

The Crystal Structure of (+)₅₈₉-Tris[(-)-*trans*-1,2-diaminocyclohexane]cobalt(III) Chloride Monohydrate ('*ob*' Isomer)

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(Received 27 January 1972)

The crystal structure of (+)₅₈₉-tris[(-)-*trans*-1,2-diaminocyclohexane]cobalt(III) chloride monohydrate, (+)₅₈₉-[Co{(-)-chxn}₃]Cl₃·H₂O ('*ob*' isomer) has been determined from three-dimensional data collected on a diffractometer. The structure was refined by the block-diagonal least-squares method to give $R=0.034$ for 1251 observed reflexions. The crystals are monoclinic with the space group $C2$. The lattice constants are $a=13.922$, $b=10.720$, $c=8.777$ Å and $\beta=108.8^\circ$ with two formula units in the unit cell. The complex ion has a pseudo symmetry D_3 . The cobalt atom has a distorted octahedral coordination of six nitrogen atoms of the ligand molecules. The distortion of the octahedron is slightly more marked than that observed in the '*lel*' isomer. The central C–C bond in the chelate ring is inclined at an angle of 72° with respect to the threefold axis, the conformation being '*ob-ob-ob*'. The shape and the size of the chelate ring as well as those of the cyclohexane ring are normal. The number of electrons around the central cobalt atom was estimated to be approximately 25.8. The absolute configuration of the complex ion is $A(\lambda\lambda\lambda)$.

Introduction

The *trans*-1,2-diaminocyclohexane molecule exists in two enantiomeric forms, since the cyclohexane ring does not allow free rotation of the N–C bonds around the central C–C bond. Such an optically active ligand in general favours the formation of one optical isomer over the other when it forms tris-bidentate complexes. The more stable isomer, (-)₅₈₉-[Co{(+)chxn}₃]Cl₃·5H₂O ('*lel*' form) has been prepared by Jaeger & Bijkerk (1937). The structure and absolute configuration of the complex ion (-)₅₈₉-[Co{(+)chxn}₃]³⁺ has already been determined (Marumo, Utsumi & Saito, 1970). The less stable isomer, '*ob*' form, was first characterized by Piper & Karipides (1964). Crystals of (+)₅₈₉-[Co{(-)chxn}₃]Cl₃·H₂O have been subjected to crystal structure analysis, in order to elucidate the conformational details of the '*ob*' isomer.

Experimental

Suitable crystals of (+)₅₈₉-tris[(-)-*trans*-1,2-diaminocyclohexane]cobalt(III) chloride monohydrate were kindly provided by Professor C. E. Schäffer. Preliminary oscillation and Weissenberg photographs showed that the crystals are monoclinic with systematic absences $hkl: h+k=2n+1$. These absences are consistent with the space groups $C2/m$ (No. 12), Cm (No. 8) and $C2$ (No. 5). The space groups $C2/m$ and Cm can be excluded since the crystals are optically active.

The intensities of the reflexions were measured on a Rigaku automated four-circle diffractometer. A crystal with approximate dimensions $0.13 \times 0.13 \times 0.19$ mm was mounted with the c axis approximately parallel to the ϕ axis of the diffractometer. Mo $K\alpha$ radiation was used. The ω - 2θ scan technique was employed. 1251

independent reflexions up to $2\theta=60^\circ$ were measured. The 400 and 002 reflexions were measured as references every fifty reflexions: the net counts of these reflexions did not alter noticeably over the period of data collection. The data were corrected for Lorentz and polarization effects. The unit-cell dimensions and their standard deviations measured on the Rigaku diffractometer (Mo $K\alpha$, $\lambda=0.7107$ Å) are $a=13.922 \pm 0.004$, $b=10.720 \pm 0.004$, $c=8.777 \pm 0.004$ Å, and $\beta=108.83 \pm 0.04^\circ$ at 23°C ; $U=1244$ Å³, $D_m=1.395$, $D_x=1.399$ g.cm⁻³ for $Z=2$, $M. W.=535.5$, linear absorption coefficient for Mo $K\alpha$, $\mu=10.62$ cm⁻¹.

In order to assess the accuracy of measurement, the intensities of pairs of equivalent reflexions ($hk0$, $hk0$) were collected. The discrepancy index, $R_{\text{exp}} = \sum ||F(hk0)| - |F(\bar{h}\bar{k}0)|| / \sum |F|$, of 0.022 was obtained.

