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# Structure of $(+)_{589}$-[1,2-Bis(dimethylphosphino)ethane]bis(ethylenediamine)cobalt(III) Tribromide Sesquihydrate, $[Co(C_2H_8N_2)_2(C_6H_{16}P_2)]Br_3.\frac{3}{2}H_2O$

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**Abstract.** $M_r = 596{\cdot}0$, monoclinic, $C2$, $a = 16{\cdot}399$ (2), $b = 8{\cdot}785$ (1), $c = 15{\cdot}679$ (2) Å, $\beta = 105{\cdot}37$ (2)°, $V = 2177{\cdot}9$ (4) Å$^3$, $Z = 4$, $D_x = 1{\cdot}82$ Mg m$^{-3}$, $\lambda$(Mo $K\alpha$) = 0·7107 A, $\mu$(Mo $K\alpha$) = 6·81 mm$^{-1}$. The structure was solved by the Patterson method and refined to a final $R$ value of 0·058 for 3345 observed reflections. The absolute configuration of the complex ion can be designated as $\Lambda$. A *trans* influence of the P atoms on the Co—N bond distance was observed: the average distances between Co and the N atoms which are in *cis* and *trans* positions with respect to the coordinated P atoms are 1·987 (9) and 2·032 (8) Å, respectively.

**Introduction.** Optically active Co$^{III}$ complexes containing alkylphosphine ligands were recently prepared to compare their spectral properties with those of the corresponding diamine Co$^{III}$ complexes (Kinoshita, Kashiwabara, Fujita, Matsumoto & Ooi, 1981). Crystals of the title compound containing dmpe $[(CH_3)_2PCH_2CH_2P(CH_3)_2]$ have been subjected to X-ray crystal structure analysis in order to determine the absolute configuration of the complex ion and to establish the relationship between the absolute configuration and the circular-dichroism (CD) spectrum.

**Experimental.** Orange plate-like crystals, elongated along **b**, preliminary determination of lattice parameters and crystal symmetry (space group $C2$ from systematic absences: $hkl$, $h + k = 2n$) made with a Weissenberg goniometer, approximate dimensions of crystal 0·5 × 0·3 × 0·2 mm, Rigaku automated four-circle diffractometer, graphite monochromator, cell parameters refined by least-squares methods on the basis of 13 independent $2\theta$ values, Mo $K\alpha$ radiation ($31 < 2\theta < 39°$, $\lambda = 0{\cdot}7107$ Å); intensity measurement performed to $2\theta = 55°$ (the $\pm h + k + l$ set), $\theta$–$2\theta$ scan technique, scan speed 2° min$^{-1}$ ($\theta$), $\pm h - k + l$ set also measured to $2\theta = 40°$; 3737 reflections measured, 3345 intensities with $|F_o| > 3\sigma(|F_o|)$ considered observed and used for the structure determination; during data collection intensities of three standard reflections decreased by 19% in $|F_o|$ owing to decay of the crystal, repeated measurements of standard reflections used to correct for the loss of scattering power; corrections for Lorentz, polarization, and absorption effects; minimum and maximum absorption corrections for $|F_o| = 1{\cdot}77$ and 2·50, respectively; structure solved by Patterson and Fourier methods, refined by block-diagonal least squares with anisotropic thermal parameters for all non-H atoms; H atoms located theoretically, those of water molecules from a difference density map; thermal parameters of H atoms not refined (fixed at 4 Å$^2$); $\sum w||F_o| - |F_c||^2$ minimized, $w = 0{\cdot}25$ for $|F_o| > 20$ and $w = 1{\cdot}0$ for $|F_o| \leq 20$; final $R = 0{\cdot}058$ and $R_w = 0{\cdot}069$ for 3345 observed reflections;* complex neutral-atom scattering factors from *International Tables for X-ray Crystallography* (1974); $F(000) = 1188$; calculations carried out on a FACOM M-160F computer at the Institute for Solid State Physics, University of Tokyo, with *UNICS* III (Sakurai & Kobayashi, 1979); final atomic parameters in Table 1.

The absolute configuration was determined by the anomalous-scattering technique. The observed and calculated intensity differences, $|F(hkl)| - |F(h\bar{k}l)|$, of seven $hkl$ and $h\bar{k}l$ pairs, for which $|F_o(hkl)|$ and $|F_o(h\bar{k}l)|$ differed by more than 50%, are compared in Table 2. The concordance in this table established the absolute structure listed in Table 1. In order to confirm this result, the enantiomeric structure was refined separately. It converged to $R = 0{\cdot}077$ and $R_w = 0{\cdot}092$ for 3345 observed reflections, and could be rejected at the 0·005 significance level (Hamilton, 1965).

