and both P—N and P—F bonds are collinear and located in apical positions.

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A New Description of the Structure of (−)$_{500}^{CD}$-mer-[Co(Ethylenediamine-N-acetate)(3-azapentane-1,5-diamine)]Br₂.$\frac{2}{3}$CH₃OH.$\frac{2}{3}$H₂O*

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Abstract. The crystal structure of (−)$_{500}^{CD}$-mer-[Co(edma)(dien)]Br₂.$\frac{2}{3}$CH₃OH.$\frac{2}{3}$H₂O has recently been reported [Kawaguchi, Fukaki, Ama, Yasui, Okamoto & Hidaka (1988). Bull. Chem. Soc. Jpn, 61, 2359–2364] in space group P1 [$a = 13.824$ (8), $b = 13.814$ (8), $c = 8.055$ (3) Å, $\alpha = 101.18$ (6), $\beta = 101.17$ (6), $\gamma = 116.32$ (5)°, $V = 1282.3$ Å³, $Z = 3$] and refined to $R_F = 0.047$ ($wR = 0.056$). The structure has now been refined in space group R3 (hexagonal axes, $a = 23.495$, $c = 8.055$ Å, $Z = 9$) to $R_F = 0.034$, based on the transformed original data. The increase in Laue symmetry – from $\bar{1}$ to $\bar{3}$ – has caused no significant changes in the geometry of the cation but the e.s.d.'s of the bonds and angles are typically half of those previously reported. A stereoview of the overall structure is presented and the possible hydrogen bonds are discussed.

Introduction. The crystal structure of (−)$_{500}^{CD}$-mer-[Co(edma)(dien)]Br₂.$\frac{2}{3}$CH₃OH.$\frac{2}{3}$H₂O (edma and dien denote ethylenediaminemonoacetato and diethylenetriamine) has recently been described (Kawaguchi, Fukaki, Ama, Yasui, Okamoto & Hidaka, 1988) (hereafter KFAYOH). A preliminary communication on the crystal structure has also been reported (Okamoto, Yasui & Hidaka, 1987). The complex was prepared and resolved according to methods described in a previous paper (Yasui, Shikiji, Koine, Ama & Kawaguchi, 1987). The structure was reported and refined by KFAYOH in space

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* Alternative nomenclature: (−)$_{500}^{CD}$-mer-(diethylenetriamine)-(ethylenediaminemonoacetato)cobalt dibromide–methanol–water (3/2/2).

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group $P1$. A total of 5001 independent reflections with $F_o > 3\sigma|F_o|$ (out of the 8064 Mo $K\alpha$ measured reflections) were used in the refinement. The authors remark that 'although there are three crystallographically independent cations in the asymmetric unit their shapes and sizes remarkably resemble one another'. The absolute configuration of the complex was determined by comparing the final R factors of two separate refinements carried out for two possible enantiomers.

All the cations were found to be in a δ spiral configuration due to the arrangement of the two *trans* N—H groups in *mer*-[Co(edma)(dien)]²⁺ and S configuration due to the asymmetric N atom of the edma ligand.

The structure can be better described and refined in space group $R3$ (No. 146).

Vectors [211], [$\bar{1}$10] and [001] define an effectively trigonal cell (hexagonal axes, $a' = 23\cdot495$, $b' = 23\cdot479$, $c' = 8\cdot055$ Å, $\alpha = 90\cdot00$, $\beta = 89\cdot95$, $\gamma = 120\cdot03°$, $V = 3847\cdot1$ Å³, $Z = 9$) and the corresponding coordinate transformation $x' = \frac{1}{3}(x - 0\cdot4521) + \frac{1}{3}(y - 0\cdot2723)$, $y' = -\frac{1}{3}(x - 0\cdot4521) + \frac{2}{3}(y - 0\cdot2723)$, $z' = -\frac{1}{3}(x - 0\cdot4521) - \frac{1}{3}(y - 0\cdot2723) + (z - 0\cdot1693)$ leads to a structure in space group $R3^*$ which we have refined, based on the original data recovered from SUP 8810. The transformation on the coordinates is such that it preserves the chirality of the structure, a fact which was checked also *via* a comparison of signs of torsion angles in the two space groups.

