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Solvent trapped valency in the [bis(pentaammineruthenium)-(μ-1,4-dicyanamidobenzene)] trication

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Abstract

Cyclic voltammetry measurements show an unprecedented solvent dependence of metal–metal coupling for the symmetric mixed valence [3,2] complex, $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{3+}$, where dicyd^{2-} is the 1,4-dicyanamidobenzene dianion. The comproportionation constant was determined to be $K_c = 10$ and 68 400 in aqueous and acetonitrile solution, respectively. The intervalence absorption band was deconvoluted from the low energy Ru(III)–cyanamide LMCT band by curve fitting analysis which gave for the [3,2] complex assuming a gaussian IT band, $E_{op} = 8190$ cm^{-1}, $\Delta\bar{\nu}_{1/2} = 4090$ cm^{-1} and $\epsilon_{max} = 2590$ M^{-1} cm^{-1} in aqueous solution and in acetonitrile solution $E_{op} = 6910$ cm^{-1}, $\Delta\bar{\nu}_{1/2} = 2640$ cm^{-1} and $\epsilon_{max} = 19\,400$ M^{-1} cm^{-1}. It is suggested that donor–acceptor interactions between the solvent and ammine protons weakens the Ru(III)–cyanamide π bond. Because the interaction between Ru(III) and the cyanamide group is crucial to superexchange, metal–metal coupling is also weakened. The acceptor properties of water may also play a role.

Keywords: Mixed valence complex; Electrochemistry; Ruthenium complexes; Ammine complexes; Dicyanamido complexes

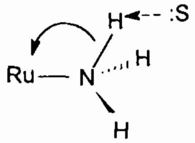
1. Introduction

For weakly coupled symmetric mixed valence complexes, Hush theory [1] gives

$$E_{op} = \chi_i + \chi_o + \Delta E \qquad (1)$$

where E_{op} is the optical energy of the intervalence transition IT, χ_i is the inner sphere reorganizational parameter, χ_o is the outer sphere reorganization parameter and ΔE takes into account any additional energy associated with excitation to either a spin–orbit or ligand field excited state. If it is assumed that χ_i and ΔE terms are independent of the nature of the solvent, then variations in E_{op} with solvent should be linearly proportional to the solvent term $(1/D_{op} - 1/D_s)$, where D_{op} and D_s are the optical and static dielectric constants of the solvent. This relationship has been demonstrated in a number of studies [2] involving symmetric mixed valence complexes. However, for asymmetric complexes of the type $[(2,2'\text{-bipyridine})_2RuCl(\mu\text{-pyrazine})Ru(NH_3)_4L]^{4+}$, studies revealed that there is a solvent donor number (*DN*) [3] dependent contribution to the Frank–Condon barrier of approximately 0.006 eV/*DN* that completely overwhelms the dielectric continuum theory derived $(1/D_{op} - 1/D_s)$ term [4]. The microscopic origin of this solvent effect was described by Curtis et al. [5] in their study of solvatochromism in the charge transfer transitions of mononuclear Ru(II) and Ru(III) ammine complexes. It was proposed that a hydrogen bonding type of interaction occurred between the solvent's non-bonding electrons and the N–H bond (Scheme 1). The strength of this interaction depends on the acidity of the ammine hydrogens which is greater for an ammine bound to Ru(III) compared to Ru(II). The net effect of this interaction is the transfer of electron density from the partially deprotonated ammine to the ruthenium ion.

In mixed valence dinuclear ruthenium complexes, the preferential solvation of the Ru(III) ammine coordination sphere creates an energy barrier to the delocalization of the odd electron and thereby decreases the magnitude of metal–metal coupling. Preferential solvation has also been shown to reduce metal–metal



Scheme 1.

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coupling in symmetric mixed valence complexes and the interaction of these complexes with crown ethers was shown to have a similar effect [6]. For the above dinuclear ruthenium complexes, the ruthenium ions are bridged by π-acceptor ligands and the dominant superexchange pathway for metal–metal coupling is expected to involve the LUMO of the bridging ligand.

In this preliminary study, we report solvent dependent metal–metal coupling in the mixed valence complex, $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{3+}$ which incorporates the π-donor bridging ligand 1,4-dicyanamidobenzene dianion. For this complex, the dominant superexchange pathway for metal–metal coupling occurs via the HOMO of the $dicyd^{2-}$ ligand [7]. The magnitude of metal–metal coupling in this complex is remarkably dependent on the nature of the outer coordination sphere and is explored by cyclic voltammetry and spectroelectrochemical studies.

