Crystal and Molecular Structure of Benzoylacetonato-[*NN'*-ethylenebis-(salicylideneiminato)]cobalt(III)–1·5 Water

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The structure of the title compound has been determined by three-dimensional *X*-ray structural analysis. The crystals are monoclinic with $a = 11{\cdot}51(1)$, $b = 19{\cdot}57(1)$, $c = 11{\cdot}42(1)$ Å, $\beta = 110{\cdot}3(1)°$, space-group $P2_1/c$, and $Z = 4$. The structure was solved by conventional Patterson and Fourier techniques and was refined anisotropically by block-diagonal least-squares methods, using 2928 independent, photographically-collected reflections, to a final R of 0·068. The cobalt(III) molecule has a normal octahedral co-ordination, with a bidentate β-diketonate ligand and a strained non-planar configuration of the quadridentate salicylaldiminate ligand. The water molecules form a hydrogen-bonded chain of four waters linking phenolate oxygens of two different molecules across a crystallographic centre of symmetry. Bond lengths are normal with a mean cobalt–oxygen distance of 1·891(4) and a mean cobalt–nitrogen distance of 1·889(5) Å. However, the molecule is distinctly strained as shown by some quite significant distortions of bond angles of the ligands and the cobalt(III) co-ordination polyhedron.

PODDAR and BISWAS[1] have reported cobalt(III) compounds with the quadridentate ligand (I) (salen) and β-diketone ligands, which are of the type [Co^{III}(salen)(β-diketonate)]. They postulated a structure in which the diketonate anion was bidentate, and hence the quadridentate salen necessarily had a non-planar configuration such as (II).

Since such compounds of non-planar salen were previously unrecognised, and must undoubtedly be strained, and since an alternative structure (III) also appeared possible, we have studied these compounds in considerably more detail. Carbon-bonded metal–β-diketone compounds are now firmly characterised,[2] and we have proved[3] that a structure such as (III), with a

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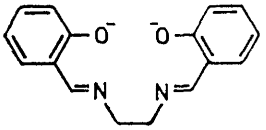
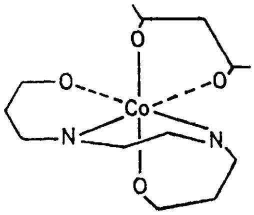
[1] S. N. Poddar and D. K. Biswas, *J. Inorg. Nuclear Chem.*, 1969, **31**, 565.

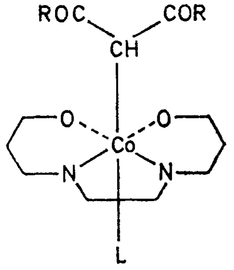
[2] D. Gibson, *Co-ordination Chem. Rev.*, 1969, **4**, 225; J. Lewis, R. F. Long, and C. Oldham, *J. Chem. Soc.*, 1965, 6740.

[3] N. A. Bailey, B. M. Higson, and E. D. McKenzie, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 591.

cobalt–carbon bond, is formed when malononitrile reacts with the oxidised Co(salen) under the same conditions used [1] to prepare the β-diketone compounds. However we can find no evidence [4] that structures such as (III) are significant in these β-diketone species, and have shown that they do have the postulated [1] structure (II).


(I)


(II)


(III)

We here present the results of a three-dimensional *X*-ray analysis of the structure of a crystalline compound of benzoylacetone (bzacH) [Co(salen)(bzac)],1·5H_2O. Whilst this work was in progress, preliminary reports were given of the structures of two other compounds with the same basic molecular structure: [Co(salen)(acac)],H_2O [5] and [Co_2(3-OMe-salen)$_3$] [6] (acac = acetylacetonate; 3-OMe-salen = 3-methoxy-salen).

EXPERIMENTAL

Green diamond-shaped prisms were obtained from acetone.[1] The crystal used for data collection had dimensions of *ca.* 0·35 × 0·25 × 0·25 mm. Unit-cell data were obtained from precession photographs.

