Ligand Properties of Quadridentate Schiff's Bases. The Crystal and Molecular Structure of the Mixed-ligand Complex [*NN'*-Ethylenebis(salicylideneiminato)](acetylacetonato)cobalt(III)–0·7 Water

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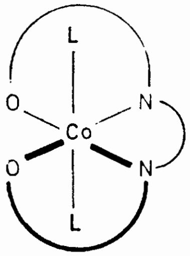
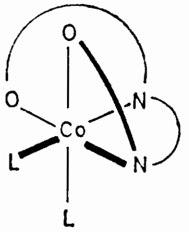
The crystal and molecular structure of the title compound has been determined from three-dimensional *X*-ray diffraction data. The crystals are orthorhombic, space-group $P2_12_12_1$, with $a = 17{\cdot}58$, $b = 13{\cdot}47$, $c = 8{\cdot}29$ Å, $Z = 4$. The structure was solved by the heavy-atom method and refined by least-squares techniques to R 0·091 for 1028 reflections, the lowest R value being obtained with the water-content 0·7H_2O per molecule. The co-ordination polyhedron of the cobalt atom is a distorted octahedron in which two *cis*-co-ordination sites are occupied by the acetylacetonato-group and the others by the quadridentate ligand in a non-planar conformation. Further investigations are reported on mixed-ligand complexes where a salen-type ligand assumes such a conformation and on binuclear cobalt complexes in which one quadridentate molecule acts as a bisbidentate ligand.

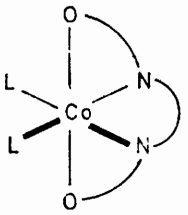
In most cobalt compounds of bis(salicylaldehyde)-ethylenedi-imine (salenH_2) the quadridentate salen ligand is found in a planar arrangement, *i.e.* with the four donor atoms almost coplanar.[1] However it has recently been suggested that it exhibits a non-planar arrangement in some lanthanide chelates[2] and in a series of [Co(salen)(dik)] (dik = β-diketonate) compounds.[3,4] This unusual structure for the salen ligand has also been suggested for some R_2Sn^{IV} (salen) (R = Me or Ph) complexes.[5] Furthermore structural evidence has been provided of the ability of salen-type ligands to act as bisbidentate ligands in binuclear cobalt complexes.[6] The planar arrangement for an octahedral Co(salen)L_2 compound is shown in (I). The twisted structures (II) and (III) can be imagined to be derived from (I) by the displacement of one or two oxygen atoms from the Co-N-N plane.



(I)



(II)



(III)

In order to study the steric and chemical requirements determining the different behaviour of the salen-type ligands, we have undertaken a structural and chemical investigation on such complexes. We now report the crystal structure of the [Co(salen)(acac)],0·7H_2O (acac = acetylacetonate) compound, a preliminary report of which has appeared.[7] We also give further evidence for the existence of twisted and bridging arrangements of salen-type ligands.

EXPERIMENTAL

X-Ray powder patterns were recorded with a cylindrical camera and Co-K_α radiation. ^1H N.m.r. spectra were recorded on a Varian HA 100 instrument with tetramethylsilane as internal reference for deuteriodimethyl sulphoxide solutions.

Crystal Data.—$C_{21}H_{21}CoO_4,0{\cdot}7H_2O$, $M = 436{\cdot}9$, Orthorhombic, $a = 17{\cdot}58 \pm 0{\cdot}03$, $b = 13{\cdot}47 \pm 0{\cdot}02$, $c = 8{\cdot}29 \pm 0{\cdot}01$ Å, $U = 1963{\cdot}1$, $D_m = 1{\cdot}47$ (by flotation), $Z = 4$, $D_c = 1{\cdot}478$, Co-K_α radiation, $\lambda = 1{\cdot}7902$ Å; μ(Co-K_α) = 23·2 cm^{-1}. Absent reflections: $h00$ for $h = 2n + 1$, $0k0$ for $k = 2n + 1$, and $00l$ with $l = 2n + 1$ indicate space-group $P2_12_12_1$ (D_2^4).