2. Experimental

2.1. Synthesis

All chemicals and solvents were reagent grade or better and used as received. The synthesis of $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{4+}$ has already been described [7]. The complex hexafluorophosphate salt was obtained by the addition of excess ammonium hexafluorophosphate to an aqueous solution of the bromide salt and recrystallized by the slow diffusion of ether into an acetone solution of the complex.

2.2. Physical measurements

Electrochemical studies were performed using a BAS CV-27 apparatus. The electrochemical cell for cyclic voltammetry in acetonitrile [8] and water [7] has already been described. Ferrocene ($E° = 665$ mV versus NHE) was used as an internal reference in acetonitrile solution [9]. Acetonitrile (Aldrich, anhydrous $<0.005\%$ water) was used as received. Tetrabutylammonium hexafluorophosphate, TBAH, (Aldrich), was recrystallized twice and vacuum dried at 120 °C overnight. Sodium perchlorate (Anachemia) was recrystallized twice. Spectroelectrochemical studies were performed with a pyrex–quartz cell of published design [10]. Visible near-IR spectra were taken on a Cary 5 spectrophotometer. The fitting of LMCT band profiles was accomplished with PeakFit v3.0 software purchased from Jandel Scientific.

3. Results

The cyclic voltammograms of the [3,3] complex $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{4+}$ in water and acetonitrile are shown in Fig. 1 and the data are summarized in Table 1. The redox assignments are based on previous studies of the free $dicyd^{2-}$ ligand [7] and mononuclear pentaammineruthenium(III) phenylcyanamide complexes [11,12].

The bridging $dicyd^{2-}$ ligand is redox active with two single-electron reduction couples shifted anodically upon coordination to Ru(III)

$$dicyd^- + e^- \rightleftharpoons dicyd^{2-} \quad L(-/2-)$$

$$dicyd^0 + e^- \rightleftharpoons dicyd^- \quad L(0/-)$$

As shown in Fig. 1(a) and (b), the L(−/2−) couple is quasi-reversible with peak to peak separation of

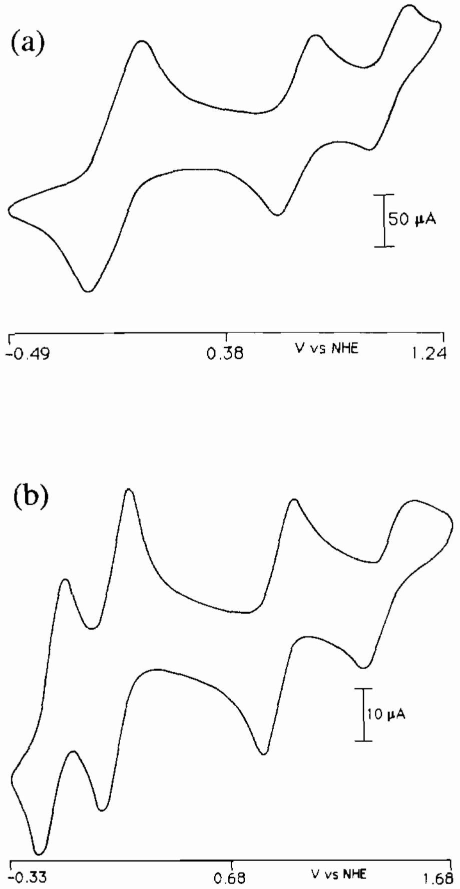

Fig. 1. Cyclic voltammetry of $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})][PF_6]_4$ in (a) aqueous and (b) acetonitrile solutions.

Table 1
Electrochemical couples[a] of the complex $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})][PF_6]_4$ in aqueous and acetonitrile solutions

Solvent	M_1	M_2	K_c[b]	L(−/2−)	L(0/−)
H_2O[c]	−0.021	−0.081	10	0.632	0.981
Acetonitrile	0.131	−0.155	68400	0.830	1.292

[a] Data in V vs. NHE.

[b] K_c is the comproportionation constant.

[c] Data is taken from Ref. [7].

approximately 65 mV independent of scan rate from 20 to 200 mV s^{-1}. The L(0/−) couple is significantly less reversible particularly in acetonitrile (Fig. 1(a)) and in both solvents the loss of reversibility of the L(0/−) couple was noticeable at scan rates less than 1.5 V s^{-1}.

