

Electron Spin Resonance Spectra of some Oxothiolato Schiff-Base Complexes of Molybdenum(V)

ALI H. AL-MOWALI

Department of Chemistry, University of Glasgow, Glasgow G12 8QQ, U.K.

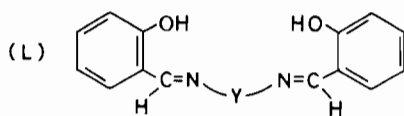
Received February 1, 1984

X-band e.s.r. spectra of $[\text{MoO}(\text{SR})\text{L}]$ complexes ($\text{L} = \text{BSEN}$, BSTN or BSOP and $\text{R} = \text{Ph}$ or *p*-tolyl) were recorded at room temperature and 77 K. The spin-Hamiltonian parameters were extracted from the spectra recorded at 298 K, and from spectra of magnetically dilute glasses taken at 77 K. These parameters and data obtained from electronic absorption spectra were used to calculate the molecular orbital coefficients for these complexes. It is pointed out that the principal values of the *g*-tensor can be used to distinguish between *cis* and *trans* isomers of the complexes.

Introduction

The structure and bonding of first-row transition metal ions with chelating Schiff-base ligands have been studied by electron spin resonance spectroscopy [1]. The *g* and metal hyperfine tensors have been used to investigate the structure and the electron distribution in these complexes. On the other hand, very little work has been done on the corresponding complexes of the early heavy transition metal ions [2, 3]. We describe in the present paper e.s.r. spectra obtained from magnetically dilute glasses containing the oxothiolato Schiff-base complexes of molybdenum(V), in order to obtain detailed information about the structure and the nature of the bonding in these complexes.

The following abbreviations have been used for the Schiff-base ligands employed in the present work:



Experimental

The oxothiolato Schiff-base complexes $[\text{MoO}(\text{SR})\text{L}]$, where L is the appropriate Schiff-base ligand and $\text{R} = \text{Ph}$ or *p*-tolyl, were prepared [4] by addition of an equimolar mixture of RSH and Et_3N in MeCN to a solution of $[\text{MoO}(\text{Cl})\text{L}]$ in MeCN and the crystalline products were purified as described earlier [4].

The e.s.r. spectra of the complexes were recorded with a Decca X3 spectrometer at 298 K and 77 K in about 10^{-4} M CH_2Cl_2 solutions. Examples of the e.s.r. spectra for $[\text{MoO}(\text{SC}_6\text{H}_5)(\text{BSEN})]$ at 298 K and for $[\text{MoO}(\text{SC}_6\text{H}_5)(\text{BSTN})]$ at 77 K are shown in Figs. 1 and 2, respectively.

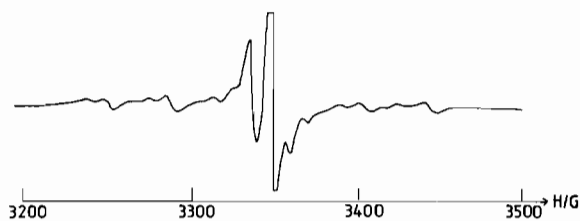


Fig. 1. The e.s.r. spectrum of $[\text{MoO}(\text{SC}_6\text{H}_5)(\text{BSEN})]$ in CH_2Cl_2 at 298 K.

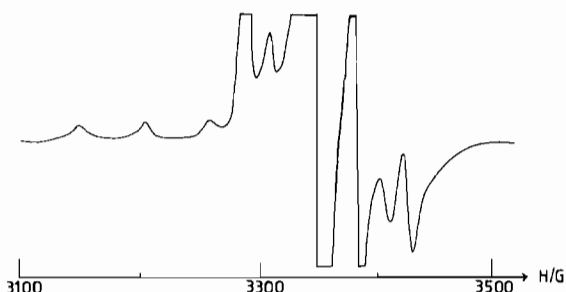


Fig. 2. The e.s.r. spectrum of $[\text{MoO}(\text{SC}_6\text{H}_5)(\text{BSTN})]$ in CH_2Cl_2 at 77 K.

