An Electron Spin Resonance Study of Substituent Effects in Adducts of Cobalt(II) Schiff-base Complexes with Dioxygen

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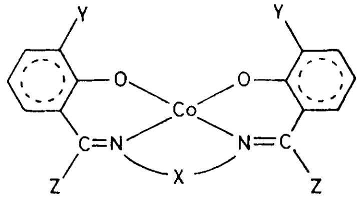
E.s.r. spectral measurements have been made on dioxygen adducts $[Co^{II}L]\cdot O_2$ of certain quadridentate Schiff-base chelates (L) of Co^{II} in frozen chloroform solutions containing pyridine or 2,6-dimethylpyridine. The effects of variation of the substituent groups in the Schiff-base ligand on the magnetic and structural parameters of the dioxygen adduct–base complex have been determined. While there is some variation in the cobalt hyperfine parameters, the Co–O–O angle lies within the range 115—120°. The widely varying *g* values and hyperfine parameters for the chelate complexes themselves may be understood on the basis of recent calculations using the angular-overlap model.

X-RAY crystallographic determinations of the structures of complexes formed by the combination of dioxygen with cobalt(II) Schiff-base chelates have provided invaluable information concerning the spatial disposition of the dioxygen molecule with respect to the cobalt(II) ion in the plane of the ligand.[1-5] The extraction of the structural data as well as the preparation of suitable compounds in crystalline form have posed considerable experimental difficulties.[6] Recent developments in the theoretical treatment of e.s.r. spectra [of complexes of dioxygen with cobalt(II) chelates] have, with the aid of information derived from the *X*-ray crystallographic studies, made possible the determination of the angle made by the dioxygen molecule with respect to the plane containing the cobalt(II) and the Schiff-base ligand.[7] It was pointed out on that occasion that models of oxygen binding must always take into account the low symmetry of the oxygenated complexes as a whole. Results for thio-Schiff-base ligands have also been reported.[8] A particular advantage of the use of e.s.r. spectroscopy to gain this type of structural information is that it does not involve the experimental difficulties encountered in the preparation of crystalline materials suitable for *X*-ray work, and makes possible a comparison of closely related systems. Thus, provided that sufficiently well resolved e.s.r. spectra are obtained, it should, in principle, be possible to detect the effects of changes in the structure of the ligand on the spatial distribution of the dioxygen molecule in its complexes with the cobalt(II) chelates. The present study was undertaken to measure the effects of varying the substituent groups in the quadridentate Schiff-base ligand *NN'*-ethylenebis(salicylideneimine) on the structural and magnetic parameters associated with the dioxygen complex of the cobalt(II) chelate of these ligands in the presence of an organic base.

The structural variations employed in this study are summarised in (1). A further structural variation is possible by the use of different bases added to the cobalt(II) chelate complexes to assist the dioxygen addition and in the cases described here the bases used were pyridine and 2,6-dimethylpyridine. In order to characterise the chelate complexes used in the oxygenation study, and to ensure that the Co^{II} was in a low-spin ground state, e.s.r. spectra were obtained in each case. It is noted that the identification of the ground state of low-spin cobalt(II) chelate complexes has been somewhat controversial[9-20] but a recent paper by Hitchman[21] appears to resolve the issues satisfactorily.



$[Co^{II}L]$ (1)

X	Y	Z	L
$[CH_2]_2$	H	H	salen
$[CH_2]_3$	H	H	salpd
$CH(Me)CH_2$	H	H	salpn
$[CH_2]_2$	H	Me	αMe - salen
$[CH_2]_2$	H	Et	αEt - salen
$[CH_2]_2$	OMe	H	3OMe - salen

RESULTS

The e.s.r. spectra of the cobalt(II) Schiff-base chelate complexes were obtained after doping them into the corresponding nickel(II) or zinc(II) complexes or by dissolution in non-co-ordinating solvents. Doping procedures usually allow a small uptake of the cobalt(II) chelates. However, well resolved spectra from which e.s.r. spectral parameters could be calculated were obtained in only a few cases and these are characterised by the familiar sets of eight lines due to the cobalt hyperfine interaction. Difficulties of this type have been mentioned previously.[22-25] The e.s.r. spectra of the cobalt(II) chelate complexes in frozen solutions of chloroform are similar to those obtained when the complexes are doped into the corresponding nickel(II) chelate complex. Unfortunately, due to the limited solubilities of some of the cobalt(II) complexes in chloroform or other non-co-ordinating solvents, it is not possible to collect e.s.r. data for a wide variety of the cobalt(II) Schiff-base complexes. The addition of pyridine to the chloroform eliminates the solubility difficulties and makes possible a comprehensive collection of e.s.r. spectral data for the cobalt(II) chelate complexes. In all cases extra hyperfine coupling is observed in the e.s.r. spectra due to the interaction of the unpaired electron of the Co^{II} with the ^{14}N nucleus of the nitrogen atom of the pyridine. In some cases,