Two one-electron Ru(3+/2+) couples are expected but only one is seen in the aqueous solution voltammogram (Fig. 1(b))

$$[3,3]+e^- \rightleftharpoons [3,2] \quad M_1$$

$$[3,2]+e^- \rightleftharpoons [2,2] \quad M_2$$

This is due to the weak coupling between the metal ions and the resultant superimposition of the two Ru(3+/2+) couples M_1 and M_2. The aqueous solution values of M_1 and M_2 in Table 1 have been previously reported [7] and were derived from an analysis developed by Richardson and Taube [13]. In acetonitrile (Fig. 1(a)), metal coupling is enhanced and separate M_1 and M_2 waves result. The M_1 couple appears quasi-reversible with peak to peak separation increasing from 60 to 110 mV over the scan rate range of 0.020 to 2 V s^{-1}. At scanning rate <2 V s^{-1}, the M_2 couple becomes irreversible with the loss of its oxidation wave and the appearance of a high anodic current wave at 0.087 V versus NHE. The high current of this anodic wave suggests that deposition of the [2,2] complex on the electrode has occurred.

Fig. 2 shows the visible near-IR absorption spectra of the complex $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{4+}$ [3,3] and its one-electron reduction product [3,2] in aqueous and acetonitrile solutions. The two-electron reduction product [2,2] does not absorb in this region. In aqueous solution (Fig. 2(A), a), the [3,3] complex shows a strong absorption centered at 890 nm (ϵ=12 800 M^{-1} cm^{-1}) associated with the two Ru(III)–cyanamide LMCT chromophores [7,11]. Reduction of the [3,3] complex results in a steady decrease in the intensity of its LMCT absorption band and a concomitant growth of a near-IR absorption tail. The spectrum of [3, 2] (Fig. 2(A), b) was obtained (λ_{max}=980 nm, ϵ=7200 M^{-1} cm^{-1}) just before the loss of isosbestic points due to the formation of [2,2]. We have assigned the near-IR tail to an IT band which is partially obscured by the relatively intense LMCT band. Re-oxidation did not result in complete regeneration of [3,3] and this is likely due to the lability of pentaammineruthenium(II) to ligand substitution.

In acetonitrile (Fig. 2(B), a), the LMCT band of the [3,3] complex shifted to lower energy and increased in intensity (λ_{max}=1095 nm, ϵ=46 200 M^{-1} cm^{-1}) compared to its aqueous solution spectrum (Fig. 2(A), a). Upon reduction of [3,3] to the [3,2] complex, (Fig. 2(B), b), a new band appears in the near-IR which we assigned to an IT transition (λ_{max}=1450 nm, ϵ=19 400 M^{-1} cm^{-1}). In contrast to the aqueous solution study, the oxidation of [3,2] to regenerate the [3,3] complex was reversible in acetonitrile.

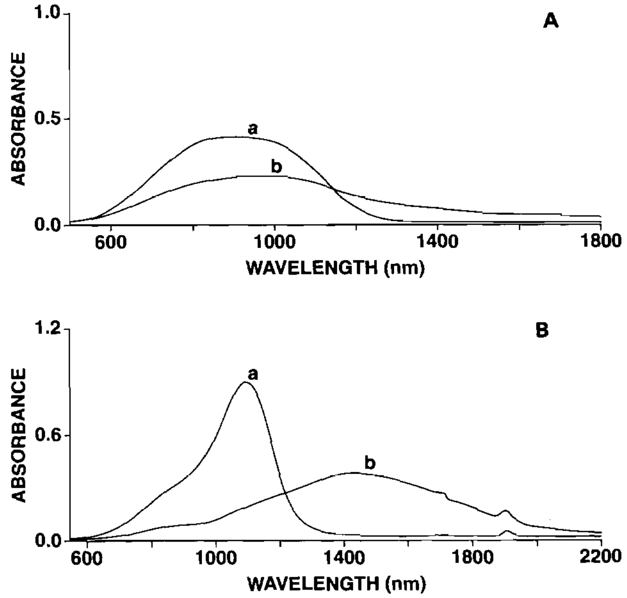

Fig. 2. Visible near-IR spectra of $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})][PF_6]_4$ and its electrochemically produced mixed valence complex in (A) D_2O solution, 3.165×10^{-5} M [3,3] (a) and [3,2] (b) (0.1 M $NaClO_4$) and (B) acetonitrile solution, 1.958×10^{-5} M, [3,3] (a) and [3,2] (b) (0.1 M TBAH). The weak absorptions at approximately 1700 and 1900 nm in (B) are instrumental artifacts that arise from large background absorption by the solvent.

