Steric Effects in the Reversible Oxygenation of Cobalt–Schiff-base-complexes. Part I. Crystal and Molecular Structure of the Optically Active and *meso*-Forms of *NN'*-Butylenebis(salicylideneiminato)cobalt(II)

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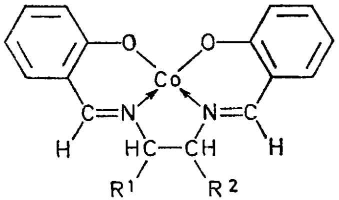
The crystal structures of the title compounds have been determined from three-dimensional *X*-ray data by conventional Fourier methods. The crystals of the optically active form are orthorhombic, space group $P2_12_12_1$, with $Z = 4$ and cell parameters $a = 10{\cdot}577$, $b = 16{\cdot}725$, and $c = 9{\cdot}603$ Å, whereas those of the *meso*-form are monoclinic, space group $P2_1/c$, with $Z = 4$ and cell parameters $a = 10{\cdot}566$, $b = 13{\cdot}449$, $c = 12{\cdot}300$ Å, and $\beta = 108{\cdot}2°$. The structures were refined by least-squares methods to R 0·050 [(+)-form, 1226 observed reflections] and 0·033 (*meso*-form, 2301 observed reflections). The molecules of both compounds are similar, the cobalt atom having a square planar stereochemistry slightly tetrahedrally distorted. The main difference is found in the butylene bridge, the methyl groups being both pseudo-axial in the optically active form, but one pseudo-equatorial and the other pseudo-axial in the *meso*-form.

RECENTLY several *X*-ray structure determinations of cobalt–Schiff-base-complexes have been performed in order to provide insight into the electronic and structural features of these well known oxygen-carriers.[1,2]

Recent preliminary results[3] have shown that steric effects may play an important role on the ability of some derivatives of *NN'*-ethylenebis(salicylideneiminato)-cobalt(II) [Co(salen); (I) $R^1 = R^2 = H$], to absorb reversibly molecular oxygen. The substitution of the hydrogen atoms of the ethylene bridge by more bulky aryl or alkyl groups provokes some critical effect on the behaviour of such oxygen carriers. The *meso*-form of the butanediamine derivative ($R^1 = R^2 = Me$) exhibits a rate of oxygen uptake in pyridine solution at least 1000 times higher than that of the corresponding optically active form. The contrary has been observed for the *meso*- and active forms of the stilbenediamine derivative ($R^1 = R^2 = Ph$).[3] We have therefore undertaken a structural study of these complexes and their pyridine derivatives in order to rationalise their different behaviour towards oxygen uptake. All these compounds are inactive towards oxygenation in the solid state, in contrast with the parent compound, Co(salen), which has been found in both active and inactive crystalline modifications.



(I)

Finally many conformational problems[4] need a more direct answer to the problem of the axial and equatorial nature of the substituents of the ethylene bridge.

We report here the crystal and the molecular structures of both *meso*- and (+)-forms of *NN'*-butylenebis-(salicylideneiminato)cobalt(II), [Co{salbn(*m*)}] and [Co-{salbn(+)}].

EXPERIMENTAL

Crystal Data.—$C_{18}H_{18}CoN_2O_2$, $M = 353{\cdot}3$. (*a*) (+)-*Form*. Orthorhombic, $a = 10{\cdot}577$, $b = 16{\cdot}725$, $c = 9{\cdot}603$ Å, $U = 1698{\cdot}8$ Å^3, D_m (by flotation) $= 1{\cdot}40$, $Z = 4$, $D_c = 1{\cdot}381$, μ(Mo-K_α) $= 10{\cdot}6$ cm^{-1}, space groups $P2_12_12_1$ (D_2^4).

(*b*) meso-*Form*. Monoclinic, $a = 10{\cdot}566$, $b = 13{\cdot}449$, $c = 12{\cdot}300$ Å, $\beta = 108{\cdot}2°$, $U = 1657{\cdot}0$ Å^3, D_m (by flotation) $= 1{\cdot}42$, $Z = 4$, $D_c = 1{\cdot}416$, μ(Mo-K_α) $= 10{\cdot}9$ cm^{-1}, space group $P2_1/c$ (C_{2h}^5).

Cell parameters were determined from Weissenberg photographs taken with Co-K_α radiation and refined with an on-line automated single-crystal Siemens diffractometer [Mo-K_α, $\lambda = 0{\cdot}7107$ Å].