Refinement. If cation B of the triclinic asymmetric unit is translated by x, $-1 + y$, $-1 + z$, subsequent transformation to space group $R3$ (hexagonal axes) yields new coordinates for the three cations, A, B and C, which are found to relate as x, y, z; $\bar{y}, x - y, z$ and $y - x, \bar{x}, z$. We have selected the transformed coordinates of cation A and of anions Br(1) and Br(3) to represent the asymmetric unit of space group $R3$. Refinement was on F using the *SHELX*77 system of programs (Sheldrick, 1977). Values of 5034 reflections coded as 'observed' were recovered from SUP 8810. Re-indexing and averaging according to point group 3 led to an R_{int} of 0·044, the number of unique reflections being 1971. Isotropic refinement converged at $R = 0\cdot093$, anisotropic refinement of the non-H atoms of the cation and the two Br anions converged at 0·054. At this stage a difference Fourier synthesis was computed in order to locate the missing methanol and water molecules. The measured density ($\rho = 1\cdot82$ g cm⁻³) and the chemical

Table 1. *Final fractional coordinates* ($\times 10^5$ *for* Co *and* Br, $\times 10^4$ *for the rest*) *and* U_{eq} ($\text{Å}^2 \times 10^4$ *for* Co *and* Br, $\text{Å}^2 \times 10^3$ *for the rest of the cation atoms*) *and* U_{iso} (*of the methanol and water molecules*, $\text{Å}^2 \times 10^2$) *values*

$$U_{eq} = \tfrac{1}{3}\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

|	x	y	z	U_{eq}/U_{iso}
Co	11741 (5)	25807 (5)	−4	171 (2)
Br(1)	25139 (4)	42198 (5)	64945 (20)	401 (2)
Br(2)	15502 (5)	21175 (5)	49728 (18)	355 (2)
O(1)	435 (3)	2430 (3)	1324 (3)	25 (1)
O(2)	164 (3)	2825 (4)	3497 (3)	33 (2)
N(1)	1681 (3)	3108 (3)	1849 (9)	21 (1)
N(2)	2020 (4)	2832 (4)	−1060 (10)	25 (2)
N(3)	1123 (3)	3293 (4)	−1163 (9)	23 (1)
N(4)	616 (3)	2023 (4)	−1784 (10)	27 (2)
N(5)	1100 (3)	1770 (3)	895 (9)	25 (1)
C(1)	570 (4)	2833 (4)	2528 (10)	24 (2)
C(2)	1296 (4)	3364 (4)	2674 (12)	25 (2)
C(3)	2355 (4)	3604 (4)	1272 (13)	29 (2)
C(4)	2553 (4)	3223 (5)	158 (12)	30 (2)
C(5)	734 (5)	3030 (5)	−2716 (13)	33 (2)
C(6)	236 (4)	2327 (5)	−2468 (12)	29 (2)
C(7)	226 (5)	1349 (5)	−1123 (15)	36 (2)
C(8)	701 (5)	1210 (5)	−257 (14)	36 (2)
CM*	132 (1)	40 (1)	373 (2)	5 (5)
OM*	141 (2)	62 (2)	516 (5)	8 (1)
OW*	0	0	629 (8)	9 (2)

*CM, OM and OW denote the methanol atoms and the water oxygen atom, respectively.

analysis (Yasui, Shikiji, Koine, Ama & Kawaguchi, 1987) suggest that there are $\frac{2}{3}$ methanol and $\frac{2}{3}$ water molecules for each cation. However, considerable disorder was found among the possible methanol and water positions. Thus, the difference synthesis showed a series of peaks (the highest electron density being 2·6 e Å⁻³) in the region of the expected methanol molecule. Additional peaks (the highest electron density being 1·3 e Å⁻³) were observed at Wyckoff positions a at 0, 0, z and we attributed these to disordered water molecules. Identification of the methanol oxygen was made on the basis of possible hydrogen bonding to the water molecule and to Br⁻ (see Table 3). The occupancies employed in the refinement are such that only 0·5 carbon and 0·3 oxygen (out of the reported $\frac{2}{3}$ methanol) and 0·1 water oxygen (out of the reported $\frac{2}{3}$) are accounted for. The low occupancy of the water oxygen together with the slightly higher value of the calculated density for $\frac{2}{3}$ water molecule ($\rho = 1\cdot835$ g cm⁻³) when compared to the experimental density ($\rho = 1\cdot82$ g cm⁻³) suggest a lower water content. We note that a density of exactly 1·82 g cm⁻³ would agree with the presence of 0·45 water molecule in the asymmetric unit. We conclude that the amount of water and perhaps methanol present has not been completely clarified.

