

The Crystal Structure of $(-)_546$ cis- β -Dinitro-(L-3,8-dimethyltriethylenetetramine)cobalt(III) Perchlorate, $(-)_546$ cis- β -[Co(NO₂)₂(L-3,8-dimetriem)]ClO₄

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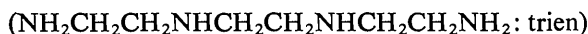
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The structure of $(-)_546$ cis- β -[Co(NO₂)₂(3,8-dimetriem)]ClO₄ has been determined from three-dimensional X-ray photographic data. The crystals are orthorhombic, space group $P2_12_12_1$, with unit-cell dimensions $a = 11.89$, $b = 13.07$, $c = 10.28$ Å. There are four formula units in the cell. The structure was solved by the heavy-atom method and refined by the anisotropic block-diagonal least-squares method to an R value of 0.093 for 883 observed reflexions. The quadridentate ligand is coordinated to the central cobalt atom with its four nitrogen atoms and the strain involved in the *cis*- β -coordination is partly alleviated by adjusting the conformation of the five-membered chelate rings. Each substituted methyl group lies in an equatorial position relative to the plane of the chelate ring. The absolute configuration of the complex ion can be described as a skew chelate pair, Δ . The conformation of the two chelate rings with methyl groups is δ and that of the other ring is λ . The configurations about the two secondary nitrogen atoms are antimeric as expected.

Introduction

There are three possible ways of coordinating a triethylenetetramine molecule

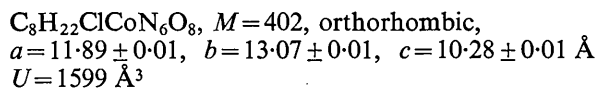


to a cobalt(III) ion, as shown in Fig. 1. Further asymmetry sources arise from the existence of the two secondary nitrogen atoms. Two isomers of the *cis*- β form are shown in Fig. 2. It has been shown that the β - R,S isomer, in which the configurations about the two secondary nitrogen atoms are antimeric, is less stable than the β - R,R isomer in which the configurations about the two nitrogen atoms are the same (Buckingham, Marzilli & Sargeson, 1967; Sargeson & Searle, 1967). This β - R,S isomer has not yet been isolated in a stable form but was obtained in the crystalline form together with the *cis*- α isomer, when a substituted trien ligand such as L-3,8-dimethyltriethylenetetramine was used (Yoshikawa, Saburi, Sawai & Goto, 1967). Freeman & Maxwell (1969) recently determined the structure of racemic *cis*- β -(chloroaquo-triethylenetetramine)cobalt(III) perchlorate (*cis*- β - R,R). The role of the asymmetric nitrogen atom in these fused-ring coordination compounds is as important as the asymmetric carbon atom in fused-ring alicyclic compounds, therefore the absolute configuration of the asymmetric nitrogen atom is crucial to the stereochemistry of rearrangement which the complex ions may undergo during reaction. The crystal structure of $(-)_546$ cis- β -[Co(NO₂)₂(L-3,8-dimetriem)]ClO₄ has been determined mainly to establish the stereochemical configuration of the complex cation.

Experimental

The specimens were kindly supplied by Professor S. Yoshikawa of this University. They are red pris-

matic crystals elongated along the c -axis. Oscillation and Weissenberg photographs were taken to determine the cell dimensions and the space group using Fe $K\alpha$ radiation ($\lambda = 1.9373$ Å). The crystal data are:



$D_m = 1.75 \text{ g.cm}^{-3}$, $D_x = 1.74 \text{ g.cm}^{-3}$, $Z = 4$, $F(000) = 784$, linear absorption coefficient for Fe $K\alpha$ radiation $\mu = 76 \text{ cm}^{-1}$, space group $P2_12_12_1$ (No. 19).