Intensity Measurements.—Three-dimensional intensity

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TABLE 1

Fractional co-ordinates ($\times 10^4$) and anisotropic temperature factors * ($\times 10^4$) of Co{salbn(+)} with estimated standard deviations in parentheses

	x	y	z	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Co	614(1)	−257(1)	1222(1)	67(1)	−4(2)	−10(3)	28(1)	−14(2)	65(1)
O(1)	1043(8)	−1292(4)	728(8)	100(8)	18(8)	19(14)	28(2)	−20(8)	92(8)
O(2)	−391(7)	−226(4)	−347(7)	86(7)	−2(9)	−6(13)	36(3)	−16(9)	80(7)
N(1)	1855(8)	−156(6)	2571(10)	69(8)	−11(11)	−25(16)	37(4)	−24(12)	104(11)
N(2)	17(10)	728(5)	1897(9)	101(9)	−4(11)	−13(17)	32(3)	−18(10)	64(9)
C(1)	1986(11)	−1721(6)	1188(14)	95(11)	−17(11)	27(26)	32(4)	3(14)	94(11)
C(2)	2235(14)	−2498(7)	630(13)	139(14)	11(14)	106(25)	33(4)	17(14)	108(13)
C(3)	3215(15)	−2971(8)	991(14)	170(18)	8(18)	51(30)	45(5)	19(17)	113(18)
C(4)	4044(17)	−2713(9)	2057(20)	158(20)	43(19)	−19(39)	45(6)	49(21)	213(25)
C(5)	3864(14)	−1986(9)	2639(17)	93(13)	41(16)	−21(33)	51(6)	18(21)	192(23)
C(6)	2801(12)	−1474(7)	2265(13)	101(12)	−3(14)	−18(23)	38(4)	22(13)	103(13)
C(7)	2712(11)	−674(8)	2980(15)	56(10)	8(14)	4(23)	50(5)	3(17)	146(16)
C(8)	1945(12)	650(7)	3202(13)	103(13)	−20(14)	−38(24)	41(4)	−59(14)	116(13)
C(9)	2803(14)	1181(8)	2342(20)	119(15)	−55(15)	−1(39)	39(5)	−34(20)	255(28)
C(10)	585(13)	944(7)	3292(12)	114(12)	−8(16)	−118(24)	47(4)	−77(12)	130(13)
C(11)	−82(16)	552(10)	4476(13)	159(17)	7(20)	−12(28)	72(7)	−18(17)	73(14)
C(12)	−842(11)	1175(7)	1389(12)	82(11)	21(12)	5(22)	40(4)	−25(13)	82(11)
C(13)	−1444(12)	1021(7)	81(12)	91(12)	9(14)	26(21)	44(5)	28(13)	78(12)
C(14)	−2321(13)	1605(8)	−412(16)	111(14)	26(16)	−54(29)	51(5)	10(18)	151(18)
C(15)	−2903(14)	1524(8)	−1730(16)	115(14)	6(17)	−63(29)	55(5)	66(17)	162(19)
C(16)	−2628(14)	823(9)	−2557(15)	126(15)	−37(17)	−25(28)	51(6)	38(17)	135(17)
C(17)	−1757(11)	262(8)	−2064(13)	88(11)	−12(16)	−33(23)	44(4)	43(17)	115(14)
C(18)	−1192(11)	332(7)	−727(11)	82(10)	−21(13)	1(18)	39(4)	37(13)	77(11)

Hydrogen atom co-ordinates; hydrogen atoms are numbered according to the atom to which they are bonded.

H(2)	1594	−2714	−174	H(14)	−2506	2126	186
H(3)	3329	−3550	476	H(15)	−3553	1979	−2096
H(4)	4757	−3140	2415	H(16)	−3093	742	−3571
H(5)	4544	−1772	3435	H(17)	−1498	−235	−2713
H(7)	3409	−499	3694	1-H(9)	2879	1761	2814
H(8)	2332	593	4279	2-H(9)	2395	1235	1313
H(10)	587	1596	3412	3-H(9)	3730	911	2259
H(12)	−1103	1715	1972				

* In the form: $\exp -(B_{11}h^2 + B_{12}hk + B_{13}hl + B_{22}k^2 + B_{23}kl + B_{33}l^2)$.

TABLE 2

Fractional co-ordinates ($\times 10^4$) and anisotropic temperature factors * ($\times 10^4$) of Co{salbn(*m*)} with estimated standard deviations in parentheses

