

There is no hydrogen bonding in the structure. The molecule has five pendant groups, each of which terminates in a methyl group, representing the extremities of the molecule. In the crystal structure the pendant groups of one molecule have weak non-bonding interactions with other molecules. Among the shorter intermolecular contacts (Table 8) there is a high frequency for the most charged atoms (*e.g.* carbonyl oxygens). This indicates that weak polar-polar interactions are the principal means by which the structure is bound together.

The crystals were kindly supplied by Dr Hans Lundström. The author thanks Professor Peder Kierkegaard and Professor Bengt Lindberg for many stimulating discussions. The author is also indebted to Dr Don Koenig for revising the English of this article. This investigation has received financial support from the Swedish Natural Science Research Council.

References

- BERMAN, H. M., CHU, S. C. & JEFFREY, G. A. (1967). *Science*, **157**, 1576–1577.
 DAHLÉN, B. (1973). *Acta Cryst.* **B29**, 595–602.
 HAMBLING, P. G. (1953). *Acta Cryst.* **6**, 98.
 HUGHES, E. W. (1941). *J. Amer. Chem. Soc.* **63**, 1737–1752.
International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press.
 JEFFREY, G. A. (1973). *Advanc. Chem. Ser.* **117**, 177–196.
 JEFFREY, G. A., POPLI, J. A. & RADOM, L. (1972). *Carbohyd. Res.* **25**, 117–131.
 LEUNG, F. & MARCHESSAULT, R. H. (1974). *Canad. J. Chem.* **52**, 2516–2512.
 LINDBERG, K. B. & KIERKEGAARD, P. (1971). *Acta Chem. Scand.* **25**, 1139–1140.
 MATHIESON, A. M. (1965). *Tetrahedron Lett.* **46**, 4137–4144.
 NORRESTAM, R. (1972). *Acta Cryst.* **A28**, 303–308.
 STEWART, R. F., DAVIDSON, E. R. & SIMPSON, W. T. (1965). *J. Chem. Phys.* **42**, 3175–3187.
 SUNDARALINGAM, M. (1968). *Biopolymers*, **6**, 189–213.

Acta Cryst. (1976). **B32**, 2021

The Crystal Structure of *meso*-Di- μ -hydroxo-bis[bis(ethylenediamine)chromium(III)] Diperchlorate Dichloride Dihydrate

BY KAREN KAAS

Chemistry Department, Royal Veterinary and Agricultural University, DK 1871 Copenhagen V, Denmark

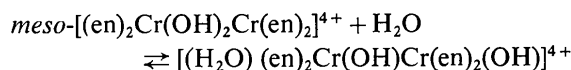
(Received 1 December 1975; accepted 5 January 1976)

$[(\text{en})_2\text{Cr} \begin{array}{c} \text{H} \\ \diagup \text{O} \diagdown \\ \text{O} \end{array} \text{Cr}(\text{en})_2](\text{ClO}_4)_2\text{Cl}_2 \cdot 2\text{H}_2\text{O}$ crystallizes in space group *Pbca* (No. 61) with $a = 18.773(8)$,

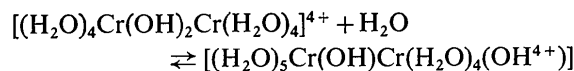
$b = 14.474(5)$, $c = 10.084(7)$ Å, $Z = 4$. There is half a formula unit in the asymmetric unit. The structure was solved by Patterson and Fourier techniques and refined by full-matrix least squares to an R of 0.044 for 2311 diffractometer-collected intensities. As the $[\text{Cr}(\text{en})_2\text{OH}]_2^{4+}$ ion contains a crystallographic inversion centre, it is the *meso* form and the bridging four-membered ring is planar. The conformation of the complex ion is 2A_2 and the Cr–Cr separation 3.059(2) Å.

