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Structure of Bis(dimethylglyoximato) [(*S*)-1-methoxycarbonylethyl] (4-pyridinecarbonitrile)cobalt(III), $C_{18}H_{25}CoN_6O_6$*

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Abstract. $M_r = 480{\cdot}4$, orthorhombic, $P2_12_12_1$, $a = 14{\cdot}575\,(2)$, $b = 16{\cdot}174\,(2)$, $c = 9{\cdot}268\,(1)$ Å, $V = 2184{\cdot}8\,(5)$ Å^3, $Z = 4$, $D_x = 1{\cdot}46$ g cm^{-3}, $T = 293$ K, $F(000) = 250$, $\mu(\text{Mo } K\alpha) = 8{\cdot}69$ cm^{-1}, $\lambda = 0{\cdot}71069$ Å, $R = 0{\cdot}058$ for 1938 observed reflections. There are no unusual bond distances or angles. The crystal shows no crystalline-state racemization on X-ray exposure. The structure found clearly explains the non-reactivity of the chiral group.

Introduction. It has been found that the chiral 1-methoxycarbonylethyl (mce) group in some crystals of bis(dimethylglyoximato)cobalt (dimethylglyoximato = 2,3-butanedione dioximato), cobaloxime, complexes is racemized by X-ray exposure without degradation of the crystallinity. In crystals of [(*R*)-1-mce] (4-chloropyridine)cobaloxime, *R*-mce-Clpy (Kurihara, Ohashi, Sasada & Ohgo, 1983), and [(*R*)-1-mce] (pyridine)-cobaloxime, *R*-mce-py (Kurihara, Ohashi & Sasada, 1982; Kurihara, Uchida, Ohashi, Sasada & Ohgo, 1984), both mce groups of the two crystallographically independent molecules are changed from the ordered enantiomeric structure to the disordered racemic one. In order to examine further details of the reaction mechanism, the crystal of the title compound, *S*-mce-cnpy, was exposed to X-rays and its structure determined.

Experimental. *S*-mce-cnpy prepared in a way similar to that reported previously (Ohgo, Takeuchi, Natori, Yoshimura, Ohashi & Sasada, 1981). Dark-red plate-like crystals obtained from an aqueous methanol solution. D_m not determined. Systematic absences $h00$: $h = 2n + 1$, $0k0$: $k = 2n + 1$, $00l$: $l = 2n + 1$. Crystal $\sim 0{\cdot}5 \times 0{\cdot}2 \times 0{\cdot}1$ mm. Rigaku AFC-4 diffractomer, graphite monochromator. Cell parameters refined by least-squares method on the basis of 15 independent 2θ values, Mo $K\alpha$ radiation ($20° < 2\theta < 30°$); no significant change in cell dimensions observed after the exposure to X-rays for one week at room temperature. Intensity measurement performed up to $2\theta = 50°$ (the $+h + k + l$ set), ω–2θ scan technique, scan speed $4°\ \text{min}^{-1}$ (θ). 2220 reflections measured; 1938 intensities with $|F_o| > 3\sigma(F_o)$ considered observed and used for the structure determination. Corrections for Lorentz and polarization; absorption and secondary extinction ignored. Direct methods (*MULTAN*78, Main Hull, Lessinger, Germain, Declercq & Woolfson, 1978) and subsequent difference Fourier calculation. Block-diagonal least squares (*HBLS*, Ohashi, 1975) with anisotropic thermal parameters for all non-H atoms; H atoms located on difference map; $\sum w(|F_o| - |F_c|)^2$ minimized, $w = 1$ for all reflections. Final $R = R_w = 0{\cdot}058$ for 1938 observed reflections. $(\Delta/\sigma)_{\max} = 0{\cdot}1$. Difference-map excursions $0{\cdot}4$ e Å^{-3}. Atomic scattering factors including anomalous-dispersion terms from *International Tables for X-ray Crystallography* (1974). Calculations carried out on FACOM-HITAC M-180 computer at this Institute.

Discussion. The final atomic parameters for the non-H atoms are in Table 1.‡ A stereoscopic drawing of the molecule with the numbering of the atoms is shown in Fig. 1. The methyl group, C(16), takes a *cis* conformation with respect to O(5) of the carbonyl group in the mce group. The torsion angles C(17)—C(15)—Co—N(4) and N(4)—Co—N(5)—C(9) are $-13{\cdot}4\,(6)°$ and $48{\cdot}9\,(7)°$, respectively. The bond distances and angles are listed in Table 2. They are in good agreement with the corresponding values of *R*-mce-Clpy, *R*-mce-py and [(*R*)-1-mce] [(*R*)-α-methylbenzylamine]cobaloxime (Ohashi & Sasada, 1977).

