Correlation of EPR Parameters with Electronic Structure in the Homologous Series of Low-Symmetry Complexes Tp*$MoOX_2$ (Tp* = Hydrotris(3,5-dimethylpyrazol-1-yl)borate; X = F, Cl, Br)

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Received August 1, 1996

In paramagnetic monometallic complexes of axial or higher symmetry, the principal axes of the molecular g and metal hyperfine, A^M, interaction matrices are required to be coincident. In lower symmetries this requirement is relaxed and the g and A^M matrices may have significantly different orientations. A few detailed investigations of the effects of low symmetry on EPR spectra have been performed,[1,2] but a comparison of the noncoincidence angles for a homologous series of discrete molecular complexes has not previously appeared. We report herein the results of oriented single-crystal EPR spectroscopy on the homologous series of Mo(V) complexes Tp*$MoOX_2$ (Tp* = hydrotris(3,5-dimethylpyrazol-1-yl)borate; X = F, Cl, Br) and have defined the trend in the noncoincidence angles between the g and A^{Mo} matrices. These complexes are particularly of interest as spectroscopic models for Mo(V) derivatives of the active sites of molybdenum containing oxidoreductase enzymes.[3] Collison, et al., have previously reported a single-crystal study of the complex Tp*$MoOCl_2$ in a Tp*$SnCl_3$ lattice.[2]

The Tp*$MoOX_2$ complexes[4] were doped into two different diamagnetic lattices, Tp*$SnBr_3$[5] and Tp*$Mn(CO)_3$.[7] Oriented single-crystal EPR spectra at room temperature were obtained at both X-band and Q-band frequencies at 10 or 15° increments of the magnetic field direction. Plots of the spectra as a function of angle for three of the samples are included in the Supporting Information. A series of spectra were collected in three mutually perpendicular planes,[8] and the data were analyzed by the Schonland method[9] to give the principal values of the g^2 and $(gA^{Mo})^2$ matrices and their directions with respect to the crystallographic planes. Due to the crystallographic symmetry[10] and the 3-fold statistical disorder in the orientation of the dopant,[11] there were multiple magnetically inequivalent sites. For each complex, however, only one combination of principal values and angles was consistent with the data in every plane.[12] For X = F and Br, extensive ligand hyperfine splittings were also observed. The detailed analysis of the ligand hyperfine will be presented elsewhere.

Table 1 summarizes the results and compares them to the noncoincidence angles between g and A^{Mo} in the molybdenum oxidoreductases. Each model complex has C_s symmetry which requires one component of the g and A^{Mo} interaction matrices to be oriented perpendicular to the symmetry plane and thus coincident.[2] In Table 1, these correspond to g_3 and A_3, which are experimentally found to be within 5° of each other. The other two components of each matrix may have any orientation in the symmetry plane. g_1 is associated with the largest A^{Mo} value and increases dramatically down the series while g_2 and g_3 exhibit more modest variations. Similar trends have also been observed in C_{4v} molybdenum oxyhalide anions[16] where they have been linked to the covalencies of the ground state and charge transfer excited states. The values for the model complexes in Table 1 compare well with the previously published work on Tp*$MoOCl_2$ in single crystals[2] and for the series of complexes in fluid solutions and frozen glasses.[4]

Of particular interest is the angle α between g_1 and A_1^{Mo}. The magnitude of α increases significantly down the series and the values are similar in magnitude to those observed in the oxidoreductase sites. It is of interest to define how the orientations of g_1 and A_1^{Mo} change relative to a fixed coordinate system and the common crystallographic coordinates provide such a fixed system. Figure 1 shows the angular dependence of g^2 and $(gA^{Mo})^2$ for analogous dopant sites for rotation in the ab (or bc*[8]) plane of Tp*$Mn(CO)_3$ crystals doped with the fluoride and bromide complexes. It is apparent from the figure that the direction of A_1^{Mo} is nearly fixed, whereas the direction of g_1 changes with respect to the crystallographic (and thus the molecular) coordinates.

These results can be interpreted by noting that previous results on these[4] and related complexes[16] have indicated that charge transfer as well as ligand field excited states play significant roles in determining the g values. The values of A^{Mo}, however, are dominated by isotropic Fermi contact and spin dipolar contributions. This implies that the directionality of the A^{Mo} axes is defined by the ground state orbital, which is localized in a plane perpendicular to the direction of largest ligand field.

