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Crystalline-State Reaction of Cobaloxime Complexes by X-ray Exposure. VI. Racemization of Tributyl- and Triphenylphosphine Complexes

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Abstract

X-ray analysis has revealed the crystal structures of [(*R*)-1-cyanoethyl]bis(dimethylglyoximato)(tributylphosphine)cobalt(III) (dimethylglyoximato = 2,3-butanedione dioximato), $[Co(C_3H_4N)(C_4H_7N_2O_2)_2\{P(C_4H_9)_3\}]$, (I), and [(*R*)-1-cyanoethyl]bis(dimethylglyoximato)(triphenylphosphine)cobalt(III) monohydrate, $[Co(C_3H_4N)(C_4H_7N_2O_2)_2\{P(C_6H_5)_3\}].H_2O$. The structures were solved by the direct method and refined by the least-squares technique. The final *R* values were 0·053 for (I) and 0·087 for (II) calculated on the basis of 2592 and 2303 independent reflections, respectively. Neither crystal showed crystalline-state racemization by X-ray exposure. This is due to the smaller volume of the cavity for each cyanoethyl group in the crystals than those in the related racemizable crystals. The Co—P distance in (II) [2·410 (3) Å] is significantly longer than that in (I) [2·316 (2) Å] and the Co atom in (II) is displaced by 0·078 (5) Å out of the mean plane of the equatorial ligands toward the phosphine ligand, although the Co—C distance in (II) [2·08 (1) Å] is approximately the same as that in (I) [2·089 (6) Å]. This would cause higher strain between the cyanoethyl group and the equatorial ligands in (II) than in (I), which is probably responsible for the faster rate of racemization by visible light in solution of (II) than those of other related complexes including (I). [Crystal data: (I): $C_{23}H_{45}CoN_5O_4P$, $M_r = 545·55$, $P2_12_12_1$, $a = 16·098\,(2)$, $b = 19·108\,(3)$, $c = 9·388\,(1)$ Å, $V = 2887·7\,(7)$ Å^3, $D_m = 1·26$, $D_x = 1·255$ g cm^{-3}, $Z = 4$, $\mu(\text{Mo}K\alpha) = 7·10$ cm^{-1}; (II): $C_{29}H_{33}CoN_5O_4P.H_2O$, $M_r = 623·53$, $P2_1$, $a = 10·388\,(1)$, $b = 15·966\,(2)$, $c = 8·782\,(1)$ Å, $\beta = 96·49\,(1)°$, $V = 1447·3\,(3)$ Å^3, $D_x = 1·431$ g cm^{-3}, $Z = 2$, $\mu(\text{Cu}K\alpha) = 54·66$ cm^{-1}.]

Introduction

In the serial studies of the crystalline-state reaction of bis(dimethylglyoximato)cobalt, cobaloxime, complexes by X-ray exposure, we have found that the modes of racemization of the cyanoethyl group are divided into two classes: order-to-disorder and order-to-order racemization as shown in Fig. 1. The former is found for crystals of [(*R*)-1-cyanoethyl][(*S*)-α-methylbenzylamine]cobaloxime, *R*-cn-*S*-mba (Ohashi & Sasada, 1977; Ohashi, Sasada & Ohgo, 1978*a*; Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1981), and [(*S*)-1-cyanoethyl][(*S*)-α-methylbenzylamine]cobaloxime, *S*-cn-*S*-mba (Ohashi, Sasada & Ohgo, 1978*b*). Each crystal contains one molecule in an asymmetric unit and the volume of its unit cell gradually increases with X-ray exposure. The latter occurs in crystals of [(*S*)-1-cyanoethyl](pyridine)cobaloxime, *S*-cn-py (Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1982), and [(*R*)-1-cyanoethyl](4-pyridinecarbonitrile)cobaloxime, *R*-cn-cnpy (Ohashi, Uchida, Sasada & Ohgo, 1983). Crystals of this class have two molecules in an asymmetric unit. The crystallographic inversion center appears between them and the unit cell contracts after the racemization. The modes of racemization seem to depend on whether or not the axial amine is chiral. We have prepared [(*R*)-1-cyanoethyl]-cobaloxime complexes with tributylphosphine and

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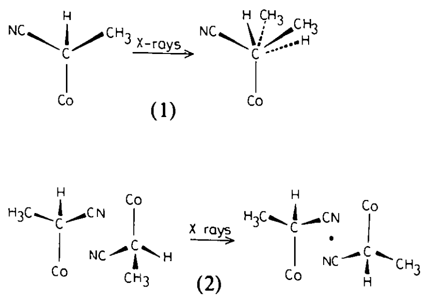

Fig. 1. The mode of racemization of the chiral 1-cyanoethyl group by X-ray exposure. The first mode, (1), is found in crystals of *R*-cn-*S*-mba and *S*-cn-*S*-mba and the second mode, (2), is observed in crystals of *S*-cn-py and *R*-cn-cnpy, the point between the two groups being a crystallographic inversion center.

triphenylphosphine (*R*-cn-tbp and *R*-cn-tpp, respectively) and examined the behavior of these crystals on X-ray exposure.

In addition, it has been realized that the chiral 1-cyanoethyl group in these complexes is easily racemized in solution on exposure to visible light. The rates of the racemization were approximately the same except for *R*-cn-tpp, which exhibits a rate which is twice as fast as the others, and its quick reaction was believed to result from the steric effect of the tpp ligand rather than from an electronic effect (Ohgo, Baba, Ohtera, Wada, Takeuchi & Hirata, 1981). In this connection, it is interesting to clarify the structural differences in the phosphine complexes.

