Optically Active Complexes of Schiff Bases. Part II.† Complexes of Cobalt(II) with Tetradentate Schiff Bases and their Reactivity with Oxygen

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Complexes of cobalt(II) with Schiff bases obtained by condensation of salicylaldehyde with substituted ethylenediamines have been synthesised together with five-co-ordinated pyridine adducts. E.s.r., electronic, and c.d. spectra and magnetic susceptibilities have been reported. Energy level schemes have been calculated by a ligand field approach in order to fit the magnetic properties and allow an assignment of the observed absorption bands. The reaction with oxygen has been studied and discussed in terms of both the electron configuration of the cobalt atom and the steric effects of substituents on the carbon atoms of the substituted ethylenediamines.

COBALT(II) complexes with tetradentate Schiff base ligands have been the subject of a large number of investigations where electronic spectra,[1] magnetic properties,[2] and some steric effects such as those [3,4] due to the length and type of the hydrocarbon chain separating the two nitrogen atoms, have been reported and discussed. The oxygen-carrying properties of these compounds were recognised in 1938 by Tsumaki [5] but only later Calvin and his co-workers [6] studied the oxygenation of *N*,*N'*-ethylenebis(salicylideneiminato)cobalt(II), Co(salen), both in solution and in the solid state. Very recently the interest in the synthesis,[7] isolation, and characterisation by physical methods [8] of 2 : 1 and 1 : 1 cobalt–oxygen adducts of these complexes has grown rapidly.

It has been shown that the ability of Co^{II} compounds to react reversibly with oxygen is not confined to the case of salicylaldehyde Schiff base compounds but to a very large set of Co^{II} complexes with π-delocalised ligands such as other tetradentate Schiff bases,[9,10] dioximes,[11] phthalocyanines,[12] synthetic [13a] and natural porphyrins,[13b] and Co^{II} vitamin B_{12} coenzyme.[14]

We report here a preparative and spectroscopic investigation of a series of such compounds derived from substituted ethylenediamines, and their reaction with oxygen.

RESULTS

Square-planar Complexes.—We have synthesised by the standard procedure (see Experimental section) the related salicylideneiminato-complexes of ethylenediamine(en), (—) and (+) propane-1,2-diamine (pn), *meso*, (+), and (—) butane-2,3-diamine (bn), *meso*, (+), and (—) cyclohexane-1,2-diamine (chxn), (—) and (+) styrene-1,2-diamine (phenen) and finally *meso*, (+), and (—) stilbene-1,2-diamine (stien).

Interestingly, all the new complexes isolated do not react in the solid state with oxygen at room temperature; and always only one crystalline form has been isolated.

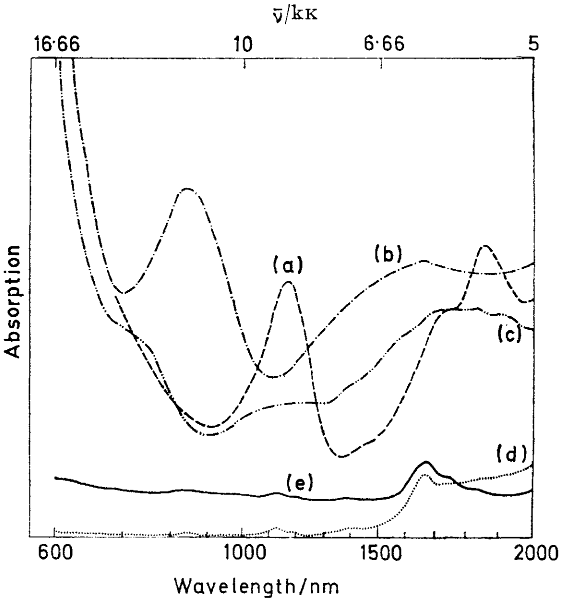

FIGURE 1 Reflectance spectra in the near-i.r. region; (a), Co(salen), active form; (b), Co(salen), inactive form; (c), Co(salen)(py); (d), salenH; (e), Zn(salen)

Reflectance spectra of all the cobalt compounds show a typical absorption band *ca.* 8·7 kK (Figure 1). Surprisingly,

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† Part I: M. Gullotti, A. Pasini, P. C. Fantucci, R. Ugo, and R. D. Gillard, *Gazzetta*, in the press.

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[13] (*a*) F. A. Walker, *J. Amer. Chem. Soc.*, 1970, **92**, 4235; (*b*) B. M. Hoffman and D. H. Petering, *Proc. Nat. Acad. Sci. U.S.A.*, 1970, **67**, 637.

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despite the inertness to oxygen, the reflectance spectra of the solid materials are similar to that of the so called ‘ active ’ crystalline form of Co(salen) which can be obtained by slow evaporation of a chloroform solution or by removing pyridine *in vacuo* at high temperature from the adduct Co(salen)(py). We can thus assume that all the new compounds reported in this paper have in the solid state a square-planar structure such as that reported for the active form of Co(salen).[15] A recent X-ray investigation [16a] of the complexes derived from (+)bn and *meso*-bn has shown that, despite a very small tetrahedral distortion, the cobalt co-ordination may be considered planar in the first approximation.

We are unable to obtain by crystallisation from ethanol or dimethylformamide, any crystalline substance corresponding to the inactive form of Co(salen), which is characterised by a new band at 11·80 kK and the complete disappearance of the band at 8·70 kK (Figure 1). This fact could be due to the difficulties of obtaining an axial intermolecular perturbation of the cobalt atom [as in the inactive form of Co(salen) [16b]] because of the presence of substituents in the carbon ring of the diamine. The absorption band *ca.* 8·7 kK may probably be related to a *d*–*d* transition; other *d*–*d* transitions, which had not been previously detected, lie between 5·0 and 6·0 kK. In fact some absorption bands, which are not to be attributed to i.r. combination bands of the ligands, are present in this region (Figure 1). The electronic spectra in this region obtained in chloroform solution are completely similar to those obtained by reflectance, the typical absorption band being shifted to 8·5—8·3 kK. Chloroform solutions are, as expected, completely stable to oxygen. We can thus conclude that in non-co-ordinating solvent all these compounds have a square-planar co-ordination and that, as already proposed,[1] this kind of co-ordination is surely related to the presence of an absorption band *ca.* 8·3—8·7 kK.

All the compounds are paramagnetic in the solid state, with values of the magnetic moment corresponding to low-spin electron configuration as in the case of Co(salen).[2] We have also determined the magnetic susceptibilities of some of the above crystalline complexes (Table 1) over a large range of temperatures. As already reported for Co(salen),[2] they behave normally with a slight decrease of the magnetic moment with the temperature and follow the Curie–Weiss law without any detectable anomaly. In conclusion, despite the small tetrahedral distortion observed in the case of (+)bn or *meso*-bn complexes,[16a] there is no sign of a thermal equilibrium between low and high spin states by changing the bulkiness of the substituents of the diamine ring.

TABLE 1

Magnetic moments [a] at two different temperatures

	μ_{eff}	
Compound	297 K	95 K
Co(salen), active	2·72 [b] (2·44)	2·57 [b] (2·32)
Co(salen), inactive	2·17 [b] (2·21)	1·80 [b] (2·00)
Co[sal(−)stien]	2·35 (2·44)	2·27 (2·32)
Co[sal *meso*-chxn]	2·31 (2·44)	2·28 (2·32)
Co(salen)(py)	2·22 [b] (2·21)	1·68 [b] (2·00)

[a] Calculated values in parentheses. [b] As reported in ref. 2.

It has been reported [8–10] that in the case of Co(salen) and similar low-spin planar cobalt tetradentate Schiff base complexes the e.s.r. signal was not detectable or broad and not resolved. Recently two independent groups have reported well resolved spectra obtained in dimethylacetamide or CH_2Cl_2–toluene [17] and in the solid state.[18] Chloroform solutions of the compounds described in this paper are paramagnetic and show at 100 K a well defined and sufficiently resolved e.s.r. spectrum; this spectrum however, does not correspond to that reported by Ochiai.[17] At room temperature it was impossible to detect any signal [as reported for Co(salen) [9]] probably because of the very short spin-lattice relaxation. In our experimental conditions (see Experimental section) we have observed that as soon as the cobalt material is dissolved in pure chloroform, there are two series of signals (Figure 2). The series at low field is due to the interaction of the unpaired electron with the cobalt nucleus ($I = 7/2$) when the magnetic field is perpendicular to the z molecular axis ($g_{1\perp}$); the other series, much more intense, is due to the components of the magnetic parameters along either x or y axes ($g_{2\perp}$) and the z axis respectively (g_{zz}). The above assignments have been obtained from the best fit of the calculation (see Experimental section).

