Inorg. Chem. **1998,** *37,* 6161−6167

Comparison of Hole-Transfer Superexchange in Dinuclear Mixed-Valence Ruthenium Complexes

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Received May 22, 1998

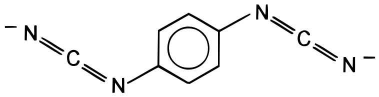
Three dinuclear complexes [{*mer*-Ru(NH_3)$_3$(bpy)}$_2$(μ-L)][ClO_4]$_4$, where L = 2,5-dimethyl- (Me_2dicyd^{2-}), 2,5-dichloro- (Cl_2dicyd^{2-}), and unsubstituted 1,4-dicyanamidobenzene dianion ($dicyd^{2-}$), have been synthesized and characterized by magnetic resonance, electrochemical, and electronic absorption spectroscopic techniques. A crystal structure of [{*mer*-Ru(NH_3)$_3$(bpy)}$_2$(μ-dicyd)][ClO_4]$_4$·3H_2O showed $dicyd^{2-}$ to be approximately planar with the cyanamido groups in an anti configuration. Crystal structure data are space group = $P\bar{1}$, with a, b, and c equal to 12.5613(1), 12.8738(1), and 16.3267(2) Å, respectively, α, β, and γ equal to 76.756(1), 83.893(1), and 69.053(2)°, respectively, $V = 2399.28(4)$ Å^3, and $Z = 2$. The structure was refined using 6112 independent reflections with $I > 2.5\sigma(I)$ to a final R factor of 0.0568. The strongly coupled mixed-valence complexes [{*mer*-Ru(NH_3)$_3$(bpy)}$_2$(μ-L)]$^{3+}$ where L = Me_2dicyd^{2-}, $dicyd^{2-}$, and Cl_2dicyd^{2-} had decreasing comproportionation constants of 1.3×10^7, 9.3×10^6, and 3.5×10^5, respectively, which are consistent with a hole transfer superexchange mechanism for metal−metal coupling. The mixed-valence properties of these complexes together with analogous systems were compared in the context of a transformation from a localized to a delocalized mixed-valence state.

Introduction

Electronic and magnetic materials based on coordination complexes, thus composed of metal centers connected by bridging ligands of some description, are of interest e.g. for their potential as molecular wires and switches. Understanding the factors controlling metal−metal coupling is central to the purposeful synthesis of such materials and to the tuning of their properties. In such systems, the electronic interaction(s) of metal centers are mediated by the orbital(s) of the bridge, and the interplay between metal and bridge orbitals are thus central in determining the behavior of the resultant system.

There has been a great deal of work on mixed-valence systems in which the bridging ligand accepts π-electron density from the lower oxidation state metal ion.[1] In these cases, the dominant pathway for metal−metal interaction is electron-transfer superexchange. Alternatively, the acceptor wave function can extend itself onto the bridging ligand when the ligand is a π-donor. This mechanism is called hole-transfer superexchange and has been observed in only a few mixed-valence complexes.[2] Nevertheless, there are numerous examples of dinuclear complexes whose metals ions undergo antiferromagnetic exchange via hole-transfer superexchange.[3] The dinuclear complexes of this study are those in which the ruthenium ions are strongly coupled by hole-transfer superexchange when the metal ions are mixed-valent $Ru^{II}-Ru^{III}$ or oxidized $Ru^{III}-Ru^{III}$.

Previous studies of the pentaammine[4] and tetraamminepyridine[5] ruthenium complexes of 2,5-dimethyl-1,4-dicyanamidobenzene (Me_2dicyd^{2-}), 1,4-dicyanamidobenzene ($dicyd^{2-}$),



2,5-dichloro-1,4-dicyanamidobenzene (Cl_2dicyd^{2-}), and 2,3,5,6-tetrachloro-1,4-dicyanamidobenzene (Cl_4dicyd^{2-}) showed that the magnitude of superexchange could be controlled by the nature of the spectator ligands as well as the substituents on the bridging ligand in a manner entirely consistent with the hole-transfer mechanism. The solvent dependence of the comproportionation constants suggested that these complexes were localized mixed-valence systems, albeit very strongly coupled. For example, [{Ru(NH_3)$_5$}$_2$(μ-dicyd)]$^{3+}$ has $K_c = 10$, in D_2O, while $K_c = 6.84 \times 10^4$, in acetonitrile.[4c,6] The terpyridinebipyridine complex [{Ru(terpy)(bipy)}$_2$(μ-dicyd)]$^{3+}$ was prepared in the hopes of creating a delocalized mixed-valence state, and indeed solvent independent properties were observed.[7]

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(1) (a) Creutz, C. *Prog. Inorg. Chem.* **1983**, *30*, 1. (b) Crutchley, R. J. *Adv. Inorg. Chem.* **1994**, *41*, 273.

(2) (a) Beley, M.; Collin, J.-P.; Louis, R.; Metz, B.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1991**, *113*, 8521. (b) Krentzien, H.; Taube, H. *J. Am. Chem. Soc*. **1976**, *98*, 6379. (c) Hage, R.; Haasnoot, J. G.; Reedijk, J.; Wang, R.; Vos, J. G. *Inorg. Chem*. **1991**, *30*, 3263. (d) Haga, M.; Matsumura-Inoue, T.; Yamabe, S. *Inorg. Chem*. **1987**, *26*, 4148. (e) Kaim, W.; Kasack, V.; Binder, H.; Roth, E.; Jordanov, J. *Angew. Chem., Int. Ed. Engl*. **1988**, *27*, 1174. (f) Ward, M. D.; *Inorg. Chem*. **1996**, *35*, 1712.

(3) For example see: Thompson, L. K.; Ramaswamy, B. S. *Inorg. Chem*. **1986**, *25*, 2664 and references therein.

(4) (a) Aquino, M. A. S. Ph.D. Thesis, Carleton University, 1991. (b) Aquino, M. A. S.; Lee, F. L.; Gabe, E. J.; Bensimon, C.; Greedan, J. E.; Crutchley, R. J. *J. Am. Chem. Soc.* **1992**, *114*, 5130. (c) Naklicki, M. L. Ph.D. Thesis, Carleton University, 1995.

(5) (a) Rezvani, A. R.; Bensimon, C.; Cromp, B.; Reber, C.; Greedan, J. E.; Kondratiev, V.; Crutchley, R. J. *Inorg. Chem.* **1997**, *36*, 3322. (b) Rezvani, A. R. Ph.D. Thesis, Carleton University, 1995.

(6) (a) Naklicki, M. L.; Crutchley, R. J. *Inorg. Chim. Acta* **1994**, *225*, 123. (b) Naklicki, M. L.; Crutchley, R. J. *J. Am. Chem. Soc.* **1994**, *116*, 6045.

10.1021/ic980576d CCC: $15.00

In this study, we report the synthesis of a fourth family of dicyd^{2-}-bridged complexes, based on a triamminebipyridine inner coordination sphere for the ruthenium centers. This new family together with the above complexes permits an examination of the effect of sequentially replacing strong σ-donor ammine spectator ligands with π-acid pyridine spectator ligands on mixed-valence state properties.

