Metal−Ligand Coupling Elements and Antiferromagnetic Superexchange in Ruthenium Dimers

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Received June 12, 1997

Antiferromagnetic exchange constants were calculated by using the Mulliken−Hush treatment for metal−ligand coupling elements (*J. Photochem. Photobiol. A: Chem.* **1994**, *82*, 47) and the valence bond model of antiferromagnetic exchange (*Inorg. Chem.* **1993**, *32*, 2850), from the spectral data of the solvent-dependent ligand-to-metal charge-transfer bands of $[\{(NH_3)_5Ru\}_2(\mu\text{-}L)]^{4+}$ complexes, where L is a substituted 1,4-dicyanamido-benzene dianion derivative. These calculated values were compared to the corresponding experimental exchange constants that were estimated from the complexes' solvent-dependent room-temperature magnetic moments. The correlation between these values is quite good, and this in turn implies that a relatively unsophisticated level of theory in conjunction with spectroscopy may be all that is necessary to predict trends in molecular properties derived from frontier orbitals.

Introduction

It would be of great value if a researcher could predict molecular properties by considering the information contained in an electronic absorption band resulting from a transition between frontier orbitals. To some extent, this has already been done for elemental properties through the definition of absolute hardness[1] and electronegativity.[2] However, an electronic transition, besides energy, also has probability (or oscillator strength), and this property in a molecule contains information about the magnitude of electronic coupling between atoms. This was first recognized by Mulliken[3] in his study of organic charge-transfer complexes and later given theoretical description by Hush[4] for metal−metal coupling in mixed-valence complexes. These systems involve photoinduced electron-transfer events and can be described under the conceptual framework of Marcus electron-transfer theory.[5] The question as to whether electron-exchange processes can be evaluated in a similar manner is intriguing insofar as it pertains to the origin and expression of molecular magnetic properties. This has immediate application to the current interest in hybrid magnetic materials based on coordination chemistry,[6] and it is the purpose of this study to demonstrate that reasonable predictions concerning the magnitude of antiferromagnetic exchange can be made from electronic absorption data.

The intramolecular interaction between two metal ions M_a and M_b, each possessing a spin $S = {}^1/_2$, can be described by the Hamiltonian

$$H = -2JS_a \cdot S_b \qquad (1)$$

where the exchange constant J is negative for antiferromagnetic exchange or positive for ferromagnetic exchange. Whether a singlet or triplet ground state is formed depends on the relative magnitude of antiferromagnetic J_{AF} and ferromagnetic J_F terms

$$2J = J_F + J_{AF} \qquad (2)$$

where J_F represents the overall spin pairing energy and J_{AF} is the energy released as a result of resonance exchange (a weak bonding interaction). In cases where metal ions are sufficiently separated to prevent through-space overlap of d orbitals, antiferromagnetic coupling can occur via the superexchange mechanism, in which bridging ligand orbitals mediate exchange. A theoretical expression for J_{AF} was first developed by Anderson,[7] who used an unrestricted Hartree−Fock formalism in his treatment of superexchange in insulators. Later, Hay, Thibeault, and Hoffmann[8] showed that J_{AF} can be analyzed in terms of pairwise interactions of dimeric molecular orbitals with the square of the splitting in energy between the members of a pair being a measure of the stabilization of the low-spin state. Their final result was shown to be equivalent to Anderson's treatment of superexchange, and extended Hueckel theory was used to evaluate the effect of geometry, electronegativity, and substituents on splitting energy. Other treatments have invoked ab initio methods[9] or have emphasized the importance of overlap between metal ions and the bridging ligand.[6a,10]

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S0020-1669(97)00728-3 CCC: $15.00

For the purposes of this study, the valence-bond theory approach to J_{AF} of Tuczek and Solomon[11] will be adopted. Their final expression for antiferromagnetic exchange was

$$-J_{AF} = \frac{{h_{d\pi}}^{4}}{\Delta^{2}}\left(\frac{1}{U} + \frac{2}{E_{DCT}}\right) \tag{3}$$

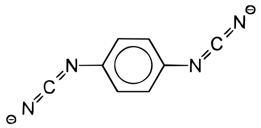
where the transfer integral (metal−ligand coupling element), $h_{d\pi,}$ corresponds to a one-electron charge transfer between the bridging ligand and the metal (i.e., an LMCT transition), Δ is the energy difference between the ground state and the LMCT excited-state associated with $h_{d\pi}$, U is the metal-to-metal charge-transfer MMCT transition energy, and E_{DCT} is the difference in energy between the ground and double-charge-transfer states. The singlet double-charge-transfer state corresponds to the simultaneous transition of one bridging ligand electron to each metal ion. It is not accounted for by Anderson theory and can have a significant contribution to ground-state antiferromagnetism.[11]

It is expected that, for a series of similar transition-metal dinuclear complexes, the energies of the charge-transfer transitions will not vary appreciably and that the greatest influence on J_{AF}, according to eq 3, will be the metal−ligand coupling element $h_{d\pi}$. Creutz, Newton, and Sutin (CNS) have shown[12] that the value of $h_{d\pi}$ can be determined from experimental CT band properties by using the expression from Mulliken and Hush

$$h_{d\pi} = \frac{3.03 \times 10^{2}}{r}(\nu_{max} f)^{1/2} \tag{4}$$

where ν_{max} is the band maximum in cm^{-1}, f is the oscillator strength of a single metal−ligand chromophore, and r is the transition moment length which is usually taken to be the separation between donor and acceptor in angstroms.[13] Equation 4 is frequently assumed to be applicable only to very weakly coupled systems; however, CNS have shown that this equation is exact in the two-state model, provided overlap can be neglected and the CT transition is polarized along the donor−acceptor axis.