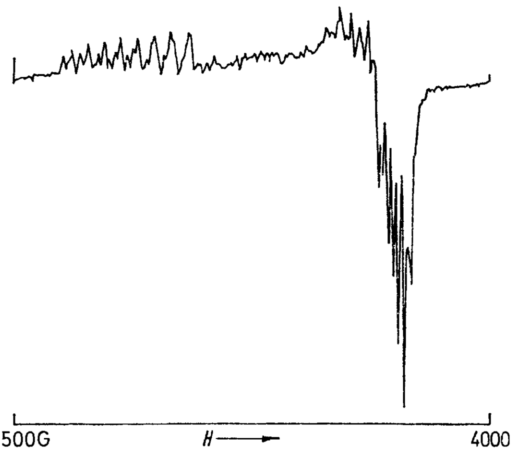

FIGURE 2 E.s.r. spectrum of Co(salen) in $CHCl_3$ at −160 °C

Both series of signals of a fresh chloroform solution show a multiplicity (Figure 2) which is higher than that expected in the case of a simple hyperfine structure (8 lines). We can thus assume that we have in solution more than one paramagnetic centre which, being all rather similar, have overlapping signals. These different centres do not involve interaction of the cobalt atom with molecular oxygen; for instance the addition of small amounts of ethanol to absolutely pure chloroform does not appreciably change the e.s.r. spectra. Only when the added ethanol is *ca.* 20% of the solution does a detectable oxygen absorption take place and a new e.s.r. signal appears *ca.* 3300 G, typical of the monomeric oxygen adducts.[8,9] We have carefully examined (see Experimental section) the e.s.r. lines due to

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the perpendicular component of the hyperfine splitting ($g_{1\perp}$) and identified in this way the lines due to the different paramagnetic centres (Figure 3a). In Table 2 we have reported the values of $g_{1\perp}$ and $A_{1\perp}$ (low field signal) for the different paramagnetic centres in the case of some complexes with different diamines.

We were in many cases unable to carry out an analysis on the series of absorption lines at high field. In fact the complexity of the high field signal was often so high, because of the strong overlap of many lines, that it was impossible to separate the many lines due to the different paramagnetic centres. However, it was possible to obtain approximate values of $g_{2\perp}$ and g_{zz} (and relative A values) in the case of Co(salen) (see Table 2) where the signal was simple enough (Figure 2a). The change in the e.s.r. spectra with time (Table 2) is as expected only if some of the paramagnetic cobalt centres remain in the solution whilst others disappear. This period of time depends on the cobalt complex; for instance in the case of (+)phenen, (−)stien, and (+)pn the rate of formation of the more stable cobalt species in chloroform solution is very high; in these cases it was possible to obtain directly the e.s.r. spectra (Figure 3b) corresponding to the final stage of the evolution of the chloroform solution observed in the case of other cobalt complexes. This final stage corresponds to the stabilisation of a species characterised by $g_{1\perp} = 3{\cdot}24$—$3{\cdot}23$ (Figure 3b).

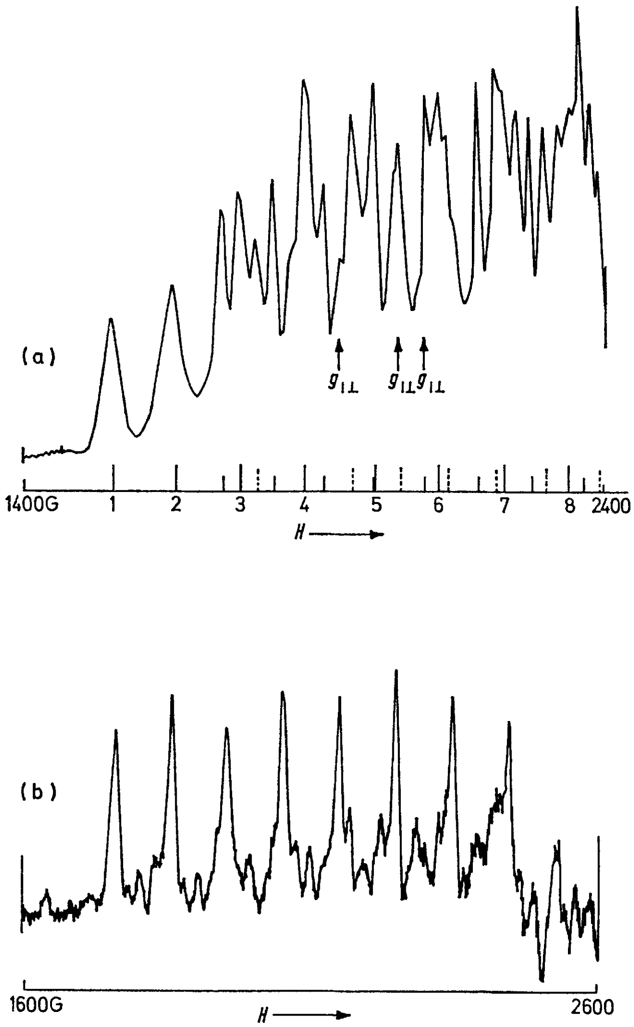

FIGURE 3 E.s.r. spectrum (−160 °C) at low field of (a), Co(sal-*meso*-chxn) after dissolution in $CHCl_3$; (b), Co[sal (+)phenen] in $CHCl_3$ after a few minutes

TABLE 2

E.s.r. data in $CHCl_3$ solutions at 113 K [a]

Compound	$g_{1\perp}$ Values at different times				$A_{1\perp}$ Values [b] at different times			
Co(salen) [c]			3·23	3·18			138	129
Co(sal *meso*-chxn)	3·59	3·28	3·24		221	168	148	
Co[sal(+)phenen]			3·24				148	
Co[sal(−)bn]	3·52		3·23	3·21	223		141	126
Co[sal(+)stien]			3·23	3·18			141	125
Co[sal(+)pn]			3·24	3·12			142	146

[a] $g_{1\perp}$ ($A_{1\perp}$) and $g_{2\perp}$ ($A_{2\perp}$) are associated with $g_{\perp}$ respectively at low and high magnetic field. [b] In cm^{-1} 10^4. [c] $g_{2\perp}$ 2·05; $A_{2\perp}$ 90; g_{zz} 1·92; A_{zz} cm^{-1} 10^4; values of these parameters for the other compounds may be only tentatively assigned as similar to those of Co(salen) because of lack of good resolution of the high field signal.

We assume that this more or less slow evolution of the paramagnetic properties of chloroform solutions of the tetradentate Schiff base cobalt complexes described in this paper must be attributed to the rate of formation of different chloroform adducts, similar to those isolated in the solid state in the case of Co(salen) [15] or similar copper complexes.[19] In these adducts the chloroform molecules probably do not interact directly with the metal ion but with the ligand atoms of the co-ordination sphere (namely oxygen in our case). Consequently the electronic situation around the cobalt ion is only perturbed and the magnetic factors are only slightly affected by the chloroform interaction.

In agreement with this picture we have observed in chloroform solution an evolution from species characterised by $g_{1\perp} = 3{\cdot}59$—$3{\cdot}52$ and $A_{1\perp} = 132$—136 G to only one species characterised by $g_{1\perp} = 3{\cdot}24$—$3{\cdot}22$ and $A_{1\perp} = 98$—94 G. The decrease of both $g_{1\perp}$ and $A_{1\perp}$ and the corresponding lower anisotropy of the e.s.r. spectrum ($g_{2\perp}$ and $A_{2\perp}$ do not seem to be very much changed) may indicate a rather minor charge-transfer from the ligand to the metal ion as expected if the oxygen atoms of the Schiff base are interacting, through hydrogen bonding, with chloroform molecules.

Similar, but better resolved spectra, have been recently obtained [20] in the solid state in the case of Co(acacen) and similar related Co^{II} compounds with substituted β-diketones. The g values of these compounds are very similar to those obtained from spectra of Co(salen) and related compounds (Table 2). We have thus calculated (in a C_{2v} symmetry) the best electron configuration which fits both g and A values, with an approach fully developed in the experimental section, which may give a picture of the ground state and of the very low lying excited states of these complexes (see later), but in order to investigate higher excited states, we needed absorption and circular dichroism (c.d.) spectra

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[19] E. N. Baker, D. Hall, and T. N. Waters, *J. Chem. Soc.* (*A*), 1970, 406.

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

which are related to electronic transitions. Lacking anisotropic data, which alone can give certain assignments to the various electronic transitions, we have tentatively studied the isotropic spectra.

TABLE 3

Reflectance spectra (kK) in the region 4—14 kK

Compound	Experimental	Compound	Experimental	Calc.	Assignments
Co(salen), active		Co[sal(−)stien][a]		1·32	$xz \rightarrow z^2$
	5·36		5·36	5·12	$x^2\text{-}y^2 \rightarrow z^2$
	5·80sh		5·80sh		*b*
	8·40		8·33	7·93	$yz \rightarrow z^2$
	9·0sh		*c*	9·13	*d*
	10·0sh		10·0sh		*d*
	14·5		14·5	15·84	$x^2\text{-}y^2 \rightarrow xy$
Co(salen), inactive	6·00	Co(salen)(py)	5·60	5·50	$xz \rightarrow z^2$
	7·50		8·70	8·35	$yz \rightarrow z^2$
	11·80		*c*	11·90	$z^2 \rightarrow xy$
	12·80		13·30	13·35	$x^2\text{-}y^2 \rightarrow z^2$

[a] All the other compounds show a similar spectrum. [b] Probably ligand absorption. [c] Probably covered by the major absorption. [d] Spin forbidden.

