The photoreaction pathway can be interpreted in terms of excited-state bonding changes. In the directly populated CT state, iron–chlorine π bonding is weakened because of population of the antibonding d_{xz} and d_{yz} metal orbitals. In addition, the iron is formally reduced. The weakened iron–chlorine coordination site probably undergoes radical attack by the iodine with homolytic cleavage of the coordinated chlorine. This radical pathway is consistent with the enhanced thermal reactivity in the presence of the radical initiator benzoyl peroxide. In addition, the trend exhibited by the photoreaction with the organic halides $CH_3CHICH_3 > CH_3I_3 > C_5H_5I \geq C_6H_5I$ is consistent with the bond energies of those halides.[24]

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Registry No. $Fe(das)_2Cl_2^+$, 47511-84-2; $Fe(das)_2Br_2^+$, 47511-80-8; $Fe(das)_2I_2^+$, 64070-44-6; $Fe(das)_2ClBr^+$, 68843-01-6; $Fe(das)_2ClI^+$, 68843-02-7; $Fe(das)_2BrI^+$, 68843-03-8.

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Determination of the Comproportionation Constant for a Weakly Coupled Mixed-Valence System by Titration of the Intervalence Transfer Band: μ-(4,4′-Bipyridyl)-bis(pentaammineruthenium)(5+)

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The change in absorbance in the region of the intervalence transition for μ-4,4′-bipyridyl-bis(pentaammineruthenium) when the fully oxidized state is titrated with a reducing agent is used to obtain the comproportionation constant for reaction I. This value (24 ± 1 at 19.0 °C) was used to calculate the extinction coefficient (8.8×10^2 M^{-1} cm^{-1}) at the band maximum (1030 nm in D_2O) and the oscillator strength corresponding to the transition. The stabilization resulting from electron delocalization in turn is calculated from the oscillator strength as 48 cal and falls far short of the stability of the mixed-valence compared to the isovalent state, which amounts to 5×10^2 cal. It seems likely that the major contribution to the stability of the mixed-valence state is the electrostatic interaction between the positively charged ends, which will favor the mixed-valence state. Calculation of this contribution using the macroscopic dielectric constant for the solvent, however, falls far short of accounting for the experimental value. When, as in this case, the contribution to stability from electron delocalization is small, the measurements would seem to provide a rather direct way of exploring the electrostatic term.

Introduction

Over the last 10 years a large number of robust molecules containing two or more metals in different oxidation states have been prepared and studied.[1–6] One important property of these mixed-valence compounds is the intervalence transfer (IT) band corresponding to a light-induced charge transfer between the metal centers.[7,8] Hush has treated these IT bands theoretically[7,9] and concludes that their intensity provides information on the extent of communication between the metal centers. In addition, the energy of these bands is related to the Franck–Condon barrier to electron transfer provided coupling between the metal centers is not very strong.

This paper is based on a reinvestigation[3–5] of the μ-(4,4′-bipyridyl)-bis(pentaammineruthenium)(5+) ion which was undertaken to obtain quantitative data on the oscillator strength of the IT band. In the work on mixed-valence molecules done heretofore, values of the equilibrium quotient governing a reaction of the type

$$[2,2] + [3,3] = 2[3,2] \qquad \text{(I)}$$

have been obtained from cyclic voltammetry data ([2,2], [3,2], and [3,3] represent the three different stages of oxidation for the binuclear species). Because the waves corresponding to the two redox stages overlap and because the waves even in well-behaved systems seldom have an ideal form, dependable values of the comproportionation[10] quotient, K_c, cannot be obtained from the electrochemical data unless K_c is greater than about 2×10^2. For some such systems, values of K_c have been estimated from the abnormally large peak to peak separations which can be observed when the waves coalesce, but in the absence of ideal behavior and of a theory even for the ideal cases connecting peak to peak separation with K_c,

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such efforts are subject to a large error. In reporting values of extinction coefficients for the intervalence band, the concentration of the mixed-valence species has often been taken to equal the total binuclear content. When K_c is 1×10^2, this introduces a 16% error into the value of ϵ, but when K_c is at the statistical value, the error amounts to a factor of 2. Because the oscillator strength for weakly coupled systems, namely, those in which K_c tends to approach 4, is a measure of the delocalization energy,[9] it becomes important to have reliable values of ϵ. We have attempted to provide such a measurement by titrating the IT band absorbance in the near-infrared region and computer fitting the data obtained to determine the value of the comproportionation quotient.

