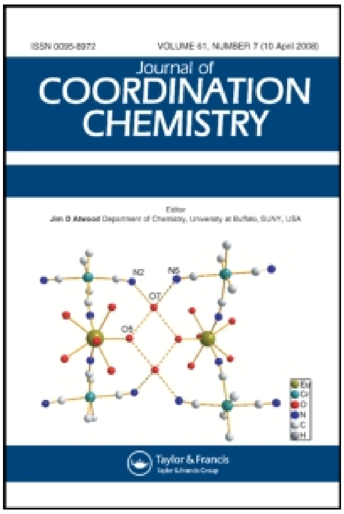

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Ali H. Al-mowali[a]; W. A. A. Kuder[a]; M. J. Bader[a]; N. N. Majead[a]
[a] Department of Chemistry, University of Basrah, Basrah, Iraq

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ELECTRON PARAMAGNETIC RESONANCE SPECTRA OF TETRAETHYLAMMONIUM TETRA (PHENYLTHIOLATO)OXOMOLYBDATE(V)

ALI H. AL-MOWALI, W. A. A KUDER, M. J. BADER and N. N. MAJEAD

Department of Chemistry, University of Basrah, Basrah, Iraq

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X-Band ESR spectra of $Et_4N[MoO(SPh)_4]$ in a range of solvents have been recorded at 77°K and 298°K and are analysed in detail. The Spin-Hamiltonian parameters have been extracted and are equated to the atomic orbital coefficients in some of the molecular orbitals involved in bonding in this compound. The unpaired electron lies in the metal-ion $4d_{xy}$ orbital and is strongly delocalized (43%) on to the sulfur ligands. Changes in the Spin-Hamiltonian parameters when a coordinated polar solvent is added to $Et_4N[MoO(SPh)_4]$ are accounted for.

INTRODUCTION

Although ESR spectra have been recorded for a large number of molybdenum(V) complexes,[1-4] relatively few reports[5,6] have been made on compounds containing Mo–S bonds. Here we describe ESR spectra obtained from glasses containing oxophenylthiolato anion in a range of solvents, and discuss the conclusions that can be drawn about electron distribution within this complex when such spectra are analysed in detail.

EXPERIMENTAL

Tetraethylammonium Tetra(Phenylthiolato)oxomolybdate(V), $Et_4N[MoO(SPh)_4]$ was prepared[6] by addition of an equimolar mixture of thiophenol and triethylamine in MeCN to a solution of Trichlorooxobis(tetrahydrofuran)molybdenum(V) in MeCN and the blue crystalline product was isolated by addition of NEt_4I. The recrystallized $Et_4N[MoO(SPh)_4]$ was used to prepare the adducts with MeCN, Pyridine, Ethanol and Dioxane by direct addition of purified solvents.

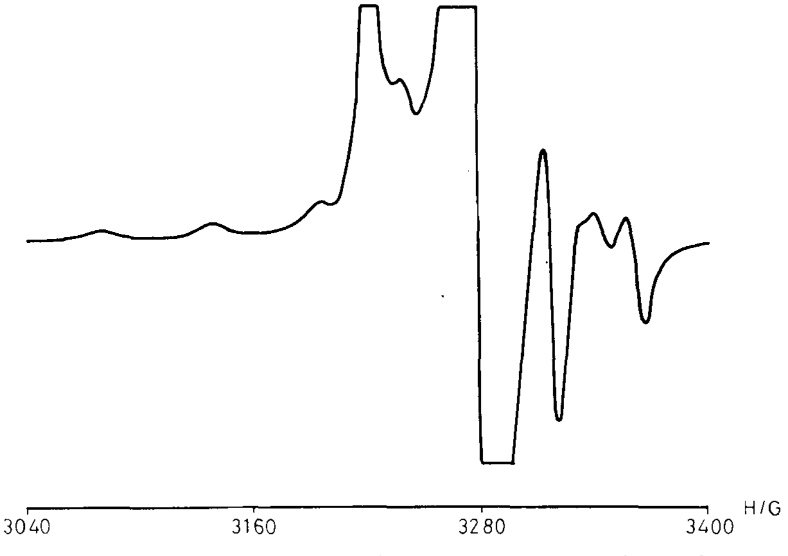

FIGURE 1 The epr spectrum of a magnetically dilute solution of $Et_4N[MoO(SPh)_4]$ in pyridine at 77°K.

ESR spectra were recorded on a Varian E-109 Spectrometer at 298°K and at 77°K in about 10^{-3} M solutions. Typical ESR spectrum of $Et_4N[MoO(SPh)_4]$ in pyridine recorded at 77°K is shown in the Figure. Visible-UV absorption spectra were recorded on a Pye-Unicam SP8-100 Spectrophotometer, using matched 1 cm quartz cells. The spectra were all solvent dependent and the positions of the absorption mixima are summarised in Table I for each solvent.