TABLE 4

Circular dichroism spectra (kK) [a] in the region 17—24 kK

Compound	Experimental	Compound	Experimental	Compound	Experimental	Compound	Experimental	Calc.	Assignments
Co[sal(−)pn] (in $CHCl_3$)	19·0sh (+0·75)	Co[sal(−)bn] (in $CHCl_3$)	18·0 (+1·0)	Co[sal(+)stien] (in $CHCl_3$)	*b*	Co[sal(−)chxn] (in $CHCl_3$)	18·0 (−0·75)	18·48	$xz \rightarrow xy$
	b		*b*		*b*		19·0 (−1·02)	18·84	$x^2\text{-}y^2 \rightarrow xy$
	20·3 (+3·70)		20·3 (+3·25)		20·1 (+4·60)		20·6 (−2·75)	18·96	$z^2 \rightarrow xy$
	21·0 (+2·50)		21·7 (+0·85)		21·0 (+1·25)		22·0 (0·0)	21·30	$yz \rightarrow xy$
	22·4 (+1·0)		22·4 (+0·85)		22·8 (−1·30)		23·6 (−4·80)	23·97	*c*
Co[sal(−)pn](py) [d] (in pyridine)	17·8 (+1·00)	Co[sal(−)bn](py) [d] (in pyridine)	18·0 (+1·40)	Co[sal(+)stien](py) [d] (in pyridine)	18·1 (+1·60)	Co[sal(−)chxn](py) [d] (in pyridine)	*b*	18·06	$xz \rightarrow xy$
	b		19·5 (+0·01)		19·7 (+1·20)		19·5 (+1·25)	19·60	$x^2\text{-}y^2 \rightarrow xy$
	21·0 (−1·20)		21·0 (−1·00)		21·5 (−0·30)		20·5 (+1·75)	20·40	$yz \rightarrow xy$
	23·0sh (+0·5)		23·0sh (+0·72)		23·0 (−0·80)		22·5sh (−1·10)	23·05	*c*

[a] ($\varepsilon_l - \varepsilon_r$) in parentheses. [b] Not observed probably because covered (in the other cases they appear as shoulders). [c] Bielectronic transition (or charge-transfer). [d] Spectra obtained in C_6H_5Cl with a small excess of pyridine are identical.

Absorption spectra in the near-i.r. region are reported in Figure 1 and Table 3. The trend of the electronic spectra in the region above 16 kK is given in Figure 4. C.d. spectra of cobalt complexes with the (−)pn Schiff bases of some substituted salicylaldehydes have been already described, while this work was in preparation, by Hipp and Baker.[21] We also obtained c.d. spectra of our compounds and examples are reported in Figure 5; one of them, namely the (−)pn compound, has been already reported by Hipp and Baker. We have been unable to examine the c.d. of the absorption bands in the near-i.r. region with the c.d. apparatus available, but the general trend of the c.d. of the absorption band *ca.* 8·5 kK has already been reported.[21]

C.d. data from *ca.* 18 kK to 23 kK are given in Table 4. As recently and independently reported by many authors [21–24] the Cotton effects of the *d–d* bands of the optically active Schiff base complexes of the type here investigated must be attributed to the perturbation of the CoN_2O_2 chromophore by the intrinsic helicity of the non-planar central chelate ring of the diamine. The total Cotton effect is related to the major stabilisation, due to steric hindrance, of one of the two conformations (λ or δ) of the ring. The c.d. spectra here reported (Table 4) are in agreement with the suggestions made by others [21] that the relatively strong Cotton effects associated with the *d–d* transitions are consistent in the case of (−)pn with an equilibrium between the axial (δ conformation of the ring) and the equatorial (λ conformation of the ring) position of the substituent, where non-bonding interactions favour the axial conformation in the case of diamines having the R absolute configuration as (−)pn (the only appreciable

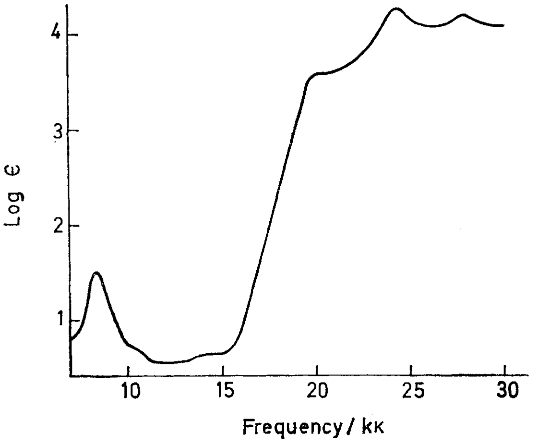

FIGURE 4 Absorption spectrum of Co[sal(+)stien] in $CHCl_3$ solution

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[21] C. J. Hipp and W. A. Baker, *J. Amer. Chem. Soc.*, 1970, **92**, 792.

[22] R. S. Downing and F. L. Urbach, *J. Amer. Chem. Soc.*, 1969, **91**, 5977; 1970, **92**, 5861.

[23] R. L. Farmer and F. L. Urbach, *Inorg. Chem.*, 1970, **9**, 2562.

[24] B. Bosnich, *J. Amer. Chem. Soc.*, 1968, **90**, 627.

steric interaction is in fact between the azomethine hydrogen and the methyl or phenyl substituent). In agreement with this point we have observed that the magnitude of the c.d. band at *ca.* 20 kK (Figure 5 and Table 4), which is definitely related to a *d–d* transition (see later), is increased by substitution of methyl by phenyl group, the latter having probably a more strong interaction with the azomethine hydrogen.

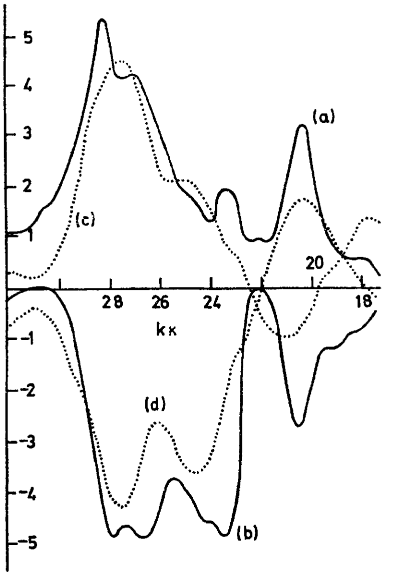

FIGURE 5 C.d. spectra; (a), Co[sal(−)bn]; (b), Co[sal(−)chxn]; (c), Co[sal(−)bn](py); (d), Co[sal(−)chxn](py)

The recent *X*-ray investigation of the (+)bn complexes has confirmed that both methyl groups are in the axial position [16a] (of course in the *meso*-bn complex one axial and one equatorial methyl group have been found). In this case, the diamine having a SS absolute configuration of the chiralic carbons, the ring must assume a λ conformation in order to let the methyls stay in the axial position. Diamines with the same absolute configuration of (−)pn, [(−)bn, (−)phenen, (+)stien] show the same c.d. spectral pattern in the region 18—25 kK, with the only exception of (−)chxn, where we have a complete inversion of the sign of the Cotton effect (Figure 5). This is an expected trend because in structurally related square planar Ni^{II} and Cu^{II} tetradentate Schiff base complexes [22] a similar behaviour has been reported and attributed to the presence of the cyclohexane ring which strongly favours the λ conformation of the chelated ring of the diamine despite the steric hindrance of the methine.

We have also observed that the circular dichroism spectra of complexes of (−)pn and (+)pn [or (−)bn and (+)bn, (+)stien and (−)stien *etc.*] correspond to enatiomeric species as expected only if Rδ and Sλ respectively are the most stable conformations. The very slight tetrahedral distortion observed in the solid state for the CoN$_2$O$_2$ chromophore lowers the local C_{2v} symmetry to C_2, introducing another element of helicity in the side chelated rings, centred about the cobalt atom. Bosnich has proposed that the corresponding Ni^{II} and Zn^{II} complexes also show such helicity in solution.[24] In fact the observation of a c.d. couplet with components of opposite signs in the region 25—30 kK (corresponding to the $\pi \longrightarrow \pi^*$ absorption band of the azomethine groups) indicates that the two azomethine groups are not strictly planar, as in a flattened tetrahedral configuration of the donor atoms.

We have also observed such a couplet (Figure 5) in the same spectral region, although not so clearly as in the case of Ni^{II},[21,22] Zn^{II},[21] and Cu^{II} [22] Schiff base complexes. In the case of (−)pn and diamines of the same absolute configuration, with the exception of (−)chxn, the couplet has the positive component at lower energies. Theory predicts [24] that when the chirality of chromophore is Λ, the negative component of the $\pi \longrightarrow \pi^*$ azomethine couplet will lie at higher energy. We can thus assume that in the case of diamines of absolute configuration R [as (−)pn, (−)bn, (−)phenen, (+)stien (see part I)] the chirality of the CoN$_2$O$_2$ chromophore is Λ. This statement is in agreement with a molecular model which shows that diamines of R absolute configuration [with the exception of (−)chxn] not only imposes the δ conformation to the chelated ring of the diamine but also the Λ (left handed) chirality to the configuration on the metal atom. Of course in the case of (−)chxn, owing to the stabilisation of the λ conformation of the ring, we should have stereoselective stabilisation of the Δ chirality of the configuration about the metal.