	x	y	z	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Co	99·0(4)	1267·0(4)	443·0(4)	63·5(3)	−0·8(6)	31·9(4)	37·1(2)	4·7(5)	44·6(2)
O(1)	309(2)	671(2)	1844(2)	86(2)	−3(3)	44(3)	51(1)	10(2)	47(1)
O(2)	1920(2)	1466(2)	948(2)	79(2)	12(3)	27(3)	52(1)	7(2)	58(2)
N(1)	−1689(3)	907(2)	−172(2)	74(2)	0(3)	35(3)	35(1)	4(3)	54(2)
N(2)	−169(3)	2007(2)	−889(2)	62(2)	11(3)	32(3)	41(1)	11(3)	60(2)
C(1)	−586(3)	203(2)	2183(3)	109(3)	6(4)	61(4)	35(2)	−5(3)	55(2)
C(2)	−174(4)	−240(3)	3286(3)	124(4)	13(5)	58(4)	56(2)	14(4)	55(2)
C(3)	−1092(4)	−740(3)	3689(3)	146(4)	0(5)	91(5)	58(2)	26(4)	71(2)
C(4)	−2439(4)	−795(3)	3026(3)	151(4)	−32(5)	113(5)	52(2)	19(4)	90(3)
C(5)	−2855(4)	−391(3)	1949(3)	106(4)	−40(5)	72(5)	58(2)	1(4)	80(3)
C(6)	−1932(3)	108(3)	1510(3)	88(3)	−10(4)	58(4)	36(2)	2(3)	61(2)
C(7)	−2419(3)	458(3)	349(3)	80(3)	−6(4)	43(4)	44(2)	2(4)	66(2)
C(8)	−2213(3)	1094(3)	−1440(3)	82(3)	6(4)	29(4)	51(2)	9(3)	53(2)
C(9)	−3731(4)	1047(3)	−1979(3)	82(4)	−20(5)	−1(5)	67(3)	25(5)	78(3)
C(10)	−1594(3)	2093(3)	−1600(3)	75(3)	11(4)	23(4)	53(2)	27(4)	60(2)
C(11)	−2224(4)	2993(3)	−1226(4)	96(4)	24(5)	85(6)	46(2)	28(5)	127(4)
C(12)	712(3)	2460(3)	−1240(3)	83(3)	17(4)	53(4)	45(2)	11(3)	58(2)
C(13)	2111(3)	2458(3)	−623(3)	81(3)	−14(4)	55(4)	50(2)	−15(4)	60(2)
C(14)	2961(4)	2977(3)	−1114(3)	100(4)	−10(5)	79(4)	63(2)	1(4)	77(2)
C(15)	4328(4)	2951(4)	−596(4)	96(4)	−33(5)	86(5)	78(3)	−13(5)	93(3)
C(16)	4865(4)	2405(3)	417(3)	78(4)	−38(5)	53(5)	73(3)	−49(5)	88(3)
C(17)	4055(4)	1914(3)	922(3)	82(3)	−16(5)	35(5)	58(2)	−31(4)	72(3)
C(18)	2657(3)	1933(3)	428(3)	76(3)	−19(4)	44(4)	43(2)	−27(3)	61(2)

Hydrogen atom co-ordinates; hydrogen atoms are numbered according to the atom to which they are bonded.

H(2)	855	−187	3820	3-H(9)	−4078	319	−1840
H(3)	−763	−1087	4528	1-H(11)	−3263	3052	−1751
H(4)	−3134	−1171	3372	2-H(11)	−1724	3669	−1330
H(5)	−3891	−445	1426	3-H(11)	−2177	2919	−339
H(7)	−3458	329	−125	H(12)	377	2869	−2042
H(8)	−1805	529	−1858	H(14)	2539	3411	−1892
H(10)	−1658	2173	−2495	H(15)	4971	3350	−974
1-H(9)	−4005	1192	−2888	H(16)	5938	2362	804
2-H(9)	−4179	1601	−1582				

* See footnote to Table 1.

data collected for both crystals on the Siemens diffractometer by the θ—2θ scan technique and Mo-K_α radiation for a maximum of 2θ angle of 50° for salbn(+) and of 60° for salbn(*m*). Reflections having $I_0 < 3\sigma(I_0)$ were rejected, the remainder being corrected for Lorentz-polarisation factors. A total of 1226 reflections for Co{salbn(+)} and of 2301 for Co{salbn(m)} were collected. No correction for absorption (μR *ca.* 0·1 for both compounds) or anomalous dispersion of the cobalt atom was applied.

Structure Determination and Refinement.—Both structures were solved by conventional Patterson and Fourier methods. After the least-squares isotropic refinement the R was 0·082 for Co{salbn(+)} and 0·061 for Co{salbn(*m*)}. After anisotropic refinement, three-dimensional difference Fourier syntheses were calculated to locate the hydrogen atoms. Estimated positions of these all occurred in regions of positive electron density. However, one methyl group of salbn(+) appeared clearly disordered and therefore its hydrogen atoms were not located and were excluded from the final refinement. The final anisotropic block-diagonal matrix least-squares refinement gave R 0·050 for salbn(+) and 0·033 for salbn(*m*). The co-ordinates and the temperature factors of the hydrogen atoms [set at $B = 5$ Å^2 for salbn(+) and 4 Å^2 for salbn(*m*)] were not allowed to vary. The final weighting schemes were $w = 1/(A + B\cdot|F_o| + C\cdot|F_o|^2)$, where $A = 6{\cdot}0\,B = 1{\cdot}0\,C = 0{\cdot}007$ for Co{salbn(+)} and $A = 5{\cdot}0$, $B = 1$, $C = 0{\cdot}005$ for Co{salbn(*m*)}, chosen to maintain $w\cdot(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and $(\sin\theta/\lambda)$. The final atomic parameters are listed in Tables 1 and 2, together with their estimated standard deviations, calculated from the residuals and the diagonal elements of the inverse matrix of the final least-squares cycle. The numbering scheme of the atoms is shown in Figure 1. Observed and calculated structure factors are listed in Supplementary Publications No. 20571 (15 pp., 1 microfiche).* Atomic scattering factors were calculated according to ref. 5.

