Electronic and Magnetic Properties of the Inactive Form of the Complex *NN'*-Ethylenebis(salicylideneiminato)cobalt(II), and of Five-co-ordinate Complexes of Cobalt(II) with Schiff's Bases

By **Carlo Busetto,† Franco Cariati,* Piercarlo Fantucci, Dario Galizzioli, and Franca Morazzoni,**
Istituto di Chimica Generale ed Inorganica, Centro C.N.R. Via Venezian 21, 20133 Milano, Italy

The dimeric structure of the inactive form of the complex [Co(salen)] [salen = *NN'*-ethylenebis(salicylideneiminato)] has been confirmed by e.s.r. measurements. From electronic and magnetic properties the structure of the complex seems to be intermediate between those of monomeric planar [Co(salen)] and square-pyramidal [Co(salen)],pyridine. All the features due to five-co-ordination are already present, so there is no electronic reason for the inactivity of the complex towards oxygen.

THE complex [Co(salen)] [salen = *NN'*-ethylenebis(salicylideneiminato)] is known to exist in two different forms: one monomeric, having a square-planar structure,[1] and the other dimeric (' inactive '), in which the cobalt ion is five-co-ordinate because of an additional bond to the Schiff's base oxygen atom of another molecule.[2] Previously we have carried out an extensive analysis on the electronic and magnetic properties of the planar complex,[3,4] the relative energies of the electronic configuration of Co^{II} being obtained. Four configurations mainly seem to contribute to the planar ground state, that with the unpaired electron in the d_{z^2} orbital being the main contributor, followed, in order of decreasing weight, by those with the unpaired electron in the d_{xz}, $d_{x^2-y^2}$, or d_{yz} orbitals. For the dimeric complex, every attempt to investigate the magnetic behaviour by e.s.r. spectroscopy had so far failed and a sure electronic-configuration diagram could not therefore be proposed. We are now able to report the results of an extensive analysis on the magnetic and electronic properties of the inactive form of the [Co(salen)] complex. These results also allow a more comprehensive discussion on the chemical behaviour of five-co-ordinate adducts of Co^{II} Schiff's base complexes.

RESULTS

So far e.s.r. investigation of the inactive form of the complex [Co(salen)] has not given any positive result, either in solution or in the solid state. In fact, in benzene, toluene, chloroform, and other non-co-ordinating solvents, the dimeric structure of the complex becomes planar and monomeric, while in pyridine, piperidine, *etc.* the complex becomes five-co-ordinate through co-ordination with a solvent molecule. On the other hand, a magnetically diluted powder of dimeric [Co(salen)] could not be obtained because co-evaporation of a mixture of the inactive form with, for example, the complex [Ni(salen)] from benzene, chloroform, pyridine, *etc.* led to the planar form or to the adduct with the solvent. As for the possibility of using the undiluted complex, unresolved paramagnetic resonance resulted.

We have found, however, that whereas on evaporation of a pyridine solution of dimeric [Co(salen)] (2%) with [Zn(salen)] (98%) the residue gave the e.s.r. spectrum of the complex [Co(salen)],pyridine,[5,6] in which the superhyperfine coupling due to the axial nitrogen atom was clearly detectable (Figure 1), the same residue, after heating at 100 °C *in vacuo* (0·4 mmHg), gave an e.s.r. spectrum with additional signals. The new resonance lines were similar in shape to those of the complex [Co(salen)],pyridine, but did not show superhyperfine coupling of the axially co-ordinated nitrogen atom (Figure 2). The residue, heated *in vacuo* at 180 °C until the pyridine was lost,[7] gave an e.s.r. spectrum consisting only of the new lines (Figure 3). Analogous spectra, though less resolved, could be obtained from mixtures of 25 and 50% [Co(salen)]. Moreover, it was found that, when the amount of the [Co(salen)] complex was increased to 25 and 50%, the changes which occurred in the case of the heated mixtures were also clearly detectable from electronic and i.r. spectra. By evaporation of a pyridine solution of the complex [Co(salen)] (25 or 50%) with [Zn(salen)] (75 or 50%), we have obtained an electronic spectrum identical to that of the complex [Co(salen)],pyridine (Figure 4); on heating the residue, the absorption frequencies changed by degrees, until we obtained an electronic spectrum identical to that of the inactive form (Figure 4). I.r. spectra show that the pyridine absorptions disappeared on heating the mixtures