The unit-cell parameters were obtained from precession photographs taken with Co-K_α radiation. The water-content was determined from the crystal analysis.

Intensity Measurements.—The *X*-ray intensity data were collected by the equi-inclination Weissenberg method by use of Co-K_α radiation and estimated visually with a calibrated scale. A total of 1028 reflections were collected. The Lorentz and polarization factors and the spot-shape correction for non-zero levels[8] were applied. No correction for extinction or absorption (μR *ca.* 0·2) was made. The anomalous dispersion of the cobalt atom has not been taken into account. The observed structure amplitudes were correlated by the method of Hamilton *et al.*[9]

Structure Determination and Refinement.—The structure was solved by Patterson and Fourier methods. After location of all the [Co(salen)(acac)]atoms, one more peak appeared on the Fourier map, which could be attributed to a water molecule of crystallization. However, the height of the peak was low for an oxygen atom, suggesting an occupancy factor for this water molecule of less than one. This occupancy factor was then determined with a series of structure-factor calculations and successive isotropic least-squares refinement. A value of 0·7H_2O per molecule gave the lowest R. Three cycles of anisotropic block-diagonal least-squares refinement reduced the R to 0·105. A successive three-dimensional difference Fourier synthesis was calculated to locate the hydrogen

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atoms. Estimated positions of these atoms all occurred in regions of positive electron density. Hydrogen atoms, excluding those of the water molecule, were then included at the calculated positions and a final anisotropic least-squares refinement reduced R to 0·091. The co-ordinates and the thermal factors (set at $B = 4$ Å^2) of the hydrogen atoms were not allowed to vary. The final weighting scheme was: $w = 1/(A + B|F_o| + C|F_o|^2)$ where $A = 10{\cdot}0$, $B = 1{\cdot}0$, and $C = 0{\cdot}005$ were chosen to maintain $w(|F_o| - |F_c|)^2$ essentially constant over all ranges of $|F_o|$ and (sin θ/λ).

TABLE 1

Fractional co-ordinates (× 10^4), with estimated standard deviations in parentheses; hydrogen atoms are numbered according to the carbon atoms to which they are bonded

	x	y	z
Co	404(1)	1751(2)	1711(3)
O(1)	712(6)	3067(9)	1314(13)
O(2)	1392(5)	1492(11)	2608(13)
O(3)	101(5)	2162(9)	3815(13)
O(4)	−567(5)	2046(10)	764(13)
N(1)	620(6)	1279(12)	−383(17)
N(2)	161(6)	390(11)	2039(14)
C(1)	978(8)	3392(17)	−50(21)
C(2)	1264(11)	4414(17)	−19(27)
C(3)	1559(9)	4804(18)	−1406(31)
C(4)	1635(9)	4301(16)	−2832(24)
C(5)	1355(10)	3309(18)	−2848(24)
C(6)	1073(8)	2859(16)	−1424(20)
C(7)	861(8)	1856(17)	−1578(23)
C(8)	424(10)	251(16)	−720(20)
C(9)	−162(9)	−16(17)	582(19)
C(10)	1479(9)	950(15)	1841(19)
C(11)	2120(8)	1118(18)	4880(24)
C(12)	2289(11)	475(18)	6143(24)
C(13)	1826(10)	−317(20)	6448(26)
C(14)	1197(10)	−544(17)	5509(22)
C(15)	1012(8)	130(15)	4233(19)
C(16)	422(8)	−154(15)	3126(22)
C(17)	−588(8)	2184(16)	4316(20)
C(18)	−1228(8)	2165(15)	3209(20)
C(19)	−1183(8)	2151(15)	1596(22)
C(20)	−720(9)	2347(19)	6050(23)
C(21)	−1891(9)	2123(20)	599(26)
O(W)	2189(11)	3355(17)	3161(24)
H(2)	1238	4860	1090
H(3)	1737	5592	−1375
H(4)	1902	4648	−3886
H(5)	1347	2875	−3984
H(7)	901	1497	−2772
1-H(8)	923	−225	−636
2-H(8)	187	177	−1926
1-H(9)	−719	296	320
2-H(9)	−236	−830	680
H(11)	2476	1780	4672
H(12)	2783	617	6904
H(13)	1977	−803	7414
H(14)	856	−1206	5740
H(16)	180	−905	3277
H(18)	−1796	2180	3758
1-H(20)	−195	2343	6715
2-H(20)	−1097	1784	6531
3-H(20)	−995	3073	6229
1-H(21)	−1744	2123	−667
2-H(21)	−2239	2781	843
3-H(21)	−2221	1472	877

