Three Polymorphs of (*rac*-1-Cyanoethyl)(pyrrolidine)cobaloxime

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Abstract

Three crystal forms were found for (*rac*-1-cyano-ethyl)bis(2,3-butanedione dioximato)(pyrrolidine)-cobalt(III). Two forms, (I) and (II), were grown from solutions of aqueous methanol and benzene–chloroform, respectively, and the third, (III), was obtained by crystalline-state racemization [Takenaka, Ohashi, Tamura, Uchida, Sasada, Ohgo & Baba (1993). *Acta Cryst.* B49, 272–277]. The structures of (I) and (II) have been determined. (I): [Co(C$_3$H$_4$N)(C$_4$H$_9$N)(C$_4$H$_7$N$_2$O$_2$)$_2$], triclinic, *P*1, *Z* = 4, *a* = 11.723 (2), *b* = 15.658 (3), *c* = 11.118 (2) Å, α = 98.71 (2), β = 90.17 (4), γ = 98.52 (3)°, *V* = 1994.2 (8) Å^3, *R* = 0.065, *wR* = 0.079, M_r = 414.4, D_m = 1.39, D_x = 1.38 Mg m^{-3}, μ(Mo *K*α) = 0.887 mm^{-1}, *F*(000) = 872, *T* = 296 K. (II): [(Co(C$_3$H$_4$N)(C$_4$H$_9$N)(C$_4$H$_7$N$_2$O$_2$)$_2$].$\frac{1}{2}$C$_6$H$_6$, monoclinic, *P*2$_1$/*a*, *Z* = 4, *a* = 16.621 (2), *b* = 18.803 (2), *c* = 9.155 (1) Å, β = 105.03 (2)°, *V* = 2763.4 (7) Å^3, *R* = 0.085, *wR* = 0.105, M_r = 531.6, D_x = 1.28 Mg m^{-3}, μ(Mo *K*α) = 0.655 mm^{-1}, *F*(000) = 1124, *T* = 296 K. Although the crystal structures are very different from each other, the cyanoethyl group conformations are well explained by reaction-cavity differences. The volume of the reaction cavity is indicative of the reactivity of the cyanoethyl groups in the crystals.

Introduction

It has been found that the chiral 1-cyanoethyl (ce) group in crystals of some bis(2,3-butanedione dioximato)cobalt(III), cobaloxime, complexes is racemized by X-ray exposure without crystal degradation (Ohashi, 1988). When the axial base ligand was replaced by other amines or phosphines, a variety of crystalline-state racemizations were observed. Roughly speaking, however, they can be divided into three modes (Tomotake, Uchida, Ohashi, Sasada, Ohgo & Baba, 1985). In the first racemization mode, a chiral group of a crystallographically independent molecule is changed to give the disordered racemates. In the second mode, there are two crystallographically independent molecules in an asymmetric unit and one of the chiral groups is inverted to the opposite configuration; the crystallographic inversion centre appears between the two molecules. In the third mode two crystallographically independent molecules are closely related by a pseudo-inversion centre, and both of the chiral groups are transformed to the disordered racemates.

It has been proposed that the packing around the ce group plays an important role in determining the reactivity of the chiral cobaloxime complex. The reaction cavity was defined as the space limited by a concave surface consisting of the spheres of the surrounding atoms around the reactive group in the crystal (Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1981). Crystalline-state racemization is observed, in any mode, when the volume of the reaction cavity is larger than 11.5 Å^3 (Takenaka, 1993).

In order to analyze the racemic structure produced by X-ray irradiation, some racemic cobaloxime crystals have been prepared from solutions containing the racemic complexes. For the complex with pyridine as an axial base ligand (which belongs to the second mode), the racemic crystal grown from aqueous methanol is the same as that produced by crystalline-state racemization (Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1982). First-mode crystals showing crystalline-state racemization have chiral axial base ligands such as (*R*)-1-phenylethyl-amine (*R*-pea; Takenaka, Kojima & Ohashi, 1993) and (*S*)-1-phenylethylamine (*S*-pea; Ohashi *et al.*, 1981). When the complex has a chiral axial base ligand, inversion of the chiral ce group converts the complex to its diastereomer. This means that the crystal produced by crystalline-state racemization cannot be obtained from solution, since the solubilities of the two diasteromers are usually different from each other.

