

## An Unusual Pyridine-Cobalt Configuration: the Crystal Structure of Bis(dimethylglyoximato)(tri-*n*-butylphosphine)(4-pyridyl)cobalt(I)

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Bis(dimethylglyoximato)(tri-*n*-butylphosphine)(4-pyridyl)cobalt(I),  $C_{25}H_{45}N_5O_4PCo$ , a 'cobaloxime', includes a pyridine ligand coordinated *via* a Co-C bond. The space group is  $P\bar{1}$  with two molecules per unit cell of dimensions  $a = 12.109$  (1),  $b = 13.142$  (2),  $c = 11.606$  (1) Å,  $\alpha = 90.317$  (12),  $\beta = 122.452$  (7),  $\gamma = 107.117$  (10)°. A full sphere of data,  $0 < 2\theta < 65^\circ$  was collected with a four-circle diffractometer using  $\theta$ - $2\theta$  scans and Nb filtered Mo  $K\alpha$  radiation. The data were corrected for absorption and averaged to give 10677 independent reflections. Full-matrix least-squares refinement gave a final  $R$  of 0.035 based on the 9027 extinction-corrected reflections with  $F > 3\sigma(F)$ . Bond distances were corrected for molecular libration. The Co-N distances average 1.891 (1) Å, the Co-C coordination distance is 1.983 (1) Å and Co-P is 2.342 (1) Å. Changes are noted in pyridine distances and angles as compared with uncoordinated pyridine and with pyridine coordinated *via* a Co-N bond.

### Introduction

Bis(dimethylglyoximato)cobalt complexes, 'cobaloximes', have been used as model compounds for the more complex cobalamins (Schrauzer, 1968*a*, 1971). Under favorable conditions some cobaloximes undergo reactions similar to the nonenzymatic reactions of coenzyme vitamin  $B_{12}$ , a biologically important cobalamin. This paper reports the structure of bis(dimethylglyoximato)(tri-*n*-butylphosphine)(4-pyridyl)cobalt(I).

The molecular structure of this cobaloxime (Fig. 1) is interesting for two reasons. It includes a pyridyl moiety coordinated through a Co-C bond, a configuration confirmed by the X-ray analysis. The bond distances and angles of the pyridyl moiety attached in this manner differ significantly from the geometry of uncoordinated pyridine (Bak, Hansen & Rastrup-Andersen, 1954) and from pyridine ligands with the usual Co-N coordination as found in other cobaloximes (Lenhert, 1967, 1972). The structure analysis also provides precise geometric data on the dimethylglyoxime ligands and the Co-N coordination which subsequent papers will compare with similar bonds in other cobaloximes, especially those considered to be model compounds for coenzyme  $B_{12}$ .

### Experimental

Crystals of bis(dimethylglyoximato)(tri-*n*-butylphosphine)(4-pyridyl)cobalt(I),  $C_{25}H_{45}N_5O_4PCo$ , were supplied by Professor G. N. Schrauzer. The compound was synthesized by reacting the cobalt(I) nucleophile with 4-bromopyridine; Schrauzer (1968*b*) has discussed the synthesis of this class of compounds elsewhere. An elemental analysis agreed with the stated formula to

within 0.3 percentage points for all elements. Precession photographs indicated a triclinic lattice. The crystal density of 1.294 g cm<sup>-3</sup>, determined by flotation in a carbon tetrachloride-hexane mixture, compares with a calculated value of 1.293 g cm<sup>-3</sup> based on two molecules (molecular weight, 596.573 daltons) per unit-cell (volume, 1458.7 Å<sup>3</sup>). The space group assumed,  $P\bar{1}$ , was confirmed by the subsequent crystal structure analysis.

A large specimen was cleaved to give a data crystal with maximum dimensions of approximately 0.4 × 0.6 × 1.2 mm and a volume of 0.157 mm<sup>3</sup>. Eastman 910 cement was used to mount the crystal so that the glass fiber (and the  $\phi$  axis of the diffractometer) made a small angle with the  $c^*$  axis and was roughly perpendicular to the long dimension of the crystal.

Accurate cell constants were determined at 21 °C from 12 reflections ( $2\theta > 80^\circ$ ) manually centered on an accurately aligned four-circle diffractometer using the Cu  $K\alpha_1$  line of the resolved doublet ( $\lambda = 1.54051$  Å). The Oak Ridge General Least-Squares program (Busing & Levy, 1962) was used with the observations (positive and negative  $2\theta$  values of the 12 Friedel pairs) to give  $a = 12.109$  (1),  $b = 13.142$  (2),  $c = 11.606$  (1) Å,  $\alpha = 90.317$  (12)°,  $\beta = 122.452$  (12)°, and  $\gamma = 107.117$  (10)°.

Intensity data were collected on a four-circle computer-controlled Picker diffractometer (FACS-I system) and a Digital Equipment Corporation PDP-8/I computer with auxiliary disc memory. The computer programs, based on the FACS-I programs, were extensively modified and adapted for use with the disc memory in this laboratory (Lenhert & Henry, 1970). The X-ray source was a standard-focus Mo tube operated at 50 kV (constant potential), 12 mA and a take-off angle of 1.8°. A 3.75 × 3.75 mm aperture defined the NaI detector opening and 1.5 mm collimators were used on the incident and diffracted beams. The pulse height analyzer was set to a 95% window centered on

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the Mo  $K\alpha$  peak. Attenuation filters (constructed of 1 to 5 thicknesses of 0.0005 in Ni foil) were automatically inserted in the diffracted beam when the count rate exceeded 8000 counts/sec.

The X-ray generator-detector system was monitored by scanning 3 standard reflections (335, 227, 174) at 2 to 6 h intervals. The intensities dropped by 6, 7 and 4% respectively during the 1100 h X-ray exposure. This probably represents a combination of X-ray damage to the crystal and a drop in X-ray output or detector sensitivity.

Reflections in the range  $0 < 2\theta < 10^\circ$  were collected with a 0.002 in Nb filter in the incident beam and Zr-Y-Al balanced filters (Young, 1961) in the diffracted beam. In the range  $10 < 2\theta < 65^\circ$  a 0.001 in Nb incident beam filter was used without balanced filters. The full sphere of reflections out to  $65^\circ$  in  $2\theta$  was measured with the  $\theta$ - $2\theta$  scan technique. The  $2\theta$  scan range was given by  $A + B \tan \theta$  where  $A = 1.1^\circ$  and  $B = 6.29^\circ$  for balanced filters and  $B = 0.69^\circ$  for  $\beta$  filter measurements. Background was measured at the end points of the scan.

