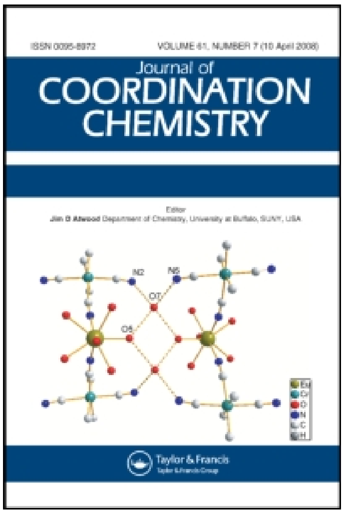

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Nola R. Bertram[a]; Diana L. Sedney[a]
[a] Thompson Chemical Laboratory, Williams College, Williamstown, MA, U.S.A.

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THE EFFECT OF A TRIDENTATE LIGAND BRIDGE UPON ELECTRON DELOCALIZATION IN A RUTHENIUM MIXED VALENCE COMPLEX

NOLA R. BERTRAM and DIANA L. SEDNEY
Thompson Chemical Laboratory, Williams College, Williamstown, MA 01267, U.S.A.

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An asymmetric binuclear ruthenium ammine complex has been synthesized using pyrazinemonocarboxylate (mcpy) as a bridging ligand. The near infrared spectrum of $[(NH_3)_5RumcpyRu(NH_3)_4]^{4+}$ exhibits at least three peaks at 1530, 1420 and 1290 nm with $\varepsilon_{1530} = 900$ M^{-1} cm^{-}. The electrochemical behavior of this complex is characterized by two reversible redox steps at 0.74 and 0.33 V corresponding to formation of the fully oxidized [3,3] and fully reduced [2,2] dimers respectively. The visible absorption spectrum of the [2,2] dimer is typical of MLCT's observed for complexes with bidentate ligands ($\lambda_{max} = 590, 485$ nm), while the mixed valence complex has only a single peak at 560 nm. A qualitative assessment of the extent of intermetal electron delocalization in the mixed valence species is presented.

Keywords: Ruthenium, dimers, binuclear, electrochemistry, synthesis

INTRODUCTION

A characteristic of many ruthenium mixed valence complexes that have been reported in the literature is the presence of a bidentate bridging ligand which occupies a single site in each ruthenium coordination sphere. The decaammine ruthenium dimers, $[(NH_3)_5Ru]_2L^{5+}$ (where L = a bidentate bridging ligand),[1] typically exhibit absorptions in the near IR region of the spectrum which have been assigned as intervalence transfer (IT) bands. The extinction coefficient of the IT band is a measure of the extent of electron delocalization between Ru(II) and Ru(III) centers. Reported values of ε range from 410 to $>10^4$ for dimers with a substantial degree of delocalization (Class III).[2] However, when the tetradentate ligand 2,5-pyrazinedicarboxylate (hereafter, *dcpy*) serves as the bridging ligand, the extinction coefficient is at the low end of this range ($\lambda_{IT} = 1510$nm, $\varepsilon = 430$M^{-1} cm^{-1})[3] even though *dcpy* is centrosymmetric and the Ru–Ru distance is expected to be comparable to that of the Creutz-Taube dimer, $\{[(NH_3)_5Ru]_2\text{pyrazine}\}^{5+}$, ($\lambda_{IT} = 1570$nm, $\varepsilon = 5000$M^{-1} cm^{-1}).[4] In an attempt to define the role of the carboxylate functionality in mediating the intervalence electron transfer, complexes containing the ligand pyrazinemonocarboxylate (*mcpy*) are currently being investigated. This asymmetric ligand offers the advantage of selective coordination as a mono- or bidentate ligand to a ruthenium metal center.

This paper details the synthesis and characterization of the mixed valence (n = 4) and fully reduced (n = 3) complexes $[(NH_3)_5Ru\textit{mcpy}Ru(NH_3)_4]^{n+}(PF_6)_n$. Coordination of the carboxylate oxygen atom opens an additional pathway for electron delocalization which is observed in both the visible and near IR spectra of the mixed valence dimer.

Materials

All starting materials were of reagent grade. The monomeric precursors were synthesized from $[Ru(NH_3)_6]Cl_3$ (ICN, K&K) following published procedures.

Deionized water was used for all aqueous solutions and an argon atmosphere was maintained throughout the syntheses.

