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Crystalline-State Reaction of Cobaloxime Complexes by X-ray Exposure. XIV. Uneven Racemization at the Independent Reaction Sites

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Abstract

Crystals of [(*R*)-1-cyanoethyl][tri(*p*-chlorophenyl)phosphine]cobaloxime [cobaloxime = bis(2,3-butanedione dioximato)cobalt(III)], $C_{29}H_{30}Cl_3CoN_5O_4P$, $[Co(C_3H_4N)(C_4H_7N_2O_2)_2(C_{18}H_{12}Cl_3P)]$, $M_r = 708{\cdot}8$, reveal crystalline-state racemization of the optically active cyanoethyl group on exposure to X-rays (Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å). At the initial stage, the crystal is triclinic, space group $P\bar{1}$, with $a = 11{\cdot}335(4)$, $b = 11{\cdot}331(4)$, $c = 13{\cdot}717(4)$ Å, $\alpha = 94{\cdot}96\ (8)$, $\beta = 83{\cdot}73\ (5)$, $\gamma = 114{\cdot}38\ (4)°$, $V = 1593\ (1)$ Å^3, $Z = 2$, $D_x = 1{\cdot}478$ g cm^{-3}, $\mu = 8{\cdot}17$ cm^{-1}, $F(000) = 728$ and $T = 293$ K. Changes in the unit-cell dimensions with exposure time are small, and after about 700 h the values become constant. From the intensity data collected for five stages during the change, the structure at each stage was determined, including the occupancy factors of the original and inverted cyanoethyl groups ($R = 0{\cdot}042$, $0{\cdot}048$, $0{\cdot}048$ and $0{\cdot}053$ for stages I, II, III and IV, respectively). The structure analysis showed that the rate of inversion of the cyanoethyl group in one of the independent molecules is much greater than that of the other. With advancing racemization, a pseudo glide plane between the two independent molecules becomes a crystallographic one and in the final stage the crystal is monoclinic, space group Cc, with $a = 19{\cdot}033(8)$, $b = 12{\cdot}308(3)$, $c = 13{\cdot}718(3)$ Å, $\beta = 96{\cdot}64(4)°$, $V = 3192(2)$ Å^3, $Z = 4$, $D_x = 1{\cdot}475$ g cm^{-3} and $R = 0{\cdot}052$. At the two symmetry-related sites, the population ratios of (*R*)- and (*S*)-cyanoethyl groups are 74(1):26(1) and *vice versa*. This characteristic racemization is discussed in terms of cavities [Ohashi, Uchida, Sasada & Ohgo (1983). *Acta Cryst.* B39, 54-61].

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Introduction

Serial studies on the crystals of [(*R*)-1-cyanoethyl]cobaloxime complexes with different base ligands have proved that in these crystals the inversion of the optically active cyanoethyl group (hereafter abbreviated to cn) occurs without degradation of the crystallinity (Ohashi & Sasada, 1977; Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1981, 1982; Ohashi, Uchida, Sasada & Ohgo, 1983; Uchida, Ohashi, Sasada, Ohgo & Baba, 1984; Tomotake, Uchida, Ohashi, Sasada, Ohgo & Baba, 1985; Ohashi, Tomotake, Uchida & Sasada, 1986). The lattice structure kept during the reaction makes possible detailed investigations of the movement of the reactive group and the effect of the surrounding molecules on it. Considering these advantages, we call such a characteristic solid-state reaction a 'crystalline-state reaction'. Depending on the molecular arrangement in the crystal, several complicated reaction modes have been observed (Kurihara, Uchida, Ohashi, Sasada, Ohgo & Baba, 1983; Tomotake *et al.*, 1985; Ohashi *et al.*, 1986). For these modes, we have defined, as a first approximation, a free space for movement of the reactive group as a 'cavity' and found a positive correlation between the cavity volume and the reaction rate (Ohashi *et al.*, 1983).

The present paper deals with the crystalline-state reactions of [(*R*)-1-cyanoethyl][tri(*p*-chlorophenyl)-phosphine]cobaloxime, the crystals of which belong to space group $P\bar{1}$ and in which two independent molecules in an asymmetric unit are related to each other by a pseudo glide operation. The reaction mechanism is discussed in terms of cavities.