The usual background correction was applied to the scans to give the integrated intensity,  $I$ . If the result was negative,  $I$  was taken as zero. To obtain the  $F^2$ , the integrated intensities were multiplied by the usual Lorentz-polarization factor, the relative scale factor derived from the standard reflections, the attenuation filter factor, and the X-ray absorption factor.

Crystal shape and orientation for the absorption correction were determined with the crystal mounted on the diffractometer. The  $\chi$  and  $\phi$  angles were adjusted to set the crystal face perpendicular to the  $\chi$  circle and parallel to the  $\omega$  axis. The distance from the  $\omega$  axis to the vertical face was then measured with the filar eyepiece of the diffractometer telescope. This distance and the  $\chi$  and  $\phi$  angles for each of the 7 crystal faces defined the crystal shape and orientation. The crystal measurements were checked for accuracy by

using the coordinates of the crystal corners calculated by *ORABS* (Wehe, Busing & Levy, 1962) to draw a stereogram of the crystal with *ORTEP* (Johnson, 1965).

The absorption correction was calculated by Gaussian integration using *ORABS*. The linear absorption coefficient calculated from mass absorption coefficients for Mo  $K\alpha$  from *International Tables for X-ray Crystallography* (1962) was  $7.04 \text{ cm}^{-1}$ . The calculated absorption factors ranged from 0.6118 to 0.8008 with an average of 0.7340.

$\sigma(I)$  was considered to arise from two sources. The first is the variance resulting from the counting statistics,  $\sigma_c^2$ . The second  $\sigma_x^2$  (expressed as a percent), is that from all other sources which affect the value obtained by repeated measurements of the same reflection (*e.g.*, short-term fluctuations in the X-ray source intensity). The combination gives  $\sigma^2(I) = \sigma_c^2 + \sigma_x^2 I^2$ .  $\sigma_x$  was estimated from repeated measurements of the standard reflections to be 0.00384. The values of  $\sigma(I)$  were scaled by the same factor used for  $I$  to give  $\sigma(F^2)$ . Then, for all reflections, including those with  $F^2 = 0$ ,  $\sigma(F) = -F + [F^2 + \sigma(F^2)]^{1/2}$ . Finally the 21523 observations were averaged and the variances combined to give 10677 independent reflections.

#### Structure determination and refinement

The crystal structure was solved by the heavy atom method using Co and P coordinates obtained from a sharpened Patterson function. A partial data set ( $2\theta < 40^\circ$ ) was used to locate and refine the remaining non-hydrogen atoms.

Initial coordinates for the 22 hydrogen atoms fixed by molecular geometry were calculated using a C-H distance of 1.0 Å and appropriate angles. The methyl hydrogen atoms were positioned by a combination of geometrical and electron density considerations as described previously (Miller, Lenhart & Joesten, 1972).

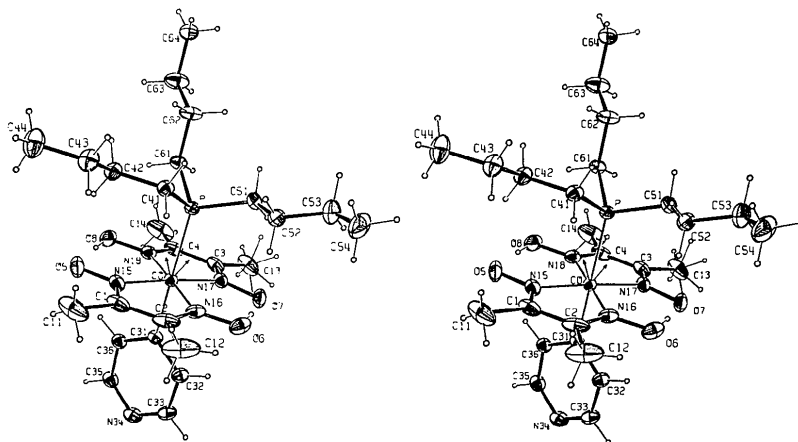


Fig. 1. Stereoscopic view of the molecule. Atom numbers are indicated, and 20% probability ellipsoids are used for all non-hydrogen atoms. The disorder in C(62) and C(63) is not shown; the free rotation in the methyl group C(13) is indicated. The two small arrows show the direction of the principal libration axis for each of the dimethylglyoxime ligands.

Table 1. Fractional coordinates and thermal parameters with standard deviations

Anisotropic thermal parameters are of the form  $T = \exp[-\frac{1}{2}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{13}hka^*c^* + 2B_{23}k lb^*c^*)]$ .  
 $M$  is the occupation factor. The first two digits of the hydrogen atom numbers correspond to the number of the adjacent carbon atom except for H(67) and H(85) which are attached to O(6) and O(8) respectively.

