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Structures of [(*R*)-1-Cyanoethyl][diethyl(phenyl)phosphine]bis(dimethylglyoximato)-cobalt(III), $C_{21}H_{33}CoN_5O_4P$ (I), and [(*R*)-1-Cyanoethyl]bis(dimethylglyoximato)-(ethyldiphenylphosphine)cobalt(III), $C_{25}H_{33}CoN_5O_4P$ (II)*

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Abstract. (I): $M_r = 509{\cdot}43$, orthorhombic, $P2_12_12_1$, $a = 14{\cdot}340$ (1), $b = 14{\cdot}451$ (1), $c = 11{\cdot}820$ (1) Å, $V = 2449{\cdot}4$ (3) Å^3, $D_m = 1{\cdot}38$, $D_x = 1{\cdot}38$ g cm^{-3}, $Z = 4$, $T = 293$ K, $F(000) = 1072$, μ(Mo $K\alpha$) = 7·97 cm^{-1}, $\lambda = 0{\cdot}71069$ Å, $R = 0{\cdot}038$ for 3020 observed reflections. (II): $M_r = 557{\cdot}47$, monoclinic, $P2_1$, $a = 8{\cdot}966$ (2), $b = 17{\cdot}567$ (2), $c = 8{\cdot}906$ (3) Å, $\beta = 109{\cdot}98$ (3)°, $V = 1318$ (1) Å^3, $D_m = 1{\cdot}41$, $D_x = 1{\cdot}41$ g cm^{-3}, $Z = 2$, $T = 293$ K, $F(000) = 584$, μ(Mo $K\alpha$) = 7·46 cm^{-1}, $R = 0{\cdot}032$ for 3045 observed reflections. Neither of the crystals reveals crystalline-state racemization at 293 K, since the cavity for the cyanoethyl group is smaller than those of related crystals showing racemization by X-rays. The Co—P bond distance is 2·313 (1) Å for (I) and 2·370 (1) Å for (II).

Introduction. It has been reported that the chiral 1-cyanoethyl (cn) group in crystals of bis(dimethylglyoximato)cobalt (dimethylglyoximato = 2,3-butanedione dioximato), cobaloxime, complexes containing some amine ligands is racemized by X-ray exposure without degradation of the crystallinity (Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1981, 1982; Ohashi, Sasada & Ohgo, 1978; Ohashi, Uchida, Sasada & Ohgo, 1983; Uchida, Ohashi, Sasada, Ohgo & Baba, 1984). However, the crystals of the cobaloxime complexes with a phosphine ligand instead of an axial amine ligand, tributylphosphine (*R*-cn-tbp) and triphenylphosphine (*R*-cn-tpp), did not reveal crystalline-state racemization (Kurihara, Uchida, Ohashi, Sasada, Ohgo & Baba, 1983). In order to account for the inactivity of the phosphine complex crystals, the crystal structures and the reactivities of the diethyl(phenyl)phosphine, [(I); *R*-cn-depp], and ethyldiphenylphosphine, [(II); *R*-cn-dpep], complexes were examined.