Thus, for a dinuclear system, J_{AF} can be calculated, provided there exist reasonable estimates or actual values of MMCT and double-charge-transfer energies and an observable bridging ligand-to-metal CT band. In addition, a true test of the above equations requires a comparison of a wide range of experimental exchange constants against those calculated. Utilization of our well-characterized dinuclear Ru(III) complexes $[\{(NH_3)_5Ru\}_2(\mu\text{-L})][PF_6]_4$, where L = 2,5-dimethyl- (Me_2dicyd^{2-}) (**1**), 2-methyl- ($Medicyd^{2-}$) (**2**), 2-methoxy- ($MeOdicyd^{2-}$) (**3**), unsubstituted ($dicyd^{2-}$) (**4**) 2,5-dichloro- (Cl_2dicyd^{2-}) (**5**), 2,3,5,6-tetrachloro- (Cl_4dicyd^{2-}) (**6**), and 2,3,5,6-tetramethyl-1,4-dicyanamidobenzene (Me_4dicyd^{2-}) (**7**), makes this test possible.



Solid-state magnetic susceptibility measurements[14] have shown that the $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ complexes are strongly antiferromagnetically coupled despite a Ru(III)−Ru(III) separation of approximately 13 Å. This is largely due to an energetically favorable superexchange pathway via the HOMO of the 1,4-dicyanamidobenzene bridging ligand. For the most strongly coupled complexes, solid-state and solution diamagnetism is observed at room temperature. Importantly, both the magnetic and LMCT band properties of these complexes are greatly perturbed in aprotic solvents by a donor−acceptor interaction between the solvent and the ammine protons.[15] This was dramatically illustrated in a previous study[16] by the decrease in oscillator strength of the low-energy LMCT band of $[\{(NH_3)_5Ru\}_2(\mu\text{-}Me_2dicyd)]^{4+}$ and the concomitant increase in the complex's magnetic moment as the donor number of the solvent was increased. This is consistent with the predicted dependence of antiferromagnetic exchange on the oscillator strength of the LMCT band according to eqs 3 and 4. In addition, the decoupling of Ru(III) ions was also observed in aqueous solutions of the dimers and it was suggested that water's ability to act as an acceptor (protonation of the cyanamide group) played an important role.

We have determined the solvent-dependent magnetic moments and LMCT band properties in dimethyl sulfoxide, acetone, acetonitrile, nitromethane, and water of seven dinuclear $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ complexes to evaluate the predictions of eqs 3 and 4.

Experimental Section

Reagents. All solvents and chemicals were reagent grade or better and were used as received unless otherwise noted. 2,5-Diaminotoluene sulfate (97%), 2-methoxy-1,4-phenylenediamine sulfate hydrate (95%), tetrabutylammonium bromide, TBAB, tetrabutylammonium hexafluorophosphate, TBAH, sodium tetraphenylborate, $NaBPh_4$, and NH_4PF_6 were purchased from Aldrich. $[(NH_3)_5Ru(H_2O)][PF_6]_2$ was prepared according literature methods.[17] CM-Sephadex C25-120 cation-exchange resin was purchased from Sigma. The syntheses of the symmetric 1,4-dicyanamidebenzene ligands have been previously reported.[14] To prepare 2-methyl- and 2-methoxy-1,4-dicyanamidebenzene, the neutral phenylenediamine had to be isolated from its sulfate salt.

Preparation of 2-Methyl-1,4-dicyanamidebenzene ($MedicydH_2$). 2,5-Diaminotoluene sulfate hydrate (30 g) was dissolved in a basic solution of potassium carbonate (69 g) in 500 mL of distilled water. This solution was extracted with 4 × 250 mL aliquots of chloroform. The chloroform extracts were dried over magnesium sulfate, filtered, and then evaporated to dryness, yielding a beige solid of the crude diamine (11.5 g, 69%). This was used without further purification to prepare the dicyanamide compound.

Benzoyl chloride (29 g) in 100 mL of acetone was added dropwise to a refluxing solution of ammonium thiocyanate (15.2 g) in 200 mL of acetone. This was followed by the dropwise addition of crude diamine (10 g) in 100 mL acetone. The reaction mixture was refluxed

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for a further 20 min, after which it was poured into 1.5 L of water. The resulting yellow precipitate was filtered off, washed with water, and then air-dried. The yellow precipitate (38.6 g) was mixed with 500 mL of 2 M NaOH and heated to a boil. After 15 min, the solution was allowed to cool to 65 °C, and then lead acetate trihydrate (72 g) in 100 mL of water was added. The temperature of the reaction mixture was maintained between 60 and 65 °C until the mixture became deep black with the formation of lead sulfide (usually within 7 min). The lead sulfide was filtered off, and to the filtrate cooled in an ice bath was added 60 mL of glacial acetic acid, which immediately precipitated the white dicyanamide product. This was filtered off, washed copiously with water, and then air-dried. The crude ligand was then dissolved in a slight excess of hot acetone, the solution was filtered, and to the boiling filtrate was added slowly an equal volume of water (or to the point of clouding). Cooling the solution gave off-white crystals which were filtered off, washed with ice-cold acetone/water solution, and finally vacuum-dried. Yield: 11.1 g (79%). Mp: dec >208 °C. Anal. Calcd for $C_9H_8N_4$: C, 62.78; H, 4.68; N, 32.54. Found: C, 62.55; H, 4.68; N, 32.58. IR (KBr): $\nu(NCN) = 2227$ cm^{-1}. ^{1}H NMR (acetone-d_6): δ 2.27 (s, 3H, CH_3), 6.91 (d, 1H, Ph), 6.94 (d, 1H, Ph), 6.96 (d, 1H, Ph), 7.14 (d, 1H, Ph), 8.25 (broad s, 2H, NH)