	$M$	$x$	$y$	$z$	$B_{11}$	$B_{22}$	$B_{33}$	$B_{12}$	$B_{13}$	$B_{23}$
Co		0.41405 (2)	0.22633 (1)	0.16200 (2)	2.24 (1)	2.99 (1)	2.49 (1)	0.83	1.10	0.62
P		0.60504 (3)	0.19216 (3)	0.34788 (3)	2.69 (1)	3.67 (2)	4.52 (1)	1.31 (1)	1.07 (1)	0.70 (1)
O(5)		0.54042 (11)	0.27310 (12)	0.01217 (11)	4.24 (5)	11.59 (10)	4.28 (5)	2.98 (6)	2.94 (4)	3.24 (6)
O(6)		0.42397 (11)	0.37299 (10)	0.35061 (11)	4.47 (5)	5.78 (6)	4.17 (5)	2.50 (5)	1.21 (4)	-0.88 (4)
O(7)		0.27136 (11)	0.18145 (10)	0.29524 (11)	4.68 (5)	7.35 (7)	4.42 (5)	2.33 (5)	3.27 (4)	1.69 (5)
O(8)		0.40232 (13)	0.08005 (11)	-0.02807 (11)	7.04 (7)	8.42 (8)	3.46 (5)	4.99 (6)	2.74 (5)	1.08 (5)
N(15)		0.52382 (11)	0.31349 (11)	0.10670 (12)	2.54 (4)	5.86 (7)	3.96 (5)	1.46 (4)	1.58 (4)	2.37 (5)
N(16)		0.46819 (11)	0.36085 (9)	0.26980 (12)	2.69 (4)	3.55 (5)	3.63 (5)	1.23 (4)	0.63 (4)	0.11 (4)
N(17)		0.29399 (10)	0.14058 (9)	0.20696 (11)	2.78 (4)	4.08 (5)	2.97 (4)	0.95 (4)	1.46 (4)	1.02 (4)
N(18)		0.35651 (12)	0.09286 (10)	0.05093 (10)	4.10 (5)	4.44 (6)	2.29 (4)	2.33 (4)	1.09 (4)	0.48 (4)
N(34)		0.01663 (11)	0.29372 (10)	-0.22050 (13)	2.82 (5)	5.18 (7)	4.43 (6)	1.58 (5)	0.96 (4)	1.48 (5)
C(1)		0.58247 (14)	0.41517 (15)	0.16279 (19)	2.54 (5)	5.30 (9)	6.63 (9)	0.96 (6)	1.41 (6)	3.46 (8)
C(2)		0.55061 (14)	0.44411 (12)	0.25956 (19)	2.55 (5)	2.93 (6)	6.61 (9)	0.75 (5)	0.21 (6)	0.90 (6)
C(3)		0.22875 (14)	0.03928 (12)	0.14387 (15)	3.29 (5)	3.83 (6)	3.59 (6)	0.37 (5)	0.88 (5)	1.34 (5)
C(4)		0.26579 (16)	0.01118 (12)	0.05249 (14)	4.88 (7)	3.22 (6)	3.01 (6)	1.35 (5)	0.46 (5)	0.30 (5)
C(11)		0.67416 (25)	0.49385 (29)	0.12856 (36)	4.41 (9)	9.74 (17)	12.94 (24)	0.95 (11)	3.54 (12)	7.71 (19)
C(12)		0.60525 (22)	0.55697 (17)	0.33905 (31)	4.36 (9)	3.51 (8)	12.32 (21)	0.76 (7)	0.49 (11)	-0.73 (10)
C(13)		0.12498 (18)	-0.03783 (15)	0.16459 (20)	4.85 (8)	6.26 (10)	6.67 (10)	-0.65 (7)	2.03 (8)	3.01 (8)
C(14)		0.20868 (37)	-0.09928 (18)	-0.03425 (29)	12.34 (23)	3.93 (10)	5.57 (11)	2.64 (11)	0.76 (13)	-0.84 (9)
C(31)		0.25077 (11)	0.25394 (10)	0.00551 (12)	2.14 (4)	2.99 (5)	3.11 (5)	0.63 (4)	1.08 (4)	0.84 (4)
C(32)		0.17902 (13)	0.30960 (12)	0.02519 (15)	2.94 (5)	4.29 (7)	3.69 (6)	1.47 (5)	1.27 (5)	0.55 (5)
C(33)		0.06564 (15)	0.32725 (13)	-0.08861 (18)	3.14 (6)	5.11 (8)	5.27 (8)	2.12 (5)	1.70 (6)	1.10 (6)
C(35)		0.08421 (14)	0.23986 (13)	-0.23926 (15)	3.30 (6)	5.32 (8)	3.26 (6)	1.39 (5)	1.10 (5)	1.19 (5)
C(36)		0.19928 (13)	0.21890 (12)	-0.13294 (14)	3.07 (5)	4.46 (7)	3.09 (5)	1.47 (5)	1.22 (4)	0.95 (5)
C(41)		0.77889 (13)	0.28913 (12)	0.41043 (14)	2.66 (5)	4.15 (6)	2.85 (5)	1.20 (5)	0.91 (4)	0.34 (5)
C(42)		0.83527 (14)	0.28026 (13)	0.32263 (15)	2.77 (5)	4.84 (7)	3.65 (6)	0.96 (5)	1.36 (5)	0.13 (5)
C(43)		0.97140 (17)	0.37287 (15)	0.37364 (19)	3.52 (7)	5.73 (9)	4.92 (8)	0.31 (6)	2.03 (6)	-0.14 (7)
C(44)		1.02931 (23)	0.36729 (20)	0.28802 (25)	5.37 (10)	7.96 (14)	7.45 (12)	-0.04 (9)	4.22 (10)	0.08 (11)
C(52)		0.60589 (16)	0.18947 (14)	0.50656 (15)	4.43 (7)	5.34 (8)	3.06 (6)	2.22 (6)	1.93 (5)	1.35 (5)
C(51)		0.67058 (17)	0.29829 (15)	0.60454 (16)	4.47 (7)	6.51 (10)	3.16 (6)	2.71 (7)	1.73 (6)	0.74 (6)
C(53)		0.66151 (24)	0.28803 (21)	0.72874 (22)	8.60 (13)	8.96 (15)	5.02 (10)	3.78 (12)	4.59 (10)	1.05 (9)
C(54)		0.73314 (28)	0.39214 (27)	0.83315 (24)	8.05 (13)	13.61 (23)	4.85 (10)	5.64 (15)	2.72 (10)	-0.96 (12)
C(61)		0.60932 (15)	0.05870 (12)	0.30970 (14)	3.53 (6)	3.76 (6)	3.30 (6)	1.50 (5)	1.29 (5)	0.72 (5)
C(621)	0.5	0.73589	0.03116	0.41929	4.46 (20)	4.63 (24)	5.96 (28)	2.84 (18)	2.04 (22)	1.69 (22)
C(622)	0.5	0.71969	0.02100	0.42729	4.33 (18)	5.16 (24)	2.52 (16)	2.41 (17)	1.35 (16)	0.80 (16)
C(631)	0.5	0.74111	-0.07141	0.38009	7.23 (30)	6.30 (30)	4.74 (28)	4.20 (24)	2.92 (27)	1.57 (23)
C(632)	0.5	0.72285	-0.08247	0.38795	5.93 (26)	3.70 (23)	8.67 (41)	2.54 (21)	2.19 (30)	1.75 (25)
C(64)		0.84280 (24)	-0.11497 (19)	0.49237 (23)	7.91 (12)	7.07 (12)	6.93 (12)	5.27 (10)	4.88 (10)	3.67 (9)

Table 1 (cont.)