Solution and refinement of the structure

The general positions of the space group $C2$ are fourfold. The two cobalt atoms and two of the six chlorine atoms are required to lie on the twofold axis, since there are only two formula units in the unit cell. The positions of the cobalt and chlorine atoms were deduced from the Patterson synthesis. The y coordinate of the cobalt atom was taken to be zero without loss of generality. These coordinates were used to calculate the structure factors. The reliability index of these F_c 's was 0.34. A three-dimensional electron density map was then calculated with all the terms, the phases of which were calculated on the basis of the cobalt and chlorine atoms. The resulting maps revealed the positions of all the remaining non-hydrogen atoms. The atomic positions and isotropic temperature factors were refined by the least-squares method with a block-diagonal program *HBL5-4* written by Dr Ashida. A weighting scheme, $w=0.2$ for $|F_o| < 15$ and $w=1$ for

all other F_o 's, was employed. The scattering factors for Co, N, C and O were those listed in *International Tables for X-ray Crystallography* (1962). After several refinement cycles the structure converged with $R=0.070$. Five further cycles of least-squares refinement were calculated in anisotropic modes. R then decreased to 0.050. A difference synthesis calculated at this stage revealed the positions of all the hydrogen atoms. After inclusion of the hydrogen atoms in the refinement a final set of least-squares calculations was carried out. Temperature factors of the hydrogen atoms were assumed to be isotropic. In the last cycle of least-squares refinement, all the parameter shifts were well within the

Table 1 (cont.)

H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc	H	K	L	Fo	Fc
2	0	-12	14	15	2	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
2	0	-14	16	15	2	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
4	0	-12	14	15	4	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
4	0	-14	16	15	4	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
6	0	-12	14	15	6	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
6	0	-14	16	15	6	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
8	0	-12	14	15	8	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
8	0	-14	16	15	8	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
10	0	-12	14	15	10	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
10	0	-14	16	15	10	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
12	0	-12	14	15	12	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
12	0	-14	16	15	12	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
14	0	-12	14	15	14	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
14	0	-14	16	15	14	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
16	0	-12	14	15	16	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
16	0	-14	16	15	16	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
18	0	-12	14	15	18	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
18	0	-14	16	15	18	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
20	0	-12	14	15	20	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
20	0	-14	16	15	20	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
22	0	-12	14	15	22	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
22	0	-14	16	15	22	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
24	0	-12	14	15	24	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
24	0	-14	16	15	24	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
26	0	-12	14	15	26	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
26	0	-14	16	15	26	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
28	0	-12	14	15	28	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
28	0	-14	16	15	28	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
30	0	-12	14	15	30	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
30	0	-14	16	15	30	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
32	0	-12	14	15	32	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
32	0	-14	16	15	32	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
34	0	-12	14	15	34	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
34	0	-14	16	15	34	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
36	0	-12	14	15	36	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
36	0	-14	16	15	36	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
38	0	-12	14	15	38	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
38	0	-14	16	15	38	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
40	0	-12	14	15	40	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
40	0	-14	16	15	40	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
42	0	-12	14	15	42	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
42	0	-14	16	15	42	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
44	0	-12	14	15	44	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
44	0	-14	16	15	44	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
46	0	-12	14	15	46	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
46	0	-14	16	15	46	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
48	0	-12	14	15	48	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
48	0	-14	16	15	48	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
50	0	-12	14	15	50	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
50	0	-14	16	15	50	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
52	0	-12	14	15	52	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
52	0	-14	16	15	52	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
54	0	-12	14	15	54	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
54	0	-14	16	15	54	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
56	0	-12	14	15	56	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
56	0	-14	16	15	56	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
58	0	-12	14	15	58	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
58	0	-14	16	15	58	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
60	0	-12	14	15	60	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
60	0	-14	16	15	60	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
62	0	-12	14	15	62	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
62	0	-14	16	15	62	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
64	0	-12	14	15	64	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
64	0	-14	16	15	64	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
66	0	-12	14	15	66	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
66	0	-14	16	15	66	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
68	0	-12	14	15	68	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
68	0	-14	16	15	68	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
70	0	-12	14	15	70	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
70	0	-14	16	15	70	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
72	0	-12	14	15	72	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
72	0	-14	16	15	72	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
74	0	-12	14	15	74	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
74	0	-14	16	15	74	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
76	0	-12	14	15	76	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
76	0	-14	16	15	76	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
78	0	-12	14	15	78	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
78	0	-14	16	15	78	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
80	0	-12	14	15	80	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
80	0	-14	16	15	80	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
82	0	-12	14	15	82	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
82	0	-14	16	15	82	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
84	0	-12	14	15	84	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
84	0	-14	16	15	84	0	-16	22	21	16	4	-7	17	11	-5	5	28	27	25
86	0	-12	14	15	86	0	-12	22	21	16	4	-7	17	11	-5	5	28	27	25
86	0	-14	16	15	86	0	-16	22	21	16									

Table 2. Atomic parameters

(a) Positional and anisotropic thermal parameters for the non-hydrogen atoms ($\times 10^4$), with their e.s.d.'s in parentheses.The β_{ij} 's are defined by: $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$.

