$$(E_{i+1} - E_0)_{i=2,3} = (E_2 - E_0) + \epsilon(\pi i^*) - \epsilon(\pi 1^*) \tag{10}$$

where $\epsilon(\pi i^*)$ is the energy of the πi^* MO of pyrazine, given by the Pariser-Parr-Pople calculation.

The $\pi 1 \rightarrow \mathrm{Ru^{III}}$ CT excitation is forbidden and is not observed in the mixed-valence ion; consequently, to estimate of the energy of $\pi i \rightarrow \mathrm{Ru^{III}}$ charge transfer we have to resort to an MO calculation on a hypothetical $\mathrm{Ru^{III}}$-pyr ion.[6] Combining all these sources of information yields the following estimates for the energies of the various excited configurations: $(E_1 - E_0) = 6.4$ kK, $(E_2 - E_0) = 17.7$ kK, $(E_3 - E_0) = {\sim}25$ kK, $(E_4 - E_0) = {\sim}45$ kK, $(E_5 - E_0) = {\sim}32.5$ kK, $(E_6 - E_0) = {\sim}60.0$ kK, $(E_7 - E_0) = {\sim}70.0$ kK. We now have all the information needed to evaluate eq 7 and 8 and thus obtain the valence delocalization parameters. The resulting values are $\gamma_1 - 0.145$ and $\gamma_0' + 0.22$.

A final point concerns the distribution of the hole in the d_{xy}, d_{xz}, and d_{yz} orbitals of $\mathrm{Ru^{III}}$, which depends on a balance between spin-orbit coupling and tetragonal distortion of the ligand field.

The hole distribution between d(0) and d(1,−1) is given by coefficients $c(0)$ and $c(1,-1)$ derived by solving a secular determinant containing the spin-orbit coupling constant of the metal and the energy difference δ between the configurations in which the hole occupies d(0) or d(1,−1) (d_{yz} and $d_{xy,xz}$ in the present case). Since NH_3 contains no π MO's, d_{xy} and d_{xz} are nonbonding, and the energy separation between d_{yz} and (d_{xy}, d_{xz}) depends only upon interactions involving the π, π^* MO's of pyrazine. The quantity δ then approximately equals the stabilization energy of the complex (when the hole is located entirely in the Ru-pyr π system) due to the $\mathrm{Ru^{II}}(d_{yz}) \rightarrow \mathrm{Ru^{III}}(d_{yz})$, $\pi \rightarrow \mathrm{Ru^{III}}(d_{yz})$ CT interaction and is given by

$$-\delta = \gamma_1^2(E_1 - E_0) + \sum_{i=1,3} \frac{C_{12}^2\beta^2(\mathrm{Ru^{III}\text{-}N})}{(E_{i+4} - E_0)} \tag{11}$$

If we take the spin-orbit coupling constant of $\mathrm{Ru^{III}}$ as 1180 $\mathrm{cm^{-1}}$ [9] and use eq 11 to estimate δ, the coefficient of the hole in d_{yz}, $c(0)$ is 0.693. Including this correction, the true valence delocalization coefficients[5] α_1 and α_0' are then −0.10 and +0.15. Our conclusion is therefore that the hole in $\mathrm{Ru^{III}}$ is delocalized onto the $\mathrm{Ru^{II}}$ in the ground state by approximately 1%.

It is worth noting that our estimate of α_1 by the perturbation method gives a value well within the range $\alpha < {}^1/_4$ required by our criterion[4] for valence trapping and class II behavior in a mixed-valence dimer with identical ligands around each site. Unfortunately, a direct test of the estimated value for α_1 is not easy. Such properties as transferred hyperfine interactions would be relevant, but the Ru Mossbauer spectrum[2] is not sufficiently resolved to yield the necessary data. There remains the intensity of the mixed-valence charge-transfer transition. The transition moment of the $\mathrm{Ru^{II}} \rightarrow \mathrm{Ru^{III}}$ excitation is given by

$$\mu(\Psi_G \rightarrow \Psi_{E1}) = (1/2)(\alpha_1 - \alpha_0')R(\mathrm{Ru^{II}\text{-}Ru^{III}})$$

Taking the $\mathrm{Ru^{II}}$-$\mathrm{Ru^{III}}$ distance R as about 6.9 Å yields $\mu = 0.81$ e Å, which agrees very nicely with our estimate from the experimental data of ref 1 of about 0.9-1.0 e Å.

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Registry No. $[(NH_3)_5Ru(pyrazine)Ru(NH_3)_5]^{5+}$, 35599-57-6.

