Table 2. *The average values of bond distances* (Å) *and bond angles* (°) *in the two* 18-*crown*-6.K⁺ *cations and an* $Mo_6O_{19}^{2-}$ *anion*

18-Crown-6(1).K(1)⁺ cation			18-Crown-6(2).K(2)⁺ cation		
C–C	1·47 (4)	[1·41–1·51]	C–C	1·45 (7)	[1·37–1·54]
C–O	1·41 (3)	[1·37–1·44]	C–O	1·42 (6)	[1·31–1·57]
K–O	2·82 (2)	[2·77–2·88]	K–O	2·79 (2)	[2·72–2·88]
C–C–O	110 (2)	[107–114]	C–C–O	109 (4)	[105–113]
C–O–C	113 (2)	[110–116]	C–O–C	113 (3)	[107–118]
		$Mo_6O_{19}^{2-}$ anion			
Mo–Mo	3·281 (2)	[3·273–3·290]	Mo–O_b–Mo	116·9 (5)	[116·2–118·0]
Mo–O_c	2·320 (10)	[2·305–2·335]	Mo–O_c–Mo	90·0 (4)	[89·4–90·6]
Mo–O_t	1·674 (11)	[1·670–1·683]	O_c–Mo–O_t	179·8 (5)	[178·2–181·6]
Mo–O_b	1·926 (11)	[1·890–1·959]	O_c–Mo–O_b	76·6 (5)	[75·8–77·6]
			O_t–Mo–O_b	103·4 (5)	[101·8–106·0]

Table 3. *Distances* (Å) *and angles* (°) *involving the potassium ions*

K(1)–$O_t(1^i)$*	2·703 (11)	K(2)–O_t(2)	2·720 (11)
K(1)–Aq	2·888 (13)	K(2)–Aq	2·926 (14)
	K(1)–Aq–K(2)	107·7 (5)	
	Aq–K(1)–$O_t(1^i)$	142·1 (3)	
	Aq–K(2)–O_t(2)	148·5 (3)	

* (i) refers to the following equivalent position: $\frac{1}{2}+x, -y, \frac{1}{2}+z$.

ment of the present crystal showed that the water molecule was released from the crystal lattice at a temperature as high as 363 K. This obviously indicates that the water molecule is not zeolitic.

The calculations were performed on a HITAC 8700/8800 computer at the Computer Centre of the University of Tokyo using a local version of *UNICS* (Sakurai, 1967).

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Structure of $(+)_{589}$-*mer*-Bis(diethylenetriamine)cobalt(III) Bromide 1·6-Hydrate

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Abstract. $C_8H_{26}CoN_6^{3+}.3Br^-.1\cdot6H_2O$, $[Co(C_4H_{13}N_3)_2]^{3+}.3Br^-.1\cdot6H_2O$, monoclinic, $P2_1$, $a = 22\cdot168$ (3), $b = 14\cdot154$ (1), $c = 8\cdot644$ (2) Å, $\beta = 96\cdot44$ (2)°, $Z = 6$, $D_x = 1\cdot973$ Mg m^{-3}, μ(Mo $K\alpha$) = 5·36 mm^{-1}. The structure has been refined to $R = 0\cdot038$ on 3537 observed reflections. The two terdentate molecules coordinate to Co in *mer* positions. The complex cation has approximate twofold symmetry. The four five-membered chelate rings take an envelope form. The absolute configuration of the complex ion may be described as *trans*-λ-NH.

Introduction. Of the three possible isomers of $[Co(dien)_2]^{3+}$, the structures of *s*-facial and *u*-facial isomers have already been reported (Kobayashi, Marumo & Saito, 1972; Konno, Marumo & Saito, 1973). A crystal of the third isomer, $(+)_{589}$-*mer*-$[Co(dien)_2]Br_3.1\cdot6H_2O$, has been subjected to X-ray crystal analysis in order to establish the absolute configuration and conformational details. The well known empirical rule relating the absolute configuration to the net chirality of the complex cannot be applied to this complex, since the net chirality is zero. The crystals

