X-RAY STRUCTURAL STUDY OF ORGANIC LIGANDS OF THE COMPLEXONE TYPE.

III. CRYSTAL AND MOLECULAR STRUCTURE OF PHOSPHONOMETHYLGLYCINE AND IMINODIACETIC-MONOMETHYLPHOSPHONIC ACID

L. M. Shkol'nikova, M. A. Porai-Koshits,
N. M. Dyatlova, G. F. Yaroshenko,
M. V. Rudomino, and E. K. Kolova

UDC 548.737

An x-ray structural study of phosphonomethylglycine (I) and iminodiacetic-monomethylphosphonic acid (II) has been carried out (diffractometer, direct method, anisotropic method of least squares, R = 0.035 and 0.050, R_W = 0.040 and 0.052 from 1712 and 1113 reflections for compounds I and II respectively). The crystals of compound I are monoclinic and those of compound II triclinic; I: a = 8.681, b = 7.981, c = 9.893 Å, β = 105.77°, d_{calc} = 1.702 g/cm^3, Z = 4, space group $P2_1/c$; II: a = 5.590, b = 7.422, c = 10.648 Å, α = 93.12, β = 95.03, γ = 90.40°, d_{calc} = 1.716 g/cm^3, Z = 2, space group $P\bar{1}$. The geometric parameters of the molecules of compounds I and II are similar. Structural proof has been obtained for the first time to show that the nitrogen atom is protonated by the proton of the phosphonic acid group, and not the carboxyl group, for the Complexones I and II, containing competing functional groups, in the crystalline state. Complexone I is obtained from Complexone II by removing one methylcarboxyl group and replacing it by a hydrogen atom. The result of this process is a change in compound I from the conformation of the molecule of compound II, directed towards the stabilization of a sterically favorable system of hydrogen bonds (HB), responsible for the similar structural motifs in the crystals of compounds I and II. This system includes HB O—H...O and N—H...O, forming dimeric ribbons, networks, and three-dimensional frameworks. In compound II, weak intramolecular HB are formed, leading to the formation of H-rings.

Phosphonomethylglycine (I), a potentially tridentate ligand, and iminodiacetic-monomethylphosphonic acid (II),* a potentially tetradentate ligand, can be regarded as derivatives of glycine with the general formula $\begin{matrix}R\\R'\end{matrix}\!>\!N{-}CH_2{-}R''$. Different combinations of the substituents R, R', and R'' make it possible to obtain a series of the most commonly encountered monoamine Complexones containing carboxyl and (or) phosphonic acid groups:

$R=H;\ R'=CH_2COOH;\ R''=COOH$
— iminodiacetic acid (IDA)
$R=R'=CH_2COOH;\ R''=COOH$
— nitrilotriacetic acid (NTA)
$R=R'=H;\ R''=PO_3H_2$
— aminomethylphosphonic acid (AMP)
$R=H;\ R'=CH_2COOH:\ R''=PO_3H_2$
— phosphonomethylglycine (PMG)
$R=R'=CH_2COOH;\ R''=PO_3H_2$
— iminodiacetic-monomethyl phosphonic acid (IDAMP);
$R=R'=CH_2PO_3H_2;\ R''=COOH$ glycine bis (methylphosphonic) acid (GP);
$R=R'=CH_2PO_3H_2;\ R''=PO_3H_2$ nitrilotriphosphonic acid (NTP).

---

*According to the IUPAC nomenclature rules, this compound is called amino-N,N-bis(methylenecarboxylic)-N-methylenephosphonic acid. In the present paper, the trivial name, which is more widely encountered in the literature, is used.

All-Union Scientific-Research Institute for Chemical Reagents and Highly Pure Chemical Substances. Translated from Zhurnal Strukturnoi Khimii, Vol. 23, No. 5, pp. 98-107, September-October, 1982. Original article submitted August 12, 1981.

