1,6-Bis-(2-hydroxyphenyl)-2,5-diaza-3,4-dimethyl-1,3,5-hexatrienatocobalt(II)

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Abstract. $CoC_{18}H_{16}N_2O_2$, monoclinic, $P2_1/c$, $Z=4$, $a=8\cdot428$ (1), $b=15\cdot425$ (3), $c=12\cdot066$ (5) Å, $\beta=90\cdot13$ (1)°; $D_m=1\cdot483$, $D_x=1\cdot488$ g cm^{-3}. The structure was solved by minimum function and heavy-atom methods, and block-diagonal least-squares refinement led to a final R of 0·045 for 2455 reflexions. The molecules are almost planar with slightly twisted and bowed shapes. The C–C bond of 1·336 (5) Å which bridges the two azomethine nitrogens is a pure double bond.

Experimental. Dark brown crystals of the title compound were kindly provided by H. Kanatomi of Kyushu University. Preliminary Weissenberg and precession photographs showed the systematic absences 0*k*0, *k* odd and *h0l*, *l* odd, indicating space group $P2_1/c$. The unit-cell parameters were obtained from a least-squares

Fig. 1. Bond lengths (Å) with their e.s.d.'s in parentheses.

Fig. 2. Bond angles (°) with their e.s.d.'s in parentheses.

procedure using 2θ values of 13 reflexions measured on a Syntex $P\bar{1}$ four-circle diffractometer with Mo $K\alpha$ radiation. The density was measured by flotation in aqueous KI solution. The crystal used for X-ray work was ground to a sphere of radius 0·155 mm.

Intensity data were collected by the θ–2θ scan technique with a variable scan rate from 4·0 to 24·0° min^{-1} and Mo $K\alpha$ radiation monochromated by a graphite crystal. 2455 independent reflexions were collected. Of these, 149 with $I<\sigma(I)$ were assigned threshold values of $0\cdot7\sigma(I)$, where $\sigma(I)$ was the standard deviation estimated from the counting statistics. The intensity data were corrected for Lorentz and polarization effects, but no corrections for absorption or extinction were made because of the low absorption coefficient and the small crystal size. An initial scale factor and over-all temperature factor were obtained by the method of Wilson (1942).

The structure was solved by a combination of minimum function and heavy-atom methods. The coordinates of the Co atom were easily deduced from a three-dimensional Patterson synthesis. Those of the 20 non-hydrogen atoms were obtained from a three-dimensional minimum function and a three-dimensional Fourier synthesis which were calculated on the basis of the coordinates of the Co atom. The two C atom positions were obtained from the subsequent three-dimensional Fourier synthesis. Refinement was carried out by the block-diagonal least-squares method with anisotropic temperature factors to an R value $[\sum(||F_o|-|F_c||)/\sum|F_o|]$ of 0·066. At this stage, all the H atoms could be located by a difference Fourier synthesis with peak heights varying from 0·33 to 0·55 e Å^{-3}. The H atoms were included in the least-squares refinement and R was reduced to 0·055. The real part of the anomalous dispersion correction for the Co atom was taken into account, but no significant shift was found in the atomic parameters or in R. Refinement was terminated when the shifts of the parameters for the non-hydrogen atoms were less than one-tenth of their estimated standard deviations. The final R value was 0·045 for all reflexions.* A final difference Fourier synthesis showed no significant features in the
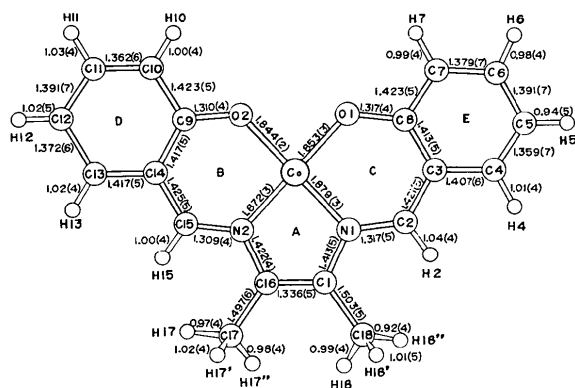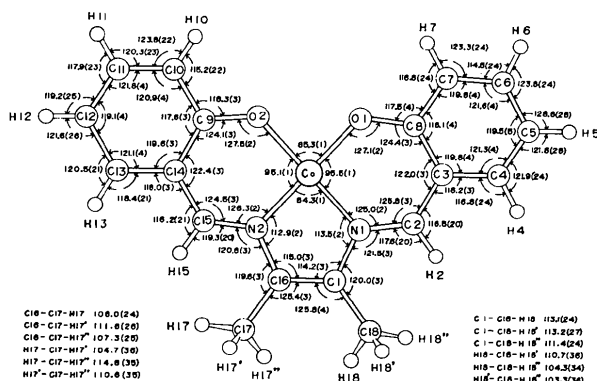
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undulations varying from -0.27 to 0.24 e Å^{-3}. The atomic scattering factors for all atoms and the real part of the anomalous dispersion factor for the Co atom were taken from *International Tables for X-ray Crystallography* (1962). In the least-squares procedure the quantity minimized was $\sum w(k|F_o| - |F_c|)^2$, where k is a scale factor and w the weight; for $|F_o| \geq 5.0$, $w = 1$, otherwise $w = 0$. The final atomic parameters are listed in Table 1.

