An Electron Spin Resonance Study of the Oxygenation of a Quadridentate Thiosalicylideneimine Cobalt(II) Chelate

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E.s.r. spectroscopy has been used to show that the cobalt(II) chelate of *NN'*-ethylenebis(thiosalicylideneiminate) (tsalen) binds ligands such as pyridine and dioxygen at low temperatures in frozen solutions. At ambient temperatures the complex reacts only very weakly with these ligands and no crystalline adducts are obtained; this contrasts markedly with the behaviour of [Co(salen)] [salen = *NN'*-ethylenebis(salicylideneiminate)] a well known oxygen-carrier. Detailed computer simulation of the spectral line shapes have been made from which a value for the Co–O–O angle in the dioxygen adduct has been deduced as well as accurate values of the *g* and *A* parameters. Reasons for the differences in the strength of axial ligand binding by the thio- and oxo-Schiff-base chelates are briefly discussed.

WE have recently described the synthesis and chemical and magnetic properties of cobalt(II) chelates of some thiosalicylideneiminato-ligands.[1-4] It was noted that quadridentate species of the [Co(tsalen)] [tsalen = *NN'*-ethylenebis(thiosalicylideneiminate)] type showed a lower affinity for the binding of ligands such as pyridine and dioxygen than is the case for the oxo-analogue, [Co(salen)] [salen = *NN'*-ethylenebis(salicylideneiminate)]. Low temperatures were required to obtain definitive evidence for the co-ordination of these molecules, and the technique of e.s.r. spectroscopy has proved particularly useful in following such interactions. Approximate *g* and *A* values, deduced by visual inspection of the spectra, have recently been reported.[3] Here we describe detailed computer simulation studies of the spectral line shapes and show that the Co–O–O angle can be deduced as well as the *g* and *A* parameters.

EXPERIMENTAL

The cobalt(II)–thiosalicylideneimine chelates were prepared as described previously.[3] E.s.r. spectra were recorded on a Varian E12 instrument at *X*-band frequencies. The variable-temperature attachment was set at 130 K. The 1 : 1 oxygen adducts were prepared in the e.s.r. tube by dissolving the Co^{II} chelate in the appropriate solvent in the presence of air, followed by rapid cooling. In one case, using pyridine, the O_2 ligand was displaced by bubbling a stream of nitrogen gas through the solution; the spectrum of the Co^{II}–pyridine adduct was then obtained.

RESULTS AND DISCUSSION

The e.s.r. spectrum of the neat solid Co^{II} chelate, [Co(tsalen)], shows reasonable resolution (Figure 1) with

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[1] A. van den Bergen, M. F. Corrigan, K. S. Murray, R. M. Slade, and B. O. West, *Inorg. Nuclear Chem. Letters*, 1974, **10**, 859.

[2] M. F. Corrigan, K. S. Murray, R. M. Sheahan, B. O. West, G. D. Fallon, and B. M. Gatehouse, *Inorg. Nuclear Chem. Letters*, 1975, **11**, 625.

[3] M. F. Corrigan and B. O. West, *Austral. J. Chem.*, 1976, **29**, 1413.

[4] K. S. Murray and R. M. Sheahan, *J.C.S. Dalton*, 1976, 999.

the hyperfine splitting of the $I = 7/2$ cobalt nuclear spin being clearly visible. Though computer simulation of the spectrum has not been attempted, it is evident from the spread of the lines that the three g values are more isotropic than is the case for the oxo-analogue, [Co(salen)], in agreement with the μ_I values determined by single-crystal susceptibility measurements.[4] The reason for the uneven separation which can be seen in parts of the hyperfine structure is not clear, but may be due to pair interactions between neighbouring cobalt ions; the compound has been shown to have a ligand-bridged dimeric structure.[2]

