Strong Metal–Metal Coupling in a Dinuclear (Terpyridine)(bipyridine)ruthenium Mixed-Valence Complex Incorporating the Bridging Ligand 1,4-Dicyanamidobenzene Dianion

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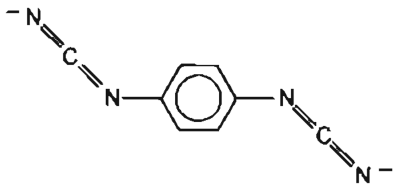
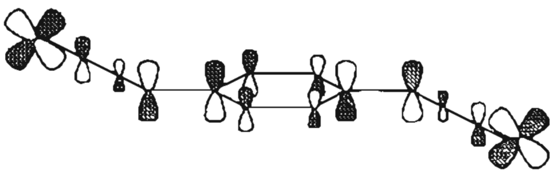
The complex, $[\{Ru(terpy)(bpy)\}_2(\mu\text{-dicyd})][PF_6]_2$, where terpy = 2,2′,2″-terpyridine, bpy = 2,2′-bipyridine, and $dicyd^{2-}$ = 1,4-dicyanamidobenzene dianion, has been synthesized and characterized by cyclic voltammetry and spectroelectrochemical methods. A quantitative absorption spectrum of the radical anion $dicyd^{\bullet-}$ has also been determined. The mixed valence ion, $[\{Ru(terpy)(bpy)\}_2(\mu\text{-dicyd})]^{3+}$ is strongly coupled with $K_c = 2.7 \times 10^7$ and has an intervalence band at $\lambda = 1090$ nm ($\epsilon_{max} = 3000\ M^{-1}\ cm^{-1}$, $\bar{\nu}_{1/2} = 1800\ cm^{-1}$). The mixed-valence properties of this complex were compared to its ammine analogue $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{3+}$ and rationalized by the perturbation of spectator ligands on the interaction of ruthenium ions with the $dicyd^{2-}$ superexchange pathway. The dependence of intervalence oscillator strength on the nature of the mixed-valence complex was also discussed.

Introduction

The mechanism for metal–metal coupling in dinuclear ruthenium complexes which incorporate the 1,4-dicyanamidobenzene dianion ($dicyd^{2-}$) bridging ligand,



is dominated by superexchange via the π HOMO of $dicyd^{2-}$. The interaction of ruthenium πd orbitals with the π HOMO of $dicyd^{2-}$ (shown schematically



where the size of the atomic orbital approximates its contribution to the molecular orbital),[1] creates a superexchange pathway which is both symmetry and energy favorable. In recent studies,[2,3] we have shown that the comproportion constants of the mixed valence complexes, $[\{(NH_3)_5Ru\}_2(\mu\text{-}L)]^{3+}$, where L = $dicyd^{2-}$ and 1,4-dicyanamido-2,5-dimethylbenzene dianion (Me_2dicyd^{2-})), are remarkably sensitive to the donor properties of the solvent. This solvent dependence classifies these complexes as valence localized class II mixed-valence systems[4] even though the magnitude of their comproportionation constants in poor donor solvents approaches that of the valence delocalized class III Creutz–Taube ion, $[\{(NH_3)_5Ru\}_2(\mu\text{-pyrazine})]^{5+}$.[5]

In this study, we have synthesized the novel dinuclear complex, $[\{Ru(terpy)(bpy)\}_2(\mu\text{-dicyd})][PF_6]_2$. Cyclic voltammetry and spectroelectrochemical methods showed that the complex, $[\{Ru(terpy)(bpy)\}_2(\mu\text{-dicyd})]^{3+}$, is a strongly coupled class III mixed-valence ion. The properties of this complex are compared to its ammine analogue, $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{3+}$, and rationalized in terms of the electronic perturbations that are introduced when an ammine ligand is replaced by pyridine.

