Infrared Study of the Class II/Class III Boundary in Mixed-Valence Dinuclear Ruthenium Complexes

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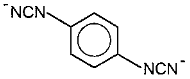
Abstract: The cyanamide stretching frequencies of the mixed-valence complexes $[\{Ru(NH_3)_5\}_2(\mu\text{-}L)]^{3+}$, *trans,trans*-$[\{Ru(NH_3)_4(py)\}_2(\mu\text{-}L)]^{3+}$ (py = pyridine), and *mer,mer*-$[\{Ru(NH_3)_3(bpy)\}_2(\mu\text{-}L)]^{3+}$ (bpy = 2,2′-bipyridine), where L is the 1,4-dicyanamidobenzene dianion and its substituted derivatives in nitromethane, acetonitrile, and dimethyl sulfoxide, were examined to determine the effects of inner- and outer-sphere perturbation on electron delocalization. The solvent-dependent infrared spectra of $[\{Ru(NH_3)_5\}_2(\mu\text{-}Me_2dicyd)]^{3+}$, where Me_2dicyd^{2-} is the 2,5-dimethyl-1,4-dicyanamidobenzene dianion, yield evidence for a transformation from localized to delocalized behavior and confirm the effect of outer-sphere perturbation on the mixed-valence state. The IR spectrum of *trans,trans*-$[\{Ru(NH_3)_4(py)\}_2(\mu\text{-}Me_2dicyd)]^{3+}$ in acetonitrile is consistent with Class III properties, and this complex's properties can be regarded as benchmarks for delocalization in our systems. It is shown that this complex obeys the general condition for delocalization in symmetric mixed-valence complexes, $2H = \lambda$, and possesses an experimental free energy of resonance exchange $\Delta G_r' = 1250$ cm^{-1} and resonance exchange integral $H = 3740$ cm^{-1}.

Introduction

Recently, we reported a quantitative study[1] of superexchange for mixed-valence polyammineruthenium complexes, incorporating the bridging ligand 1,4-dicyanamidobenzene ($dicyd^{2-}$),



and its substituted derivatives. Metal−metal coupling in these complexes can be dramatically perturbed by donor−acceptor interactions between the nonbonding electrons of the solvent and the protons of the ammine ligands, and range from very weak (Class II)[2] to very strong. The comproportionation constants of the latter were comparable to that of the Creutz−Taube ion, a recognized Class III complex.[3]

The free energy of comproportionation is given by[1]

$$\Delta G_c = \Delta G_s + \Delta G_e + \Delta G_i + \Delta G_r + \Delta G_{AF} \qquad (1)$$

where ΔG_s reflects the statistical distribution of the comproportionation equilibrium, ΔG_e accounts for the electrostatic repulsion of the two like-charged metal centers, ΔG_i is an inductive factor dealing with competitive coordination of the bridging ligand by the metal ions, ΔG_r is the free energy of resonance exchange, and ΔG_{AF} is the free energy of antiferromagnetic exchange. To account for there being 2 mol of mixed-valence complex in the comproportionation equilibrium, we define $\Delta G_r = 2\Delta G_r'$, where $\Delta G_r'$ is the free energy of resonance exchange per mixed-valence complex.

We were able to factor out the free energy of resonance exchange, $\Delta G_r'$, from the free energy of comproportionation, ΔG_c, for the majority of our mixed-valence complexes, and compare these experimental values against those calculated by using the method of Creutz, Newton, and Sutin.[1,4] The agreement between experiment and theory was quite reasonable, and strongly supported the relationship between coupling elements and charge-transfer band oscillator strengths.

It would be of some theoretical and practical importance to know the magnitude of resonance exchange energy required to achieve a delocalized state in a mixed-valence complex. The above polyammineruthenium complexes appear to span the range from valence-trapped to delocalized but definitive evidence for the delocalized state has not yet been obtained. In this regard, infrared spectroscopy has been recognized as a powerful means to examine electron transfer in mixed-valence complexes, as its time scale (10^{-13} s) gives an almost instantaneous view of the state of a fluxional molecule.[5]

Previous infrared spectroscopic studies[5] have shown that for a valence-trapped complex (Class II), the two different metal centers have distinguishable spectral features that will slowly coalesce as coupling between metal centers increases. The IR spectrum of a Class III complex will resemble that of its fully reduced and fully oxidized states, but with an important difference: the energy of a given IR band in the mixed-valence complex will be the average of that found for the analogous band in the complex's fully oxidized and fully reduced states.

For our systems, we will show that polarization of the cyanamide bridging ligand can have a significant effect on ν(NCN) and that because of this it is more appropriate to state that the frequency of the ν(NCN) of a Class III complex is the average of the ν(NCN) bands of a similar Class II complex.

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[1] Evans, C. E. B.; Naklicki, M. L.; Rezvani, A. R.; White, C. A.; Kondratiev, V. V.; Crutchley, R. J. *J. Am. Chem. Soc.* **1998**, *120*, 13096.

[2] Robin, M. B.; Day, P. *Adv. Inorg. Chem. Radiochem.* **1967**, *10*, 247.

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

[4] Creutz, C.; Newton, M. D.; Sutin, N. *J. Photochem. Photobiol. A Chem.* **1994**, *82*, 47.

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We report an infrared spectroscopic study of our mixed-valence complexes both to confirm the effects of outer- and inner-sphere perturbation on metal−metal coupling observed previously[1] and to identify the Class II−Class III boundary in the infrared time scale.

Experimental Section

Physical Measurements. IR spectroelectrochemistry was performed with use of an OTTLE cell based upon the design of Hartl.[6,7] The infrared spectra of the [III−III], [II−III], and [II−II] species were taken at ambient temperature, focusing on the range of the deprotonated cyanamide stretch (2200−1950 cm^{-1}), using a Bomem Michelson 120 FTIR spectrophotometer.

