

The Crystal Structure of $(-)$ ₅₈₉-*u*-facial-Bis(diethylenetriamine)cobalt(III) Hexacyanocobaltate(III) Dihydrate, $(-)$ ₅₈₉-*u*-facial-[Co(dien)₂][Co(CN)₆].2H₂O

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The crystal structure of $(-)$ ₅₈₉-*u*-facial-bis(diethylenetriamine)cobalt(III) hexacyanocobaltate(III) dihydrate, $(-)$ ₅₈₉-*u*-facial-[Co(dien)₂][Co(CN)₆].2H₂O, has been determined from three-dimensional X-ray data collected by an automated four-circle diffractometer. The compound crystallizes in the orthorhombic system with $a = 13.942$, $b = 32.370$, $c = 9.418$ Å and $Z = 8$ in space group $B22_12$. The structure has been refined by block-diagonal least-squares methods to an R value of 0.035 for 2510 reflexions. There are two isomeric complex cations in an asymmetric unit. They both have a twofold axis and the absolute configuration can be designated as skew chelate pairs $\Delta\Delta$. However, the conformations of the two chelate rings formed by a dien molecule in one complex ion are $\delta\lambda$, while those in the other are $\lambda\lambda$.

Introduction

All the possible isomers of bis(diethylenetriamine)cobalt(III) ion, $[\text{Co}(\text{dien})_2]^{3+}$, were isolated and characterized by Keene, Searle, Yoshikawa, Imai & Yamasaki (1970). As part of a series of investigations on the structures of the complex cation in the $[\text{Co}(\text{dien})_2]^{3+}$ system (Kobayashi, Marumo & Saito, 1972), the crystal of $(-)$ ₅₈₉-*u*-facial-[Co(dien)₂][Co(CN)₆].2H₂O has been subjected to X-ray crystal analysis in order to establish the absolute configuration and conformational details.

Experimental

Orange red crystals of $(-)$ ₅₈₉-*u*-facial-bis(diethylenetriamine)cobalt(III) hexacyanocobaltate(III) dihydrate were kindly supplied by Professor Yamasaki of Nagoya University. They belong to the orthorhombic system, with unit-cell dimensions: $a = 13.942$ (3), $b = 32.370$ (5) and $c = 9.418$ (1) Å. The observed systematic

absences: hkl for $h+l \neq 2n$ and $0k0$ for $k \neq 2n$, indicate the space group $B22_12$. There are eight formula units of $\text{Co}(\text{C}_4\text{H}_{13}\text{N}_3)_2\text{Co}(\text{CN})_6 \cdot 2\text{H}_2\text{O}$ in the unit cell ($D_x = 1.61$ g cm⁻³, $D_m = 1.59$ g cm⁻³). A crystal specimen shaped into a sphere of diameter 0.23 mm was mounted with the a axis parallel to the φ axis of a goniostat of a Rigaku automated four-circle diffractometer. The ω -scan technique was employed with a scanning speed of 2° per min in ω . Mo $K\alpha$ radiation monochromated by a graphite crystal was used. Scanning range was calculated from the formula: $1.5^\circ + 0.5^\circ \tan \theta$. Backgrounds were counted both at the beginning and at the end of each scan for 10 sec. 2758 independent intensities were measured up to $2\theta = 55^\circ$. 2510 of these had significantly non-zero intensities. The intensities were corrected for the Lorentz and polarization factors. No corrections were made for absorption in view of the small μ_r value of 0.2. The structure amplitudes obtained were put on an absolute scale by comparison with the calculated values at a later stage.