We have in fact observed that the azomethine couplet has in this latter case (see Figure 5) the positive component at higher energies, as expected. Of interest is the fact that our conclusions agree with those independently reached in the case of similar square planar Ni^{II} [24] and Cu^{II} [22] complexes. C.d. has also been used to distinguish the *d–d* transitions in a major band envelope of the electronic absorption spectrum (Figures 4 and 5, and Table 4). In this approach we have tentatively localised the *d–d* transitions which appear in the lower energy region between 18—23 kK. Above 23 kK *d–d* transitions are certainly too mixed or covered by charge transfer and intraligand absorptions also in the c.d. spectrum.[21] In first approximation as already stated the *cis*-CoN$_2$O$_2$ chromophore may be considered nearly planar (C_{2v} symmetry) in chloroform solution (Figure 6). We have thus used a ligand field approach as developed by some of us [25] to obtain electronic energy levels which fit some of the physical data reported above.

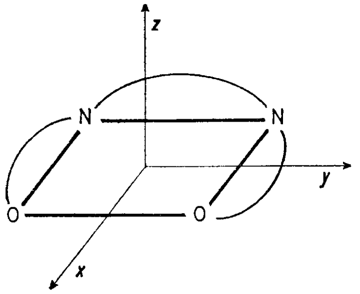

FIGURE 6 The choice of co-ordinates for the CoN$_2$O$_2$ chromophore

Very recently, while this paper was in preparation, a rather similar parametric ligand field calculation has been developed.[26] It is known that a simple ligand field approach does not allow the characterisation of the electronic anisotropy in the *xy* plane (see Figure 6); consequently it could

[25] F. Cariati, A. Sgamellotti, and V. Valenti, *Atti Accad. naz. Lincei, Rend. Classe Sci. fis. mat. nat.*, 1968, **45**, 76.

[26] L. M. Engelhardt and M. Green, *J.C.S. Dalton*, 1972, 724 and references therein.

be useful to consider only a local D_{4h} symmetry.[26] However if we consider not only the CoN_2O_2 chromophore, but the ligand as a whole, a C_{2v} symmetry, related to a certain anisotropy in the x and y axes, must be in any case considered. This rhombic perturbation has been for instance clearly detected in the e.s.r. spectra. Overlap calculations have shown that the origin of the anisotropy stays probably in the different π interactions outside the xy plane between the cobalt d orbitals and the π orbitals of the carbon atoms of the phenyl ring and of the ethylenic bridge of the diamine.

The energy levels have been calculated using the perturbation matrices in the case of a d^7 electron configuration in a C_{2v} field, where the electronic repulsion and the spin–orbit coupling have been fully considered. In a previous study, where the complete perturbation matrices used here were described, only the D_{4h} symmetry was reported.[25] In order to introduce the rhombic anisotropy, we have modified the above matrices introducing the rhombic perturbation terms and removing the degeneracy of the e_g orbitals * (see Experimental section). The following values of major parameters have been used: $-0{\cdot}4$ kK for the spin–orbit coupling constant ξ, as proposed by Griffith,[27] a ratio 1 : 7 for the parameters B and C of electrostatic repulsion, as already used in other tetragonal compounds,[28] and finally the value of $-0{\cdot}5$ kK for the parameter R, which describes the field interaction of d_{z^2} and $d_{x^2-y^2}$ orbitals, which in a rhombic C_{2v} symmetry belong to the same irreducible representation.

The other field parameters (see Experimental section) have been considered to be satisfactory when we could fit both magnetic properties (μ_{eff} and g values) and electronic transitions. The final values obtained from the best fit are completely reasonable and in good agreement with those used by other authors. With this approach (see Experimental section for details) we have obtained a ground state where the unpaired electron stays mainly in the d_{z^2} orbital. The values of g factors have thus been recalculated by considering the magnetic interactions which take place between the complete eigen-functions describing the ground state. A satisfactory agreement has again been observed between experimental and calculated values.

Of note then is that the ground state is described not only by the configuration where the unpaired electron is localised in the d_{z^2} orbital but also, although at much less extent, by those configurations where the unpaired electron stays in the d_{xz}, d_{yz}, and $d_{x^2-y^2}$ orbitals (only doublet states are considered of course) with the following major distribution of the unpaired electron: d_{z^2} (90%), d_{xz} (5%), d_{yx} (0·1%), $d_{x^2-y^2}$ (0·7%). Besides the ground state eigen-function does not contain only doublet states but also a minor contribution of quartet states, particularly that in which the unpaired electrons stay in d_{z^2}, $d_{x^2-y^2}$, d_{yz} orbitals (1·3%). It is thus important to point out now that, by considering the ground state and energy levels proposed by Hipp and Baker [21] where the unpaired electron stays in the $d_{x^2-y^2}$ orbital, it would be impossible to obtain a satisfactory agreement between calculated and experimental g values. Besides also the calculated values of μ_{eff} at different temperatures would be much lower than the experimental ones (*ca.* 1·8 B.M. at room temperature also considering spin–orbit coupling).

We have then calculated values of μ_{eff} at different temperatures based on the energy levels here proposed; the results are reported in Table 1. The agreement between calculated and experimental values of μ_{eff} is satisfactory and what is more important, the observed temperature variation is close to that calculated. We can thus conclude that our description of the d electron distribution fits, in a better way, the magnetic properties than the one already proposed.[21]

The ground state configuration here proposed differs also from that proposed on the basis of e.s.r. data by Ochiai [17] who also places the odd electron in the $d_{x^2-y^2}$ orbital (using our choice of axes). As a matter of fact, as already pointed out, the e.s.r. data reported by this author [17] (obtained in dimethyl acetamide or CH_2Cl_2–toluene solutions) differ greatly from ours, despite the fact that absorption spectra show that in these solvents the square planar species is the only one present as in our case. The ground state configuration here proposed is not unusual for square planar low spin Co^{II} compounds; for instance it was assumed in rather similar complexes such as Co^{II} phthalocyanine,[26] or in the case of *trans*-$Co(PPh_3)_2$(mesitylene)$_2$ and related compounds.[29]

Of course, in absence of an anisotropic study such as that described in ref. 29, we are actually unable to define perfectly the magnetic rhombic anisotropy. However this latter point means only that we cannot define the relative position of d_{xz} and d_{yz} orbitals. Once having defined the ground state, we have also attempted an investigation of excited states with the help of isotropic electronic spectra and c.d. data.

The allowed *d–d* transitions, which can be detected in the electronic and c.d. spectra (see Tables 3 and 4) have been tentatively assigned considering our ligand field calculations (see Experimental section). With our values of field parameters one expected a group of two spin-allowed *d–d* bands in the near-i.r. region. Hipp and Baker [21] have shown, both from the shape of the isotropic absorption and c.d. spectra, that the band *ca.* 8·5 kK is definitively asymmetric with at least two or three components. They have thus assigned to this complex absorption all the spin-allowed, one electron transitions of the near-i.r. region. We have confirmed that the absorption *ca.* 8·5 kK is definitively asymmetric but however, (Figure 1), we have also found new *d–d* absorption bands *ca.* 5·36 and 5·80 kK, which have not been considered by those authors.

Our calculations (see Table 3) assign the absorption bands of the near-i.r. region to the following transitions: $d_{x^2-y^2} \longrightarrow d_{z^2}$ *ca.* 5·36—5·80 kK and (d_{xz} or d_{yz}) $\longrightarrow d_{z^2}$ *ca.* 8·5 kK. The complexity of the band *ca.* 8·5 kK may be due to the presence of spin-forbidden transitions (see Table 3) which become stronger by the mixing up with spin-allowed transitions of similar energies. The assignment of the electronic *d–d* transitions which lie in the visible region is difficult because, as already reported, the visible absorption spectra show very intense bands starting at 16—18 kK (Figure 4) which must be assigned as metal to ligand charge-transfer [21] and prevent the easy location of the *d–d* bands, which occur as weak shoulders on the major absorptions. However, as already reported, we have distinguished with the help of the c.d. spectra, some of the

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* In D_{4h} symmetry we have the following assignments: $d_{z^2} = a_{1g}$; $d_{x^2-y^2} = b_{2g}$; $d_{xy} = b_{1g}$; $d_{xz,yz} = e_g$.

[27] J. S. Griffith, 'The Theory of Transition-metal Ions,' Cambridge University Press, 1961, p. 342.

[28] H. B. Gray and C. J. Ballhausen, *J. Amer. Chem. Soc.*, 1963, **85**, 260.