Introduction

The present structure analysis was initiated as part of recent studies of the equilibrium between μ -hydroxo and di- μ -hydroxo binuclear complexes of Cr^{III} . The equilibrium



is established unexpectedly fast. Both the forward and reverse rate constants are several orders of magnitude greater than those for water exchange in $[\text{Cr}(\text{H}_2\text{O})_6]^{3+}$. The equilibrium constant is 40 times greater than that for the corresponding equilibrium



(Springborg & Toftlund, 1975, 1976).

Although $[(\text{en})_2\text{Cr}(\text{OH})_2\text{Cr}(\text{en})_2]^{4+}$ was first isolated by Pfeiffer & Stern (1908), the configuration was not established until the present structure analysis. The isomer investigated was the *meso* form. The *rac* form has now been isolated by Springborg & Toftlund (private communication). A structure analysis of μ -hydroxo-bis[bis(ethylenediamine)hydroxochromium(III)] perchlorate hydrate is in progress. The crystallographic investigation is intended, *inter alia*, to elucidate the influence of different ligands and of

steric effects on the geometry of the bridging system, in order to decide whether the antiferromagnetic superexchange coupling between the two Cr atoms is correlated to the Cr–O–Cr angle.

Experimental

The crystal used for data collection was prepared as described by Springborg & Toftlund (1975). Photographs showed that $h0l$ were absent for $l \neq 2n$, $0kl$ for $k \neq 2n$ and $hk0$ for $h \neq 2n$, so the space group is $Pbca$. The cell dimensions obtained from least-squares refinement of a series of diffractometer-measured 2θ angles (Mo $K\alpha$, $\lambda = 0.71069 \text{ \AA}$) are $a = 18.773 (8)$, $b = 14.474 (5)$, $c = 10.084 (7) \text{ \AA}$, $V = 2740 \text{ \AA}^3$. The formula weight is $684.3 (\text{Cr}_2\text{C}_8\text{H}_{38}\text{N}_8\text{O}_{12}\text{Cl}_4)$; D_o , measured by flotation at $24^\circ\text{C} = 1.66 (1)$, $D_x = 1.66 (2) \text{ g cm}^{-3}$ for $Z = 4$, corresponding to half a formula unit (*i.e.* half a complex ion, one ClO₄⁻ ion, one Cl⁻ ion, and one water molecule) per asymmetric unit. $\mu(\text{Mo } K\alpha) = 12.8 \text{ cm}^{-1}$.

All X-ray data were obtained on a Nonius three-circle automatic diffractometer with graphite-monochromated Mo $K\alpha$ radiation. The crystal ($0.28 \times 0.28 \times 0.55 \text{ mm}$) was sealed in a glass capillary and oriented with c along the ϕ axis of the goniometer. The

ω scanning mode was used, scan speed $1.2^\circ \text{ min}^{-1}$. Each reflexion was scanned over a range of 1.2° . Background was measured on each of the scan range limits for half the scanning time. A standard reflexion was remeasured after each 25 reflexions. Intensities for all 3192 independent reflexions in an octant in reciprocal space in the range $2.5^\circ \leq \theta \leq 28.0^\circ$ were measured. In the range $2.5^\circ \leq \theta \leq 15.0^\circ$ all reflexions in a hemisphere were measured and the intensities in this range were taken as an average of the intensities of four symmetry-related reflexions. 2414 reflexions had structure factors greater than 2.5 times their corresponding standard deviations obtained from counting statistics, and were considered observed. No absorption correction was applied, as a calculation showed that the corrections amounted to less than $\pm 1.5\%$.