Experimental. (I) and (II) prepared in a way similar to that reported previously (Ohgo, Takeuchi, Natori, Yoshimura, Ohashi & Sasada, 1981); orange plate-like crystals obtained from aqueous methanol solutions. D_m by flotation in CCl_4/C_6H_{12} solutions. Systematic absences: $h00$, $h = 2n+1$, $0k0$, $k = 2n+1$, $00l$, $l = 2n+1$ (I), and $0k0$, $k = 2n+1$ (II). Crystal dimensions 0·5 × 0·4 × 0·3 mm (I) and 0·4 × 0·4 × 0·2 mm (II). Rigaku AFC-4 diffractometer, graphite monochromator. Cell parameters refined by least-squares method on the basis of 12 (I) and 15 (II) independent 2θ values [Mo $K\alpha$ radiation, $25° < 2\theta < 30°$ (I) and $28° < 2\theta < 30°$ (II), $\lambda = 0{\cdot}71069$ Å]. Intensity measurement performed up to $2\theta = 55°$; range of hkl, 0 to 18, 0 to 18 and 0 to 15 (I) and −11 to 10, 0 to 22 and 0 to 11 (II). ω–2θ scan technique, scan speed 4° min^{-1} (θ). No significant variation of intensity in three standard reflections. 3172 (I) and 3135 (II) reflections measured, 3020 (I) and 3045 (II) intensities with $|F_o| > 3\sigma(|F_o|)$ considered observed and used for the structure determination. Lorentz and polarization corrections, absorption ignored. Direct methods (*MULTAN*78, Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). Full-matrix least squares (*SHELX*76, Sheldrick 1976) with anisotropic thermal parameters for all non-H atoms. H atoms located on difference map. $\sum w(|F_o| - |F_c|)^2$ minimized, with $w = [\sigma^2(F_o) + C(F_o)^2]^{-1}$, $C = 0{\cdot}0020$ (I) and 0·0012 (II). Final $R = 0{\cdot}038$ (I) and 0·032 (II), and $R_w = 0{\cdot}043$ (I) and 0·035 (II) for 3020 (I) and 3045 (II) observed reflections. Max. (Δ/σ) 0·2 (I) and 0·3 (II).

* Crystalline-State Reaction of Cobaloxime Complexes by X-ray Exposure. XI.

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Table 1. *Final atomic coordinates* ($\times 10^5$ *for* Co *and* P, *and* $\times 10^4$ *for* C, N *and* O) *and equivalent isotropic thermal parameters for* R-cn-depp (I)

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

	x	y	z	B_{eq}(Å^2)
Co	42924 (3)	34890 (3)	8322 (3)	2·7
P	43099 (6)	19340 (5)	3695 (7)	2·6
N(1)	5272 (2)	3679 (2)	−195 (2)	3·0
N(2)	3589 (2)	3735 (2)	−476 (3)	3·5
N(3)	3308 (2)	3317 (2)	1865 (3)	3·7
N(4)	5004 (2)	3267 (2)	2140 (2)	3·1
O(1)	6177 (2)	3562 (2)	89 (2)	3·8
O(2)	2643 (2)	3739 (2)	−478 (3)	5·2
O(3)	2405 (2)	3374 (2)	1550 (3)	5·0
O(4)	5943 (2)	3273 (2)	2146 (2)	3·8
C(1)	5055 (3)	3875 (2)	−1231 (3)	3·5
C(2)	4046 (3)	3929 (3)	−1389 (3)	3·8
C(3)	3538 (3)	3130 (3)	2894 (4)	4·1
C(4)	4541 (3)	3099 (2)	3069 (3)	3·6
C(5)	5760 (4)	4007 (3)	−2155 (4)	5·1
C(6)	3572 (4)	4153 (4)	−2484 (4)	6·2
C(7)	2850 (4)	2935 (4)	3813 (4)	6·5
C(8)	5007 (4)	2913 (3)	4175 (4)	5·1
C(9)	4266 (3)	4866 (2)	1324 (3)	4·0
C(10)	5196 (3)	5265 (2)	1301 (3)	3·8
C(11)	3565 (3)	5485 (3)	760 (5)	5·7
N(5)	5907 (3)	5612 (3)	1286 (4)	5·6
C(12)	3348 (2)	1295 (2)	1011 (3)	3·5
C(13)	3193 (3)	293 (3)	658 (5)	5·4
C(14)	4204 (2)	1732 (2)	−1138 (3)	2·9
C(15)	4980 (3)	1684 (3)	−1831 (3)	3·8
C(16)	4860 (3)	1564 (3)	−3002 (4)	5·0
C(17)	3976 (4)	1500 (3)	−3451 (3)	5·1
C(18)	3214 (3)	1562 (3)	−2779 (3)	4·9
C(19)	3313 (3)	1691 (3)	−1632 (3)	3·9
C(20)	5403 (2)	1388 (2)	800 (3)	3·5
C(21)	5558 (3)	375 (3)	468 (4)	4·5

