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Structure of (–)₅₈₉Bis[(1*R*,2*R*)-1,2-cyclohexanediamine](3,3'-dimethyl-2,2'-bipyridine)cobalt(III) Bromide Diperchlorate Monohydrate

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Abstract. [Co(C₆H₁₄N₂)₂(C₁₂H₁₂N₂)₂]³⁺.Br⁻.2ClO₄⁻.H₂O, [C₂₄H₄₀CoN₆]³⁺.Br⁻.2ClO₄⁻.H₂O, *M_r* = 768.4, orthorhombic, *P*2₁2₁2₁, *a* = 12.298 (1), *b* = 30.394 (4), *c* = 8.599 (1) Å, *U* = 3214 (1) Å³, *Z* = 4, *D_m* = 1.59, *D_x* = 1.59 Mg m⁻³, λ(Mo *K*α) = 0.7107 Å, μ(Mo *K*α) = 2.10 mm⁻¹. The final *R* value is 0.052 for 2749 independent reflections collected by X-ray diffractometry. The complex cation, (–)₅₈₉[Co(*R*,*R*-chxn)₂(3,3'-dmbpy)]³⁺ (chxn: *trans*-1,2-cyclohexanediamine; dmbpy: dimethyl-2,2'-bipyridine), has approximate twofold symmetry, and its absolute configuration can be designated as *A* (λλ,λ-dmbpy).

Introduction. When the two H atoms at the 3 and 3' positions of 2,2'-bipyridine are replaced by bulky methyl groups, the two pyridine moieties are no longer coplanar on forming a chelate ring. Thus 3,3'-dmbpy may coordinate to the cobalt(III) ion with a stereospecific conformation depending on the configuration. As part of a series of structure determinations of cobalt(III) complexes containing 3,3'-dmbpy (Sato & Saito, 1978), crystals of (–)₅₈₉[Co(*R*,*R*-chxn)₂(3,3'-dmbpy)]Br(ClO₄)₂.H₂O were subjected to X-ray structure analysis in order to reveal the conformational details of the complex ion and to establish an empirical

rule relating its absolute configuration and circular-dichroism spectrum. Orange-red plate-like crystals of the title compound were kindly supplied by Dr T. M. Suzuki (Suzuki & Kimura, 1977). Weissenberg photographs showed them to be orthorhombic with the systematic absences *h*00, 0*k*0 and 00*l* for odd indices, determining the space group as *P*2₁2₁2₁. For X-ray work a spherical specimen 0.5 mm in diameter was prepared. Intensities and cell dimensions were measured on a Rigaku automated four-circle diffractometer. Data were collected by the ω-scan technique to a maximum 2θ value of 55° with Mo *K*α radiation (λ = 0.7107 Å) monochromated by a graphite plate. Of the 4158 measured unique reflections, 2749 with |*F_o*| > 3σ(|*F_o*|) were considered as observed. The intensities were corrected for Lorentz-polarization and absorption effects.

The structure was solved by the heavy-atom method, and refined by block-diagonal least squares with anisotropic thermal parameters for the non-hydrogen atoms. With *R* = 0.068 (*R* = ∑|Δ*F*|/∑|*F_o*|), all the H atoms appeared in a difference synthesis, except for those of the methyl groups. At this stage the thermal parameter of H(C2) was –3.5 Å² and the C(2)–H(C2) distance was 1.25 (7) Å. This unusual result could be accounted

for if a hydroxyl group was attached to C(2) with a population of about $\frac{1}{2}$. The population of O(C2) was refined by full-matrix least squares and converged to 0.354 (9), where C(2)—O(C2) was 1.36 (3) Å. The final R dropped to 0.052 and $R_2 = 0.052$ $\{R_2 = [\sum w(\Delta F)^2 / \sum w(F_o)^2]^{1/2}$ for 2749 reflections. The largest shift/error ratio was 0.4 and the final difference synthesis showed no peaks of height greater than 0.5 e Å⁻³. The refinement for the structure without a hydroxyl group converged with $R = 0.054$ and $R_2 = 0.055$. This latter structure can be rejected at the 0.005 significance level by Hamilton's (1965) test. A weighting scheme, $w = 0.5$ for $|F_o| < 20$ and $w = 1$ for $|F_o| \geq 20$, was employed. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974). The atomic coordinates are listed in

Table 1.* The average isotropic temperature factor for H was 4.5 (2.2) Å².