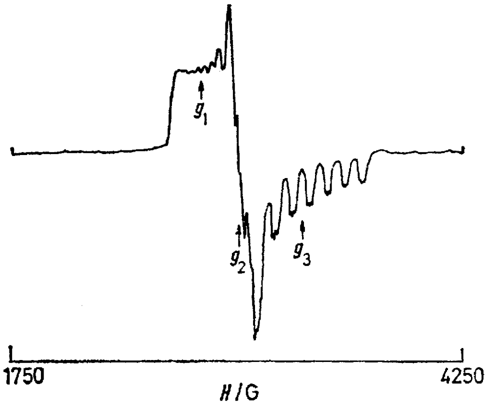

FIGURE 1 E.s.r. spectrum of [Zn(salen)]–[Co(salen)] mixed powder evaporated from a pyridine solution of the complexes [Co(salen)] (2%) and [Zn(salen)] (98%)

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† L. S. R. Snam Progetti, San Donato Milanese.

[1] W. P. Schaeffer and R. E. Marsh, *Acta Cryst.*, 1969, **B25**, 1675.

[2] S. Brückner, M. Calligaris, G. Nardin, and L. Randaccio, *Acta Cryst.*, 1969, **B25**, 1671.

[3] C. Busetto, F. Cariati, A. Fusi, M. Gullotti, F. Morazzoni, A. Pasini, R. Ugo, and V. Valenti, *J.C.S. Dalton*, 1973, 754.

[4] C. Bussetto, F. Cariati, P. Fantucci, D. Galizzioli, and F. Morazzoni, *Inorg. Nuclear Chem. Letters*, 1973, **9**, 313.

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[7] R. H. Bailes and M. Calvin, *J. Amer. Chem. Soc.*, 1947, **69**, 1886.

and the inactive [Co(salen)] frequencies then became evident (Figures 5 and 6).

While we are unable to explain the [Co(salen)]–[Zn(salen)] mixed powder behaviour, we think that the planar [Co(salen)] and the [Zn(salen)] complexes, on mixing, can give rise to a dimeric complex in which the cobalt atom of a monomeric unit is co-ordinated to the oxygen atom of the Schiff's base of a zinc monomeric unit. This complex is obviously not the inactive form of the [Co(salen)] complex, but it remains the same irrespective of the [Co(salen)] : [Zn(salen)] ratio and shows the electronic properties of the inactive form. The e.s.r. signals of the mixture heated at 180 °C have to be ascribed to a magnetic interaction similar to that in the dimeric [Co(salen)] complex and we assign definitely to the latter the *A* and *g* magnetic-tensor values found for the mixture. In Table 1 are reported the magnetic-tensor values and the electronic absorption frequencies of the inactive form of the complex [Co(salen)] compared with those of the monomeric [Co(salen)] and [Co(salen)],pyridine complexes.

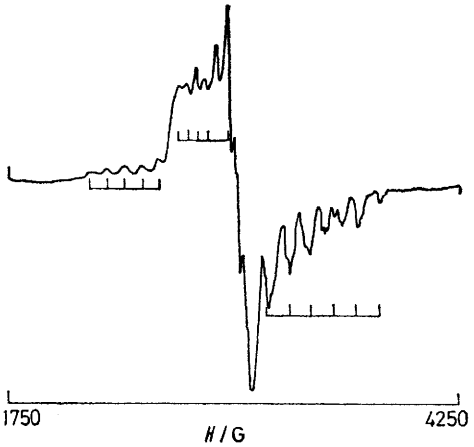

FIGURE 2 E.s.r. spectrum of [Zn(salen)]–[Co(salen)] mixed powder, evaporated from a pyridine solution of the complexes [Co(salen)] (2%) and [Zn(salen)] (98%), heated at 100 °C *in vacuo* (0·4 mmHg). Resonance lines due to 'inactive' [Co(salen)] are indicated

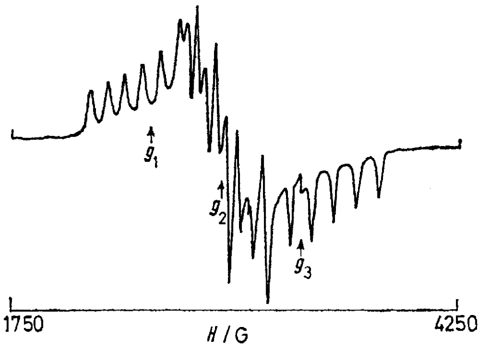

FIGURE 3 E.s.r. spectrum of [Zn(salen)]–[Co(salen)] mixed powder, evaporated from a pyridine solution of the complexes [Co(salen)] (2%) and [Zn(salen)] (98%), after heating at 180 °C *in vacuo* (0·4 mmHg)

