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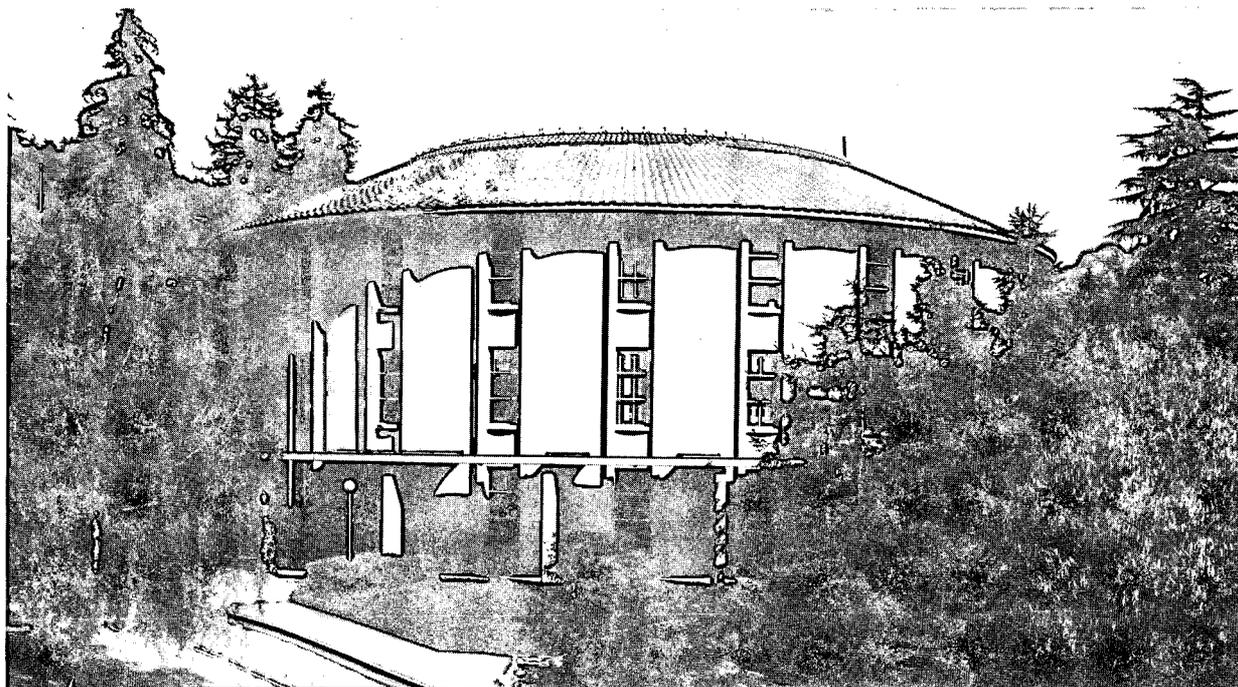
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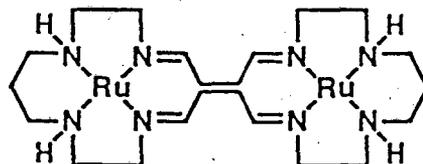
Evidence for a New Valence-Averaged Mixed-Valence Di-ruthenium Complex

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Summary: A new mixed-valence $[\text{Ru}_2(\text{C}_{20}\text{H}_{36}\text{N}_8)\text{Cl}_4]^+$ species has been prepared which exhibits a narrow, intense NIR band ($\lambda_{\text{max}} = 805 \text{ nm}$, $\epsilon = 68,000 \text{ M}^{-1} \text{ cm}^{-1}$), and has a 920 mV separation between successive oxidations to the $(\text{Ru}^{2+}, \text{Ru}^{3+})$ levels.

