

# SYNTHESIS AND X-RAY DIFFRACTION STUDY OF 5,5,7,12,12,14-HEXAMETHYL-1,4,8,11- TETRAAZACYCLOTETRADECA-N-ACETIC ACID DIHYDROPERCHLORATE

A. A. Chuiko, V. K. Bel'skii, A. G. Kol'chinskii,  
and S. S. Sil'chenko

*The dihydroperchlorate of 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-N-acetic acid (I) was obtained by the exchange reaction of the dihydrobromide with silver perchlorate. A planar structure of the ligand molecule with methyl and CH<sub>2</sub>COOH groups that deviate from the plane of the macroring was established as a result of x-ray diffraction analysis. Numerous hydrogen bonds with the participation of a carboxy group, amino nitrogen atoms, and crystallization water molecules were detected.*

The introduction of an additional functional group into tetraazamacrocyclic ligands makes it possible to obtain compounds that stabilize metal ions in unusual oxidation states and are simultaneously capable of covalent immobilization in an inorganic or polymeric matrix [1-3]. We have previously reported the immobilization of the macrocyclic complex of nickel with 5,5,7,12,12,14-hexamethyl-1,4,8,11-tetraazacyclotetradeca-N-acetic acid (I) on dispersed silicas [4].

The carboxy-perchlorate pair should be regarded as a successful combination of an anion and an addition functional group in a molecule of the complex being grafted. The additional (with respect to the principal MN<sub>4</sub> coordination node) carboxy group makes it possible to accomplish grafting to widely used aminopropyl-substituted silicas. The perchlorate anion ensures high solubility of the complex being grafted in most solvents. It is also resistant to the action of oxidizing and reducing agents, which makes it possible to investigate the redox properties of a grafted complex over a wide range of redox potentials. A convenient starting compound for the synthesis of such complexes is I·2HClO<sub>4</sub>. We obtained the diperchlorate by the exchange reaction of the previously described [5] I·2HBr with silver perchlorate. The following absorption bands are observed in the IR spectrum of the compound:  $\nu_{\text{ClO}_4}$  1100 cm<sup>-1</sup>, carboxy group  $\nu_{\text{C=O}}$  1740 cm<sup>-1</sup>,  $\nu_{\text{C-N}}$  1615 cm<sup>-1</sup>, and  $\nu_{\text{NH}}$  3300 cm<sup>-1</sup>. The broad asymmetrical band at 3500 cm<sup>-1</sup> is evidently related to the absorption of OH groups linked by a hydrogen bond. The structure of the molecule disregarding the anions and the crystallization water molecules is shown in Fig. 1. The coordinates of the nonhydrogen atoms are presented in Table 1, while some of the interatomic distances and angles are given in Tables 2 and 3, respectively.

The macrocyclic ligand molecule has a virtually planar structure with methyl C<sub>(17)</sub> and C<sub>(14)</sub> atoms and a pendant CH<sub>2</sub>COOH group that deviate from the plane of the macroring.

The carboxy hydrogen atom does not participate in the formation of hydrogen bonds, while the O<sub>(2)</sub> atom bonded to it is linked to the hydrogen atom attached to the N<sub>(3)</sub> atom of another molecule of the macrocyclic ligand. The interatomic distances are as follows: N...O 3.186 Å, N-H 0.80 Å, and H...O 2.47 Å. Angle NHO is 149°. An intermolecular hydrogen bond also develops between the N<sub>(2)</sub> atom through the amino nitrogen atom with the oxygen atom of the perchlorate anion [O<sub>(23)</sub>]: N...O 2.939 Å, N-H 0.91 Å, H...O 2.04 Å, and angle NHO 166°. One of the perchlorate anions, which is linked to one of the water molecules by a hydrogen bond [O<sub>(24)</sub>-H<sub>(1)</sub>W1...O<sub>W1</sub>], is situated on the same side of the plane of the macrocyclic ligand as the pendant group. This hydrogen bond is characterized by the following parameters: O...O 2.936 Å, O-H 1.01 Å, H...O 2.30 Å, and angle OHO 120°.