Experimental

Crystals of the present complex were obtained from an aqueous methanol solution. Preliminary unit-cell dimensions and space group were deduced from

Table 1. *Crystallographic data at room temperature*

	Stage						
	I	II	III	IV	V Triclinic	V Monoclinic	VI
a (Å)	11·335 (4)	11·335 (3)	11·333 (3)	11·324 (4)	11·332 (3)	19·033 (8)	19·039 (6)
b (Å)	11·331 (4)	11·332 (3)	11·333 (4)	11·324 (4)	11·334 (4)	12·308 (3)	12·307 (2)
c (Å)	13·717 (4)	13·725 (3)	13·707 (3)	13·717 (4)	13·718 (3)	13·718 (3)	13·705 (3)
α (°)	94·96 (8)	95·25 (6)	95·27 (7)	95·41 (8)	95·48 (6)		
β (°)	83·73 (5)	83·92 (4)	84·15 (5)	84·35 (6)	84·34 (4)	96·64 (4)	96·67 (3)
γ (°)	114·38 (4)	114·27 (2)	114·24 (3)	114·18 (4)	114·22 (2)		
V (Å^3)	1593 (1)	1596 (1)	1595 (1)	1594 (1)	1595 (1)	3192 (2)	3190 (2)
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$	Cc	Cc
Z	2	2	2	2	2	4	4

photographs. Intensity measurement was performed at room temperature for the five different stages on a Rigaku four-circle diffractometer. A crystal used for measurement of stage I was exposed to X-rays for 3000 s for determining the orientation matrix. Crystal size 0·3×0·3×0·4 mm, graphite-monochromated Mo $K\alpha$ radiation (50 kV, 25 mA), $\omega/2\theta$ scan, scan rate 8°(2θ) min^{-1}, scan width (1·0+0·35 tan θ)°, stationary background counts accumulated for 5 s before and after each scan, $3<2\theta<55°$, 7306 independent reflexions, h −14 to 14, k −14 to 14, l 0 to 17. Intensity measurement for stage I took 77 h. Lorentz and polarization corrections, absorption effects neglected. Another crystal of 0·5×0·5×0·6 mm, taken from the same crystallization batch, was mounted on the diffractometer for the continuous X-ray exposure and the intensity measurements for the stages II–V. The exposure time was recorded by a timer that worked only when the window of the X-ray tube was open. By use of the hot-air flow method, the crystal was kept at 343 K, but before intensity data collection the crystal was slowly cooled to room temperature and after the measurement it was heated to 343 K. Unit-cell dimensions at every stage were determined with 18 reflexions ($21<2\theta<30°$). Crystal data at room temperature for each stage are given in Table 1. The stages were characterized by the total exposure time; stage II 43–121 h, stage III 235–313 h, stage IV 421–495 h and stage V 602–680 h. Until the end of the stage II, the X-ray generator was operated at 50 kV and 20 mA, and then at 45 kV and 20 mA. Experimental details of the intensity measurement were the same as those for stage I. Since the structure analysis established the space group at stage V to be Cc, the monoclinic unit-cell dimensions are also given in Table 1. To examine gradual changes over a long period, intensity data were collected with the same crystal after it had been kept in a dark room at room temperature for 10 months. This is called stage VI.

Structure determination

Stage I. The crystal structure was solved with *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by block-diagonal least squares with *SHELX*76 (Sheldrick, 1976) and *HBLS V* (Ohashi, 1975). The crystal contains two independent molecules, *A* and *B*. After some cycles of the refinement, the difference electron density map showed a significant peak, the location of which corresponded to the methyl group of the inverted cn group in *B* (hereafter abbreviated to *B*-cn). Random disorder of the cn groups with *R* and *S* configurations was introduced in the refinement, the bond lengths and angles of the cn group being constrained, and the same isotropic temperature factors for the asymmetric C atoms in *B* being assumed. Occupancies of (*R*)- and (*S*)-cn were 0·74(1) and 0·26(1), respectively. The methyl groups of the 2,3-butanedione dioximato group and that of *A*-cn were refined as a rigid body in which C—H was 1·00 Å and ∠H—C—H a tetrahedral angle, and thermal motion of the H atoms was isotropic. The H atoms attached to the asymmetric C atoms and those in the phenyl groups were located geometrically. $\sum w(|F_o|-|F_c|)^2$ was minimized, where $w^{-1}=\sigma^2(|F_o|)+c|F_o|^2$ with $c=0{\cdot}00124$. $R=0{\cdot}042$ ($wR=0{\cdot}059$) for 6954 reflexions with $|F_o|\geq 3\sigma(|F_o|)$.

Stage II. The atomic coordinates for stage I were taken as a starting model, the *B*-cn group with *S* configuration being omitted. The difference map showed peaks due to the (*S*)-cn group. The refinement process was the same as that for stage I.

Stages III *and* IV. Refinement of stage III was initiated from the results of the stage II. Peaks corresponding to the inverted configuration of *A*-cn, in addition to those of *B*-cn, appeared. Similar refinement was undertaken for stage IV. Structural differences from stage III are negligible.