Experimental Section

Materials. House-line distilled water was purified by redistillation from alkaline permanganate. Traces of oxygen were removed from argon (99.995%) by passing it through a scrubbing tower charged with 0.25 M chromium(II) (from $Cr(ClO_4)_3$) in 0.5 M $HClO_4$ over zinc/mercury amalgam. 4,4′-Bipyridyl dihydrochloride (Aldrich) and europium oxide (Research Chemicals) were used as supplied. D_2O–DCl (0.1 M) was prepared by diluting 12.1 M D_2O–DCl (International Chemical and Nuclear) with D_2O (MSD Isotopes, Merck). Europic solutions were prepared by dissolving a weighed amount of Eu_2O_3 in 0.1 M D_2O–DCl.

$[Ru(NH_3)_5Cl]Cl_2$ was prepared from the corresponding hexaammine trichloride (Matthey Bishop) following the literature procedure.[11] *Caution*! Although no shock-induced explosion of the following compound was encountered, an explosion occurred upon heating!

μ-(4,4′-Bipyridyl)-bis(pentaammineruthenium(III)) Perchlorate Dihydrate. $[Ru(NH_3)_5Cl]Cl_2$ (200 mg, 0.68 mmol) was suspended in 18 mL of distilled water, degassed by a steady stream of argon, and reduced for 1 h over zinc/mercury amalgam. 4,4′-Bipyridyl dihydrochloride (60 mg 0.26 mmol) was suspended in 2 mL of distilled water. Sodium hydroxide (0.28 mL, 1.88M (0.53 mmol) was added slowly with stirring producing a precipitate of fine, white needles of neutral ligand. The suspension was purged with argon for 1 h. The reduced ruthenium solution was transferred to the ligand solution via a stainless steel needle and allowed to react under argon for 8 h in the absence of light. The purple solution formed was acidified with 1 mL of 6 M HCl and oxidized by bubbling chlorine gas through it until all traces of purple were removed. A crude product was precipitated by adding the oxidized solution to 200 mL of rapidly stirred acetone. The filtered solid was washed with acetone and ether before air-drying. The anion was exchanged by dissolving the chloride salt in 10 mL of water and precipitating the complex by addition of an equal volume of saturated sodium perchlorate in water. The crude perchlorate was filtered, washed with ethanol and ether, and air-dried. The perchlorate salt was recrystallized from 10 mL of hot 0.1 M $HClO_4$ yielding red needles. The crystalline product was collected, washed with cold 0.1 M $HClO_4$, ethanol, and ether, and dried in a vacuum desiccator; yield 180 mg (60%). Calcd for $[(Ru(NH_3)_5)_2\text{-}4,4'\text{-bipy}](ClO_4)_6 \cdot 2H_2O$: C, 10.34; H, 3.64; N, 14.48. Found: C, 10.15; H, 3.62; N, 14.37.[12] Though using ClO_4^- as the counterion is hazardous, it does result in a cleaner, more crystalline product than is the case with anions used heretofore. The results reported here are much closer[3] to the calculated than is the case for the tosylate salt and have been obtained in like quality for repeat preparations.

Instrumentation. All electronic spectra were recorded on a Beckman Model 5270 spectrophotometer using matched quartz cells.

Electrochemical measurements were made using a Princeton Applied Research Model 173 potentiostat and Model 175 universal programmer system. Formal potentials were measured by cyclic voltammetry using a carbon paste electrode. Carbon paste was purchased from Bio-Rad, Inc. Potentials were measured against a saturated calomel electrode (SCE) at 25 °C and are uncorrected for junction potentials. Potentials were corrected to the normal hydrogen electrode scale by adding 0.244 V to the observed value. The voltammetric measurements were made in a standard H cell, with the test solution compartment separated from the reference electrode compartment by a fine porosity glass frit.

