(+)589-(3,3'-Dimethyl-2,2'-bipyridine)bis(ethylenediamine)cobalt(III) Chloride Diperchlorate Monohydrate

By S. Sato and Y. Saito

The Institute for Solid State Physics, The University of Tokyo, Roppongi-7, Minato-ku, Tokyo 106, Japan

Abstract. $C_{16}H_{30}N_6Cl_3CoO_9$, orthorhombic, $P2_12_12_1$ (No. 19), $a = 16\cdot754$ (2), $b = 18\cdot311$ (2), $c = 8\cdot129$ (1) Å, $U = 2493\cdot6$ Å^3, $Z = 4$, $D_m = 1\cdot68$ (by flotation in chloroform/methyl iodide), $D_x = 1\cdot64$ g cm^{-3}, FW 615·7, μ(Mo $K\alpha$) $= 10\cdot9$ cm^{-1}. The final R is 0·036 for 3711 independent observed reflexions. The conformation of one of the two ethylenediamine chelate rings is disordered. The absolute configuration of the complex cation can be designated as $\varLambda$ (δ-dmbpy, δ, 90% λ and 10% δ).

Introduction. Crystals of the title compound were kindly provided by Dr T. M. Suzuki (Suzuki & Kimura, 1977). They are dark orange-red needles elongated along *c*. A spherically shaped crystal of 0·5 mm in diameter was used for data collection up to $2\theta = 60°$ on a Rigaku automated four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation ($\lambda = 0\cdot7107$ Å), the θ–2θ scan technique being employed. Of 4083 independent reflexions 3711 with $|F_o| > 3\sigma(|F_o|)$ were considered as observed, and used in the structure analysis. The intensities were corrected for Lorentz and polarization factors. No absorption

Table 1. *Positional parameters* ($\times 10^4$ *for non-hydrogen atoms*; $\times 10^3$ *for hydrogen atoms*)

The C atoms corresponding to 10% δ-en ring are indicated by a prime.

	x	y	z
Co	2950 (0)	3425 (0)	2037 (1)
N(1)	3579 (1)	2782 (1)	583 (3)
N(2)	2626 (2)	2494 (1)	3006 (3)
N(3)	2111 (2)	3395 (1)	356 (3)
N(4)	2169 (2)	3997 (1)	3300 (3)
N(5)	3381 (2)	4346 (1)	1171 (4)
N(6)	3795 (2)	3506 (2)	3706 (3)
C(1)	4041 (2)	2976 (2)	−672 (4)
C(2)	4234 (2)	2502 (2)	−1933 (4)
C(3)	3879 (2)	1816 (2)	−1947 (4)
C(4)	3380 (2)	1601 (2)	−655 (4)
C(5)	3315 (2)	2071 (2)	673 (4)
C(6)	2952 (2)	1903 (2)	2274 (4)
C(7)	2984 (2)	1223 (2)	3075 (4)
C(8)	2563 (2)	1163 (2)	4547 (5)
C(9)	2173 (3)	1753 (2)	5226 (5)

Table 1 (*cont.*)