Experimental Section

Reagents. Unless otherwise noted, all solvents and reagents were purchased from Aldrich, Anachemia, or Alfa Aesar, were reagent grade or better, and were used as received. Argon (industrial grade) was purchased from BOC, and sulfur dioxide (99.98%) from Matheson. Laboratory grade acetone (Anachemia) was distilled in glass. Acetonitrile for spectroscopy and electrochemistry was Anachemia Accusolv grade and was distilled in glass from phosphorus pentoxide under reduced pressure and stored under argon. The electrochemistry internal reference, ferrocene (J. T. Baker), was purified by sublimation, and the electrolyte tetrabutylammonium hexafluorophosphate (TBAH) was recrystallized twice from 2:1 ethanol/water and vacuum-dried overnight at 120 °C. Syntheses of the ligands 2,5-dimethyl-1,4-dicyanamidobenzene ($Me_2dicydH_2$), 1,4-dicyanamidobenzene ($dicydH_2$), and 2,5-dichloro-1,4-dicyanamidobenzene ($Cl_2dicydH_2$) have been previously reported.[4] $[Ru(NH_3)_5Cl]Cl_2$ was synthesized according to the method of Clarke,[8] and *trans*-$[Ru(NH_3)_4(SO_2)Cl]Cl$ according to the method of Vogt.[9]

Preparation of [*mer*-Ru(NH$_3$)$_3$(bpy)(SO$_4$)]Cl. The procedure outlined hereafter is a modification (eliminating an isolation step) of the method of Curtis.[10] Bipyridine (1.54 g, 9.6 mmol) was dissolved in acetone (10 mL) and the volume made up to 100 mL with water. Solid *trans*-$[Ru(NH_3)_4(SO_2)Cl]Cl$ (1.50 g, 4.9 mmol) was added to the solution which was heated with stirring to 50−70 °C for 1.5 h. To the cooled, gravity-filtered solution was added 1:1 0.4 M HCl:30% H_2O_2 (50 mL combined volume, ∼50× excess). The new solution was stirred for 30 min to ensure complete oxidation and was solvent stripped on a rotary evaporator at 55 °C to a total volume of ∼25 mL, and the product precipitated by the addition of 15 volume equiv of acetone and overnight refrigeration. Crystallization of the resultant oil was effected by decantation of the supernatant liquid, dissolution of the oil in water (∼25 mL), and the slow addition of 8 equiv of acetone. The mixture was allowed to sit at room temperature for several hours and was then placed in a freezer overnight to maximize the yield of russet-orange flakes of [*mer*-$Ru(NH_3)_3(bpy)(SO_4)]Cl$. These were collected by vacuum filtration and washed with acetone and ether (1.52 g, 3.5 mmol, 70% yield).

Preparation of [*mer*-Ru(NH$_3$)$_3$(bpy)(H$_2$O)][B(Ph)$_4$]$_2$. [*mer*-$Ru(NH_3)_3(bpy)(SO_4)]Cl$ (1.0 g, 2.3 mmol) was dissolved in water (75 mL), thrice degassed, and transferred to freshly prepared Zn/Hg amalgam (15 g) in an ice bath. The solution darkens from dark orange to a deep red almost immediately, yet the reduction was allowed to continue for 30 min; we occasionally vented the solution, to ensure completion. The solution was then transferred to a beaker, and the product precipitated by the pipetwise addition of a solution of $NaBPh_4$ (3.0 g in 25 mL H_2O). The purple precipitate was collected by vacuum filtration and immediately vacuum-dried, yielding [*mer*-$Ru(NH_3)_3(bpy)(H_2O)][B(Ph)_4]_2$ (1.99 g, 2.1 mmol, 92% yield).

Preparation of [{*mer*-Ru(NH$_3$)$_3$(bpy)}$_2$(μ-dicyd)][ClO$_4$]$_4$·2H$_2$O. 1,4-Dicyanamidobenzene (0.12 g, 0.78 mmol) was dissolved in acetone (100 mL) and thrice degassed on a double-manifold vacuum line equipped with argon as the inert gas. Solid [*mer*-$Ru(NH_3)_3(bpy)(H_2O)][B(Ph)_4]_2$ (1.50 g, 1.55 mmol) was added, and the solution degassed one additional time. After 16−24 h stirring under argon the solution was decanted into an Erlenmeyer flask and stirred open to air for an additional 16−24 h. Addition of solid tetrabutylammonium bromide, TBAB (6 g, ∼25× excess), to the solution, resulted in the precipitation of the mixed-valence complex, [{*mer*-$Ru(NH_3)_3(bpy)\}_2(\mu$-dicyd)]Br_3 (0.75 g, 0.74 mmol, 95% yield). This crude product was dissolved in water (100 mL) and treated with a solution of cerium(IV) ammonium nitrate (0.43 g, 0.74 mmol) in water (15 mL), and the resultant solution stirred for 20 min to ensure complete oxidation. [{*mer*-$Ru(NH_3)_3(bpy)\}_2(\mu$-dicyd)][PF_6]$_4$ was precipitated by the addition of solid ammonium hexafluorophosphate (9 g, ∼45× excess), collected by vacuum filtration, and washed sparingly with water. The PF_6^- salt was metathesized by dissolution in acetonitrile (30 mL), gravity filtration, and precipitation by addition of solid TBAB (3 g, ∼12× excess). The bromide salt [{*mer*-$Ru(NH_3)_3(bpy)\}_2(\mu$-dicyd)]Br_4 (0.48 g, 0.44 mmol, 60% yield) was then dissolved in a minimum of 1 M NaCl (∼75 mL), loaded onto a CM Sephadex C25 cation exchanger column (typically 1 in. diameter and 18 in. length, prepared with 1 M NaCl), and eluted under pressure with 1 M NaCl. The golden brown product band (typical volume ∼200 mL) eluted second after a small reddish band consistent with the mixed-valent complex, and the purified product was precipitated by addition of solid sodium perchlorate (1 g/10 mL of eluent), yielding [{*mer*-$Ru(NH_3)_3(bpy)\}_2(\mu$-dicyd)][ClO_4]$_4$ (0.29 g, 0.25 mmol, 55% yield) which was collected by vacuum filtration and washed sparingly with cold water. (**Caution!** *Perchlorate salts are sensitive and potentially explosive, particularly when dry. Extreme caution must be exercised when handling these salts!*) Once dry, the complex was recrystallized from acetonitrile by ether diffusion. Multiple recrystallizations afforded X-ray-quality crystals. Overall (approximate) yield from starting reagents was 30%. Elem. anal. Calcd: C, 27.87; H, 3.51; N, 16.25. Found: C, 27.77; H, 3.43; N, 15.95.

Preparation of [{*mer*-Ru(NH$_3$)$_3$(bpy)}$_2$(μ-Me$_2$dicyd)][ClO$_4$]$_4$·1.25MeCN. This complex was prepared in the same manner as its dicyd^{2-} analogue, including all molar ratios for the reagents. The neutral ligand, 1,4-dicyanamido-2,5-dimethylbenzene, did not, however, dissolve fully in acetone, and the reaction was performed heterogeneously. Overall (approximate) yield from starting reagents was 40%. Elem. anal. Calcd: C, 31.23; H, 3.69; N, 17.09. Found: C, 31.60; H, 3.47; N, 16.75.

Preparation of [{*mer*-Ru(NH$_3$)$_3$(bpy)}$_2$(μ-Cl$_2$dicyd)][ClO$_4$]$_4$·0.5MeCN. This complex was prepared in the same manner as its dicyd^{2-} analogue, including molar ratios for all reagents except cerium(IV) ammonium nitrate, for which the optimum ratio of oxidant/complex was found to be 0.8:1. As was the case with $Me_2dicydH_2$, neutral 1,4-dicyanamido-2,5-dichlorobenzene did not dissolve fully in acetone in the first step, and the reaction was performed heterogeneously. No trace of unreacted ligand was noticed after the initial reaction period. The crude bromide salt was purified by metathesis first to a PF_6^- salt and then back to a Br^- salt prior to performing the oxidation. This step was found to be necessary to avoid overoxidation of the complex, and the attendant loss of yield during column purification. Overall (approximate) yield from starting reagents was 25%. Elem. anal. Calcd: C, 27.64; H, 2.99; N, 16.12. Found: C, 27.81; H, 3.07; N, 15.85.