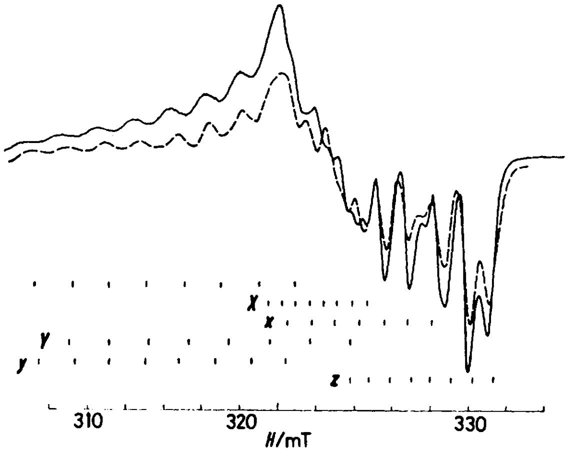


FIGURE 1 E.s.r. spectrum at −140 °C and 9.143 GHz of [Co(2Et-salen)]·O_2·py. (— — —) Computed spectrum based on the parameters in Table 5. Note that signal heights have not been normalised to the same value

on increasing the amount of pyridine, the ligand hyperfine-coupling data point to the formation of a cobalt(II) Schiff-base chelate complex containing two axially co-ordinated pyridine molecules.

TABLE 1

Magnetic parameters for some four-co-ordinate cobalt(II) Schiff-base chelate complexes

Complex	Magnetic diluant	g_x	g_y	g_z	A_x^{Co}	A_y^{Co}	A_z^{Co}	Ref.
[Co(salen)]	[Ni(salen)] single crystal	3.805 ± 0.005	1.66 ± 0.01	1.74 ± 0.01	291 ± 1	22 ± 6	30 ± 5	12
	[Ni(salen)]	3.80	2.07	1.79	284		20	24
[Co(salen)]·$CHCl_3$	[Ni(salen)]·$CHCl_3$	3.80	1.72	1.75	292	24	16	25
[Co(salen)]	$CHCl_3$	3.20	2.14	1.92	133	90	22.3	24
	CH_2Cl_2	3.32	1.96	1.91	149	34	38	25
[Co(3OMe-salen)]	[Ni(3OMe-salen)]	3.32(2)	1.98(4)	1.90(0)	150	37	26	This work

Hyperfine constants are in units of 10^{-3} cm^{-1}.

It is generally acknowledged that oxygenation of cobalt(II) Schiff-base chelate complexes is more readily achieved at low temperatures rather than at room or higher temperatures.[26-28] We found that addition of as little as 1% v/v of pyridine to the solutions gave a well resolved spectrum at 77 K which is characteristic of the cobalt(II) chelate-dioxygen complex. A typical result is shown in Figure 1.

TABLE 2

Magnetic parameters for [Co(salen)] doped into [Zn(salen)]

g_x	g_y	g_z	A_x^{Co}	A_y^{Co}	A_z^{Co}	Ref.
2.69	2.31	2.00(2)	125.9	58.4	110.3	24
2.72 ± 0.01	2.32 ± 0.01	2.00(3) ± 0.005	121 ± 1	65 ± 1	112 ± 1	This work

Hyperfine constants are in units of 10^{-4} cm^{-1}.

The spectra observed at above the freezing point of the solvent mixture consist of eight hyperfine lines from which isotropic g and A values may be determined.

