Figure 1. Structure, labeling scheme, and selected interatomic distances of $[Fe(C_{10}H_{19}N_8)(CO)(CH_3)]$.

F's $\geq 2\sigma$. All of the hydrogen atoms were located on a difference Fourier and then their positions were recalculated assuming normal geometry and a C–H distance of 0.95 Å. These were then included, but at fixed positions, in the final refinement. See paragraph at the end of the paper regarding supplementary material.

The structure consists of six-coordinate iron(II) coordinated to a macrocyclic ligand, a molecule of carbon monoxide, and a methyl group (Figure 1). The $CH_3FeC\equiv O$ axis is constrained to lie on the intersection of two perpendicular crystallographic mirror planes.[13]

The most significant aspect of the structure is that the Fe^{II}–CH_3 distance, 2.077 (5) Å, is markedly longer than might be predicted on the basis of known Co^{III}–C distances and the Fe–C distance, 1.933 (3) Å, of an iron(III)–aryl complex.[2] A similar lengthening of metal–carbon distance can be expected to occur on the interaction of carbon monoxide with alkyl corrins and could easily account for increased ease of cobalt–carbon bond rupture. The observed bond lengthening must be attributed to the weakening produced by the overriding trans effect of carbon monoxide. The remaining interatomic distances are normal. The Fe(II)–N distances, 1.900 (2) Å, are shorter than observed for most low-spin Fe(II)–N distances but are comparable to those found in the bisimidazole–bis(DMG) complex of Fe(II),[14] which also has "pure" α-diimine chelate moieties. The Fe(II) is displaced slightly, 0.187 Å, toward the carbon monoxide molecule from the least-square plane of the four nitrogen atoms.

Supplementary Material Available. A listing of atomic coordinates and structure factor amplitudes will appear following these pages in the microfilm edition of this volume of the journal. Photocopies of the supplementary material from this paper only or microfiche (105 × 148 mm, 24× reduction, negatives) containing all of the supplementary material for the papers in this issue may be obtained from the Journals Department, American Chemical Society, 1155 16th St., N.W., Washington, D. C. 20036. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche, referring to code number JACS-74-7826.

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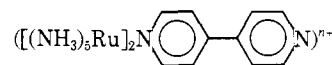
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Mixed Valence Complexes of Ruthenium Ammines with 4,4'-Bipyridine as Bridging Ligand

Sir:

Previous work on the complexes

$$([(NH_3)_5Ru]_2N\!\!-\!\!\bigcirc\!\!-\!\!\bigcirc\!\!-\!\!N)^{n+}$$

(n = 4, 5, and 6 to be denoted [2,2], [2,3], and [3,3] respectively) gave contradictory spectral and electrochemical results.[1-4] There did, however, seem to be agreement on the point that the stability of the mixed valence state when 4,4'-bipyridine bridges the ruthenium atoms is much less than for pyrazine as the bridging group.[5,6] In view of the current interest[7] in mixed valence complexes and of the fact that the nature of the ion

$$([(NH_3)_5Ru]_2N\!\!\bigcirc\!\!N)^{5+}$$
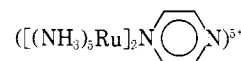
is not yet understood, we felt it worthwhile to investigate the 4,4'-bipyridine system further in the hope of illuminating the subject of mixed valence complexes.

The [2,2] species was formed by the reaction in acetone under argon of $(NH_3)_5RuOH_2(PF_6)_2$ and 4,4'-bipyridyl in 2:1 molar ratio. After 2 hr in the dark, the [2,2] complex

$$[(NH_3)_5RuN\!\!-\!\!\bigcirc\!\!-\!\!\bigcirc\!\!-\!\!NRu(NH_3)_5](C_7H_7SO_3)_6\cdot H_2O$$

I
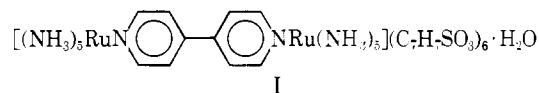
was precipitated by the addition of two volumes of ether. Oxidation of the [2,2] ion with Br_2 in 0.1 M HCl was followed by precipitation of the tosylate salt of the [3,3] ion. *Anal.* Calcd for **I**: C, 40.2; H, 4.1; N, 10.8; Ru, 13.0. Found: C, 37.9; H, 4.96; N, 10.4; Ru, 12.3.[8] The [3,3] perchlorate salt was formed by dissolving the tosylate complex in H_2O, passing the solution through Bio Rad AG1X2 resin in the perchlorate form, and evaporating to dryness.