The positions of the hydrogens were calculated and introduced into the final stages of least squares and refined. Some of the hydrogens [those attached

Table 2. *Molecular dimensions (Å and °) of the*
$(-)^{CD}_{500}$-*mer-[Co(edma)(dien)]$^{2+}$ cation*

The numbering system is that given by KFAYOH in their Fig. 2.
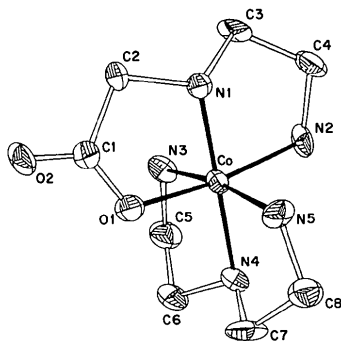
Co—O1	1·914 (6)	N2—C4	1·492 (11)
Co—N1	1·922 (7)	N3—C5	1·489 (12)
Co—N2	1·963 (7)	N4—C6	1·501 (11)
Co—N3	1·972 (7)	N4—C7	1·476 (13)
Co—N4	1·944 (7)	N5—C8	1·495 (11)
Co—N5	1·962 (7)	C1—C2	1·533 (12)
O1—C1	1·280 (10)	C3—C4	1·496 (14)
O2—C1	1·226 (10)	C5—C6	1·485 (14)
N1—C2	1·471 (10)	C7—C8	1·486 (14)
N1—C3	1·495 (10)		

O1—Co—N1	84·2 (3)	Co—N1—C3	109·5 (6)
O1—Co—N2	170·5 (3)	C2—N1—C3	116·7 (7)
O1—Co—N3	89·3 (3)	Co—N2—C4	108·1 (6)
O1—Co—N4	92·5 (3)	Co—N3—C5	109·4 (6)
O1—Co—N5	89·1 (3)	Co—N4—C6	108·2 (5)
N1—Co—N2	86·3 (3)	Co—N4—C7	107·7 (6)
N1—Co—N3	95·9 (3)	C6—N4—C7	116·3 (7)
N1—Co—N4	176·6 (3)	Co—N5—C8	109·7 (6)
N1—Co—N5	93·8 (3)	O1—C1—O2	124·7 (8)
N2—Co—N3	91·2 (3)	O1—C1—C2	115·0 (7)
N2—Co—N4	97·0 (3)	O2—C1—C2	120·3 (8)
N2—Co—N5	92·1 (3)	N1—C2—C1	107·1 (6)
N3—Co—N4	85·1 (3)	N1—C3—C4	104·2 (7)
N3—Co—N5	170·0 (3)	N2—C4—C3	110·3 (7)
N4—Co—N5	85·1 (3)	N3—C5—C6	109·1 (8)
Co—O1—C1	114·8 (5)	N4—C6—C5	104·6 (7)
Co—N1—C2	107·7 (5)	N4—C7—C8	105·8 (7)
		N5—C8—C7	107·9 (7)

to N(3), N(5) and C(8)] had to be refined as 'riding atoms'.

During the final cycles of least squares several low angle reflections (110, 030, 01$\bar{1}$ and their equivalents in space group $R3$) were detected for which the value of F_{obs} was considerably lower than that of F_{calc}. These discrepancies were attributed to extinction and the reflections omitted.

Full-matrix least squares [1961 unique reflections, unit weights, 242 parameters refined (scale factor, anisotropic displacement factors for the ordered non-H atoms, isotropic for the 'major orientation' of the methanol and water molecules and of the hydrogens)] converged at $R_F = 0·034$. Max. and min. heights in the final map were 0·55 and $-0·49$ e Å^{-3} with a $(\Delta/\sigma)_{max}$ value of 0·31 for the non-H atoms.

A re-check of the absolute configuration has also been performed; a refinement of the enantiomeric

atomic parameters (the λ spiral configuration) converged at the higher value of $R = 0·044$.

Final positional parameters and equivalent displacement factors of the non-H atoms are presented in Table 1.*

Discussion. The change in space group requires the asymmetric unit to consist of only one cation, two Br anions and $\frac{2}{3}$ methanol and water molecules. The molecular dimensions of the cation are presented in Table 2.

Since the space-group change involves only an increase in Laue symmetry from $\bar{1}$ to $\bar{3}$, there are no significant alterations in the bond lengths and angles (Schomaker & Marsh, 1979; Marsh & Herbstein, 1988). However, we note that due to the significantly lower R factor attained for the present refinement the e.s.d.'s of the distances and angles are usually half of those reported in space group $P1$.

A stereoview (Johnson, 1965) of the overall structure is presented in Fig. 1. The structure is characterized by extensive hydrogen bonding (Table 3). Four types of hydrogen bonds occur: carbonyl···HN, Br···HN, O(methanol)···O(water) and O(methanol)···Br. The criteria for deciding whether hydrogen bonds of the N—H···Br type are formed are d(N—H···Br) < 3·6 Å and the closeness to linearity of the N—H···Br angle. The interaction will be weakened but not eliminated for approaches not meeting these criteria. Obviously, characterization of a particular approach as a hydrogen bond contains some elements of arbitrariness. In view of the deviations of the relevant angles from linearity we regard the contacts listed in Table 3 to represent weak hydrogen bonds.