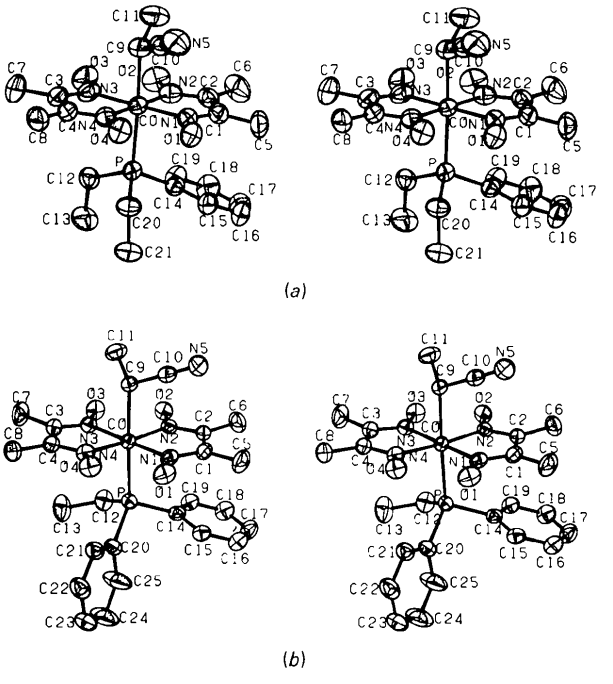

Fig. 1. *ORTEP* drawings of (*a*) *R*-cn-depp (I), and (*b*) *R*-cn-dpep (II), with the numbering of the atoms.

Table 2. *Final atomic coordinates* ($\times 10^5$ *for* Co *and* P, *and* $\times 10^4$ *for* C, N *and* O) *and equivalent isotropic thermal parameters for* R-cn-dpep (II)

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

	x	y	z	B_{eq}(Å^2)
Co	26526 (4)	25000	9438 (4)	2·3
P	44445 (9)	26406 (4)	35919 (8)	2·7
N(1)	4345 (3)	2279 (2)	221 (3)	2·9
N(2)	2772 (3)	1441 (2)	1299 (3)	2·7
N(3)	927 (3)	2717 (2)	1625 (3)	3·0
N(4)	2419 (3)	3547 (2)	416 (3)	3·1
O(1)	5064 (3)	2816 (2)	−401 (3)	4·3
O(2)	1804 (3)	1070 (1)	1921 (3)	3·9
O(3)	228 (3)	2184 (2)	2238 (3)	4·1
O(4)	3288 (3)	3889 (2)	−346 (3)	4·0
C(1)	4787 (4)	1576 (2)	281 (4)	3·4
C(2)	3855 (4)	1077 (2)	924 (4)	3·3
C(3)	400 (4)	3411 (2)	1435 (4)	3·5
C(4)	1290 (4)	3905 (2)	723 (4)	3·4
C(5)	6077 (5)	1312 (3)	−304 (5)	5·4
C(6)	4082 (5)	229 (2)	1110 (5)	5·0
C(7)	−1004 (5)	3660 (3)	1852 (6)	5·6
C(8)	945 (5)	4732 (2)	352 (5)	5·0
C(9)	1013 (3)	2294 (2)	−1346 (3)	3·0
C(10)	1648 (4)	1779 (2)	−2221 (4)	3·7
C(11)	−618 (4)	2022 (2)	−1423 (4)	4·9
N(5)	2128 (4)	1356 (2)	−2914 (4)	5·6
C(12)	3483 (4)	2638 (3)	5116 (4)	4·4
C(13)	2844 (7)	3424 (3)	5370 (5)	6·4
C(14)	5802 (4)	1833 (2)	4167 (4)	3·0
C(15)	7203 (4)	1840 (2)	3796 (4)	3·5
C(16)	8238 (4)	1226 (2)	4203 (5)	4·2
C(17)	7881 (5)	600 (3)	4950 (5)	4·7
C(18)	6501 (5)	590 (2)	5321 (5)	4·5
C(19)	5459 (4)	1197 (2)	4926 (4)	3·7
C(20)	5807 (5)	3444 (2)	4206 (5)	3·7
C(21)	5786 (4)	4056 (2)	3237 (4)	3·5
C(22)	6814 (5)	4668 (3)	3788 (6)	5·0
C(23)	7890 (6)	4661 (3)	5319 (7)	5·9
C(24)	7929 (7)	4054 (4)	6276 (7)	8·5
C(25)	6892 (8)	3449 (3)	5764 (6)	7·8

