

The Crystal Structure of Tris(1-phenyl-1,2-propanedione-2-oximato)cobalt(III)–Benzene(1/1), $[\text{Co}(\text{C}_9\text{H}_8\text{NO}_2)_3]\cdot\text{C}_6\text{H}_6$

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The title compound crystallizes in the triclinic space group $P\bar{1}$ with $Z=2$ and with unit cell dimensions $a=10.316(10)$, $b=12.318(10)$, $c=12.695(19)$ Å, $\alpha=76.34(10)$, $\beta=74.42(11)$, and $\gamma=89.36(7)^\circ$. The structure was solved by direct methods with the MULTAN program and refined by full-matrix least-squares technique to an R value 0.041 for 2646 observed reflections. The cobalt(III) in the complex is octahedrally coordinated by three oxime nitrogen and three carbonyl oxygen atoms such that the three nitrogen atoms are mutually *cis*. There are no closer interactions between the complex and the solvent benzene molecules. The average C–N, N–O, C–O, C1–C2 bond lengths and the CNO angle are 1.348(7), 1.252(6), 1.279(6), 1.421(8) Å, and $121.4(5)^\circ$, respectively. The results are compared with those obtained earlier for similar ligands in free and metal-coordinated states.

In earlier X-ray studies we found the metal chelates formed by 1,2-nitrosonaphthols \rightleftharpoons 1,2-naphthoquinone oximes to have a quinone oximato structure.^{1–3} For comparative purposes the investigation has now been extended to include a typical carbonyl-oxime ligand of aliphatic character. Unlike 1,2-nitrosonaphthols, aliphatic carbonyl-oximes are poor metal chelating agents and the complexes, if formed at all, are often amorphous and unstable.⁴ The crystalline cobalt(III) chelate of 1-phenyl-1,2-propanedione-2-oxime is easily prepared, however, and the results of an X-ray structure analysis of it are given here. The structure of the uncoordinated ligand acid has been described earlier by the authors.⁵

EXPERIMENTAL

Crystal preparation. The complex compound was prepared by adding $\text{Na}_3[\text{Co}(\text{NO}_2)_6]$ (1 mol), dissolved in a small quantity of water, to a hot methanolic solution of 1-phenyl-1,2-propanedione-2-oxime (3 mol). The precipitated product was dissolved in a benzene–chloroform mixture (1:1), from which brown-red prisms were separated after the solution had slowly evaporated almost to dryness. Anal. C, H, N. The amount of solvent was determined thermogravimetrically as 12% (calc. 12.5%).

Crystal and intensity data. Preliminary photographic work showed the crystals to be triclinic. The space group $P\bar{1}$ was assumed and later confirmed by successful refinement of the structure. A crystal with approximate dimensions $0.3 \times 0.3 \times 0.3$ mm was mounted on a Syntex $P2_1$ diffractometer and precise cell parameters were determined by a least-squares refinement of 15 automatically centered reflections. The crystal data for $[\text{Co}(\text{C}_9\text{H}_8\text{NO}_2)_3]\cdot\text{C}_6\text{H}_6$ are:

$a=10.316(10)$, $b=12.318(10)$, $c=12.695(19)$ Å,
 $\alpha=76.34(10)$, $\beta=74.42(11)$, $\gamma=89.36(7)^\circ$,

Space group $P\bar{1}$, $Z=2$, $D_x=1.37$ g cm⁻³, $D_m=1.3$ g cm⁻³ (by flotation),

$\lambda(\text{MoK}\alpha)=0.7107$ Å, $\mu=6.5$ cm⁻¹ (MoK α)

X-Ray intensities were measured by the ω scan technique ($3^\circ < 2\theta < 50^\circ$) with graphite monochromated MoK α radiation. The scan rate varied from 2 to 29° min⁻¹, depending on the intensity of the reflection. The three reflections checked periodically during the data collection showed no crystal decomposition. Of the 3946 recorded reflections, 2646 with $I > 3\sigma(I)$ were used for the structure analysis. The intensities were corrected for Lorentz and polarization effects.

Structure determination and refinement. The structure was solved by direct methods with the MULTAN program.⁶ The cobalt and the atoms in its coordination sphere could be localized in the

Table 1. Fractional atomic coordinates ($\times 10^4$) and anisotropic thermal parameters^a ($\times 10^3$) for non-hydrogen atoms. The three different values for the parameters refer to atoms in ligands A, B and C, respectively. The values in Table 2 and Figure 2 refer to the same order of ligands.