The behaviour of the complex [Co(salbn)] [salbn = *NN'*-1-methylpropylenebis(salicylideneiminato)] seems to confirm the nature of the heated Zn–Co mixture. Actually the complex [Co(salbn)], mixed with [Zn(salbn)] and evaporated from pyridine, showed the electronic and e.s.r. spectrum of the complex [Co(salbn)],pyridine; on heating *in vacuo* up to 180 °C, no evidence of dimerization was found. Mixed dimerization seems to occur only when the dimeric cobalt complex exists, as in the case of [Co(salen)],

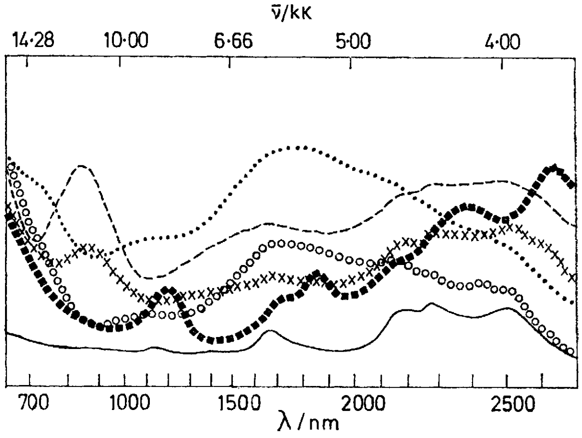

FIGURE 4 Reflectance electronic spectra: (——) [Zn(salen)]; (– – – –) undiluted 'inactive' [Co(salen)]; (• • • •), undiluted [Co(salen)],pyridine; (○), [Co(salen)]–[Zn(salen)] mixed powder evaporated from a pyridine solution of the complexes [Co(salen)] (25%) and [Zn(salen)] (75%); (×), [Co(salen)]–[Zn(salen)] and mixed powder evaporated from a pyridine solution of the complexes [Co(salen)] (50%) and [Zn(salen)] (50%) after heating at 180 °C *in vacuo*; (■), [Co(salen)]–[Ni(salen)] mixed powder evaporated from a pyridine solution of the complexes [Co(salen)] (50%) and [Ni(salen)] (50%) after heating at 180 °C *in vacuo*

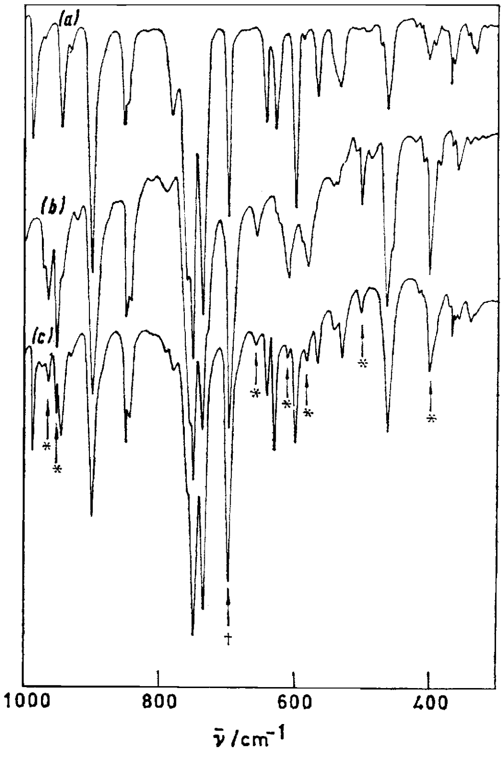

FIGURE 5 I.r. spectra on KBr samples (*a*) [Zn(salen)],pyridine; (*b*) [Co(salen)],pyridine; and (*c*) [Zn(salen)]–[Co(salen)] evaporated from a pyridine solution of the complexes [Co(salen)] (50%) and [Zn(salen)] (50%) after heating at 100 °C. Bands marked with an asterisk are due to the complex [Co(salen)],pyridine; those with a dagger are due to co-ordinated pyridine

so that the mixture [Zn(salen)]–[Co(salen)] very probably has the same structure as that of dimeric [Co(salen)].