Experimental Section

Physical Measurements. The equipment used to perform cyclic voltammetry, IR, ^{1}H-NMR, and UV–vis–near-IR spectroscopy has been described in a previous paper.[6] Spectroelectrochemistry was performed with a pyrex-quartz cell of published design,[7] on acetonitrile solutions containing 1.0×10^{-5} M $[\{Ru(terpy)(bpy)\}_2(\mu\text{-dicyd})][PF_6]_2$ and 0.1 M tetrabutylammonium hexafluorophosphate (TBAH) electrolyte. Platinum-mesh working, platinum-wire counter and silver-wire reference electrodes were used. The solutions were degassed and agitated by bubbling argon through a Teflon needle. The potential at the working electrode was controlled by using a BAS CV-27 apparatus. Aldrich anhydrous acetonitrile and Anachemia accusolv grade dimethylformamide (DMF) were used as received. TBAH was recrystallized twice from ethanol and vacuum dried at 110 °C overnight. TBAB, tetrabutylammonium tetraphenylborate was synthesized by combining aqueous solutions of $NaBPh_4$ and tetrabutylammonium bromide. TBAB was separated, washed with water and vacuum dried at 110 °C overnight. Ferrocene ($E° = 665$ mV vs NHE)[8] was used as an internal reference. Elemental analysis was performed by Canadian Microanalytical Services Ltd.

Reagents. All chemicals and solvents were reagent grade or better and used as received. 2,2′,2″-Terpyridine (terpy) and 2,2′-bipyridine (bpy) were purchased from Aldrich. 1,4-Dicyanamidebenzene (di-

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cydH$_2$),[1] [AsPh$_4$]$_2$[dicyd],[1] Ru(terpy)Cl$_3$,[9] and [Ru(bpy)(terpy)Cl][PF$_6$][10] were prepared by following literature procedures.

Preparation of [{Ru(bpy)(terpy)}$_2$(μ-dicyd)][PF$_6$]$_2$·DMF. A mixture of [[Ru(bpy)(terpy)Cl][PF$_6$] (224 mg, 0.33 mmol) and AgPF$_6$ (0.85 mg, 0.33 mmol) was placed in acetone (50 mL) and stirred at a reflux for 3 h. The reaction mixture was then filtered and to the filtrate was added dicydH$_2$ (27 mg, 0.17 mmol). The solution was vacuum degassed and then stirred with slight heating (25−30 °C) under argon overnight. The solvent was removed and the crude product purified by column chromatography by using grade V alumina type WA-1 (Sigma) and a 2:1 mixture of CH$_2$Cl$_2$/CH$_3$CN as eluent. Three major bands were eluted in the order: a yellow band (possibly deprotonated ligand), a purple band (a mononuclear Ru(II)−terpy derivative), and finally a brown band of the dinuclear complex. The product eluent was evaporated to dryness and the product recrystallized by the diffusion of ether into a dimethylformamide solution of the complex. Dark-brown fine crystals of the dinuclear complex were collected and washed with ether and vacuum dried. Yield: 51 mg, 21%. Anal. Calcd for C$_{61}$H$_{49}$N$_{15}$P$_2$F$_{12}$Ru$_2$: C, 48.83 (ppm); H, 3.27; N, 14.01. Found: C, 48.08; H, 3.59; N, 14.33. ^{1}H NMR in dimethyl sulfoxide-d_6, relative to TMS at 0.00 ppm: DMF resonances at 2.74 (3 H, singlet), 2.91 (3 H, singlet) and 7.95 (1 H, singlet); phenyl protons at 5.50 (4 H, singlet); terpy and bpy protons at 7.13 (2 H, triplet), 7.39 (2 H, doublet), 7.41 (4 H, triplet), 7.65 (4 H, doublet), 7.82 (2 H, triplet), 8.01 (4 H, triplet), 8.10 (2 H, triplet), 8.24 (2 H, triplet), 8.40 (2 H, triplet), 8.67 (4 H, doublet), 8.70 (2 H, doublet), 8.81 (4 H, doublet), 8.94 (2 H, doublet), 9.65 (2 H, doublet).

Results

The crude product of the reaction of [Ru(terpy)(bpy)Cl]$^+$ with neutral dicydH$_2$ is suggested to be the dinuclear complex [{Ru(terpy)(bpy)}$_2$(μ-dicydH$_2$)]$^{4+}$, based on the observation of a protonated cyanamide ν(NCN) band at 2250 cm^{-1} in the IR spectrum of the crude product obtained by reducing the reaction solution to dryness.[11] It seems likely that the dicydH$_2$ is actually bound to Ru(II) at this stage because the bromide salt of the crude complex (precipitated by the addition of tetrabutylammonium bromide to the reaction solution) still possesses a protonated cyanamide ν(NCN) band at 2225 cm^{-1}. Deprotonation of the bridging ligand apparently occurred during purification by chromatography using grade V alumina as shown by the characteristic anionic cyanamide ν(NCN) band observed at 2151 cm^{-1} and the stoichiometry required by the elemental analysis for the final product [{Ru(terpy)(bpy)}$_2$(μ-dicyd)]$^{2+}$. The deprotonation of the bridging ligand was not pursued further in this study.

