Structure of the Racemate Produced by X-ray Exposure of Bis(2,3-butanedione dioximato)[(R)-1-methoxycarbonylethyl](pyridine)cobalt(III)

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Abstract. $C_{17}H_{26}CoN_5O_6$, $[Co(C_5H_5N)(C_4H_7N_2O_2)_2(C_4H_7O_2)]$, $M_r = 455.36$, monoclinic, $P2_1/n$, $a = 9.288$ (1), $b = 19.952$ (2), $c = 11.397$ (1) Å, $\beta = 94.10$ (2)°, $V = 2106.6$ (5) Å^3, $Z = 4$, $D_x = 1.436$ g cm^{-3}, μ(Mo $K\alpha$) = 8.91 cm^{-1}. The structure was solved by the direct method and refined by constrained least squares. The final R was 0.089 for 2087 reflections. Molecules are packed in pairs across a center of symmetry so that the disordered 1-methoxycarbonylethyl groups of the two molecules are sandwiched by the two (2,3-butanedione dioximato)-cobalt moieties and face each other.

Introduction. It has been found that the chiral 1-cyanoethyl group, $-C^*H(CH_3)CN$, bonded to cobalt in the crystals of complexes of bis(2,3-butanedione dioximato)cobalt (cobaloxime), is racemized by X-ray exposure without degradation of the crystallinity (Ohashi & Sasada, 1977a; Ohashi, Sasada & Ohgo, 1978; Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1981, 1982). In order to examine the crystalline-state racemization more extensively, the reacting group was replaced by the 1-methoxycarbonylethyl group (mce group). The complex of [(R)-1-mce](pyridine)cobaloxime (1) also revealed racemization by X-ray exposure at room temperature. However, it was impossible to collect the three-dimensional intensity data at the initial stage, since the rate of racemization was too rapid. This paper presents the structure of the racemate from (1) by X-ray exposure.

Unit-cell dimensions were determined by a least-squares fit to setting angles for 12 reflections on a Rigaku four-circle diffractometer. Initially a, b, c, β, and V were 9.289 (3), 21.058 (6), 11.498 (4) Å, 94.16 (3)°, and 2243 (1) Å^3, respectively, with space group $P2_1$. After a week they converged to the values given in the *Abstract*. Intensities of $h0l$ reflections with $h + l$ odd became negligibly small. This indicated that the space group changed from $P2_1$ to $P2_1/n$, so that the enantiomeric crystal was transformed to the racemic one.

Intensity data of the racemate up to $2\theta \le 45°$ were collected using a crystal of $0.35 \times 0.30 \times 0.10$ mm with Mo $K\alpha$ radiation monochromatized by graphite, an ω–2θ scan at 8° (2θ) min^{-1} for a scan range of $(1.0 + 0.35 \tan\theta)°$. Stationary background counts were accumulated for 5 s before and after each scan. 2087 reflections with $|F_o| \ge 3\sigma(|F_o|)$ were used for the structure determination. No corrections for the absorption and extinction were made. The structure was solved by the direct method using *MULTAN* 78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and refined by constrained least squares with *SHELX* 76 (Sheldrick, 1976) in order to avoid the parameter interaction between the disordered mce groups. In the

Table 1. *Final atomic coordinates* ($\times 10^4$) *for non-hydrogen atoms with e.s.d.'s in parentheses and equivalent isotropic thermal parameters* (Å^2)