Recently it was found that crystals of [(*R*)-1-cyanoethyl](pyrrolidine)cobaloxime (*R*-pyrr) race-mize in the first mode (Takenaka, Ohashi, Tamura, Uchida, Sasada, Ohgo & Baba, 1993). In order to examine the racemic crystal more precisely, we tried to prepare it from various solutions. Two different crystals were obtained using different solvents. One was grown from aqueous methanol, crystal (I), and the other grown from a benzene–chloroform solution, crystal (II).

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Table 1. *Atomic coordinates and equivalent isotropic thermal parameters,* B_{eq} (Å²), *for non-H atoms in* (I)

$$B_{eq} = (4/3)\sum_i\sum_j B_{ij}\,\mathbf{a}_i\mathbf{a}_j$$

	x	y	z	B_{eq}		x	y	z	B_{eq}
Co(1A)	0.79694	0.75184	0.68943	3.82 (3)	Co(1C)	0.7069 (1)	0.30248 (9)	0.8320 (1)	3.70 (3)
N(1A)	0.806 (1)	0.6700 (7)	0.5469 (8)	5.6 (3)	N(1C)	0.8558 (7)	0.3708 (5)	0.8554 (7)	4.5 (2)
N(2A)	0.9087 (8)	0.6891 (6)	0.7461 (8)	5.1 (3)	N(2C)	0.7970 (8)	0.2117 (6)	0.7834 (8)	4.6 (2)
N(3A)	0.7937 (8)	0.8361 (6)	0.8295 (8)	5.2 (3)	N(3C)	0.5594 (6)	0.2365 (6)	0.8104 (7)	4.4 (2)
N(4A)	0.6861 (7)	0.8108 (6)	0.6357 (8)	4.7 (2)	N(4C)	0.6185 (7)	0.3920 (6)	0.8814 (8)	4.7 (2)
O(1A)	0.740 (1)	0.6692 (7)	0.4460 (7)	8.7 (4)	O(1C)	0.8690 (7)	0.4545 (5)	0.8950 (8)	6.7 (3)
O(2A)	0.9522 (8)	0.7093 (6)	0.8603 (7)	6.6 (3)	O(2C)	0.7472 (7)	0.1302 (5)	0.7430 (7)	5.6 (2)
O(3A)	0.8554 (8)	0.8364 (6)	0.9304 (6)	6.7 (3)	O(3C)	0.5437 (7)	0.1496 (5)	0.7640 (7)	5.6 (2)
O(4A)	0.6382 (7)	0.7895 (6)	0.5215 (8)	7.3 (3)	O(4C)	0.6647 (8)	0.4760 (5)	0.9170 (9)	7.3 (3)
C(1A)	0.873 (1)	0.6133 (9)	0.554 (1)	7.0 (4)	C(1C)	0.9424 (8)	0.3273 (7)	0.8368 (9)	4.4 (3)
C(2A)	0.932 (1)	0.6240 (8)	0.669 (1)	5.8 (4)	C(2C)	0.9062 (8)	0.2345 (7)	0.7903 (9)	4.0 (3)
C(3A)	0.722 (1)	0.8914 (7)	0.824 (1)	5.4 (3)	C(3C)	0.4725 (9)	0.276 (1)	0.8376 (9)	5.7 (4)
C(4A)	0.6581 (9)	0.8776 (8)	0.705 (1)	5.9 (4)	C(4C)	0.506 (1)	0.3678 (9)	0.8819 (9)	5.7 (3)
C(5A)	0.887 (2)	0.543 (1)	0.447 (2)	11.7 (8)	C(5C)	1.066 (1)	0.3677 (9)	0.856 (1)	6.4 (4)
C(6A)	1.018 (1)	0.566 (1)	0.705 (2)	8.4 (5)	C(6C)	0.991 (1)	0.1720 (9)	0.756 (1)	6.6 (4)
C(7A)	0.710 (2)	0.964 (1)	0.928 (1)	8.8 (5)	C(7C)	0.349 (1)	0.231 (1)	0.821 (1)	8.0 (5)
C(8A)	0.576 (1)	0.936 (1)	0.676 (2)	9.1 (6)	C(8C)	0.422 (1)	0.433 (1)	0.920 (1)	8.1 (5)
N(5A)	0.9292 (7)	0.8307 (6)	0.6236 (8)	4.8 (2)	N(5C)	0.7239 (7)	0.2764 (6)	1.0057 (7)	4.7 (2)
C(9A)	1.020 (1)	0.880 (1)	0.712 (1)	8.4 (5)	C(9C)	0.648 (1)	0.200 (1)	1.046 (1)	7.6 (5)
C(10A)	1.096 (1)	0.946 (1)	0.644 (1)	7.7 (5)	C(10C)	0.681 (2)	0.206 (2)	1.180 (2)	9.7 (7)
C(11A)	1.025 (1)	0.9539 (9)	0.532 (1)	7.0 (4)	C(11C)	0.711 (2)	0.296 (2)	1.224 (1)	9.7 (7)
C(12A)	0.904 (1)	0.9003 (9)	0.553 (1)	6.3 (4)	C(12C)	0.716 (1)	0.349 (1)	1.109 (1)	8.5 (5)