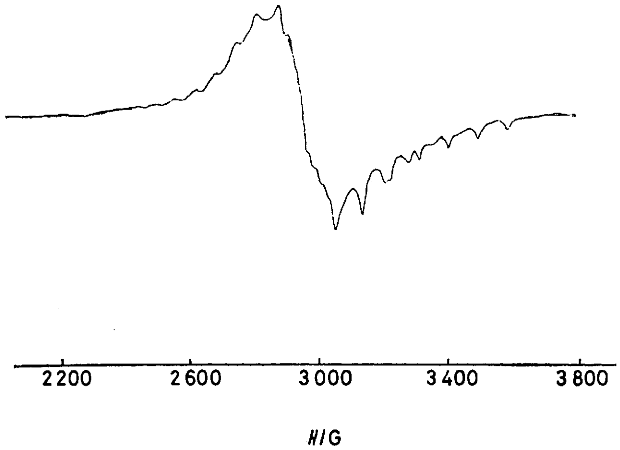


FIGURE 1 E.s.r. spectrum of powdered [Co(tsalen)] at 130 K. (Microwave frequency 9 150 MHz)

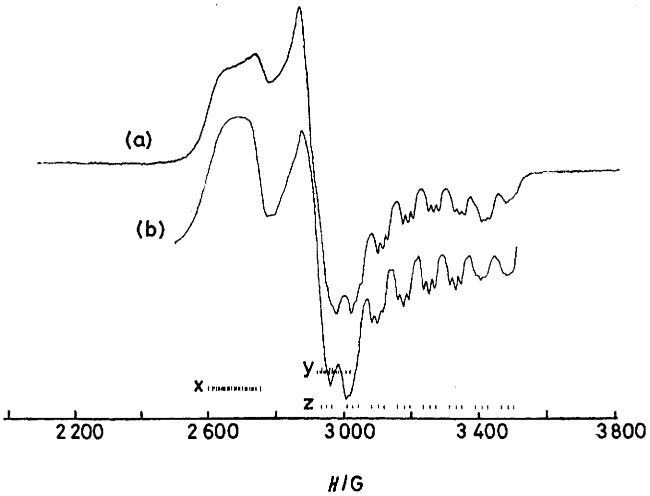
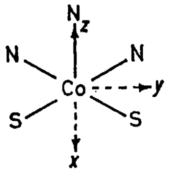


FIGURE 2 E.s.r. spectrum of [Co(tsalen)] in neat frozen pyridine, 130 K. (a) Observed spectrum; (b) computer-simulated spectrum (Microwave frequency 9 146 MHz)

In the absence of air, frozen pyridine solutions of [Co(tsalen)] show the well resolved spectrum displayed in Figure 2(a). This spectrum is typical of low-spin d^7 cobalt(II) chelates of the [Co(chelate)(py)] type;[5] the cobalt and axial nitrogen ($I = 1$) hyperfine structure is well resolved in the z direction but overlap occurs in the x and y directions. Using programs and theory described previously[6] the line shape has been simulated [Figure 2(b)] and the parameters thus obtained are given in Table 1. Table 1 also includes the dependence of the x and z components of the line width on the nuclear quantum number, m_I. The relationships quoted were determined empirically by means of the computer simulation. This phenomenon is due to motional effects,[7] but they have not been analysed in detail. The stick spectra are particularly useful in fitting spectra of this type. The x and y directions must lie in the cobalt–ligand plane midway between the S,S and S,N atoms, respectively, while the z direction lies along the Co–pyridine bond. The degree of anisotropy in the g values is characteristic of five-co-ordinate species of this type which have a $d^1_{z^2}$ orbital ground state, the anisotropy being dominated by the close approach of the d_{yz} orbital to the d_{z^2} orbital. The magnitudes of the g and hyperfine parameters for [Co(tsalen)(py)] are very similar to those of [Co(salen)(py)].[7-9] Thus the electronic structures of these two species, which show such differing stabilities, are similar. We have recently shown,[4] in the case of [Co(salen)(py)], that the low-lying excited quartet states are close to the doublet ground state derived from $d^1_{z^2}$.