Two series of equi-inclination Weissenberg photographs were taken with Mn-filtered Fe $K\alpha$ radiation

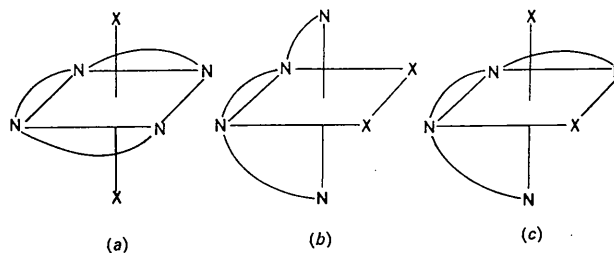


Fig. 1. Possible cobalt-triethylenetetramine coordination. (a) *trans*, (b) *cis*- α , (c) *cis*- β .

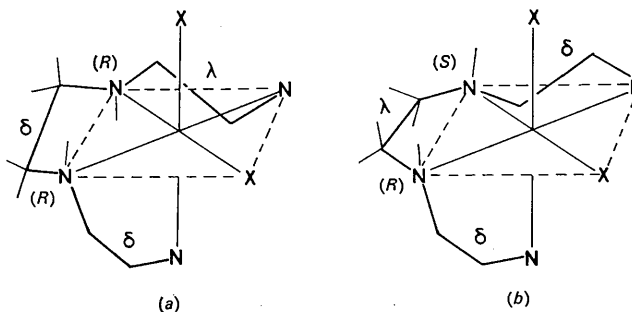


Fig. 2. (a) R,R -*cis*- β and (b) R,S -*cis*- β isomers.

around the c axis up to the seventh layer and around the a axis up to the second layer. The multiple-film technique was used. 883 independent reflexions were collected. The intensities were estimated visually with a standard film strip and were converted to $F_o(hkl)$ by applying the usual Lorentz, polarization and spot-shape corrections. No correction was made for either absorption or extinction. One of the crystals used for the c axis rotation had a cross section of 0.18×0.15 mm, and that for the a axis rotation a cross section of 0.24×0.28 mm. The two series of intensity data were correlated and reduced to a common scale. The data

were brought to the absolute scale by comparison with the calculated values at a later stage.

Determination and refinement of the structure

The coordinates of the cobalt and chlorine atoms could be easily located from a three-dimensional Patterson synthesis. The positions of other lighter atoms were determined by routine application of the heavy atom method. Six cycles of block-diagonal least-squares refinement using isotropic temperature factors reduced the R value (defined as $\sum |F_o| -$

Table 1. *Fractional atomic coordinates and anisotropic thermal parameters*

The estimated standard deviations are given in parentheses. The temperature factor expression used was

