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**DINUCLEAR PENTAAMMINERUTHENIUM COMPLEXES
BRIDGED BY DICYANAMIDOBENZENE LIGANDS**

by

MANUEL A.S. AQUINO, B.Sc., M.Sc.

A thesis submitted to
the Faculty of Graduate Studies and Research
in partial fulfilment of
the requirements for the degree of
Doctor of Philosophy

Department of Chemistry

Carleton University

Ottawa, Ontario

June, 1991

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Chair, Department of Chemistry

Thesis Supervisor

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July 18, 1991

ABSTRACT

The π -donor bridging ligand 1,4-dicyanamidebenzene dianion (Dicyd^{2-}) and four of its derivatives, 1,4-dicyanamide-2,3,5,6-tetrachlorobenzene dianion (TC-Dicyd^{2-}), 1,4-dicyanamide-2,5-dichlorobenzene dianion (DC-Dicyd^{2-}), 1,4-dicyanamide-2,3,5,6-tetramethylbenzene dianion (TM-Dicyd^{2-}) and 1,4-dicyanamide-2,5-dimethylbenzene dianion (DM-Dicyd^{2-}), were synthesized as tetraphenylarsonium salts. These ligands have been fully characterized by IR spectroscopy, cyclic voltammetry and X-ray crystallography. The X-ray structure determinations show all of the ligands except TM-Dicyd^{2-} to be planar and in the anti configuration. TM-Dicyd^{2-} shows significant out-of-plane distortion. Six corresponding dinuclear ruthenium complexes, $\{\mu\text{-Dicyd-}[(\text{NH}_3)_5\text{Ru}]_2\}(\text{ClO}_4)_4$ (1), $\{\mu\text{-TC-Dicyd-}[(\text{NH}_3)_5\text{Ru}]_2\}\text{Cl}_4$ (2), $\{\mu\text{-DC-Dicyd-}[(\text{NH}_3)_5\text{Ru}]_2\}\text{Cl}_4$ (3), $\{\mu\text{-TM-Dicyd-}[(\text{NH}_3)_5\text{Ru}]_2\}(\text{ClO}_4)_4$ (4), $\{\mu\text{-DM-Dicyd-}[(\text{NH}_3)_5\text{Ru}]_2\}(\text{ClO}_4)_4$ (5) and $\{\mu\text{-Dicyd-}[(\text{NH}_3)_5\text{Ru}]_2\}(\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)_4$ (6), have been synthesized and characterized by elemental analysis, cyclic voltammetry, UV-Vis-NIR and IR spectroscopy and magnetic susceptibility. An X-ray crystal structure of (6) was determined and it was found that a linear and a bent form of the dimer existed in the unit cell. The mixed-valence complexes, (III,II), of the above were shown to be weak electronically coupled cases with an intervalence charge transfer (IT) band being resolvable in complex (2) only, leading to an H_{ab} of 185 cm^{-1} . The weakness of the electronic coupling in solution is mostly likely due to rapid rotation of the phenyl ring. Temperature dependent magnetic susceptibility measurements of the oxidized dimers, (III,III), showed moderate to

strong antiferromagnetic behaviour. Isotropic spin-only models of the data yielded the magnetic coupling constants, J , for each complex. They are as follows: (2), -61.9 cm^{-1} ; (3), -95.9 cm^{-1} ; (4), -53.5 cm^{-1} and (6), -100 cm^{-1} . Complexes (1) and (5) were found to be diamagnetic at room temperature with $|J|$ estimated at $> 400 \text{ cm}^{-1}$. Antiferromagnetic coupling of this magnitude between magnetic centers separated by $13.2 \text{ \AA}$ is unprecedented. Extended Hückel Molecular Orbital (EHMO) calculations were performed and show that the two highest occupied molecular orbitals on the ligand lie closer in energy to the metal orbitals than the ligand LUMO. These orbitals can provide an extended or conductive π -system which should lead to efficient magnetic coupling either by superexchange or spin polarization mechanisms. A reassessment of Coffmann and Büttner's limit function, is made. Its application to "insulating" systems appears valid, however, it does not seem to predict maximum J values for semiconducting (or conducting) systems such as the ones in this study.

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**This work is dedicated to my wife, Nicola,
and to my parents, Ann and Ron Aquino.**

**"...To know that what is impenetrable to us really exists,
manifesting itself as the highest wisdom and the most
radiant beauty which our dull facilities can comprehend
only in the most primitive forms—this knowledge, this
feeling, is at the center of true religiousness.**

**In this sense, and in this sense only, I belong to the
ranks of the devoutly religious men."**

Albert Einstein

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LIST OF ABBREVIATIONS

Me	methyl
Bu	butyl
Ph	phenyl
OAc	acetate anion
OTs	tosylate anion
pyz	pyrazine
bipy	2,2'-bipyridine
bipy'	4,4'-bipyridine
bpa	1,2-bis(4-pyridyl)ethane
dien	diethylenetriamine
phen	1,10-phenanthroline
tacn	N,N',N''-trimethyl-1,4,7-triazacyclononane
TBAB	tetrabutylammoniumbromide
TBAH	tetrabutylammoniumhexafluorophosphate
DCNQI	N,N'-dicyano-1,4-benzoquinonediimine
TCNQ	7,7,8,8-tetracyanoquinonediimethane
TTF	tetrathiafulvalene
HOMO	highest occupied molecular orbital
LUMO	lowest unoccupied molecular orbital

CHAPTER 1

INTRODUCTION

1.1 Background

The study of electron transfer and electron exchange in polymetallic complexes is very important to experimentalist and theoretician alike.¹⁻³ To the experimentalist there is clear application in the design and synthesis of chemical models for the active sites of many metalloproteins as well as the creation of novel electronic and magnetic solid-state materials.

Many proteins contain active sites which consist of two or more metal ions bridged by various chemical groups. These bridges can range from simple small anions such as O^{2-} or S^{2-} to more elaborate groups such as carboxylate or imidazole. Some examples of dinuclear metal sites found in proteins include: methemerythrin,⁴⁻⁶ which contains two Fe(III) ions bridged by one oxo and two carboxylato groups, and is used for oxygen fixation; two-iron ferredoxin,⁷⁻¹⁰ which has two Fe(III) ions bridged by two S^{2-} anions and functions as an electron carrier; and more recently, catalase,¹¹⁻¹³ which has an active site similar to hemerythrin except that Fe(III) is replaced by Mn(III) and functions in converting H_2O_2 to H_2O and O_2 . Modelling these and other biological systems and studying their metal-metal interactions will lead to a better understanding of the properties and functions of the actual metalloproteins.

The design of solid-state magnetic and electronic materials has gained increasing attention over the last ten years.^{14,15} A large and eclectic variety of these compounds exist. They include such systems as: donor-acceptor or charge-transfer complexes such as tetrathiafulvalene-tetracyanoquinonemethane

(TTF-TCNQ)¹⁶ and its variants, a highly conducting organic charge-transfer complex which displays metallic behaviour down to 54 K; the organic "linear chain" compounds such as the tetracyanoplatinates or Krogmann salts^{17,18} (eg. $K_2[Pt(CN)_4]$) which are partially oxidized materials that exhibit metallic behaviour at room temperature; and transition metal macrocyclic ligand complexes such as metallophthalocyanines^{19,20} which form efficient π -stacking conductors. More recently, metal radicals such as metal nitroxides^{15,21,22} and radical anion metal salts of dicyanoquinonediimine derivatives (DCNQI)²³ have shown great promise as magnetic and electronic materials respectively. The DCNQI's will be discussed in greater detail later in this chapter.

To the theoretician, a better insight into the mechanisms governing electron transfer and electron exchange can be gained. In the case of the former, superexchange mechanisms²⁴ involving either electron transfer or hole transfer from one metal to the other are mediated by the nature of the intervening bridge. Varying the nature of this bridge will lead to the preference of one form of transfer over the other. In the case of electron exchange, spin polarization mechanisms have recently been invoked to explain interactions in dinuclear copper complexes.² Understanding of the mechanism can in turn lead to better theories explaining such things as the distance^{25,26} and solvent^{27,28} dependencies of these processes.

This thesis deals with the spectroscopic, electrochemical, and magnetic properties of dinuclear ruthenium complexes bridged by an organic ligand. The choice of ruthenium as the metal is dictated by the fact that few redox couples simultaneously meet the criteria that states differing by one oxidation unit are stable and that they each form robust complexes. Among classical complexes, the III/II couples of the iron group offer the most abundant examples. However, ruthenium has the advantage over iron in that its complexes are always low-spin

(i.e. Ru(III) d^5 (l.s.), Ru(II) d^6 (l.s.)) while many iron complexes are high spin and tend to be labile. Ruthenium also has the advantage over osmium since the desired complexes are usually easier and cheaper to prepare. These properties, as we shall see, simplify the study of electronic coupling (since it is easier to synthesize robust Ru(III)—Bridge—Ru(II) complexes) and magnetic coupling (since low spin Ru(III)—Bridge—Ru(III) complexes only have one unpaired electron on each metal).

Before considering the system which is the subject of this thesis however, a more detailed discussion of electronic and magnetic coupling in diruthenium complexes will be given.

1.2 Intervalence Transitions in Diruthenium Complexes

To study electron transfer in dinuclear bridged systems one must first generate a "mixed-valence" complex.²⁹ This simply means that the oxidation states of the metals involved must differ by one unit. (I)

In the discussions that follow we will assume that the systems are symmetric, that is, both ends of the bridge are identical and hence both metals have the same coordination environments. It will also be assumed that these metal environments have octahedral or near octahedral symmetry.

The first major diruthenium mixed-valence complex to be synthesized was the Creutz-Taube (II) ion in 1969³⁰ and it still demands much work today.³¹⁻³³ Since then a vast array of these kinds of complexes have been made.³⁴⁻³⁷

(II)

However, before considering any of the specific complexes in any detail the concept of electronic coupling must be further defined in a general sense.

The mechanism of electron transfer between two metal centers linked by a bridge is referred to as *superexchange*. This can manifest itself in two major ways: electron transfer and hole transfer. Electron transfer occurs by the transfer of an electron from the d orbital on the electron-rich metal (M) via the vacant lowest unoccupied molecular orbital (LUMO), usually a π^* orbital, of the bridge, to the appropriate d orbital on the electron deficient metal (M^+). This pathway will be favored when the energies of the metal orbitals are close to that of the ligand LUMO. (III)

(III)

However, when the energies of the metal orbitals are closer to that of the ligand π highest occupied molecular orbital (HOMO), a hole transfer mechanism whereby the positive hole is transferred from the electron deficient metal center (M^+) via the π HOMO of the bridge to the electron rich metal center (M), is favored. (IV)

One can also view this latter process as a double electron transfer where one has concurrent transfer of an electron from the bridge π molecular orbital to M^+ and M to the bridge π orbital. The preference of one mechanism over the other in a particular system is dictated by the nature of the bridging ligand.

Robin and Day³⁸ have distinguished three broad classes of mixed-valence materials. Class I compounds show virtually no interaction between M and M^+ centers, either because the M—Bridge— M^+ distance is very large or the M and M^+ environments are extremely different. These mixed-valence materials only display the properties of the corresponding isolated mononuclear M and M^+

complexes. In effect the metal valences are totally localized. At the other extreme are Class III systems. Here the interaction between M and M^+ is so great that the properties due to the isolated monomers are absent and only new properties intrinsic to the $(M\text{---}Bridge\text{---}M)^+$ unit are observed. In this case the charge is totally delocalized over the two metals. In between lie Class II systems which show slightly perturbed M and M^+ properties and may also show features not associated with the isolated monomer units.

To illustrate the classification scheme more clearly consider the potential energy diagram for symmetric systems shown in Figure 1.1. Here the left-hand parabola represents the potential energy surface for $M\text{---}Bridge\text{---}M^+$ (electron on the left-hand side); the right-hand curve is for $M^+\text{---}Bridge\text{---}M$ (electron on right-hand side).

Figure 1.1 Potential energy versus nuclear configuration for a symmetric mixed-valence complex. (from ref. 34)

The curves split at their intersection by $2H_{ab}$, where H_{ab} is the resonance energy between the two states and is a measure of the degree of electronic coupling between M and M^+ . The energy barrier to thermal electron transfer (from left to right) is defined as E_{th} . Optical electron transfer occurs when light of the appropriate energy ($E_{op} = \lambda = h\nu$) is absorbed and the system passes vertically from the lower surface to the upper surface. If one assumes that $E_{th} = \Delta G_{th}^*$ and H_{ab} is small we can define E_{op} as:

$$E_{op} = \lambda = 4\Delta G_{th}^* \quad (1.1)$$

Therefore, mixed-valence ions should display absorption bands that occur at $h\nu = \lambda$. These are called metal to metal charge transfer (MMCT) bands or intervalence transfer (IT) bands.

In Figure 1.2a we see the potential energy surface for a Class I system. This is one in which there is no electronic coupling between metal sites and hence $H_{ab} = 0$ (there is no splitting at the intersection of the curves). As the interaction is increased as in Class II systems (Figure 1.2b) splitting occurs between the curves and H_{ab} becomes significant. The thermal barrier to electron transfer is decreased and coupling occurs. E_{th} can be expressed as:

$$E_{th} = (\lambda/4) - H_{ab} \quad (1.2)$$

In Class III systems (Figure 1.2c), H_{ab} , and hence the coupling, is so large ($H_{ab} > \lambda/2$) that the barrier to electron transfer is removed. The two minima corresponding to the localized mixed-valence ions M —Bridge— M^+ and M^+ —Bridge— M are gone and a single minima due to the delocalized

Figure 1.2 Potential energy versus nuclear configuration for a symmetric mixed-valence complex as a function of λ and H_{ab} . a) Class I b) Class II c) Class III (from ref. 34).

$(\text{M}—\text{Bridge}—\text{M})^+$ is present.

The most common way of assessing H_{ab} , and hence the electronic coupling, experimentally is by analysis of the intervalence transfer (IT) band(s). The intensity and position of this band (at $\lambda = h\nu$) depends on H_{ab} . Since $H_{ab} = 0$ for Class I systems an IT band may not be observable. For Class II systems the IT band is expected to have measurable intensity since H_{ab} is small but significant and for Class III complexes $h\nu = 2H_{ab}$ (see Figure 1.2c). Therefore, the position of the IT band for a Class II ion is related to E_{th} , but for a Class III ion it is related directly to H_{ab} .

Evaluation of H_{ab} can be accomplished directly using the spectral analysis developed by Hush.³⁹ For moderately coupled systems (Class II):

$$H_{ab} = 2.05 \times 10^{-2} \left[\frac{\epsilon_{\max} \Delta \nu_{\frac{1}{2}}}{\nu_{\max}} \right]^{\frac{1}{2}} \frac{\nu_{\max}}{r} \quad (1.3)$$

where $\epsilon_{\max}$ is the molar absorptivity ($\text{M}^{-1} \text{cm}^{-1}$) at the band maximum, $\Delta \nu_{\frac{1}{2}}$ is the bandwidth at half intensity (in cm^{-1}), $\nu_{\max}$ is the band maximum (in cm^{-1}) and r is the separation between the metal centers (in Å). For Class III systems (as mentioned above):

$$H_{ab} = \frac{h\nu_{\max}}{2} \quad (1.4)$$

The second major way of assessing the degree of electronic coupling experimentally is by determining the comproportionation constant (K_c).⁴⁰ For a diruthenium complex in which each ruthenium can have an oxidation state of II or

III the mixed-valence state can be represented as (III,II) and is stabilized with respect to the isovalent states (III,III) and (II,II). The degree of this stabilization is reflected in K_c (i.e. the larger K_c is, the greater the electronic coupling).

Determining K_c experimentally is readily done electrochemically when the values of the reduction potentials (E^0) governing the two stages of the reduction

are well separated. K_c can then be obtained from the Nernst equation (at 25 °C).

$$\log K_c = 16.9 (E_1^0 - E_2^0) \quad (1.7)$$

The task is somewhat more difficult as K_c approaches the statistical value of 4 and E_1^0 and E_2^0 are not well separated.

A second method for determining K_c is by a spectrophotometric titration of the IT band⁴¹ using an appropriate oxidant if the (II,II) species is used as the starting complex or a reductant if the (III,III) species is used. Computer fitting of the IT absorbance versus percent complex oxidized (reduced) plot, yields K_c . This method has its drawbacks in that a well isolated IT band is needed to perform the titration and the complex must be relatively inert to side reactions after it is oxidized or reduced.

The electronic coupling data for a series of selected diruthenium-pentaammine complexes with various bridging ligands is given in Table 1.1

TABLE 1.1 Electronic Coupling Data for Selected $[\text{Ru}(\text{NH}_3)_5]_2\text{L-L}^{5+}$ Complexes

L-L	$H_{ab}(\text{eV})$	K_c	Class (Ref.)
0.048	20	II (41,42) ^a
0.012	6.7	II (42) ^a
0.062	≈ 26	II (42) ^a
0.029	21	II (43) ^a
0.39	4×10^6	III (44) ^b
0.4–0.6	10^{10}	III (45) ^a
$\text{N}\equiv\text{C}-\text{C}\equiv\text{N}$	0.44	$>10^{13}$	III (46) ^a
0.53	$>10^{10}$	III (47) ^b

^aCoupling mechanism is electron transfer. ^bCoupling mechanism is hole transfer.

The first four entries are all weakly coupled Class II systems where H_{ab} is small (< 0.1 eV) and K_c is also small (< 100). The last four entries are strongly coupled Class III systems where H_{ab} is substantial (> 0.35 eV) and K_c is very large ($> 10^6$). It should also be noted that only one example exists, where the ligand is *t*-butylmalonitrile,⁴⁷ in which the mechanism of electronic coupling is hole transfer. This is also the only bridging ligand in the table that is a π -base, all of the others are π -acids. This fact and the fact that strong coupling is seen was a major factor contributing to the design of the present system.

1.3 Magnetic Properties of Diruthenium Complexes

In dealing with magnetic exchange in dinuclear metal complexes we are concerned with the simplest case in which the metals are in the same oxidation state (V) and they are low spin (i.e. Ru(III)). Consequently each metal contains only one unpaired electron and $s = 1/2$.

The Hamiltonian one can use for metal-metal exchange in dimers is of the form:⁴⁸

$$H = -2JS_1 \cdot S_2 \quad (1.8)$$

This is called an isotropic or Heisenberg Hamiltonian, where S_1 and S_2 correspond to the spin vectors on the individual metals, and from it arise two major types of interactions. By convention when J is negative the coupling is termed anti-

ferromagnetic (i.e. a spin-paired or singlet ground state exists in the dimer) and when J is positive one obtains ferromagnetic coupling (a spin aligned or triplet ground state). This is shown using a state description below (VI).

(VI)

Here we see the two types of interactions. On the left of each diagram are the free paramagnetic ($s = 1/2$) ions with uncorrelated spins. When they form a dimer via a diamagnetic bridging ligand the states split into singlet and triplet with an interaction energy of $-2J$.

Experimentally J can be evaluated by variable temperature magnetic susceptibility measurements. However, before discussing the temperature dependence of magnetic susceptibilities in dimers one must first consider paramagnetism in mononuclear complexes.

To a first approximation the susceptibility, χ , varies inversely with temperature. This is described by the Curie Law:

$$\chi = C/T \quad (1.9)$$

where C is the Curie constant and T is the absolute temperature. Therefore, a plot of χ^{-1} versus T gives a straight line with slope C^{-1} .

There are many instances in which the Curie Law is not obeyed. (The Curie law is really the magnetic equivalent of the ideal gas law). Deviations can occur, for instance, by the presence of an energy level whose population changes greatly over a measured temperature range. Another source of deviations is the magnetic interactions between paramagnetic ions as we shall see for dimers below. In these instances, a modification of the Curie Law gives the Curie-Weiss Law:

$$\chi = C/(T - \theta) \quad (1.10)$$

where the correction term, θ , has units of temperature. It can be obtained empirically from the intercept of a plot of χ^{-1} versus T . When θ is negative it is called antiferromagnetic in sign and when it is positive it is ferromagnetic in sign.

The simplest model for the analysis of susceptibility data for $s = 1/2$ spin coupled dimers is the so-called Bleaney-Bowers equation:^{48,49}

$$\chi_m = (2 N g^2 \beta^2 / 3kT) [1 - 1/3 \exp(-2J/kT)]^{-1} \quad (1.11)$$

where J is the exchange coupling constant (as defined in (VI) above), g is the powder averaged g -value and β is the Bohr magneton.

Inspection of this equation shows that for negative J (antiferromagnetic) χ has a maximum (Figure 1.3). This usually occurs at $J/kT_m \cong -4/5$ (where T_m is the temperature at the maximum χ).

Figure 1.3 A plot of the Bleaney-Bowers equation for an $s = 1/2$ spin coupled dimer with a typical set of parameters, $g = 2.2$ and $2J/k = -30$ K. (from ref. 48).

For positive J (ferromagnetic) an $S = 1$ spin only Curie Law susceptibility is obtained as $2J/kT$ becomes large, i.e. at low temperatures (Figure 1.4).

Figure 1.4 The Bleaney-Bowers equation (dashed line) for $S = 1$, $g = 2.2$ and $J/k = 30$ K compared with the Curie Law (solid line) with $s = 1/2$ per mole and $g = 2.2$. (from ref. 48).

The susceptibilities for positive J as calculated from the Bleaney-Bowers equation do not differ greatly from the Curie Law for $s = 1/2$. Only at very low

temperatures with respect to $2J/k$ is there any deviation. This is due to the extra factor of 2 which is needed when comparing a mole of spins, $s = 1/2$, with a mole of dimers with individual ions of spin, $s = 1/2$.

Examples of the application of equation 1.11, especially for first row transition metal complexes, are too numerous to mention.⁵⁰ The most famous example, copper acetate, $[\text{Cu}(\text{OAc})_2 \cdot \text{H}_2\text{O}]_2$, was investigated by Bleaney and Bowers themselves.⁴⁹ However, much less work has been done on second and third row transition metals, including dinuclear ruthenium complexes.⁵¹⁻⁵⁵

Table 1.2 summarizes the J values and metal-metal distances of various ligand bridged complexes of ruthenium(III). It is quite evident from the data that as the metal-metal distance increases the extent of the magnetic coupling is greatly diminished. The strongest coupling was observed for the diruthenium complexes with monoatomic, O^{2-} , bridges. There was even diamagnetic behaviour reported for $[(\text{tacn})_2\text{Ru}_2(\mu\text{-O})(\mu\text{-CH}_3\text{CO}_2)](\text{PF}_6)_2$, although this was thought to be due to a direct Ru-Ru bond.^{54,55} The degree of coupling in the complexes where the metal-metal separation was greater than 6 Å was so small it was beyond the sensitivity of the instrumentation used,^{51,52} and determination of antiferromagnetic versus ferromagnetic coupling was impossible.