Discussion. The bond lengths and angles corrected for thermal motions (except for the H atoms) and atom numbering scheme are shown in Figs. 1 and 2.

The molecule has almost planar configuration consisting of the two chemically equivalent moieties. The chemically equivalent bond lengths of these moieties are in good agreement with each other. The Co atom is nearly square coordinated by the two N and two O atoms with mean Co–O and mean Co–N bond lengths of 1.848 (4) and 1.876 (3) Å respectively. These values may be compared with 1.835 (4), 1.869 (5) Å for Co–O

and 1.829 (5), 1.864 (5) Å for Co–N in bis(salicylalde-hyde)ethylenediiminecobalt(II) chloroform solvate (Schaefer & Marsh, 1969) in which the Co atom has the same coordination as this complex. The bond angles at the Co atom differ by *ca.* 5° from 90°. N(1)–C(2), 1.317 (5) Å, and N(2)–C(15), 1.309 (4) Å, in the two azomethines of the fully conjugated Schiff base have considerable double-bond character, and C(1)–C(16), 1.336 (5) Å, which bridges N(1) and N(2) is clearly a pure double bond. The C–C bond lengths outside the salicylaldimine parts are somewhat shorter than those within them, as pointed out by Lingafelter & Braun (1966), this phenomenon is observed in many salicylaldimine chelates and is almost independent of the nature of the metal ion. The C–H bond lengths in the two salicylaldimine parts vary from 0.94 (5) to 1.04 (4) Å with an average value of 1.006 (9) Å, and those in the two methyl groups vary from 0.92 (4) to 1.02 (4) Å with an average value of 0.979 (14) Å. These values are in agreement with those obtained in the other structures (Sutton, 1965).

Table 1. *Fractional atomic coordinates and temperature factors*

Numbers in parentheses here and elsewhere in this paper are the estimated standard deviations in the least significant digits.

(a) Non-hydrogen atoms
All values have been multiplied by 10^5. The anisotropic temperature factors are expressed in the form:
$$\exp\{-(h^2 B_{11} + k^2 B_{22} + l^2 B_{33} + hk B_{12} + hl B_{13} + kl B_{23})\}.$$