Preparation of 2-Methoxy-1,4-dicyanamidebenzene (MeOdicydH$_2$). This was prepared similarly to the methyl analogue. From 12.5 g of the crude 2-methoxy-1,4-phenylenediamine was obtained 12 g (83%) of recrystallized product. Mp: dec >155 °C. Anal. Calcd for $C_9H_8ON_4$: C, 57.44; H, 4.28; N, 29.77. Found: C, 56.91; H, 4.50; N, 28.98. IR (KBr): $\nu(NCN) = 2232$ cm^{-1}. ^{1}H NMR (acetone-d_6): δ 3.90 (s, 3H, OCH_3), 6.73 (d, 1H, Ph), 6.76 (d, 1H, Ph), 6.78 (d, 1H, Ph), 7.09 (d, 1H, Ph), 8.40 (broad s, 2H, NH)

The ruthenium dimer complexes **1**, **4**, **5**, **6**, and **7** have been previously prepared as chloride or perchlorate salts.[14] In this study, the complexes' counteranion was usually hexafluorophosphate; however, solubility in nitromethane was significantly improved if tetraphenylborate was selected. In either case, the appropriate complex was metathesized from an aqueous solution of the complex halide salt by the addition of excess $NaBPh_4$ or NH_4PF_6.[18] The synthetic procedure described below was used for complexes **1**, **2**, **3**, **4**, and **7**. Its main advantages in comparison to previous methods are the improved yields, the avoidance of inert-atmosphere techniques, and the use of the neutral ligand. For complexes **5** and **6**, the synthesis[14] requiring the tetraphenylarsonium salt of the dianion ligand was used. Elemental analyses of these complexes agreed with their formulation.[18]

Preparation of $[\{(NH_3)_5Ru\}_2(\mu\text{-Medicyd})][PF_6]_4\cdot 0.75$acetone (2). Acetone (50 mL) was added to freshly prepared $[(NH_3)_5Ru(H_2O)][PF_6]_2$ (1.0 g) and MedicydH$_2$ (174 mg). The mixture was stirred while being exposed to the atmosphere for 1 h, during which the solution color change from golden yellow to green. The solution was then gravity-filtered and the crude bromide salt of the product precipitated from solution by the addition of excess TBAB. This was filtered off, dried, and then purified by cation exchange chromatography on CM-Sephadex C25-120 resin (for 0.71 g of the crude bromide complex, the column dimensions were 30 cm height by 3.7 cm diameter). Elution with 1.0 M NaCl of the green product band was preceded by yellow and blue bands. The product was forced out of the eluent by the addition of $NaBPh_4$, filtered off, washed with water, and air-dried. Dissolving the tetraphenylborate complex salt in acetone followed by the addition of TBAB gave the bromide complex salt which was then converted to the hexafluorophosphate salt by the addition of NH_4PF_6 to a concentrated aqueous solution of the complex bromide salt. Ether diffusion into an acetone solution of the complex gave bluish green crystals of the complex. Yield: 0.24 g (20%). Anal. Calcd for $C_{11.25}H_{40.5}N_{14}O_{0.75}F_{24}P_4Ru_2$: C, 11.62; H, 3.51; N, 16.86. Found: C, 11.66; H, 3.47; N, 17.01. IR: $\nu(NCN) = 2096$ cm^{-1}.

Preparation of $[\{(NH_3)_5Ru\}_2(\mu\text{-MeOdicyd})][PF_6]_4$ (3). This complex was prepared similarly to the Medicyd analogue. From 0.5 g of $[(NH_3)_5Ru(H_2O)][PF_6]_2$ was obtained 0.185 g (32%) of bluish green crystalline complex. Anal. Calcd for $C_9H_{36}N_{14}OF_{24}P_4Ru_2$: C, 9.50; H, 3.19; N, 17.22. Found: C, 9.80; H, 3.20; N, 16.65. IR: $\nu(NCN) = 2106$ cm^{-1}.

Physical Measurements. The equipment used to perform IR (KBr disk) and UV−vis−near-IR spectroscopy has been described in a previous paper.[19] The LMCT absorption bands of the complexes were non-Gaussian, and so the standard equation for oscillator strength could not be used. The oscillator strength was calculated by fitting the band profiles to a set of Gaussian bands with PeakFit v3.0 software from Jandel Scientific and then summing the oscillator strengths of each Gaussian band determined from $f = 4.61 \times 10^{-9}(\epsilon_{max}\nu_{1/2})$, where ϵ_{max} is the extinction coefficient in M^{-1} cm^{-1} and $\nu_{1/2}$ is the bandwidth at half peak height.