Determination and refinement of the structure

The positions of the Cr and the two Cl atoms were deduced from a sharpened Patterson synthesis. An E map phased by these three atoms showed nine more of the non-hydrogen atoms. A new E map revealed the remaining five non-hydrogen atoms. All atoms were assumed to be non-ionized and scattering factors were from Cromer & Mann (1968). Isotropic full-matrix

Table 1. Final parameters (and *e.s.d.*'s) of non-hydrogen atoms

$$\text{T.F.} = \exp [-2\pi^2(U_{11}a^*h^2 + 2U_{12}a^*b^*hk + 2U_{13}a^*c^*hl + U_{22}b^*k^2 + 2U_{23}b^*c^*kl + U_{33}c^*l^2)].$$

Thermal parameters are in $\text{\AA}^2 \times 10^3$. Positional parameters are $\times 10^4$.

	x	y	z	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Cr	-19.5 (2)	442.2 (2)	1377.1 (4)	2.93 (2)	2.03 (2)	1.90 (2)	-0.17 (2)	0.07 (2)	-2.45 (1)
Cl(1)	-24.3 (4)	3356.6 (4)	389.0 (7)	4.95 (4)	3.19 (3)	3.24 (4)	-0.37 (4)	0.16 (4)	0.39 (3)
Cl(2)	2483.0 (4)	3510.1 (6)	1062.1 (9)	3.6 (4)	5.58 (5)	5.41 (6)	-0.04 (4)	-0.27 (4)	-0.36 (4)
O(1)	458.6 (9)	536 (1)	-336 (2)	4.1 (1)	2.88 (9)	2.7 (1)	-1.41 (8)	0.75 (9)	-0.36 (8)
O(2)	2630 (1)	3501 (2)	2449 (3)	9.5 (2)	11.6 (2)	6.2 (2)	-2.2 (2)	-2.7 (2)	0.6 (2)
O(3)	1737 (1)	3571 (2)	877 (3)	3.6 (1)	12.4 (2)	8.8 (2)	-0.1 (1)	-0.1 (1)	-0.5 (2)
O(4)	2830 (1)	4284 (2)	475 (3)	7.6 (2)	7.1 (2)	9.2 (2)	-0.7 (1)	2.0 (2)	0.8 (2)
O(5)	2743 (1)	2684 (2)	484 (4)	11.0 (2)	7.1 (2)	12.3 (3)	1.3 (2)	2.2 (2)	-2.1 (2)
O(6)	1373 (2)	3123 (2)	4073 (3)	9.7 (2)	7.6 (2)	9.5 (2)	4.4 (2)	1.7 (2)	-0.2 (2)
N(1)	600 (1)	1483 (1)	2213 (2)	4.3 (1)	3.0 (1)	3.2 (1)	-0.1 (1)	-0.4 (1)	-0.6 (1)
N(2)	765 (1)	-385 (1)	2250 (2)	4.1 (1)	3.7 (1)	3.0 (1)	0.5 (1)	0.4 (1)	-0.2 (1)
N(3)	-807 (1)	1402 (1)	959 (2)	4.0 (1)	3.0 (1)	2.8 (1)	0.0 (1)	-0.4 (1)	-0.0 (1)
N(4)	-651 (1)	254 (1)	3057 (2)	4.3 (1)	3.0 (1)	2.6 (1)	0.0 (1)	0.1 (1)	-0.1 (1)
C(1)	1328 (2)	1101 (2)	2465 (3)	3.8 (2)	4.8 (2)	4.5 (2)	-0.4 (1)	-0.6 (2)	-0.9 (2)
C(2)	1223 (2)	187 (2)	3140 (3)	4.4 (2)	5.1 (2)	3.4 (2)	1.1 (1)	-1.2 (1)	-0.6 (1)
C(3)	-1223 (2)	1617 (2)	2183 (3)	4.6 (2)	4.9 (2)	4.0 (2)	1.7 (2)	0.1 (2)	-0.6 (2)
C(4)	-1356 (2)	713 (2)	2889 (4)	4.2 (2)	5.9 (2)	4.3 (2)	0.6 (2)	1.2 (2)	0.7 (2)

