The ligands cis to the terminal oxo or sulfido ligand remain constant in **1** and **2**, and thus to a good approximation the character of the ground state remains unchanged.[11] Since the composition of the ground state mainly determines the magnitudes of the principal A tensor elements (see eq A10–A13 in Appendix), relatively little change in the principal **A** tensor values on substituting sulfido for oxo is anticipated.

Our present observations show that merely changing an oxygen donor ligand for a sulfur donor ligand does not necessarily increase the $g$ values and decrease the $A$ values of a Mo(V) complex. Such changes are dependent at least on the ligand type, and probably on the position of substitution relative to the other ligands. Three mechanisms that would lead to *increases* in the $g$ values upon replacing an oxygen donor atom by a sulfur donor atom are as follows:

(i) Admixture of charge-transfer states involving significant contributions from appropriate metal d orbitals. Such excited charge-transfer states mix into the ground state under metal spin–orbit coupling to give contributions with the sign opposite from those involving simple d–d excitations.[21,22] This mechanism can give $g$ values $\geq 2.0023$.

(ii) Increased covalency of the metal–ligand bond leading to delocalization of the unpaired electron and reduction of the metal molecular orbital coefficients in the d–d contribution to the $g$ values. This mechanism will only permit $g$ values $\leq 2.0023$.

(iii) The increased value of the single electron spin–orbit coupling constant of sulfur vs. oxygen. This mechanism can decrease the amount by which some $g_{ii}$ are reduced from 2.0023.

It is difficult to completely separate these mechanisms from one another, but the $[HB(Me_2pz)_3]MoOXY$ complexes (X, Y = monoanions) and **1** and **2** have enabled us to investigate the effects of a variety of single-ligand substitutions on the EPR spectra of a six-coordinate Mo(V) center of known stereochemistry. Our previous study[7] showed that $g$ values $\geq 2.0023$ correlate with the observation of low-energy charge-transfer transitions and points to the importance of (i) since this mechanism is the only one cited that can raise $g$ above 2.0023. That study also confirmed that two $RS^-$ ligands cis to a terminal oxo ligand produce $g$ values approaching or exceeding 2.

The present results for **1** and **2** demonstrate for the first time that a terminal sulfido ligand bound to Mo(V) produces *lower* $g$ values than a terminal oxo ligand. The lower $g$ values for **2** correlate with the lower energy of the first d–d transition of **2**, as expected from ligand field theory (Appendix). Mechanisms i–iii may also contribute to the final EPR parameters for **1** and **2**, but these mechanisms cannot be the dominant factors in the observed differences in $g$ values between **1** and **2**.

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**Appendix.** For **g** and **A** tensors in $C_s$ symmetry with $z$ parallel to Mo=E and $y$ perpendicular to the mirror plane, d-orbital mixings in the antibonding molecular orbitals are

$$\phi_1 = \alpha[a_1 d_{x^2-y^2} + b_1 d_{xz} + c_1 d_{z^2}] \qquad a_1 > b_1, c_1 \qquad \text{(A1)}$$

$$\phi_2 = \beta[a_2 d_{x^2-y^2} + b_2 d_{xz} + c_2 d_{z^2}] \qquad b_2 > a_2, c_2 \qquad \text{(A2)}$$

$$\phi_5 = \epsilon[a_5 d_{x^2-y^2} + b_5 d_{xz} + c_5 d_{z^2}] \qquad c_5 > a_5, b_5 \qquad \text{(A3)}$$

$$\phi_3 = \gamma[e_3 d_{xy} + f_3 d_{yz}] \qquad e_3 > f_3 \qquad \text{(A4)}$$

$$\phi_4 = \delta[e_4 d_{xy} + f_4 d_{yz}] \qquad f_4 > e_4 \qquad \text{(A5)}$$

Using $\phi_1$ (mainly $d_{x^2-y^2}$) as the ground state and $\Delta_i$ ($i$ = 2–5) as the energy separations between $\phi_1$ and $\phi_i$, we have

$$g_{zz} = 2.0023 - \frac{2\xi(\alpha\gamma)^2(2a_1e_3 + b_1f_3)^2}{\Delta_3} - \frac{2\xi(\alpha\delta)^2(2a_1e_4 + b_1f_4)^2}{\Delta_4} \qquad \text{(A6)}$$

$$g_{xx} = 2.0023 - \frac{2\xi(\alpha\gamma)^2[b_1e_3 + (a_1f_3 + 3^{1/2}c_1f_3)]^2}{\Delta_3} - \frac{2\xi(\alpha\delta)^2[b_1e_4 + (a_1f_4 + 3^{1/2}c_1f_4)]^2}{\Delta_4} \qquad \text{(A7)}$$