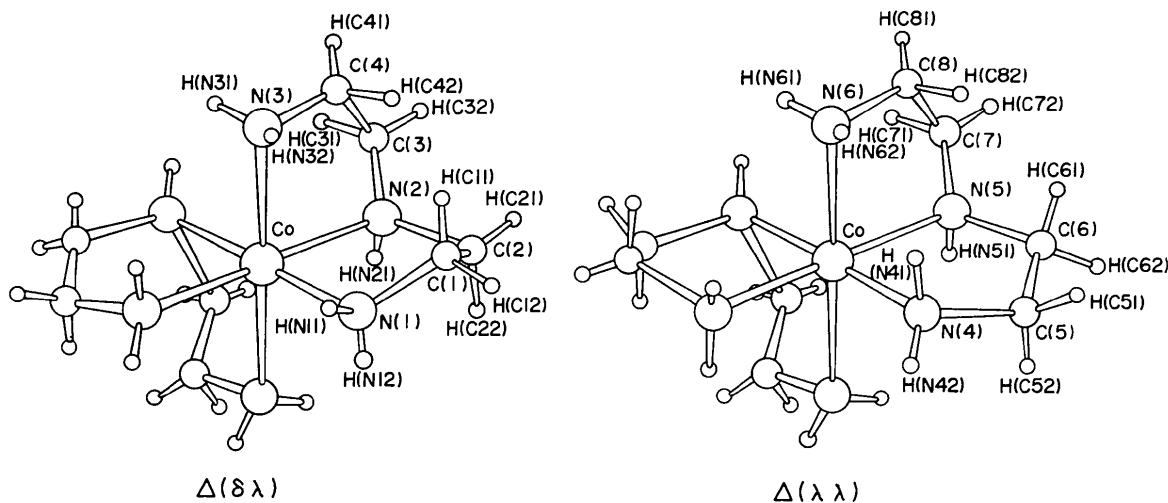


Fig. 1. Perspective drawings of the complex cations.

Determination and refinement of the structure

The structure was solved straightforwardly by the heavy-atom method. Positions of the cobalt atom were deduced from three-dimensional Patterson maps. The positions of the cobalt atoms were used to calculate structure factors, whose phases were used with the ob-

served $|F(hkl)|$ to calculate a three-dimensional electron density synthesis. Successive Fourier syntheses revealed the complete structure. These atomic positions were refined using block-diagonal least-squares methods. The R value at this stage was 0.066, where anisotropic temperature factors were used. Difference synthesis was carried out, which revealed all the hydrogen atoms except those belonging to the two oxygen atoms. The final least-squares calculation was made including the contribution of these hydrogen atoms. Temperature factors for the hydrogen atoms were assumed to be isotropic. After several cycles of refinement the R value was reduced to 0.035 for the 2510 observed reflexions. At this stage positional shifts were all less than one fourth of the standard deviations of the positional parameters. Unit weight was given to all the reflexions. The atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962). The final set of coordinates and their estimated standard deviations are listed in Table 1. Corresponding thermal parameters are given in Table 2 with their estimated standard deviations. The observed and calculated structure amplitudes are listed in Table 3.

Table 1. *Final positional parameters and their standard deviations (in parentheses)*

The values have been multiplied by 10^4 .

	x	y	z
Co(1)	0 (0)	0 (0)	1005 (1)
Co(2)	1685 (1)	2500 (0)	0 (0)
Co(3)	484 (1)	1169 (0)	5552 (1)
N(1)	650 (4)	- 334 (1)	2445 (5)
N(2)	723 (3)	- 323 (1)	- 408 (5)
N(3)	1087 (3)	388 (1)	924 (5)
N(4)	712 (4)	2445 (2)	1477 (6)
N(5)	2620 (3)	2487 (2)	1565 (5)
N(6)	1753 (4)	3104 (1)	223 (5)
N(7)	- 1398 (5)	731 (2)	6162 (9)
N(8)	2419 (4)	1582 (2)	5084 (7)
N(9)	- 410 (5)	1981 (2)	6501 (6)
N(10)	1300 (4)	372 (2)	4344 (6)
N(11)	- 101 (5)	1342 (2)	2518 (6)
N(12)	872 (4)	995 (2)	8655 (6)
C(1)	1478 (4)	- 560 (2)	1818 (7)
C(2)	1207 (4)	- 678 (2)	316 (7)
C(3)	1394 (4)	- 40 (2)	- 1152 (6)
C(4)	1855 (4)	239 (2)	- 54 (7)
C(5)	1143 (6)	2263 (2)	2762 (7)
C(6)	2112 (5)	2457 (2)	2964 (6)
C(7)	3190 (5)	2874 (2)	1496 (7)
C(8)	2495 (5)	3228 (2)	1267 (7)
C(9)	- 693 (4)	896 (2)	5877 (7)
C(10)	1685 (4)	1427 (2)	5277 (5)
C(11)	- 66 (5)	1674 (2)	6145 (6)
C(12)	1019 (4)	665 (2)	4880 (6)
C(13)	124 (5)	1286 (2)	3668 (6)
C(14)	772 (4)	1057 (2)	7465 (6)
O(1)	- 511 (4)	1836 (1)	138 (6)
O(2)	2448 (6)	1412 (3)	2006 (7)
H(N11)	867 (49)	- 144 (19)	3251 (72)
H(N12)	190 (52)	- 516 (21)	2903 (75)
H(N21)	339 (49)	- 424 (20)	- 1105 (74)
H(N31)	900 (47)	662 (20)	522 (75)
H(N32)	1392 (57)	408 (23)	1839 (85)
H(N41)	457 (54)	2722 (20)	1739 (77)
H(N42)	148 (56)	2270 (21)	1104 (79)
H(N51)	3046 (52)	2257 (21)	1536 (78)
H(N61)	1903 (51)	3240 (21)	- 706 (79)
H(N62)	1115 (50)	3213 (21)	491 (80)
H(C11)	2101 (52)	- 384 (20)	1842 (76)
H(C12)	1652 (50)	- 830 (21)	2385 (74)
H(C21)	1811 (44)	- 759 (19)	- 248 (72)
H(C22)	738 (45)	- 924 (19)	330 (70)
H(C31)	1012 (47)	139 (19)	- 1884 (69)
H(C32)	1913 (49)	- 208 (19)	- 1697 (74)
H(C41)	2169 (49)	492 (20)	- 525 (76)
H(C42)	2365 (48)	89 (20)	498 (70)
H(C51)	713 (49)	2330 (19)	3705 (74)
H(C52)	1233 (56)	1959 (22)	2637 (81)
H(C61)	1975 (52)	2726 (20)	3346 (77)
H(C62)	2519 (49)	2301 (20)	3637 (77)
H(C71)	3696 (52)	2842 (20)	632 (80)
H(C72)	3556 (49)	2928 (20)	2367 (73)
H(C81)	2843 (51)	3479 (20)	900 (78)
H(C82)	2190 (53)	3311 (21)	2197 (79)

