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## Structure of a Nickel(II) Perchlorate Complex of a 14-Membered Tetraaza Macrocyclic

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**Abstract.**  $[\text{Ni}(\text{C}_{16}\text{H}_{36}\text{N}_4)](\text{ClO}_4)_2$ ,  $M_r = 542.10$ , monoclinic,  $P2_1/a$ ,  $a = 9.222(7)$ ,  $b = 14.636(9)$ ,  $c = 9.670(7)$  Å,  $\beta = 114.0(3)^\circ$ ,  $U = 1192.3$  Å<sup>3</sup>,  $Z = 2$ ,  $D_m = 1.46(2)$ ,  $D_x = 1.51$  g cm<sup>-3</sup>,  $\lambda(\text{Mo K}\alpha) = 0.7107$  Å,  $\mu = 19.5$  cm<sup>-1</sup>,  $F(000) = 572$ , room temperature, final  $R = 0.070$  for 1179 [ $I > 4\sigma(I)$ ] independent observed reflections. The structure of the cation  $[\text{NiL}]^{2+}$ , where  $L$  is the macrocyclic ligand *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, has crystallographically imposed  $\bar{1}$  symmetry. The bond lengths and angles of both the cation and the anions are normal. The Ni atom sits in the plane of the four N atoms in the macrocycle [Ni–N 1.942(6) and 1.941(9) Å]. The two perchlorate ions are in approximately axial positions but they are each attached to the cation *via* two O···H–N hydrogen bonds [O···N 3.07(1) and 3.09(1) Å] rather than *via* Ni···O interactions [Ni···O 3.34(1) Å].

**Introduction.** Metal complex cations of the type  $[\text{ML}]^{n+}$ , where  $L$  is *C-meso*-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane, are well known since they were first prepared by Curtis (1964). Structures of the nickel complex cation  $[\text{NiL}]^{2+}$  have been reported for the acetylacetonate perchlorate by Curtis, Swann & Waters (1973), the chloride by Ito &

Toriumi (1981), the fluoride by Toriumi & Ito (1981), and the bromide by Ito, Toriumi & Ito (1981). Both low-spin and high-spin isomers of the bromide and the chloride are known.

**Experimental.** Orange platelets of the title compound isolated from slow evaporation of an aqueous solution in the presence of an excess of thiourea. Density measured by flotation in  $\text{CCl}_4$ /ligroin. Crystal of approximate size  $0.2 \times 0.4 \times 0.4$  mm mounted on Stoe Stadi-2 diffractometer to rotate about the  $a$  axis. Cell dimensions calculated from  $2\theta$  measurement of 20 reflections ( $2\theta$  range  $30$  to  $40^\circ$ ). Intensity data collected *via* variable-width  $\omega$  scan, background counts 20 s, step-scan rate  $0.033^\circ \text{ s}^{-1}$ , width  $(1.5 + \sin\mu/\tan\theta)$ . Absorption and extinction corrections not applied. Standard reflections  $h22$  measured every  $2\theta$  measurements for each layer; no significant change in intensity. 2082 reflections measured with  $2\theta_{\text{max}} 50^\circ$ ,  $h$  0 to 10,  $k$  0 to 17 and  $l$  –10 to 10. 1785 unique reflections,  $R_{\text{int}} = 0.03$ . 1179 data with  $I > 4\sigma(I)$  used in subsequent calculations.

Structure solved by Patterson method using *SHELX76* (Sheldrick, 1976) on Amdahl V7A computer. All non-hydrogen atoms refined anisotropically before hydrogen atoms located. Positional and thermal