The final atomic parameters are listed in Tables 1 and 2 together with their estimated standard deviations, which were derived from the residuals and the diagonal elements of the inverse matrix of the last least-squares cycle. The final anisotropic temperature factor of the water molecule was 5·2(4) Å^2. The numbering scheme of the atoms is shown in Figure 1. Observed and calculated structure factors are listed in Supplementary Publication No. 20274 (6pp., 1 microfiche).*

TABLE 2

Anisotropic temperature factors * (× 10^4) with estimated standard deviations in parentheses

	B_{11}	B_{12}	B_{13}	B_{22}	B_{23}	B_{33}
Co	17(1)	0(2)	9(3)	52(2)	−15(6)	161(3)
O(1)	26(3)	−7(9)	24(14)	22(10)	65(23)	160(17)
O(2)	11(3)	−11(9)	−5(12)	62(11)	13(23)	150(16)
O(3)	20(3)	−18(9)	10(12)	36(10)	−34(20)	124(16)
O(4)	10(3)	17(9)	13(12)	64(12)	1(24)	149(17)
N(1)	11(3)	−7(10)	40(16)	30(12)	−36(28)	168(22)
N(2)	15(3)	−7(10)	42(13)	26(12)	−87(25)	104(17)
C(1)	15(4)	5(15)	30(19)	75(20)	−12(43)	161(27)
C(2)	39(7)	−4(19)	33(32)	26(19)	−44(46)	250(38)
C(3)	24(5)	−1(16)	−24(30)	38(19)	92(55)	348(51)
C(4)	21(5)	25(16)	47(22)	70(20)	41(42)	20(33)
C(5)	24(5)	7(17)	−37(23)	68(20)	66(49)	212(32)
C(6)	15(4)	−10(14)	−4(19)	73(18)	18(35)	126(25)
C(7)	17(4)	13(15)	25(20)	85(19)	−27(48)	170(27)
C(8)	25(5)	−8(17)	22(23)	51(17)	−43(35)	131(24)
C(9)	23(5)	−21(15)	24(20)	75(20)	−21(35)	108(23)
C(10)	22(5)	27(15)	3(19)	58(16)	−119(32)	111(21)
C(11)	9(4)	3(15)	−11(21)	75(20)	−38(46)	219(33)
C(12)	28(6)	3(18)	−41(25)	87(21)	10(45)	164(30)
C(13)	33(6)	63(18)	−29(27)	98(22)	−4(53)	198(36)
C(14)	29(5)	17(17)	25(24)	54(19)	53(40)	163(28)
C(15)	14(4)	9(12)	46(18)	34(16)	1(33)	128(24)
C(16)	18(4)	−16(14)	55(24)	42(16)	−30(37)	184(27)
C(17)	12(5)	−9(14)	−2(18)	87(19)	21(36)	125(24)
C(18)	12(4)	−13(13)	28(19)	86(17)	−97(35)	120(22)
C(19)	11(4)	−2(13)	19(20)	58(16)	4(39)	177(27)
C(20)	22(5)	34(18)	54(22)	11(22)	23(44)	156(26)
C(21)	17(5)	−10(17)	49(22)	121(25)	51(49)	219(34)

