Steric Strain in Cobalt(III) Compounds. Crystal and Molecular Structure of Dibenzoylmethanato-*O,O′*-[*NN′*-*o*-phenylenebis(salicylideneiminato)]-cobalt(III)

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A preparative study is reported of the mixed-ligand cobalt(III) compounds with β-diketonate or related ester anions and the quadridentate ligand of the title compound. Although the quadridentate ligand was expected to remain in a planar configuration in such compounds, several β-diketonate species can be made in which the diketone is *O,O*-bidentate and the quadridentate ligand is in the same non-planar configuration that *NN′*-ethylenebis-(salicylideneiminate) adopts in related compounds. This is proven, and the details of the steric strain in the molecule are revealed, by an *X*-ray structural study of the title compound. The orange-brown crystals are monoclinic with $a = 16.89(2)$, $b = 16.47(1)$, $c = 9.84(1)$ Å, $\beta = 90.86(5)°$, space group $P2_1/n$, and $Z = 4$. A total of 3 091 independent reflections were obtained on a diffractometer. The structure was solved by conventional Patterson and Fourier techniques and was refined to a final R of 0.059. The octahedral cobalt(III) molecular species contains an *O,O*-bidentate β-diketonate anion, and the quadridentate Schiff-base ligand is in the non-planar *cis*-β configuration. The steric strain is taken up not only in the expected bond-angle distortions, but also in significant bond-length changes. Whereas the two Co–N distances are not significantly different [1.906(4) and 1.902(5) Å], nor are the two Co–O distances for the β-diketonate [1.897(4) and 1.894(4) Å], yet the two Co–O distances for the quadridentate ligand differ by 8σ. The distance to the ' out-of-plane ' oxygen is long [1.912(4) Å] and that to the ' in-plane ' oxygen is shorter than normal [1.880(4) Å]. Bond angles at the cobalt range between 83.5(2) and 96.5(2)°. In contrast to the diketonates, both ethyl acetoacetate and diethyl malonate form *C*-bonded unidentate compounds, with the quadridentate ligand in the planar configuration.

Cobalt(III) alkyls of type (I) {O–N–N–O = ligand (II) for A = $-[CH_2]_2-$} can be formed by a direct reaction between cobalt(III) and carbon species with an activated methyl or methylene group.[1,2]

Acetone gives such a cobalt–carbon-bonded species [1] [(I) for R^1 = COMe, and R^2 = H], but β-diketonates do not. Instead they bond in an *O,O*-bidentate mode (III),[3-5] with the quadridentate ligand {(II), for R =

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[1] A. Bigotto, G. Costa, G. Mestroni, G. Pellizer, A. Puxeddu, E. Reisenhofer, L. Stefani, and G. Tauzher, *Inorg. Chim. Acta Rev.*, 1970, **4**, 41.

[2] N. A. Bailey, B. M. Higson, and E. D. McKenzie, *Inorg. Nuclear Chem. Letters*, 1971, **7**, 591; D. Cummins, B. M. Higson, and E. D. McKenzie, *J.C.S. Dalton*, 1973, 414; D. Cummins, Ph.D. Thesis, Sheffield, 1974.

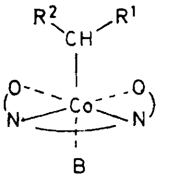
[3] S. N. Poddar, and D. K. Biswas, *J. Inorg. Nuclear Chem.*, 1969, **31**, 565; R. J. Cozens and K. S. Murray, *Austral. J. Chem.*, 1972, **25**, 911.

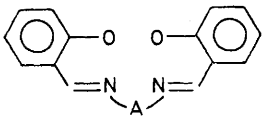
[4] M. Calligaris, G. Nardin, and L. Randaccio, *Chem. Comm.*, 1970, 1079; *J.C.S. Dalton*, 1972, 543.

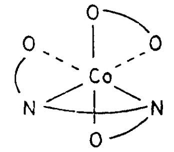
[5] D. Cummins, B. M. Higson, and E. D. McKenzie, *J.C.S. Dalton*, 1973, 1359.

$-[CH_2]_2-$, $-CH_2-CHMe-$, or $-CH_2-CMe_2-$} in a strained[6] (*cis*-β) configuration.

