

Crystal Structure of $(-)_589$ -Tris-(+ *trans*-1,2-diaminocyclopentane)cobalt (III) Chloride Tetrahydrate, $(-)_589$ -[Co (+cptn)]Cl₃·4H₂O

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The crystal structure of $(-)_589$ -tris-(+ *trans*-1,2-diaminocyclopentane)cobalt(III) chloride tetrahydrate, $(-)_589$ [Co(+cptn)]Cl₃·4H₂O, has been determined from three-dimensional data collected by a diffractometer. The structure was refined by the full-matrix least-squares method. Refinement was unusually difficult due to large correlation coefficients between parameters, associated with a non-orthogonality of the *a* and *b* axes. The final *R* index is 0.12 for 786 observed reflexions. Crystals are hexagonal with space group *P*6₂2. Lattice constants are *a* = 11.871, *c* = 30.803 Å, with six formula units in the unit cell. The complex ion is mononuclear with pseudo-symmetry *D*₃. Three ligands are bonded to the cobalt atom through six nitrogen atoms. The five-membered chelate rings are not planar. Their shape and size are similar to those of [Co(en)₃]³⁺. The conformation of the chelate ring is '1el'. The cyclopentane rings take half-chair conformation. Some strain is introduced in the bond angles of the chelate ring due to fused-ring formation.

Introduction

Jaeger & Blumendal (1928) first prepared tris-(*trans*-1,2-diaminocyclopentane)cobalt(III) salts in a series of early investigations of stereochemical behaviour of complex ions containing dissymmetric ligands. Severe strain in bond angles is introduced by the *trans* fusion of two five-membered rings which is necessary if cptn* is to act as a bidentate ligand. Thus, a binuclear structure, [Co₂(cptn)₇(H₂O)₂]⁶⁺, was proposed for this ion (Phillips & Royer, 1965). The crystal-structure determination of tris-(*trans*-1,2-diaminocyclopentane)cobalt(III) chloride tetrahydrate, $(-)_589$ [Co(+cptn)]Cl₃·4H₂O, has been undertaken to establish the structure of the complex ion and to explain the conformational feature of the chelate rings. The optical rotatory dispersion curve and circular dichroism spectrum of this complex ion are somewhat different from those of the analogous complex ions such as [Co(en)₃]³⁺ and [Co(chxn)₃]³⁺ (Ito, Marumo & Saito, 1970). Thus, evidence for the absolute configuration of this complex ion from its optical properties is ambiguous. It was also the purpose of this investigation to determine the absolute configuration of the complex ion by means of X-rays and to clarify the relation between the absolute configuration and circular dichroism of the transition metal complexes.

Experimental

The complex was synthesized by heating an aqueous solution of sodium tris(carbonato)cobaltate(III) and *trans*-1,2-diaminocyclopentane hydrochloride. The resulting racemic mixture was resolved as the *d*-tartrate chloride double salts. Optically active [Co(cptn)]Cl₃

was separated using Amberlite A.G. IRA-400. The compound was recrystallized from water. Crystals used for X-ray work were grown by slow evaporation of an aqueous solution. They are red in colour and hexagonal-bipyramidal. The crystals easily lose the water of crystallization and disintegrate when exposed to air at room temperature. Specimens were protected from the atmosphere by a thin layer of grease during X-ray exposure. Cell dimensions, determined from higher-order reflexions recorded on Weissenberg photographs, were later refined by employing data obtained on a single-crystal diffractometer with Mo *K*α radiation ($\lambda = 0.7107$ Å).

Crystal data are: Co(C₅H₁₂N₂)₃Cl₃·4H₂O,
F.W. 537.4;

Hexagonal, *a* = 11.871 ± 0.002, *c* = 30.803 ± 0.003 Å,
U = 3759 Å³;

*D*_m = 1.420 g.cm⁻³, *Z* = 6, *D*_x = 1.425 g.cm⁻³;

Space group *P*6₂2 (*D*₆², No. 178) or *P*6₃22 (*D*₆³, No. 179);

F(000) = 1716;

Linear absorption coefficient for Mo *K*α, $\mu = 10.6$ cm⁻¹.

The crystals were reformed into spheres of diameter about 0.20 mm. Initial intensity data, from which the structure was solved, were collected using the equi-inclination Weissenberg technique and were measured visually. Layers *0kl*~*4kl*, taken with Cu *K*α radiation, gave a total of 412 independent reflexions. Intensity data on which the final atomic parameters are based were measured on a Rigaku automatic four-circle diffractometer. The crystal specimen was mounted with the *c* axis parallel to the φ axis of the diffractometer. The ω scan technique was employed. Mo *K*α radiation monochromatized by an LiF crystal was used. A set of standard reflexions was measured every 50 reflexions during data collection to check the electronic stability of the instrument and to check any crystal deteriora-

* *trans*-1,2-diaminocyclopentane.

tion. Fluctuations in the intensities of the standard reflexions were within 2~3%.

A total of 1200 intensities was measured, up to $2\theta = 55^\circ$. Of these, 414 were less than 3σ over the background, where σ is given by $|F|/2I_0[I_P + (B_1 + B_2)(T_P/2T_B)^2]^{1/2}$, where I_P and I_0 are the total intensity and net intensity, respectively. Both B_1 and B_2 are background counts and T_P , T_B are the time required for the measurements of peak and background intensities. Intensities were corrected for Lorentz and polarization factors, but corrections for absorption ($\mu r = 0.12$) and extinction were not made.