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

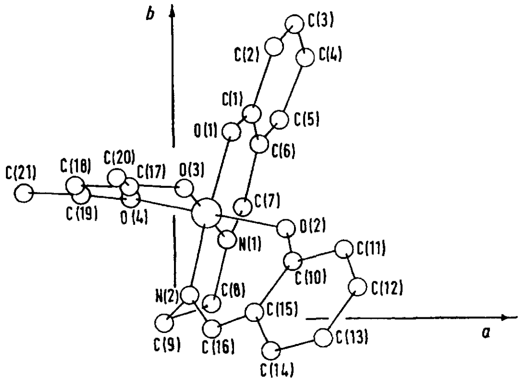

FIGURE 1 Projection of the molecule along the [001] plane and numbering scheme used

Atomic scattering factors were taken from ref. 10 for cobalt, from ref. 11 for oxygen, carbon, and hydrogen, and from ref. 12 for nitrogen.

Calculations.—All calculations were performed on an IBM 7044 computer using programs written by Im-

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* For details of Supplementary Publications see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. will be supplied as full size copies).

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mirzi[13] and Albano *et al.*[14] A program written by us was used to calculate the best molecular-plane equations, according to Schomaker *et al.*[15]

Preparation of Compounds.—All chemicals were commercial grade, except the Schiff's base complexes, which were prepared by published procedures.

Co(salen)(acac),$0·7H_2O$. Dark green crystals were obtained by the method of ref. 3 from Co(salen) and acacH in the air.

Co(salen)(salicylaldehydato),H_2O. The dark green compound was obtained similarly (Found: C, 58·8; H, 4·55; N, 5·85. Calc. for $C_{23}H_{21}CoN_2O_5$: C, 59·6; H, 4·55; N, 6·00%).

Co_2(3-MeOsalen)$_3$,$2H_2O$,2dmso (3-MeOsalen *is 3-methoxy-salen*, dmso *is dimethyl sulphoxide*). The greenish compound was obtained by two procedures, (i) from Co(3-MeOsalen) and 3-MeOsalenH_2 and (ii) from Co(AcO)$_2$,$4H_2O$ and 3-MeOsalenH_2 in the molar ratio of 2 : 3. Oxygen was bubbled through the reaction mixture which was then gently heated under reflux in dimethyl sulphoxide. After *ca.* 2 h the product separated out, and was washed and dried under vacuum. The *X*-ray powder spectra in both cases were identical and coincident with the calculated spectrum derived from the single-crystal *X*-ray data already reported.[6] Procedure (ii) gives a much greater yield and the elemental analysis was performed only on this product (Found: C, 53·4; H, 5·36; Co, 8·97; N, 6·56. Calc. for $C_{58}H_{70}Co_2N_6O_{16}S_2$: C, 54·0; H, 5·48; Co, 9·14; N, 6·52%).

Co_2(salen)$_3$,H_2O. The green compound was prepared in methanol by procedure (ii) (Found: C, 61·3; H, 4·44; Co, 12·8; N, 8·88. Calc. for $C_{48}H_{44}Co_2N_6O_7$: C, 61·6; H, 4·75; Co, 12·6; N, 8·99%).

RESULTS AND DISCUSSION

The Structure.—The salen ligand adopts in the [Co(salen)(acac)] compound the twisted arrangement (II), the acac group acting as chelate ligand. The hypothesis of Poddar and Biswas[3] has thus been confirmed. The crystals are built up of discrete [Co(salen)(acac)] units. The acac group occupies two *cis*-positions of a distorted octahedron around the cobalt atom, the polyhedron being completed by the quadridentate ligand as shown in Figure 1.

Bond-lengths and -angles are listed in Table 3 together with their estimated standard deviations. The co-ordination and salen-ligand bond lengths appear to be the same, within experimental error, as the mean values obtained for the planar Co(salen) derivatives.[16] Almost all the bond-lengths and -angles involving the acac group are quite normal for octahedral Co^{III}(acac) complexes.[17] The difference between the two distances C(17)–C(18) and C(18)–C(19) is probably due to the low accuracy in the location of carbon atoms.