Table 2. *Final thermal parameters and their standard deviations (in parentheses)*

The values have been multiplied by 10^4 and refer to the expression:

$$\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl)].$$

Mean isotropic temperature factor of all the hydrogen atoms is 2.34 \AA^2 .

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co(1)	23 (0)	3 (0)	46 (1)	0 (0)	0 (0)	0 (0)
Co(2)	28 (0)	4 (0)	48 (1)	0 (0)	0 (0)	- 3 (0)
Co(3)	30 (0)	4 (0)	51 (1)	1 (0)	- 6 (1)	- 1 (0)
N(1)	37 (3)	5 (0)	63 (5)	1 (1)	7 (3)	- 1 (1)
N(2)	28 (2)	4 (0)	60 (5)	0 (1)	- 3 (3)	3 (1)
N(3)	29 (2)	5 (0)	73 (5)	- 1 (1)	- 4 (3)	0 (1)
N(4)	43 (3)	8 (1)	92 (6)	- 1 (1)	21 (4)	- 8 (2)
N(5)	38 (2)	5 (0)	54 (4)	1 (1)	- 11 (3)	1 (1)
N(6)	52 (3)	5 (0)	66 (6)	2 (1)	- 5 (4)	- 4 (1)
N(7)	50 (4)	12 (1)	202 (12)	- 9 (1)	2 (6)	- 10 (2)
N(8)	48 (3)	8 (1)	95 (6)	- 5 (1)	- 1 (4)	- 2 (2)
N(9)	85 (5)	6 (1)	115 (7)	8 (1)	- 23 (5)	- 9 (2)
N(10)	46 (3)	8 (1)	111 (7)	5 (1)	- 14 (4)	- 11 (2)
N(11)	82 (5)	11 (1)	82 (6)	- 4 (2)	- 27 (5)	1 (2)
N(12)	61 (4)	9 (1)	78 (6)	0 (1)	- 5 (4)	9 (2)
C(1)	37 (3)	6 (1)	90 (7)	3 (1)	17 (4)	- 3 (2)
C(2)	39 (3)	6 (0)	90 (8)	3 (1)	3 (4)	0 (2)
C(3)	34 (3)	7 (1)	83 (6)	- 1 (1)	13 (4)	0 (2)
C(4)	31 (3)	6 (1)	105 (7)	- 2 (1)	13 (4)	1 (2)
C(5)	67 (5)	9 (1)	82 (8)	- 2 (2)	21 (5)	1 (0)
C(6)	65 (4)	8 (1)	56 (6)	- 5 (2)	- 1 (4)	0 (2)
C(7)	40 (3)	8 (1)	77 (7)	- 5 (1)	- 11 (4)	1 (2)
C(8)	73 (5)	5 (1)	81 (7)	0 (1)	- 23 (5)	- 4 (2)
C(9)	40 (3)	6 (1)	98 (8)	- 1 (1)	- 8 (4)	- 6 (2)
C(10)	44 (3)	5 (1)	46 (6)	0 (1)	- 2 (3)	0 (1)
C(11)	43 (3)	6 (1)	66 (6)	2 (1)	- 13 (4)	1 (1)
C(12)	34 (3)	6 (1)	61 (6)	0 (1)	- 12 (4)	- 2 (1)
C(13)	44 (3)	6 (1)	77 (6)	0 (1)	- 6 (4)	- 4 (1)
C(14)	36 (3)	4 (0)	83 (7)	- 1 (1)	- 9 (4)	1 (1)
O(1)	57 (3)	10 (1)	134 (7)	- 6 (1)	- 16 (4)	0 (2)
O(2)	159 (8)	46 (2)	122 (9)	64 (3)	68 (7)	35 (4)