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

	x	y	z			
Co	0.0328 (2)	0.1903 (2)	0.0485 (2)			
Cl	0.3154 (5)	0.2039 (5)	0.5067 (5)			
N(1)	0.0982 (12)	0.2070 (13)	-0.1276 (14)			
N(2)	-0.0651 (12)	0.0853 (13)	-0.0346 (17)			
N(3)	-0.0362 (13)	0.1537 (11)	0.2132 (13)			
N(4)	0.1530 (13)	0.0944 (14)	0.0986 (18)			
N(5)	0.1228 (14)	0.3011 (13)	0.1192 (17)			
N(6)	-0.0823 (13)	0.2933 (12)	0.0180 (15)			
C(1)	0.0406 (20)	0.1295 (17)	-0.2188 (19)			
C(2)	-0.0062 (19)	0.0392 (18)	-0.1494 (19)			
C(3)	-0.0882 (19)	-0.0184 (18)	-0.2303 (22)			
C(4)	-0.1062 (18)	0.0148 (17)	0.0662 (23)			
C(5)	-0.1322 (20)	0.0811 (19)	0.1901 (21)			
C(6)	0.0567 (17)	0.1103 (17)	0.3012 (19)			
C(7)	0.0119 (18)	0.0593 (16)	0.4234 (21)			
C(8)	0.1319 (23)	0.0449 (18)	0.2266 (24)			
O(1)	0.0989 (14)	0.3431 (10)	0.2218 (12)			
O(2)	0.2011 (11)	0.3358 (11)	0.0526 (15)			
O(3)	-0.1436 (11)	0.3234 (12)	0.1039 (13)			
O(4)	-0.0989 (12)	0.3247 (13)	-0.0947 (15)			
O(5)	0.2585 (20)	0.2583 (22)	0.6091 (27)			
O(6)	0.4331 (13)	0.1941 (18)	0.5439 (21)			
O(7)	0.2685 (17)	0.1029 (14)	0.4955 (24)			
O(8)	0.2981 (23)	0.2598 (19)	0.3820 (24)			
	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{13}
	($\times 10^4$)	($\times 10^4$)	($\times 10^4$)	($\times 10^4$)	($\times 10^4$)	($\times 10^4$)
Co	32 (2)	31 (2)	41 (3)	-9 (4)	2 (5)	0 (5)
Cl	47 (4)	39 (4)	75 (7)	4 (8)	-40 (9)	-6 (10)
N(1)	8 (11)	25 (12)	31 (18)	-77 (23)	31 (23)	-26 (27)
N(2)	16 (12)	34 (11)	41 (19)	-43 (21)	19 (27)	-12 (28)
N(3)	23 (12)	24 (10)	24 (15)	-39 (21)	55 (24)	17 (21)
N(4)	19 (13)	35 (13)	88 (26)	-23 (22)	8 (30)	-9 (31)
N(5)	44 (13)	6 (10)	88 (23)	-27 (25)	-68 (31)	34 (30)
N(6)	44 (13)	16 (10)	29 (18)	14 (21)	-40 (25)	14 (26)
C(1)	52 (19)	35 (14)	24 (22)	46 (34)	-17 (37)	42 (33)
C(2)	59 (22)	46 (17)	23 (24)	-12 (32)	87 (38)	-2 (33)
C(3)	46 (20)	34 (16)	55 (28)	18 (31)	-71 (39)	-34 (36)
C(4)	41 (18)	34 (15)	66 (29)	-17 (30)	-25 (41)	44 (38)
C(5)	44 (18)	47 (17)	31 (26)	17 (32)	50 (36)	19 (36)
C(6)	34 (18)	38 (15)	18 (22)	17 (28)	-6 (33)	19 (32)
C(7)	47 (19)	32 (14)	51 (27)	-51 (29)	29 (37)	-31 (33)
C(8)	86 (24)	29 (16)	54 (29)	8 (34)	35 (46)	36 (36)
O(1)	102 (16)	22 (10)	10 (15)	0 (21)	-25 (27)	-4 (20)
O(2)	30 (11)	47 (11)	72 (18)	-63 (19)	22 (26)	-26 (25)
O(3)	27 (10)	41 (11)	64 (17)	44 (19)	63 (23)	8 (25)
O(4)	48 (12)	49 (12)	79 (19)	36 (23)	8 (27)	-39 (27)
O(5)	115 (25)	179 (30)	268 (46)	123 (43)	23 (57)	-261 (64)
O(6)	59 (14)	95 (16)	195 (29)	-12 (29)	130 (37)	-48 (49)
O(7)	109 (20)	48 (13)	251 (41)	-37 (28)	-218 (49)	50 (41)
O(8)	181 (30)	122 (22)	191 (36)	-117 (44)	-120 (58)	232 (49)

was employed. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1962).

Since the ligand was prepared from L-alanine the known absolute configuration of the two asymmetric carbon atoms can be used as internal reference asymmetric centres to determine the absolute configuration of the whole complex ion (Mathieson, 1956). Final atomic parameters and their estimated standard deviations are listed in Table 1. They correctly represent the absolute configuration referred to the right-handed axes. The observed and calculated structure amplitudes are compared in Table 2. Calculations were carried out on the HITAC 5020 E at the Computer Centre of this University.