Appropriate solvent of recrystallization peaks were observed in the ^1H NMR spectra of each of the complexes.

Physical Measurements. Infrared spectra were obtained as KBr mulls using a Bomem Michelson 120 FTIR spectrophotometer, and data were analyzed using Bomem Grams/386 v3.04 Level II software. ^1H NMR spectra were obtained using a Bruker AMX-400 spectrometer at ambient temperatures with Ultra-Imperial Grade PP-507 sample tubes (Wilmad) and were referenced to solvent resonances or TMS. For the Evans method experiments Special Stem Coaxial Inserts (Wilmad) were also required and referencing was exclusively to TMS. UV−vis−NIR spectra were obtained using a Varian Cary 5 UV−vis−NIR Spectrophotometer at ambient temperatures using quartz cells of either 1.000 or 0.200 cm path length from Hellma (Canada) Limited at 600 nm/min with a data interval of 0.333 nm, a spectral bandwidth of 2.00 nm, and a signal averaging time of 0.033 s vs solvent backgrounds. Error in the wavelength measurements is ±0.01 nm in the visible and ±0.1 nm in the NIR region. Cyclic voltammograms were obtained

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(7) Rezvani, A. R.; Evans, C. E. B.; Crutchley, R. J. *Inorg. Chem.* **1995**, *34*, 4600.

(8) (a) Clarke, R. E. M.Sc. Thesis, University of California at Santa Barbara, 1978. (b) Chang, J. P.; Fung, E. Y.; Curtis, J. C. *Inorg. Chem.* **1986**, *25*, 4233.

(9) Vogt., L. H., Jr.; Katz, J. L.; Wiberley, S. E. *Inorg. Chem.* **1965**, *8*, 1157.

(10) Chang, J. P.; Fung, E. Y.; Curtis, J. C. *Inorg. Chem.* **1986**, *25*, 4233.

Table 1. Crystal Data and Structural Refinement Information for the X-ray Structural Determination of [{*mer*-Ru$(NH_3)_3$(bpy)}$_2$(μ-dicyd)]$[ClO_4]_4 \cdot 3H_2O$

empirical formula	$C_{28}H_{44}Cl_4N_{14}O_{19}Ru_2$
fw	1224.71
temperature	298(2) K
wavelength	0.710 73 Å
crystal system	triclinic
space group	$P\bar{1}$
unit cell dimensions	$a = 12.5613(1)$ Å $\alpha = 76.756(1)°$ $b = 12.8738(1)$ Å $\beta = 83.893(1)°$ $c = 16.3267(2)$ Å $\gamma = 69.053(2)°$
volume	2399.28 (4) Å^3
Z	2
density (calculated)	1.695 Mg/m^3
abs coeff	0.936 mm^{-1}
F(000)	1236
crystal size	$0.30 \times 0.20 \times 0.20$ mm
θ range for data collcn	1.73 to 22.50°
limiting indices	$-16 \leq h \leq 16$, $-13 \leq k \leq 16$, $-21 \leq l \leq 21$
no. of reflcns collcd	10 023
no. of indep reflcns	6112 [R(int) = 0.0271]
abs cor	none
refinement method	full-matrix least-squares on F^2
nos. of data/restraints/parameters	6106/1624/571
goodness-of-fit on F^2	1.033
final R indices [$I > 2\sigma(I)$]^a	$R1 = 0.0568$, $wR2 = 0.1473$
R indices (all data)^a	$R1 = 0.0629$, $wR2 = 0.1557$
largest diff peak and hole	0.919 and −0.892 e Å^{-3}

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. $wR2 = (\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2)^{1/2}$.

Table 2. Selected Bond Lengths and Angles[a] for [{*mer*-Ru$(NH_3)_3$(bpy)}$_2$(μ-dicyd)]$[ClO_4]_4$

Ru(1)−N(12)	1.978 (8)	Ru(1)−N(5)	2.139 (8)
Ru(1)−N(2)	2.049 (7)	N(11)−C(27)	1.309 (14)
Ru(1)−N(1)	2.070 (7)	N(11)−C(26)	1.335 (13)
Ru(1)−N(3)	2.138 (8)	N(12)−C(27)	1.172 (12)
Ru(1)−N(4)	2.139 (8)		

N(12)−Ru(1)−N(2)	95.0 (3)	C(27)−N(11)−C(26)	122.6 (9)
N(12)−Ru(1)−N(1)	173.6 (3)	C(27)−N(12)−Ru(1)	174.1 (8)
N(1)−Ru(1)−N(3)	97.6 (3)	C(28)−N(14)−Ru(2)	178.1 (8)
N(2)−Ru(1)−N(3)	176.3 (3)	N(12)−C(27)−N(11)	169.2 (10)
N(3)−Ru(1)−N(5)	88.8 (3)	N(14)−C(28)−N(13)	173.9 (11)
N(4)−Ru(1)−N(5)	177.6 (3)		

[a] Bond lengths are in Å, and angles are in degrees. Standard deviations are given in parentheses following each listed value. The numbering scheme is available in Figure 1.

using a BAS CV-27 voltammograph and BAS X-Y recorder at a constant temperature of 25 °C, maintained with a Haake D8-G refrigerated bath and circulator. The cell is configured for a working volume of ∼15 mL and is double-hulled to permit temperature control via the water bath. It was fitted with a Teflon cap through which the electrodes and argon bubbler were introduced to the cell via predrilled holes. The electrodes consisted of platinum disk working and counter electrodes (BAS, 1.6 mm diameter), a silver wire pseudo-reference electrode with ferrocene ($E° = 0.665$ V vs NHE in acetonitrile[11]) added as the internal reference, and 0.1 M TBAH as the supporting electrolyte. For aqueous solutions the working electrode was a disk of glassy carbon (BAS, 5 mm diameter), the counter electrode a platinum disk (BAS, 1.6 mm diameter), the reference electrode a saturated calomel electrode (SCE, $E° = 0.224$ V vs NHE at 25 °C) assembly (Accumet), and 0.1 M KCl was used as the supporting electrolyte. The error in electrochemical measurements is estimated to be ±5 mV. Analyte concentrations were on the order of 10^{-3} M, the solutions were deoxygenated by bubbling with argon for 20−30 min, and an argon blanket was maintained throughout the experiment. Spectroelectrochemistry was performed using an OTTLE cell based on the design of Hartl[12] and using gold-foil (500 lines/inch, 60% transmittance, Buckbee Mears) working and counter electrodes and a Ag/AgCl reference electrode. Spectra were obtained on the same Cary 5 Spectrophotometer as was used for electronic absorption spectroscopy vs appropriate backgrounds of solvent and electrolyte at a scan rate of 1200 nm/min, and potentials were controlled using the same BAS CV-27 as was used for cyclic voltammetry. At any given potential, the system was allowed to come to equilibrium ($i \approx 0$ μA) prior to acquisition of the spectrum. Elemental analyses were performed by Canadian Microanalytical Services, Ltd. (Delta, B.C., Canada).