Calculations.—All calculations were carried out on an IBM 7044 computer, with programs described in ref. 6. A local program was used to obtain best molecular planes, whose equations were calculated according to ref. 7.

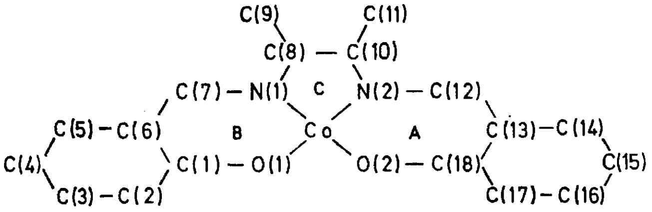

FIGURE 1 Numbering scheme of the atoms for Co{salbn(+)} and Co{salbn(*m*)} molecules

RESULTS AND DISCUSSION

The Structure.—The stereochemistry of the cobalt atom in both compounds is essentially square-planar as previously suggested.[3] However a tetrahedral distortion is found which appears significant as compared with other cobalt(II) salen compounds. The difference is shown in Figure 2, where a side-view of these molecules is compared with that of Co(salen); the displacement of the atoms of the group O_2CoN_2 from the plane passing through the four donor atoms is given under each sketch. It seems likely that such a distortion is due to the repulsive interactions involving the methyl groups of the ethylene bridge. Since the trigonal configuration of the nitrogen atoms is preserved (see bond angles around nitrogen atoms, Table 4), strains are alleviated by a slightly tetrahedral arrangement around the cobalt atom. The bond lengths and angles are reported in Tables 3 and 4 together with their estimated standard deviations. Bond lengths of the two molecules appear to be not significantly different and are in agreement with those reported for a series of salen complexes.[8] We note that the co-ordination Co–O distances in the four-co-ordinate cobalt complexes seem to be shorter than those of five- and six-co-ordinate species. The only significant difference is in the bond angles and deals with the five-membered ring of the ethylene bridges. The N–CH–CH_3 angle in both complexes has the usual tetrahedral value when the carbon atom is bound to an axial methyl group, whereas it assumes the significantly higher value of 115·6(4)° when it is bound to an equatorial one. This angle strain is certainly due to the steric hindrance be-

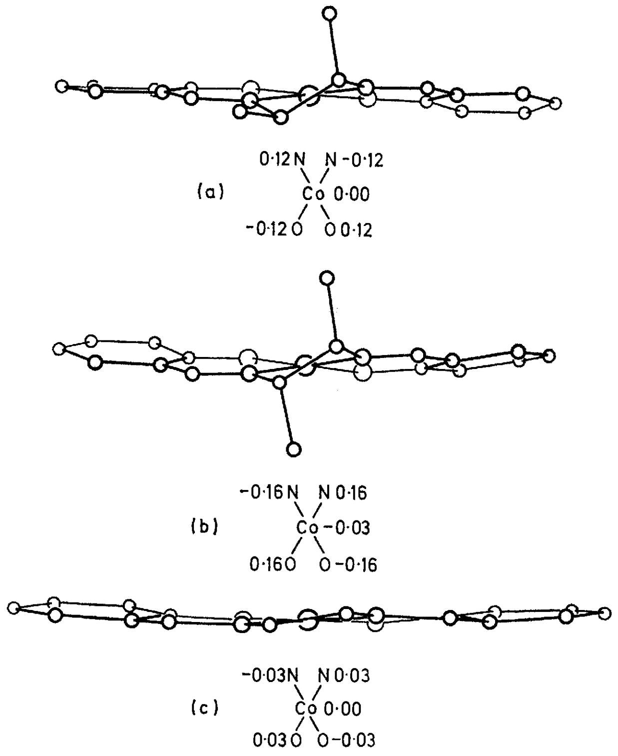

FIGURE 2 A side-view of: (a) Co{salbn(*m*)}, (b) Co{salbn(+)}, and (c) Co(salen),$CHCl_3$. Displacement of the Co, N, and O atoms from the best molecular plane of the donor atoms is shown below in each case

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* For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20.

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tween the equatorial methyl group and the methine group as confirmed by the comparison of the values of the distances (H)C · · · CH_3(ax) which range from 3·15—3·24 Å, and (H)C · · · CH_3(eq) which is 2·87 Å. The other bond angles are as expected. The equations of the most significant least-squares planes are shown in Table 5.