Stage V. Since the changes in the unit-cell dimensions suggested the possibility of a monoclinic cell for stage V, the unit cell was transformed by $\mathbf{a}'=\mathbf{b}-\mathbf{a}$, $\mathbf{b}'=-(\mathbf{a}+\mathbf{b})$ and $\mathbf{c}'=\mathbf{c}$. The space group was assigned as Cc from the systematic extinction. Starting parameters in this space group were obtained by $x'=(y-x)/2$, $y'=-(x+y)/2+1{\cdot}377$ and $z'=z$. Refinement was performed in a similar manner.

Stage VI. Refinement was undertaken starting from the parameters of stage V. Since the structure hardly changed, a full refinement was not undertaken.

Details of the analysis are given in Table 2. Atomic scattering factors including anomalous-dispersion terms were taken from *International Tables for X-ray*

Table 2. *Details of the refinement*

	Stage I	II	III	IV	V
Total exposure time (h)	1-78	43-121	235-313	421-495	602-680
c^*	0·00124	0·00408	0·00130	0·00114	0·00126
Max. Δ/σ	0·3	0·1	0·7	0·2	0·3
Max. $\Delta\rho$ (e Å^{-3})	0·5	0·7	0·4	0·5	0·8
Occupancy (%)					
(*S*)-cn in *A*	0	0	21 (2)	22 (2)	26 (1)
(*S*)-cn in *B*	26 (1)	53 (1)	67 (2)	65 (1)	74 (1)
N†	6954	6965	6789	6749	6597
R	0·042	0·048	0·048	0·053	0·052
wR	0·059	0·072	0·058	0·061	0·059

* Coefficient in the weight function, $w^{-1}=\sigma^2(|F_o|)+c|F_o|^2$.
† Number of reflexions with $|F_o|\geq 3\sigma(|F_o|)$.

Crystallography (1974). The final atomic coordinates are listed in Table 3,* where the atom numbering shown in Fig. 1 is followed by *A* or *B* to indicate the atoms in the independent molecules. For the newly appearing (*S*)-cn groups, the atoms in molecule *A* are labelled by *D* and those in *B* by *C*. At stage V (monoclinic), the atoms in the minor cn group are primed.

Results and discussion

Changes in the unit-cell dimensions

As mentioned in the previous section, stages II-VI were undertaken with one crystal on the goniometer. To accelerate the reaction, the crystal was kept at 343 K during X-ray exposure, but the intensity data were collected at room temperature. On raising of the temperature after the end of the intensity measurements for stage II, linear-expansion coefficients for *a*, *b* and *c* were $10{\cdot}41\times10^{-5}$, $7{\cdot}76\times10^{-5}$ and $4{\cdot}36\times10^{-5}$ K^{-1} respectively. The expansion of the cell was anisotropic, but in the later stages it became more isotropic. Table 1 lists the unit-cell dimensions at each stage. The values for *a* and *b* are the same within experimental error and the sum of α and β approaches 180° with increasing exposure. This suggested that the unit cell is monoclinic at the final stage, and the structure analysis established the space group to be *Cc*. Except for the elevation of the symmetry, the changes in the unit-cell dimensions are very small and the cell volume remains nearly constant.

Crystal structure

Fig. 2 shows the crystal structure at stage I viewed along the *a* axis. The two independent molecules are arranged in a head-to-tail manner with respect to the axial ligands along [1$\bar{1}$1]; the *A*-cn group fits into the depression formed by three *p*-chlorophenyl groups of the phosphine of *B*, and *vice versa*. Each cn group is completely isolated from the other cn groups. There are pseudo *c* and *n* glide planes parallel to (110) between the two independent molecules, except for the chiral cn groups. These local symmetries are converted into the crystallographic ones with advancing inversion of cn. Fig. 3 illustrates the crystal structure

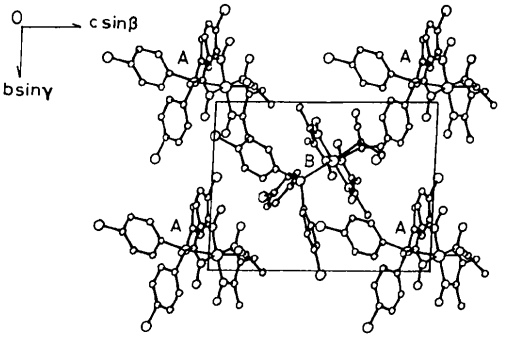

Fig. 2. Crystal structure at stage I, projected along the *a* axis.