Crystal Data.—$C_{26}H_{26}CoN_2O_{5.5}$, M = 513·5, Monoclinic, a = 11·51(1), b = 19·57(1), c = 11·42(1) Å, β = 110·3(1)°, U = 2410·8 Å^3, D_m = 1·414 (by flotation), Z = 4, D_c = 1·420. $F(000)$ = 1068. Space-group, $P2_1/c$ (C^5_{2h}, No. 14) from systematic absences: $\{h0l\}$, for $l = 2n + 1$, and $\{0k0\}$, for $k = 2n + 1$. Mo-K_α radiation, λ = 0·7107 Å, μ(Mo-K_α) = 7·9 cm^{-1}.

Photographic *X*-ray data for the layers $hk0$—5, 0—5kl, and $hk2h$ were collected by precession methods using zirconium-filtered Mo-K_α radiation, and intensities were estimated visually. Corrections were applied for Lorentz and polarisation effects, and for the splitting of the $K_{\alpha,1} - K_{\alpha,2}$ doublet. No corrections were made for absorption. Data were scaled together by means of common reflections to give 2928 independent reflections.

The Patterson function calculated from this data set gave the position of the heavy atom (cobalt), from which, after one cycle of least-squares refinement, an observed Fourier synthesis gave the positions of the remaining atoms except the water molecules and the hydrogen atoms. Five cycles of block-diagonal least-squares refinement of positional and isotropic thermal parameters reduced R to 0·169.

A difference Fourier synthesis then revealed two oxygen atoms of separate water molecules with peak-heights of *ca.* 4·6 and 1·6 eÅ^{-3}. The positions of these were consistent with a hydrogen-bonded water chain linking oxygen atoms of the salen moieties of two molecules across the centre of symmetry (see Results and Discussion section). The rela-

TABLE 1

Atomic positions (× 10^4) with estimated standard deviations and the calculated hydrogen positions (× 10^3)

Atom	x/a	y/b	z/c
Co	2411·0(8)	1372·2(3)	0911·7(7)
O(1)	1085(4)	1099(2)	−0531(4)
O(2)	2877(4)	0467(2)	1465(4)
O(3)	1326(4)	1358(2)	1827(4)
O(4)	3710(4)	1653(2)	2364(4)
O(5)	2532(6)	0714(3)	4146(6)
O(6)	0780(14)	0611(5)	5162(13)
N(1)	1993(5)	2272(2)	0285(5)
N(2)	3511(5)	1417(3)	0021(5)
C(1)	−0188(6)	0406(3)	−2142(6)
C(2)	0865(6)	0485(3)	−0907(6)
C(3)	1527(6)	−0086(3)	−0310(6)
C(4)	2473(6)	−0070(2)	0827(6)
C(5)	3150(5)	−0705(3)	1413(5)
C(6)	2717(6)	−1362(3)	0971(6)
C(7)	3403(7)	−1936(3)	1516(7)
C(8)	4510(7)	−1872(3)	2484(7)
C(9)	4963(7)	−1228(3)	2914(7)
C(10)	4281(6)	−0651(3)	2394(6)
C(11)	0432(6)	1805(3)	1736(6)
C(12)	−0395(6)	1670(3)	2341(6)
C(13)	−1333(7)	2118(4)	2289(7)
C(14)	−1467(8)	2732(4)	1617(8)
C(15)	−0666(8)	2878(3)	1019(7)
C(16)	0311(6)	2429(3)	1037(6)
C(17)	1087(6)	2621(3)	0381(6)
C(18)	4779(5)	1328(3)	2670(6)
C(19)	5474(7)	1229(3)	3947(7)
C(20)	6628(7)	0889(4)	4287(8)
C(21)	7106(7)	0651(5)	3414(10)
C(22)	6440(7)	0770(4)	2152(9)
C(23)	5286(6)	1090(3)	1777(7)
C(24)	4694(7)	1280(4)	0484(7)
C(25)	2668(6)	2503(3)	−0521(6)
C(26)	3023(7)	1871(4)	−1088(6)
H(1^1)	−049	090	−252
H(1^2)	008	012	−280
H(1^3)	−094	015	−198
H(3)	128	−058	−078
H(6)	183	−141	021
H(7)	306	−244	117
H(8)	504	−233	289
H(9)	584	−118	367
H(10)	462	−015	276
H(12)	−029	119	287
H(13)	−197	199	279
H(14)	−222	309	156
H(15)	−079	336	049
H(17)	090	311	−010
H(19)	509	140	466
H(20)	717	080	527
H(21)	802	040	373
H(22)	683	059	144
H(24)	526	131	−014
H(25^1)	209	284	−125
H(25^2)	350	278	002
H(26^1)	223	164	−181
H(26^2)	373	197	−150