In a further attempt to obtain β-diketonate compounds of type (I), we have now used the more rigidly planar ligand salph (II; $A = o-C_6H_4$). However, even in this case, type (III) compounds are formed, and accordingly we have done an *X*-ray structural analysis of one of them to investigate the strain in the ligand system.[7]


(I)


(II)


(III)

EXPERIMENTAL

Preparation of Compounds.—In all preparative reactions, the same method was used. Air was drawn through a suspension of [Co(salph)] (2.0 g) in methanol (100 ml) for 2 h. The resulting solution was filtered, and N_2 was passed through it for 30 min. A slight excess of the β-diketone or ester in methanol (30 ml) was then added; the flask was stoppered, and the mixture set aside until a solid product had separated out. The exclusion of light from the reaction had no noticeable effect on the purity of the solids isolated. The crystalline compounds isolated by this method are listed in Table 1.

TABLE 1

The compounds isolated, the analytical data, and the key to the abbreviations used for the diketones and esters

	Abbreviation key [a]		Analyses							
			Found (%)				Calc. (%)			
Compound	R^3	R^4	C	H	N	S	C	H	N	S
[Co(salph)(tfta)]	CF_3	thenoyl	56.5	3.7	4.8	5.6	56.5	3.2	4.7	5.4
$[Co(salph)(py)_2][tfta]$			59.3	4.3	7.7	5.2	60.6	3.7	7.4	4.3
[Co(salph)(dbm)]	Ph	Ph	70.2	4.3	4.6		70.4	4.2	4.7	
[Co(salph)(eaa)(MeOH)]	Me	OEt	61.5	5.1	5.6		60.7	5.1	5.2	
[Co(salph)(eaa)(py)]			64.0	4.9	7.2		63.5	5.3	8.0	
$[Co(salph)(dem)(H_2O)]\cdot3H_2O$	OEt	OEt	54.1	5.5	4.6		53.7	4.8	4.2	
$[Co(salph)(dem)(py)]\cdot2H_2O$			59.2	4.7	6.3		59.4	5.3	6.5	
[Co(salen)(ea)]	Me	OEt	58.0	5.3	6.1		58.0	5.3	6.2	
acac	Me	Me								
bzac	Me	Ph								

[a] R^3 and R^4 are the different substituents on the basic C_3HO_2 framework of the diketonates and ester anions [py = pyridine; salph = (II) for $A = o-C_6H_4$; and salen = (II) for $A = C_2H_4$].

The species containing pyridine (Table 1) were obtained by dissolving the parent diketone species in pyridine and adding water.

Other β-diketones were tried, without success. Benzoylacetone, acetylacetone, cyclohexane-1,3-dione, and dimedone each gave brown powders with little crystallinity (very poorly defined *X*-ray powder patterns), and attempts to purify them, either by recrystallisation or by elution from a short alumina column with chloroform, produced only totally amorphous brown powders. Hexafluoroacetylacetone and ω-nitroacetophenone did give, in some cases, crystalline products (*X*-ray powder patterns) but the analytical data gave very poor correlations with expected figures. None of the i.r. spectra of these products had C=O stretching frequencies above 1 650 cm^{-1}. From a previous attempt[5] to prepare the benzoylacetone compound by refluxing the mixture, we obtained only $[Co(bzac)_3]$, and in several cases we also detected some of the tris-diketonates here (mass spectra).

The compound [Co(salen)(eaa)] was made for comparison, but attempts to make a pure sample of the dem analogue were unsuccessful.

Physical Measurements.—I.r. spectra were obtained on a PE 457 grating instrument, using Nujol mulls; ^1H n.m.r. spectra were obtained on a Varian HA 100 instrument.

Crystal Structure Determination.—The orange-brown crystal, obtained from methanol for data collection, was an irregular fragment of dimensions *ca*. 0.28 × 0.17 × 0.38 mm.