The acac group and the two salicylideneiminato residues (sal) are nearly planar, as it can be seen from Table 4 which lists relevant least-squares planes. The main features of the overall geometry of the molecule are well described by the angles between the planes passing through these groups and the three equatorial planes of the octahedron around the cobalt atom. These are shown in Figure 2, together with the planes involved. The plane of the sal(1) group is nearly parallel to its corresponding co-ordination plane O(1), O(3), N(1), N(2) (dihedral angle 5·0°) whereas the plane of the sal(2) group makes an angle of 29·3° with the co-ordination plane O(1), O(2), O(4), N(2). The more marked deviation from coplanarity of the sal(2) group is not unexpected, if the twisted arrangement (II) can be imagined as being derived from the planar (I) structure by the displacement of O(2) from the O(1), N(1), N(2) plane. In fact, inspection of models shows that the sal(2) group must be bent away from its corresponding co-ordination plane in order to allow the

TABLE 3

Bond-lengths (Å) and -angles (°) with estimated standard deviations in parentheses

(*a*) Bond-lengths

Co–O(1)	1·88(1)	C(2)–C(3)	1·37(3)
Co–O(2)	1·92(1)	C(3)–C(4)	1·37(3)
Co–O(3)	1·91(1)	C(4)–C(5)	1·42(3)
Co–O(4)	1·92(1)	C(5)–C(6)	1·42(3)
Co–N(1)	1·89(1)	C(6)–C(7)	1·41(3)
Co–N(2)	1·90(2)	C(8)–C(9)	1·54(2)
O(1)–C(1)	1·30(2)	C(10)–C(11)	1·44(2)
O(2)–C(10)	1·27(2)	C(11)–C(12)	1·39(3)
O(3)–C(17)	1·28(2)	C(12)–C(13)	1·37(3)
O(4)–C(19)	1·29(2)	C(13)–C(14)	1·39(3)
N(1)–C(7)	1·33(3)	C(14)–C(15)	1·43(3)
N(1)–C(8)	1·45(3)	C(15)–C(16)	1·44(2)
N(2)–C(9)	1·44(2)	C(17)–C(18)	1·45(2)
N(2)–C(16)	1·25(2)	C(17)–C(20)	1·47(3)
C(1)–C(2)	1·47(3)	C(18)–C(19)	1·34(3)
C(1)–C(6)	1·36(3)	C(19)–C(21)	1·50(2)

(*b*) Bond-angles

O(1)–Co–O(2)	88·8(5)	C(1)–C(2)–C(3)	118·5(20)
O(1)–Co–O(3)	88·1(5)	C(2)–C(3)–C(4)	125·0(22)
O(1)–Co–O(4)	89·4(5)	C(3)–C(4)–C(5)	116·0(19)
O(1)–Co–N(1)	95·7(6)	C(4)–C(5)–C(6)	121·0(19)
O(1)–Co–N(2)	175·8(5)	C(1)–C(6)–C(5)	121·1(20)
O(2)–Co–O(3)	87·2(4)	C(5)–C(6)–C(7)	115·3(17)
O(2)–Co–O(4)	177·9(5)	N(1)–C(7)–C(6)	125·3(18)
O(2)–Co–N(1)	96·5(5)	N(1)–C(8)–C(9)	104·3(15)
O(2)–Co–N(2)	88·4(6)	N(2)–C(9)–C(8)	103·6(14)
O(3)–Co–O(4)	93·8(4)	O(2)–C(10)–C(11)	119·2(17)
O(3)–Co–N(1)	174·8(5)	O(2)–C(10)–C(15)	124·5(15)
O(3)–Co–N(2)	94·9(5)	C(11)–C(10)–C(15)	116·2(16)
O(4)–Co–N(1)	82·7(5)	C(10)–C(11)–C(12)	121·4(19)
O(4)–Co–N(2)	93·3(5)	C(11)–C(12)–C(13)	119·9(18)
N(1)–Co–N(2)	81·5(6)	C(12)–C(13)–C(14)	122·9(21)
Co–O(1)–C(1)	125·0(12)	C(13)–C(14)–C(15)	117·2(19)
Co–O(2)–C(10)	121·8(10)	C(10)–C(15)–C(14)	122·2(15)
Co–O(3)–C(17)	124·6(10)	C(10)–C(15)–C(16)	118·7(15)
Co–O(4)–C(19)	123·3(11)	C(14)–C(15)–C(16)	117·9(17)
Co–N(1)–C(7)	123·6(14)	N(2)–C(16)–C(15)	124·7(18)
Co–N(1)–C(8)	116·7(11)	O(3)–C(17)–C(18)	121·8(14)
C(7)–N(1)–C(8)	119·3(15)	O(3)–C(17)–C(20)	118·0(14)
Co–N(2)–C(9)	109·5(11)	C(18)–C(17)–C(20)	119·8(13)
Co–N(2)–C(16)	125·9(12)	C(17)–C(18)–C(19)	125·8(14)
C(9)–N(2)–C(16)	121·8(17)	O(4)–C(19)–C(18)	125·7(14)
O(1)–C(1)–C(2)	115·1(17)	O(4)–C(19)–C(21)	113·6(16)
O(1)–C(1)–C(6)	126·6(20)	C(18)–C(19)–C(21)	120·2(14)
C(2)–C(1)–C(6)	118·0(17)		