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

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‡ Lists of structure factors, anisotropic thermal parameters for non-H atoms, and positional and thermal parameters for H atoms have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39492 (11 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Table 1. *Final atomic coordinates* (×10⁴) *and equivalent isotropic thermal parameters* (Å²) *for non-*H *atoms*

$$B_{eq} = \tfrac{8}{3}\pi^2 \textstyle\sum_i \sum_j U_{ij} a_i^* a_j^* \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	B_{eq}
Co	673 (1)	2078 (1)	2439 (1)	2·5
N(1)	595 (5)	1785 (4)	462 (7)	3·4
N(2)	1712 (4)	1378 (4)	2302 (7)	2·9
N(3)	720 (4)	2342 (4)	4420 (6)	2·8
N(4)	−333 (3)	2821 (3)	2496 (8)	2·9
O(1)	−104 (4)	2035 (4)	−385 (6)	4·5
O(2)	2267 (4)	1259 (4)	3454 (7)	4·3
O(3)	1343 (4)	2001 (4)	5330 (6)	4·2
O(4)	−791 (4)	3050 (4)	1320 (6)	3·9
C(1)	1236 (6)	1305 (5)	−30 (9)	3·7
C(2)	1907 (6)	1088 (5)	1031 (9)	3·7
C(3)	114 (5)	2865 (5)	4905 (8)	3·6
C(4)	−483 (5)	3181 (5)	3752 (9)	3·2
C(5)	1215 (8)	984 (7)	−1515 (10)	5·6
C(6)	2766 (6)	624 (6)	725 (12)	5·2
C(7)	−24 (7)	3062 (7)	6437 (10)	5·1
C(8)	−1169 (6)	3833 (6)	3960 (11)	4·6
N(5)	1526 (4)	3062 (4)	1926 (7)	3·1
C(9)	1317 (6)	3589 (5)	895 (11)	4·3
C(10)	1895 (7)	4194 (6)	428 (12)	5·1
C(11)	2778 (6)	4254 (5)	1011 (11)	4·3
C(12)	2992 (6)	3736 (6)	2108 (11)	5·2
C(13)	2356 (5)	3159 (5)	2548 (12)	4·4
C(14)	3431 (8)	4831 (6)	457 (12)	5·6
N(6)	3946 (7)	5289 (6)	14 (13)	8·1
C(15)	−123 (5)	1033 (4)	2921 (8)	2·8
C(16)	317 (6)	446 (5)	4015 (11)	4·5
C(17)	−1025 (5)	1308 (5)	3432 (9)	3·6
O(5)	−1245 (4)	1416 (4)	4663 (7)	5·4
O(6)	−1600 (4)	1449 (4)	2311 (8)	4·5
C(18)	−2442 (6)	1849 (8)	2683 (18)	7·6

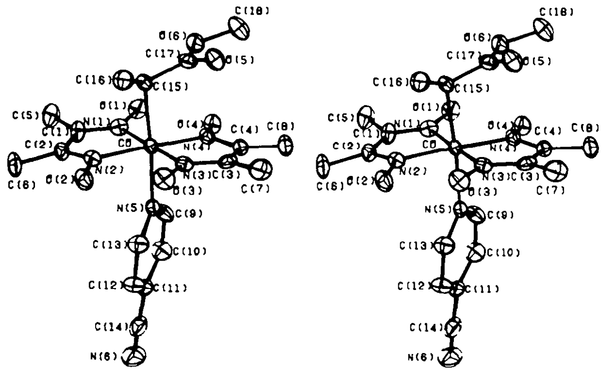

Fig. 1. Stereoscopic drawing (*ORTEP*; Johnson, 1965) of *S*-mce-cnpy.

The crystal structure viewed along the c axis is shown in Fig. 2, in which several short contacts are given. The mce group is surrounded by the 4-pyridinecarbonitrile ligands and the cobaloxime moieties of neighboring molecules. The same structure was obtained after exposure to X-rays for one week at room temperature. However, the crystal was gradually decomposed by X-ray irradiation at 353 K. This suggests that the racemization proceeds, destroying the lattice structure, only at high temperatures. The mce group in the present crystal is isolated from the other mce groups and is closely packed with the surrounding molecules as shown in Fig. 2; this arrangement may be unfavorable for crystalline-state reaction.

