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Electron Paramagnetic Resonance Investigation of Some 11-Tungstoruthenate(III) Polyoxoanions

Charles C. Rong,[a][‡] Hyunsoo So,*[b] and Michael T. Pope*[a]

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EPR spectra of three Keggin structure polyoxotungstates containing ruthenium(III), $[PW_{11}O_{39}Ru(L)]^{4-}$ (L = H_2O, pyridine, dimethyl sulfoxide), have been recorded at 77 K and yield details of the symmetry and ligand field parameters of the embedded low-spin d^5 ruthenium cation. The magnitudes of the *g* tensors and ^{99,101}Ru hyperfine coupling constants of the dmso derivative show that the unpaired electron occupies a d_{xy}-type orbital as a result of the axial component of the ligand field with $\Delta(d_{xy} - d_{xz},d_{yz}) \approx 6200\ cm^{-1}$. A weak broad absorption in the electronic spectrum at ca. 5600 cm^{-1} is consistent with this interpretation. A smaller rhombic component imposed by the polytungstate ligand further splits the d_{xz} and d_{yz} orbitals ($< 2000\ cm^{-1}$). The orbital reduction factor *k* of the dmso complex (0.69) is significantly smaller than those for the aqua and pyridine derivatives (0.80, 0.83), and this implies that, as previously found for the Ru^{II} analog, the dmso ligand is *S*-bonded in the Ru^{III} complex.

Introduction

The recognition that transition-metal cations could be incorporated into lacunary polyoxotungstate and -molybdate anions, especially those based on the Keggin structure, has a history dating back to the 1960s.[1] It soon became evident that such transition-metal-substituted polyoxometalates (TMSP) could be considered as oxidation-resistant analogs of metalloporphyrins, and subsequent investigations have generated a voluminous literature describing the use of TMSP as catalysts (or catalyst precursors) for a broad variety of oxidative reactions.[2] In particular, much attention has been focused on polytungstates incorporating ruthenium in view of that element's documented catalytic activity in other molecular environments.

Several years ago we reported the synthesis and characterization of salts containing the anion $[PW_{11}O_{39}Ru^{II}(L)]^{5-}$, where L = H_2O and a variety of *S*-bonded ligands (sulfides and sulfoxides) and activated alkenes such maleic and crotonic acids.[3] Each of these polyoxoanions could be oxidized to the paramagnetic Ru^{III} derivative, and in the case where L = H_2O to the oxidoruthenium(IV) and -(V) versions. We have noted that the Ru^{III} anions yield well-defined EPR spectra that allow the present detailed analysis of the symmetry and the ligand field parameters imposed upon the ruthenium cation by the structure of the lacunary 11-tungstophosphate anion.

Results and Discussion

Three anions $[PW_{11}O_{39}Ru^{III}(L)]^{4-}$ (Figure 1) have been studied as tetra-*n*-butylammonium salts, where L is H_2O (**1**-aq), dimethyl sulfoxide (**1**-dmso), and pyridine (**1**-py).

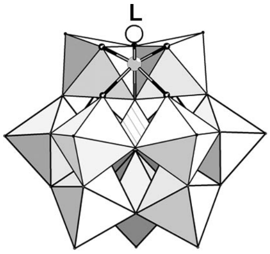

Figure 1. Representation of the structure of $[PW_{11}O_{39}Ru(L)]^{4-}$ in mixed polyhedral and bond version. Ru = gray sphere, L = white sphere.

The EPR spectrum of **1**-dmso at 77 K, together with its simulation, is shown in Figure 2. The three major lines are characteristic of a rhombic system as expected, and the high-field line also shows hyperfine satellites from ^{99}Ru ($I = 5/2$; 12.7%) and ^{101}Ru ($I = 5/2$; 17.1%). Both magnetic isotopes have very similar nuclear moments and are indistinguishable in the EPR spectra. The spectra of **1**-aq. and **1**-py (Supporting Information) are similar to that of **1**-dmso except that hyperfine features are not observed owing to

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[a] Department of Chemistry, Georgetown University,
Box 571227, Washington, DC 20057, USA
Fax: +1-202-687-6209
E-mail: popem@georgetown.edu
[b] Department of Chemistry, Sogang University,
Seoul, South Korea
E-mail: hyunso@sogang.ac.kr
[‡] Current address: Army Research Laboratory,
Adelphi, MD 20783, USA

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the increased width of the high-field lines in these cases. Experimental EPR parameters confirmed by the spectral simulations are given in Table 1.