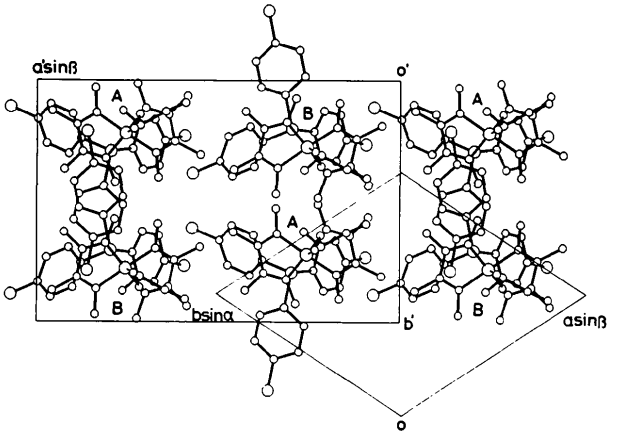

Fig. 3. Crystal structure at stage V, projected along the *c* axis. Relations between the monoclinic and triclinic cells are indicated. Primed letters represent the monoclinic cell.

* Lists of structure factors, anisotropic thermal parameters for non-H atoms, positional and thermal parameters for H atoms, bond lengths and angles at stages I and V and atomic coordinates at the intermediate stages II-IV have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43494 (99 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

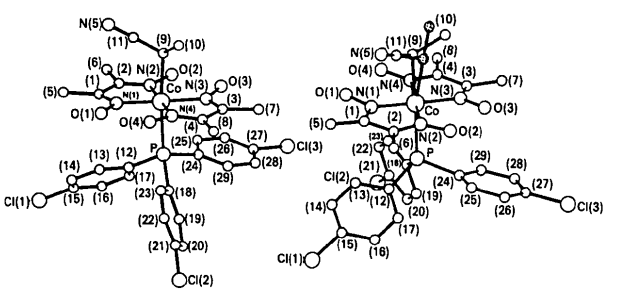

Fig. 1. Structures of molecules *A* and *B* at the stage I, with atom numbering. Atoms of (*S*)-cn disordered in *B* are shaded.

Table 3. *Final atomic coordinates* ($\times 10^5$ *for* Co *and* $\times 10^4$ *for the other non-*H *atoms) and equivalent isotropic temperature factors* (Å^2)