Results and Discussion

E.s.r. Spectra

The e.s.r. spectra of $[\text{MoO}(\text{SR})(\text{BSTN})]$ and $[\text{MoO}(\text{SR})(\text{BSOP})]$ in CH_2Cl_2 solutions at room

temperature were well resolved, and each one consisted of a central intense line corresponding to the molybdenum ($I = 0$) nucleus and six relatively weak hyperfine lines on either side of the central line arising from $\text{Mo}^{95,97}$ ($I = 5/2$). The e.s.r. spectrum of $[\text{MoO}(\text{SC}_6\text{H}_5)(\text{BSEN})]$ in CH_2Cl_2 was complicated and consisted of two partially overlapping e.s.r. spectra of the type described for $[\text{MoO}(\text{SC}_6\text{H}_5)(\text{BSTN})]$ and $[\text{MoO}(\text{SC}_6\text{H}_5)(\text{BSOP})]$, indicating the presence of two paramagnetic species.

The e.s.r. spectra of the $[\text{MoO}(\text{SR})\text{L}]$ complexes have the same characteristic features as those for $[\text{MoO}(\text{Cl})\text{L}]$, where $\text{L} = \text{BSTN}$, BSOP and BSEN , obtained in solutions at room temperature which have been assigned *cis*, *trans* and mixture of *cis* and *trans* isomers for $[\text{MoOCl}(\text{BSTN})]$, $[\text{MoOCl}(\text{BSOP})]$ and $[\text{MoOCl}(\text{BSEN})]$ respectively [3] on the basis of IR spectropic measurements (*cis* and *trans* refer to the position of the Cl ligand with respect to the oxo group). It is therefore, highly likely that $[\text{MoO}(\text{SR})\text{L}]$ complexes have the same geometries, when Cl^- is replaced by SR. Table I lists the isotropic g_0 and A_0 obtained from the analysis of the e.s.r. spectra for these complexes.

The e.s.r. spectra of a frozen solution of $[\text{MoO}(\text{SR})(\text{BSTN})]$ and $[\text{MoO}(\text{SR})(\text{BSOP})]$ at 77 K were all characteristic of one unpaired electron moving in an axially symmetric orbital. Therefore the magnetic data could be fit to the usual spin-Hamiltonian [5] and analysed using the method already described [6]. The spin-Hamiltonian parameters calculated by this method are listed in Table II. In the case of $[\text{MoO}(\text{SC}_6\text{H}_5)(\text{BSEN})]$, the frozen e.s.r. spectrum was too broad and complex to analyse, which again

TABLE I. Isotropic Spin-Hamiltonian Parameters for Oxothiolato Schiff-Base Complexes. The A_0 values are in units of cm^{-1} . Limits of error are $g_0 \pm 0.0005$, $A_0 \pm 0.00005 \text{ cm}^{-1}$.

Complex	g_0	A_0
$[\text{MoO}(\text{SC}_6\text{H}_5)(\text{BSEN})]$	1.9847, 1.9784	0.00350, 0.00386
$[\text{MoO}(\text{SC}_6\text{H}_5)(\text{BSTN})]$	1.9847	0.00350
$[\text{MoO}(\text{SC}_6\text{H}_4\text{Me-p})(\text{BSTN})]$	1.9844	0.00353
$[\text{MoO}(\text{SC}_6\text{H}_5)(\text{BSOP})]$	1.9784	0.00386
$[\text{MoO}(\text{SC}_6\text{H}_4\text{Me-p})(\text{BSOP})]$	1.9781	0.00388

TABLE II. Spin-Hamiltonian Parameters for Oxothiolato Schiff-Base Complexes. All hyperfine tensor components are in units of cm^{-1} . Limits of error for g_{\parallel} and g_{\perp} are ± 0.0005 , for A_{\parallel} and A_{\perp} ± 0.0005 .