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formation of the five-membered ring without drastic strain. The difference between the two sal groups is also reflected in the tetrahedral distortion of N(2) atom, which is displaced *ca.* 0·15 Å from the Co, N(2), C(9), C(16) plane, whereas the corresponding displacement of N(1) atom is *ca.* 0·06 Å. The plane of the acac group makes an angle of 17·9° with the co-ordination plane O(2), O(3), O(4), N(1) and of 75·1 and 60·5° with the planes of the sal(1) and sal(2) groups. The latter planes form an angle of 58·6°. The ethylene bridge has a nearly gauche conformation, the torsional angle around the CH_2–CH_2 being 44·3°. The C(8) and C(9) atoms are both displaced from the O(1), O(3), N(1), N(2) plane by 0·19 and 0·74 Å towards O(4).

TABLE 4

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

Plane (1): O(1), O(3), N(1), N(2) $16{\cdot}332x - 2{\cdot}673y + 2{\cdot}590z = 0{\cdot}629$

[O(1) 0·054, O(3) −0·054, N(1) −0·058, N(2) 0·058]

Plane (2): O(2)—(4), N(1) $5{\cdot}334x + 12{\cdot}437y - 1{\cdot}950z = 2{\cdot}044$

[O(2) 0·046, O(3) −0·047, O(4) 0·049, N(1) −0·048]

Plane (3): O(1), O(2), O(4), N(2) $-6{\cdot}127x + 3{\cdot}290y + 7{\cdot}502z = 1{\cdot}577$

[O(1) −0·018, O(2) 0·018, O(4) 0·017, N(2) −0·017]

Plane (4): O(1), N(1), C(1)—(7) $16{\cdot}154x - 3{\cdot}748y + 2{\cdot}320z = 0{\cdot}348$

[O(1) −0·043, N(1) 0·085, C(1) −0·051, C(2) 0·035, C(3) 0·044, C(4) 0·024, C(5) −0·060, C(6) −0·017, C(7) −0·019]

Plane (5): O(2), N(2), C(10)—(16) $-10{\cdot}094x + 7{\cdot}650y + 4{\cdot}889z = 1{\cdot}076$

[O(2) −0·064, N(2) 0·057, C(10) 0·036, C(11) 0·026, C(12) −0·020, C(13) −0·009, C(14) −0·007, C(15) 0·072, C(16) −0·091]

Plane (6): O(3), O(4), C(17)—(21) $0{\cdot}801x + 13{\cdot}414y - 0{\cdot}654z = 2{\cdot}649$

[O(3) 0·009, O(4) 0·000, C(17) −0·049, C(18) −0·053, C(19) 0·038, C(20) 0·046, C(21) 0·009]

The intramolecular distances between non-bonded atoms are quite normal, only the O(4) ··· C(9) distance (2·87 Å) being shorter than the sum of the van der Waals radii.