$$B_{eq} = \frac{4}{3}\sum_i \sum_j B_{ij}\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Stage I				
Co(*A*)	40077 (5)	91129 (7)	3975 (6)	2·8
N(1*A*)	5628 (4)	9616 (4)	−325 (4)	3·4
N(2*A*)	3993 (5)	7445 (4)	111 (4)	3·7
N(3*A*)	2406 (5)	8647 (5)	1167 (4)	3·6
N(4*A*)	4079 (4)	10776 (4)	739 (4)	3·2
O(1*A*)	6437 (4)	10855 (4)	−490 (4)	4·7
O(2*A*)	3043 (5)	6387 (4)	467 (4)	4·9
O(3*A*)	1649 (5)	7405 (4)	1392 (4)	4·9
O(4*A*)	5114 (4)	11857 (4)	500 (4)	3·9
C(1*A*)	5985 (6)	8699 (6)	−689 (5)	4·2
C(2*A*)	5007 (7)	7408 (6)	−424 (5)	4·3
C(3*A*)	2062 (6)	9550 (7)	1471 (5)	4·2
C(4*A*)	3036 (6)	10831 (6)	1228 (5)	4·1
C(5*A*)	7261 (9)	8945 (11)	−1227 (8)	6·3
C(6*A*)	5122 (11)	6132 (8)	−681 (9)	7·4
C(7*A*)	794 (9)	9334 (10)	2074 (7)	6·8
C(8*A*)	2989 (10)	12119 (9)	1518 (7)	6·5
C(9*A*)	4780 (7)	9074 (7)	1690 (5)	4·7
C(10*A*)	4864 (9)	10137 (10)	2496 (6)	6·4
C(11*A*)	6009 (7)	8953 (6)	1499 (6)	4·7
N(5*A*)	6968 (7)	8808 (7)	1336 (6)	6·2
P(*A*)	2866 (1)	8808 (1)	−1033 (1)	2·7
Cl(1*A*)	5472 (2)	7351 (2)	−5015 (2)	6·8
Cl(2*A*)	1939 (3)	13397 (3)	−2639 (3)	8·9
Cl(3*A*)	−2726 (2)	4524 (2)	178 (2)	7·0
C(12*A*)	3556 (4)	8290 (4)	−2179 (3)	3·1
C(13*A*)	4797 (5)	9133 (5)	−2520 (4)	4·4
C(14*A*)	5394 (5)	8847 (5)	−3400 (4)	5·0
C(15*A*)	4743 (5)	7726 (5)	−3924 (4)	4·1
C(16*A*)	3517 (5)	6877 (5)	−3603 (4)	4·6
C(17*A*)	2934 (5)	7165 (5)	−2730 (4)	4·2
C(18*A*)	2585 (4)	10152 (4)	−1469 (4)	3·4
C(19*A*)	1635 (6)	9884 (6)	−2111 (5)	5·0
C(20*A*)	1426 (6)	10888 (7)	−2462 (5)	5·9
C(21*A*)	2183 (5)	12129 (6)	−2190 (4)	4·9
C(22*A*)	3151 (6)	12407 (5)	−1595 (5)	5·0
C(23*A*)	3352 (5)	11415 (5)	−1229 (4)	4·2
C(24*A*)	1218 (4)	7551 (4)	−777 (3)	3·0
C(25*A*)	999 (4)	6255 (4)	−810 (4)	3·6
C(26*A*)	−220 (5)	5326 (4)	−526 (4)	4·2
C(27*A*)	−1205 (5)	5709 (5)	−177 (4)	4·4
C(28*A*)	−1002 (5)	6984 (6)	−105 (4)	4·6
C(29*A*)	217 (4)	7915 (4)	−415 (4)	3·7
Co(*B*)	83888 *	35010 *	53987 *	2·8
N(1*B*)	7861 (4)	1925 (5)	4673 (4)	3·4
N(2*B*)	10033 (5)	3466 (5)	5078 (4)	3·7
N(3*B*)	8905 (5)	5073 (5)	6158 (4)	3·8
N(4*B*)	6740 (4)	3485 (5)	5779 (4)	3·3
O(1*B*)	6596 (4)	1141 (4)	4551 (4)	4·5
O(2*B*)	11123 (4)	4398 (5)	5390 (4)	5·3
O(3*B*)	10158 (5)	5761 (5)	6344 (4)	5·3
O(4*B*)	5634 (4)	2474 (4)	5565 (4)	4·1
C(1*B*)	8767 (7)	1552 (7)	4303 (5)	4·4
C(2*B*)	10052 (6)	2478 (7)	4536 (5)	4·2
C(3*B*)	8019 (8)	5444 (7)	6481 (5)	4·6
C(4*B*)	6733 (7)	4517 (7)	6272 (5)	4·3
C(5*B*)	8505 (11)	305 (9)	3768 (7)	6·3
C(6*B*)	11296 (8)	2325 (11)	4215 (9)	7·6
C(7*B*)	8293 (11)	6691 (10)	7097 (8)	7·7
C(8*B*)	5482 (10)	4685 (11)	6574 (7)	7·1
C(10*B*)	8363 (14)	3136 (10)	7600 (5)	6·1
C(10*C*)	7524 (36)	2636 (26)	7523 (12)	8·3
C(11*B*)	8588 (6)	1454 (5)	6448 (5)	4·7
N(5*B*)	8905 (7)	636 (5)	6318 (5)	5·9