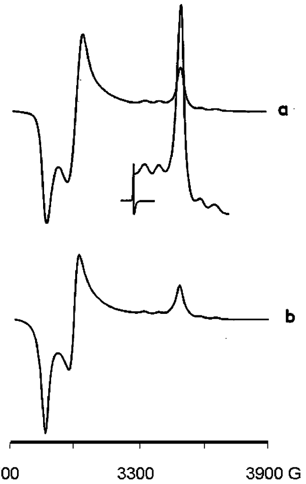

Figure 2. X-band EPR spectrum of **1**-dmso at 77 K (a) experimental (b) simulation.

Table 1. Experimental EPR parameters.[a]

Anion	g_1	g_2	g_3	A_1	A_2	A_3
1-aq	2.494	2.311	1.697			
1-py	2.579	2.338	1.603			
1-dmso	2.296	2.192	1.877	< 20	< 20	60

[a] Hyperfine parameters in 10^{-4} cm^{-1}.

Interpretation of the EPR Parameters

We use the method of Bleaney and O'Brien,[4] which has been applied to other low-spin 4d^5 ruthenium complexes.[5] This approach assumes that only the octahedral t_{2g} orbitals are included in the basis set. In the most general case the lowest Kramers doublet can be written as

$$\Psi^+ = A|1^+\rangle + B|\xi^-\rangle + C|-1^+\rangle$$

$$\Psi^- = A|-1^-\rangle - B|\xi^+\rangle + C|1^-\rangle$$

where $|1\rangle = -(1/\sqrt{2})(d_{xz} + id_{yz})$, $|-1\rangle = (1/\sqrt{2})(d_{xz} - id_{yz})$, $|\xi\rangle = id_{xy}$, and the superscripts + and – represent the α and β spin wave functions, respectively. Operating on these functions with the magnetic moment operator ($kL + g_eS$) yields equations for g values in terms of the coefficients A, B and C, and the orbital reduction factor k.

$$g_x = 2[2AC - B^2 + \sqrt{2}kB(C - A)]$$

$$g_y = -2[2AC + B^2 + \sqrt{2}kB(C + A)]$$

$$g_z = -2[1 - 2B^2 + k(A^2 - C^2)]$$

Because $A^2 + B^2 + C^2 = 1$, values for A, B, and C can be determined from the experimental g values, and these can then be used to determine the ligand field parameters Δ and V in terms of the spin-orbit coupling constant λ:

$$V/\lambda = (2A + \sqrt{2}B)C/(A^2 - C^2)$$

$$\Delta/\lambda = -A/(\sqrt{2}B) - 0.5 + (A/2C)(V/\lambda)$$

where Δ represents the separation of the d_{xy} orbital from the d_{xz} and d_{yz} orbitals generated by an axial distortion, and V represents the separation between the d_{xz} and d_{yz} orbitals by a rhombic distortion. A positive value of Δ means that the d_{xy} orbital has a higher energy than the d_{xz}, d_{yz} orbitals.

The signs of the g values cannot be determined experimentally, and all possible combinations of signs must be considered to interpret them. Comparing the experimental g values with the values in the literature, only two acceptable solutions can be found. We note that McGarvey has presented useful guidelines for assigning and analyzing the principal g values for low-spin d^5 complexes.[6] Application of these guidelines to our data, see Supporting Information, also leads to the same two solutions. These solutions are presented in Table 2.

Table 2. Two possible acceptable fits to the experimental g values.

	Solution 1			Solution 2		
	1-aq	**1**-py	**1**-dmso	**1**-aq	**1**-py	**1**-dmso
g_x	–2.494	–2.579	–2.296	–1.697	–1.603	–1.877
g_y	–2.311	–2.338	–2.192	–2.311	–2.338	–2.192
g_z	1.697	1.603	1.877	–2.494	–2.579	–2.296
A	0.232	0.264	0.151	0.846	0.852	0.833
B	0.972	0.964	0.988	0.530	0.518	0.552
C	–0.029	–0.036	–0.020	0.060	0.072	0.031
k	0.80	0.83	0.69	1.14	1.15	1.09
Δ/λ	3.36	2.96	5.14	–0.18	–0.22	–0.10
V/λ	–1.01	–1.00	–1.56	0.21	0.24	0.11

Solution 1 has a positive Δ, which corresponds to the electron hole in the d_{xy} orbital. Solution 2 corresponds to the hole in the ($d_{xz} \pm d_{yz}$) orbitals and very small axial and rhombic distortions. An acceptable range for the orbital reduction factor k is controversial. Some authors[7] use $0.75 < k < 2.0$, whereas others[5b,8] prefer lower values. Since all of our values except one are in the former range we consider both solutions to be acceptable. However, further insight into the symmetry of the ruthenium ion in **1**-dmso can be provided by the magnitude of the observed hyperfine coupling constants.