Table 1. Atomic coordinates ( $\times 10^4$ ) and equivalent isotropic thermal parameters ( $\text{\AA}^2 \times 10^3$ ) with estimated standard deviations in parentheses

$$U_{eq} = \frac{1}{3} \sum_i \sum_j a_i \cdot a_j U_{ij}$$

	x	y	z	$U_{eq}$
Ni	5000*	5000*	0*	81 (2)
Cl(12)	2053 (3)	6353 (2)	1547 (4)	132 (4)
O(13)	2049 (9)	5510 (6)	2189 (10)	190 (13)
O(14)	1493 (12)	7024 (7)	2161 (15)	244 (20)
O(15)	1024 (15)	6307 (8)	31 (13)	206 (20)
O(16)	3596 (9)	6564 (6)	1657 (14)	276 (19)
N(1)	3396 (8)	4301 (5)	-1604 (8)	79 (9)
C(2)	2273 (12)	3945 (7)	-969 (13)	98 (15)
C(3)	3231 (13)	3596 (7)	533 (13)	120 (16)
N(4)	4368 (8)	4318 (5)	1386 (8)	91 (10)
C(5)	5599 (12)	4005 (6)	2826 (11)	109 (13)
C(6)	6437 (13)	4829 (6)	3718 (11)	106 (14)
C(7)	7519 (12)	5344 (7)	3140 (12)	101 (13)
C(8)	4783 (17)	3517 (8)	3731 (14)	154 (20)
C(9)	6755 (14)	3362 (8)	2554 (16)	153 (19)
C(10)	8377 (15)	6082 (9)	4244 (15)	117 (22)

\* Parameter fixed.

parameters of H atoms in imine groups allowed to refine independently. H atoms bonded to the same C atom refined as rigid group with the same thermal parameter and fixed C-H distance of 0.95 Å. Layers were given individual scale factors. Weighting scheme  $w = 1/\sigma^2(F)$ ,  $\sigma(F)$  taken from counting statistics. Final  $R(F) = 0.070$  ( $wR = 0.071$ ,  $S = 6.329$ ) and all final shift/e.s.d.  $< 0.04$ . In final difference map, max. and min. peaks 0.75,  $-0.39 \text{ e \AA}^{-3}$ . Scattering factors from *International Tables for X-ray Crystallography* (1974). Atomic coordinates are given in Table 1, interatomic distances and angles in Table 2.\*

**Discussion.** Many nickel(II) complexes of the macrocycle *C-meso-5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradecane* (or *meso-Me<sub>6</sub>[14]aneN<sub>4</sub>*) are known. Of the known structures so far reported only that of the acetylacetonate perchlorate compound does not have four coplanar N atoms. When the Ni atom is in the plane of the N atoms the imine groups become chiral centres and many conformers are possible resulting from the direction of the imine H in relation to the plane of the macrocycle. The five known structures all have the conformation shown in Fig. 1. The title molecule is no exception and is represented in Fig. 2. Bond distances and angles in the coordinated macrocycle are within the range reported. The two Ni-N bond distances of 1.942 (6) and 1.941 (9) Å are typical of those found in low-spin divalent nickel complexes in which the metal atom is coplanar with four nitrogen

\* Lists of structure factors, anisotropic thermal parameters and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 43466 (13 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

donors (Madaule-Aubry & Brown, 1968; Madaule-Aubry, Busing & Brown, 1968; Hawkinson & Fleischer, 1969). The six-membered rings take the stable chair form while the *gauche* conformation is adopted by the five-membered rings.