	x	y	z	B_{eq}
Co	5879 (1)	6654 (1)	3717 (1)	2.8
O(1)	7493 (7)	6689 (4)	5926 (5)	5.1
O(2)	2819 (7)	6702 (4)	3281 (6)	4.7
O(3)	4254 (7)	6612 (4)	1512 (6)	4.7
O(4)	8954 (7)	6628 (4)	4161 (6)	5.3
N(1)	6207 (7)	6681 (4)	5363 (5)	3.8
N(2)	3947 (6)	6684 (4)	4096 (5)	3.4
N(3)	5571 (7)	6596 (3)	2077 (5)	3.5
N(4)	7830 (6)	6607 (4)	3353 (6)	3.7
C(1)	5041 (10)	6698 (5)	5956 (7)	3.8
C(2)	3699 (10)	6693 (5)	5208 (7)	3.8
C(3)	6712 (10)	6535 (5)	1496 (8)	4.0
C(4)	8048 (10)	6552 (5)	2259 (9)	4.5
C(5)	5132 (13)	6711 (6)	7280 (8)	6.2
C(6)	2237 (10)	6699 (5)	5670 (10)	5.9
C(7)	6658 (14)	6473 (7)	162 (8)	7.4
C(8)	9525 (10)	6452 (5)	1774 (9)	5.5
N(5)	5928 (7)	7684 (3)	3662 (5)	3.1
C(9)	4932 (9)	8031 (5)	3029 (7)	3.9
C(10)	4902 (10)	8716 (5)	2952 (8)	4.7
C(11)	5966 (11)	9080 (5)	3587 (8)	4.6
C(12)	6999 (11)	8709 (5)	4250 (9)	4.9
C(13)	6936 (8)	8042 (5)	4295 (7)	3.7
C(14)	5757 (5)	5616 (3)	3870 (3)	4.8
C(15P)	4784 (10)	5272 (7)	2948 (11)	5.8
C(16P)	7242 (5)	5381 (7)	3788 (14)	14.1
O(5P)	7672 (15)	5060 (10)	2986 (15)	12.2
O(6P)	7686 (18)	5250 (10)	4911 (14)	8.9
C(17P)	9168 (21)	5048 (20)	4982 (47)	15.4
C(15Q)	7157 (11)	5268 (8)	4214 (10)	6.4
C(16Q)	5205 (11)	5385 (5)	2702 (5)	9.6
O(5Q)	5856 (15)	5039 (8)	2049 (8)	9.4
O(6Q)	3802 (13)	5282 (8)	2849 (14)	7.5
C(17Q)	3013 (41)	5081 (16)	1782 (22)	14.3

final refinement, the non-hydrogen atoms were refined anisotropically, and the atoms of the disordered mce groups were constrained tightly to have the same bond distances as observed in the structure of [(R)-1-mce]-[(R)-α-methylbenzylamine]cobaloxime (2) (Ohashi & Sasada, 1977b). The methyl hydrogen atoms were refined under constraint with the fixed C—H distance of 1·08 Å. The occupancy factors of the disordered mce groups, P and Q, converged to 0·46 (1) and 0·54 (1), respectively. The weighting scheme $w = [\sigma(|F_o|)^2 + 0.00236F_o^2]^{-1}$ was employed. The final R value was 0·089 for 2087 reflections. Atomic scattering factors were taken from International Tables for X-ray Crystallography (1974). The final atomic coordinates are given in Table 1.*

Discussion. The molecular structure with the disordered mce groups and the numbering of the atoms is shown in Fig. 1. Bond distances and angles of the cobaloxime moiety listed in Table 2 are in good agreement with the corresponding ones for (2) and related cobaloxime complexes (Ohashi, Sasada, Takeuchi & Ohgo, 1980a, b). The torsional angles of N(3)—Co—N(5)—C(9), N(4)—Co—C(14)—C(16P) and N(3)—Co—C(14)—C(16Q) are 47·3 (7), 7·6 (8) and 11·5 (6)°, respectively. The molecule with the disordered mce groups has an approximate mirror plane lying perpendicular to the cobaloxime plane and passing through the long axis of cobaloxime.

Fig. 2 shows the crystal structure viewed along the c axis. Molecules are packed in pairs across a center of symmetry. There is no unusually short contact between

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* Lists of structure factors, anisotropic thermal parameters for non-hydrogen atoms, and positional and thermal parameters for hydrogen atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 36895 (12 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
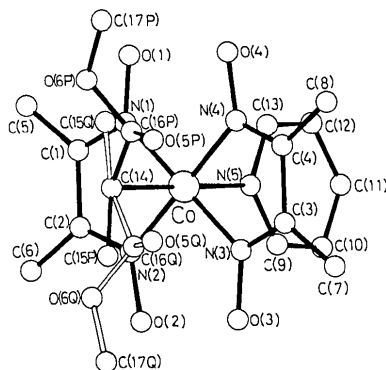
Table 2. *Bond lengths* (Å) *and angles* (°) *with e.s.d.'s in parentheses*