[29] R. B. Bentley, F. E. Mabbs, W. R. Smail, M. Gerloch, and J. Lewis, *J. Chem. Soc.* (*A*), 1970, 3003.

d–d bands from the overlapping charge transfer absorptions at least in the lower energy region (16—23 kK). In this region when the diamine is (−)pn, three clear Cotton effects have been detected at around 15·5 (positive), 18·0 (negative), 20·0 (positive).

We have always found, when the diamine has an absolute configuration corresponding to that of (−)pn, that the c.d. curve is in agreement with the presence at least of three Cotton effects in the 15—21 kK region (Figure 5). Our assignments of the electronic transitions corresponding to these bands are reported in Table 4.

Our assignments do not correspond to those previously done,[21] but they seem to be more reliable. In fact all the electronic transitions corresponding to our assignments are magnetically allowed in agreement with the observed Cotton effects. On the contrary other authors,[21] in order to explain the presence of a relatively small c.d. corresponding to the 18·0 kK transition (which they assign to $d_{z^2} \longrightarrow d_{x^2-y^2}$ which does not possess magnetic dipole character) were obliged to invoke some mixing with the $d_{xy} \longrightarrow d_{x^2-y^2}$ transition under the influence of the C_{2v} field. The remaining bands in the visible–u.v. region are mainly charge transfer or intraligand absorptions; we have not tried any assignment, which in a ligand field approach is certainly hopeless although, using the qualitative approach of Bosnich,[24] they could be attempted.[21]

Five-co-ordinate Complexes.—Square planar cobalt(II) Schiff base complexes interact easily with donor bases to form five-co-ordinated species; these adducts can be isolated in the solid state and the structure of the pyridine compound Co(salen)(py) has been reported.[30]

Although six-co-ordinated species have been reported to form in the case of other similar Co^{II} species,[31] we have been unable to detect the formation of such species at room temperature in the presence of a large excess of donor bases (which may be used as solvents). We have thus obtained the five-co-ordinated pyridine adducts of some of our compounds (see Table 5) as red-brown air stable crystalline materials. In solution they react smoothly and in a reversible way, as already reported for Co(salen)(py),[7] with oxygen. E.s.r. spectra of Co(salen)(py) or related compounds have been already reported by different authors:[8,17,26] they all concluded that the unpaired electron stays mainly in the d_{z^2} orbital.

Using the ligand field approach previously described, we have calculated the energy levels, which may fit the e.s.r. (see Experimental section) and electronic transitions, arriving at a similar conclusion. The general trend of the electronic levels is not changed much, when compared to that of the related square planar compounds, with the major exception of the much lower splitting of the e_g orbitals (which are d_{yz} and d_{xz} in a D_{4h} symmetry). This latter point, which is suggested by overlap calculations, is in agreement with the experimental lower rhombic anisotropy of the tensor g,[8,17,26] that some authors [8] were in fact unable to resolve. Moreover the d_{z^2} orbital, which is the highest occupied d orbital, is shifted at higher energy in respect to its relative position in the square planar compounds. The calculations (carried out as in the case of square planar compounds) have given values of the g tensor which are in very good agreement with the experimental ones.

In conclusion the ground state is described by an electron configuration which is completely similar to that proposed up to now for all the low spin five-co-ordinated Co^{II} complexes.[32] We have thus tried an investigation of the electronic transitions observed in the isotropic electronic and c.d. spectra. In Table 3 we have reported the observed *d–d* electron transitions, probably between doublet states, which may give us some information on the position of some excited states. The absorption spectra show two clear features: the disappearance of the sharp absorption bands *ca.* 8·5 and 6 kK (Figure 1) and a rather strong envelope of charge transfer bands where only one of the *d–d* transitions can be detected as a shoulder (Table 3) *ca.* 13 kK. Also in this case c.d. spectra (Figure 5) may be used in detecting *d–d* transitions in the region 18—23 kK. At least two (and probably three) Cotton effects due to *d–d* transitions are centred (see Figure 5 and Table 4) *ca.* 18·5—18 kK (positive), 21·5—20·5 kK (negative), and 23 kK (negative) [in the case of (−)pn and diamines of the same absolute configuration]. The assignments are given in Table 4 together with the calculated values for each transition.

The relatively strong and anomalous temperature dependence of the values of the magnetic moment [compared for instance with the slight influence in the case of square planar complexes (Table 1)] suggests the existence of low lying quartet states [2] in the case of five-co-ordinated compounds. Despite the fact that through spin–orbit coupling and by mixing with spin-allowed transitions some spin-forbidden transitions may sometimes become strong enough to be observed, generally it is difficult, through absorption spectra, to define the position of excited states which cannot easily be reached by electron excitation because they correspond fundamentally to spin-forbidden transitions.

In the ligand field calculation we have found that we have, above the doublet ground state $^2A_1$, a quartet state which corresponds to the ^4E state (considering simply a D_{4h} symmetry) and lies *ca.* 1000 cm^{-1} above the ground state. Such a value is slightly too high to give, by mixing of the ground and excited states, a temperature dependence of the calculated magnetic moment in agreement with that reported by Earnshaw and coworkers.[2] In order to obtain a better agreement we needed an energy difference of *ca.* 800 cm^{-1} or less; such a change is acceptable if we consider that either we have some vibrationally excited states which lie *ca.* 200 cm^{-1} above the ground state or that our energies are calculated with uncertainties of ± 300 cm^{-1}. The calculated magnetic moment of Co(salen)(py) (see Experimental section for details of calculations) is with this assumption in acceptable agreement with the experimental one (Table 1). The very close proximity of an excited quartet state to the double ground state has been recently confirmed by the observed spin equilibrium doublet–quartet in the case of five-co-ordinated species of Co(salen), where the base is an imidazole derivative.[33]

The c.d. spectra need more discussion because they show some other interesting features. First we have a complete inversion of the Cotton effects in the region 18—22 kK, particularly *ca.* 20 kK, when compared to those of the

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[30] M. Calligaris, D. Minichelli, G. Nardin, and L. Randaccio, *J. Chem. Soc.* (*A*), 1970, 2411.

[31] (*a*) L. D. Rollman and S. I. Chan, *Inorg. Chem.*, 1971, **10**, 1978, and references therein; (*b*) L. G. Marzilli, P. A. Marzilli, and J. Halpern, *J. Amer. Chem. Soc.*, 1970, **92**, 5752; (*c*) A. Rockenbaner, É. Budó-Záhonyi, and L. Simandi, personal communication.

[32] M. Ciampolini, *Structure and Bonding*, 1969, **6**, 83.

[33] L. G. Marzilli and P. A. Marzilli, *Inorg. Chem.*, 1972, **11**, 457.

corresponding square planar complexes (Figure 5), whilst they remain rather similar in the region above 23 kK, where we have mainly charge transfer and intra-ligand $\pi \longrightarrow \pi^*$ transitions. Such behaviour has not been reported [22] in the case of related Cu^{II} Schiff base complexes of (−)pn and (−)chxn, where only a lower intensity of the Cotton effects has been observed on going from chloroform to pyridine solution.

The structure of Co(salen)(py) [30] corresponds to a slightly distorted square planar pyramid, where the chelated ring of the diamine is not too much distorted from planarity. If this feature is maintained also in the case of carbon substituted diamines, we should expect a relatively small magnitude of the c.d. bands (due to *d–d* transitions) which are directly related to the amount of the ring distortion which induces, through the effect of asymmetric carbon atoms of the diamine, the stabilisation of one intrinsically asymmetric conformation (either δ or λ) of the ring.[21] We have in fact a decrease (with respect to the case of square-planar complexes) of the magnitude of the Cotton effect in the region 18—22 kK (Figure 5); however such a decrease is not so large as expected if a large difference of the ring distortion in square planar and five-co-ordinated compounds was involved.

This trend may be due either to the difficulty of extending the results obtained in the solid state to those reached from solution studies (where different non-bonding interactions may take place) or to the fact that the intensity of the c.d. bands in that region is related to the mixing of *d–d* transitions with totally allowed electronic transitions of the same symmetry such as the charge transfer bands which are associated with the same energy region. In this latter case the strength of the Cotton effect is mainly due to these transitions and less affected by the ring conformation which perturbs mainly the internal *d–d* transition of the cobalt ion. The inversion of the Cotton effect pattern in the region 18—22 kK may suggest a complete inversion of the diamine ring conformation on going from square planar to five-co-ordinated species.

However, in other similar five-co-ordinated complexes such as the sal-(+)pn complexes of vanadyl ion,[23] it has been observed that the inversion of the conformation of the chelated ring is always followed by an inversion of the configuration about the metal atom (that is there is a $\lambda \rightleftharpoons \delta$ and $\Delta \rightleftharpoons \Lambda$ interdependence). Besides in the case of vanadyl (−)pn complex the δ conformation of the chelated ring was still the preferred one as in the case of square planar complexes, no ring inversion being observed.

