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Spectroelectrochemistry of the Multistep Redox System $\{(\mu\text{-bpym})[\mathrm{Ru(NH_3)_4}]_2\}^{n+}$, $n = 2-6$, in a Nonaqueous Medium

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The dinuclear complex ion $\{(\mu\text{-bpym})[\mathrm{Ru(NH_3)_4}]_2\}^{4+}$, isolated as the tetrakis(hexafluorophosphate) salt, undergoes two reversible oxidation and two reversible reduction processes in dry acetonitrile/0.1 M n-$\mathrm{Bu_4NPF_6}$. The more accessible 3+, 4+, and 5+ states were characterized spectroelectrochemically (UV/vis/NIR). The EPR-active 3+ form ($g_1 = 2.0089$, $g_2 = 1.9967$, $g = 1.9308$, $\langle g \rangle = 1.9785$) is best described as a complex between the bpym radical anion and two tetraammineruthenium(II) fragments. The 5+ state, on the other hand, is EPR silent down to 3.5 K due to rapid relaxation involving metal-based orbitals; it exhibits a weak absorption in the 3200 $\mathrm{cm^{-1}}$ region which may be associated with the intervalence-transfer (IT) transition. Although the question of (de)-localization in the mixed-valent 5+ species cannot be answered from the available data, the comproportionation constant of $10^{5.1}$ signifies strong metal−metal interaction under these conditions.

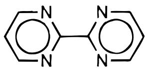
Introduction

The characterization of the redox system $\{(\mu\text{-pz})[\mathrm{Ru(NH_3)_5}]_2\}^{n+}$, $n = 4-6$, with the mixed-valent Creutz−Taube ion ($n = 5$) as intermediate[1] has contributed significantly to the field of electron transfer.[2] That system was studied in aqueous and aprotic media,[3] and both electrochemical steps were found to involve primarily metal-centered orbitals: $(\mathrm{Ru^{II}})_2$, $(\mathrm{Ru^{2.5}})_2$, $(\mathrm{Ru^{III}})_2$. Although the lowest transition of the $(\mathrm{Ru^{II}})_2$ form ($n = 4$) was attributed to an MLCT transition to the π^* orbital of the bridging ligand,[1] it was not possible to reduce that (4+) ion further because of an apparently very negative reduction potential and poor solubility in many aprotic solvents.[4]

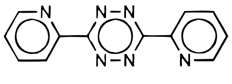
In one attempt to extend Creutz−Taube ion chemistry, Ruminski and Petersen reported a study of $\{(\mu\text{-bpym})[\mathrm{Ru(NH_3)_4}]_2\}^{n+}$ ions (bpym = 2,2′-bipyrimidine) in aqueous solution where the bridging ligand acted as bis-chelate system.[5] Neither reduction nor a fully reversible second oxidation process was observed; the latter was attributed to dissociative tendencies yielding aqua complexes. Although the 5+ ion was described as a mixed-valent species, there was no report of the usually expected[2,3] long-wavelength intervalence-transfer (IT) band.

In a previous similar approach, the dinuclear bpym-bridged complex ions $\{(\mu\text{-bpym})[\mathrm{Ru(bpy)_2}]_2\}^{n+}$, $n = 4$, 5[6] and $n = 3$[7] were investigated in aqueous and aprotic solution.

Exploring the chemistry and spectroscopy of specifically designed analogues[8] of the Creutz−Taube ion,[1] we discovered that d^5/d^6 mixed-valent systems with conjugated bis-chelate bridging ligands such as 2,2′-bipyrimidine or 3,6-bis(2-pyridyl)-1,2,4,5-tetrazine (bptz) showed only very weak IT absorptions despite large comproportionation constants K_c.[8a,b]



bpym



bptz

Considering the frequently strong solvent dependence of charge-transfer bands and redox potentials of mixed-valent systems,[2,3,9] we began an investigation of the title system with special emphasis on (i) studying the reduction behavior in addition to the expected two-step oxidation, (ii) searching for the IT band of the (5+) mixed-valent intermediate by spectroelectrochemical methods, and (iii) measuring the EPR response of the paramagnetic states.