Crystallography. Crystallographic data and refinement parameters are detailed in Table 1. Unit-cell parameters were calculated from reflections obtained from 60 data frames collected at different sections of the Ewald sphere. No symmetry higher than triclinic was evident from the diffraction data or unit-cell parameters. Data were collected on a Siemens SMART CCD diffractometer using a multirun routine which collects two-dimensional data frames with an effective coverage of >80% of the Ewald sphere. The E statistics strongly suggested the centric option and solution in $P\bar{1}$ yielded chemically reasonable and computationally stable results. A trial application of semiempirical absorption corrections based on redundant data at varying effective azimuthal angles yielded T_{max}/T_{min} at unity and was ignored.

Standard Lorentz polarization correction was applied. The anions were located each statistically disordered with a 50/50 site distribution. Three cocrystallized water molecules of hydration were also located. All non-hydrogen atoms were refined with anisotropic displacement coefficients except those atoms on the anions and solvent molecules which were refined isotropically. All hydrogen atoms were treated as idealized contributions excepting those hydrogen atoms on the water molecules which were ignored but included in calculations for intrinsic properties.

The structure was solved by direct methods, completed by subsequent Fourier syntheses and refined with full-matrix least-squares methods.

All scattering factors and anomalous dispersion coefficients are contained in the SHELXTL 5.03 program library.[13] Further crystallographic details are deposited with the Cambridge Crystallographic Data Centre (http://www.ccdc.cam.ac.uk) under the depository number 100738.

Results

The triammine complexes can be isolated as golden-brown air-stable crystals after repeated recrystallizations. In aqueous, acetonitrile or nitromethane solutions, the complexes appear stable. However, in acetone or DMSO solutions, partial autoreduction to the mixed-valence complex was observed.

Selected bond lengths and angles from the structural determination of [{*mer*-Ru$(NH_3)_3$(bpy)}$_2$(μ-dicyd)]$[ClO_4]_4$ have been placed in Table 2. Table 2 presents a minimum data set of the cyanamide group and the coordination sphere about the Ru1 ion. A labeled ORTEP drawing for this complex is given as Figure 1. Of significance is the anti conformation of the cyanamide groups, which was found to be the case for [{Ru$(NH_3)_5$}$_2$(μ-dicyd)][OTs]$_4$,[4] OTs = tosylate, but not for [{*trans*-Ru$(NH_3)_4$(py)}$_2$(μ-dicyd)]$[PF_6]_4$,[5] which adopted a syn conformation. Unlike the case of [{Ru$(NH_3)_5$}$_2$(μ-dicyd)][OTs]$_4$, only a single coordination mode of the ligand was found in the crystal structure of [{*mer*-Ru$(NH_3)_3$(bpy)}$_2$(μ-dicyd)]$[ClO_4]_4$.

The bond angles for the NCN moieties themselves (169 and 174°) and for the N*C*−*N*−*Ru* bonds (174 and 178°) were close to linear, as is expected since such conformations maximize π-overlap, and hence coupling, in the system. Similar coordination angles were seen in both the pentaammine[4] and tetraammine[5] complexes of dicyd^{2-}, and the NCN angle in the free

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(11) Gennett, T.; Milner, D. F.; Weaver, M. J. *J. Phys. Chem.* **1985**, *89*, 2787.

(12) Krejcik, M.; Danek, M.; Hartl, F. *J. Electroanal. Chem.* **1991**, *317*, 179.

(13) Sheldrick, G. M. *SHELXTL Program Library*, Version 5.03; Siemens Analytical X-ray Instruments Division: Madison, WI, 1994.

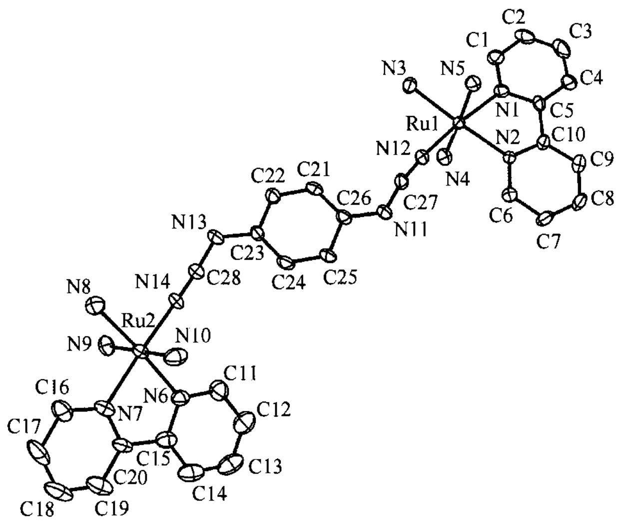

Figure 1. ORTEP of the [{*mer*-Ru(NH$_3$)$_3$(bpy)}$_2$(μ-dicyd)]$^{4+}$ cation.

ligand (as a tetraphenylarsonium salt) is 174°.[14] Regardless of small variations in individual bonds between systems, overall Ru(1)−Ru(2) throughspace separation is unaffected, being 13.1 Å in both [{*mer*-Ru(NH$_3$)$_3$(bpy)}$_2$(μ-dicyd)][ClO$_4$]$_4$ and [{Ru(NH$_3$)$_5$}$_2$(μ-dicyd)][OTs]$_4$. The much shorter value of 10.9 Å for [{*trans*-Ru(NH$_3$)$_4$(py)}$_2$(μ-dicyd)][PF$_6$]$_4$ is due to the syn conformation of its cyanamide moieties.

It is interesting to note that the growth of X-ray-quality crystals was extremely sensitive to ambient humidity. When recrystallizations of the triammine complexes yielded powders, associated solvent molecules were acetonitrile, not water.

For [{*mer*-Ru(NH$_3$)$_3$(bpy)}$_2$(μ-L)]$^{4+}$ where L = Me$_2$dicyd^{2-} and dicyd^{2-}, Evans method[15,16] determination of the paramagnetic susceptibility of the complexes in acetonitrile solution showed no splitting of the TMS reference peak. This suggests that the complexes are either diamagnetic or only very weakly paramagnetic.[17] On the other hand, for [{*mer*-Ru(NH$_3$)$_3$(bpy)}$_2$(μ-Cl$_2$dicyd)]$^{4+}$, two TMS resonances were observed whose separation is consistent with a magnetic susceptibility of 0.785 μ_B/Ru^{III}. In agreement with these results, the 400 MHz ^{1}H NMR spectra of both the L = dicyd^{2-} and L = Me$_2$dicyd^{2-} complexes show no evidence of paramagnetic shifting, while paramagnetic shifting, particularly of the axial ammine protons, was seen in the acetonitrile spectra of the L = Cl$_2$dicyd^{2-} complex (Table 3). Similar, although far more dramatic, paramagnetic effects were observed with the [{Ru(NH$_3$)$_5$}$_2$(μ-L)]$^{4+}$ complexes, where L is a dicyd^{2-} derivative.[16,18] For these latter complexes, the nature of the bridging ligand and the solvent influence the magnitude of antiferromagnetic exchange and hence the thermal population of the triplet excited state.

The 1-D nitromethane spectrum of the aromatic region of [{*mer*-Ru(NH$_3$)$_3$(bpy)}$_2$(μ-Me$_2$dicyd)][ClO$_4$]$_4$ is provided as Supporting Information. We believe the spectrum of bipyridine, bound to Ru(III) yet in a diamagnetic environment, to be unique in the literature. Assignment of the bipyridine proton resonances (Figure 2 indicates the labeling of the hydrogens) was effected via 2-D COSY and NOESY techniques. The latter spectrum indicated a strong through-space interaction of the 3 and 3′ protons, as well as an interaction between proton 6 and the hydrogens of the equatorial ammine. With the couplings indicated by the COSY spectrum, this information allowed the individual resonances to be assigned not only to a specific position on a ring, but also to a specific ring of bipyridine.