Titration of the IT band. Solutions of μ-(4,4′-bipyridyl)-bis(pentaammineruthenium(III)) perchlorate and Eu^{3+} (12.0 and 25.6 mM, respectively) were prepared and degassed with a steady stream of argon dried by passage through a scrubbing tower of concentrated sulfuric acid and saturated with D_2O in a second tower. The europic solution was reduced over excess zinc/mercury amalgam for 30 min. The sample solution was continuously circulated through a flow-through 0.1-cm quartz cell by means of a Masterflex Model 7016 peristaltic pump. Connections were made using Teflon tubing joined with Luer fittings or septum caps. Oxygen leakage was checked by repetitively scanning the spectrum of chromium(II) over 1 h and found to be minimal. Successive reductions were accomplished by transferring the europous solution via a glass syringe fitted with a platinum needle. A clean syringe was used for each addition. The sample solution was allowed to equilibrate (30 s) before recording the absorbance. Measurements were made at room temperature (19 ± 0.5 °C). Absorbance values were corrected for dilution and solvent absorption. The measurements of the intervalence band were made in 0.1 M DCl in D_2O.

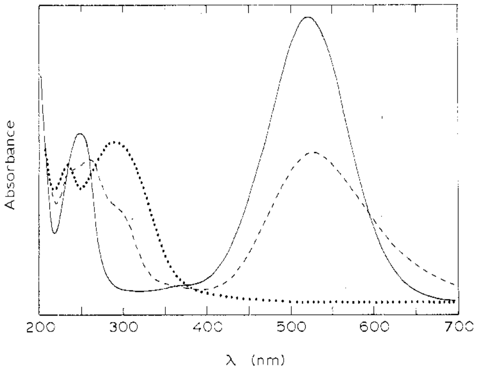


Figure 1. Absorption spectra for [2,2] (—), [2,3] ([2,3] spectrum corrected for equilibrium concentrations of [2,2] and [3,3], - - -), and [3,3] (···) forms of $[((NH_3)_5Ru)_2\text{-}4,4'\text{-bpy}]$ in 0.1 M HCl at 20 °C.

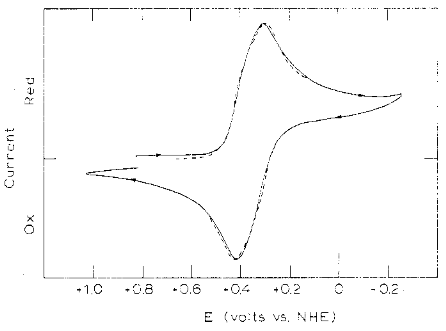


Figure 2. Cyclic voltammogram of $[((NH_3)_5Ru)_2\text{-}4,4'\text{-bpy}]^{6+}$ in 0.1 M HCl: scan rate 100 mV/s (—), simulation (- - -). The shoulders are obvious only when the comparison is made with the trace for a reversible one-electron process; they manifest themselves as swellings on the parts of the profiles which lie between the maxima.

Table I. Absorption Spectra for μ-(4,4′-Bipyridyl)-bis(pentaammineruthenium)(4+,5+,6+)[a]

[2,2][b]		[2,3][c]		[3,3]	
λ, nm	ϵ, M^{-1} cm^{-1}	λ, nm	ϵ, M^{-1} cm^{-1}	λ, nm	ϵ, M^{-1} cm^{-1}
249	1.50×10^4	238	1.11×10^4	235	1.13×10^4
365 sh		260	1.22×10^4	290	1.35×10^4
521	2.62×10^4	290 sh			
		365 sh			
		525	1.28×10^4		

[a] In 0.1 M HCl at ambient temperature. [b] Formed by reducing the [3,3] with excess zinc/mercury amalgam. [c] Formed by mixing equal volumes of [2,2] and [3,3]. Values are corrected for equilibrium concentrations of [2,2] and [3,3].

Results

UV–visible data for the binuclear complex in the [2,2], [2,3], and [3,3] states are shown in Figure 1 and summarized in Table I. Cyclic voltammetry in 0.1 M HCl showed two overlapping waves with only a single maximum resolved for

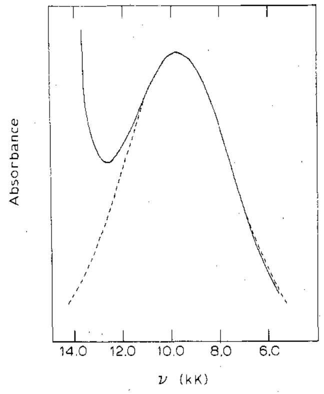


Figure 3. IT band for $[((NH_3)_5Ru)_2\text{-}4,4'\text{-bpy}]^{5+}$ in 0.1 M D_2O–DCl (—) and calculated Gaussian band shape (- - -).