$[(NH_3)_5Ru$*mcpy*$Ru(NH_3)_4](PF_6)_3$, (I): The dimer was prepared from $[(NH_3)_5Ru$*mcpy*$](PF_6)^5$ and *cis*-$[(NH_3)_4RuCl_2]Cl$.[6] The dichloro complex was added to a minimum volume of deaerated water, reduced over Zn/Hg amalgam, and combined with the ruthenium pentaammine complex. The dark indigo solution was stirred under argon for three hours and then filtered, reduced in volume and precipitated as the hexafluorophosphate salt, using a large excess of ethanol. The solid product was recovered by filtration, washed with ethanol, and vacuum dried. The dimer is subject *via* atmospheric oxidation to a mixed valence species so that experimental data was obtained using freshly prepared samples. An alternative synthesis, using $[(NH_3)_5Ru$*mcpy*$](PF_6)^5$ and *cis*-$[(NH_3)_4RuCl_2]Cl$.[6] The dichloro complex was added to a the dimer, but chromatographic separation on a Sephadex column indicated the presence of impurities. Therefore the synthetic route initially described is preferred.

$[(NH_3)_5Ru$*mcpy*$Ru(NH_3)_4](PF_6)_4$, (II): The mixed valence complex was obtained by partial oxidation of dimer I. A concentrated aqueous solution of I was oxidized with an aqueous solution of ceric ammonium nitrate (in 0.1M H_2SO_4; 1/2 mol Ce(IV)/mol dimer I. Complex II was recovered after the addition of excess aqueous NH_4PF_6 solution, followed by excess alcohol. The solid product was filtered, washed with a little ethanol and air dried.

Instrumentation

Absorption spectra were recorded on Cary 219, Perkin-Elmer Lambda 3 (UV-Vis region) and Cary 14 (near IR) spectrophotometers. A Perkin-Elmer 283B IR spectrophotometer was used to obtain IR spectra of the dimers prepared in KBr disks. Cyclic voltammograms were measured on an IBM 225 Voltammetric Analyzer using a glassy carbon working electrode, a platinum wire counter electrode, and a saturated standard calomel electrode as the reference electrode. The reduction potentials were obtained in 0.1 M KCl aqueous solutions and the values reported are *vs* SHE using the $[Ru(NH_3)_6]^{3+/2+}$ couple ($E^\circ = +0.05$ V)[7] as a standard. A Beckman Century SS-1 Expanded Scale pH Meter was used for pH measurements.

RESULTS AND DISCUSSION

UV-Visible Spectra

The spectra of I and II are shown in Fig. 1. A broad metal-to-ligand charge transfer (MLCT) is the dominant feature in the visible absorption spectrum of each dimer. The shoulder at 485nm in the spectrum of I is considered to be a MLCT to the metallocycle which is formed through coordination of the COO^- group. This spectrum is unchanged over a pH range of 0.1 to 7, and thus *mcpy* is likely to be coordinatively saturated, in agreement with the IR spectra discussed below. Partial oxidation of I to yield complex II produces a 30nm blue shift in the position of the main band. When the bridging ligand is 2,5-pyrazine dicarboxylate (*dcpy*) rather than *mcpy*, a similar hypsochromic shift in the principle MLCT band is also observed. This has been attributed to the decreased π-backbonding ability of the Ru^{III} species ($-[Ru(NH_3)_5]^{3+}$) now at athe remote end of the Ru^{II}-*mcpy* moiety instead of the divalent $-[Ru(NH_3)_5]^{2+}$ group. When monodentate ligands (at each metal center) are used, a red shift is observed upon oxidation of the [2,2] dimers. In the case of the Creutz-Taube complex $\{[(NH_3)_5Ru]_2\text{pyrazine}\}^{n+}$, $\lambda_{max} = 547, 565$nm for n = 4, 5 respectively and the electrostatic effect of replacing a 2+ charge with 3+ is considered to be the dominant