Bleaney and O'Brien have presented expressions for these constants. With the z axis of the g tensor along a cubic axis, and with the x and y axes each making an angle β with a cubic axis, the constants are given by

$$A_x = P[-(2B^2 + 6C^2\cos4\beta + 11\sqrt{2}AB + 2AC - 17\sqrt{2}BC)/7 + \kappa(B^2 + 2AC)]$$

$$A_y = P[-(2B^2 + 6C^2\cos4\beta + 11\sqrt{2}AB - 2AC - 17\sqrt{2}BC)/7 + \kappa(B^2 - 2AC)]$$

$$A_z = P[(12 - 28A^2 - 16B^2 + 6\sqrt{2}AB)/7 + \kappa(1 - 2B^2)]$$

where κ is the core-polarization constant and $P = 2g_N\beta_e\beta_N\langle r^{-3}\rangle$.

A useful parameter related to κ is the core polarization hyperfine field per unit spin:

$$\chi = -1.5\kappa\langle r^{-3}\rangle$$

Although the signs of the hyperfine coupling constants are not known, P, κ, $\langle r^{-3}\rangle$, and χ can be calculated for various combinations of signs, and a proper combination can yield acceptable values of P, etc. The sign of P must be negative for the nuclear g factors of ^{99}Ru and ^{101}Ru are both negative, $-0.25\beta_N$ and $-0.28\beta_N$, respectively. As both $<r^{-3}>$ and χ are expected to be reduced by covalency from their free ion values, $<r^{-3}>_{4d} = 6.5$ au and $\chi = -8.5$ au, they should not exceed these values. Therefore, these values may be taken as criteria for determining the best solution. The A_x and A_y values cannot be determined from the spectrum, but simulation indicates that they are less than 0.002 cm^{-1}. Although the angle β is not known, the term containing cos4β should be negligibly small for both solutions. The coefficients of Solution 1 (Table 2) give acceptable $<r^{-3}>$ and χ values for $A_z = 0.0060$ cm^{-1} and $-0.0031 < (A_x + A_y)/2 < -0.0001$ cm^{-1}. For example if it is assumed that $(A_x + A_y)/2 = -0.0020$ cm^{-1}, the results would be $P = -0.00395$ cm^{-1}, $\kappa = 1.14$, $<r^{-3}> = 4.5$ au, and $\chi = -7.7$ au. The values of A_x and A_y can then be calculated to be -0.0022 and -0.0018 cm^{-1}, respectively. In contrast, no reasonable value of $<r^{-3}>$ could be obtained from the coefficients of Solution 2, and we therefore conclude that Solution 1 is the only acceptable result for the ligand field parameters of Ru^{III} in the three tungstoruthenate polyoxoanions.

The values of Δ/λ for the three complexes correspond to the energy separation between the half-filled d_{xy} orbital and the d_{xz},d_{yz} orbitals generated by the axial distortion from ideal octahedral geometry. The similar values for **1**-aq (3.36) and **1**-py (2.96) differ significantly from that for **1**-dmso (5.14). The free ruthenium ion spin-orbit parameter λ is reported[5a] to be 1197 cm^{-1} so that Δ for **1**-dmso should be ca. 6150 cm^{-1} (1625 nm). The electronic spectrum of a solution of **1**-dmso in acetonitrile is shown in Figure 3. The broad weak band (ε = 24 L mol^{-1} cm^{-1}) at ca. 1800 nm is consistent with this argument. The corresponding transitions for the other complexes could not be observed owing to strong solvent absorption at wavelengths > 2200 nm. As indicated by the values shown in Table 2 the effects of the rhombic component, V, of the ligand field are much smaller than Δ and range from ca. 1800 to 2000 cm^{-1}.