C(13A)	0.674 (1)	0.6671 (9)	0.759 (1)	6.3 (4)	C(13C)	0.707 (1)	0.336 (1)	0.660 (1)	6.5 (4)
C(14A)	0.594 (2)	0.603 (1)	0.669 (2)	12.0 (8)	C(14C)	0.790 (2)	0.304 (2)	0.569 (1)	11.1 (8)
C(15A)	0.608 (1)	0.7135 (9)	0.846 (1)	6.3 (4)	C(15C)	0.589 (1)	0.3297 (8)	0.612 (1)	5.3 (3)
N(6A)	0.550 (1)	0.7455 (9)	0.915 (1)	8.1 (4)	N(6C)	0.499 (1)	0.3235 (8)	0.573 (1)	7.6 (4)
Co(1B)	0.2053 (1)	0.2481 (1)	0.3101 (1)	4.06 (3)	Co(1D)	0.2930 (1)	0.73431 (9)	0.1920 (1)	4.02 (3)
N(1B)	0.2067 (8)	0.3315 (6)	0.4516 (8)	5.0 (3)	N(1D)	0.4132 (7)	0.6660 (6)	0.1690 (7)	4.8 (2)
N(2B)	0.3380 (7)	0.3244 (6)	0.2844 (8)	4.9 (3)	N(2D)	0.4216 (8)	0.8248 (7)	0.2299 (8)	6.0 (3)
N(3B)	0.2054 (8)	0.1646 (7)	0.1690 (8)	5.2 (3)	N(3D)	0.1720 (7)	0.8018 (6)	0.2122 (7)	4.9 (2)
N(4B)	0.0666 (7)	0.1762 (6)	0.3395 (8)	5.0 (2)	N(4D)	0.1685 (6)	0.6444 (5)	0.1530 (8)	4.8 (2)
O(1B)	0.1253 (7)	0.3227 (6)	0.5362 (7)	6.4 (2)	O(1D)	0.3918 (8)	0.5775 (6)	0.1394 (8)	7.0 (3)
O(2B)	0.4019 (7)	0.3110 (6)	0.1796 (8)	6.3 (3)	O(2D)	0.4022 (8)	0.9077 (6)	0.2646 (9)	7.8 (3)
O(3B)	0.2847 (7)	0.1682 (6)	0.0838 (7)	6.7 (3)	O(3D)	0.1915 (7)	0.8886 (5)	0.2511 (8)	6.4 (2)
O(4B)	0.0027 (6)	0.1929 (6)	0.4322 (8)	6.4 (3)	O(4D)	0.1790 (8)	0.5590 (5)	0.1219 (8)	6.8 (3)
C(1B)	0.2921 (8)	0.3967 (7)	0.465 (1)	5.1 (3)	C(1D)	0.5182 (9)	0.7080 (9)	0.1847 (8)	5.8 (3)
C(2B)	0.3693 (8)	0.3914 (8)	0.363 (1)	5.2 (3)	C(2D)	0.5206 (8)	0.8018 (9)	0.2198 (9)	5.6 (3)
C(3B)	0.120 (1)	0.0998 (8)	0.155 (1)	5.6 (3)	C(3D)	0.0684 (7)	0.7597 (7)	0.1878 (8)	4.7 (3)
C(4B)	0.0363 (9)	0.1056 (7)	0.252 (1)	5.4 (3)	C(4D)	0.0655 (9)	0.6652 (7)	0.1526 (8)	5.1 (3)
C(5B)	0.302 (1)	0.468 (1)	0.574 (1)	8.3 (5)	C(5D)	0.620 (1)	0.658 (1)	0.168 (1)	8.3 (5)
C(6B)	0.474 (1)	0.461 (1)	0.357 (1)	7.6 (5)	C(6D)	0.630 (1)	0.867 (1)	0.245 (1)	8.8 (5)
C(7B)	0.107 (1)	0.0294 (9)	0.044 (1)	7.2 (4)	C(7D)	-0.040 (1)	0.8023 (9)	0.203 (1)	6.6 (4)
C(8B)	-0.074 (1)	0.0466 (8)	0.256 (1)	6.9 (4)	C(8D)	-0.043 (1)	0.6035 (9)	0.120 (1)	6.9 (4)
N(5B)	0.3080 (6)	0.1847 (6)	0.4072 (7)	4.3 (2)	N(5D)	0.3149 (7)	0.7529 (6)	0.0155 (7)	5.0 (2)
C(9B)	0.407 (1)	0.1474 (9)	0.344 (1)	6.8 (4)	C(9D)	0.296 (2)	0.843 (1)	-0.017 (1)	9.4 (6)
C(10B)	0.457 (1)	0.0971 (8)	0.435 (1)	6.4 (4)	C(10D)	0.305 (2)	0.831 (2)	-0.156 (2)	11.2 (8)
C(11B)	0.355 (1)	0.0663 (8)	0.508 (1)	6.3 (4)	C(11D)	0.278 (1)	0.732 (2)	-0.200 (1)	11.6 (9)
C(12B)	0.255 (1)	0.1124 (8)	0.471 (1)	6.5 (4)	C(12D)	0.256 (1)	0.687 (1)	-0.085 (1)	8.8 (5)
C(13B)	0.117 (1)	0.3207 (9)	0.215 (1)	6.9 (4)	C(13D)	0.283 (1)	0.710 (1)	0.368 (1)	9.4 (6)
C(14B)	0.062 (2)	0.396 (1)	0.289 (2)	10.0 (6)	C(14D)	0.370 (2)	0.708 (2)	0.443 (1)	17 (1)
C(15B)	0.028 (1)	0.2620 (8)	0.132 (1)	5.4 (3)	C(15D)	0.173 (1)	0.719 (1)	0.417 (1)	7.2 (4)
N(6B)	-0.0409 (9)	0.2215 (8)	0.068 (1)	7.1 (3)	N(6D)	0.088 (1)	0.725 (1)	0.463 (1)	10.3 (6)