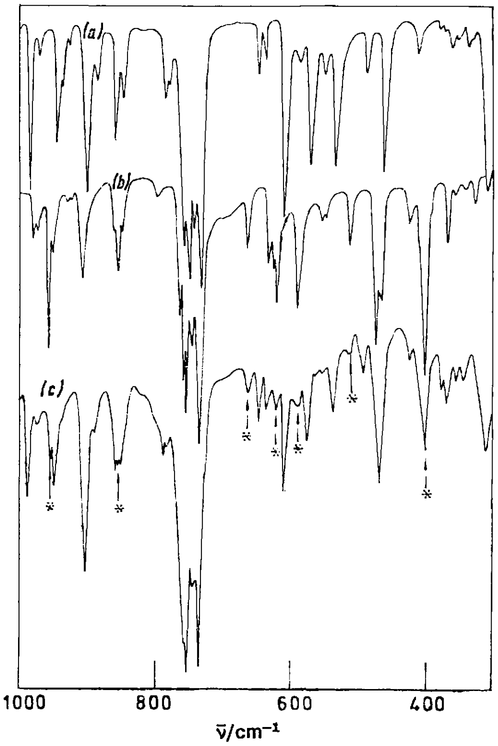

FIGURE 6 I.r. spectra on KBr samples: (*a*) [Zn(salen)]; (*b*) ' inactive ' [Co(salen)]; and (*c*) [Zn(salen)]–[Co(salen)] mixed powder evaporated from a pyridine solution of the complexes [Co(salen)] (50%) and [Zn(salen)] (50%) after heating at 180 °C. Bands marked with an asterisk are due to ' inactive ' [Co(salen)] in the mixed powder

We have also carried out magnetic susceptibility measurements on a [Zn(salen)]–[Co(salen)] mixed powder which was evaporated from pyridine and heated at 180 °C; the components were [Co(salen)] (48·4 mg) and [Zn(salen)] (52·35 mg). The value of χ_g was $2{\cdot}430 \times 10^{-6}$ at 298 K; hence, taking into account the diamagnetic corrections due to [Zn(salen)] in the mixture and to ligand contribution (see Experimental section), we have $\mu_{eff} = 2{\cdot}16$ B.M. for the complex [Co(salen)] in the mixture. This value is in accord with that obtained by Earnshaw *et al.* (2·17 B.M.)[8] for the undiluted inactive form at 298 K. Thus it is confirmed that the [(Co(salen)]–[Zn(salen)] mixture has the same structure as that of the dimeric complex [Co(salen)].

TABLE 1

E.s.r. parameters

Complex	g_1	g_2	g_3	10^4A_1	10^4A_2 (cm⁻¹)	10^4A_3	Δ_1/kK	Δ_2/kK	10^4P/cm⁻¹	k
[Co(salen)] monomeric [a]	3·2	2·14	1·91	133	90	22·3		8·3		
	(3·19)	(2·16)	(1·90)	(133)	(−77)	(22·3)	(2·0)	(8·25)	(256)	(0·4)
[Co(salen)] ' inactive ' [b]	2·69	2·31	2·002	125·9	58·4	110·4	4·0	6·0		
	(2·69)	(2·31)	(1·97)	(90)	(44)	(100)	(3·4)	(6·7)	(142)	(−0·2)
[Co(salen)],pyridine [c]	2·41	2·24	2·012	41·4	24·4	90·8 [d]	6·0	9·0		
	(2·41)	(2·24)	(1·98)	(41·4)	(21·1)	(90·8)	(5·7)	(9·3)	(131)	(−0·16)

All spectra have been recorded at 100 K; calculated values are in parentheses. salen = *NN'*-Ethylenebis(salicylideneiminato).

[a] In chloroform solution. [b] Recorded on a [Zn(salen)] (98%)–[Co(salen)] (2%) mixture after heating at 180 °C (see text). [c] Recorded on a [Zn(salen)] (98%)–[Co(salen)] (2%) mixture before heating. [d] The superhyperfine coupling constant for ^{14}N is $11{\cdot}74 \times 10^{-4}$ cm⁻¹.