Table 3. Chemical Shift Data[a] (in ppm) for the Complexes [{*mer*-Ru(NH$_3$)$_3$(bpy)}$_2$(μ-L)][ClO$_4$]$_4$ (L = Me$_2$dicyd^{2-}, dicyd^{2-}, and Cl$_2$dicyd^{2-}) in Various Solvents (NM, AN, and DMSO)

	Ligand						
	Me$_2$dicyd^{2-}		dicyd^{2-}			Cl$_2$dicyd^{2-}	
	NM	AN	NM	AN	DMSO	NM	AN
3	8.59	8.56	8.64	8.68	9.71	8.95	9.40
3′	8.47	8.40	8.48	8.40	8.65	8.53	8.27
4	8.24	8.15	8.30	8.16	8.37	8.30	7.40
4′	8.05	7.98	8.04	7.96	8.03	8.04	8.00
5	7.82	7.79	7.87	7.90	7.21	8.12	8.52
5′	7.59	7.51	7.57	7.50	6.81	7.40	6.99
6	9.02	8.80	8.93	∼8.57	∼5.66	8.12	5.85
6′	9.16	8.91	8.96	8.59	5.22	7.99	6.20
L$_H$	7.64	−	∼8	−	5.61	∼7.78	−
L$_{Me}$	2.20	−	N/A	N/A	N/A	N/A	N/A
A$_{eq}$	3.17	2.97	3.14	2.96	3.89	3.51	3.77
A$_{ax}$	2.19	2.09	2.42	2.54	13.87	4.63	10.23

[a] Bipyridine hydrogens are represented by the numbers (see Figure 2), the bridging ligand hydrogens and methyl groups by L$_H$ and L$_{me}$, respectively, and the equatorial and axial ammines by A$_{eq}$ and A$_{ax}$, respectively. (The equatorial ammine is that in the plane of the bipyridine rings.)

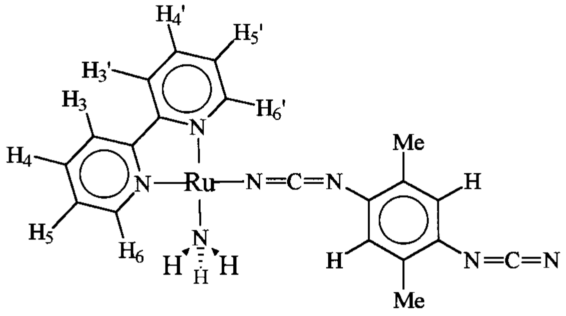

Figure 2. Schematic representation of the equatorial coordination plane about one ruthenium center in [{*mer*-Ru(NH$_3$)$_3$(bpy)}$_2$(μ-Me$_2$dicyd)]$^{4+}$ showing the hydrogen numbering scheme for bipyridine. Peaks due to bridging ligand hydrogens (H) or methyl groups (Me) are so labeled.

A significant steric interaction between the 3 and 3′ protons causes these to be the most deshielded in [Ru(bpy)$_3$]$^{2+}$ and a number of other spectra of bpy-containing ruthenium complexes.[19] In the diamagnetic triammines, however, the 6 position protons are the most deshielded, and this may be attributable to inductive effects associated with the higher oxidation state of the metal.

Examination of the three complexes of this study via cyclic voltammetry in acetonitrile showed four well-separated redox events (see Supporting Information). At more negative poten-

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

(15) (a) Evans, D. F. *J. Chem. Soc.* **1959**, 2003. (b) Philips, W. D.; Poe, M. *Methods Enzymol.* **1972**, *24*, 304. (c) Schubert, E. M. *J. Chem. Educ.* **1992**, *69*, 62.

(16) Naklick, M. L.; White, C. A.; Plante, L. L.; Evans, C. E. B.; Crutchley, R. J. *Inorg. Chem.* **1998**, *37*, 1880.

(17) The digital resolution of the Bruker AMX-400 NMR spectrometer was between 0.3 and 0.5 Hz depending on sweep width.

(18) Naklick, M. L.; Crutchley, R. J. *Inorg. Chem.*, submitted.

(19) (a) Lyttle, F. E.; Petrosky, L. M.; Carlson, L. R. *Anal. Chim. Acta* **1971**, *57*, 239. (b) Orellana, G.; Ibarra, C. A.; Santoro, J. *Inorg. Chem.* **1988**, *27*, 1025. (c) Anderson, P. A.; Deacon, G. B.; Haarmann, K. H.; Keene, F. R.; Meyer, T. J.; Reitsma, D. A.; Skelton, B. W.; Strouse, G. F.; Thomas, N. C.; Tweadway, J. A.; White, A. H. *Inorg. Chem.* **1995**, *34*, 6145. (d) Heijden, M.; van Vliet, P. M.; Haasnoot, J. G.; Reedijk, J. *J. Chem. Soc., Dalton Trans.* **1993**, 3675. (e) Rutherford, T. J.; Reitsma, D. A.; Keene, F. R. *J. Chem. Soc., Dalton Trans.* **1994**, 3659. (f) Bryant, G. M.; Ferguson, J. E. *Aust. J. Chem.* **1971**, *24*, 441. (g) Predieri, G.; Vignali, C.; Gianfranco, D.; Scolastica, S. *Inorg. Chim. Acta* **1993**, *205*, 145.

Table 4. Redox Couples and Comproportionation Constants as a Function of Ligand for $[\{mer\text{-Ru(NH}_3)_3\text{(bpy)}\}_2(\mu\text{-L})][\text{ClO}_4]_4$[a]

ligand	$L^{0/-}$	$L^{-/2-}$	$E°_{M2}$	$E°_{M1}$	ΔE^b	$K_c{}^c$
$\text{Me}_2\text{dicyd}^{2-}$	0.633	0.439	−0.203	−0.624	421	1.3×10^7
dicyd^{2-}	0.699	0.446	−0.138	−0.550	412	9.3×10^6
$\text{Cl}_2\text{dicyd}^{2-}$	0.830	0.511	0.001	−0.327	328	3.5×10^5

[a] Data reported in V vs ferrocene in acetonitrile. [b] $\Delta E = = E°_{M2} - E°_{M1}$ in mV. [c] $K_c = \exp[16.91(\Delta E)]$, for ΔE in V.

tials are the metal-centered events of eq 1, with the two couples at higher potentials being formally assigned as the ligand-centered events $L^{0/-}$ and $L^{-/2-}$. Although the peaks were

$$[\text{Ru}^{II}-\text{Ru}^{II}] \xrightleftharpoons{E°_{M1}} [\text{Ru}^{III}-\text{Ru}^{II}] \xrightleftharpoons{E°_{M2}} [\text{Ru}^{III}-\text{Ru}^{III}] \qquad (1)$$

separated sufficiently for determination of $E_{1/2}$ values, they were insufficiently separated to permit proper measurement of the peak currents using standard methods.[20] The metal-centered couples ($E°_{M1}$ and $E°_{M2}$) and the ligand-centered couple $L^{-/2-}$ had the appearance of unity or near unity $i_{pc}:i_{pa}$ current ratios, and thus of chemical reversibility. The $L^{0/-}$ couples occurred close to the solvent limit, and were not in all cases sufficiently resolved for such a characterization to be made. Anodic−cathodic peak-to-peak ($E_{pa} - E_{pc}$) separations of ca. 60 mV, invariant with scan rate over the range 0.050−0.500 V/s for the couples of the L = dicyd^{2-} complex revealed these to be electrochemically reversible as well as chemically reversible. The L = $\text{Me}_2\text{dicyd}^{2-}$ complex's couples had $E_{pa} - E_{pc}$ values of 65−70 mV, varying with scan rate by ca. 10 mV over the same range as for the L = dicyd^{2-} complex. These couples are thus best characterized as electrochemically quasi-reversible, while those for L = $\text{Cl}_2\text{dicyd}^{2-}$, with $E_{pa} - E_{pc}$ values of ca. 100 mV, varying with scan rate by 100 mV over the range 0.050−0.500 V/s, are best described as electrochemically irreversible.