A new di-ruthenium complex prepared by aerobic oxidative dehydrogenation of $\text{trans}[\text{Ru}(\text{cyclam})\text{Cl}_2]\text{Cl}$ cyclam = 1,4,8,11-tetrazacyclotetradecane has been investigated. Although the structure has not yet been unequivocally established by X-ray crystal structure analysis, mass spectral, optical, infrared and elemental analysis data are consistent with formulation of the new complex as the ruthenium analogue of a di-iron complex we recently described.¹ The di-ruthenium complex isolated after aerobic oxidation of ruthenium(III)cyclam is the $(\text{Ru}^{2+}, \text{Ru}^{3+})$ mixed valence



1 (Each Ru has two Cl axial ligands)

species, $[\text{Ru}_2(\text{C}_{20}\text{H}_{36}\text{N}_8)\text{Cl}_4]^+$. This species has a delocalized π system bridging two tetraaza-macrocycles, and as a result of this feature, the low-spin di-iron(II) complex exhibits an intense near-infrared electronic band ¹ (λ max = 874nm, ϵ = 24,000 $\text{M}^{-1}\text{cm}^{-1}$). The mixed-valence (Ru^{2+} , Ru^{3+}) and isoalent (Ru^{2+} , Ru^{2+}) dinuclear analogues have similar intense low-energy spectral features.

The initial ethanol solution in which the $[\text{Ru}(\text{cyclam})\text{Cl}_2]\text{Cl}_3$ was prepared² 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 as well as a NIR band at 800 nm. Chromatography on a Sephadex LH-20 column yielded several bands; only a purple band eluting after the $[\text{Ru}(\text{cyclam})\text{Cl}_2]^+$ 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 732.2. 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 $\text{C}_{20}\text{H}_{36}\text{N}_8\text{Cl}_4\text{Ru}_2$ (mass = 732.0) is virtually identical to the experimental pattern. This result establishes the di-nuclear nature of the species and is consistent with the same degree of unsaturation as in the well-characterized di-iron complex.

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

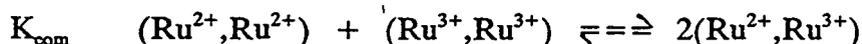
and reprecipitated as a chloride salt by addition of tetrabutylammonium chloride. Elemental analysis³ of these salts were consistent with formulation of the complex as $[\text{Ru}_2(\text{C}_{20}\text{H}_{36}\text{N}_8)\text{Cl}_4]\text{X}$ ($\text{X} = \text{Cl}^-$ or PF_6^-). The infrared spectrum of the PF_6^- salt shows $\nu_{\text{N-H}}$ at 3212 cm^{-1} , $\nu_{\text{C=N}}$ at 1624 cm^{-1} , $\nu_{\text{C=C}}$ at 1578 cm^{-1} , and ν_{PF_6} at 843 cm^{-1} and 555 cm^{-1} . All but the N-H stretch are absent in the infrared spectrum of $t - [\text{Ru}(\text{cyclam})\text{Cl}_2]\text{Cl}$. Magnetic susceptibility measurements were made on the chloride salt. The material showed Curie behavior to 5 K and had a magnetic moment of $1.66\ \beta\text{M}$ 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 $(\text{Ru}^{2+}, \text{Ru}^{3+})$ 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 $+0.27\text{ V}$ and $+1.19\text{ V}$. The redox process at $+0.27\text{ V}$ is assigned to $(\text{Ru}^{2+}, \text{Ru}^{2+})$ oxidation to $(\text{Ru}^{2+}, \text{Ru}^{3+})$, while that at $+1.19\text{ V}$ is due to oxidation to the $(\text{Ru}^{3+}, \text{Ru}^{3+})$ level. Oxygen has the oxidizing capacity to generate the mixed-valence $(\text{Ru}^{2+}, \text{Ru}^{3+})$ 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 ($12,420\text{ cm}^{-1}$) with a molar absorptivity coefficient of $68,000\text{ M}^{-1}\text{ cm}^{-1}$ and a width at half-maximum of $1,100\text{ cm}^{-1}$. The mixed-valence

species can be reduced at 0.0 V to form the (Ru²⁺,Ru²⁺) compound. This species also exhibits an intense NIR band (Fig. 1), ($\lambda_{\max} = 910 \text{ nm}$, $\epsilon = 19,000 \text{ M}^{-1} \text{ cm}^{-1}$). The corresponding absorption band in the (Fe²⁺,Fe²⁺) species has been assigned to a particularly low-energy metal to ligand charge transfer (MLCT)¹. It seems reasonable to also assign the 910 nm band in the (Ru²⁺,Ru²⁺) analogue as an MLCT. 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 The energy of this band shows essentially no solvent dependence (solvents CH₃CN, water, ethanol). This is consistent⁴ with designation of the mixed-valence complex as a valence-averaged, Robin and Day⁵ 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 iso-valent (Ru³⁺,Ru³⁺) species leads to a comproportionation constant of 3.5×10^{15} .