The present work was undertaken in order to determine the crystal structures of (I) and (II) and to compare these two forms with the racemic crystal (III) which was produced by crystalline-state racemization of the R-pyrr crystal. The structure of (III) has already been reported (Takenaka, Ohashi *et al.*, 1993).

Experimental

Crystal (I)

Crystal (I) was grown from an aqueous methanol solution of the racemic complex which was in turn prepared by the method reported previously (Ohgo, Takeuchi, Natori, Yoshimura, Ohashi & Sasada, 1981).

A crystal, 0.4 × 0.3 × 0.2 mm, was mounted on a Rigaku AFC-4 four-circle diffractometer. Mo $K\alpha$ graphite-monochromated radiation was used (40 kV,

20 mA, $\lambda = 0.7107$ Å). Unit-cell parameters were determined from 15 2θ values in the range $20 \le 2\theta \le 25°$. Three-dimensional intensity data were measured up to $\sin\theta/\lambda \le 0.65$ Å^{-1} ($-13 \le h \le 13$, $-18 \le k \le 18$, $0 \le l \le 13$) by means of an $\omega-2\theta$ scan technique at 8° min^{-1} in 2θ. Three monitored reflexions did not show significant variation. A total of 7013 reflexions were measured, of which 6295 with $|F| > 3\sigma(F)$ were used.

The structure was solved by direct methods using *MULTAN*78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by the full-matrix least-squares technique in *SHELX*76 (Sheldrick, 1976), based on F and with $w = [\sigma^2(|F_o|) + 0.0019|F_o|^2]^{-1}$. Anisotropic thermal parameters were applied to non-H atoms. H atoms bonded to O were refined with fixed thermal parameters, those belonging to pyrrolidine or C(13) were located by

Table 2. *Atomic coordinates and equivalent isotropic thermal parameters, B_{eq} (Å^2), for non-H atoms in* (II)

Site occupancies of C(14R) and C(14S) are 0.688 (6) and 0.312 (6), respectively.

