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Evidence for a New Valence-Averaged Mixed-Valence Diruthenium Complex

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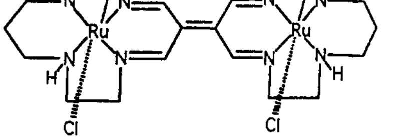
A new diruthenium complex prepared by aerobic oxidative dehydrogenation of *trans*-[Ru(cyclam)Cl_2]Cl (cyclam = 1,4,8,11-tetraazacyclotetradecane) has been investigated. Although the structure has not yet been unequivocally established by X-ray crystal structure analysis, the mass spectral, optical, infrared, and elemental analysis data are consistent with formulation of the new complex as the ruthenium analogue of a diiron complex we recently described.[1] The diruthenium complex isolated after aerobic oxidation of ruthenium(III) cyclam is the (Ru^{2+},Ru^{3+}) mixed- valence species $[Ru_2(C_{20}H_{36}N_8)Cl_4]^+$ (**1**).



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The structure of the related (Fe^{2+},Fe^{2+}) compound $[Fe_2(C_{20}H_{36}N_8)(CH_3CN)_4](ClO_4)_4{\cdot}2CH_3CN$ has been determined by X-ray analysis and has a delocalized π system bridging two tetraaza macrocycles. As a result of this feature, the low-spin diiron(II) complex exhibits an intense near-infrared electronic band[1] (λ_{max} 874 nm, ϵ = 24 600 $M^{-1}cm^{-1}$). The isovalent (Ru^{2+},Ru^{2+}) dinuclear analogue in this study has a very similar spectrum, including an intense low-energy band.

The initial ethanol solution in which the [Ru(cyclam)Cl_2]Cl_3 was prepared[2] was stirred for several days in contact with air. During this time, the solution color changed from yellow to black. The spectrum of this reaction solution contained multiple absorption bands throughout the visible region as well as a near-IR band at 800 nm. Chromatography on a Sephadex LH-20 column with 0.12 M HCl yielded several bands; only a purple band eluting after the [Ru(cyclam)Cl_2]$^+$ starting material had a NIR transition.

The FAB mass spectrum of the solid obtained after solvent evaporation of the purple band gave convincing evidence for **1**. The mass peaks for the ion are centered at *m/z* 732. Ruthenium has five isotopes with abundances greater than 10%, and this leads to a very distinctive isotopic distribution pattern. The computer-simulated pattern for the composition $C_{20}H_{36}N_8Cl_4Ru_2$ is virtually identical to the experimental pattern. This result establishes the dinuclear nature of the species and is consistent with the same degree of unsaturation as in the well-characterized diiron complex.

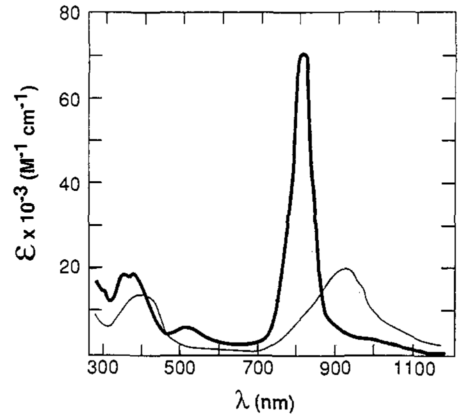

Figure 1. UV–vis spectra of $[Ru_2(C_{20}H_{36}N_8)Cl_4]^+$ (heavy line) and $[Ru_2(C_{20}H_{36}N_8)Cl_4]$ (thin line) in acetonitrile.

The purple species eluted from the column can be precipitated from ethanol by the addition of aqueous KPF_6. This solid can be redissolved in organic solvents and reprecipitated as a chloride salt by addition of tetrabutylammonium chloride. Elemental analyses[3] of these salts were consistent with formulation of the complex as $[Ru_2(C_{20}H_{36}N_8)Cl_4]X$ (X = Cl^- or PF_6^-). The infrared spectrum of the PF_6 salt shows ν_{N-H} at 3212 cm^{-1}, $\nu_{C=N}$ at 1624 cm^{-1}, $\nu_{C=C}$ at 1578 cm^{-1}, and ν_{PF_6} at 843 and 555 cm^{-1}. All but the N–H stretch are absent in the infrared spectrum of *trans*-[Ru(cyclam)Cl_2]Cl. Magnetic susceptibility measurements were made on the chloride salt. The material showed Curie behavior to 5 K and had a magnetic moment of 1.66 μ_B indicating one unpaired electron. The conclusion we draw from these data is that the species obtained from air oxidation of the starting ruthenium(III) cyclam complex is indeed the mixed-valence, formally (Ru^{2+},Ru^{3+}) dinuclear complex.