Coffman and Buettner²⁵ have proposed a limit function for long-range ferromagnetic and antiferromagnetic exchange in exchange-coupled dimers;

$$|2J_{\text{lim}}| = 1.35 \times 10^7 \exp(-1.80R) \quad (1.12)$$

where J is the magnetic exchange coupling constant (in cm^{-1}) and R is the distance between metal ions (in Å). This expression was derived from the fitting of a general exponential function, $J = A \exp(-\alpha R)$, to experimental data for

Table 1.2. Magnetic Coupling Data for Ligand-Bridged Ruthenium(III) Complexes

Complex ^a	M—M (Å)	J (cm ⁻¹)	Ref.
$\{[\text{Ru}(\text{NH}_3)_5]_2\text{pyz}\}(\text{OTs})_6$	6.8	$ J < 0.2$	51,56
$\{[\text{Ru}(\text{bpy})_2\text{Cl}]_2\text{bpy}'\}(\text{ClO}_4)_4$	11.3		
$\{[\text{Ru}(\text{bpy})_2\text{Cl}]_2\text{pyz}\}(\text{ClO}_4)_4$	6.9	$ J < 2$	34,52
$\{[\text{Ru}(\text{bpy})_2\text{Cl}]_2\text{bpa}\}(\text{ClO}_4)_4$	—		
$\{[\text{Ru}(\text{bpy})_2\text{NO}_2]_2\text{O}\}(\text{PF}_6)_2$	3.69	-87	53,57
$\{[\text{Ru}(\text{phen})_2\text{NO}_2]_2\text{O}\}(\text{ClO}_4)_2$	—	-60	53
$[\text{L}_2\text{Ru}_2(\mu\text{-O})(\mu\text{-OAc})_2](\text{PF}_6)_2$	3.26	diamag.	54,55
$[\text{L}_2\text{Ru}_2(\mu\text{-OH})(\mu\text{-OAc})_2](\text{PF}_6)_2$	—	-218	54,55

^aAbbreviations: pyz = pyrazine, OTs = tosylate, bpy = 2,2'-bipyridyl, bpy' = 4,4'-bipyridyl, bpa = 1,2-bis(4-pyridyl)ethane, phen = 1,10-phenanthroline, OAc = acetate, L = N,N',N'-trimethyl-1,4,7-triazacyclononane.

superexchange coupling as a function of distance. The equation predicts negligible coupling, $|J| < 0.5 \text{ cm}^{-1}$, at distances greater than 10 Å. All the systems studied to that point, 1979, fell within the boundaries of this limit function.

The limit function has held up quite well until this day, however, there have been two notable exceptions. In a study⁵⁸ that explored the distance dependence of magnetic coupling between two Cu(II) ions bridged by 4,4'-bipyridine (VII), 2J was found to be -0.9 cm^{-1} for a metal-metal separation of

11.1 Å. Equation 1.12 predicts $|2J_{\text{lim}}| = 0.03 \text{ cm}^{-1}$.

(VII)

In the second study Chaudhuri *et al.*⁵⁹ showed the existence of moderately strong antiferromagnetic coupling ($J = -70 \text{ cm}^{-1}$) between Cu(II) ions in a μ -terephthalato complex (VIII) in which the metal-metal separation was 11.25 Å. Here the equation predicts $|2J_{\text{lim}}| = 0.02 \text{ cm}^{-1}$.

(VIII)

One can conclude from these cases that it is not unreasonable to expect that a serious challenge to the above limit could be made. Through the judicious design of a bridging ligand, such as one possessing an extended π system lying close in energy to the metal orbitals, mediation of electron exchange could be more efficient.

1.4 System Design and the DCNQI's

The initial goal of this thesis was to design a dinuclear ruthenium system which displayed strong electronic coupling in the mixed-valence (III,II) state as well as strong magnetic coupling in the fully oxidized (III,III) state over distances

greater than 10 Å. To accomplish this end the superexchange mechanism of hole transfer was explored further. This mechanism of electronic coupling was shown by Taube⁴⁷ to lead to Class III behaviour for a *t*-butylmalonitrile bridged mixed-valence complex (see Table 1.1). Here, the through bond metal-metal distance is approximately 9 Å. The fully oxidized, (III,III), form displayed a very low magnetic moment at room temperature ($\mu_B = 0.98$) which is indicative of a strong interaction between the Ru(III) ions. (Follow-up variable temperature measurements are not in the literature).

The major criteria that must be considered in the design of a system can now be addressed.

1. Redox Properties of the Bridge – In order for a hole transfer mechanism to be operable, coupling must occur through the bridging ligand π molecular orbital (HOMO). That is to say, the HOMO of the bridge must lie close in energy to that of the metal t_{2g} orbitals. Therefore, a π -donor ligand that can preferentially reduce one Ru(III) site and not the other would generate a mixed-valence radical bridged species which should show strong coupling. The ideal ligand should have two one-electron redox potentials that bracket that of the Ru(II/III) couple of the metal fragment.

2. Tunability – Built into the system should be some means of varying the energy of the both the bridging ligand and metal orbitals involved in the coupling interaction. This can be done, for instance, by varying certain substituents on the bridge (eg. from electron withdrawing to electron donating) or by varying the co-ligands on the metal (eg. from NH_3 to 2,2'-bipyridyl).

3. Symmetry – A symmetric bridging ligand is employed to simplify the thermodynamics of the electron transfer between the metals. That is, both metal centers have identical ligand environments and hence $\Delta G^\circ = 0$ for the electron

transfer in the mixed-valence system,

since the identical species exists on both sides of the equation. This greatly simplifies the analysis of the electronic coupling, especially the electrochemical evaluation of K_c (see pg. 10).

4. Planarity – The planarity of the overall system is very important in optimizing both the electronic and magnetic coupling. Maximum planarity and linearity of the free ligand should, in most cases, lead to planarity in the complex and hence maximize the overlap of electronic and magnetic orbitals. However, it should be noted that a ligand that is planar and rigid in the solid state may not maintain this rigidity in solution and consequently coupling may be compromised.

5. Stability – Of course, it is frequently desirable to have a complex that is relatively inert to ligand substitution, air stable, light stable, heat stable and can be readily synthesized in high yields. This, in many cases, is the most difficult criterion to meet.

As mentioned earlier, the choice of metal will be ruthenium. The Ru(III/II) redox couple in $[\text{Ru}(\text{NH}_3)_5\text{X}]^{n+}$ type complexes lies in the range $0 \rightarrow 0.5$ V vs. NHE and provides easy access to both oxidation states. The reduced (Ru(II)) forms of these complexes are readily synthesized and can be used as substitutionally labile precursors for the synthesis of bridged dimers.⁶⁰ The design of the bridging ligand is more critical since most of the above criteria must be met.

In the mid-1980's a series of novel acceptors for charge-transfer (CT) complexes, based on the already well established TCNQ acceptor, were synthesized. These were the bis-aza-analogues of TCNQ known as

N,N'-dicyano-1,4-benzoquinonediimines or DCNQI's.^{61,62}

Hünigs group and others went on to extensively characterize a large variety of these compounds⁶³⁻⁶⁵ and employ them in CT complexes⁶⁶⁻⁶⁸ and, perhaps even more extensively, in radical anion metal salts.^{23,69-74} The room temperature conductivity of some of these compounds is shown in Table 1.3.

Table 1.3 Room Temperature Conductivity of Compounds with DCNQI Acceptors

Complex Stoichiometry ^a	Conductivity ($\Omega^{-1} \text{ cm}^{-1}$)	Ref.
DCNQI·TTF	4.2×10^{-4}	61
DC-DCNQI·TTF	5.0×10^{-3}	61
(DM-DCNQI) ₂ Cu	$1 - 2 \times 10^2$	23,67,72
	5×10^5 (3.5 K)	
(DM-DCNQI) ₂ Ag	100	67,72
(DM-DCNQI) ₂ Li	300	67,72
(DM-DCNQI) ₂ Tl	50	71

^aAbbreviations: DC = 2,5-dichloro-, DM = 2,5-dimethyl-

The first two entries are charge transfer (CT) salts and more than 25 of these derivatives have been made. Their conductivities are in the semi-conductor range and are similar to their TCNQ counterparts. The radical anion metal salts, however, show remarkably high conductivities. Most of these, and close to 50 have been synthesized, show metal-insulator transition temperatures in the range 70–230 K but the (2,5-dimethyl-DCNQI)Cu₂ derivative shows metallic behaviour down to 1.5 K with a conductivity at 3.5 K of $5 \times 10^5 \Omega^{-1} \text{cm}^{-1}$.²³ There are no analogous TCNQ complexes showing similar properties.

The redox properties of the DCNQI's were determined by Hünig *et al.*⁶³ These were expected to be close to those of the TCNQ's since the functional

Table 1.4 Redox Potentials for Selected DCNQI's⁶³ and TCNQ's.^{63,75,76}

		DCNQI ^a		TCNQ ^a	
R ¹	R ²
		E ₁ (V)	E ₂	E ₁ (V)	E ₂
Cl	Cl	0.13	0.76	—	—
Cl	H	0.00	0.65	-0.10	0.41 ^b
H	H	-0.25	0.39	-0.28	0.39
CH ₃	H	-0.38	0.21	-0.38	0.10 ^b
CH ₃	CH ₃	-0.39	0.05	-0.40	—

^aCH₂Cl₂/Bu₄NBF₄/Pt vs. Ag/AgCl/CH₃CN. ^bCH₃CN/Hg/LiClO₄ vs. SCE.

SCHEME 1.1

groups were similar. The redox and proton equilibria of DCNQI is shown in Scheme 1.1. The measured redox potentials for the DCNQI's and the corresponding TCNQ values (where available) are given in Table 1.4.

It can be seen from these redox potentials that the fully oxidized DCNQI's (L^0) should be as good, if not better acceptors, than the TCNQ's and this has been borne out. However, what is more interesting, is the fact that the fully reduced forms, L^{2-} or LH_2 , should be powerful π electron donors. (This is important since it makes the ligand more amenable to hole transfer in a dinuclear metal complex). Varying the substituent R group gives one the tunability one needs and the DCNQI's are also symmetrical. Therefore, the first three criteria listed above have been met. The DCNQI's are relatively planar⁶¹ and it is expected that the doubly reduced forms would be planar as well, although the increased single bond character between the phenyl carbon and amide nitrogen may lead to the cyanamide moiety (NCN) twisting out of the plane somewhat. Some of the properties listed in Criterion 5 may have to be compromised, however, although relative ease of synthesis based on the DCNQI's should be achievable. The objectives of this thesis can now be outlined.

1.5 Research Aims

There were four major goals of this research:

1. To synthesize and characterize a series of doubly reduced DCNQI's or dicyanamidebenzenes (Dicyd's);

$$R^1 = R^2 = Cl$$

$$R^1 = R^2 = H$$

$$R^1 = R^2 = CH_3$$

$$R^1 = Cl \quad R^2 = H$$

$$R^1 = CH_3 \quad R^2 = H$$

2. To synthesize and characterize the corresponding diruthenium(III) pentaammine complexes;

3. To investigate the spectroscopic and electrochemical properties of the mixed-valent form of the metal complexes and;

4. To investigate the magnetic properties of the oxidized form of the metal complexes.

CHAPTER 2

EXPERIMENTAL

2.1 Starting Materials

2.1.1 Reagents for Ligand Syntheses

Ammonium thiocyanate (reagent grade, Fisher Scientific Co.), benzoyl chloride (99%, reagent grade, Aldrich Chem. Co.), lead acetate trihydrate (reagent grade, Anachemia), 1,4-phenylenediamine (97%, Aldrich Chem. Co.), 2,5-dimethyl-1,4-phenylenediamine (97%, Aldrich Chem. Co.), 2,3,5,6-tetramethyl-1,4-phenylenediamine (97%, Aldrich Chem. Co.), 2,5-dichloro-1,4-phenylenediamine (Aldrich Chem. Co.), sodium hydroxide (lab grade, Anachemia), tetraphenylarsonium chloride hydrate (97%, Aldrich Chem. Co.) and glacial acetic acid (99.7%, reagent grade, Anachemia) were used without further purification. 2,3,5,6-tetrachloro-1,4-phenylenediamine was previously prepared by A. Bostock from 1,4-phenylenediamine and thionyl chloride.⁷⁷

2.1.2 Reagents for Metal Complex Syntheses

Ruthenium(III) chloride hydrate (Aldrich Chem. Co.), hydrazine monohydrate (98%, Aldrich Chem. Co.), ammonium hexafluorophosphate (99.99%, Aldrich Chem. Co.), tetrabutylammonium bromide (99%, Aldrich Chem. Co.), hydrochloric acid (36.5–38.0%, reagent grade, Anachemia) and sulfuric acid (95–98%, reagent grade, Anachemia) were used as received. Zinc/mercury amalgam was prepared by first cleaning zinc metal (mossy, reagent grade,

Anachemia) with 1M HCl then treating with a saturated solution of mercurous chloride (reagent grade, Anachemia).

Chloropentaammineruthenium(III) chloride: This was prepared by a method similar to that of Clarke.⁷⁸ 10 g (0.048 mol) of $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ was slowly added to a solution of 82 mL (1.7 mol) 98% hydrazine in 100 mL of water and allowed to stir for 16 hours. The solution was then put on ice and 250 mL of concentrated HCl was added very slowly. (**Caution:** This reaction is extremely exothermic). After all of the HCl was added the solution was allowed to reflux for 2 hours, then allowed to cool in the fridge for 2 hours. The yellow–orange crystals that formed were filtered off and recrystallized from 500 mL of 0.1 M HCl. The final yield of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was 8.64 g (62%).

Aquopentaammineruthenium(II) hexafluorophosphate: This was prepared, under argon, in a similar manner to that of Sullivan *et al.*⁷⁹ 0.75 g (2.6 mmol) of $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ was dissolved with stirring in 75 mL of 0.1 M H_2SO_4 . The solution was filtered and placed into a 100 mL round bottom flask. 18 g of freshly prepared Zn/Hg amalgam was placed in a separate round bottom flask and both flasks were degassed on a vacuum line. The flask containing the Zn/Hg amalgam was placed in an ice bath and the $[\text{Ru}(\text{NH}_3)_5\text{Cl}]\text{Cl}_2$ solution transferred to it. This solution was allowed to react for 30 minutes with intermittent venting to remove any evolved H_2 gas. 6 g (0.036 mol) of NH_4PF_6 were then dissolved in 30 mL of distilled water, filtered, placed into a round bottom flask and degassed. The reduced ruthenium solution was then transferred back to this flask and immediate precipitation of $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{PF}_6)_2$ was afforded. The solution was allowed to stir for 10 minutes and then filtered through a medium glass frit. The pale

yellow precipitate was washed with 5 mL of cold water, 5 mL cold methanol and 25 mL cold diethyl ether and then dried *in vacuo* overnight. When stored under argon in the freezer the product can be used for up to 2 months. The yield of $[\text{Ru}(\text{NH}_3)_5(\text{H}_2\text{O})](\text{PF}_6)_2$ was 1.15 g (90%).

2.1.3 Solvents

Dimethyl sulphoxide (distilled in glass, Caledon Labs), diethyl ether (anhydrous, Caledon Labs) and ethanol (absolute, Consolidated Alcohols Ltd.) were used without further purification. Acetone (Spectro grade, Caledon Labs) was used as received or distilled in glass before use. Acetonitrile (HPLC grade, Caledon Labs) was stored over alumina before use. Methanol (Spectro grade, Caledon Labs) was used as received or distilled over magnesium before use. Deuterium Oxide (99.9 atom % D, MSD Isotopes) was used as received. d_4 -methanol and d_6 -ethanol (99.8 atom % D, Aldrich Chem. Co.) were used as received.

2.1.4 Electrolytes and Ion Exchange Resins

Sodium chloride (99+%, reagent grade, Anachemia) and sodium perchlorate (anhydrous, reagent grade, Anachemia) were used as received. Tetrabutylammonium hexafluorophosphate (98%, Aldrich Chem. Co.) was recrystallized from ethanol and dried *in vacuo* at elevated temperatures before use.

CM-Sephadex C25 cation exchange resin (bead size: 40–120 microns, Sigma) was used as received.

2.2 Syntheses of the Bridging Ligands

1,4-Dicyanamidebenzene (H₂Dicyd): Benzoyl chloride (14.0 g, 0.1 mol) in 100 mL of acetone was added to a refluxing solution of ammonium thiocyanate (7.6 g, 0.1 mol) in 100 mL of acetone. The mixture was further refluxed until a yellow color appeared. 1,4-phenylenediamine (5.4 g, 0.05 mol) in 100 mL of acetone was then added dropwise (using a pressure equalizing dropping funnel) and the entire mixture refluxed for a further 15 minutes. The solution was then slowly added to 1500 mL of distilled water with vigorous stirring. The solution was then filtered and the precipitate washed with 150 mL of acetone followed by 150 mL of water and then 150 mL of acetone again. The pale yellow solid (thiourea derivative) was then air-dried before continuing.

The dried product (20.3 g, 0.0465 mol) was dissolved in basic solution (21.5 g, 0.5 mol NaOH in 250 mL of water) and boiled for 10 minutes. The solution was then cooled to 80 °C and a solution of lead acetate trihydrate (37.9 g, 0.1 mol) in 100 mL of water was added slowly with constant stirring. Stirring was maintained until the solution had turned completely black. The temperature should be maintained between 60 and 80 °C. The solution was then filtered on ice to cool the filtrate. The cooled filtrate was then neutralized by the addition of 29.4 mL glacial acetic acid. A white precipitate was formed, filtered off and washed with copious amounts of water until the smell of acetic acid was minimal. (If the precipitate appears slightly green, more acid should be added). The crude product was then dried *in vacuo*. If desired, the crude product can be recrystallized by dissolving it in an excess amount of hot acetone to produce a dark blue solution. The solution was then filtered and concentrated and an equal volume of distilled water was added to it. The solution, which should now be lighter in colour, was

then allowed to cool in the fridge. The crystals which formed were filtered and washed with cold 50/50 (v/v) acetone/water and dried *in vacuo*. In most cases, however, the crude H₂Dicyd was suitable for synthesizing the dianion.

Tetraphenylarsonium salt of the 1,4-Dicyanamidebenzene Dianion ([AsPh₄)₂[Dicyd]]: This reaction was performed under argon on a vacuum line. 0.48 g (0.003 mol) of H₂Dicyd and 3.0 g (0.075 mol) of NaOH were placed in a 100 mL round bottom flask and purged with argon. Previously degassed water (30 mL) was transferred to this flask and the mixture stirred until the solids were completely dissolved. 2.6 g (0.006 mol) of tetraphenylarsonium chloride hydrate was dissolved in 30 mL of 2.5 M NaOH and degassed. The ligand solution was transferred to this solution and the desired product formed as a yellow precipitate. This solution was filtered and the precipitate washed with three 10 mL aliquots of ice cold water and dried *in vacuo*. The final red product was air-sensitive and hygroscopic and was stored in the freezer under argon. Yield = 1.9 g (69%).

1,4-Dicyanamide-2,5-dimethylbenzene (DM-H₂Dicyd): This was prepared in a similar manner to that of H₂Dicyd except that 6.8 g (0.05 mol) of 2,5-dimethyl-1,4-phenylenediamine was used in the place of the 1,4-phenylenediamine and the reaction temperature was not allowed to rise above 70 °C during the addition of the lead acetate. This was done to prevent any dimerization.

Tetraphenylarsonium salt of the 1,4-Dicyanamide-2,5-dimethylbenzene Dianion ([AsPh₄)₂[DM-Dicyd]]: This was prepared in a similar manner to that of [AsPh₄)₂[Dicyd] using 0.56 g (0.003 mol) of the DM-H₂Dicyd instead. Yield = 2.1 g (73%).

1,4-Dicyanamide-2,3,5,6-tetramethylbenzene (TM-H₂Dicyd): This was prepared in the same way as H₂Dicyd except that 8.2 g (0.05 mol) of 2,3,5,6-tetramethyl-1,4-phenylenediamine was used instead of 1,4-phenylenediamine and the temperature was not allowed to rise above 70 °C during the addition of the lead acetate. The product can be recrystallized from hot methanol, if desired.

Tetraphenylarsonium salt of the 1,4-Dicyanamide-2,3,5,6-tetramethylbenzene Dianion ([AsPh₄]₂[TM-Dicyd]): This was prepared in a similar way to that of [AsPh₄]₂[Dicyd] using 0.65 g (0.003 mol) of the TM-H₂Dicyd instead. Yield = 1.9 g (65%).

1,4-Dicyanamide-2,5-dichlorobenzene (DC-H₂Dicyd): This was prepared in a similar manner to H₂Dicyd except for the following starting amounts: ammonium thiocyanate (9.12 g, 0.12 mol), benzoyl chloride (16.8 g, 0.12 mol) and 2,5-dichloro-1,4-phenylenediamine (5.31 g, 0.03 mol). The 4:1 molar ratio was used to ensure completeness of reaction. As before, the temperature was not allowed to rise above 70 °C after addition of the lead acetate.

Tetraphenylarsonium salt of the 1,4-Dicyanamide-2,5-dichlorobenzene Dianion ([AsPh₄]₂[DC-Dicyd]): This was synthesized in the same way as [AsPh₄]₂[Dicyd] using 0.68 g (0.003 mol) of the DC-H₂Dicyd instead. Yield = 2.5 g (84%).

1,4-Dicyanamide-2,3,5,6-tetrachlorobenzene (TC-H₂Dicyd): This was prepared in a similar way to H₂Dicyd except for the following starting quantities:

ammonium thiocyanate (13.7 g, 0.18 mol), benzoyl chloride (25.2 g, 0.18 mol) and 2,3,5,6-tetrachloro-1,4-phenylenediamine (7.38 g, 0.03 mol). A 6:1 molar ratio was necessary in this reaction to ensure completeness. This compound was used without further purification to prepare the dianion.

Tetraphenylarsonium salt of the 1,4-Dicyanamide-2,3,5,6-tetrachloro-benzene Dianion ([AsPh₄]₂[TC-Dicyd]): This was prepared in the same way as [AsPh₄]₂[Dicyd] using 0.89 g of the TC-H₂Dicyd instead. Yield = 2.1 g (66%).