Experimental Section

The complex $\{(\mu\text{-bpym})[\mathrm{Ru(NH_3)_4}]_2\}(\mathrm{PF_6})_4$ was obtained and characterized as described previously for the analogous perchlorate.[5]

Instrumentation. EPR spectra were recorded in the X band on a Bruker System ESP 300 equipped with a Bruker ER035M gaussmeter

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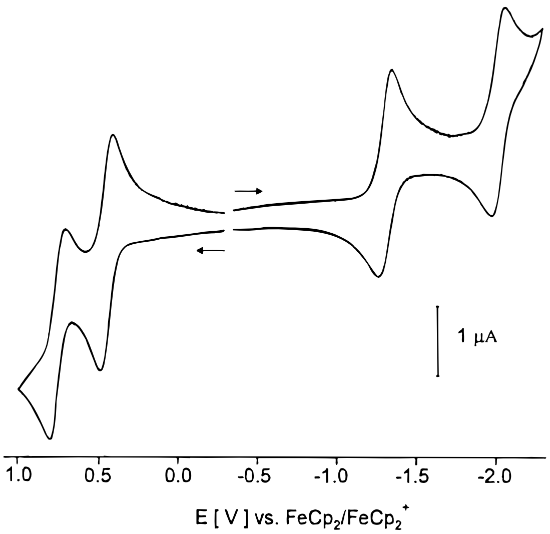

Figure 1. Cyclic voltammograms (oxidation and reduction) of $\{(\mu\text{-bpym})[\mathrm{Ru(NH_3)_4}]_2\}(\mathrm{PF_6})_4$ (10^{-3} M) in acetonitrile/0.1 M n-$\mathrm{Bu_4NPF_6}$ at 100 mV/s scan rate (298 K).

and an HP 5350B microwave counter. EPR spectral simulations were performed using the Bruker WINEPR SimFonia 1.25 program. Infrared spectra were obtained using a Perkin-Elmer Paragon 1000 PC instrument. UV/vis/NIR absorption spectra were recorded on a Bruins Instruments Omega 10 spectrophotometer. Cyclic voltammetry was carried out in dried acetonitrile/0.1 M n-$\mathrm{Bu_4NPF_6}$ using a three-electrode configuration (glassy carbon electrode, Pt counter electrode, Ag/AgCl reference) and a PAR 273 potentiostat and function generator. The ferrocene/ferrocenium couple served as internal reference. Spectroelectrochemical measurements were performed using an optically transparent thin-layer electrode (OTTLE) cell[10] for UV/vis spectra and a two-electrode capillary for EPR studies.[7] Potentials and electrolysis time were optimized empirically following spectral response.

Results

In contrast to the results reported[5] for the aqueous solution, the starting material $\{(\mu\text{-bpym})[\mathrm{Ru(NH_3)_4}]_2\}(\mathrm{PF_6})_4$ showed in acetonitrile two reversible one-electron reduction processes in addition to the oxidation features (Figure 1).

The potentials vs $\mathrm{FeCp_2}^{+/0}$ for cyclovoltammetrically reversible one-electron processes are +0.45 and +0.75 V (oxidation) and −1.31 and −2.02 V (reduction). These values lead to comproportionation constants K_c of $10^{5.1}$ (5+ ion) and $10^{12.0}$ (3+ state), calculated as follows:

$$K_c = [\mathrm{M}^{n+}]^2/[\mathrm{M}^{(n-1)+}][\mathrm{M}^{(n+1)+}] = 10^{\Delta E/59\,(\mathrm{mV})}$$

where

$$2\mathrm{M}^{n+} \rightleftharpoons \mathrm{M}^{(n-1)+} + \mathrm{M}^{(n+1)+}$$

Spectroelectrochemistry in the UV/vis region confirmed the reversible behavior within the 3+/4+/5+ redox series, the 2+ and 6+ states were not sufficiently long-lived for conventional spectroelectrochemistry at room temperature. Figure 2 shows the changes occurring upon the oxidation $\{(\mu\text{-bpym})[\mathrm{Ru(NH_3)_4}]_2\}^{4+\rightarrow 5+}$, and Table 1 contains the corresponding data.

Table 1. UV/Vis Absorption Data for $\{(\mu\text{-bpym})[\mathrm{Ru(NH_3)_4}]_2\}^{n+}$ in Different Oxidation States[a]

complex	absorption maxima $\lambda_{\max}$, nm (ϵ, 10^4 M^{-1} cm^{-1})
$\{(\mu\text{-bpym})[\mathrm{Ru(NH_3)_4}]_2\}^{3+}$	325 (1.81), 398 (1.05), 467 (sh), 502 (sh), 630 (0.25)
$\{(\mu\text{-bpym})[\mathrm{Ru(NH_3)_4}]_2\}^{4+}$	260 (2.01), 423 (1.72), 630 (sh), 691 (0.42)
$\{(\mu\text{-bpym})[\mathrm{Ru(NH_3)_4}]_2\}^{5+}$	260 (1.86), 438 (0.81), 701 (0.20)

[a] From OTTLE spectroelectrochemistry in acetonitrile/0.1 M n-$\mathrm{Bu_4NPF_6}$.