Results and discussion

Fig. 3 shows the arrangement of the complex ions in the unit cell viewed along the *c* axis. Complex cations and perchlorate anions are alternately repeated along the *b* and *c* axes.

A perspective drawing of the complex cation is presented in Fig. 4, which also represents the absolute configuration. A cobalt atom is surrounded nearly

octahedrally by four nitrogen atoms from the trien ligand and two nitrogen atoms of the nitro groups. The nitro groups are in *cis*-positions. The bond lengths and angles are listed in Table 3 with their e.s.d.'s. The two nitrogen atoms, N(5) and N(6), of the two nitro groups are coordinated at a distance of 1.94 Å, which is shorter than those between the cobalt atom and the other four nitrogen atoms of the chelating molecule.

There exist three chelate rings and the absolute configuration of the complex ion can be described as a skew chelate pair, Δ . The N-Co-N bond angles which form the chelate rings I, II and III are compressed to 85.0°, 86.7° and 86.0° respectively. The bond angles around the two secondary nitrogen atoms and adjacent asymmetric carbon atoms show significant deviation from the normal tetrahedral angle:

C(4)N(2)C(2)	117.9	(1.6)*
C(6)N(3)C(5)	113.5	(1.6)
C(7)C(6)C(8)	116.2	(2.1)
N(2)C(2)C(1)	103.5	(1.7)

* The estimated standard deviations are given in parentheses.

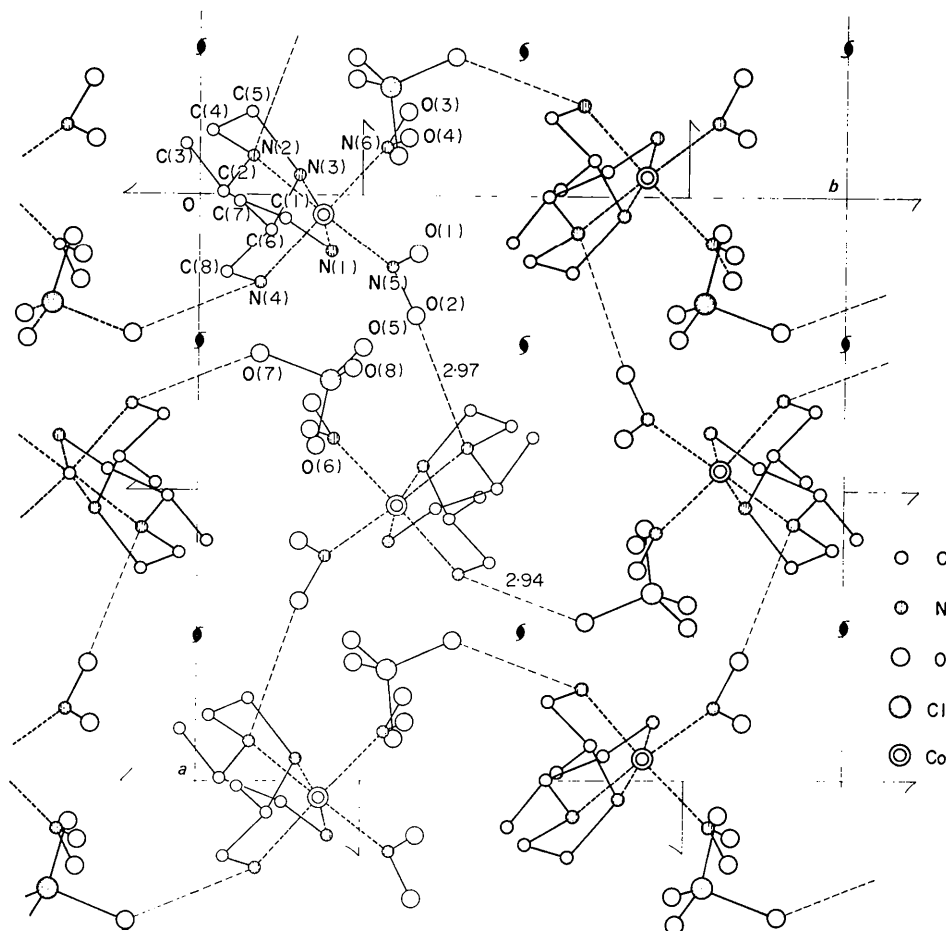


Fig. 3. Projection of the structure along the *c* axis.