The cyclic voltammograms of the mononuclear complex [Ru(terpy)(bpy)Cl]$^+$ and the dinuclear complex [{Ru(terpy)(bpy)}$_2$(μ-dicyd)]$^{2+}$ in DMF solutions are compared in Figure 1. The cyanamide anion group is a pseudo halogen and is expected to perturb the Ru(III/II) couple in much the same way as a chloride anion ligand. Thus, for the dinuclear complex, Figure 1B, the Ru(III/II) couples occur in approximately the same region as the Ru(III/II) couple of [Ru(terpy)(bpy)Cl]$^+$ at 1.025 V vs NHE (Figure 1A) but are split into two one-electron waves (at 0.250 and 0.690 V vs NHE) because of significant metal−metal coupling. The Ru(III/II) reduction couples for both complexes appear quasi-reversible with an average separation between cathodic and anodic waves of 70 mV that is largely independent of scan rate between 50−250 mV/s. From the difference in Ru(III/II) couples of the dinuclear complex (ΔE = 440 mV), the comproportionation constant (K_c) for the formation of the Ru(III/II) mixed-valence complex was determined to be 2.7 × 10^7. This comproportionation constant is approximately the same as that found for the Creutz−Taube ion [{(NH$_3$)$_5$Ru}$_2$(μ-pyrazine)]$^{5+}$ (K_c = 8.54 × 10^6 in DMF)[5] and by analogy, is supportive of a class III assignment for the mixed-valence complex of this study.[4]

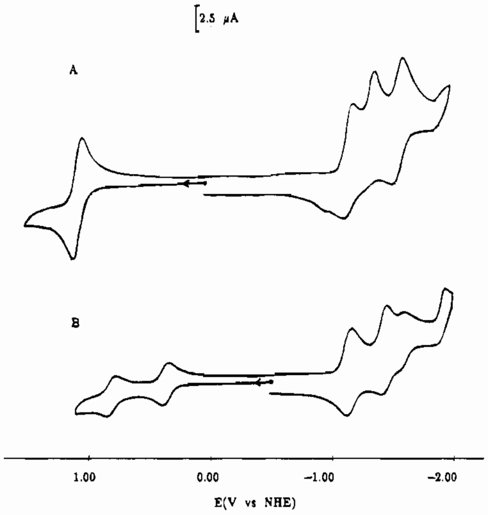

Figure 1. Cyclic voltammograms: (A) [Ru(bpy)(terpy)Cl][PF$_6$]; (B) [{Ru(terpy)(bpy)}$_2$(μ-dicyd)][PF$_6$]$_2$ in dimethylformamide.

The PF$_6^-$ salt of the dinuclear complex proved sparingly soluble in all but strong donor solvents and this severely limited studies of solvent-dependent properties. However, the tetraphenylborate salt of the complex was sufficiently soluble in acetonitrile to permit a cyclic voltammetry study. At a scan rate of 100 mV/s and with 0.025 M TBAB electrolyte, two Ru(III/II) couples were observed at 0.415 and 0.840 V vs NHE which is roughly the same separation between Ru(III/II) couples (ΔE) that is observed in DMF. In contrast, [{(NH$_3$)$_5$Ru}$_2$(μ-Me$_2$dicyd)]$^{4+}$, shows dramatic solvent perturbation of metal−metal coupling where in nitromethane ΔE = 368 mV, while in DMSO ΔE = 198 mV.[2] The solvent dependence of these Ru(III/II) couples was suggested to be caused by the donor−acceptor interaction between the solvent molecules and the ammine ligands. Importantly, this effect is absent in [{Ru(terpy)(bpy)}$_2$(μ-dicyd)]$^{2+}$.