Solvents and Reagents. Organic solvents (Anachemia *Accusolv* grade unless otherwise noted) were dried with an appropriate reagent, distilled in glass at reduced pressure, and stored under argon. Acetonitrile was distilled in the presence of phosphorus pentoxide. Dimethyl sulfoxide (DMSO) and nitromethane (HPLC grade, 96+%, Sigma) were dried overnight with and distilled in the presence of aluminum oxide (neutral, chromatography grade, Woelm), which had been previously activated by heating to 300 °C for 3 h. The reagent complex, *mer*-$[Ru(NH_3)_3(bpy)(H_2O)][BPh_4]_2$,[8] and 2,3-dichlorophenylcyanamide (2,3-Cl_2pcydH)[9] were prepared by literature methods.

Complexes. The syntheses of the dinuclear complexes $[\{Ru(NH_3)_5\}_2(\mu\text{-}L)][PF_6]_4$,[10] *trans*,*trans*-$[\{Ru(NH_3)_4(py)\}_2(\mu\text{-}L)][PF_6]_4$ (py = pyridine),[11] and *mer*,*mer*-$[\{Ru(NH_3)_3(bpy)\}_2(\mu\text{-}L)][ClO_4]_4$ (bpy = 2,2′-bipyridine),[7,8a] where L is 2,5-dimethyl-1,4-dicyanamidobenzene (Me_2dicyd^{2-}) and 1,4-dicyanamidobenzene ($dicyd^{2-}$), and that of the mononuclear complex $[Ru(NH_3)_5(2,3,5,6\text{-}Cl_4pcyd)][ClO_4]_2$, where 2,3,5,6-$Cl_4pcyd^-$ is 2,3,5,6-tetrachlorophenylcyanamido,[12] have been reported.

Preparation of *mer*-$[Ru(NH_3)_3(bpy)(2,3\text{-}Cl_2pcyd)][ClO_4]_2$. 2,3-Dichlorophenylcyanamide (0.2 g, 1.3 mmol) was dissolved in acetone (100 mL) and degassed three times on a double-manifold vacuum line equipped with argon as the inert gas. Solid *mer*-$[Ru(NH_3)_3(bpy)(H_2O)][BPh_4]_2$ (1 g, 1.0 mmol) was quickly added and the solution was degassed one final time. After 16 h of stirring, tetrabutylammonium bromide, TBAB (3.0 g), was added to the solution to precipitate the complex, *mer*-$[Ru(NH_3)_3(bpy)(2,3\text{-}Cl_2pcyd)]Br$ (0.43 g). The product was dissolved in distilled water (50 mL) and oxidized with a solution of cerium(IV) ammonium nitrate (0.39 g, 0.66 mmol) in distilled water (15 mL). The solution was stirred for 10 min and *mer*-$[Ru(NH_3)_3(bpy)(2,3\text{-}Cl_2pcyd)][PF_6]_2$ (0.40 g) was precipitated from the solution by the addition of ammonium hexafluorophosphate (1.2 g). The product was converted to a bromide salt by the addition of TBAB (2 g) to an acetonitrile (20 mL) solution of the complex. *mer*-$[Ru(NH_3)_3(bpy)(2,3\text{-}Cl_2pcyd)]Br_2$ (0.2 g) was dissolved in a minimum of 1 M NaCl (∼20 mL), loaded onto a CM Sephadex C25 cation exchange column, and eluted with 1 M NaCl. The blue/green product band was preceded by a purple band containing the Ru(II) complex. The desired complex was precipitated by the addition of solid sodium perchlorate (1 g/10 mL of eluent). *mer*-$[Ru(NH_3)_3(bpy)(2,3\text{-}Cl_2pcyd)][ClO_4]_2$ (0.15 g, 22% yield from starting materials) was collected by vacuum filtration and was washed sparingly with cold water. (**Caution!** *Perchlorate salts are potentially explosive, particularly when dry. Exercise caution when handling these salts.*) The complex was recrystallized by ether diffusion into a concentrated acetonitrile solution. Anal. Calcd for $C_{17}H_{20}Cl_4N_7O_8Ru$: C, 29.45; H, 2.91; N, 14.14. Found: C, 29.72; H, 3.29; N, 14.35. IR (KBr) ν(NCN) 2117 cm^{-1}.

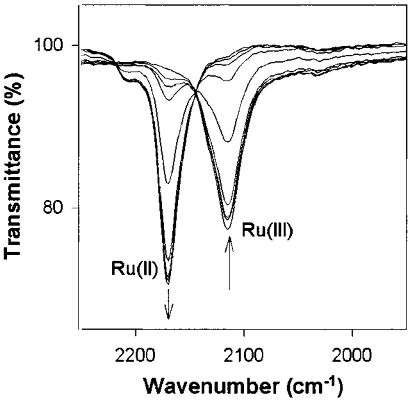

Figure 1. IR spectra showing the reduction of the Ru(III) complex, *mer*-$[Ru(NH_3)_3(bpy)(2,3\text{-}Cl_2pcyd)][ClO_4]_2$ in nitromethane, to the fully reduced Ru(II) complex.

Results

A number of spectra have been placed in Supporting Information. These spectra are denoted in the text by the capital letter S preceding the figure number.