TABLE 1

E.s.r. parameters for [Co(tsalen)(py)] (frozen pyridine solution)



g_x	2.44	A_x	21.0×10^{-4} cm^{-1}
g_y	2.20	A_y	10.0×10^{-4} cm^{-1}
g_z	2.033	A_z	72.0×10^{-4} cm^{-1}
		axial N $A_\perp^N$	15.0×10^{-4} cm^{-1}
		axial N $A_\parallel^N$	16.0×10^{-4} cm^{-1}

line widths/G

σ_x	$35 + 5m_I$
σ_y	20
σ_z	$9 + 0.4m_I^2$

The spectrum of the Co$^{\text{II}}$ chelate is dramatically altered on formation of the 1 : 1 oxygen adduct, obtained on admittance of air. Thus, as is now well documented,[10] the g values lie close to the free-electron value, and the hyperfine structure arising from the cobalt nucleus is still present but is much reduced in magnitude. The odd electron now resides on the O$_2$ molecule and the compound has the Co$^{\text{III}}$–superoxo-formulation.[11] The spectral line shape of the oxygen adduct appears to be dependent on the nature of the solvent, which presumably occupies the sixth (axial) position *trans* to the O$_2$ moiety. The

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[5] B. M. Hoffman, D. L. Diemente, and F. Basolo, *J. Amer. Chem. Soc.*, 1970, **92**, 61.

[6] J. R. Pilbrow and M. E. Winfield, *Mol. Phys.*, 1973, **25**, 1073.

[7] R. Neiman and D. Kivelson, *J. Chem. Phys.*, 1961, **35**, 156.

[8] C. Busetto, F. Cariati, P. Fantucci, D. Gallizzioli, and F. Morazzoni, *J.C.S. Dalton*, 1973, 1712.

[9] E. Ochiai, *J. Inorg. Nuclear Chem.*, 1973, **35**, 1727, 3375.

[10] F. Basolo, B. M. Hoffman, and J.A. Ibers, *Accounts Chem. Res.*, 1975, **8**, 384.

[11] L. Vaska, *Accounts Chem. Res.*, 1976, **9**, 175.

spectrum in frozen dimethylformamide (dmf) solution is shown in Figure 3(a) together with the computer-simulated spectrum, Figure 3(b). All the features of the spectrum have been reproduced, both in their positions and intensities. The theoretical model employed has been described previously [12] using orientations of the principal g and A factors shown in Figure 4. The best-fit parameters are given in Table 2. Two aspects are noteworthy. First the g values are rhombic and not axial as is usually reported for spectra of this type, though admittedly the difference between g_x and g_z is very small. Secondly, the simulation of the line shape is significantly improved by inclusion of the Co–O–O angle (labelled α) with a magnitude of up to 10°. Alternatively an exactly equivalent result may be obtained with α *ca.* 90° and by suitable relabelling of axes. Thus, with the resolution shown, the angle obtained is close to zero, *i.e.* the O_2 molecule lies close to being perpendicular (or parallel) to the cobalt–chelate plane. The e.s.r. spectrum in this case is unable to distinguish between the two possible arrangements.

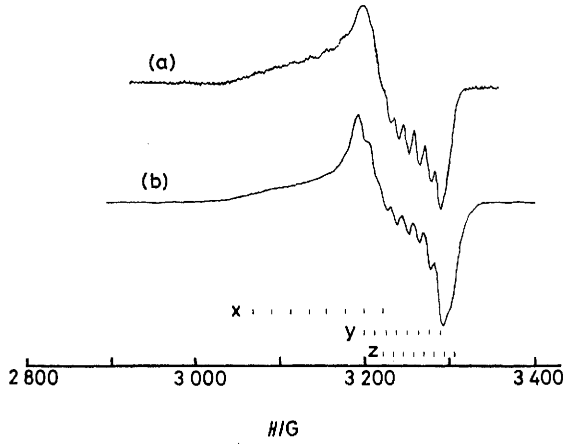

FIGURE 3 E.s.r. spectrum of [Co(tsalen)(O_2)] in frozen dimethylformamide, 130 K. (a) Observed spectrum; (b) computer-simulated spectrum (Microwave frequency 9 147 MHz)