Solution magnetic susceptibility measurements were determined by the Evans method,[20] with a Bruker AMX-400 NMR spectrometer at 300 K. TMS was used as an internal reference in nonaqueous solutions, while DSS was used as an internal reference in deuterium oxide. Special stem coaxial insert tubes (dimensions: 203 mm × 4 mm o.d.) with a capillary reference volume of 60 μL (capillary dimensions: 50 mm × 2.5 mm o.d.) were made of precision grade Pyrex by the Wilmad Glass Co.

The NMR method for magnetic susceptibility measurements was originally developed by Evans for NMR instruments whose magnetic fields were perpendicular to the sample tube axis. Modern instruments generally have magnetic fields parallel to the sample tube axis, and this changes the form of the Evans method expression[21] for mass susceptibility χ_g to

$$\chi_g = \frac{-3\Delta f}{4\pi F m} + \left[\chi_0 + \frac{\chi_0(d_0 - d_s)}{m}\right] \tag{5}$$

where Δf is the observed frequency shift in Hz of the reference resonance, F is the fixed probe frequency in Hz of the NMR spectrophotometer, χ_0 is the mass susceptibility in cm^3 g^{-1} of the solvent, m is the mass in grams of the complex per cm^3 of solution, and d_0 and d_s are the densities in g cm^{-3} of the solvent and solution, respectively. The term in the square brackets is a correction to the solvent's density and hence diamagnetism because of the addition of solute. The complex concentration for all the solutions studied was 11 mM, except in nitromethane, where the solubility of the complexes limited the concentration to 1.8 mM. At these concentrations, the solution density is approximated by $d_0 + m$,[22] and the mass susceptibility simplifies to

$$\chi_g = \frac{-3\Delta f}{4\pi F m} \tag{6}$$

The diamagnetic correction to the molar susceptibility χ_m for each complex was calculated[18] from Pascal's constants,[23] and the effective magnetic moment μ_{eff} was calculated by using the standard equation

$$\mu_{eff} = 2.828(\chi_{m'}T)^{1/2} \quad (\mu_B) \tag{7}$$

where $\chi_{m'}$ is the corrected molar susceptibility and T is the temperature in K.

An orbital contribution to the magnetic moment might be expected for a low-spin Ru(III) ion in an octahedral ligand field. However, low

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Table 1. Oscillator Strengths of the Lowest Energy LMCT Bands, Metal−Ligand Coupling Elements, LMCT Excited-State Energies, and Calculated Antiferromagnetic Exchange Constants for $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ in Dimethyl Sulfoxide Solution[a]

L	ν_{max}	f	$h_{d\pi}$[b]	Δ	$-J_{AF}$[c]
$MeOdicyd^{2-}$	10 230	0.376	2040	5310	70
Me_2dicyd^{2-}	9 890	0.372	2000	4970	70
$Medicyd^{2-}$	10 310	0.346	1970	5390	60
$dicyd^{2-}$	11 060	0.351	2050	6140	50
Cl_2dicyd^{2-}	12 640	0.275	1940	7720	30
Cl_4dicyd^{2-}	13 970	0.223	1840	9050	20
Me_4dicyd^{2-}	10 500	0.352	2000	5580	60

[a] All data have units of cm^{-1} except oscillator strength, which is unitless. [b] Calculated according to eq 4. $r = 6.5$ Å, and f is divided by 2. See text for details. [c] Calculated according to eq 3. See text for details.

Table 2. Oscillator Strengths of the Lowest Energy LMCT Bands, Metal−Ligand Coupling Elements, LMCT Excited State Energies, and Calculated Antiferromagnetic Exchange Constants for $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ in Acetone Solution[a]

L	ν_{max}	f	$h_{d\pi}$[b]	Δ	$-J_{AF}$[c]
$MeOdicyd^{2-}$	8970	0.591	2400	4050	220
Me_2dicyd^{2-}	8950	0.550	2310	4030	200
$Medicyd^{2-}$	9050	0.553	2330	4130	190
$dicyd^{2-}$	9200	0.477	2180	4280	140
Cl_2dicyd^{2-}	10380	0.400	2120	5460	80
Cl_4dicyd^{2-}	12790	0.299	2040	7870	30
Me_4dicyd^{2-}	9280	0.656	2570	4360	260

[a] All data have units of cm^{-1} except oscillator strength, which is unitless. [b] Calculated according to eq 4. $r = 6.5$ Å, and f is divided by 2. See text for details. [c] Calculated according to eq 3. See text for details.

Table 3. Oscillator Strengths of the Lowest Energy LMCT Bands, Metal−Ligand Coupling Elements, LMCT Excited State Energies, and Calculated Antiferromagnetic Exchange Constants for $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ in Acetonitrile Solution[a]

L	ν_{max}	f	$h_{d\pi}$[b]	Δ	$-J_{AF}$[c]
$MeOdicyd^{2-}$	8900	0.730	2660	3970	350
Me_2dicyd^{2-}	8920	0.684	2570	4000	300
$Medicyd^{2-}$	9020	0.642	2510	4100	360
$dicyd^{2-}$	9140	0.606	2450	4220	230
Cl_2dicyd^{2-}	9940	0.468	2250	5020	110
Cl_4dicyd^{2-}	12000	0.366	2180	7080	50
Me_4dicyd^{2-}	9360	0.732	2760	4440	330

[a] All data have units of cm^{-1} except oscillator strength, which is unitless. [b] Calculated according to eq 4. $r = 6.5$ Å, and f is divided by 2. See text for details. [c] Calculated according to eq 3. See text for details.