The C-C distance in the central chelate ring, 1.57 Å, is somewhat longer and those in the chelate rings of the two ends, 1.49 and 1.46 Å, are shorter than the normal C-C bond distance of 1.54 Å. This result is in contrast to those of Freeman & Maxwell (1969). In the case of *cis*- β -[Co(trien)ClOH₂] (ClO₄)₂, the former is shorter than the latter. The steric strain which arises from *cis*- β -coordination of the substituted trien ligand appears to be partly accommodated by the above mentioned geometrical distortion of the ligand.

The absolute configurations about the two asymmetric nitrogen atoms are antimeric [N(2): *R*, N(3): *S*]. This is the first time that this type of conformational isomer has been reported.

One of the terminal five-membered chelate rings, I (Fig. 5), is in the eclipsed envelope conformation, that is, the four atoms, Co, N(1), N(2), C(1), are coplanar, while the carbon atom with the methyl group, C(2), is off this plane at a distance of 0.66 Å. The other terminal ring, III, is rather different and the two carbon atoms, C(6), C(8), are off the plane formed by the cobalt and two nitrogen atoms at distances of 0.53 and 0.33 Å respectively. On the other hand, the central chelate ring, II, has an unsymmetrical skew conformation and the carbon atoms C(4), C(5) lie at -0.44 and 0.19 Å respectively from the plane through N(2), Co and N(3). In the crystal of *cis*- β -*R,R*[Co(trien)ClOH₂] (ClO₄)₂, two outer chelate rings have unsymmetrical skew conformation and the

central one is envelope type. The Newman projections of the chelate rings along the central C-C bond are shown in Fig. 6. The dihedral angles between the planes of the chelate rings are:

$$\text{I-II, } 175.2, \text{ II-III, } 85.5, \text{ I-III, } 85.8^\circ.$$

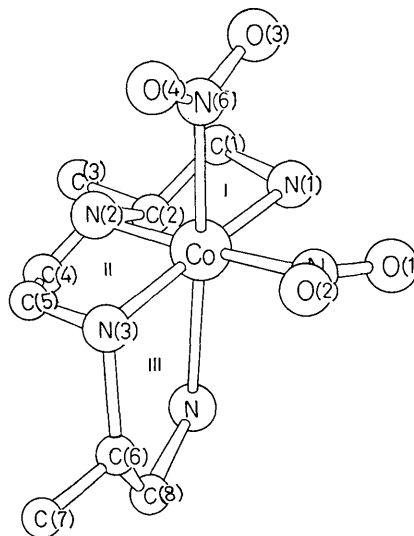


Fig. 4. A perspective drawing of the complex ion, $(-)_546$ -[Co(NO₂)₂(L-3,8-dimetriene)]⁺.