M	x	y	z	B(Å <sup>2</sup> )	H(Å <sup>2</sup> )	x	y	x	y	y	B(Å <sup>2</sup> )
H(67)	0.3647 (19)	0.2983 (16)	0.3365 (18)	7.56	H(422)	0.7740 (16)	0.2802 (12)	0.7740 (16)	0.2802 (12)	0.2282 (16)	5.64
H(85)	0.4612 (19)	0.1542 (15)	-0.0116 (18)	6.72	H(431)	1.0358 (18)	0.3786 (14)	1.0358 (18)	0.3786 (14)	0.4648 (18)	7.45
H(111)	0.6615 (28)	0.5604 (21)	0.1424 (31)	12.70	H(432)	0.9525 (18)	0.4403 (15)	0.9525 (18)	0.4403 (15)	0.3664 (19)	7.74
H(112)	0.7678 (25)	0.5185 (19)	0.2072 (25)	11.87	H(441)	0.9616 (22)	0.3699 (18)	0.9616 (22)	0.3699 (18)	0.1925 (23)	10.32
H(113)	0.6547 (34)	0.4580 (30)	0.0640 (33)	13.99	H(442)	1.1099 (21)	0.4282 (17)	1.1099 (21)	0.4282 (17)	0.3161 (20)	9.08
H(121)	0.5647 (25)	0.6009 (19)	0.2807 (25)	11.88	H(443)	1.0534 (21)	0.3009 (16)	1.0534 (21)	0.3009 (16)	0.2853 (21)	9.08
H(122)	0.5743 (24)	0.5490 (19)	0.3977 (25)	9.68	H(511)	0.5105 (16)	0.1550 (12)	0.5105 (16)	0.1550 (12)	0.4743 (15)	5.70
H(123)	0.7031 (25)	0.5853 (18)	0.3886 (24)	12.10	H(512)	0.6522 (17)	0.1430 (13)	0.6522 (17)	0.1430 (13)	0.5497 (17)	6.45
H(131)	0.0340	-0.0223	0.1152	11.00	H(521)	0.7635 (19)	0.3289 (15)	0.7635 (19)	0.3289 (15)	0.6390 (19)	8.19
H(132)	0.0376	-0.0825	0.0745	11.00	H(522)	0.6280 (18)	0.3481 (14)	0.6280 (18)	0.3481 (14)	0.5590 (17)	6.94
H(133)	0.1034	-0.1151	0.1307	11.00	H(531)	0.5728 (22)	0.2564 (18)	0.5728 (22)	0.2564 (18)	0.7014 (22)	9.43
H(134)	0.1655	-0.0875	0.2276	11.00	H(532)	0.7056 (22)	0.2316 (17)	0.7056 (22)	0.2316 (17)	0.7768 (21)	9.61
H(135)	0.1620	-0.0272	0.2683	11.00	H(541)	0.6951 (24)	0.4428 (18)	0.6951 (24)	0.4428 (18)	0.7934 (23)	9.90
H(136)	0.0962	0.0053	0.2121	11.00	H(542)	0.7300 (25)	0.3823 (19)	0.7300 (25)	0.3823 (19)	0.9144 (24)	11.68
H(141)	0.2655 (26)	-0.1295 (21)	-0.0105 (26)	10.92	H(543)	0.8320 (22)	0.4189 (18)	0.8320 (22)	0.4189 (18)	0.8753 (22)	9.90
H(142)	0.1575 (35)	-0.1330 (25)	-0.0286 (36)	13.18	H(611)	0.5206 (16)	0.0052 (13)	0.5206 (16)	0.0052 (13)	0.2818 (16)	6.26
H(143)	0.1578 (25)	-0.0959 (19)	-0.1226 (24)	11.33	H(612)	0.6082 (14)	0.0564 (11)	0.6082 (14)	0.0564 (11)	0.2299 (15)	4.87
H(321)	0.2041 (14)	0.3350 (11)	0.1157 (15)	5.10	H(621)	0.8170	0.0833	0.8170	0.0833	0.4482	7.19
H(331)	0.0162 (16)	0.3611 (13)	-0.0721 (16)	6.47	H(622)	0.7141	0.0189	0.7141	0.0189	0.5009	8.19
H(351)	0.0481 (15)	0.2152 (12)	-0.3394 (16)	5.92	H(631)	0.6407	-0.1332	0.6407	-0.1332	0.3554	10.06
H(361)	0.2482 (14)	0.1838 (11)	-0.1543 (14)	4.76	H(632)	0.7486	0.0683	0.7486	0.0683	0.3084	10.81
H(411)	0.7744 (14)	0.3588 (12)	0.4136 (14)	4.95	H(641)	0.9296 (21)	-0.0568 (17)	0.9296 (21)	-0.0568 (17)	0.5616 (21)	9.64
H(412)	0.8407 (14)	0.2824 (11)	0.4989 (15)	4.84	H(642)	0.8494 (22)	-0.1819 (18)	0.8494 (22)	-0.1819 (18)	0.4661 (22)	10.44
H(421)	0.8558 (16)	0.2100 (13)	0.3250 (16)	6.24	H(643)	0.8175 (23)	-0.1429 (18)	0.8175 (23)	-0.1429 (18)	0.5484 (22)	10.44

Final hydrogen coordinates were established by refinement except as noted.

Initial hydrogen-atom temperature factors were taken as 1.2 times the isotropic equivalent of the adjacent carbon atom. At a later stage they were adjusted according to  $\Delta B = -2B\Delta\rho/\rho_0$ , where  $\Delta\rho$  is the difference density and  $\rho_0$  the observed electron density at the hydrogen position and  $B$  is the isotropic temperature factor for the hydrogen atom.

The hydrogen atoms located between O(6) and O(7) and between O(5) and O(8) were initially placed equidistant from the oxygen atoms. Refinement moved each hydrogen atom to a different dimethylglyoxime ligand with an O-H distance of about 1.0 Å. The hydrogen atoms on the methyl group, C(13), failed to refine. Examination of the difference electron-density suggested disorder which was approximated by six equally spaced half-hydrogen atoms.

According to chemical evidence (Schrauzer, 1970) the pyridine ligand is attached to cobalt through a Co-C bond rather than the more common Co-N link. The Co-C attachment was confirmed by refining a model with pyridine atoms C(31) and N(34) interchanged. The arrangement with Co-C pyridine coordination gave a smaller residual electron-density difference at the two atomic sites, an  $R=0.004$  lower, and reasonable thermal parameters for the two atoms, clearly supporting the chemical evidence.

After further refinement of all heavy-atom parameters and hydrogen atom coordinates, an extinction correction (Zachariasen, 1968) was made. An extinction parameter,  $r^*$ , was calculated for each of the 25 most intense reflections using an average value of  $\bar{T}$  (0.04392 cm), the effective crystal thickness,  $F_o$  (uncorrected) and  $F_c$  for each reflection. The average value of  $r^*$ ,  $1.663 \times 10^{-5}$  was then used to correct all the  $F_o$  and the corrected values were used in all subsequent calculations.