Infrared Spectroelectrochemistry of the Mononuclear Complexes. The infrared spectroelectrochemistry of *mer*-$[Ru(NH_3)_3(bpy)(2,3\text{-}Cl_2pcyd)][ClO_4]_2$ is shown in Figure 1. In addition, Figure S1, showing the spectroelectrochemical reduction of $[Ru(NH_3)_5(2,3,5,6\text{-}Cl_4pcyd)]^{2+}$, is available in the Supporting Information. For both mononuclear Ru(III) complexes, reduction causes a decrease in the lower energy ν(NCN) band and the development of a new absorbance at higher energy that we assign to ν(NCN) for cyanamide bound to Ru(II). The intensity of this new stretch for the pentaammineruthenium(II) complex (Figure S1) is significantly weaker than that of the triamminebipyridineruthenium(II) complex (Figure 1). Oxidation of the Ru(II) complexes fully regenerated the spectra of the Ru(III) complexes. Importantly, the shift of ν(NCN) to higher frequencies upon metal ion reduction is opposite to that observed for the stretching vibrations of coordinated carbonyl and cyanide ligands[5] and is a consequence of the polarizability of the cyanamide group as discussed below.

Infrared Spectroelectrochemistry of the Dinuclear Complexes. Starting with a given [III,III] complex, spectroelectrochemical generation of its mixed-valence complex spectrum was judged to be complete upon the loss of the first set of isosbestic points and the appearance of a second set of isosbestic points,

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(5) (a) Ito, T.; Hamaguchi, T.; Nagino, H.; Yamaguchi, T.; Kido, H.; Zavarine, I. S.; Richmond, T.; Washington, J.; Kubiak, C. P. *J. Am. Chem. Soc.* **1999**, *121*, 4625. (b) Ketterle, M.; Kaim, W.; Olabe, J. A.; Parise, A. R.; Fiedler, J. *Inorg. Chim. Acta* **1999,** *291*, 66. (c) Demadis, K. D.; Neyhart, G. A.; Kober, E. M.; Meyer, T. J. *J. Am. Chem. Soc.* **1998**, *120*, 7121. (d) Wu, R.; Koske, S. K.; White, R. P.; Anson, C. E.; Jayasooriya, U. A.; Cannon, R. D.; Nakamoto, T.; Katada, M.; Sano, H. *Inorg. Chem.* **1998**, *37*, 1913. (e) Omberg, K. M.; Schoonover, J. R.; Meyer, T. J. *J. Phys. Chem.* **1997**, *101*, 9531. (f) Kaim, W.; Bruns, W.; Kohlmann, S.; Krejcik, M. *Inorg. Chim. Acta* **1995**, *229*, 143−151. (g) Chin, T. T.; Lovelace, S. R.; Geiger, W. E.; Davis, C. M.; Grimes, R. N. *J. Am. Chem. Soc.* **1994**, *116*, 9359. (h) Geiger, W. E.; Pierce, D. T. *Inorg. Chem.* **1994**, *33*, 373. (i) Wu, R.; Poyraz, M.; Sowrey, F.; Anson, C. E.; Wocadlo, S.; Powell, A. K.; Jayasooriya, U. A.; Cannon, R. D. *J. Chem. Soc., Chem. Commun.* **1994**, 4625. (j) Atwood, C. G.; Geiger, W. E.; Rheingold, A. L. *J. Am. Chem. Soc.* **1993**, *115*, 5310. (k) Bruns, W.; Kaim, W.; Waldhor, E.; Krejcik, M. *J. Chem. Soc., Chem. Commun.* **1993**, 1868. (l) Atwood, C. G.; Geiger, W. E. *J. Am. Chem. Soc.* **1993**, *115*, 5310. (m) Delville, M.-H.; Rittinger, S.; Astruc, D. *J. Chem. Soc., Chem. Commun.* **1992**, 519.

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

(7) Evans, C. E. B. Ph.D. Thesis, Carleton University, 1998.

(8) (a) Evans, C. E. B.; Yap, G. P. A.; Crutchley, R. J. *Inorg. Chem.* **1998**, *37*, 6161. (b) Chang, J. P.; Fung, E. Y.; Curtis, J. C. *Inorg. Chem.* **1986**, *25*, 4233.

(9) Crutchley, R. J.; Naklicki, M. L. *Inorg. Chem.* **1989**, *28*, 1955.

(10) (a) 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. (b) Aquino, M. A. S. Ph.D. Thesis, Carleton University, 1991. (c) Naklicki, M. L. Ph.D. Thesis, Carleton University, 1995. (d) Naklicki, M. L.; Crutchley, R. J. *Inorg. Chim. Acta* **1994**, *225*, 123.

(11) (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.

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

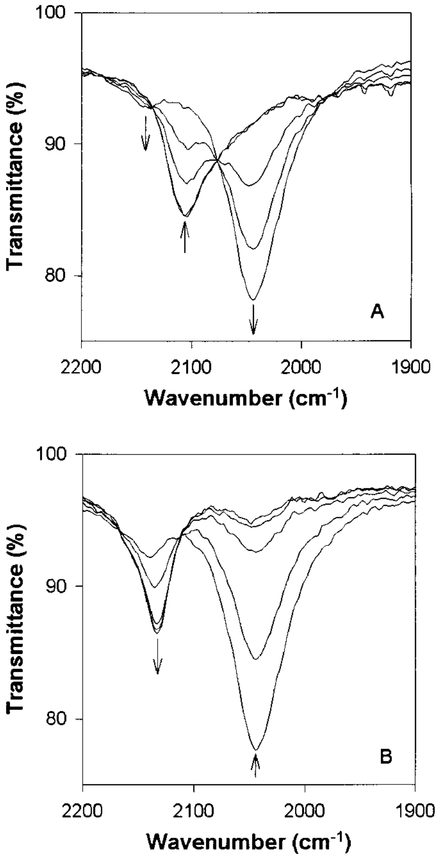

Figure 2. (a) IR spectra showing the reduction of the [III,III] complex, [{Ru(NH$_3$)$_5$}$_2$(μ-Me$_2$dicyd)][PF$_6$]$_4$ in DMSO, to the [III,II] complex. (b) IR spectra showing the reduction of the mixed valence complex to the [II,II] complex.