Absolute configuration

The absolute configuration was determined by using the absorption-edge technique. Equi-inclination Weis-

enberg photographs were taken with Cu K α radiation. Table 4 lists some of the observed relations between intensities of *hkl* and *hkl* with calculated *F* values.

Table 3. Observed and calculated structure factors ($\times 10^3$)

Table with multiple columns for h, k, l and F values. The table is organized into several sections based on the magnitude of the structure factor indices. Each section contains rows of data points with their corresponding observed and calculated values.

lengths and angles with their estimated standard deviations in the complex ions are given in Table 5.

Table 5. *Interatomic distances and bond angles within the complex ions with their estimated standard deviations in parentheses*

Co(1)···N(1)	1.957 (5) Å	Co(2)···N(4)	1.951 (5) Å
Co(1)···N(2)	1.970 (4)	Co(2)···N(5)	1.968 (4)
Co(1)···N(3)	1.969 (4)	Co(2)···N(6)	1.970 (4)
C(1)···N(1)	1.489 (8)	C(5)···N(4)	1.474 (9)
C(2)···N(2)	1.496 (7)	C(6)···N(5)	1.499 (7)
C(3)···N(2)	1.487 (7)	C(7)···N(5)	1.486 (8)
C(4)···N(3)	1.493 (8)	C(8)···N(6)	1.482 (9)
C(1)···C(2)	1.514 (9)	C(5)···C(6)	1.503 (11)
C(3)···C(4)	1.517 (8)	C(7)···C(8)	1.515 (9)
N(1)Co(1)N(2)	86.4 (2)°	N(4)Co(2)N(5)	85.7 (2)°
Co(1)N(1)C(1)	110.8 (3)	Co(2)N(4)C(5)	109.8 (4)
N(1)C(1)C(2)	107.5 (5)	N(4)C(5)C(6)	107.6 (4)
C(1)C(2)N(2)	110.2 (3)	C(5)C(6)N(5)	109.9 (5)
C(2)N(2)Co(1)	109.3 (3)	C(6)N(5)Co(2)	110.3 (3)
N(2)Co(1)N(3)	85.4 (1)	N(5)Co(2)N(6)	84.9 (1)
Co(1)N(3)C(4)	111.8 (3)	Co(2)N(6)C(8)	111.8 (3)
N(3)C(4)C(3)	108.0 (4)	N(6)C(8)C(7)	109.7 (3)
C(4)C(3)N(2)	108.3 (4)	C(8)C(7)N(5)	107.6 (4)
C(3)N(2)Co(1)	108.2 (2)	C(7)N(5)Co(2)	107.6 (2)
Co(3)···C(9)	1.889 (6) Å	C(9)···N(7)	1.150 (9) Å
Co(3)···C(10)	1.890 (6)	C(10)···N(8)	1.153 (8)
Co(3)···C(11)	1.889 (5)	C(11)···N(9)	1.154 (8)
Co(3)···C(12)	1.903 (5)	C(12)···N(10)	1.144 (8)
Co(3)···C(13)	1.883 (6)	C(13)···N(11)	1.142 (8)
Co(3)···C(14)	1.881 (6)	C(14)···N(12)	1.147 (8)
C(9)Co(3)C(11)	90.3 (2)°	C(9)Co(3)C(12)	89.6 (2)°
C(9)Co(3)C(13)	90.9 (2)	C(9)Co(3)C(14)	86.6 (2)
C(11)Co(3)C(13)	89.8 (2)	C(11)Co(3)C(14)	88.3 (2)
C(12)Co(3)C(13)	87.9 (2)	C(12)Co(3)C(14)	94.0 (2)
C(10)Co(3)C(11)	91.0 (2)	C(10)Co(3)C(12)	89.2 (2)
C(10)Co(3)C(13)	91.0 (2)	C(10)Co(3)C(14)	91.6 (2)
Co(3)C(9)C(7)	175.8 (5)	Co(3)C(10)N(8)	178.7 (5)
Co(3)C(11)N(9)	179.3 (3)	Co(3)C(12)N(10)	173.0 (3)
Co(3)C(13)N(11)	177.3 (5)	Co(3)C(14)N(12)	174.5 (5)