The cyclic voltammogram of **1** as the PF_6 salt was determined in acetonitrile relative to a Ag/Ag^+ reference electrode. The compound exhibits two reversible waves at +0.27 and +1.19 V. The redox process at +0.27 V is assigned to (Ru^{2+},Ru^{2+}) oxidation to (Ru^{2+},Ru^{3+}), while that at +1.19 V is due to oxidation to the (Ru^{3+},Ru^{3+}) level. Oxygen has the oxidizing capacity to generate the mixed-valence (Ru^{2+},Ru^{3+}) species, which is the one obtained from the synthesis.

The unusual electronic spectrum of the mixed-valence complex is shown in Figure 1. There is a very narrow, intense NIR band that dominates the spectrum. This band has a λ_{max} at 805 nm (12 420 cm^{-1}) with a molar absorbancy coefficient of 68 000 M^{-1} cm^{-1} and a width at half-maximum of 1 100 cm^{-1}. The mixed-valence species can be reduced at 0.0 V to form the (Ru^{2+},Ru^{2+}) compound. This species also exhibits an intense NIR band (Figure 1), (λ_{max} = 910 nm, ϵ = 19 000 M^{-1} cm^{-1}). The corresponding absorption band in the (Fe^{2+},Fe^{2+}) species has been assigned to a particularly low-energy metal-to-ligand charge transfer (MLCT).[1] It seems reasonable to assign the 910-nm band in the (Ru^{2+},Ru^{2+}) analogue as a MLCT as well.

The very narrow, much more intense 805-nm band in the mixed-valence compound is tentatively assigned as a transition from a delocalized ($Ru^{2.5+}$,$Ru^{2.5+}$) ground state to an excited state.[4] Class II[5] or intermediate-coupled mixed-valence compounds frequently exhibit a new electronic transition not seen in the lower or higher isovalent forms. This intervalence-transfer (IT) or light-induced metal-to-metal charge-transfer band frequently occurs in the long-wavelength visible or the near-infrared spectral regions. Class III or valence-averaged compounds should also undergo light

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(3) Anal. Calcd for $[Ru_2(C_{20}H_{36}N_8)Cl_4]PF_6$: C, 27.37; H, 4.14; N, 12.77. Found: C, 27.01; H, 4.19; N, 11.95. Calcd for $[Ru_2(C_{20}H_{36}N_8)Cl_4]Cl$: Ru, 26.32; Cl, 23.08. Found: Ru, 27.25; Cl, 21.54.

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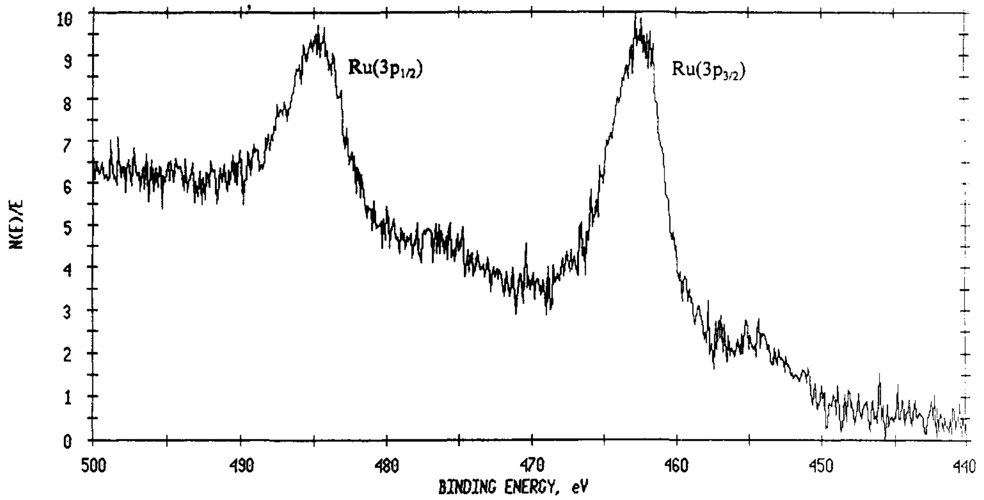

Figure 2. XPS spectrum of $[Ru_2(C_{20}H_{36}N_8)Cl_4]PF_6$. Sample prepared by evaporation of 10^{-4} M solution in acetonitrile.

absorption by virtue of their mixed-valence nature. The odd electron, though, is completely delocalized on all time scales, and the electronic transition is not properly called an IT band. The position of the mixed-valence band for a class III ion is related to the degree of electronic coupling, H_{AB}, between the metals according to the widely used Hush model.[6] The value of H_{AB} for **1** is 6200 cm^{-1} ($H_{AB} = 1/(2\lambda_{max})$). This large value is consistent with a class III compound. Furthermore, recent work[7] indicates that the Hush formalism underestimates H_{AB} in strongly coupled systems. The energy of the mixed-valence band of **1** shows essentially no solvent dependence (solvents CH_3CN, water, and ethanol). This again is consistent[4] with designation of the mixed-valence complex as a valence-averaged, Robin and Day[5] class (III) species.