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[4] B. M. Higson and E. D. McKenzie, to be published.

[5] M. Calligaris, G. Nardin, and L. Randaccio, *Chem. Comm.*, 1969, 1248.

[6] M. Calligaris, G. Nardin, and L. Randaccio, *Chem. Comm.*, 1970, 1079.

tive peak-heights were consistent with the presence of one full and one half water, as suggested by the chemical analyses and the measured density. Accordingly, they were inserted as such into the set of atomic positions, and their unexceptionable behaviour on further refinement was taken as proof of the assignment. No attempt has been made to refine population parameters of the half oxygen.

TABLE 2

Anisotropic thermal parameters * ($\times 10^5$)

Atom	b_{11}	b_{22}	b_{33}	b_{23}	b_{13}	b_{12}
Co	837(1)	142(0)	741(1)	18(1)	390(2)	−23(1)
O(1)	948(7)	185(2)	802(6)	18(5)	132(13)	56(5)
O(2)	962(7)	142(1)	822(6)	−80(5)	307(12)	−39(5)
O(3)	815(6)	197(1)	839(6)	144(6)	436(12)	49(6)
O(4)	871(6)	180(1)	876(6)	23(5)	248(12)	−72(5)
O(5)	1953(13)	432(3)	1464(10)	372(10)	456(22)	−394(11)
O(6)	2541(31)	314(5)	2203(28)	556(20)	2705(58)	571(21)
N(1)	989(8)	171(2)	822(8)	107(6)	420(15)	−112(6)
N(2)	985(8)	263(2)	774(7)	124(7)	667(15)	98(8)
C(1)	1035(11)	271(3)	871(10)	14(9)	197(21)	−48(9)
C(2)	885(10)	217(2)	975(9)	−14(8)	521(19)	−91(8)
C(3)	908(10)	192(2)	908(10)	−99(8)	357(19)	32(8)
C(4)	761(8)	167(2)	849(8)	−7(7)	703(17)	−44(7)
C(5)	781(8)	156(2)	832(9)	42(7)	729(17)	31(7)
C(6)	1003(10)	141(2)	1218(11)	−28(9)	751(21)	−76(8)
C(7)	1223(12)	162(2)	1153(11)	38(8)	1007(23)	−59(8)
C(8)	1215(12)	199(2)	1084(11)	181(8)	1123(23)	147(9)
C(9)	1067(11)	208(3)	1132(11)	101(8)	751(22)	153(8)
C(10)	987(10)	181(2)	875(9)	−9(8)	272(19)	19(8)
C(11)	872(9)	162(2)	762(8)	−58(7)	317(17)	−45(7)
C(12)	945(10)	266(3)	978(10)	−109(9)	742(21)	−23(9)
C(13)	1257(13)	302(3)	1249(13)	−201(11)	1072(26)	128(11)
C(14)	1329(14)	303(3)	1521(15)	0(12)	1018(28)	361(11)
C(15)	1400(14)	244(3)	1157(12)	10(9)	829(25)	330(10)
C(16)	1003(10)	173(2)	906(10)	6(8)	349(19)	97(8)
C(17)	1041(10)	157(2)	854(9)	92(7)	296(19)	26(8)
C(18)	836(9)	179(2)	972(9)	98(8)	533(18)	−203(8)
C(19)	1111(12)	222(3)	1187(12)	125(9)	23(23)	−230(9)
C(20)	944(12)	352(4)	1605(16)	263(13)	−80(27)	−158(11)
C(21)	978(12)	485(5)	2019(20)	701(17)	611(31)	230(13)
C(22)	1069(12)	381(4)	1953(19)	269(30)	986(30)	208(12)
C(23)	862(10)	231(2)	1221(12)	164(21)	853(21)	−66(8)
C(24)	1238(13)	293(3)	1297(13)	254(25)	962(25)	139(11)
C(25)	1086(11)	245(3)	908(10)	340(21)	605(21)	−30(9)
C(26)	1264(13)	343(3)	890(10)	275(23)	881(23)	96(11)