Table 3. Bond lengths and angles with their *e.s.d*'s

Bond length		Bond angle	
Co-N(1)	1.983 (0.015) Å	N(1)-Co-N(2)	85.0 (0.6)°
Co-N(2)	1.994 (0.016)	Co-N(2)-C(2)	110.0 (1.2)
Co-N(3)	1.943 (0.014)	N(2)-C(2)-C(1)	103.5 (1.7)
Co-N(4)	1.969 (0.017)	C(2)-C(1)-N(1)	113.3 (1.6)
Co-N(5)	1.941 (0.017)	C(1)-N(1)-Co	108.1 (1.1)
Co-N(6)	1.923 (0.016)	N(2)-Co-N(3)	86.6 (0.6)
N(1)-C(1)	1.542 (0.027)	Co-N(3)-C(5)	109.8 (1.2)
N(2)-C(2)	1.500 (0.027)	N(3)-C(5)-C(4)	109.1 (1.7)
N(2)-C(4)	1.471 (0.029)	C(5)-C(4)-N(2)	107.0 (1.7)
N(3)-C(5)	1.503 (0.028)	C(4)-N(2)-Co	108.8 (1.3)
N(3)-C(6)	1.536 (0.025)	N(3)-Co-N(4)	85.5 (0.6)
N(4)-C(8)	1.489 (0.031)	Co-N(4)-C(8)	112.7 (1.3)
C(1)-C(2)	1.487 (0.031)	N(4)-C(8)-C(6)	108.3 (1.9)
C(2)-C(3)	1.487 (0.032)	C(8)-C(6)-N(3)	110.4 (1.7)
C(4)-C(5)	1.572 (0.033)	C(6)-N(3)-Co	107.5 (1.1)
C(6)-C(7)	1.520 (0.030)	O(5)-Cl-O(6)	107.6 (1.3)
C(6)-C(8)	1.455 (0.033)	O(5)-Cl-O(7)	109.2 (1.4)
N(5)-O(1)	1.223 (0.022)	O(5)-Cl-O(8)	108.9 (1.5)
N(5)-O(2)	1.241 (0.022)	O(6)-Cl-O(7)	108.3 (1.0)
N(6)-O(3)	1.217 (0.021)	O(6)-Cl-O(8)	113.7 (1.2)
N(6)-O(4)	1.244 (0.021)	O(7)-Cl-O(8)	109.1 (1.3)
Cl-O(5)	1.440 (0.028)	Co-N(5)-O(1)	122.0 (1.3)
Cl-O(6)	1.456 (0.018)	Co-N(5)-O(2)	118.6 (1.3)
Cl-O(7)	1.438 (0.019)	O(1)-N(5)-O(2)	119.2 (1.6)
Cl-O(8)	1.491 (0.026)	Co-N(6)-O(3)	123.4 (1.3)
		Co-N(6)-O(4)	119.0 (1.2)
		O(3)-N(6)-O(4)	117.6 (1.5)
		N(5)-Co-N(6)	86.3 (0.7)

The conformation of the two chelate rings with methyl groups is δ and that of the other ring is λ , and methyl groups lie in an equatorial position relative to the plane of the chelate rings.

N-O distances in the nitro groups average to 1.23 Å, the average O-N-O angles being 119.5°. They are in agreement with those found in other nitro complexes (for example, Cotton & Edwards, 1968; Bertrand & Carpenter, 1966).

The average Cl-O distance, 1.46 Å, is comparable to the distances in perchlorate ions found in other structures. However, appreciable distortion of the O-Cl-O angles was observed: the largest O-Cl-O value is $114.7 \pm 1.2^\circ$ and the smallest, $106.9 \pm 1.3^\circ$.

There are two short contacts which may be considered to be hydrogen bonds. One, 2.94 Å, is found between the perchlorate oxygen atom O(7) and the ligand nitrogen atom N(4), and the other, 2.97 Å, is found between the oxygen atom O(2) of the nitro group and the ligand nitrogen atom N(2). There are also short C...O contacts in the range 3.13 - 3.29 Å found between ligand carbon atoms and oxygen atoms of the nitro groups. These contacts might suggest that weak C-H...O bonds are present (Sutor, 1963). Interatomic distances less than 3.5 Å are listed in Table 4.