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* Anisotropic displacement factors of the non-H atoms, coordinates and isotropic displacement factors of the H atoms and a list of structure factors have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 52359 (14 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.
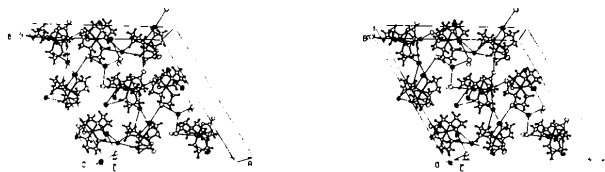

Fig. 1. *ORTEP* stereoview of the unit cell of $(-)^{CD}_{500}$-*mer*-[Co(edma)(dien)]Br$_2$.$\frac{2}{3}$CH$_3$OH.$\frac{2}{3}$H$_2$O. The displacement ellipsoids are 50% probability distributions for the non-H atoms of the cation and Br anions, and of convenient size for the 'major orientations' of the disordered methanol and water molecules and for the H atoms. The hydrogen bonds listed in Table 3 are shown by thin lines. All the eight hydrogen bonds involving the cation are shown for the moiety situated at the centre of the unit cell.

Table 3. *Geometrical details* (Å *and* °) *of possible hydrogen bonds*

The e.s.d.'s of the bonds are ~0·1 Å for N—H, O—H and Br⋯H; ~0·007 Å for Br⋯N; ~0·01 Å for N⋯O; ~0·04 Å for Br⋯OM and OM⋯OW. The e.s.d.'s of the angles are ~7°.

Reference atom Donor (D)	Acceptor	D—H	D⋯A	H⋯A	D—H⋯A
N(1)—HN(1)	Br(2^i)	1·00	3·335	2·38	160
N(2)—HN(21)	Br(1^{ii})	0·81	3·475	2·81	141
N(2)—HN(22)	Br(1^{iii})	0·90	3·516	2·83	134
N(3)—HN(31)	Br(1^{ii})	1·08	3·445	2·47	149
N(3)—HN(32)	O(2^{iv})	1·08	2·91	1·89	156
N(4)—HN(4)	Br(2^{ii})	1·28	3·347	2·18	150
N(5)—HN(52)	Br(1^{iii})	1·08	3·453	2·50	146
OM*	Br(2^i)		3·38		
OW*	OM*		3·02		

Symmetry code: (i) x, y, z; (ii) $x, y, -1 + z$; (iii) $\frac{2}{3} - y, \frac{1}{3} + x - y, \frac{1}{3} + z - 1$; (iv) $\frac{1}{3} - y, \frac{2}{3} + x - y, \frac{2}{3} + z - 1$.

* The H atoms of the disordered methanol and water molecules could not be identified.

The proposed hydrogen bonding is such that each cation forms eight hydrogen bonds in seven of which the N—H groups act as donors (to the Br anions and to the carbonyl group of an adjacent cation). The scheme is completed by an eighth hydrogen bond involving the carbonyl oxygen as acceptor. This leads to an arrangement in which each cation is linked to four adjacent cations, two *via* hydrogen bonding to Br(1) and two involving hydrogen bonds of the N—H carbonyl type.

The packing of the linked cations is such that it leaves cavities around the threefold axes which accommodate the disordered methanol and water molecules together with the Br(2) anion.

Each of the Br(2) anions in the cavity is hydrogen bonded to two N—H groups belonging to cations related by translation along c and to methanol which in turn is presumably hydrogen bonded to the water molecule situated on the threefold axis.

We assume that the water molecule, when present, acts as a donor only, with the requirements of three-fold symmetry attained in a disordered fashion.

The two Br anions are involved in different numbers of hydrogen bonds. Thus, Br(1) forms four such bonds to two adjacent cations, whereas Br(2) is involved in three such bonds; two to the N—H groups and one to the methanol.

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Structure of *cyclo*(-*N*-Hydroxyglycyl-L-phenylalanyl-)

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Abstract. 3-Benzyl-1-hydroxy-2,5-piperazinedione, $C_{11}H_{12}N_2O_3$, $M_r = 220.2$, orthorhombic, $P2_12_12_1$, $a = 14.523 (7)$, $b = 11.622 (4)$, $c = 6.293 (1)$ Å, $V = 1062 (1)$ Å^3, $Z = 4$, $D_m = 1.368 (4)$, $D_x = 1.377$ Mg m^{-3}, λ(Cu $K\alpha$) = 1.5418 Å, $\mu = 0.808$ mm^{-1}, $F(000) = 464.0$, $T = 296$ K, $R = 0.055$, $wR = 0.074$, for 768 observations. The diketopiperazine (DKP) ring is almost planar, the C(3) atom deviating most from the plane. The benzene ring is folded over the DKP ring, with dihedral angle of 49°

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