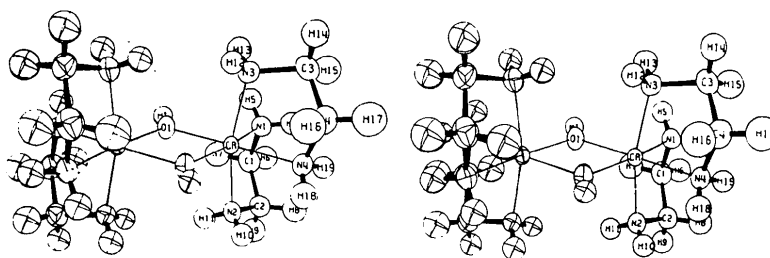


Fig. 1. Stereoscopic drawing of the complex ion. The thermal ellipsoid encloses 50% probability. As the ion has the symmetry $\bar{1}$, it is the *meso* form.

least-squares refinement led to an R of 0.09 [$R = \sum w(|F_o| - |F_c|) / \sum w|F_o|$].

A difference map at this stage showed all H atoms except the two of the water molecule. The positions of the peaks ($0.3\text{--}0.7 \text{ e } \text{\AA}^{-3}$) were in accordance with those calculated from the positions of the atoms to which the H atoms are bonded. In the following cycles of anisotropic full-matrix least-squares refinement the H atoms were included as a fixed contribution in the structure factor calculation, but not refined. This refinement led to an R of 0.045 after inclusion of the water H atoms in calculated positions. 103 reflexions were excluded from the last cycles of refinement as the difference in background count (probably due to a slight missetting of the crystal) amounted to more than 10% of the intensity. Finally the positional and isotropic thermal parameters of the H atoms were refined in separate cycles alternating with anisotropic refinement of the non-hydrogen atoms. The final R was 0.044 (2311 reflexions, less-thans not included). At this stage the shifts of all

parameters were less than 0.4 times their estimated standard deviations (average shift/error 0.11).

During the later stages of refinement the weighting scheme was $1/w = 0.00001|F|^3 - 0.04|F| + 1 + 2\sigma^2|F|$. The maximum weight used was 2. A final analysis of $\sum w(F_o - |F_c|)^2$ as a function of F_o and $\sin \theta$ showed smooth distribution indicating the validity of the weighting scheme. The final atomic parameters are listed in Tables 1 and 2.*

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31600 (13 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

Table 2. Final parameters (and *e.s.d.*'s) of hydrogen atoms

	Positional parameters are $\times 10^3$.			$U \times 100 \text{ \AA}^2$
	<i>x</i>	<i>y</i>	<i>z</i>	
H(1)	70 (1)	88 (2)	-53 (2)	3.1 (6)
H(2)	178 (2)	365 (3)	421 (4)	9. (1.)
H(3)	157 (2)	270 (4)	454 (6)	18.0 (2)
H(4)	40 (1)	168 (2)	296 (3)	4.4 (7)
H(5)	62 (1)	197 (2)	166 (3)	4.2 (7)
H(6)	162 (1)	150 (2)	302 (3)	5.6 (8)
H(7)	156 (2)	108 (2)	153 (3)	6.1 (9)
H(8)	95 (1)	27 (2)	404 (3)	5.0 (8)
H(9)	166 (1)	-15 (2)	338 (3)	5.1 (8)
H(10)	56 (1)	-83 (2)	263 (3)	3.9 (8)
H(11)	103 (1)	-61 (2)	165 (3)	3.9 (7)
H(12)	-111 (1)	121 (2)	42 (3)	3.3 (7)
H(13)	-63 (1)	190 (2)	58 (3)	4.3 (8)
H(14)	-167 (1)	191 (2)	190 (3)	4.4 (7)
H(15)	-90 (1)	202 (2)	281 (3)	5.5 (8)
H(16)	-164 (2)	27 (2)	240 (3)	7. (1.)
H(17)	-162 (2)	87 (2)	375 (3)	7. (1.)
H(18)	-69 (1)	-30 (2)	328 (3)	4.4 (8)
H(19)	-45 (1)	50 (2)	370 (2)	3.3 (7)

