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Structure and Absolute Configuration of $(+)_{589}$-(2-Cyanoethyl)bis[(*E,E*)-1-phenyl-1,2-propanedione dioximato-*N,N'*](pyridine)cobalt(III), $[Co(C_3H_4N)(C_9H_9N_2O_2)_2(C_5H_5N)]$

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Abstract. $M_r = 546{\cdot}47$, monoclinic, $P2_1$, $a = 9{\cdot}736$ (1), $b = 15{\cdot}991$ (3), $c = 8{\cdot}653$ (1) Å, $\beta = 109{\cdot}638$ (8)°, $V = 1268{\cdot}9$ (3) Å^3, $Z = 2$, $D_m = 1{\cdot}42$, $D_x = 1{\cdot}431$ g cm^{-3}, Mo $K\alpha$, $\lambda = 0{\cdot}71069$ Å, $\mu = 7{\cdot}52$ cm^{-1}, $F(000) = 284$, $T = 293$ K, $R = 0{\cdot}041$ for 2203 observed reflections. The two phenyl groups are *trans* to each other in the equatorial ligands so that the molecule is chiral. The absolute configuration was determined to be *C*. The axial Co—C and Co—N bonds are 2·005 (5) and 2·094 (4) Å respectively.

Introduction. The title complex was enantioselectively prepared from the reaction of [(*R*)-1-phenylethylamine]bis[(*E,E*)-1-phenyl-1,2-propanedione dioximato]cobalt(I) with acrylonitrile followed by the displacement of the chiral amine with pyridine. The 2-cyanoethyl group, $-CH_2CH_2CN$, in the powdered sample of the complex was also found to be changed into a 1-cyanoethyl group, $-CH(CH_3)CN$, on exposure to visible light (Ohgo & Takeuchi, 1984). In order to examine the mechanisms of the enantioselective reaction and the solid-state '2—1 isomerization', the crystal structure of the title compound has been determined.

Experimental. Orange needle-like crystals from benzene–hexane solution; D_m by flotation in C_6H_{12}/CCl_4 solution; systematic absences: $0k0$, $k = 2n + 1$; crystal dimensions 0·3 × 0·2 × 0·15 mm; Rigaku AFC-4 diffractometer; graphite monochromator; cell parameters refined by least-squares method on basis of 15 independent 2θ values; $15 < 2\theta < 33°$; intensity measurement performed up to $2\theta = 50°$; range of *hkl* −10 to 11, 0 to 18 and −10 to 0; ω–2θ scan, scan speed 2° min^{-1}(θ), scan width $(1{\cdot}0 + 0{\cdot}35\tan\theta)°$; background 5 s before and after each scan; three standard reflections monitored every 50 reflections, no significant variation in intensities; 2319 reflections measured, 2203 with $|F_o| > 3\sigma(|F_o|)$ considered observed and used for structure determination; corrections for Lorentz and polarization, absorption 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 with $w = [\sigma^2(F_o) + (0{\cdot}03F_o)^2]^{-1}$; max. (Δ/σ) 0·4; $\Delta\rho$ excursions in final difference map 0·4 e Å^{-3}; absolute configuration determined by Cu $K\alpha$ radiation with 10 Friedel pairs; atomic scattering factors including anomalous terms from *International Tables for X-ray Crystallography* (1974); calculation carried out on FACOM-HITAC system M-180 computer at this Institute.

Discussion. The final atomic parameters for non-H atoms are in Table 1.† The stereoscopic drawing of the molecule with the numbering of the atoms is shown in Fig. 1. Bond distances and angles are listed in Table 2. The two phenyl groups in the equatorial ligands are *trans* to each other. This causes the chirality in the molecule. The absolute configuration is *C* (Brown, Cook & Sloan, 1975), which confirms the proposed mechanism of the enantioselective reaction (Ohgo & Takeuchi, 1984). The torsion angles C(25)—C(24)—Co—N(3), N(1)—Co—N(5)—C(19), N(1)—C(1)—C(5)—C(10) and N(3)—C(3)—C(12)—C(13) are −21·3 (4), 24·4 (4), −55·2 (8) and 41·6 (8)°, respectively.