Creutz[1] and Lavallee and Fleischer[2] had reported band maxima of the [2,2] ion in the visible at 513 and 542 nm, respectively. We observed λ_{max} for the [2,2] ion at 521 nm but noted that when the [2,2] complex is left in the presence of a strong reducing agent (*e.g.*, Eu^{2+}, Cr^{2+}, Zn(Hg)) for hours, λ_{max} shifts from 521 nm to shorter wavelengths with a decrease in intensity. The product is presumably the binu-
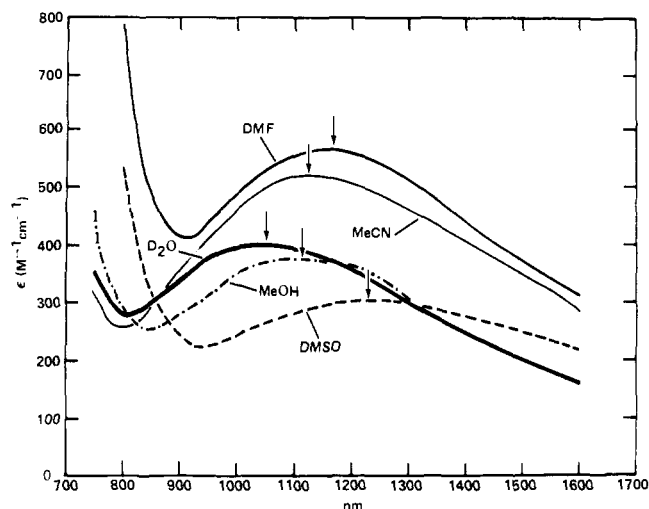
Figure 1. The near-infrared band for the [2+,3+] species in various solvents. Molar extinction coefficients are calculated assuming that, when equal amounts of [2+,2+] and [3+,3+] are mixed, half of the material is present as [2+,3+].

clear ion with one of the rings reduced. In accord with observations made with substituted pyridine Ru(II) ammines, the band is expected to be at higher energy when the assumed reduction takes place.

The discrepancy with the spectrophotometric results of Lavallee, et al., is not real. Their paper contains a typographical error: 542 nm should read 524 nm and the revised result is in satisfactory agreement with ours.

On titrating a solution containing [3,3] with $(NH_3)_5RuOH_2^{2+}$, no shift in the visible band occurs during the titration, though the intensity does increase on reduction (the [3,3] complex has zero absorption at 521 nm). Results to be described presently show that the [2,3] complex is formed and one must, therefore, conclude that its absorption maximum coincides with that of the [2,2] form.

Cyclic voltammetry measurements in 0.1 F HCl on a platinum button electrode show a single wave centered at 0.35 V $vs.$ nhe with a peak separation of 114 mV. Graphic superposition of cyclic voltammetry waves of

$$(NH_3)_5RuN \underset{\text{}}{\bigcirc} \overset{O}{\underset{NH_2}{\diagup}}$$
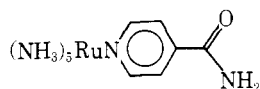
separated by between 35 and 75 mV[9] gave an acceptable facsimile of the cyclic voltammogram of the [3,3] complex. The difference in formal potentials implies that significant concentrations of the [2,3] species are in equilibrium with the [2,2] and [3,3] complexes and lead to a value of the equilibrium constant of reaction 1 close to the statistical value of 4 with an upper limit of 20.

$$[2,2] + [3,3] \overset{K}{=} 2[2,3] \tag{1}$$
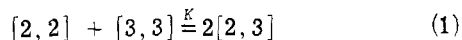
Fleischer and Lavallee[3] concluded from their cyclic voltammetry results that [3,3] is reduced to [2,2] directly and reversibly. We consider this part of their work to be faulty on two counts. For a reversible two electron reduction, a peak to peak separation in cyclic voltammetry of about 30 mV is expected[10] and not the value of 60 mV reported by them. Secondly, the measuring indicator electrode used by them is not suitable for this system because mercury oxidizes at the potentials characteristic of the system under investigation.

On titrating the [3,3] tosylate salt in D_2O–0.1 M DCl with $(NH_3)_5RuOH_2^{2+}$ a band appeared at 930 nm which reached a maximum absorbance at 1 equiv of reducing

agent per binuclear complex (cf. Figure 1). With further reduction, the band dropped in intensity and the maximum shifted to higher energy. We attribute the latter effect to the mixing of the tail of the visible band with the NIR transition. The NIR absorption was observed by Creutz[1,11] and was attributed to the

$$[2,3] \xrightarrow{h\nu} [3,2]^*$$
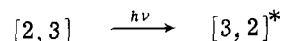
intervalence transition.[12] Lavallee and Fleischer[3] did not find the absorption, a fact which we are unable to explain.