The complex ion shows a negative Cotton effect in the longer wavelength circular dichroism band in the region of the octahedral (T_{1g}) absorption, and the net chirality of the complex ion is Δ . Consequently the simple empirical rule between the sign of the longer

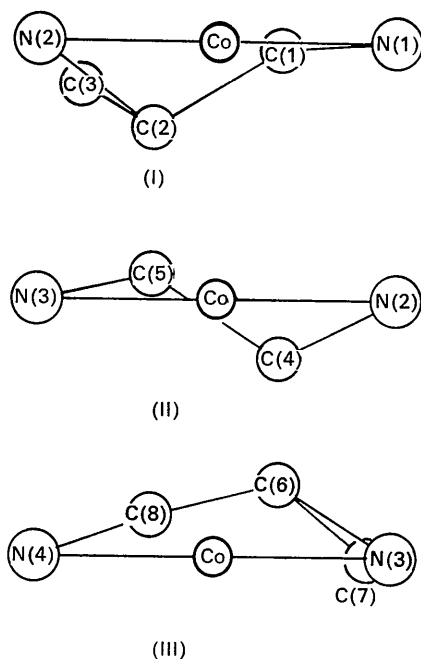


Fig. 5. Conformation of the chelate rings.

wavelength circular dichroism band and the net chirality was found to hold even in the case of the quadridentate ligands as well as in the case of the sixidentate ligands (Muto, Marumo & Saito, 1969).

Table 4. Interatomic distances less than 3.5 Å

	Distance	Symmetry operation applied to second atom
N(3)-O(4)	3.13	1
O(2)-C(5)	3.25	1
O(2)-O(4)	3.21	1

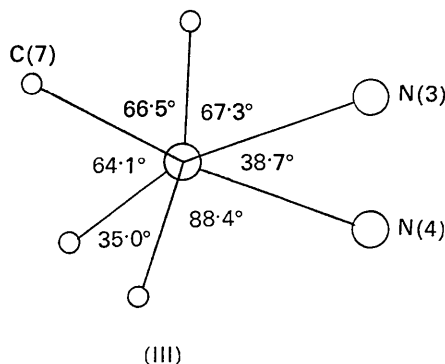
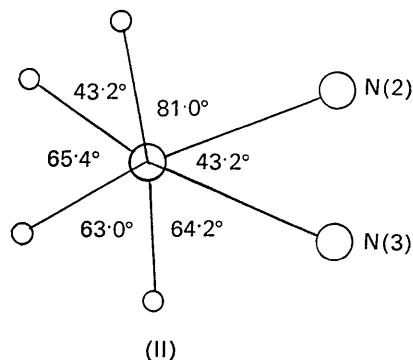
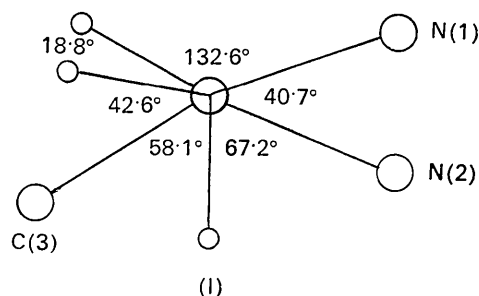


Fig. 6. Newman projections of the chelating ligand. The projections are: ring(I), the C(1)-C(2) bond; ring(II), the C(4)-C(5) bond; and ring(III), the C(6)-C(8) bond.

Table 4 (cont.)

O(2)-N(2)	3.16	1
O(8)-O(4)	3.34	1
N(3)-O(3)	3.37	1
N(6)-O(3)	3.11	1
O(2)-C(4)	3.37	1
O(2)-O(3)	3.22	1
O(1)-C(4)	3.27	2
O(3)-C(8)	3.38	2
O(1)-C(5)	3.13	2
O(1)-C(7)	3.46	2
O(3)-C(7)	3.47	2
O(7)-C(8)	3.29	3
O(6)-C(5)	3.43	3
O(4)-N(6)	3.25	4

Key to symmetry operations

1	0.5 + x, 0.5 - y, -z
2	-x, 0.5 + y, 0.5 - z
3	0.5 - x, -y, 0.5 + z
4	x, y, 1.0 + z