Table 2. *Bond distances* (Å) *and angles* (°) *of S*-mce-cnpy

Co–N(1)	1·895 (7)	C(3)–C(4)	1·469 (11)
Co–N(2)	1·894 (7)	C(3)–C(7)	1·468 (14)
Co–N(3)	1·886 (6)	C(4)–C(8)	1·466 (13)
Co–N(4)	1·897 (7)	N(5)–C(9)	1·316 (12)
Co–N(5)	2·076 (6)	N(5)–C(13)	1·349 (13)
Co–C(15)	2·098 (7)	C(9)–C(10)	1·361 (15)
N(1)–O(1)	1·349 (9)	C(10)–C(11)	1·399 (15)
N(1)–C(1)	1·298 (11)	C(11)–C(12)	1·353 (15)
N(2)–O(2)	1·353 (9)	C(11)–C(14)	1·429 (15)
N(2)–C(2)	1·299 (11)	C(12)–C(13)	1·377 (15)
N(3)–O(3)	1·357 (9)	C(14)–N(6)	1·131 (16)
N(3)–C(3)	1·304 (10)	C(15)–C(16)	1·530 (13)
N(4)–O(4)	1·331 (9)	C(15)–C(17)	1·467 (11)
N(4)–C(4)	1·320 (11)	C(17)–O(5)	1·198 (11)
C(1)–C(2)	1·431 (12)	C(17)–O(6)	1·354 (11)
C(1)–C(5)	1·471 (14)	O(6)–C(18)	1·429 (18)
C(2)–C(6)	1·487 (14)		

N(1)–Co–N(2)	80·5 (3)	C(2)–C(1)–C(5)	124·8 (8)
N(1)–Co–N(3)	178·1 (3)	N(2)–C(2)–C(1)	112·7 (7)
N(1)–Co–N(4)	98·0 (3)	N(2)–C(2)–C(6)	122·7 (8)
N(1)–Co–N(5)	90·3 (3)	C(1)–C(2)–C(6)	124·6 (8)
N(1)–Co–C(15)	88·4 (3)	N(3)–C(3)–C(4)	112·1 (7)
N(2)–Co–N(3)	99·9 (3)	N(3)–C(3)–C(7)	124·5 (8)
N(2)–Co–N(4)	176·6 (3)	C(4)–C(3)–C(7)	123·2 (8)
N(2)–Co–N(5)	87·9 (3)	N(4)–C(4)–C(3)	113·0 (7)
N(2)–Co–C(15)	88·6 (3)	N(4)–C(4)–C(8)	123·1 (8)
N(3)–Co–N(4)	81·8 (3)	C(3)–C(4)–C(8)	123·9 (7)
N(3)–Co–N(5)	91·6 (3)	Co–N(5)–C(9)	121·6 (6)
N(3)–Co–C(15)	89·7 (3)	Co–N(5)–C(13)	121·9 (6)
N(4)–Co–N(5)	89·0 (3)	C(9)–N(5)–C(13)	116·3 (8)
N(4)–Co–C(15)	94·4 (3)	N(5)–C(9)–C(10)	123·6 (9)
N(5)–Co–C(15)	176·4 (3)	C(9)–C(10)–C(11)	119·7 (10)
Co–N(1)–O(1)	122·2 (5)	C(10)–C(11)–C(12)	117·3 (10)
Co–N(1)–C(1)	116·5 (6)	C(10)–C(11)–C(14)	121·3 (10)
O(1)–N(1)–C(1)	121·2 (7)	C(12)–C(11)–C(14)	121·4 (10)
Co–N(2)–O(2)	120·7 (5)	C(11)–C(12)–C(13)	119·1 (10)
Co–N(2)–C(2)	116·8 (6)	N(5)–C(13)–C(12)	123·7 (10)
O(2)–N(2)–C(2)	122·2 (7)	C(11)–C(14)–N(6)	179·8 (13)
Co–N(3)–O(3)	122·5 (5)	Co–C(15)–C(16)	114·2 (6)
Co–N(3)–C(3)	117·3 (5)	Co–C(15)–C(17)	108·7 (5)
O(3)–N(3)–C(3)	120·2 (6)	C(16)–C(15)–C(17)	110·5 (7)
Co–N(4)–O(4)	122·8 (5)	C(15)–C(17)–O(5)	126·3 (8)
Co–N(4)–C(4)	115·6 (6)	C(15)–C(17)–O(6)	111·0 (7)
O(4)–N(4)–C(4)	121·1 (7)	O(5)–C(17)–O(6)	122·7 (8)
N(1)–C(1)–C(2)	113·4 (8)	C(17)–O(6)–C(18)	115·0 (9)
N(1)–C(1)–C(5)	121·7 (8)		