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Table 1. *Positional parameters with their standard deviations in parentheses*

	x	y	z
Br(1)	0·39019 (6)	0·95135 (14)	0·17496 (14)
Br(2)	0·34470 (6)	0·67037 (13)	0·96607 (17)
Br(3)	0·41867 (5)	0·49975 (12)	0·62272 (13)
Br(4)	0·33413 (5)	0·32161 (13)	0·21792 (13)
Br(5)	0·01754 (5)	0·38172 (14)	0·45639 (13)
Br(6)	0·17370 (6)	0·76070 (12)	0·53182 (15)
Br(7)	0·06219 (6)	0·61067 (12)	0·08658 (16)
Br(8)	0·26585 (6)	0·13482 (12)	0·53417 (17)
Br(9)	0·14458 (6)	0·24264 (12)	0·87947 (14)
Co(1)	0·10731 (6)	0·92499 (14)	0·98136 (15)
N(1)	0·0528 (4)	0·8226 (8)	0·8909 (9)
N(2)	0·0419 (4)	0·9588 (8)	1·1043 (10)
N(3)	0·1521 (4)	1·0282 (8)	1·0975 (10)
N(4)	0·1480 (4)	0·8338 (8)	1·1328 (9)
N(5)	0·1713 (4)	0·8945 (8)	0·8544 (9)
N(6)	0·0792 (4)	1·0150 (8)	0·8138 (9)
C(1)	−0·0075 (5)	0·8357 (12)	0·9542 (12)
C(2)	0·0046 (5)	0·8693 (11)	1·1149 (13)
C(3)	0·0680 (5)	0·9979 (11)	1·2547 (12)
C(4)	0·1123 (6)	1·0731 (11)	1·2100 (12)
C(5)	0·1965 (5)	0·7865 (11)	1·0623 (14)
C(6)	0·2249 (5)	0·8520 (11)	0·9542 (12)
C(7)	0·1833 (5)	0·9742 (9)	0·7578 (12)
C(8)	0·1230 (5)	1·0103 (10)	0·6867 (12)
Co(2)	0·21539 (6)	0·44822 (15)	0·54073 (15)
N(7)	0·1406 (3)	0·5279 (7)	0·5335 (9)
N(8)	0·2115 (4)	0·4439 (8)	0·7655 (9)
N(9)	0·2899 (3)	0·3703 (8)	0·5879 (9)
N(10)	0·2649 (4)	0·5656 (7)	0·5410 (9)
N(11)	0·2188 (4)	0·4488 (8)	0·3208 (9)
N(12)	0·1659 (4)	0·3345 (8)	0·5010 (9)
C(9)	0·1221 (5)	0·5372 (11)	0·6932 (12)
C(10)	0·1779 (5)	0·5299 (10)	0·8112 (12)
C(11)	0·2727 (5)	0·4310 (12)	0·8462 (12)
C(12)	0·2994 (5)	0·3507 (11)	0·7568 (12)
C(13)	0·2798 (5)	0·5838 (10)	0·3804 (13)
C(14)	0·2313 (4)	0·5454 (10)	0·2665 (12)
C(15)	0·1647 (5)	0·4009 (11)	0·2409 (12)
C(16)	0·1613 (5)	0·3079 (10)	0·3304 (12)
Co(3)	0·46894 (6)	0·83976 (14)	0·68841 (14)
N(13)	0·4650 (4)	0·7086 (8)	0·7698 (9)
N(14)	0·5268 (4)	0·8603 (8)	0·8701 (8)
N(15)	0·4822 (4)	0·9750 (8)	0·6477 (10)
N(16)	0·5309 (4)	0·7991 (8)	0·5563 (9)
N(17)	0·4130 (4)	0·8180 (8)	0·5010 (9)
N(18)	0·3962 (4)	0·8716 (8)	0·7913 (9)
C(17)	0·5113 (5)	0·6961 (10)	0·9050 (12)
C(18)	0·5174 (5)	0·7892 (10)	0·9939 (11)
C(19)	0·5267 (5)	0·9594 (10)	0·9174 (12)
C(20)	0·5265 (5)	1·0159 (11)	0·7685 (12)
C(21)	0·5031 (5)	0·7783 (10)	0·3970 (11)
C(22)	0·4376 (5)	0·7461 (10)	0·4037 (12)
C(23)	0·3516 (5)	0·8006 (10)	0·5463 (14)
C(24)	0·3436 (5)	0·8782 (12)	0·6686 (12)
O(1)	0·2810 (5)	0·1226 (10)	0·0210 (14)
O(2)	0·2535 (4)	0·9518 (9)	0·3072 (10)
O(3)	0·4089 (4)	0·1144 (8)	0·4338 (9)
O(4)	0·3831 (4)	0·0938 (8)	0·8143 (11)
O(5)	0·0006 (7)	0·6476 (11)	0·4653 (18)*