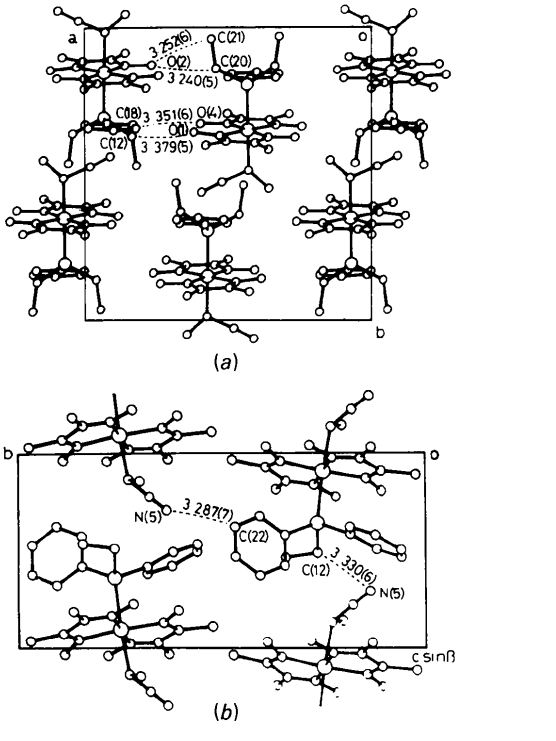

Fig. 2. Crystal structures (*a*) viewed along **c** for *R*-cn-depp (I) and (*b*) viewed along **a** for *R*-cn-dpep (II). Distances are in Å.

Excursions in final difference map, 0·6 (I) and 0·2 (II) e Å^{-3}. Atomic scattering factors including anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). Calculations carried out on the FACOM-HITAC system M-180 computer at this Institute.

Discussion. Final atomic parameters for non-H atoms are given in Table 1 (I) and Table 2 (II).* *ORTEP* drawings (Johnson, 1965) of the molecules with the numbering of the atoms are shown in Fig. 1. The crystal structures are shown in Fig. 2. Neither of the present complexes reveals crystalline-state racemization at 293 K. If the racemization were observed, the ordered cn group would convert into the disordered racemates as found in the crystals of [(*R*)-1-cn][(*S*)-α-methylbenzylamine]cobaloxime, *R*-cn-*S*-mba (Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1981), and [(*S*)-1-cn][(*S*)-α-methylbenzylamine]cobaloxime, *S*-cn-*S*-mba (Ohashi, Sasada & Ohgo, 1978), since each crystal has only one molecule in an asymmetric unit and the cn group is isolated from the other cn groups in the crystal structure. In order to compare the structures around the cn groups with those of the other related crystals, the cavities for the cn groups in the crystals were calculated in the same way as reported previously (Ohashi, Uchida, Sasada & Ohgo, 1983). The volumes of the cavities of (I) and (II) are 8·40 and 10·18 Å^3, respectively, which are smaller than those of *R*-cn-*S*-mba (14·53 Å^3), *S*-cn-*S*-mba (12·23 Å^3), *R*-cn-tbp (10·64 Å^3) and *R*-cn-tpp (11·31 Å^3). The latter two crystals did not reveal racemization at 293 K. The small sizes of the cavities of the present crystals clearly explain the non-reactivity on X-ray exposure.