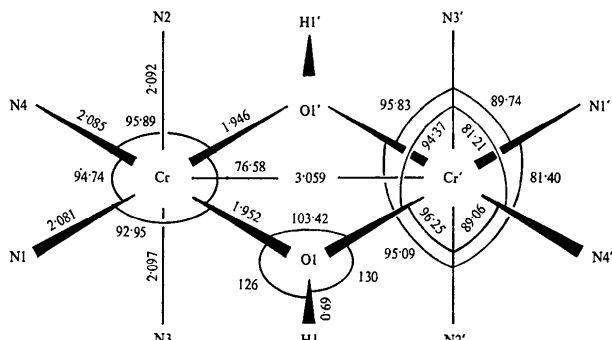


Fig. 2. Bond distances and angles of the coordination octahedron.

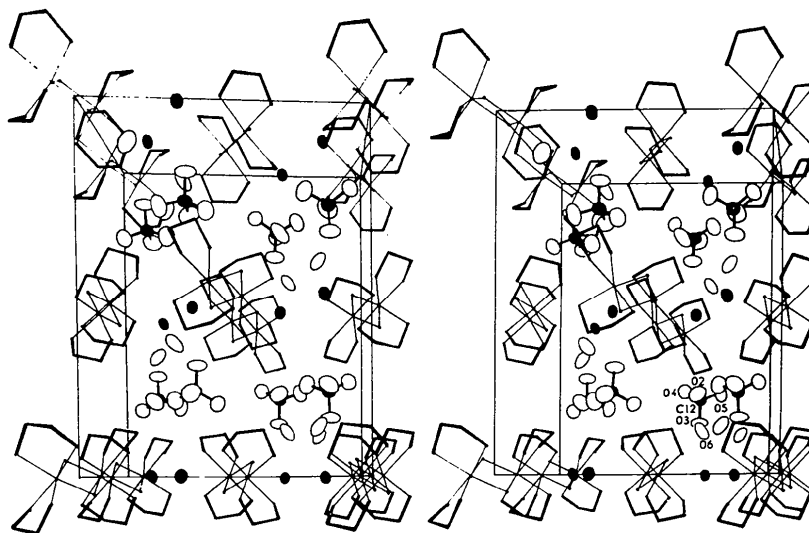


Fig. 3. Stereoscopic illustration of the contents of the unit cell. The view is down c , with a vertical and b horizontal. Thermal ellipsoids are shown for the perchlorate and the chloride ions and the water molecule. The filled ellipsoids are chlorine atoms. The hydrogen atoms have been omitted for clarity.

The input tapes for the diffractometer were produced on an IBM 1130 computer by *INDIFF* (Sørensen, unpublished). The remaining calculations were performed on the IBM 370/165 computer at NEUCC, Lundtofte, Denmark. NRC 2 (*A Picker data reduction program*) (Ahmed, 1966) and the X-RAY System (Stewart, Kruger, Ammon, Dickinson & Hall, 1972) were used. The drawings were prepared by *ORTEP* (Johnson, 1965).

Description and discussion of the structure

The structure consists of binuclear [Cr(en)₂OH]₂⁴⁺ cations, ClO₄⁻ and Cl⁻ anions, and water molecules held together by electrostatic forces and hydrogen bonds. The geometry of the cation and atomic labelling are shown in Fig. 1. The labelling of the anions and the water molecule is shown in Fig. 3.

Table 3. *Interatomic distances (Å) and angles (°)*

Symmetry notation given in Table 5.