Table 4. Oscillator Strengths of the Lowest Energy LMCT Bands, Metal−Ligand Coupling Elements, LMCT Excited State Energies, and Calculated Antiferromagnetic Exchange Constants for $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ in Nitromethane Solution[a]

L	ν_{max}	f	$h_{d\pi}$[b]	Δ	$-J_{AF}$[c]
$MeOdicyd^{2-}$	9040	0.726	2670	4120	330
Me_2dicyd^{2-}	9080	0.718	2660	4160	320
$Medicyd^{2-}$	9040	0.661	2550	4120	280
$dicyd^{2-}$	9030	0.675	2570	4110	290
Cl_2dicyd^{2-}	9180	0.537	2310	4260	170
Cl_4dicyd^{2-}	10500	0.409	2160	5580	80

[a] All data have units of cm^{-1} except oscillator strength, which is unitless. [b] Calculated according to eq 4. $r = 6.5$ Å, and f is divided by 2. See text for details. [c] Calculated according to eq 3. See text for details.

Table 5. Oscillator Strengths of the Lowest Energy LMCT Bands, Metal−Ligand Coupling Elements, LMCT Excited State Energies, and Calculated Antiferromagnetic Exchange Constants for $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ in Aqueous Solution[a]

L	ν_{max}	f	$h_{d\pi}$[b]	Δ	$-J_{AF}$[c]
$MeOdicyd^{2-}$	10 100	0.398	2090	5090	80
Me_2dicyd^{2-}	9 790	0.388	2030	4870	80
Me_2dicyd^{2-} [d]	18 480	0.078	1250	13560	1
Me_2dicyd^{2-} [e]	13 620	0.125	1360	8700	5
$Medicyd^{2-}$	10 360	0.364	2020	5440	60
$dicyd^{2-}$	11 500	0.351	2090	6580	50
Cl_2dicyd^{2-}	12 600	0.337	2150	7680	40
Cl_4dicyd^{2-}	14 070	0.209	1790	9150	10
Me_4dicyd^{2-}	12 630	0.266	1910	7710	20

[a] All data have units of cm^{-1} except oscillator strength, which is unitless. [b] Calculated according to eq 4. $r = 6.5$ Å, and f is divided by 2. See text for details. [c] Calculated according to eq 3. See text for details [d] In 1.2 M DCl solution. [e] In 0.12 M DCl solution.

coordination sphere symmetry can result in quenching of orbital angular momentum, and this is suggested to be the case for the complexes of this study because of the acceptable fits of the temperature dependence of the magnetic susceptibility of these complexes using the spin-only Bleaney−Bowers expression.[14]

Results

Representative electronic absorption spectra of the ruthenium dimer complexes have been published.[24] The spectral data for the lowest energy LMCT band of the ruthenium dimers in DMSO, acetone, acetonitrile, nitromethane, and water appear respectively in Tables 1−5. Also included in these tables are the metal−ligand coupling elements $h_{d\pi}$ and exchange constants $-J_{AF}$ that were calculated according to eqs 4 and 3, respectively. To calculate $h_{d\pi}$, the value of r in eq 4 was taken as 6.5 Å, the distance between Ru(III) and the midpoint of the bridging $dicyd^{2-}$ ligand. The oscillator strength in eq 4 is that of a single ruthenium(III)−cyanamide chromophore and has been approximated by dividing the oscillator strengths in Tables 1−5 by a factor of 2. In eq 3, Δ was estimated from

$$\nu_{max} = \Delta + \chi \tag{8}$$

where ν_{max} is the optical energy at ϵ_{max} of the low-energy LMCT band and χ is an energy term which arises from Franck−Condon excitation into excited vibrational levels and is related to inner- and outer-sphere reorganizational energies. The value of χ is assumed to be constant[25] and is given a value of 0.61 eV, which was obtained from the intercept of a plot of the difference in Ru(III/II) and ligand(0/1−) couples versus ν_{max} for a series of mononuclear pentaammineruthenium phenylcyanamide complexes.[26] The values of U and E_{DCT} in eq 3 were assumed to be constant for the series of complexes studied.[27] The MMCT energy U was estimated[28] to be 20 970 cm^{-1} from the difference between the PES d orbital binding energies of $[Ru(NH_3)_6][Cl]_3$

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(24) Naklicki, M. L.; Crutchley, R. J. *Inorg. Chim. Acta* **1994**, *225*, 123.

(25) While the inner-sphere contribution to χ is expected not to vary significantly, the outer coordination sphere contribution will vary with solvent in proportion to $(1/D_{op} - 1/D_s)$ where D_{op} and D_s are optical and static dielectric constants of the solvent, respectively. A plot of the solvent dependence of MMCT band energies for the mixed-valence complex $[\{(NH_3)_5Ru\}_2(\mu\text{-4,4'-bipyridine})]^{5+}$ versus $(1/D_{op} - 1/D_s)$ shows that χ in acetonitrile is a good average. See: Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1.

(26) Crutchley, R. J.; McCaw, K.; Lee, F. L.; Gabe, E. J. *Inorg. Chem.* **1990**, *29*, 2576.

(27) Certainly, charge-transfer transitions are sensitive to metal and ligand orbital energies as well as the nature of the solvent, and this approximation will create scatter in the correlation to follow. However, for these complexes, MMCT and E_{DCT} are expected to follow the same minor variation in energy as that seen for the LMCT bands in Tables 1−5.

(28) The rationale for this method of estimating U has been published: Didziuslis, S. V.; Cohen, S. L.; Gerwirth, A. A.; Solomon, E. I. *J. Am. Chem. Soc.* **1988**, *110*, 250. See also ref 7.