Complex	g_{\parallel}	g_{\perp}	A_{\parallel}	A_{\perp}
$[\text{MoO}(\text{SC}_6\text{H}_5)(\text{BSTN})]$	2.0162	1.9689	0.00554	0.00250
$[\text{MoO}(\text{SC}_6\text{H}_4\text{Me-p})(\text{BSTN})]$	2.0160	1.9688	0.00556	0.00253
$[\text{MoO}(\text{SC}_6\text{H}_5)(\text{BSOP})]$	1.9892	1.9730	0.00605	0.00278
$[\text{MoO}(\text{SC}_6\text{H}_4\text{Me-p})(\text{BSOP})]$	1.9892	1.9728	0.00608	0.00279

suggests that two isomers for this complex are also present in the frozen solutions.

Infra-red spectroscopy has previously been used [3] to distinguish between *cis* and *trans* isomers for $[\text{MoO}(\text{Cl})\text{L}]$ complexes, but unfortunately the infra-red spectra of the complexes studied here do not enable us to discriminate between these isomers since all compounds show broad absorptions at 330–380 cm^{-1} due to Mo–S bond stretching frequency. However, it is possible to obtain similar information from the e.s.r. data obtained from analysis of the e.s.r. spectra at 77 K. The g-tensor components for $[\text{MoO}(\text{SR})\text{L}]$ listed in Table II could be used to distinguish the *cis* from *trans* isomers. For the complexes $[\text{MoO}(\text{SR})(\text{BSTN})]$ in which the SR group is assumed to be *cis* to the oxygen atom, the quantity g_{\parallel} was greater than the spin only value 2.0023 while for the complexes $[\text{MoO}(\text{SR})(\text{BSOP})]$ in which the SR group is assumed to be *trans* to the oxygen atom, the quantity g_{\parallel} was smaller than the spin only value. The increase in the values of g_{\parallel} for the *cis* isomers compared with *trans* isomers could be attributed to the effect of the spin-orbit coupling with sulfur ligand in the basal plane of the complexes, since the spin-orbit coupling with light atoms such as oxygen or nitrogen is relatively small.

Bonding in Oxothiolato Schiff-Base Complexes

The data obtained from the e.s.r. and optical spectra can now be used to obtain values for the coefficients in the molecular orbitals for the complexes, and hence to obtain information about the bonding. Because of the axially symmetric spin-Hamiltonian parameters we assume that $[\text{MoO}(\text{SR})\text{L}]$ complexes have effectively C_{4v} symmetry, with the unpaired electron in an antibonding orbital $\psi^*(B_2)$. The explicit form of the magnetically important molecular orbitals appropriate to this symmetry are as in eqns. (1)–(4):

$$\psi^*(B_2) = \beta_2 d_{xy} - \beta'_2 \phi(B_2) \quad (1)$$

$$\psi^*(E) = \epsilon d_{xz} - \epsilon' \phi(E) \quad (2)$$

or d_{yz}

$$\psi^*(B_1) = \beta_1 d_{x^2-y^2} - \beta'_1 \phi(B_1) \quad (3)$$

$$\psi(B_1) = \beta'_1 d_{x^2-y^2} + \beta_1 \phi(B_1) \quad (4)$$

where ϕ are the ligand group orbitals of appropriate symmetry. These basic functions are perturbed by spin-orbit coupling, Zeeman and hyperfine interactions. The e.s.r. parameters may be expressed as functions of the coefficients of the orbitals (1)–(4). These functions have been shown to be [7–9] as in eqns. (5)–(9):

$$g_{\parallel} = 2.0023 - 2 \left[\frac{(2\beta_1\beta_2\zeta_{Mo} - \beta'_1\beta'_2\zeta_L)(2\beta_1\beta_2 - \beta'_1\beta'_2)}{\Delta E(B_1^*)} - \frac{(2\beta'_1\beta_2\zeta_{Mo} + \beta_1\beta'_2\zeta_L)(2\beta'_1\beta_2 + \beta_1\beta'_2)}{\Delta E(B_1)} \right] \quad (5)$$

$$g_{\perp} = 2.0023 - \frac{2\zeta_{Mo}\beta_2^2\epsilon^2}{\Delta E(E^*)} \quad (6)$$