Fig. 3 shows the projection of each molecule onto the mean plane of the cobaloxime moiety. The torsional

* Lists of structure factors, anisotropic thermal parameters for non-H atoms, positional and thermal parameters for H atoms and bond angles for the two crystals have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39532 (34 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

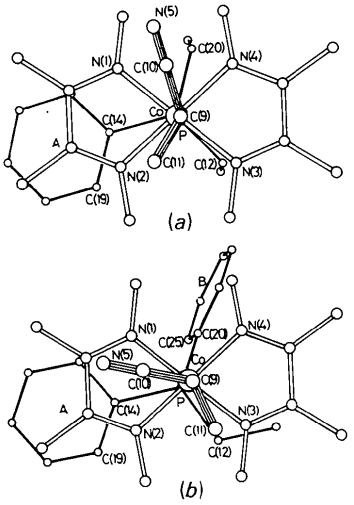

Fig. 3. Projections of the molecules onto the mean planes of the cobaloxime moieties: (*a*) *R*-cn-depp (I) and (*b*) *R*-cn-dpep (II).

Table 3. *Torsion angles* (°) *around the* Co—C *and* Co—P *bonds and the dihedral angles* (°) *between the mean planes of the cobaloxime and the phenyl rings for* *R*-cn-depp (I), *R*-cn-dpep (II) *and* *R*-cn-tpp

	R-cn-depp (I)	*R*-cn-dpep (II)	*R*-cn-tpp
C(10)--C(9)–Co–N(1)	33·6 (3)	−26·1 (3)	−136·3 (10)*
N(3)–Co–P–C(12)	−6·9 (2)	−14·6 (2)	−18·9 (5)
N(2)–Co–P–C(14)	−27·0 (2)	−31·8 (2)	39·6 (5)
N(4)–Co–P–C(20)	33·5 (2)	28·1 (2)	22·5 (5)
Dihedral angle between			
Co(dmg)$_2$ and ring *A*	19·3 (1)	16·1 (1)	15·9 (4)
Co(dmg)$_2$ and ring *B*		84·7 (1)	87·1 (4)
Co(dmg)$_2$ and ring *C*			39·7 (4)

* C(11)–C(9)–Co–N(1) in the original paper.

Table 4. *Bond distances* (Å) *of* *R*-cn-depp (I) *and* *R*-cn-dpep (II)

	R-cn-depp (I)	*R*-cn-dpep (II)
Co–P	2·313 (1)	2·370 (1)
Co–N(1)	1·878 (3)	1·880 (3)
Co- N(2)	1·880 (3)	1·883 (3)
Co–N(3)	1·883 (3)	1·884 (3)
Co–N(4)	1·880 (3)	1·893 (3)
Co–C(9)	2·074 (4)	2·098 (3)
P–C(12)	1·825 (4)	1·839 (4)
P–C(14)	1·812 (3)	1·825 (4)
P–C(20)	1·827 (4)	1·824 (4)
N(1)–O(1)	1·351 (4)	1·363 (4)
N(1)–C(1)	1·295 (5)	1·292 (5)
N(2)–O(2)	1·356 (5)	1·347 (4)
N(2)–C(2)	1·295 (5)	1·299 (4)
N(3)–O(3)	1·350 (5)	1·341 (4)
N(3)–C(3)	1·288 (5)	1·297 (5)
N(4)–O(4)	1·347 (4)	1·337 (4)
N(4)–C(4)	1·305 (5)	1·297 (5)
C(1)–C(2)	1·461 (6)	1·457 (5)
C(1)–C(5)	1·500 (6)	1·496 (7)
C(2)–C(6)	1·496 (7)	1·506 (6)
C(3)–C(4)	1·454 (6)	1·463 (5)
C(3)–C(7)	1·495 (7)	1·494 (7)
C(4)–C(8)	1·493 (6)	1·498 (6)
C(9)–C(10)	1·453 (6)	1·433 (5)
C(9)–C(11)	1·502 (7)	1·518 (6)
C(10)–N(5)	1·136 (6)	1·140 (6)
C(12)–C(13)	1·522 (7)	1·541 (7)
C(14)–C(15)	1·384 (5)	1·404 (5)
C(14)–C(19)	1·406 (5)	1·394 (5)
C(15)–C(16)	1·405 (6)	1·388 (6)
C(16)–C(17)	1·377 (7)	1·378 (6)
C(17)–C(18)	1·354 (7)	1·386 (6)
C(18)–C(19)	1·376 (6)	1·381 (6)
C(20)–C(21)	1·532 (6)	
C(20)–C(21)		1·375 (6)
C(20)–C(25)		1·396 (8)
C(21)–C(22)		1·392 (7)
C(22)–C(23)		1·375 (8)
C(23)–C(24)		1·357 (9)
C(24)–C(25)		1·383 (10)