Note: Crystals of all the dianion ligands were grown by slowly cooling a saturated solution of crude ligand in hot dimethyl sulphoxide in an inert atmosphere (glove-box). X-ray crystal structures of all the dianions (as tetraphenylarsonium salts) were obtained and are reported in the next section. In most cases the dianion ligands were used without further purification to prepare the dinuclear complexes.

2.3 Syntheses of Dinuclear Metal Complexes

CAUTION: Perchlorate salts are hazardous and tend to ignite when agitated or scraped. They should only be handled in small quantities (< 100 mg) and contact with organic solvents should be avoided.

(μ -1,4-Dicyanamidobenzene)bis(pentaammineruthenium(III)) Perchlorate [Ru₂Dicyd](ClO₄)₄: 0.51 g (0.55 mmol) of [AsPh₄]₂[Dicyd] and 0.60 g (1.2 mmol) of [Ru(NH₃)₅(H₂O)](PF₆)₂ were placed in a 100 mL round bottom flask and purged with argon on a vacuum line. 80 mL of acetone was placed in a separate

flask and degassed. The acetone was then transferred to the reactant flask and the mixture stirred under argon for 2 hours. The yellow solution slowly turned green. The solution was then filtered through a medium glass frit, to remove the precipitated AsPh_4PF_6 , and exposed to air for 30 minutes to ensure complete oxidation. To this dark green solution was then added a solution of 3.6 g (11 mmol) tetrabutylammonium bromide in 20 mL of acetone and immediate precipitation of the crude dark green bromide salt occurred. This was then filtered through a fine glass frit and the collected precipitate was washed with 30 mL of cold acetone. The crude product was dried *in vacuo* before proceeding. Yield = 400 mg (86%).

The crude bromide salt was purified by dissolving it in a minimum amount of 0.3 M NaCl, filtering and loading the solution onto a 2.5 cm $\times$ 30 cm column of CM-Sephadex C25 cation exchange resin. Elution with a 0.3 M NaCl solution separated out a yellow band which was most likely due to unreacted ligand. Elution with a 1.0 M NaCl solution separated out a blue band (a mononuclear species with a charge of +2), followed by a green-blue band (the desired dinuclear complex with a charge of +4) and a very slow moving purple band (probably due to a protonated form of the dinuclear complex with a charge of +5). The green-blue band was completely eluted ($\approx$ 80 mL total volume) and added to a solution of 10g NaClO_4 in 15 mL of distilled water. This solution was placed in the fridge and precipitation of the perchlorate salt was afforded after about one hour. The fine precipitate was collected on a fine glass frit and washed with 0.5 mL of ice cold water, then dried *in vacuo*. The column pure product was recrystallized by ether diffusion. This was accomplished by dissolving the complex in a solution of 10 mL acetone and 1 mL distilled water in a small beaker and then placing it into a glass jar containing about 50 mL of diethyl ether. Precipitation of

microcrystalline product occurred after about 5 hours. The supernatant was then decanted and the product dried *in vacuo*. Yield = 60 mg (12%, based on starting reagents). Anal. Calcd.(%) for $C_8H_{34}N_{14}Cl_4O_{16}Ru_2 \cdot 4H_2O$: C, 9.62; H, 4.24; N, 19.64. Found(%): C, 9.75; H, 4.06; N, 19.26.

(μ -1,4-Dicyanamido-2,5-dimethylbenzene)bis

(pentaammineruthenium(III)) Perchlorate $[Ru_2(DM-Dicyd)](ClO_4)_4$: This complex was prepared in a similar way to $[Ru_2Dicyd](ClO_4)_4$, however, the following reagent amounts were used: $[Ru(NH_3)_5(H_2O)](PF_6)_2$ (0.50 g, 1 mmol); $[AsPh_4]_2[DM-Dicyd]$ (0.44 g, 0.45 mmol) and tetrabutylammonium bromide (3.0 g, 9 mmol). Yield = 380 mg (92%). Purification of this complex was also carried out in a similar manner to that of $[Ru_2Dicyd](ClO_4)_4$ except only 2–3 drops of water were used along with the 10 mL of acetone in the recrystallization and the yield was 74 mgs. (18%). Anal. Calcd.(%) for $C_{10}H_{38}N_{14}Cl_4O_{16}Ru_2 \cdot 1/6 C_3H_6O$: C, 13.08; H, 4.08; N, 20.34. Found(%): C, 13.06; H, 3.97; N, 20.12.

(μ -1,4-Dicyanamido-2,3,5,6-tetramethylbenzene)bis

(pentaammineruthenium(III)) Perchlorate $[Ru_2(TM-Dicyd)](ClO_4)_4$: This complex was prepared in a similar way to $[Ru_2Dicyd](ClO_4)_4$ with the following starting reagent amounts: $[Ru(NH_3)_5(H_2O)](PF_6)_2$ (0.54 g, 1.1 mmol); $[AsPh_4]_2[TM-Dicyd]$ (0.49 g, 0.5 mmol) and tetrabutylammonium bromide (3.2g, 10 mmol). Yield = 360 mg (88%). Purification of this complex was carried out in a similar fashion to that of $[Ru_2Dicyd](ClO_4)_4$ except that only 2–3 drops of water were used in the recrystallization. The yield was 78 mg (19%). Anal. Calcd.(%) for $C_{12}H_{42}N_{14}Cl_4O_{16}Ru_2 \cdot 1/6 C_3H_6O$: C, 15.13; H, 4.37; N, 19.76. Found(%): C, 15.25; H, 4.40; N, 19.84.

(μ -1,4-Dicyanamido-2,5-dichlorobenzene)bis

(pentaammineruthenium(III)) Chloride [Ru₂(DC-Dicyd)]Cl₄: The crude bromide salt was again synthesized in a manner similar to that of [Ru₂Dicyd](ClO₄)₄ using the following reagent amounts: [Ru(NH₃)₅(H₂O)](PF₆)₂ (0.49 g, 1 mmol); [AsPh₄]₂[DC-Dicyd] (0.40 g, 0.4 mmol) and tetrabutylammonium bromide (2.6 g, 8 mmol). Yield = 336 mg (85%). Purification of this complex was accomplished in a slightly different fashion. Elution from the cation exchange column required the use of 2.0 M NaCl to isolate the desired product. The eluted product ($\approx$ 200–250 mL) was concentrated by roto-evaporation and allowed to cool in the fridge overnight. The chloride salt which formed was filtered off and washed with 10 drops of ice cold water and then dried *in vacuo*. The dried product could be recrystallized out of water by acetone diffusion. The yield was 53 mg (17%). Anal. Calcd.(%) for C₈H₃₂N₁₄Cl₆Ru₂·3H₂O: C, 12.11; H, 4.79; N, 24.71. Found(%): C, 12.23; H, 4.58; N, 24.58.

(μ -1,4-Dicyanamido-2,3,5,6-tetrachlorobenzene)bis

(pentaammineruthenium(III)) Chloride [Ru₂(TC-Dicyd)]Cl₄: This complex was prepared in a similar manner to that of [Ru₂Dicyd](ClO₄)₄ using the following reagent amounts: [Ru₂(NH₃)₅(H₂O)](PF₆)₂ (0.49 g, 1 mmol); [AsPh₄]₂[TC-Dicyd] (0.42 g, 0.4 mmol) and tetrabutylammonium bromide (2.6 g, 8mmol). Yield = 337 mg (94%). Purification was carried out in the same fashion as for the [Ru₂(DC-Dicyd)]Cl₄ complex. The yield of the chloride salt was 20 mg (6%). Anal. Calcd.(%) for C₈H₃₀N₁₄Cl₈Ru₂·1/6 C₃H₆O: C, 12.48; H, 3.82; N, 23.97; Cl, 34.68. Found(%): C, 12.35; H, 3.85; N, 24.45; Cl, 34.55.

(μ -1,4-Dicyanamidobenzene)bis(pentaammineruthenium(III))

p-Toluenesulphonate [Ru₂(Dicyd)](CH₃C₆H₄SO₃)₄: This complex was prepared by R. J. Crutchley using a different method from that mentioned above. [Ru(NH₃)₅Cl]Cl₂ was reacted with the thallium salt of the 1,4-dicyanamidobenzene dianion in 1-methyl-2-pyrrolidinone for a period of about a week. It was isolated as a crude bromide salt and X-ray quality crystals were grown from an aqueous solution of the salt containing *p*-toluenesulphonate by acetone diffusion. The resulting crystal structure information was provided to the author for use in this thesis.

2.4 Physical Measurements

2.4.1 Infrared and NMR Spectra

Infrared spectra were recorded on a Bomem Michelson 120 spectrophotometer interfaced with a NEC Powermate i Advanced Personal Computer or a Perkin-Elmer 1600 Series FTIR spectrophotometer. Both spectrophotometers were online to a Hewlett-Packard Colorpro Plotter. All samples were prepared as KBr (oven dried) disks. Reference spectra of air were run prior to all sample spectra. Variable temperature ¹³C NMR were run on a Varian XL200 NMR spectrophotometer.

2.4.2 Electronic Spectra

Electronic spectra were recorded on a Perkin-Elmer Lambda 4B UV/Vis spectrophotometer online to an Epson FX-85 printer, a Cary 14 UV/Vis/NIR spectrophotometer or a Cary 5 UV/Vis/NIR spectrophotometer interfaced with a Raven 386/16 Personal Computer online to a Hewlett-Packard Laserjet IID

printer. All samples were run using matching quartz cells and a background correction was performed before each run.

2.4.3 Cyclic Voltammetry

Cyclic voltammetry was performed by using a PAR Model 170 electrochemistry system or a BAS CV-27 online to a BAS X-Y recorder. The electrochemical cell consisted of a double-jacketed glass container with an inner volume of approximately 15 mL. Cell temperature was controlled by means of a Haake D8-G refrigerated bath and circulator (accuracy ± 0.02 °C). The cell was fitted with a Teflon plug through which holes had been drilled to permit insertion of electrodes and an argon gas inlet and outlet tube. Non-aqueous cyclic voltammetry was performed in dry acetonitrile (0.1 M tetrabutylammonium hexafluorophosphate, TBAH) at 25 °C with a three-electrode system consisting of a platinum-disk working (BAS 1.6 mm diameter) and wire counter electrodes and a silver-wire quasi-reference electrode. Ferrocene ($E^\circ = 0.400$ V vs NHE) was used as an internal reference.⁸⁰ Aqueous cyclic voltammetry was performed in distilled water (pH $\approx$ 7, 0.1 M NaCl or 0.1 M NaClO₄) at 25 °C with a three electrode system consisting of a glassy-carbon working (BAS 5 mm diameter), platinum wire counter and saturated calomel reference electrodes.

2.4.4 X-ray Structure Determinations

Crystal structure determinations were performed at the National Research Council (NRC) Canada by Florence Lee, Corinne Bensimon and Eric Gabe. For all the bridging ligands the diffracted intensities were collected on a Nonius diffractometer using Mo K α radiation, with a 2θ scan technique with profile analysis.⁸¹ The diffracted intensities for [Ru₂(Dicyd)](CH₃C₆H₄SO₃)₄ were

collected at 295 K with Cu K α radiation using the $\theta/2\theta$ scan technique with profile analysis as before. The space groups were determined by systematic absences only.

The structures were solved by direct methods and refinements were done by full matrix least-squares. All the hydrogens were found by differences fourier. Their positional and isotropic thermal parameters were refined. All the calculations were performed with the NRCVAX Crystal Structure Package.⁸² Details on various other parameters for the individual compounds as well as bond distances and bond angles are presented in the appropriate sections.

2.4.5 Magnetic Susceptibility Measurements

Variable-temperature magnetic susceptibility measurements were performed at the Institute for Materials Research at McMaster University, Hamilton, Ontario, by Prof. J.E. Greedan and C.V. Stager using a Quantum Design Superconducting Quantum Interference Device (SQUID) magnetometer. The data analysis was performed by J.N. Reimers using the non-linear least squares fitting program GENFIT (M. Eitel, McMaster Univ., 1985).

2.5 Theoretical Calculations

Extended Hückel Molecular Orbital (EHMO) calculations were performed on the ligands using FORTICON 8⁸³ obtained through the Quantum Chemistry Program Exchange (QCPE), Indiana University, Dept. of Chemistry. Calculations were performed on a Raven 386 PC equipped with a 80387 coprocessor and using Microsoft Fortran 5.0. Data input files were constructed using bond length and bond angle information obtained from the relevant X-ray crystal structures and are listed in the Appendix.

CHAPTER 3

THE BRIDGING LIGANDS

3.1 Synthesis

In most cases the synthesis of the various Dicyd's was accomplished in a similar fashion to that of Hünig *et al.*⁶² by starting with the appropriately substituted phenylenediamine (Scheme 3.1). The phenylenediamines were reacted with benzoyl thiocyanate (formed from the reaction of benzoyl chloride with ammonium thiocyanate) to form (A) which upon heating in base gave the thiourea derivative (B). (B) was desulfurized with a heavy metal salt, lead(II) acetate, and upon gentle heating the dicyanamide dianion (C) was formed *in situ*. The dianion was then protonated with acetic acid and precipitated from solution as (D). The protonated H₂Dicyd (D) was then converted to a tetraphenylarsonium salt (E), [AsPh₄]₂[Dicyd], by deprotonation in base followed by addition of tetraphenylarsonium chloride in excess. The final product, (E), was soluble in various common organic solvents such as dimethylsulfoxide, methanol, ethanol and acetone.

During these syntheses care had to be taken to ensure complete deprotonation of H₂Dicyd in the conversion to [AsPh₄]₂[Dicyd], otherwise the product would consist of a mixture of protonated and deprotonated forms. This was readily diagnosed by using infrared spectroscopy. In the infrared, $\nu(\text{C}\equiv\text{N})$ for H₂Dicyd's occur at $\approx 2300\text{ cm}^{-1}$ whereas $\nu(\text{N}=\text{C}=\text{N})$ for Dicyd²⁻ dianions occur at $\approx 2100\text{--}2150\text{ cm}^{-1}$ (See Section 3.2).

Scheme 3.1

Another problem encountered during the synthesis of these compounds was their tendency to dimerize. Dimerization usually occurs during the desulfurization step if excessive heat is used (Scheme 3.2). The temperature must not be allowed to rise above 70°C for any length of time. Dimer formation can be detected using infrared spectroscopy. A strong band at $\approx 1680\text{ cm}^{-1}$ is present due to $\nu(\text{C}=\text{N})$ of the dimer (**F**).

Scheme 3.2

3.2 Infrared Spectroscopy

The infrared spectra of the five Dicyd's are shown in Figures 3.1–3.5. They all show the characteristic strong $\nu(\text{N}=\text{C}=\text{N})$ stretch in the range $2070\text{--}2110\text{ cm}^{-1}$ and strong aromatic $\nu(\text{C}=\text{C})$ stretches around $1400\text{--}1500\text{ cm}^{-1}$. These stretching frequencies are summarized in Table 3.1. It should be noted that as the electron withdrawing nature of the substituent on the phenyl rings increase (from CH_3 to Cl) so do the $\nu(\text{N}=\text{C}=\text{N})$ stretches. This is due to the increased electron density

Figure 3.1 IR Spectrum of $[\text{AsPh}_4]_2[\text{Dicyd}]$ (KBr Disk).

Figure 3.2 IR Spectrum of $[\text{AsPh}_4]_2[\text{DM-Dicyd}]$ (KBr Disk).

Figure 3.3 IR Spectrum of $[\text{AsPh}_4]_2[\text{TM-Dicyd}]$ (KBr Disk).

Figure 3.4 IR Spectrum of $[\text{AsPh}_4]_2[\text{DC-Dicyd}]$ (KBr Disk).

Figure 3.5 IR Spectrum of $[\text{AsPh}_4]_2[\text{TC-Dicyd}]$ (KBr Disk).

Table 3.1 Characteristic IR Bands for the Five Dicyd Ligands (cm⁻¹).

Ligand	$\nu(\text{N}=\text{C}=\text{N})^{\text{a}}$	$\nu(\text{C}=\text{C})^{\text{a}}$
TM-Dicyd ²⁻	2077(s)	1438(m),1402(m)
DM-Dicyd ²⁻	2093(s)	1498(m),1478(m),1438(m)
Dicyd ²⁻	2089(s)	1485(s),1437(m)
DC-Dicyd ²⁻	2100(s)	1483(m),1461(s),1439(s)
TC-Dicyd ²⁻	2104(s)	1481(m),1435(s)

^a s = strong, m = medium, w = weak.

on the amide nitrogen, leading to a shortening of the nitrile bond length from 1.19 Å in TM-Dicyd²⁻ to 1.16 Å in TC-Dicyd²⁻. Other major bands of note seen in these spectra include: weak aromatic C–H stretches in the range 3000–3100 cm⁻¹ and C–H bends in the range 680–760 cm⁻¹. The large broad band at $\approx$ 3380 cm⁻¹ was due to water, both in the ligands which are quite hygroscopic as well as the KBr itself.

3.3 X-Ray Crystallography

Crystals of each of the tetraphenylarsonium salts of the bridging ligands were readily grown from saturated dimethyl sulfoxide solutions. In most cases they were large rhombohedral shaped crystals which ranged in colour from yellow ([AsPh₄]₂[TC-Dicyd]) to orange ([AsPh₄]₂[Dicyd]) to red ([AsPh₄]₂[TM-Dicyd]).

Table 3.2 Crystallographic Data for [AsPh₄]₂[Dicyd].

Parameter	Value ^a
Empirical Formula	As ₂ N ₄ C ₅₆ H ₄₄
Formula Weight	922.82
Crystal Dimensions (mm)	0.20 × 0.20 × 0.25
Space Group	P2 ₁ /a
a, (Å)	9.7659(6)
b, (Å)	21.6128(13)
c, (Å)	11.1040(7)
β, (deg.)	110.560(10)
Z, (molecules/cell)	2
F(000), (electrons)	947.79
Vol., (Å ³)	2194.42(23)
d _{calc.} , (g/cm ³)	1.397
Lin. Abs. Coeff. (μ, mm ⁻¹)	1.56
Radiation, (Å)	0.70930
2θ(max), deg.	44.8
# Reflections Measured	4910
# Unique Reflections	2848
# Unique Reflections (I _{net} > 2.5σ (I _{net}))	1804
Last Least Squares Cycle Calcd.	53 atoms, 347 parameters, 1804 reflections
R _f (sig. refl.) ^b	0.040
R _w (sig. refl.) ^c	0.034
Goodness of Fit ^d	1.290
R _f (all refl.)	0.091
R _w (all refl.)	0.043
Max. shift/σ	0.633
Last D-map:	
Deepest Hole, (e/Å)	-0.360
Highest Peak, (e/Å)	0.340
Sec. Ext. Coeff.	0.150037

^aESD's are in parentheses and refer to the last digit printed.

^bR_f = Σ||F_o| - |F_c|| / Σ|F_o|. ^cR_w = [Σw(|F_o| - |F_c|)² / Σ(w|F_o|)²]^{1/2} where w = 1/σ²I.

^dGoodness of Fit = [Σw(|F_o| - |F_c|)² / (No. of refl. - No. of parameters)]^{1/2}

Table 3.3 Crystallographic Data for [AsPh₄]₂[DM-Dicyd].

Parameter	Value ^a
Empirical Formula	As ₂ N ₄ C ₅₈ H ₄₈
Formula Weight	950.88
Crystal Dimensions (mm)	0.20 × 0.20 × 0.20
Space Group	P 2 ₁ /n
a, (Å)	9.8860(14)
b, (Å)	16.416(5)
c, (Å)	14.909(3)
β, (deg.)	99.391(17)
Z, (molecules/cell)	2
F(000), (electrons)	1991.58
Vol., (Å ³)	2387.2(10)
d _{calc.} , (g/cm ³)	1.323
Lin. Abs. Coeff. (μ, mm ⁻¹)	2.87
Radiation, (Å)	0.70930
2θ(max), deg.	46.9
# Reflections Measured	3759
# Unique Reflections	3530
# Unique Reflections (I _{net} > 2.5σ(I _{net}))	1648
Last Least Squares Cycle Calcd.	56 atoms, 122 parameters, 1648 reflections
R _f (sig. refl.) ^b	0.084
R _w (sig. refl.) ^c	0.050
Goodness of Fit ^d	3.34
R _f (all refl.)	0.203
R _w (all refl.)	0.051
Max. shift/σ	0.029
Last D-map:	
Deepest Hole, (e/Å)	-0.920
Highest Peak, (e/Å)	0.790
Sec. Ext. Coeff.	0.114497

^aESD's are in parentheses and refer to the last digit printed.

^bR_f = $\Sigma ||F_0| - |F_c|| / \Sigma |F_0|$. ^cR_w = $[\Sigma w(|F_0| - |F_c|)^2 / \Sigma (w|F_0|)^2]^{1/2}$ where $w = 1/\sigma^2 I$.

^dGoodness of Fit = $[\Sigma w(|F_0| - |F_c|)^2 / (\text{No. of refl.} - \text{No. of parameters})]^{1/2}$

Table 3.4 Crystallographic Data for [AsPh₄]₂[TM-Dicyd].

Parameter	Value ^a
Empirical Formula	As ₂ N ₄ C ₆₆ H ₅₂
Formula Weight	966.84
Crystal Dimensions (mm)	0.20 × 0.25 × 0.30
Space Group	P2 ₁ /n
a, (Å)	12.6115(24)
b, (Å)	14.3029(17)
c, (Å)	13.6986(14)
β, (deg.)	100.820(10)
Z, (molecules/cell)	2
F(000), (electrons)	1011.79
Vol., (Å ³)	2427.0(6)
d _{calc.} , (g/cm ³)	1.323
Lin. Abs. Coeff. (μ, mm ⁻¹)	1.41
Radiation, (Å)	0.70930
2θ(max), deg.	44.8
# Reflections Measured	7669
# Unique Reflections	3142
# Unique Reflections (I _{net} > 2.5σ(I _{net}))	2180
Last Least Squares Cycle Calcd.	53 atoms, 299 parameters, 2180 reflections
R _f (sig. refl.) ^b	0.051
R _w (sig. refl.) ^c	0.051
Goodness of Fit ^d	2.427
R _f (all refl.)	0.090
R _w (all refl.)	0.055
Max. shift/σ	0.130
Last D-map:	
Deepest Hole, (e/Å)	-0.340
Highest Peak, (e/Å)	0.450
Sec. Ext. Coeff.	0.070806

^aESD's are in parentheses and refer to the last digit printed.