Determination and refinement of the structure

The general position is 12-fold for the space group $P6_122$ or $P6_522$. The cobalt atom must lie on a set of special positions, since there are only six formula units in the unit cell. Thus, the complex ion is required to have a twofold axis of rotation. Six chloride ions must also lie on a set of sixfold positions. The interpretation of the three-dimensional Patterson map was difficult due to accidental overlapping of peaks. The cobalt and the chlorine atoms were located after several structures were tested, by calculating the structure amplitudes. Cobalt atoms lie near the threefold screw axis and the arrangement is approximately hexagonal close-packed. When the positions of the heavy atoms were fixed, the remaining non-hydrogen atoms were located straightforwardly from successive Fourier syntheses. The usual R value ($\sum|F_o| - |F_c|/\sum|F_o|$) was 0.30 at this stage. Atomic scattering factors as well as corrections for anomalous dispersion were taken from *International Tables for X-ray Crystallography* (1962). Refinement was carried out by the full-matrix least-squares program *FLS4* written by Drs Sakurai, Nakatsu & Iwasaki with isotropic temperature factors. After six cycles, the R value reduced to 0.20 for all the 412 observed reflexions. The weighting scheme, a modification of Cruickshank's method (Cruickshank, Pilling, Bujosa, Lovell & Truter, 1961) was employed: $1/w = c - |F_o| + a|F_o|^2$ if $|F_o| \leq F_{\min}$ and $|F_o| \geq F_{\max}$, otherwise $1/w = d$. Further refinement was carried out by full-matrix least-squares methods, using anisotropic temperature factors. A preliminary set of visual data did not improve below $R = 0.17$. The existence of large correlation coefficients between some pairs of parameters caused oscillation of the corresponding parameters and the appearance of many negative temperature factors. All correlation coefficients with values greater than 0.40 are listed in Table 1. All atoms at the general positions showed large correlations between x and y , β_{11} and β_{12} , β_{22} and β_{12} , and β_{13} and β_{23} . All these arise from the non-orthogonality of the a and b axes, and such correlations are always found in the structure based on non-orthogonal axes (Templeton, 1959). After this stage, intensity data collected by the diffractometer were used for the refinement. A large damping factor of 0.3 was applied to all parameter shifts to

prevent oscillation. The structure began to converge slowly and, after seven cycles of refinement with anisotropic thermal parameters, R reduced to 0.14. After the introduction of hydrogen atoms obtained from the difference synthesis (the missing hydrogen atom attached to N(3) was supplied by calculated values), a final set of least-squares calculations was carried out, but the parameters of hydrogen atoms were not varied. Temperature factors of the hydrogen atoms were assumed to be isotropic and were given the same values as those of the atoms to which the hydrogen atoms were attached. A total of eight cycles was computed before the shifts were less than the corresponding standard deviations for non-hydrogen atoms. The topography of the final difference synthesis is flat within $0.7 \text{ e.}\text{\AA}^{-3}$. The final structure does not differ appreciably from that based on the visual data. It appears that convergence is first achieved easily and rapidly with intensity data of sufficient accuracy. The final R value is 0.121 for 786 observed reflexions.

Table 1. Correlation coefficients greater than 0.40 from the final cycle of the least-squares refinement

Values are multiplied by 10 ² .				
	x, y	β_{11}, β_{12}	β_{22}, β_{12}	β_{13}, β_{23}
Cl(2)	59	68	62	61
N(1)		57	48	41
N(2)	72	74	77	70
N(3)	61	68	69	58
C(2)	52	59	71	58
C(3)	50	53	58	56
C(4)	58	67	61	57
C(5)		43	43	
C(6)	48	66	58	50
C(7)	40	49	53	41
C(8)	44	58	64	53
O(1)	65	64	71	67
O(2)		64		

The absolute structure was determined by using the absorption-edge technique. Equi-inclination Weissenberg photographs were taken with $\text{Cu K}\alpha$ radiation. Table 2 lists some of the observed relations between intensities of hkl and $h\bar{k}\bar{l}$ with calculated values. Comparison of observed and calculated differences shows that $P6_122$ is the true space group and the complex ion, $(-)_589[\text{Co}(\text{cptn})_3]$, has the absolute configuration illustrated in Fig. 1.

Table 2. Reflexions used to determine the absolute configuration

h	k	l	$ F_o(hkl) ^2$	Observed	$ F_c(h\bar{k}\bar{l}) ^2$
$\bar{1}$	4	2	552	>	492
$\bar{1}$	4	4	476	>	416
$\bar{1}$	4	21	156	>	116
$\bar{2}$	5	1	352	<	404
$\bar{2}$	5	3	372	<	436

Table 3 gives calculated and observed structure amplitudes. Final atomic parameters with their stan-