* The expression for the temperature factor is: $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + klb_{23} + hlb_{13} + hkb_{12})]$.

Further refinement with isotropic thermal parameters now reduced R to 0·12, and with anisotropic thermal parameters to 0·080.

A difference Fourier revealed most of the hydrocarbon hydrogen atoms at the expected positions. The mean peak-height was 0·35 eÅ^{-3} and no other density >0·3 eÅ^{-3} was observed, except for residual peaks of 0·6 eÅ^{-3} at distances of *ca.* 1 Å from the cobalt atom. The density around the water chain was ill-defined, with no peak >0·25 eÅ^{-3}, so that unambiguous assignment of the hydrogen atoms of the water molecules was not possible. Except for these, the hydrogen-atom positions were calculated assuming C–H 1·08 Å. For the methyl group, two of the hydrogen atoms were generated from the position of the carbon and that of the highest peak (0·35 eÅ^{-3}) corresponding to a reasonable hydrogen position. These (with isotropic thermal vibrations of 7·3 Å^2) were included, but not varied, in the further refinement.

Further cycles of block-diagonal least-squares refinement reduced R to 0·069. Introduction of a non-unit weighting scheme of the form: $w = 1/\{1 + [(|F_o| - b)/a]^2\}$, where $a = 2000$ and $b = 1800$, caused further convergence to 0·067. Allowance for the anomalous scattering of the cobalt atom increased R marginally to 0·068, but reduced the shifts in the positional parameters.

The atomic positions with estimated standard deviations are listed in Table 1, together with the calculated positions of the hydrogen atoms; and the anisotropic thermal parameters are listed in Table 2. The molecular geometry of the cobalt(III) species and the atom numbering system are given in Figure 1, and the hydrogen-bonded water chain in Figure 2. Hydrogen atoms are given the same numbers as

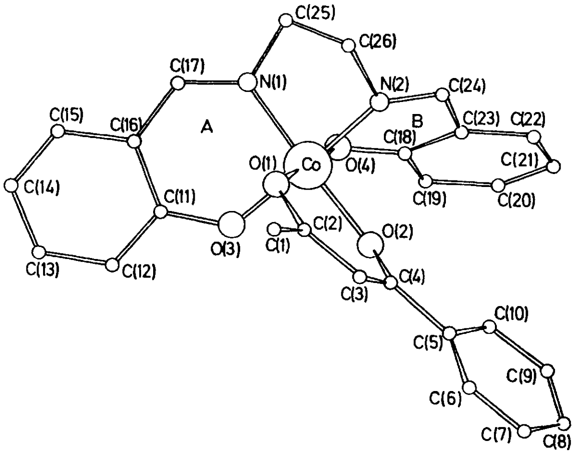

FIGURE 1 The molecular geometry of Co(salen)(bzac) with the atom and chelate-ring labelling system

the carbon atoms to which they are bonded, with superior figures denoting the different hydrogens attached to the same atom.