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TABLE 1. Coordinates of the Atoms ( $\cdot 10^4$ )

Atom	x	y	z	Atom	x	y	z
Cl(1)	7446	4498(1)	4953	C(1)	3598(8)	3724(4)	780(6)
O(11)	8162(13)	4784(7)	6202(9)	C(2)	4327(8)	3097(4)	1773(6)
O(12)	5822(9)	4800(6)	4363(9)	C(3)	5770(8)	2558(4)	1608(6)
O(13)	7297(13)	3659(5)	5139(11)	C(4)	6127(8)	1390(4)	144(7)
O(14)	8588(13)	4621(10)	4347(11)	C(5)	5328(8)	1041(4)	-1148(7)
Cl(2)	1599(3)	-863(1)	-3017(2)	C(6)	4428(9)	1394(4)	-3425(7)
O(21)	943(11)	-1656(4)	-2970(9)	C(7)	4000(7)	2106(4)	-4336(5)
O(22)	2405(11)	-603(5)	-1767(6)	C(8)	2452(7)	2640(3)	-4355(4)
O(23)	2639(12)	-863(5)	-3770(8)	C(9)	1561(6)	3555(3)	-2798(4)
O(24)	215(10)	-324(5)	-3524(7)	C(10)	2185(6)	3939(3)	-1495(4)
O(1)	-799(7)	213(4)	-1291(6)	C(11)	952(6)	2944(3)	-421(4)
O(2)	6078(10)	3819(5)	-2379(8)	C(12)	655(5)	2127(3)	-1099(4)
O(1)	1661(5)	1790(3)	-1500(5)	C(13)	2436(9)	4316(4)	1288(6)
O(2)	-845(6)	1810(3)	-1155(5)	C(14)	7132(7)	3063(4)	1284(7)
N(1)	2519(6)	3341(3)	-457(4)	C(15)	6509(8)	2028(4)	2784(5)
N(2)	4958(6)	1982(3)	501(4)	C(16)	5679(10)	808(5)	-3764(6)
N(3)	5094(6)	1687(3)	-2103(5)	C(17)	844(7)	2153(4)	-4625(6)
N(4)	2875(6)	3020(3)	-3043(5)	C(18)	2235(10)	3320(4)	-5325(6)

TABLE 2. Bond Lengths in the  $I\cdot 2HClO_4\cdot 2H_2O$  Molecule

Bond	d Å	Bond	d Å
Cl(1)—O(11)	1,410(9)	Cl(2)—O(23)	1,38(1)
Cl(1)—O(12)	1,385(7)	Cl(2)—O(24)	1,412(8)
Cl(1)—O(13)	1,398(9)	C(6)—C(16)	1,54(1)
Cl(1)—O(14)	1,34(1)	C(1)—C(2)	1,505(9)
Cl(2)—O(21)	1,413(8)	C(3)—C(15)	1,529(9)
Cl(2)—O(22)	1,408(7)	C(6)—C(7)	1,511(9)