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(4) Nipales, N. S.; Westmoreland, T. D. *Inorg. Chem.* **1995**, *34*, 3374−3377.
(5) Tp*$SnBr_3$[6] crystallizes in the monoclinic space group $P2_1/n$ with a = 11.519(2) Å, b = 13.574(2) Å, c = 14.439(1) Å, β = 104.22(1)°, and Z = 4. Full crystallographic details will be published elsewhere.
(6) Lobbia, G. G.; Bonati, F.; Cecchi, P.; Lorenzotti, A.; Pettinary, C. *J. Organomet. Chem.* **1991**, *403*, 317−323.
(7) Tp*$Mn(CO)_3$ was synthesized by heating KTp* and $Mn(CO)_5Br$ in THF followed by recrystallization from acetone. Tp*$Mn(CO)_3$ crystallizes in the monoclinic space group $P2_1/c$ with a = 8.0007(3) Å, b = 13.9831(4) Å, c = 18.6916(6) Å, β = 97.8800(10)°, and Z = 4. Full crystallographic details will be published elsewhere.
(8) In each case the ac plane was identified from linearly polarized microscopy. The other two planes were either ab and bc* or a*b and bc, since the a and c axes could not be unambiguously assigned.
(9) Schonland, D. S. *Proc. Phys. Soc. (London)* **1959**, *73*, 788−792.
(10) Each site in each lattice is related by the 2-fold screw axis to another magnetically inequivalent site.
(11) The oxo group may substitute for any of the three Br atoms in the Tp*$SnBr_3$ lattice or for any CO in the Tp*$Mn(CO)_3$ lattice.
(12) In addition to the six possible orientations of the site, there are ambiguities in the signs of off-diagonal elements of the g^2 matrix.[9] The solutions presented in the table were chosen on the basis of the following criteria: (1) At least one g and A^{Mo} component must be coincident (in practice, within 10° of each other). (2) g_1 correlates with the largest A^{Mo} component. (3) The g and A^{Mo} values and their relative orientations must be consistent with both the isotropic and powder spectra.
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S0020-1669(96)00913-5 CCC: $14.00 © 1997 American Chemical Society

Table 1. Principal Values and Noncoincidence Angles for g and A^{Mo} Interaction Matrices of Tp*$MoOX_2$ Complexes and Xanthine Oxidase Active Site Derivatives[a]

	g_1	g_2	g_3	A_1^{Mo}	A_2^{Mo}	A_3^{Mo}	α (deg)	ref
model complexes								
Tp*$MoOF_2$[b]	1.901	1.957	1.946	85.0	38.2	33.4	17	this work
Tp*$MoOCl_2$[c,d]	1.9698	1.9420	1.9315	76.2	36.2	22.1	31	this work
	(1.969	1.939	1.931	71.6	33.8	33.4	34)	2b
Tp*$MoOBr_2$[c]	2.067	1.943	1.936	81.2	31.8	26.4	57	this work
xanthine oxidase								
very rapid[e]								
xanthine	2.0252	1.9550	1.9494	44.4	18.2	19.1	36, 8 [f]	14
2-oxo-6-methylpurine	2.0229	1.9518	1.9446	42.2	20.2	21.2	42, 7 [f]	14
rapid type 1[e]								
1-methylxanthine	1.9866	1.9691	1.9646	61.7	24.8	24.8	20	13
formamide	1.9901	1.9710	1.9666	61.4	24.7	25.7	18	14
rapid type 2	1.9897	1.9681	1.9617	60.4	24.7	24.8	20	13
slow	1.9706	1.9655	1.9542	65.4	26.2	27.1	33	13
sulfite oxidase								
low-pH form	2.007	1.974	1.968	56.7	25.0	16.7	18	15
high-pH form	1.990	1.966	1.954	54.4	21.0	11.3	14, 22 [f]	15

[a] A^{Mo} values are given in units of 10^{-4} cm^{-1}. [b] Tp*$Mn(CO)_3$ lattice. [c] Tp*$SnBr_3$ lattice. [d] Values in parentheses were obtained in a Tp*$SnCl_3$ lattice.[2b] [e] The parameters were obtained with the indicated substrates. [f] The second angle represents rotation about the z axis prior to rotation in the xz plane.[12]