	<i>x</i>	<i>y</i>	<i>z</i>	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Co	5000 (0)	5000 (0)	5000 (0)	23 (0)	35 (1)	58 (1)	0 (0)	10 (1)	0 (0)
Cl(1)	0 (0)	633 (2)	0 (0)	108 (2)	81 (2)	94 (3)	0 (0)	70 (2)	0 (0)
Cl(2)	2816 (1)	2183 (2)	5630 (2)	37 (1)	107 (2)	181 (3)	-22 (1)	20 (1)	52 (2)
N(1)	3516 (3)	4870 (5)	3860 (4)	25 (2)	51 (5)	70 (5)	-12 (3)	9 (3)	9 (5)
N(2)	5105 (3)	3742 (4)	3397 (5)	21 (2)	44 (4)	90 (6)	-2 (2)	6 (3)	15 (4)
N(3)	4769 (3)	6363 (4)	6347 (5)	38 (3)	49 (4)	48 (5)	-4 (3)	21 (3)	-5 (4)
C(1)	3338 (4)	4232 (5)	2285 (6)	24 (3)	47 (4)	62 (7)	-1 (3)	11 (3)	5 (5)
C(2)	4093 (4)	3180 (4)	2577 (6)	23 (3)	37 (4)	74 (7)	-1 (3)	12 (3)	9 (5)
C(3)	4022 (4)	2513 (5)	1012 (6)	43 (3)	48 (4)	87 (7)	3 (3)	27 (4)	17 (5)
C(4)	2932 (5)	2026 (6)	203 (7)	58 (4)	73 (6)	102 (8)	-13 (4)	20 (5)	-31 (6)
C(5)	2158 (5)	3045 (6)	-30 (7)	47 (4)	86 (7)	92 (8)	-11 (4)	4 (5)	3 (6)
C(6)	2254 (4)	3751 (6)	1521 (6)	22 (3)	67 (5)	92 (8)	0 (3)	9 (4)	-5 (5)
C(7)	5154 (4)	7572 (5)	5910 (5)	31 (3)	36 (4)	60 (6)	-3 (3)	17 (4)	-4 (4)
C(8)	4735 (4)	8723 (5)	6492 (6)	42 (3)	44 (4)	94 (8)	0 (3)	24 (4)	16 (5)
C(9)	5113 (4)	9898 (7)	5905 (7)	53 (3)	49 (5)	158 (9)	-6 (5)	24 (5)	-22 (8)
O(1)	2960 (8)	4981 (16)	7052 (14)	234 (11)	439 (22)	677 (31)	35 (21)	211 (16)	32 (36)

Table 2 (cont.)

(b) Positional and isotropic thermal parameters for the hydrogen atoms ($\times 10^4$).

	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>
H(1)	3287 (45)	4386 (59)	4495 (73)	1.6 (1.4)
H(2)	3269 (44)	5597 (55)	3744 (69)	1.6 (1.4)
H(3)	5303 (45)	4149 (60)	2687 (73)	1.7 (1.4)
H(4)	5541 (44)	3216 (60)	3850 (70)	1.7 (1.4)
H(5)	4129 (44)	6412 (61)	6152 (71)	1.5 (1.4)
H(6)	5047 (44)	6210 (62)	7301 (70)	1.5 (1.4)
H(7)	3537 (39)	4806 (64)	1593 (62)	1.5 (1.3)
H(8)	3983 (41)	2589 (60)	3454 (67)	1.6 (1.3)
H(9)	4501 (47)	1724 (64)	1083 (74)	2.4 (1.6)
H(10)	4160 (46)	3089 (60)	278 (75)	2.4 (1.6)
H(11)	2793 (52)	1308 (71)	909 (82)	3.3 (1.8)
H(12)	2916 (52)	1638 (70)	-823 (85)	3.3 (1.7)
H(13)	1478 (51)	2795 (70)	-384 (82)	3.3 (1.8)
H(14)	2185 (53)	3558 (72)	-816 (81)	3.3 (1.8)
H(15)	2218 (46)	3219 (61)	2217 (74)	2.3 (1.6)
H(16)	1638 (49)	4440 (60)	1338 (77)	2.4 (1.6)
H(17)	5942 (41)	7514 (60)	6343 (67)	1.4 (1.3)
H(18)	3974 (50)	8723 (66)	6011 (74)	2.4 (1.6)
H(19)	4968 (50)	8708 (70)	7684 (77)	2.4 (1.5)
H(20)	5790 (49)	9918 (87)	6462 (75)	3.5 (1.5)
H(21)	4796 (53)	10607 (68)	6294 (81)	3.3 (1.7)

Table 3. Observed and calculated intensity relations between some *hkl* and $h\bar{k}l$ reflexions

<i>h</i>	<i>k</i>	<i>l</i>	$F_c^2(hkl)$	Observed relations	$F_c^2(h\bar{k}l)$
4	2	0	625	>	196
$\bar{1}\bar{1}$	1	1	961	>	376
$\bar{1}\bar{2}$	2	1	85	<	361
$\bar{1}\bar{1}$	3	1	237	<	729
$\bar{1}\bar{1}$	3	2	182	<	475