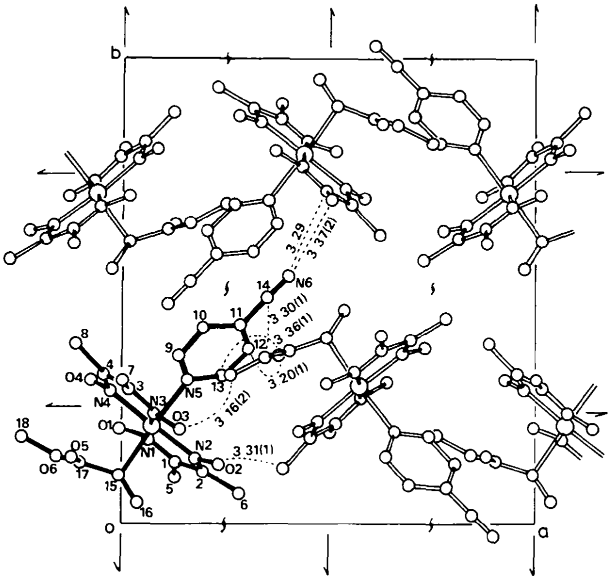

Fig. 2. Crystal structure viewed along the c axis. Interatomic distances less than 3·4 Å are shown. The contacts along the c axis are C(7)···O(1) 3·38 (1) and O(3)···C(5) 3·36 (1) Å.

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The Structure of PbI_2–Pyridine Adducts. I. Lead(II) Iodide–Pyridine (2/4), *catena*-Di-μ-iodo-bis(pyridine)lead(II), $[Pb_2I_4(C_5H_5N)_4]$

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Abstract. $M_r = 1238{\cdot}4$, trigonal, $P3_121$, $a = 10{\cdot}103\ (1)$, $c = 24{\cdot}584\ (3)$ Å, $U = 2173{\cdot}1\ (4)$ Å^3, $Z = 3$, $D_m = 2{\cdot}78$, $D_x = 2{\cdot}84$ Mg m^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 15{\cdot}7$ mm^{-1}, $F(000) = 1632$, room temperature, final $R = 0{\cdot}069$ for 1630 unique reflections. The two independent Pb atoms are on the twofold axes and are surrounded by four I and two N atoms. One Pb atom has regular octahedral coordination with the two pyridine molecules in *trans* positions, whereas the other exhibits very distorted octahedral coordination with the two pyridine molecules in *cis* positions. The two Pb atoms are alternately linked through the two bridging I atoms to form a helical chain along **c**.

Introduction. Lead(II) iodide (PbI_2) reacts with some Lewis bases and its specific yellow color disappears. When the reaction products are allowed to stand in air they recover the original yellow color, indicating the loss of the Lewis bases. These facts seem to indicate that the Lewis bases intercalate between the layers of PbI_2 to form 'intercalation compounds' (Koshkin, Mil'ner, Kukol', Zabrodskii, Dmitriev & Brintsev, 1976; Rybalka & Miloslavskii, 1976).

Independently, Wharf, Gramstad, Makhija & Onyszchuk (1976) discovered that pyridine (py), a typical Lewis base, forms two types of adducts with PbI_2: $PbI_2(py)_2$ and $PbI_2(py)$. They proposed a linear chain structure for $PbI_2(py)_2$ on the basis of infrared spectra, where the two py molecules coordinate to the metal atom in *trans* positions. However, they could not confirm it by single-crystal X-ray diffraction, because the compound was obtained as a fine powder.

We have succeeded in crystallizing the two adducts and determined the crystal structures in order to see whether intercalation occurs or not. This paper deals with one of the two products, $PbI_2(py)_2$.

Experimental. Preparation as described by Wharf *et al.* (1976). The powder sealed was with ethanol in a branched glass tube, as shown in Fig. 1. An end of the branch containing the powder was kept at 333 K in a water bath and the other kept at ambient temperature (*ca* 293 K). After a week, crystals grew in the lower-temperature region. Crystal shows similar IR spectrum but much sharper X-ray powder diffraction pattern than those of original powder sample. Crystals

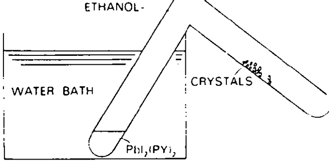

Fig. 1. Preparation of the crystals.

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