Table 3. Observed and calculated structure amplitudes

#	K	L	IP01	IP01	#	K	L	IP01	IP01	#	K	L	IP01	IP01	#	K	L	IP01	IP01
0	0	0	410.88	396.57	0	10	7	39.14	21.76	4	2	0	170.81	171.13	3	4	30	29.98	17.29
0	0	10	151.83	151.83	1	1	1	151.83	151.83	4	2	0	87.06	87.06	3	5	7	31.92	27.27
0	0	20	137.94	137.94	1	1	1	107.85	107.85	2	2	0	53.00	53.00	3	5	7	31.92	27.27
0	0	30	117.96	117.96	1	1	1	67.87	67.87	2	2	0	33.00	33.00	3	5	7	31.92	27.27
0	0	40	97.98	97.98	1	1	1	27.90	27.90	2	2	0	13.00	13.00	3	5	7	31.92	27.27
0	0	50	77.99	77.99	1	1	1	7.92	7.92	2	2	0	3.00	3.00	3	5	7	31.92	27.27
0	0	60	57.99	57.99	1	1	1	2.94	2.94	2	2	0	1.00	1.00	3	5	7	31.92	27.27
0	0	70	37.99	37.99	1	1	1	0.98	0.98	2	2	0	0.33	0.33	3	5	7	31.92	27.27
0	0	80	17.99	17.99	1	1	1	0.33	0.33	2	2	0	0.11	0.11	3	5	7	31.92	27.27
0	0	90	7.99	7.99	1	1	1	0.11	0.11	2	2	0	0.03	0.03	3	5	7	31.92	27.27
0	0	100	0.99	0.99	1	1	1	0.03	0.03	2	2	0	0.01	0.01	3	5	7	31.92	27.27
0	1	0	117.96	117.96	1	1	20	79.83	79.83	2	2	0	28.00	28.00	3	5	22	23.92	20.00
0	1	10	97.98	97.98	1	1	20	29.85	29.85	2	2	0	18.00	18.00	3	5	22	23.92	20.00
0	1	20	77.99	77.99	1	1	20	9.87	9.87	2	2	0	8.00	8.00	3	5	22	23.92	20.00
0	1	30	57.99	57.99	1	1	20	2.90	2.90	2	2	0	2.00	2.00	3	5	22	23.92	20.00
0	1	40	37.99	37.99	1	1	20	0.93	0.93	2	2	0	0.67	0.67	3	5	22	23.92	20.00
0	1	50	17.99	17.99	1	1	20	0.30	0.30	2	2	0	0.23	0.23	3	5	22	23.92	20.00
0	1	60	7.99	7.99	1	1	20	0.10	0.10	2	2	0	0.08	0.08	3	5	22	23.92	20.00
0	1	70	0.99	0.99	1	1	20	0.03	0.03	2	2	0	0.03	0.03	3	5	22	23.92	20.00
0	1	80	0.03	0.03	1	1	20	0.01	0.01	2	2	0	0.01	0.01	3	5	22	23.92	20.00
0	1	90	0.01	0.01	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	100	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	110	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	120	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	130	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	140	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	150	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	160	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	170	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	180	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	190	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	200	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	210	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	220	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	230	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	240	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	250	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	260	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	270	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	280	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	290	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	300	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	310	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	320	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	330	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	340	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	350	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	360	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	370	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	380	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	390	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	400	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	410	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	420	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	430	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	440	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	450	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	460	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	470	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	480	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	490	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	500	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	510	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	520	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	530	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	540	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	550	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	560	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	570	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	580	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	590	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	600	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	610	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	620	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	630	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	640	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	650	0.00	0.00	1	1	20	0.00	0.00	2	2	0	0.00	0.00	3	5	22	23.92	20.00
0	1	660	0.00	0.00	1	1	20	0.00											

standard deviations are listed in Table 4. The rather large standard deviations are certainly due to parameter interactions.

Description and discussion of the structure

Fig. 1 shows a perspective drawing of the complex ion. It has rigorous symmetry C_2 , but pseudo-symmetry D_3 . Each ligand molecule is coordinated to the cobalt atom with its nitrogen atoms, functioning as a bidentate ligand. The complex ion is mononuclear, and does not agree with a binuclear structure proposed by Phillips & Royer (1965). Table 5 lists interatomic distances and bond angles within the complex ion. Standard deviations are somewhat larger than usual owing to parameter interactions. Consequently, it is impracticable to discuss bond lengths and angles in detail. Bond lengths and angles, averaged by assuming D_3 symmetry, of the chelate rings are shown in Fig. 2. The cobalt atom has a slightly distorted octahedral coordination of six nitrogen atoms, with an average Co-N distance of 2.00 Å. The C-C and C-N distances agree with single-bond distances within experimental errors.

The N-Co-N angles in five-membered chelate rings are all less than 90° and average 86.7° . The triangle N(1')-N(2)-N(3') is rotated by about 5.5° with respect to the

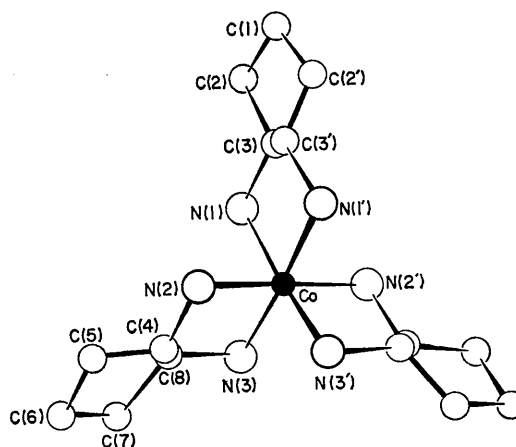


Fig. 1. Perspective drawing of the complex ion, $(-)_589[\text{Co}(\text{cptn})_3]^{3+}$, viewed along the direction perpendicular to the upper triangle formed by three nitrogen atoms.

Table 4. *Final atomic parameters*

E.s.d.'s are given in parentheses.

(a) Positional parameters ($\times 10^4$)

	x	y	z
Co	7059 (2)	3529 (2)	0833 (0)
Cl(1)	5610 (6)	1221 (6)	2500 (0)
Cl(2)	5654 (8)	5072 (8)	2892 (2)
N(1)	5644 (19)	1854 (18)	0577 (6)
N(2)	7137 (21)	2666 (23)	1377 (6)
N(3)	8379 (21)	3111 (24)	0593 (6)
C(1)	2230 (14)	1115 (14)	0833 (0)
C(2)	3125 (32)	0741 (28)	0615 (9)
C(3)	4443 (19)	1964 (24)	0608 (7)
C(4)	8300 (24)	2555 (25)	1332 (7)
C(5)	8469 (28)	1591 (28)	1600 (8)
C(6)	9491 (34)	1372 (26)	1348 (9)
C(7)	9570 (25)	1920 (25)	0897 (11)
C(8)	8323 (26)	2062 (28)	0883 (7)
O(1)	5686 (24)	3553 (26)	2015 (6)
O(2)	6773 (51)	0000 (0)	0000 (0)
O(3)	6683 (30)	8341 (30)	0833 (0)

(b) Thermal parameters ($\times 10^4$), based on $\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl$.