Description of the structure and discussion

The complex cation has rigorous symmetry C_2 , but has a pseudo symmetry D_3 , as can be seen in Fig. 1. Each ligand molecule is coordinated to the cobalt atom with its nitrogen atoms. All the C-C bonds in the chelate rings are inclined at an angle of 72° with respect to the threefold axis of rotation, *i.e.* the com-

plex ion has 'ob' conformation. In the 'lel' isomer of this complex ion the C-C bond makes an angle of only 12° with its threefold axis. Table 4 lists the interatomic distances and bond angles within the complex ion with their standard deviations. The cobalt atom has a distorted octahedral coordination of nitrogen atoms with distances ranging from 1.973 to 1.991 Å. These values are slightly shorter than those observed in the 'lel' isomer (Marumo *et al.*, 1970). The angles NCoN in the chelate ring are 84.4 and 84.2° , being slightly smaller than the average value of 86.7° in the case of the 'lel' isomer. The octahedron is distorted around the threefold axis: the upper triangle formed by the three nitrogen atoms is rotated counterclockwise by about 9° with respect to the lower triangle of the three remaining nitrogen atoms, while the angle of distortion is 7° in the 'lel' isomer. The distance between the two triangles of the nitrogen atoms is 2.270 Å and is shorter by about 0.07 Å than that observed in the 'lel' isomer. The five-membered chelate ring is puckered. Two carbon atoms C(77) and C(7) lie at 0.378 Å above and below the plane of Co, N(3) and N(33). C(2) lies 0.378 Å above and C(1) lies 0.369 Å below the plane of Co, N(1) and N(2). These conformational features agree with those of the related complexes; however, the deviations of the carbon atoms from the coordination plane are slightly smaller than those observed in the 'lel' isomer (0.47, 0.50 Å). The average C-C and C-N bond lengths of 1.516 and 1.494 Å are quite normal. Somewhat larger values observed in the 'lel' isomer may be due to neglect of the contribution of hydrogen atoms. The absolute configuration of the complex ion can be designated as $A(\lambda\lambda\lambda)$ according to the IUPAC Convention (1968).

The crystal structure projected along the *c* axis is presented in Fig. 2. The complex lies on a twofold axis of rotation along the *b* axis. It is surrounded by six chloride ions. They form a distorted octahedron around the complex cation. Intermolecular contacts less than 3.5 Å are listed in Table 5. The oxygen atoms

of the water molecules have a distorted tetrahedral coordination. O(1) is surrounded by three chloride ions Cl(1), Cl(2) and Cl(22) and one amino nitrogen atom N(1), as shown in Fig. 2. There may be weak hydrogen bonds between Cl and N atoms and between N and O atoms similar to those observed in the related structures (for example, Iwata, Nakatsu & Saito, 1969; Marumo *et al.*, 1970).

Table 4. Interatomic distances and angles within the complex ion, with their estimated standard deviations

Co—N(1)	1.989 (3) Å	Co—N(2)	1.991 (5) Å
Co—N(3)	1.973 (5)	N(1)—C(1)	1.493 (7)
N(2)—C(2)	1.488 (6)	N(3)—C(7)	1.500 (7)
C(1)—C(2)	1.507 (7)	C(7)—C(77)	1.517 (6)
C(2)—C(3)	1.526 (8)	C(3)—C(4)	1.544 (8)
C(4)—C(5)	1.502 (9)	C(5)—C(6)	1.527 (9)
C(6)—C(1)	1.531 (7)	C(7)—C(8)	1.524 (8)
C(8)—C(9)	1.520 (10)	C(9)—C(99)	1.520 (8)
N(1)—H(1)	0.894 (69)	N(1)—H(2)	0.846 (59)
N(2)—H(3)	0.876 (70)	N(2)—H(4)	0.830 (58)
N(3)—H(5)	0.853 (61)	N(3)—H(6)	0.819 (56)
C(1)—H(7)	0.967 (65)	C(2)—H(8)	1.047 (65)
C(3)—H(9)	1.067 (68)	C(3)—H(10)	0.957 (70)
C(4)—H(11)	1.046 (79)	C(4)—H(12)	0.987 (78)
C(5)—H(13)	0.936 (68)	C(5)—H(14)	0.894 (77)
C(6)—H(15)	0.850 (68)	C(6)—H(16)	1.105 (67)
C(7)—H(17)	1.042 (54)	C(8)—H(18)	1.006 (64)
C(8)—H(19)	0.992 (65)	C(9)—H(20)	0.912 (61)
C(9)—H(21)	0.994 (78)		

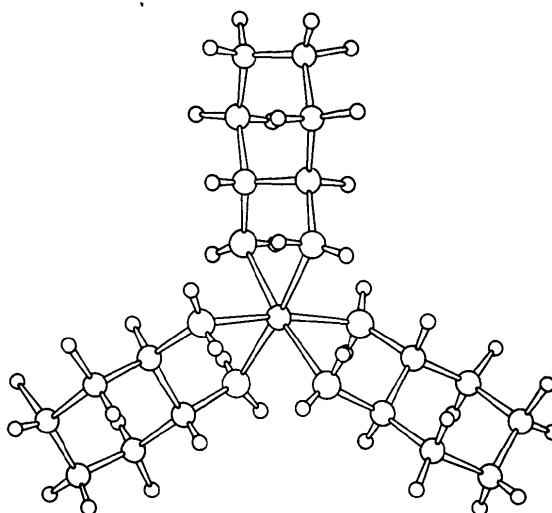


Fig. 1. A perspective drawing of the complex ion, (+)₅₈₉-[Co{(-)-chxn}₃]³⁺.

