tested. Both, however, were parameterized to mimic the results of single-configuration ab initio SCF methods. Detailed studies by Schaeffer[22] and Goddard[23] have shown that such procedures do not give satisfactory results for potential surfaces, due to their neglect of election correlation. In MINDO/3 and MNDO electron correlation is tacitly taken into account by modification of the repulsion integrals, as originally suggested by Pariser and Parr.[26]

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Notes

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Single-Crystal Electron Paramagnetic Resonance of Binuclear Mo(V) Complexes. μ-Oxo-bis(oxotetraphenylporphinatomolybdenum(V))

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The chemistry of molybdenum(V) complexes is dominated by the formation of strong Mo–O bonds. Binuclear Mo(V) species typically contain either a single oxo bridge or two oxo bridges and terminal MO═O groups although other species are known. The species containing a single oxo bridge are diamagnetic and the terminal Mo═O groups are cis to the linear Mo–O–Mo bridge.[1] However, the binuclear oxomolybdenum(V) porphyrins,[2,3] with molecular formula $O_3Mo_2(por)_2$,[4] have a nearly linear[5] O═Mo—O—Mo═O group and are paramagnetic. The paramagnetism marks the porphyrin derivatives as unique among well-characterized binuclear Mo(V) complexes. An interaction between the unpaired electrons on the two molybdenum atoms, which almost surely have the ground state $(4d_{xy})^1$,[1,6] would be expected. We have studied the EPR of a single crystal of $O_3Mo_2(TPP)_2$ in order to measure this interaction as well as the other magnetic parameters accessible to measurement.

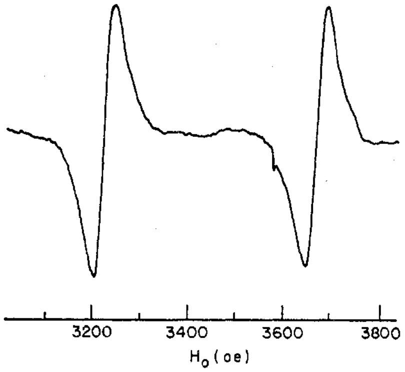

Figure 1. EPR spectrum observed at room temperature from a single crystal of $(MoTPP)_2O_3$.

Results and Discussion

The crystal structure of $O_3Mo_2(TPP)_2$ involves a four-molecule unit cell,[5] with the molecules so distributed that they are magnetically equivalent. Thus, one should see only one species in the EPR spectrum. We performed rotations about three orthogonal axes defined for convenience in the external morphology of the crystal. At each orientation, the spectrum consisted of a pair of lines which we interpreted as the spectrum of one triplet species with a zero-field splitting. We, therefore, set out to fit the spectrum to a spin Hamiltonian

$$H = g_{\parallel}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + D[S_z^2 - {}^1/_3 S(S + 1)]$$

In this equation $S = 1$, the z axis lies along the Mo–Mo direction, x and y are chosen arbitrarily in the plane perpendicular to z, and $g_{\parallel}$, $g_{\perp}$, and D have their conventional meanings. In our rotations about each axis (covering 180°) we found two local maxima in the splitting and one minimum which was essentially zero. One of the maxima was the same size in all three rotations; the other varied. We interpreted the equal maxima as representing the orientation in the plane of the rotation at which the magnetic field is perpendicular to the line connecting the two molybdenum atoms. There is, of course, one such position in all three planes of rotation. The maxima which differed in each rotation were interpreted as representing the position in the plane of rotation at which the magnetic field lay nearest to the Mo–Mo line. The angle between the magnetic field and the Mo–Mo direction differs in each plane, so the maxima differ. These assumptions allowed us to calculate D, the zero-field splitting parameter, and also to fix the orientation of the Mo–Mo direction in our coordinate system. We then examined the spectrum at the indicated orientation and found a splitting of D, as expected. We thus considered that we had verified our assignment. We find $D = 2548$ MHz.