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* Lists of structure factors, anisotropic thermal parameters and mean-square displacement tensors have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 38086 (26 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. *Positional parameters* ($\times 10^4$; *for* H $\times 10^3$) *and equivalent isotropic temperature factors* (*Hamilton,* 1959)

| | $x$ | $y$ | $z$ | $B_{eq}$(Å$^2$) |
|---|---|---|---|---|
| Br(1) | 6153 (1) | 5000 | 4153 (1) | 4·2 |
| O(*W*1) | 5000 | 7271 (14) | 5000 | 4·9 |
| O(*W*2) | 9564 (6) | 6855 (13) | 6972 (7) | 5·7 |
| Br(2) | 8636 (1) | 6386 (2) | 8509 (1) | 3·9 |
| Br(3) | 6465 (1) | 5751 (1) | 9137 (1) | 3·4 |
| Co | 7776 (1) | 6075 (1) | 2096 (1) | 1·8 |
| N(1) | 8720 (5) | 7101 (10) | 1764 (5) | 2·3 |
| N(2) | 7799 (5) | 4628 (10) | 1090 (5) | 2·4 |
| N(3) | 6967 (5) | 7483 (9) | 1247 (6) | 2·6 |
| N(4) | 6720 (5) | 5064 (10) | 2213 (5) | 2·4 |
| P(1) | 7910 (2) | 7661 (3) | 3263 (2) | 2·2 |
| P(2) | 8588 (2) | 4502 (3) | 3101 (2) | 2·2 |
| C(1) | 8774 (7) | 6587 (13) | 868 (7) | 3·0 |
| C(2) | 8568 (7) | 4899 (13) | 771 (6) | 2·8 |
| C(3) | 6074 (7) | 7263 (13) | 1302 (8) | 3·4 |
| C(4) | 5985 (7) | 5578 (16) | 1466 (8) | 3·9 |
| C(5) | 8366 (7) | 6583 (12) | 4279 (7) | 2·8 |
| C(6) | 9048 (6) | 5565 (12) | 4120 (6) | 2·5 |
| C(7) | 7005 (7) | 8635 (14) | 3466 (8) | 3·5 |
| C(8) | 8658 (8) | 9196 (13) | 3283 (7) | 3·4 |
| C(9) | 9456 (8) | 3476 (14) | 2836 (8) | 3·5 |
| C(10) | 7990 (7) | 3021 (12) | 3477 (8) | 3·2 |
| H(C1)1 | 942 (7) | 679 (15) | 81 (8) | |
| H(C1)2 | 834 (7) | 725 (15) | 36 (8) | |
| H(C2)1 | 844 (7) | 456 (14) | 8 (8) | |
| H(C2)2 | 909 (8) | 423 (15) | 117 (8) | |
| H(C3)1 | 564 (8) | 764 (14) | 69 (9) | |
| H(C3)2 | 598 (7) | 795 (15) | 185 (8) | |
| H(C4)1 | 540 (7) | 536 (14) | 164 (8) | |
| H(C4)2 | 599 (8) | 493 (15) | 87 (8) | |
| H(C5)1 | 788 (7) | 591 (16) | 444 (8) | |
| H(C5)2 | 863 (7) | 738 (15) | 482 (8) | |
| H(C6)1 | 959 (7) | 625 (15) | 404 (8) | |
| H(C6)2 | 927 (7) | 478 (14) | 467 (8) | |
| H(C7)1 | 669 (8) | 933 (14) | 289 (8) | |
| H(C7)2 | 656 (7) | 782 (15) | 360 (8) | |
| H(C7)3 | 722 (8) | 940 (14) | 404 (8) | |
| H(C8)1 | 843 (7) | 992 (14) | 271 (8) | |
| H(C8)2 | 871 (7) | 989 (15) | 388 (8) | |
| H(C8)3 | 927 (7) | 874 (14) | 330 (8) | |
| H(C9)1 | 921 (7) | 282 (15) | 224 (8) | |
| H(C9)2 | 992 (8) | 428 (14) | 275 (8) | |
| H(C9)3 | 974 (8) | 271 (14) | 338 (8) | |
| H(C10)1 | 768 (7) | 229 (14) | 292 (8) | |
| H(C10)2 | 841 (8) | 232 (14) | 398 (8) | |
| H(C10)3 | 751 (7) | 353 (14) | 376 (8) | |
| H(N1)1 | 932 (7) | 682 (14) | 225 (8) | |
| H(N1)2 | 863 (7) | 833 (15) | 176 (8) | |
| H(N2)1 | 724 (7) | 482 (15) | 54 (8) | |
| H(N2)2 | 780 (7) | 346 (15) | 132 (8) | |
| H(N3)1 | 699 (7) | 723 (15) | 57 (8) | |
| H(N3)2 | 716 (7) | 866 (14) | 140 (8) | |
| H(N4)1 | 660 (7) | 538 (14) | 284 (8) | |
| H(N4)2 | 679 (8) | 383 (14) | 219 (8) | |
| H(O*W*1) | 520 (7) | 645 (13) | 479 (8) | |
| H(O*W*2)1 | 949 (7) | 733 (15) | 666 (8) | |
| H(O*W*2)2 | 922 (7) | 580 (15) | 646 (8) | |