Computer Simulation of E.S.R. Spectra of the Low-spin Cobalt(II) *Schiff-base Chelate Complexes and the Dioxygen Adducts*.—The e.s.r. spectra of the monomeric cobalt(II) species reported here may be described by the spin Hamiltonian (1) for orthorhombic symmetry where $S = \frac{1}{2}$

$$\mathscr{H} = \sum_{i=x,y,z} (\beta g_i B_i + A_i^{Co} I_i) S_i \qquad (1)$$

and $I = \frac{7}{2}$ for Co^{II}, β is the Bohr magneton, and the g and A values have their usual meaning. In order to account for the presence of ligand hyperfine structure from the two N atoms of the chelate complexes, or N atoms from pyridine used as a solvent in certain cases, we may add to equation (1) an expression (2) for *each* nitrogen, where X, Y, and Z

$$\sum_{J=X,Y,Z} A_J^N S_J I_J \qquad (2)$$

are the principal axes of the individual cobalt–nitrogen hyperfine interaction. For nitrogen (^{14}N), $I^N = 1$.

Computer simulation of the experimental spectra was carried out as previously described.[29] Although the program can handle monoclinic symmetry of the g and A tensors, and in certain cases here the overall molecular symmetry may be low, the spectra did not require more parameters than those of equations (1) and (2). To within the errors quoted in the results (Tables 1—4), the nitrogen hyperfine structure is isotropic.

In Tables 1—4 the following convention has been used in designating spin-Hamiltonian parameters. For the four-co-ordinate chelate complexes the largest g value was assigned as g_x, the smallest as g_y. For the five- and six-co-ordinate chelate complexes g_z is taken as the smallest g value, but g_x and g_y cannot be assigned unambiguously. These designations agree with what many workers have used in studies of Schiff-base chelate complexes based on single-crystal data, where the x and y axes are placed in the molecular plane [see (1)] with x along the bisector of the N–Co–N angle. (It is noted that the same e.s.r. spectrum would result if the axis labels were permuted among themselves.)

The spin-Hamiltonian parameters calculated for [Co(salen)] and [Co(3OMe-salen)] doped into the corresponding nickel(II) complexes are listed in Table 1 where they may be compared with the parameters reported for [Co(salen)] doped into [Zn(salen)], as shown in Table 2. In the doped zinc system a large reduction in g_x occurs and the value of A_z is increased compared with the doped nickel(II) system. In the presence of pyridine or 2,6-dimethylpyridine, nitrogen hyperfine coupling is observed on the high-field lines. The calculated parameters for the five-co-ordinate cobalt(II) chelate complexes are given in Table 3 while the parameters obtained from the computer simulation of the e.s.r. spectra of the six-co-ordinate cobalt(II) species are shown in Table 4.

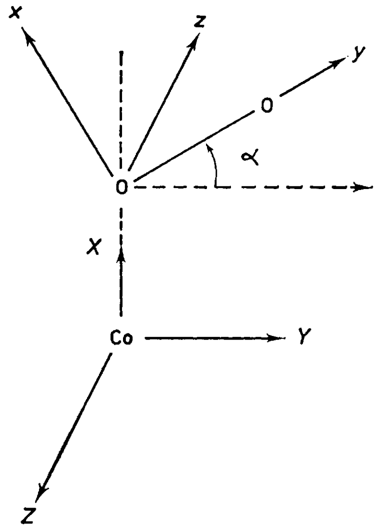


FIGURE 2 Arrangement of principal axes for models of Co–O_2 complexes. Co–O–O angle = (α + 90)°

Computer simulation of the e.s.r. spectra due to cobalt(II) chelate–dioxygen adducts may be accounted for by the spin Hamiltonian (3) which takes into account the non-coincidence of the g and A axes in the xy plane,[7] and is based on a

$$\mathscr{H} = \beta(g_xS_xB_x + g_yS_yB_y + g_zS_zB_z) + A_XS_XI_X + A_YS_YI_Y + A_ZS_ZZ_Z \quad (3)$$

consideration of the molecular model shown in Figure 2. As in equation (1), $S = \frac{1}{2}$ and $I = \frac{7}{2}$. The axis system in this case has been chosen to conform with our previous paper on the oxygenation of tetrasulphonated porphyrins.[17] It must be noted that the direction of the X and Y axes within the molecule has not been determined from our results.