Three one electron ligand reduction waves are observed between −1.0 and −2.0 V, in the voltammogram of [Ru(terpy)(bpy)Cl]$^+$, Figure 1A. The first reduction wave probably corresponds to the reduction of the coordinated terpy ligand because of the greater stability of terpy's π^* orbital, compared to that of bpy[10a,12]

$$[\mathrm{Ru^{II}(terpy)(bpy)Cl}]^+ + e^- \rightleftharpoons [\mathrm{Ru^{II}(terpy^{\bullet -})(bpy)Cl}] \quad (1)$$

The above couple occurs at a potential of −1.100 V vs NHE with cathodic and anodic peak separation (70 mV) independent of scan rate from 50 to 250 mV/s. This is followed closely by the irreversible reduction of the coordinated bpy ligand

$$[\mathrm{Ru^{II}(terpy^{\bullet -})(bpy)Cl}] + e^- \rightarrow [\mathrm{Ru^{II}(terpy^{\bullet -})(bpy^{\bullet -})Cl}]^- \quad (2)$$

The cathodic peak maximum of this couple occurred at −1.320 V vs NHE and a weak anodic wave that is associate with this couple is seen at approximately −0.9 V vs NHE. This anodic wave does not appear unless the potential is swept past −1.320

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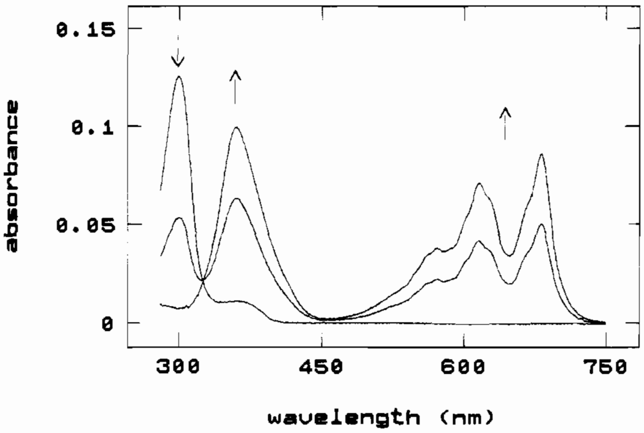

Figure 2. Spectroelectrochemical oxidation of $[\mathrm{AsPh_4}]_2[\mathrm{dicyd}]$, 4.63 × 10^{-6} M, in acetonitrile solution, forming the radical anion dicyd$^{\bullet-}$.

V. The irreversibility of this reduction step is suggested to be due to the loss of the chloride ligand. The third reduction wave probably corresponds to the second reduction of the terpy ligand.

For the dinuclear complex, Figure 1B, ligand reduction couples analogous to those of the mononuclear complex are expected between −1.0 and −2.0 V. The first reduction couple (terpy$^{0/-}$ = −1.250 V vs NHE), appears reversible with cathodic to anodic peak separations of 70 mV, independent of scan rates between 50 and 250 mV/s. The second reduction wave (bpy$^{0/-}$ = −1.550 vV vs NHE) approaches reversibility at scan rates greater than 250 mV/s where the anodic peak current starts to match that of the cathodic peak. It is important to note that the current of these ligand reduction couples is twice that of the Ru(III/II) couples at anodic potentials and that this is consistent with one electron ligand reductions at each end of the complex at the same potential. However, the third reduction step, the terpy$^{-/2-}$ couple, is split into two one-electron redox waves and strongly suggests intramolecular ligand−ligand coupling in the (terpy^{2-}, terpy^{-}) complex. It is possible that these couples may be Ru(II/I) couples although previous studies support ligand-centered reductions.[13] The first terpy$^{-/2-}$ redox wave appears quasi-reversible although its overlap with the bpy redox wave makes this a difficult judgement. The second wave is irreversible with significant loss of anodic current at scan rates less than 100 mV/s. The instability of these reduction products prevented spectroelectrochemical characterization.