Table 2. *Determination of the absolute configuration*

| | | | $\lvert F(hkl)\rvert - \lvert F(h\bar{k}l)\rvert$ | |
|---|---|---|---|---|
| $h$ | $k$ | $l$ | obs. | calc. |
| 6 | 4 | 0 | 13·3 | 10·4 |
| $\bar{9}$ | 3 | 3 | −11·2 | −7·8 |
| $\overline{12}$ | 2 | 4 | −7·8 | −7·3 |
| $\bar{4}$ | 4 | 4 | −6·9 | −8·6 |
| $\bar{3}$ | 3 | 6 | −11·6 | −14·9 |
| $\bar{3}$ | 1 | 7 | −7·2 | −8·9 |
| $\bar{4}$ | 4 | 9 | −6·9 | −7·9 |

**Discussion.** A perspective view of the complex cation is shown in Fig. 1. The complex has a pseudo twofold axis through the Co and the midpoint of the C(5)—C(6) bond of the dmpe ligand. The central Co atom is surrounded octahedrally by the two P atoms of dmpe and the four N atoms of the ethylenediamine (en) ligands. The absolute configuration of the present complex is $\Lambda$ in agreement with the prediction based on the CD spectrum (Ohishi, Kashiwabara & Fujita, 1980). The empirical rule for tris-chelated $d^6$ or $d^3$ complexes with five-membered chelate rings states that those complexes showing a positive CD band on the longer-wavelength side of the first absorption region have absolute configuration $\Lambda$ (Saito, 1979). Bond lengths and bond angles are listed in Table 3. A *trans* influence of the P atoms on the Co—N bond distances is observed. N(2) and N(3) are in the *trans* position with respect to the coordinated P(1) and P(2), respectively. The mean value of the Co—N(2) and Co—N(3) bonds is 2·032 (8) Å, which is longer by 0·045 Å than that of the Co—N(1) and Co—N(4) bonds. The *trans* influence of the P atoms was also recognized in $(+)_{589}$-$\Delta$-*fac*-$[Co\{NH_2CH_2CH_2P(CH_3)_2\}_3]Br_3.3H_2O$ (Kinoshita *et al.,* 1981). The conformation of the five-membered chelate ring formed by the dmpe ligand is presented in Fig. 2. It takes a $\lambda$ symmetrical skew conformation. The dihedral angle P(1)—C(5)—C(6)—P(2) is 51·4 (8)°, which is a little greater than the N—C—C—N angles of

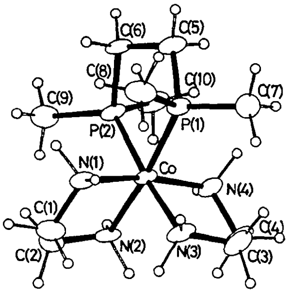

Fig. 1. An *ORTEP* drawing of the complex ion with thermal ellipsoids scaled at the 50% probability level (Johnson, 1965). H atoms are represented by circles of radius 0·08 Å.

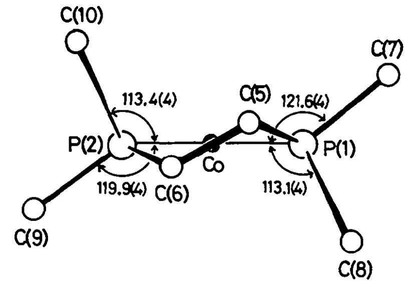

Fig. 2. The dmpe ligand viewed along the line through the Co atom and the midpoint of the P(1)—P(2) axis. The Co—P—$CH_3$ bond angles (°) are shown.

the en ligands, 45·8 (11) and 48·8 (11)°. The P—Co—P angle is 84·2 (1)°, which is nearly the same as the mean N—Co—N angle of 84·4 (4)° spanned by the en chelate rings. Mean Co—P and P—C bond distances are 2·256 (3) and 1·823 (13) Å, respectively. The Co—P(1)—C(7) and Co—P(2)—C(9) angles average 120·8 (4)°, greater than the mean of 113·3 (4)° for the Co—P(1)—C(8) and Co—P(2)—C(10) angles, as a result of the staggered configuration of the C(5)—C(6) ethylene group.

