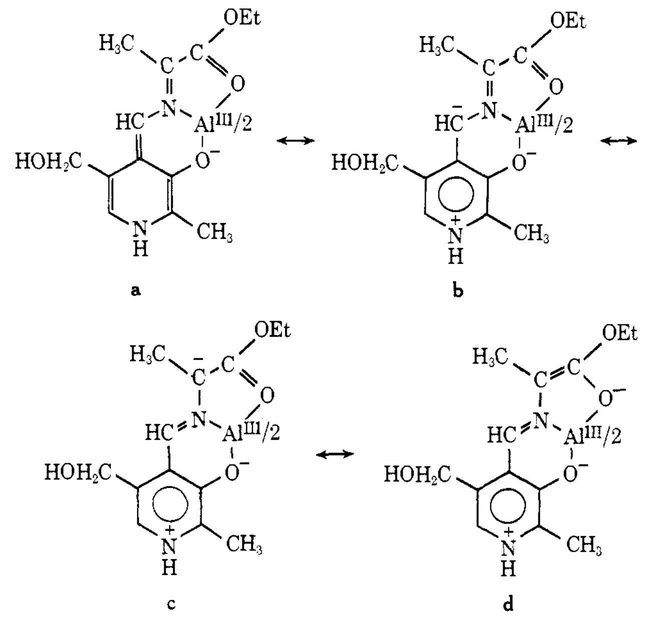
Scheme I



case, the nitrogen would bear part of the negative charge of the carbanion. We assume a considerable contribution of structure d to the stability of the carbanion. This assumption comes from the approximate planarity of the ligand, the powerful affinity of aluminum ion for hydroxide ion and oxygen containing groups,[7] and the fact that the species could be observed with ester but not with carboxylate forms of $\alpha$-keto acids.

Maley and Bruice, in their nonenzymatic transamination system with 1-methyl-3-hydroxy-4-formylpyridinium chloride, did not observe the species absorbing in the 500-nm region,[8] which they did observe with 1-methyl-4-formylpyridinium iodide.[4c]

In the study of the interactions of a variety of analogs of pyridoxal phosphate with apoaspartate aminotransferase, Metzler and coworkers[9] reported the appearance of a small peak at 485 nm on addition of glutamate to a mixture of the apoenzyme and *O*-methyl pyridoxal phosphate. With analogs having a 3-phenolic group, a corresponding absorption was not observed. These facts suggest that a free phenolic or phenolate group prevents the appearance of the carbanion. The role of aluminum ion in the present system would be to coordinate strongly to the phenolate oxygen and to the carbonyl oxygen of ester group and to stabilize the carbanion in the chelate form.

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(9) F. S. Furbish, M. L. Fonda, and D. E. Metzler, *Biochemistry*, **8**, 5169 (1969).

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## Mixed Oxidation States in Osmium Ammine Dinitrogen Complexes

*Sir:*

In pursuing our interests in the coordination chemistry of dinitrogen, we have succeeded in preparing binuclear ammine complexes of osmium with dinitrogen as a bridging group. These are remarkable in the ease with which the [II–II] species are oxidizable to the $[OsNNOs]^{5+}$ unit, the kinetic stability of the oxidized forms, and the wealth of low-energy transitions which the mixed valence complexes exhibit. In contrast to the unit, where electronic coupling between the metal centers appears to be quite weak,[1,2] in $[OsNNOs]^{5+}$ it is strong enough so that the molecules behave as Robin and Day class III systems.[3]

The green ions $[H_2O(NH_3)_4OsNNOs(NH_3)_5]^{5+}$ (**1**)[4] and $[Cl(NH_3)_4OsNNOs(NH_3)_5]^{4+}$ (**2**)[4] were synthesized by heating $[(NH_3)_5OsN_2]^{2+}$ [5] (0.3 *M*) with *cis*-$[(NH_3)_4Os(N_2)_2]^{2+}$ [6] (0.15 *M*) at 70° under argon for 36 hr. Following acidification with HCl and oxidation by air, the blue-green solution was subjected to ion exchange chromatography, using a column of Bio-Rad AG 50W-X2 resin in the acid form. Species **2** was elutable with 4 *M* HCl and **1** by 5 *M* HCl. Moving somewhat more slowly than **1** was a blue band and further ion exchange was necessary to resolve this band from **1**. Tosylate salts of **1** and **2** were precipitated and submitted for analysis. *Anal.* Calcd for $[H_2O(NH_3)_4OsNNOs(NH_3)_5](C_7H_7SO_3)_5 \cdot H_2O$: C, 28.9; H, 4.6; N, 10.6. Found: C, 28.9; H, 4.6; N, 10.9. Calcd for $[Cl(NH_3)_4OsNNOs(NH_3)_5](C_7H_7SO_3)_4 \cdot H_2O$: C, 25.8; H, 4.4; N, 11.8; Cl, 2.7. Found: C, 25.2; H, 4.3; N, 11.9; Cl, 2.6. Oxidation of **1** with an excess of Ce(IV) yielded 0.9 mol of $N_2$/mol of complex.