The Co—C and Co—N(5) bonds are significantly shorter and longer than the corresponding ones, respectively, in the cobaloxime complexes with the 1-cyanoethyl group and 4-substituted pyridines as axial ligands: pyridine complex, 2·053 (4) (Co—C) and

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† Lists of structure factors, anisotropic thermal parameters for non-H atoms, positional and thermal parameters for H atoms, bond angles and the relationship between $|F_o|$ in ten Friedel pairs have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 39706 (13 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* ($\times 10^5$ *for* Co, $\times 10^4$ *for* C, N *and* O *atoms) and equivalent isotropic thermal parameters,* B_{eq} (Å^2)

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

	x	y	z	$B_{\rm eq}$
Co	29569 (6)	14104	43253 (7)	2·7
N(1)	4312 (4)	2154 (3)	5759 (4)	3·1
N(2)	3313 (4)	809 (3)	6303 (4)	3·2
N(3)	1650 (4)	664 (2)	2869 (4)	2·8
N(4)	2638 (4)	2009 (2)	2369 (4)	3·0
O(1)	4754 (4)	2858 (2)	5235 (4)	3·7
O(2)	2697 (4)	54 (2)	6363 (4)	4·2
O(3)	1284 (4)	−61 (2)	3395 (4)	3·9
O(4)	3303 (4)	2735 (2)	2309 (4)	3·8
C(1)	4748 (5)	1953 (3)	7314 (5)	3·2
C(2)	4173 (5)	1152 (3)	7625 (5)	3·2
C(3)	1086 (5)	901 (3)	1336 (5)	3·0
C(4)	1679 (5)	1709 (3)	1059 (5)	3·0
C(5)	5741 (5)	2498 (3)	8623 (6)	3·3
C(6)	5320 (6)	2776 (4)	9901 (7)	4·4
C(7)	6175 (7)	3291 (4)	11085 (7)	5·5
C(8)	7498 (6)	3541 (4)	11008 (7)	5·1
C(9)	7924 (7)	3284 (5)	9737 (9)	6·5
C(10)	7075 (7)	2757 (5)	8561 (7)	5·8
C(11)	4534 (7)	761 (4)	9263 (6)	4·5
C(12)	−7 (6)	441 (3)	31 (6)	3·5
C(13)	−1175 (6)	53 (4)	333 (6)	4·2
C(14)	−2196 (6)	−397 (4)	−903 (7)	5·2
C(15)	−2099 (7)	−418 (4)	−2457 (7)	5·2
C(16)	−948 (7)	−73 (4)	−2755 (6)	4·8
C(17)	86 (6)	344 (4)	−1527 (7)	4·3
C(18)	1215 (6)	2182 (4)	−518 (6)	4·3
N(5)	1203 (4)	2018 (3)	4731 (4)	3·1
C(19)	1297 (6)	2816 (3)	5213 (6)	3·8
C(20)	167 (7)	3237 (4)	5507 (7)	4·9
C(21)	−1118 (7)	2830 (4)	5251 (8)	5·5
C(22)	−1230 (6)	2019 (5)	4790 (8)	5·6
C(23)	−67 (6)	1627 (3)	4520 (7)	4·4
C(24)	4693 (5)	862 (3)	3999 (6)	3·5
C(25)	4539 (6)	−22 (4)	3371 (7)	4·9
C(26)	5879 (6)	−290 (4)	3118 (7)	4·6
N(6)	6971 (6)	−443 (4)	2952 (7)	6·7

Table 2. *Bond distances* (Å)