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 Further characterization of this interesting new di-ruthenium complex is underway.

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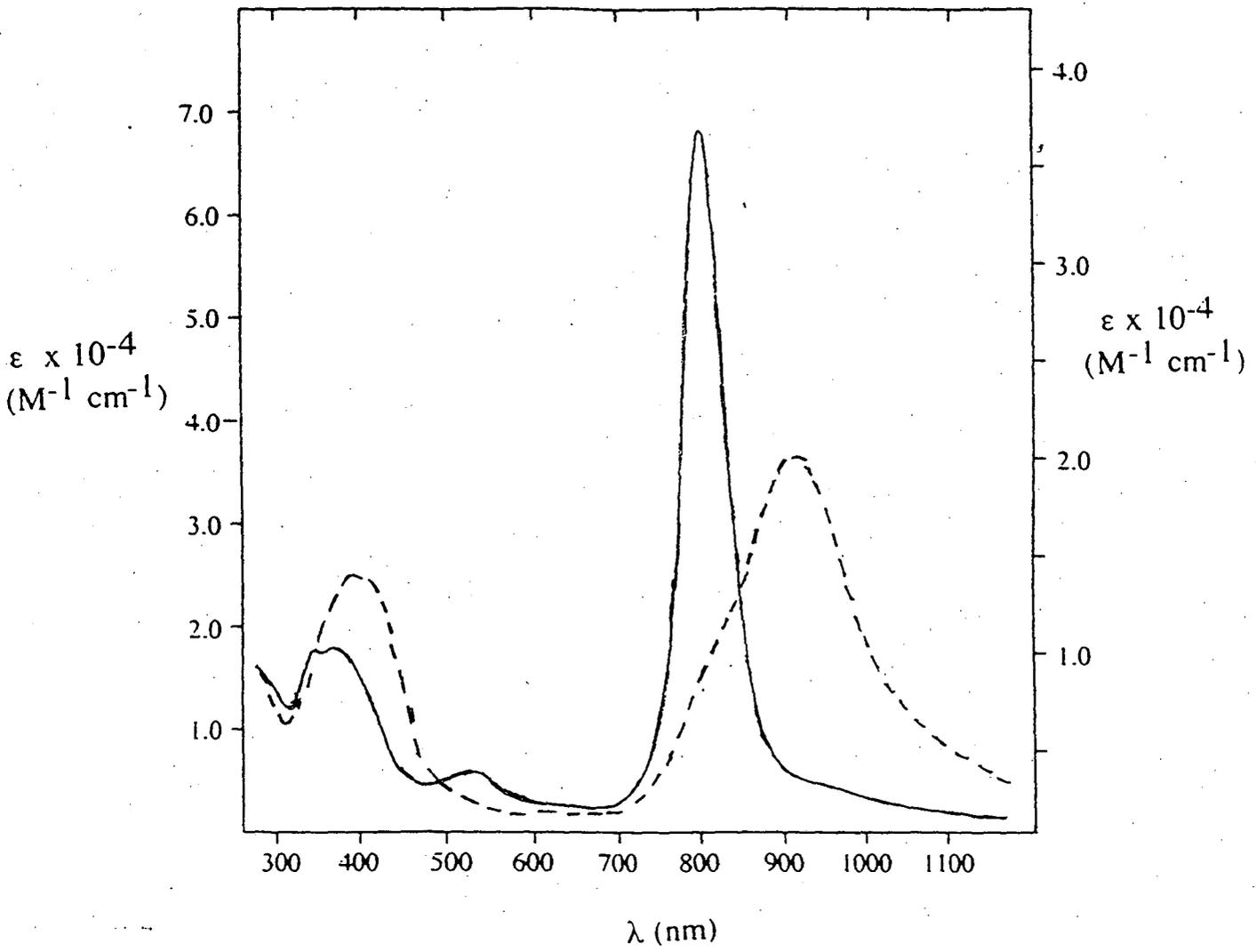
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Figure Caption

Figure 1. Electronic Spectra: — ($\text{Ru}^{2+}, \text{Ru}^{3+}$), left axis; ---- ($\text{Ru}^{2+}, \text{Ru}^{2+}$), right axis.



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