^bR_f = Σ||F_o| - |F_c|| / Σ|F_o|. ^cR_w = [Σw(|F_o| - |F_c|)² / Σ(w|F_o|)²]^{1/2} where w = 1/σ²I.

^dGoodness of Fit = [Σw(|F_o| - |F_c|)² / (No. of refl. - No. of parameters)]^{1/2}

Table 3.5 Crystallographic Data for [AsPh₄]₂[DC—Dicyd].

Parameter	Value ^a
Empirical Formula	As ₂ Cl ₂ N ₄ C ₅₆ H ₄₂
Formula Weight	991.71
Crystal Dimensions (mm)	0.30 × 0.40 × 0.20
Space Group	P2 ₁ /n
a, (Å)	9.8673(23)
b, (Å)	18.3696(19)
c, (Å)	13.1791(11)
β, (deg.)	102.875(14)
Z, (molecules/cell)	2
F(000), (electrons)	1011.8
Vol., (Å ³)	2328.8(6)
d _{calc.} , (g/cm ³)	1.414
Lin. Abs. Coeff. (μ, mm ⁻¹)	1.59
Radiation, (Å)	0.70930
2θ(max), deg.	44.9
# Reflections Measured	3068
# Unique Reflections	3041
# Unique Reflections (I _{net} > 2.5σ(I _{net}))	2685
Last Least Squares Cycle Calcd.	53 atoms, 374 parameters, 2685 reflections
R _f (sig. refl.) ^b	0.026
R _w (sig. refl.) ^c	0.020
Goodness of Fit ^d	4.02
R _f (all refl.)	0.033
R _w (all refl.)	0.020
Max. shift/σ	0.208
Last D-map:	
Deepest Hole, (e/Å)	-0.290
Highest Peak, (e/Å)	0.260
Sec. Ext. Coeff.	0.842389

^aESD's are in parentheses and refer to the last digit printed.

^bR_f = Σ||F_o| - |F_c|| / Σ|F_o|. ^cR_w = [Σw(|F_o| - |F_c||)² / Σ(w|F_o|)²]^{1/2} where w = 1/σ²I.

^dGoodness of Fit = [Σw(|F_o| - |F_c||)² / (No. of refl. - No. of parameters)]^{1/2}

Table 3.6 Crystallographic Data for [AsPh₄]₂[TC-Dicyd].

Parameter	Value ^a
Empirical Formula	AsCl ₂ N ₂ C ₂₈ H ₂₀
Formula Weight	530.30
Crystal Dimensions (mm)	0.20 × 0.20 × 0.40
Space Group	P1
a, (Å)	10.0609(10)
b, (Å)	10.2590(11)
c, (Å)	12.0028(14)
α, β, γ, (deg.)	101.936(11), 103.436(8), 90.783(10)
Z, (molecules/cell)	2
F(000), (electrons)	549.9
Vol., (Å ³)	1176.42
d _{calc.} , (g/cm ³)	1.497
Lin. Abs. Coeff. (μ, mm ⁻¹)	1.69
Radiation, (Å)	0.70930
2θ(max), deg.	0.0
# Reflections Measured	8199
# Unique Reflections	5627
# Unique Reflections (I _{net} > 2.5σ(I _{net}))	3606
Last Least Squares Cycle Calcd.	53 atoms, 379 parameters, 3606 reflections
R _f (sig. refl.) ^b	0.048
R _w (sig. refl.) ^c	0.029
Goodness of Fit ^d	1.974
R _f (all refl.)	0.095
R _w (all refl.)	0.031
Max. shift/σ	1.506
Last D-map:	
Deepest Hole, (e/Å)	-0.790
Highest Peak, (e/Å)	0.900
Sec. Ext. Coeff.	0.051620

^aESD's are in parentheses and refer to the last digit printed.

^bR_f = Σ||F_o| - |F_c|| / Σ|F_o|. ^cR_w = [Σw(|F_o| - |F_c||)² / Σ(w|F_o|)²]^{1/2} where w = 1/σ²I.

^dGoodness of Fit = [Σw(|F_o| - |F_c||)² / (No. of refl. - No. of parameters)]^{1/2}

Figure 3.6 $[\text{AsPh}_4]_2[\text{Dicyd}]$ a) ORTEP plot showing atom labelling scheme and 50% probability ellipsoids. Hydrogen atoms and $[\text{AsPh}_4]^+$ cations are not shown for clarity. b) Stereoview of the unit cell.

Figure 3.7 $[\text{AsPh}_4]_2[\text{DM-Dicyd}]$ a) ORTEP plot showing atom labelling scheme and 50% probability ellipsoids. Hydrogen atoms and $[\text{AsPh}_4]^+$ cations are not shown for clarity. b) Stereoview of the unit cell.

Figure 3.8 $[\text{AsPh}_4]_2[\text{TM-Dicyd}]$ a) ORTEP plot showing atom labelling scheme and 50% probability ellipsoids. Hydrogen atoms and $[\text{AsPh}_4]^+$ cations are not shown for clarity. b) Stereoview of the unit cell.

Figure 3.9 $[\text{AsPh}_4]_2[\text{DC-Dicyd}]$ a) ORTEP plot showing atom labelling scheme and 50% probability ellipsoids. Hydrogen atoms and $[\text{AsPh}_4]^+$ cations are not shown for clarity. b) Stereoview of the unit cell.

Figure 3.10 $[\text{AsPh}_4]_2[\text{TC-Dicyd}]$ a) ORTEP plot showing atom labelling scheme and 50% probability ellipsoids. Hydrogen atoms and $[\text{AsPh}_4]^+$ cations are not shown for clarity. b) Stereoview of the unit cell.

Table 3.7 Selected Bond Lengths (Å) and Angles (°) for Dicyd²⁻.

C(2)—H(2)	0.98(5)	C(1)—C(2)—H(2)	115(3)
C(1)—C(2)	1.399(9)	C(1)—C(2)—C(3)	123.0(5)
C(2)—C(3)	1.385(9)	C(2)—C(1)—C(3) ^a	114.9(5)
C(1)—N(1)	1.388(8)	C(2)—C(1)—N(1)	119.1(5)
N(1)—C(4)	1.299(10)	C(1)—N(1)—C(4)	118.7(5)
N(2)—C(4)	1.172(10)	N(1)—C(4)—N(2)	174.1(6)

Out-of-Plane Distances (Å)

N(1): 0.031(13) C(2): 0.097(16) N(2): 0.201(19)

Table 3.8 Atomic Parameters x, y, z and B_{iso} ^a for Dicyd²⁻.

	x	y	z	B_{iso}
N(1)	0.5426(5)	0.29489(22)	0.3650(4)	3.8(3)
N(2)	0.7843(6)	0.36206(24)	0.3644(5)	5.2(3)
C(1)	0.5270(6)	0.4465(3)	0.4335(5)	3.1(3)
C(2)	0.3900(7)	0.4595(3)	0.4413(5)	3.5(3)
C(3)	0.3637(6)	0.5106(3)	0.5151(5)	3.1(3)
C(4)	0.6726(9)	0.3799(3)	0.3684(5)	3.7(3)
H(2)	0.312(5)	0.4301(22)	0.397(4)	4.0
H(3)	0.268(5)	0.5181(23)	0.503(5)	3.8

^a B_{iso} is the mean of the principal axes of the thermal ellipsoid.

NOTE: Estimated Standard Deviations (ESD's) are in brackets and refer to the last digit printed.

Table 3.9 Selected Bond Lengths (Å) and Angles (°) for DM-Dicyd²⁻.

C(3)—H(3)	1.100(18)	C(2)—C(4)—C(5)	121.4(17)
N(1)—C(1)	1.18(3)	C(3) ^a —C(2)—C(4)	118.2(15)
N(2)—C(1)	1.28(3)	C(2)—C(4)—C(3)	120.3(17)
N(2)—C(2)	1.426(22)	N(2)—C(2)—C(4)	123.9(18)
C(4)—C(5)	1.525(24)	C(1)—N(2)—C(2)	120.9(16)
C(2)—C(4)	1.39(3)	N(1)—C(1)—N(2)	177.9(23)

Out-of-Plane Distances (Å)			
N(2): -0.02(4)	C(1): 0.06(5)	N(1): 0.15(7)	

Table 3.10 Atomic Parameters x,y,z and B_{iso}^a for DM-Dicyd²⁻.

	x	y	z	B _{iso}
N(1)	-0.0677(21)	0.7900(12)	0.1941(13)	8.3(14)
N(2)	0.0982(14)	0.8657(9)	0.1148(9)	4.5(9)
C(1)	0.0057(22)	0.8250(12)	0.1591(13)	4.9(15)
C(2)	0.0557(22)	0.9329(9)	0.0563(11)	3.4(11)
C(3)	0.0929(22)	1.0388(11)	-0.0481(10)	4.2(11)
C(4)	0.1415(19)	0.9737(11)	0.0059(11)	4.0(11)
C(5)	0.2898(16)	0.9473(10)	0.0078(11)	5.1(10)
H(3)	0.083	1.190	-0.096	4.8

^aB_{iso} is the mean of the principal axes of the thermal ellipsoid.

NOTE: Estimated Standard Deviations (ESD's) are in brackets and refer to the last digit printed.

Table 3.11 Selected Bond Lengths (Å) and Angles (°) for TM-Dicyd²⁻.

C(4)—C(1)	1.531(12)	C(4)—C(1)—C(2)	121.7(7)
C(1)—C(3) ^a	1.405(12)	C(1)—C(2)—C(3)	121.8(7)
C(1)—C(2)	1.416(12)	C(2)—C(1)—C(3) ^a	117.8(8)
C(2)—N(1)	1.410(11)	C(1)—C(2)—N(1)	120.8(8)
N(1)—C(5)	1.283(14)	C(2)—N(1)—C(5)	121.6(7)
C(5)—N(2)	1.187(14)	N(1)—C(5)—N(2)	174.6(9)
C(3)—C(6)	1.547(10)	C(4)—C(1)—C(3) ^a	121.0(7)

Out-of-Plane Distances (Å)

N(1): -0.11(3) C(5): 0.70(4) N(2): 1.41(5)

Table 3.12 Atomic Parameters x,y,z and B_{iso}^a for TM-Dicyd²⁻.

	x	y	z	B _{iso}
N(1)	0.5471(6)	0.4492(4)	0.3157(6)	4.9(4)
N(2)	0.5952(6)	0.5569(5)	0.1903(6)	6.1(4)
C(1)	0.5983(7)	0.5327(5)	0.4743(6)	4.0(4)
C(2)	0.5238(7)	0.4779(5)	0.4079(6)	3.9(4)
C(3)	0.4283(6)	0.4440(5)	0.4337(6)	3.7(4)
C(4)	0.7062(6)	0.5625(6)	0.4483(6)	5.2(5)
C(5)	0.5725(7)	0.5082(7)	0.2534(7)	4.3(5)
C(6)	0.3520(6)	0.3826(5)	0.3582(5)	4.6(4)

^aB_{iso} is the mean of the principal axes of the thermal ellipsoid.

NOTE: Estimated Standard Deviations (ESD's) are in brackets and refer to the last digit printed.

Table 3.13 Selected Bond Lengths (Å) and Angles (°) for DC-Dicyd²⁻.

Cl(1)—C(3)	1.740(3)	Cl(1)—C(3)—C(2)	118.92(21)
C(2)—C(3)	1.392(4)	C(2)—C(3)—C(4)	122.10(24)
C(3)—C(4)	1.379(4)	C(3)—C(2)—C(4) ^a	114.96(24)
N(2)—C(2)	1.392(3)	N(2)—C(2)—C(3)	119.53(23)
N(2)—C(1)	1.301(4)	N(2)—C(2)—C(4) ^a	125.51(25)
N(1)—C(1)	1.160(4)	C(1)—N(2)—C(2)	118.38(22)
C(4)—H(4)	0.857(21)	N(1)—C(1)—N(2)	174.2(3)

Out-of-Plane Distances (Å)

N(2): 0.003(3) C(1): 0.216(5) N(1): 0.305(6)

Table 3.14 Atomic Parameters *x,y,z* and *B*_{iso}^a for DC-Dicyd²⁻.

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{iso}
Cl	0.31768(7)	0.96919(4)	1.05046(6)	4.88(4)
C(1)	0.0179(3)	0.80482(17)	0.95150(22)	4.30(16)
C(2)	0.0495(3)	0.92818(15)	0.98368(18)	3.55(14)
C(3)	0.1394(3)	0.98515(15)	1.02200(19)	3.49(13)
C(4)	-0.0916(3)	0.94632(16)	0.96122(21)	3.75(14)
N(1)	-0.0486(3)	0.75236(13)	0.93366(21)	6.16(15)
N(2)	0.10354(22)	0.85947(13)	0.97190(18)	4.64(13)
H(4)	-0.1556(21)	0.9144(11)	0.9427(16)	3.0(6)

^a*B*_{iso} is the mean of the principal axes of the thermal ellipsoid.

NOTE: Estimated Standard Deviations (ESD's) are in brackets and refer to the last digit printed.

Table 3.15 Selected Bond Lengths (Å) and Angles (°) for TC-Dicyd²⁻.

Cl(1)—C(1)	1.728(4)	Cl(1)—C(1)—C(2)	120.1(3)
C(1)—C(2)	1.374(6)	C(1)—C(2)—C(3)	122.3(4)
C(1)—C(3)	1.426(6)	Cl(2)—C(2)—C(3)	115.7(3)
C(3)—N(1)	1.360(6)	C(2)—C(3)—N(1)	118.9(4)
N(1)—C(4)	1.299(6)	C(3)—N(1)—C(4)	130.1(4)
C(4)—N(2)	1.167(4)	N(1)—C(4)—N(2)	168.8(5)
Cl(2)—C(2)	1.744(4)	C(1) _a —C(3)—C(2)	112.5(4)

Out-of-Plane Distances (Å)

Cl(1): 0.047 Cl(2): 0.013 N(1): 0.015(6) C(4): 0.153(12) N(2): 0.290(16)

Table 3.16 Atomic Parameters x, y, z and B_{iso} ^a for TC-Dicyd²⁻.

	x	y	z	B_{iso}
Cl(1)	0.88530(12)	0.54855(12)	0.24951(9)	4.34(6)
Cl(2)	1.18638(12)	0.48099(13)	0.32588(10)	4.78(7)
C(1)	0.9483(4)	0.5234(4)	0.3896(3)	2.86(21)
C(2)	1.0816(4)	0.4915(4)	0.4242(4)	3.01(21)
C(3)	0.8569(4)	0.5354(4)	0.4654(4)	2.91(22)
N(1)	0.7241(4)	0.5678(3)	0.4438(3)	3.66(19)
C(4)	0.6503(5)	0.6087(4)	0.3551(4)	3.35(23)
N(2)	0.5684(4)	0.6489(4)	0.2865(3)	5.09(25)

^a B_{iso} is the mean of the principal axes of the thermal ellipsoid.

NOTE: Estimated Standard Deviations (ESD's) are in brackets and refer to the last digit printed.

The relevant X-ray crystallographic data and data collection details are summarized in Tables 3.2–3.6. An ORTEP diagram and stereoview of the unit cell for each ligand are shown in Figures 3.6–3.10. Selected bond lengths and bond angles, out-of-plane distances, as well as the atomic positional parameters and isotropic thermal displacement parameters (B_{iso}) are shown in Tables 3.7–3.16. The refinement in all cases was quite good with the unweighted residual (R_f) for all significant reflections being less than 5%.

All of the ligands except TM-Dicyd²⁻ are planar, the terminal nitrile nitrogen being no more than 0.3 Å out of the plane formed by the central phenyl ring. The cyanamide (N–C–N) groups in all cases are trans to each other and close to linear, with the N–C–N bond angle ranging from 168.8°–177.9°. In TM-Dicyd²⁻ the cyanamide moiety is bent significantly out of the phenyl ring plane (see Fig. 3.8). The terminal nitrogen is 1.4 Å out of the plane. The reason for this is most likely due to the steric hindrance that the methyl groups impart on the cyanamide groups thereby pushing them out of the plane.

The nitrile bond length varies from 1.6 Å to 1.9 Å depending on the electron withdrawing nature of the substituents on the phenyl ring, i.e. the more electron withdrawing the substituent, the shorter the bond. An easy way of seeing why these bond changes take place is by comparing the two resonance forms that exist for cyanamides.

As the electron withdrawing nature of R_1 and R_2 increases, resonance form (II) becomes more favored. The phenyl ring carbon to cyanamide bond length varies from 1.43 Å in DM-Dicyd²⁻ to 1.36 Å in TC-Dicyd²⁻ which is also explainable by the above reasoning and fall in the range of average to short C-N single bonds.⁸⁴ Finally, the ring carbon-carbon bonds have lengths typical of substituted benzenes with the bond lengths of adjacent carbons not attached to the cyanamide groups being slightly shorter (≈ 0.01 – 0.05 Å) than the others.

Each dianion has, of course, associated with it two tetraphenylarsonium (AsPh_4)⁺ cations. Data for these has not been included since it is not relevant to any future discussions. Tetraphenylarsonium was a convenient and useful counterion to use in the synthesis and crystal growth of these ligands. A thallium salt of Dicyd²⁻ has recently been prepared.⁸⁵

3.4 Cyclic Voltammetry

The cyclic voltammetry of the five bridging ligands was performed in acetonitrile using a platinum working and counter electrode, a silver wire pseudo-reference electrode and the ferrocene/ferrocenium couple (0.400 V vs. NHE) as an internal reference.⁸⁰ The five cyclic voltammograms are shown in Figures 3.11–3.15 and the redox potentials are summarized in Table 3.17. All of the ligands showed two characteristic one-electron redox processes.

The dependence of the reversibility of the two processes on the scan rate was investigated. The anodic to cathodic peak separation (ΔE_{a-c}) for the first of

Figure 3.11 Cyclic Voltammogram of $[\text{AsPh}_4]_2[\text{Dicyd}]$ in acetonitrile.

Figure 3.12 Cyclic Voltammogram of $[\text{AsPh}_4]_2[\text{DM-Dicyd}]$ in acetonitrile.

Figure 3.13 Cyclic Voltammogram of $[\text{AsPh}_4]_2[\text{TM-Dicyd}]$ in acetonitrile.

Figure 3.14 Cyclic Voltammogram of $[\text{AsPh}_4]_2[\text{DC-Dicyd}]$ in acetonitrile.

Figure 3.15 Cyclic Voltammogram of $[\text{AsPh}_4]_2[\text{TC-Dicyd}]$ in acetonitrile.

Table 3.17 Ligand Redox Potentials^{a,b,c}

Ligand	$E_{L_1}^0$	$E_{L_2}^0$	$\Delta E^0(\log K)$
TM-Dicyd ²⁻	-0.565(130)	-0.070(60)	0.495(8.4)
DM-Dicyd ²⁻	-0.545(130)	+0.095(60)	0.640(10.8)
Dicyd ²⁻	-0.465(125)	+0.210(65)	0.675(11.4)
DC-Dicyd ²⁻	-0.175(75)	+0.465(60)	0.640(10.8)
TC-Dicyd ²⁻	-0.025(80)	+0.570(70)	0.595(10.1)

^aVolts vs. NHE. ^bNumbers in brackets refer to ΔE_{a-c} in mV at 100 mV/s scan rate. ^cMeasured on ≈ 1 mM solutions in acetonitrile at 25° C at a scan rate of 100 mV/s. Ionic strength = 0.1M tetrabutylammoniumhexafluorophosphate (TBAPF₆).

these couples ($E_{L_1}^0$) was found to increase upon increasing the scan rate and is therefore defined as quasi-reversible. (For example, for DM-Dicyd²⁻ $\Delta E_{a-c} = 105$ mV at 20 mV/s and 230 mV at 200 mV/s). The second couples' peak to peak separation was scan rate independent and hence this process was reversible. In all cases the anodic to cathodic current ratios (I_a/I_c) at a scan rate of 100 mV/s were close to unity. This is indicative of chemical reversibility.

The separations of the respective redox couples ($E_{L_2}^0 - E_{L_1}^0$) and hence the thermodynamic stability of the radical anion form of the ligand ($L^{\cdot-}$) are given (along with the corresponding equilibrium constants, K) in the last column in Table 3.17. The stability constants increase and reach a maximum on going from TM-Dicyd²⁻ to Dicyd²⁻ and then drop off slightly on going to TC-Dicyd²⁻. A very similar pattern was seen in the data of Hünig *et al.*⁶³ (difference in the first

two columns in Table 1.4) for the DCNQi redox behaviour in methylene chloride. (Recall that DCNQi is the two electron oxidation product of Dicyd²⁻). The reason for this trend is not clear at present. In all cases, however, logK was greater than 8 and therefore all the radical anion intermediates show great thermodynamic stability. The trends in $E_{L_1}^0$ and $E_{L_2}^0$ are dependent on the nature of the phenyl substituent with both couples becoming more anodic as the electron withdrawing ability of the substituent increases. A similar trend was also reported by Hünig⁶³ who went further to find a relatively good correlation between $E_{L_2}^0$ and Hammett σ -constants. The five ligands span a range of 0.54 eV for $E_{L_1}^0$ and 0.64 eV for $E_{L_2}^0$. Hence, a good degree of "tunability" is possible.

3.5 Nuclear Magnetic Resonance

NMR was not used as a primary characterization tool for the ligands. The ¹H NMR were quite complicated owing to the phenyl ring protons on the [AsPh₄]⁺ cations and were not investigated further. ¹³C NMR was used in an attempt to determine the energy barrier to rotation about the phenyl ring carbon-cyanamide amide nitrogen bond (i.e. the activation energy of syn/anti isomerization). This was accomplished by running low temperature ¹³C NMR of the [AsPh₄]₂[DC-Dicyd] ligand in both *d*₄-methanol (m.p. = -94°C) and in *d*₆-ethanol (m.p. = -130°C). The ¹³C NMR in *d*₄-methanol at four different temperatures are shown in Figure 3.16. These gave the best results. The room temperature NMR (Figure 3.16a) shows the resonance assignments. As the temperature is lowered the four DC-Dicyd²⁻ carbon resonances slowly broaden, with the cyanamide carbon resonance (d) being the first to disappear into the baseline at $\approx -60^\circ\text{C}$. As the temperature is lowered further, ideally, two distinct resonances corresponding to syn and anti isomers should be observed. However,

Figure 3.16 200 MHz ^{13}C NMR of $[\text{AsPh}_4]_2[\text{DC-Dicyd}]$ at various temperatures. a) Room temperature (22°C) run showing resonance assignments and chemical shifts. b) -15°C.