	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	42 (2)	37 (3)	4 (0)	21 (2)	0 (0)	3 (1)
Cl(1)	151 (16)	76 (7)	28 (3)	38 (7)	1 (6)	0 (0)
Cl(2)	124 (10)	89 (9)	8 (1)	68 (7)	-7 (2)	-5 (2)
N(1)	61 (21)	50 (19)	3 (2)	24 (18)	-1 (5)	5 (5)
N(2)	89 (25)	128 (31)	5 (2)	93 (24)	21 (7)	19 (7)
N(3)	80 (26)	128 (32)	6 (3)	83 (25)	12 (6)	5 (7)
C(1)	10 (14)	37 (26)	16 (5)	5 (14)	0 (0)	-2 (10)
C(2)	132 (42)	60 (33)	9 (3)	23 (31)	5 (9)	-4 (9)
C(3)	19 (19)	66 (28)	7 (3)	39 (21)	-4 (6)	-11 (7)
C(4)	73 (31)	44 (26)	5 (2)	38 (24)	-7 (7)	2 (7)
C(5)	86 (33)	99 (33)	9 (3)	46 (29)	-8 (9)	1 (8)
C(6)	161 (49)	19 (26)	9 (3)	6 (30)	4 (11)	22 (9)
C(7)	83 (30)	21 (27)	16 (4)	21 (25)	-11 (11)	-10 (9)
C(8)	95 (29)	110 (37)	3 (2)	55 (26)	11 (8)	10 (8)
O(1)	219 (38)	139 (30)	10 (3)	126 (29)	3 (9)	5 (8)
O(2)	323 (83)	604 (90)	22 (9)	302 (90)	-13 (13)	-26 (13)
O(3)	214 (48)	243 (84)	56 (18)	107 (48)	0 (0)	55 (30)

triangle N(1)–N(2')–N(3) from the position expected for a regular octahedron. The distance between the triangles N(1')–N(2)–N(3') and N(1)–N(2')–N(3) is 2.32 Å. All three C–C bonds in the chelate ring point along the threefold axis of the octahedron. Hence, the configura-

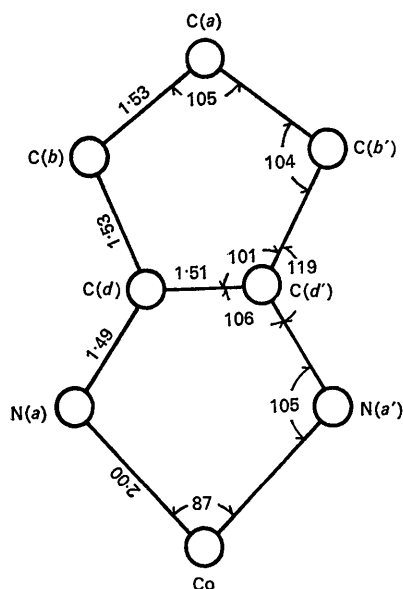


Fig. 2. Bond lengths and angles of a chelate ring, averaged by assuming D_3 symmetry.

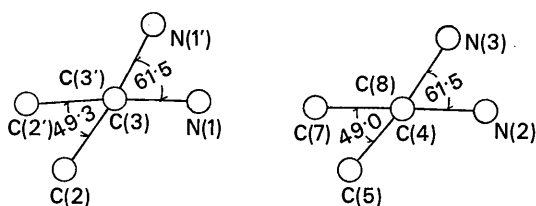


Fig. 3. Newman projections down the bond C(3)–C(3') and C(4)–C(8).

tion of the complex ion is of the type *lel-lel-lel* (Corey & Bailar, 1959). These structural features are common to all the *lel* isomers of tris-diamine cobalt(III) complexes with five-membered chelate rings. The angle Co–N(*a*)–C(*d*) is 104.9°, which is slightly smaller than the corresponding value of 106.4° observed in the tris(*trans*-1,2-diaminocyclohexane)cobalt(III) ion; the value of the N(*a*)–C(*d*)–C(*d'*) angle is 105.5°, and agrees well with those observed in the *lel* isomers of the complex ions, [Co(en)₃]³⁺ and [Co(chxn)₃]³⁺. The five-membered chelate ring is puckered. Two carbon atoms, C(3) and C(3'), lie at 0.37 Å above and below the plane formed by Co, N(1) and N(1'). C(4) lies 0.44 Å above, and C(8) lies 0.37 Å below, the plane of Co, N(2) and N(3). These conformational features also agree very well with those of the related complexes.

Newman projections down the bond C(3)–C(3') and C(4)–C(8) are presented in Fig. 3. The cyclopentane ring has a half-chair conformation. Some strain is introduced in the bond angles due to fused-ring formation. Angles C(*b*)–C(*d*)–C(*d'*) of 101° and N(*a*)–C(*d*)–C(*b*) of 119° deviate largely from the normal tetrahedral angle. Corresponding angles in the *trans*-1,2-diaminocyclohexane analogue are 112 and 110° respectively. This strain appears to affect the circular dichroism of the complex ion in solution, as discussed later. Boyd's (1968) technique of minimizing conformational potential energy has been applied to a free *trans*-1,2-diaminocyclopentane molecule. The obtained conformation of the molecule with minimum conformational energy is compared with that observed in the complex ion, [Co(cptn)₃]³⁺ in Table 6. Conformation of the cyclopentane ring observed in crystals of (–)₅₈₉[Co(+cptn)₃]Cl₃·4H₂O agrees well with that calculated by the minimization procedure. Large distortions of bond angles occur at N(*a*)–C(*d*)–C(*b*) and N(*a*)–C(*d*)–C(*d'*). In fact, the N(*a*)···N(*a'*) distance of 3.14 Å decreases in length to 2.76 Å when the molecule forms a chelate ring. In calculating minimum potential