angles around the Co—C and Co—N bonds and the dihedral angles between the mean planes of the cobaloxime and phenyl rings are listed in Table 3, in which the corresponding values of *R*-cn-tpp are also given. The conformations of the phosphine ligands of *R*-cn-depp and *R*-cn-dpep are very similar to that of *R*-cn-tpp. The rotation angle around the Co—C bond of *R*-cn-dpep has a similar value to those of *R*-cn-tpp and *R*-cn-tbp, whereas that of *R*-cn-depp is similar to those of *R*-cn-*S*-mba and *S*-cn-*S*-mba.

Bond distances of the two molecules are listed in Table 4. The Co—P distance of *R*-cn-depp is approximately the same as that of *R*-cn-tbp, 2·316 (2) Å. The Co—P bond of *R*-cn-dpep is significantly longer than that of *R*-cn-depp and is shorter than that of *R*-cn-tpp, 2·410 (3) Å. The difference in the Co—P distances of the phosphine complexes may be explained by the steric repulsion between the cobaloxime moiety and the phosphine ligand. The Co—C distances are similar to those of *R*-cn-tbp, 2·089 (6) Å, and *R*-cn-tpp, 2·08 (1) Å. Other distances are in good agreement with those of the related complexes.

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Neutron Diffraction Study at 37 K of Sodium Triaqua(ethylenediaminetetraacetato)samarate(III) Pentahydrate, $Na[Sm(C_{10}H_{12}N_2O_8)(H_2O)_3].5H_2O$*

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Abstract. $M_r = 605{\cdot}7$, orthorhombic, *Fdd*2, $T = 37$ (2) K, $a = 19{\cdot}416$ (10), $b = 35{\cdot}315$ (15), $c = 12{\cdot}014$ (6) Å, $V = 8238$ (7) Å^3, $Z = 16$, $D_x = 1{\cdot}953$ g cm^{-3}; $T = 298$ (3) K, $a = 19{\cdot}457$ (10), $b = 35{\cdot}530$ (15), $c = 12{\cdot}108$ (6) Å, $D_x = 1{\cdot}922$, $D_m = 1{\cdot}906$ g cm^{-3}, $\lambda = 1{\cdot}300$ Å, $\mu = 165$ mm^{-1}, $F(000) = 1231 + 46i$ fm. $R = 0{\cdot}059$ based on F^2 and $R_w = 0{\cdot}080$ for 1795 independent reflections (including those with $F_o^2 \leq 0{\cdot}0$) out of 1947 measured and 434 parameters. The refinement was partially anisotropic. All H atoms were located revealing an extensive H-bond network incorporating two water molecules in a disordered arrangement around the twofold axis.

Introduction. The neutron diffraction study of $NaSmA.8H_2O$ (A = edta) originally was undertaken in order to evaluate methods of phase determination based on multiwavelength data exploiting the anomalous scattering of ^{149}Sm for thermal neutrons. A preliminary report of the determination using room-temperature data obtained at three neutron wavelengths, including location of most of the H atoms, was given by Koetzle & Hamilton (1975). The structure is isomorphous with a number of lanthanide–edta complexes investigated by

* Research at Brookhaven National Laboratory performed under contract with the US Department of Energy, Office of Basic Energy Sciences.

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