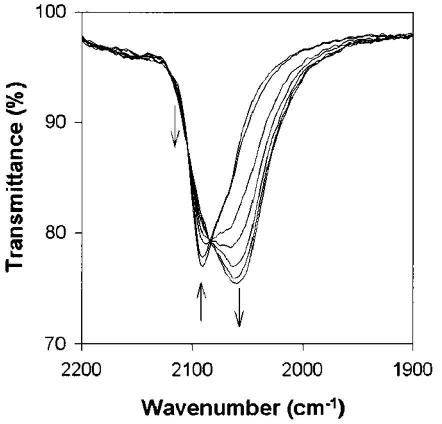

Figure 3. IR spectra showing the reduction of the [III,III] complex, [{Ru(NH$_3$)$_5$}$_2$(μ-Me$_2$dicyd)][PF$_6$]$_4$ in acetonitrile, to the mixed-valence [III,II] complex. The [II,II] complex is not stable in acetonitrile.

the latter indicating the formation of the [II,II] complex from the [III,II] complex. These changes were coincident with previously reported transformations in the UV−vis−NIR spectral region for the reduction of the dinuclear complexes.[1,7,10c,11b] All spectral changes were reversible with greater than 95% recovery of the [III,III] complex's spectrum from that of the [II,II] complex.

Pentaammineruthenium Dinuclear Complexes. Figures 2−4 show the results of the spectroelectrochemistry studies performed on [{Ru(NH$_3$)$_5$}$_2$(μ-Me$_2$dicyd)][PF$_6$]$_4$ in three solvents of varying donor strength.[13] In DMSO, two new ν(NCN) bands arise upon reduction of the [III,III] complex to the mixed-valence species (Figure 2A): an intense absorbance at lower energy (2040 cm^{-1}) and a weak band at higher energy (2160 cm^{-1}). Upon further reduction to the [II,II] complex (Figure 2B), the lower energy band disappears and the higher energy band intensifies. The analogous dicyd^{2-} complex [{Ru(NH$_3$)$_5$}$_2$(μ-dicyd)][PF$_6$]$_4$ in DMSO shows similar spectral changes (see Figure S2) except that, for the [III,II] complex, the higher energy ν(NCN) band is more intense.

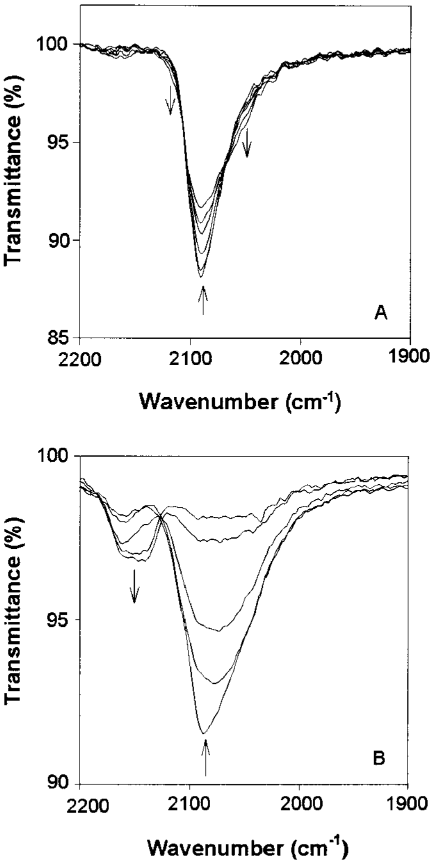

Figure 4. (a) IR spectra showing the reduction of the [III,III] complex, [{Ru(NH$_3$)$_5$}$_2$(μ-Me$_2$dicyd)][PF$_6$]$_4$ in nitromethane, to the [II$^1/_2$,II$^1/_2$] complex. (b) IR spectra showing the reduction of the mixed-valence complex to the [II,II] complex.

In acetonitrile, reduction to the mixed-valence complex (Figure 3) causes a broadening of the ν(NCN) band, and a shift to lower energy (2060 cm^{-1}). Further reduction to the [II,II] complex results in a loss of reversibility. This is likely due to the lability of anion ligands when coordinated to Ru(II) and the competitive coordination of the solvent.

The infrared spectrum of the mixed-valence complex, [{Ru(NH$_3$)$_5$}$_2$(μ-Me$_2$dicyd)]$^{3+}$ in nitromethane (Figure 4A), shows a decrease in the oscillator strength of the ν(NCN) vibration centered at 2090 cm^{-1} and some increase in the peak width relative to the [III,III] complex. In Figure 4B, the reduction of the mixed-valence complex causes the loss of this band and the growth of a new but weaker band at higher energies (2150 cm^{-1}).

Tetraamminepyridineruthenium Dinuclear Complex. Figure 5 shows the spectral transformations upon reduction of *trans,trans*-[{Ru(NH$_3$)$_4$(py)}$_2$(μ-Me$_2$dicyd)][PF$_6$]$_4$ in acetonitrile to the mixed-valence and fully reduced species. Similarly to the pentaammine case in nitromethane, the reduction of this complex to its mixed-valence state results in a decrease in

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[13] Gutmann, V. *The Donor−Acceptor Approach to Molecular Interactions*; Plenum Press: New York, 1978.