Table 6. Effective Magnetic Moments[a] and Estimated Antiferromagnetic Exchange Constants[b] for $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{4+}$ in Various Solvents

	DMSO		acetone		acetonitrile		nitromethane		water	
L	μ_{eff}	$-2J_{est}$	μ_{eff}	$-2J_{est}$	μ_{eff}	$-2J_{est}$	μ_{eff}	$-2J_{est}$	μ_{eff}	$-2J_{est}$
MeOdicyd^{2-}	1.23	390	0.73	650	0.65	710	0.60	740	1.38	310
Me$_2$dicyd^{2-}	1.16	420	0.75	640	0.73	660	*c*		1.27	370
									1.43[d]	290
									1.34[e]	340
Medicyd^{2-}	1.25	380	0.75	640	0.73	660	0.62	730	1.38	310
dicyd^{2-}	1.25	380	0.88	570	0.79	620	0.64	720	1.35	330
Cl$_2$dicyd^{2-}	1.38	310	1.19	410	1.11	450	0.93	540	1.60	200
Cl$_4$dicyd^{2-}	1.42	290	1.30	350	1.30	350	1.24	380	1.86	36
Me$_4$dicyd^{2-}	1.24	380	0.78	630	0.79	620			1.50	260

[a] Per Ru(III) ion with units of Bohr magneton. [b] In cm^{-1}, calculated according to eq 9. [c] Diamagnetic. [d] In 1.2 M DCl solution. [e] In 0.12 M DCl solution.

and $[Ru(en)_3][ZnCl_4]$, where en is ethylenediamine.[29] The energy of the double-charge-transfer transition was estimated to be 31 400 cm^{-1} by assuming that it is the sum of stepwise LMCT transitions (10 000 cm^{-1} each), the energy difference between first and second oxidation potentials of the dicyd^{2-} ligand (5400 cm^{-1})[14] and a pairing energy term (6000 cm^{-1}) of a Ru(II) d orbital.[30] It is important to recognize that the double-charge-transfer excited-state term in eq 3 ($2/E_{DCT}$) contributes the most to the stability of the singlet ground state and that this is a consequence of the polarizability of the bridging ligand.

The antiferromagnetic exchange constants $-2J_{est}$ (Table 6) for the complexes in solution were estimated[31] from the magnetic moments, μ_{eff}, of the Ru(III) dimers in solution at $T = 298$ K, according to

$$-2J_{est} = kT \ln\left(\frac{3.0003g^2}{{\mu_{eff}}^2} - 3\right) \tag{9}$$

Thompson and Ramaswamy showed that this expression,[32] when fitted to literature values of $-2J$ for a wide selection of Cu(II) dimers, gave a sensible mean g value (2.198 ± 0.008) for Cu(II) and a mean room temperature (295.6 ± 4.5 K). In addition, these authors proposed that realistic estimates of exchange integrals could be obtained for antiferromagnetically coupled Cu(II) dimers by use of the graphical fit or eq 9 itself.[33] The use of this equation for Ru(III) dimers assumes that orbital angular momentum is largely quenched (see Experimental Section) and the coordination geometry is the same for all the complexes in solution. The latter assumption is important because it has been shown that the average g value[34] of mononuclear Ru(III) complexes can range from 2.01 to 2.36, depending upon the degree of tetragonal and rhombic distortions.[35] Because it was not possible to measure the average g values of the complexes in solution at room temperature,[36] we chose the g value for the Ru(III) dimers in solution to be 2.20 on the basis of values found for monoclear Ru(III) complexes[35,37] and those found for the mixed-valence complexes $[\{(NH_3)_5Ru\}_2(\mu\text{-L})]^{5+}$, where L = pyrazine[38] or quinone diimine[39] ($g = 2.28$ or 2.25, respectively).

Discussion

The trend in experimental antiferromagnetic exchange constants $-2J_{est}$ in Table 6, increasing in magnitude as electron-withdrawing substituents are replaced with electron-donating substituents on the bridging ligand, reflects the dependence of hole transfer superexchange on the ease of bridging ligand oxidation.[14,18] However, the data associated with $[\{(NH_3)_5Ru\}_2(\mu\text{-Me}_4\text{dicyd})]^{4+}$ appear not to follow this trend, and this is probably due to nonplanarity of the bridging ligand.

Optimal superexchange coupling in the complexes of this study requires a planar dicyd^{2-} bridging ligand and a linear Ru(III)−cyanamide bond because this geometry maximizes the π overlap between the bridging ligand HOMO and πd orbitals of the Ru(III) ions.[14] Crystal structures[40] of Me$_2$dicyd^{2-}, dicyd^{2-}, Cl$_2$dicyd^{2-}, and Cl$_4$dicyd^{2-} all show this planar geometry and anti conformation of the cyanamide groups to be preferred, with this preference maintained upon coordination, at least in the solid state.[41] On the other hand, the crystal structure[42] of Me$_4$dicyd^{2-} showed that the steric repulsion between methyl and cyanamide groups was enough to force the cyanamide groups out of the phenyl ring plane while retaining the anti conformation. The significance of conformation upon antiferromagnetic exchange was supported by variable-temperature solid-state magnetic susceptibility studies[42,43]

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(29) Shepard, R. E.; Proctor, A.; Henderson, W. W.; Myser, T. K. *Inorg. Chem.* **1987**, *26*, 2440.