TABLE I
Band maxima (10^2 m^{-1}) in the visible-UV absorption spectra of $Et_4N[MoO(SPh)_4]$ in various solvents

Solvent	d ← d transitions	Metal ion ← sulfer charge transfer
CCl_4	18 000, 30900	34 900
Dioxane	16 700, 30900	34 800
MeCN	16 700, 30800	34 800
C_5H_5N	16 500, 30800	34 800
EtOH	16 400, 30800	34 700

RESULTS AND DISCUSSION

The ESR spectra were all characteristic of one unpaired electron moving in an axially symmetric orbital, and so the Spin-Hamiltonian has the form

$$\mathcal{H} = g_{\|}\beta H_z S_z + g_{\perp}\beta(H_x S_x + H_y S_y) + A S_z I_z + B(S_x I_x + S_y I_y) \quad (1)$$

The nuclear spin quantum number, I, for ^{95}Mo (natural abundance 15.78%) and ^{97}Mo (natural abundance 9.60%) are both 5/2. The magnetic dipole moments of these isotopes differ by only 1% and, since we were not able to resolve any molybdenum isotopic fine structure, all absorption spectra were analysed using methods already described.[7] Iterative computation of the ESR spectra lead to the Spin-Hamiltonian parameters listed in Table II. The quantity $g_{\|}$ was greater than $g_{\perp}$, a situation which is unusual in d^1 species subjected to a tetragonal ligand field, and it therefore follows[8-10] that charge transfer from sulfur ligand to the central metal ion must be considered in accounting for the Spin-Hamiltonian parameters.

TABLE II
Spin-Hamiltonian parameters for $Et_4N[MoO(SPh)_4]$ in various solvents. All hyperfine tensor components are in units of m^{-1}. Limits of error for $g_{\|}$, $g_{\perp}$ and $\langle g \rangle$ are ±0.0005, for A, B and $\langle a \rangle$ ±0.005.

Solvent	$g_{\|}$	$g_{\perp}$	A	B	$\langle g \rangle$	$\langle a \rangle$
CCl_4	2.0198	1.9768	0.543	0.271	1.9911	0.362
Dioxane	2.0194	1.9759	0.533	0.258	1.9904	0.349
MeCN	2.0191	1.9755	0.513	0.245	1.9900	0.334
C_5H_5N	2.0190	1.9754	0.512	0.244	1.9899	0.333
EtOH	2.0190	1.9750	0.510	0.234	1.9897	0.326

More precise information can be obtained about electron distributions within this complex if the Spin-Hamiltonian parameters are equated with the coefficients in appropriate linear combinations of atomic orbitals. According to ligand field theory, molybdenum-ion orbitals combine with ligand group orbitals ϕ with appropriate symmetry to form the following magnetically important bonding and antibonding molecular orbitals in a C_{4v} complex

$$\begin{aligned}
\psi^*(B_2) &= \beta_2 d_{xy} - \beta_2'\phi(B_2)\\
\psi^*(E) &= \epsilon\, d_{xz} - \epsilon'\,\phi(E)\\
&\quad \text{or } d_{yz} \qquad (2)\\
\psi^*(B_1) &= \beta_1 d_{x^2-y^2} - \beta_1'\phi(B_1)\\
\psi(B_1) &= \beta_1' d_{x^2-y^2} + \beta_1\phi(B_1)
\end{aligned}$$

Where the unpaired electron is in the antibonding orbital $\psi^*(B_2)$. Spin-orbit coupling at the central metal-ion and at the sulfur ions, Zeeman interactions and hyperfine interactions all perturb the combinations of the orbital functions (2) with the various allowed electronic spin functions, and if the matrix elements of these interactions are equated with those of the Spin-Hamiltonian (1) then the Spin-Hamiltonian parameters can be expressed as functions of the coefficients of the molecular orbitals. These functions have been shown to be[8-10]

$$g_{\|} = 2.0023 - 2\left[\frac{(2\beta_1\beta_2\xi_{Mo} - \beta_1'\beta_2'\xi_s)(2\beta_1\beta_2 - 2\beta_1'\beta_2')}{\Delta E(B_1^*)} - \frac{(2\beta_1'\beta_2\xi_{Mo} + \beta_1\beta_2'\xi_s)(2\beta_1'\beta_2 + \beta_1\beta_2')}{\Delta E(B_1)}\right] \quad (3)$$

$$g_{\perp} = 2.0023 - \frac{2\xi_{Mo}\beta_2^2\epsilon^2}{\Delta E(E^*)} \quad (4)$$

$$A = P\left[-K - \frac{4}{7}\beta_2^2 - 8\xi_{Mo}\beta_2^2\left(\frac{\beta_1^2}{\Delta E(B_1^*)} - \frac{\beta_1'^2}{\Delta E(B_1)}\right) - \frac{6}{7}\frac{\xi_{Mo}\beta_2^2\beta_1^2}{\Delta E(E^*)}\right] \quad (5)$$