A difference synthesis indicated disorder in the region of C(62) and C(63) along one butyl chain. As an expedient, the large apparent motion perpendicular to the chain was approximated according to Kartha & Ahmed (1960) by replacing C(62) and C(63) with half atoms separated by about 0.25 Å. The anisotropic thermal parameters but not the coordinates were refined in subsequent least-squares calculations. Hydrogen atom positions were calculated from the average positions of the half atoms and were not subsequently refined.

The atomic scattering factors for neutral Co, P, O, N and C tabulated by Cromer & Mann (1968) and H scattering factors calculated by Stewart, Davidson & Simpson (1965) were used. Co and P were corrected for the real part of the anomalous dispersion.

The final cycles of full-matrix least-squares were performed on blocks of parameters corresponding to groups of atoms (butyl chains, dimethylglyoxime ligands and pyridine) with the scale factor, Co and P included in each group. This reduced  $R$  to 4.15% for

Table 2. Observed and calculated structure factors

The running index is I. F<sub>o</sub> and F<sub>c</sub> have been multiplied by 10. The extinction correction has been applied to F<sub>o</sub> and all values changed by more than 0.5% are marked with an X.

Table with multiple columns containing numerical data for structure factors, including indices and values for F<sub>o</sub> and F<sub>c</sub>.

Table 2 (cont.)

A large table of numerical data with multiple columns and rows, containing various numbers and some text labels like '10-11', '10-10', etc.

Table 2 (cont.)

A large table containing numerical data organized in columns, with various labels and symbols interspersed throughout the rows.

Table 2 (cont.)

A large table of numerical data with multiple columns and rows, containing various numbers and some text labels like '1-11-11', '1-11-11', etc.





all 10677 reflections and 3.48% for the 9027 reflections with  $F_o > 3\sigma(F_o)$ . The final weighted  $R$  index,  $R' = \{[\sum w(|F_o| - |F_c|)^2] / \sum w F_o^2\}^{1/2}$  was 0.034 for all reflections. For nonhydrogen atoms, the average shift to error ratio was less than 0.05 with a maximum ratio of 0.45 for the  $x$  parameter of C(14). The quantity minimized in the least-squares calculation was  $\sum w(|F_o| - |F_c|)^2$  where the weights, which ranged from 0.13 to 3.5, were proportional to  $1/\sigma^2(F_o)$ .

A final difference synthesis calculated with all reflections showed a maximum residual electron density of  $0.34 \text{ e } \text{Å}^{-3}$  in the region of the disordered butyl moiety and a minimum of  $-0.32 \text{ e } \text{Å}^{-3}$  near the cobalt atom.

The atomic parameters and their standard deviations (calculated from the inverse matrix of the normal equations) are displayed in Table 1. Table 2 shows the observed and calculated structure factors.

Structure factor, Fourier, bond distance and angle, and least-squares calculations were carried out with the X-RAY 67 program system (Stewart, 1967).

### Description and discussion of the structure

#### Non-bonded contacts

Fig. 2 shows the contents and immediate surroundings of a unit cell. The molecule nearest the origin (*a*) is shown in greater detail in Fig. 1. The molecules are packed fairly tightly in all directions with no significant voids, but there are no hydrogen bonds between molecules. Van der Waals forces maintain the intermolecular integrity of the system.

There are no remarkably short intermolecular distances as examination of the 35 contacts listed in Table 3 will show. Most of the intermolecular contacts with the dimethylglyoxime ligands tend to reduce motion normal to the plane of these ligands but to allow rotation about the C(34)–Co–P axis. The principal points of contact involve the methyl groups C(11) and C(13) on opposite sides of the molecule, the pyridine, and the butyl chains. Two of the butyl chains have their orientation stabilized by intramolecular contacts with

the equatorial ligands; the third, C(61)···C(64) suffers some disorder in the C(62), C(63) region in spite of 7 contacts with adjacent molecules.

Table 3. Intermolecular and selected intramolecular contacts

All intermolecular contacts with contact radii less than 1.3 Å for H, 1.55 Å for N, 1.45 Å for O and 1.75 Å for aromatic carbon are shown.

		Symmetry operation
H(321)···N(16)	2.60 Å	1
H(321)···H(67)	2.41	1
H(321)···O(6)	2.49	1
H(361)···O(8)	2.47	1
H(361)···N(18)	2.54	1
H(361)···H(85)	2.36	1
H(411)···C(1)	2.86	1
H(411)···C(2)	2.90	1
H(422)···O(5)	2.56	1
H(422)···N(15)	2.75	1
H(432)···H(112)	2.53	1
H(511)···O(7)	2.64	1
H(511)···N(17)	2.74	1
H(522)···O(6)	2.48	1
H(611)···N(18)	2.85	1
H(611)···C(4)	2.82	1
H(612)···N(18)	2.81	1
H(412)···N(34)	2.74	2
H(621)···H(351)	2.57	2
H(521)···N(34)	2.78	2
H(543)···H(331)	2.34	2
H(132)···H(131)	2.49	3
C(33)···H(133)	2.79	3
C(3)···H(131)	2.92	3
H(131)···H(131)	2.47	3
C(32)···H(132)	3.04	3
H(361)···H(632)	2.36	4
H(351)···H(642)	2.48	4
O(8)···H(632)	2.72	4
C(35)···H(111)	3.02	5
C(36)···H(111)	2.93	5
C(35)···H(112)	3.05	5
H(135)···H(622)	2.24	6
H(531)···H(631)	2.33	6
O(7)···H(643)	2.55	6

Symmetry operations: 1,  $(x, y, z)$ ; 2,  $(x+1, y, z+1)$ ; 3,  $(-x, -y, -z)$ ; 4,  $(-x+1, -y, -z)$ ; 5,  $(-x+1, -y+1, -z)$ ; 6,  $(-x+1, -y+1, -z+1)$ .

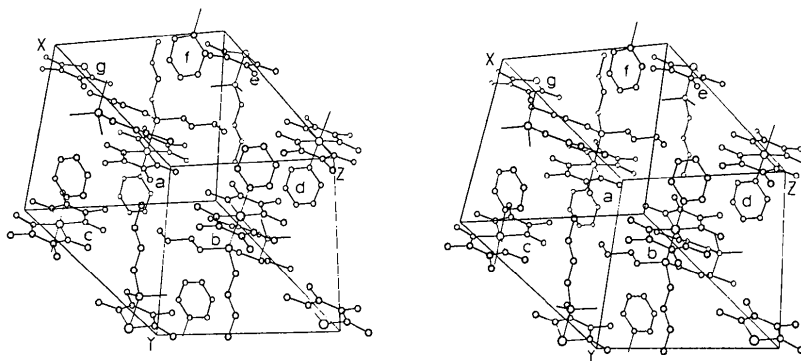


Fig. 2. Stereogram of intermolecular packing. The molecules shown correspond to the atomic coordinates of Table 1 as follows: (a)  $(x, y, z)$ ; (b)  $(1-x, 1-y, 1-z)$ ; (c)  $(1-x, 1-y, -z)$ ; (d)  $(x, y, z+1)$ ; (e)  $(1-x, -y, 1-z)$ ; (f)  $(x+1, y, z+1)$ ; (g)  $(1-x, -y, -z)$ .