Atom	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
C1	2227(5)	4434(4)	1053(4)	39(3)	44(3)	42(3)	6(2)	-15(2)	-4(2)
	4610(5)	3630(4)	3432(4)	31(3)	43(3)	34(3)	-2(2)	-0(2)	-3(2)
	201(5)	2390(4)	4634(4)	35(3)	34(3)	47(3)	2(2)	-14(2)	0(2)
C2	3233(6)	3737(4)	624(4)	48(4)	40(3)	40(3)	2(2)	-1(3)	-5(2)
	4520(5)	2436(4)	3870(4)	27(3)	50(3)	46(3)	-1(2)	-4(2)	-2(2)
	69(5)	1721(4)	3907(5)	35(3)	35(3)	51(3)	-1(2)	-7(3)	-8(2)
C3	3898(7)	3750(5)	588(5)	72(5)	70(4)	43(4)	8(3)	0(3)	-7(3)
	5363(7)	1730(5)	4528(5)	57(4)	58(4)	71(4)	9(3)	-23(3)	-3(3)
	-1085(6)	945(5)	4009(5)	38(4)	58(4)	69(4)	-9(3)	-10(3)	-16(3)
C4	1846(6)	5485(4)	374(4)	53(4)	43(3)	37(3)	-1(3)	-10(3)	-6(2)
	5658(5)	4401(5)	3495(4)	40(3)	57(3)	34(3)	-11(3)	-8(2)	-4(3)
	-776(5)	2363(4)	5738(4)	38(3)	43(3)	46(3)	6(2)	-11(2)	-8(2)
C5	517(6)	5809(5)	656(5)	61(4)	50(3)	60(4)	2(3)	-19(3)	-8(3)
	5328(6)	5488(5)	3538(5)	51(4)	61(4)	47(3)	-8(3)	-8(3)	-10(3)
	-1012(6)	3342(5)	6111(5)	60(4)	61(4)	56(4)	-6(3)	-14(3)	-15(3)
C6	172(7)	6816(5)	73(6)	59(5)	63(4)	98(5)	15(3)	-35(4)	-18(4)
	6284(8)	6269(6)	3539(6)	90(6)	69(4)	69(5)	-19(4)	-20(4)	-23(4)
	-1908(8)	3330(6)	7145(6)	87(5)	81(5)	78(5)	21(4)	-14(4)	-45(4)
C7	1145(8)	7531(5)	-769(6)	117(7)	51(4)	66(4)	19(4)	-35(4)	-2(3)
	7577(8)	5957(6)	3511(6)	79(6)	92(5)	83(5)	-36(4)	-31(4)	-12(4)
	-2530(8)	2341(7)	7823(6)	88(6)	94(6)	72(5)	2(4)	13(4)	-27(4)
C8	2465(8)	7230(5)	-1027(6)	101(6)	51(4)	59(4)	6(4)	-15(4)	6(3)
	7925(6)	4882(6)	3476(6)	40(4)	105(6)	79(5)	-23(4)	-20(4)	-3(4)
	-2308(7)	1360(6)	7478(6)	71(5)	80(5)	68(5)	-7(4)	17(4)	-5(4)
C9	2826(7)	6210(5)	-480(5)	65(4)	53(4)	54(4)	-0(3)	-12(3)	1(3)
	6985(6)	4103(5)	3451(5)	46(4)	74(4)	57(4)	-8(3)	-15(3)	-2(3)
	-1441(6)	1364(5)	6432(5)	66(4)	53(4)	48(4)	6(3)	10(3)	-6(3)
N	3474(4)	2918(3)	1449(4)	35(3)	42(3)	50(3)	-2(2)	-3(2)	-8(2)
	3470(4)	1962(3)	3673(4)	40(3)	38(2)	51(3)	-4(2)	-9(2)	1(2)
	1128(4)	1896(3)	2974(4)	46(3)	36(2)	47(3)	-1(2)	-11(2)	-7(2)
O1	1592(3)	4166(3)	2102(3)	43(2)	42(2)	40(2)	-1(2)	-7(2)	-4(2)
	3725(4)	4068(3)	2958(3)	39(2)	41(2)	49(2)	-4(2)	-13(2)	-1(2)
	1236(3)	3074(3)	4339(3)	42(3)	45(2)	42(2)	-8(2)	-8(2)	-8(2)
O2	4304(4)	2199(3)	1250(3)	61(3)	58(3)	62(3)	20(2)	5(2)	-9(2)
	3209(4)	921(3)	4013(4)	73(3)	37(2)	78(3)	-9(2)	-22(2)	7(2)
	1181(4)	1388(3)	2219(3)	60(3)	59(2)	53(2)	-6(2)	-9(2)	-25(2)
Co	2443(1)	2976(1)	2910(1)	39(1)	36(1)	40(1)	-5(1)	-6(1)	-2(1)

Table 1. Continued.