Estimation of the number of electrons around the cobalt atom

An attempt has been made to estimate the number of electrons around the central cobalt atom by integrating

Table 4 (cont.)

N(1)—Co—N(2)	84.21 (14)°	N(3)—Co—N(33)	84.37 (13)°
Co—N(1)—C(1)	109.43 (28)	Co—N(2)—C(2)	109.98 (29)
Co—N(3)—C(7)	110.15 (29)	N(1)—C(1)—C(2)	106.76 (30)
N(2)—C(2)—C(1)	106.20 (19)	N(3)—C(7)—C(77)	105.59 (26)
C(1)—C(2)—C(3)	111.05 (34)	C(2)—C(3)—C(4)	109.93 (47)
C(3)—C(4)—C(5)	111.86 (26)	C(4)—C(5)—C(6)	112.85 (40)
C(5)—C(6)—C(1)	110.29 (45)	C(6)—C(1)—C(2)	110.99 (22)
C(77)—C(7)—C(8)	110.28 (28)	C(7)—C(8)—C(9)	110.22 (45)
C(8)—C(9)—C(99)	112.27 (34)		
H(1)—N(1)—H(2)	113.4 (4.1)	H(3)—N(2)—H(4)	109.4 (4.9)
Co—N(1)—H(1)	104.5 (3.8)	Co—N(2)—H(3)	106.2 (4.1)
Co—N(1)—H(2)	108.2 (1.6)	Co—N(2)—H(4)	109.3 (2.7)
C(1)—N(1)—H(1)	109.2 (3.8)	C(2)—N(2)—H(3)	108.9 (4.1)
C(1)—N(1)—H(2)	111.9 (1.6)	C(2)—N(2)—H(4)	112.8 (2.7)
H(5)—N(3)—H(6)	109.6 (5.6)	Co—N(3)—H(5)	106.7 (4.1)
Co—N(3)—H(6)	110.6 (3.8)	C(7)—N(3)—H(5)	109.5 (4.1)
C(7)—N(3)—H(6)	110.3 (3.8)	N(1)—C(1)—H(7)	107.2 (2.8)
C(2)—C(1)—H(7)	104.9 (2.9)	C(6)—C(1)—H(7)	112.5 (2.8)
N(2)—C(2)—H(8)	103.4 (2.8)	C(1)—C(2)—H(8)	108.5 (2.8)
C(3)—C(2)—H(8)	113.5 (2.8)	N(3)—C(7)—H(17)	106.1 (3.0)
C(77)—C(7)—H(17)	106.8 (3.0)	C(8)—C(7)—H(17)	113.5 (3.0)
C(1)—C(6)—H(15)	101.0 (3.5)	C(1)—C(6)—H(16)	116.7 (2.6)
C(5)—C(6)—H(15)	107.6 (3.5)	C(5)—C(6)—H(16)	111.3 (2.7)
H(15)—C(6)—H(16)	109.2 (4.4)	H(13)—C(5)—H(14)	102.2 (5.5)
C(6)—C(5)—H(13)	103.0 (4.0)	C(6)—C(5)—H(14)	111.8 (3.9)
C(4)—C(5)—H(13)	116.3 (3.9)	C(4)—C(5)—H(14)	110.2 (3.9)
H(11)—C(4)—H(12)	106.2 (5.1)	C(3)—C(4)—H(11)	108.6 (3.0)
C(3)—C(4)—H(12)	106.9 (4.1)	C(5)—C(4)—H(11)	110.7 (3.0)
C(5)—C(4)—H(12)	112.3 (4.1)	H(9)—C(3)—H(10)	107.0 (4.0)
C(4)—C(3)—H(9)	105.2 (2.2)	C(4)—C(3)—H(10)	107.0 (3.4)
C(2)—C(3)—H(9)	117.5 (2.2)	C(2)—C(3)—H(10)	109.7 (3.4)
H(18)—C(8)—H(19)	112.5 (5.3)	C(7)—C(8)—H(18)	109.0 (3.7)
C(7)—C(8)—H(19)	108.2 (3.7)	C(9)—C(8)—H(18)	107.0 (3.7)
C(9)—C(8)—H(19)	110.0 (3.7)	H(20)—C(9)—H(21)	107.2 (4.9)