The electrochemical parameters also support assignment of the mixed-valence compound as valence-averaged ($Ru^{2.5+}$,$Ru^{2.5+}$). The large 920-mV difference in the potentials for formation of the mixed-valence and isovalent (Ru^{3+},Ru^{3+}) species corresponds to a comproportionation constant of 3.5×10^{15}:

$$K_{com}\quad (Ru^{2+},Ru^{2+}) + (Ru^{3+},Ru^{3+}) \rightleftarrows 2(Ru^{2+},Ru^{3+})$$

This indicates a great deal of resonance stabilization of the mixed-valence form. This K_{com} value is the largest we are aware of in mixed-valence transition-metal literature and is indicative of a delocalized ground state.[4]

The most direct evidence for complete delocalization of the ground state comes from X-ray photoelectron spectroscopy. Data were obtained with a Perkin-Elmer PHI 5300 using Mg Kα radiation. High-resolution data were taken in the 275–290 and 440–500-eV binding energy regions. Peaks occur in the lower energy region due to ruthenium (Ru $3d_{3/2}$ and Ru $3d_{5/2}$) and to carbon (C 1s) electron transitions. At the higher energy region, the peaks are due to ruthenium alone (Ru $3p_{1/2}$ and Ru $3p_{3/2}$).

A class II (localized ground state) mixed-valence species will clearly exhibit two metal core level photopeaks of equal integrated intensity on the very short time scale (10^{-17} s) of the XPS experiment. These peaks would correspond to the Ru^{2+} and Ru^{3+} ions. However, models proposed by Hush[8] and Citrin and Ginsburg[9] predict this same "doublet" photoemission spectrum from a delocalized (class III) ground state if the metals are only weakly coupled. This is due to the high polarizability of the valence orbital in such complexes. Under the influence of a core hole, the valence orbital is predicted to relax strongly and the system becomes localized. There are then two photoionized states, a lower energy state in which the unpaired valence orbital electron is localized on the photoionized ruthenium and a higher energy state in which the valence electron is on the other center. This is the case for the Creutz–Taube mixed-valence ion, $[(H_3N)_5Ru(pyrazine)Ru(NH_3)_5]^{5+}$. The Creutz–Taube ion has been widely studied, and the preponderance of evidence indicates that it is a class III species.[9] However, its XPS spectrum still has doublet ruthenium photopeaks with 1:1 integrated intensity and binding energies close to those of the isovalent (Ru^{2+},Ru^{2+}) and (Ru^{3+},Ru^{3+}) compounds. Therefore, as has been pointed out,[10] if a doublet spectrum is observed, XPS cannot distinguish between a class II complex and a mixed-valence dimer with a delocalized ground state and relatively weak metal-to-metal interactions. However, if the spectrum is *not* split but shows just a single line for each transition, then that is unambiguous evidence for one kind of ruthenium, in this case designated as $Ru^{2.5+}$.

The XPS spectrum of **1** in the 500–440-eV region is shown in Figure 2. The two photopeaks corresponding to the ruthenium $3p_{1/2}$ and $3p_{3/2}$ spin–orbit components are shown. (The $3d_{3/2}$ and $3d_{5/2}$ peaks are partially obscured by the large C 1s photopeak.) The important point is that each is a single peak indicating only one oxidation level for ruthenium. This result clearly indicates that the ground state of **1** is strongly coupled and delocalized on all accessible time scales.

In a previous paper, Citrin and Ginsburg[9] noted that sample preparation was important in obtaining correct experimental results with the Creutz–Taube ion. Accordingly, we used two independent preparations of **1** and two different methods of mounting the sample. One was evaporation of an acetonitrile solution (10^{-4} M, PF_6 salt) onto a precleaned silicon wafer, and the other was pressing a solid sample onto double-sided tape. In all cases only single peaks were observed. Likewise, sample degradation through radiation damage is a concern. Survey scans done before and after long-term data acquisition indicated no significant change.

We are currently attempting to grow X-ray quality crystals of **1**. Also, we are examining the effects of changing the axial ligands on the spectral and redox properties.

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