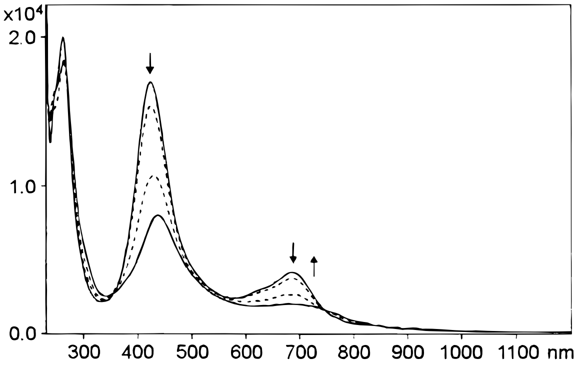

Figure 2. UV/vis spectroelectrochemical response upon the reversible oxidation $\{(\mu\text{-bpym})[\mathrm{Ru(NH_3)_4}]_2\}^{4+\rightarrow 5+}$ (8×10^{-4} M) in acetonitrile/0.1 M n-$\mathrm{Bu_4NPF_6}$ at 298 K.

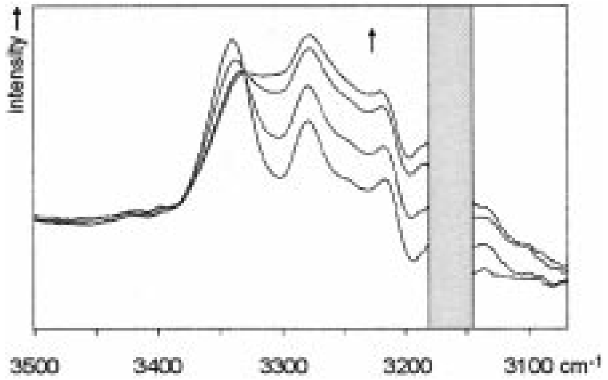

Figure 3. IR spectroelectrochemical response upon the reversible oxidation $\{(\mu\text{-bpym})[\mathrm{Ru(NH_3)_4}]_2\}^{4+\rightarrow 5+}$ (5×10^{-3} M) in acetonitrile/0.1 M n-$\mathrm{Bu_4NPF_6}$ at 298 K. Shaded area: solvent absorption.

In the search for the IT band, we extended the spectroelectrochemistry into the near-infrared (NIR) region (Figure 3). Upon oxidation from the 4+ to the 5+ form, we observed an increase of intensity underlying the NH vibrational bands between 3100 and 3350 cm^{-1} (Figure 3). We attribute this increase to a weak electronic (IT) transition.

Whereas all attempts to observe EPR spectra failed for the electrochemically generated 5+ form, even at 3.5 K in glassy frozen solution, the 3+ state yielded a rhombic EPR signal under those conditions (Figure 4) which could be simulated using the following parameters: $g_1 = 2.0089$, $g_2 = 1.9967$, $g = 1.9308$, $A_2 = 0.70$ mT (2H), $A_1 \approx 0.5$ mT (^{99,101}Ru). At room temperature, an isotropic signal with $\langle g \rangle = 1.9785$ was observed.

Discussion

Changing from aqueous solution to aprotic acetonitrile extends the electrochemical potential window so that two reversible reduction processes become accessible in addition to both oxidation steps. Another result of the solvent change is the increase in the comproportionation constant K_c(5+) from $10^{3.2}$ (ΔE 190 mV) to $10^{5.1}$ (ΔE 300 mV); the Creutz−Taube ion exhibits $K_c = 10^{7.3}$ in acetonitrile.[3] This observation suggests a stabilization of the $\mathrm{Ru^{II}/Ru^{III}}$ mixed-valent state. The value of $K_c(3+) = 10^{12.0}$ (ΔE 710 mV) is in agreement with

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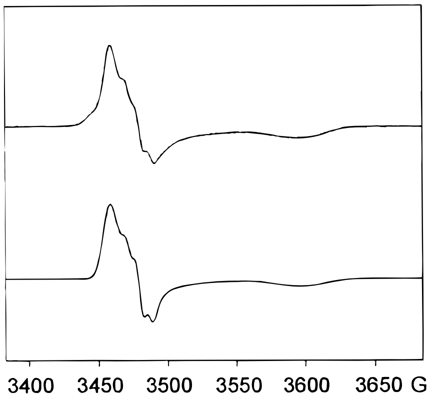

Figure 4. Top: EPR spectrum of electrogenerated $\{(\mu\text{-bpym})[\mathrm{Ru(NH_3)_4}]_2\}^{3+}$ (10^{-4} M) in frozen acetonitrile/0.1 M *n*-$\mathrm{Bu_4NPF_6}$ at 110 K (microwave frequency 9.7347 GHz). Bottom: Computer-simulated spectrum.