Figure 3.16 (Cont.) c) -50°C. d) -60°C, coalescence.

when the temperature drops below -60°C , precipitation of the ligand occurs at the concentrations needed to maintain an adequate signal. If the concentration of the ligand is dropped sufficiently to prevent precipitation the signal is not strong enough and no distinct resonances appear.

Therefore only a rough estimate of the upper limit of the activation energy (E_a) can be made from this data. An equation for the rate of syn/anti interconversion at coalescence has been determined by Gutowsky and Holm,⁸⁶

$$k_{\text{int}} = \sqrt{2\pi} \Delta\nu_0 \quad (3.1)$$

where $\Delta\nu_0$ is the frequency separation of the peaks in the absence of interchange (i.e. in the slow exchange limit where $\tau\Delta\nu_0 \gg 1$ and τ is the mean lifetime of each species). Since the data presented only covers fast and intermediate exchange, an estimate of $\Delta\nu_0$ using the broadened line of the cyanamide carbon at -60°C will be used. The peak width at half height is approximately 2 ppm or 400 Hz which leads to a value of $k_{\text{int}} \approx 1000 \text{ s}^{-1}$. Using the Arrhenius equation,

$$k_{\text{int}} = \kappa \frac{kT}{h} \exp(-E_a/RT) \quad (3.2)$$

where k_{int} is defined as above, k is Boltzman's constant, h is Planck's constant

and κ is the transmission coefficient and is assumed to be unity for intramolecular processes,^{87,88} one can obtain the activation energy (E_a). This was found to be ≈ 9 kcal mol⁻¹. Since $\Delta\nu_0$ is more than likely larger than 400 Hz this value of E_a can be considered an upper limit (i.e. $E_a \leq 9$ kcal mol⁻¹).

The activation energy for syn/anti isomerization of the N-cyanoimine group of various DCNQI derivatives was found to be in the range 13–17 kcal mol⁻¹ by Hünig *et al.*⁶² For the DCNQI's there is a double bond between the ring carbon and the amide nitrogen (1.30 Å in DCNQI).⁶¹ For DC-Dicyd²⁻ (as well as Dicyd²⁻) the bond length is 1.39 Å and the significantly lower E_a is consistent. Therefore, the barrier to rotation about this bond is greatly reduced on going from DCNQI to Dicyd²⁻ and the latter will not necessarily maintain its planar rigidity in solution.

3.6 Electronic Spectra

The electronic spectra of the ligands were not investigated in any detail since the ligands were extremely air sensitive *in situ* and the spectra are largely obscured by the strong $\pi \rightarrow \pi^*$ transitions due to the eight phenyl rings of the tetraphenylarsonium cations. The spectra of [AsPh₄]₂[TC-Dicyd] and [AsPh₄][DC-Dicyd] were recorded in methanol and the key transitions are reported along with the dinuclear metal complexes in Section 4.4.1.

CHAPTER 4

DINUCLEAR METAL COMPLEXES

4.1 Synthesis

Although the synthesis of the various diruthenium(III)pentaammine ligand complexes appears relatively straightforward (see Scheme 4.1) the route travelled was not. $[\text{Ru}(\text{NH}_3)_5(\text{OH}_2)](\text{PF}_6)_2$ was reacted with the appropriate Dicyd²⁺ ligand in a 2.2:1 ratio. (This slight excess over 2:1 was found to give an optimum yield). The reaction mixture was air-oxidized and a crude bromide salt (B) isolated. Purification of this crude salt was then afforded by using cation-exchange chromatography followed by isolation by an appropriate anion (C) and then careful recrystallization, usually from a mixed solvent system. In many cases molecules of solvation, such as acetone, water and even ether, are present in the pure product. Drying the product for any length of time at

Scheme 4.1

elevated temperatures leads to the decomposition of the complex. In most cases the yields were quite low ($\approx 20\%$) due to the fact that several different products were formed, the lability of the second ruthenium coordination site and the loss of material precipitating or "sticking" to the column resin.

The column chromatography afforded a most colorful display of the several species that were formed as the reaction was quenched. Since a cation-exchange resin was used the species with the lowest positive charge were eluted first. The general order of the bands for most of the complexes was: (1) a yellow-orange band most likely due to unreacted ligand which would have a charge of -2 , and moved quite rapidly; (2) a much slower moving blue band characterized by UV-Vis and IR spectroscopy as a mononuclear $[\text{Ru}(\text{NH}_3)_5\text{HDicyd}]^{2+}$ but with no consistent elemental analysis; (3) a violet band which was not characterized but was most likely due to the protonated form of the previous band, i.e., $[\text{Ru}(\text{NH}_3)_5\text{H}_2\text{Dicyd}]^{3+}$; (4) the desired blue-green product band $[\text{Ru}_2(\text{Dicyd})]^{4+}$ and; (5) a very slow moving purple band almost certainly due to a protonated dimer, either $[\text{Ru}_2(\text{HDicyd})]^{5+}$ or $[\text{Ru}_2(\text{H}_2\text{Dicyd})]^{6+}$. These latter specie(s) were also seen when acid was added to a solution of (4).

Precipitation onto the column appeared to be a problem for the chloro-substituted complexes, $[\text{Ru}_2(\text{TC-Dicyd})]^{4+}$ and $[\text{Ru}_2(\text{DC-Dicyd})]^{4+}$. These complexes generally moved down the column much slower than the others and the more concentrated electrolyte solutions needed to elute them added to the problem of precipitation and resulted in the lowest product yields of the dinuclear complexes.

The final products, whether they were chloride or perchlorate salts, were soluble in water and dimethylsulfoxide. The latter were also slightly soluble in acetone. The recrystallized complexes could usually be stored under argon in the

freezer for up to a year without losing their integrity. Exposure to air and light would turn the blue-green microcrystalline product black within six months. Regeneration of the original product from this was not attempted.

4.2 Infrared Spectroscopy

The infrared spectra of the five complexes are shown in Figures 4.1–4.5. They all display the characteristic $\nu(\text{N}=\text{C}=\text{N})$ stretch shifted very slightly to lower energies with respect to the free ligands (see Table 3.1). This shift in most cases is only $\approx 2 \text{ cm}^{-1}$. The shift to lower frequencies is consistent with the π -stabilization imparted by the Ru(III) on the cyanamide moiety. However, this shift is not as large as may be expected due to the "push-pull" effect the Ru(III) has on the distribution of electron density over the cyanamide group. A lengthening of the terminal C–N bond due to electron density being shifted to Ru(III) leads to a shortening of the internal N–C bond due to electron density being shifted from the amide nitrogen and the overall N–C–N "length" remains relatively unchanged. Hence, only small changes are observed in the infrared. The specific bond length changes as they apply to $[\text{Ru}_2(\text{Dicyd})]^{4+}$ versus Dicyd^{2-} will be discussed in the next section.

The NH_3 stretches are seen in the range $3100\text{--}3350 \text{ cm}^{-1}$ and the bending mode is seen at $\approx 1620 \text{ cm}^{-1}$. Similar values were reported by Nakamoto⁸⁹ for mononuclear ruthenium(III)pentaammine complexes. In three of the complexes; $[\text{Ru}_2(\text{Dicyd})](\text{ClO}_4)_4$, $[\text{Ru}_2(\text{DM-Dicyd})](\text{ClO}_4)_4$ and $[\text{Ru}_2(\text{TM-Dicyd})](\text{ClO}_4)_4$, the characteristic vibrations of the perchlorate anion show up in the range $1085\text{--}1110 \text{ cm}^{-1}$. This range is also consistent with ionic perchlorate complexes reported by Nakamoto.⁸⁹ All of the important infrared bands seen in these dinuclear complexes are summarized in Table 4.1.

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Figure 4.1 IR Spectrum of $[\text{Ru}_2(\text{Dicyd})](\text{ClO}_4)_4$, (KBr Disk).

Figure 4.2 IR Spectrum of [Ru₂(DM-Dicyd)](ClO₄)₄, (KBr Disk).

Figure 4.3 IR Spectrum of [Ru₂(TM-Dicyd)](ClO₄)₄, (KBr Disk).

Figure 4.4 IR Spectrum of [Ru₂(DC-Dicyd)]Cl₄, (KBr Disk).

Figure 4.5 IR Spectrum of [Ru₂(TC-Dicyd)]Cl₄, (KBr Disk).

Table 4.1 Characteristic IR Bands for the Five Metal Complexes (cm⁻¹)^a

Complex	$\nu(\text{NCN})$	$\delta(\text{NH}_3)$	$\nu(\text{ClO})$
[Ru ₂ (TM-Dicyd)](ClO ₄) ₄	2068(s)	1619(m)	1110(s)
[Ru ₂ (DM-Dicyd)](ClO ₄) ₄	2088(s)	1623(m)	1088(s)
[Ru ₂ (Dicyd)](ClO ₄) ₄	2087(s)	1625(m)	1091(s)
[Ru ₂ (DC-Dicyd)]Cl ₄	2098(s)	1624(m)	—
[Ru ₂ (TC-Dicyd)]Cl ₄	2102(s)	1623(m)	—

^as = strong, m = medium.

4.3 X-Ray Crystallography

The growth of X-ray quality crystals of the dinuclear complexes proved quite difficult. Nevertheless, one of them, [Ru₂(Dicyd)](CH₃PhSO₃)₄, was crystallographically characterized. The X-ray crystallographic data and data collection parameters are given in Table 4.2. An ORTEP diagram and the unit cell are shown in Figure 4.6 and a labelling scheme is given in Figure 4.7. Finally, selected bond lengths and angles as well as atomic positional parameters are summarized in Tables 4.3 and 4.4.

The refinement of this crystal structure was reasonable, with the unweighted residual (R_f) for the significant reflections being 6.3%. The unit cell was quite large with a volume of 5580 Å³. This is due to the fact that it contains two distinct coordination forms of the [Ru₂(Dicyd)]⁴⁺ dimer. As can be seen in Figures 4.6a and 4.7 there is a "linear" form (A) in which the Ru(1)–N(6)–C(1) bond angle is 175° and a "bent" form (B) in which the corresponding bond angle

Table 4.2 Crystallographic Data for $[\text{Ru}_2(\text{Dicyd})](\text{CH}_3\text{PhSO}_3)_4 \cdot \text{acetone}$

Parameter	Value ^a
Empirical Formula	$\text{Ru}_2\text{S}_4\text{O}_{13}\text{N}_{14}\text{C}_{39}\text{H}_{60}$
Formula Weight	1263.35
Crystal Dimensions (mm)	$0.20 \times 0.20 \times 0.10$
Space Group	$\text{P2}_1/\text{c}$
a , (Å)	7.5861(6)
b , (Å)	23.0450(19)
c , (Å)	32.078(3)
β , (deg.)	95.771(7)
Z , (molecules/cell)	4
$F(000)$, (electrons)	2207
Vol., (Å ³)	5579.5
$d_{\text{calc.}}$, (g/cm ³)	1.504
Lin. Abs. Coeff. (μ , mm ⁻¹)	6.33
Radiation, (Å)	1.54056 (Cu)
$2\theta(\text{max})$, deg.	99.8
# Reflections Measured	5746
# Unique Reflections	5728
# Unique Reflections ($I_{\text{net}} > 2.5\sigma(I_{\text{net}})$)	3947
Last Least Squares Cycle Calcd.	134 atoms, 415 parameters, 3947 reflections
R_f (sig. refl.) ^b	0.063
R_w (sig. refl.) ^c	0.048
Goodness of Fit ^d	3.71
R_f (all refl.)	0.097
R_w (all refl.)	0.049
Max. shift/ σ	0.604
Last D-map:	
Deepest Hole, (e/Å ³)	-0.610
Highest Peak, (e/Å ³)	1.110

^aESD's are in parentheses and refer to the last digit printed.

^b $R_f = \Sigma||F_o| - |F_c|| / \Sigma|F_o|$. ^c $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma(w|F_o|)^2]^{1/2}$ where $w = 1/\sigma^2 I$.

^dGoodness of Fit = $[\Sigma w(|F_o| - |F_c|)^2 / (\text{No. of refl.} - \text{No. of parameters})]^{1/2}$

Figure 4.6 $[\text{Ru}_2(\text{Dicyd})](\text{CH}_3\text{PhSO}_3)_4 \cdot \text{acetone}$ ORTEP plot with 50% probability ellipsoids. Hydrogen atoms and $[\text{CH}_3\text{PhSO}_3]^-$ anions are not shown for clarity. b) Stereoview of the unit cell.

Figure 4.7 Diagram showing the atomic labelling scheme for $[\text{Ru}_2(\text{Dicyd})]^{4+}$.

Table 4.3 Selected Bond Lengths (Å) and Angles (°) for $[\text{Ru}_2(\text{Dicyd})]^{4+}$.

Ru(1)–N(1)	2.078(10)	N(1)–Ru(1)–N(2)	92.0(4)
Ru(1)–N(2)	2.118(10)	N(1)–Ru(1)–N(4)	178.1(4)
Ru(1)–N(5)	2.138(11)	N(1)–Ru(1)–N(6)	89.2(4)
Ru(1)–N(6)	1.938(11)	N(2)–Ru(1)–N(3)	179.6(4)
Ru(2)–N(8)	2.129(10)	N(2)–Ru(1)–N(6)	88.1(4)
Ru(2)–N(9)	2.119(11)	N(5)–Ru(1)–N(6)	177.9(4)
Ru(2)–N(10)	2.121(11)	N(8)–Ru(2)–N(10)	86.9(4)
Ru(2)–N(11)	2.161(12)	N(8)–Ru(2)–N(11)	176.5(5)
Ru(2)–N(12)	2.103(11)	N(8)–Ru(2)–N(13)	87.4(5)
Ru(2)–N(13)	1.969(13)	N(9)–Ru(2)–N(10)	177.0(4)
N(6)–C(1)	1.151(19)	N(10)–Ru(2)–N(13)	93.7(5)
N(7)–C(1)	1.298(19)	N(12)–Ru(2)–N(13)	174.8(5)
N(7)–C(2)	1.376(17)	Ru(1)–N(6)–C(1)	175.1(10)
N(13)–C(5)	1.188(24)	Ru(2)–N(13)–C(5)	149.8(12)
N(14)–C(5)	1.28(3)	N(6)–C(1)–N(7)	171.5(15)
N(14)–C(6)	1.468(23)	C(1)–N(7)–C(2)	119.7(12)
C(2)–C(3)	1.406(20)	N(7)–C(2)–C(3)	117.6(12)
C(2)–C(4)	1.386(20)	N(7)–C(2)–C(4)	124.2(13)
C(3)–C(4) ^a	1.386(20)	C(3)–C(2)–C(4)	118.2(12)
C(6)–C(7)	1.40(3)	C(2)–C(3)–C(4) ^a	120.8(12)
C(6)–C(8)	1.28(3)	N(13)–C(5)–N(14)	169.6(18)
C(8)–C(7) ^b	1.49(3)	N(14)–C(6)–C(7)	110.5(17)
Ru(1)–Ru(1) ^a	13.11(10)	N(14)–C(6)–C(8)	127.2(18)
Ru(2)–Ru(2) ^a	13.27(11)	C(5)–N(14)–C(6)	117.1(15)
Ru(1)–Ru(2)	7.61(5)	C(7)–C(6)–C(8)	122.2(17)
		C(6)–C(7)–C(8) ^b	116.9(16)

Table 4.4 Atomic Parameters x, y, z and B_{iso}^a for $[Ru_2(Dicyd)]^{4+}$.

	x	y	z	B_{iso}
Ru(1)	0.97921(15)	0.84318(5)	0.16553(4)	3.03(6)
Ru(2)	0.47067(16)	0.56419(5)	0.19502(4)	3.92(7)
N(1)	0.7062(13)	0.8482(4)	0.1666(3)	3.22(25)
N(2)	1.0122(13)	0.9318(4)	0.1820(3)	3.5(3)
N(3)	0.9483(13)	0.7553(4)	0.1490(3)	3.25(25)
N(4)	1.2620(14)	0.8350(5)	0.1650(3)	3.6(3)
N(5)	1.0025(15)	0.8191(4)	0.2302(3)	3.9(3)
N(6)	0.9512(14)	0.8670(4)	0.1073(3)	3.3(3)
N(7)	0.8912(14)	0.8965(5)	0.0341(4)	4.3(3)
N(8)	0.6705(14)	0.6072(4)	0.1646(3)	4.1(3)
N(9)	0.2659(14)	0.6192(5)	0.1683(3)	4.9(3)
N(10)	0.6763(14)	0.5118(5)	0.2247(3)	4.7(3)
N(11)	0.2780(17)	0.5158(6)	0.2262(4)	4.3(3)
N(12)	0.5007(15)	0.6243(5)	0.2446(4)	4.1(3)
N(13)	0.4339(17)	0.5137(5)	0.1454(4)	5.6(3)
N(14)	0.3110(19)	0.4967(6)	0.0724(5)	7.7(4)
C(1)	0.9280(19)	0.8845(6)	0.0736(5)	4.2(4)
C(2)	0.9485(17)	0.9479(6)	0.0184(4)	3.4(3)
C(3)	0.8906(17)	0.9617(6)	-0.0234(4)	3.5(3)
C(4)	1.0614(18)	0.9865(6)	0.0410(4)	4.1(3)
C(5)	0.3868(24)	0.5077(8)	0.1092(6)	6.9(5)
C(6)	0.422(3)	0.4990(7)	0.0375(6)	6.6(5)
C(7)	0.3195(24)	0.4879(8)	-0.0007(7)	8.6(6)
C(8)	0.586(3)	0.5126(7)	0.0392(5)	6.7(5)

^a B_{iso} is the mean of the principal axes of the thermal ellipsoid.

NOTE: Estimated Standard Deviations (ESD's) are in brackets and refer to the last digit printed.

is only 150° . The existence of two forms may be due to crystal packing forces, the nature of the counterion or perhaps even the presence of the acetone of solvation. A crystal structure of the same complex with a different counterion may provide the answer.

Let us now consider specific bond length and bond angle changes in the $[\text{Ru}_2(\text{Dicyd})]^{4+}$ complex in comparison to the free ligand, Dicyd^{2-} (Section 3.3). As already alluded to in the previous section, the overall N—C—N length does not change significantly upon coordination. The nitrile bond length, N(6)—C(1), in the linear form, (A), is 1.15 Å and in the bent form, (B), N(13)—C(5) is 1.19 Å compared with a value of 1.17 Å in the free Dicyd^{2-} . The internal amide nitrogen to carbon bond is 1.30 Å in (A) (N(7)—C(1)) and 1.28 Å in (B) (N(14)—C(5)) compared with 1.30 Å in Dicyd^{2-} . However, the bond that connects the cyanamide group to the phenyl ring does show some marked changes. In form (A) N(7)—C(2) is 1.38 Å which is close to that of the free Dicyd^{2-} value of 1.39 Å but the corresponding bond in form (B) N(14)—C(6) is longer at 1.47 Å and one can conclude that there is little double bond character here. Typical N—C single bonds are 1.43 Å.⁸⁴ Also when comparing the ring carbon—carbon bond lengths, those for the linear form are quite similar to the free ligand, however, the bent form phenyl ring bonds show significant distortion. They range from 1.28 Å (C(6)—C(8)) to 1.49 Å (C(8)—C(7)b) whereas in the free ligand they only range from 1.39–1.40 Å.

A crystal structure determination has been reported for a mononuclear ruthenium phenylcyanamide complex,⁹⁰ $[(\text{NH}_3)_5\text{Ru}(2,3\text{-Cl}_2\text{pcyd})][\text{SO}_4] \cdot \text{C}_2\text{H}_5\text{OH}$ where pcyd^- is the phenylcyanamide anion, and shows similar bond length and angle values to the linear form, (A), reported here. The Ru—N—C bond angle was found to be 171.4° , the nitrile bond length, 1.17 Å, and the amide nitrogen to

Figure 4.8 Diagram showing complete contents of the unit cell (including counterions and acetone of solvation) with labelling scheme.

cyanamide carbon bond length, 1.31 Å. The amide nitrogen to phenyl ring carbon bond is somewhat intermediate to those reported here at 1.42 Å.

The ruthenium atoms in both dimer types are in essentially octahedral environments. None of the N–Ru–N angles deviate by more than 4° from a right angle. The ruthenium–cyanamide bond in (A), Ru(1)–N(6), is 1.94 Å and in (B), Ru(2)–N(13) is 1.97 Å compared with a value of 1.98 Å in the mononuclear complex.⁹⁰ There does not appear to be any significant *trans*-effect on the ammine trans to the cyanamide since all of the ruthenium–ammine nitrogen

bonds in both forms are quite similar, ranging from 2.08–2.16 Å. The values for the mononuclear complex ranged from 2.10–2.14 Å.

The overall planarity of complex dimer form (A) with respect to the free ligand appears reasonably well maintained. The best plane formed by N(6)–Ru(1)–N(2)–N(5)–N(3) is tilted by only 12° with respect to the phenyl ring formed by C(2)–C(3)–C(4)a–C(2)a–C(3)a–C(4). However, the same dihedral angle for form (B), measured between the best planes formed by N(13)–Ru(2)–N(8)–N(11)–N(12) and C(6)–C(7)–C(8)b–C(6)b–C(7)b–C(8), is 30° and planarity is essentially lost. The key difference in this form being, of course, the non-linearity of the Ru(2)–N(13)–C(5) bond angle.

Finally and most importantly, the intra- and intermolecular metal–metal distances reported in Table 4.3 should be mentioned. For dimer (A) the Ru(1)–Ru(1)a through bond distance (shortest path) is 15.7 Å and the through space distance is 13.1 Å. For dimer (B) the Ru(2)–Ru(2)b through bond distance is 15.9 Å and the through space distance is 13.3 Å. The intermolecular distance for Ru(1)–Ru(2) is 7.6 Å.

4.4 Electronic Spectra

4.4.1 Spectral Assignments

The UV–Vis–(NIR) spectra for the five dinuclear complexes are shown in Figures 4.9–4.13. Electronic absorption data for all of the complexes as well as two of the ligands are reported in Table 4.5. An extensive discussion on the individual band assignments has appeared elsewhere for mononuclear penta-ammineruthenium(III) phenylcyanamide complexes^{90,91} and only a brief discussion will be presented here.

Figure 4.9 UV-Vis-NIR absorption spectrum of $[\text{Ru}_2(\text{Dicyd})](\text{ClO}_4)_4$ in D_2O . Inset shows NIR region. $[\text{Ru}_2(\text{Dicyd})]^{4+} = 8.74 \times 10^{-5} \text{ M}$.

