

Table 3. Torsion angles (°) in some centrosymmetric Ni^{II} meso-Me₆[14]aneN₄ cations and in L.2H₂O

Torsion angles	(1)	(2)	(3)	(4)	(5)	(6)	(7)
N(1)–C(2)–C(3)–N(4)	52.1 (1)	51.9	56.6	53.5	51.9	57.4	66.3
C(2)–C(3)–N(4)–C(5)	–169.9 (1)	–175.6	–169.2	175.2	179.0	–170.1	–171.3
C(3)–N(4)–C(5)–C(6)	–167.6 (1)	179.6	–175.3	167.5	172.4	178.9	–176.0
N(4)–C(5)–C(6)–C(7)	–71.1 (1)	–68.3	–81.1	–57.7	–64.0	–78.1	–72.5
C(5)–C(6)–C(7)–N(1 ¹)	61.7 (1)	67.5	64.9	70.4	70.3	68.5	68.5
C(6)–C(7)–N(1 ¹)–C(2 ¹)	–169.6 (1)	175.5	–174.1	167.5	168.8	–178.1	–164.2
C(7)–N(1 ¹)–C(2 ¹)–C(3 ¹)	179.9 (1)	175.3	–178.1	170.3	172.4	177.1	176.1

References: (1) this work; (2), (3) low-spin and high-spin nickel chloride complexes (Ito & Toriumi, 1981); (4), (5) low-spin and high-spin nickel bromide complexes (Ito, Toriumi & Ito, 1981); (6) high-spin nickel fluoride complex (Toriumi & Ito, 1981); (7) L.2H₂O (Gluziński, Krajewski & Urbańczyk-Lipkowska, 1980).

Hydrogen bonding plays an important role in all the known structures, including the title compound. The two perchlorate ions position themselves above and below the plane of the macrocycle in such a way that two of the oxygen atoms are hydrogen-bonded to the imine H atoms. Dimensions of these bonds are: O(13)···H(41) 2.18 (1), O(13)···N(4) 3.09 (1) Å, O(13)···H(41)–N(4) 161 (1)°, O(16)···H(11¹) 2.21 (1), O(16)···N(1¹) 3.07 (1) Å, O(16)···H(11¹)–N(1¹) 150 (1)°. Atom O(16) is 3.34 (1) Å away from the Ni atom and the bond angle O(16)···Ni–N(4) is 75 (1)°. The Ni atom may therefore be considered as having two distant ligands in the axial positions.

Torsion angles of the macrocycle in the title compound, in the nickel dihalide complexes and in the metal-free dihydrate are given in Table 3. Values for the other compounds are obtained from a search of the

Cambridge Structural Database (1986) files. There is general agreement between the corresponding angles in this series of compounds, irrespective of whether the compound is low-spin or high-spin. The agreement between the title compound and the metal-free dihydrate is fairly remarkable, considering that the latter is not constrained by a central coordinated metal ion. Such a conformation is probably adopted to facilitate the operation of the extensive hydrogen bonding present in these two compounds.

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A Neutron Structural Study of Semicarbazide Hydrochloride

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Abstract. CH₅N₃O⁺.Cl[–], *M_r* = 111.5, orthorhombic, *P*2₁2₁2₁, *a* = 7.53 (1), *b* = 13.18 (2), *c* = 4.67 (1) Å, *V* = 463.5 Å³, *Z* = 4, *D_x* = 1.598 g cm^{–3}, neutron wavelength = 1.036 Å, *μ_c* = 0.45 cm^{–1}, *F*(000) = 232, *T* = 298 K, final *R* = 0.02 (on *F*) for 319 independent reflections. The crystal structure was determined by three-dimensional neutron data collected on a TDC-312 computer-controlled four-circle diffractometer. The atomic parameters were refined with a full-matrix least-squares technique. The structure is held together

by a three-dimensional network of N–H···Cl and N–H···O hydrogen bonds. The present structural analysis along with electrical and spectroscopic studies contradict the reported ferroelectric phase transition of the compound.