$$B_{eq} = (4/3)\Sigma_i\Sigma_j B_{ij}\mathbf{a}_i\mathbf{a}_j$$

	x	y	z	B_{eq}
Co	0.46935 (3)	0.26150 (3)	0.52078 (6)	3.04 (2)
N(1)	0.5029 (2)	0.2592 (2)	0.3408 (5)	4.0 (1)
N(2)	0.5208 (2)	0.3507 (2)	0.5344 (5)	4.0 (1)
N(3)	0.4358 (3)	0.2639 (3)	0.7015 (4)	4.4 (1)
N(4)	0.4190 (2)	0.1713 (2)	0.5088 (5)	4.0 (1)
O(1)	0.4897 (3)	0.2028 (2)	0.2467 (4)	5.5 (1)
O(2)	0.5252 (3)	0.3951 (2)	0.6525 (4)	5.6 (1)
O(3)	0.4498 (3)	0.3204 (2)	0.7956 (4)	5.9 (1)
O(4)	0.4173 (3)	0.1264 (2)	0.3935 (5)	6.0 (1)
C(1)	0.5392 (3)	0.3148 (3)	0.3069 (6)	4.3 (1)
C(2)	0.5503 (3)	0.3702 (3)	0.4221 (6)	4.3 (1)
C(3)	0.3942 (3)	0.2096 (3)	0.7305 (6)	4.7 (1)
C(4)	0.3850 (3)	0.1542 (3)	0.6166 (7)	4.9 (2)
C(5)	0.5698 (4)	0.3227 (4)	0.1671 (7)	6.7 (2)
C(6)	0.5913 (4)	0.4405 (3)	0.4190 (9)	6.7 (2)
C(7)	0.3621 (4)	0.2052 (5)	0.8679 (7)	7.8 (2)
C(8)	0.3411 (5)	0.0864 (4)	0.6236 (9)	8.0 (2)
N(5)	0.3537 (2)	0.3027 (2)	0.4133 (4)	3.6 (1)
C(9)	0.3388 (4)	0.3795 (3)	0.4246 (8)	6.4 (2)
C(10)	0.2543 (4)	0.3956 (4)	0.3164 (9)	7.3 (2)
C(11)	0.2418 (4)	0.3367 (4)	0.2044 (8)	7.4 (2)
C(12)	0.3153 (4)	0.2875 (4)	0.2519 (7)	7.1 (2)
C(13)	0.5801 (3)	0.2169 (3)	0.6327 (7)	5.0 (1)
C(14R)	0.6066 (7)	0.2224 (6)	0.803 (1)	7.6 (2)
C(14S)	0.587 (2)	0.148 (1)	0.659 (3)	7.6 (2)
C(15)	0.6492 (3)	0.2391 (3)	0.5773 (6)	5.1 (1)
N(6)	0.7043 (3)	0.3562 (4)	0.5316 (7)	7.5 (2)
C(B1)	0.3653 (6)	0.4498 (5)	0.957 (1)	8.6 (2)
C(B2)	0.3736 (5)	0.5043 (5)	1.060 (1)	8.6 (2)
C(B3)	0.3186 (6)	0.5572 (5)	1.037 (1)	8.8 (3)
C(B4)	0.2560 (6)	0.5574 (5)	0.917 (1)	8.8 (3)
C(B5)	0.2449 (5)	0.5040 (7)	0.8132 (9)	9.8 (2)
C(B6)	0.3008 (6)	0.4480 (6)	0.8376 (9)	8.8 (2)
C(B7)	0.0676 (6)	0.4677 (5)	0.975 (1)	9.1 (2)
C(B8)	0.0338 (5)	0.4400 (5)	1.077 (1)	7.9 (2)
C(B9)	0.0301 (6)	0.5252 (6)	0.886 (1)	9.8 (2)

geometric calculations, and methyl groups were treated as rigid groups with constraints on C—H = 1.0 Å. Positions of H atoms are required later in order to calculate the reaction cavity and the packing potential energy. A total of 1018 parameters were refined. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). Final R and wR values were 0.065 and 0.079, respectively, $S = 1.20$, and $\Delta/\sigma < 0.35$. No peak higher than 0.5 e Å^{-3} was found in the difference map except for a peak between molecules (0.75 e Å^{-3}). No absorption or extinction corrections were applied. The atomic parameters for non-H atoms are given in Table 1.*

Crystal (II)

Crystal (II) was grown from a benzene–chloroform solution. A crystal, 0.6 × 0.5 × 0.3 mm,

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was mounted in a glass capillary. Unit-cell parameters were determined in the range $22 \leq 2\theta \leq 30°$. Three-dimensional intensity data were measured using Mo $K\alpha$ radiation (45 kV, 20 mA, $\lambda = 0.7107$ Å) up to $\sin\theta/\lambda \leq 0.65$ Å^{-1} ($-21 \leq h \leq 20$, $0 \leq k \leq 24$, $0 \leq l \leq 11$). The orientation matrix was redetermined when the intensity of standard reflexions varied by more than $6\sigma(|F|)$. A total of 6665 reflexions were measured, of which 5105 with $|F| > 3\sigma(|F|)$ were used. Other conditions were the same as for crystal (I).