Figure 4.10 UV-Vis-NIR absorption spectrum of $[\text{Ru}_2(\text{DC-Dicyd})]\text{Cl}_4$ in D_2O . $[\text{Ru}_2(\text{DC-Dicyd})]^{4+} = 3.98 \times 10^{-5} \text{ M}$.

Figure 4.11 UV-Vis-NIR absorption spectrum of $[\text{Ru}_2(\text{TM-Dicyd})](\text{ClO}_4)_4$ in D_2O . Inset shows NIR region. $[\text{Ru}_2(\text{TM-Dicyd})]^{4+} = 7.20 \times 10^{-5} \text{ M}$.

Figure 4.12 UV-Vis-NIR absorption spectrum of $[\text{Ru}_2(\text{DM-Dicyd})](\text{ClO}_4)_4$ in D_2O . $[\text{Ru}_2(\text{DM-Dicyd})]^{4+} = 4.53 \times 10^{-5} \text{ M}$.

Figure 4.13 (top) UV-Vis absorption spectrum for the reduction of $[\text{Ru}_2(\text{TC-Dicyd})]\text{Cl}_4$ showing fully oxidized (III,III), mixed valent (II,III), and reduced (II,II), species. (bottom) NIR region of the same reduction showing presence of IT transition in (II,III) species. $[\text{Ru}_2(\text{TC-Dicyd})]^{4+} = 8.30 \times 10^{-5} \text{ M}$.

Table 4.5 Electronic Spectroscopy Data for the Free Ligands and the Dinuclear Metal Complexes^a

Compound	$\pi^* \leftarrow \pi$	LMCT	
		$b_1^* \leftarrow b_2$	$b_1^* \leftarrow b_1$
<u>Ligand</u>^b			
[AsPh ₄] ₂ [TC-Dicyd]	218(4.86),283(4.23) 373(3.54)	—	—
[AsPh ₄] ₂ [DC-Dicyd]	220(4.91),293(4.46) 366(3.62)	—	—
<u>Complex</u>			
[Ru ₂ (TC-Dicyd)]Cl ₄	225(4.54),278(4.23) 325(sh)	402(3.67)	713(3.93)
[Ru ₂ (DC-Dicyd)]Cl ₄	216(4.55),272(4.49) 320(3.91)	376(3.76)	803(4.13)
[Ru ₂ (Dicyd)](ClO ₄) ₄	211(4.53),266(4.20) 345(3.62)	385(3.62)	865(4.12) ^c
[Ru ₂ (DM-Dicyd)](ClO ₄) ₄	211(4.53),264(4.26) 307(3.85)	352(3.70)	892(4.20) 1046(4.24)
[Ru ₂ (TM-Dicyd)](ClO ₄) ₄	213(4.58),252(4.16) 353(3.50)	465(3.50)	795(3.91) 975(3.85)

^a All ligand data were recorded in acetonitrile. All complex data recorded in D₂O. Values are in nm (log ϵ in parenthesis). sh = shoulder.

^b Cyanamide absorptions complicated by tetraphenylarsonium counterions.

^c Broad band.

As mentioned earlier, the anionic cyanamide group is a resonance stabilized π -system ($\text{Ph-N}^-\text{C}\equiv\text{N} \leftrightarrow \text{Ph-N}=\text{C}=\text{N}^-$) which when coordinated to Ru(III) should shift its resonance to the $\text{Ph-N}=\text{C}=\text{N}^-$ form. The three atom π -system contains two pairs of non-bonding electrons of π -symmetry that can delocalize into it. This leads to two orthogonal molecular orbitals, π_1 and π_2 . If one focusses on the Ru(III)-NCN chromophore the two ligand orbitals, upon mixing with the appropriate metal orbitals, give rise to two ligand to metal charge transfer (LMCT) transitions in the visible region of the spectrum. The lower energy LMCT bands (710–1950 nm) have been assigned to an allowed $b_1^* \leftarrow b_1$ ($d\pi^* \leftarrow \pi_1$) transition and the higher energy LMCT (350–465 nm) to a formally symmetry forbidden $b_1^* \leftarrow b_2$ ($d\pi^* \leftarrow \pi_2$) transition. In the complex spectra, the UV region usually contains three strong bands which are also seen in the ligand spectra of $[\text{AsPh}_4]_2[\text{DC-Dicyd}]$ and $[\text{AsPh}_4]_2[\text{TC-Dicyd}]$ and are assigned to ligand based $\pi^* \leftarrow \pi$ transitions. The band positions for these transitions are quite similar in the complex and free ligand, however, the intensities are much larger in the free ligand owing to the additional phenyl rings of the tetraphenylarsonium cations.

In most cases the band properties for the dimers are similar to the monomers with two notable exceptions. The $d\pi^* \leftarrow \pi_1$ transition is shifted to somewhat lower energies and both LMCT bands have approximately twice the intensity of the analogous mononuclear complexes. Compare, for instance, $[\text{Ru}_2(\text{DC-Dicyd})]\text{Cl}_4$, which has LMCT transitions at 376 and 803 nm and extinction coefficients of 6200 and 13500 $\text{M}^{-1} \text{cm}^{-1}$ respectively, with $[\text{Ru}(2,3\text{-Cl}_2\text{pcyd})](\text{ClO}_4)_2$, which has bands at 356 and 629 nm and extinction coefficients of 2900 and 5200 $\text{M}^{-1} \text{cm}^{-1}$ respectively. The approximate doubling in intensity is, of course, consistent with the fact that there are two Ru(III) units

present. The lowering of the low energy LMCT band energy is probably due to the fact that the DC-Dicyd²⁻ HOMO lies higher in energy than the corresponding HOMO of 2,3-Cl₂pcyd²⁻. The DC-Dicyd²⁻ is also much easier to oxidize than 2,3-Cl₂pcyd⁻ ($E^0 = -0.175$ V vs. NHE for DC-Dicyd²⁻ versus 0.617 V vs. NHE for 2,3-Cl₂pcyd⁻).

A curious feature of the last three complexes in Table 4.5 is the splitting of the low energy LMCT band. A similar splitting has been seen for the mononuclear complexes that contain electron donating species (methyl and methoxy) on the phenyl ring.^{92,93} Fine structure is also seen in the high energy LMCT transition of [Ru(2,3-Cl₂pcyd)](ClO₄)₂ mentioned above. The origin in both cases was blamed on vibronic interactions or possibly underlying ligand field transitions. In the present case the possibility of syn/anti isomerization had to be investigated. This was accomplished by measuring the electronic spectrum of [Ru₂(DM-Dicyd)](ClO₄)₄ over a range of temperatures and monitoring the separated peaks. The spectra were run from 6.5°C to 86.5°C and very little change was observed in the band splitting. Over this temperature range the band at 898 nm shifted little and decreased in intensity by < 10%. The band at 1046 nm shifted to lower energies (≈ 1082 nm at 86.5°C) and increased by $\approx 6\%$ in intensity. Although the changes are small, they are still consistent with there being distinct syn and anti isomers present. However, if syn and anti isomers are present, it is unlikely that the splitting would *increase* as the electron donating ability of the cyanamide increased since the phenyl ring to amide nitrogen bond length also increases (see Section 3.3) thus leading to more facile rotation and *less* chance of separate syn and anti isomers. The barrier to rotation for [AsPh₄]₂[DC-Dicyd] has already been determined to be small (see Section 3.3). There is, however, still the possibility that a coupled form of the

dimer exists at low temperature and a decoupled form at higher temperatures. This will require further investigation over a larger temperature range.

Another possible explanation for the splitting is the fact that the crystal structure of $[\text{Ru}_2(\text{Dicyd})](\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)_4$ shows two distinct dimers and each dimer would have its own slightly different LMCT band energy. These two forms could exist in solution for the above dimer as well as its perchlorate salt and the perchlorate salts of $[\text{Ru}_2(\text{DM-Dicyd})]^{4+}$ and $[\text{Ru}_2(\text{TM-Dicyd})]^{4+}$ which show significantly larger splittings.

4.4.2 Intervalence Charge Transfer and Electronic Coupling

In order to investigate the intervalence charge transfer properties of these complexes a suitable method for the generation of the mixed-valent, (II,III) species, had to be found. Since all of the dimers are in the fully oxidized, (III,III) forms it was found that reduction over Zn/Hg amalgam *in situ*, while monitoring the electronic absorption spectrum, was effective in generating first the green (II,III) species and then the fully reduced yellow (II,II) species. If the reduction was allowed to proceed for more than five hours, in most cases decomposition would occur and a grey precipitate would inevitably form in the flask. The three vis-NIR spectra for the $[\text{Ru}_2(\text{TC-Dicyd})]\text{Cl}_4$ complex are shown in Figure 4.13. All of the other complexes show similar reduction characteristics in the ultra-violet and visible spectral regions. However, as the electron donating ability of the phenyl ring substituents increases it becomes harder to fully reduce the complexes to the (II,II) form and premature precipitation occurs. The one marked difference between the $[\text{Ru}_2(\text{TC-Dicyd})]\text{Cl}_4$ reduction spectra and the others can be seen in the bottom of Figure 4.13. Here it is clearly observed that a band forms at ≈ 1220 nm, reaches a maximum and then diminishes. This band

has been assigned to an intervalence transfer (IT) transition of the (II,III) mixed-valent $[\text{Ru}_2(\text{TC-Dicyd})]^{3+}$. The band is not observed in the (III,III) or (II,II) species or the free ligand. The proximity of this band to the low energy LMCT does not rule out its presence in the other complexes, whose LMCT bands move to lower energies thereby possibly obscuring any IT band. (The presence of a very weak shoulder on the low energy side of the LMCT in the $[\text{Ru}_2(\text{DC-Dicyd})]\text{Cl}_4$ reduction spectra appears to be real, but its weakness and closeness to the much more intense band make it very difficult to analyze). The band in Figure 4.13 for $[\text{Ru}_2(\text{TC-Dicyd})]^{3+}$, while still a shoulder, can at least be roughly diagnosed.

Using the Hush model^{26,39} for weak electronically coupled systems, expressed in Equation 1.3 and again below, a good estimate of the upper limit of the electronic coupling constant in the $[\text{Ru}_2(\text{TC-Dicyd})]^{3+}$ complex can be achieved.

$$H_{ab} = 2.05 \times 10^{-2} \left[\frac{\epsilon_{\max} \Delta \nu_{\frac{1}{2}}}{\nu_{\max}} \right]^{\frac{1}{2}} \frac{\nu_{\max}}{r}$$

The parameter values for $[\text{Ru}_2(\text{TC-Dicyd})]^{3+}$ are: $\epsilon_{\max} \leq 600 \text{ M}^{-1} \text{ cm}^{-1}$, $\Delta \nu_{\frac{1}{2}} = 4100 \text{ cm}^{-1}$, $\nu_{\max} = 8200 \text{ cm}^{-1}$ and $r = 13.2 \text{ \AA}$. This leads to a value of $H_{ab} \leq 185 \text{ cm}^{-1}$ (0.02 eV) which falls in the category of weakly coupled, Class II, systems.^{34,38} Hush also predicted the bandwidth ($\Delta \nu_{\frac{1}{2}}$) for weakly coupled system to be given by,

$$\Delta \nu_{\frac{1}{2}} = (2310 \nu_{\max})^{\frac{1}{2}} \quad (4.1)$$

and the calculated bandwidth of 4300 cm^{-1} is comparable to the observed value of 4100 cm^{-1} . Significantly narrower bands, on the order of a factor of two or even three are seen in strongly coupled, Class III, systems. For example, the *t*-butyl-malonitrile bridged species mentioned in the Introduction (see Table 1.1) shows a $\Delta\nu_{\frac{1}{2}} = 2100\text{ cm}^{-1}$ ($\nu_{\text{max}} = 8500\text{ cm}^{-1}$) but from Equation 4.1, $\Delta\nu_{\frac{1}{2}} = 4400\text{ cm}^{-1}$.

The H_{ab} value for any of the other dinuclear complexes will not be significantly different from the above value since no major spectral changes (other than a diminishing in LMCT intensities) occur upon reduction. It would seem, therefore, that all of the systems show very weak electronic coupling. This spectral evidence alone is not sufficient and further proof from the electrochemical properties of these complexes is presented next.

4.5 Cyclic Voltammetry

4.5.1 Redox Potentials

The cyclic voltammograms of all five complexes in aqueous solution are shown in Figures 4.14–4.18. They all show similar patterns of one larger redox process followed by two smaller ones. These can be broken down as follows (see Scheme 4.2): the first redox process with a half wave potential defined as E_M^* is actually two closely overlapping one-electron transfer processes centered at the metals (i.e. consecutive $\text{Ru}^{2+}/3+$ couples, $E_{M_1}^0$ and $E_{M_2}^0$). The smaller waves consist of ligand centered redox processes (i.e. $\text{L}^{2-}/-$ and $\text{L}^{-}/0$ couples, $E_{L_1}^0$ and $E_{L_2}^0$). The redox potentials are summarized in Table 4.6.

Figure 4.14 Cyclic voltammogram of $[\text{Ru}_2(\text{Dicyd})](\text{ClO}_4)_4$ in H_2O (0.1 M NaCl) at a scan rate of 100 mV s^{-1} .

Figure 4.15 Cyclic voltammogram of $[\text{Ru}_2(\text{DM-Dicyd})](\text{ClO}_4)_4$ in H_2O (0.1 M NaCl) at a scan rate of 100 mV s^{-1} .

Figure 4.16 Cyclic voltammogram of $[\text{Ru}_2(\text{TM-Dicyd})](\text{ClO}_4)_4$ in H_2O (0.1 M NaCl) at a scan rate of 100 mV s^{-1} .

Figure 4.17 Cyclic voltammogram of $[\text{Ru}_2(\text{TC-Dicyd})]\text{Cl}_4$ in H_2O (0.1 M NaClO_4) at a scan rate of 100 mV s^{-1} .

Figure 4.18 Cyclic voltammograms of $[\text{Ru}_2(\text{DC-Dicyd})]\text{Cl}_4$ in H_2O (0.1 M NaClO_4) at scan rates of 100 mV s^{-1} . a) positive scan limit: 0.8 V vs. SCE. b) positive scan limit: 1.2 V vs. SCE.

Scheme 4.2

Table 4.6 Redox Potentials for the Dinuclear Complexes^a

Complex ^b	E _M [*]	E _{L₁} ^o	E _{L₂} ^o
Ru ₂ (TM-Dicyd)	-0.083	0.475	0.822
Ru ₂ (DM-Dicyd)	-0.073	0.539	0.912
Ru ₂ (Dicyd)	-0.051	0.632	0.981
Ru ₂ (DC-Dicyd)	-0.003	0.814	1.13
Ru ₂ (TC-Dicyd)	-0.033	0.892	1.03 ^c

^a Values are in volts vs. NHE. E_m^* corresponds to two overlapping one-electron transfer processes. ^b The counterions have been left out for clarity. ^c Anodic potential only.

The evidence for the first wave consisting of two unresolvable metal centered waves is threefold. First, the current intensity (anodic peak height + cathodic peak height) is approximately twice as large as that for the two smaller ligand centered waves. This is consistent with the fact that two electrons are involved instead of one. Second, the anode peak to cathode peak separation is scan rate independent (20–200 mV/s) but significantly greater than the 59 mV predicted for a reversible couple. There is actually a slight shoulder evident in the CV of $[\text{Ru}_2(\text{DM-Dicyd})](\text{ClO}_4)_4$ (see Figure 4.15). This is evidence for two closely spaced but not identical reversible one-electron couples. The cyclic voltammograms of similar mononuclear $[\text{Ru}(\text{NH}_3)_5\text{pcyd}](\text{ClO}_4)_2$ complexes show reversible metal centered waves with separations of 60 mV.⁹¹ And third, the position of the half-wave potential (E_M^*) at slightly less than 0 V vs. NHE is comparable to that seen for the $\text{Ru}^{2+/3+}$ couple for the same $[\text{Ru}(\text{NH}_3)_5\text{pcyd}](\text{ClO}_4)_2$ complexes mentioned above. For example, $E^0(\text{Ru}^{2+/3+})$ for $\text{Ru}(\text{NH}_3)_5(2,3\text{-Cl}_2\text{pcyd})^{2+/3+}$ is -0.095 V vs. NHE.

It should also be noted that with regards to the second point just mentioned, Taube and coworkers^{41,42,94} have seen similar large peak to peak separations for dinuclear rutheniumpentaammine complexes bridged by various bipyridine ligands.

The smaller, ligand based waves, are shifted to much more anodic potentials than the corresponding free ligand waves. This shift ranges from 0.92 V to 1.1 V for $E_{L_1}^0$ and from 0.67 V to 0.89 V for $E_{L_2}^0$. This effect is almost certainly due to the π -stabilization afforded the ligand upon complexation. The two ligand waves are scan rate dependent but in most cases the anodic to cathodic current ratios are close to unity. The exceptions being those that are close to the solvent limit, i.e. $[\text{Ru}_2(\text{DC-Dicyd})]\text{Cl}_4$ and $[\text{Ru}_2(\text{TC-Dicyd})]\text{Cl}_4$.

They are both, therefore, classified as quasi-reversible.

For the above mentioned complexes whose second ligand potentials ($E_{L_2}^0$) are high and close to the solvent limit (≈ 1.3 V vs NHE for H_2O at a pH of 7) complications arise (see Figures 4.17 and 4.18). For $[Ru_2(DC-Dicyd)]Cl_4$ the metal centered wave (E_M^*) and the first ligand wave ($E_{L_1}^0$) behave in a similar way to those of the other complexes (Figure 4.18a), however, as the potential is raised past the second ligand oxidation potential chemical reversibility is lost and on the return reduction sweep significant loss of current intensity in the corresponding reduction (cathodic) waves is seen as well as some additional waves (Figure 4.18b). In the case of $[Ru_2(TC-Dicyd)]Cl_4$ it is not possible to go beyond the second ligand oxidation potential since the solvent limit is reached first. Some loss of reduction current intensity is observed on the return sweep if the potential is maintained at > 1.0 V vs. NHE for any length of time (> 20 seconds).

4.5.2 The Comproportionation Constant and Electronic Coupling

In order to assess the electronic coupling using the redox potentials, the individual metal potentials must be determined. This means E_M^* must be resolved into two separate potentials, $E_{M_1}^0$ and $E_{M_2}^0$, as defined in Scheme 4.2. Once this has been accomplished K_c , as defined in Equation 4.2, is easily determined from the difference in these two potentials.

Myers and Shain⁹⁵ have developed a method of determining ΔE^0 from the experimentally determined values of $E_p - E_{p/2}$ (the difference between the peak

potential and the half peak potential). Calculations were carried out by them, using numerical methods derived earlier,⁹⁶ and a data set obtained. Using their data a plot can be constructed and the appropriate values obtained. The method can be used for both stationary-pulse voltammetry or cyclic voltammetry.

Richardson and Taube⁹⁴ have extended this work and applied it to binuclear ruthenium pentaammines. In this work a much more extensive data set was constructed where ΔE^0 could be determined from ΔE_p (the anode to cathode peak separation) as well as from $E_p - E_{p/2}$. Using the data given in reference 94 a plot of ΔE_p versus ΔE^0 was constructed and is shown in Figure 4.19. Once ΔE^0 has been determined, the individual E_M^0 values for the two one-electron transfer steps can be determined from a plot of $|E_{p(\text{cathodic})} - E_1^0|$ (data also obtained from reference 94) versus ΔE^0 . This plot is shown in Figure 4.20. Table 4.7 summarizes the metal centered redox potentials and reports the K_c values which were determined using Equation 1.7.

Before discussing the K_c values that were obtained, mention must be made of the two major assumptions that are made in using the above analysis. First, each separate redox process must be reversible over a wide scan range and second, the switching potential (E_s) must be at least 250 mV beyond (i.e. more negative than) E_M^* to minimize peak distortion. The second criterion has been met and the first appears to be valid.

The values for the comproportionation constants (K_c) reported in the last column of Table 4.7 are all less than 30 with the value for $\text{Ru}_2(\text{TM-Dicyd})$ approaching the statistical limit of 4. Similar low values of K_c were reported by Sutton and Taube^{41,42} for various bipyridine bridged ruthenium pentaammines which showed comparable electrochemical behaviour to the complexes investigated here. They reported values from 6.7 for a μ -(4,4'-dipyridyl-

Figure 4.19 Plot of ΔE_p versus ΔE^0 for the data in reference 94.

Figure 4.20 Plot of $|E_{p(cat)} - E_1^0|$ versus ΔE^0 for the data in reference 94.

Table 4.7 Metal Centered Redox Potentials and Comproportionation Constants^a

Complex ^b	ΔE_p	ΔE^0	$E_{M_1}^0$	$E_{M_2}^0$	K_c
Ru ₂ (TM-Dicyd)	72	50	-0.108	-0.058	7
Ru ₂ (DM-Dicyd)	120	85	-0.117	-0.032	28
Ru ₂ (Dicyd)	85	60	-0.081	-0.021	10
Ru ₂ (DC-Dicyd)	110	78	-0.042	0.036	21
Ru ₂ (TC-Dicyd)	92	65	-0.067	-0.002	13

^a ΔE_p refers to the anodic to cathodic peak to peak separation. ΔE^0 is the actual separation between the individual metal redox couples ($E_{M_2}^0 - E_{M_1}^0$). All potential values are in mV. K_c is unitless. ^b The counterions have been left out for clarity.

methane) bridged species to 26 for a μ -(4,4'-dipyridylamine) bridged complex. In all cases they observed an intervalence transfer (IT) band which was relatively weak ($\epsilon_{\max} < 1000 \text{ M}^{-1} \text{ cm}^{-1}$) and the bandwidth ($\Delta\nu_{\frac{1}{2}}$) was equal to or greater than that predicted by the Hush model in Equation 4.1. Their conclusion was that their complexes fell into the Class II category of weakly coupled systems. This conclusion must also be arrived at in the present case since the parallels with Taube's systems, both through the spectroscopic and electrochemical data, are strong. Thermodynamically a low K_c value means that the "plateau" of stability for the mixed-valent (II,III) system is quite narrow and that its existence is transient upon reduction of the (III,III) complex (or oxidation of the (II,II)). This also explains why it is difficult to isolate pure solid (II,III) mixed-valence complexes.