Introduction. The molecular crystal of semicarbazide hydrochloride (SEM-HCl) is made up of protonated semicarbazide cations and chloride ions with an ionic character due to hydrochloric acid. The crystal struc-

ture of SEM-HCl was solved from room-temperature X-ray data by Nardelli, Fava & Gerardi (1965). In this investigation possible changes in nonhydrogen bond angles and lengths of semicarbazide in the ionic and coordinated states were discussed. Positions of the hydrogen atoms were derived on the basis of bonding configuration of the molecules. After the structural investigation a second-order unusually close ferroelectric phase transition in SEM-HCl was reported at 292 and 294 K by Rocaries & Boldrini (1971) on the basis of dielectric constant measurements and room-temperature (293–294 K) X-ray diffuse scattering. But in these X-ray photographic studies no change in space group ($P2_12_12_1$) was observed at temperatures of 273 and 294 K. Hence, the existence and full explanation of the above reported transitions are not yet very clear, nor is knowledge of the accurate dimensions of hydrogen bonding. For the better understanding of these phenomena we have carried out systematic studies of structural, electrical, optical and spectroscopic properties of this material. In the present communication we are reporting our high-precision neutron structural study of the SEM-HCl crystal at room temperature (298 ± 1 K).

Experimental. Optically high-quality single crystals of SEM-HCl grown from aqueous solution of the basic compound (99.9% pure) by slow evaporation technique. Compound crystallized as colourless prisms elongated along [001] in orthorhombic system. Neutron diffraction data recorded at room temperature [298 (1) K] with the TDC-312 computer-controlled four-circle diffractometer (Sequeira *et al.* 1978) at the CIRUS reactor, Trombay. The crystal of size $7.3 \times 2.9 \times 2.9$ mm was cut from a large single crystal and mounted with its c axis parallel to the ϕ axis of the diffractometer. θ - 2θ step scanning, 330 independent reflections ($+h$, $+k$, $+l$) collected up to $(\sin\theta)/\lambda = 0.45 \text{ \AA}^{-1}$. The unit-cell parameters were refined with 20 high-angle reflections. Systematic absences were consistent with space group $P2_12_12_1$. The variation in mutual agreement factor for the intensity of one standard reflection repeated after every 20 reflections was found to be well within 2%.

The atomic parameters reported by Nardelli *et al.* (1965) were used as the starting parameters. The data were reduced to structure factors with the program *DATRED* [Rajagopal, Srikanta & Sequeira, 1973 (unpublished)] which also includes the absorption correction program *ORABS* (Wehe, Busing & Levy, 1962). Max., min. values of absorption correction 0.90, 0.85. A total of 319 reflections [$I > \sigma(I)$] were used in the final least-squares refinement. The number of degrees of freedom and structure parameters varied in the final cycle were 208 and 110 respectively. All hydrogen atoms in the unit cell were located in a difference Fourier map from neutron data and the

Table 1. Fractional coordinates with e.s.d.'s in parentheses

	x	y	z
Cl	0.2544 (2)	0.1399 (1)	0.9646 (4)
O	0.7574 (4)	0.0873 (3)	0.8218 (6)
N1	0.9276 (3)	0.1608 (2)	0.4795 (7)
N2	0.6330 (3)	0.1326 (2)	0.39639 (6)
N3	0.4914 (3)	0.0659 (2)	0.4576 (6)
C	0.7756 (3)	0.1251 (2)	0.5813 (6)
H1	1.0303 (2)	0.1669 (5)	0.6152 (6)
H2	0.9344 (2)	0.1917 (7)	0.2874 (1)
H3	0.6592 (9)	0.1346 (5)	0.1823 (8)
H4	0.4319 (9)	0.0836 (5)	0.6550 (6)
H5	0.3970 (1)	0.0782 (6)	0.3009 (2)
H6	0.53489 (9)	-0.0086 (5)	0.4547 (2)