The structure was solved using *MULTAN78* and refined with *SHELX76* where $w = [\sigma^2(|F_o|) + 0.0024|F_o|^2]^{-1}$. The methyl of the ce group was treated as a disordered structure and was refined isotropically with the same thermal parameters for both C atoms. Other non-H atoms were refined anisotropically. H atoms were treated using the same methods as for crystal (I) except for those bonded to C(13) which were not included. A total of 339 parameters were refined. The site occupancy of the ce group was $R:S = 0.688:0.312$ (6). Final R and wR values were 0.085 and 0.105, respectively, $S = 1.05$, and $\Delta/\sigma < 0.27$. No peak higher than 0.73 e Å^{-3} (0.9 Å from Co) was found in the difference map. Atomic parameters are given in Table 2.

Results and discussion

Molecular and crystal structure

The crystal structure of (I) is shown in Fig. 1(a). There are four independent molecules, A, B, C and D, in the asymmetric unit. Molecules A and B have ce groups with the R configuration, whereas molecules C and D have S-ce groups. The N atom of the ce group of molecule A is hydrogen bonded to the NH group of the pyrrolidine of the neighbouring molecule D and the N atom of the ce group of molecule D forms an N···HN hydrogen bond with another A molecule. These hydrogen bonds connect molecules A and D along [10$\bar{1}$] as columns of type A–D–A–D. By contrast, the ce group of molecule C is hydrogen bonded to the NH group of the pyrrolidine of molecule B and the ce group of molecule B is bonded to the NH group of another C molecule. This second column, which is composed of C–B–C–B chains, runs along [101] in the vicinity of the A–D column. In both columns ce groups which have the opposite configuration to each other are connected alternately, since molecules A and B have the R and molecules C and D have the S configuration. Distances relating the hydrogen bonds are listed in Table 3.

Fig. 1(b) shows the crystal structure of (II). The asymmetric unit consists of one complex and two solvent benzene molecules. One of the benzene molecules lies on an inversion centre and the other

occupies a general position. These solvent molecules form columns along the *a* axis. The distances between the benzene rings are not equivalent. The N atom of the ce group is hydrogen bonded to the NH group of the pyrrolidine of neighbouring molecules which are related by a glide plane and the molecules are connected in the form of a column along the *a* axis. Hydrogen-bonded distances are also given in Table 3.

In (III) the N atom of the ce group is hydrogen bonded to the solvent water molecule, which forms a hydrogen bond with the NH group of the pyrrolidine of the neighbouring molecule and the O atom of the cobaloxime moiety of another molecule. The hydrogen bonds form a three-dimensional network.

The molecular structures of (I) and (II), together with the numbering systems, are shown in Fig. 2, in which only molecule A of (I) is shown for clarity. Selected bond distances and angles are listed in Table 4. The corresponding distances and angles are substantially the same. The ce group of (II) has a disordered structure, but the occupancy factors of the two methyl groups, C(14R) and C(14S), are different.

Table 3. *Hydrogen-bond distances* (Å)

(I)

N(6A)···N(5D')	2.99 (1)	N(6C)···N(5B)	3.24 (1)
N(6B)···N(5C'')	3.11 (1)	N(6D)···N(5A''')	3.07 (1)

(II)

N(6)···N(5'''')	3.156 (7)

Symmetry codes: (i) x, y, $z + 1$; (ii) $x - 1$, y, $z - 1$; (iii) $x - 1$, y, z; (iv) $x + \frac{1}{2}$, $-y + \frac{1}{2}$, z.

Conformation of the cyanoethyl group

Fig. 3 shows the conformations of the ce groups, projected onto the cobaloxime planes, for each of the three crystals. All of the cyano groups in the ce groups are located in the direction of the long axes of the cobaloxime planes. Similar conformations have been observed in crystals of the related (*R*)-1-

(a)

(b)

Fig. 1. Crystal structures of (a) (I) and (b) (II). Hydrogen bonds are indicated by dotted lines.

(a)

(b)

Fig. 2. Molecular structures, with atom-numbering schemes, for (a) molecule A in (I) and (b) (II).