Fig. 3 shows a projection of the structure along **b**. The O(*W*1) atoms lie on twofold axes parallel to **b**. Water molecules O(*W*1) and O(*W*2) are linked to the $\mathrm{Br}(1)^-$ ion by weak hydrogen bonds: Br(1)···O(*W*1) = 3·26 (1), Br(1)···O(*W*2) = 3·32 (1) Å. Two complex cations related by a unit translation along **b** are linked to $\mathrm{Br}(2)^-$ and $\mathrm{Br}(3)^-$ anions by weak hydrogen bonds: N(3)—H(N3)2···Br(2)···H(N4)2—N(4) and N(1)—H(N1)2···Br(3)···H(N2)2—N(2). The distances Br···N and Br···H(N) are 3·4–3·7 and 2·4–2·9 Å, respectively.

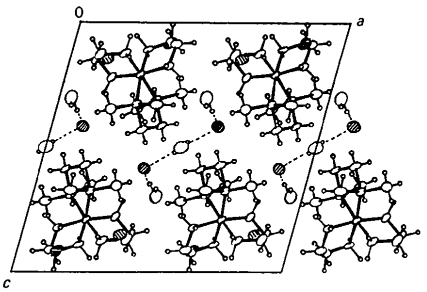

Fig. 3. A projection of the crystal structure along **b**. The hatched ellipsoids indicate $\mathrm{Br}^-$ ions. Hydrogen bonds are marked by broken lines.

Table 3. *Bond lengths* (Å) *and angles* (°)

| | | | |
|---|---|---|---|
| Co—N(1) | 1·976 (9) | P(1)—C(5) | 1·834 (10) |
| Co—N(2) | 2·034 (8) | P(1)—C(7) | 1·813 (13) |
| Co—N(3) | 2·030 (8) | P(1)—C(8) | 1·817 (13) |
| Co—N(4) | 1·998 (8) | P(2)—C(6) | 1·832 (9) |
| Co—P(1) | 2·264 (3) | P(2)—C(9) | 1·823 (13) |
| Co—P(2) | 2·248 (3) | P(2)—C(10) | 1·820 (12) |
| N(1)—C(1) | 1·502 (14) | C(1)—C(2) | 1·520 (16) |
| N(2)—C(2) | 1·493 (15) | C(3)—C(4) | 1·517 (18) |
| N(3)—C(3) | 1·502 (15) | C(5)—C(6) | 1·503 (15) |
| N(4)—C(4) | 1·510 (13) | | |
| | | | |
| N(1)—Co—N(2) | 84·5 (4) | Co—N(4)—C(4) | 109·2 (6) |
| N(1)—Co—N(3) | 88·3 (3) | Co—P(1)—C(5) | 108·3 (3) |
| N(1)—Co—N(4) | 170·3 (4) | Co—P(1)—C(7) | 121·6 (4) |
| N(1)—Co—P(1) | 91·0 (3) | Co—P(1)—C(8) | 113·1 (4) |
| N(1)—Co—P(2) | 96·0 (3) | C(5)—P(1)—C(7) | 104·8 (5) |
| N(2)—Co—N(3) | 90·9 (3) | C(5)—P(1)—C(8) | 104·5 (5) |
| N(2)—Co—N(4) | 89·3 (3) | C(7)—P(1)—C(8) | 103·1 (6) |
| N(2)—Co—P(1) | 173·6 (2) | Co—P(2)—C(6) | 109·2 (3) |
| N(2)—Co—P(2) | 91·7 (2) | Co—P(2)—C(9) | 119·9 (4) |
| N(3)—Co—N(4) | 84·3 (3) | Co—P(2)—C(10) | 113·4 (4) |
| N(3)—Co—P(1) | 93·5 (2) | C(6)—P(2)—C(9) | 106·6 (5) |
| N(3)—Co—P(2) | 175·1 (2) | C(6)—P(2)—C(10) | 102·4 (5) |
| N(4)—Co—P(1) | 95·7 (3) | C(9)—P(2)—C(10) | 103·9 (6) |
| N(4)—Co—P(2) | 91·7 (3) | N(1)—C(1)—C(2) | 108·6 (9) |
| P(1)—Co—P(2) | 84·2 (1) | N(2)—C(2)—C(1) | 108·0 (9) |
| Co—N(1)—C(1) | 110·8 (6) | N(3)—C(3)—C(4) | 106·0 (9) |
| Co—N(2)—C(2) | 110·5 (6) | N(4)—C(4)—C(3) | 109·3 (9) |
| Co—N(3)—C(3) | 111·2 (7) | P(1)—C(5)—C(6) | 108·2 (7) |
| | | P(2)—C(6)—C(5) | 107·2 (7) |

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