From Figure 5 we can infer that the azomethine couplet region *ca.* 28 kK is not changed very much on going from Co[sal(−)pn] to Co[sal(−)pn](py). Consequently the Λ configuration about the metal atom is still maintained, which probably means that we have not an inversion of the δ chelated ring of the diamine. In fact when such an inversion takes place [as probably in the case of (−)chxn pyridine complex (Figure 5)], we observe in the same time an inversion of the azomethine couplet related to an inversion of the configuration about the cobalt. In fact the (−)pn and (−)chxn pyridine complexes have a mirror-image relationship between the signs of the bands of the c.d. spectrum (see Figure 5). We can thus conclude that the inversion observed in the c.d. spectra *ca.* 20 kK may be probably attributed only to a different amount of distortion from planarity of the chelated ring of the diamine but towards the same conformation. This point may be supported by the assumption made by some authors [21] who have correlated in these complexes the sign of the c.d. of *d–d* bands using a simple rationalisation such as a right-handed octet rule which considers the amount of the displacement of chelate ring atoms from planarity.

However our conclusion must be proved by an *X*-ray investigation (which is under way in the case of Co[sal(+)bn](py) and Co(sal *meso*-bn)(py). There are still a few points of a certain interest to be discussed; for instance considering the reflectance spectra (Figure 1 and Table 3) of Co(salen) (active form), Co(salen)(py) and finally Co(salen) (inactive form) we observe that the spectrum of the inactive form of Co(salen) has a general pattern between those of the corresponding active form and of Co(salen)(py). This is an expected behaviour because from the *X*-ray structure [16] it appears that the cobalt atom in the crystalline inactive form of Co(salen) has a tetragonal perturbation which corresponds to a weak five-co-ordination. As support to this latter point we have that the magnetic moment (see Table 1) has a value and a temperature dependence in agreement with such a tetragonal perturbation.

The Reaction with Oxygen.—All the cobalt complexes, when dissolved in pyridine or dimethylformamide, react rather easily with oxygen in a reversible way; in anhydrous solvents many cycles of oxygenation and deoxygenation (for instance by bubbling dry nitrogen or argon in the oxygenated solution) can be obtained (the oxygenation and deoxygenation processes can be followed on 10^{-3}—10^{-4}M solutions through the changes of the absorption spectra in the region *ca.* 25 kK).

The oxygen adducts of complexes derived from diamines different from en are more soluble than the 2 : 1 oxygen adduct [LCo(salen)]$_2$O$_2$ (where L is a donor base) and they do not precipitate at room temperature from rather concentrated solutions (10^{-2}M). However we have been able to obtain in some cases dark-brown crystalline samples of some 2 : 1 oxygen adducts (see Table 5) by mild concentration of the oxygenated pyridine solution in a stream of dry oxygen and at a temperature of −50°. The presence

TABLE 5

Analytical data of cobalt complexes

Compound	Calc.			Found		
	C	H	N	C	H	N
Co(salen)	59·1	4·3	8·6	58·9	4·5	8·7
Co[sal(−)pn]	60·2	4·8	8·3	59·2	4·8	8·1
Co[sal(+)pn]	60·2	4·8	8·3	59·4	4·8	8·2
Co(sal *meso*-bn)	61·2	5·1	7·9	59·6	5·2	7·5
Co[sal(+)bn]	61·2	5·1	7·9	60·9	5·4	7·6
Co[sal(−)chxn]	63·3	5·3	7·4	62·6	5·4	7·2
Co[sal(+)chxn]	63·3	5·3	7·4	64·3	5·5	7·6
Co(sal *meso*-chxn)	63·3	5·3	7·4	63·5	5·2	7·4
Co[sal(+)stien]	69·9	5·4	5·8	69·5	5·3	5·4
Co[sal(−)stien]	69·9	5·4	5·8	69·2	5·5	5·6
Co(sal *meso*-stien)	69·9	5·4	5·8	68·3	4·5	5·7
Co(salen)(py)	61·8	4·7	10·0	61·7	4·7	10·1
Co[sal(+)bn](py)	64·1	5·3	9·7	64·4	5·3	10·0
Co[sal *meso*-bn)(py)	64·1	5·3	9·7	64·2	5·3	9·6
[Co[salen)(py)]$_2$O$_2$	60·0	4·6	10·0	59·4	4·3	10·2
{Co[sal(−)pn](py)}$_2$O$_2$	60·8	4·9	9·7	61·3	4·8	10·2
[Co(sal *meso*-bn)(py)]$_2$O$_2$	61·6	5·2	9·4	61·0	5·3	9·2
{Co[sal(+)stien](py)}$_2$O$_2$	69·2	4·7	7·3	69·1	4·4	7·6
{Co[sal(+)chxn](py)}$_2$O$_2$	63·3	5·3	8·9	62·8	4·3	9·3
[Co(salen)DMF]$_2$O$_2$	55·1	5·1	10·1	54·4	4·6	9·5
{Co[sal(−)pn]DMF}$_2$O$_2$	56·0	5·4	9·8	55·6	5·4	9·7
[Co(sal *meso*-bn)DMF]$_2$O$_2$	57·0	9·5	5·7	56·0	8·9	5·6
{Co[sal(+)stien]DMF}$_2$O$_2$	65·7	5·1	7·4	66·0	4·5	7·4

of bound molecular oxygen in the samples was confirmed by analysis, evolution of oxygen by treatment with $CHCl_3$ and by the reversibility of their pyridine solutions towards the reformation of the non-oxygenated cobalt complexes.

Rather similar dark-brown materials, which however are hydroxo-cobalt(III) species, may be obtained when the work up is not sufficiently careful (presence of water in the solvent) and too long. These compounds, which have a completely similar elemental analysis, may be easily recognised by the absence of oxygen evolution by treatment with $CHCl_3$ and by the presence in the i.r. spectrum of a rather broad OH absorption *ca.* 3100—3000 cm^{-1}.

We have shown, as already briefly reported in a preliminary way [34] that five-co-ordinated species (in equilibrium with the square planar species) were formed by addition of an amine to a chlorobenzene or nitrobenzene solution of the cobalt complexes. These solutions react also smoothly with oxygen confirming once again that five-co-ordination is directly related to the ' activation ' of the cobalt atom towards oxygen. In fact, after addition of bases to the $CHCl_3$ or CCl_4 solutions of the cobalt complexes, where we did not observe the formation of five-co-ordinated species at room temperature, a reaction with oxygen was not apparent although it has been reported to take place at -100 °C [10] when the formation of some five-co-ordinated species probably takes place. In this respect the properties of dimethylformamide solutions of square planar cobalt(II) complexes are rather relevant. They react, as already reported,[7,8] rather smoothly with oxygen at room temperature despite the fact that electronic, c.d., and o.r.d. spectra show that the major form present in solution at room temperature is the square planar complex.[34] We could say that in these conditions at least 95—98% of the cobalt atoms have in dimethylformamide solutions the square planar co-ordination geometry.

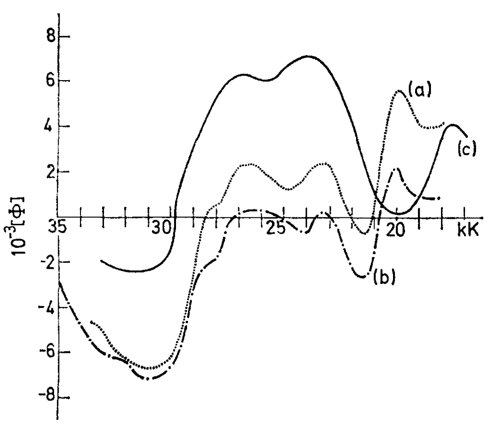

FIGURE 7 O.r.d. spectra of Co[sal(−)pn] in (a), $CHCl_3$; (b), DMF; and (c), pyridine

If we compare the absorption band *ca.* 8·5 kK we could not find a decrease of intensity on going from chloroform to dimethylformamide solution, although in the o.r.d. spectra (Figure 7) the rotation *ca.* 20 kK is lower in dimethylformamide than in chloroform, as it could be expected if a certain amount of a five-co-ordinated species, which has an opposite Cotton effect, is present. E.s.r. investigations have shown that at liquid-nitrogen temperature in dimethylformamide a mixture of square planar and five-co-ordinated species is present.

In conclusion five-co-ordination is an essential feature for oxygenation but it is not always necessary to have a large concentration of a thermodynamically stable five-co-ordinated species, in order to obtain oxygen uptake at a reasonable rate. In agreement with this latter point we have observed that oxygen is taken up, although very slowly, in the presence of an excess of very weak bases like alcohols, ethers, and water, which do not form very stable five-co-ordinated adducts of the square planar Co^{II} complexes at very low temperatures. Consequently the previous statement [7] that five-co-ordination is an essential feature for oxygenation must be changed; only the presence of a donor σ base appears to be an essential feature for oxygenation.