Co–N(1)	1·880 (8)	C(3)–C(7)	1·523 (10)
Co–N(2)	1·876 (8)	C(4)–C(8)	1·528 (10)
Co–N(3)	1·874 (7)	N(5)–C(9)	1·326 (12)
Co–N(4)	1·890 (8)	N(5)–C(13)	1·345 (12)
Co–N(5)	2·058 (7)	C(9)–C(10)	1·370 (15)
Co–C(14)	2·083 (7)	C(10)–C(11)	1·387 (15)
O(1)–N(1)	1·315 (11)	C(11)–C(12)	1·391 (15)
O(2)–N(2)	1·350 (10)	C(12)–C(13)	1·334 (14)
O(3)–N(3)	1·342 (10)	C(14)–C(15P)	1·501 (15)
O(4)–N(4)	1·343 (11)	C(14)–C(16P)	1·466 (17)
N(1)–C(1)	1·318 (12)	C(14)–C(15Q)	1·501 (17)
N(2)–C(2)	1·305 (12)	C(14)–C(16Q)	1·466 (13)
N(3)–C(3)	1·294 (12)	C(16P)–O(5P)	1·208 (25)
N(4)–C(4)	1·282 (13)	C(16P)–O(6P)	1·342 (25)
C(1)–C(2)	1·459 (14)	O(6P)–C(17P)	1·431 (57)
C(1)–C(5)	1·506 (10)	C(16Q)–O(5Q)	1·208 (19)
C(2)–C(6)	1·491 (10)	C(16Q)–O(6Q)	1·342 (19)
C(3)–C(4)	1·464 (14)	O(6Q)–C(17Q)	1·431 (42)

N(1)–Co–N(2)	81·9 (3)	N(2)–C(2)–C(6)	124·9 (8)
N(1)–Co–N(3)	178·0 (3)	C(1)–C(2)–C(6)	123·7 (8)
N(1)–Co–N(4)	97·5 (3)	N(3)–C(3)–C(4)	112·6 (8)
N(1)–Co–N(5)	90·0 (3)	N(3)–C(3)–C(7)	123·2 (8)
N(1)–Co–C(14)	87·2 (3)	C(4)–C(3)–C(7)	124·1 (8)
N(2)–Co–N(3)	98·7 (3)	N(4)–C(4)–C(3)	113·2 (9)
N(2)–Co–N(4)	178·8 (3)	N(4)–C(4)–C(8)	124·8 (8)
N(2)–Co–N(5)	89·9 (3)	C(3)–C(4)–C(8)	121·8 (8)
N(2)–Co–C(14)	87·4 (3)	Co–N(5)–C(9)	121·4 (6)
N(3)–Co–N(4)	81·8 (3)	Co–N(5)–C(13)	122·0 (6)
N(3)–Co–N(5)	91·9 (3)	C(9)–N(5)–C(13)	116·5 (8)
N(3)–Co–C(14)	91·0 (3)	N(5)–C(9)–C(10)	124·4 (9)
N(4)–Co–N(5)	91·1 (3)	C(9)–C(10)–C(11)	118·5 (10)
N(4)–Co–C(14)	91·6 (3)	C(10)–C(11)–C(12)	116·4 (10)
N(5)–Co–C(14)	176·3 (3)	C(11)–C(12)–C(13)	121·4 (10)
Co–N(1)–O(1)	124·4 (6)	N(5)–C(13)–C(12)	122·7 (9)
Co–N(1)–C(1)	115·6 (6)	Co–C(14)–C(15P)	115·4 (6)
O(1)–N(1)–C(1)	120·0 (8)	Co–C(14)–C(16P)	104·8 (7)
Co–N(2)–O(2)	123·4 (6)	Co–C(14)–C(15Q)	115·5 (7)
Co–N(2)–C(2)	117·5 (6)	Co–C(14)–C(16Q)	104·7 (6)
O(2)–N(2)–C(2)	119·1 (8)	C(15P)–C(14)–C(16P)	109·4 (9)
Co–N(3)–O(3)	123·1 (6)	C(15Q)–C(14)–C(16Q)	109·4 (8)
Co–N(3)–C(3)	116·3 (6)	C(14)–C(16P)–O(5P)	125·5 (15)
O(3)–N(3)–C(3)	120·6 (8)	C(14)–C(16P)–O(6P)	103·2 (13)
Co–N(4)–O(4)	123·9 (6)	O(5P)–C(16P)–O(6P)	121·6 (18)
Co–N(4)–C(4)	116·0 (7)	C(16P)–O(6P)–C(17P)	109·7 (26)
O(4)–N(4)–C(4)	120·1 (8)	C(14)–C(16Q)–O(5Q)	125·5 (11)
N(1)–C(1)–C(2)	113·5 (8)	C(14)–C(16Q)–O(6Q)	102·4 (10)
N(1)–C(1)–C(5)	121·7 (8)	O(5Q)–C(16Q)–O(6Q)	121·5 (13)
C(2)–C(1)–C(5)	124·8 (8)	C(16Q)–O(6Q)–C(17Q)	112·3 (19)
N(2)–C(2)–C(1)	111·5 (8)		