	x	y	z	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
Co	9124 (5)	14130 (3)	-4537 (4)	1156 (6)	382 (2)	521 (4)	-7 (6)	291 (7)	54 (4)
O(1)	11070 (28)	7955 (17)	-17607 (20)	1618 (40)	516 (14)	577 (20)	-197 (37)	370 (43)	-98 (25)
O(2)	29394 (27)	17936 (17)	-7438 (20)	1342 (37)	582 (15)	685 (22)	-287 (37)	637 (43)	-175 (27)
N(1)	-11295 (31)	10087 (18)	-1206 (23)	1196 (40)	370 (15)	669 (25)	50 (37)	302 (47)	122 (28)
N(2)	6670 (30)	20765 (19)	8305 (23)	1164 (40)	425 (16)	559 (23)	92 (37)	379 (45)	92 (28)
C(1)	-17364 (38)	13406 (24)	8819 (30)	1149 (49)	431 (20)	773 (33)	96 (46)	584 (59)	61 (37)
C(2)	-19444 (41)	4569 (25)	-7281 (32)	1335 (53)	417 (20)	840 (35)	-66 (49)	25 (64)	145 (39)
C(3)	-14587 (44)	1031 (24)	-17580 (31)	1683 (60)	386 (20)	702 (32)	-53 (52)	-112 (66)	168 (37)
C(4)	-25193 (53)	-4447 (30)	-23241 (37)	2176 (79)	565 (26)	963 (42)	-530 (70)	-385 (88)	-127 (49)
C(5)	-21433 (61)	-7923 (32)	-33239 (41)	2790 (99)	590 (28)	1061 (46)	-714 (82)	-813 (104)	-105 (54)
C(6)	-6832 (62)	-6026 (31)	-37981 (37)	3111 (105)	573 (27)	777 (39)	-285 (83)	-216 (99)	-166 (49)
C(7)	4016 (54)	-725 (29)	-32759 (33)	2496 (83)	559 (25)	616 (34)	-233 (71)	-29 (80)	-108 (43)
C(8)	285 (45)	2992 (24)	-22298 (29)	1809 (61)	385 (20)	586 (31)	-33 (52)	-47 (67)	95 (35)
C(9)	37566 (39)	23746 (24)	-1957 (29)	1281 (50)	420 (19)	616 (29)	-48 (46)	172 (57)	140 (35)
C(10)	52760 (43)	26133 (29)	-6051 (33)	1351 (57)	670 (26)	822 (36)	-322 (58)	589 (68)	14 (46)
C(11)	61771 (47)	32151 (32)	-698 (38)	1412 (62)	765 (29)	1059 (43)	-548 (66)	360 (78)	47 (54)
C(12)	56559 (50)	36240 (32)	8889 (39)	1697 (70)	739 (30)	1121 (45)	-715 (72)	95 (85)	-188 (56)
C(13)	42024 (46)	34068 (28)	13136 (34)	1641 (63)	549 (24)	846 (37)	-218 (59)	-58 (73)	-190 (44)
C(14)	32175 (39)	27913 (24)	7773 (29)	1299 (50)	419 (19)	631 (30)	28 (47)	183 (58)	75 (35)
C(15)	17090 (40)	26121 (24)	12517 (29)	1331 (51)	446 (20)	607 (29)	93 (48)	193 (58)	-32 (36)
C(16)	-8014 (38)	19250 (24)	13708 (30)	1195 (49)	441 (20)	693 (31)	222 (46)	637 (58)	14 (36)
C(17)	-11843 (49)	24059 (30)	24131 (36)	1810 (69)	681 (27)	915 (39)	-177 (67)	1207 (80)	-288 (50)
C(18)	-33076 (44)	10275 (30)	13100 (37)	1265 (57)	671 (26)	1101 (43)	-199 (59)	817 (75)	10 (51)

(b) Hydrogen atoms
The hydrogen atoms are labelled so that they have the same number as the carbon atom to which they are bonded. The coordinate values have been multiplied by 10^4. The average estimated standard deviation of the isotropic temperature factors is 1.0 Å^2.