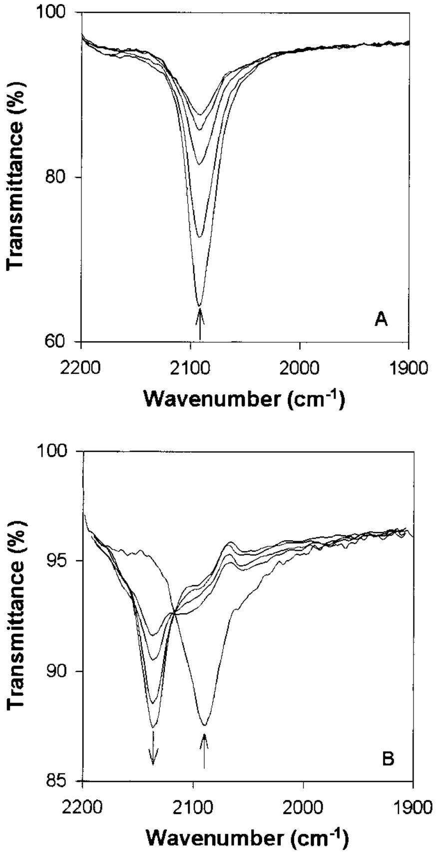


Figure 5. (a) IR spectra showing the reduction of the [III,III] complex, *trans,trans*-[{Ru(NH$_3$)$_4$(py)}$_2$(μ-Me$_2$dicyd)][PF$_6$]$_4$ in acetonitrile, to the [II$^1/_2$,II$^1/_2$] complex. (b) IR spectra showing the reduction of the mixed-valence complex to the [II,II] complex.

oscillator strength, but with no apparent broadening of the band (Figure 5A). The spectrum of the fully reduced complex (Figure 5B) shows the further loss of the low-energy ν(NCN) vibration and the appearance of a new absorption at higher wavenumbers (2135 cm^{-1}).

Triamminebipyridineruthenium Dinuclear Complexes. Figures 6−8 show the results of the spectroelectrochemistry performed on *mer,mer*-[{Ru(NH$_3$)$_3$(bpy)}$_2$(μ-Me$_2$dicyd)]$^{4+}$ in DMSO, acetonitrile, and nitromethane, respectively. In addition, the results of analogous studies on *mer,mer*-[{Ru(NH$_3$)$_3$(bpy)}$_2$-(μ-dicyd)]$^{4+}$ have been placed in Supporting Information (Figure S3−S5). For the most part, these complexes all show similar behavior despite changes in the outer coordination sphere and in the substituents on the dicyd^{2-} bridge. Generally speaking, in all three solvents, reduction to the mixed-valence state results in a decrease in the intensity of the ν(NCN) vibration, with no significant broadening of the peak, similar to that of *trans,trans*-[{Ru(NH$_3$)$_4$(py)}$_2$(μ-Me$_2$dicyd)][PF$_6$]$_4$ in acetonitrile (Figure 5). Further reduction to the [II,II] complex causes the appearance of a new band at higher energies. The exception to this behavior is the mixed-valence spectrum of *mer,mer*-[{Ru(NH$_3$)$_3$(bpy)}$_2$-(μ-dicyd)]$^{3+}$ in DMSO (see Figure S3A), which shows the ν(NCN) band to be significantly broader and shifted to lower energies as well as to have reduced oscillator strength relative to the [III,III] ν(NCN) band.

The [III,III] spectra in Figures 7A and 8A have an additional weak band at higher frequencies that is not observed for either the pentaammine or tetraammine dinuclear [III,III] complexes or for *mer,mer*-[{Ru(NH$_3$)$_3$(bpy)}$_2$(μ-dicyd)]$^{4+}$ (see Figures S3−S5). This band does not appear to be an artifact, and reduces in intensity with reduction of the [III,III] complex. We believe that two ν(NCN) bands arise from either the syn and anti conformations of the bridging ligand or symmetric and antisymmetric combinations of ν(NCN).

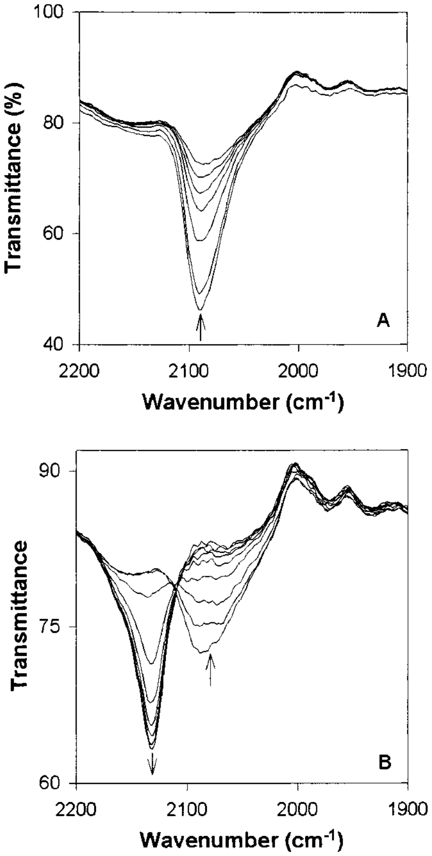
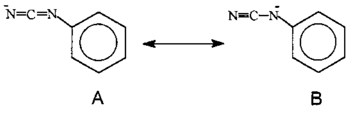


Figure 6. (a) IR spectra showing the reduction of the [III,III] complex, *mer,mer*-[{Ru(NH$_3$)$_3$(bpy)}$_2$(μ-Me$_2$dicyd)][ClO$_4$]$_4$ in DMSO, to the [II$^1/_2$,II$^1/_2$] complex. (b) IR spectra showing the reduction of the mixed-valence complex to the [II,II] complex

Discussion

Interpretation of the IR spectroelectrochemical studies requires an understanding of the effect of resonance on the cyanamide group. The protonated cyanamide group shows an infrared stretch with the most nitrile character and typically has ν(NCN) $\approx$ 2250 cm^{-1}.[12] Upon deprotonation, two pairs of nonbonding electrons are delocalized in a three-atom π-system, generating two resonance forms