One might expect that D in this compound would be due almost entirely to spin dipolar coupling between the electrons on the two molybdenum atoms. If the electrons can be treated as point dipoles localized on the Mo nuclei, $D = g^2\beta^2/R^3$, with R the Mo–Mo distance. Our values of D result in an estimated R of 3.9 Å, vs. a measured value of 3.8 Å, so the assumption may be considered to be justified.

About 25% of naturally occurring Mo consists of the isotopes ^{95}Mo and ^{97}Mo with spins of $^5/_2$ and very similar magnetic moments.[7] We were able to resolve hyperfine structure well only near the parallel orientation, when the magnetic field lies near the Mo–Mo direction. We attempted to describe the hyperfine structure seen from the complexes containing one isotope with nuclear spin by adding to the spin-Hamiltonian the terms:

$$H' = A_{\parallel} I_z S_z + A_{\perp}(I_x S_x + I_y S_y)$$

Here $I = {}^5/_2$ and, strictly speaking, there should be two pairs of terms as above, one for ^{95}Mo species and one for ^{97}Mo. Since the two have such similar magnetic moments, they will have similar hyperfine constants; however, we cannot resolve their effects. $A_{\parallel}$ and $A_{\perp}$ have the conventional meanings. On the parallel orientation, we obtain a splitting constant of 40.3 G, or 112.8 MHz.

The interpretation of the hyperfine splitting of dimeric species depends on the splitting between the singlet and triplet spin states, called the exchange splitting.[8] The details have been worked out[8] for a system containing two identical nuclei with spin, but the results are, in general, similar if only one of the nuclei has a hyperfine coupling. This is the situation in our experiment, in which the transitions we observe correspond to dimers with one magnetic nucleus. The striking qualitative aspect of the results is that the observed hyperfine splitting equals the hyperfine coupling of the electron with the magnetic nucleus if the exchange splitting is small but only half the hyperfine coupling if the exchange splitting is large. When the hyperfine constant and the exchange splitting are comparable, the spectrum becomes complex and extra transitions may appear. Our data are, in principle, consistent with either limiting case. We see no evidence for extra transitions, but we could not see them readily, were they present, because the spectrum is quite broad. We are inclined to believe that the exchange splitting is large, compared with the hyperfine coupling. This belief is based on the facts that the coupling constant decreases as we go away from the parallel orientation and that, in the solution spectrum, the average coupling constant is 140.8 MHz. As discussed below, the solution spectrum is to be assigned to a monomeric species, but it is reasonable to assume that such a species would have an isotropic hyperfine constant not greatly different from that of the dimer. One then sees that the observed parallel splitting must be only half the parallel hyperfine coupling. Unfortunately, we cannot follow the hyperfine splitting far enough away from parallel to obtain the perpendicular hyperfine splitting and an average hyperfine splitting to compare with the solution value. Use of the solution value for the crystal results in a predicted perpendicular splitting of 49 MHz. The extremely limited angular data we have are consistent with this but can hardly be said to support it because of poor resolution.

The hyperfine structure suggests that the exchange splitting is large compared to 0.007 cm^{-1}. We sought to set an upper limit on the splitting by comparing the spectra at room temperature and at 77 K. We found that the spectrum displayed, as best we could tell, Curie-law behavior over this temperature range. Thus the exchange splitting must be less than perhaps 25 cm^{-1}.

The rather broad limits we have set on the exchange splitting show, nevertheless, the splitting to be rather small. This is expected, since there are not reasonably strong exchange paths connecting the two unpaired electrons.

There is a small but definite angular variation of the center of the spectrum, corresponding to an angular dependence of the spectroscopic splitting factor. The variation is sufficiently small compared to the breadth of the lines (some 150 MHz) and to the spread of the spectrum that we have not gotten an accurate angular variation. It is clear, however, that $g_{\perp} < g_{\parallel}$, $\Delta g = 0.008$, and $\bar{g}$ is quite close to g_0. This is quite a small variation in g. It suggests that the splitting between the d_{xy} orbital and the d_{xz}, d_{yz} orbitals is rather large, since coupling between these is responsible for the derivation of $g_{\perp}$ from g_0 in a crystal field model. The fact that $g_{\perp} < g_{\parallel}$ is consistent with a d_{xy} ground state, since $g_{\parallel}$ involves coupling between d_{xy} and $d_{x^2-y^2}$, much more distant in energy.