0022-4766/82/2305-0737\$07.50

TABLE 1. Coordinates of the Atoms Other Than Hydrogen ($\times 10^4$) and the Hydrogen Atoms ($\times 10^3$) in Compound I

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
P	—510(0)	2755(0)	745(0)	C(3)	4847(1)	1077(2)	1482(1)
O(1)	—438(1)	2812(1)	—828(1)	H(O1)	7(3)	362(3)	—87(2)
O(2)	—996(1)	4414(1)	1216(1)	H(O4)	698(3)	98(3)	154(2)
O(3)	—1476(1)	1232(1)	868(1)	H(N)	159(2)	6(2)	211(2)
O(4)	6356(1)	835(2)	2167(1)	H(N)1	181(2)	29(2)	69(2)
O(5)	4351(1)	1764(2)	367(1)	H(C1)	226(2)	308(2)	126(2)
N	2068(1)	652(1)	1630(1)	H(C1)1	167(3)	269(3)	266(2)
C(1)	1561(2)	2420(2)	1747(1)	H(C2)	413(3)	78(3)	330(2)
C(2)	3794(2)	362(2)	2328(2)	H(C2)1	396(3)	—78(3)	246(2)

X-ray structural studies have previously been carried out only for monoamine Complexones containing as functional group only carboxyl (IDA [1, 2], NTA [3]) or phosphonic acid (AMP [4], NTP [5]) groups. Our aim was to study the structure of modified Complexones combining phosphorus-containing acid groups and carboxyl groups, since these Complexones should show an increased coordination activity and specificity of action and should therefore have a number of advantages over classical Complexones. The results of the x-ray structural study of compounds I and II were presented at the Third All-Union Conference on Organic Crystal Chemistry in May 1981. It was later found that the structure of compound I had been studied simultaneously by other workers, who published their results in a brief communication [6]. These results coincide practically completely with the results of our study. The accuracy of the determination of the atom coordinates in our case is higher by a factor of 2-3. The values of the factors R and R_W are 0.035 and 0.040 in our case and 0.057 and 0.058 in [6].

Sheldrick and Morr gave emphasis to the discussion of the conformation of the molecule, and did not deal with the packing of the molecules or a comparison of the behavior of the phosphonic acid and carboxyl groups with respect to the formation of the zwitterion.

The present paper gives a comparative discussion of the influence of the nature and number of different functional groups on the structure of the molecule and the crystal for Complexones I and II.

EXPERIMENTAL

Complexone II was obtained by the reaction of IDA with formaldehyde and phosphorus trichloride. Complexone I was obtained by the dimethylcarboxylation of compound II in the presence of sulfuric acid and hydrogen peroxide.

The lamellar crystals of compound I with the composition $C_3H_8O_5NP$ and the isometric crystals of compound II with the composition $C_5H_{10}O_7NP$ were grown from aqueous solutions of the corresponding compounds. The crystals of compounds I and II belong to the monoclinic and triclinic systems respectively, with lattice parameters I: a = 8.681(4), b = 7.981(7), c = 9.893(10) Å, β = 105.77(6)°, V = 660(2) Å^3, d_{calc} = 1.702(5) g/cm^3, Z = 4, space group $P2_1/c$; II: a = 5.590(2), b = 7.422(3), c = 10.648(5) Å, α = 93.12(4), β = 95.03(3), γ = 90.40(3)°, V = 439.4(6) Å^3, d_{calc} = 1.716(2) g/cm^3, Z = 2, space group $P\bar{1}$.

The experimental material (2101 and 2016 independent reflections for compounds I and II respectively) was obtained on a CAD-4 automatic diffractometer using Mo radiation. The intensity of the reflections was measured by the ω-scanning method, maximum angle θ 31 and 27° for compounds I and II respectively. The linear dimensions of the crystal were: I 0.12 × 0.70 × 0.80; II 0.25 × 0.25 × 0.25 mm. All the calculations were carried out using the ENX-SDP set of programs on a PDP 11/t-55 minicomputer.