* Population 0·87 (2).

were kindly provided by Professor J. Fujita of Nagoya University. An initial unit cell and the space group were provided by a series of Weissenberg photographs. A least-squares refinement of the unit-cell dimensions based on 16 2θ values of high-angle reflections obtained by diffractometry gave the accurate cell dimensions.

Because the specimen deteriorated during exposure to X-rays, two spherically shaped crystals 0·30 and 0·36 mm in diameter were used for the data collection. The combined data included 3537 unique reflections with $|F_o| \geq 5\sigma(|F_o|)$ (variances based on counting statistics) which were classified as observed. Lorentz, polarization and absorption corrections were applied. The structure was solved by routine application of the heavy-atom method. All the atoms were then refined by a block-diagonal least-squares method. With $R = 0\cdot06$, the isotropic thermal factor of O(5) was unusually large. Thus the population of O(5) was refined by the full-matrix least-squares method. All the H atoms, except those of the water molecules, were located from a difference synthesis. With anisotropic thermal parameters for nonhydrogen atoms and isotropic ones for H, further refinement cycles gave a final R value of 0·038 ($R = \sum|\Delta F|/\sum|F_o|$) and $R_2 = 0\cdot035$ $\{R_2 = (\sum w|\Delta F|^2/\sum w|F_o|^2)^{1/2}$, $w = [\sigma^2(|F_o|) + (0\cdot015|F_o|)^2]^{-1}\}$. Scattering factors for H atoms were taken from Stewart, Davidson & Simpson (1965) and all others including anomalous-scattering components for Co and Br from *International Tables for X-ray Crystallography* (1974). The final atomic coordinates are given in Table 1.* The absolute structure was determined by the anomalous-scattering technique. 22 hkl and $h\bar{k}l$ pairs were examined on Weissenberg photographs recorded using Cu $K\alpha$ radiation. In Table 2* the observed and calculated differences are compared, for which $|F(hkl)|$ and $|F(h\bar{k}l)|$ differed by more than

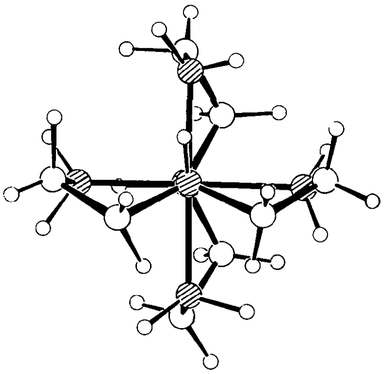

Fig. 1. A perspective drawing of the complex ion $(+)_{589}$-*mer*-$[Co(dien)_2]^{3+}$.

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* Lists of structure factors, anisotropic thermal parameters, the positional and thermal parameters of the H atoms, a complete list of interatomic distances and bond angles within the complex ions, and Tables 2 and 4 have been deposited with the British Library Lending Division as Supplementary Publication No. SUP 34528 (30 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

15%. The concordance in Table 2 indicated that $(+)_{589}$-*mer*-$[Co(dien)_2]^{3+}$ has the absolute configuration illustrated in Fig. 1. The enantiomeric structure was refined in the same way and converged at residuals $R = 0{\cdot}050$ and $R_2 = 0{\cdot}051$. Application of the R-factor ratio test shows that the latter may be rejected at the 0·005 confidence level in favor of the former (Hamilton, 1965).