$$g_{yy} = 2.0023 - \frac{2\xi(\alpha\beta)^2[(a_1b_2 - b_1a_2) + 3^{1/2}(b_1c_2 - c_1b_2)]^2}{\Delta_2} - \frac{2\xi(\alpha\epsilon)^2[(a_1b_5 - b_1a_5) + 3^{1/2}(b_1c_5 - c_1b_5)]^2}{\Delta_5} \qquad \text{(A8)}$$

$$g_{xz} = g_{zx} = \frac{2\xi(\alpha\gamma)^2[b_1e_3 + a_1f_3 + 3^{1/2}c_1f_3][2a_1e_3 + b_1f_3]}{\Delta_3} + \frac{2\xi(\alpha\delta)^2[b_1e_4 + a_1f_4 + 3^{1/2}c_1f_4][2a_1e_4 + b_1f_4]}{\Delta_4} \qquad \text{(A9)}$$

where $\xi$ is the metal single-electron spin–orbit coupling constant. Ignoring terms in $1/\Delta$, we have

$$A_{zz} \approx P\left[-\alpha^2K - \frac{2\alpha^2}{7}(4a_1^2 + b_1^2 - 2) - (2.0023 - g_{zz})\right] \qquad \text{(A10)}$$

$$A_{xx} \approx P\left[-\alpha^2K - \frac{2\alpha^2}{7}(a_1^2 + b_1^2 + 3c_1^2 + 2(3^{1/2})a_1c_1 - 2) - (2.0023 - g_{xx})\right] \qquad \text{(A11)}$$

$$A_{yy} \approx P\left[-\alpha^2K - \frac{2\alpha^2}{7}(a_1^2 + 4b_1^2 + 3c_1^2 - 2(3^{1/2})a_1c_1 - 2) - (2.0023 - g_{yy})\right] \qquad \text{(A12)}$$

$$A_{xz} = A_{zx} \approx P\left[\frac{2\alpha^2}{7}(3a_1b_1 + 3^{1/2}b_1c_1) + g_{xz}\right] \qquad \text{(A13)}$$

**Registry No.** **1**, 31371-06-9; **2**, 109390-37-6; *fac*-$[(NH_3)_3MoOCl_2]^+$, 109390-38-7; *fac*-$[(NH_3)_3MoSCl_2]^+$, 109390-39-8.

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# Structural, ESR, and Electrochemical Properties of Two $[Rh_2(ap)_4]^+$ Geometric Isomers (ap = 2-Anilinopyridinate). A True Mixed-Valent Rhodium(II)-Rhodium(III) Complex

*Sir:*

Numerous theoretical and experimental ESR studies have been reported for $Rh_2^{5+}$ complexes containing carboxylate,[1,2] amidate,[3]

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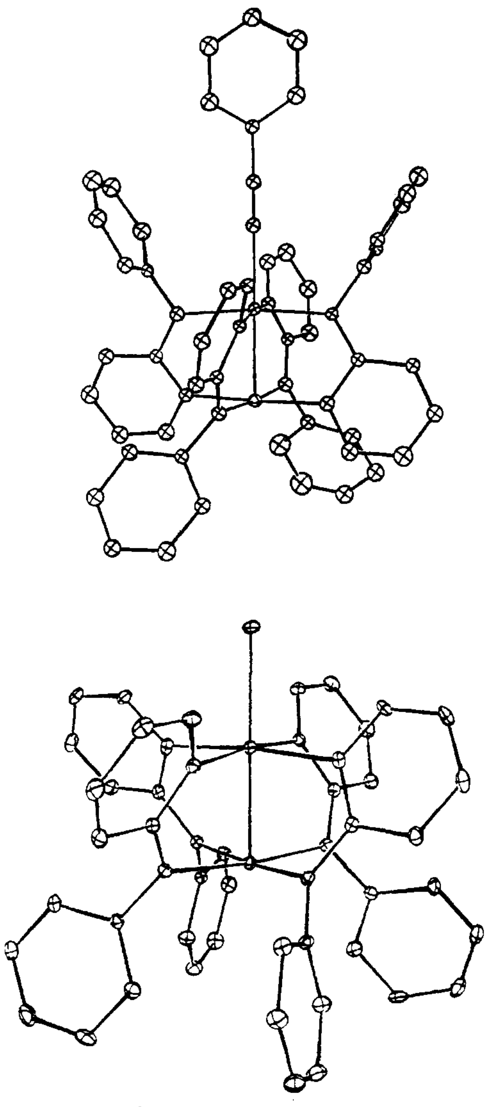

**Figure 1.** Structures of (top) $Rh_2(ap)_4(C_6H_5CN)$ (compound **1**) and (bottom) $Rh_2(ap)_4Cl$ (compound **2**).

and amidinate[4] bridging ligands. The symmetry of the odd-electron orbital has been reported to be Rh–Rh $\sigma$, Rh–Rh $\pi^*$, or Rh–Rh $\delta^*$. These assignments were based on theoretical values of the **g** tensors resulting from calculations on axially symmetric bisadducts of $[Rh_2(O_2CR)_4]^+$.[1,2] Until recently, all experimental ESR studies on dirhodium radical-cation complexes have shown the unpaired electron to be equally distributed over the two metal centers.