The crystal is composed of complex cations, complex anions and water molecules. There are two crystallographically independent complex cations in an asymmetric unit. One lies on the diad axis parallel to the *c* axis and the other is on the diad axis parallel to the *a* axis. Two dien molecules are coordinated to the central cobalt atom by six nitrogen atoms, adopting *u*-facial configurations. Both cations can be designated

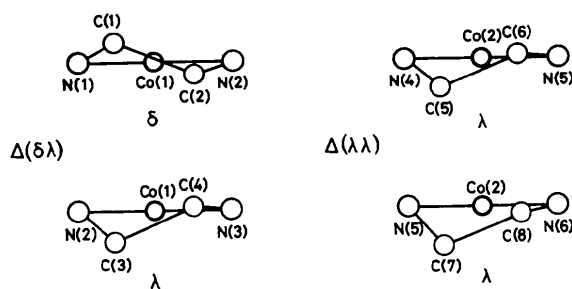


Fig. 3. Conformation of the chelate rings.

as skew chelate pairs $\Delta\Delta$. This is in conformity with the results of a circular dichroism study (Keene *et al.*, 1970). However, the conformations of the two chelate rings formed by a dien molecule are different in the two cations in the asymmetric unit. In the complex cation *A*, which lies on the diad axis parallel to the *c* axis, they are $\delta\lambda$, whereas they are $\lambda\lambda$ in the complex ion *B* on the diad axis parallel to the *a* axis. The interatomic distances and bond angles in the two crystallographically independent complex cations correspond pretty well with each other, though the conformations of the chelate rings are different. Only the CNC angle at the secondary nitrogen atom is significantly different: CNC in *A* is 113.9° , while that in *B* is 110.4° . The C-C and C-N distances are in agree-

Table 6. *Intermolecular distances less than 3.5 Å*

Key to symmetry operations		Distances	Symmetry operation applied to second atom
(1)	<i>x</i> , <i>y</i> , <i>z</i>		
(2)	$-0.5+x$, <i>y</i> , $-0.5+z$		
(3)	$0.5+x$, <i>y</i> , $-0.5+z$		
(4)	<i>x</i> , <i>y</i> , $-1+z$		
O(1)···N(4)		2.897 (7) Å	(1)
O(1)···N(11)		2.812 (8)	(1)
O(1)···N(4')		3.262 (7)	(1)
O(1)···N(6')		3.180 (7)	(1)
O(2)···N(8)		2.951 (9)	(1)
O(2)···C(5)		3.376 (12)	(1)
O(2)···C(10)		3.260 (8)	(1)
O(2)···N(6')		2.791 (9)	(1)
O(2)···C(8')		3.296 (10)	(1)
N(1)···N(10)		3.040 (7)	(1)
N(3)···N(10)		3.235 (7)	(1)
C(5)···N(11)		3.457 (9)	(1)
C(6)···N(8)		3.493 (9)	(1)
N(1')···N(10)		3.256 (7)	(1)
N(1')···N(11)		3.350 (7)	(1)
N(1')···C(12)		3.438 (7)	(1)
N(1')···C(13)		3.463 (7)	(1)
C(1')···N(11)		3.244 (9)	(1)
C(2')···N(11)		3.361 (8)	(1)
O(1)···N(8)		3.001 (7)	(2)
C(2')···N(8)		3.505 (8)	(2)
C(3')···N(10)		3.421 (8)	(2)
C(4')···N(10)		3.294 (8)	(2)
O(2)···N(7)		2.843 (11)	(3)
O(2)···C(9)		3.262 (11)	(3)
C(4)···N(7)		3.127 (9)	(3)
N(5)···N(9)		3.197 (8)	(3)
C(7)···N(9)		3.488 (9)	(3)
C(7')···N(9)		3.464 (9)	(3)
O(1)···N(9)		3.461 (8)	(4)
N(3)···N(12)		2.918 (7)	(4)
C(3)···N(12)		3.433 (8)	(4)
C(4)···N(12)		3.056 (8)	(4)
N(2')···N(12)		3.232 (7)	(4)
C(2')···N(12)		3.450 (8)	(4)
C(3')···N(7)		3.377 (9)	(4)
N(4')···N(9)		3.086 (6)	(4)
N(6')···N(12)		3.335 (7)	(4)
C(5')···N(9)		3.340 (10)	(4)
C(8')···N(8)		3.493 (9)	(4)
C(8')···N(12)		3.384 (9)	(4)