The absolute configuration of the complex cation was assigned as Δ with reference to the known absolute configuration of (-)-*trans*-1,2-cyclohexanediamine (Marumo, Utsumi & Saito, 1970). In order to confirm the absolute configuration, equi-inclination Weissenberg photographs were taken with Cu $K\alpha$ radiation. In Table 2* the observed and calculated differences, for

* Lists of structure amplitudes and thermal parameters, observed and calculated intensity relations between some Bijvoet pairs (Table 2), and a table of the relevant interatomic distances have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34171 (21 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 1. *Positional parameters* ($\times 10^4$; for Co and Br $\times 10^5$; for H $\times 10^3$)

	x	y	z		x	y	z
Co	53591 (9)	40145 (4)	31962 (16)	H(N3)1	413 (6)	447 (2)	472 (9)
N(1)	4695 (7)	3532 (2)	4372 (9)	H(N3)2	490 (8)	433 (3)	572 (11)
N(2)	4033 (5)	3960 (2)	1953 (10)	H(N4)1	653 (7)	455 (2)	244 (9)
N(3)	4721 (6)	4414 (3)	4724 (9)	H(N4)2	580 (9)	449 (3)	98 (12)
N(4)	5869 (5)	4555 (2)	2125 (8)	H(N5)1	720 (6)	422 (3)	392 (9)
N(5)	6753 (6)	3982 (2)	4322 (8)	H(N5)2	662 (4)	397 (2)	524 (6)
N(6)	6061 (6)	3627 (2)	1685 (9)	H(N6)1	572 (7)	334 (3)	181 (12)
C(1)	5016 (9)	3386 (3)	5697 (14)	H(N6)2	610 (5)	372 (2)	90 (7)
C(2)	4371 (10)	3132 (3)	6703 (15)	H(C1)	565 (5)	345 (2)	621 (7)
C(3)	3344 (10)	3066 (4)	6298 (17)	H(C2)	466	305	765
C(4)	2941 (9)	3215 (3)	4876 (19)	O(C2)	479 (3)	300 (1)	812 (4)
C(5)	3671 (8)	3432 (3)	3878 (13)	H(C3)	274 (7)	290 (3)	700 (11)
C(6)	3423 (7)	3602 (3)	2326 (13)	H(C8)	202 (6)	351 (2)	-47 (9)
C(7)	2675 (8)	3420 (4)	1283 (16)	H(C9)	288 (5)	414 (2)	-135 (7)
C(8)	2496 (9)	3661 (4)	-44 (18)	H(C10)	415 (7)	438 (3)	60 (10)
C(9)	3013 (9)	4044 (4)	-373 (13)	H(C13)	584 (5)	484 (2)	498 (7)
C(10)	3812 (8)	4177 (4)	647 (12)	H(C14)	463 (6)	498 (2)	233 (9)
C(11)	1755 (15)	3179 (7)	4757 (33)	H(C15)1	656 (6)	540 (2)	285 (9)
C(12)	2180 (12)	2955 (5)	1471 (23)	H(C15)2	599 (6)	541 (2)	155 (10)
C(13)	5211 (7)	4868 (3)	4496 (10)	H(C16)1	460 (9)	578 (3)	292 (13)
C(14)	5286 (7)	4944 (3)	2808 (9)	H(C16)2	540 (5)	599 (2)	306 (8)
C(15)	5841 (9)	5379 (3)	2479 (12)	H(C17)1	579 (6)	563 (2)	536 (9)
C(16)	5249 (10)	5751 (3)	3320 (14)	H(C17)2	475 (7)	586 (3)	558 (10)
C(17)	5106 (10)	5674 (3)	4979 (14)	H(C18)1	377 (9)	511 (3)	494 (13)
C(18)	4570 (9)	5230 (3)	5287 (12)	H(C18)2	451 (5)	515 (2)	626 (7)
C(19)	7341 (8)	3585 (3)	3742 (12)	H(C19)	715 (6)	333 (2)	411 (9)
C(20)	7250 (7)	3591 (3)	2027 (11)	H(C20)	752 (5)	385 (2)	168 (8)
C(21)	7795 (9)	3207 (3)	1200 (14)	H(C21)1	739 (6)	295 (2)	174 (11)
C(22)	8970 (10)	3169 (4)	1814 (20)	H(C21)2	773 (10)	316 (4)	7 (16)
C(23)	9033 (10)	3151 (4)	3553 (18)	H(C22)1	943 (10)	339 (4)	182 (16)
C(24)	8490 (9)	3550 (4)	4318 (16)	H(C22)2	920 (8)	293 (3)	118 (12)
Br	62103 (9)	42205 (3)	-17703 (13)	H(C23)1	881 (10)	282 (4)	391 (14)
Cl(1)	4880 (3)	7407 (1)	2745 (5)	H(C23)2	975 (10)	308 (3)	403 (13)
Cl(2)	3439 (2)	5520 (1)	9311 (3)	H(C24)1	886 (6)	378 (2)	402 (8)
O(1)	5028 (10)	7732 (3)	3895 (15)	H(C24)2	846 (10)	350 (4)	525 (14)
O(2)	4291 (12)	7064 (4)	3259 (16)	H(O9)1	828 (5)	492 (2)	345 (8)
O(3)	4347 (12)	7600 (4)	1524 (19)	H(O9)2	887 (10)	472 (4)	320 (16)
O(4)	5854 (10)	7259 (5)	2273 (20)				
O(5)	2934 (9)	5650 (4)	10690 (13)				
O(6)	2657 (7)	5398 (4)	8262 (14)				
O(7)	4203 (10)	5217 (4)	9518 (13)				
O(8)	3986 (13)	5855 (4)	8652 (17)				
O(9)	8288 (5)	4701 (2)	3290 (10)				

which $|F(hkl)|$ and $|F(\bar{h}\bar{k}l)|$ differed by more than 20%, are compared.