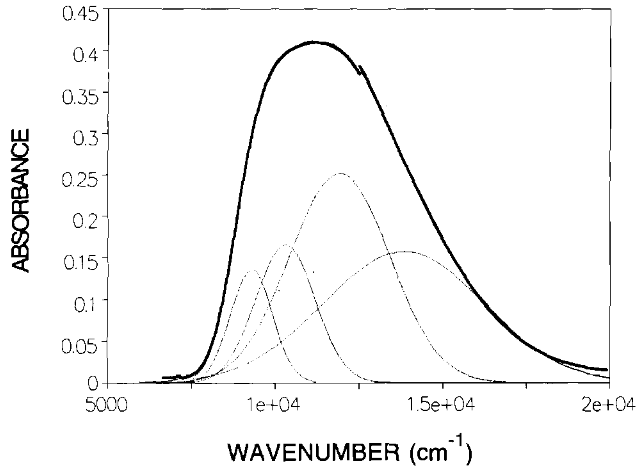

Fig. 3. Multiple gaussian fit of the LMCT band of $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{4+}$ (Fig. 2(A), a). The glitch at 12 500 cm^{-1} is an instrumental artifact.

The proximity of LMCT and IT transitions in Fig. 2 does not permit a Hush model treatment of IT band properties. This problem can be overcome by using non-linear curve fitting software to deconvolute the IT transition from the LMCT transitions. Fig. 3 shows a multiple gaussian fit of the LMCT band of the [3,3]

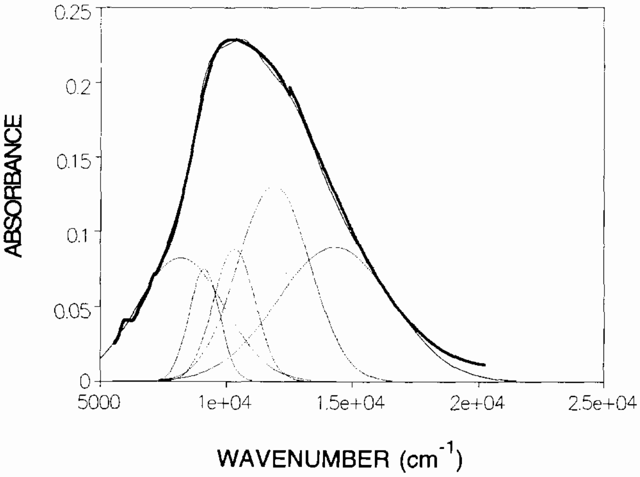

Fig. 4. Multiple gaussian fit of the LMCT band of $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{3+}$ (Fig. 2(A), b). The glitch at 12 500 cm^{-1} is an instrumental artifact.

complex in aqueous solution[1]. This fit (keeping the relative properties of the gaussian contributions constant) and the addition of a low energy gaussian band (the IT transition) was then used to model the band profile of the [3,2] complex in aqueous solution (Fig. 2(A), b). For the [3,2] complex in aqueous solution, the fit (Fig. 4) had a square of the correlation coefficient $R^2=0.998$ and gave for the low energy gaussian IT band, $E_{op}=8190$ cm^{-1}, bandwidth at one-half peak height $\Delta\bar{\nu}_{1/2}=4090$ cm^{-1} and $\epsilon_{max}=2590$ M^{-1} cm^{-1}. For the [3,2] complex in acetonitrile solution (Fig. 2(B), b) a similar analysis had $R^2=0.996$ and gave for the low energy gaussian IT band, $E_{op}=6910$ cm^{-1}, bandwidth at one-half peak height $\Delta\bar{\nu}_{1/2}=2640$ cm^{-1} and $\epsilon_{max}=19\,400$ M^{-1} cm^{-1}.

In the above analyses, two main assumptions have been made. The first is that the IT transition can be described by a single gaussian band, a condition which is not always seen experimentally [14]. Second, the energy and the band shape of the LMCT transition does not change upon reduction of one of the Ru(III)–cyanamide chromophores. A good test of the second, assumption is given by the [Ru(III),Cu(II)] complex, $[(NH_3)_5Ru(\mu\text{-dicyd})Cu(L)]^{2+}$ where L = 1,3-bis(2′-pyridylimino)isoindolinato [15]. For this system in acetonitrile, the Ru(III)–cyanamide LMCT band has approximately the same profile as that seen in Fig. 2(B), a and has $\lambda_{max}=1086$ nm.