Cyclic voltammetry of the free dicyd^{2-} molecule in acetonitrile showed two redox couples corresponding to dicyd$^{-/2-}$ = −0.215 and dicyd$^{0/-}$ = 0.460 V vs NHE.[1] These couples shift anodically when coordinated to Ru(III). For example, the dicyd$^{-/2-}$ and dicyd$^{0/-}$ couples occur at 0.830 and 1.292 V vs NHE in the cyclic voltammogram of $[\{(\mathrm{NH_3})_5\mathrm{Ru}\}_2(\mu\text{-dicyd})]^{4+}$ in acetonitrile solution.[3] For the complex *trans*-$[\{(\mathrm{NH_3})_4\mathrm{Ru}(\mathrm{pyridine})\}_2(\mu\text{-dicyd})]^{4+}$, the replacement of one ammine ligand with pyridine shifted the dicyd$^{-/2-}$ and dicyd$^{0/-}$ couples to 0.965 and 1.340 V vs NHE respectively.[14] An even greater anodic shift of these couples can be expected for $[\{\mathrm{Ru(terpy)(bpy)}\}_2(\mu\text{-dicyd})]^{4+}$. Unfortunately, these couples were not observed up to DMF's anodic limit of 1.75 V vs NHE, and attempts to observed these couples in solvents with greater anodic limits were frustrated by the poor solubility of the complex.

Spectroelectrochemistry was performed on acetonitrile solutions of the free dicyd^{2-} ligand to obtain the radical anion absorption spectrum (Figure 2). The absorbance spectrum of the fully oxidized ligand in acetonitrile solution has been obtained[15] and consists of a broad band centered at 330 nm (ε = 29 500 M^{-1} cm^{-1}). Solutions of 1,4-dicyanamidobenzene dianion and its substituted derivatives are very air sensitive and upon oxidation to the radical anion give blue solutions which show a characteristic three-band pattern in the visible region (Figure 2). It is important to note that oxidation of $[\{\mathrm{Ru(terpy)(bpy)}\}_2(\mu\text{-dicyd})]^{2+}$ acetonitrile solutions to obtain the absorption spectrum of the mixed-valence [3,2] complex (Figure 3) and the fully oxidized [3,3] complex (Figure 4) does not result in the appearance of the radical anion chromophore and further supports the Ru(III/II) couple assignments. Reversibility was indicated by the return of the absorption spectrum of [2,2] upon reduction of [3,3].

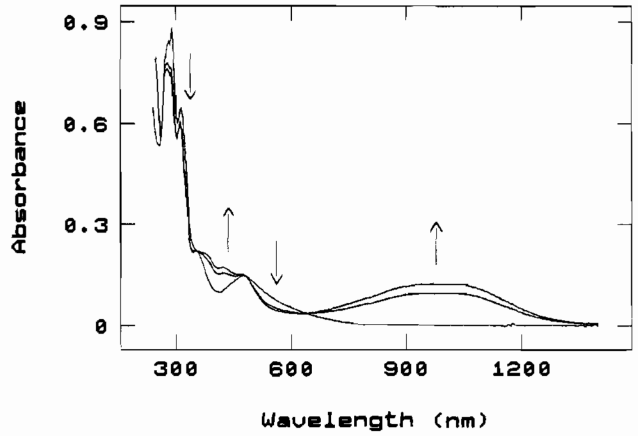

Figure 3. Spectroelectrochemical oxidation of $[\{\mathrm{Ru(terpy)(bpy)}\}_2(\mu\text{-dicyd})]^{2+}$ forming the mixed-valence [3,2] complex, 1.0 × 10^{-5} M in acetonitrile solution.

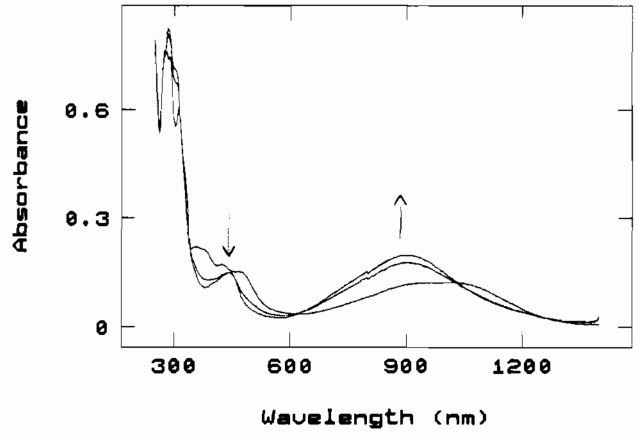

Figure 4. Spectroelectrochemical oxidation of $[\{\mathrm{Ru(terpy)(bpy)}\}_2(\mu\text{-dicyd})]^{3+}$ forming the [3,3] complex, 1.0 × 10^{-5} M in acetonitrile solution.