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Contribution No. 13996 from the Division of Chemistry,
National Research Council of Canada, Ottawa, Canada

Resonance Raman Spectra of a Complex Containing the Rhenium-Iron Bond

S. Sunder[1] and H. J. Bernstein*

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Bennet, *et al.*,[2] have synthesized a novel complex, shown in Figure 1A, of the formula $(CO)_2Rh{\cdot}C_7H_7{\cdot}Fe(CO)_3$. The Rh-Fe distance of 2.76 Å indicates the presence of a metal-metal bond.[2,3] This note reports the resonance Raman spectrum of this complex. The compound is dark brown and it is difficult to obtain its conventional Raman spectrum.[4] The absorption spectrum of this compound is shown in Figure 1. There is a strong maximum at about 4400 Å which has a tail covering the whole visible region.

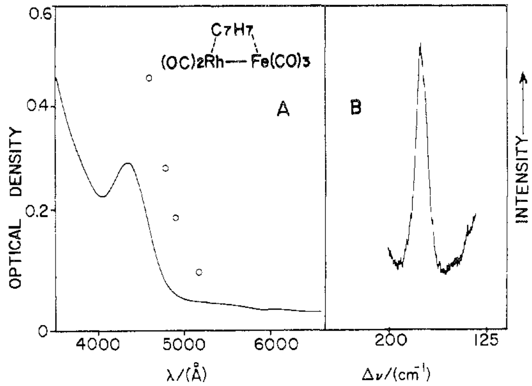

Figure 1. (A) Absorption spectra of a 4.3×10^{-4} *M* solution of $(CO)_2Rh{\cdot}C_7H_7{\cdot}Fe(CO)_3$ (path length 0.2 cm); relative intensity of the Raman band with different exciting radiations is indicated by circles. (B) Raman band observed using the 4880-Å laser line (resolution 4 $\mathrm{cm^{-1}}$).

The absorption spectrum was recorded with a Cary 14 spectrophotometer. Raman spectra were recorded using a Spex 1400 monochromator and an Ar^+ ion laser. The solutions of the complex were prepared in $CHCl_3$ under an atmosphere of dry N_2. The Raman spectra were recorded using a spinning-sample cell.[5] The ν_4 band of chloroform[6] was used as an internal reference to study the intensity of the band due to the complex as a function of the frequency of the exciting radiation.

The Raman spectrum of the solution of the complex showed a band at 172 ± 2 $\mathrm{cm^{-1}}$ in addition to the bands due to the solvent. The band is strongly polarized and is shown in Figure 1 as obtained from a 10^{-3} *M* solution of the complex with the 4880-Å line of the Ar^+ laser. Three other lines in the Ar^+ laser at 4579, 4765, and 5145 Å were also used and the dependence of the intensity of the band on the exciting frequency is also shown in Figure 1.

The band is polarized ($\rho \approx 0.1$ with 4880 Å) and can be assigned to the Rh-Fe stretching vibration giving a value of

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0.63 mdyn/Å for the Rh–Fe bond force constant, if one ignores the presence of all other atoms. On the other hand, the force constant will have a value of 1.3 mdyn/Å if one considers it as a diatomic molecule with two atoms of atomic weights equal to those of the $Rh(CO)_2$ and $Fe(CO)_3$ moieties but ignores the effect of C_7H_7 ligand. The first value of the force constant so obtained is close to that reported for the Mn–Mn bond while the second value is closer to that reported for the Fe–Fe bond in similar compounds.[4] The intensity of the Raman band increases upon moving into the regions of higher absorption (Figure 1). The band observed with the 4579-Å line is 7 times stronger than that observed with the 5145-Å line. This is in agreement with the current literature on resonance Raman spectra.[7]

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Contribution from the Department of Inorganic and Analytical Chemistry, The Hebrew University of Jerusalem, Jerusalem, Israel