Table 2. Bond distances (Å) and angles (°) with e.s.d.'s in parentheses

Ni-N(1)	1.942 (6)	C(2)-C(3)	1.451 (14)
Ni-N(4)	1.941 (7)	C(3)-N(4)	1.480 (11)
Cl(12)-O(13)	1.381 (8)	N(4)-C(5)	1.467 (11)
Cl(12)-O(14)	1.353 (9)	C(5)-C(6)	1.500 (12)
Cl(12)-O(15)	1.386 (11)	C(5)-C(8)	1.542 (14)
Cl(12)-O(16)	1.417 (7)	C(5)-C(9)	1.523 (13)
N(1 <sup>1</sup> )-C(7)	1.473 (10)	C(6)-C(7)	1.527 (13)
N(1)-C(2)	1.496 (11)	C(7)-C(10)	1.498 (14)
N(1)-C(7 <sup>1</sup> )	1.473 (7)		
N(1 <sup>1</sup> )-Ni-N(4)	93.7 (2)	Ni-N(4)-C(3)	109.1 (5)
N(1)-Ni-N(4)	86.3 (3)	Ni-N(4)-C(5)	118.8 (5)
O(13)-Cl(12)-O(14)	112.3 (1)	C(3)-N(4)-C(5)	113.9 (7)
O(13)-Cl(12)-O(15)	107.8 (6)	N(4)-C(5)-C(6)	108.3 (7)
O(14)-Cl(12)-O(15)	106.2 (7)	N(4)-C(5)-C(8)	108.4 (8)
O(13)-Cl(12)-O(16)	110.3 (5)	C(6)-C(5)-C(8)	107.6 (8)
O(14)-Cl(12)-O(16)	111.1 (5)	N(4)-C(5)-C(9)	110.8 (8)
O(15)-Cl(12)-O(16)	108.9 (7)	C(6)-C(5)-C(9)	111.2 (9)
Ni-N(1 <sup>1</sup> )-C(7)	123.9 (4)	C(8)-C(5)-C(9)	110.4 (9)
Ni-N(1)-C(2)	106.6 (5)	C(5)-C(6)-C(7)	116.6 (8)
Ni-N(1)-C(7 <sup>1</sup> )	123.9 (4)	C(6)-C(7)-C(6)	110.6 (7)
C(2)-N(1)-C(7 <sup>1</sup> )	109.2 (5)	N(1 <sup>1</sup> )-C(7)-C(6)	112.6 (8)
N(1)-C(2)-C(3)	107.0 (7)	C(6)-C(7)-C(10)	109.3 (9)
C(2)-C(3)-N(4)	108.2 (8)		

(i): Symmetry element  $1-x, 1-y, -z$ .

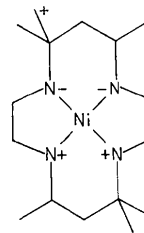


Fig. 1. Schematic diagram of  $[\text{NiL}]^{2+}$ . + and - signs at the N atoms refer to hydrogen atoms above and below the plane of the macrocycle. The other + and - signs refer to directions of the two axial methyl groups.

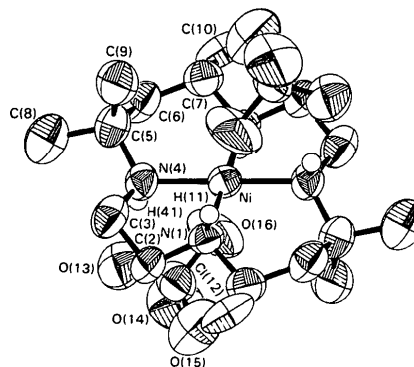


Fig. 2. The structure of the molecule with numbering scheme. Thermal ellipsoids are shown at 50% probability.

Table 3. Torsion angles (°) in some centrosymmetric Ni<sup>II</sup> meso-Me<sub>6</sub>[14]aneN<sub>4</sub> cations and in L.2H<sub>2</sub>O

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 <sup>1</sup> )	61.7 (1)	67.5	64.9	70.4	70.3	68.5	68.5
C(6)–C(7)–N(1 <sup>1</sup> )–C(2 <sup>1</sup> )	–169.6 (1)	175.5	–174.1	167.5	168.8	–178.1	–164.2
C(7)–N(1 <sup>1</sup> )–C(2 <sup>1</sup> )–C(3 <sup>1</sup> )	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.2H<sub>2</sub>O (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(11<sup>1</sup>) 2.21 (1), O(16)···N(1<sup>1</sup>) 3.07 (1) Å, O(16)···H(11<sup>1</sup>)–N(1<sup>1</sup>) 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.** CH<sub>5</sub>N<sub>3</sub>O<sup>+</sup>.Cl<sup>–</sup>, *M<sub>r</sub>* = 111.5, orthorhombic, *P*2<sub>1</sub>2<sub>1</sub>2<sub>1</sub>, *a* = 7.53 (1), *b* = 13.18 (2), *c* = 4.67 (1) Å, *V* = 463.5 Å<sup>3</sup>, *Z* = 4, *D<sub>x</sub>* = 1.598 g cm<sup>–3</sup>, neutron wavelength = 1.036 Å, *μ<sub>c</sub>* = 0.45 cm<sup>–1</sup>, *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-