Crystal Data.—$C_{35}H_{25}N_2O_4Co$, $M = 596.5$, Monoclinic, $a = 16.89(2)$, $b = 16.47(2)$, $c = 9.84(1)$ Å, $\beta = 90.86(5)°$, $U = 2\,738$ Å^3, $D_m = 1.440$ g cm^{-3} (by flotation), $Z = 4$, $D_c = 1.446$ g cm^{-3}, $F(000) = 1\,232$. Mo-K_α radiation, $\lambda = 0.710\,69$ Å, $\mu(\text{Mo-}K_\alpha) = 7.00$ cm^{-1}. Space group $P2_1/n$ (a non-standard setting of C_{2h}^5, No. 14) from systematic absences.

Data were collected on a Stoe Stadi-2 two-circle diffractometer, by use of graphite-monochromated Mo-K_α radiation. All reflections within a 2θ diffraction sphere of 50° were scanned and those with $I < 3\sigma$ were discarded. Corrections were applied for Lorentz and polarisation factors, and for absorption by a Gaussian integration method. 19 Of the low-angle reflections were later discarded because the observed intensities were significantly lower than the calculated ones, thus suggesting extinction. 3 091 Independent reflections were used in the final analysis.

The structure was solved by conventional Patterson and Fourier techniques. Block-diagonal least-squares refinement of the positional and isotropic thermal parameters reduced *R* to 0.081; the introduction of anisotropic thermal parameters for the cobalt reduced *R* to 0.076; but the use of

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[6] N. A. Bailey, B. M. Higson, and E. D. McKenzie, *J.C.S. Dalton*, 1972, 503.

[7] D. Cummins, E. D. McKenzie, and H. Milburn, *Inorg. Chim. Acta*, 1975, **12**, L17.

TABLE 2

Atomic positions ($\times 10^4$) and calculated hydrogen positions ($\times 10^3$) with isotropic thermal parameters (Å ^{2}), with estimated standard deviations in parentheses

Atom	x/a	y/b	z/c	B
Co	393.2(4)	1 894.2(4)	600.0(7)	[a]
N(1)	84(3)	868(3)	1 313(4)	2.75(1)
N(2)	1 378(3)	1 646(3)	1 466(4)	3.11(1)
O(1)	−576(2)	2 097(2)	−302(4)	3.52(1)
O(2)	833(2)	1 488(2)	−1 044(4)	3.26(1)
O(3)	7(2)	2 311(2)	2 260(4)	3.28(1)
O(4)	691(2)	2 934(2)	−40(4)	3.20(1)
C(1)	−1 139(3)	1 573(3)	−562(6)	3.13(2)
C(2)	−1 776(4)	1 798(4)	−1 371(7)	4.24(2)
C(3)	−2 404(4)	1 289(4)	−1 604(8)	5.33(2)
C(4)	−2 448(5)	535(4)	−964(8)	5.72(3)
C(5)	−1 843(4)	300(4)	−115(7)	4.45(2)
C(6)	−1 171(3)	795(3)	135(6)	3.12(2)
C(7)	−577(3)	507(3)	1 039(6)	3.06(2)
C(8)	603(3)	608(3)	2 384(6)	2.99(2)
C(9)	1 285(3)	1 069(3)	2 547(6)	3.20(2)
C(10)	1 832(4)	920(4)	3 580(7)	4.52(2)
C(11)	1 689(4)	273(4)	4 453(7)	5.11(2)
C(12)	1 030(4)	−205(4)	4 270(7)	5.00(2)
C(13)	476(4)	−51(4)	3 250(7)	4.17(2)
C(14)	2 053(3)	1 786(4)	931(6)	3.46(2)
C(15)	2 123(3)	2 055(3)	−456(6)	3.24(2)
C(16)	2 835(4)	2 428(4)	−886(7)	4.14(2)
C(17)	2 922(4)	2 600(4)	−2 247(7)	4.83(2)
C(18)	2 352(4)	2 371(4)	−3 166(7)	4.65(2)
C(19)	1 663(4)	1 980(4)	−2 783(6)	3.84(2)
C(20)	1 521(3)	1 845(4)	−1 394(6)	3.08(2)
C(21)	162(3)	3 016(3)	2 733(6)	2.73(1)
C(22)	521(3)	3 640(3)	2 009(6)	3.12(2)
C(23)	739(3)	3 578(3)	663(6)	2.70(2)
C(24)	1 043(3)	4 286(3)	−134(6)	2.95(2)
C(25)	982(4)	5 084(4)	335(6)	3.70(2)
C(26)	1 231(4)	5 726(4)	−489(7)	4.31(2)
C(27)	1 554(4)	5 568(4)	−1 713(7)	4.68(2)
C(28)	1 631(4)	4 782(4)	−2 192(7)	4.91(2)
C(29)	1 366(4)	4 143(4)	−1 390(6)	4.02(2)
C(30)	−65(3)	3 141(4)	4 165(5)	3.04(2)
C(31)	−318(4)	3 893(4)	4 649(7)	4.30(2)
C(32)	−527(4)	3 979(4)	6 009(8)	5.12(2)
C(33)	−462(4)	3 317(4)	6 899(7)	4.72(2)
C(34)	−241(4)	2 575(4)	6 418(7)	4.33(2)
C(35)	−51(4)	2 476(4)	5 050(6)	3.72(2)
H(2)	−175	233	−182	[b]
H(3)	−284	146	−221	
H(4)	−290	17	−112	
H(5)	−187	−23	33	
H(7)	−68	−1	150	
H(10)	231	126	370	
H(11)	207	15	518	
H(12)	94	−66	489	
H(13)	0	−39	314	
H(14)	254	170	148	
H(16)	103	158	−110	
H(17)	341	286	−255	
H(18)	243	248	−413	
H(19)	125	182	−345	
H(22)	63	415	248	
H(25)	75	519	123	
H(26)	118	629	−17	
H(27)	174	602	−227	
H(28)	186	468	−308	
H(29)	141	358	−171	
H(31)	−34	436	402	
H(32)	−70	451	636	
H(33)	−60	338	786	
H(34)	−22	211	705	
H(35)	12	194	470	