### Bond distances and angles

The bond distances have been corrected for thermal motion using the computer program *ORSBA* (Johnson, 1970a) which fits either a rigid body or a segmented body to the molecular motion described by the anisotropic thermal parameters. In this instance, the complete Schomaker & Trueblood (1968) description was used including screw, translation and libration motions. The molecule does not behave as a single rigid body. However, the 4 groups consisting of the cobalt taken together with each of the 2 dimethylglyoxime ligands, the pyridine ligand and the 4 atoms of the tributylphosphine ligand nearest to it, behave, to a good approximation, as rigid bodies. The reaction center (Johnson, 1970b) for each of the 4 groups is near the cobalt atom showing that, to a good approximation, each group behaves as if it were pivoted at cobalt. Table 4 gives the parameters describing the motion along with the standard error of  $U(i,j)$  for the four molecular segments treated here as rigid bodies. In Fig. 1 the left and right arrows show the principal libration axes for the right and left dimethylglyoxime ligands, respectively. The fit deteriorates significantly when both dimethylglyoxime ligands are treated as a single rigid unit.

The corrected bond distances and angles obtained from the rigid-body treatment are shown in Fig. 3. They are listed in Tables 5 and 6 along with the uncorrected values. Standard deviations as calculated from the least-squares refinement are included in the tables. Chemically equivalent bond distance averages (corrected for libration) are: Co-N, 1.891 Å; C-N, 1.305; N-O(H), 1.343; N-O, 1.355; C-C(Me), 1.511; C-C, 1.455; P-C, 1.836. Pyridine distances and angles are discussed below. The average C-H distances (for those hydrogen positions which were refined) are: methyl groups, 0.906 Å; methylene groups, 0.943 and pyridine, 0.965.

### The phosphine ligand

The phosphine ligand coordinates to the cobalt center through a Co-P bond of 2.342 (1) Å. The bonding geometry of the phosphorus atom is distorted tetrahedral. The close proximity of the equatorial ligands to the  $\alpha$  and  $\beta$  carbon atoms of the butyl triad forces the three chains away from the equatorial plane, increasing the Co-P-C angles by about 5° and decreasing the C-P-C angles by a like amount.

The n-butyl groups are planar to within an r.m.s. deviation of 0.05 Å due to the steric effects of the hydrogen atoms on adjacent carbon atoms. It is interesting to note the angles between each of the three planes and the equatorial plane: C(40)'s plane, 27°; C(50)'s plane, 23°; C(60)'s plane, 88°. The two n-butyl groups which make acute angles with the equatorial plane are in contact at the  $\alpha$  and  $\beta$  carbon atoms. The C(60)'s chain where C(62) and C(63) show disorder has intramolecular contacts only at the  $\alpha$  carbon, C(61). Intermolecular contacts, especially C(62) and C(63),

are with points to one side of the chain, allowing greater freedom of motion than in any other part of the molecule. These contact distances are listed in Table 3.

### The pyridine ligand

Coordination of pyridine through a Co-C bond effectively replaces the hydrogen atom on C(31) with cobalt. This contrasts with the usual Co-N coordination where the unpaired electrons of the free pyridine

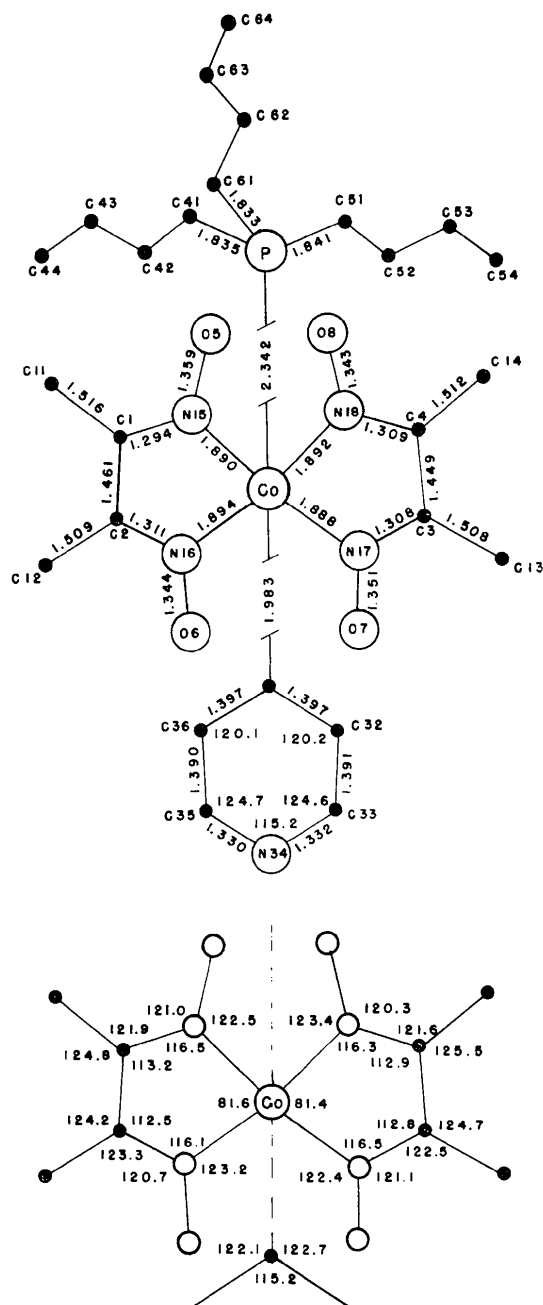


Fig. 3. Intramolecular bond distances and angles. All distances and angles shown have been corrected for librational motion as discussed in the text.

molecule are shared with cobalt. The effects of this 'substitution' are seen by comparing the pyridine bond distances and angles for the most accurate determinations to date on uncoordinated pyridine, pyridine with Co-C coordination and pyridine with Co-N coordination. These results are shown in Table 7. Comparison of uncoordinated and Co-C coordinated pyridine supports the conclusion that Co-C coordination has no effect on the C-C pyridine distances but probably a small effect on the C-N distances. Co-N coordination shortens the C-C pyridine bonds (as compared with uncoordinated pyridine) but has no effect on the C-N distances.