The structures of compounds I and II were determined automatically by the direct method using the program MULTAN. All the atoms other than hydrogen were located in the E-synthesis. The refinement of the positional and thermal parameters was carried out by the full-matrix method of least squares first in the isotropic and then in the anisotropic approxima-

TABLE 2. Coordinates of the Atoms Other than Hydrogen ($\times 10^4$) and the Hydrogen Atoms ($\times 10^3$) in Compound II

Atom	x/a	y/b	z/c	Atom	x/a	y/b	z/c
P	943(0)	618(0)	1869(0)	C(4)	—1409(8)	3387(6)	3955(4)
O(1)	1406(6)	2138(4)	941(3)	C(5)	—1225(8)	2212(6)	5079(4)
O(2)	1005(6)	—1216(4)	1207(3)	H(O1)	68(8)	192(6)	37(4)
O(3)	2678(5)	974(4)	3013(3)	H(O4)	—692(9)	723(7)	149(5)
O(4)	—5419(7)	6565(5)	1346(4)	H(O6)	—301(9)	37(7)	573(5)
O(5)	—6279(6)	5252(5)	3105(4)	H(N)	—431(9)	242(7)	307(5)
O(6)	—3087(6)	1145(5)	5084(3)	H(C1)	—238(7)	—3(5)	286(4)
O(7)	481(6)	2334(5)	5852(3)	H(C1)1	—311(8)	43(6)	153(5)
N	—2931(6)	2622(5)	2821(4)	H(C2)	—389(7)	339(5)	107(4)
C(1)	—2113(8)	838(6)	2279(4)	H(C2)1	—177(9)	462(7)	180(5)
C(2)	—3265(8)	4014(6)	1854(4)	H(C4)	—203(7)	454(5)	420(4)
C(3)	—5177(9)	5334(6)	2201(5)	H(C4)1	18(9)	363(6)	371(5)

TABLE 3. Bond Lengths d (Å) and Valence Angles ω (deg) in Compound I

Bond	d	Bond	d
P—O(1)	1,575(1)	O(1)—H(O1)	0,79(3)
P—O(2)	1,502(1)	O(4)—H(O4)	0,93(2)
P—O(3)	1,500(1)	N—H(N)1	0,94(2)
P—C(1)	1,821(1)	C(1)—H(C1)	1,02(2)
N—C(1)	1,492(2)	C(1)—H(C1)1	0,91(2)
N—C(2)	1,488(2)	C(2)—H(C2)	0,98(2)
C(2)—C(3)	1,509(2)	C(2)—H(C2)1	0,92(2)
C(3)—O(4)	1,315(2)	N—H(N)	0,86(2)
C(3)—O(5)	1,202(2)		

Angle	ω	Angle	ω
O(1)PO(2)	111,78(6)	PC(1)H(C1)	107(1)
O(1)PO(3)	106,09(6)	PC(1)H(C1)1	109(1)
O(1)PC(1)	104,08(7)	NC(1)H(C1)	103(1)
O(2)PO(3)	118,61(6)	H(C1)C(1)H(C1)1	116(2)
O(2)PC(1)	106,22(6)	NC(1)H(C1)1	110(1)
O(3)PC(1)	109,13(6)	C(1)NH(N)	106(1)
PC(1)N	111,42(9)	C(1)NH(N)1	112(1)
C(1)NC(2)	113,2(1)	C(2)NH(N)	104(1)
NC(2)C(3)	111,7(1)	C(2)NH(N)1	110(1)
C(2)C(3)O(4)	109,1(1)	H(N)NH(N)1	111(2)
C(2)C(3)O(5)	124,1(1)	NC(2)H(C2)	110(1)
O(4)C(3)O(5)	126,7(1)	NC(2)H(C2)1	110(1)
PO(1)H(O1)	104(2)	C(3)C(2)H(C2)	112(1)
C(3)O(4)H(O4)	111(2)	C(3)C(2)H(C2)1	109(1)
		H(C2)C(2)H(C2)1	101(2)

tion with allowance for secondary extinction from 1712 reflections with $I \geqslant 2\sigma$ for compound I and 1113 reflections with $I \geqslant 3\sigma$ for compound II. The coordinates of all the H atoms were found from difference syntheses. After the refinement of the structure in the anisotropic-isotropic (for the H atoms) approximation, the final values of R and R_W for compound (I) were those given above, and those for compound (II) $R = 0.050$, $R_W = 0.052$. In the method of least squares, the weighting scheme $w = 1/\sigma\ (F_i)^2$ was used for compounds I and II.