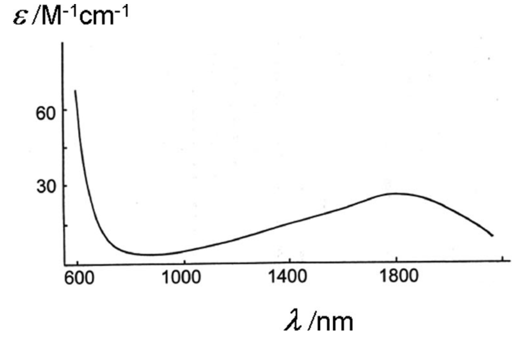

Figure 3. Near-IR absorption spectrum of **1**-dmso in acetonitrile.

Recent ^{182}W Mössbauer data[10] for several Keggin polytungstates $[\mathrm{XW_{12}O_{40}}]^{n-}$ show that an individual tungsten atom experiences an asymmetry parameter, η (which is roughly analogous to the rhombic distortion, V/λ, discussed here) that *increases* from ca. 0.30 to ca. 1.0 as the oxidation state of X *decreases*. It would be of interest to discover whether this change is paralleled by other yet-to-be-synthesized $[\mathrm{XW_{11}O_{39}Ru^{III}(L)}]^{n-}$ anions.

The observed variations in the orbital reduction factor k [0.80 (aq), 0.83 (py) vs. 0.69 (dmso)] imply a greater degree of covalency for the dmso–Ru bond. It is plausible to ascribe this to an S-bonded isomer as was found to be the case for the Ru^{II} complex.[3] Although S-bonded Ru^{II} complexes are commonplace, it has been noted[9] that the pentammineruthenium(III)–dmso complex undergoes spontaneous isomerization (Ru–S to Ru–O, $k = 7 \times 10^{-2}$ s^{-1}). However, the stabilization of the S-bonded isomer in **1**-dmso is consistent with the other experimental evidence (especially W NMR spectra) demonstrating that the lacunary cavity in polyoxometalates functions as a "π-acceptor" macrocyclic ligand as a result of the vacant d_{xy}-type orbitals of the adjacent W^{VI} atoms.[3]

Conclusions

Analysis of the EPR spectra of ruthenium(III) incorporated in Keggin structure polytungstates provides detailed insights into the magnitudes of the axial and rhombic components of the ligand field imposed by the lacunary ligand $[\mathrm{PW_{11}O_{39}}]^{7-}$. The larger ligand field and lower orbital reduction factor of the dmso complex compared with the corresponding values for the aqua and pyridine derivatives suggest that the dmso ligand is S-bonded to the Ru^{III} center of the polytungstate.

Experimental Section

The preparation and identification of tetra-n-butylammonium salts of **1**-aq and **1**-py have been described in the previous paper.[3] Preparation of the corresponding salt of **1**-dmso was achieved as follows. An aqueous solution containing brown $\mathrm{Cs_4[PW_{11}O_{39}Ru^{II}(dmso)]}$[3b] [48 mg in 15 mL of sulfate buffer (pH = 3)] was electrolytically oxidized by 1 Faraday/mol at a graphite cloth electrode at +0.75 V vs. SCE. The resulting pale yellow solution displayed the same cyclic voltammogram as the Ru^{II} anion with the open-circuit voltage shifted from less than 0 V to more than +0.70 V. The desired salt was precipitated by the addition of 100 mg of tetra-n-butylammonium hydrogen sulfate. The isolated salt was washed with water and air-dried. ^{31}P NMR (CD$_3$CN): $\delta = -31$ ppm ($\nu_{0.5}$ = 820 Hz) [cf. $\delta = -10.8$ ppm ($\nu_{0.5}$ = 2.0 Hz) for the Ru^{II} anion in D$_2$O].

EPR spectra were recorded with a Varian E-4 X-band spectrometer at 77 K. The polyoxometalate samples were prepared as solutions in acetonitrile to which an equal volume of toluene was added to ensure the formation of a good glass at 77 K. Programs for the spectral simulation and calculation of the ligand field parameters were written by H. S.[11]

Supporting Information (see footnote on the first page of this article): Traces of experimental EPR spectra of **1**-aq and **1**-py; analysis of the g values according to ref.[6]

Acknowledgments

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[11] The EPR simulation program was a modification of EPRPOW originally written by L. K. White and R. L. Belford (University of Illinois).

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