Experimental

R-cn-tbp and *R*-cn-tpp were prepared according to the method reported for *S*-cn-py (Ohgo, Takeuchi, Natori, Yoshimura, Ohashi & Sasada, 1981).

R-cn-tbp

Orange plate-like crystals were obtained from an aqueous methanol solution. Preliminary unit-cell dimensions and the space group were obtained from photographs. Systematic absences are $h = 2n + 1$ for $h00$, $k = 2n + 1$ for $0k0$ and $l = 2n + 1$ for $00l$. Crystal data are listed *in the Abstract.* A crystal 0·4 × 0·4 × 0·3 mm was mounted on a Rigaku four-circle diffractometer equipped with Mo$K\alpha$ radiation monochromated by graphite. The unit-cell dimensions were obtained by means of the least-squares technique with 18 reflections in the range $20° \leq 2\theta \leq 30°$. The determination of the cell dimensions was repeated continuously at 293 K. No significant change was observed after 100 h. The three-dimensional intensity data were collected using the same crystal. Reflections within $2\theta \leq 50°$ were measured by an $\omega/2\theta$ scan; the scanning rate was $4°(\omega)\ \mathrm{min}^{-1}$ for a scan range of $(1{\cdot}0 + 0{\cdot}35 \tan\theta)°$. Stationary background counts were accumulated for 5 s before and after each scan. A total of 2910 reflections were observed, of which 2592 $[|F_o| \geq 3\sigma(F_o)]$ were used for the structure determination. No corrections for absorption or extinction were made.

The structure was solved by the direct method with the *MULTAN*78 program (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by full-matrix least squares with the *SHELX*76 program (Sheldrick, 1976). Positions of most of the H atoms were obtained from a difference map and those of the others were calculated geometrically. In the final refinement, the C—H distance was constrained to have a fixed length (1·0 Å) and the three H atoms of the methyl groups to have the same isotropic thermal parameter. No significant peaks higher than 0·5 e Å^{-3} were found in the final difference map. The atomic scattering factors including the anomalous-dispersion terms were taken from *International Tables for X-ray Crystallography* (1974). The final *R* was 0·053 for 2592 reflections. Atomic coordinates for non-hydrogen atoms are given in Table 1.

Even when the temperature was raised to 343 K, the cell dimensions did not change by X-ray exposure. However, the reflection intensities gradually decreased and the crystal decomposed.

Table 1. *Final atomic coordinates* (×10^5 *for* Co *and* P; ×10^4 *for* C, N *and* O) *and equivalent isotropic thermal parameters* (Å^2) *for non-hydrogen atoms of R-cn-tbp*

$$B_{\mathrm{eq}} = \tfrac{1}{3}\textstyle\sum_i\sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i . \mathbf{a}_j.$$

	x	y	z	B_{eq}
Co	53495 (5)	29988 (4)	27731 (8)	3·1
N(1)	5248 (3)	3237 (2)	4700 (5)	3·7
N(2)	4190 (3)	2943 (3)	2922 (6)	4·3
N(3)	5465 (3)	2732 (2)	852 (5)	3·6
N(4)	6518 (3)	3030 (2)	2637 (5)	3·4
O(1)	5904 (3)	3344 (2)	5539 (4)	4·8
O(2)	3710 (3)	2727 (3)	1814 (5)	5·3
O(3)	4816 (3)	2548 (3)	18 (6)	5·4
O(4)	6997 (3)	3225 (2)	3735 (5)	4·8
C(1)	4488 (4)	3277 (3)	5207 (7)	4·5
C(2)	3873 (4)	3089 (4)	4165 (7)	4·8
C(3)	6211 (4)	2682 (3)	385 (7)	4·1
C(4)	6842 (4)	2867 (3)	1410 (8)	4·1
C(5)	4309 (6)	3443 (6)	6743 (8)	7·2
C(6)	2930 (5)	3079 (7)	4410 (11)	7·4
C(7)	6402 (6)	2418 (4)	−1116 (10)	6·1
C(8)	7749 (5)	2871 (5)	1123 (11)	6·4
C(9)	5367 (4)	1935 (3)	3280 (6)	4·6
C(10)	5211 (7)	1739 (4)	4832 (8)	7·2
C(11)	6114 (5)	1600 (3)	2796 (8)	5·4
N(5)	6714 (4)	1339 (3)	2443 (9)	8·5
P	52672 (9)	41638 (7)	21109 (17)	3·5
C(*B*11)	6271 (4)	4531 (3)	1601 (8)	4·4
C(*B*12)	6296 (6)	5292 (4)	1125 (10)	6·6
C(*B*13)	7177 (7)	5601 (5)	1047 (13)	7·9
C(*B*14)	7568 (9)	5742 (7)	2432 (17)	11·7
C(*B*21)	4600 (6)	4330 (5)	599 (9)	6·2
C(*B*22)	3690 (6)	4435 (6)	908 (13)	8·5
C(*B*23)	3199 (8)	4685 (12)	−337 (18)	11·2
C(*B*24)	2346 (10)	4843 (9)	53 (23)	14·7
C(*B*31)	4882 (5)	4789 (4)	3443 (7)	4·8
C(*B*32)	5457 (5)	4987 (4)	4649 (9)	5·8
C(*B*33)	5033 (9)	5505 (7)	5644 (13)	9·9
C(*B*34)	5552 (12)	5689 (8)	6888 (15)	12·3