The spectrum of a solution of $O_3Mo_2(TPP)_2$ in chloroform has been measured previously.[2] As we have stated, this spectrum must be assigned to a monomeric species, contrary to previous interpretations. The lines are quite sharp, the width being only some 4.0 MHz. We can estimate a line width expected for the dimer from the angular variation of the spectrum, mentioned above. If we assume a correlation time for tumbling of 10^{-11} s, and it could hardly be less than this, we get an expected line width of some 350 MHz, far greater than observed.

The solution spectrum displays Mo hyperfine coupling, with a constant of 140.8 MHz, as mentioned, and also coupling to the nitrogens of the porphyrin with a coupling constant of 7.0 MHz. It, thus, appears to be the same as a spectrum observed by Newton and Davis from solutions of MoTPP(O)(OH) in CH_2Cl_2.[9]

We measured the solution spectrum in chloroform and in benzene and obtained the same spectrum. We cannot say what fraction of the solute was dissociated. We saw no evidence for a dimer spectrum, but it would be rather broad, as mentioned, and hard to observe in the presence of the monomer spectrum.

In summary, the EPR parameters of $O_3Mo_3(TPP)_2$ provide a picture of a pair of nearly independent Mo(V) units, each having its unpaired electron localized strongly in the d_{xy} orbital. The weak coupling between the Mo(V) units might be expected because there are no efficient exchange paths between two d_{xy} orbitals through an intermediate oxygen. Nevertheless, in other weakly coupled d^1 dimeric systems, such as the vanadyl tartrates[10] or the molybdenum(V)–glutathione complex,[11] the paramagnetic centers are more widely separated than in the case at hand.

Experimental Section

Single crystals of the compound were mounted on a device allowing rotation about one axis and were studied with a conventional X-band EPR spectrometer (Varian V-4500) at room temperature.

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Ultraviolet Photoelectron Spectra of Some $Cr(CO)_5L$ Complexes Containing Organosulfide and Organophosphine Ligands

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Ultraviolet photoelectron spectroscopy (UV PES) has become an important tool for studying those transition-metal carbonyl complexes which are sufficiently volatile.[1] In this report we present the results obtained from UV PES measurements on some R_2S and R_3P complexes of $Cr(CO)_5$, providing a comparison between the electronic behavior of the R_2S and R_3P ligands, as well as the various substituents R. Although the range of complexes of this type which can be successfully used for UV PES measurements is limited by involatility on one hand and insufficient vapor-phase stability on the other hand, most of the complexes described below could be obtained in a sufficiently pure state to give good-quality spectra. While small amounts of impurity appeared in the spectra of some of the complexes (see Experimental Section), only the divinyl sulfide complex was unstable enough to prevent its handling and analysis as a pure material. Although its UV PES data showed the evidence of decomposition, useful information could still be obtained.

No UV PES study on R_2S complexes appears to have been previously reported. The spectra of $Cr(CO)_5L$ complexes (where L = NH_3, PH_3, NMe_3, PMe_3) have been measured by Lloyd.[2]

Results and Discussion

The IP values below 12 eV are listed in Table I. The observed bands are due to ionization from orbitals predominantly on the chromium and the R_2S (or R_3P) ligands, while orbitals largely CO in character give rise to peaks above 12 eV.[2,3] The splitting of the ionization from the chromium d orbitals (IP_1, IP_2) results from a breakdown of the degeneracy of the filled t_{2g} orbitals into e and b_2 components. Lloyd has assigned the first peak to the e orbital on the basis of intensity considerations,[2] but it is not clear that this is so in the present study.