The spin-Hamiltonian parameters obtained from the computer simulations of the spectra are listed in Table 5. Figure 1 shows both experimental and simulated spectra for [Co(αEt-salen)]·O_2 in pyridine. The parameters which show the largest variation as a result of alterations to the ligand structure are A_x, A_z and α. Of the g values, that designated g_z shows a variation outside the range of the determined error from the computer simulations. The angle, α, which lies in the range 25—30°, also reflects this sensitivity to ligand structure such that a change of 1° effects a discernible change in the computed spectrum. The region affected most by variations in α is the high-field peak positions. The reason why changes in α bring about changes in the e.s.r. spectrum has been outlined previously.[7, 29]

DISCUSSION

A number of attempts have been made to correlate the reactivity of cobalt(II) Schiff-base chelate complexes towards dioxygen with the details of the electronic structures of these complexes. Ochiai [27] postulated two orderings of the energy levels to account for the difference in reactivity of [Co(salen)] in different environments, such that the reactive chelates have a d_{z^2} ground state and unreactive species a $d_{x^2-y^2}$ ground state.[30] Busetto *et al.*[24] suggested that the so-called 'inactive' as well as the 'active' forms of [Co(salen)] have a d_{z^2} ground state, the difference in reactivity depending

TABLE 3

Magnetic parameters for some five-co-ordinate cobalt(II) Schiff-base chelate complexes

Complex	Magnetic diluant	g_x	g_y	g_z	A_x^{Co}	A_y^{Co}	A_z^{Co}	A_z^{N}	Ref.
[Co(salen)]·py	[Zn(salen)]	2.41	2.24	2.012	414	24.4	90.8		24
	1% v/v in py–$CHCl_3$	2.464 ± 0.005	2.244 ± 0.005	2.024 ± 0.005	40 ± 2	10 ± 2	93 ± 1	15 ± 1	This work
[Co(αMe-salen)]·py	50% v/v in py–$CHCl_3$	2.417 ± 0.005	2.353 ± 0.005	2.022 ± 0.05	60.0 ± 2	10 ± 2	95 ± 1	15 ± 1	This work
[Co(3OMe-salen)]·py	Nematic liquid crystal	2.40	2.23	2.015	50	10	89.4	14.7	16
	50% v/v in py–$CHCl_3$	2.412 ± 0.005	2.217 ± 0.005	2.017 ± 0.0005	53 ± 2	5 ± 2	95 ± 1	17 ± 1	This work

Hyperfine constants are in units of 10^{-4} cm^{-1}.

TABLE 4

Magnetic parameters for six-co-ordinate [Co(salen)]·2py

Magnetic diluant	g_x	g_y	g_z	A_x^{Co}	A_y^{Co}	A_z^{Co}	A_z^{N}	Ref.
Pyridine	2.354	2.27	2.028	20	20	77		9
50% v/v py—$CHCl_3$	2.322 ± 0.004	2.227 ± 0.005	1.982 ± 0.002	10 ± 2	15 ± 2	80 ± 1	13 ± 1	This work

Hyperfine constants are in units of 10^{-4} cm^{-1}.

TABLE 5

Magnetic parameters for the $[Co^{II}L]\cdot O_2$ adducts [a]

L	g_y	g_x	g_z	A_Y	A_X	A_Z	α
salen	2.081 ± 0.002	2.010 ± 0.005	1.990 ± 0.002	19 ± 1	7.3 ± 0.05	7.5 ± 0.5	28 ± 1
salpd	2.081	2.010	1.990	18	7.3	7.5	28
salpn	2.081	2.010	1.990	19	7.3	7.5	28
αMe-salen	2.081	2.010	1.994	20.5	7.0	10.0	30
αEt-salen	2.081	2.010	1.994	20.5	7.0	10.0	30
3OMe-salen	2.083	2.008	1.996	20.0	11.4	8.0	25
salen [b]	2.083	2.008	1.996	20.0	11.4	8.0	25

[a] Hyperfine constants are in units of 10^{-4} cm^{-1}. Fitting errors are constant in each column. The magnetic diluant was 50% v/v py–$CHCl_3$ except where stated otherwise. [b] Diluant was 2,6Me_2-py–$CHCl_3$.

on the ordering of the orbitals of the excited states. Carter *et al.*[31] have proposed that an important parameter in determining the oxygen affinity of cobalt(II) chelate complexes is the electron density at the Co^{II} as measured by the redox potential, regardless of the subtleties in electronic structure. Thus for a number of cobalt(II) chelate complexes a linear relation exists between the equilibrium constant, which represents the oxygen uptake, and the reversible polarographic half-wave potential.