two bpym-centered reduction processes as was reported for other dinuclear complexes $\mathrm{L}_n\mathrm{M}(\mu\text{-bpym})\mathrm{ML}_n$.[11]

The UV/vis spectroelectrochemical results show the expected decrease of the metal-to-ligand charge transfer (MLCT) bands[5,11] at 691 and 423 nm. The 3+ ion exhibits several little resolved bands in the near-UV and visible regions (Table 1) which do not completely fit the pattern of other dinuclear complexes $\mathrm{L}_n\mathrm{M}(\mu\text{-bpym}^{\bullet-})\mathrm{ML}_n$,[12] thus indicating some degree of metal d/ligand π^* orbital mixing (see below). For the 5+ ion, there is no evidence for a long-wavelength IT absorption except for the feature emerging around 3200 cm^{-1} which still exhibits NH vibrational stretching bands but also a broad underlying absorption (Figure 3). We attribute this absorption to the IT transition which is expectedly weak for bis-chelate complexes, due to unfavorable overlap of corresponding orbitals:[8a,b] $\{(\mu\text{-bptz})[\mathrm{Ru(NH_3)_4}]_2\}^{5+}$ has $\epsilon = 500\ \mathrm{M^{-1}\ cm^{-1}}$ at $\lambda_{\max} = 1453$ nm ($K_\mathrm{c} = 10^{15.0}$),[8a] and $\{(\mu\text{-bpym})[\mathrm{Mo(CO)_4}]_2\}^{+}$ ($K_\mathrm{c} \approx 10^{8}$)[8b] exhibits a weak broad band around 3700 nm (2700 cm^{-1}). These data are consistent with a weak band in the 3200 cm^{-1} region for $\{(\mu\text{-bpym})[\mathrm{Ru(NH_3)_4}]_2\}^{5+}$.

The EPR results confirm the above assignment of states: as a predominantly metal-centered mixed-valent species, the 5+ ion remains EPR silent, probably because of rapid relaxation involving close-lying excited states and high spin−orbit coupling contributions from the heavy metal centers.[8] Remarkably, the oxidized mononuclear compound $[(\mathrm{bpym})\mathrm{Ru(NH_3)_4}]^{3+}$ is not EPR silent at 3.5 K but exhibits the typical features of a $\mathrm{Ru^{III}}$ ($4\mathrm{d}^5$) species:[4] $g_1 = 2.920$, $g_2 = 2.527$, $g_3 = 2.050$.

The 3+ state exhibits the expected[4,13] features for a complex between the bpym radical anion and two tetraammineruthenium(II) fragments: The EPR signal is still observable at room temperature and the g components are not too different from the free-electron value of 2.0023. Nevertheless, the g anisotropy is rather large (Figure 4) and the $\langle g \rangle$ value of 1.9785 is lower than that of related species such as $\{(\mu\text{-bpym})[\mathrm{Ru(bpy)_2}]_2\}^{3+}$ ($\langle g \rangle = 1.9890$),[7] $[(\mathrm{bpym})\mathrm{Ru(NH_3)_4}]^{+}$ ($\langle g \rangle = 1.9893$)[4] or $\{(\mu\text{-bpym})[\mathrm{Mo(CO)_4}]_2\}^{-}$ ($\langle g \rangle = 2.0022$),[13] the generally low g values being typical for that particular system.[7,13] Hyperfine contributions could be detected for ruthenium ($A_1 = 0.5$ mT) and hydrogen ($A_2 = 0.70$ mT, assigned to $\mathrm{H}^{5,5'}$); both values are in agreement with the occupation of a predominantly bpym-based orbital by the added single electron.[13,14] In comparison to the case of the mononuclear radical complex $[(\mathrm{bpym})\mathrm{Ru^{II}(NH_3)_4}]^{+}$ ($g_{1,2} = 2.003$, $g_3 = 1.965$),[4] the close-to-axial symmetry is maintained for dinuclear $\{(\mu\text{-bpym})[\mathrm{Ru^{II}(NH_3)_4}]_2\}^{3+}$; however, the g anisotropy measured as $g_1 - g_3$ has doubled from 0.038 to 0.078—reflecting the sizable and nonnegligible contributions from the transition metal to the ligand-based singly occupied MO.

Summarizing, the use of dry aprotic acetonitrile allowed us not only to stabilize the mixed-valent state and discover the IT band in the infrared region but also to observe and study the reduced form, thus indirectly confirming the MLCT character of the lowest excited state of the precursor system. Although the localization/delocalization question could not be decisively answered for the mixed-valent 5+ species, the increased comproportionation constant indicates much stronger Coulombic metal−metal interaction under aprotic conditions.

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