The green species $([Cl(NH_3)_4Os]_2N_2)^{3+}$ (**3**)[4] was prepared by heating *cis*-$[(NH_3)_4Os(N_2)_2]^{2+}$ in solution at 70° for 36 hr and then for *ca.* 0.5 hr at 90° after oxidation. The complex was eluted with 3 *M* HCl and was precipitated as the chloride salt. *Anal.* Calcd for $[(Cl(NH_3)_4Os)_2N_2]Cl_3 \cdot H_2O$: H, 3.5; N, 18.9; Cl, 24.0. Found: H, 3.3; N, 19.1; Cl, 23.2.

When a solution containing the blue species mentioned above was heated in 1 *M* HCl under argon, **1** and **2** were obtained in about 20 and 50% yields, respectively. On the basis of this evidence, and the band structure in the ir in the N≡N stretch region, we take the blue species to be $[N_2(NH_3)_4OsNNOs(NH_3)_5]^{5+}$ (**4**).

A portion of the ir spectrum of compounds containing **2** and **3** is shown in Figure 1. It is clear that a band ascribable to the N≡N stretch is virtually absent in **3** but that it has a moderate intensity in **2** (the ir band of present interest is of intermediate intensity in **1**). The Raman spectrum of **3** in solution shows a strong

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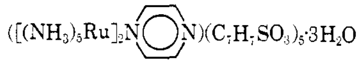
(1) C. Creutz and H. Taube, *J. Amer. Chem. Soc.*, **91**, 3988 (1969).

(2) C. Creutz, M. L. Good, and G. Chandra, private communication. Mössbauer spectroscopy shows two different kinds of Ru atoms to be present at low temperature in



(3) M. B. Robin and P. Day, *Advan. Inorg. Chem. Radiochem.*, **10**, 247 (1967).

(4) Because the starting material has a cis configuration, we take this configuration to be preserved when the binuclear species are formed. This assumption is in accord with the assignment of the far-visible–near-ir absorptions.

(5) A. D. Allen and J. R. Stevens, *Chem. Commun.*, 1147 (1967).

(6) H. A. Scheidegger, J. N. Armor, and H. Taube, *J. Amer. Chem. Soc.*, **90**, 3263 (1968).

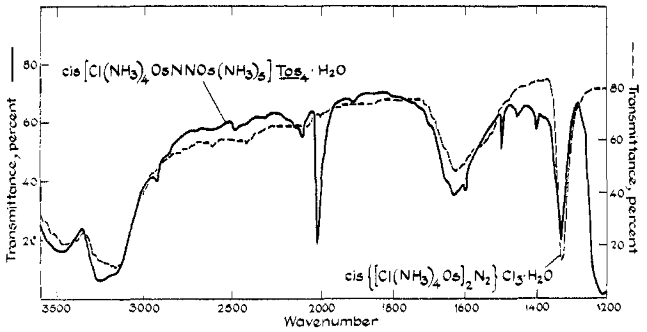


Figure 1. Infrared spectra (KBr) of *cis*-$[Cl(NH_3)_4OsNNOs(NH_3)_5]Tos_4 \cdot H_2O$ and *cis*-$\{[Cl(NH_3)_4Os]_2N_2\}Cl_3 \cdot H_2O$ in the dinitrogen stretch region (Tos = tosylate anion).

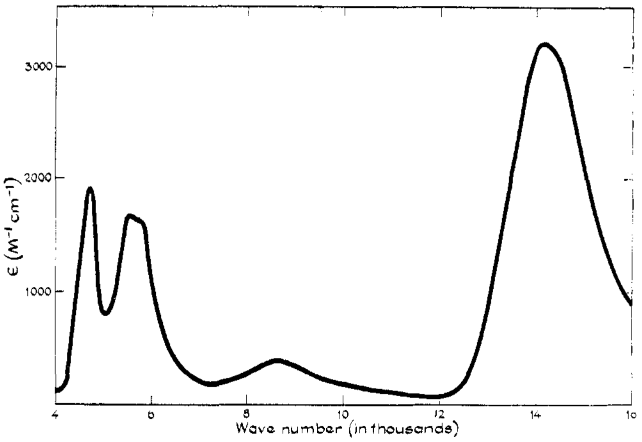


Figure 2. The low-energy spectrum of $[(H_2O)(NH_3)_4OsNNOs(NH_3)_5]^{5+}$ (tosylate anion) in 0.12 *M* $DCl-D_2O$ solution, measured in matched 0.1-cm cells.