The absorption spectrum of the [2,2] complex (Figure 3) shows MLCT bands at 356 and 478 nm that are typical of Ru(II)(terpy)(bpy) chromophores.[10,16] Upon oxidation to the mixed-valence [3,2] complex, a new band grows in centered at approximately 950 nm with a band maximum at 1006 nm (ϵ_{max} = 1.2 × 10^4 M^{-1} cm^{-1}). The asymmetry of this broad band is suggested to arise from the overlap of the Ru(III)−cyanamide LMCT chromophore and an intervalence transition (IT). A spectroscopic analysis of the Ru(III)−cyanamide LMCT chromophore has shown that two LMCT transitions arise from the interaction of Ru(III) with the two nondegenerate π_{nb} molecular

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orbitals of the cyanamide group.[17] The absorption spectrum of the fully oxidized [3,3] complex (Figure 4) clearly shows these two LMCT transitions at 443 and 900 nm and also shows that upon oxidation of [3,2] to [3,3] near-IR absorbance intensity is lost. This is taken as evidence for the presence of an intervalence transition which was estimated from the absorption spectrum of [3,2] to have λ_{max} at 1090 nm (ϵ_{max} = 5600 M^{-1} cm^{-1}, $\bar{\nu}_{1/2}$ = 1800 cm^{-1}).[18]

Spectroelectrochemistry of the dinuclear complex was also performed on DMF solutions and the growth of the [3,2] complex spectrum was essentially identical to that obtained in Figure 3 (isosbestic points in acetonitrile solutions, 356, 475, and 641 nm, compared to those in DMF, 357, 490, and 649 nm). There is also a slight red shift of the band maximum to 1066 nm (ϵ_{max} = 1.2 × 10^4 M^{-1} cm^{-1}). Unfortunately, incomplete reversibility in DMF solutions was noted when regeneration of [2,2] from [3,3] showed significant loss of absorption intensity.

Discussion

The replacement of the ammine ligands with the pyridine moieties of bpy and terpy ligands is expected to increase the stability of the ruthenium d-orbitals in both the 2+ and 3+ oxidation states because of pyridine's π-acceptor properties and pyridine's poorer σ-donor properties compared to the ammine ligand. The effect this has on the Ru(III) ion can be readily seen by a comparison of the Ru(III/II) couples of $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{4+}$ which occur at 0.131 and −0.155 V vs NHE[3] with those of $[\{Ru(terpy)(bpy)\}_2(\mu\text{-dicyd})]^{2+}$ which occur at 0.840 and 0.415 V vs NHE in acetonitrile solutions. The increased stability of the Ru(III) d-orbitals increases the covalency of its π-interaction with the cyanamide groups of the bridging ligand and causes a similar anodic shift of $dicyd^{2-}$-centered redox couples (see Results). As a consequence of this enhanced π-interaction, metal-metal coupling in the mixed-valence complex results in a delocalized class III system.

In previous studies, we have shown that the magnitude of metal−metal coupling in the mixed-valence complex, $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{3+}$, was strongly dependent on the donor and acceptor properties of the solvent.[2,3] The comproportionation constant of this complex was shown to increase from 10 to 68 000 in aqueous and acetonitrile solutions, respectively. In addition, the IT band properties of this complex in aqueous solution were consistent with a weakly coupled class II system but in acetonitrile solution, the IT band properties (λ_{max} = 1447 nm, ϵ_{max} = 20100 M^{-1} cm^{-1}, $\bar{\nu}_{1/2}$ = 2640 cm^{-1}), do not fit Hush model predictions and suggest that the complex is borderline between class II and class III systems in acetonitrile solution. If we compare the IT band properties of this complex in acetonitrile solution with those of the class III mixed-valence complex of this study, $[\{Ru(terpy)(bpy)\}_2(\mu\text{-dicyd})]^{3+}$ (λ_{max} = 1090 nm, ϵ_{max} = 5600 M^{-1} cm^{-1}, $\bar{\nu}_{1/2}$ = 1800 cm^{-1}), an obvious difference in intervalence transition, energies, intensities and band widths is apparent and can be explained by a transition from valence localized to delocalized mixed-valence system.