|	x	y	z	B (Å^2)		x	y	z	B (Å^2)
H(2)	-3069 (42)	279 (24)	-449 (30)	2.7	H(13)	3790 (42)	3700 (24)	2018 (30)	2.9
H(4)	-3549 (49)	-586 (28)	-1936 (34)	4.4	H(15)	1463 (43)	2917 (24)	1963 (30)	2.9
H(5)	-2845 (53)	-1161 (30)	-3707 (37)	5.5	H(17)	-1152 (48)	3024 (27)	2249 (34)	4.3
H(6)	-311 (48)	-855 (27)	-4498 (33)	4.1	H'(17)	-334 (53)	2318 (30)	3003 (37)	5.4
H(7)	1443 (47)	81 (27)	-3600 (33)	3.9	H''(17)	-2212 (49)	2193 (28)	2675 (35)	4.5
H(10)	5630 (45)	2293 (25)	-1281 (32)	3.4	H(18)	-3645 (49)	1328 (28)	1999 (34)	4.4
H(11)	7289 (47)	3368 (27)	-357 (33)	3.9	H'(18)	-3355 (55)	380 (31)	1408 (39)	6.0
H(12)	6399 (53)	4036 (30)	1293 (37)	5.4	H''(18)	-4115 (45)	1138 (26)	811 (32)	3.6
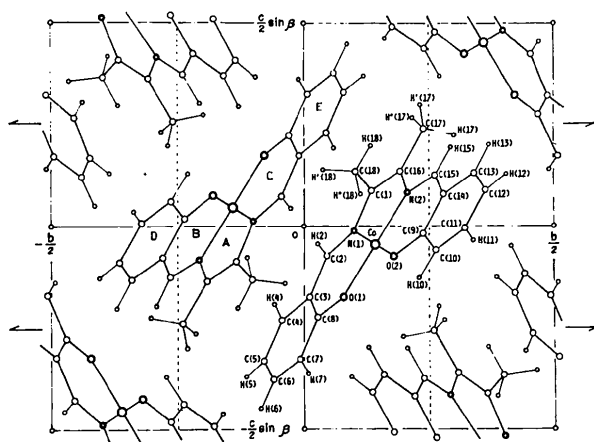
Fig. 3. Molecular arrangement projected down the a axis.

The two benzene rings (D and E) are planar with mean deviations of 0·0053 and 0·0015 Å from the respective least-squares planes. The other two six-membered rings (B and C) and the five-membered ring (A) are nearly planar, the mean deviations from the respective least-squares planes being 0·0149, 0·0173 and 0·0194 Å. A χ^2 test on the least-squares plane through the two N and two O atoms with a mean deviation of 0·039 Å indicates that the Co coordination is slightly distorted from a square planar geometry. The distortion from the coordination expected for square planar dsp^2 hybridization on the Co atom may be attributable to the pure double bond C(1)–C(16). In addition, there are slight bendings of the D and E rings to the same side of the molecular plane about C(9)–C(14) and C(3)–C(8) respectively. Thus the molecule is very slightly twisted and bowed, and the mean deviation is 0·075 Å from the least-squares plane for the whole molecule.

Inspection of the thermal motion ellipsoids drawn with *ORTEP* (Johnson, 1965) suggested that the molecule is librating about a point close to its centroid. The root-mean-square deviation of the difference between the observed and calculated U_{ij} values is 0·0062 Å² for the rigid-body model of the whole molecule. The molecular arrangement projected down the a axis is shown in Fig. 3. The mean interplanar spacing between the molecules which are related by a centre of symmetry is 3·386 Å, and the distance between the Co atoms of these molecules is 4·7509 (9) Å. Only three intermolecular distances are slightly shorter than the van der Waals contacts: 3·333 (5) Å between C(1) in (x,y,z) and C(8) in $(\bar{x},\bar{y},\bar{z})$, 3·332 (4) Å between Co in (x,y,z) and C(2) in $(\bar{x},\bar{y},\bar{z})$, and 2·53 (4) Å between H(15) in (x,y,z) and O(1) in $(x,\frac{1}{2}-y,\frac{1}{2}+z)$. The other contacts are normal.

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Trichloro-μ-trichloro-tris(tri-n-butylphosphine)dirhodium(III)

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Abstract. $Rh_2(PBu_3)_3Cl_6$, $Rh_2P_3Cl_6C_{36}H_{81}$, monoclinic, $P2_1/c$, $a = 12·670$ (13), $b = 26·828$ (10), $c = 16·887$ (20) Å, $\beta = 118·98$ (16)°, $Z = 4$, $d_x = 1·306$ (14), $d_m = 1·359$ (3) g cm⁻³, $V = 5021$ Å³. The molecule has a confacial bioctahedral structure with three chlorine bridges, each of which is *trans* to one phosphine and one terminal chlorine. There are two phosphines on one Rh and one on the other.

Introduction. Binuclear complexes of Rh(III) are known with either two or three halogen bridges (Chatt, Johnson & Shaw, 1964; Allen & Gabuji, 1971;