$$A_{\parallel} = P \left[-K - 4/7\beta_2^2 - 8\zeta_{Mo}\beta_2^2 \times \left(\frac{\beta_1^2}{\Delta E(B_1^*)} - \frac{\beta_1'^2}{\Delta E(B_1)} \right) - 6/7 \frac{\zeta_{Mo}\beta_2^2\beta_1^2}{\Delta E(E^*)} \right] \quad (7)$$

$$A_{\perp} = P \left[-K + 2/7\beta_2^2 - 11/7 \frac{\zeta_{Mo}\beta_2^2\beta_1^2}{\Delta E(E^*)} \right] \quad (8)$$

$$A_0 = -PK - (2.0023 - g_0)P \quad (9)$$

Here ζ_{Mo} and ζ_L are the spin-orbit coupling constants of the molybdenum and the equatorial sulfur and/or oxygen ions respectively, K is the isotropic Fermi contact parameter and $\Delta E(\psi)$ and $\Delta E(\psi^*)$ are the energies of the appropriate bonding and anti-bonding excited levels (relative to that of the $\psi^*(B_2)$ level). Spin-orbit coupling of the ligand nitrogen has been ignored due to its small size relative to that of the sulfur and oxygen ligands. For all oxothiolato Schiff-base complexes g_{\parallel} is greater than g_{\perp} and therefore in eqns. (5) and (7) we have allowed for mixing of states obtained by exciting bonding electrons, but we have not considered similar effects in eqns. (6) and (8).

In order to evaluate the molecular orbital coefficients from equations (5)–(9), the values of ζ_{Mo} , ζ_L , P and the electronic excitation energies $\Delta E(B_1^*)$, $\Delta E(B_2^*)$ and $\Delta E(E^*)$ must be known. The values of ζ_{Mo} and P for the molybdenum ion were taken [10] to be those 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 [10, 11] to be 820 cm^{-1} and -0.0055 cm^{-1} respectively. ζ_L values for the sulfur and oxygen ions were assumed to be identical with the values for the free atoms, *i.e.* 382 cm^{-1} and 151 cm^{-1} respectively [12].

The electronic spectra of the *cis* and *trans* complexes in CH_2Cl_2 were obtained in the region $10,000 \text{ cm}^{-1}$ and $30,000 \text{ cm}^{-1}$. In the case of *cis* complexes, only a weak absorption at *ca.* $24,000 \text{ cm}^{-1}$ and a very intense charge transfer band at *ca.* $17,500 \text{ cm}^{-1}$ were observed. The high energy transition may be assigned to the d–d transition $\Delta E(B_1^*)$ while the low energy transition may be assigned to $\Delta E(B_1)$ in which an electron transfers from an orbital, which is essentially the sulfur molecular orbital, to that orbital which contains the unpaired electron. The other d–d transition is believed to be masked by the charge transfer band and a lower limit of $17,000 \text{ cm}^{-1}$ is assigned to $\Delta E(E^*)$. In the case of *trans* complexes a weak absorption at *ca.* $25,000 \text{ cm}^{-1}$, a very weak inflexion at $16,000 \text{ cm}^{-1}$ and an intense charge transfer band at *ca.* $17,000 \text{ cm}^{-1}$ were observed. The weak transitions at $25,000 \text{ cm}^{-1}$ and $16,000 \text{ cm}^{-1}$ may be assigned to the d–d transitions $\Delta E(B_1^*)$ and $\Delta E(E^*)$ respectively while the intense band at $17,000 \text{ cm}^{-1}$ may be assigned to $\Delta E(B_1)$ in which an electron transfers from an orbital, which is partially the oxygen molecular orbital, to that orbital which contains the unpaired electron.

The assignment of the electronic transitions together with the value of ζ_{Mo} , ζ_L and P now allow us to calculate K , β_2 , β_1 and ϵ from eqns. (5)–(9). The parameters obtained in this way for the *cis* and *trans* complexes are listed in Table III.

TABLE III. K and Molecular Orbital Coefficients for Oxothiolato Schiff-Base Complexes.