Table 3

Bond lengths (Å), with estimated standard deviations in parentheses, for the two compounds

	Co{salbn(+)}	Co{salbn(*m*)}
Co–O(1)	1·845(7)	1·848(3)
Co–O(2)	1·851(7)	1·861(2)
Co–N(1)	1·880(9)	1·878(3)
Co–N(2)	1·852(9)	1·860(3)
O(1)–C(1)	1·31(1)	1·317(5)
O(2)–C(18)	1·31(1)	1·320(5)
N(1)–C(7)	1·29(2)	1·304(6)
N(1)–C(8)	1·48(1)	1·501(4)
N(2)–C(12)	1·27(1)	1·303(5)
N(2)–C(10)	1·51(1)	1·498(5)
C(1)–C(2)	1·43(2)	1·418(5)
C(1)–C(6)	1·41(2)	1·417(5)
C(2)–C(3)	1·35(2)	1·402(6)
C(3)–C(4)	1·42(2)	1·411(6)
C(4)–C(5)	1·35(2)	1·369(5)
C(5)–C(6)	1·46(2)	1·432(6)
C(6)–C(7)	1·47(2)	1·435(5)
C(8)–C(9)	1·52(2)	1·537(6)
C(8)–C(10)	1·52(2)	1·544(6)
C(10)–C(11)	1·49(2)	1·525(6)
C(12)–C(13)	1·43(2)	1·443(4)
C(13)–C(14)	1·43(2)	1·422(6)
C(13)–C(18)	1·42(2)	1·425(5)
C(14)–C(15)	1·41(2)	1·394(5)
C(15)–C(16)	1·45(2)	1·402(7)
C(16)–C(17)	1·40(2)	1·382(7)
C(17)–C(18)	1·42(2)	1·420(5)

Table 4

Bond angles (°), with estimated standard deviations in parentheses, for the two compounds

	Co{salbn(+)}	Co{salbn(*m*)}
O(1)–Co–O(2)	87·6(3)	87·0(1)
O(1)–Co–N(1)	95·2(4)	94·0(1)
O(1)–Co–N(2)	172·0(4)	173·0(1)
O(2)–Co–N(1)	167·8(4)	171·9(1)
O(2)–Co–N(2)	93·6(4)	93·9(1)
N(1)–Co–N(2)	85·2(4)	86·1(1)
Co–O(1)–C(1)	127·9(7)	128·1(2)
Co–O(2)–C(18)	128·3(7)	128·8(2)
Co–N(1)–C(7)	127·1(9)	127·6(2)
Co–N(1)–C(8)	114·5(9)	111·7(3)
C(7)–N(1)–C(8)	118·0(10)	120·3(3)
Co–N(2)–C(10)	112·4(7)	113·5(3)
Co–N(2)–C(12)	128·5(8)	128·1(2)
C(10)–N(2)–C(12)	118·9(9)	118·4(3)
O(1)–C(1)–C(2)	120·9(11)	118·0(3)
O(1)–C(1)–C(6)	123·7(10)	124·1(3)
C(2)–C(1)–C(6)	115·4(11)	118·0(4)
C(1)–C(2)–C(3)	125·3(12)	120·1(3)
C(2)–C(3)–C(4)	118·9(13)	121·2(4)
C(3)–C(4)–C(5)	119·1(15)	119·7(5)
C(4)–C(5)–C(6)	122·3(14)	120·1(4)
C(1)–C(6)–C(5)	118·7(11)	120·9(3)
C(1)–C(6)–C(7)	121·9(11)	122·1(4)
C(5)–C(6)–C(7)	118·9(12)	117·0(3)
N(1)–C(7)–C(6)	124·0(12)	123·9(3)
N(1)–C(8)–C(9)	110·4(11)	115·6(4)
N(1)–C(8)–C(10)	104·9(9)	104·3(3)
C(9)–C(8)–C(10)	114·1(10)	114·6(3)
N(2)–C(10)–C(8)	104·4(9)	104·8(3)
N(2)–C(10)–C(11)	112·5(11)	110·4(3)
C(8)–C(10)–C(11)	110·4(11)	114·0(4)
N(2)–C(12)–C(13)	123·2(11)	124·0(3)
C(12)–C(13)–C(14)	117·2(11)	117·9(3)
C(12)–C(13)–C(18)	123·0(11)	122·3(3)
C(13)–C(14)–C(15)	120·9(12)	120·6(4)
C(14)–C(15)–C(16)	118·8(13)	119·5(5)
C(15)–C(16)–C(17)	119·4(13)	120·8(4)
C(16)–C(17)–C(18)	121·9(12)	121·4(3)
O(2)–C(18)–C(13)	123·3(10)	122·8(3)
O(2)–C(18)–C(17)	117·7(10)	119·4(3)
C(13)–C(18)–C(17)	118·9(11)	117·9(4)

Table 5

Equations of least-squares planes and, in square brackets, distances (Å) of atoms from the planes. The equations are referred to the crystal axes and *x*, *y*, *z* are fractional co-ordinates

(*a*) Co{salbn(+)}

Plane (1): O(1), O(2), N(1), N(2)

$$7{\cdot}241x + 6{\cdot}983y - 5{\cdot}738z = -0{\cdot}404$$

[O(1) −0·161, O(2) 0·162, N(1) 0·163, N(2) −0·164, Co −0·032]

Plane (2): O(1), N(1), C(1)—(7)

$$-6{\cdot}216x - 6{\cdot}782y + 6{\cdot}724z = 0{\cdot}719$$

[O(1) −0·001, N(1) −0·037, C(1) 0·013, C(2) 0·010, C(3) +0·036, C(4) −0·009, C(5) 0·001, C(6) 0·063, C(7) −0·004]