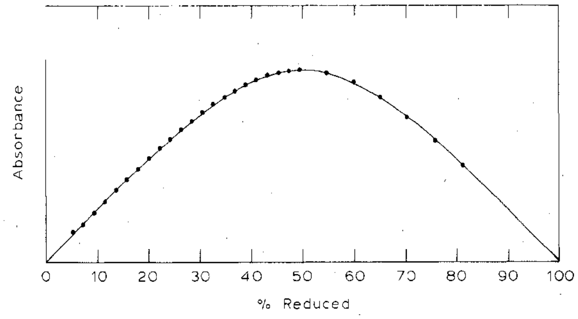


Figure 4. Titration data for reduction of $[((NH_3)_5Ru)_2\text{-}4,4'\text{-bpy}]^{6+}$ by Eu^{2+} in 0.1 M D_2O–DCl and calculated titration curve (—) obtained from computer-determined K_c. λ 1030 nm; [dimer] = 1.2 × 10^{-2} M; 1-mm cell.

the oxidation and reduction processes, the remaining maxima appearing as shoulders (Figure 2).

Figure 3 shows a plot of the IT band on an energy scale. The dotted curve represents the calculated Gaussian curve based on the observed half-width at half-height. The half-width was determined on the low-energy side of the band because of overlap with the visible band at the high-energy side. Hush's[7] theory gives the band full-width in the high temperature limit as $\Delta\nu_{1/2} = (2310\nu)^{1/2}$ where $\Delta\nu_{1/2}$ is the band full-width at half-height and ν is the band maximum (both in cm^{-1}). The observed band is found to be about 10% broader than the calculated band (0.52 vs. 0.48 μm^{-1}). Bands broader than those calculated have been observed for many weakly coupled mixed-valence systems. Exceptions to this behavior have been observed for ruthenium pentaammine complexes bridged by pyrazine,[1] cyanogen,[13] and *tert*-butylmalononitrile[14] where the metal centers are believed to be strongly coupled.

The data obtained in the titration of the intervalence band are shown in Figure 4. Absorption values were corrected for dilution. The data were computer fitted as described below to yield a value of K_c (24 ± 1) which was used to obtain a calculated curve shown as a solid line in Figure 4. Data collection was discontinued after 1.6 equiv of Eu^{2+} had been added because at this point precipitation of the complex ensued.

Because the magnitude of the absorbance of the IT band is a function of the extinction coefficient to be determined, it is necessary to fit the experimental curve (cf. Figure 4) by the use of ratios. The absorbance at 1 equiv of reductant or oxidant is chosen as the reference point because this maximum is easily determined with a minimum error. The ratios of this value to ten variable points along the curve are determined and compared to similar ratios calculated for three values of K_c. The points were chosen between 0 and 1 equiv of europous ion to minimize the error introduced by correction for dilution. The sign of the sum of the differences between the observed and calculated ratios was used to determine the limits on the experimental value. These new limits and their average were chosen and the interpolation procedure was repeated until the range of K_c became acceptably small. Error analysis was approximated by altering computer-generated data and observing the effect on the determined value of K_c.

For K_c = 20, a 1% error in a single data point results in about a 1% error in K_c and the percent mixed-valence species present. By the inclusion of a number of such points, random errors will cancel and the accuracy will be improved. The absorbance at the equivalence point is an exception because this value is used as a reference for calculating the observed ratios; a 1% error in it will result in a 4% change in the determined value of K_c and a similar alteration in the percent mixed-valence species present. However, for an absorbance maximum in the range 0.5–1.0 units, the error is easily reduced below 1% when many data points are taken around the equivalence point. As K_c increases, the curves become less and less sensitive to its value. This tends to decrease the accuracy of K_c as determined from the data, but in a limited range at least, the effect described is offset by the fact that the fraction of binuclear converted to the [3,2] state becomes less sensitive to the value of K_c. At worst, in the range $4 < K_c <$ ca. 200, the situation is superior to that encountered in cyclic voltammetry where the error in ΔE_f is often on the order of ±10 mV even when the waves are resolvable. When K_c is small, the waves overlap which increases the error in determining it.