Complex	K	β_2	β_1	ϵ
[MoO(SC ₆ H ₅)(BSTN)]	0.62	0.78	0.84	0.82
[MoO(SC ₆ H ₄ Me-p)(BSTN)]	0.62	0.79	0.84	0.83
[MoO(SC ₆ H ₅)(BSOP)]	0.67	0.86	0.88	0.80
[MoO(SC ₆ H ₄ Me-p)(BSOP)]	0.68	0.87	0.89	0.80

The values of β_2 in Table III, which indicate the extent of in-plane π -bonding between the metal $4d_{xy}$ orbital and the ligand π -orbitals, show that in each case the unpaired electron lies in the metal $4d_{xy}$ orbital and is strongly delocalised, onto ligands in the case of *cis* complexes whereas relatively less delocalisation of this electron is found in the *trans* complexes. The decrease in the values of β_2 for the *cis* complexes can be attributed to the presence in the basal plane of the complexes, of the sulfur ligand known to be a good π -bonding ligand.

The values of β_1 in Table III indicate the extent of in-plane σ -bonding between the metal $4d_{x^2-y^2}$ orbital and the ligand σ -orbital, showing a considerable degree of covalency in the metal–ligand bonds for both *cis* and *trans* complexes. These data also show that the bonding in the *cis* complexes is stronger than in the *trans* complexes.

The values of ϵ are a measure of the extent of the out-of-plane π -bonding between the metal $4d_{xz}$ and $4d_{yz}$ orbitals and the ligand π -orbitals. These values again show an appreciable degree of covalency in the metal–ligand bonds for both *cis* and *trans* complexes, and that there is slightly more covalency in the *trans* complexes than in the *cis* complexes.

From the above results it may be concluded that the coordination of only one sulfur atom in the equatorial position is sufficient to cause great influence on both in-plane σ and π -bonding, and hence to cause the g_{\parallel} value to be greater than the spin-only value. Coordination of sulfur atoms in the axial position exerts little effect on out-of-plane π -bonding and therefore increases slightly the magnitude of g_{\perp} . This axial coordination should presumably have the greatest influence on the σ -bonding coefficient of the $4d_{z^2}$ orbital, but this cannot be evaluated since neither g nor the A values involve this energy level.

Acknowledgements

The author gratefully acknowledges Dr. A. L. Porte for providing laboratory facilities and the University of Glasgow for hospitality.

References

- 1 A. B. Goodman and J. B. Raynor, *Adv. Inorg. Chem. Radiochem.*, **13**, 135 (1970).
- 2 J. R. Dilworth, C. A. McAuliffe and B. J. Sayle, *J. Chem. Soc. Dalton Trans.*, 849 (1977).
- 3 C. A. McAuliffe, F. P. McCullough, M. J. Parrott, C. A. Rice, B. J. Sayle and W. Levason, *J. Chem. Soc. Dalton Trans.*, 1762 (1977).
- 4 K. Dey, R. K. Maiti and J. K. Bahr, *Transition Met. Chem.*, **6**, 346 (1981).
- 5 A. Abragam and M. H. L. Pryce, *Proc. R. Soc. London, Ser. A*, **205**, 135 (1951).
- 6 A. H. Al-Mowali and A. L. Porte, *J. Chem. Soc. Dalton Trans.*, 50 (1975).
- 7 H. Kon and N. E. Sharpless, *J. Chem. Phys.*, **42**, 906 (1965).
- 8 K. DeArmond, B. B. Garrett and H. S. Gutowsky, *J. Chem. Phys.*, **42**, 1019 (1965).
- 9 H. Kon and N. E. Sharpless, *J. Phys. Chem.*, **70**, 105 (1966).
- 10 P. T. Monoharan and M. T. Rogers, *J. Chem. Phys.*, **49**, 5510 (1968).
- 11 L. A. Dalton, R. D. Bereman and C. H. Brubaker, *Inorg. Chem.*, **8**, 2477 (1969).
- 12 P. W. Atkins, 'Quanta: a Handbook of Concepts', Clarendon Press, Oxford, p. 271 (1974).