The rather high reactivity of dimethylformamide solutions cannot be easily explained, although a completely similar feature has been reported to take place in the oxygenation of cobalt(II) porphyrins.[35] We have found, using a constant pressure burette (see Experimental section) that in pyridine solution oxygen uptake is only 3 or 4 times faster than in dimethylformamide, however with nitrogen donor bases the rate of oxygen uptake increases by increasing the basicity of the axial ligand. For instance addition of very small amounts of dimethylamine to a dimethylformamide solution of the cobalt complexes suddenly increases by many times the rate of oxygen uptake which, with our apparatus, becomes thus completely diffusion controlled. A similar connection with donor properties of the nitrogen axial ligands has been reported in the case of the thermodynamic stabilities of Co^{II}–porphyrin oxygen adducts.[35]

A rather qualitative preliminary investigation on the relative rates of oxygen uptake of either pyridine or dimethylformamide solutions has shown some interesting and unexpected features clearly related to steric effects. While all the complexes of different diamines show comparable rates of absorption [with the exception of (+)chxn and *meso*-chxn complexes which react two or three times faster than the others] the *meso*-stien and (+)bn complexes react more slowly (at least 100 times more slowly than the others) both in pyridine and dimethylformamide.

In order to have a better knowledge of the steric and electronic effects on the oxygenation reaction we are carrying out quantitative spectroscopic determinations of the rates and the equilibrium constants of the reaction with oxygen; the preliminary data, to be published in a future paper, are in agreement with the qualitative description reported here.

In 10^{-2}M solution at room temperature the amount of oxygen absorbed either in dimethylformamide or pyridine is lower than the expected for a 1 : 1 adduct and usually is between 1 : 1 and 1 : 2. However this does not mean that the 1 : 2 adduct is the major component of the oxygenated solutions; in fact visible and o.r.d. spectra in dimethylformamide show that, after oxygen uptake, there is still in solution a remarkable amount of the starting square planar complexes. Recent volumetric determinations,[36] e.s.r. studies [8d] and our preliminary investigations on equilibrium constants obtained by spectroscopic techniques have shown

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[34] F. Cariati, A. Fusi, M. Gullotti, F. Morazzoni, A. Pasini, F. Salghetti, and R. Ugo, *Chimica e Industria* (*Milan*), 1971, **53**, 264.

[35] (*a*) H. C. Stynes and J. A. Ibers, *J. Amer. Chem. Soc.*, 1972, **94**, 1559, and references therein; (*b*) J. A. Ibers reported at Symposium on activation of small molecules, June 20—22, Buffalo, 1972.

[36] M. Green and D. Mettrick, *J. Inorg. Nuclear Chem. Letters*, 1970, **6**, 149.

that the 1 : 2 adduct is probably only a minor component of the oxygenated solutions when 10^{-2}M solutions of the cobalt complex are considered. The easier isolation from these solutions of the 1 : 2 adducts is generally due to their lower solubility despite the major concentration in solution, particularly when diluted, of the 1 : 1 adducts.

The oxygenation reaction of the complexes studied in this paper is definitively exothermic, in fact by increasing the temperature to 35—40 °C we could not observe oxygen uptake by a 10^{-2}M dimethylformamide solution of Co(salen). Thermodynamic studies made on Co(acacen)(py) [37] and cobalt–porphyrin complexes [35] are completely in agreement with this latter point.

CONCLUSION

It is known that in low spin d^7 compounds the three most plausible ground states are (in D_{4h} symmetry for the sake of simplicity) $^2A_1$, $^2B_2$, and ^2E which correspond to an electron hole in d_{z^2}, $d_{x^2-y^2}$, and (d_{xz}, d_{yz}) orbitals respectively.

We have found, in agreement with others, that in five-co-ordinated compounds studied in this paper, the $^2A_1$ ground state becomes the most important, by approach along the z axis of the ligand. However we have also observed that the $^2A_1$ ground state is still the most stable in square planar Co(salen) and similar derivatives despite the absence of an axial perturbation, but the total ground state has now a major ^2E and $^2B_1$ character (Figure 8). Another interesting point is related to the energy difference of d_{xz} and d_{yz} orbitals which is greater in square planar than in five-co-ordinated species (see Figure 8) and to the presence of low lying quartet excited states in five-co-ordinated species.

It is now well established that the tendency to react with oxygen increases by introducing an axial perturbation and is also related to the basic strength of the axial ligand. We have determined that the major electronic changes on going from square planar to five-co-ordinated species are the greater localisation of the unpaired electron in the d_{z^2} orbital and the presence of low lying quartet excited states.

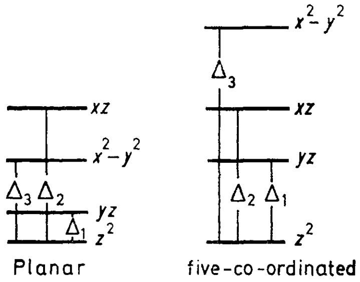

FIGURE 8 Relative energies of different electron configurations in square planar and five-co-ordinated compounds (the orbital in which the hole is located characterizes each energy)

Whilst the first point means that we have an increased radical reactivity of the cobalt atom,[38] the latter cannot be easily correlated with the observed increased reactivity with oxygen. However, it might be an important point because with a basic axial ligand of biological interest, such as imidazole, the cross-over between doublet and quartet ground state was been found to be very low lying.[33] The reaction with oxygen does not depend only on the axial ligand but it is also related to the characteristic of the field in the x,y plane. While an extended reactivity with oxygen has been observed in a large series of complexes where the ligands in the x and y plane are not too strong [39] it is known that with largely delocalised ligands (porphyrins [37] and phthalocyanines [12]), where presumably we have a stronger field, the oxygen addition takes place less easily and usually requires very low temperatures and the presence of strong bases in the axial positions. This point cannot be settled with a ligand field approach; for this reason molecular orbital calculations are under way to obtain a more complete and detailed description of the electronic structures of these complexes.

We can thus finally briefly discuss the steric effects which we have reported in this paper and have been recently confirmed by a preliminary thermodynamic investigation. They may be related to two factors: the repulsive interaction of the axial substituents of the diamine ring with the oxygen molecules approaching the cobalt atom or the repulsive interaction with the axial donor base L which is then maintained at a greater distance from the cobalt atom than it is usually in Co(salen)L. We believe that X-ray investigations under way on some pyridine adducts will make the choice between these two hypotheses easier.

EXPERIMENTAL

Preparation of Complexes.—The diamines were synthesised and resolved as reported in Part I of this series; Schiff bases have been also obtained as described in the same paper. Square planar cobalt(II) compounds have been obtained by reacting, under nitrogen, a hot alcoholic solution of cobalt acetate with an alcoholic solution of an equimolecular amount of the Schiff base. Red or brown-red crystalline materials separated on cooling the solution.

Pyridine adducts have been isolated as brown-red materials by slow evaporation in a stream of dry nitrogen of a pyridine solution of the cobalt Schiff base complexes. Analyses of all the compounds prepared are reported in Table 5. Oxygen compounds have been obtained in a few cases (see Table 5) as dark-brown crystalline materials by bubbling dry oxygen into a solution of the cobalt complexes in anhydrous pyridine or dimethylformamide; after evaporation to small volume and by cooling to −50° for a day microcrystals separated.

Spectroscopic and Magnetic Measurements.—Solution and reflectance electronic spectra were carried out on a Beckman DK 2A spectrophotometer; the reflectance spectrum of the active form of Co(salen) was obtained in a nitrogen atmosphere by protecting the crystalline material with a thin glass.

E.s.r. spectra were obtained on a Varian 4502-11 spectrometer, at a field modulation of 100 kHz. The apparatus

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[37] G. Amiconi, M. Brunori, E. Antonini, G. Tauzher, and G. Costa, *Nature*, 1970, **228**, 549.

[38] P. B. Chock and J. Halpern, *J. Amer. Chem. Soc.*, 1969, **91**, 582, and references therein.

[39] Shizuo Fujiwara, Tokuko Watanabe, and Hiroshi Tadana, *J. Co-ordination Chem.*, 1971, **1**, 195.

has a control of both magnetic field and temperature. The resonance frequencies have been derived by standardisation *with* DPPH. Samples in deoxygenated chloroform have been prepared as already reported.[8d] Magnetic susceptibilities have been obtained with the Gouy method. The magnetic balance (with a Chan balance) had an automatic control of the temperature from −194° to +25 °C. Measurements have been made in all this range of temperatures by increasing slowly the temperature by shifts of *ca.* 20°.

C.d. spectra were obtained on a Cary 61 spectrophotometer; o.r.d. spectra on a Perkin-Elmer spectropolarimeter.

Measurement of Oxygen Absorption.—The determination of the relative rates of oxygen absorption have been carried with a constant pressure burette already described; [40] the pure and dry solvents, degassed by refluxing *in vacuo* for a few hours, were saturated with oxygen in the reactor; the solid materials were then added without stirring and they usually dissolved in a few seconds to give *ca.* 10^{-2}M solutions (*ca.* 50 mg in *ca.* 25 ml of solvent). By vigorous magnetic stirring oxygen absorption from the gas phase suddenly took place. The rate of oxygen absorption was not much altered by changing the rate of stirring or the gas–liquid surface area.