Deprotonation of the cyanamide group will shift ν(NCN) to lower energies ($\approx$2120 cm^{-1}),[12] but the magnitude of this effect will depend on the contribution of a given resonance form to the electronic structure of the cyanamide ligand, as influenced by the nature of the metal ion. Resonance form A should have ν(NCN) similar to that of organic carbodiimides (for R−N=C=N−R, ν(NCN) ranges from 2100 to 2150 cm^{-1})[14] while resonance form B should have a ν(NCN) that approaches that of neutral phenylcyanamides ($\approx$2250 cm^{-1}). In addition, the ν(NCN) band of dicyd^{2-} derivatives is shifted to lower frequencies by approximately 20 cm^{-1} compared to that of similar phenylcyanamide ligands.[10b,12]

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[14] Kurzer, F.; Douraghi-Zadeh, K. *Chem. Rev.* **1967**, *67*, 107

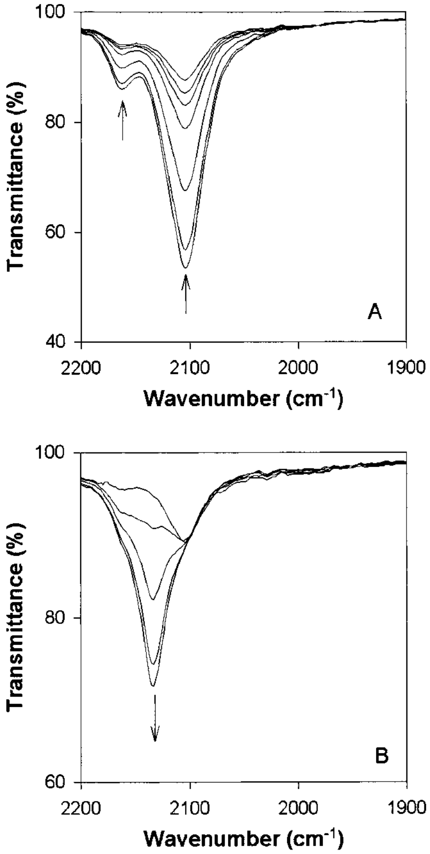


Figure 7. (a) IR spectra showing the reduction of the [III,III] complex, *mer,mer*-[{Ru(NH$_3$)$_3$(bpy)}$_2$(μ-Me$_2$dicyd)][ClO$_4$]$_4$ in acetonitrile, to the [II$^1/_2$,II$^1/_2$] complex. (b) IR spectra showing the reduction of the mixed-valence complex to the [II,II] complex

Mononuclear Complexes. Upon reduction to Ru(II), the ν(NCN) band of both triammine bipyridine and pentaammine complexes undergo shifts to higher energy. We suggest that this hypsochromic shift is due to the greater contribution of resonance form B to the cyanamide group when the nitrile moiety is coordinated to Ru(II). Nitrile ligands are π-acceptors and are expected to be favored by the π-donor Ru(II) ion.[15] In contrast to Figure 1, the ν(NCN) band in the IR spectrum of the pentaammineruthenium(II) complex (Figure S1) shows a noticeable decrease in oscillator strength compared to that of the Ru(III) complex. This decrease is due to a smaller dipole moment created by the vibration and is largely the consequence of electronic factors involving the metal ion, its coordination sphere, and the cyanamide ligand. For example, protonated phenylcyanamide ligands have very strong ν(NCN) bands, but when coordinated to pentaammineruthenium(II), this band practically disappears.[16,17] Variations in the oscillator strength of ν(NCN) bands are also seen for the [III,II] and [II,II] dinuclear complexes.

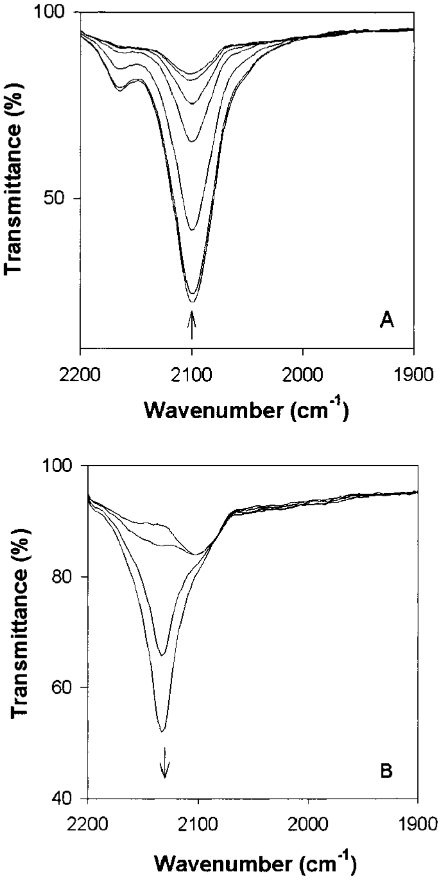
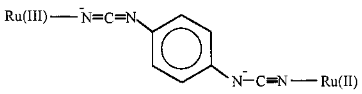


Figure 8. (a) IR spectra showing the reduction of the [III,III] complex, *mer,mer*-[{Ru(NH$_3$)$_3$(bpy)}$_2$(μ-Me$_2$dicyd)][ClO$_4$]$_4$ in nitromethane, to the [II$^1/_2$,II$^1/_2$] complex. (b) IR spectra showing the reduction of the mixed-valence complex to the [II,II] complex.

Dinuclear Complexes. The spectrum of [{Ru(NH$_3$)$_5$}$_2$(μ-Me$_2$dicyd)]$^{3+}$ in DMSO (Figure 2A) is entirely consistent with a Class II complex. We know from the reduction of the mononuclear Ru(III) complex, [Ru(NH$_3$)$_5$(bpy)(2,3-Cl$_2$pcyd)]$^{2+}$, Figure 1, that ν(NCN) shifts to higher frequencies. Thus, the band at 2160 cm^{-1} in Figure 2A is assigned to the cyanamide group bound to Ru(II). This leaves the band at 2040 cm^{-1} to the cyanamide bound to Ru(III) and its shift to lower energies relative to that of the [III,III] complex can be rationalized by the dominating contribution of resonance form A to the cyanamide group as shown below.