The benzene molecule

C11	7127(10)	-528(8)	2607(8)	135(8)	104(7)	113(8)	-5(6)	4(6)	-33(6)
C12	6081(9)	-297(7)	2173(9)	90(7)	96(6)	153(9)	-6(5)	-16(6)	-41(6)
C13	6253(13)	-378(9)	1031(11)	184(12)	129(9)	184(12)	-26(8)	-109(10)	33(8)
C14	7576(14)	-715(9)	446(9)	247(14)	131(9)	87(7)	-42(9)	-15(8)	-15(6)
C15	8530(11)	-889(8)	1017(10)	150(9)	98(7)	181(11)	-11(7)	23(8)	-69(9)
C16	8341(10)	-825(8)	2066(10)	120(8)	93(7)	166(10)	-15(6)	-36(7)	-3(7)

^a The anisotropic thermal parameters are of the form $\exp[-2\pi(h^2a^{*2}U_{11} + \dots + 2klb^*c^*U_{23})]$.

initial *E* map, and subsequent Fourier syntheses gave the positions of the other non-hydrogen atoms. The refinement was carried out by block-diagonal least-squares calculations (X-RAY system, 1976)⁷ with the non-hydrogen atoms refined anisotropi-

cally. All hydrogen atoms except those of the benzene molecule were located on a difference Fourier map. The refinement was then continued with a mixed thermal mode, with the hydrogen atoms isotropic. The function to be minimized was

Table 2. Fractional atomic coordinates ($\times 10^3$), isotropic thermal parameters ($\times 10^3$) and bond distances (Å) for hydrogen atoms.

Atom	x	y	z	U_{iso}	Bond length
H1(C3)	479(7)	406(6)	-84(6)	112(24)	0.94(7)
	578(7)	212(5)	490(5)	95(22)	0.93(8)
	-188(5)	113(4)	449(4)	54(16)	0.95(5)
H2(C3)	394(6)	295(5)	-68(5)	93(22)	1.02(7)
	601(6)	138(5)	408(5)	93(21)	0.93(6)
	-87(6)	14(5)	430(5)	73(18)	1.02(6)
H3(C3)	334(6)	417(5)	-108(5)	74(19)	1.01(6)
	474(8)	107(6)	516(6)	126(27)	1.07(6)
	-130(7)	101(6)	328(6)	120(28)	0.99(8)
H(C5)	-9(5)	529(4)	123(5)	64(17)	0.93(5)
	443(4)	571(4)	357(4)	34(13)	0.96(5)
	-56(6)	400(5)	563(5)	76(18)	0.93(5)
H(C6)	-86(6)	700(5)	36(5)	75(19)	1.07(6)
	597(7)	705(6)	356(6)	106(24)	1.01(7)
	-215(6)	402(5)	733(5)	90(21)	0.94(7)
H(C7)	93(7)	825(5)	-112(6)	101(23)	0.95(6)
	825(6)	652(5)	347(5)	91(21)	0.97(7)
	-315(8)	234(6)	859(6)	124(27)	1.01(7)
H(C8)	314(7)	782(6)	-156(6)	109(24)	1.01(6)
	888(8)	468(6)	329(6)	121(27)	0.99(8)
	-276(7)	69(6)	792(6)	111(24)	0.93(6)
H(C9)	378(6)	596(5)	-64(5)	72(18)	1.01(9)
	724(6)	333(4)	336(5)	70(18)	1.01(9)
	-125(5)	61(4)	618(4)	61(16)	1.05(6)

$w(|F_o| - |F_c|)^2$, where $w = 1/(50.0 + |F_o| + 0.006|F_o|^2)$. The final R value ($R = \sum ||F_o| - |F_c|| / \sum |F_o|$) was 0.041 for 2646 observed reflections; the average shift/e.s.d. value of variable parameters was 0.09.

The atomic scattering factors for the non-hydrogen atoms were those of Cromer and Mann⁸ and for the hydrogen atom those of Stewart, Davidson and Simpson.⁹ The anomalous dispersion corrections ($\Delta f'$, $\Delta f''$) were included for Co.¹⁰

Atomic parameters for the non-hydrogen and hydrogen atoms are listed in Tables 1 and 2, respectively. The calculated C-H bond distances in the complex moiety are also included in Table 2. The solvent benzene molecules are relatively loosely bound in the structure, and the benzene carbon atoms show considerably higher thermal vibrations than the other non-hydrogen atoms, as is common. The observed C-C bond lengths in the benzene molecule are in the range 1.31–1.47 Å, with a mean standard deviation of 0.02 Å.