R-cn-tpp

Very thin plate-like crystals were obtained from an aqueous methanol solution. Experimental details are nearly the same as those for *R*-cn-tbp and the crystal data are also listed in the *Abstract*. A crystal 0·4 × 0·2 × 0·01 mm was mounted on the diffractometer. Cu$K\alpha$ radiation monochromated by graphite was used to obtain a gain in intensity. Accurate cell dimensions were obtained with 17 reflections in the range $40° \leq 2\theta \leq 60°$. The unit-cell dimensions did not change significantly by X-ray exposure for a week at 293 K. The three-dimensional intensity data within $2\theta \leq 125°$ were collected with an $\omega/2\theta$ scan; the scanning rate was 2° (ω) min^{-1} for a scan range of $(1{\cdot}0 + 0{\cdot}15 \times \tan\theta)°$. A total of 2394 reflections were measured, of which 2303 $[|F_o| \geq 3\sigma(F_o)]$ were considered as observed. No corrections for absorption or extinction were made.

The structure was solved by the direct method and refined by block-diagonal least squares with the modified *HBLS* program (Ohashi, 1975). After several cycles of refinement, a solvent water molecule appeared in the difference map. Positions of the H atoms were calculated geometrically and refined with fixed isotropic thermal parameters. In the final difference map, a few peaks of 0·8–1·4 e Å^{-3} were found within 1·0 Å from the Co and P atoms. Others were lower than 0·6 e Å^{-3}. The final R was 0·087 for 2303 reflections. Atomic coordinates for non-hydrogen atoms are given in Table 2.[*]

Table 2. *Final atomic coordinates* (×10^4) *and equivalent isotropic thermal parameters* (Å^2) *for non-hydrogen atoms of R-cn-tpp*

$$B_{eq} = \tfrac{1}{3}\textstyle\sum_i \sum_j B_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Co	2931 (1)	6030 (1)	1084 (2)	2·0
N(1)	3476 (8)	6206 (7)	−850 (11)	3·2
N(2)	3293 (8)	7176 (6)	1254 (10)	2·5
N(3)	2490 (9)	5832 (6)	3096 (11)	2·8
N(4)	2730 (8)	4849 (6)	988 (9)	2·2
O(1)	3518 (8)	5593 (7)	−1901 (9)	4·2
O(2)	3169 (9)	7617 (5)	2531 (9)	3·6
O(3)	2402 (8)	6442 (5)	4142 (8)	3·4
O(4)	2970 (8)	4402 (5)	−265 (9)	3·3
C(1)	3852 (11)	6954 (8)	−1192 (15)	3·6
C(2)	3819 (10)	7519 (8)	120 (15)	3·4
C(3)	2260 (10)	5057 (8)	3436 (13)	2·8
C(4)	2424 (9)	4474 (7)	2195 (12)	2·7
C(5)	4368 (14)	7186 (10)	−2654 (16)	4·7
C(6)	4311 (14)	8407 (9)	112 (20)	4·9
C(7)	1956 (13)	4799 (9)	4969 (14)	4·0
C(8)	2356 (13)	3558 (8)	2368 (17)	4·1
C(9)	4846 (11)	5877 (8)	2015 (13)	3·4
C(10)	5857 (12)	5781 (9)	861 (15)	4·1
C(11)	5073 (12)	5188 (10)	3073 (16)	4·3
N(5)	5248 (12)	4629 (11)	3908 (19)	8·0
P	756 (2)	6408 (2)	67 (3)	2·5
C(12)	826 (9)	7320 (7)	−1220 (12)	2·3
C(13)	759 (12)	7185 (7)	−2771 (12)	3·1
C(14)	937 (12)	7858 (8)	−3761 (14)	3·7
C(15)	1193 (13)	8650 (8)	−3137 (15)	3·8
C(16)	1260 (12)	8782 (8)	−1592 (15)	3·6
C(17)	1099 (11)	8109 (7)	−636 (14)	3·1
C(18)	−331 (10)	5698 (7)	−1147 (11)	2·4
C(19)	−1596 (11)	5906 (7)	−1529 (14)	3·4
C(20)	−2445 (11)	5416 (10)	−2423 (16)	4·3
C(21)	−2013 (11)	4668 (8)	−2978 (12)	3·2
C(22)	−772 (13)	4442 (8)	−2616 (14)	3·5
C(23)	125 (11)	4961 (8)	−1676 (13)	2·9
C(24)	−329 (10)	6709 (7)	1520 (12)	2·5
C(25)	−1010 (11)	7445 (8)	1486 (13)	3·4
C(26)	−1886 (13)	7610 (9)	2570 (15)	4·0
C(27)	−2020 (13)	6999 (10)	3702 (16)	4·4
C(28)	−1344 (12)	6273 (9)	3710 (16)	4·4
C(29)	−505 (10)	6125 (9)	2640 (12)	3·1
O(*w*)	4513 (11)	3259 (9)	5798 (14)	7·1

Results

Perspective drawings of *R*-cn-tbp and *R*-cn-tpp with the numbering of the atoms are shown in Fig. 2. Selected bond distances and angles of the two molecules are given in Tables 3 and 4, respectively. The Co—P distance in *R*-cn-tpp, 2·410 (3) Å, is significantly longer than that in *R*-cn-tbp, 2·316 (2) Å. Similar Co—P(tpp) and Co—P(tbp) distances have been found in crystals of methyl(tpp)cobaloxime, 2·418 (1) Å (Bresciani-Pahor, Calligaris, Randaccio & Marzilli, 1979), isopropyl(tpp)cobaloxime, 2·412 (4) Å (Randaccio, Bresciani-Pahor, Toscano & Marzilli, 1980) and 4-pyridyl(tbp)cobaloxime, 2·342 (1) Å (Adams & Lenhert, 1973). The Co—C distances of the present phosphine complexes are approximately the same and are significantly longer than those of the amine complexes: 2·056 (6) Å in *R*-cn-*S*-mba at 173 K (Ohashi, Sasada, Takeuchi, & Ohgo, 1980*a*), 2·059 (9) Å in *S*-cn-*S*-mba at 173 K (Ohashi, Sasada, Takeuchi & Ohgo, 1980*b*), 2·053 (4) Å in *rac*-cn-py (Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1982), and 2·065 (3) Å in *rac*-cn-cnpy (Ohashi, Uchida, Sasada & Ohgo, 1983).