We suggest that the carbodiimide resonance form dominates because of the high polarizability of the dianion ligand and the asymmetry of metal charges that allows electron density to be preferentially polarized toward Ru(III). A similar assignment of ν(NCN) bands is appropriate for [{Ru(NH$_3$)$_5$}$_2$(μ-dicyd)]$^{3+}$ in DMSO (Figure S2).

From previous studies[1] on [{Ru(NH$_3$)$_5$}$_2$(μ-Me$_2$dicyd)]$^{3+}$, the magnitude of metal−metal coupling increased as the donor number of the solvent decreased. Thus, with DMSO, acetonitrile, and nitromethane having donor numbers[13] of 29.8, 14.1, and 2.7, respectively, Figures 2−4 show the transformation of ν(NCN) as a function of increasing metal−metal coupling. In contrast to [{Ru(NH$_3$)$_5$}$_2$(μ-Me$_2$dicyd)]$^{3+}$ in DMSO (Figure 2), the mixed-valence complex in acetonitrile (Figure 3) shows only a single band, broader and shifted to lower energies relative to that of its [III,III] complex. This is consistent with an intermediate case between valence-trapped and valence-delocalized states.[5a,18] In Figure 4A, [{Ru(NH$_3$)$_5$}$_2$(μ-Me$_2$dicyd)]$^{3+}$, in nitromethane, shows reduced broadening compared to Figure

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[15] Ford, P. C. *Coord. Chem. Rev.* **1970**, *5*, 75.

[16] Naklicki, M. L.; Crutchley, R. J. *Inorg. Chem.* **1989**, *28*, 4226.

[17] We suggest that this variation in ν(NCN) band strength has similar origins to that observed for the ν(C≡C) band of symmetric and asymmetric acetylenes but further study is required.

[18] The temperature dependence of the IR spectra was examined in the range of −10 to 50 °C but no significant effects were noted.

3 and no shift in energy compared to its [III,III] spectrum. The slight broadening of this band may indicate that the mixed-valence complex is not quite delocalized. However, the energy of ν(NCN) is unchanged relative to the [III,III] complex and this is exactly what one expects for the delocalized case of our systems if the energy of ν(NCN) is the average of the two bands seen in the valence-trapped case (Figure 2A).

Replacing the ammine ligands with pyridine moieties has the effect of stabilizing the ruthenium d-orbitals and increasing metal−metal coupling.[8a] Thus, the behavior of the mixed-valence complex, *mer,mer*-$[\{Ru(NH_3)_3bpy\}_2(\mu\text{-}Me_2dicyd)]^{3+}$ in DMSO, acetonitrile, and nitromethane, should reflect a more delocalized state. In all three solvents, Figures 6−8, the spectral changes are very similar to that of the pentaammine analogue in nitromethane (Figure 4A), except that there is little evidence for band broadening. These data are consistent with Class III behavior for *mer,mer*-$[\{Ru(NH_3)_3bpy\}_2(\mu\text{-}Me_2dicyd)]^{3+}$ in these solvents. The mixed-valence complex *mer,mer*-$[\{Ru(NH_3)_3(bpy)\}_2(\mu\text{-}dicyd)]^{3+}$ (Figures S3−S5) shows similar behavior in nitromethane and in acetonitrile but in DMSO, the most strongly donating solvent, the spectral changes in Figure S5A resemble that of Figure 3. We argue that the strength of the solvent's interaction with ammine protons traps the odd electron on a ruthenium ion and is a consequence of weaker superexchange metal−metal coupling mediated by the $dicyd^{2-}$ bridging ligand compared to Me_2dicyd^{2-} as shown in previous studies.[1]

The main objective of this study was to determine a free energy benchmark for delocalization in our mixed-valence systems. The experimental $\Delta G_r'$ values of our dinuclear complexes were factored from the free energy of comproportionation[19] by experimentally determining the free energy of antiferromagnetic exchange for each complex and estimating a single value for the nonresonance exchange contributions ΔG_{nr}, where $\Delta G_{nr} = \Delta G_s + \Delta G_e + \Delta G_i$. Previous studies suggested[1] that ΔG_{nr} should be increased by 200 cm^{-1}. Accordingly, all the $\Delta G_r'$ values in this discussion have been reduced from those reported in ref 1.

For $[\{Ru(NH_3)_5\}_2(\mu\text{-}Me_2dicyd)]^{3+}$ in DMSO and acetonitrile, $\Delta G_r' = 400$ and 1010 cm^{-1}, respectively.[1] At 1010 cm^{-1}, valence trapping is indicated by the broadening and energy shift of the cyanamide stretch due to overlapping ν(NCN) bands. Unfortunately, the $\Delta G_r'$ value for this complex in nitromethane could not be factored from the free energy of comproportionation because a value of the free energy of antiferromagnetic exchange was unattainable.[20] We sought a complex with a higher $\Delta G_r'$ value than 1010 cm^{-1} to find the threshold above which delocalized behavior is observed. The IR spectroelectrochemistry of *trans,trans*-$[\{Ru(NH_3)_4(py)\}_2(\mu\text{-}Me_2dicyd)]^{3+}$ (Figure 5) is very similar to that of *mer,mer*-$[\{Ru(NH_3)_3(bpy)\}_2(\mu\text{-}Me_2dicyd)]^{3+}$ (Figures 6−8), and we suggest that it indicates a delocalized mixed-valence state. Because the free energy of resonance exchange for this tetraammine complex is 1250 cm^{-1}, it seems reasonable to propose that the onset of delocalization with respect to the infrared time scale occurs between $\Delta G_r' = 1010$ cm^{-1} and $\Delta G_r' = 1250$ cm^{-1}. Hence, we can conclude with confidence that the $\Delta G_r'$ value of 1250 cm^{-1} is a free energy benchmark for delocalization in our systems.[21] These systems span the complete range of Class II to Class III complexes and interpretation of their spectroscopic and physical properties must reflect this transformation.[1]