[a] The anisotropic thermal parameters for the cobalt were, in order, 0.00242(0), 0.00187(0), 0.00627(1), 0.00035(1), 0.00122(1), and 0.00052(1), where the expression for the temperature factor is: $\exp[-(h^2b_{11} + k^2b_{22} + l^2b_{33} + klb_{23} + hlb_{13} + hkb_{12})]$. [b] Fixed isotropic thermal parameters of 5 Å^2 were used.

anisotropic thermal parameters for the other atoms could not be justified.

A difference-Fourier revealed peaks in most positions where hydrogen atoms were expected, the mean peak height being 0.3 eÅ^3. Accordingly, hydrogen atom positions were calculated (assuming C–H 0.98 Å), and included (with isotropic thermal parameters of 5.0 Å^2) but not varied in the final refinement to *R* 0.059.

Atomic scattering factors were taken from ref. 8. Observed structure amplitudes and calculated structure factors are available from the authors (Sheffield) and deposited as Supplementary Publication No. SUP 21547 (20 pp., 1 microfiche).*

Programmes used are part of the Sheffield *X*-ray system. Calculations were performed on the Sheffield University ICL 1907 computer. Final atomic positional and vibrational parameters, with estimated standard deviations, are listed in Table 2.

RESULTS AND DISCUSSION

All solid compounds (Table 1) were characterised by their *X*-ray powder diffraction patterns (which are available from the authors) and their i.r. spectra. Preparations were more difficult than with the salen analogues. The same range[5] of diketones was tried, but only for the few listed in Table 1 have we been able to characterise properly the 1 : 1 mixed-ligand compounds.

Structural assignment, *i.e.* the distinction between structures (I) and (III), was based on the C=O stretching frequencies of the i.r. spectra, as before.[5] The *O,O*-bidentate structure for the dbm compound is confirmed by the *X*-ray structural analysis.[7]

There are general parallels with, but differences in detail from, the behaviour of the salen analogues. For example, the ^{1}H n.m.r. spectra (especially the azomethine resonances) of [Co(salph)(tfta)] show that it retains structure (III) in chloroform, but rearranges to the ionic species [Co(salph)(solvent)$_2$][tfta] in pyridine and dimethyl sulphoxide. However, the conversion into the ionic form is apparently complete for the salph compound, but only partial for the salen analogue.[5] The compound [Co(salph)(py)$_2$][tfta] has been isolated and characterised (Table 1).