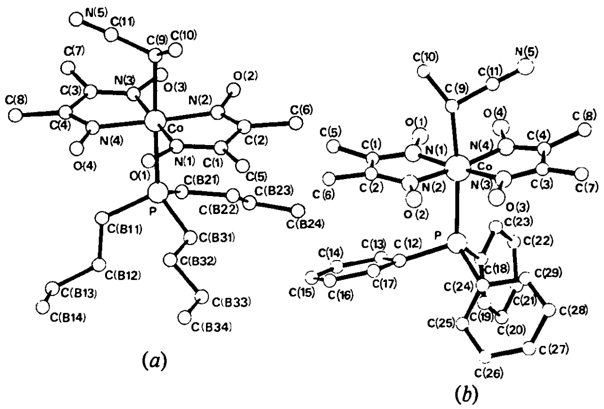

Fig. 2. Perspective drawings of (*a*) *R*-cn-tbp and (*b*) *R*-cn-tpp with the numbering of the atoms.

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[*] Lists of structure factors, anisotropic thermal parameters, H-atom parameters and bond distances and angles of the phosphine ligands for *R*-cn-tbp and *R*-cn-tpp have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38432 (25 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 3. *Selected bond distances* (Å) *of R-cn-tbp and R-cn-tpp*

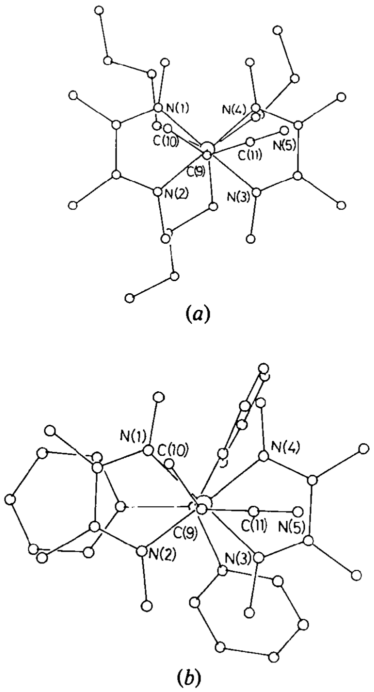
	R-cn-tbp	*R*-cn-tpp		*R*-cn-tbp	*R*-cn-tpp		*R*-cn-tbp	*R*-cn-tpp
Co—N(1)	1·873 (5)	1·87 (1)	N(3)—O(3)	1·351 (7)	1·35 (1)	C(9)—C(10)	1·525 (12)	1·55 (2)
Co—N(2)	1·874 (6)	1·87 (1)	N(3)—C(3)	1·283 (9)	1·30 (2)	C(9)—C(11)	1·437 (10)	1·44 (2)
Co—N(3)	1·883 (5)	1·90 (1)	N(4)—O(4)	1·341 (7)	1·36 (1)	C(11)—N(5)	1·137 (11)	1·16 (2)
Co—N(4)	1·885 (5)	1·90 (1)	N(4)—C(4)	1·303 (9)	1·29 (2)	P—C(*B*11)	1·825 (8)	
Co—C(9)	2·089 (6)	2·08 (1)	C(1)—C(2)	1·437 (10)	1·47 (2)	P—C(*B*21)	1·808 (10)	
Co—P	2·316 (2)	2·410 (3)	C(1)—C(5)	1·505 (13)	1·49 (2)	P—C(*B*31)	1·838 (8)	
N(1)—O(1)	1·332 (7)	1·35 (2)	C(2)—C(6)	1·535 (15)	1·51 (2)	P—C(12)		1·85 (1)
N(1)—C(1)	1·314 (8)	1·30 (2)	C(3)—C(4)	1·444 (10)	1·46 (2)	P—C(18)		1·85 (1)
N(2)—O(2)	1·359 (8)	1·34 (1)	C(3)—C(7)	1·527 (12)	1·48 (2)	P—C(24)		1·86 (1)
N(2)—C(2)	1·304 (10)	1·31 (2)	C(4)—C(8)	1·484 (13)	1·47 (2)			