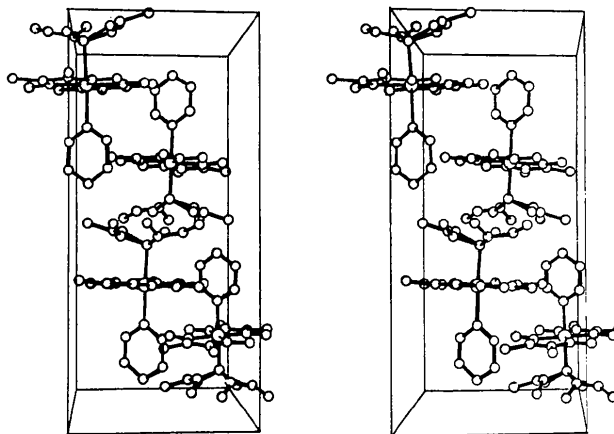Fig. 1. Perspective view of the molecule, showing the atom numbering.

Fig. 2. Stereoview of the packing of the molecules. The origin is at the lower left-hand corner, a is horizontal, b is vertical and c towards the viewer.
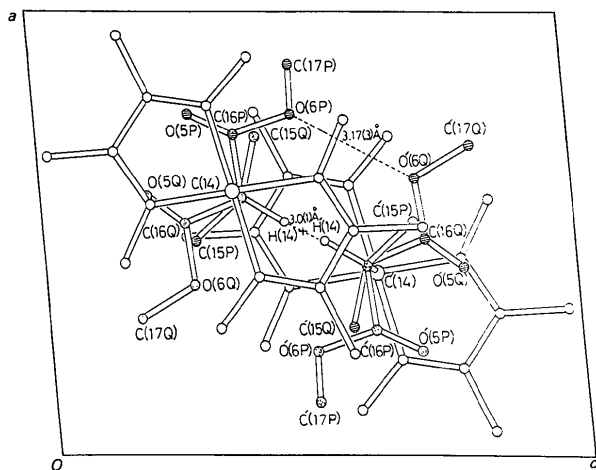
Fig. 3. Projection of the two complexes related by an inversion center (+). The pyridine ligands are omitted for clarity. The disordered pair of mce groups are sandwiched by the two cobaloxime planes and face each other.

the molecules. The two disordered mce groups are sandwiched by the two cobaloxime moieties and face each other. Fig. 3 is a view along the normal to the mean plane of cobaloxime, showing the contacts between the mce groups. The distances of $O(6P)\cdots O'(6Q)$ and $H(14)\cdots H'(14)$ are 3·17 (3) and 3·0 (1) Å, respectively. This suggests that the two mce groups around the inversion center can independently take the R or S configuration at random. The situation is different from the racemization by X-ray exposure in the crystals of the complexes containing the cyanoethyl group (Ohashi, Sasada & Ohgo, 1978; Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1981), in which the cyanoethyl group is isolated from the other reactive groups. The face-to-face contact of the two reactive mce groups is probably responsible for such a rapid racemization.

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