sharp peak at 1999 $cm^{-1}$ and **2** shows a Raman peak at 1995 $cm^{-1}$. Since in the symmetrically substituted species, **3**, the $N \equiv N$ stretch is virtually absent in the ir, we conclude that in it the Os atoms become equivalent on the time scale of the lifetime of a vibrational state; *i.e.*, internal electron transfer (to the extent that this has meaning) must take place with $\tau_{1/2}$ shorter than *ca.* $10^{-13}$ sec.

The ions of mixed oxidation state are stable in acidic aqueous solution for days, in marked contrast to $[(NH_3)_5OsN_2]^{3+}$, which loses $N_2$ at a specific rate of $2 \times 10^{-2}$ $sec^{-1}$ at 25°.[7] The comparison of rates supports the view that an Os atom in the mixed oxidation state species cannot usefully be regarded as being akin to Os(III) in mononuclear complexes.

The uv spectra of **1**, **2**, and **3** are very similar, each showing a peak at 41.3–41.5 kK (log $\epsilon$ ~4.6) and a shoulder at ~37.0 kK. Both bands appear to be d to $\pi^*$ transitions. All show a strong band in the visible: 14.1 kK (log $\epsilon$ 3.5), 14.1 (3.5), 13.9, and 14.5 for **1**–**4**, respectively. It should be noted that a band at 13.2 kK is reported for $[(NH_3)_5RuNNOs(NH_3)_5]^{5+}$ (**5**).[8] The near-infrared spectrum of **1** is shown in Figure 2. From the band intensities and the fact that only minor shifts are observed on deuteration, we conclude that the bands arise from electronic transitions. The chloride salt of **3** shows peaks at 4.7, 5.2, and 7.7 kK in descending intensity. The spectrum of **2** was measured in DCl in $D_2O$, yielding values of extinction coefficients: 4.6 kK ($\epsilon$ $2.3 \times 10^3$ $M^{-1}$ $cm^{-1}$), 5.9 ($1.6 \times 10^3$), 8.5 ($4.1 \times 10^2$), the 4.6-kK band being split in KBr. The visible–near-ir bands are absent from the [II–II] species produced by reduction of **1**.[9] The low-lying d levels appear to be best described by molecular orbitals delocalized over both metal centers, as has been assumed for $[((NH_3)_5Ru)_2N_2]^{4+}$.[10] We have made a tentative assignment of levels for **1**[11] as $(x_1z_1 - x_2z_2) < (y_1z_1 - y_2z_2) < x_1y_1 < x_2y_2 < (y_1z_1 + y_2z_2) < (x_1z_1 + x_2z_2) \ll \pi^*x(N_2) \sim \pi^*y(N_2)$, assigning the visible–near-ir absorptions to transitions from the lower lying levels to the half-occupied $(x_1z_1 + x_2z_2)$ and the uv absorptions to transitions from $(x_1z_1 + x_2z_2)$ and $(y_1z_1 + y_2z_2)$ to $\pi^*(N_2)$. In **3** the $x_1y_1$ and $x_2y_2$ levels appear to become degenerate and thus only four visible–near-ir absorption bands are observed. Fewer bands still would be expected were $H_2O$ or Cl in **1**, **2**, or **3** to lie along the *z* axis. For **5**, which has $C_{4v}$ symmetry, we have found bands only at 4.3 and 7.7 kK in the near-ir.

Oxidation of **2** in acid with 1 equiv of Ce(IV) yields a blue solution ($\bar{\nu}_{max}$ at 19.5 and 16.1 kK, the latter being very broad), which on reducing with $Fe^{2+}$ regenerates **2**. We take the oxidized species to contain the [III–III] moiety. The kinetic stability of this ion may be enough to make feasible isolation in the solid state.

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(9) The yellow, air-sensitive reduced solution shows a single very intense absorption at 38.7 kK, similar to the band seen for $[((NH_3)_5Ru)_2N_2]^{4+}$ [D. F. Harrison, E. Weissberger, and H. Taube, *Science*, **159** 320 (1968)].

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(11) Assuming an eclipsed configuration and placing the $Os-OH_2$ bond in the *xz* plane.