Table 4. *Selected bond angles* (°) *of R-cn-tbp and R-cn-tpp*

	R-cn-tbp	*R*-cn-tpp		*R*-cn-tbp	*R*-cn-tpp		*R*-cn-tbp	*R*-cn-tpp
N(1)—Co—N(2)	81·7 (2)	81·2 (4)	Co—N(2)—C(2)	116·4 (5)	116·5 (8)	N(4)—C(4)—C(8)	123·6 (7)	124·4 (11)
N(1)—Co—N(3)	178·3 (2)	176·2 (5)	O(2)—N(2)—C(2)	121·9 (6)	120·2 (10)	C(3)—C(4)—C(8)	124·9 (7)	123·1 (11)
N(1)—Co—N(4)	98·3 (2)	98·7 (5)	Co—N(3)—O(3)	123·3 (4)	123·6 (7)	Co—C(9)—C(10)	117·0 (5)	116·4 (9)
N(1)—Co—C(9)	91·1 (2)	90·0 (5)	Co—N(3)—C(3)	116·1 (5)	116·2 (8)	Co—C(9)—C(11)	111·9 (5)	115·0 (9)
N(1)—Co—P	91·1 (2)	89·7 (4)	O(3)—N(3)—C(3)	120·4 (5)	120·2 (10)	C(10)—C(9)—C(11)	109·3 (6)	105·9 (11)
N(2)—Co—N(3)	98·9 (2)	99·0 (4)	Co—N(4)—O(4)	122·1 (4)	121·9 (7)	C(9)—C(11)—N(5)	178·4 (9)	179·1 (18)
N(2)—Co—N(4)	178·5 (2)	174·5 (4)	Co—N(4)—C(4)	116·9 (5)	117·5 (8)	Co—P—C(*B*11)	112·9 (2)	
N(2)—Co—C(9)	86·6 (3)	84·8 (4)	O(4)—N(4)—C(4)	121·0 (5)	120·5 (10)	Co—P—C(*B*21)	114·4 (3)	
N(2)—Co—P	91·0 (2)	87·6 (3)	N(1)—C(1)—C(2)	112·4 (6)	110·4 (12)	Co—P—C(*B*31)	117·5 (2)	
N(3)—Co—N(4)	81·1 (2)	80·7 (4)	N(1)—C(1)—C(5)	122·5 (7)	124·9 (13)	C(*B*11)—P—C(*B*21)	104·6 (4)	
N(3)—Co—C(9)	87·3 (2)	86·3 (4)	C(2)—C(1)—C(5)	124·9 (7)	124·4 (12)	C(*B*11)—P—C(*B*31)	103·1 (3)	
N(3)—Co—P	90·5 (2)	94·1 (3)	N(2)—C(2)—C(1)	113·1 (7)	112·9 (11)	C(*B*21)—P—C(*B*31)	102·7 (4)	
N(4)—Co—C(9)	91·9 (2)	89·7 (5)	N(2)—C(2)—C(6)	121·2 (8)	124·6 (12)	Co—P—C(12)		108·9 (4)
N(4)—Co—P	90·5 (2)	98·0 (3)	C(1)—C(2)—C(6)	125·6 (8)	122·5 (12)	Co—P—C(18)		123·1 (4)
C(9)—Co—P	176·5 (2)	172·3 (4)	N(3)—C(3)—C(4)	114·4 (6)	113·3 (10)	Co—P—C(24)		115·2 (4)
Co—N(1)—O(1)	122·6 (4)	123·3 (8)	N(3)—C(3)—C(7)	121·9 (7)	122·6 (11)	C(12)—P—C(18)		101·2 (5)
Co—N(1)—C(1)	116·4 (4)	118·4 (9)	C(4)—C(3)—C(7)	123·7 (7)	123·9 (11)	C(12)—P—C(24)		106·5 (5)
O(1)—N(1)—C(1)	121·0 (5)	118·3 (11)	N(4)—C(4)—C(3)	111·5 (6)	112·3 (10)	C(18)—P—C(24)		100·1 (5)
Co—N(2)—O(2)	121·7 (5)	122·9 (7)						

Bond angles of the cobaloxime moiety and the cyanoethyl group in *R*-cn-tbp are in good agreement with the corresponding ones in *S*-cn-py and *R*-cn-cnpy. In *R*-cn-tpp, on the other hand, three of the four N—Co—P angles deviate significantly from 90°. The Co—P bond makes an angle of 84·6 (2)° with the mean plane composed of the four N atoms of cobaloxime. Similar angles are found for methyl(tpp)cobaloxime, 85·5°, and isopropyl(tpp)cobaloxime, 83·5°. In the cyanoethyl group of *R*-cn-tpp, the Co—C(9)—C(11) angle is greater and C(10)—C(9)—C(11) is smaller than the corresponding angles in *R*-cn-tbp. Other distances and angles of the two complexes are in fair agreement with each other and essentially the same as those of the related cyanoethyl cobaloxime complexes so far determined.

The conformations around the Co—C bond in the present two complexes are different from those of the above amine cobaloximes: the cyano groups of the present phosphine complexes lie on the glyoximato plane as shown in Fig. 3, whereas those of the amine complexes are situated over the gap between the two glyoxime ligands. The torsion angles C(11)—C(9)—Co—N(4) are −22·8 (5) and −37·6 (10)° for *R*-cn-tbp and *R*-cn-tpp, respectively. Such conformations probably elongate the Co—C



(*a*)

(*b*)

Fig. 3. Conformations of the axial ligands in (*a*) *R*-cn-tbp and (*b*) *R*-cn-tpp.