The couples were all characterized as one-electron events, supported by the measurement of a bpy-centered redox event in the DMSO spectrum of $[\{mer\text{-Ru(NH}_3)_3\text{(bpy)}\}_2(\mu\text{-Me}_2\text{dicyd})]^{4+}$ with peak currents twice those of the other couples in the voltammogram, representing the one-electron $\text{bpy}^{0/-}$ events occurring at each ruthenium center. $E°$ of the various couples was estimated as the average of E_{pa} and E_{pc} and have been collected in Table 4.

The stability of the mixed-valence state is quantified by the comproportionation constant, K_c, which is defined for the equilibrium shown in eq 2.

$$[\text{Ru}^{II}-\text{Ru}^{II}] + [\text{Ru}^{III}-\text{Ru}^{III}] \xrightleftharpoons{K_c} 2[\text{Ru}^{III}-\text{Ru}^{II}] \qquad (2)$$

Equation 2 may be viewed as the sum of the redox events described in eq 1, and K_c is thus available experimentally from the difference between the two metal-centered redox events via eq 3, where $\Delta E = E°_{M2} - E°_{M1}$ and the other terms have their usual meanings.

$$\Delta E = \frac{RT}{nF} \ln K_c \qquad (3)$$

Comproportionation constants of the complexes of this study have been placed in Table 4.

Table 5. Electronic Absorption Data[a] of the Low-Energy LMCT Transition for $[\{mer\text{-Ru(NH}_3)_3\text{(bpy)}\}_2(\mu\text{-L})]^{4+}$ Complexes and the IT Transition for $[\{mer\text{-Ru(NH}_3)_3\text{(bpy)}\}_2(\mu\text{-L})]^{3+}$ Complexes, in Acetonitrile

ligand	LMCT ν_{max} (f, ϵ_{max})	IT ν_{max} (ϵ_{max}, $\nu_{1/2}$)
$\text{Me}_2\text{dicyd}^{2-}$	9510 (0.827, 5.53×10^4)	7970 (1.18×10^4, 1760)
dicyd^{2-}	8940 (0.894, 7.05×10^4)	7580 (1.85×10^4, 1940)
$\text{Cl}_2\text{dicyd}^{2-}$	8340 (0.813, 7.60×10^4)	6910 (2.80×10^4, 2440)

[a] ν_{max} and $\nu_{1/2}$ are in cm^{-1}, ϵ_{max} in L mol^{-1} cm^{-1}, and f, the oscillator strength, is unitless.

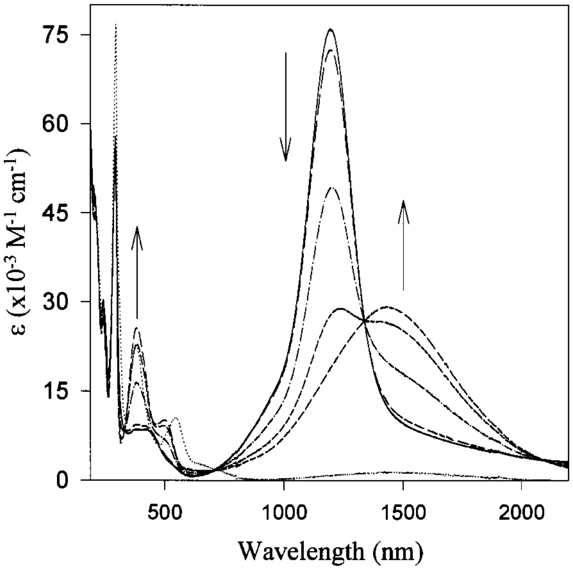

Figure 3. Absorption spectra showing the reduction of the $\text{Ru}^{III}-\text{Ru}^{III}$ complex, $[\{mer\text{-Ru(NH}_3)_3\text{(bpy)}\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$ in acetonitrile, to the mixed-valent $\text{Ru}^{III}-\text{Ru}^{II}$ complex. The spectrum of the fully reduced $\text{Ru}^{II}-\text{Ru}^{II}$ complex (···) is also shown.

Electronic absorption spectra of fully oxidized (i.e. $\text{Ru}^{III}-\text{Ru}^{III}$) complexes of dicyd ligands are dominated by intense low-energy bands which have been assigned as LMCT transitions[4,5] between the high-energy π-HOMO of the dianion ligand and a metal-centered πd orbital, or LCAO of both metals' orbitals. In a spectoscopic analysis of the mononuclear complexes,[21] such transitions were assigned in C_{2v} microsymmetry, and the lowest-energy LMCT transition of the dinuclear complexes has, by analogy, been labeled $b_1{}^* \leftarrow b_1$. The idealized geometry of the dinuclear complexes assuming anti-conformation of the cyanamide groups is, however, C_{2h} in which symmetry the corresponding assignment would be $b_g{}^* \leftarrow b_g$.[22] The spectral data associated with this transition for the triammine complexes of this study appear in Table 5.

Figure 3 shows the spectroelectrochemical data for $[\{mer\text{-Ru(NH}_3)_3\text{(bpy)}\}_2(\mu\text{-Cl}_2\text{dicyd})][\text{ClO}_4]_4$ in acetonitrile. The reduction of the $\text{Ru}^{III}-\text{Ru}^{III}$ complex to the $\text{Ru}^{III}-\text{Ru}^{II}$ complex was accompanied by a decrease in the intensity of the LMCT band and the appearance of a low-energy band (or shoulder in the spectra of the more strongly coupled systems) which increased in intensity as the LMCT band decreased. This low-energy shoulder was assigned as a metal−metal charge-transfer (MMCT) band (also commonly called an intervalence transition

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(20) (a) Mabbott, G. A. *J. Chem. Educ.* **1983**, *60*, 697. (b) Kissinger, P. T.; Heineman, W. R. *J. Chem. Educ.* **1983**, *60*, 702. (c) Harris, D. C. *Quantitative Chemical Analysis*, 2nd ed.; W. H. Freeman and Company: New York, 1987.

(21) (a) Crutchley, R. J.; Naklicki, M. L. *Inorg. Chem.* **1989**, *28*, 1955. (b) Crutchley, R. J.; McCaw, K.; Lee, F. L.; Gabe E. J. *Inorg. Chem.* **1990**, *29*, 2576. (c) Evans, C. E. B.; Ducharme, D.; Naklicki, M. L.; Crutchley, R. J. *Inorg. Chem.* **1995**, *34*, 1350.

(22) Naklicki, M. L.; Evans C. E. B.; Crutchley, R. J. *J. Mol. Struct.* **1997**, *405*, 87.