Cr...Cr	3.059 (2)	O(1)-Cr-N(1)	92.95 (9)
Cr-O(1)	1.952 (2)	O(1)-Cr-N(2)	95.09 (9)
Cr-O(1 ¹)	1.946 (2)	O(1)-Cr-N(3)	95.83 (9)
Cr-N(1)	2.081 (2)	O(1)-Cr-O(1 ¹)	76.58 (8)
Cr-N(2)	2.092 (2)	N(1)-Cr-N(2)	81.40 (9)
Cr-N(3)	2.072 (2)	N(1)-Cr-N(3)	89.74 (9)
Cr-N(4)	2.085 (3)	N(1)-Cr-N(4)	94.74 (9)
N(1)-C(1)	1.497 (4)	N(2)-Cr-N(4)	89.06 (9)
N(2)-C(2)	1.493 (4)	N(2)-Cr-O(1 ¹)	96.25 (8)
N(3)-C(3)	1.492 (4)	N(3)-Cr-N(4)	81.21 (9)
N(4)-C(4)	1.491 (4)	N(3)-Cr-O(1 ¹)	94.37 (9)
C(1)-C(2)	1.501 (4)	N(4)-Cr-O(1 ¹)	95.89 (9)
C(3)-C(4)	1.511 (5)	Cr-O(1)-Cr ¹	103.42 (8)
Cl(2)-O(2)	1.426 (3)	N(1)-C(1)-C(2)	106.4 (2)
Cl(2)-O(3)	1.415 (3)	C(1)-C(2)-N(2)	106.9 (2)
Cl(2)-O(4)	1.424 (3)	N(3)-C(3)-C(4)	107.2 (2)
Cl(2)-O(5)	1.417 (3)	C(3)-C(4)-N(4)	107.0 (2)
Cr...N(1) C(1)	108.2 (2)	O(2)-Cl(2)-O(3)	108.8 (2)
Cr...N(2)-C(2)	110.0 (2)	O(2)-Cl(2)-O(4)	109.0 (2)
Cr...N(3)-C(3)	110.2 (2)	O(2)-Cl(2)-O(5)	109.2 (2)
Cr...N(4)-C(4)	110.7 (2)	O(3)-Cl(2)-O(4)	110.4 (2)
		O(3)-Cl(2)-O(5)	109.8 (2)
		O(4) Cl(2) O(5)	109.6 (2)

Conformation of the complex ion

The distances and angles are given in Table 3, and those of the inner coordination sphere around the Cr atoms in Fig. 2. As [Cr(en)₂OH]₂⁴⁺ contains a crystallographic inversion centre, it is the *meso* form and the

bridging four-membered ring is planar. N(1) lies 0.11 Å above the plane defined by the bridging unit, N(4) and H(1) lie 0.12 and 0.07 Å below respectively. Similar bridging rings are found in [Cr(gly)₂OH]₂ (Veal, Hatfield, Jeter, Hempel & Hodgson, 1973), [Cr(phen)₂OH]₂Cl₄·6H₂O (Veal, Hatfield & Hodgson, 1973) and [Cr(phen)₂OH]₂I₄·4H₂O (Scaringe, Singh, Eckberg, Hatfield & Hodgson, 1975). For comparison, average values of the respective geometries are given in Table 4.

The four independent Cr-N separations are in the range 2.072 (2) to 2.092 (2) Å, mean 2.083 (8) Å. The distances and angles of the ethylenediamine chelate rings are all approximately the same as previously reported values for Cr^{III} ethylenediamine complexes (Raymond, Corfield & Ibers, 1968; Raymond & Ibers, 1968). The C-H distances are in the range 0.97-1.05 Å and the N-H distances 0.83-0.90 Å, e.s.d. 0.03 Å. Bond angles which involve one H atom are also quite normal 104-116°, e.s.d. 2°. The ethylenediamine rings have the C-C bond nearly parallel to the pseudo three-fold axis (the angle is 177° in both cases), so the conformation can be described as $\lambda\lambda A_2^2$ in the nomenclature proposed by Thewalt, Jensen & Schäffer (1972). The intramolecular H-H distances give no hint as to why the *meso* and not the *rac* form is found. The geminal H-H distances are all near 2.41 (4) Å, the shortest vicinal H-H distance is 2.21 Å, whereas the closest approach between H atoms belonging to different Cr atoms is 2.27 (4) Å between H(11) and H(12¹) in the *meso* form. Calculations have shown that the corresponding distance in a *rac* form would not differ significantly if the conformations of the chelate rings were not changed [H(11)-H(11¹) = 2.29 (4) Å].