Table 5. *Torsion angles (°) of the phosphine ligands in R-cn-tbp and R-cn-tpp*

tbp ligand		tpp ligand	
N(4)–Co–P–C(*B*11)	−6·1 (3)	N(2)–Co–P–C(12)	−39·6 (5)
N(3)–Co–P–C(*B*21)	−44·5 (4)	N(4)–Co–P–C(18)	−22·5 (5)
N(1)–Co–P–C(*B*31)	15·5 (3)	N(3)–Co–P–C(24)	−18·9 (5)
Co–P–C(*B*11)–C(*B*12)	−179·2 (5)	Co–P–C(12)–C(17)	74·3 (10)
Co–P–C(*B*21)–C(*B*22)	−86·2 (8)	Co–P–C(18)–C(23)	8·4 (11)
Co–P–C(*B*31)–C(*B*32)	−74·4 (6)	Co–P–C(24)–C(29)	57·6 (10)
P–C(*B*11)–C(*B*12)–C(*B*13)	−166·8 (7)		
P–C(*B*21)–C(*B*22)–C(*B*23)	−170·4 (11)		
P–C(*B*31)–C(*B*32)–C(*B*33)	179·8 (7)		
C(*B*11)–C(*B*12)–C(*B*13)–C(*B*14)	72·9 (13)		
C(*B*21)–C(*B*22)–C(*B*23)–C(*B*24)	174·4 (15)		
C(*B*31)–C(*B*32)–C(*B*33)–C(*B*34)	−177·0 (11)		

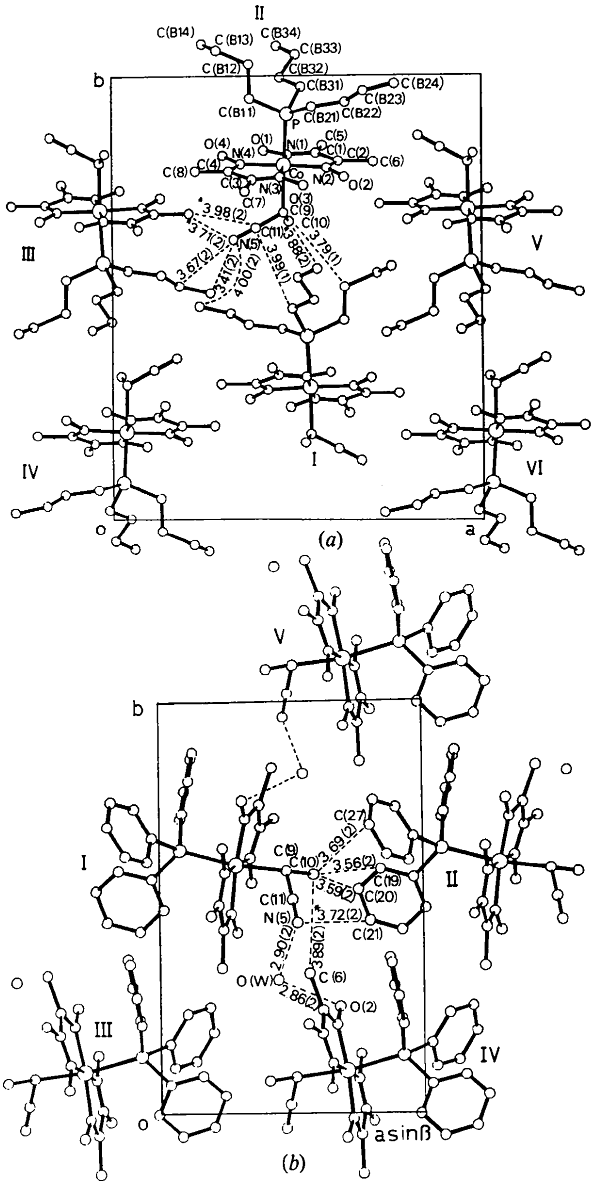


Fig. 4. Crystal structures of (*a*) *R*-cn-tbp and (*b*) *R*-cn-tpp, viewed along the *c* axis. Several short intermolecular distances (Å) around the cyanoethyl group are also shown. The distances marked with asterisks indicate that the molecules belong to the neighboring unit cell along the *c* axis.

bonds in *R*-cn-tbp and *R*-cn-tpp. The torsion angles in the tbp and tpp moieties are listed in Table 5. The three phenyl rings of the tpp ligand makes angles of 15·9 (4), 39·7 (4) and 87·1 (4)° to the mean plane of cobaloxime. Similar angles are found in methyl(tpp)-cobaloxime, 16·5, 40·6 and 76·9, and isopropyl(tpp)-cobaloxime, 21·2, 41·5 and 77·8°. The acute dihedral angles between the planes of the two glyoximato groups are 1·5 (4) and 9·4 (7)° for *R*-cn-tbp and *R*-cn-tpp, respectively, the two planes being bent away from the tbp and tpp ligands. The corresponding angles observed in 4-pyridyl(tbp)cobaloxime, methyl(tpp)cobaloxime and isopropyl(tpp)cobaloxime are 4·4, 13·6 and 14°, respectively. The conformational similarity among them suggests that the conformation observed in the crystal is inherent and is also kept in solution.

The crystal structures of *R*-cn-tbp and *R*-cn-tpp are shown in Fig. 4, in which short intermolecular distances around the cyanoethyl group are also given. The cyano group of *R*-cn-tpp makes a hydrogen bond with a solvent water molecule, which is also hydrogen-bonded to the O(2) atom of cobaloxime in the neighboring molecule. The N···O and O···O distances are 2·90 (2) and 2·86 (2) Å, respectively. These hydrogen bonds link molecules along the *b* axis. Both of the cyanoethyl groups in the crystals of *R*-cn-tbp and *R*-cn-tpp have usual van der Waals contact with the neighboring molecules, except with the hydrogen-bonded water molecule in the *R*-cn-tpp crystal, and they are isolated from the cyanoethyl groups of the neighboring molecules as observed in *R*-cn-*S*-mba and *S*-cn-*S*-mba crystals. This is distinct from the crystal structures of *S*-cn-py and *R*-cn-cnpy, in which the cyanoethyl groups of two crystallographically independent molecules are related by a pseudo inversion and contact with each other.