The titration method is useful also for impure samples provided the contaminants do not absorb in the same region as the IT band and they have half-cell potentials sufficiently different from those of the binuclear complex. If the electrochemical condition is met, the concentration of the binuclear complex can be determined by titration.

Discussion

The value of the comproportionation constant for μ-(4,4'-bipyridyl)-bis(pentaammineruthenium)(5+) mixed-valence complex was determined as 24 at 19.0 °C and is believed to be precise to ±1 with 90% confidence. An independent determination at a slightly different temperature (20.8 °C) yielded a value of 23. Taking account of the value of K_c, we found the molar extinction coefficient to be 880 M^{-1} cm^{-1}[15] for the IT band observed at 1030 nm in 0.1 M D_2O–DCl. Numerical values for the oscillator strength (f = 2.13 × 10^{-2}), dipole strength (D = 0.4 Å), transition dipole moment ($|M|$ = 2.15 × 10^{-10} Å esu), and mixing coefficient (a = 4.15 × 10^{-2}) were calculated by applying eq 1–4 derived

$$f = (4.6 \times 10^{-9})\epsilon_{\max}\Delta\nu_{1/2} \tag{1}$$

$$D = (f/(1.085 \times 10^{-5})\nu)^{1/2} \tag{2}$$

$$|M| = (4.803 \times 10^{-10})D \tag{3}$$

$$a = Dr^{-1} \tag{4}$$

by Hush.[7] A value of 10.8 Å was chosen as the internuclear distance estimated from CPK space-filling models.

We are interested in assessing the factors that contribute to the stability of the mixed-valence state relative to the isovalent ones. Among them is stabilization by electron delocalization. The basis for calculating the delocalization energy from the spectrophotometric data is outlined in the following.

A weakly interacting mixed-valence system can be dealt with by considering two states (ψ_1 and ψ_2) corresponding to the unpaired electron being centered primarily on metals 1 or 2 keeping the nuclei at fixed positions. They correspond to the intersections of a vertical line with the potential energy profiles in a Marcus diagram.[16] As the interaction between these states is increased by electron delocalization, the mixing of the excited state (ψ_2) into the ground state (ψ_1) becomes more prominent. Assuming mixing of the first excited state only, the forms of the ground and excited state wave functions are

$$\psi_g = \psi_1 + a\psi_2$$

$$\psi_e = b\psi_1 + \psi_2$$

respectively, where a^2 or $b^2 << 1$. Because these interactions are small for weakly coupled systems, the approach developed by Mulliken[17] for weak charge-transfer complexes is applicable. Using the wave functions above, the expression for the energy of the states obtained by solving the secular determinant is given by

$$E(1 - S_{12}^2) = (1/2)(E_1° + E_2°) - S_{12}H_{12} \pm \sqrt{(\Delta/2)^2 + \beta_1\beta_2} \quad (5)$$

$$\Delta = E_2° - E_1°$$

$$\beta_1 = H_{12} - E_1°S_{12}$$

$$\beta_2 = H_{12} - E_2°S_{12}$$

where S_{12} is the overlap integral ($\langle\psi_1|\psi_2\rangle$), $E_1°$ and $E_2°$ are the unperturbed energies for the ground and first excited states, H_{12} is the resonance integral between the two states ($\langle\psi_1|H|\psi_2\rangle$), and H is the Hamiltonian for the system. The corresponding equations for the mixing coefficients are

$$a = -(H_{12} - S_{12}E_g)/(E_2° - E_g) \quad (6)$$

$$b = -(H_{12} - S_{12}E_g)/(E_1° - E_e) \quad (7)$$

where E_g and E_e are the perturbed energies for the ground and excited states, respectively. If $S_{12} << 1$ as expected for a weakly coupled system and the corrections in the energies are small compared to the difference between the ground and excited states (i.e., $\Delta \simeq E_e - E_g = h\nu_{IT}$; ν_{IT} is the energy of the intervalence transfer band expressed in wave numbers), then expressions 5–7 simplify to

$$E = \frac{E_1° + E_2°}{2} \pm \sqrt{(\Delta/2)^2 + H_{12}^2} \quad (8)$$

$$a = -\frac{H_{12}}{\Delta} \simeq -\frac{H_{12}}{h\nu_{IT}} \quad (9)$$

$$b = -\frac{H_{12}}{-\Delta} = -a \quad (10)$$

The two cases of interest occur at the intersection of the zero-order potential energy surfaces and at the bottom of the potential well. At the intersection point $E_1° = E_2°$ and the energy expression reduces to