phase was based on X-ray nonhydrogen atom positions. Full-matrix least-squares refinement of the structure with anisotropic temperature factors converged to a final R value (on F) of 0.02, $wR = 0.05$. Positional fractional coordinates of all the atoms are given in Table 1.* Weighting scheme used $w = 1/[\sigma^2 + (0.04y_0)^2]$. $(\Delta/\sigma)_{\max} = 0.035$; $-0.5 < \Delta\rho < 0.6 \text{ e \AA}^{-3}$. Atomic scattering factors from *International Tables for X-ray Crystallography* (1974). Other program used: *ORFLS* (Busing, Martin & Levy, 1962).

Discussion. All the atoms are positioned and numbered as in Fig. 1. The important bond lengths and angles are given in Table 2. The carbazide molecule is protonated at the amino group attached to the imino group. The C–N1 bond length [1.326 (4) Å] agrees well with the shortened partial double bond (N=C=O) of 1.322 Å whereas the C–N₂ bond length [1.382 (4) Å] is between partial double and single (1.472 Å) bond lengths. The C–O bond length is close to the standard double-bond length. The carbazide molecule is non-planar and highly distorted, as can be seen from the equations of planes and the torsion angles given in Table 3.

Torsion angles around the C–N2 bond indicate that the N2–H₃ and N2–N3 bonds are considerably distorted by about 20° from the trigonal coordination around N2, thereby reducing the π -bonding character of the C–N2 bond. This is also consistent with the significantly longer bond length observed for C–N2, and may be due to steric and strong hydrogen-bonding considerations involving the terminal NH₃ group. Detailed hydrogen-bond geometry is given in Table 4. A packing diagram of the cell is given in Fig. 2.

The structure is held together by a three-dimensional network of N–H...Cl and N–H...O hydrogen bonds. Two hydrogens of –NH₃⁺ and one of the –NH₂ groups

* Lists of structure factors and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43493 (8 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

are strongly hydrogen-bonded to the chloride ions, while the third hydrogen of the $-\text{NH}_3^+$ and the imino hydrogen are bonded to the neighbouring carboxyl oxygens. The remaining hydrogen of the $-\text{NH}_2$ group is in van der Waals contact with the chloride ions.

It is interesting to note that no significant diffuse scattering could be observed with our neutron diffraction data recorded at room temperature [298 (1) K] which is close to the transition temperature of 294 K. Further, the noncentrosymmetric space group $P2_12_12_1$ determined in the present studies at 298 (1) K suggests no ferroelectric-paraelectric (FE-PE) transition in this compound. The combination of previous X-ray studies (Rocaries & Boldrini, 1971) with our present structural analysis does not suggest any FE-PE transition at 292 or 294 K. Our dielectric, spontaneous polarization and

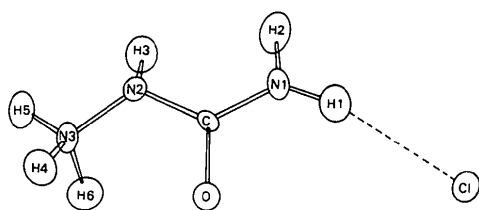


Fig. 1. Geometry of all the atoms in the SEM-HCl molecule.

Table 4. Hydrogen-bond geometry with e.s.d.'s in parentheses

$X-H\cdots Y$	$X-H$ (Å)	$H\cdots Y$ (Å)	$X-H\cdots Y$ (°)
$N1-H1\cdots Cl$	1.003 (10)	2.375 (8)	166.1 (5)
$N1-H2\cdots Cl$	0.987 (11)	2.856 (10)	132.1 (6)
$N2-H3\cdots O$	1.020 (10)	1.946 (11)	156.6 (6)
$N3-H4\cdots Cl$	1.051 (9)	2.106 (9)	162.1 (5)
$N3-H5\cdots Cl$	1.033 (11)	2.070 (10)	163.1 (6)
$N3-H6\cdots O$	1.036 (9)	1.978 (9)	138.7 (5)