Discussion. A perspective drawing of $(+)_{589}$-*mer*-$[Co(dien)_2]^{3+}$ is shown in Fig. 1. There are three crystallographically independent complex cations in an asymmetric unit; however, their shape and size are remarkably similar. Thus the averaged bond lengths and angles are shown in Table 3. The two ligand molecules coordinate to the central Co atom in *mer* positions with three N atoms forming a distorted octahedral complex. The Co—N(secondary) bond of 1·940 (8) Å is significantly shorter than the Co—N(terminal) bond of 1·981 (9) Å, in contrast to the observed results for the dien ligand in the *u*-facial isomer (Konno *et al.*, 1973). The angle subtended by the two terminal N atoms of a dien ligand at the central Co atom is 170·0 (4)°. The three ligating N atoms of the ligand and the Co atom are nearly planar and the two planes formed by Co and the three N atoms make an angle of 90·0 (6)°. The five-membered chelate ring takes an envelope form; one of the methylene C atoms that is bonded to the secondary N atom is shifted by 0·61 (4) Å from the plane formed by the Co atom and the two ligating N atoms. The conformations of the two fused chelate rings are δ and λ respectively. The geometry of the complex cation agrees well with the results of conformational analysis (Yoshikawa, 1976). The net chirality of this complex ion is zero. The optical activity arises from the dissymmetric disposition of the methylene groups with respect to the coordination plane and the chiral arrangement of the two *trans* N—H bonds. The complex ion can be designated as *trans*-λ-NH, providing that the chirality is defined by the line joining the two H atoms and the line joining the two secondary N atoms (IUPAC, 1971). Richardson (1972) derived the sector rules which relate the sign of the net *d–d* rotatory strength to the geometry of the complex. In his derivation, the perturbation treatment was carried out to the second order in both the wave function and the rotatory strength. The author predicted that the *trans*-λ-NH isomer will yield a negative net rotatory strength based on a molecular model. The calculation based on the observed geometry of this complex ion indeed gives negative rotatory strength which agrees with the observed CD (Kojima, Iwagaki, Yoshikawa & Fujita, 1977; Keene, Searle & Mason, 1970).

Table 3. *Averaged interatomic distances* (Å) *and bond angles* (°) *within the complex ions*

Values in parentheses are mean errors.

Co—N(H$_2$)	1·981 (9)	Co—N(H$_2$)—C	109·3 (6)
Co—N(H)	1·940 (8)	Co—N(H)—C	109·5 (6)
C—N(H$_2$)	1·493 (13)	N(H$_2$)—Co—N(H)	85·1 (4)
C—N(H)	1·482 (13)	N(H$_2$)—Co—N(H$_2$)	170·0 (4)
C—C	1·514 (16)	C—C—N(H$_2$)	108·7 (9)
		C—C—N(H)	104·7 (9)
		C—N(H)—C	116·2 (9)

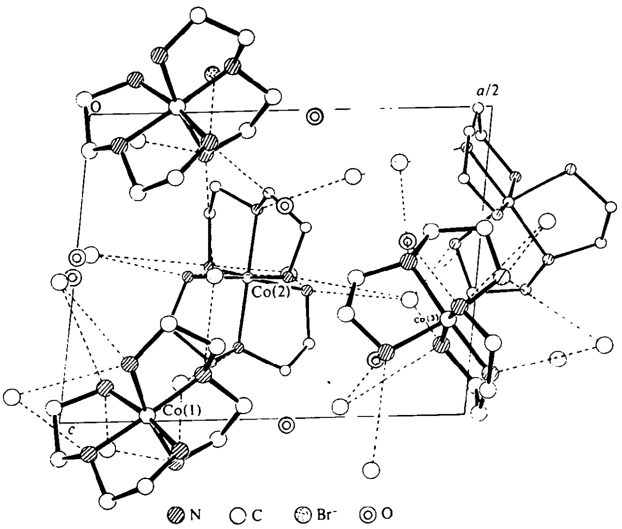

Fig. 2. A projection of the crystal structure along **b**.

The packing diagram is shown in Fig. 2. Relevant interatomic distances outside the complex ions are listed in Table 4.* In the crystal packing the three crystallographically independent complex ions are quite irregularly oriented; however, their HN—Co—NH axes are all approximately parallel to (010). N(3) and N(15) form N—H···O hydrogen bonds of 2·931 (13) and 3·047 (12) Å respectively. All the other atoms are bonded to the bromide ions. The N···Br distances range from 3·303 (9) to 3·606 (9) Å. They are indicated by broken lines in Fig. 2.