Co—N(1)	1·896 (4)	C(5)—C(10)	1·381 (9)
Co—N(2)	1·891 (4)	C(6)—C(7)	1·359 (9)
Co—N(3)	1·885 (4)	C(7)—C(8)	1·371 (10)
Co—N(4)	1·877 (4)	C(8)—C(9)	1·363 (11)
Co—N(5)	2·094 (4)	C(9)—C(10)	1·365 (11)
Co—C(23)	2·005 (5)	C(12)—C(13)	1·394 (8)
N(1)—O(1)	1·337 (6)	C(12)—C(17)	1·390 (8)
N(1)—C(1)	1·307 (7)	C(13)—C(14)	1·391 (9)
N(2)—O(2)	1·356 (6)	C(14)—C(15)	1·380 (9)
N(2)—C(2)	1·291 (6)	C(15)—C(16)	1·349 (9)
N(3)—O(3)	1·337 (5)	C(16)—C(17)	1·366 (9)
N(3)—C(3)	1·309 (6)	N(5)—C(19)	1·335 (7)
N(4)—O(4)	1·339 (5)	N(5)—C(23)	1·342 (7)
N(4)—C(4)	1·295 (6)	C(19)—C(20)	1·385 (9)
C(1)—C(2)	1·458 (7)	C(20)—C(21)	1·360 (9)
C(1)—C(5)	1·497 (7)	C(21)—C(22)	1·350 (10)
C(2)—C(11)	1·480 (8)	C(22)—C(23)	1·381 (9)
C(3)—C(4)	1·467 (7)	C(24)—C(25)	1·504 (8)
C(3)—C(12)	1·464 (7)	C(25)—C(26)	1·456 (9)
C(4)—C(18)	1·491 (8)	C(26)—N(6)	1·146 (9)
C(5)—C(6)	1·375 (8)		

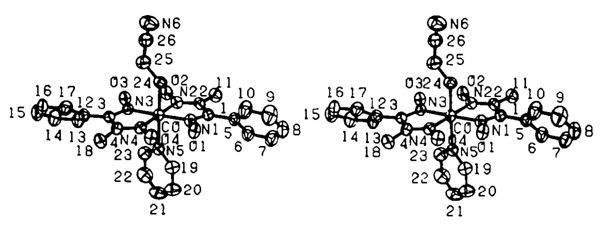

Fig. 1. Stereoscopic drawing (*ORTEP*; Johnson, 1965) with the numbering of atoms.

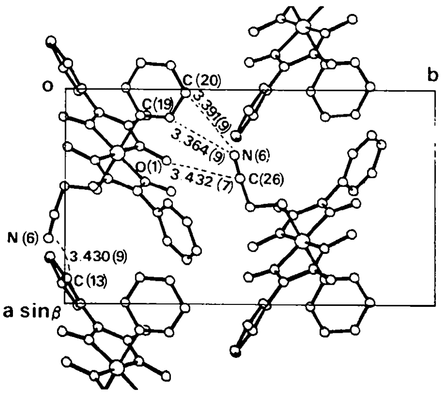

Fig. 2. Crystal structure viewed along the *c* axis. Short interatomic distances less than 3·5 Å are shown.

2·047 (3) Å (Co—N) (Ohashi, Yanagi, Kurihara, Sasada & Ohgo, 1982); 4-pyridinecarbonitrile, 2·052 (6) (Co—C) and 2·065 (3) Å (Co—N) (Ohashi, Uchida, Sasada & Ohgo, 1983); and 4-methylpyridine, 2·05 (1) (Co—C) and 2·058 (8) Å (Co—N) (Uchida, Ohashi, Sasada, Ohgo & Baba, 1984). The sum of the distances of Co—C and Co—N are approximately the same in both types of complexes. Other distances and angles are in good agreement with the corresponding values in the related cobaloxime complexes.

The crystal structure viewed along the *c* axis is shown in Fig. 2, in which several short contacts are given. The reactive 2-cyanoethyl group is surrounded by the pyridine ligands and the cobaloxime moieties of the neighboring molecules. There appears to be no void space around the group. The 2—1 isomerization is impossible without degradation of the crystallinity.

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