The IP values obtained here may be compared with the value of 8.4 eV found for $Cr(CO)_6$.[3] Thus the R_2S and R_3P ligands appear to place a significantly greater electronic charge at the chromium site than the CO. There is no material difference between the effect of the R_2S and R_3P ligands in this respect. Results obtained from C–O stretching frequency measurements appear to present clear evidence that R_2S is a poorer π acceptor than corresponding R_3P,[4] but this difference may be compensated by a weaker σ-donor ability on the part of the R_2S ligand.[5] Graham has discussed the interrelationship between the two properties.[4]

Table I. Vertical Ionization Potentials[a] of $Cr(CO)_5L$

L	IP_1 [b]	IP_2 [b]	IP_3 [c]	IP_4 [c]
$(C_2H_5)_3P$	7.44[d]	7.58	9.67	11.1[e]
$(CH_3)_3P$[f]	7.58[d]	7.72	10.00	
$(C_2H_3)_3P$	7.52[d]	7.66	9.60	10.33[g]
$(C_2H_5)_2S$	7.45	7.67	9.71	11.48
$(CH_3)_2S$	7.59	7.79	10.00	12.10
$(C_2H_3)_2S$	7.6_1	7.8_0	9.48	
$(CH_3)(CH_2Cl)S$	7.74	7.90	10.27	

[a] In eV. [b] Assigned to the chromium d orbitals–see text. [c] Assigned to the ligand orbitals with some admixture of metal character–see text. [d] Shoulder. [e] Additional band at 11.3 eV. [f] Data taken from ref 2. [g] Assigned to the vinyl groups. Additional ligand bands at 10.76 eV and 12.0 eV.

Table II. Appropriate Ionization Potential[a] Data for R_3P and R_2S [b]

Compd	IP_1	IP_2
$(CH_3)_3P$	8.60[c]	11.3
$(C_2H_5)_3P$	8.31[c]	10.4
$(C_2H_3)_3P$	8.51[c]	9.89
$(CH_3)_2S$[d]	8.69[e]	11.20[f]
$(C_2H_5)_2S$[d]	8.46[e]	10.70[f]
$(C_2H_3)_2S$	8.42[e]	
$(CH_3)(CH_2Cl)S$	9.17[e]	

[a] In eV. [b] Data for $(CH_3)_3P$ taken from ref 9. All other values obtained in this laboratory. [c] Assigned to the lone-pair (a_1) orbital. [d] Reference 8 gives: for $(CH_3)_2S$, IP_1 = 8.67 eV, IP_2 = 11.2 eV; for $(C_2H_5)_2S$, IP_1 = 8.44 eV, IP_2 = 10.7 eV. [e] Assigned to the b_1 orbital–see text. [f] Assigned to the a_1 orbital–see text.

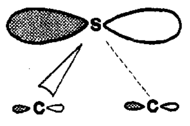
Table III. Increase in Ligand Orbital Ionization Energies[a] upon Complexation with the $Cr(CO)_5$ Group

Ligand	b_1	a_1
$(CH_3)_3P$		1.40
$(C_2H_5)_3P$		1.36
$(C_2H_3)_3P$		1.09
$(CH_3)_2S$	1.31	0.90
$(C_2H_5)_2S$	1.25	0.78
$(C_2H_3)_2S$	1.06	
$(CH_3)(CH_2Cl)S$	1.10	

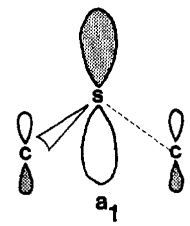
[a] In eV.

The variation of d orbital IP values with the substituent R reflects qualitatively the ability of R to increase the electron density at sulfur or phosphorus[6] (which in turn may be passed on to chromium). Discussions of the effect of substituents directly on the donor atom are frustrated, however, by the unknown differences in the bond angle about the donor atom, with the resulting change in hybridization affecting the nature of the donor orbitals.

The remaining IP's below 12 eV are derived from ligand orbitals, with some chromium orbital character introduced as a result of complexation. Most interesting from the standpoint of the bonding between R_2S ligands and electron acceptors is the fate of the highest occupied R_2S molecular orbitals upon complexation. A sample calculation was performed on dimethyl sulfide complexed to a reference acid (in this case BH_3), using the CNDO/2 technique.[7] The B–S distance was varied in steps from 2.0 to 3.0 Å. In the uncomplexed R_2S the two highest occupied molecular orbitals are of the type[8]



b_1



a_1