4.6 Variable Temperature Magnetic Susceptibility

4.6.1 Curve Fitting

Magnetic susceptibility measurements of all of the complexes were made over the temperature range 5–300 K using a superconducting quantum interference device (SQUID) magnetometer. The measurements were made at McMaster University, Hamilton, by Professor John E. Greedan using 30–50 mg of the complex in either pellet or powder form. The fitted plots of molar magnetic susceptibility versus temperature are shown in Figures 4.21–4.25. The raw data was fitted using a modified version of the Bleaney–Bowers equation for $S = 1/2$ spin-coupled dimers mentioned in the Introduction (Equation 1.11) and shown below.

$$\chi_m = C/(T-\theta) + (2Ng^2\beta^2/3kT)[1-1/3\exp(-2J/kT)]^{-1} + \chi_0 \quad (4.3)$$

Here g is the powder averaged g -value and J is the exchange coupling constant the same as in Equation 1.11 but two other terms have been added. The first, a Curie–Weiss term, corrects for any paramagnetic impurity at low temperatures (seen in all of these complexes) and χ_0 , which is a correction for any background paramagnetism. Using the least-squares fitting program GENFIT the raw data was fitted by optimizing J , g , C , θ and χ_0 .

Four of the six complexes show characteristic antiferromagnetic behaviour. The curve shapes are similar to that shown in Figure 1.3. (Note that data for both $[\text{Ru}_2(\text{Dicyd})](\text{ClO}_4)_4$ and $[\text{Ru}_2(\text{Dicyd})](\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)_4$ was collected). The broad maxima in these cases is characteristic of *intramolecular* exchange. *Intermolecular* antiferromagnetic couplings usually result in a phase transition to

Figure 4.21 Molar magnetic susceptibility from 5 to 300 K in a 1.0 T field for $[\text{Ru}_2(\text{Dicyd})](\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)_4$. (The solid line is a fit to equation 4.3 which yields the parameters in Table 4.8).

Figure 4.22 Molar magnetic susceptibility from 5 to 300 K in a 1.0 T field for $[\text{Ru}_2(\text{TM-Dicyd})](\text{ClO}_4)_4$. (The solid line is a fit to equation 4.3 which yields the parameters given in Table 4.8).

Figure 4.23 Molar magnetic susceptibility from 5 to 300 K in a 1.0 T field for $[\text{Ru}_2(\text{DC-Dicyd})]\text{Cl}_4$. (The solid line is a fit to equation 4.3 which yields the parameters given in Table 4.8).

Figure 4.24 Molar magnetic susceptibility from 5 to 300 K in a 1.0 T field for $[\text{Ru}_2(\text{TC-Dicyd})]\text{Cl}_4$. (The solid line is a fit to equation 4.3 which yields the parameters given in Table 4.8).

Figure 4.25 Molar magnetic susceptibility from 5 to 300 K in a 1.0 T field for $[\text{Ru}_2(\text{TC-Dicyd})]\text{Cl}_4$. (The solid line is a fit to the Ising model, see equation 4.6, which yields the parameters given in Table 4.8).

a long-range ordered state which gives a sharp maximum at the transition temperature (Neel temperature). Intermolecular exchange is seen in monomeric Ru(III) complexes with similar ligands but the effect occurs at much lower temperatures than those observed here.⁴⁸ Each ruthenium(III) has a low spin d^5 configuration and therefore has one unpaired electron. The susceptibility at high temperatures is low because the spins on each metal are randomly oriented with respect to each other. As the temperature is decreased the spins become increasingly aligned until χ_m reaches a maximum at T_c (the critical temperature). As the temperature is lowered further, χ_m decreases dramatically as the spins become paired. χ_m should theoretically drop to zero as the temperature is decreased further. All of the complexes here have a singlet

Table 4.8 Summary of Magnetic Susceptibility Data^a

Complex	g	J	C	θ
$[\text{Ru}_2(\text{TM-Dicyd})](\text{ClO}_4)_4$	1.76	-53.5	0.047	-2.2
$[\text{Ru}_2(\text{DM-Dicyd})](\text{ClO}_4)_4$	—	diag.	—	—
$[\text{Ru}_2(\text{Dicyd})](\text{ClO}_4)_4$	—	diag.	—	—
$[\text{Ru}_2(\text{Dicyd})](\text{OTs})_4$	1.95	-100	0.014	-0.651
$[\text{Ru}_2(\text{DC-Dicyd})](\text{ClO}_4)_4$	1.69	-95.9	0.019	0.440
$[\text{Ru}_2(\text{TC-Dicyd})]\text{Cl}_4$	1.96	-61.9	0.11	-21.6
$[\text{Ru}_2(\text{TC-Dicyd})]\text{Cl}_4^b$	$g_x = g_y = 0$ $g_z = 2.13$	-96.6	0.0804	-13.0

^a Measured from 5–300 K in a 1.0 T field. Units are: J (cm^{-1}); C ($\text{emu cm}^{-3} \text{K}^{-1}$) and θ (K). ^b Ising model.

ground-state. However, very small amounts of paramagnetic impurity, which in the present case are most likely due to the presence of oxidized Dicyd²⁻ and possibly mononuclear Ru(III), cause the curve to rise sharply. This effect can be corrected for in the fitting process by adding the Curie-Weiss term, mentioned above, to the Bleaney-Bowers equation. This takes into account the molar amount of paramagnetic impurity.

Two complexes, [Ru₂(Dicyd)](ClO₄)₄ and [Ru₂(DM-Dicyd)](ClO₄)₄, show reproducible *diamagnetic* behaviour at room temperature. A summary of the coupling constants, *g*-values and C and θ parameters is given in Table 4.8. It should be noted that the *g* values all fall in the range of typical Ru(III) complexes, however, they must be treated with caution. In the present data analysis, the main effect of the paramagnetic impurity will be to reduce *g* artificially.

The fit for [Ru₂(TC-Dicyd)]Cl₄ (Figure 4.24) is significantly poorer than the rest. This is possibly due to *g*-factor anisotropy. (The above model is valid only for a relatively isotropic *g*-tensor). The data for this complex was therefore fitted to the highly anisotropic Ising model^{97,98} (Figure 4.25). To understand this model the Heisenberg Hamiltonian (Equation 1.8) can be rewritten as;

$$H = -2J[\gamma(S_{1x}S_{2x} + S_{1y}S_{2y}) + S_{1z}S_{2z}] \quad (4.4)$$

and one observes that with $\gamma = 1$ the Heisenberg Hamiltonian is generated using all the spin components of the vectors *S*₁ and *S*₂. However, a very anisotropic expression, called the Ising model is obtained when γ is set equal to zero. The essence of this model is that spins have only two orientations, up or down or +1/2 and -1/2, the eigenvalues of the *S*_z. A dimer will therefore exhibit four

states: $+1/2, +1/2$; $+1/2, -1/2$; $-1/2, +1/2$; and $-1/2, -1/2$. For any particular pair, the Hamiltonian can be written as;

$$H = -2JS_{z1}S_{z2} + g\mu_B H_z(S_{z1} + S_{z2}) \quad (4.5)$$

where the parameters have their usual meanings and H_z is the external magnetic field. From this it is easy to obtain the eigenvalues, write out the partition function and derive the expression for the molar magnetic susceptibility. (For more detail see reference 48).

$$\chi_{\parallel} = \frac{2Ng_z^2\mu_B^2}{kT} - \left[\frac{1 + e^{-J/kT} \cosh(g_z\mu_B H_z/kT)}{[e^{-J/kT} + \cosh(g_z\mu_B H_z/kT)]^2} \right] \quad (4.6)$$

This gives the susceptibility, $\chi_{\parallel}$, parallel to the z -axis. It should be noted that an extra factor of 2 in the denominator is required to refer to a mole of magnetic ions.

The fit of this model to the $[\text{Ru}_2(\text{TC-Dicyd})](\text{ClO}_4)_4$ data is only marginally better than before, with improvement near χ_{max} but poorer at higher temperatures. Parameters for both models are given in Table 4.8. More information about this system may need to be obtained by performing single-crystal measurements or ESR. For Ru(III) systems the latter is complicated by spin-orbit coupling.

The models used for these analyses neglect orbital angular momentum contributions which are important for Ru(III) , t_{2g}^5 systems. Drillon and Georges⁹⁹ have developed procedures for including the orbital contribution for various t_{2g}^n electron configurations, but analytical expressions are not, as yet,

available. Nevertheless, the use of the Bleaney–Bowers equation should provide a very good first approximation of the magnetic coupling constant, J .

4.6.2 Magnetic Coupling

All of the dinuclear complexes display either moderate or strong antiferromagnetic coupling, two of them being diamagnetic at room temperature. The J values range from -53 cm^{-1} to -100 cm^{-1} for the four complexes which show a maximum in χ_m . The diamagnetic complexes have $|J| > 400 \text{ cm}^{-1}$. This behaviour is truly unprecedented in the literature over these distances. With the through space metal to metal separations being about $13.2 \text{ \AA}$, and the through bond distance even longer ($\approx 15\text{--}16 \text{ \AA}$), Coffman and Beuttner's model (Equation 1.12) predicts $|J| = 5 \times 10^{-4} \text{ cm}^{-1}$! Surely this model is inadequate in predicting the magnitude of coupling in these systems and raises questions about the actual exchange mechanism. Intramolecular coupling could occur via the L^2 bridging ligand by superexchange and/or spin polarization mechanisms. These mechanisms and how they may apply to the present systems will be discussed in greater detail in the next chapter where they are put in the context of molecular orbital calculations.

However, whichever mechanism is operating here one point appears relatively clear from the data in Table 4.8, increased planarity leads to increased coupling. The complex with the lowest J value, $[\text{Ru}_2(\text{TM-Dicyd})](\text{ClO}_4)_4$, has the bridging ligand which showed the greatest deviation from planarity (terminal cyanamide nitrogen is $1.4 \text{ \AA}$ out of the phenyl ring plane). This distortion is not expected to change dramatically upon complexation. If anything, the steric hindrance should be worse. $[\text{Ru}_2(\text{TC-Dicyd})]\text{Cl}_4$, which also has a relatively lower J value with respect to the other complexes, should also deviate from

planarity. Although the free ligand did not show a great deal of out of plane distortion (terminal nitrogen was only 0.3 Å out of the phenyl ring plane) it is expected that this distortion will increase upon coordination to the $-\text{Ru}(\text{NH}_3)_5$ moieties due to the increased steric hindrance of the four chlorines.

The other four complexes should be relatively planar because of either the lack of substituents on the phenyl ring or the "2,5" positioning of the substituents which is trans to the NCN and hence on the "wrong" side to impart any steric hindrance on the coordinated metal. These four complexes show the greatest degree of magnetic coupling. The increased planarity leads to increased overlap of the appropriate magnetic orbitals on the metal with an orbital that spans the ligand, facilitating electron exchange (see Chapter 5).

A significant difference in the magnetic coupling exists between $[\text{Ru}_2(\text{Dicyd})](\text{ClO}_4)_4$ and $[\text{Ru}_2(\text{Dicyd})](\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3)_4$, the former showing diamagnetic behaviour at room temperature and the latter relatively strong anti-ferromagnetic coupling with $J = -100 \text{ cm}^{-1}$. Recall that the latter, whose crystal structure was determined, had two dimer forms in the unit cell, "linear" and "bent" in a ratio of 1:1. It doesn't seem unreasonable to expect the linear form to show greater exchange than the bent form and hence the bent form probably serves to attenuate or suppress the coupling. This may not be the case for $[\text{Ru}_2(\text{Dicyd})](\text{ClO}_4)_4$. Here the counterions are "spherical" and should not distort the crystal lattice as the $\text{CH}_3\text{C}_6\text{H}_4\text{SO}_3^-$ ions seem to do (see Figure 4.8). Therefore, in $[\text{Ru}_2(\text{Dicyd})](\text{ClO}_4)_4$ it is possible that only the linear form is present and greatly increased coupling is therefore observed. Indisputable proof of this, however, will only come from a crystal structure.

The dependence of J on the nature of the counterion has not, in itself, been studied to any great extent. Hendrickson and coworkers^{100,101} saw only minor

changes in J for dinuclear copper complexes with different counterions. $[\text{Cu}_2(\text{tren})_2(\text{Im})]^{3+}$ ($\text{tren} = 2,2',2''$ -triaminotriethylamine, $\text{Im} = \text{imidazole}$) shows a J value of -38 cm^{-1} when PF_6^- is the counterion and a value of -40 cm^{-1} when ClO_4^- is the counterion. These counterions, however, are both "spherical". $[\text{Cu}_2(\text{tren})_2(\text{PPD})]^{4+}$ ($\text{PPD} = p$ -phenylenediamine) shows J values of -35 cm^{-1} with NO_3^- , -26 cm^{-1} with ClO_4^- and -20 cm^{-1} with PF_6^- . Again, not a very large deviation. More recently, Chaudhuri and Oder¹⁰² also saw only minor changes in J when a truly asymmetric, albeit small, counterion was used. In the complex $[\text{Cu}_2\text{L}_2(\mu\text{-SCN})_2]^{2+}$ (where $\text{L} = 1,4,7$ -trimethyl-1,4,7-triazacyclononane) the J value was -15 cm^{-1} when SCN^- was the counterion and -20 cm^{-1} when the "spherical" ClO_4^- was used. This, again, is not a significant enough difference from which to draw any definite conclusions.

CHAPTER 5

COUPLING MECHANISMS

5.1 Introduction

Both electronic and magnetic coupling were briefly outlined in the Introduction (Sections 1.2 and 1.3). Some of the relevant points will be reiterated here along with some additional detail to put what follows in some context.

For weakly coupled mixed-valence systems the degree of electronic coupling between donor and acceptor wavefunctions can be obtained from the Hush equation (Equation 1.3) where H_{ab} can be described as the *electronic* resonance exchange integral. This equation, derived from perturbation theory, is only applicable to weak electronically coupled systems, such as ours. Here the assumption is made that the overlap between the donor and acceptor wavefunctions is zero.

The magnitude of H_{ab} is, of course, dependent on the nature of the bridging ligand. This dependence is dictated, not only by r (in Equation 1.3), but by the extent to which the ligand can enhance coupling via a superexchange mechanism.¹⁰³ For a superexchange mechanism to operate, the donor and acceptor wavefunctions must have the correct symmetry and energy to interact with the LUMO or HOMO of the bridging ligand. This interaction leads to a slight delocalization of the donor or acceptor wavefunction onto the bridge which leads to increased electronic coupling between the redox sites. As detailed explicitly in Section 1.2, superexchange may occur via the empty LUMO (electron transfer) or via the filled HOMO (hole transfer). Examples of the former are quite

abundant in the literature, however, the latter has received far less attention. Our systems were designed, in part, to address this.

The magnetic interaction between the spins for two atoms, 1 and 2, was represented by the Heisenberg Hamiltonian (Equation 1.8).

$$H = -2JS_1 \cdot S_2$$

Two theoretical approaches have been developed to determine J , the exchange coupling constant. Hoffmann¹⁰⁴ has used perturbation theory to treat the weak magnetic interaction of two $S = 1/2$ spins in *orthogonal* magnetic orbitals and obtained,

$$J = V_{12} - (2H_{12}^2)/J_{11} - J_{12} \quad (5.1)$$

V_{12} is the potential exchange integral which represents the overall spin pairing energy. This is the ferromagnetic term. The second term is antiferromagnetic in nature and consists of the *magnetic* resonance exchange integral H_{12} and the Coulomb repulsion integrals J_{11} and J_{12} . The term that dominates dictates the kind of coupling observed.

Kahn *et al.*¹⁰⁵ have used a somewhat different approach in which they stress the importance of magnetic orbital overlap and the use of *nonorthogonal* magnetic orbitals to obtain the magnetic interaction between two $S = 1/2$ spins.

$$J = (V_{12} - J_{12}) - H_{12}S_{12} \quad (5.2)$$

Here V_{12} , J_{12} and H_{12} have the same meaning as in Equation 5.1 but nonorthogonal

orbitals are used. S_{12} is the overlap integral. Both of these treatments are essentially equivalent and can be used to effectively predict trends in magnetic coupling when the dominant effect is the direct interaction between magnetic orbitals. To obtain a more quantitative picture of antiferromagnetic coupling more rigorous methods are needed. De Loth¹⁰⁶ has performed *ab initio* calculations that show second order effects to be important.

The electronic and magnetic resonance exchange integrals, H_{ab} and H_{12} , cannot be directly equated, however, under identical conditions general trends in one should be reflected in the other (i.e. if H_{ab} is measured for a series of complexes one should be able to qualitatively predict the trend in their magnetic coupling).

5.2 Molecular Orbital Considerations

As alluded to in the previous chapter, there are two major mechanisms which can operate for magnetic exchange: superexchange and spin polarization. It must be stressed that these mechanisms are not mutually exclusive and both could contribute to the observed magnetic coupling. They depend to a large degree on the nature of the bridging ligand orbital that interacts with the magnetic orbital of the metal. The magnetic orbital in our case, Ru(III) (low spin d^5), is a π -symmetry d orbital. This orbital could interact with the appropriate ligand orbital and more specifically with the appropriate p orbital contribution on the nitrile nitrogen. (For the definition of the coordinate axes see Figure 5.1).

Extended Hückel molecular orbital (EHMO) calculations have been carried out on the five dicyanamidobenzene bridging ligands to determine the nature, ordering and to a certain extent, the energy of the frontier orbitals. The FORTICON 8 program was used to perform the calculations and the data input

files for the five ligands are given in the Appendix. These files were constructed by using the crystal structure data in Chapter 3. The ligands were placed in the xy plane and the x, y and z Cartesian coordinates of each atom were determined. All of the ligands except for TM-Dicyd²⁻ were assumed to be planar. Execution of the program yields the overlap matrix, the energy levels of the molecular orbitals, the coefficients of the atomic orbitals that make up the molecular orbitals, the reduced overlap matrix, reduced charge matrix, the net atomic charges and atomic orbital occupations and the reduced energy matrix. Figure 5.1 shows the LUMO (lowest unoccupied molecular orbital) and the two highest energy occupied molecular orbitals of Dicyd²⁻. The lobe sizes are proportional to the coefficients given by the EHMO program. The two occupied orbitals are similar to those defined earlier by Crutchley *et al.*⁹¹ for phenylcyanamides, however, their ordering is reversed. The EHMO calculations of the other Dicyd derivatives show similar orbital orderings and coefficients with a relatively high lying LUMO and two closely spaced "HOMO's". A summary of the energies of these three orbitals obtained from the calculations is given in Table 5.1. The energy difference of the two highest occupied orbitals ranges from 0.54 V to 0.77 V. If one examines the orbitals in Figure 5.1 more closely one sees that the LUMO (π^*) is predominantly phenyl ring centered with little contribution from the NCN moieties. The HOMO (π_1) has a much greater delocalized character with significant p_z contributions on most of the atoms and is a prime candidate for an efficient coupling pathway. The next highest orbital (π_2) which is orthogonal to π_1 also shows some delocalized nature with respect to the mostly p_y and p_x contributions. Here, however, the NCN moiety is not coupled directly into the phenyl ring as is π_1 and at first glance does not appear to be a candidate for magnetic exchange. We will see below that it too can serve as an indirect coupling pathway.

Figure 5.1 Frontier orbitals of Dicyd^{2-} from EHMO calculations. Energies are in eV. Minor orbital contributions are omitted for clarity.

Table 5.1 Frontier Orbital Energies (in eV) from EHMO Calculations

Ligand	HOMO(1st)	HOMO(2nd)	LUMO
TC-Dicyd ²⁻	-11.58	-12.26	-9.97
DC-Dicyd ²⁻	-11.71	-12.48	-9.70
Dicyd ²⁻	-11.66	-12.42	-8.25
DM-Dicyd ²⁻	-11.50	-11.99	-8.14
TM-Dicyd ²⁻	-11.70	-12.24	-8.04

A qualitative energy level diagram has been constructed showing the interaction between the phenylcyanamide ligand and Ru(III).⁹¹ This is reproduced in Figure 5.2a. If the magnetic coupling is now treated as a perturbation of the singly occupied b_2^* orbitals resulting from the interaction of the two separate Ru(III) ions and the ligand, the very simple two electron interaction scheme shown in Figure 5.2b results. Here the energy separation between the ground-state singlet and excited triplet states is equal to $2J$ and J is negative corresponding to the antiferromagnetic coupling. As we saw in the previous chapter this perturbation ranges from $\approx 100 \text{ cm}^{-1}$ ($-2J$) to greater than 800 cm^{-1} (for the diamagnetic cases).

Before we go on to discuss the individual coupling mechanisms in greater detail a slight digression will be made to consider some other information provided by the EHMO calculations.

Figure 5.2 a) Qualitative energy level scheme for the orbitals resulting from π interactions between phenylcyanamide and Ru(III). b) Perturbation of two b_1^* orbitals leading to magnetic coupling.

The NCN^- moiety can be considered a pseudo-halogen. Indeed, the phenylcyanamides were designed as novel π -donors whose electronic properties could be probed systematically.^{107,108} With this in mind a net "effective charge" can be assigned to NCN^- , which consists of the sum of the net charges on each of the three atoms. The net atomic charges are given by the EHMO calculations and are summarized in Table 5.2. The last column contains the net "effective charge". From this data it is clear that as the electron withdrawing nature of the phenyl ring substituent increases the "effective charge" on the NCN^- decreases. This is as one would expect. However, it is the way it decreases on going from DC-Dicyd²⁻ to TC-Dicyd²⁻ that is somewhat more subtle.

Table 5.2 Net Atomic and Effective Charges on the Cyanamide Groups

Ligand	N(amide)	C	N(nitrile)	" NCN^- " ^a
TC-Dicyd ²⁻	-0.776	0.946	-1.281	-1.111
DC-Dicyd ²⁻	-0.886	0.973	-1.244	-1.157
Dicyd ²⁻	-0.877	0.975	-1.268	-1.170
DM-Dicyd ²⁻	-0.869	0.978	-1.296	-1.187
TM-Dicyd ²⁻	-0.860	0.972	-1.329	-1.217

^a Net charge on cyanamide (sum of previous three columns).

On going from TM-Dicyd²⁻ to DC-Dicyd²⁻ the net negative charge on the amide nitrogen increases and that of the nitrile nitrogen decreases. The charge on the carbon remains relatively unchanged. However, on going from DC-Dicyd²⁻ to TC-Dicyd²⁻ the negative charge on the amide nitrogen drops dramatically and that on the nitrile nitrogen rises slightly. The charge on the carbon drops somewhat. There appears to be some "give and take" of electron density in this trend. However, the net effect is still seen as a decrease in the overall "effective charge" on the NCN⁻ group.

This change in effective charge reflects the "tunability" (see pg. 19) built into these ligands. A plot of $\ln |2J|$ vs. the effective charge is shown in Figure 5.3.