DISCUSSION

The aim of our discussion is to connect the electronic and magnetic properties of the inactive form of the [Co(salen)] complex with a more comprehensive investigation on five-co-ordinate Co^{II} Schiff's base complexes. E.s.r. parameters of ' inactive ' [Co(salen)] are discussed in connection with the electronic *d–d* transitions, so that absorption frequencies calculated from e.s.r. data are in accordance with the experimental electronic bands. We have used a calculation method which reproduces, with a second-order approximation, the *g* and *A* tensor experimental values and allows us to obtain the ground state of Co^{II} in the dimeric complex. It was assumed that *g*, *A*, and the molecular axes were approximately coincident. The same method has also been used for the monomeric [Co(salen)] complex and for [Co(salen)],pyridine.[3,4,9,10]

The ground state of ' inactive ' [Co(salen)] was found to be as in equation (1) (the three-holes approximation is

$$\phi_{\pm} = b_3|(xy)^2(z^2)\rangle \pm b_2|(xy)^2(xz)\rangle + ib_1|(xy)^2(yz)\rangle \quad (1)$$

$$\text{where } b_1 = \frac{\sqrt{3}}{2}\frac{\zeta}{\Delta_1} = -0{\cdot}1016$$

$$\Delta_1 = E(yz) - E(z^2) = 3{\cdot}4 \text{ kK}$$

$$b_2 = \frac{\sqrt{3}}{2}\frac{\zeta}{\Delta_2} = -0{\cdot}0513$$

$$\Delta_2 = E(xz) - E(z^2) = 6{\cdot}7 \text{ kK}$$

$$b_3 = 0{\cdot}9935$$

$$\zeta = \text{spin-orbit coupling constant} = -0{\cdot}4 \text{ kK}$$

adopted). The unpaired electron is mainly in the d_{z^2} orbital and the *g* values were assigned as g_1 to $g_\perp'$ or $g_\perp''$, g_2 to $g_\perp''$ or $g_\perp'$, and g_3 to $g_\parallel$. The calculated values of Δ_1 and Δ_2 were in accordance with the absorption bands at 4·0 and 6·0 kK; these correspond to $d_{xz,yz} \longrightarrow d_{z^2}$ and $d_{yz,xz} \longrightarrow d_{z^2}$ transitions. (The calculation method does not allow differentiation of d_{xz} from d_{yz}.) From the electronic spectrum of ' inactive ' [Co(salen)] we can derive another absorption frequency, at 11·8 kK, which

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[8] A. Earnshaw, P. C. Hewlett, E. A. King, and L. F. Larkworthy, *J. Chem. Soc.* (*A*), 1968, 241.

[9] C. Busetto, F. Cariati, P. Fantucci, D. Galizzioli, and F. Morazzoni, *Gazzetta*, 1972, **102**, 321.

[10] C. Busetto, F. Cariati, P. Fantucci, D. Galizzioli, F. Morazzoni, and V. Valenti, *Gazzetta*, 1972, **102**, 1040.

does not result from the e.s.r. calculations. Nevertheless we think this band could be assigned to a $d_{x^2-y^2} \longrightarrow d_{z^2}$ transition, on the same grounds as used in our assignment of the bands at 5·5 and 13·3 kK, respectively, in the spectra of the monomeric [Co(salen)] complex and of [Co(salen)],pyridine complexes.[3,4,10]

In addition to three bands previously assigned, the electronic spectra of ' inactive ' [Co(salen)], [Co(salen)],pyridine, and of the various mixtures contained other bands, at 6·1, 4·55, 4·35, and 4 kK, that were already present in the [Zn(salen)] spectrum. These bands are due to vibrational modes of the ligand exalted by the stronger electronic absorptions. The shape of the electronic bands was better resolved in the mixture spectra, as the presence of the [Zn(salen)] complex reveals the vibrational modes (Figure 4); moreover the vibrational modes were unchanged in every complex or mixture and only three frequencies, or frequency ranges, varied and have to be related to electronic modes of the paramagnetic complexes.