Perchlorate ion

The ClO₄⁻ ion is an almost perfect tetrahedron. Distances and angles are given in Table 3. The average Cl-O distance is 1.420 (5) Å and the average O-Cl-O angle 109.5 (6)°.

Water molecule

The water molecule is hydrogen-bonded to the bridging hydroxy group of the complex ion [O(6)...O(1¹¹) = 2.658 Å]. The water H(2) and H(3) were initially placed on the lines connecting the water O and the two nearest perchlorate O atoms,

Table 4. *Geometry of the bridging ring*

	[Cr(phen) ₂ OH] ₂ ⁴⁺		[Cr(gly) ₂ OH] ₂ ‡	[Cr(en) ₂ OH] ₂ ⁴⁺
	chloride*	iodide†		
Cr-Cr (Å)	3.008	2.986	2.974	3.059
Cr-O (Å)	1.927	1.920	1.967	1.949
Cr-O-Cr (°)	102.7	102.1	98.2	103.4

* Veal, Hatfield & Hodgson (1973).

† Veal, Hatfield, Jeter, Hempel & Hodgson (1973).

‡ Scaringe, Singh, Eckberg, Hatfield & Hodgson (1975).

Table 5. *Hydrogen bond distances (Å) and angles (°)*

Key to symmetry operations			
i	$1+x$	$\frac{1}{2}-y$	$z-\frac{1}{2}$
ii	$x+\frac{1}{2}$	$\frac{1}{2}-y$	\bar{z}
iii	x	$\frac{1}{2}-y$	$\frac{1}{2}+z$
iv	\bar{x}	$y+\frac{1}{2}$	$\frac{1}{2}-z$
	X...H-Y	X...H	$\angle X...H-Y$
Cl(1)...	N(1) 3.480 (3)	Cl(1)...	H(5) 2.67 (3) 150
Cl(1)...	N(1 ⁱ) 3.418 (3)	Cl(1)...	H(4 ⁱ) 2.58 (3) 157
Cl(1)...	N(2 ^{iv}) 3.305 (3)	Cl(1)...	H(10 ^{iv}) 2.53 (3) 154
Cl(1)...	N(3) 3.239 (2)	Cl(1)...	H(13) 2.40 (2) 160
Cl(1)...	N(4 ⁱ) 3.310 (3)	Cl(1)...	H(19 ⁱ) 2.50 (3) 165
Cl(1)...	N(4 ^{iv}) 3.407 (2)	Cl(1)...	H(18 ^{iv}) 2.73 (3) 141
O(2)...	O(6) 2.925 (4)	O(2)...	H(2) 2.40 (4) 108
O(3)...	O(6 ⁱ) 3.128 (4)	O(3)...	H(3 ⁱ) 2.30 (6) 162
O(4)...	N(3 ⁱⁱ) 3.103 (4)	O(4)...	H(12 ⁱⁱ) 2.31 (2) 160
O(6)...	O(1 ⁱⁱⁱ) 2.658 (3)	O(6)...	H(1 ⁱⁱⁱ) 1.97 (2) 175

O(6)···O(2)=2.925 Å and O(6)···O(3ⁱⁱ)=3.128 Å. But, as can be seen from the temperature factors, they did not refine well.

Packing

The structure is built from two different kinds of layers oriented perpendicular to *a*. One consists of complex ions and Cl⁻ ions, the other of ClO₄⁻ ions and water molecules (Fig. 3). In the first layer each complex ion is surrounded by six Cl⁻ ions and each Cl⁻ ion by three complex ions. The closest approaches in this layer are six hydrogen bonds between a Cl⁻ ion and six amine groups (Table 5). The complex ions have two hydrogen bonds to the water-perchlorate layer,

one from the bridging hydroxy group to the water molecule, and one from an amine group to a ClO₄⁻ ion.