By contrast, the ester compounds in the salph series have ν(C=O) above 1 700 cm^{-1} and are clearly of structural type (I). They give a further indication that, as expected, the salph quadridentate ligand is more reluctant to adopt the non-planar configuration. The salen compound of ethylacetoacetate is *O,O*-bidentate.

X-Ray Structure Analysis.—The molecular geometry is shown in the Figure, with details of the atom numbering scheme. Bond lengths and angles are given in Table 3, and details of some least-squares planes and the angles between them are in Table 4.

The molecule [Co(salph)(dbm)] has the same basic

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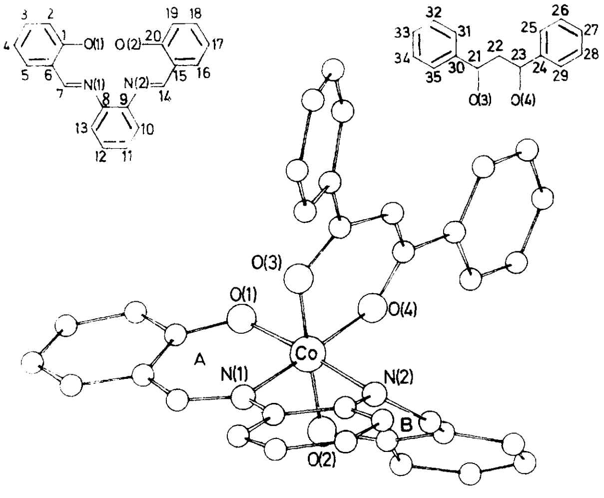
* See Notice to Authors No. 7, in *J.C.S. Dalton*, 1975, Index issue.

[8] 'International Tables for Crystallography,' vol. III, Kynoch Press, Birmingham, 1962.

structure as [Co(salen)(bzac)] [6] and [Co(salen)(acac)].[4] The cobalt has the normal octahedral co-ordination for the +3 oxidation state, the β-diketonate is *O,O*-bidentate, and the quadridentate ligand has a non-planar (*cis*-β) configuration. Bond lengths are mostly normal, although, as in [Co(salen)(bzac)] there are a variety of angular distortions. There are no intermolecular contacts significantly shorter than the sum of the van der Waals radii.



The molecular geometry of [Co(salph)(dbm)] with the atom and chelate-ring labelling system

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–N(1)	1.906(4)	Co–O(2)	1.912(4)
Co–N(2)	1.902(5)	Co–O(3)	1.897(4)
Co–O(1)	1.880(4)	Co–O(4)	1.894(4)

(ii) Bond angles

N(1)–Co–N(2)	83.5(2)	N(2)–Co–O(4)	96.2(2)
N(1)–Co–O(1)	95.2(2)	O(1)–Co–O(2)	90.5(2)
N(1)–Co–O(2)	96.5(2)	O(1)–Co–O(3)	92.0(2)
N(1)–Co–O(3)	84.5(2)	O(1)–Co–O(4)	85.2(2)
N(1)–Co–O(4)	177.7(2)	O(2)–Co–O(3)	177.2(2)
N(2)–Co–O(1)	177.4(2)	O(2)–Co–O(4)	85.8(2)
N(2)–Co–O(2)	87.5(2)	O(3)–Co–O(4)	93.2(2)
N(2)–Co–O(3)	90.1(2)		

(*b*) The β-diketone ligand

(i) Bond lengths

O(3)–C(21)	1.277(6)	C(28)–C(29)	1.393(10)
O(4)–C(23)	1.269(6)	C(24)–C(29)	1.379(8)
C(21)–C(22)	1.394(8)	C(21)–C(30)	1.481(8)
C(22)–C(23)	1.384(8)	C(30)–C(31)	1.396(9)
C(23)–C(24)	1.500(8)	C(31)–C(32)	1.397(10)
C(24)–C(25)	1.398(8)	C(32)–C(33)	1.402(10)
C(25)–C(26)	1.401(9)	C(33)–C(34)	1.365(10)
C(26)–C(27)	1.355(10)	C(34)–C)35)	1.399(9)
C(27)–C(28)	1.385(10)	C(35)–C(30)	1.399(8)