The calculations were carried out on a FACOM 230-48 computer at this Institute with a local version of *UNICS* (Ashida, 1967). Part of the calculation was performed on a HITAC 8800/8700 computer at the Computer Center of the University of Tokyo. The authors are grateful to Professor J. Fujita for supplying the crystal specimen. Part of the cost of this research was met by a Scientific Research Grant from the Ministry of Education, to which the author's thanks are due.

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* See deposition footnote.

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Dichloro[(2*S*,S*R*)-*S*-methylcysteine *S*-oxide]platinum(II) Hydrate

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Abstract. $[Pt(C_4H_9NO_3S)Cl_2].H_2O$, M_r = 435·30, monoclinic, *C*2, *a* = 17·721 (7), *b* = 5·386 (2), *c* = 11·781 (4) Å, *β* = 104·8 (1)° (at 294 K), *V* = 1090·2 (11) $Å^3$, *μ* = 13·92 mm^{-1} (Mo *Kα*), D_o = 2·65 (2), D_c = 2·653 Mg m^{-3} (*Z* = 4). The amino acid coordinates to Pt^{II} through N and S. The five-membered chelate ring has the *λ* conformation and an equatorial carboxyl group. The S—O and S—CH_3 bond vectors make almost equal angles with the plane of coordination (50·1 and 57·8° respectively). The Pt–S distance of 2·182 (3) Å is the shortest Pt–S distance found thus far in any Pt^{II} complex.

Introduction. The title compound was prepared by combining stoichiometric amounts of K_2PtCl_4 and (2*S*,S*R*)-*S*-methylcysteine *S*-oxide in hot aqueous solution, in an adaptation of the method used by Volshtein & Mogilevkina (1963) to make $PtCl_2$-(methionine). It was recrystallized from hot dilute HCl. The prismatic crystal used in this work had the dimensions 0·38 × 0·079 × 0·061 mm.

The space group *C*2 was unambiguously determined from the systematic absences, *h* + *k* odd for all *hkl*, noted on precession photographs; the compound was known to be optically active. The crystal was mounted on a Picker FACS-1 computer-controlled four-circle diffractometer. Accurate cell dimensions were obtained by a least-squares refinement of the setting angles of 12 general reflections having 2*θ* in the range 45–50° and using Mo $K\alpha_1$ radiation. The crystal was accurately aligned with [010] coincident with the *φ* axis of the diffractometer. To determine the severity of the absorption problem the 020 reflection was measured (by repeated *θ*–2*θ* scans) at *χ* = 90° and at 10° intervals from *φ* = 0° to *φ* = 350°. The variation in intensity as a function of *φ* (defined as maximum – minimum/average) was 20%. The data were corrected for absorption. Data-collection procedures and computer programs for the reduction of the data, for the application of an empirical correction to account for absorption by the *β* filter, for the absorption correction, and for solution and refinement of the structure were as described by Churchill & DeBoer (1973). Details specific to this case are summarized in Table 1.

A set of 1928 unique data was collected out to a 2*θ* of 50°. During the latter stages of refinement it was found that a small subset of these was systematically low. Review of the data-collection procedures and the standards gave evidence for intermittent instrument malfunction. Ultimately seven (hkl, $h\bar{k}l$) pairs for which $\Delta F_{obs}/\sigma > 20$ were omitted from the analysis.

An original 'observed' Fourier synthesis phased by the Pt alone allowed location of all the donor atoms; all non-hydrogen light atoms were then found in successive difference Fourier analyses. Calculations were performed on an IBM 370/158 computer. Atom scattering factors were taken from Cromer & Waber (1965) and for H from Stewart, Davidson & Simpson (1965). Refinement included the use of anisotropic thermal parameters for all non-hydrogen atoms and insertion of nine 'riding' H atoms (all the non-water H atoms) in idealized positions with *d*(N—H) = 0·87 Å, *d*(C—H) = 0·95 Å (Churchill, 1970). The positional parameters of the H atoms were constrained to vary with the positional parameters of their attached C or N atoms. An overall isotropic thermal parameter for all the H

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* To partially fulfill requirements for a PhD at UICC (1977).

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