P(*B*)	8763 (1)	4710 (1)	3969 (1)	2·7
Cl(1*B*)	10158 (2)	2033 (2)	22 (2)	6·6
Cl(2*B*)	4222 (2)	5644 (2)	2338 (2)	7·5
Cl(3*B*)	13014 (2)	10265 (2)	5107 (2)	7·1
C(12*B*)	9268 (4)	4002 (4)	2835 (3)	2·9
C(13*B*)	8356 (5)	2835 (6)	2482 (4)	4·9
C(14*B*)	8612 (6)	2232 (6)	1613 (4)	5·4
C(15*B*)	9811 (5)	2783 (5)	1111 (4)	3·9
C(16*B*)	10735 (5)	3943 (5)	1428 (4)	4·7
C(17*B*)	10447 (5)	4546 (5)	2287 (4)	4·1
C(18*B*)	7446 (4)	5017 (4)	3537 (4)	3·3
C(19*B*)	7721 (5)	5987 (5)	2904 (4)	4·7
C(20*B*)	6736 (6)	6189 (6)	2531 (5)	5·2
C(21*B*)	5458 (5)	5402 (5)	2809 (4)	4·5
C(22*B*)	5166 (5)	4435 (6)	3418 (4)	4·7
C(23*B*)	6150 (4)	4216 (5)	3802 (4)	4·1
C(24*B*)	10020 (4)	6348 (4)	4192 (3)	3·1
C(25*B*)	11324 (4)	6575 (5)	4147 (4)	3·7
C(26*B*)	12256 (5)	7790 (5)	4405 (4)	4·2
C(27*B*)	11851 (5)	8741 (5)	4760 (4)	4·5
C(28*B*)	10555 (5)	8530 (5)	4864 (4)	4·5
C(29*B*)	9642 (5)	7328 (5)	4568 (4)	3·9
C(9*B*)	8005 (9)	2391 (7)	6628 (6)	4·17 (15)
C(9*C*)	8523 (21)	2723 (12)	6688 (11)	4·17 (15)
Stage V (monoclinic)				
Co	25559 *	72122 (3)	4013 *	3·0
N(1)	2002 (2)	6159 (3)	−309 (3)	3·7
N(2)	1728 (2)	8031 (3)	98 (3)	3·9
N(3)	3112 (2)	8248 (3)	1154 (2)	3·9
N(4)	3365 (2)	6357 (2)	762 (2)	3·3
O(1)	2229 (2)	5131 (2)	−452 (3)	4·9
O(2)	1662 (2)	9047 (2)	433 (3)	5·1
O(3)	2857 (2)	9242 (2)	1363 (2)	5·3
O(4)	3393 (2)	5302 (2)	541 (2)	4·3
C(1)	1374 (2)	6433 (4)	−668 (4)	4·5
C(2)	1210 (2)	7556 (4)	−432 (4)	4·5
C(3)	3741 (3)	7979 (4)	1474 (3)	4·7
C(4)	3897 (2)	6847 (4)	1238 (3)	4·4
C(5)	860 (3)	5652 (5)	−1224 (5)	7·0
C(6)	506 (3)	8100 (6)	−713 (7)	7·6
C(7)	4253 (4)	8701 (6)	2069 (5)	7·5
C(8)	4581 (3)	6286 (5)	1545 (5)	6·7
C(9)	2152 (5)	6882 (6)	1717 (7)	4·6
C(9′)	2164 (13)	6421 (16)	1585 (15)	3·5
C(10)	2632 (4)	6268 (7)	2486 (5)	6·3
C(10′)	2323 (12)	7018 (21)	2596 (14)	6·2
C(11)	1464 (3)	6303 (4)	1496 (4)	5·1
N(5)	912 (3)	5934 (4)	1349 (4)	6·5
P	2970 (1)	7959 (1)	−1038 (1)	2·9
Cl(1)	935 (1)	7318 (1)	−5000 (1)	7·0
Cl(2)	5718 (1)	6131 (1)	−2655 (2)	8·1
Cl(3)	3613 (1)	12871 (1)	135 (1)	7·3
C(12)	2359 (2)	7859 (3)	−2172 (3)	3·2
C(13)	2189 (3)	6812 (3)	−2514 (4)	4·9
C(14)	1762 (3)	6639 (4)	−3377 (4)	5·4
C(15)	1482 (2)	7520 (4)	−3911 (3)	4·3
C(16)	1643 (3)	8556 (4)	−3596 (4)	4·9
C(17)	2083 (3)	8717 (3)	−2745 (3)	4·3
C(18)	3784 (2)	7441 (3)	−1465 (3)	3·3
C(19)	4128 (3)	8062 (4)	−2109 (4)	5·0
C(20)	4732 (3)	7652 (4)	−2472 (4)	5·6
C(21)	4965 (2)	6625 (4)	−2199 (4)	4·9
C(22)	4623 (3)	6014 (4)	−1601 (4)	5·1
C(23)	4021 (2)	6408 (3)	−1222 (3)	4·2
C(24)	3161 (2)	9400 (3)	−807 (3)	3·3
C(25)	2617 (2)	10166 (3)	−862 (3)	3·9
C(26)	2764 (3)	11238 (3)	−586 (4)	4·4
C(27)	3442 (3)	11538 (3)	−226 (4)	4·8
C(28)	3982 (2)	10783 (4)	−135 (4)	4·7
C(29)	3833 (2)	9718 (3)	−433 (3)	3·9