References

- AHMED, F. R. (1966). NRC 2 revised by ALCOCK & SØRENSEN. *World List of Crystallographic Computer Programs*. Utrecht: Oosthoek.
- CROMER, D. T. & MANN, J. B. (1968). *Acta Cryst.* **A24**, 321-324.
- JOHNSON, C. K. (1965). *ORTEP*. Oak Ridge National Laboratory Report ORNL-3794.
- PFEIFFER, P. & STERN, R. (1908). *Z. anorg. Chem.* **58**, 272-296.
- RAYMOND, K. N., CORFIELD, P. W. R. & IBERS, J. A. (1968). *Inorg. Chem.* **7**, 1362-1372.
- RAYMOND, K. N. & IBERS, J. A. (1968). *Inorg. Chem.* **7**, 2333-2338.
- SCARINGE, R. P., SINGH, P., ECKBERG, R. P., HATFIELD, W. E. & HODGSON, D. J. (1975). *Inorg. Chem.* **14**, 1127-1133.
- SPRINGBORG, J. & TOFTLUND, H. (1975). *Chem. Commun.* pp. 422-423.
- SPRINGBORG, J. & TOFTLUND, H. (1976). *Acta Chem. Scand.* **A30**. In the press.
- STEWART, J. M., KRUGER, G. J., AMMON, H. L., DICKINSON, C. S. & HALL, S. R. (1972). The X-RAY system, version of June 1972. Tech. Rep. TR 192. Computer Science Center, Univ. of Maryland, College Park, Maryland.
- THEWALT, U., JENSEN, K. A. & SCHÄFFER, C. E. (1972). *Inorg. Chem.* **11**, 2129-2136.
- VEAL, J. T., HATFIELD, W. E. & HODGSON, D. J. (1973). *Acta Cryst.* **B29**, 12-20.
- VEAL, J. T., HATFIELD, W. E., JETER, D. Y., HEMPEL, J. C. & HODGSON, D. J. (1973). *Inorg. Chem.* **12**, 342-346.

Acta Cryst. (1976). **B32**, 2025

Silipramine: a Group IV Analog of Imipramine Hydrochloride. The Crystal and Molecular Structure of 5-Methyl-5-(3-dimethylaminopropyl)-10,11-dihydro-5H-dibenzo[*b,f*]-silepin Hydrochloride Hydrate

BY EUGENE R. COREY AND JOYCE Y. COREY

Department of Chemistry, University of Missouri - St. Louis, St. Louis, Missouri 63121, U.S.A.

AND MILTON D. GLICK

Department of Chemistry, Wayne State University, Detroit, Michigan 48202, U.S.A.

(Received 28 October 1975; accepted 6 January 1976)

The structure of silipramine hydrochloride hydrate, C₂₀H₂₇NSi.HCl.H₂O, monoclinic, in space group *P*₂₁/*c* with *a*=15.667 (3), *b*=9.085 (2), *c*=14.548 (3) Å, β=91.16 (2)°, *Z*=4, has been determined by iterative application of the Σ₂ relationship and refined by full-matrix least-squares techniques to a conventional *R* of 0.046 for 1896 counter reflections. The silipramine molecule adopts a folded boat conformation with a dihedral angle between benzo group planes of 141.8° and an extended dimethylaminopropyl side chain in the pseudo-axial position on the silicon heteroatom. Generalized parameters for the description of stereochemical features of dibenzoheteroepins are discussed.

Introduction

There is a general interest in the structural features of dibenzotricyclic derivatives because of their central

nervous system activity (antidepressants and tranquilizers). As part of a synthetic and structural program of silicon analogs of tricyclic compounds, we wish to report the first solid state structural study of a