TABLE 2

E.s.r. parameters for the 1 : 1 oxygen adducts [Co(tsalen)-(L)(O_2)] (frozen solution)

	L = dimethyl-formamide	L = pyridine *
g_x	2.014 ± 0.002	2.001 ± 0.002
g_y	2.077 ± 0.002	2.086 ± 0.002
g_z	2.002 ± 0.001	2.003 ± 0.002
A_x (10^4 cm^{-1})	12 ± 0.5	7 ± 0.5
A_y (10^4 cm^{-1})	21 ± 0.5	20 ± 0.5
A_z (10^4 cm^{-1})	11 ± 0.5	14 ± 0.5
α	0 ± 10°	15 ± 10°
line widths/G:		
σ_x	8	10
σ_y	35	15
σ_z	10	10

* The tsalen and *NN'*-trimethylenebis(thiosalicylideneiminato) compounds give identical spectra.

The spectrum of the oxygen adduct in frozen pyridine solution, though broadly similar to that in dmf, shows differences in detail (Figure 5). It has, for instance, more resolution in the x region. It does not show hyperfine structure due to the nitrogen atom of pyridine, though it is highly likely that pyridine is bonded in the sixth position. A perfect simulation of the spectrum has not been achieved in this case, but most of the features have been obtained. As is sometimes the case in line-fittings of the present kind, which involve a large number of variable parameters (*i.e.* three g values, three A values, three line-width parameters, and the angle α), we found that improving the fitting of one part of the spectrum tended to worsen the fit slightly in other regions. In contrast to the dmf spectrum there is, however, no doubt that the cobalt–dioxygen angle in pyridine solution is non-zero, with the value 105 ± 10° [from the present results it is not possible to distinguish (90 + 15) from (180 − 15)° but X-ray results available on these kinds of oxygen adducts [10,11] would favour the former]. The fairly large degree of uncertainty in the value of the angle arises from a lack of resolution in the regions of the spectrum which are arrowed in Figure 5. Both of these regions are very sensitive to small changes in α when it has a magnitude of 15° or greater, this sensitivity arising from the effect that α has on the hyperfine splitting.

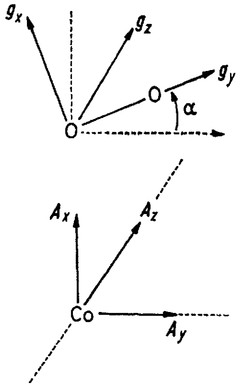

FIGURE 4 Arrangement of the principal axes for the [Co-(chelate)(O_2)] (the yz plane is the Schiff-base-ligand plane)

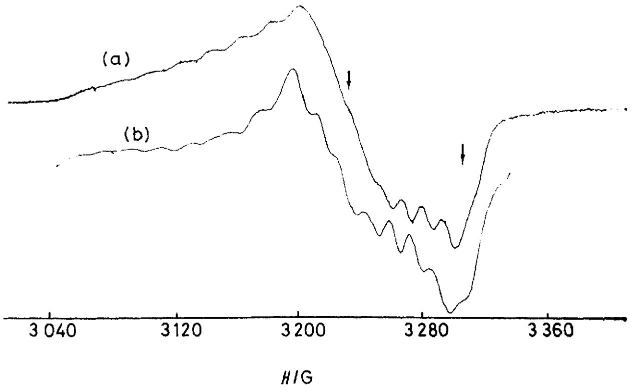

FIGURE 5 E.s.r. spectrum of [Co(tsalen)(O_2)] in frozen pyridine, 130 K. (a) Observed spectrum; (b) computer-simulated spectrum (Microwave frequency 9 150 MHz)