ment, within experimental errors, with the values observed in the *s-facial* isomer (Kobayashi, Marumo & Saito, 1972). All the observed Co–N distances are normal for Co(III) complexes of linear aliphatic polyamines. The chelate rings formed by a dien ligand in the complex cation *A* have eclipsed envelope and symmetrical skew conformations, while those in the complex cation *B* are both eclipsed envelope conformations. They are shown in Fig. 3. The Newman projections along the C–C bonds are illustrated in Fig. 4. All the dihedral angles N–C–C–N are in the range 43–45° and are much smaller than that in a typical *gauche* structure. The bond distances and angles in the hexacyanocobaltate(III) anion are listed in Table 5. They may be compared with those observed in $(-)_589\text{-}[\text{Co}(\text{penten})][\text{Co}(\text{CN})_6] \cdot 2\text{H}_2\text{O}$ (Muto, Marumo & Saito, 1970). The closest approach between complex cations and anions occurs between the terminal nitrogen atom of the cation and the nitrogen atom of the anion: N(3)···N(12) and N(4)···N(9) are 2.918 and 3.086 Å respectively. The positions of hydrogen atoms attached to N(3) and N(4) suggest that N(3)···N(12) and N(4)···N(9) are hydrogen bonds. The water molecules are surrounded by two nitrogen atoms of the anion and a terminal nitrogen atom of the cation as indicated by broken lines in Fig. 2. These N···O distances are mostly less than 3 Å. Other interatomic distances less than 3.5 Å between complexes are listed in Table 6.

The authors are grateful to Professor K. Yamasaki of Nagoya University for supplying the specimens. The computations for the structure analysis were carried out on the FACOM 270-30 computer at this institute. Part of the cost of this investigation was met

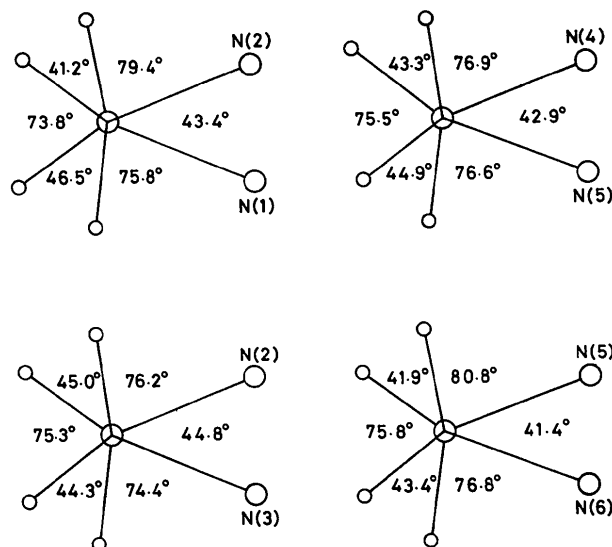


Fig. 4. Newman projections along the C–C bonds in the chelate ring.

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The Crystal Structure of CsMnCl_3

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The crystal structure of CsMnCl_3 , determined from Weissenberg data, is trigonal, space group $R\bar{3}m$. The hexagonal cell contains 9 molecules and has dimensions $a = 7.29$ (1) and $c = 27.48$ (5) Å. The c parameter accommodates 9 close-packed layers of composition CsCl_3 and the Mn ions are octahedrally coordinated by Cl ions. The structure is closely related to that of CsNiCl_3 .

Introduction

Many complex halides of composition CsMCl_3 , where M represents a metal ion in the first transition series, have the same structure as CsNiCl_3 (Tishchenko, 1955), which consists of hexagonally close-packed CsCl_3 layers with Ni octahedrally coordinated by Cl ions

such that the Ni–Cl octahedra share opposite faces to form infinite chains of composition $(\text{NiCl}_3)_n^{n-}$ parallel to c , the space group being $P6_3/mmc$ with $a \approx 7.2$ Å, $c/a \approx 0.82$ and $Z = 2$. Recent work (Goodyear & Kennedy, 1972) has shown that CsMnBr_3 also has this structure.

An investigation of the unit cell of CsMnCl_3 by Kes-