Table 4. *Selected bond distances* (Å), *angles* (°) *and torsion angles* (°)

	(I)				(II)	(III)
	A	*B*	*C*	*D*		
Co—C(13R)	2.05 (1)	2.05 (2)			2.041 (5)	2.062 (9)
Co—C(13S)			2.06 (1)	2.05 (1)	=	2.073 (7)
C(13R)—C(14R)	1.51 (2)	1.56 (2)			1.51 (1)	1.50 (2)
C(13S)—C(14S)			1.49 (2)	1.32 (2)	1.31 (3)	1.54 (1)
C(13R)—C(15R)	1.42 (2)	1.49 (2)			1.432 (8)	1.47 (1)
C(13S)—C(15S)			1.46 (2)	1.42 (2)	=	1.45 (1)
C(15R)—N(6R)	1.14 (2)	1.13 (1)			1.148 (8)	1.11 (1)
C(15S)—N(6S)			1.12 (2)	1.13 (2)	=	1.12 (1)
Co—C(13R)—C(14R)	117 (1)	117 (1)			118.3 (6)	116.7 (8)
Co—C(13S)—C(14S)			120 (1)	127 (1)	121 (1)	114.4 (5)
Co—C(13R)—C(15R)	110.5 (9)	110.0 (9)			113.8 (4)	110.3 (7)
Co—C(13S)—C(15S)			111.2 (8)	112 (1)	=	111.8 (5)
C(14R)—C(13R)—C(15R)	110 (1)	110 (1)			107.5 (6)	111.1 (9)
C(14S)—C(13S)—C(15S)			114 (1)	118 (1)	108 (1)	110.4 (7)
N(1)—Co—C(13R)—C(14R)	−30 (1)	−13 (1)			−17.7 (6)	12.4 (7)
N(2)—Co—C(13S)—C(14S)			−15 (1)	−40 (2)	2 (1)	25.4 (5)
N(3)—Co—C(13R)—C(15R)	24 (1)	39.9 (9)			34.5 (5)	65.0 (6)
N(3)—Co—C(13S)—C(15S)			22 (1)	23 (1)	=	53.7 (5)

cyanoethyl cobaloximes which have tributylphosphine (Kurihara, Uchida, Ohasi, Sasada, Ohgo & Baba, 1983), triphenylphosphine (Kurihara *et al.*, 1983), ethyldiphenylphosphine (Tomotake, Uchida, Ohashi, Sasada, Ohgo & Baba, 1984), 3-methylpyridine (Ohashi, Tomotake, Uchida & Sasada, 1986), tri(*p*-chlorophenyl)phosphine (Danno, Uchida, Ohashi, Sasada, Ohgo & Baba, 1987), and *R*-pyrr (Takenaka, Ohashi *et al.*, 1993) as axial base ligands. Potential calculations for *R-S*-pea and *S-S*-pea complexes reveal that this conformation is energetically less stable than that in which the cyano group lies along the short axis of the cobaloxime plane (Ohashi, 1977). The energy gap between these conformations was calculated to be about 4 kJ mol⁻¹ and the effects of hydrogen bonding of

the ce groups and packing forces around the ce group could override this energy.

In order to explain the various ce group conformations, the reaction cavity was drawn for the crystals described here. Fig. 3 shows the ce group cavities, the volumes of which are listed in Table 5. It can be clearly seen that the cavities of molecules *A* and *B* in (I) have volumes smaller than 10 Å³ and their shapes are only suitable for acceptance of *R*-ce groups. However, the cavities of molecules *C* and *D* are large enough to accommodate either *R*- or *S*-ce groups and therefore the ce groups of molecules *C* and *D* may be converted to the disordered structures if the crystal is irradiated with visible light or X-rays. The
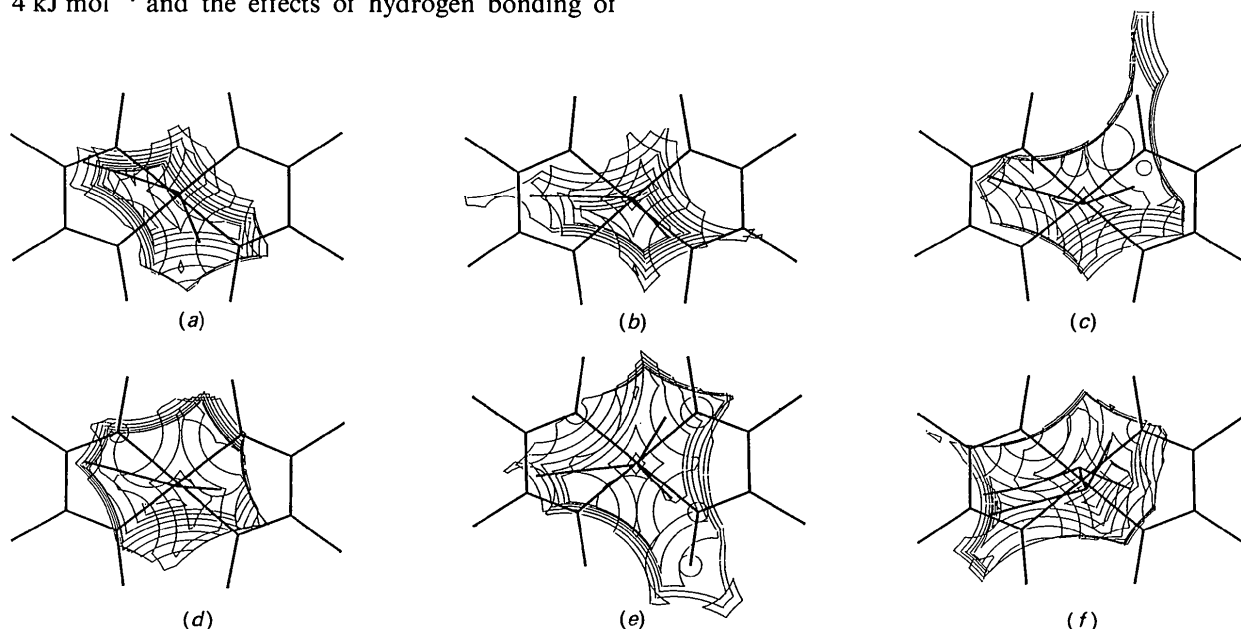