4. Discussion

The comproportionation constant K_c is a measure of mixed valence complex stability in solution [16]. The unprecedented K_c solvent dependence of the [3,2] complex (Table 1) is consistent with a transformation from weakly coupled Class II properties in aqueous solution to strongly coupled Class III properties in acetonitrile. The Hush treatment of weakly coupled symmetric mixed valence complexes [1] derived the following relationship to calculate intervalence band width at half-peak height

$$\Delta\bar{\nu}_{1/2}=(2310E_{op})^{1/2} \tag{2}$$

For the [3,2] complex in D_2O, the calculated $\Delta\bar{\nu}_{1/2}=4350$ cm^{-1} is in close agreement with the curve fitted value of 4090 cm^{-1}. In contrast, for [3,2] in acetonitrile, the calculated $\Delta\bar{\nu}_{1/2}=4000$ cm^{-1} is considerably larger than that found by curve fitting analysis ($\Delta\bar{\nu}_{1/2}=2640$ cm^{-1}) and this is characteristic of strongly coupled mixed valence systems. The [3,2] complex in acetonitrile solution is probably not a fully delocalized Class III system but it is at the very least intermediate between Class II and Class III. The origin of this solvent dependent metal–metal coupling deserves further discussion.

The stabilization energy of superexchange metal–metal coupling in $[\{(NH_3)_5Ru\}_2(\mu\text{-dicyd})]^{3+}$ results from the mixing of the ground state with an excited LMCT state

$$\overset{\uparrow}{M_a}-\overset{\uparrow\downarrow}{L}-\overset{\uparrow\downarrow}{M_b}\xrightarrow{\text{LMCT}}\overset{\uparrow\downarrow}{M_a}-\overset{\uparrow}{L}-\overset{\uparrow\downarrow}{M_b}\longrightarrow\overset{\uparrow\downarrow}{M_a}-\overset{\uparrow\downarrow}{L}-\overset{\uparrow}{M_b} \tag{3}$$

The magnitude of this stabilization depends on a close symmetry and energy match between the metal dπ orbitals and the π HOMO of the bridging dicyd^{2-} ligand. In addition, the π HOMO must span the entire bridging ligand and interact simultaneously with both metal ions to be an effective superexchange pathway. In previous studies [12,17], we have shown that the oscillator strength f of the Ru(III)–cyanamide LMCT band can be qualitatively related to the π overlap integral S of the Ru(III)–cyanamide bond

$$f\approx(1.085\times10^{-5})G\bar{\nu}S^2R^2 \tag{4}$$

where G is the degeneracy of the transition, $\bar{\nu}$ is the energy of LMCT band at ϵ_{max} and R is the transition dipole moment length. Both inner and outer sphere perturbations of the Ru(III)–cyanamide π bond obeyed this qualitative relationship. Importantly, for mononuclear pentaammineruthenium(III) complexes of phenylcyanamide ligands, the LMCT oscillator strength and by inference the π overlap integral increased with decreasing solvent donor number [17]. It was suggested that solvents with large donor numbers strongly interact with the ammine hydrogens causing electron density to flow to Ru(III) (see Scheme 1) and thereby weaken

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[1] The four gaussian bands which were used to fit the LMCT band profile were chosen arbitrarily and do not reflect expected transitions.

the Ru(III)–cyanamide π bond. Water is also an electron acceptor and can weaken the Ru(III)–cyanamide bond by protonation of the cyanamide group. It is therefore not unexpected that the LMCT oscillator strength of the [3,3] complex shows the same solvent dependence increasing from 0.34 in D_2O to 0.60 in acetonitrile[2]. From this result it seems reasonable to infer that the Ru(III)–cyanamide π overlap is greater in acetonitrile than in water and that this explains the solvent dependence of metal–metal coupling in the [3,2] complex.

We have synthesized dinuclear tetraammine- and pentaammineruthenium complexes of substituted 1,4-dicyanamidobenzene dianion bridging ligands in order to perform comprehensive studies of the solvent dependence of metal–metal coupling in mixed valence complexes. These studies will be presented in the near future.

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[2] This is the total oscillator strength from two Ru(III)–cyanamide chromophores.

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