The interesting intermolecular distances are those involving the water oxygen atom, which forms two bent hydrogen bonds with the oxygen atoms of the salen ligand [O(1) ··· O(W) 3·04 (2), and O(2) ··· O(W) 2·91(3) Å].

Ligand Properties.—The reaction of Co^{II}(salen) with β-diketones [3] and oxygen is to give cobalt(III) derivatives in which the salen ligand has been rearranged from a planar to a twisted conformation (II) by the displacement of only one oxygen atom from the equatorial plane of the planar isomer. The preceding oxidation of cobalt(II) seems to be indispensible to the reaction, which does not in fact occur under nitrogen,[18] although it takes place starting from $(OH^-)Co^{III}$ (salen),H_2O.[4] The same reaction is given by similar chelate agents like salicylaldehyde. The arrangement (II) has also been found for the salen-type ligand in the binuclear complexes [Co_2(salen)$_3$] in which one quadridentate Schiff's base molecule acts as chelating agent.[7] The unusual chelating ability of salen-type ligands is also shown by the formation of the binuclear complexes through the same reaction between Co(salen) and chelating agents, where the Schiff's base plays the same role as a β-diketone. The same arrangement has been proposed for rhodium–salen complexes.[19] On the other hand it must be noted that the bridging ability is determined by the steric requirements of the different Schiff's bases. In fact, such a bridging ability would be more probable with polymethylene derivatives because of the inherent difficulty in forming the $Co\langle{}^{N}_{N}\rangle[CH_2]_n$ ring when $n > 3$, and of the decrease of steric hindrance in the formation of polynuclear complexes. The latter polymeric structure has been recently suggested for *NN'*-polymethylenebis(salicylideneiminato)nickel(II) complexes.[20]

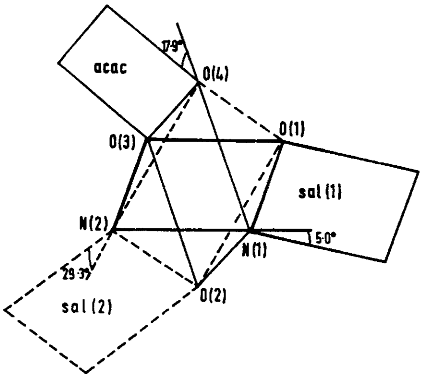

FIGURE 2 The overall geometry of the molecule

N.m.r. Spectra.—The *X*-ray results of [Co(salen)acac] show that the two methine hydrogens of the salen ligand are not equivalent, as they are in the planar (I) complexes. This suggested that n.m.r. spectral analysis could provide information about the actual arrangement of the quadridentate ligand. In fact the CH=N resonance is observed as singlet [21] when salen is planar, whereas the n.m.r. spectra in dimethyl sulphoxide show for [Co(salen)(acac)] two peaks at δ 8·04 and 7·81 and for [Co(salen)(salicylaldehydato)] two at δ 8·12 and 7·90 p.p.m. The agreement between the n.m.r. and *X*-ray results gives us confidence in using n.m.r. results to deduce the overall structure of this type of complex. From similar considerations, Murray and

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[18] G. Mestroni, personal communication.

[19] R. J. Cozens, K. S. Murray, and B. O. West, *J. Organometallic Chem.*, 1971, **27**, 399.

[20] W. C. Hoyt and G. W. Everett, jun., *Inorg. Chem.*, 1969, **8**, 2013.

[21] H. A. O. Hill, K. G. Morallee, G. Pellizer, G. Mestroni, and G. Costa, *J. Organometallic Chem.*, 1968, **11**, 167.

co-workers[5] have suggested a twisted structure of the salen ligand in R_2Sn^{IV} (salen) (R = Me or Ph) compounds.*

In binuclear complexes possessing a centre of symmetry, which is probably retained in solution, intramolecular steric hindrance causes three different kinds of methine hydrogens to be present, and hence three peaks would be expected in the CH=N resonance region. Unfortunately, the binuclear compounds which we examined are practically insoluble in all common solvents and n.m.r. spectra were not resolved.

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* A recent structure determination in our laboratory has shown that the two methyl grougs are actually *trans*-bonded.