In the present investigation attention is focused on the molecular properties of the dioxygen complex formed by the cobalt(II) Schiff-base chelates. The angle α, which measures the tilt of the oxygen upwards from the plane containing the cobalt(II) ion, determined here is closely similar to the more recent X-ray crystallographic determination of this angle. Taking as a point of comparison the structural and magnetic parameters associated with the dioxygen complex of [Co(salen)], increasing the length of the bridging group as in [Co(salpd)] and [Co(salpn)] has little or no effect on the g, A, or α values. The result of substitution of H by Me or Et as in [Co(αMe-salen)] or [Co(αEt-salen)] is to increase the values of A_Z and α, while A_X and A_Y remain close to the values observed for [Co(salen)]. On the other hand, substitutions in the phenyl groups as in [Co(3OMe-salen)] results in a decrease in the value of α and a clearly observed increase in A_X, while A_Y and A_Z remain largely unaltered. It is interesting to note that the decrease in α brought about in [Co(3OMe-salen)], and accompanied by an increase in A_X, also occurs as a result of substitution of the base pyridine by the stronger base 2,6-dimethylpyridine. The values of α, in the range 25—30°, produce Co–O–O angles of 115—120°. These may be compared with that predicted originally by Griffith [32] on the basis of sp^2 hybridisation. Results for dioxygen-thio-Schiff-base complexes were found to correspond to a smaller Co–O–O angle.[8]

Although our results do not enable the orientation of the dioxygen molecule to be determined uniquely, symmetry considerations would suggest an arrangement such that the Y direction should lie along the bisector of the N–Co–N angle. Thus, we would expect the dioxygen molecule to lie in the mirror plane of the chelates.

Finally, some comment on the ground state of the low-spin cobalt(II) complexes themselves is in order. McGarvey [13] considered the contribution of low-lying quartet states as well as the effect of possible configuration interaction between the d_{z^2} and $d_{x^2-y^2}$ orbitals in the $^2A_1$ ground state. It was proposed that in the four-co-ordinate cobalt(II) complexes the unpaired electron occupies a d_{xy} orbital and that the $3d$ orbitals are arranged as $(d_{xz})^2(d_{x^2-y^2})^2(d_{z^2})^2(d_{yz})^1(d_{xy})^0$ in order of increasing energy with the $d_{x^2-y^2}$, d_{z^2}, and d_{yz} orbitals being close together. On the other hand, evidence has been presented for a $3d_{z^2}$ ground-state electronic configuration from the pattern of isotropic shifts in the ^1H n.m.r. spectrum of [Co(salen)] in $S(CD_3)_2O$.[20] It was also suggested that a spin equilibrium between high- and low-spin forms may exist. Cariati *et al.*[15] have pointed out that even if the ground state has the d_{yz} configuration a weak axial perturbation provided by an attachment of an extra ligand molecule may be all that is necessary to obtain the d_{z^2} configuration since the energy difference between the two levels is quite small. Hitchman [21] has used the angular-overlap model to determine g and A values for [Co(salen)] in certain circumstances and has obtained good agreement between theory and experiment. The results show that certain cases fall into the d_{z^2} ground-state category, others into the d_{yz} ground state. Thus the results in Table 1 for four-co-ordinate chelate complexes are consistent with a d_{yz} ground state. In comparing [Co(salen)] doped into the corresponding nickel and zinc salts (Tables 1 and 2) with Hitchman's results [21] it is evident that the former cobalt system has a d_{yz} ground state, the latter d_{z^2}. The five-co-ordinate chelate complexes (Table 3) are not so readily accounted for on the basis of the particular results given by Hitchman [21] since he did not consider cases where the in-plane g values were nearly isotropic. The exception is the [Co(salen)]·py complex doped into [Zn(salen)] which is consistent with a d_{z^2} ground state as in the four co-ordinate case. The six-co-ordinate chelate complexes (Table 4), identified by the characteristic e.s.r. splittings resulting from a nitrogen atom on each pyridine, clearly have d_{z^2} ground states.

EXPERIMENTAL

E.s.r. spectra were recorded by means of a Varian E12 spectrometer. The Schiff-base ligands were prepared by condensation of the appropriate aldehyde or ketone with the diamine followed by conversion into the cobalt(II) chelate complexes. The composition of each product was established by elemental analysis.

R. L. L. acknowledges a Monash Graduate Scholarship. This work was supported, in part, by the Australian Research Grants Committee.

[8/201 *Received, 7th February*, 1978]

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