(ii) Bond angles

O(3)–C(21)–C(22)	124.9(5)	C(32)–C(33)–C(34)	119.9(6)
O(3)–C(21)–C(30)	114.7(5)	C(33)–C(34)–C(35)	120.4(6)
C(22)–C(21)–C(30)	120.4(5)	C(34)–C(35)–C(30)	120.4(6)
C(21)–C(22)–C(23)	124.0(5)	C(23)–C(24)–C(25)	122.0(5)
O(4)–C(23)–C(24)	112.6(5)	C(23)–C(24)–C(29)	118.7(5)
O(4)–C(23)–C(22)	124.6(5)	C(25)–C(24)–C(29)	119.2(5)
C(22)–C(23)–C(24)	122.8(5)	C(24)–C(25)–C(26)	119.6(6)
C(21)–C(30)–C(31)	122.2(5)	C(25)–C(26)–C(27)	119.9(6)
C(21)–C(30)–C(35)	118.8(5)	C(26)–C(27)–C(28)	121.5(6)
C(31)–C(30)–C(35)	119.6(5)	C(27)–C(28)–C(29)	118.8(6)
C(30)–C(31)–C(32)	120.0(6)	C(28)–C(29)–C(24)	120.9(8)
C(31)–C(32)–C(33)	120.1(7)		

Table 3 (*Continued*)

(*c*) The salph ligand

(i) Bond lengths

O(1)–C(1)	1.297(7)	C(8)–C(9)	1.387(8)
O(2)–C(20)	1.351(7)	C(9)–C(10)	1.386(9)
N(1)–C(7)	1.290(7)	C(10)–C(11)	1.393(10)
N(1)–C(8)	1.427(7)	C(11)–C(12)	1.373(10)
N(2)–C(9)	1.436(7)	C(12)–C(13)	1.386(10)
N(2)–C(14)	1.284(7)	C(8)–C(13)	1.399(9)
C(1)–C(2)	1.414(9)	C(14)–C(15)	1.442(8)
C(2)–C(3)	1.367(10)	C(15)–C(16)	1.421(9)
C(3)–C(4)	1.396(11)	C(16)–C(17)	1.386(10)
C(4)–C(5)	1.367(10)	C(17)–C(18)	1.363(10)
C(5)–C(6)	1.416(9)	C(18)–C(19)	1.388(9)
C(1)–C(6)	1.429(9)	C(19)–C(20)	1.409(8)
C(6)–C(7)	1.412(9)	C(15)–C(20)	1.406(8)

(ii) Bond angles

Co–O(1)–C(1)	125.8(4)	C(6)–C(7)–N(1)	125.5(5)
Co–O(2)–C(20)	114.2(3)	N(1)–C(8)–C(9)	114.9(5)
Co–N(1)–C(7)	125.0(4)	N(1)–C(8)–C(13)	125.8(5)
Co–N(1)–C(8)	111.7(3)	C(9)–C(8)–C(13)	119.3(5)
C(7)–N(1)–C(8)	122.4(5)	N(2)–C(9)–C(8)	112.1(5)
Co–N(2)–C(9)	111.7(3)	N(2)–C(9)–C(10)	125.6(5)
Co–N(2)–C(14)	123.6(4)	C(8)–C(9)–C(10)	122.1(5)
C(9)–N(2)–C(14)	122.0(5)	C(9)–C(10)–C(11)	117.9(6)
O(1)–C(1)–C(2)	117.9(5)	C(10)–C(11)–C(12)	120.4(6)
O(1)–C(1)–C(6)	124.2(5)	C(11)–C(12)–C(13)	121.9(7)
C(2)–C(1)–C(6)	117.9(5)	C(12)–C(13)–C(8)	118.4(6)
C(1)–C(2)–C(3)	121.5(6)	N(2)–C(14)–C(15)	121.9(5)
C(2)–C(3)–C(4)	121.1(7)	C(14)–C(15)–C(16)	119.8(5)
C(3)–C(4)–C(5)	119.0(7)	C(14)–C(15)–C(20)	118.6(5)
C(4)–C(5)–C(6)	122.2(6)	C(16)–C(15)–C(20)	121.2(5)
C(1)–C(6)–C(5)	118.4(5)	C(15)–C(16)–C(17)	118.8(6)
C(5)–C(6)–C(7)	118.4(5)	C(16)–C(17)–C(18)	120.2(6)
C(1)–C(6)–C(7)	123.2(5)	C(17)–C(18)–C(19)	122.3(6)
C(18)–C(19)–C(20)	119.5(6)	O(2)–C(20)–C(15)	123.7(5)
C(15)–C(20)–C(19)	117.8(5)	O(2)–C(20)–C(19)	118.4(5)