The solvent dependence of the intervalence band maximum was investigated. The [2,3] complex was generated in the following manner. A known amount of the [3,3] complex with the appropriate anion was dissolved in the solvent; 1.5 ml of the [3,3] solution was reduced over Zn(Hg) and 1.5 ml was degassed with argon for 10 min; the two solutions were mixed, and the NIR region was examined.[13] Unless the value of K for reaction 1 is strongly solvent dependent, in none of the systems is the formation of the [2,3] species complete. The considerations based on the band maxima are independent of this feature, and it should also be noted that the apparent extinction coefficients in the different solvents at the NIR maximum did not vary widely.

Hush's theory[12] for the effect of solvent on the intervalence transition leads to eq 2, where E_{outer} is the outer

$$E_{outer} = \left(\frac{1}{a_{III}} + \frac{1}{a_{II}} - \frac{1}{d}\right) e^2 \left(\frac{1}{n^2} - \frac{1}{D}\right) \tag{2}$$

sphere Franck–Condon activation energy, a_{III} and a_{II} are the diameter of dielectric saturation of the Ru(III) and Ru(II) centers, d is the distance between the Ru centers, e is the electronic charge, n is the refractive index, and D is the static dielectric constant.

A plot of the energy of the NIR transition in D_2O, methanol, acetonitrile, N,N-dimethylformamide, dimethyl sulfoxide, and acetone $vs.$ $(1/n^2 - 1/D)$ gives a straight line with an intercept 3.5 kK. The intercept is interpreted[12] as the Franck–Condon inner sphere optical activation energy. The difference between the energy of the transition and the intercept is E_{outer}. For D_2O the calculated solvent activation energy using Laidler's[14] values for dielectric saturation and eq 2 is 7.6 kK and the observed value is 6.1 kK.

The band width in the high temperature limit is given by Hush[12] as: $\bar{\nu} = (\Delta\bar{\nu}_{1/2})^2/2310$ where ν is the band maximum and $\bar{\nu}^{1/2}$ is the band width at half height (both in cm^{-1}). The calculated band width is 4.8 kK while the observed is 7.3 kK. The behavior is different from the pyrazine case where the band width is too narrow by a factor of about 2. The oscillator strengths for the NIR transition, however, are comparable: 4,4'-bipyridine (2.7 × 10^{-2}) and pyrazine (3.5 × 10^{-2}), the former calculated assuming K for reaction 1 to be 4. The mixing coefficient, however, is smaller in the 4,4'-bipyridine case due to the greater distance between the ruthenium centers.

Experiments in which the derivatives substituted symmetrically by isonicotinamide at the cis and trans positions were used show slight shifts in the band maxima to longer wavelength but do not show a diminished intensity. Thus they do not help to explain why in the systems reported by Adeyemi, et al.,[15] the NIR band is not observed.

Though the present results to not explain some of the puzzling features of the pyrazine-bridged ion, they are reassuring on the point that in the present system, with weak coupling, many of the features are understood on the basis of Hush's theories.[16] The conclusion that coupling is weak rests on two lines of evidence. Firstly, the equilibrium constant for reaction 1 is close to the statistical value (contrast this with the pyrazine-bridged case where the equilibrium

constant is *ca.* 10^6). Secondly, the πd–π^* transition except for the matter of intensity for [2,3] is so like that of the [2,2].

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Intervalence Transfer in Unsymmetrical, Ligand-Bridged Dimeric Complexes of Ruthenium

Sir:

The properties of the mixed-valence ions, $[(NH_3)_5Ru(pyz)Ru(NH_3)_5]^{5+}$ and $[(bipy)_2ClRu(pyz)RuCl(bipy)_2]^{3+}$ (pyz is pyrazine; bipy is 2,2'-bipyridine).[1-4] are consistent with the presence of discrete ruthenium(II) and ruthenium(III) sites. For the pentaammine mixed-valence dimer, an intense, near-infrared band has been found which has been assigned to an intervalence transfer (IT) transition.[1,2] However, the half-width and solvent dependence of the band are not consistent with the model developed by Hush.[5,6] For the 2,2'-bipyridine mixed-valence dimer, no band attributable to an IT transition has been found.[3]

We have prepared dimeric, mixed, pentaammine-2,2'-bipyridine complexes in order to compare their mixed-valence and IT properties with the symmetric dimers. The complexes, $[(NH_3)_5Ru(L)RuCl(bipy)_2]^{3+}$ (L is pyrazine (pyz), 4,4'-bipyridine (4,4'-bipy), *trans*-1,2-bis(4-pyridyl)ethylene (BPE), and 1,2-bis(4-pyridyl)ethane (BPA)), were prepared by the reactions between [Ru-

Table I. Intervalence Transfer Bands for the Transition

$[(NH_3)_5Ru^{III}(L)Ru^{II}Cl(bipy)_2]^{4+} \xrightarrow{h\nu}$

$[(NH_3)_5Ru^{II}(L)Ru^{III}Cl(bipy)_2]^{4+*}$ [a]