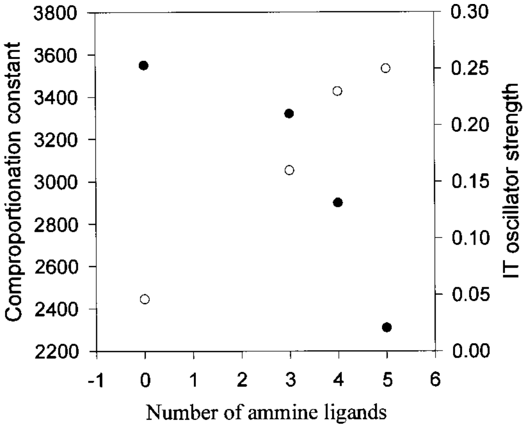

Figure 4. Plot showing the effect of replacing ammine ligands with pyridine moieties on the free energy of comproportionation (●) and the IT oscillator strength (○) of ruthenium dinuclear complexes in acetonitrile: $[\{Ru(NH_3)_5\}_2(\mu\text{-dicyd})]^{3+}$ for $n = 5$, $[\{trans\text{-}Ru(NH_3)_4(pyridine)\}_2(\mu\text{-dicyd})]^{3+}$ for $n = 4$, $[\{mer\text{-}Ru(NH_3)_3(bpy)\}_2(\mu\text{-dicyd})]^{3+}$ for $n = 3$, and $[\{Ru(terpy)(bpy)\}_2(\mu\text{-dicyd})]^{3+}$ for $n = 0$.

(IT) band because the charge transfer occurs between metals of differing oxidation states). Further reduction of the $Ru^{III}-Ru^{II}$ complex caused the loss of the LMCT-IT isosbestic points, and a decrease in the intensity of the IT band to vanishing (or very nearly vanishing), consistent with expectations for a $Ru^{II}-Ru^{II}$ complex. Unlike their pentaammine and tetraammine analogues, whose reductions to the $Ru^{II}-Ru^{II}$ complex were irreversible due to lability of this state to ligand exchange, nearly reversible regeneration of the $Ru^{III}-Ru^{III}$ complex was possible for the triammines, with the proper band shape and ca. 95% of the original spectrum's intensity regained upon oxidation of the $Ru^{II}-Ru^{II}$ complex.

In all three triammine complexes, as was similarly the case for the pentaammine and tetraammine complexes, the IT and LMCT bands overlapped to some extent. The experimental IT bands thus had to be deconvoluted from the band envelope of the mixed-valence complex. An example of this fitting procedure has been deposited in the Supporting Information. The LMCT band for the $Ru^{III}-Ru^{III}$ complex, $[\{mer\text{-}Ru(NH_3)_3(bpy)\}_2(\mu\text{-dicyd})]^{4+}$, was first modeled by using three Gaussian bands. The low-energy band envelope of the $Ru^{III}-Ru^{II}$ complex was fitted by assuming that the remaining LMCT chromophore was largely unaffected by reduction, (i.e. the ν_{max} and $\Delta\nu_{1/2}$ values and relative intensities of the three Gaussian bands used to fit the LMCT were held constant), and that any change in absorbance could be attributed to an additional IT band of Gaussian shape. The resulting IT band properties for the triammine complexes are compiled in Table 5. This technique and examples of the multiple-Gaussian fitting have been previously presented,[6] and yielded extremely good results for the pentaammines. In fact, for all three families of complexes, the low-energy side of the mixed-valence complexes could be well modeled. The fitting of the high-energy side, however, was poorer, and became progressively worse as the modeled systems became more strongly coupled.

Discussion

The stability of the mixed-valence state of a dinuclear complex is determined by all the factors which act to stabilize or destabilize not only the mixed-valence complex itself, but also the fully oxidized and fully reduced complexes of eq 2. Accordingly, a number of factors contribute to K_c, and, because of this, the free energy of comproportionation, ΔG_c, may only be considered a qualitative measure of "metal−metal coupling" when the resonance exchange term's contribution is dominant. Sutton and Taube proposed[23] the following four contributions to ΔG_c,

$$\Delta G_c = \Delta G_s + \Delta G_e + \Delta G_i + \Delta G_r \qquad (4)$$

where ΔG_r is the free energy of resonance exchange, while ΔG_s, ΔG_e, and ΔG_i, are related, respectively, to the statistical distribution of eq 2, to electrostatic repulsion of the two (like-charged) metal centers, and to inductive factors arising from the nature of a dinuclear complex. As noted by Sutin,[24] an additional term is needed when there is significant stabilization of the $Ru^{III}-Ru^{III}$ complex by antiferromagnetic exchange.[4] Including such a term, eq 4 is expanded to the form of eq 5.

$$\Delta G_c = \Delta G_s + \Delta G_e + \Delta G_i + \Delta G_r + \Delta G_{ex} \qquad (5)$$

It is important to realize that unlike the terms of eq 4, ΔG_{ex} acts to shift the equilibrium of eq 2 to the left, diminishing the magnitude of the comproportionation constant. Its sign is thus opposite those of the other four terms.

It is possible to derive an estimate of the nonexchange contributions to the comproportionation free energy, $\Delta G_{ne} = \Delta G_s + \Delta G_e + \Delta G_i$ by measuring the comproportionation constant under conditions in which resonance and antiferromagnetic exchange are very small. This can be accomplished by taking advantage of the extreme solvent dependence of metal−metal coupling previously demonstrated by the $[\{Ru(NH_3)_5\}_2(\mu\text{-dicyd})]^{4+/3+}$ complexes.[4c,25] In aqueous solution, the magnetic properties of $[\{Ru(NH_3)_5\}_2(\mu\text{-}Cl_4dicyd)]^{4+}$ are consistent with isolated Ru(III) ions[16] and for $[\{Ru(NH_3)_5\}_2(\mu\text{-}Cl_4dicyd)]^{3+}$, $K_c = 13$.[4c] This value of K_c is approximated to be due entirely to the nonresonance contributions and to be constant for the Ru−dicyd−Ru series of complexes. The term ΔG_s has a constant value for symmetrical systems and ΔG_e is largely dependent on the metal−metal separation which should be effectively invariant for the complexes studied. The variation in ΔG_i is suggested to be small as all the complexes involve the same Ru−dicyd−Ru moiety perturbed by the nature of the substituents on the phenyl ring and the nature of the spectator ligands. When ΔG_{ne} is small and approximately constant, any significant variation in the comproportionation constants between similar complexes must therefore be due to the values of ΔG_r and ΔG_{ex} recognizing that an increase in the free energy of comproportionation can only result from a dominant contribution by ΔG_r.

The comproportionation constants, K_c, as a function of bridging ligand for the pentaammine, tetraamminepyridine, and bipyridineterpyridine mixed-valence dinuclear ruthenium complexes together with the triamminebipyridine complexes of this study have been compiled in Table 6. It is evident from these data that metal−metal coupling increases both as the energy of the π-HOMO is raised (by removing electron-withdrawing substituents or by introducing electron-donating substituents on the phenyl ring) and as the energy of the metal πd is lowered through the replacement of ammine ligands with pyridine ligands. Both these trends support the conclusion that hole transfer is the dominant superexchange pathway in these systems, and that the degree of metal−metal coupling may be maximized by minimizing the energy gap between metal and ligand orbitals.

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[23] Sutton, J. E.; Taube, H. *Inorg. Chem.* **1981**, *20*, 3125.
[24] Sutin, N. Personal communication.
[25] Naklicki, M. L.; Crutchley, R. J. *J. Am. Chem. Soc.* **1994**, *116*, 6045.