	x	y	z
C(10)	2253 (2)	2415 (2)	4458 (4)
C(11)	2896 (2)	915 (2)	−843 (5)
C(12)	3488 (3)	588 (2)	2552 (5)
C(13)	1434 (2)	3884 (2)	809 (5)
C(14)	1359 (2)	3852 (2)	2635 (5)
C(15)	3970 (3)	4654 (2)	2357 (6)
C(16)	4402 (3)	4048 (3)	3137 (6)
C(15')	4290 (15)	4386 (14)	1904 (37)
C(16')	4094 (17)	4267 (16)	3836 (39)
Cl(1)	2152 (1)	5734 (0)	2066 (1)
Cl(2)	473 (1)	412 (1)	2201 (1)
Cl(3)	5301 (1)	1942 (1)	3263 (1)
O(1)	1237 (2)	247 (2)	1574 (5)
O(2)	453 (3)	1143 (2)	2768 (6)
O(3)	−121 (2)	359 (2)	955 (6)
O(4)	294 (2)	−78 (2)	3522 (5)
O(5)	5966 (3)	1523 (3)	3599 (6)
O(6)	5525 (3)	2642 (3)	3179 (14)
O(7)	4674 (3)	1932 (4)	4340 (6)
O(8)	4997 (2)	1733 (4)	1725 (5)
O(9)	1296 (2)	2027 (2)	127 (8)
H(N3)1	195 (2)	292 (2)	15 (4)
H(N3)2	230 (2)	352 (2)	−47 (4)
H(N4)1	249 (3)	458 (3)	333 (9)
H(N4)2	216 (2)	389 (2)	475 (5)
H(N5)1	363 (2)	430 (2)	49 (4)
H(N5)2	311 (2)	469 (2)	116 (5)
H(N6)1	401 (2)	307 (2)	385 (5)
H(N6)2	362 (2)	369 (2)	490 (6)
H(C1)	427 (2)	343 (2)	−77 (4)
H(C2)	460 (2)	273 (2)	−270 (4)
H(C3)	392 (2)	151 (2)	−282 (4)
H(C8)	254 (2)	72 (2)	509 (5)
H(C9)	188 (2)	175 (2)	629 (6)
H(C10)	208 (2)	271 (2)	487 (6)
H(C11)1	252 (2)	86 (2)	15 (6)
H(C11)2	256 (2)	97 (2)	−179 (5)
H(C11)3	316 (3)	52 (3)	−118 (7)
H(C12)1	318 (2)	21 (2)	214 (6)
H(C12)2	394 (2)	68 (2)	184 (5)
H(C12)3	370 (3)	29 (2)	360 (7)
H(C13)1	94 (2)	367 (2)	55 (6)
H(C13)2	161 (2)	445 (2)	60 (5)
H(C14)1	120 (2)	342 (2)	307 (6)
H(C14)2	100 (2)	426 (2)	309 (5)
H(C15)1	423 (2)	493 (2)	198 (5)
H(C15)2	367 (3)	484 (3)	322 (7)
H(C16)1	472 (2)	395 (3)	221 (6)
H(C16)2	470 (2)	420 (2)	443 (6)
H(O9)1	114 (2)	179 (2)	97 (6)
H(O9)2	103 (3)	225 (3)	−11 (7)

correction was applied. The cell dimensions were obtained by a least-squares method from the θ values for 45 high-angle reflexions measured on the diffractometer.

The structure was solved by the conventional heavy-atom method. The positions of all the H atoms were identified in subsequent difference-Fourier maps. The structure was refined by the block-diagonal least-squares method with anisotropic thermal parameters for non-hydrogen atoms and isotropic for H. The scattering factors for non-hydrogen atoms and the anomalous-scattering corrections for Co and Cl were taken from *International Tables for X-ray Crystallography* (1974). For H the values given by Stewart, Davidson & Simpson (1965) were used. The weights employed were $w = [\sigma^2(|F_o|) + (0 \cdot 01|F_o|)^2]^{-1}$. The absolute structure was determined by the anomalous-dispersion technique by comparison of observed and calculated intensity relations for some Bijvoet pairs on equi-inclination Weissenberg photographs taken with Cu $K\alpha$ radiation (hkl and $\bar{h}kl$, $l = 1$ and 2).*

At a later stage of the refinement, the C atoms of one en ring showed larger thermal parameters than the others. The difference syntheses suggested conformational disorder of the en ring, $\delta = \lambda$, similar to that reported for tris(ethylenediamine)chromium(III) complexes (Brouty, Spinat, Whuler & Herpin, 1977; Whuler, Brouty, Spinat & Herpin, 1977). Accordingly, the disordered model was refined by the full-matrix least-squares method to a final R of 0·036, and led to a conformational disorder of 90% λ-en and 10% δ-en rings. The refinement for the ordered structure converged at $R = 0 \cdot 037$. The ordered structure can be rejected at a 0·005 significance level by Hamilton's $\mathscr{R}$ test (Hamilton, 1965).