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References

- BERTRAND, J. A. & CARPENTER, D. A. (1966). *Inorg. Chem.* **5**, 515.
 BUCKINGHAM, D. A., MARZILLI, P. A. & SARGESON, A. M. (1967). *Inorg. Chem.* **6**, 1032.
 COTTON, F. A. & EDWARDS, W. T. (1968). *Acta Cryst.* **B24**, 474.
 FREEMAN, H. C. & MAXWELL, I. E. (1969). *Inorg. Chem.* **8**, 1293.
International Tables for X-ray Crystallography (1962). Vol. III. Birmingham: Kynoch Press.
 MATHIESON, A. MCL. (1956). *Acta Cryst.* **9**, 317.
 MUTO, A., MARUMO, F. & SAITO, Y. (1969). *Inorg. Nucl. Chem. Letters*, **5**, 85.
 SARGESON, A. M. & SEARLE, G. H. (1967). *Inorg. Chem.* **6**, 2172.
 SUTOR, D. J. (1963). *J. Chem. Soc.* p. 1105.
 YOSHIKAWA, S., SABURI, M., SAWAI, T. & GOTO, M. (1969). *Proc. XII ICCS*, Sydney, p. 155.

Acta Cryst. (1970). **B26**, 1414

The Crystal and Molecular Structure of Copper(II) Chloride-Bis-(*N,N*-dimethylacetamido)thioether

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The crystal structure of copper(II) chloride-bis-(*N,N*-dimethylacetamido)thioether has been determined by three-dimensional X-ray analysis employing Patterson and Fourier techniques. The atomic parameters were refined by the full-matrix least-squares method to a final *R* index of 0.106 for 838 observed reflexions which were photographically recorded. The space group is *P* $\bar{1}$ with *Z* = 2 and cell dimensions of $a = 11.15 \pm 0.01$, $b = 8.17 \pm 0.01$, $c = 7.77 \pm 0.01$ Å, $\alpha = 95.7 \pm 0.3$, $\beta = 97.4 \pm 0.4$ and $\gamma = 96.9 \pm 0.4^\circ$. The central copper atom is pentacoordinated with the ligands arranged in a square-pyramidal configuration.

Pentacoordinated complexes of copper(II) are known in the trigonal-bipyramidal and square-pyramidal configurations (Barclay, Hoskins & Kennard, 1963; Gillard & Wilkinson, 1963). The molecule of copper(II) chloride-bis-(*N,N*-dimethylacetamido)thioether is an example of the latter type of fivefold coordination.

The brilliant green crystals of CuCl₂·C₈H₁₆N₂O₂S crystallize in a triclinic lattice, space group *P* $\bar{1}$. The following unit-cell dimensions were obtained from measurements made on oscillation, precession and Weissenberg photographs:

$$a = 11.15 \pm 0.01, \quad b = 8.17 \pm 0.01, \quad c = 7.77 \pm 0.01 \text{ \AA}$$

$$\alpha = 95.7 \pm 0.3, \quad \beta = 97.4 \pm 0.4, \quad \gamma = 96.9 \pm 0.4^\circ.$$

The crystal density measured by flotation is 1.63 g.cm⁻³ from which it follows that the unit cell contains

two molecules (calculated density = 1.62 g.cm⁻³). Using the multiple-film equi-inclination Weissenberg technique with Cu *K*α radiation, intensities were collected by visual comparison with a calibrated strip for 838 independent reflexions. Layer lines with *k* = 0 to 4 were recorded with oscillation about the *b* axis.

A crystal of spherical shape (diameter ~ 0.2 mm) was used for the intensity measurements. The standard Lorentz and polarization corrections were made as well as absorption corrections according to *International Tables for X-ray Crystallography* (1962).

The structure was solved employing three-dimensional Patterson and Fourier syntheses. Refinement using equal weighting was carried out by means of a full-matrix least-squares program (Busing, Martin & Levy, 1962) which minimizes the function $\sum \omega(F_o - F_c)^2$. With individual isotropic thermal parameters for the