(30) Here we have assumed that the pairing energy of the bridging ligand's HOMO cancels out the pairing energy of a 4d orbital in Ru(II). The value of 6000 cm^{-1} was calculated according to: Lever, A. B. P *Inorganic Electronic Spectroscopy*, 2nd ed.; Elsevier: New York, 1984; p 218.

(31) Thompson, L. K.; Ramaswamy, B. S. *Inorg. Chem.* **1986**, *25*, 2664.

(32) Equation 9 is derived from the substitution of the Van Vleck expression for magnetic susceptibility into eq 7.

(33) It is also possible to determine $-2J$ from temperature-dependent chemical shift data. See: Cotton, F. A.; Eglin, J. L.; Hong, B.; James, C. A. *J. Am. Chem. Soc.* **1992**, *114*, 4915. The solvents used in this study have a limited temperature range and are not optimal for these measurements. In addition, the donor−acceptor interaction between the solvent and ammine protons is expected to be temperature dependent.

(34) The average g was calculated according to $g = [(g_1^2 + g_2^2 + g_3^2)/3]^{1/2}$.

(35) LaChance-Galang, K. J.; Doan, P. E.; Clarke, M. J.; Rao, U.; Yamano, A.; Hoffman, B. M. *J. Am. Chem. Soc.* **1995**, *117*, 3529.

(36) No EPR signal was observed for the complexes in solution at room temperature or as glasses at 77 K.

(37) Medhi, O. K.; Agarwala, U. *Inorg. Chem.* **1980**, *19*, 1381.

(38) Hush, N. S.; Edgar, A.; Beattie, J. K. *Chem. Phys. Lett.* **1980**, *69*, 128.

(39) Joss, S.; Reust, H.; Ludi, A. *J. Am. Chem. Soc.* **1981**, *103*, 981.

(40) Aquino, M. A. S.; Crutchley, R. J.; Lee, F. L.; Gabe, E. J.; Bensimon, C. *Acta Crystallogr.* **1993**, *C49*, 1543.

(41) A crystal structure of *trans*-$[\{(NH_3)_4Ru(\text{pyridine})\}_2(\mu\text{-dicyd})]^{4+}$ showed the dicyd bridging ligand to be planar but with cyanamides in the syn conformation: Rezvani, A. R.; Bensimon, C.; Cromp, B.; Reber, C.; Greedan, J. E.; Kondratiev, V. V.; Crutchley, R. J. *Inorg. Chem.* **1997**, *36*, 3322. A crystal structure of the pentaammine analogue in ref 14 showed a planar bridging ligand with cyanamides in the anti conformation.

(42) Aquino, M. A. S.; Crutchley, R. J.; Lee, F. L.; Gabe, E. J.; Bensimon, C. *Acta Crystallogr.* **1993**, *C49*, 1543.

(43) Recent high-temperature magnetic susceptibility measurements have raised our lower limit for $-J$ from that reported in ref 14.

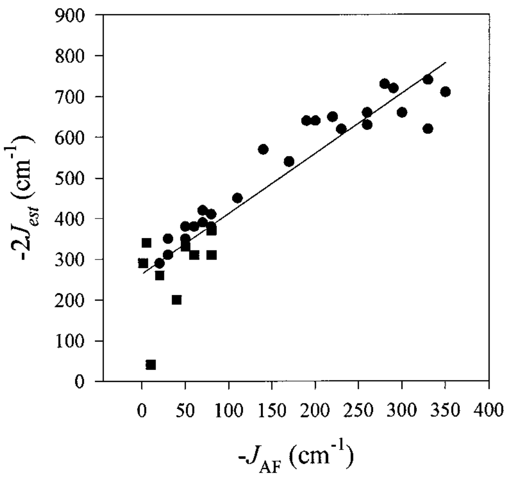

Figure 1. Plot of calculated versus estimated antiferromagnetic exchange constants for the complexes in aprotic solvents (solid circles) and the complexes in aqueous solutions (solid squares). The data for the plot appear in Tables 1−6. The equation for the line is $2J_{est} = 1.5J_{AF} - 260$; $R^2 = 0.86$.

which yielded $-2J \geq 1000$ cm^{-1} for [{(NH$_3$)$_5$Ru}$_2$(μ-Me$_2$dicyd)][ClO$_4$]$_4$ in contrast to $-2J = 107$ cm^{-1} for [{(NH$_3$)$_5$Ru}$_2$(μ-Me$_4$dicyd)][ClO$_4$]$_4$. The latter result is considerably attenuated from that expected if only the donor properties of the substituents are important to the energy of the superexchange pathway, suggesting the existence of geometric factors. In solution, the barriers to rotation of the cyanamide group between in-plane and out-of-plane anti conformations for dicyd^{2-} and Me$_4$dicyd^{2-} ligands were calculated[44] to be 3.5 and 8.9 kcal/mol, respectively, with the most stable conformer in agreement with that found by the above crystallographic studies. The preference of Me$_4$dicyd^{2-} for the out-of-plane anti conformation is expected to be retained upon coordination and in solution and thus to comprise the aforementioned geometric factor. It is important to note that the solution $-2J_{est}$ values for [{(NH$_3$)$_5$Ru}$_2$(μ-Me$_4$dicyd)]$^{4+}$ are significantly greater than the solid-state result. This is consistent with rotation into conformations for which superexchange is stronger.