The general criterion for delocalization in symmetric mixed-valence complexes can be seen in the dependence of the thermal barrier to electron transfer ΔG_{th} on the donor−acceptor resonance exchange integral H,[22,23]

$$\Delta G_{th} = \frac{\lambda}{4}\left(1 - \frac{2H}{\lambda}\right)^2 \tag{2}$$

where λ is the energy of photoinduced electron transfer that can be estimated from the energy of the intervalence transition in a weakly coupled symmetric Class II complex.[3] Thus, when $2H = \lambda$, there will be no thermal barrier to electron movement in the mixed-valence state. For the Class III system, *trans,trans*-$[\{Ru(NH_3)_4(py)\}_2(\mu\text{-}Me_2dicyd)]^{3+}$ in acetonitrile, the intervalence band energy was found[1] to equal $2H = 7480$ cm^{-1}. We estimate $\lambda = 7670$ cm^{-1} for the tetraammineruthenium mixed-valence complexes, from the intervalence band energy of the weakly coupled Class II complex, *trans,trans*-$[\{Ru(NH_3)_4(py)\}_2(\mu\text{-}Cl_4dicyd)]^{3+}$ in DMSO.[1] The difference between $2H$ and λ, while not large, may be significant. Endicott[24] has suggested that when the difference in energy between intervalence and ligand-to-metal charge transfer states is small, symmetric and antisymmetric mixing of these states would significantly perturb the energies and oscillator strengths of the charge-transfer transitions.

It is also possible to estimate the magnitude of resonance exchange required to achieve a delocalized state in our mixed-valence systems. For a Class III system,

$$\Delta G_r' = H - \frac{\lambda}{4} \tag{3}$$

Because $\Delta G_r' = 1250$ cm^{-1} for *trans,trans*-$[\{Ru(NH_3)_4(py)\}_2(\mu\text{-}Me_2dicyd)]^{3+}$ in acetonitrile and $\lambda/4 = 1920$ cm^{-1}, (estimated from the intervalence band energy of the Class II complex, *trans,trans*-$[\{Ru(NH_3)_4(py)\}_2(\mu\text{-}Cl_4dicyd)]^{3+}$ in DMSO), eq 3 yields $H = 3170$ cm^{-1}.[25] This is very close to $H = 3360$ cm^{-1}, calculated by using the method of Creutz, Newton, and Sutin,[4] but lower than that derived from the complex's intervalence band energy $H = 3740$ cm^{-1}. As we have greater confidence in the latter value, this probably indicates that $\lambda/4$ has been underestimated and requires further research to derive experimental values.

To conclude, infrared spectroelectrochemical studies of pentaammine, tetraamminepyridine, and triamminebipyridineruthenium mixed-valence complexes have shown that these complexes span the entire range of Class II to Class III behavior. The IR spectrum of *trans,trans*-$[\{Ru(NH_3)_4(py)\}_2(\mu\text{-}Me_2dicyd)]^{3+}$ in acetonitrile is consistent with Class III properties. In comparison to the IR spectra of our mixed-valence systems, we suggest that this complex's properties can be regarded as benchmarks for delocalization in our complexes. It is shown that this complex obeys the general condition for delocalization

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[19] An uncertainty of ±10 mV in an electrochemical measurement results in an error of approximately ±160 cm^{-1} in ΔG_c, an 8% error in the case of $[\{Ru(NH_3)_4(py)\}_2(\mu\text{-}Me_2dicyd)]^{3+}$ in acetonitrile.

[20] Naklicki, M. L.; White, C. A.; Plante, L. L.; Evans, C. E. B.; Crutchley, R. J. *Inorg. Chem*. **1998**, *37*, 1880.

[21] Rapid intramolecular exchange (10^{12} s^{-1}) can result in spectral coalescence but with some band broadening. Intramolecular exchange approaching 10^{13} s^{-1} is required to achieve complete coalescence. See ref 5a.

[22] Sutin, N. *Prog. Inorg. Chem.* **1983**, *30*, 441.

[23] Nelson, S. F. *Chem. Eur. J.* **2000**, *6*, 581.

[24] Macatangay, A. W.; Endicott, J. F. *Inorg. Chem.* **2000**, *39*, 437.

[25] The complex in acetonitrile possesses a larger outer-sphere reorganizational energy compared to that in DMSO and this difference can be calculated by using the dielectric continuum model (see ref 3a, eq 5). Thus, $\Delta\lambda_{outer}/4 = 200$ cm^{-1} and, by using eq 3, $H = 3370$ cm^{-1}, an even closer agreement to the value of H calculated by the method of Creutz, Newton, and Sutin.

in symmetric mixed-valence complexes, $2H = \lambda$, and possesses an experimental free energy of resonance exchange $\Delta G_r' = 1250$ cm^{-1} and resonance exchange integral $H = 3740$ cm^{-1}.

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Supporting Information Available: Figures showing the IR spectroelectrochemistry performed on $[Ru(NH_3)_5(2,3,5,6\text{-}Cl_4pcyd)]^{2+}$ in acetonitrile, $[\{Ru(NH_3)_5\}_2(\mu\text{-dicyd})][PF_6]_4$ in DMSO, and *mer*,*mer*-$[\{Ru(NH_3)_3(bpy)\}_2(\mu\text{-dicyd})]^{4+}$ in DMSO, acetonitrile, and nitromethane (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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