TABLE 3. Angles between the Bonds in the  $I\cdot 2HClO_4\cdot 2H_2O$  Molecule

Angle	Deg	Angle	Deg
O(11)—Cl(1)—O(12)	113,1(6)	O(11)—Cl(1)—O(13)	102,1(7)
O(12)—Cl(1)—O(13)	107,7(6)	O(11)—Cl(1)—O(14)	107,8(7)
O(12)—Cl(1)—O(14)	115,9(7)	O(13)—Cl(1)—O(14)	109,4(9)
O(21)—Cl(2)—O(22)	107,9(5)	O(21)—Cl(2)—O(23)	109,9(6)
O(22)—Cl(2)—O(23)	114,3(5)	O(21)—Cl(2)—O(24)	108,5(5)
O(22)—Cl(2)—O(24)	106,2(5)	O(23)—Cl(2)—O(24)	109,7(5)
C(1)—N(1)—C(10)	110,9(4)	C(1)—N(1)—C(11)	113,0(5)
C(10)—N(1)—C(11)	111,6(4)	C(3)—N(2)—C(4)	117,0(4)
C(5)—N(3)—C(6)	114,2(5)	C(8)—N(4)—C(9)	117,2(4)
N(1)—C(1)—C(2)	112,3(5)	N(1)—C(1)—C(13)	113,1(5)
C(2)—C(1)—C(13)	109,7(6)	C(1)—C(2)—C(3)	119,2(6)
N(2)—C(3)—C(2)	106,9(5)	N(2)—C(3)—C(14)	108,2(6)
C(2)—C(3)—C(14)	111,9(6)	N(2)—C(3)—C(15)	107,4(5)
C(2)—C(3)—C(15)	109,7(6)	C(14)—C(3)—C(15)	112,6(5)
N(2)—C(4)—C(5)	112,0(5)	N(3)—C(5)—C(4)	109,9(50)
N(3)—C(6)—C(7)	110,7(5)	N(3)—C(6)—C(16)	112,2(5)
C(7)—C(6)—C(16)	110,4(6)	C(6)—C(7)—C(8)	117,6(6)
N(4)—C(8)—C(7)	106,1(4)	N(4)—C(8)—C(17)	109,3(5)
C(7)—C(8)—C(17)	112,3(5)	N(4)—C(8)—C(18)	108,9(4)
C(7)—C(8)—C(18)	109,7(5)	C(17)—C(8)—C(18)	110,4(5)
N(4)—C(9)—C(10)	111,9(4)	N(1)—C(10)—C(9)	113,7(4)
N(1)—C(11)—C(12)	112,6(4)	O(1)—C(12)—O(2)	123,5(5)
O(1)—C(12)—C(11)	124,8(4)	O(2)—C(12)—C(11)	111,7(5)

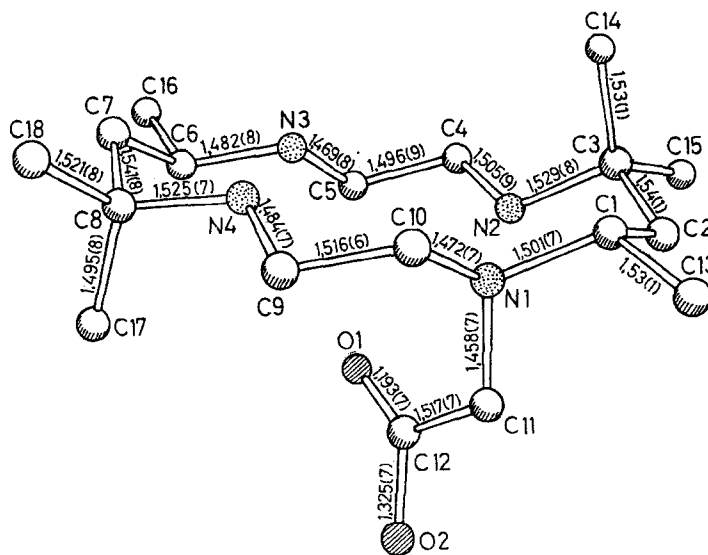


Fig. 1. Molecular structure of the ligand.

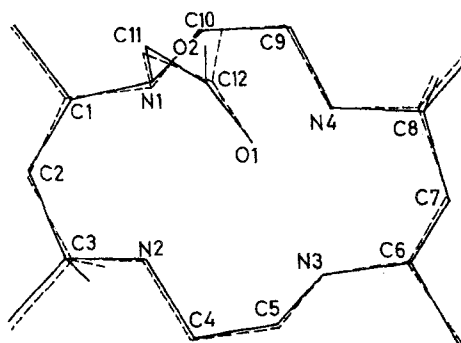


Fig. 2. Superimposed  $\text{H}_2\text{I}^{2+}$  molecular skeletons in the lattices of the dihydroperchlorate salt (continuous line) and the hydrate of the dihydrobromide salt (dash line).

Yet another molecule of water and another perchlorate anion are situated on the other side of the plane of the macrocyclic ligand. The distance between them is too great for the development of a hydrogen bond. The perchlorate ion remains free, while the water molecule is linked through its oxygen atom by a hydrogen bond with the protonated  $\text{N}_{(4)}$  atom. The distances and angle are as follows:  $\text{N}\dots\text{O}$  2.829 Å,  $\text{N}-\text{H}$  0.88 Å,  $\text{H}\dots\text{O}$  1.96 Å, and angle  $\text{NHO}$  169°.