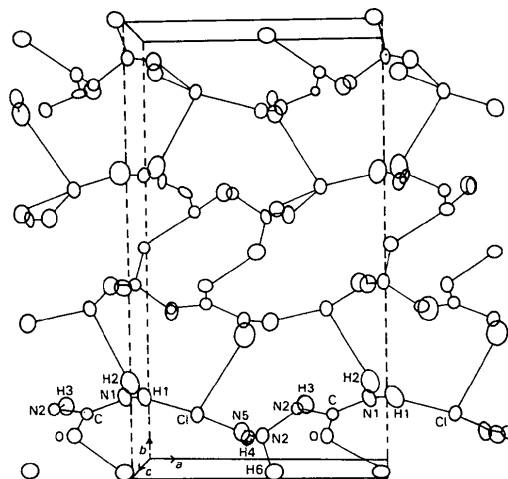


Fig. 2. Packing diagram of the cell.

Table 2. Some important interatomic bond distances (Å) and angles (°) with e.s.d.'s in parentheses

$H1-Cl$	2.375 (8)	$N2-H3$	1.020 (10)
$N1-H1$	1.003 (10)	$N3-N2$	1.412 (3)
$N1-H2$	0.987 (11)	$N3-H6$	1.036 (9)
$C-N1$	1.326 (4)	$N3-H4$	1.051 (9)
$C-O$	1.234 (4)	$N3-H5$	1.033 (11)
$N2-C$	1.382 (4)		
$Cl-H1-N1$	166.0 (8)	$C-N2-H3$	117.7 (4)
$H1-N1-C$	117.8 (5)	$H3-N2-N3$	111.1 (4)
$N1-C-O$	124.4 (3)	$N2-N3-H4$	111.2 (4)
$O-C-N2$	120.7 (3)	$N2-N3-H5$	106.1 (4)
$C-N2-N3$	114.5 (2)	$N2-N3-H6$	110.4 (4)
$H1-N1-H2$	120.1 (7)	$H4-N3-H5$	107.1 (5)
$H2-N1-C$	121.2 (5)	$H4-N3-H6$	110.9 (6)
$N1-C-N2$	114.9 (3)	$H5-N3-H6$	110.9 (6)

Table 3. Equations of planes and torsion angles (°)

	Equation of plane			
(1) O, C, N1, N2	$0.221x_1 - 0.902y_1 - 0.371z_1 + 1.207 = 0$			
(2) O, C, N1, N2, H3	$0.268x_1 - 0.920y_1 - 0.285z_1 + 0.703 = 0$			
(3) O, C, N1, N2, N3	$0.335x_1 - 0.875y_1 - 0.351z_1 + 0.410 = 0$			
(4) O, C, N2, N3	$0.427x_1 - 0.800y_1 - 0.422z_1 + 0.060 = 0$			
	Deviations from planes (Å)			
	(1)	(2)	(3)	(4)
C	-0.004	-0.032	-0.039	0.085
O	0.001	0.074	-0.036	-0.046
N1	0.001	-0.021	0.103	0.400
N2	0.001	-0.153	-0.167	-0.077
N3	0.441	0.278	0.133	0.038
H1	-1.800	-2.085	-2.451	-2.820
H2	-0.014	-0.114	0.094	0.489
H3	0.360	0.132	0.195	0.372
$O-C-N1-H11$	35.7	$C-N2-N3-H31$	64.3	
$O-C-N1-H12$	1.6	$C-N2-N3-H32$	-171.3	
$O-C-N2-H4$	-19.5	$C-N2-N3-H33$	-57.6	
$O-C-N2-N3$	-154.8			

spectroscopic measurements along three different crystallographic principal axes have also not yielded any information regarding a ferroelectric phase transition between 123 and 323 K, which gives full support to our structural analysis.

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