* Fixed.

at stage V, projected along the *c* axis, where the reaction between the monoclinic and original triclinic cells is indicated. A similar change in symmetry, from a pseduo to a true glide plane, has been observed in a crystal of [(*R*)-1-cyanoethyl](4-methylpyridine)cobaloxime (Uchida *et al.*, 1984).

Molecular structure

Fig. 1 shows the molecular structure at stage I, where molecule *B* contains randomly inverted (*S*)-cn groups whose atoms are shaded. Except for the inverted cn group appearing in *A* after stage III, the structures are at all stages very similar to each other. Selected molecular dimensions are given in Table 4. Corresponding bond lengths and angles at all the stages are in good agreement with each other within experimental error.

Table 4. *Selected bond lengths* (Å) *and angles* (°)

	Stage I		
	Molecule *A*	Molecule *B*	Stage V
Co—N(1)	1·875 (5)	1·865 (5)	1·871 (4)
Co—N(2)	1·890 (6)	1·883 (6)	1·877 (4)
Co—N(3)	1·891 (6)	1·884 (6)	1·886 (4)
Co—N(4)	1·873 (5)	1·878 (5)	1·884 (3)
Co—C(9)	2·073 (8)	2·090 (10)	2·083 (10)
Co—C(9′)		2·089 (23)	2·102 (24)
Co—P	2·390 (2)	2·389 (1)	2·392 (1)
P—C(12)	1·839 (5)	1·833 (5)	1·835 (4)
P—C(18)	1·838 (5)	1·832 (5)	1·833 (4)
P—C(24)	1·840 (5)	1·839 (5)	1·832 (4)
N(1)—Co—N(2)	81·9 (2)	81·6 (2)	81·3 (2)
N(3)—Co—N(4)	81·1 (2)	81·3 (2)	81·0 (2)
N(1)—Co—N(4)	97·6 (2)	98·3 (2)	98·3 (2)
N(2)—Co—N(3)	99·3 (2)	98·8 (3)	99·3 (2)
N(1)—Co—C(9)	92·6 (3)	85·8 (3)	94·2 (3)
N(1)—Co—P	93·2 (2)	92·6 (2)	93·2 (1)
Co—P—C(12)	116·8 (2)	115·2 (2)	115·9 (1)
Co—P—C(18)	120·4 (2)	120·3 (2)	120·1 (1)
Co—P—C(24)	107·4 (2)	108·6 (2)	107·9 (1)

The structures of molecules *A* and *B* are mirror images of each other; approximately in the early stages (except for the cn groups) and exactly in the final stage. The deviations from mirror symmetry at stage I are especially significant, though small, in the conformations of the three phenyl groups in the phosphine. In *A*, torsion angle Co—P—C(12)—C(13) is −61·5(4), Co—P—C(18)—C(23) is 22·5(5) and Co—P—C(24)—C(25) is −77·3(4)°, whereas the corresponding values in *B* are 66·4(4), −22·1(5) and 77·1(4)°, respectively. The conformations of triphenylphosphine in the present complex are similar to those in [(*R*)-1-cyanoethyl](triphenylphosphine)cobaloxime (Kurihara *et al.*, 1983).

The plane of one phenyl group [C(18)–C(23)] in each molecule makes dihedral angle of about 72° with the cobaloxime plane, leading to some close contacts between the planes [O(4)···C(23) 3·130(6) and N(4)···C(23) 3·123(6) Å]. The large bond angle found for Co—P—C(18) may result from such repulsion (Kurihara *et al.*, 1983; Kinoshita, Yokota, Matsumoto, Ooi, Kashiwabara & Fujita, 1983).

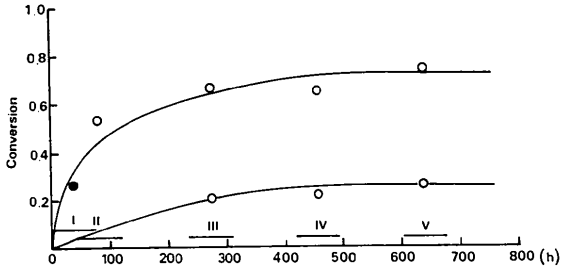

Fig. 4. Conversion into (*S*)-cn *versus* exposure time (h) at 343 K. The duration of intensity measurements for each stage is indicated by a horizontal bar. However, the conversion at stage I occurs at room temperature.

Racemization of the cyanoethyl group

Although the change in unit-cell dimensions is very small, the structure determination shows directly that the proportion of inverted cn groups increases gradually. Fig. 4 plots the conversion into (*S*)-cn groups in *A* and *B* *versus* the exposure time at 343 K. The conversion rate of *B*-cn is much greater than that of *A*-cn. It is noted that *B*-cn is inverted even at room temperature. After an exposure time of about 700 h, the change reaches an equilibrium at which 26% of *A*-cn and 74% of *B*-cn are inverted. Since the two reaction sites are related by a glide symmetry at stage V, the whole crystal is racemic. Such a characteristic racemate structure has not been observed previously. In the crystalline-state racemization of [(*R*)-1-cyanoethyl](3-methylpyridine)cobaloxime (Ohashi *et al.*, 1986), the cn groups of the two independent molecules, *A*- and *B*-cn, are inverted into the opposite configuration in the early stages with an increase in volume of the unit cell. The conversion rate of *B*-cn