Fig. 3. Cavity around the cyanoethyl group projected onto the cobaloxime plane. Contours are drawn in sections separated by 0.2 Å. (*a*) Molecule *A* in (I), (*b*) molecule *B* in (I), (*c*) molecule *C* in (I), (*d*) molecule *D* in (I), (*e*) (II), (*f*) (III).

Table 5. *Cavity volume* ($Å^3$) *and packing potential energy* (*PPE*; kJ mol^{-1})

A, B, C and *D* refer to the packing potential energy for the respective molecule (see text). *R* and *S* refer to the configuration of the cyanoethyl group.

	Cavity	PPE Crystal	Molecule
Crystal (I)			
		−562.7	
A	9.4		−168.2
B	6.9		−177.0
C	12.9		−165.3
D	13.8		−163.8
Crystal (II)			
	14.2	−236.8	
R			−159.8
S			−159.8
Crystal (III)			
	12.6	−166.4	

volume of the cavity in (II) is larger than that in (I) and large enough to accommodate either *R*- or *S*-ce groups and is therefore responsible for the disordered structure. Since the cavity in (III) is smaller than in (II), the cyano group must adjust its position in order to accommodate the inverted methyl group. The difference in cavity size (14.2 and 12.6 $Å^3$) may be responsible for the different disordered structures.

Packing potential energy

In order to explain the conformation of the ce group in each molecule more quantitatively, packing potential energies were calculated for all of the crystals using the program *OPEC* (Gavezzotti, 1983). Pairwise potentials were applied, which are functions of interatomic distances. Atom pairs within 7 Å separation were included. The packing potential energy for each molecular fragment was calculated as,

$$E_i = \sum_{j \in S} E_{ij} + \overset{\text{asymmetric unit}}{\underset{i \neq j}{\sum}} E_{ij},$$

where E_{ij} is the potential energy between molecular fragments *i* and *j*, and *S* refers to the surrounding molecules in the neighbouring asymmetric unit. Contributions from atom pairs involved in hydrogen bonding were omitted because the packing potential energy does not depend on electrostatic effects. The results are listed in Table 5. The reaction cavity is a function of interatomic distance and direction from neighbouring atoms around the reactive group weighted by the van der Waals radii of the surrounding atoms. The packing potential energy is another function of interatomic distances but is weighted by the interatomic energy of the atom pair which is

specific to the pair and embedded in the parameters of the pairwise potential. For (I), the order of the packing potential energy for each molecule is *B, A, C* and *D*. This result coincides excellently with the cavity-size order for the ce group.

The packing potential energies for each conformation of (II) are equal as listed in Table 5. However, the site occupancy factor was determined to be *R:S* = 0.69:0.31, approximately 2:1, by the structure analysis. This difference in site occupancy cannot be explained by the packing potential energy. The volume of the reaction cavity for (II) is 14.2 $Å^3$, larger than the value of 11.5 $Å^3$ which is required for first-mode racemization to take place (Takenaka, Ohashi *et al.*, 1993). It can be supposed that the site occupancy of each methyl in the ce group of (II) will become equal to 0.5:0.5 if it is exposed to visible light or X-rays.

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