The plot of estimated versus calculated antiferromagnetic exchange constants for the complexes in aprotic and protic solvents is shown in Figure 1. The strong correlation between $-2J_{est}$ and $-J_{AF}$ suggests that both eqs 3 and 4 are realistic models; however, the linear least-squares fit of the data points ($2J_{est} = 1.5J_{AF} - 260$) is at odds with eq 2, which predicts unity slope and positive intercept for constant J_F.[45] It is clear from Figure 1 that eq 3 underestimates antiferromagnetic exchange.[46] If the derivation of eq 3 is accepted, the greatest source of potential error is the estimate of metal−ligand coupling $h_{d\pi}$ from the oscillator strength of the low-energy LMCT band and eq 4.

When calculating $h_{d\pi}$, we have estimated[47] the oscillator strength of a single ruthenium(III)−cyanamide chromophore by dividing the dinuclear oscillator strengths in Tables 1−5 by a factor of 2. The mononuclear complexes [(NH$_3$)$_5$Ru(Me$_2$dicyd)]$^+$, [(NH$_3$)$_5$Ru(dicyd)]$^+$, and [(NH$_3$)$_5$Ru(Cl$_2$dicyd)]$^+$ in aqueous solution gave low-energy LMCT oscillator strengths of 0.215, 0.169, and 0.155, respectively.[48] These values are approximately a factor of 2 smaller than those in Table 5 for the corresponding dinuclear complexes, and this gives us confidence that our estimate is reasonable. On the other hand, our estimate of $r = 6.5$ Å in eq 4 may be a source of significant error. Covalency in the Ru(III)−cyanamide bond would have the effect of decreasing the transition dipole moment length, which would increase the calculated value of $h_{d\pi}$ and hence J_{AF}.

The negative intercept of the equation for the line in Figure 1 implies the existence of a solvent-independent mechanism for antiferromagnetic superexchange that is large enough to compensate for J_F.[49] In a previous study, it was shown that both the dicyd^{2-} ligand's HOMO and SHOMO are suitable mediators for superexchange. The HOMO was shown to be orthogonal to the dicyd^{2-} plane whereas the SHOMO was in the plane. The donor−acceptor interaction of the solvent with the ammine protons has the effect of weakening the π bond between the Ru(III) ions and the cyanamide groups[50] and thereby weakening superexchange via the bridging ligand's π symmetry orbitals. The LMCT oscillator strength of [{(NH$_3$)$_5$Ru}$_2$(μ-Me$_2$dicyd)]$^{4+}$ in Table 5 was measured under acidic conditions (1.2 M DCl), where protonation of the coordinated cyanamide can occur,[51] and yet the Ru(III) ions were still antiferromagnetically coupled with $-J_{est} = 290$ cm^{-1}. One might have reasoned that protonation should have removed the π superexchange pathways; however, extended Huekel calculations of the fully protonated planar[52] bridging ligand dicydH$_2$ show a π HOMO spanning the entire molecule. This π HOMO is at higher energy but can nevertheless serve as a superexchange pathway. Another possibility is a σ-bonding superexchange pathway. This would be less sensitive to solvent perturbations because of stronger bonding.

The above discussion supports the contention that the valence bond model of antiferromagnetic superexchange (eq 3) in conjunction with the Mulliken−Hush treatment of metal−ligand coupling elements (eq 4) is a reasonable model that can be used to rationalize the trend of antiferromagnetic exchange in the complexes of this study. The generality of this approach may be limited to second- and third-row transition metals. Ab initio calculations of magnetic exchange coupling in linear oxo-bridged dinuclear complexes of Ti(III), V(III), and Cr(III) showed that it was necessary to consider *all* the single and double excitations of the valence electrons with multireference configuration interaction calculations to obtain reasonable agreement with experiment.[9b]

Acknowledgment. We are grateful to the Natural Sciences and Engineering Research Council of Canada for financial support. We also thank Johnson-Matthey Ltd. for the loan of ruthenium trichloride hydrate.

IC970728P

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(44) Tripos Sybyl software.

(45) J_F is essentially an electron-pairing term which should remain constant for a series of similar complexes

(46) Conversely, J_{est} may be overestimated. However, only a minor variation in the magnitude of J_{est} is calculated by using eq 9 for the experimental range of $g = 2.0-2.4$ for Ru(III) complexes.

(47) A similar approximation was made when $h_{d\pi}$ was calculated from MLCT oscillator strengths. See ref 12.

(48) Naklicki, M. L.; White, C. A.; Krondratiev, V. V.; Crutchley, R. J. *Inorg. Chim. Acta* **1996**, *242*, 63.

(49) This ferromagnetic term is not expected to be large in any case. See: (a) Okamura, M. Y.; Fredkin, D. R.; Isaacson, R. A.; Feher, G. In *Tunneling in Biological Systems*; Chance, B., DeVault, D. C., Frauenfelder, H., Marcus, R. A., Schrieffer, J. R., Sutin, N., Eds.; Academic Press: New York, 1974; p 729. (b) Bertrand, P. *Chem. Phys. Lett.* **1985**, *113*, 104. If J_F is small, it could well be canceled by second-order antiferromagnetic contributions. See ref 9a.

(50) The ammine becomes more "amide-like" and contributes π electron density to Ru(III).

(51) Naklicki, M. L.; Crutchley, R. J. *Inorg. Chem.* **1989**, *28*, 4226.

(52) Hyperchem energy minimization of dicydH$_2$ gave a planar conformer with anti cyanamide groups.