Atomic scattering factors and the anomalous dispersion corrections are taken from ref. 7. Observed and calculated structure factors are listed in Supplementary Publication No. SUP 20282 (27 pp., 1 microfiche) *, together with a Table of the dimensions and orientations of the thermal ellipsoids of vibration of the atoms.

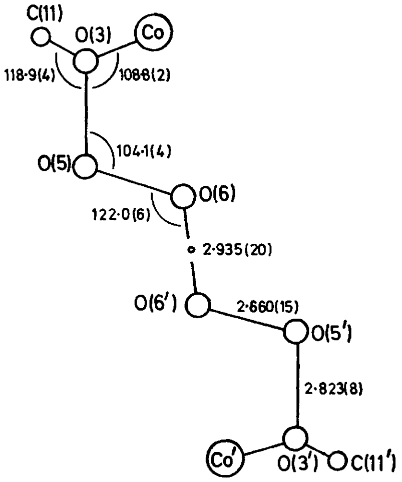

FIGURE 2 The hydrogen-bonded water chain with bond lengths (Å) and angles (°). Estimated standard deviations are given in parentheses

RESULTS AND DISCUSSION

Details of the various bond lengths and angles are given in Table 3. There are no intermolecular contacts shorter than the sum of the van der Waals' radii.

The molecule [Co(salen)(bzac)] has the same basic structure (Figure 1) as that of [Co(salen)(acac)].[5] The cobalt has the normal octahedral co-ordination for oxidation state $+3$, the β-diketonate anion is oxygen-bonded bidentate, and the salen has the *cis*-β configuration [8] of a facultative quadridentate ligand.

Bond lengths are generally normal, but a variety of angular distortions are observed. The salen ligand adopts a significantly strained configuration about the metal, and there are also significant distortions of the co-ordination polyhedron of the latter.

The Cobalt(III) *Co-ordination Polyhedron.*—The Co–O and Co–N bond lengths are all very similar at *ca.* 1·89 Å. The four Co–O bond lengths appear to be identical [mean 1·891(4)]; but the Co–N distances of 1·898(5) and 1·881(5), although not experimentally different, may reflect the different bonding situations of the two nitrogen atoms.

The bond angles at cobalt deviate significantly from 90°, ranging between 83·3(2) and 95·3(2)°. Such devi-

TABLE 3

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

(*a*) The co-ordination sphere of the metal

(i) Bond lengths

Co–O(1)	1·893(4)	Co–O(4)	1·888(4)
Co–O(2)	1·896(4)	Co–N(1)	1·898(5)
Co–O(3)	1·887(4)	Co–N(2)	1·881(5)

(ii) Bond angles

O(1)–Co–O(2)	94·3(2)	O(2)–Co–N(2)	93·3(2)
O(1)–Co–O(3)	89·4(2)	O(3)–Co–O(4)	89·5(2)
O(1)–Co–O(4)	178·8(2)	O(3)–Co–N(1)	95·3(2)
O(1)–Co–N(1)	85·0(2)	O(3)–Co–N(2)	178·0(2)
O(1)–Co–N(2)	91·9(2)	O(4)–Co–N(1)	94·7(2)
O(2)–Co–O(3)	88·1(2)	O(4)–Co–N(2)	98·2(2)
O(2)–Co–O(4)	86·2(2)	N(1)–Co–N(2)	83·3(2)
O(2)–Co–N(1)	176·5(2)		

(*b*) The diketone ligand

(i) Bond lengths

O(1)–C(2)	1·271(8)	C(5)–C(6)	1·409(9)
O(2)–C(4)	1·270(7)	C(6)–C(7)	1·388(9)
C(1)–C(2)	1·515(9)	C(7)–C(8)	1·372(10)
C(2)–C(3)	1·392(9)	C(8)–C(9)	1·387(10)
C(3)–C(4)	1·375(9)	C(9)–C(10)	1·385(9)
C(4)–C(5)	1·495(8)	C(5)–C(10)	1·396(9)