The Binuclear Molybdenum(III)-Aquo Ion

Michael Ardon* and Arnold Pernick

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Reduction of acid solutions of molybdenum(VI) by a cadmium reductor or a Jones reductor produces green solutions of molybdenum(III).[1] Similar green solutions are produced by electrolytic reduction of Mo(VI) in HCl (2–4 *M*).[2] Forster and Fricke[3] attributed the green color to a hexaaquomolybdenum(III) ion. Wardlaw and coworkers[4] belived that the main species in these solutions were $MoO(H_2O)_5^+$ and $MoO(H_2O)_4Cl$. Hartmann and Schmidt[2] measured the absorption spectra of the green solutions of molybdenum(III) in HCl, HBr, and H_2SO_4 and reported similar spectra for these three acids. The authors concluded from this similarity that the three solvents contained one and the same species, namely, a green hexaaquo ion $Mo(H_2O)_6^{3+}$. Bowen and Taube[5] investigated the products of the aquation of the hexachloromolybdenum(III) ion in the noncomplexing acid solutions of *p*-toluenesulfonic acid (HPTS) and trifluoromethylsulfonic acid. They separated the aquation products by ion-exchange chromatography and identified a pale yellow tripositive ion as $Mo(H_2O)_6^{3+}$. These results were confirmed by other investigators[6-8] and could not be reconciled with Hartmann's assignment of a hexaaquo structure to the green Mo(III) species, since existence of two isomeric hexaaquomolybdenum(III) ions was ruled out. It was also pointed out[5] that the strong absorption of the green species at 600 nm was incompatible with a $Mo(H_2O)_6^{3+}$ structure in view of the position of Mo in the second row of the transition elements. Bowen and Taube[5] concluded that the green species was a condensation product of Mo(III). A di-*μ*-oxo structure was recently proposed[9] for the green Mo^{III}-EDTA complex $[Mo_2O_2EDTA(H_2O)_4]^{2-}$. Haight and Boston[10] suggested that the related structure $Mo_2O_2^{2+}$ could be attributed to Hartmann's green species. The present investigation was undertaken in order to identify this green molybdenum(III) species.

Experimental Section

Materials. "Baker Analyzed" Na_2MoO_4 and Fluka HPTS were used. BioRad Dowex 50-X2 cation-exchange resin was used both for ion-exchange columns and for batch equilibration experiments. All ion-exchange separations and batch experiments were conducted under nitrogen at ~2°. All Mo(III) solutions prepared by reduction of Mo(VI) in HPTS were 0.01 *M* in Mo and 1 *M* in acid. Mo(III) preparations in other acids were 0.01 *M* in Mo and in acid concentrations as specified.

Analytical Work. The oxidation number of the blue-green ion was determined as follows. Aliquots of the green species eluted from the ion-exchange column were discharged into excess Fe(III) before and after reduction with a Jones reductor (to Mo(III)) and the Fe(II) resulting from oxidation of Mo to Mo(VI) was titrated with $KMnO_4$. Analyses of samples that were rereduced gave identical titer with those of the original green solution, thus confirming the oxidation state of +3 for this ion. The oxidation state did not change in solutions kept for 1 week under nitrogen. $KMnO_4$ titrations of solutions containing HPTS were conducted at 0°. Under these conditions, no oxidation of HPTS occurred. In the ion-exchange batch experiments, Mo(III) was analyzed spectrophotometrically at 624 nm or 360 nm. A Cary 14 spectrophotometer was used for all spectral measurements. An Alpha Scientific magnetic susceptibility instrument with a Model 6000 electromagnet was used for the magnetic measurements.

Results and Discussion

Preliminary experiments indicated that the green Mo(III) solutions in hydrochloric and sulfuric acids contained a mixture of molybdenum(III) species, whereas the solution obtained by reduction of Mo(VI) in HPTS contained a single Mo(III) species. A solution of 0.01 *M* Mo(III) in 1 *M* HPTS, prepared by a Jones reductor, was diluted with water and absorbed on a cooled Dowex 50-X2 cation-exchange column. All operations following the reduction were carried out under nitrogen. A sharp blue-green band was absorbed on the column and could not be eluted with 2 *M* HPTS but could be slowly eluted with 3 *M* HPTS, indicating an ionic charge of 4+. The absorption spectrum (Figure 1) had three maxima at 360 nm (ϵ 306), at 572 nm (ϵ 39), and at 624 nm (ϵ 43). Identical results were obtained when a cadmium reductor was used instead of the Jones reductor.

Charge Per Molybdenum Atom. A solution of 0.01 *M* Mo(III) in 1 *M* HPTS was diluted with water and absorbed on the cation-exchange column. Elution with 1 *M* HPTS removed the Zn^{2+} ion (introduced by the Jones reductor), and the blue-green band was eluted with 3 *M* HPTS. This fraction was diluted with water and reabsorbed on a small cation-exchange column until all the H^+ ions were replaced by molybdenum ions. The absorbed molybdenum was eluted with acid and the number of millimoles of molybdenum in the eluent was determined. The capacity of the column was determined by elution of the acid form with

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