The largest g value is assumed to lie along the O–O bond

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[12] J. A. de Bolfo, T. D. Smith, J. F. Boas, and J. R. Pilbrow, *J.C.S. Dalton*, 1976, 1495.

direction and is similar in magnitude to that observed in dmf. The g_x value in the latter solvent is slightly larger than that in pyridine. The A_x value is also somewhat larger though the other A values are of similar magnitude. The directions of the in-plane A tensors relative to the metal–ligand bonds are not known with certainty but probably lie midway between them as is the case in the cobalt(II) precursors. (*N.B.* The in-plane hyperfine tensors are labelled A_y and A_z in the oxygenated species compared with A_x and A_y in the deoxygenated system.)

E.s.r. measurements have been made [13] on a 1 : 1 oxygen adduct of a related [Co{N_2S_2}] chelate, *i.e.* [Co(tacacen)(py)(O_2)] [tacacen = *NN'*-ethylenebis(thioacetylacetoneiminate)] $g_{x,z}$ 1.997, g_y 2.085, $A_{x,z}$ 10.4 G, A_y 21.3 G.* The magnetic parameters are similar in magnitude to those of the present system. A bent Co–O_2 linkage was proposed but the value of the angle was not evaluated. It is pertinent also to compare the parameters for oxygenated [Co(tsalen)] with those for the oxygenated oxo-analogue, [Co(salen)]. In frozen pyridine–chloroform (1 : 20) the latter showed [14] g and A values very similar to those of [Co(tsalen)(O_2)] in neat pyridine. The Co–O–O angle in the salen case was found to be larger, *i.e.* 117°, which is very close to that recently found by Schaefer and his co-workers in accurate *X*-ray structures of 1 : 1 oxygen adducts of substituted salen chelates.[15]

The stability of the 1 : 1 oxygen adduct of [Co(tsalen)] with pyridine as the axial base is less than that of [Co(salen)]; it has not been possible to date, however, to crystallize either adduct at ambient temperatures. A 2 : 1 oxygen-bridged species has been isolated for [Co(salen)] but not for [Co(tsalen)]. Though the pyridine adduct of [Co(tsalen)] and its 1 : 1 oxygenated product are only stabilized at low temperatures, once formed, the results of the present work show that their electronic features are similar to those of the salen analogues. The reasons for the difference in stability are not immediately obvious but are probably similar to those proposed [13] for the [Co(tacacen)]–[Co(acacen)] [acacen = *NN'*-ethylenebis(acetylacetoneiminate)] derivatives. First, the sulphur donor atoms facilitate withdrawal of electron density from cobalt by in-plane d-d_π back bonding which lowers the electron density on cobalt thus making it a less effective oxygen carrier. Our recent magnetic studies also showed that d_π bonding between the cobalt atom and the pyridine or O_2 p_π orbitals also play a part, being much weaker for the thio-ligands.[4] Secondly, the ability of the cobalt(II) chelate to oxygenate has been shown by Carter *et al.*[13] to be dependent on the ease of oxidation to the Co^{III} state. Electrochemical determinations of the $E_{\frac{1}{2}}$ values for the present thio-Schiff-base chelates are currently in progress to test this postulate.

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[7/011 *Received, 4th January, 1977*]

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* 1 G = 10^{-4} T.

[13] M. J. Carter, D. P. Rillema, and F. Basolo, *J. Amer. Chem. Soc.*, 1974, **96**, 392.

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[15] A. Avdeef and W. P. Schaefer, *J. Amer. Chem. Soc.*, 1976, **98**, 5153; R. S. Gall, J. F. Rogers, W. P. Schaefer, and G. G. Christoph, *ibid.*, p. 5135.