Plane (3): O(2), N(2), C(12)—(18)

$$7{\cdot}870x + 8{\cdot}144y - 4{\cdot}393z = -0{\cdot}304$$

[O(2) −0·036, N(2) 0·076, C(12) −0·012, C(13) −0·037, C(14) −0·035, C(15) 0·020, C(16) 0·029, C(17) 0·041, C(18) −0·045]

(*b*) Co{salbn(*m*)}

Plane (1): O(1), O(2), N(1), N(2)

$$-3{\cdot}671x + 11{\cdot}322y + 6{\cdot}175x = 1{\cdot}663$$

[O(1) 0·122, O(2) −0·123, N(1) −0·122, N(2) 0·123, Co 0·009]

Plane (2): O(1), N(1), C(1)—(7)

[O(1) 0·051, N(1) −0·054, C(1) 0·024, C(2) −0·033, C(3) −0·054, C(4) 0·011, C(5) 0·039, C(6) 0·036, C(7) −0·020]

Plane (3): O(2), N(2), C(12)—(18)

O(2) 0·052, N(2) −0·050, C(12) −0·021, C(13) 0·029, C(14) 0·044, C(15) 0·007, C(16) −0·048, C(17) −0·034, C(18) 0·020]

Conformational Aspects.—Both methyl groups are pseudo-axial in the (+)-compound, whereas one is pseudo-axial and the other pseudo-equatorial in the *meso*-compound. The only example of an axial methyl group in this type of complex is in the five-co-ordinate *NN'*-propylenebis(salicylideneiminato)copper(II) complexes.[9] On the other hand many sources claim that an axial substituent is less favoured than the equatorial analogue in octahedral complexes with substituted ethylenediamine chelates.[10] Two reasons may be invoked to explain the difference. First the tetrahedral nature of the nitrogen atoms in the ethylenediamine chelate favours the equatorial substituent, whereas their trigonal nature in the Schiff-base complexes favours an axial substituent. The second is that all those ethylenediamine substituted complexes in which equatorial groups are found, are octahedral, and the axial methyl group is destabilized by interaction with other donor atoms bonded to the metal. The tetrahedral distortion of the CoN_2O_2 group imposes on the whole molecule a flat helical conformation. We have already noticed[8] that the distortion occurring in the whole molecule of previously studied Co(salen) complexes are those leading to either an umbrella-shape or stepped conformations, with the CoN_2O_2 atoms always nearly coplanar. On the other hand in Fe(salen) compounds a tetrahedral distortion was also found.[8] In the present case only a tetrahedral distortion is practically detected, the angle between the planes of the two halves of the salbn ligand being 10·3 in the *meso*- and 17·9° in the (+)-form. The torsional angles which define the conformation in both cases are nearly equal, the rotation angles around the N(1)–C(8), C(8)–C(10), and C(10)–N(2) bonds being 151, 44, and 148° for the (+)- and 145·8, 45·6, and 147·0° for the *meso*-form. Thus in the latter case the two methyl groups are in a pseudo-*trans*-conformation (162°), whereas in the former compound they assume a nearly *gauche* conformation (53°).

Because of the dissymmetry of the $\mathrm{CoO_2N_2}$ chromophore, arising from the tetrahedral distortion, the side rings A and B (see Figure 1) confer helicity which is opposite to that of the central ring C (see Figure 1).[4] The pseudo-bisaxial conformation of the methyl groups of the (+)-complex in the solid state is probably maintained in solution. In fact an approximate conformational energy calculation, taking into account non-bonded interactions and bond-angle strains, gives an energy difference between the conformation of the ring of the (+)- and *meso*-forms of *ca.* 3·5 kcal mol^{-1}, the optically active being the more stable. The contributions of the H · · · H, C · · · C, and C · · · H non-bonded interactions to the conformational energy were calculated by employing the potential functions suggested in ref. 11. Because the only significant difference in the bond angles between the two compounds is found in the N(1)–C(8)–C(10) angle, only this strain contribution to the total energy has been introduced, assuming a value of 0·8 kcal mol^{-1}.[12] Hence this calculation suggests that the pseudo-bisequatorial conformation should be at least 4·0 kcal mol^{-1} higher in energy than the pseudo-bisaxial one.

Crystal Packing.—The crystals of the two compounds are built up by discrete Co(salbn) molecules, but their packings differ significantly. In the *meso*-form, the molecules are associated around the symmetry centre in pairs, with close intermolecular contacts (see Table 6) in a way similar to that observed in Co(salen),$\mathrm{CHCl_3}$. Thus the packing is more efficient than that of the optically active form, where no pairing of molecules has been detected, in agreement with the significant difference in the density values. The difference is mainly due to the steric hindrance of the axial methyl groups which prevent a too close approach of the molecules for the (+)-compound.