A list of the observed and calculated structure factors is obtainable from the authors on request.

DESCRIPTION AND DISCUSSION OF THE STRUCTURE

Fig. 1 illustrates the molecular structure. The same numbering scheme has been adopted for each of the three ligand molecules, which are distinguished from each other by the letters A, B and C. The bond lengths and angles for the non-hydrogen atoms of the complex constituents are shown in Fig. 2.

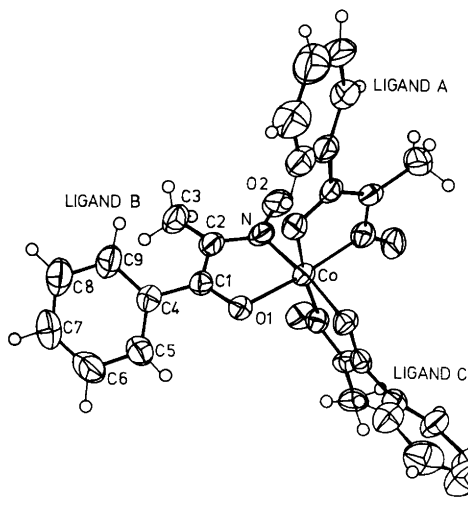


Fig. 1. ORTEP drawing of the complex molecule showing the atom numbering scheme used. The non-hydrogen atoms are represented by their thermal ellipsoids with 50% probability.

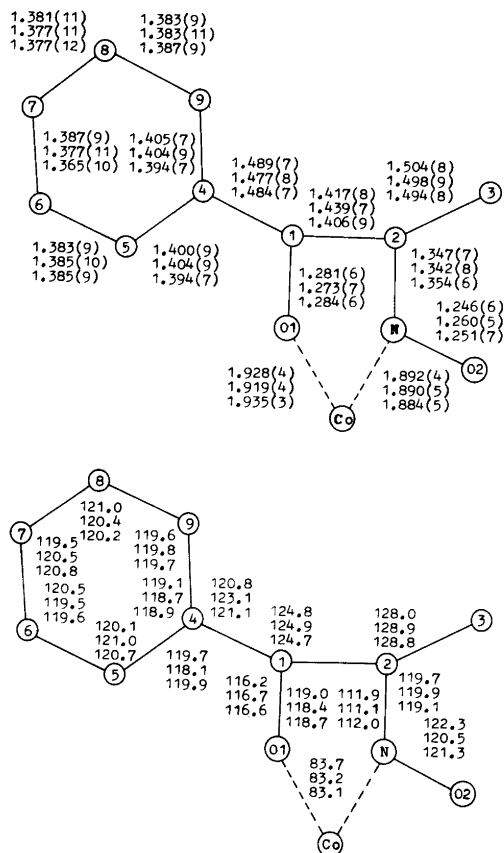


Fig. 2. Bond lengths (Å) and angles (°). The estimated standard deviations for the bond angles are 0.2–0.7°.

The coordination about cobalt is *cis*-octahedral with five-membered chelate rings. Such geometry could be anticipated: thus far the presence of five-membered chelate rings, *i.e.* coordination through oxime nitrogen and quinone oxygen, has been established in all complexes of the series,^{1-3,11-14} and *cis*-octahedral geometry about the metal has been found in those few cases where tris chelates have been studied.¹²⁻¹⁴

The three Co-N bond lengths are in the range 1.884–1.892 Å, with a mean of 1.889 Å, and the equivalent values for Co-O are 1.919–1.935 Å with a mean of 1.927 Å. These distances are very similar to those found in *fac*-tris(isonitrosoacetylacetonato)cobalt(III) (mean distances 1.891 and 1.925 Å),¹⁴ which is the only other cobalt complex of known structure containing a carbonyl-oxime

Table 3. Selected structural details.

Torsion angles (°)	Ligand A	Ligand B	Ligand C
NC2C1O1	-6.6	1.1	1.5
C3C2C1O1	166.5	-175.3	-174.1
C4C1C2N	172.8	-179.2	-178.2
Deviations (Å) from the plane CoNO1			
C1	0.190	-0.016	-0.022
C2	0.125	-0.004	-0.005
O2	-0.101	0.036	0.035

function. The coordination octahedron about cobalt found here is not seriously distorted from regular octahedral with the N-Co-N angles of *ca.* 94°, N-Co-O angles in the range 83–94°, and O-Co-O angles of 89–93°.