The cobalt(III) *co-ordination polyhedron*. The Co–O and Co–N bond lengths are, on average, slightly longer than those in [Co(salen)(bzac)] [6] (1.898 *vs.* 1.891 Å, respectively). The two Co–N distances are not significantly different, nor are the two Co–O distances for the β-diketonate, but the two Co–O distances for the quadridentate ligand differ by 8σ. The distance to the ' out-of-plane ' oxygen is 1.912(4) Å, whereas that to the ' in-plane ' oxygen is shorter than normal at 1.880(4) Å.

The bond angles at the cobalt range between 83.5(2) and 96.5(2)°, so the deviations from the ideal are a little larger than in [Co(salen)(bzac)].[6]

The salph *ligand*. The strain in this ligand is taken up mainly in angular distortions in one half of the molecule. The angular strain in the salicylaldimine ring B (Figure) is quite clearly shown by comparison with ring A, for which the bond lengths and angles are close to those observed in most relatively unstrained salicylaldimine chelate compounds.[9] The light atoms of ring A are closely coplanar (Table 4), the cobalt being 0.17 Å out of this plane, whereas those of ring B deviate quite considerably from the least-squares plane, the cobalt being 1.00 Å out of this plane {some 0.14 Å farther than in the

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[9] M. Calligaris, G. Nardin, and L. Randaccio, *Co-ordination Chem. Rev.*, 1972, **7**, 385.

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 *). Deviations (Å) 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(1), N(1)	0.3549	−0.4520	−0.8184	−1.6607
[O(4) −0.076, N(2) 0.073]				
Plane (2):				
Co, O(2), N(2)	0.3394	0.9152	−0.2174	2.9489
[O(1) −0.052, O(3) 0.044]				
Plane (3):				
Co, O(3), O(4)	−0.8997	0.1146	−0.4212	−0.4808
[N(1) −0.010, O(2) −0.085]				
Plane (4):				
C(1)–C(6)	0.4804	−0.4133	−0.7736	−1.6051
[N(1) 0.073, O(1) −0.057, C(7) −0.006]				
Plane 5:				
C(8)—(13)	0.5088	−0.6045	−0.6129	−1.5284
[N(1) −0.066, N(2) 0.179]				
Plane (6):				
C(15)—(20)	0.4340	−0.8950	−0.1027	−1.4278
[N(2) −0.145, O(2) −0.043, C(14) 0.200]				
Plane (7):				
C(24)–(29)	0.9627	−0.0638	0.4256	1.0878
[C(21) −0.049, C(22) 0.139, C(23) −0.068]				
Plane (8):				
C(30)—(35)	−0.9473	−0.2270	−0.2259	−1.9165
[C(21) −0.040, C(22) −0.697, C(23) −0.742]				
Plane (9):				
O(1), N(1), C(1), C(6), C(7)	0.4688	−0.3966	−0.7892	−1.5619
[Co 0.166, N(1) 0.032, O(1) −0.027, C(1) 0.025, C(6) 0.010, C(7) −0.040]				
Plane (10):				
O(2), N(2), C(14), C(15), C(20)	−0.3636	0.9262	0.0994	1.7094
[Co 1.000, N(2) 0.106, O(2) −0.059, C(14) −0.150, C(15) 0.075 C(20) 0.028]				
Plane (11):				
O(3), O(4), C(21) −(23)	−0.8962	0.3099	−0.3176	0.4815
[Co −0.290, O(3) 0.011, O(4) −0.019, C(21) −0.006, C(22) −0.014, C(23) 0.028, C(24) 0.108, C(36) −0.027]				
Plane (12):				
Co, C(7), C(8)	0.5109	−0.5001	−0.6993	−1.6582
[N(1) 0.082]				
Plane (13):				
Co, C(9), C(14)	0.0168	−0.8096	−0.5868	−2.8611
[N(2) −0.141]				
Plane (14):				
Co, N(1), N(2)	−0.3201	0.4478	0.8349	1.6803
[C(7) −0.136, C(8) 0.411, C(9) 0.519, C(14) −0.704]				