The final atomic coordinates are listed in Table 1. The mean isotropic temperature factor of the H atoms is $U = 0 \cdot 06$ (1) Å^2, defined by $\exp[-8\pi^2 U(\sin\theta/\lambda)^2]$.

Discussion. Fig. 1 shows a partial projection of the crystal structure along c. The absolute configuration is $\varLambda$ (IUPAC, 1971) in agreement with the assignment based on the sign of CD in the first absorption region (Suzuki & Kimura, 1977). The bidentate ligand dmbpy is coordinated to the Co atom with an average Co—N distance of 1·964 (2) Å and N—Co—N angle of 82·5 (1)°. The bond lengths and angles in the Co–dmbpy ring are shown in Fig. 2: the angles Co—N—C and N—C—C in the five-membered chelate ring are much smaller than 120°, and rather close to the normal

tetrahedral angle. The C—C bond in the dmbpy chelate ring is inclined at an angle of 15·1° with respect to the pseudo threefold axis; the conformation of the chelate ring is δ as expected from a molecular model (Suzuki & Kimura, 1977). The fact that the chelate ring specifically takes the δ conformation may be attributed to escape from the repulsion between the fused py ring and the H atoms of the adjacent Co–en ring. The chelate ring is of the eclipsed envelope type, the dihedral angles being 16·2, 0·6 and 28·2° for N(2)—Co—N(1)—C(5), N(1)—Co—N(2)—C(6) and N—C—C—N, respectively. Each of the py rings is nearly planar with no atom being displaced more than 0·08 Å from its least-squares plane; however, the two rings are not coplanar but are twisted about the 2,2' C—C bond with a dihedral angle of 32·4° owing to repulsion between the two methyl groups. The distance between the methyl C atoms is 2·994 (6) Å with the shortest contact of 2·30 (6) Å between their H atoms. Fig. 3 shows a projection of the complex cation along the line through the midpoint of the dmbpy N atoms and the Co atom. The py ring A is inclined at an angle of 24·4° with respect to the NCoN plane, and the ring B at 13·7°. The 2,2' C—C bond makes an angle of 8·9° to ring A and 2·1° to ring B. The tilt angles of the C—CH$_3$ bond to the appropriate py ring are 11·8° for ring A and 9·7° for B. This unsymmetrical conformation of the dmbpy ligand can probably be ascribed to the strong repulsion between ring A and the perchlorate ion.

Conformational details of the en chelate rings are listed in Table 2. The bond lengths and angles are normal except for the disordered δ ring.
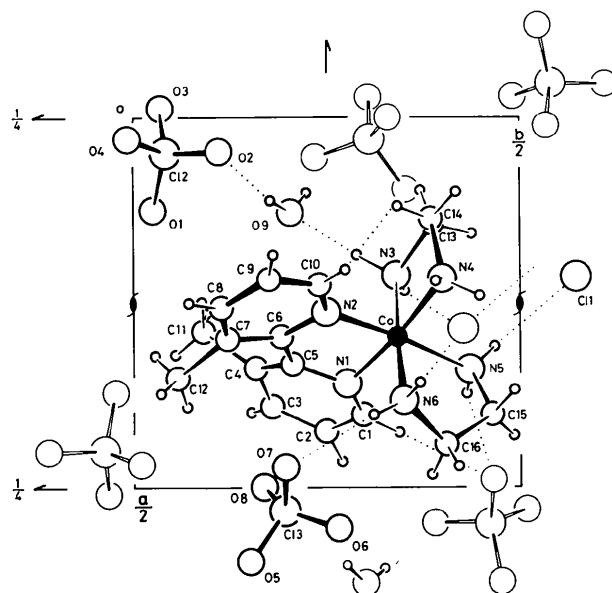