Coordination clearly has an effect on the pyridine bond angles. In the Co-C case, the largest effect is on the C-C-C angle at the coordination site which decreases nearly 3°. The adjacent C-C-C angles increase

by 1.5°. These changes are consistent with the idea that they are produced by distortion resulting from contacts between the equatorial ligands and adjacent pyridine atoms.

Pyridine ligands with Co-N coordination which are without intramolecular contacts near the C-C-C angles show these angles within about 0.5° of those in uncoordinated pyridine. The nitrogen end shows C-N-C and N-C-C angles which also differ somewhat from those in the uncoordinated pyridine. In this case the C-N-C angle increases somewhat with a corresponding decrease in the N-C-C angles. Here the strains introduced by coordination are presumably smaller since the Co-N distance is longer (2.043 Å) than the Co-C(4) distance (1.983 Å).

The heavy atoms of the pyridine ligand are planar to within 0.005 Å and the pyridine plane makes an

Table 4. Rigid-body analysis of molecular libration

Atoms in rigid unit	Standard error of $U(I, J)$	Reaction center coordinates*			Principal value of libration	Direction cosines of libration axes*			Principal axes of translation
		X	Y	Z					
Co, N(15), N(16) O(5), O(6), C(1) C(2), C(11), C(12)	0.0027 Å <sup>2</sup>	-0.081 Å	0.153 Å	0.231 Å	6.3° 3.9 3.3	0.845 0.293 0.447	-0.096 -0.739 0.667	0.525 -0.607 -0.597	0.205 Å (r.m.s.) 0.189 0.164
Co, N(17), N(18) O(7), O(8), C(3) C(4), C(13), C(14)	0.0035	-0.378	-0.518	-0.209	6.3 4.5 3.3	0.133 -0.882 0.452	-0.438 -0.462 -0.772	0.889 -0.096 -0.447	0.197 0.192 0.154
Co, N(34), C(31) C(32), C(33) C(35), C(36)	0.0024	-0.356	0.118	-0.486	6.6 2.7 2.4	0.537 -0.840 0.076	-0.297 -0.272 -0.915	0.790 0.469 -0.396	0.207 0.186 0.170
Co, P, C(41) C(51), C(61)	0.0017	0.678	0.622	-0.518	3.5 2.6 1.3	0.384 -0.031 0.923	-0.418 -0.897 0.143	0.824 -0.440 -0.357	0.200 0.188 0.158

\* In terms of a Cartesian system with the origin at the cobalt atom, x along **a**, y along **c**\* × **a** and z along **c**\*.

Table 5. Intramolecular distances (Å) before and after correction for molecular libration

Co—P	2.339 (1)	2.342†	O(7)—H(67)	1.501 (18)
Co—N(15)	1.876 (2)	1.890	O(6)—H(67)	0.981 (19)
Co—N(16)	1.880 (1)	1.894	O(5)—O(8)	2.470 (2)
Co—N(17)	1.874 (1)	1.888	O(6)—O(7)	2.477 (2)
Co—N(18)	1.875 (1)	1.892	C(31)—C(32)	1.388 (3)
Co—C(31)	1.979 (1)	1.983	C(32)—C(33)	1.389 (2)
N(15)—C(1)	1.284 (2)	1.294	C(33)—N(34)	1.324 (2)
N(16)—C(2)	1.301 (2)	1.311	N(34)—C(35)	1.322 (3)
N(17)—C(3)	1.297 (2)	1.308	C(35)—C(36)	1.387 (2)
N(18)—C(4)	1.299 (2)	1.309	C(36)—C(31)	1.389 (2)
N(15)—O(5)	1.349 (2)	1.359	P—C(41)	1.831 (1)
N(16)—O(6)	1.334 (2)	1.344	C(41)—C(42)	1.520 (3)
N(17)—O(7)	1.340 (2)	1.351	C(42)—C(43)	1.521 (2)
N(18)—O(8)	1.333 (2)	1.343	C(43)—C(44)	1.504 (4)
C(1)—C(11)	1.504 (4)	1.516	P—C(51)	1.837 (2)
C(2)—C(12)	1.497 (3)	1.509	C(51)—C(52)	1.523 (2)
C(3)—C(13)	1.497 (3)	1.508	C(52)—C(53)	1.507 (4)
C(4)—C(14)	1.498 (3)	1.512	C(53)—C(54)	1.499 (4)
C(1)—C(2)	1.450 (3)	1.461	P—C(61)	1.829 (2)
C(3)—C(4)	1.437 (3)	1.449	C(61)—C(62)	1.523*
O(5)—H(85)	1.506 (18)		C(62)—C(63)	1.450*
O(8)—H(85)	0.968 (18)		C(63)—C(64)	1.491*

\* Not included in final least-squares cycles, distances calculated from the average position of C(621), C(622) and C(631), C(632).

† This column is corrected for molecular libration.

Table 6. *Intramolecular angles (°) and standard deviations before and after correction for molecular libration*