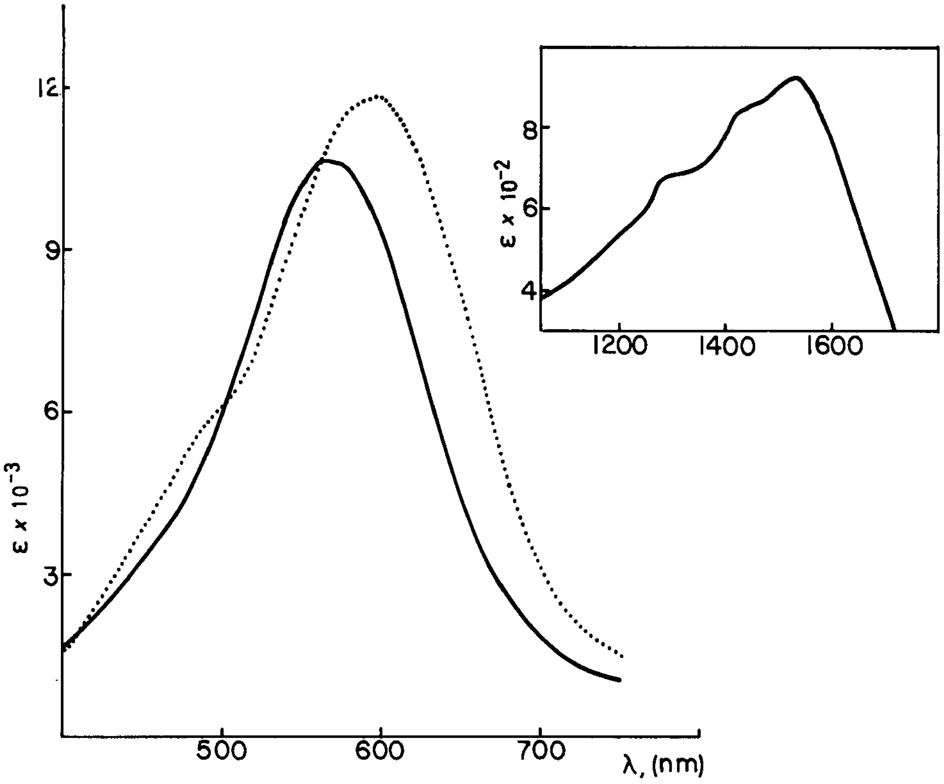

FIGURE 1 The visible absorption spectra of $[(NH_3)^5Ru$ *mcpy* $Ru(NH_3)_4]^{n+}$ in aqueous solution: I, (. . .), n = 3 and (——), n = 4. The near infrared spectrum of II is shown in the inset.

contribution to the decrease in the π^* ligand level. The disappearance of the shoulder at 485nm in the spectrum of the [2,3] dimer suggests the oxidation state assignment $[(NH_3)_5Ru^{II}$*mcpy*$Ru^{III}(NH_3)_4]^{4+}$. The metallocycle absorption is expected to be lost when Ru^{II} is oxidized to Ru^{III}. In the case of the symmetric *depy* dimer,[3] the two MLCT absorptions are maintained in the mixed valence spectrum since a Ru^{II}-metallocycle still exists.

IR Spectra

The IR spectrum of dimer I is primarily of interest to confirm the mode of coordination between ruthenium tetraammine and the carboxylate functionality. The symmetric and asymmetric -CO stretching frequencies occur at 1360 and 1625 cm^{-1}, respectively (as compared to 1370 and 1621 cm^{-1} for the potassium salt of the free ligand). These frequencies are indicative of a strong ionic interaction between the ruthenium atom and the carboxylate group. Therefore the coordination spheres of the ruthenium atoms are formally inequivalent, with one metal center bound to six nitrogen atoms and the second ruthenium atom bound to one oxygen atom and five nitrogen atoms.

TABLE I
Reduction Potentials of Ruthenium Ammine Monomer/Dimer Pairs

Monomer	$E_{1/2}(V)^2$	Dimer	$E_{1/2}(V)$
$[(NH_3)_4Ru$*mcpy*$]^{2+/+}$	0.37^b	$[(NH_3)_4Ru$*mcpy*$Ru(NH_3)_5]^{5+/4+/3+}$	0.74, 0.33^c
$[(NH_3)_5Ru$*mcpy*$]^{2+/+}$	0.51^b		
$[(NH_3)_5Rupyrazine]^{3+/2+}$	0.49^d	$\{[(NH_3)_5Ru]_2pyrazine\}^{6+/5+/4+}$	0.74, 0.35^d
$\{(NH_3)_4Ru$*dcpy*$\}^{2+/+}$	0.41^e	$\{[(NH_3)_4Ru]_2$*dcpy*$\}^{4+/3+/2+}$	0.62, 0.32^c

[a]Measured in 0.1M KCl *vs* NHE; [b]Ref. 5; [c]This work; [d]Ref. 1; [e]Ref. 3.