$$B = P\left[-K + \frac{2}{7}\beta_2^2 - \frac{11}{7}\frac{\xi_{Mo}\beta_2^2\beta_1^2}{\Delta E(E^*)}\right] \qquad (6)$$

$$\langle a\rangle = -PK - (2.0023 - \langle g\rangle)P \qquad (7)$$

Where ξ_{Mo} and ξ_s are the spin-orbit coupling constants of the molybdenum and sulfur ions respectively, K is the isotropic contact term and $\Delta E(\psi)$ and $\Delta E(\psi^*)$ are the energies of the appropriate bonding and antibonding excited levels (relative to that of the $\psi^*(B_2)$ level). $g_\parallel$ is greater than $g_\perp$ in this molecule and therefore in Eqs. (3) and (5) we have allowed for mixing of states obtained by exciting bonding electrons but we have not considered similar effects in Eqs. (4) and (6).

In order to obtain the values of the molecular orbital coefficients from Eqs. (3)–(6), estimates of the values of ξ_{Mo}, ξ_s and P together with the assignment of the band maxima in the visible-UV absorption spectra were needed. The values of ξ_{Mo} and P for the molybdenum ion were taken[11] to be that of Mo^{3+} since the effective charge on molybdenum is expected to be less than its oxidation number by two units, and have been shown[11,12] to be 82 000 m^{-1} and -0.55 m^{-1} respectively. ξ_s value for the sulfur atom was assumed to be identical with the value for the free atom, i.e. 38 200 m^{-1}.[13]

The relative intensities, effects of solvents on the positions of the maxima, and consistency with the ESR data, all indicate that the band maxima in the visible-UV absorption spectra listed in Table I should be assigned to the transitions listed below.

Band maximum ($10^2 m^{-1}$)	Transition
16 700	$\psi^*(E) \leftarrow \psi^*(B_2)$
30 800	$\psi^*(B_1) \leftarrow \psi^*(B_2)$
34 800	$\psi^*(B_2) \leftarrow \psi(B_1)$

The value of ξ_{Mo}, ξ_s and P together with the assignment of the band maxima now enable the values of K, β_2, β_1 and ϵ to be evaluated using Eqs. (3)–(7). The parameters obtained in this way are listed in Table III.

Since the molecular orbital that contains the unpaired electron, has zero electron spin density at the molybdenum nucleus and does not mix with the metal 4s orbital in C_{4v} symmetry, there is no direct way of putting unpaired electron density on the nucleus. The non zero values of K, must then arise from the Spin-Polarization.

The values of β_2 in Table III, which reflects the degree of delocalisation of in-plane π-bonding electron on to the ligands, show that in each case the unpaired electron lies in the metal-ion $4d_{xy}$ and it is strongly (43%) delocalised on to the sulfur atoms.

TABLE III

K values and molecular orbital coefficients for $Et_4N[MoO(SPh)_4]$ in various solvents

Solvent	K	β_2	β_1	ϵ
CCl_4	0.65	0.760	0.880	0.813
Dioxane	0.62	0.754	0.882	0.806
MeCN	0.59	0.750	0.881	0.800
C_5H_5N	0.59	0.750	0.881	0.798
EtOH	0.58	0.747	0.880	0.795

The values of β_1 and ϵ in Table III, which reflects the degree of delocalization of σ and out-of-plane π-bonding electrons away from sulfur atoms into metal-ion $4d_{x_2-y_2}$ and $4d_{xy}$ or $4d_{yz}$ respectively, also shows that these electrons are strongly delocalized.

Addition of polar solvent to the sixth co-ordination position[14,15] of $Et_4N[MoO(SPh)_4]$ has no measurable effect on σ-bonding to the metal-ion $4d_{x_2-y_2}$ orbital, and it has little effect on the transition energies $|\Delta E(B_1)|$. Hence co-ordinating solvent does not alter $g_\parallel$. On the other hand, in the case of in-plane π-bonding to the metal-ion $4d_{xy}$ orbital, and of out-of-plane π-bonding to the metal-ion $4d_{xz}$ and $4d_{yz}$ orbitals, the coordinated solvent does cause very small additional drifts of electrons away from the central metal ion and also decreases the magnitudes of the transition energies $|\Delta E(E)|$. The addition of polar solvent therefore noticeably decreases the magnitude of $g_\perp$ and the magnitudes of the magnetic hyperfine tensor components. This polar solvent should presumably have the greatest influence on σ-bonding to the metal-ion $4d_{z_2}$ orbital, but this involves molecular orbitals of A_1 symmetry which are inaccessible to us since they do not affect the paramagnetic properties of these complexes.

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