Table 5. *Interatomic distances and bond angles within the complex ion*

E.s.d.'s are given in parentheses.			
Co·····N(1)	2.015 (16) Å	C(1)·····C(2)	1.500 (29) Å
Co·····N(2)	1.990 (22)	C(2)·····C(3)	1.512 (32)
Co·····N(3)	2.007 (21)	C(3)·····C(3')	1.519 (32)
N(1)·····C(3)	1.498 (25)	C(4)·····C(5)	1.502 (43)
N(2)·····C(4)	1.458 (28)	C(5)·····C(6)	1.566 (36)
N(3)·····C(8)	1.507 (43)	C(6)·····C(7)	1.519 (33)
		C(7)·····C(8)	1.572 (32)
		C(4)·····C(8)	1.509 (35)
N(1)–Co–N(1')	87.6 (0.8)°	C(2)–C(1)–C(2')	104.4 (2.1)°
N(2)–Co–N(3)	86.6 (0.9)	C(1)–C(2)–C(3)	105.6 (2.3)
Co–N(1)–C(3)	104.4 (1.5)	C(2)–C(3)–C(3')	99.5 (2.2)
Co–N(2)–C(4)	104.9 (1.4)		
Co–N(3)–C(8)	105.5 (1.7)	C(4)–C(5)–C(6)	105.4 (2.2)
N(1)–C(3)–C(3')	106.5 (1.9)	C(5)–C(6)–C(7)	105.6 (2.2)
N(2)–C(4)–C(8)	108.9 (2.1)	C(6)–C(7)–C(8)	102.2 (2.2)
N(3)–C(8)–C(4)	103.0 (2.6)	C(7)–C(8)–C(4)	102.5 (2.2)
N(1)–C(3)–C(2)	119.4 (2.4)	C(8)–C(4)–C(5)	99.9 (2.4)
N(2)–C(4)–C(5)	120.7 (2.3)		
N(3)–C(8)–C(7)	116.7 (2.2)		

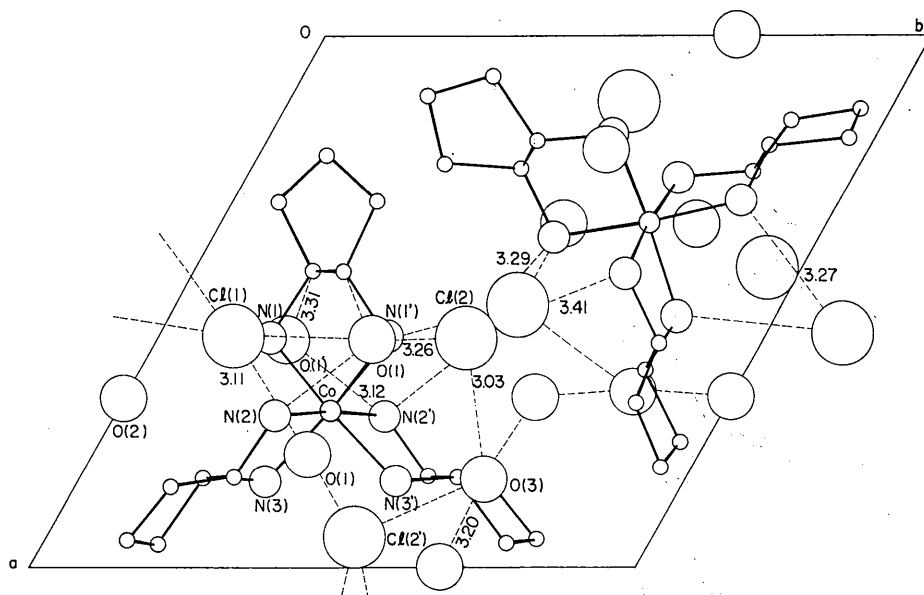


Fig. 4. Atomic arrangement viewed along the c axis near $z = \frac{1}{3}$. Broken lines indicate close contacts.

energy, energies of bond-length distortion and angle bending were determined by using average values of force constants reported by Nakagawa & Shimanouchi (1966), Schachtschneider & Snyder (1963) and Westheimer (1956). For torsional energy and energy of non-bonded interaction, the expressions of Lowe (1968) and of Liquori, Damiani & Elefante (1968) were used respectively.

chloride ion Cl(1) on the twofold axis is surrounded by two nitrogen atoms on one side and by two water molecules on the other side, Cl(2) is also surrounded by two nitrogen atoms and two water-oxygen atoms. There may be three types of weak hydrogen bonds, *i.e.*, $\text{N}-\text{H} \cdots \text{O}$, $\text{O}-\text{H} \cdots \text{Cl}^-$ and $\text{N}-\text{H} \cdots \text{Cl}^-$, similar to those found in the structures of $(-)\text{Co}(\text{en})_3\text{Cl}_3 \cdot \text{H}_2\text{O}$ (Iwata, Nakatsu & Saito, 1969) and $(-)\text{Co}(\text{en})_3\text{Cl}_3 \cdot 4\text{H}_2\text{O}$ (Iwata, Nakatsu & Saito, 1969) and $(-)\text{Co}(\text{en})_3\text{Cl}_3 \cdot 4\text{H}_2\text{O}$ (Iwata, Nakatsu & Saito, 1969).