We recently reported the synthesis of $[Rh_2(dpb)_4]^+$ (dpb = *N,N'*-diphenylbenzamidinate), which has an unequal distribution of electron density on the two rhodium ions.[4] In this paper we report the synthesis of two geometric isomers of $[Rh_2(ap)_4]^{0/+}$ (ap = 2-anilinopyridinate). One of these isomers has a complete polarization of the odd electron, thus giving the first true mixed-valent rhodium(II)–rhodium(III) complex.

The complex $Rh_2(ap)_4$ can exist in four geometric forms. The synthesis of $Rh_2(ap)_4$ was previously reported by Tocher and Tocher,[5] but no crystal structure was determined to establish the identity of any geometric isomer. We have repeated the synthesis of this complex using the synthetic procedure described in the literature.[5] The major product was recrystallized in the presence of benzonitrile to obtain a crystal suitable for structure determination. The molecular structure of this complex is illustrated in Figure 1. The complex (compound **1**) consists of a dirhodium(II) ion bridged by four 2-anilinopyridinate ions and one axial benzonitrile ligand. Each rhodium is equatorially bound to two pyridine nitrogens ($N_P$) and two anilino nitrogens ($N_A$) trans to their own kind. Compound **1** has a Rh–Rh bond distance of 2.412 (1) Å. The average Rh–$N_P$ and Rh–$N_A$ bond distances are 2.035 (9) and 2.041 (8) Å, and the Rh–$N_{axial}$ bond distance is 2.189 (9) Å. Steric crowding by the axial ligand forces a torsional twist of the two equatorial planes by 14°.

**Figure 2.** ESR spectra: (top) electrogenerated $[Rh_2(ap)_4]^+$ at 77 K, trans isomer (compound $1^+$) in $CH_3CN$ containing 0.1 M TBAP; (middle) $[Rh_2(ap)_4]^+$, trans isomer (compound $1^+$) in $C_2H_4Cl_2$ containing 0.1 M (TBA)Cl; (bottom) $Rh_2(ap)_4Cl$ (compound **2**) in $CH_2Cl_2$.

An oxidized dirhodium complex, $Rh_2(ap)_4Cl$, was obtained from the reaction of $Rh_2(OOCCH_3)_4$ in a melt of 2-anilinopyridine. The molecular structure of $Rh_2(ap)_4Cl$ (compound **2**) is also shown in Figure 1 and reveals the complex to have a geometric arrangement of bridging ligands different from that of **1**. The Rh–Rh bond distance of compound **2** is 2.406 (1) Å. One rhodium ion is bound to four pyridine nitrogens ($N_P$) and an axial chloride ion. The Rh–$N_P$ and Rh–Cl bond distances are 2.048 (3) and 2.421 (3) Å. Four anilino nitrogens ($N_A$) are bound to the other Rh with an average bond distance of 2.008 (3) Å, and the axial site is vacant. A 23.4° torsional twist of the equatorial planes is observed.

The cyclic voltammetry of compounds **1** and **2** in dichloromethane shows two reversible redox processes, which are given by reactions 1 and 2. The axially bound benzonitrile may or may

$$Rh^{II}_2 \rightleftarrows Rh^{II}Rh^{III} + e^- \qquad (1)$$

$$Rh^{II}Rh^{III} \rightleftarrows Rh^{III}_2 + e^- \qquad (2)$$

not be present in $CH_2Cl_2$. Half-wave potentials for oxidation of compound **1** in dichloromethane (0.1 M TBAP) are 0.03 and 0.73 V vs. SCE while for compound **2** there is a reduction at $E_{1/2}$ =

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**Table I.** Values of $g_\perp$, $g_\parallel$, and $A_\parallel$ for the Two Geometrical Isomers of $[Rh_2(ap)_4]^+$ (ap = 2-Anilinopyridinate) at 77 K in Various Solvents

| formula | compd no. | solvent | $g_\perp$ | $g_\parallel$ | $A_\parallel$, $10^4$ $cm^{-1}$ |
|---|---|---|---|---|---|
| $[Rh_2(ap)_4]^{+a}$ | $1^+$ | $CH_2Cl_2$ | 2.076, 2.054 | 1.954 | 16.77 |
| $[Rh_2(ap)_4]^{+a}$ | $1^+$ | $CH_3CN$ | 2.062, 2.053 | 1.955 | 19.77 |
| $[Rh_2(ap)_4]^{+b}$ | $1^+$ | $CH_2ClCH_2Cl$ | 2.082 | 1.943 | 20.84 |
| $Rh_2(ap)_4Cl$ | 2 | THF | 2.093 | 1.946 | 23.3 |
| $Rh_2(ap)_4Cl$ | 2 | $CH_2Cl_2$ | 2.095 | 1.948 | 24.56 |
| $Rh_2(ap)_4Cl$ | 2 | $CH_2ClCH_2Cl$ | 2.089 | 1.946 | 19.63[c] |