(ii) Bond angles

O(1)–C(2)–C(1)	114·4(5)	C(4)–C(5)–C(6)	122·3(5)
C(1)–C(2)–C(3)	119·9(6)	C(4)–C(5)–C(10)	119·5(5)
O(1)–C(2)–C(3)	125·7(6)		
		C(6)–C(5)–C(10)	118·2(6)
C(2)–C(3)–C(4)	124·3(6)	C(5)–C(6)–C(7)	120·2(6)
		C(6)–C(7)–C(8)	120·8(6)
C(3)–C(4)–C(5)	121·4(5)	C(7)–C(8)–C(9)	119·8(7)
C(3)–C(4)–O(2)	125·0(6)	C(8)–C(9)–C(10)	120·1(6)
O(2)–C(4)–C(5)	113·6(5)	C(5)–C(10)–C(9)	120·9(6)

(*c*) The salen ligand

(i) Bond lengths

O(3)–C(11)	1·327(7)	C(16)–C(17)	1·401(9)
O(4)–C(18)	1·319(7)		
N(1)–C(17)	1·284(8)	C(18)–C(19)	1·412(9)
N(1)–C(25)	1·467(9)	C(19)–C(20)	1·415(11)
N(2)–C(24)	1·306(9)	C(20)–C(21)	1·376(13)
N(2)–C(26)	1·488(9)	C(21)–C(22)	1·397(13)
		C(22)–C(23)	1·395(12)
C(11)–C(12)	1·383(9)	C(18)–C(23)	1·418(9)
C(12)–C(13)	1·375(11)		
C(13)–C(14)	1·405(12)	C(23)–C(24)	1·440(10)
C(14)–C(15)	1·355(12)		
C(15)–C(16)	1·439(9)	C(25)–C(26	1·517(10
C(11)–C(16)	1·439(9)		

(ii) Bond angles

Co–O(3)–C(11)	126·3(4)	N(1)–C(17)–C(16)	126·2(6)
Co–O(4)–C(18)	118·3(4)	N(1)–C(25)–C(26)	107·2(6)
		N(2)–C(26)–C(25)	101·7(6)
Co–N(1)–C(17)	124·7(4)	N(2)–C(24)–C(23)	121·4(7)
Co–N(1)–C(25)	113·8(4)		
C(17)–N(1)–C(25)	120·8(5)	O(4)–C(18)–C(19)	118·8(6)
		O(4)–C(18)–C(23)	123·1(6)
Co–N(2)–C(24)	125·1(5)	C(19)–C(18)–C(23)	118·1(6)
Co–N(2)–C(26)	111·2(4)	C(18)–C(19)–C(20)	119·3(7)
C(24)–N(2)–C(26)	119·9(6)	C(19)–C(20)–C(21)	122·3(8)
		C(20)–C(21)–C(22)	118·5(9)
O(3)–C(11)–C(12)	119·0(6)	C(21)–C(22)–C(23)	120·9(8)
O(3)–C(11)–C(16)	121·7(5)	C(18)–C(23)–C(22)	120·9(7)
C(12)–C(11)–C(16)	119·3(6)	C(22)–C(23)–C(24)	119·3(7)
C(11)–C(12)–C(13)	121·5(7)	C(18)–C(23)–C(24)	119·1(6)
C(12)–C(13)–C(14)	120·2(7)		
C(13)–C(14)–C(15)	119·4(8)		
C(14)–C(15)–C(16)	122·4(7)		
C(11)–C(16)–C(15)	117·1(6)		
C(15)–C(16)–C(17)	118·4(6)		
C(11)–C(16)–C(17)	124·6(6)		

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

[7] 'International Tables for *X*-ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

[8] A. M. Sargeson and G. H. Searle, *Nature*, 1963, **200**, 356; *Inorg. Chem.*, 1965, **4**, 45.

ations are larger than normal for the compounds of such ligands, and they have their origin in the various ligand steric constraints (see later).