Ligand Field Calculations.—The calculations were based on perturbation of d^7 configuration by the ligand field Hamiltonian, including electron repulsion and spin–orbit coupling, where the empirical parameters Dq, Dt, Ds, B, C, ζ have their usual definition.[41] The equivalence of d^7 to three d holes was used throughout. The details of the calculation of the matrix elements have been already reported and discussed in the case of D_{4h} symmetry.[25] We have slightly changed this previous work in order to consider the C_{2v} symmetry by introducing the two new parameters R and T of rhombic distortion defined as:

$$R = \langle d_{x^2-y^2}/V_{\mathrm{romb}}/d_{z^2}\rangle;$$
$$T = \langle d_{xz}/V_{\mathrm{romb}}/d_{xz}\rangle = -\langle d_{yz}/V_{\mathrm{romb}}/d_{yz}\rangle$$

In this approach the two 30 × 30 matrices E' and E'' of D_{4h} symmetry transform into an unique 60 × 60 matrix.* The choice of values of empirical ligand field parameters has been made by fitting first the e.s.r. factors and then the *d–d* electronic transitions (see later for details). The best values of this fitting are:

Parameter/kK	Square planar	Five-co-ordinated
Dq	+1·85	+1·9
Dr	+2·61	+2·61
Ds	+4·16	+1·76
B	+0·5	+0·5
C	+3·5	+3·5
ζ	−0·4	−0·4
R	−0·5	−1·5
T	−0·35	−1·0

Calculation of E.S.R. Factors and d–d *Transition.*—The evaluation of g and A factors of square planar and five-coordinate complexes have been carried out in the following way.

(1) We have constructed a set of eigenfunctions, corresponding to a C_{2v} symmetry, based upon real metal d orbitals, where the coefficients of the linear combination between configurations of doublet (ground and excited) are obtained from spin–orbit coupling interaction.

(2) We have thus applied the first order perturbation theory to give the eigenfunctions of Kramers doublets which result as follows:

$$\phi^{\pm} = N|\Gamma \pm \tfrac{1}{2}\rangle - \sum_{\Gamma' M_s'} \frac{\langle \Gamma' M_s'|\xi l.s|\Gamma \pm \frac{1}{2}\rangle}{E(\Gamma') - E(\Gamma)}|\Gamma' M_s'\rangle$$

Where Γ is the ground state doublet in absence of spin–orbit coupling and Γ' is the excited state doublet respectively.

(3) We have derived the principal g and A values by use of these wavefunctions and of the magnetic moment operator as follows:

$$g_{zz} = 2\langle \phi^+|Kl_z + 2S_z|\phi^+\rangle$$
$$g_{xx} = 2\langle \phi^+|Kl_x + 2S_x|\phi^-\rangle$$
$$g_{yy} = 2i\langle \phi^+|Kl_y + 2S_y|\phi^-\rangle$$
$$A_{zz} = 2P\langle \phi^+|\mathscr{H}_z - kS_z|\phi^+\rangle$$
$$A_{xx} = 2P\langle \phi^+|\mathscr{H}_x - kS_x|\phi^-\rangle$$
$$A_{yy} = 2Pi\langle \phi^+|\mathscr{H}_y - kS_y|\phi^-\rangle$$

where K is the Stevens constant, k a parameter called Fermi constant which describes the contact term in the hyperfine interaction and $\mathscr{H}$ is an operator already reported and described.[42] The above magnetic factors have been calculated considering the various possible ground states. The only satisfactory fitting of the principal g and A values has been obtained considering a ground state which corresponds to a hole in the d_{z^2} orbital. In these calculations * we have used the following relations derived from the above general equations:

$$g_{zz} = 2b_3^2 - 2b_2^2 - 2b_1^2 + 4Kb_1b_2$$
$$g_{xx} = 2b_1^2 - 2b_2^2 + 2b_3^2 - 4\sqrt{3}Kb_1b_3$$
$$g_{yy} = 2b_3^2 + 2b_2^2 - 2b_1^2 - 4\sqrt{3}Kb_2b_3$$
$$A_{zz} = 2P\left[-\frac{1}{7}b_2^2 + \frac{2}{7}b_3^2 - \frac{1}{7}b_1^2 + \frac{\sqrt{3}}{7}b_1b_3 + \frac{\sqrt{3}}{7}b_2b_3 + 2b_1b_2 - \frac{k}{2}(b_3^2 - b_2^2 - b_1^2)\right]$$
$$A_{xx} = 2P\left[-\frac{2}{7}b_1^2 - \frac{1}{7}b_2^2 - \frac{1}{7}b_3^2 - \frac{3}{7}b_1b_2 - 2\sqrt{3}b_1b_3 - \frac{\sqrt{3}}{7}b_2b_3 - \frac{k}{2}(b_1^2 - b_2^2 + b_3^2)\right]$$
$$A_{yy} = 2P\left[-\frac{1}{7}b_3^2 - \frac{2}{7}b_2^2 - \frac{1}{7}b_1^2 - \frac{3}{7}b_1b_2 - \frac{\sqrt{3}}{7}b_1b_3 - 2\sqrt{3}b_2b_3 - \frac{k}{2}(b_3^2 + b_2^2 - b_1^2)\right]$$
$$b_1 = \frac{\sqrt{3}}{2}\frac{\zeta}{\Delta_1};\quad b_2 = \frac{\sqrt{3}}{2}\frac{\zeta}{\Delta_2};\quad b_3 = N$$
$$\Delta_1 = E\big((d_{xy})^2d_{yz}\big) - E\big((d_{xy})^2d_{z^2}\big)$$
$$\Delta_2 = E\big((d_{xy})^2d_{xz}\big) - E\big((d_{xy})^2d_{z^2}\big)$$

The large experimental anisotropy has required the retention of all the second-order terms; it was therefore impossible

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* The programme may be obtained on request from the authors.

[40] G. Pregaglia, D. Morelli, F. Conti, G. Gregorio, and R. Ugo, *Discus. Faraday Soc.*, 1968, **46**, 110.

[41] B. N. Figgis, ' Introduction to Ligand Fields,' Wiley, New York, 1966.

[42] R. M. Golding, ' Applied Wave Mechanics,' Van Nostrand, London, 1969.

to simplify the equations to obtain g and A values as reported in the case of bis(1,2-dicyanoethylene-1,2-dithiolato)cobalt(II).[43] With the following values of the constants:

$$K = 1;\ k = 0{\cdot}406;\ P = 257{\cdot}10^{-4}\ \mathrm{cm}^{-1};\ b_1 = -0{\cdot}176;\ b_2 = -0{\cdot}039;\ b_3 = 0{\cdot}9835$$

we have obtained in the case of square planar complexes a rather satisfactory fitting with experimental values (experimental values are in parentheses):

$$g_{1\perp} = 3{\cdot}19\ (3{\cdot}18) \qquad A_{1\perp} = 133\ (138)$$
$$g_{2\perp} = 2{\cdot}14\ (2{\cdot}05) \qquad A_{2\perp} = -82{\cdot}6\ (90)$$
$$g_{zz} = 1{\cdot}89\ (1{\cdot}92) \qquad A_{zz} = 22{\cdot}31\ (22)$$

We have been unable to carry out the same analysis in the case of the pyridine adducts owing to the lack of good data of all the six e.s.r. anisotropic factors.[8,17]

We must point out that we can obtain directly from the above relations in the case of square planar complexes two d–d transitions, namely $d_{xz} \longrightarrow d_{z^2}$ and $d_{yz} \longrightarrow d_{z^2}$ which lie at *ca.* 2000 and *ca.* 8700 cm^{-1} respectively. The *ca.* 8700 cm^{-1} transition corresponds to the absorption band observed at *ca.* 8·3—8·7 kK in the electronic spectra. The other d–d transitions which we have detected in the electronic absorption and c.d. spectra have thus been fitted by the ligand field approach described before, introducing the best values of the ligand field parameters (see ligand field calculations). Of course in the case of five-co-ordinated complexes, where we had indirectly a good knowledge of the most stable ground state configuration,[33] we have obtained the ground state directly by fitting the d–d transitions that we have been able to detect.

Once we have been able to define the best ligand field parameters, we have calculated again the g values taking into account the complete ligand field eigenfunction where however only the most important multiplets have been considered (weight $> 5 \times 10^{-3}$). This corresponds to the evaluation of a 20 × 20 matrix. The calculated values (taking $K = 1$) are:

	Square planar	Five-co-ordinated
$g_{1\perp}$	3·59 (3·18)	2·31 (2·26)
$g_{2\perp}$	2·01 (2·05)	2·31 (2·26)
g_{zz}	1·89 (1·92)	2·09 (2·03)

In parentheses we have given the experimental values (those of five-co-ordinated compounds have been taken from refs. 8 and 26).

Calculation of Magnetic Moments.—These have been calculated by using the Van Vleck approach[41] with a simplified ground state eigenfunction where only the most important multiplets have been considered (weight $> 5 \times 10^{-3}$).

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[43] A. H. Maki, N. Edelstein, A. Davidson, and R. H. Holm, *J. Amer. Chem. Soc.*, 1964, **86**, 4580.