TABLE 6

Intermolecular distances (Å) <4 Å with estimated standard deviations in parentheses for Co{salbn(*m*)}

Co · · · Co$^{\mathrm{I}}$	3·564(1)	C(6) · · · C(12$^{\mathrm{I}}$)	3·743(6)
Co · · · O(1$^{\mathrm{I}}$)	3·757(3)	C(6) · · · C(13$^{\mathrm{I}}$)	3·606(6)
Co · · · N(1$^{\mathrm{I}}$)	3·449(3)	C(6) · · · C(18$^{\mathrm{I}}$)	3·556(5)
Co · · · C(1$^{\mathrm{I}}$)	3·960(4)	C(7) · · · C(13$^{\mathrm{I}}$)	3·951(6)
Co · · · C(7$^{\mathrm{I}}$)	3·740(4)	C(7) · · · C(17$^{\mathrm{I}}$)	3·732(5)
Co · · · C(8$^{\mathrm{I}}$)	3·862(4)	C(7) · · · C(18$^{\mathrm{I}}$)	3·351(6)
O(1) · · · N(1$^{\mathrm{I}}$)	3·582(4)	C(4) · · · C(9$^{\mathrm{II}}$)	3·888(6)
O(1) · · · N(2$^{\mathrm{I}}$)	3·777(4)	C(5) · · · C(9$^{\mathrm{II}}$)	3·759(6)
O(1) · · · C(8$^{\mathrm{I}}$)	3·263(5)	C(2) · · · C(3$^{\mathrm{III}}$)	3·769(5)
O(2) · · · N(1$^{\mathrm{I}}$)	3·318(4)	C(3) · · · C(3$^{\mathrm{III}}$)	3·874(5)
O(2) · · · C(6$^{\mathrm{I}}$)	3·694(5)	C(7) · · · C(16$^{\mathrm{IV}}$)	3·926(7)
O(2) · · · C(7$^{\mathrm{I}}$)	3·172(5)	C(9) · · · C(15$^{\mathrm{IV}}$)	3·997(7)
O(2) · · · C(8$^{\mathrm{I}}$)	3·492(5)	C(11) · · · C(15$^{\mathrm{IV}}$)	3·993(7)
O(2) · · · C(9$^{\mathrm{I}}$)	3·899(6)	O(1) · · · C(12$^{\mathrm{V}}$)	3·378(5)
N(1) · · · C(18$^{\mathrm{I}}$)	3·943(5)	O(1) · · · C(13$^{\mathrm{V}}$)	3·990(4)
N(2) · · · C(1$^{\mathrm{I}}$)	3·582(5)	O(1) · · · C(14$^{\mathrm{V}}$)	3·619(4)
N(2) · · · C(2$^{\mathrm{I}}$)	3·894(5)	O(2) · · · C(14$^{\mathrm{V}}$)	3·507(4)
N(2) · · · C(6$^{\mathrm{I}}$)	3·845(5)	C(1) · · · C(11$^{\mathrm{V}}$)	3·866(7)
C(1) · · · C(8$^{\mathrm{I}}$)	3·812(6)	C(1) · · · C(12$^{\mathrm{V}}$)	3·721(5)
C(1) · · · C(12$^{\mathrm{I}}$)	3·754(6)	C(2) · · · C(11$^{\mathrm{V}}$)	3·887(6)
C(2) · · · C(12$^{\mathrm{I}}$)	3·829(5)	C(2) · · · C(12$^{\mathrm{V}}$)	3·855(6)
C(3) · · · C(12$^{\mathrm{I}}$)	3·920(6)	C(3) · · · C(11$^{\mathrm{V}}$)	3·899(6)
C(4) · · · C(12$^{\mathrm{I}}$)	3·976(7)	C(4) · · · C(11$^{\mathrm{V}}$)	3·869(6)
C(4) · · · C(13$^{\mathrm{I}}$)	3·810(6)	C(5) · · · C(11$^{\mathrm{V}}$)	3·864(6)
C(4) · · · C(14$^{\mathrm{I}}$)	3·690(6)	C(6) · · · C(11$^{\mathrm{V}}$)	3·863(6)
C(5) · · · C(12$^{\mathrm{I}}$)	3·873(6)	O(2) · · · C(3$^{\mathrm{VI}}$)	3·918(5)
C(5) · · · C(13$^{\mathrm{I}}$)	3·441(6)	O(2) · · · C(4$^{\mathrm{VI}}$)	3·876(5)
C(5) · · · C(14$^{\mathrm{I}}$)	3·618(6)	N(2) · · · C(3$^{\mathrm{VI}}$)	4·000(4)
C(5) · · · C(15$^{\mathrm{I}}$)	3·928(6)	C(3) · · · C(12$^{\mathrm{VII}}$)	3·881(5)
C(5) · · · C(17$^{\mathrm{I}}$)	3·928(5)	C(3) · · · C(13$^{\mathrm{VII}}$)	3·789(6)
C(5) · · · C(18$^{\mathrm{I}}$)	3·645(6)	C(3) · · · C(18$^{\mathrm{VII}}$)	3·862(6)

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $-x, -y, -z$
II $-1-x, -y, -z$
III $-x, -y, 1-z$
IV $-1+x, y, z$
V $x, \frac{1}{2}-y, \frac{1}{2}+z$
VI $-x, \frac{1}{2}+y, \frac{1}{2}-z$
VII $-x, -\frac{1}{2}+y, \frac{1}{2}-z$