Angles between planes (°)

(1)—(9)	7.5	(5)—(14)	161.0
(2)—(10)	45.4	(6)—(10)	175.6
(3)—(11)	12.7	(7)—(8)	159.5
(4)—(5)	14.4	(7)—(11)	164.6
(4)—(9)	1.5	(8)—(11)	31.7
(5)—(6)	34.4	(12)—(13)	34.5

analogous [Co(salen)(bzac)] compound}. The angular distortions in ring B are larger than those in the bent salen ligand. The Co–O(2)–C(20) angle is 114.2(3)° and the Co–N(2)–C(14) angle is 123.6(4)° in the salph compound, compared to 118.3(4) and 125.1(5)° respectively in [Co(salen)(bzac)].

The difference between the angle subtended at the cobalt by N(1) and O(1) [95.2(2)°], which corresponds to the normal situation [9] and that subtended by N(2) and O(2) [87.5(2)°] is also marked, this difference being *ca.* 26% greater than that observed in [Co(salen)(bzac)].

Angular strain in the phenylenediamine ring is apparent in the smaller-than-trigonal angles at the carbon atoms C(8) and C(9), especially the N(2)–C(9)–C(8) angle which is only 112.1(5)°. The phenylene is 19° out of planarity with the [Co, N(1), N(2)] plane. The co-ordination polyhedra of the azomethine nitrogens are non-planar. N(2) is 0.14 Å out of the [Co, C(9), C(14)] plane whereas N(1) is 0.08 Å out of the [Co, C(7), C(8)] plane.

The distortions observed add up to a significant steric strain in the salph ligand in this configuration. The quadridentate ligand would obviously prefer to be in an essentially planar configuration, this preference being somewhat greater than in [Co(salen)(bzac)].

The dbm ligand. Bond lengths and angles in the β-diketonate are normal, but the ligand adopts an unstable conformation.

The two phenyl substituents (rings C and D in the Figure) are not quite coplanar with the C_3O_2 chelate ring, but are twisted from this plane by angles of 31.7 and 15.4°, respectively, with a dihedral angle of 159.5° between them (Table 4). This parallels the situation in bicyclic aromatic systems such as biphenyl and *p,p'*-bitolyl, for which coplanarity of the rings is a strained conformation.[10] Further rotation of the phenyl rings out of the chelate ring plane is prevented by intermolecular contacts. However, some extra relief of strain caused by the close contact of the hydrogen atoms H(22), H(25), and H(31) is indicated by the angular distortions at C(21) and C(23). The phenyl rings are pushed away from each other, so that the O(3)–C(21)–C(30) angle is 114.7 and O(4)–C(23)–C(24) 112.6°.

The conformation of this ligand also contributes to the distortion of the cobalt polyhedron. O(4) is 0.08 Å out of the [Co, N(1), O(1)] plane in the same direction as O(3). The large angle subtended by O(3) and O(4) at the cobalt [93.2(2)°] suggests that the deviation should be in the opposite direction. However, in such a case, H(29) would be too close to C(15) and C(19) of the salicylaldimine chelate ring. The marked difference in the angles O(1)–Co–O(4) and N(2)–Co–O(4) {which is twice as large as that observed in [Co(salen)(bzac)]} probably has a similar origin.

These results illustrate a general point about steric effects in metal chelate compounds. They are important and give a good rationalisation of much experimental data. However, they cannot be put on any reliable

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

quantitative scale relative to the total bonding energy in the molecule in all of its possible forms, so predictions about structure have to be based on limited extrapolations from experimental data.

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