N(15)-Co-N(16)	81.64 (6)	81.63†	C(13)-C(3)-C(4)	124.7 (2)	124.7†
N(16)-Co-N(17)	98.54 (6)		N(18)-C(4)-C(14)	121.6 (3)	121.6
N(17)-Co-N(18)	81.46 (6)	81.44	N(18)-C(4)-C(3)	113.0 (2)	112.9
N(18)-Co-N(15)	98.26 (6)		C(14)-C(4)-C(3)	125.4 (3)	125.5
P-Co-C(31)	179.2 (19)		Co-N(18)-O(8)	123.3 (1)	123.4
N(15)-Co-C(31)	88.38 (6)		Co-N(18)-C(4)	116.2 (2)	116.3
N(16)-Co-C(31)	89.80 (5)		C(4)-N(18)-O(8)	120.4 (2)	120.3
N(17)-Co-C(31)	87.81 (5)		N(18)-O(8)-H(85)	100.3 (16)	
N(18)-Co-C(31)	88.85 (5)		Co-C(31)-C(32)	122.8 (1)	122.7
N(15)-Co-P	92.43 (4)		C(36)-C(31)-Co	122.3 (2)	122.1
N(16)-Co-P	90.32 (3)		C(36)-C(31)-C(32)	114.9 (2)	115.2
N(17)-Co-P	91.38 (3)		C(31)-C(32)-C(33)	120.3 (2)	120.2
N(18)-Co-P	91.03 (4)		C(32)-C(33)-N(34)	124.7 (2)	124.6
Co-N(15)-O(5)	122.5 (1)	122.5	C(33)-N(34)-C(35)	114.9 (2)	115.2
Co-N(15)-C(1)	116.5 (2)	116.5	N(34)-C(35)-C(36)	124.9 (2)	124.8
C(1)-N(15)-O(5)	121.0 (2)	121.0	C(35)-C(36)-C(31)	120.3 (2)	120.1
N(15)-C(1)-C(11)	121.9 (3)	121.9	Co-P-C(41)	116.66 (6)	116.66
N(15)-C(1)-C(2)	113.2 (2)	113.2	Co-P-C(51)	113.97 (6)	113.92
C(11)-C(1)-C(2)	124.8 (2)	124.8	Co-P-C(61)	112.86 (4)	112.85
N(16)-C(2)-C(12)	123.3 (3)	123.3	C(41)-P-C(51)	103.16 (7)	103.21
N(16)-C(2)-C(1)	112.5 (2)	112.5	C(51)-P-C(61)	103.40 (9)	103.45
C(12)-C(2)-C(1)	124.2 (2)	124.2	C(61)-P-C(41)	105.41 (8)	105.40
Co-N(16)-O(6)	123.2 (1)	123.2	P-C(41)-C(42)	116.9 (1)	
Co-N(16)-C(2)	116.1 (2)	116.1	C(41)-C(42)-C(43)	112.5 (2)	
C(2)-N(16)-O(6)	120.8 (2)	120.7	C(42)-C(43)-C(44)	113.9 (2)	
N(16)-O(6)-H(67)	102.0 (16)		P-C(51)-C(52)	116.8 (2)	
Co-N(17)-O(7)	122.5 (1)	122.4	C(51)-C(52)-C(53)	112.8 (2)	
Co-N(17)-C(3)	116.5 (2)	116.5	C(52)-C(53)-C(54)	114.5 (3)	
C(3)-N(17)-O(7)	121.0 (2)	121.1	P-C(61)-C(62)	118.0*	
N(17)-C(3)-C(13)	122.5 (2)	122.5	C(61)-C(62)-C(63)	115.6*	
N(17)-C(3)-C(4)	112.8 (2)	112.8	C(62)-C(63)-C(64)	118.0*	

\* Not included in final least-squares cycles, angles calculated from the average position of C(621), C(622) and C(631), C(632).

† This column is corrected for molecular libration.

Table 7. *Comparison of average pyridine distances and angles*

	(a) Uncoordinated	(b) Co-C(4)	(c) Co-N
Co-C(4)		1.983 (1) Å	
Co-N			2.043 (1) Å
N(1)-C(2)	1.342 (5) Å	1.331 (2)	1.340 (1)
C(2)-C(3)			
C(5)-C(6)	1.391 (5)	1.390 (2)	1.378 (1)
C(3)-C(4)			
C(5)-C(4)	1.398 (5)	1.397 (2)	1.372 (1)
C(6)-N(1)-C(2)	116.7°	115.2 (2)°	117.47 (8)°
N(1)-C(2)-C(3)	124.0	124.7 (1)	122.69 (5)
N(1)-C(6)-C(5)			
C(2)-C(3)-C(4)	118.6	120.1 (1)	119.28 (5)
C(6)-C(5)-C(4)	118.1	115.2 (2)	118.60 (8)

(a) Microwave results of Bak, Hansen & Rastrup-Andersen (1954) for uncoordinated pyridine.

(b) This work. Pyridine coordinated *via* Co-C(4).

(c) Average values for 3 independent structure determinations, each of comparable accuracy with the present study. Pyridine coordinated *via* Co-N (Lenhert, 1972). Corrections for molecular libration not applied. Estimated corrections about 0.005 Å or less.

angle of 89.0° with the plane of the equatorial ligands. The orientation of the pyridine plane, approximately

parallel to the N-O bonds of the equatorial ligands, is characteristic of the cobaloximes (Lenhert, 1972).

#### The equatorial ligands

The cobalt coordination is distorted from square planar geometry by the five-membered rings formed by the dimethylglyoxime ligands. The inter-ring N-Co-N angles of about 81.5° (Table 6) and the extra-ring angles of 98.5° are characteristic of the cobaloximes. Intramolecular O-H...O hydrogen bonds of 2.47 Å connect the two ligands. Both hydrogen atoms were located unambiguously; each has a clear association with only one of the two dimethylglyoxime ligands (Table 5) as shown by least-squares refinement of the hydrogen atom positions and the final difference synthesis.

All atoms of the equatorial ligands are planar to within an r.m.s. deviation of 0.06 Å as shown in Table 8. If only the 5 atoms of each ligand ring are included in the plane calculations, the dihedral angle between the planes of the two five-membered ligand rings, C<sub>2</sub>N<sub>2</sub>Co, is 4.4°. This bending as well as the individual deviations of several of the atoms apparently results from intramolecular contacts with the axial ligands. The effects of these contacts (listed in Table 3) can best be seen by examining the stereopair, Fig. 1. Contacts with the pyridyl moiety especially between H(361), N(18) and O(8) tilt one ligand, and contacts between H(321), N(16) and O(6) tilt the other ligand, but in the

opposite direction. The tilt axis bisects the N-Co-N inner ring angle. Contacts between the tributylphosphine ligand, especially between H(411), C(1) and C(2) on one ligand and H(611) and C(4) on the other tilt each dimethylglyoxime ligand toward the pyridine side.

Table 8. Deviations from least-squares planes

	2DMG	DMG1	DMG2
Co	0.077* Å	0.006* Å	-0.012* Å
N(15)	-0.006*	-0.006*	
N(16)	0.042*	-0.007*	
N(17)	0.035*		0.014*
N(18)	0.067*		0.012*
C(1)	-0.027*	0.002*	
C(2)	0.003*	0.004*	
C(3)	-0.022*		-0.008*
C(4)	0.001*		-0.005*
C(11)	-0.082*	0.006	
C(12)	-0.013*	0.012	
C(13)	-0.119*		-0.051
C(14)	-0.047*		-0.023
O(5)	-0.054*	-0.033	
O(6)	0.028*	-0.053	
O(7)	0.012*		0.001
O(8)	0.104*		0.024
H(67)	0.057	-0.058	
H(85)	0.087		-0.028

Dihedral angles between the planes: 2DMG-DMG1, 2.2°; 2DMG-DMG2, 2.2°; DMG1-DMG2, 4.4°.

\* Denotes atoms included in the least-squares fit.

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