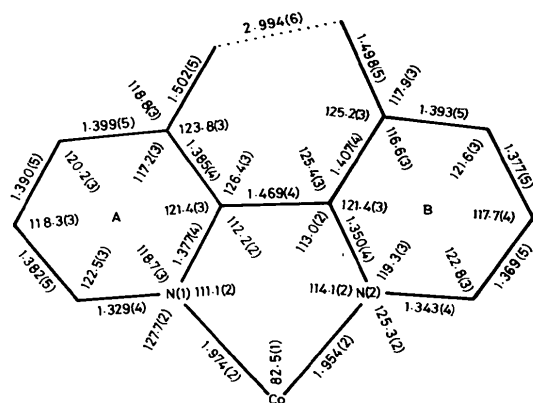Fig. 1. A partial projection of the structure along c. The dotted lines indicate hydrogen bonds.

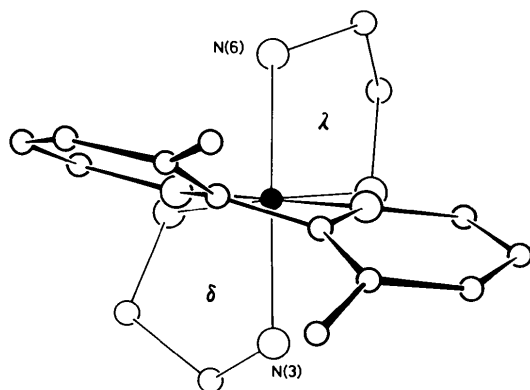Fig. 2. Bond lengths (Å) and angles (°) in the dmbpy ring.

Fig. 3. A projection of the complex cation viewed along a line through the midpoint of the dmbpy N atoms and the Co atom.

One perchlorate anion takes a nearly normal tetrahedral configuration with a mean Cl(2)—O distance of 1·421 (4) Å. This value agrees well with those observed in a recent investigation (Berglund, Thomas & Tellgren, 1975). The other shows the commonly observed tendency to slight disorder or high thermal vibration: the mean length of the Cl(3)—O bonds is 1·372 (5) Å. Fairly short C···O distances are observed, for example, for C(10)···O(5), 3·306 (6) Å. These short contacts might indicate the weak hydrogen bonds suggested by Sutor (1963). The complex cations, anions and water molecules are linked by hydrogen bonds to form a three-dimensional network.

The calculations were performed on a FACOM 230-48 computer of this Institute with a local version of the

Table 2. *Bond lengths (Å) and angles (°) in the ethylenediamine chelate rings*

The values for 10% δ conformation are omitted.

	δ	90% λ
Bond lengths		
Co—N	1·960 (3)	1·965 (3)
	1·966 (3)	1·966 (3)
N—C	1·492 (4)	1·490 (5)
	1·484 (4)	1·494 (5)
C—C	1·491 (5)	1·469 (6)
Bond angles		
N—Co—N	84·4 (1)	85·3 (1)
Co—N—C	110·9 (2)	109·7 (2)
	108·8 (2)	109·1 (2)
N—C—C	106·6 (3)	108·6 (3)
	106·2 (3)	107·4 (3)
Inclination angles of the C—C bonds to the pseudo threefold axis	8·5°	63·0°

References

Berglund, B., Thomas, J. O. & Tellgren, R. (1975). *Acta Cryst.* **B31**, 1842–1846.
Brouty, C., Spinat, P., Whuler, A. & Herpin, P. (1977). *Acta Cryst.* **B33**, 1913–1920.
Hamilton, W. C. (1965). *Acta Cryst.* **18**, 502–510.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
IUPAC (1971). *Nomenclature of Inorganic Chemistry*, 2nd ed., pp. 75–83. London: Butterworths.
Stewart, R. F., Davidson, E. R. & Simpson, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
Sutor, D. J. (1963). *J. Chem. Soc.* pp. 1105–1110.
Suzuki, T. M. & Kimura, T. (1977). *Bull. Chem. Soc. Jpn*, **50**, 391–395.
Whuler, A., Brouty, C., Spinat, P. & Herpin, P. (1977). *Acta Cryst.* **B33**, 2877–2885.