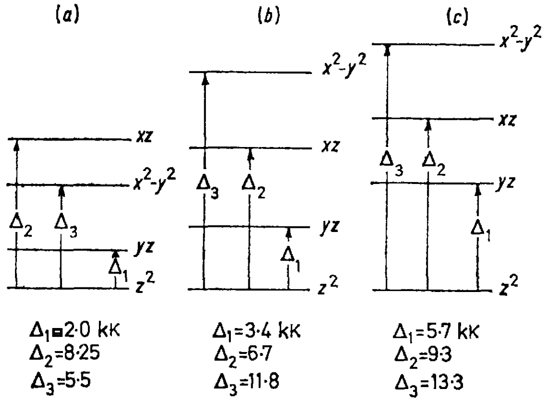

FIGURE 7 Energy-level diagrams: (*a*) monomeric [Co(salen)]; (*b*) ' inactive ' [Co(salen)]; (*c*) [Co(salen)],pyridine. Electronic configurations are symbolized by the orbital containing the unpaired electron

In Figure 7 is shown the energy-level diagram for ' inactive ' [Co(salen)] compared with those of the monomeric complex and [Co(salen)],pyridine. The calculated values of g and A tensors, the P parameter, the Fermi constant, and electronic absorption frequencies are reported in Table 1. The Stevens constant was taken as unity. From the energy-level diagrams we make the following observations.

(*a*) The configuration $(xz)^2(yz)(x^2-y^2)^2(z^2)^2$, which in the monomeric [Co(salen)] complex is at 2·0 kK, with respect to the ground state, shifts to 3·4 and 5·7 kK in going respectively to ' inactive ' and to pyridine complexes.

(*b*) The $(xz)^2(yz)^2(x^2-y^2)(z^2)^2$ configuration is at 5·5 kK from the ground state in the planar complex and shifts to 11·8 and 13·3 kK in the ' inactive ' and pyridine complexes.

(*c*) The xy plane anisotropy, calculated from the energy difference between the $(xz)(yz)^2(x^2-y^2)^2(z^2)^2$ and $(xz)^2(yz)(x^2-y^2)^2(z^2)^2$ configurations, decreases from the planar (6·0 kK) to the ' inactive ' and pyridine complexes (3·0 kK).

The relative energies of the configurations here proposed for ' inactive ' [Co(salen)] differ from those proposed in our previous paper[3] only on the grounds of electronic spectra. This complex seems to have an electronic behaviour intermediate between those of the planar and pyridine complexes, though all properties due to five-co-ordination, such as the d_{z^2} and $d_{x^2-y^2}$ displacements and the xy lower anisotropy, are already present. Dimerization of the [Co(salen)] complex suffices to change a planar structure to a five-co-ordinated structure, and thus we confirm, by spectroscopic and magnetic analysis, the X-ray measurements of Brückner *et al.*[2] We shall use the intermediate behaviour of ' inactive ' [Co(salen)] to explain the electronic perturbations which occur by degrees to the cobalt ion on passing from a planar to a pyridine complex.

It is well known that co-ordination of basic molecules to planar Co^{II} Schiff's base complexes increases their reactivity towards oxygen. Until now we had thought that the increased reactivity in going from planar to pyridine complexes arises from the greater weight of the $(xz)^2(yz)^2(x^2-y^2)^2(z^2)$ configuration in the ground state of the five-co-ordinate complex; in fact our calculation approach shifts the $(xz)^2(yz)(x^2-y^2)^2(z^2)^2$ configuration from the ground state, because of five-co-ordination. When a complex molecule is interacting with oxygen, electron transfer may be easier the more the unpaired electron is in the $(xz)^2(yz)^2(x^2-y^2)^2(z^2)$ configuration. On the basis of our new results, we think that the large displacement of the $(xz)^2(yz)^2(x^2-y^2)(z^2)^2$ configuration must also have some effect on the reactivity towards oxygen; actually the displacement is a peculiar feature of five-co-ordination, being already present in ' inactive ' [Co(salen)], where the fifth ligand (the oxygen atom of the Schiff's base of another molecule) is weaker than pyridine. In order to connect the shift with the different reactivity of planar and pyridine complexes, we have carried out an overlap calculation between cobalt d and oxygen p orbitals. The calculation used the superoxide structure of Rodley and Robinson;[11] the results are shown in Table 2. It is quite clear that only the d_{z^2}, d_{xz}, and d_{yz} orbitals overlap with the oxygen p orbitals, so that while the unpaired electron in these orbitals can be transferred to oxygen, that in the $d_{x^2-y^2}$ orbital cannot. The weight of the $(xz)^2(yz)^2(x^2-y^2)(z^2)^2$ configuration, higher in the ground state of the planar complex than in the five-co-ordinate complex, could

TABLE 2

Summary of overlap calculation for cobalt d and oxygen p orbitals *

	px_1	py_1	pz_1	px_2	py_2	pz_2
d_{z^2}	0	0	−0·1050	0·0040	0	−0·0070
d_{xz}	0·0400	0	0	0·0008	0	0·0060
d_{yz}	0	0·0400	0	0	0·018	0
$d_{x^2-y^2}$	0	0	0	−0·0002	0	−0·0013

* The subscripts 1 and 2 indicate the atoms of co-ordinated dioxygen, 1 being that nearest to the cobalt atom.