Although the bond lengths and angles in the chelate rings appear to be essentially equivalent, some differences in the chelation conformation do exist. The chelate rings involving ligands B and C are relatively planar, whereas slight but significant deviations from planarity can be found for ligand A. The different puckering of the chelate ring of ligand A as compared with the other two rings, and which most probably arises from packing considerations, is revealed in the values of the torsion angle NC2C1O1 together with the deviations of atoms C1 and C2 from the plane CoNO1. These values for each of the chelate rings, together with some other structural details, are listed in Table 3.

In our studies on nitrosophthalato \rightleftharpoons naphthoquinone oximate complexes^{1–3} we have observed that chelation with a metal ion (Cu^{2+} , Ni^{2+} or Zn^{2+}) brings about the following changes in the ligand geometry: (i) the C=O and C=N distances are lengthened from their respective free ligand values of 1.22 ± 0.02 and 1.30 ± 0.01 Å to 1.28 ± 0.02 and 1.36 ± 0.02 Å, (ii) the N-O and C1-C2 distances are shortened from their free ligand values of 1.37 ± 0.02 and 1.49 ± 0.03 Å to 1.26 ± 0.01 and 1.43 ± 0.01 Å, and (iii) the CNO angle of $112 \pm 2^\circ$ is opened up to $121 \pm 2^\circ$. The mean values of the present C1-O1, C2-N, C1-C2, and N-O2 bond lengths and the C2NO2 bond angle are 1.279, 1.348, 1.421, 1.252 Å, and 121.4° , respectively. The corresponding free ligand values have been previously reported as 1.231(4), 1.278(4), 1.501(5), 1.405(4) Å, and $113.0(2)^\circ$ (in the free ligand the oxime nitrogen and carbonyl oxygen are roughly in *trans*-

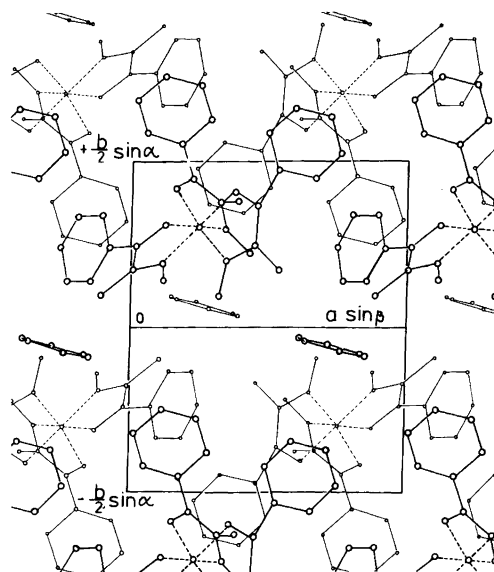


Fig. 3. A packing diagram of $[\text{Co}(\text{C}_9\text{H}_8\text{NO}_2)_3] \cdot \text{C}_6\text{H}_6$ as viewed down the *c* axis.

position, the torsion angle NC2C1O1 being 155°).⁵ These values are in excellent agreement with the results given above for the free and metal-coordinated naphthoquinone oximes. The C-O and C-N bond lengths, and the CNO angle obtained in this study are also very similar to those reported for the iron(II) and cobalt(III) complexes of isonitrosoacetylacetone, which seem to be the only other metal chelates of aliphatic carbonyl-oximes studied by X-rays. However, the N-O bond [$1.22(2)$ Å] in these two complexes is possibly somewhat shorter than the one found here.¹⁴ As a whole it can still be maintained that aliphatic carbonyl-oximes and nitrosophenol \rightleftharpoons quinone oxime compounds yield metal chelates of essentially similar structure with no marked effects arising from the aromatic ring system.

The low density of the present compound (1.3 g cm^{-3}) suggests a loose packing of the complex and the solvent in the unit cell. In fact, there are only four intermolecular distances below 3.45 Å, and none of these is associated with the solvent benzene molecule, which simply fills gaps in the structure and is held by van der Waals forces. It may be noted, too, that three of the intermolecular contacts mentioned (3.23–3.35 Å), comprising two oxime oxygen-carbon contacts and a carbon-carbon contact, occur between A ligands, while the

fourth is an oxime oxygen – carbon contact of 3.29 Å between ligands B and C. Fig. 3 shows a view of the molecular packing.

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