Figure 5.3 Plot of $\ln |2J|$ vs. effective charge for the four complexes: 1) $[\text{Ru}_2(\text{TC-Dicyd})\text{Cl}_4]$ (Heisenberg model), 2) $[\text{Ru}_2(\text{DC-Dicyd})\text{Cl}_4]$, 3) $[\text{Ru}_2(\text{Dicyd})(\text{ClO}_4)_4]$ and 4) $[\text{Ru}_2(\text{DM-Dicyd})(\text{ClO}_4)_4]$. The J values are taken from Table 4.8 and the effective charge from Table 5.2.

If one omits the data for $[\text{Ru}_2(\text{TM-Dicyd})](\text{ClO}_4)_4$ (not shown in Figure 5.3) since this complex probably deviates significantly from planarity, one can see that as the charge on "NCN" becomes more negative the magnetic coupling increases. The two highest lying HOMO's are those of Dicyd^{2-} and DM-Dicyd^{2-} (Table 5.1) and the complexes formed from these ligands show the strongest magnetic coupling (diamagnetic at room temperature). In these cases one has the best energy matching of ligand and metal orbitals. Only the lower limits of $2J$ are plotted for $[\text{Ru}_2(\text{Dicyd})](\text{ClO}_4)_4$ and $[\text{Ru}_2(\text{DM-Dicyd})](\text{ClO}_4)_4$ and it would seem that many more data points are needed in order to derive a solid correlation, however, there does appear to be a significant trend. It does appear possible, therefore, to "tune" these systems in such a way as to optimize the magnetic coupling between the metal sites, assuming that there are no significant conformational differences between complexes.

5.3 Superexchange

Now let us address the first and probably the most common mechanism of magnetic coupling: superexchange. For superexchange to operate the appropriate magnetic orbital on the metal must interact with a high lying ligand HOMO or low lying ligand LUMO of the correct symmetry and energy. If we assume the metal d orbitals of Ru(III) to lie somewhere around -11.2 eV ,¹⁰⁹ then interaction with any of the five ligand LUMO's is unlikely (all lie above -10.0 eV and are not well extended over the ligand) and superexchange should occur via the HOMO as shown in Figure 5.4 for the Dicyd^{2-} ligand. The d_{xz} orbital on each ruthenium overlaps well with the nitrile nitrogen p_z orbital available on the HOMO and the extended pathway is complete and continuous.

It is clear that any out-of-plane deviation by either the ligand (i.e. the NCN bending out of the phenyl ring plane or simply a twisting of the ring itself) or the $\text{Ru}(\text{NH}_3)_6$ moiety will reduce the overlap and hence reduce the coupling.

Figure 5.4 Diagram showing the interaction of the metal d_{xy} orbitals with the Dicyd^{2-} ligand HOMO; the most likely pathway for superexchange.

5.4 Spin Polarization

Spin polarization involves the interaction of ligand HOMO's which are *orthogonal* to the magnetic orbitals. This is a quantum mechanical effect in which the spin of the metal electron is induced to "align" with the spin of the electron on the ligand. A recent example of this was seen for a dinuclear iron(III) complex,¹¹⁰ in which the spins of the $d\pi$ electrons of the metal induced the same spins on a resorcinol type bridging ligand and thereby propagated a ferromagnetic interaction between the iron centers.

To look at this mechanism in greater detail let us consider an earlier, and perhaps now classic, example of spin polarization of a bridging ligand orbital upon orthogonal metal orbitals. This involves the μ -azido bridged copper(II) complexes.¹¹¹⁻¹¹³ The π_g molecular orbital of the bridging network (Figure 5.5) plays a dominant role in the interaction between the copper(II) ions. The electrons can, at any instant, reside at the ends of the molecular orbital.

Figure 5.5 The azide π_g molecular orbital showing the electron spins.

The absence of significant overlap density in the π_g orbital (there is a node at the central nitrogen) pushes the two paired electrons occupying the same molecular orbital towards the two extremities of the system (arrows in Figure 5.5). This serves to magnify the spin polarization.

When the N_3 group bridges in an end on fashion the lone spin of the single bridging nitrogen aligns the spins on the two copper ions and a triplet ground state occurs and hence ferromagnetic coupling is observed. However, when the azide bridges in an end-to-end manner electrons in the π_g orbital, at any given instant, are at opposite ends of the bridge and have opposite spins and thus induce opposite spins in the copper ions. Therefore the copper spins are antiferromagnetically

coupled, leading to a singlet ground-state at low temperature. These arguments are indeed borne out by experiment, since in the former type complexes J is found to be positive and in the latter J is negative (indeed some are even diamagnetic at room temperature).¹¹⁴

A similar situation may arise in our system involving the d_{xz} magnetic orbital and the π_2 ligand orbital which is orthogonal to π_1 . Here one could envision the paired spins of the π_2 orbital lying, at any instant, at opposite ends of the orbital near the terminal nitrogens and inducing the electrons on the metal d_{xy} orbitals to have opposite spins from each other. Therefore, in the present system, as with the end-to-end bonded azide above there does not need to be a direct interaction between an extended bridging ligand HOMO and the magnetic orbitals for antiferromagnetic coupling to occur.

It should be noted that the interaction of the metal d_{xy} orbitals with π_2 ligand orbital leads to a "bent" conformation if the optimal overlap is considered (Figure 5.6). The Ru—N—C angle would be $\approx 150^\circ$ which is the same as that seen

Figure 5.6 Diagram showing the interaction of the ruthenium d_{xy} orbitals with the second highest occupied molecular orbital of Dicyd^{2-} (π_2).

for the bent conformation of $[\text{Ru}_2(\text{Dicyd})]^{4+}$ in the crystal structure (see Section 4.3). It is therefore possible that the two forms seen in the crystal structure correspond to ruthenium orbitals interacting with both the π_1 and π_2 ligand orbitals (which are relatively close in energy).

The question as to which mechanism is operating or whether even both are operating to a certain degree simultaneously is difficult to answer. It would appear that the most likely mechanism is superexchange since the ligand HOMO is closer to the metal orbital energies than the next highest lying occupied molecular orbital. However, the accuracy of the ligand orbital energies is questionable since configuration interaction or electron–electron repulsion interactions are not taken into account in these calculations and these effects have been found to be important in magnetic exchange interactions.¹¹⁵ More detailed theoretical study of this system is needed. This could include EHMO calculations on the entire system (i.e. including the $\text{Ru}(\text{NH}_3)_5$ groups) and possibly *ab initio* calculations in which configuration interactions are taken into account and from which more reliable energy level values could be extracted.

5.5 Failure of the Coffman and Buettner Limit Function

Whichever mechanism is operating, one thing is clear, the magnetic coupling observed in these complexes is much stronger than Coffman and Buettner's²⁵ limit function predicts (Equation 1.12 and below), given the large metal–metal

$$|2J_{\text{lim}}| = 1.35 \times 10^7 \exp(-1.80R)$$

separations. The problem with their model is not so much that it is wrong, quite to the contrary, for the experimental data they used it works quite well. The

problem is really in the data set itself. All of their data involves "insulating" compounds, and they state that there is a dominance of σ -bonding in the superexchange process. This leads to relatively low lying ligand HOMO's and high lying LUMO's, neither of which would provide strong overlap with the metal magnetic orbitals. The novelty of the present system was, of course, inherent in its design from the outset. The Dicyd²⁻ derivatives are exceedingly good π -donors, they have destabilized, high lying HOMO's which as we saw above lie very close to the ruthenium 3d orbitals in energy. Therefore, the mechanism for the present exchange process, whether it be superexchange or spin polarization, is fundamentally different from those systems investigated by Coffman and Buettner. Ours involve conducting π -systems, theirs, insulating σ -networks.

One very interesting and notable exception to Coffman and Buettner's limit function at that time were a series of dinuclear copper(II) complexes synthesized by Felthouse and Hendrickson.¹⁰¹ One complex in particular, with a benzidine bridge showed significant antiferromagnetic coupling, $J = -4 \text{ cm}^{-1}$ at a Cu-Cu distance of 12.3 Å. This J value is well above that predicted by the limit function of 0.002 cm^{-1} . CNDO/2 calculations were performed on benzidine and it was concluded that not only were the ligand " σ -orbitals" involved in the propagation of the exchange interaction but that the involvement of the high lying " π -orbitals" could not be discounted, the copper(II) ions being in a distorted tetrahedral environment. Coffman and Buettner pointed out that the closest *intermolecular* Cu-Cu distance in this complex was 7.5 Å and that using this value for R in the above equation leads to an $|J|$ value greater than 4 cm^{-1} . The crystal structure of this compound showed that no counterions were responsible for such an interaction, however, a hydrogen bonded pathway may exist.

Despite the fact that Hendrickson's complex may have been brushed aside by

Coffman and Buettner, since then, two more examples of antiferromagnetic exchange over large distances in copper(II) compounds have appeared.^{58,59} These were outlined in the Introduction (pgs 17–19). Here the bridging ligands were 4,4'-bipyridine and terephthalate. Although the result for the former was ambiguous since a clear distinction between intra- and intermolecular coupling could not be made, the results for the latter clearly exceeded the CB limit. ($J = -70 \text{ cm}^{-1}$ at a Cu–Cu distance of 11.25 Å). This appears to be the only example of a direct conflict with the CB function since the major coupling pathway evoked was σ in nature, involving the $d_{x^2-y^2}$ magnetic orbital on Cu(II) (square-pyramidal environment) and a coplanar σ -ligand orbital.

Returning to the present system, it appears to be the first example of long-range antiferromagnetic coupling through an extended ligand π -system and involving ruthenium d_{xz} and/or d_{xy} magnetic orbitals. It would seem then that the CB limit function is not appropriate for these complexes. The basis of the limit function is the general exponential decay function;

$$J_{\text{ex}} = A \exp(-\alpha R) \quad (5.3)$$

where J_{ex} and R have their usual meanings. This was empirically derived to model the distance dependence of J_{ex} for the systems they studied. This type of function has been frequently used to describe the distance dependence of electron transfer rates through bridged systems as well as electronic coupling¹¹⁶ (Equation

$$H_{\text{ab}} = H_0 \exp(-\alpha R) \quad (5.4)$$

5.4). Here H_0 is the electronic resonance exchange integral when donor and

acceptor wavefunctions are at van der Waals separation. The α parameter can be viewed as an "attenuation factor". The smaller its value the slower the exponential decay of J_{ex} , H_{ab} , or k , the rate of electron transfer, with distance. α is frequently related to electron tunneling through a square potential barrier.¹¹⁷ Using a standard quantum-mechanical tunneling formula, α equals $(2/\hbar)(2mV_0)^{1/2}$ where m is the mass of the electron, V_0 the height of the potential barrier and $\hbar$ is $h/2\pi$. (An α value of $1.46 \text{ \AA}^{-1}$ corresponds to a potential barrier of 2.0 eV). Miller^{118,119} has shown that, at least for electron transfer in certain donor-acceptor systems, α can be small. This is frequently due to electron interactions propagating not only through empty orbitals in the "medium" between donor and acceptor (the LUMO pathway) but also through filled orbitals (HOMO hole tunneling). The more favorable the hole tunneling, the lower α becomes. This could also be the case for exchange coupled systems, such as ours, in which there are high lying "HOMO's" to efficiently mediate the interactions. This means that the α value of 1.80 in the CB limit function is almost certainly too high for the present systems.

To get an accurate value of α for systems like ours in which π coupling mechanisms are operating, more magnetic data over a range of metal-metal distances is needed. A crude estimate of α in the present case can be made if we assume that the pre-exponential factor, A , remains the same (this is not unreasonable since it represents J_{ex} at van der Waals separation). If we use the complex for which we have an accurate metal-metal distance, $[\text{Ru}_2(\text{Dicyd})](\text{OTs})_4$, then for a value of $|J| = 100 \text{ cm}^{-1}$ at a distance of $13.2 \text{ \AA}$ we obtain an α value of $0.84 \text{ \AA}^{-1}$. This is substantially lower than the $1.80 \text{ \AA}^{-1}$ obtained by Coffmann and Buettner, but it needs further verification in other conducting complexes where the coupling pathway and metal-metal distances are unambiguous as well as over longer metal-metal distances.

5.6 Coupling in (III,III) Versus (II,III) Complexes

Contrary to the relatively strong antiferromagnetic coupling seen in the fully oxidized (III,III) complexes studied in this thesis, when the mixed-valence (II,III) complex is generated in solution only very weak *electronic* coupling is seen. The mixed-valence ion is classified as being a valence-trapped or localized Class II system. Since H_{ab} was only determined in the case of $[Ru_2(TC-Dicyd)]Cl_4$ a comparison of H_{ab} values with J_{ex} is not possible. It would probably be unfair to compare these two properties even if more H_{ab} values had been determined. The measurements of H_{ab} and J_{ex} were not performed under similar conditions. Electronic coupling is almost certainly weak due to the dynamics (ring rotation) of the system in solution. As has been mentioned several times, the phenyl ring to cyanamide bond is long and has predominant single bond character and therefore there is ample rotational freedom about it. This will greatly reduce the overlap in the extended π -system if the hole transfer is occurring via the HOMO (which is most likely since the LUMO lies too high in energy) and significantly reduce the electronic coupling. If the hole transfer pathway occurs via the next highest lying ligand orbital then not only will the above be a problem but the transfer will be symmetry forbidden as well (see Figure 5.6). The energy of the Ru(II) metal orbitals with respect to those of Ru(III) may also be a factor, although this difference should be small.

Magnetic coupling was measured in the solid-state and the conditions for coupling appear to be optimized. Here, the system is "locked-in position" and the maximum overlap of magnetic and ligand orbitals can occur (aside from minor perturbations due to crystal-packing effects and the nature of the counterions). Even if this were not the case spin polarization provides a mechanism whereby a contiguous pathway may not be necessary but strong exchange could still occur.

CHAPTER 6

CONCLUSIONS AND FUTURE STUDIES

The recent interest in the acceptor properties of the dicyanoquinone-diimines (DCNQI's) in charge-transfer complexes has opened up new avenues in the development of novel electronic materials. This thesis has achieved the aims that were outlined in Section 1.5. It has dealt with the synthesis and characterization of the doubly reduced forms of these acceptor compounds, the dicyanamidebenzenes, and their use as bridging ligands in dinuclear ruthenium pentaammine complexes. The synthesis and characterization of these dimers was detailed and the investigation of their electronic properties using spectroscopic and electrochemical techniques has shown that only weak electronic coupling occurs in the mixed-valent forms. Variable temperature magnetic susceptibility data of the fully oxidized forms was consistent with moderate to strong antiferromagnetic behaviour. The major reason for the weak electronic coupling in the former case is probably due to the nonrigidity of the overall system in solution, whereas for the latter, rigidity is maintained in the solid-state and the overall system is relatively planar leading to near optimal magnetic interactions. The unprecedented magnetic coupling in these systems has led to a reassessment of the Coffman and Büttner limit function, outlined in the Introduction, which predicts an upper limit for J_{ex} , the magnetic coupling constant, at long intermetallic distances. Coffman and Büttner's model may be appropriate for systems in which the predominant coupling mechanism involves an insulating σ pathway, but not in the present system in which π -interactions predominate. Our systems can be viewed

as semi-conducting or even conducting, as opposed to insulating. All of our J_{ex} values lie well above those predicted by the limit function (usually by greater than 10^6). A re-evaluation of the "attenuation factor", a , in the exponential decay equation must be made for these types of systems. The decay of J_{ex} with distance is obviously much slower and a will be substantially lower. Future studies will be geared to synthesizing similar complexes with a range of metal-metal distances.

The first strategy would be to extend the length of the bridge and hence the extended π -system and see if this effects the magnetic coupling. The system below (I) has already been synthesized by R.J. Crutchley and the author and

preliminary characterization is in progress. The crystal structure of the bridging ligand has been determined and shows it to be relatively planar with the dihedral angle (or twist angle) between the two phenyl rings being only 8° .

Another modification that can be made is the changing of the coligands on each ruthenium from the good donor NH_3 groups to π -acids such as bipyridine and/or terpyridine. This will stabilize the +2 oxidation state and raise the redox potential, which should significantly effect both the electronic and magnetic properties of dinuclear complexes such as (II). Since the metal orbitals will be stabilized there should be better energy matching with the ligand HOMO which

will hopefully increase the electronic and magnetic coupling and increase the conducting properties of the system. Coordination of the π -donor Dicyd²⁻ derivatives to Ru(terpy)(bipy)²⁺ moieties may prove difficult and the use of the diprotonated H₂Dicyd derivatives which have some π -acid properties may be necessary. Free rotation about the phenyl ring carbon to amide nitrogen bond will also still be a problem in solution.

Finally, a much more drastic change would be to substitute ruthenium for a different metal, such as copper or nickel. Complexes like (III) are also currently under study. (L³ is a tris chelating ligand such as diethylenetriamine).

The potential of the dicyanamidobenzene ligands and their derivatives in the design of dinuclear and polynuclear materials with interesting electronic and magnetic properties is so large, the surface has barely been scratched! It is hoped that this thesis has, to a small extent, laid the groundwork for future design and study of related systems.

APPENDIX

LIGAND INPUT DATA FILES FOR EHMO CALCULATIONS

NOTE: The first row in each data set contains four numbers which represent the number of hydrogen atoms, the number of heavy atoms (maximum of 40), the charge on the compound and the method used (0, 1, 2 or 3), respectively. The total number of atoms can not exceed 50. This is followed by the x, y, and z coordinates of each atom (hydrogens must be listed first) and a last line indicating the heavy atoms in the order they appear in the coordinate list. The atom labels correspond to those of the crystal structures in Section 3.3.

TC-Dicyd²⁻

0 16 -2 0

Atom	x	y	z
C(1)	2.041	-1.249	0.000
C(1)a	0.677	1.249	0.000
C(2)	0.677	-1.249	0.000
C(2)a	2.041	1.249	0.000
C(3)	0.000	0.000	0.000
C(3)a	2.708	0.000	0.000
C(4)	-2.197	-0.994	0.000
C(4)a	4.905	0.994	0.000
N(1)	-1.360	0.000	0.000
N(1)a	4.068	0.000	0.000
N(2)	-3.108	-1.724	0.000
N(2)a	5.816	1.724	0.000
Cl(1)	2.856	-2.773	0.000
Cl(1)a	-0.148	2.773	0.000
Cl(2)	-0.155	-2.787	0.000
Cl(2)a	2.863	2.787	0.000
C C C C C C C C N N N NCLCLCLCL			

DC-Dicyd²⁻

2 14 -2 0

Atom	x	y	z
H(4)	0.395	1.957	0.000
H(4)a	2.484	-1.957	0.000
C(3)	2.129	1.177	0.000
C(3)a	0.750	-1.177	0.000
C(4)	0.750	1.177	0.000
C(4)a	2.129	-1.177	0.000
C(2)	2.879	0.000	0.000
C(2)a	0.000	0.000	0.000
C(1)	4.890	-1.144	0.000
C(1)a	-2.011	1.144	0.000
N(2)	4.271	0.000	0.000
N(2)a	-1.392	0.000	0.000
N(1)	5.542	-2.103	0.000
N(1)a	-2.663	2.103	0.000
Cl(1)	2.966	2.703	0.000
Cl(1)a	-0.087	-2.703	0.000
C C C C C C C C N N N NCLCL			

Dicyd²⁻

4 12 -2 0

Atom	x	y	z
H(2)	0.268	2.032	0.000
H(3)	2.619	2.032	0.000
H(2)a	2.619	-2.032	0.000
H(3)a	0.268	-2.032	0.000
C(1)	0.000	0.000	0.000
C(2)	0.751	1.179	0.000
C(3)	2.136	1.179	0.000
C(1)a	2.887	0.000	0.000
C(2)a	2.136	-1.179	0.000
C(3)a	0.751	-1.179	0.000
C(4)	-2.012	1.139	0.000
C(4)a	4.899	-1.139	0.000
N(1)	-1.388	0.000	0.000
N(1)a	4.275	0.000	0.000
N(2)	-2.678	2.104	0.000
N(2)a	5.565	-2.104	0.000
C C C C C C C C N N N N			

DM-Dicyd²⁻

8 14 -2 0

Atom	x	y	z
H(5)a	3.064	-3.028	0.953
H(5a)a	-0.256	3.028	0.953
H(5)b	2.312	-3.376	-0.551
H(5a)b	0.496	3.376	-0.551
H(5)c	3.614	-2.074	-0.551
H(5a)c	-0.806	2.074	-0.551
H(3)	1.734	-3.530	0.000
H(3)a	1.074	3.530	0.000
C(1)	4.943	1.184	0.000
C(1)a	-2.135	-1.184	0.000
C(2)	2.808	0.000	0.000
C(2)a	0.000	0.000	0.000
C(3)	0.714	-1.193	0.000
C(3)a	2.094	1.193	0.000
C(4)	2.094	-1.193	0.000
C(4)a	0.714	1.193	0.000
C(5)	2.789	-2.551	0.000
C(5)a	0.019	2.551	0.000
N(1)	5.464	2.141	0.000
N(1)a	-2.656	-2.141	0.000
N(2)	4.234	0.000	0.000
N(2)a	-1.426	0.000	0.000
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Atom	x	y	z
H(6a)a	-0.363	3.036	0.953
H(6a)b	0.389	3.384	-0.551
H(6a)c	-0.913	2.082	-0.551
H(4a)a	-0.363	-3.036	0.953
H(4a)b	0.389	-3.383	-0.551
H(4a)c	-0.913	-2.082	-0.551
H(4)a	3.132	3.036	0.953
H(4)b	2.380	3.384	-0.551
H(4)c	3.682	2.082	-0.551
H(6)a	3.132	-3.036	0.953
H(6)b	2.380	-3.384	-0.551
H(6)c	3.682	-2.082	-0.551
C(2)a	0.000	0.000	0.000
C(3)a	0.682	1.226	0.000
C(1)a	0.682	-1.226	0.000
C(2)	2.769	0.000	0.000
C(3)	2.087	-1.226	0.000
C(1)	2.087	1.226	0.000
C(4)a	-0.088	-2.559	0.000
C(4)	2.857	2.559	0.000
C(6)a	-0.088	2.559	0.000
C(6)	2.857	-2.559	0.000
C(5)a	-2.401	0.000	0.700
C(5)	5.172	0.000	-0.700
N(1)a	-1.406	0.000	-0.110
N(1)	4.177	0.000	0.110
N(2)a	-3.352	0.000	1.410
N(2)	6.123	0.000	-1.410

C C C C C C C C C C C N N N N

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