Electrochemistry

The cyclic voltammogram of dimer I contains a reversible peak at $E_{1/2} = 0.33$ and 0.74V. Using these two values as the [2,2]/[2,3] and [2,3]/[3,3] potentials respectively, the comproportionation constant is 9×10^6. The mixed valence dimer therefore does not disproportionate to any appreciable extent and any contribution from the [2,2] and [3,3] dimers in the calculation of the extinction coefficients of II has been neglected.

The reduction potentials of some monomer/dimer pairs are reported in Table I. Usually when ruthenium atoms are separated by a single aromatic ring (r ~7 Å), the first reduction potential of the dimer is more positive than that of the monomer due to charge stabilization through addition of a 3+ charge at the remote end of the ligand bridge. The second reduction potential, though, is more negative than the corresponding monomer value as observed for the pyrazine and *dcpy* pairs in Table I. The shift to more negative potentials may be the result of now having a π-donor(Ru^{II}) at the remote end of the ligand bridge The *mcpy* dimer follows this same trend and the following reductions are assumed to occur.

$$[(NH_3)_5Ru^{III}mcpyRu^{III}(NH_3)_4]^{5+} \xrightarrow{-e^-} [(NH_3)_5Ru^{II}mcpyRu^{III}(NH_3)_4]^{4+}$$

$$[(NH_3)_5Ru^{II}mcpyRu^{III}(NH_3)_4]^{4+} \xrightarrow{-e^-} [(NH_3)_5Ru^{II}mcpyRu^{II}(NH_3)_4]^{3+}$$

Reduction of the pentaammine side of the complex is expected to occur more readily than the tetraammine side if the E_0 values of the respective monomeric analogs are compared (0.51 *vs* 0.37V). When the electrochemical reduction is monitored spectroscopically it is not until after the second reduction step that the shoulder at 485nm ascribed to the metallocycle MLCT appears in the spectrum.

Near IR Spectrum

The near IR spectrum of the mixed valence dimer in D_2O is shown in the inset of Fig. 1. Solutions of the fully reduced [2,2] and fully oxidized [3,3] dimers in D_2O do not absorb in this region of the spectrum. The broad spectrum observed is composed of multiple intervalence transfer bands with the lowest energy band having a peak maximum at 1530nm. The presence of shoulders at 1420 and 1290nm is responsible for the asymmetry on the high energy side of the IT band.

The non-classical shape of these absorptions precludes quantitative assessment of the degree of electron delocalization according to the Hush theory.[8] However, the low molar extinction coefficient ($\varepsilon_{1530} = 900M^{-1}\ cm^{-1}$) which is proportional to the IT transition moment indicates that the degree of delocalization is small and the ruthenium valence states are nearly trapped. This value of ε is intermediate between that reported for the similarly shaped near IR spectrum of $\{[NH_3)_4Ru]_2dcpy\}^{3+}$ and the Creutz-Taube complex. As might have been predicted, the degree of electron delocalization is greater in the case of the tridentate *vs* the tetradentate bridging ligand. Such comparisons based on coordination number may be overly simplistic since *mcpy* is not a centrosymmetric ligand like the other two.

Multiple coordination by the bridging ligand in the mixed valence complexes causes the intermetal electron transfer to proceed along competing pathways with the net effect of decreased probability of transition along any one path. The extent of electron transfer should be more properly considered as proportional to the sum of several transition moments in such cases.

CONCLUSIONS

A mixed valence complex containing a tridentate ligand bridge has been prepared. Although coordination by the carboxylate substituent on the pyrazine ring produces only small changes in the visible spectrum of the dimer, compared with previously synthesized ruthenium ammine mixed valence species, the near IR spectrum is unusual and appears to be a composite of several absorptions of similar, low intensities. The presence of multiple coordination sites produces splitting of the $d\pi$–π^*–$d\pi$ molecular orbitals so that several intervalence transfers become allowed.

Throughout this paper the bridging ligand has been denoted as asymmetric, but this raises an interesting question concerning the classification of II. Mixed valence complexes are designated as symmetric or asymmetric based upon the ligands occupying the terminal metal coordination sites. Introduction of asymmetry has been shown both theoretically and experimentally[9] to increase the energy of the intervalence transfer. In this case the terminal ligands are all ammines and the ruthenium coordination spheres are sufficiently similar so that the onset of the IT bands occurs at 1530nm which is comparable in energy to *symmetric* mixed valence complexes.

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