$$E = E_{1,2}° \pm H_{12} \quad (11)$$

while at the bottom of the potential well $E_2° > E_1°$ and the quantity $[(\Delta/2)^2 + H_{12}^2]^{1/2}$ must be simplified using the binomial expansion. Truncation after two terms yields

$$E_g = E_1° - H_{12}^2/|\Delta| \quad (12)$$

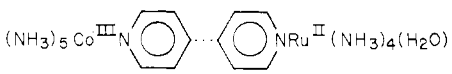
$$E_e = E_2° + H_{12}^2/|\Delta| \quad (13)$$

These expressions are also obtained from degenerate and nondegenerate perturbation theory, respectively.

Equations 11–13 indicate that the corrections to the zero-order energies due to resonance between the states can be calculated from H_{12} and ν_{IT}. The value of the resonance integral can be calculated from the mixing coefficient (eq 4) using eq 9. The calculated mixing coefficient indicates the unpaired electron spends 99.8% of its time associated primarily with the Ru(II) center; the extent of delocalization is small and the molecule falls within the weakly interacting category of mixed-valence complexes. The calculated energy correction for the bottom of the well is 48 cal/mol while at the intersection point the splitting ($2H_{12}$) is calculated to be 2.3 kcal/mol. The latter value assumes the mixing coefficient does not change with the geometry of the system.

It should be noted that the energy correction at the bottom of the well is calculated assuming $a = b$. Since in these ligand-bridged systems the interaction does not occur significantly by direct orbital overlap between the metal orbitals but by mixing in excited states which involve also the ligands,[18] b will be greater than a so that in actuality the delocalization energy at the bottom of the well is somewhat overestimated.

The value calculated for this splitting at the intersection region is sufficiently large so that the transmission coefficient for thermal electron transfer will be close to unity and thermal transfer is expected to be adiabatic.[19] Observations[20] made on the rates of the intramolecular redox processes in complexes of the type



where coupling between the 4,4′ positions of the pyridine rings is varied by suitable chemical modifications suggest that the reaction is in, or at least close to, the adiabatic regime for the case of 4,4′-bipyridine as the bridging group. In a system such as this where the acceptor orbital has σ symmetry while the carrier has π, the mismatch is presumably met by a distortion of the coordination sphere about the Co(III) center, and this requirement contributes to the high activation energy which is observed (~19 kcal).

The value of $K_c = 24$ provides a measure of the stability of the [2,3] state relative to [2,2] + [3,3]. Converted to energy units this becomes $RT \ln 24/4$ (the factor 4 is the purely statistical contribution to K_c) or ~500 cal per [3,2] unit. If the metal ions are far enough apart, trapping of charge by the solvent will make no contribution to the stability of the mixed relative to the isovalent state. It is unlikely that there are any electronic effects in the [2,2] and [3,3] states which particularly stabilize them. In an earlier paragraph, the stabilization of the [2,3] by electronic delocalization was shown to contribute only 50 cal. The major contribution to the 500 cal registered may well be the simple electrostatic repulsion of the charge which gives the 2[3,2] distribution a slight advantage in stability over [2,2] + [3,3]. This contribution (w) was calculated as 90 cal/mol using the following equations:

$$w = \frac{Z_1Z_2e^2}{D_s r(1 + \kappa r)} \quad (14)$$

$$\kappa = \frac{8\pi Ne^2\mu d}{1000D_s kT} \quad (15)$$

where Z_1 and Z_2 are the charges on the metal centers, e is the electronic charge in esu, D_s is the dielectric constant (80), r is the separation between metal centers (10.8×10^{-8} cm), N is Avogadro's number, μ is the ionic strength (0.1 M), d is the density of the solvent (1.11 g/mL), k is the Boltzmann constant in erg/deg, and T is the temperature (293 °C). The sum of the two contributions which have been identified is much less than the experimental value of 500 cal. It is altogether likely that the electrostatic term is grossly underestimated. Since the electronic contribution is so small in weakly interacting systems, the value of K_c may be a rather sensitive way of determining the electrostatic term in solution.