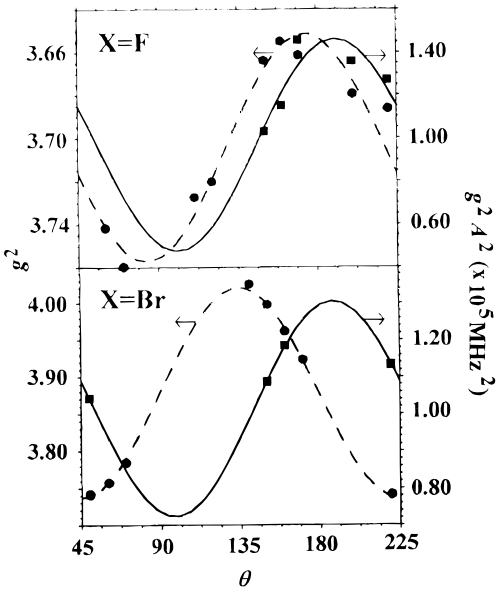

Figure 1. Angular dependencies of g^2 and $(gA^{Mo})^2$ in the ab (or bc*) plane of Tp*$Mn(CO)_3$ for (top) Tp*$MoOF_2$ and (bottom) Tp*$MoOBr_2$. The angle θ is relative to the b axis of the crystal. The data are represented by circles (g^2) and squares $(gA^{Mo})^2$. Solid and dashed curves represent fits of the data to the Schonland equations.[9]

For the Tp*$MoOX_2$ complexes, this direction is approximately along the Mo═O axis, which is constant for analogous sites in each of the doped crystals. The anisotropy of the g matrix, however, is defined by the anisotropy of excited state mixing into the ground state. For the complexes under consideration the ligand field state contributions are expected to be relatively constant since the energies of the ligand field states vary only modestly.[4,17] Charge transfer contributions, however, vary considerably due both to the increasing covalency and the decreasing energy of these excited states down the series. Thus differences in the angle α between complexes seem to primarily reflect the influence of the charge transfer excited states on electronic structure.

For dimethyl sulfoxide reductase, MCD[18] and resonance Raman[19] spectroscopic studies have suggested that the dominant charge transfer interaction is with the dithiolene moiety of the molybdopterin cofactor. An analogous transition is expected for other oxidoreductases. The orientation of this charge transfer state orbital with respect to the ground state orbital should change as the orientation of the ground state orbital responds to changes in the direction of the strongest ligand field. Within this interpretive framework the large α for the very rapid signals suggests significant dithiolene interaction, which is consistent with the high g_1 value.[16] The relatively low values of α for the rapid type 1 signals indicate that the orientation of the ground state orbital has changed and that the charge transfer interaction with the dithiolene cofactor has decreased. This interpretation is also consistent with the relatively low g values observed.[20] These results suggest that the noncoincidence angles of EPR parameters may be correlated with specific electronic structural features related to the effective ligand fields of molybdenum oxidoreductase active site derivatives.

Acknowledgment. Dr. R. Weber of Bruker Instruments, and Prof. H. Frank, Dr. V. Chynwat, and Mr. R. Desamero of the University of Connecticut, Storrs, CT, are gratefully acknowledged for providing access to Q-band EPR spectrometers. Dr. S. DeGala and Dr. V. G. Young are acknowledged for the crystal structure analyses. The authors also acknowledge the National Institutes of Health for support.

Supporting Information Available: Contour plots of the angular variation of the EPR spectra for the doped crystals in three mutually perpendicular planes (3 pages). Ordering information is given on any current masthead page.

IC960913N

(17) Density functional calculations of $[MoOX_4(H_2O)]^-$ anions[16b] show that the orbital compositions and energies of the ground state and first three ligand field excited states for X = Br are very similar to those for X = Cl.

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(20) A reviewer has suggested that the protonation of the terminal sulfido group in xanthine oxidase may account for the orientation dependence on the basis of the covalency of the site in the plane *cis* to the oxo group. While such effects must certainly play a role in the overall electronic structures of the sites, A^{Mo} values for the xanthine oxidase active site derivatives indicate that there are relatively small differences in the net covalency.[16a] The slow signal is the least covalent and would be expected to have the smallest α, in contrast to the experimental results.[13,14] The conclusion that charge transfer excited states are responsible for the *differences* between derivatives seems the most reasonable on the basis of the available evidence.