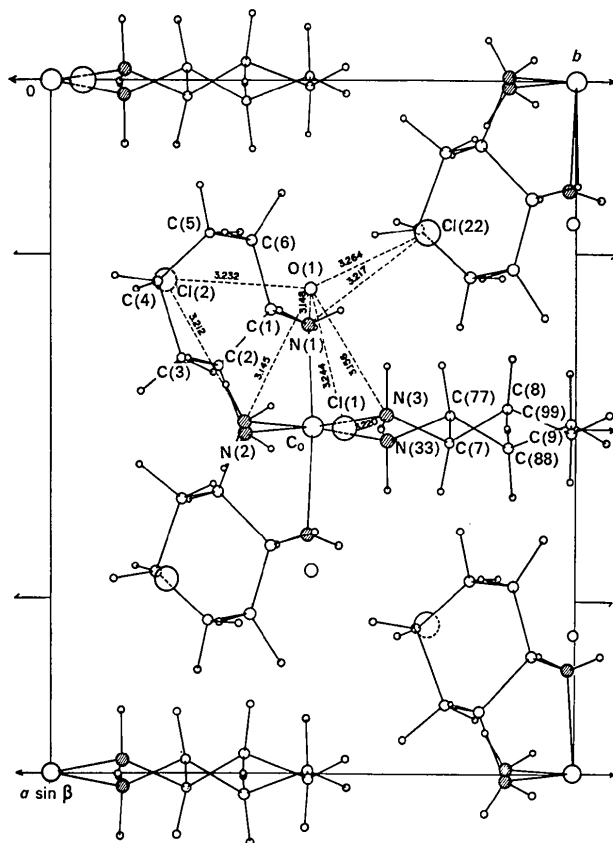


Fig. 2. A projection of the structure along the c axis. Broken lines indicate some close contacts.

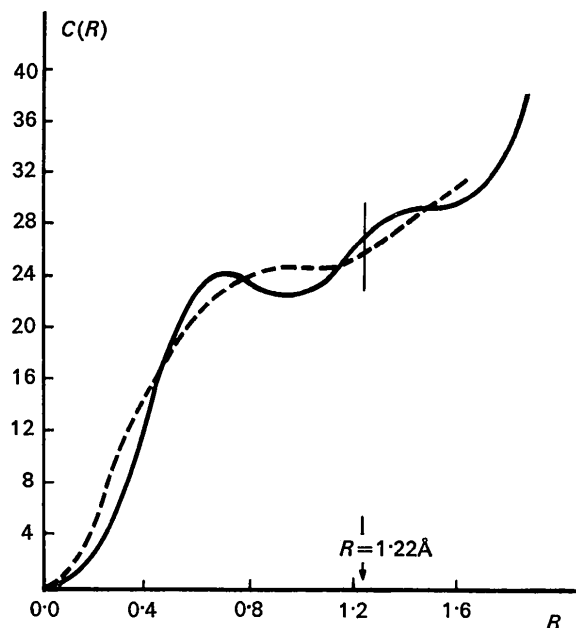


Fig. 3. Number of electrons around the cobalt atom; — number of electrons in a sphere of radius R , $C(R)$. - - - $C(R)$ corrected for termination error.

Table 5. Interatomic distances less than 3.5 \AA outside the complex ions

N(1)···O(1)	3.148 (14) Å
N(2)···O(1)	3.145 (14)
N(3)···O(1)	3.156 (15)
N(1)···Cl(22)	3.217 (5)
N(2)···Cl(2)	3.212 (4)
N(3)···Cl(1)	3.220 (4)
O(1)···Cl(1)	3.244 (10)
O(1)···Cl(2)	3.232 (17)
O(1)···Cl(22)	3.264 (15)

the electron density within a sphere around it. Electron density at a point \mathbf{r} in the unit cell is:

$$\rho(\mathbf{r}) = \frac{1}{V} \sum \sum \sum F(hkl) \exp[-2\pi i (\mathbf{S} \cdot \mathbf{r})]$$

where

$$\mathbf{S} = h\mathbf{a}^* + k\mathbf{b}^* + l\mathbf{c}^*. \quad (1)$$

$C(R)$, the number of electrons in a sphere of radius R with its centre at \mathbf{r}_i , can be obtained by integrating equation (1).

$$C(R) = \frac{1}{V} \left[\frac{4}{3}\pi R^3 F(000) + \frac{1}{2\pi^2} \sum \sum \sum \frac{1}{S^3} F(hkl) \right. \\ \times \exp[-2\pi i (\mathbf{S} \cdot \mathbf{r}_i)] \\ \left. \times (-2\pi SR \cos 2\pi SR + \sin 2\pi SR) \right]. \quad (2)$$

If we assume a spherical charge distribution around the cobalt atom, we have

$$\rho(R) = \frac{1}{4\pi R^2} \frac{dC(R)}{dR}. \quad (3)$$

$C(R)$ was calculated by using observed $F(hkl)$'s according to equation (2). The results plotted against R give the full line shown in Fig. 3. Though $C(R)$ is an increasing function of R , the experimental curve shows a slight downward trend around $R=0.9 \text{ \AA}$, which might be due to the termination effect in the Fourier series. The effect was corrected from the following consideration: the electron density which has the termination effect can be written as follows

$$\rho(\mathbf{R}) = \int F(\mathbf{S})g(\mathbf{S}) \exp[-2\pi i (\mathbf{S} \cdot \mathbf{R})] d\mathbf{S} \\ = \int \rho^*(\mathbf{R} + \mathbf{\Pi})\Phi(\mathbf{\Pi})d\mathbf{\Pi} \quad (4)$$

where $g(\mathbf{S})$ is a step function ($=1$ $|\mathbf{S}| \leq S_{\max}$, $=0$ $|\mathbf{S}| > S_{\max}$), $\Phi(\mathbf{\Pi})$ a Fourier transform of $g(\mathbf{S})$, and $\rho^*(\mathbf{R})$ a true (error free) electron density.