Table 6. Comparison of molecular geometry of the ligand in the crystal with that calculated by energy minimization

	Observed	Calculated
$\text{C}(a) \cdots \text{C}(b)^*$	1.53 Å	1.53 Å
$\text{C}(b) \cdots \text{C}(d)$	1.53	1.52
$\text{C}(d) \cdots \text{C}(d')$	1.51	1.52
$\text{N}(a) \cdots \text{C}(d)$	1.49	1.49
$\text{C}(b)-\text{C}(a)-\text{C}(b')$	105°	106°
$\text{C}(a)-\text{C}(b)-\text{C}(d)$	104	104
$\text{C}(b)-\text{C}(d)-\text{C}(d')$	101	102
$\text{N}(a)-\text{C}(d)-\text{C}(d')$	106	112
$\text{N}(a)-\text{C}(d)-\text{C}(b)$	119	112

* See Fig. 2.

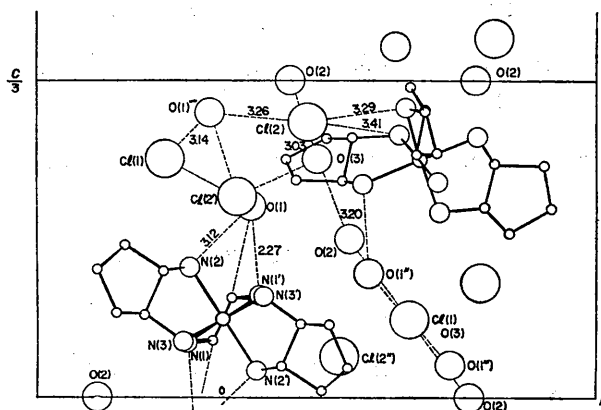


Fig. 5. Atomic arrangement projected on the bc plane.

A partial projection of the structure around $z = \frac{1}{3}$ along the c axis is shown in Fig. 4. Relations around a complex ion are illustrated in Fig. 5. The general features of the structure are broadly similar to those of $(-)\text{Co}(\text{en})_3\text{Cl}_3 \cdot \text{H}_2\text{O}$ (Marumo, Utsumi & Saito, 1970). Stacking of the complex cations is related to hexagonal closest-packing. The cobalt atom is on a twofold axis and slightly off the threefold axis. The pseudo-threefold axis of the complex ion is inclined about 22° to the c axis. Interatomic distances less than 3.5 Å outside the complex ions are listed in Table 7. The

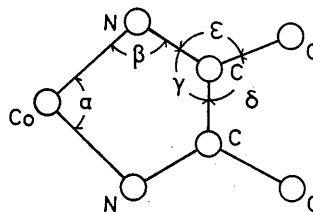


Fig. 6. Geometrical diagram of complex ions (see Table 8).

[Co(+chxn)₃]Cl₃·5H₂O (Marumo, Utsumi & Saito, 1970). These hydrogen bonds are indicated by broken lines in Figs. 4 and 5. In fact, the relative arrangement of the complex ions, chloride ions and water molecules is related to that found in the structures of analogous compounds mentioned above. O(1) has nearly-tetrahedral surroundings but O(2) and O(3) possess irregular coordinations. This explains why O(2) and O(3) have larger temperature factors than O(1).

Table 7. Intermolecular distances less than 3.5 Å

E.s.d.'s are given in parentheses.		Symmetry operation applied to second atom	
Cl(1)···O(1)	3.108 (32) Å		1
Cl(1)···N(3)	3.274 (21)		2
Cl(2)···N(1)	3.293 (19)		3
Cl(2)···N(2)	3.412 (34)		3
Cl(2)···O(1)	3.258 (26)		1
Cl(2)···O(3)	3.031 (28)		6
O(1)···N(1)	2.866 (26)		4
O(1)···N(2)	3.122 (41)		1
O(1)···C(3)	3.254 (28)		4
O(3)···O(2)	3.204 (48)		5
1.	$x,$	$y,$	z
2.	$x-y,$	$x-1.0,$	$z+\frac{1}{6}$
3.	$x-y,$	$x,$	$z+\frac{1}{6}$
4.	$x,$	$x-y,$	$-z+\frac{1}{6}$
5.	$x,$	$y+1.0,$	z
6.	$y,$	$z,$	$z+\frac{1}{6}$

Geometry of complex ions and optical activity

Table 8 lists geometrical values for a series of *lel* isomers of tris-diamine cobalt(III) complexes with five-membered chelate rings. Corresponding values for the tris-(1,3-diaminopropane)cobalt(III) ion are also included for reference. The geometrical diagram for use with Table 8 is shown in Fig. 6. Values in Table 8 are averaged by assuming an appropriate symmetry of the chelate ring for each case. Some optical properties are also listed in Table 8. Fig. 7 shows the circular dichroism spectra of the complex ions. Usually, they give two circular dichroism bands with opposed signs in the region of the first absorption band. The longer wavelength band has positive rotatory strength, reflecting the same absolute configuration *A* (IUPAC, 1968). The first absorption band of (+)₅₈₉[Co(en)₃]³⁺ and (-)₅₈₉[Co(+chxn)₃]³⁺ is observed around 470 mμ, whereas that of (-)₅₈₉[Co(+cptn)₃]³⁺ is shifted towards a longer wavelength at 490 mμ. Correspondingly, the red shift is also observed in the circular dichroism spectrum of (-)₅₈₉[Co(+cptn)₃]³⁺. McCaffery & Mason (1963) measured the circular dichroism of single crystals of Na(+)₅₈₉[Co(en)₃]₂Cl₇·6H₂O, of which the crystal structure was already known (Nakatsu, Shiro, Saito & Kuroya, 1957), and they assigned the longer wavelength component to that of *E* symmetry and the shorter wavelength component to that of *A*₂ symmetry. The circular dichroism spectrum of (-)₅₈₉[Co(+chxn)₃]³⁺ can be assigned in the same

way as that of (+)₅₈₉[Co(en)₃]³⁺, since the optical rotatory dispersion curve and circular dichroism spectrum resemble those of (+)₅₈₉[Co(en)₃]³⁺. Unlike these two complex ions, the circular dichroism spectrum of (-)₅₈₉[Co(+cptn)₃]³⁺ is somewhat different: the longer wavelength band has smaller rotatory strength than the shorter one. The longer wavelength band predominates in the first two members of the series. Ion-pair effect and anisotropy in polarized light absorption of the single crystal indicated that the longer wavelength band is *E* (Ito, Marumo & Saito, 1970). The ratio of the rotatory strength of the *E* and *A*₂ bands is given in the last line but one of Table 8.