TABLE 7

Intermolecular distances (Å) <4 Å with their estimated standard deviations in parentheses for Co{salbn(+)}

C(11) · · · C(16$^{\mathrm{I}}$)	3·95(2)	O(2) · · · C(8$^{\mathrm{VII}}$)	3·97(2)
C(11) · · · C(17$^{\mathrm{I}}$)	3·80(2)	O(2) · · · C(9$^{\mathrm{VII}}$)	3·87(2)
C(9) · · · C(15$^{\mathrm{II}}$)	3·95(2)	C(1) · · · C(8$^{\mathrm{VII}}$)	3·57(2)
C(5) · · · C(13$^{\mathrm{III}}$)	3·94(2)	C(1) · · · C(9$^{\mathrm{VII}}$)	3·81(2)
C(4) · · · C(9$^{\mathrm{IV}}$)	3·86(2)	C(2) · · · C(8$^{\mathrm{VII}}$)	3·97(2)
C(2) · · · C(11$^{\mathrm{V}}$)	3·98(2)	C(2) · · · C(9$^{\mathrm{VII}}$)	3·85(2)
C(2) · · · C(12$^{\mathrm{V}}$)	3·91(2)	C(6) · · · C(11$^{\mathrm{VII}}$)	3·92(2)
C(3) · · · C(12$^{\mathrm{V}}$)	3·83(2)	Co · · · C(16$^{\mathrm{VIII}}$)	3·50(2)
C(4) · · · C(14$^{\mathrm{V}}$)	3·87(2)	O(2) · · · C(16$^{\mathrm{VIII}}$)	3·55(2)
C(5) · · · C(14$^{\mathrm{V}}$)	3·91(2)	N(2) · · · C(16$^{\mathrm{VIII}}$)	3·66(2)
O(1) · · · C(3$^{\mathrm{VI}}$)	3·63(2)	N(2) · · · C(17$^{\mathrm{VIII}}$)	3·95(2)
O(1) · · · C(4$^{\mathrm{VI}}$)	3·79(2)	C(11) · · · C(16$^{\mathrm{VIII}}$)	3·87(2)
O(2) · · · C(3$^{\mathrm{VI}}$)	3·41(2)	C(11) · · · C(17$^{\mathrm{VIII}}$)	3·90(2)
O(2) · · · C(4$^{\mathrm{VI}}$)	3·87(2)	C(12) · · · C(16$^{\mathrm{VIII}}$)	3·85(2)
Co · · · C(7$^{\mathrm{VII}}$)	3·98(1)	C(12) · · · C(17$^{\mathrm{VIII}}$)	3·80(2)
Co · · · C(8$^{\mathrm{VII}}$)	3·94(1)	C(13) · · · C(16$^{\mathrm{VIII}}$)	3·95(2)
O(1) · · · C(8$^{\mathrm{VII}}$)	3·40(2)	C(13) · · · C(17$^{\mathrm{VIII}}$)	3·97(2)
O(1) · · · C(9$^{\mathrm{VII}}$)	3·48(2)	C(3) · · · C(17$^{\mathrm{IX}}$)	3·97(2)
O(2) · · · C(7$^{\mathrm{VII}}$)	3·63(1)		

Roman numerals as superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z:

I $x, y, 1+z$
II $\frac{1}{2}+x, \frac{1}{2}-y, -z$
III $\frac{1}{2}-x, -y, \frac{1}{2}+z$
IV $1-x, -\frac{1}{2}+y, \frac{1}{2}-z$
V $-x, -\frac{1}{2}+y, \frac{1}{2}-z$
VI $-\frac{1}{2}+x, -\frac{1}{2}-y, -z$
VII $\frac{1}{2}-x, -y, -\frac{1}{2}+z$
VIII $-\frac{1}{2}-x, -y, \frac{1}{2}+z$
IX $\frac{1}{2}+x, -\frac{1}{2}-y, -z$

Many metal–salen-type complexes have been found as dimers in the solid state.[8] The factors which favour the dimeric as opposed to the monomeric structure and *vice versa* have been suggested on the basis of *X*-ray results for a series of copper, iron, and cobalt derivatives.[8] In Co{salbn(+)}, the methyl groups in the axial positions destabilize the dimeric species because of their interactions with the atoms of the other Co(salbn) unit. On the other hand, because the electronic and steric factors, which can prevent dimerization, are

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not evident in the *meso*-form, it seems likely that essentially a more favourable crystal packing determines the monomeric arrangement. The influence of the crystal packing on the delicate balance between monomeric and dimeric structure is clearly shown by the ClFe(salen) crystal structures. In fact this compound, which exists as a dimer in the solid state, is built up by monomer units when it co-crystallizes with nitromethane.[13]

The presence of monomeric four-co-ordinate cobalt complexes may account for the inactivity [3] towards oxygenation in the solid state.[1] In any case the 'self protecting' effect [1a] of the closed crystal packing, found in these crystals, does not leave voids through which oxygen can diffuse.

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