Table 6. Comproportionation Constants, K_c, and the Oscillator Strengths of the Intervalence Band[a] as a Function of Bridging Ligand for the Pentaammine (A5),[b] Tetraamminepyridine (A4P),[b] Triamminebipyridine (A3B),[b] and Bipyridineterpyridine (BT)[c] Mixed-Valence Dinuclear Ruthenium Complexes

	metal inner coordination sphere			
ligand	A5[d]	A4P[e]	A3B[f]	BT[g]
Me_2dicyd^{2-}	5.6×10^5 (0.22)	5.2×10^6 (0.19)	1.3×10^7 (0.096)	−
$dicyd^{2-}$	6.9×10^4 (0.25)	1.2×10^6 (0.23)	9.3×10^6 (0.16)	2.7×10^7 (0.046)
Cl_2dicyd^{2-}	3.9×10^3 (0.25)	2.7×10^4 (0.26)	3.5×10^5 (0.31)	−
Cl_4dicyd^{2-}	3.3×10^2 (0.14)	7.2×10^2 (0.26)	−	−

[a] Oscillator strength in parentheses. [b] In acetonitrile solution. [c] In dimethylformamide. [d] Reference 4c. [e] Reference 5. [f] This work. [g] Reference 7.

Figure 4 shows the variation of the free energy of comproportionation, ΔG_c, with the number of ammine spectator ligands for the four L = $dicyd^{2-}$ complexes. The change in ΔG_c becomes less with each successive replacement of an ammine by a pyridine moiety such that a limiting free energy of comproportionation would appear to be approached in the case of $[\{Ru(terpy)(bpy)\}_2(\mu\text{-dicyd})]^{3+}$. It might be suggested that metal−metal coupling is also reaching a limiting value. However, the antiferromagnetic exchange term ΔG_{ex} is also expected to increase in magnitude as pyridine replaces the ammine ligands and could very well cancel out any increase in ΔG_r.[5]

The intervalence oscillator strengths of these complexes are also compiled in Table 6 and Figure 4 shows the trend in oscillator strengths as ammine ligands are replaced by pyridine moieties. It is clear that the IT oscillator strength f decreases with increasing metal−metal coupling. This is contrary to the predictions of the Hush model of resonance exchange in weakly coupled mixed-valence systems

$$h_{d\pi} = \frac{3.03 \times 10^2}{r}(\nu_{max} f)^{1/2} \tag{6}$$

which suggests that the first-order wave functions used in the derivation of the above expression are not appropriate for these complexes. Alternatively, the transition moment length r may be decreasing as metal−metal coupling increases.

The complexes in Table 6 are all strongly coupled mixed-valence systems but the question remains whether some of them are delocalized or, according to the Robin and Day classification, Class III systems.[26] The Creutz−Taube ion $[\{Ru(NH_3)_5\}_2(\mu\text{-pyrazine})]^{5+}$ has been studied exhaustively and recent work seems to be best interpreted in terms of a delocalized mixed-valence state for this ion.[1b,27] Comparing the comproportionation constant for the Creutz−Taube ion in acetonitrile,[28] 1.9 × 10^7, against those of Table 6 shows that both $[\{Ru(terpy)(bpy)\}_2(\mu\text{-dicyd})]^{3+}$ and $[\{mer\text{-}Ru(NH_3)_3(bpy)\}_2(\mu\text{-}Me_2dicyd)]^{3+}$ have comproportionation constants consistent with Class III behavior. Indeed, if it were not for the diminishing effect of the antiferromagnetic exchange term ΔG_{ex}, which is not significant in the Creutz−Taube ion,[29] many of the complexes in Table 6 might be also be deemed Class III from their K_c values. One of the criteria for a delocalized mixed-valence state, however, has been the demonstration of solvent independence of metal−metal coupling, and in this respect the complexes in Table 6, with the exception[7] of $[\{Ru(terpy)(bpy)\}_2(\mu\text{-dicyd})]^{3+}$, would appear to be Class II. Whereas the comproportionation constant of Creutz−Taube ion shows only very weak solvent dependence, the comproportionation constant for $[\{mer\text{-}Ru(NH_3)_3(bpy)\}_2(\mu\text{-}Me_2dicyd)]^{3+}$ varies from $K_c = 1.3 \times 10^7$ to 67, in acetonitrile and aqueous solution, respectively. This extraordinary solvent dependent metal−metal coupling arises from the extreme polarizability of the Ru−dicyd−Ru bridge which is a necessary requirement for efficient hole-transfer superexchange. It is important to note that photoelectron spectroscopy of the Creutz−Taube ion showed two different ruthenium ions whereas only one is expected if the mixed-valence state is delocalized.[30] Hush showed[31] that, if the ion is polarizable, this result would occur even if the ion was Class III. In this context, some of our complexes could be considered Class III, as is the Creutz−Taube ion. In fact, in less strongly donating solvents (e.g. nitromethane, acetonitrile, acetone) the behavior of both $[\{mer\text{-}Ru(NH_3)_3(bpy)\}_2(\mu\text{-}Me_2dicyd)]^{3+}$ and $[\{mer\text{-}Ru(NH_3)_3(bpy)\}_2(\mu\text{-dicyd})]^{3+}$ is solvent independent, suggesting perhaps that the polarizability of these ions leads to their Class III behavior being “softer” than that of the Creutz−Taube ion.

It would be of interest to obtain a measure of antiferromagnetic exchange in the $Ru^{III}-Ru^{III}$ complexes of Table 6, to gain an estimate of ΔG_r. Unfortunately, the stability of $[\{Ru(terpy)(bpy)\}_2(\mu\text{-dicyd})]^{4+}$ precludes magnetic measurements of what is expected to be the strongest antiferromagnetically coupled system. Nevertheless, magnetic measurements of the $Ru^{III}-Ru^{III}$ complexes are possible for the other systems and we hope to present a more quantitative study soon.

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.

Supporting Information Available: Full listings of crystal structure data, tables of atomic parameters, anisotropic thermal parameters, bond lengths, and bond angles and figures showing the 400 MHz ^1H NMR spectrum of $[\{mer\text{-}Ru(NH_3)_3(bpy)\}_2(\mu\text{-}Me_2dicyd)][ClO_4]_4$, the cyclic voltammogram of $[\{mer\text{-}Ru(NH_3)_3(bpy)\}_2(\mu\text{-dicyd})][ClO_4]_4$, and the deconvolution of the IT band from the visible−NIR spectrum of $[\{mer\text{-}Ru(NH_3)_3(bpy)\}_2(\mu\text{-dicyd})]^{3+}$ (12 pages). Ordering information is given on any current masthead page.

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(26) Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

(27) Petrov, V.; Hupp, J. T.; Mottley, C.; Mann, L. C. *J. Am. Chem. Soc.* **1994**, *116*, 2171.

(28) Creutz, C.; Chou, M. H. *Inorg. Chem.* **1987**, *26*, 2995.

(29) Bunker, B. C.; Drago, R. S.; Hendrickson, D. N.; Richman, R. M.; Kessell, S. L. *J. Am. Chem. Soc.* **1978**, *100*, 3805.

(30) (a) Citrin, P. H. *J. Am. Chem. Soc.* **1973**, *95*, 6472. (b) Speer, L. O.; Allan, C. B.; MacQueen, D. B.; Otvos, J. W.; Calvin, M. *J. Am. Chem. Soc.* **1994**, *116*, 2187.

(31) (a) Beattie, J. K.; Hush, N.; Taylor, P. R. *Inorg. Chem.* **1976**, *15*, 992. (b) Hush, N. *Chem. Phys.* **1975**, *10*, 361.