The most striking aspect of these data is that the shape and size of an octahedron, formed by six nitrogen atoms around the cobalt atom as well as those of the five-membered chelate ring, are practically the same throughout the series of complex ions. The symmetry of the complex ions is *D*₃. The octahedron is slightly distorted around the threefold axis: the upper triangle formed by three nitrogen atoms is rotated counter-clockwise by about 5° with respect to the lower triangle of the three remaining nitrogen atoms. This distortion of the octahedron, due to formation of the chelate rings, may give rise to a twisted ligand field, from which the optical activity of these complex ions will arise.

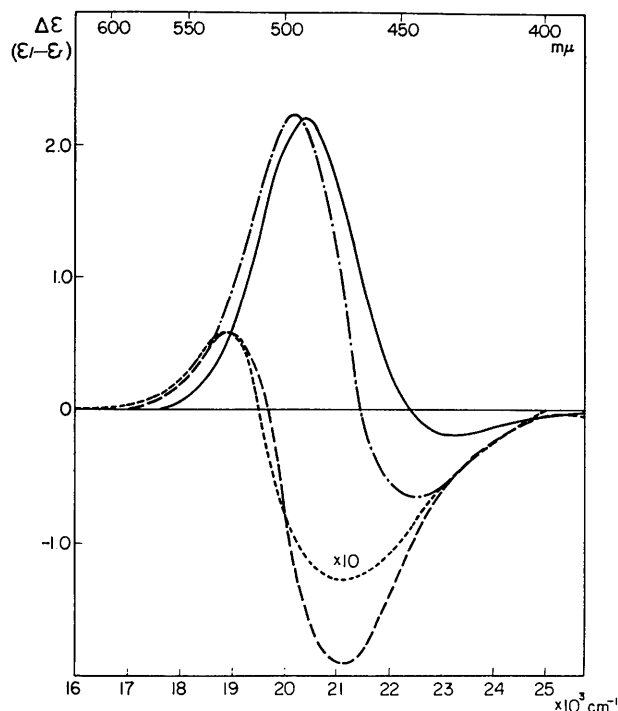


Fig. 7. Circular dichroism spectra of some tris-diamine cobalt(III) complexes in aqueous solutions.

- (+)₅₈₉[Co(en)₃]Cl₃
- - - (-)₅₈₉[Co(+chxn)₃]Cl₃
- · - · (-)₅₈₉[Co(+cptn)₃]Cl₃
- · · · (-)₅₈₉[Co(tn)₃]Br₃

No appreciable strain is introduced in bond angles on forming a chelate ring for the complex ions, (+)₅₈₉[Co(en)₃]³⁺ and (-)₅₈₉[Co(+chxn)₃]³⁺. In the case of (-)₅₈₉[Co(cptn)₃]³⁺, however, bond angles δ and ε deviate largely from the normal tetrahedral angle. Angle β is also smaller than the normal tetrahedral angle. In fact, the N...N distance of 3.14 Å decreases in length to 2.76 Å when a strain-free ligand molecule forms a chelate ring. Such a strain in bond angles due to fused-ring formation appears to weaken the ligand field. This change in the ligand field might cause the red shifts of the first absorption band and both components of circular dichroism spectrum. The observed reversal of rotatory strength of the two components of circular dichroism might also be attributable to this change in the ligand field. There is an interesting trend for the angle Co-N-C (designated as β in Table 8) to decrease with an increase of A/E in the series. Note that the general pattern of the circular dichroism of (-)₅₈₉[Co(tn)₃]³⁺ is remarkably similar to that of (-)₅₈₉[Co(+cptn)₃]³⁺, though the rotatory strength of the former is smaller than that of the latter by a factor of 10. Considerable strain in bond angles is also introduced in the formation of the complex ion, (-)₅₈₉[Co(tn)₃]³⁺ (Nomura, Marumo & Saito, 1969). This fact appears to suggest that the misalignment of the lone-pair orbital of the ligand atom might influence the rotatory strength of the two circular dichroism bands as Liehr (1964) suggested.

To sum up, the important factor that governs the rotatory strength of $d-d$ transitions in metal complexes

is considered from the evidence of X-ray crystal analysis to be the cumulative effect of various distortions of the ligand atoms, which may give rise to a twisted crystal field.

Fourier syntheses and least-squares calculations were carried out on the HITAC 5020E computer, Computer Centre of the University of Tokyo, with programs ANSR-2, RSFR-6 and FLS-4 of the UNICS system. Preliminary calculations were performed on the FACOM 270-30 computer at this Institute. Part of the cost of this research was met by a Scientific Research Grant of the Ministry of Education, to which the authors' thanks are due.