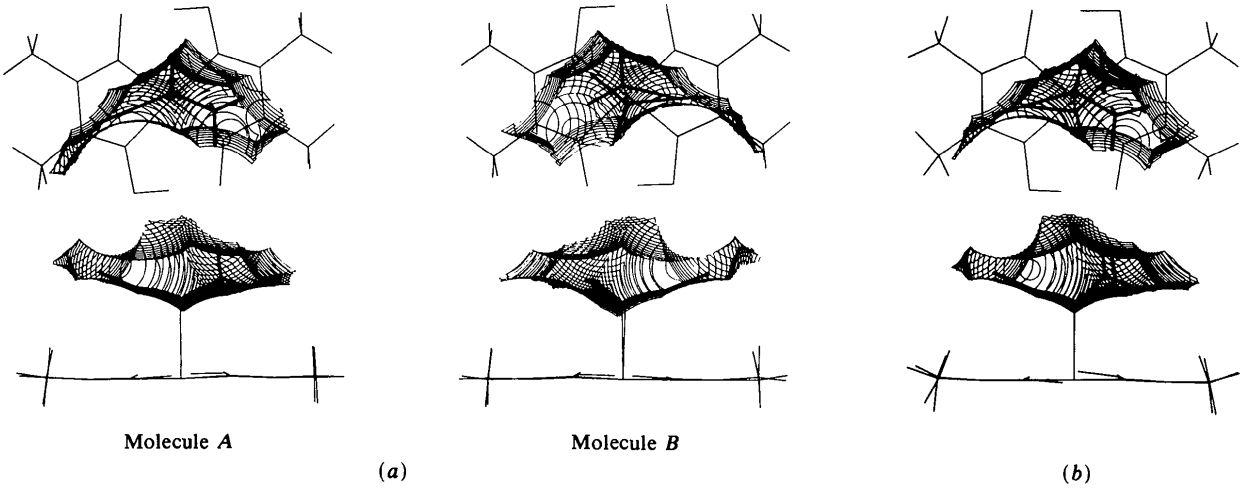

Fig. 5. Cavities at stage I (*a*) and stage V (*b*). The mirror-imaged cavity at stage V corresponding to the *B* cavity is omitted. Contours are drawn in sections separated by 0·1 Å. Upper diagrams are views along the normal to the mean plane of cobaloxime, and lower diagrams their side views.

Table 5. *Volume of the cavity* (Å^3)

	Stage				
	I	II	III	IV	V
A-cn	9·5	9·4	10·0	9·9	10·1
B-cn	10·0	10·1	10·1	10·0	

is about twice that of *A*-cn. After racemization of the crystal as a whole with a 400 h exposure, *B*-cn still continues the inversion, whereas *A*-cn is restored to the original configuration. The volume of the unit cell begins to decrease, and it is suggested that the crystal finally becomes an ordered racemate. In the present crystal, the volume of the cell is kept almost constant, and the back-conversion into the original configuration does not occur.

We have interpreted successfully the reaction behaviour of cobaloxime complexes in terms of 'cavities' - spaces in which the atomic centres of the reactive group can be located freely. Cavities for *A*- and *B*-cn groups (hereafter abbreviated to *A* and *B* cavities) are drawn from the determined crystal structures. Fig. 5 illustrates the cavities at stages I and V, viewed along the normal to, and the short axis of, the cobaloxime skeleton. Shapes of the cavities at the other stages are very similar to the corresponding ones at stage I.

The volumes of the *A* and *B* cavities are 9·5 and 10·0 Å^3, respectively, as shown in Table 5. These values seemed, at the first sight, to be correlated to the different rates of conversion of *A*- and *B*-cn groups, but such an explanation is ambiguous because the latter cavity already contains some inverted cn groups. In addition, these volumes are too small to allow the inversion, considering that each cavity is isolated from the others (Kurihara *et al.*, 1983). However, the cavity wall consists of the tri(*p*-chlorophenyl)phosphine ligand which is rather flexible, and this 'softness' could produce the inversion of the cn group.

To interpret such reaction behaviour, another factor should be taken into account. As seen from Fig. 5, the (*R*)-cn group is well fitted in the *A* cavity; in other words, it is energetically favourable. The presence of (*R*)-cn in the *B* cavity, on the other hand, may be disadvantageous, because the *B* cavity is an approximate mirror image of the *A* cavity. Such a shape effect would accelerate the inversion of *B*-cn from *R* to *S*. However, the accommodation of the preferable enantiomer in the respective cavity leaves a void which can be filled by the opposite enantiomer. Thus, the void offers an entropy gain by mixing cn groups with different configurations. The population ratio of (*R*)- and (*S*)-cn at each site would then be determined by a balance between the enthalpy and entropy terms. Crystalline-state reaction of [(R)-1-cyanoethyl](diphenylmethylphosphine)cobaloxime gives a 1:1 disordered racemate at each of the two independent reaction sites, since the volumes of the corresponding cavities are quite large. This reaction has been classified as mode III, in comparison with the features of the foregoing reactions of cobaloxime complexes (Tomotake *et al.*, 1985). Thus, the present racemization is considered as some modification of mode III, as the enthalpy effect should play a role as well as the entropic driving force. It should be emphasized that the slight difference of the cavity gives rise to the variety of the reaction.

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