Discussion

Racemization in solution

Structural parameters around the Co atoms in the related tbp and tpp cobaloxime complexes so far determined are summarized in Table 6. The Co—P bonds in the tpp complexes are significantly longer than those in the tbp complexes and the Co atom of the tpp complex is displaced out of the equatorial plane toward the phosphine ligand, probably in order to avoid the short contacts between the phenyl groups of the tpp ligand and the cobaloxime moiety. A similar trend has been observed for tbp and tpp cobaloxime complexes containing an axial Cl ligand; the Co—P distances are 2·271 (2) and 2·258 (2) Å in Cl(tbp)cobaloxime (Bresciani-Pahor, Calligaris & Randaccio, 1980) and 2·327 (4) Å in Cl(tpp)cobaloxime (Bruckner & Randaccio, 1974), and the displacements of the Co atom from the mean plane are 0·04 and 0·05 Å, respectively, in these complexes.

The Co—C distance of *R*-cn-tpp, on the other hand, is approximately the same as that of *R*-cn-tbp. This suggests that the cyanoethyl group of *R*-cn-tpp must sustain a stronger steric repulsion from the cobaloxime moiety than that of *R*-cn-tbp. Several short contacts in the *R*-cn-tbp and *R*-cn-tpp complexes are shown in Fig. 5. The cyano group of *R*-cn-tpp is hydrogen-bonded with the water molecule. The intermolecular hydrogen bond makes the Co—C(9)—C(11) angle greater than the usual tetrahedral one and causes looser contacts between the cyano group and the cobaloxime moiety in *R*-cn-tpp than in *R*-cn-tbp. If the Co—C(9)—C(11) angle of *R*-cn-tpp were the same as that of *R*-cn-tbp, the cyano group would have closer contacts with the equatorial ligands in *R*-cn-tpp than in *R*-cn-tbp as observed in other intramolecular contacts. Such steric repulsions found in *R*-cn-tpp do not seem to disappear even if the cyanoethyl group has a similar conformation in solution as that of the amine cobaloxime complexes and probably accelerate the Co—C bond cleavage by visible light. Consequently, the rate of racemization of *R*-cn-tpp is faster than those of *R*-cn-tbp and the other amine cobaloxime complexes.

Table 6. *Structural parameters around the* Co *atom in the tbp and tpp complexes*

The value *d* is the displacement of the Co atom from the mean plane of four N atoms of cobaloxime toward the phosphine ligand

Axial ligand		*d* (Å)	Co—P (Å)	Co—C (Å)
tbp	cyanoethyl	0·026 (3)	2·316 (2)	2·089 (6)
tbp	4-pyridyl	0·02	2·342 (1)	1·983 (1)
tpp	cyanoethyl	0·078 (5)	2·410 (3)	2·08 (1)
tpp	methyl	0·11	2·418 (1)	2·026 (6)
tpp	isopropyl	0·17	2·412 (4)	2·22 (2)

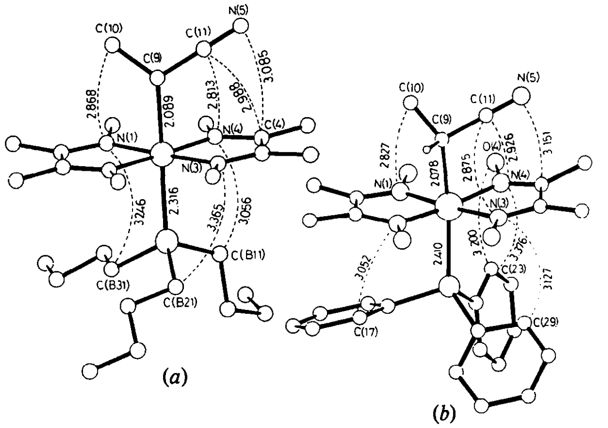


Fig. 5. Several short contacts (Å) between the axial ligands and the cobaloxime moiety in (*a*) *R*-cn-tbp and (*b*) *R*-cn-tpp.

Racemization in the crystalline state

Neither of the present complexes reveals crystalline-state racemization at 293 K. The cyanoethyl groups of the two crystals are surrounded by the butyl or phenyl groups and the cobaloxime moieties of the neighboring molecules as shown in Fig. 4. If crystalline-state racemization were observed, the present two crystals should belong to the first class; the ordered cyanoethyl group would convert into the disordered racemates. The interatomic distances between the cyanoethyl groups and the neighboring atoms in Fig. 4 indicate that the cyanoethyl groups of the two crystals are rather tightly packed among the neighboring molecules. Moreover, the N atom of the cyanoethyl group in *R*-cn-tpp is hydrogen-bonded to the water molecule.

In order to examine the degree of packing more quantitatively, the cavities for the cyanoethyl groups of the two crystals are calculated in the same way as reported previously (Ohashi, Uchida, Sasada & Ohgo, 1983), and are shown in Fig. 6. In both cavities, there is no void space for the inversion of the cyanoethyl group as observed in the *R*-cn-*S*-mba crystal, which belongs to the first class. The volumes of the cavities were calculated to be 10·64 and 11·31 $Å^3$ for the *R*-cn-tbp and *R*-cn-tpp crystals, respectively. They are smaller than that of *R*-cn-*S*-mba, 12·95 $Å^3$ at 173 K, at which crystalline-state racemization was no longer observed. The small sizes of the cavities of the present crystals clearly explain the non-reactivity on X-ray exposure.