[a] Electrochemically generated in 0.10 M TBAP solution. $g_\parallel$ is split into a 1:2:1 triplet. The counterion is noncoordinating $ClO_4^-$. [b] Electrochemically generated in 0.10 M (TBA)Cl solution. $g_\parallel$ appears to result from two overlapping signals with the major contribution being a doublet. The counterion is coordinating $Cl^-$. [c] Solution contains 0.1 M TBAP.

−0.41 V (the reverse of eq 1) and an oxidation at $E_{1/2} = 0.52$ V.

The radical cations $1^+$ and 2 were investigated by ESR spectroscopy. The resulting ESR spectra of the two geometric isomers are shown in Figure 2, and the values of $g_\perp$, $g_\parallel$, and $A_\parallel$ are listed in Table I. Compound $1^+$ was electrochemically generated by oxidation of the neutral complex at a constant potential of 0.3 V in dichloromethane containing either a 0.1 M TBAP or a 0.1 M (TBA)Cl solution. Compound 2 was already in the mixed Rh(II)–Rh(III) oxidation state and was used as isolated.

Both compounds are ESR-active at room temperature in dichloromethane solutions and give $g$ values of 2.033 and 2.050. Compound $1^+$ gives a rhombic ESR spectrum in frozen glass (77 K) in $CH_3CN$ and $CH_2Cl_2$. The value of $g_\parallel$ is split into a 1:2:1 triplet when the counterion is $ClO_4^-$ and into a multiplet when the counterion is $Cl^-$. In the latter case, the signal appears to result from a mixing of two signals giving an unsymmetrical doublet with a shoulder.

The following equilibrium between $[Rh_2(ap)_4]^+$ and $Cl^-$ is possible:

$$[Rh_2(ap)_4]^+ \overset{Cl^-}{\rightleftharpoons} Rh_2(ap)_4Cl \overset{Cl^-}{\rightleftharpoons} [Rh_2(ap)_4Cl_2]^- \quad (3)$$

The unligated and dichloride species in eq 3 are axially symmetric and should show a 1:2:1 triplet for $g_\parallel$. It is doubtful, however, that the dichloride adduct exists in solution since both $1^+$ and 2 appear to only form monoadducts. The oxidized monochloride adduct could give a doublet or doublet of doublets for $g_\parallel$ depending on the degree of polarization of the odd electron orbital. Compound 2 gives an axial ESR spectrum at 77 K in both THF and $CH_2Cl_2$ and has $g_\parallel$, which is split into a doublet. This shows conclusively that the odd electron is localized on only one rhodium ion and that compound 2 (which contains one axially bound $Cl^-$ ligand) is a true Rh(II)–Rh(III) mixed-valent complex.

The localization of the odd electron in compound 2 could be caused by three factors: the effect of axial monoligation, the different equatorial coordination spheres about the two rhodium ions, and the twist angle of the two equatorial rhodium planes. The two rhodium atoms in $[Rh_2(dpb)_4]^+$[4] and $1^+$ are equatorially equivalent within each dimer unit. Both complexes still have an unequal distribution of spin density on the two rhodium atoms in bonding solvents and/or in the presence of coordinating anions. This suggests that axial polarization and not differences in equatorial bonding environment is the most significant factor. At present there is insufficient information to evaluate the importance of the torsional twist of the two rhodium planes.

In summary, dirhodium ($Rh_2^{5+}$) complexes have now been identified in which the odd-electron spin density is equally distributed[3] ($g_\parallel$ split into a 1:2:1 triplet), unequally distributed[4] ($g_\parallel$ split into a 1:1:1:1 doublet of doublets), and localized on only one metal ($g_\parallel$ split into a doublet). Only three dirhodium complexes ($[Rh_2(dpb)_4]^+$, $1^+$, and 2) have been reported to date that show an unequal distribution of the odd electron on the two metal centers. All of these complexes appear to exclusively form monoadducts. In the case of compound 2, the axial polarization is enhanced by unequal equatorial and axial bonding on the two rhodium ions. These results raise questions regarding the nature of the HOMO of these molecules and the driving force for the localization of the odd electron. Further theoretical and experimental studies are in progress.

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**Registry No.** $Rh_2(ap)_4(C_6H_5CN)$, 109532-20-9; $Rh_2(ap)_4$, 99243-16-0; $Rh_2(ap)_4^+$, 99243-17-1; $Rh_2(ap)_4Cl$, 109532-21-0.

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