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Table 8. Geometries* of the chelate ring and optical activity

Complex	E.s.d.'s are given in parentheses.			
	(+) ₅₈₉ [Co(en) ₃] Cl ₃ ·H ₂ O	(-) ₅₈₉ [Co(+chxn) ₃] Cl ₃ ·5H ₂ O	(-) ₅₈₉ [Co(+cptn) ₃] Cl ₃ ·4H ₂ O	(-) ₅₈₉ [Co(tn) ₃] Br ₃ ·H ₂ O
Symmetry	D ₃	D ₃	D ₃	C ₃
Absolute configuration:	<i>A</i> ($\delta\delta\delta$)	<i>A</i> ($\delta\delta\delta$)	<i>A</i> ($\delta\delta\delta$)	<i>A</i>
Co-N	1.978 (4) Å	2.019 (10) Å	2.004 (12) Å	2.000 (12) Å
N-C	1.49 (1)	1.51 (2)	1.49 (2)	1.47 (2)
C-C	1.51 (1)	1.56 (3)	1.51 (2)	1.54 (3)
α	85.3 (2)°	86.7 (6)°	87.0 (6)°	94.5 (7)°
β	108.4 (3)	106.4 (7)	104.8 (9)	117.4 (10)
γ	105.5 (4)	105.7 (9)	105.5 (13)	112.8 (10)
δ		112.0 (10)	101.0 (13)	
ε		110.8 (9)	118.9 (13)	
θ †	55.0	59.0	61.5	
References	Iwata, Nakatsu & Saito (1969)	Marumo, Utsumi & Saito (1970)		Nomura, Marumo & Saito (1969)
Absorption spectra	λ_{\max}	λ_{\max}	λ_{\max}	λ_{\max}
	469 m μ	472 m μ	490 m μ	489 m μ
Circular dichroism spectra	$\Delta\varepsilon$	$\Delta\varepsilon$	$\Delta\varepsilon$	$\Delta\varepsilon$
	493	495	529	532
	$\Delta\varepsilon$	$\Delta\varepsilon$	$\Delta\varepsilon$	$\Delta\varepsilon$
	-0.195	-0.66	-1.91	-0.13
	λ_{\max}	λ_{\max}	λ_{\max}	λ_{\max}
	429	442	474	474
	A/E	A/E	A/E	A/E
	0.10	0.24	4.38	2.30
References	Mason & Norman (1966)			

* See Fig. 6 for diagram.

† θ : dihedral angle N-C-C-N.

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The Crystal Structure of 4b,9a-Dibromo-9,10-dihydroindeno[1,2-*a*]indene

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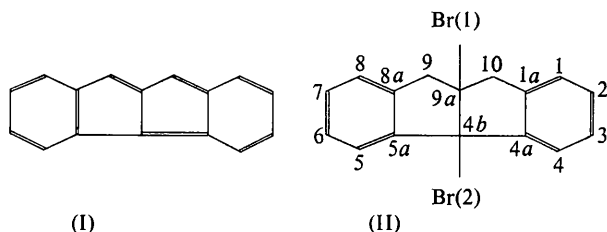
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Crystals of 4b,9a-dibromo-9,10-dihydroindeno[1,2-*a*]indene, $C_{16}H_{12}Br_2$, are monoclinic with cell dimensions of $a=11.430$, $b=7.794$, $c=16.248$ Å, $\beta=110.68^\circ$, $Z=4$ and space group $P2_1/c$. The structure has been determined from three-dimensional X-ray data collected by photographic methods. Positional and thermal parameters were refined by the block-diagonal least-squares method to an R value of 0.10 for 1864 observed reflexions. The molecule is butterfly-shaped: two indane nuclei are fused with the C(4b)–C(9a) bond in common. It is folded at this C–C bond, the planes of the two indane rings making an angle of 111° . The conformation of the Br–C(4b)–C(9a)–Br group is staggered, and the distance between the two Br atoms is as short as 3.362 Å, indicating that the molecule is overcrowded.

Introduction

An organic semiconductor, indeno[1,2-*a*]indene (I), originally synthesized by Haga & Miura (1969), is easily hydrogenated to form 9,10-dihydroindeno[1,2-*a*]indene. The double bond at the centre of the molecule is easily brominated to form 4b,9a-dibromo-9,10-dihydroindeno[1,2-*a*]indene (II). Inspection of a molecular model reveals that the *trans* dibromo isomer hardly exists owing to great strain in the molecule, and the *cis* dibromo isomer should be overcrowded because the Br...Br distance is as short as 2.8 Å. Thus, a *gauche* structure is most probable. All attempts to determine the chemical structure of the molecule by means of mass spectroscopy, nuclear magnetic resonance and infrared spectroscopy did not succeed. The crystal-structure analysis of the compound (II) was undertaken to establish the molecular structure and conformation.



Experimental

The crystals used for X-ray analysis were grown from a carbon tetrachloride solution. They are colourless, transparent, and are stable to X-ray radiation in the air. Cell dimensions were obtained from Weissenberg photographs taken with Cu $K\alpha$ radiation ($\lambda=1.5418$ Å). Copper-powder diffraction lines were superposed on the films for calibration purposes.

Crystal data are: 4b,9a-dibromo-9,10-dihydroindeno[1,2-*a*]indene, $C_{16}H_{12}Br_2$, M.W. 364.08; monoclinic, $a=11.430 \pm 0.006$, $b=7.794 \pm 0.003$, $c=16.248 \pm 0.006$ Å, $\beta=110.68 \pm 0.06^\circ$, $Z=4$, $U=1354$ Å³, $D_x=1.785$, $D_m=1.778$ g.cm⁻³, $F(000)=712$, $\mu(\text{Cu } K\alpha)=82.4$ cm⁻¹, space group $P2_1/c$ (No. 14, C_{2h}^2).

Intensities of reflexions were recorded on multiple-film equi-inclination Weissenberg photographs with Cu $K\alpha$ radiation. Crystals of maximum dimensions 0.10 mm were used. Six layers, $h0l \sim h5l$, were collected around the b axis and three layers, $0kl \sim 2kl$, were collected around the a axis. Intensities were estimated visually by comparison with a standard scale. A total of 1864 independent reflexions was observed. The intensities covered a range of about 6000:1. Usual Lorentz and polarization corrections, and Phillips spot-shape corrections were made. Relative intensities were placed on an approximately absolute scale by Wilson's method.