It should be noted that the volume of the cavity for the cyanoethyl group does not show any direct correspondence to the density of the crystal. The densities and the volumes of the cavities for the cyanoethyl groups of *R*-cn-*S*-mba at 293 and 173 K and *R*-cn-tbp and *R*-cn-tpp are listed in Table 7. The packing density, D_p, also given in the table, is defined as V_m/V_u, where V_m is the volume of the molecules in a unit cell and V_u is the volume of the unit cell. V_m was calculated numerically, assuming that each atom is a sphere with its van der Waals radius (Bondi, 1964).

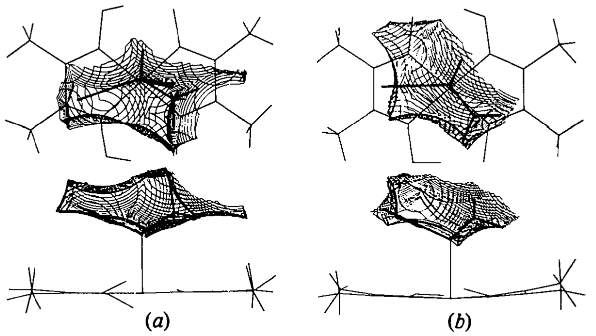


Fig. 6. Cavities for the cyanoethyl group viewed along the normal to the mean plane of cobaloxime and parallel to the plane in (*a*) *R*-cn-tbp and (*b*) *R*-cn-tpp crystals. Contours are drawn in sections separated by 0·1 Å.

Table 7. *The density, D_x, the packing density D_p, and the volume of the cavity for the cyanoethyl group, V_{cav}, in crystals of R-cn-S-mba at* 293 *and* 173 K, *and R-cn-tbp and R-cn-tpp at* 293 K

	R-cn-*S*-mba		*R*-cn-tbp	*R*-cn-tpp
	293 K	173 K	293 K	293 K
D_x (g cm^{-3})	1·388	1·421	1·255	1·431
D_p*	0·690	0·710	0·665	0·718
V_{cav} (Å^3)	14·53	12·95	10·64	11·31

* D_p for the closest packing of spheres is 0·741.

Although the density and the packing density of the *R*-cn-tbp crystal are smaller than the corresponding densities of *R*-cn-*S*-mba at 293 and 173 K and *R*-cn-tpp, the volume of the cavity is the smallest among the four cavities. This suggests that the void space in the cavity for the cyanoethyl group is essential for crystalline-state racemization and the volume of the cavity for the reactive group is a good guide as to whether or not the reactive group is actually racemized by X-ray exposure.

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References

Adams, W. W. & Lenhert, P. G. (1973). *Acta Cryst.* **B29**, 2412–2425.

Bondi, A. (1964). *J. Phys. Chem.* **68**, 441–451.

Bresciani-Pahor, N., Calligaris, M. & Randaccio, L. (1980). *Inorg. Chim. Acta*, **39**, 173–179.

Bresciani-Pahor, N., Calligaris, M., Randaccio, L. & Marzilli, L. G. (1979). *Inorg. Chim. Acta*, **32**, 181–187.

Bruckner, S. & Randaccio, L. (1974). *J. Chem. Soc. Dalton Trans.* pp. 1017–1022.

International Tables for X-ray Crystallography (1974). Vol. IV, pp. 71–151. Birmingham: Kynoch Press.

Main, P., Hull, S. E., Lessinger, L., Germain, G., Declercq, J. P. & Woolfson, M. M. (1978). *MULTAN78. A System of Computer Programs for the Automatic Solution of Crystal Structures from X-ray Diffraction Data.* Univs. of York, England, and Louvain, Belgium.

Ohashi, Y. (1975). Unpublished version of an original program by T. Ashida.

Ohashi, Y. & Sasada, Y. (1977). *Nature (London)*, **267**, 142–144.

Ohashi, Y., Sasada, Y. & Ohgo, Y. (1978*a*). *Chem. Lett.* pp. 457–460.

Ohashi, Y., Sasada, Y. & Ohgo, Y. (1978*b*). *Chem. Lett.* pp. 743–746.

Ohashi, Y., Sasada, Y., Takeuchi, S. & Ohgo, Y. (1980*a*). *Bull. Chem. Soc. Jpn*, **53**, 627–634.

Ohashi, Y., Sasada, Y., Takeuchi, S. & Ohgo, Y. (1980*b*). *Bull. Chem. Soc. Jpn*, **53**, 1501–1509.

Ohashi, Y., Uchida, A., Sasada, Y. & Ohgo, Y. (1983). *Acta Cryst.* **B39**, 54–61.

Ohashi, Y., Yanagi, K., Kurihara, T., Sasada, Y. & Ohgo, Y. (1981). *J. Am. Chem. Soc.* **103**, 5805–5812.

Ohashi, Y., Yanagi, K., Kurihara, T., Sasada, Y. & Ohgo, Y. (1982). *J. Am. Chem. Soc.* **104**, 6353–6359.

Ohgo, Y., Baba, S., Ohtera, C., Wada, H., Takeuchi, S. & Hirata, H. (1981). Joint Meeting of CSJ and SPSJ in Niigata. Abstract, p. 41.

Ohgo, Y., Takeuchi, S., Natori, Y., Yoshimura, J., Ohashi, Y. & Sasada, Y. (1981). *Bull. Chem. Soc. Jpn*, **54**, 3095–3099.

Randaccio, L., Bresciani-Pahor, N., Toscano, P. J. & Marzilli, L. G. (1980). *J. Am. Chem. Soc.* **102**, 7372–7373.

Sheldrick, G. M. (1976). *SHELX76*. Program for crystal structure determination. Univ. of Cambridge, England.