The Salen Ligand.—The strain here is conveniently noted under three headings. It is apparent largely as angular distortions, and none of the bond-length differences are experimentally significant.

(*a*) Angular strain in the ' en ' chelate ring is apparent in: (i) the smaller-than-tetrahedral angles at the methylene carbon atoms, especially the angle N(2)–C(26)–C(25), which is only 101·7°; (ii) the conformation of the chelate ring [C(25) is almost exactly in the Co, N(1), N(2) plane]; and (iii) the acute angle subtended by N(1) and N(2) at the cobalt, which at 83·3° is much less than the more normal 87°.[9]

(*b*) The co-ordination polyhedra of the azomethine nitrogens [especially N(2)] are non-planar. N(2) is 0·17 Å out of the plane of Co, C(24), and C(26), and N(1) 0·08 Å out of the plane of Co, C(17), and C(25).

(*c*) The angular strain in the salicylaldimine ring B (Figure 1) is quite clearly shown by comparison with ring A, for which the bond lengths and angles are very close to those observed in most relatively unstrained salicylaldimine chelate compounds.[10] The light atoms of ring A are closely co-planar (Table 4) with the cobalt 0·21 Å out of this plane, whereas those of ring B all deviate markedly from the least-squares plane, and the cobalt is 0·86 Å out of this plane (Table 4).

C(17), but not C(24), is in the same plane (Table 4) as the phenyl ring to which it is attached.

Further there is a marked difference between the angle subtended at the cobalt by N(1) and O(3) (95·3°, which corresponds to the normal situation [10]) and the acute angle subtended by N(2) and O(4) (89·2°).

Together these distortions must add up to a quite significant steric strain for the salen ligand in its adopted configuration, and it would obviously prefer an essentially planar configuration. It is also apparent that the chances of salen adopting a *cis*-α-configuration [8] (a possibility noted by Calligaris *et al.*[5]) must be negligible.

The Benzoylacetonato-ligand.—Bond distances and angles in the β-diketonate ligand are all normal within experimental error, but the ligand adopts an unstable configuration which may also contribute to angle strain at the cobalt atom.

The phenyl substituent is nearly co-planar with the six-membered C_3O_2Co chelate ring (angle between planes 13·7°). This moiety is closely equivalent to the bicyclic aromatic systems such as biphenyl, for which co-planarity of the rings is a strained situation,[11] and in the present case strain is indicated by the relatively short calculated H · · · H interaction [H(3) · · · H(6) 1·96 Å]. Further rotation of the phenyl group out of the chelate-ring plane, which would relieve this strain, is inhibited by intermolecular contacts.

This configuration of the ligand may also contribute to distortion of the cobalt co-ordination polyhedron. Thus O(2) is 0·03 Å out of the Co, O(3), N(1) plane, in the direction of O(1). Yet with the large angle subtended by O(2) and O(1) at the cobalt [94·3(2)°], O(2) would be expected to be out of this plane in the other direction. But in such a case, H(10) would be too close to C(18) and C(23) of the salicylaldimine chelate ring. The marked difference in the angles O(3)–Co–O(2) and N(2)–Co–O(2) may have a similar origin.

TABLE 4

Equations of the least-squares planes given in the form $lX + mY + nZ = d$ (where X, Y, and Z are co-ordinates in Å referred to the axes a, b^*, and c'). The deviations of various atoms from these planes are given in square brackets. Angles between some of the planes are listed at the end of the Table