Discussion. The molecular configuration of $(-)_589[\text{Co}(\text{R,R}\text{-chxn})_2(3,3'\text{-dmbpy})]^{3+}$ in the crystal structure is illustrated in Fig. 1 together with the atomic numbering scheme. The Δ absolute configuration of the present complex agrees with the assignment based on the sign of the CD in the first absorption region (Suzuki & Kimura, 1977). The bidentate ligand dmbpy is coordinated to the Co with an average Co–N distance of 1.959 (8) Å and N–Co–N angle of 82.7 (3)°. The bond lengths and angles in the Co–dmbpy ring are shown in Fig. 2. The C–C bond in the dmbpy chelate ring is inclined at an angle of 15.8° to the pseudo-threefold axis; the conformation of the chelate ring formed by dmbpy is λ , as expected from a molecular model (Suzuki & Kimura, 1977). A projection of the complex cation along the pseudo-twofold axis is shown in Fig. 3. The two pyridine moieties of the dmbpy are twisted in such a way that they can avoid repulsion by the *R,R*-chxn ligands. The pyridine (py) rings are essentially planar (r.m.s. deviations from the least-squares planes are 0.029 and 0.033 Å). They are inclined at angles of 17.3 and 16.9° to the N(1)–Co–N(2) plane, and 1.6 and 5.4° to the C(5)–C(6) bond axis. The twist angle around C(5)–C(6) is 29.4°. The tilt angles of each C–CH₃ bond axis to the appropriate py ring

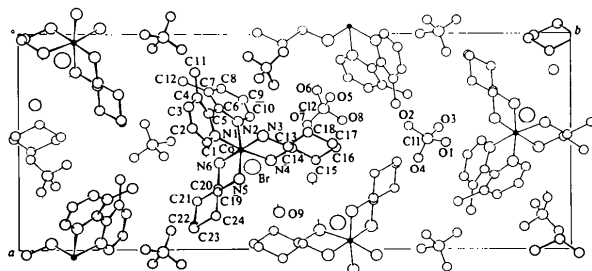


Fig. 1. A projection of the crystal structure along *c*. Dotted lines indicate hydrogen bonds.

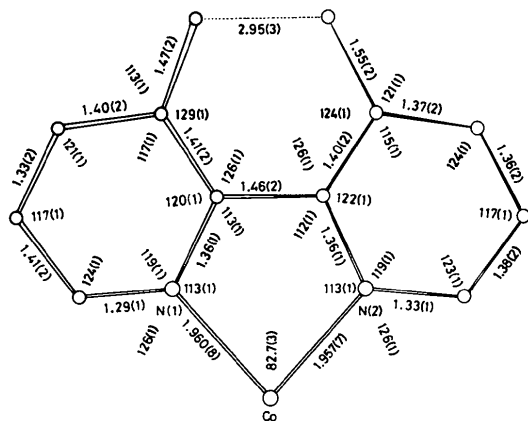


Fig. 2. Bond lengths (Å) and angles (°) in the dmbpy ring.

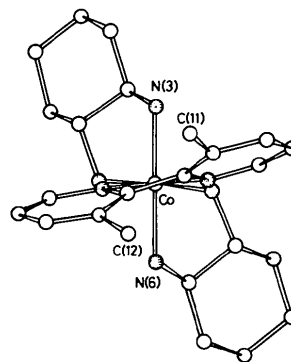


Fig. 3. A projection of the complex cation along the pseudo-twofold axis.

are 11.5 and 10.1°, and the distance between the two methyl C atoms is 2.95 (3) Å. The C–C bonds in the two chelate rings formed by chxn ligands are inclined at 6.8 and 7.4° to the pseudo-threefold axis, respectively. The mean Co–N distance in the Co–chxn rings is 1.967 (8) Å with an N–Co–N angle of 85.3 (3)°. The shape and size of the chxn ligands are normal.

The complex cation has an approximate twofold symmetry axis through the Co and the midpoint of the central C–C bond in dmbpy. The reason the disordered hydroxyl group is specifically bonded to C(2) may be explained as follows: around C(2) there is a space to accommodate O(C2); moreover, it is located favorably to form an O–H...O hydrogen bond of 2.71 Å with O(2). On the other hand, the calculated position for a hydroxyl group bonded to C(9) is too close to O(5), the O...O distance being as short as 2.43 Å. It is not known whether the hydroxy derivative was an impurity in the starting materials or was formed during the synthetic procedure.

The authors are grateful to Dr T. M. Suzuki for supplying the crystal specimen. The calculations were carried out on the FACOM 230-48 computer at this Institute with a local version of *UNICS* (Sakurai, 1967). Part of the calculation was performed on a HITAC 8800/8700 computer at the Computer Center of The University of Tokyo. Part of the cost of this research was met by a Scientific Research Grant from the Ministry of Education, to which the authors' thanks are due.

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