As a check to the validity of the procedure for determining K_c, the value obtained was used to calculate ΔE_f, i.e., the difference in potential for the two stages [3,3 − 3,2] and [3,2 − 2,2], and a simulated cyclic voltammogram was produced by summing two reversible, one-electron waves separated by

ΔE_f. The simulated cyclic voltammogram closely matches the observed as shown in Figure 2. Calculations[4] show that after the waves coalesce, the peak-to-peak separation as read from the oxidation and reduction maxima will decrease as K_c becomes smaller. When $K_c = 4$, ΔE_f for two separate stages is 36 mV, and the peak-to-peak separation observed when the waves corresponding to the two stages are superimposed will be 59 mV. The amplitude will, however, correspond to the flow of 2 electrons rather than 1 electron per molecule. The simulated cyclic voltammogram has a slightly larger value of peak-to-peak separation than the observed, which is likely a result of incomplete resolution in the latter.

After we obtained a value of K_c, the spectrum recorded for a solution nominally containing the [3,2] species was corrected for the contributions by the [2,2] and [3,3] forms in equilibrium with it. The spectrum shown in Figure 1 for the [3,2] species has been obtained in this manner. The prominent features in the spectrum of the [2,2] are the bands in the visible and near-UV region arising from $\pi^* \leftarrow \pi d$ and $\pi^* \leftarrow \pi$ transitions, respectively, while the weak band at ~380 nm is probably a ligand field transition. The Ru(III) species shows the $\pi^* \leftarrow \pi$ transition at higher energy than is the case for the fully reduced, and the weak band observed in the latter is absent. The strong and rather broad band in the near-UV region probably arises from a $\pi d \leftarrow \pi$ transition (perhaps transitions). As expected for a weakly coupled system, the mixed-valence species combines the features of both the [2,2] and [3,3]. Some perturbations are, however, worth noting. The $\pi^* \leftarrow \pi d$ transition is at slightly lower energy than is the case for the [2,2] species, and most of the tailing to lower energies is intrinsic to the band and cannot be accounted for by the intervalence absorption. The oscillator strengths for the transitions are 0.51 and 0.28 ([2,2] and [3,2], respectively). The $\pi^* \leftarrow \pi$ absorption is composite as is expected for a species containing both Ru(II) and Ru(III) and there is a definite shift for each of them to lower energy, possibly suggesting a significant change in the structure of the bridging group as the oxidation states of the metal change.

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Registry No. $[((NH_3)_5Ru)_2\text{-}4,4'\text{-bpy}]^{5+}$, 54065-65-5; $[((NH_3)_5Ru)_2\text{-}4,4'\text{-bpy}](ClO_4)_6$, 69042-75-7; $[Ru(NH_3)_5Cl]Cl_2$, 18532-87-1; $[((NH_3)_5Ru)_2\text{-}4,4'\text{-bpy}]^{4+}$, 36451-88-4.

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Direct Observation of Singlet–Triplet Separation in Dimeric Copper(II) Acetate by Neutron Inelastic Scattering Spectroscopy

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The singlet–triplet separation in $Cu_2(CD_3COO)_4 \cdot 2D_2O$ has been determined by neutron inelastic scattering spectroscopy. Its value is 298 ± 4 cm^{-1}. Within experimental error there is no temperature dependence of the singlet–triplet separation between 10 and 300 K. Magnetic susceptibility measurements on $Cu_2(CH_3COO)_4 \cdot 2H_2O$ and $Cu_2(CD_3COO)_4 \cdot 2D_2O$ reveal that deuteration has no measurable effect on the exchange coupling.

Introduction

Since the pioneering work of Bleaney and Bowers in 1952[1] a great deal has been written about the electronic structure of copper(II) acetate and related binuclear complexes.[2] There is today no mechanism of coupling of the two paramagnetic copper(II) ions accepted by everyone working in this field. It is not our intention to add one more opinion. Rather, we want to report an experiment which is of some significance to this question.

Inelastic scattering of thermal neutrons is a powerful tool for the study of low-energy excitations in crystalline transition-metal and lanthanide compounds.[3] It offers an alternative to infrared and Raman spectroscopy on the one hand and bulk techniques such as heat capacity and magnetic susceptibility measurements on the other hand. In the case of magnetically

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