As a first approximation, we adopt the analytical expression for the atomic scattering factors given by Forsyth & Wells (1959) to calculate the function $\rho^*(\mathbf{R})$ and write it as $\rho_0^*(\mathbf{R})$. If $\rho(\mathbf{R})$ has a value $\rho_1(\mathbf{R})$ when $\rho^*(\mathbf{R})$ is $\rho_0^*(\mathbf{R})$ in equation (4), the difference between $\rho_0^*(\mathbf{R})$ and $\rho_1(\mathbf{R})$ is considered to be a correction

for the termination effect. Thus $\varrho_2^*(\mathbf{R})$, given by the following equation, is a better approximation for $\varrho^*(\mathbf{R})$.

$$\varrho_2^*(\mathbf{R}) = \varrho(\mathbf{R}) + [\varrho_0^*(\mathbf{R}) - \varrho_1(\mathbf{R})], \quad (5)$$

where

$$\varrho_1(\mathbf{R}) = \int \varrho_0^*(\mathbf{R} + \mathbf{R}_1) \Phi(\mathbf{R}_1) d\mathbf{R}_1.$$

$\varrho_2^*(\mathbf{R})$ was used in place of $\varrho_0^*(\mathbf{R})$ and the calculation was repeated. After two cycles $\varrho_2^*(\mathbf{R})$ converged. $C(R)$, corrected for termination error, is plotted in Fig. 3 (dotted line). Thus the number of electrons around the cobalt atom in a sphere of radius 1.22 Å (covalent radius of Co) is estimated to be 25.8. The value is quite plausible and seems to support the electroneutrality rule of Pauling (1960).

Residual electron density

At the final stage of refinement a three-dimensional difference synthesis including all the atoms was calculated in order to detect any residual electron density. The result is shown in Fig. 4 for one chelate ring. Areas of low negative and positive density were observed throughout the unit cell, but an interesting feature is that there remain higher peaks in the spaces between the non-hydrogen atoms. This is similar to the effects which were reported, for example, by Hartman & Hirschfeld (1966), Hvoslev (1968), Delaplane & Ibers (1969) and Verschoor & Keulen (1971). In particular, the highest peaks appear between the cobalt and nitrogen atoms and are just off the line joining these atoms, and are outside the chelate ring. A similar feature was observed for all the crystallographically independent cobalt–nitrogen bonds.

In order to examine this point more closely, a difference Fourier synthesis composed of the coefficients $(F_o - F_c')$'s was calculated, using all the observed data up to $\sin \theta/\lambda = 0.70$. F_c' is the structure factor calculated by excluding one electron in the lone pair orbital of each nitrogen atom, *i.e.* by assuming the atomic scattering factor of the nitrogen atom to be the sum of the mean scattering factors of one *1s*, two *2s* and three *2p* electrons (Fukamachi, 1971):

$$F_c' = \sum f_j \exp 2\pi i \mathbf{r}_j \cdot \mathbf{S} + f_N \exp 2\pi i \mathbf{r}_N \cdot \mathbf{S} \\ (f_N = 2f_{1s} + f_{2s} + f_{2p_x} + f_{2p_y} + f_{2p_z}).$$

The symmetry of the complex cation is 2. This implies that there exist three crystallographically independent but chemically equivalent regions in the difference synthesis. The result of averaging these regions is shown in Fig. 5. The peak height is $0.4 \pm 0.07 \text{ e.}\text{\AA}^{-3}$ and the distance of the peak from the atomic centre of nitrogen is 0.43 Å, in agreement with the calculated value of Dawson (1964) ($B = 2 \text{ \AA}^2$, $\sin \theta/\lambda = 0.65$), whereas another peak of height $0.4 \pm 0.07 \text{ e.}\text{\AA}^{-3}$ lies nearly on the line joining the nitrogen and the carbon atoms. The fact that the peak position is slightly off

the Co–N direction appears to indicate that the lone pair orbital is not oriented directly towards the central cobalt atom. In the calculation of the rotatory strength of optically active complexes, this effect should be taken into account.

The authors are grateful to Professor C. E. Schäffer for providing crystals of $(+)_589\text{-tris}\{(-)\text{-trans}\text{-}1,2\text{-diaminocyclohexane}\}\text{cobalt(III) chloride monohydrate}$. Part of the cost of this investigation was met by a Scientific Research Grant from the Ministry of Education, to which the authors' thanks are due.