The energy of the IT band of a class II system arises from inner and outer sphere reorganizational energies. On the other hand, the IT band energy of a class III ion reflects the magnitude of metal−metal coupling and is estimated to be twice the resonance exchange integral H_{ad}.[4] For $[\{Ru(terpy)(bpy)\}_2(\mu\text{-dicyd})]^{3+}$, H_{ad} is estimated to be 0.57 eV.

The oscillator strength of an electronic transition is given by the expression[19]

$$f = (1.085 \times 10^{11})G\bar{\nu}M^2 \tag{3}$$

where G refers to the degeneracy of the states concerned, $\bar{\nu}$ is the energy of the transition in cm^{-1}, and M is the transition moment. Experimentally, oscillator strength is evaluated from band properties by the expression

$$f = 4.61 \times 10^{-9}\epsilon_{max}\bar{\nu}_{1/2} \tag{4}$$

In the case of a weakly coupled class II system, Hush[20] approximated the transition moment of an intervalence transition by the expression

$$M \approx e\alpha R \tag{5}$$

where R represents the transition dipole moment length, e is the electronic charge and α is the mixing coefficient of donor and acceptor wave functions. The increase in oscillator strength for the intervalence band of $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{3+}$ in going from aqueous to acetonitrile solutions[3] can therefore be ascribed to an enhanced mixing of donor and acceptor wavefunctions since R remains the same. In addition, the magnitude of metal−metal coupling increases with increasing intervalence oscillator strength.[20]

For a strongly coupled class III system, the approximations used to derive eq 5 are no longer valid and the transition dipole moment is more appropriately given by[21]

$$M \approx eS_{ad}R \tag{6}$$

where S_{ad} is the overlap integral between donor and acceptor wave functions. Studies of $[(NH_3)_5Ru(L)]^{2+}$ where L is a phenylcyanamide anion derivative, have shown that variations in ligand to metal charge transfer (LMCT) oscillator strength be rationalized in terms of the overlap integral between Ru(III) πd orbitals and the π HOMO of the cyanamide ligand.[21] For the IT band of $[\{Ru(terpy)(bpy)\}_2(\mu\text{-dicyd})]^{3+}$, the contribution of S_{ad} to the oscillator strength is unknown. However, what can be said with confidence is that a class III complex will have greater charge delocalization in both ground and excited states and that this would result in a smaller change in electron distribution upon IT excitation. Therefore, R is smaller for a class III complex compared to a class II complex and this accounts to a significant degree for the difference in IT oscillator strength that is observed for $[\{Ru(terpy)(bpy)\}_2(\mu\text{-dicyd})]^{3+}$ and $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{3+}$ complexes.

The variation in intervalence oscillator strength f_{it} that is observed for other mixed-valence complexes can now be understood within the context of this study. For example, the mixed-valence complex $[\{(NH_3)_4Ru\}_2(\mu\text{-bptz})]^{5+}$ where bptz is 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine, has a large K_c (10^{15}) but only a small ϵ_{max}(IT) = 500 M^{-1} cm^{-1}.[22,23] This is a strongly coupled system in which the delocalization of the odd electron in both ground and excited states results in R being small for the intervalence transition. The f_{it} of this complex is signifi-

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cantly smaller than other class III systems[4,23] and this may be explained by variations in S_{ad}. The mixed-valence complex, $[(\text{tterpy})\text{Ru})_2(\mu\text{-tpbp})]^{3+}$ where tterpy is 4′-*p*-tolyl-2,2′,6,6′,2″-terpyridine and tpbp is tetrapydinebiphenyl dianion, has a relatively small K_c (600) but large $\epsilon_{max}(\text{IT}) = 27\,000\ \text{M}^{-1}\ \text{cm}^{-1}$.[24] This is a class II system in which the combination of large R an large α results in an unusually large intervalence ϵ_{max}. The importance of the overlap integral S_{ad} in eq 6 to the f_{it} of class III ions requires further investigation. It contains the factors of relative symmetry and energy which can play an important role in determining the probability of an electronic transition and magnitude of metal−metal coupling. We intend to examine the relationship between Ru(III)−cyanamide LMCT and Ru(III)−Ru(III) IT transitions and the magnitude of metal−metal coupling for both class II and class III systems in a future study.

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