Ion	kK	$\lambda_{max},$[a] nm	ϵ
$[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{4+}$	10.4	960	530
$[(NH_3)_5Ru(pyz)Ru(NO_2)(bipy)_2]^{4+}$	12.7	790	
$[(NH_3)_5Ru(pyz)Ru(CH_3CN)(bipy)_2]^{5+}$	13.3 (sh)	750 (sh)	
$[(NH_3)_5Ru(4,4'-bipy)RuCl(bipy)_2]^{4+}$	14.4 (sh)	695 (sh)	>300
$[(NH_3)_5Ru(BPE)RuCl(bipy)_2]^{4+}$	14.7 (sh)	680 (sh)	>300
$[(NH_3)_5Ru(BPA)RuCl(bipy)_2]^{4+}$	—	—	—

[a] In deaerated acetonitrile, ± 3 nm.

$(NH_3)_5H_2O](PF_6)_2 \cdot H_2O$ and $[Ru(bipy)_2(L)Cl](PF_6)$[8] in acetone. The complexes were isolated as hexafluorophosphate salts and had satisfactory elemental analyses.

Voltammetry at a Pt-bead electrode in 0.1 M $[(n-C_4H_9)_4N](PF_6)$-acetonitrile solutions showed that the dimeric complexes undergo two, reversible, one-electron oxidations. From the available spectral and electrochemical data, the initial site of oxidation in the one-electron oxidized dimers, $[(NH_3)_5Ru(L)RuCl(bipy)_2]^{4+}$, is localized largely on the pentaammine end giving $[(NH_3)_5Ru^{(III)}$-$(L)Ru^{(II)}Cl(bipy)_2]^{4+}$. Localized oxidation at the pentaammine end is the expected result since, on the average, monomeric $[Ru(bipy)_2(L)Cl]^+$ complexes are more difficult to oxidize than $[Ru(NH_3)_5L]^{2+}$ by ~0.4 V.[9] Solutions containing the mixed-valence +4 ions in acetonitrile can be prepared by stoichiometric oxidation using Br_2 or Ce(IV).

For the BPA-bridged dimers, $[(NH_3)_5Ru(BPA)Ru-Cl(bipy)_2]^{4+/3+}$ there is no evidence for even weak metal-metal interactions across the bridging ligand. For example, the spectra of the +3 and +4 ions are virtually the sum of the spectra of the monomeric components, $[Ru(bipy)_2(B-PA)Cl]^+$ and $[Ru(NH_3)_5BPA]^{2+}$ or $[Ru(NH_3)_5BPA]^{3+}$. No metal-metal interaction occurs in the BPA dimers because of the saturated $-CH_2CH_2-$ linkage; when the bridging ligand has an intact π system (pyz, 4,4'-bipy, or BPE), the effects of weak metal-metal interactions are observed in spectral and reduction potential data and in the appearance of IT bands for the mixed-valence ions.

Intervalence transfer bands found for the mixed-valence, dimeric complexes are given in Table I. No bands are observed for the +3 ions in this spectral region. The assignment of the near-infrared bands to IT transitions for the pyrazine-bridged complexes is based on several lines of evidence. By replacing Cl^- in $[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{4+}$ by NO_2^- or CH_3CN, the IT band maximum shifts to higher energies. The IT transition (eq 1) is expected to

$[(NH_3)_5Ru^{III}(pyz)Ru^{II}Cl(bipy)_2]^{4+} \xrightarrow{h\nu}$

$[(NH_3)_5Ru^{II}(pyz)Ru^{III}Cl(bipy)_2]^{4+*}$ (1)
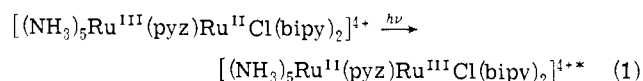
shift to higher energies since the bis-2,2'-bipyridine center is more difficult to oxidize when Cl^- is replaced by NO_2^- or CH_3CN.[11] Band half-widths on the order of 4-8 kK are expected for IT bands.[5,6,10] A band half-width of 5.8 kK is found for the IT band in $[(NH_3)_5Ru(pyz)Ru(Cl)-(bipy)_2]^{4+}$ which is in reasonable agreement with the half-width predicted in an equation given by Hush.[6,7] Hush has suggested that the energy of IT bands should vary with $(1/n^2 - 1/D)$ where n is the index of refraction and D the static dielectric constant for a given solvent.[6] The IT band for the ion, $[(NH_3)_5Ru(pyz)RuCl(bipy)_2]^{4+}$, has the expected solvent dependence (using acetonitrile, nitrobenzene, and dilute, aqueous perchloric acid).

The IT bands for the mixed-valence ions containing BPE or 4,4'-bipy are at higher energies, and therefore appear as well-defined shoulders on the tail of the lowest d(Ru) →