	l	*m*	*n*	*d*
Plane (1): Co, O(3), N(1)	0·4789	0·3670	0·7975	2·9199
[O(2) −0·026, N(2) 0·047]				
Plane (2): Co, O(4), N(2)	−0·1855	0·9559	−0·2276	1·8971
[O(1) 0·017, O(3) 0·050]				
Plane (3): Co, O(1), O(2)	0·8539	−0·0214	−0·5201	1·4953
[O(4) −0·036, N(1) 0·113]				
Plane (4): C(11)—(16)	0·3420	0·4605	0·8191	3·0834
[O(3) 0·018, N(1) −0·040, C(17) −0·011]				
Plane (5): C(18)—(23)	0·4743	0·8797	0·0351	4·5005
[O(4) 0·014, N(2) −0·148, C(24) 0·193]				
Plane (6): C(5)—(10)	0·7510	0·0465	−0·6587	1·2440
[C(4) 0·058]				
Plane (7): O(3), N(1), C(11), C(16), C(17)	0·3520	0·4666	0·8114	3·1003
[Co −0·206, O(3) 0·010, N(1) −0·010, C(11) −0·011, C(16) 0·000, C(17), 0·011]				
Plane (8): O(4), N(2), C(18), C(23), C(24)	0·4235	0·9056	0·0218	4·3299
[Co −0·855, O(4) 0·065, N(2) −0·111, C(18) −0·033, C(23) −0·078, C(24) 0·156]				
Plane (9): O(1), O(2), C(2)—(4)	0·8766	0·1134	−0·4676	1·7727
[Co 0·191, O(1) 0·016, O(2) −0·010, C(1) −0·055, C(2) −0·024 C(3) 0·012, C(4) 0·006, C(5) 0·050]				
Plane (10): Co, C(24), C(26)	0·1358	0·8621	0·4882	3·1194
[N(2) −0·171]				
Plane (11): Co, C(17), C(25)	0·4060	0·4083	0·8176	2·8744
[N(1) 0·076]				
Plane (12): Co, N(1), N(2)	0·4569	0·3687	0·8095	2·8832
[O(2) −0·029, O(3) 0·047, C(25) −0·031, C(26) −0·689]				

Angles between planes (°)

(1)–(7)	9·3	(4)–(7)	0·8
(2)–(8)	38·5	(5)–(8)	3·4
(3)–(9)	8·4	(6)–(9)	13·7

We [4] have no evidence for the apparently less strained

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[9] B. Bosnich, R. D. Gillard, E. D. McKenzie, and G. A. Webb, *J. Chem. Soc.* (*A*), 1966, 1331.

[10] M. Gerloch, E. D. McKenzie, and A. D. C. Towl, *J. Chem. Soc.* (*A*), 1969, 2850, and references therein; M. Calligaris, D. Minichelli, G. Nardin, and L. Randaccio, *J. Chem. Soc.* (*A*), 1971, 2702, and references therein.

[11] G. Casalone, C. Mariani, A. Mugnoli, and M. Simonetta, *Acta Cryst.*, 1969, **B25**, 1741.

isomer in which the positions of the methyl and phenyl substituents are interchanged.

The Hydrogen-bonded Water Chain.—The full water molecule is hydrogen bonded to the phenolic oxygen atom O(3) at an O(3) · · · O(5) distance of 2·82 Å, and the half-water molecule is so placed that it forms, with O(5), a chain of four water molecules across a crystallographic centre of symmetry. Thus the waters link symmetry-related [Co(bzac)(salen)] molecules (Figure 2). All oxygen–oxygen contacts are within the range expected for hydrogen bonding and all angles subtended at the oxygen atoms are fairly close to tetrahedral (Figure 2).

One explanation of the occurrence of O(6) with only half population could be that O(6) only occurs on one side of the inversion centre at any one time, the occurrence being random (*i.e.*, some molecules could have a chain of two water molecules attached to O(3), and some only one molecule). However, since only one site has been observed for O(6), and this is such (Figure 2) that the formation of the full water chain is facilitated, a preferred explanation is that approximately half the pairs of [Co(bzac)(salen)] molecules are linked by a full chain of four water molecules, and the remainder have only the O(5) water molecules directly attached to them. In this latter case, the population of O(6) would not be constrained to 0·5, although peak-heights suggested this value.

As can be seen from Figure 2, hydrogen atoms cannot be associated with the water molecules in an ordered way so as to conform to the space-group symmetry. Thus the failure of the difference Fourier to show such atoms is partially explained.

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