Another hydrogen atom attached to  $\text{N}_{(4)}$  participates in the formation of an intramolecular hydrogen bond with the carboxy oxygen atom:  $\text{N}\dots\text{O}$  3.014 Å,  $\text{N}-\text{H}$  0.79 Å,  $\text{H}\dots\text{O}$  2.32 Å, and angle  $\text{NHO}$  148°.

Thus the position of the pendant group is fixed by both an intermolecular hydrogen bond and an intramolecular hydrogen bond.

The protonated  $\text{N}_{(2)}$  and  $\text{N}_{(4)}$  atoms are situated along the diagonal of the molecule, but the distance between them is great enough to lead to mutual repulsion of the delocalized positive charges. The length of the  $\text{N}_{(2)}-\text{N}_{(4)}$  diagonal turns out to be extremely close to the length of the other  $\text{N}_{(1)}-\text{N}_{(3)}$  diagonal: 4.143 Å and 4.198 Å, respectively.

One of the two protons attached to the  $\text{N}_{(2)}$  atom forms a weak intramolecular hydrogen bond with the  $\text{N}_{(3)}$  atom with  $\text{N}_{(2)}-\text{H}_{(2)}\text{N}_{(2)}\dots\text{N}_{(3)}$ ,  $\text{N}-\text{H}$  1.03 Å,  $\text{H}\dots\text{N}$  2.62 Å,  $\text{N}\dots\text{N}$  2.98 Å, and angle  $\text{NHN}$  100°. Thus both ethylenediamine bridges in the  $\text{I}\cdot 2\text{HClO}_4$  molecule are linked by hydrogen bonds — one with the participation of the carboxy part of the pendant group, and the other through a hydrogen bond between nitrogen atoms.

The superimposed  $\text{H}_2\text{I}^{2+}$  molecular skeletons in the lattices of the dihydrate of the dihydroperchlorate salt (continuous line) and the previously investigated [5] hydrate of the dihydrobromide salt (dash line) are presented in Fig. 2.

In the significantly similar structures the greatest differences are observed in the position of the pendant group, which in the case of the dihydroperchlorate is inclined to the plane of the macroring at a greater angle. The reason for this difference is evidently an intermolecular hydrogen bond in which the O<sub>(2)</sub> atom participates.

## EXPERIMENTAL

To obtain I·2HClO<sub>4</sub>·2H<sub>2</sub>O, an equivalent amount of silver perchlorate was added to a saturated aqueous solution of I·2HBr·H<sub>2</sub>O [5]. The silver bromide was removed by filtration and washed with distilled water. The filtrate was evaporated slowly, and the product crystallized out in the form of clear rhombic crystals. The yield was quantitative.

The IR spectra were recorded with a UR-20 spectrometer. The x-ray diffraction experimentation was carried out with a Syntex P1 automatic diffractometer [ $\lambda$  (Mo K $\alpha$ ),  $\beta$  filter,  $\theta/2\theta$  scanning]. The C<sub>18</sub>H<sub>80</sub>N<sub>4</sub>Cl<sub>2</sub>O<sub>10</sub> crystals were monoclinic with  $a = 8.248(1)$ ,  $b = 16.353(4)$ ,  $c = 11.143(2)$  Å,  $\beta = 108.31(1)^\circ$ ,  $V = 1426.9$  Å<sup>3</sup>,  $Z = 2$ , space group Pc, and  $d_{\text{calc}} = 1.110$  g/cm<sup>3</sup>.

The structure was decoded by the direct method and was refined by the complete-matrix method of least squares up to  $R = 0.045$  and  $R_w = 0.055$ . A total of 2232 independent reflections with  $I \geq 3\sigma(I)$  was used in the calculations. All of the calculations were carried out with a Nova-3 computer by means of programs of the SHELXTL complex realized in the Nicolet-R<sub>3</sub> system.

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