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[11] G. A. Rodley and W. T. Robinson, *Nature*, 1972, **235**, 438.

prevent electron transfer to oxygen. We conclude that 'inactive' [Co(salen)] should be 'active' towards oxygen, on the grounds of its electronic structure; the reason for its inactivity may be that proposed by Brückner *et al.*,[2] who, by *X*-ray analysis, found the packing of dimeric [Co(salen)] to be unfavourable to oxygen absorption.

EXPERIMENTAL

The complexes were synthesized as previously reported.[7,12] The [Zn(salen)]–[Co(salen)] powder mixture was prepared as follows. Weighed amounts of pure [Co(salen)] and [Zn(salen)] were dissolved in pyridine; the solution was then evaporated and a solid residue obtained. The solid was heated under vacuum (0·4 mmHg) at 100 °C and then at 180 °C (*ca.* 2 h), in order to expel the co-ordinated pyridine.[7]

E.s.r. spectra were recorded using a Varian 4502-11 spectrometer, at a field modulation of 100 kHz. Reflectance electronic spectra were recorded on a Beckman DK-2A spectrophotometer, and i.r. spectra on a Perkin-Elmer 621 spectrophotometer. Magnetic susceptibilities were measured at 298 K by the Gouy method. The tube was calibrated with $Co[Hg(SCN)_4]$ and diamagnetic corrections were calculated from Pascal constants. All manipulations were carried out in an inert-gas atmosphere to prevent oxidation.

Calculations.—The lack of a single-crystal e.s.r. spectrum prevented the experimental assignment of g and A tensor values. From both solution and diluted-powder spectra we could not derive the magnetic axis directions, so we had to use a calculation method which allows assignment of the ground state and of the magnetic-tensor components. We have taken the molecular axes with the z axis perpendicular to the CoN_2O_2 plane and the x and y axes bisecting, respectively, the N–Co–N and O–Co–N angles; g and A are coincident with the molecular axes. With this approximation we have calculated, through the magnetic operators, g and A expressions for all possible ground states; that is with the unpaired electron in the d_{z^2}, d_{xz}, or d_{yz}, or $d_{x^2-y^2}$ orbitals.

In each ground state g and A experimental values were tentatively assigned. The first possibility is g_1 to $g_{\parallel}$, g_2 to $g_{\perp}'$, and g_3 to $g_{\perp}''$, and the second possibility is g_1 to $g_{\perp}'$, $g_3(g_2)$ to $g_{\perp}''$, and $g_2(g_3)$ to $g_{\parallel}$. The third possibility of exchanging $g_{\perp}'$ with $g_{\perp}''$ is not useful, because $g_{\perp}'$ and $g_{\perp}''$ expressions are symmetric with respect to this exchange. Satisfactory agreement with the experimental values of g and A tensors, and of electronic absorption bands, can be obtained only if the values g_1 to $g_{\perp}'$ or $g_{\perp}''$, g_2 to $g_{\perp}''$ or $g_{\perp}'$, and g_3 to $g_{\parallel}$ are assigned, and if the ground state has the unpaired electron in the d_{z^2} orbital. Magnetic axes with analogous orientation have been recently reported for the bis complex of cobalt(II) with pentane-2,4-dithione, which has also very similar g values.[13] The expressions for the g and A tensors have been reported in a previous paper.[3]

Similar calculations were carried out on the assumption that the x and y principal magnetic axes are at 45° to the previous molecular axes; we still obtained a good fitting of the g and A magnetic tensors, with no change in the ground state. Actually, provided no exchange between $g_{\parallel}$ and $g_{\perp}$ occurs, the rotation of the magnetic axes in the plane does not move the unpaired electron from its position.

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[12] C. Floriani and F. Calderazzo, *J. Chem. Soc.* (*A*), 1969, 946.

[13] A. K. Gregson, R. L. Martin, and S. Mitra, *Chem. Phys. Letters*, 1970, **5**, 310.