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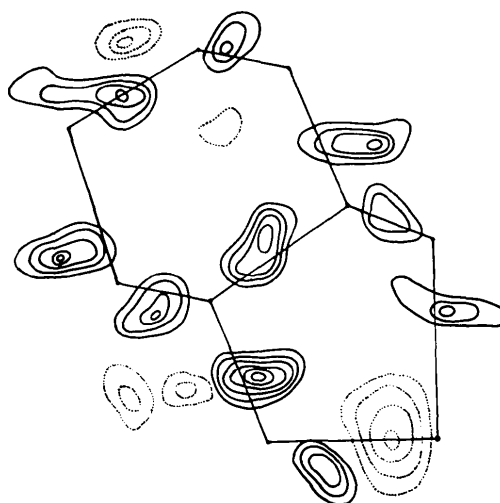


Fig. 4. The residual electron density. The contour interval is $0.02 \text{ e.}\text{\AA}^{-3}$; the lowest contour is $0.08 \text{ e.}\text{\AA}^{-3}$; negative contours are shown as broken lines.

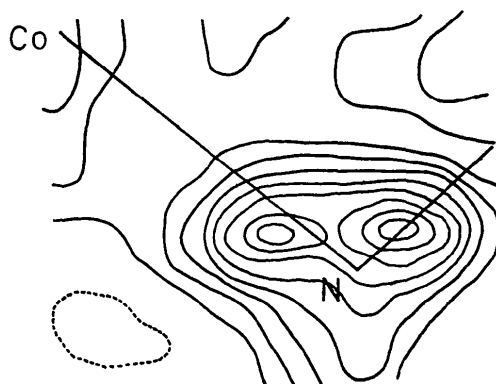


Fig. 5. Final difference synthesis composed of the coefficients $(F_o - F_c')$. The contour interval is $0.05 \text{ e.}\text{\AA}^{-3}$; negative contours are shown as broken lines; zero contours are omitted.

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The Crystal and Molecular Structure of 1,2,4,5-Tetra-*t*-butylbenzene

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(Received 1 May 1972)

The crystal structure of a monoclinic modification of 1,2,4,5-tetra-*t*-butylbenzene has been determined using three-dimensional Cu $K\alpha$ counter data. The final R index is 7.5%. The benzene ring with the adjacent quaternary carbon atoms is planar within the limits of accuracy. The benzene ring has angular deviations up to 10° from a regular hexagon. The exocyclic C-C bonds have lengths of 1.57 Å. There are indications of disorder involving the *t*-butyl groups.

Introduction

Because of the strong steric interaction of the bulky *t*-butyl groups in *o*-*t*-butylbenzenes considerable distortion of the benzene ring is to be expected. Dale (1961) on the evidence of infrared and ultraviolet spectra for 1,2,4 tri-*t*-butylbenzene was led to conclude that *ortho*-positioned *t*-butyl groups cause a (probably small) out of plane distortion of the benzene ring. A similar conclusion was drawn by Hoogzand & Hübel (1961) from the IR and UV spectra of 1,2,4,5-tetra-*t*-butylbenzene (TTBB). As the IR spectrum indicated the loss of centrosymmetry a chair-like distortion was considered impossible and a boat-like deformation was assumed. Arnett, Sanda, Bollinger & Barber (1967) have determined the strain energy resulting from a pair of *ortho*-positioned *t*-butyl groups as 22.3 ± 0.5 kcal/mole. They see no conclusive evidence from n.m.r., IR or UV spectra or from the reactivity of these compounds for a warping of the ring. The only indication for an appreciable influence on the aromatic π -electron system according to these authors is a noticeable decrease of the diamagnetic susceptibility exaltation relative to benzene.

It is borne out by the structure determination of monoclinic TTBB (preliminary communication: van Bruynsvoort, Eilermann, van der Meer & Stam, (1968) that there is indeed a strong deformation of the benzene ring, without, however, affecting the planarity of the ring.

Two other *o*-*t*-butyl aromatics have recently been investigated: 4,5-di-*t*-butylimidazole (DTBI, Visser & Vos, 1971*a*) and 2,3-di-*t*-butylquinoxaline (DTBQ, Visser & Vos, 1971*b*). Here also the planarity of the aromatic ring is not or little affected.

Experimental

Recrystallization of TTBB from alcohol yielded two modifications, an orthorhombic and a monoclinic one. At about 80° the orthorhombic crystals transform irreversibly into the monoclinic form. The monoclinic modification was chosen for a crystal structure determination.

The monoclinic crystals were usually rhombohedral blocks with the forms $\{011\}$ and $\{10\bar{1}\}$ predominant and smaller faces $\{110\}$. The cell constants were determined from zero-layer Weissenberg diagrams about $[010]$, $[001]$ and $[101]$, calibrated with Al powder lines. A least-squares procedure applied to 45 reflexions of high θ yielded:

$$\begin{aligned} a &= 10.910 (3) \text{ \AA} \\ b &= 9.988 (3) \\ c &= 10.051 (3) \\ \beta &= 112.29 (2)^\circ. \end{aligned}$$

The numbers in parentheses are standard deviations. The space group is $P2_1/n$. Because of the scarcity of the material no experimental density was determined.