The coordinates of the atoms in the structures of compounds I and II are given in Tables 1 and 2 respectively. The table of temperature correction constants can be obtained

TABLE 4. Bond Lengths d (Å) and Valence Angles ω (deg) in Compound II

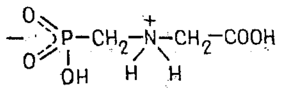
Bond	d	Bond	d
P—O(1)	1,574(4)	O(7)—C(5)	1,203(6)
P—O(2)	1,500(3)	O(1)—H(O1)	0,71(6)
P—O(3)	1,500(3)	O(4)—H(O4)	0,84(6)
P—C(1)	1,806(5)	O(6)—H(O6)	0,92(6)
N—C(1)	1,505(6)	N—H(N)	0,85(6)
N—C(2)	1,499(6)	C(1)—H(C1)	0,94(5)
N—C(4)	1,498(7)	C(1)—H(C1)1	0,96(6)
C(2)—C(3)	1,511(7)	C(2)—H(C2)	0,97(5)
O(4)—C(3)	1,324(7)	C(2)—H(C2)1	0,95(6)
O(5)—C(3)	1,191(6)	C(4)—H(C4)	0,96(5)
C(4)—C(5)	1,516(7)	C(4)—H(C4)1	0,97(6)
O(6)—C(5)	1,304(6)		

Angle	ω	Angle	ω
O(1)PO(2)	110,8(2)	PC(1)—H(C1)1	106(3)
O(1)PO(3)	106,4(2)	NC(1)H(C1)	107(3)
O(1)PC(1)	107,4(2)	NC(1)H(C1)1	112(3)
O(2)PO(3)	116,9(2)	H(C1)C(1)H(C1)1	104(4)
O(2)PC(1)	104,4(2)	C(1)NH(N)	106(4)
O(3)PC(1)	110,6(2)	C(2)NH(N)	107(4)
PC(1)N	119,4(4)	C(4)NH(N)	106(4)
C(1)NC(2)	112,8(6)	NC(2)H(C2)	107(3)
C(1)NC(4)	115,0(4)	NC(2)H(C2)1	109(4)
C(2)NC(4)	109,8(4)	C(3)C(2)H(C2)	106(3)
NC(2)C(3)	110,2(4)	C(3)C(2)H(C2)1	111(4)
O(4)C(3)C(2)	109,2(4)	H(C2)C(2)H(C2)1	113(5)
O(5)C(3)C(2)	124,5(5)	C(3)O(4)H(O4)	110(4)
O(4)C(3)O(5)	126,2(5)	NC(4)H(C4)	108(3)
NC(4)C(5)	115,1(4)	NC(4)H(C4)1	108(3)
O(6)C(5)C(4)	112,2(4)	C(5)C(4)H(C4)	110(3)
O(7)C(5)C(4)	120,8(5)	C(5)C(4)H(C4)1	110(3)
O(6)C(5)O(7)	127,0(5)	H(C4)C(4)H(C4)1	106(4)
PO(1)H(O1)	107(5)	C(5)O(6)H(O6)	115(4)
PC(1)H(C1)	108(3)		

from the authors. The bond lengths and valence angles are given in Tables 3 and 4. Figure 1a and b gives the configurations of the molecules of compounds I and II respectively, together with the numbering of the atoms.

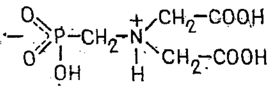
DISCUSSION OF RESULTS

The molecules of compounds I and II exist in the zwitterion form with the negative charge localized on the phosphonic acid group:



$^{-}O_2P(OH)-CH_2-\overset{+}{N}H_2-CH_2-COOH$

I



$^{-}O_2P(OH)-CH_2-\overset{+}{N}H(CH_2-COOH)_2$

II

The suggestion, previously made many times, that it is the phosphononic acid group that is deprotonated, because of its higher acidity, in competition with the carboxyl group has been confirmed by studying the spectra of Complexones with mixed functional groups. In particular, Grigor'ev, Voronezheva, and Dyatlova, from the infrared spectra of compound II

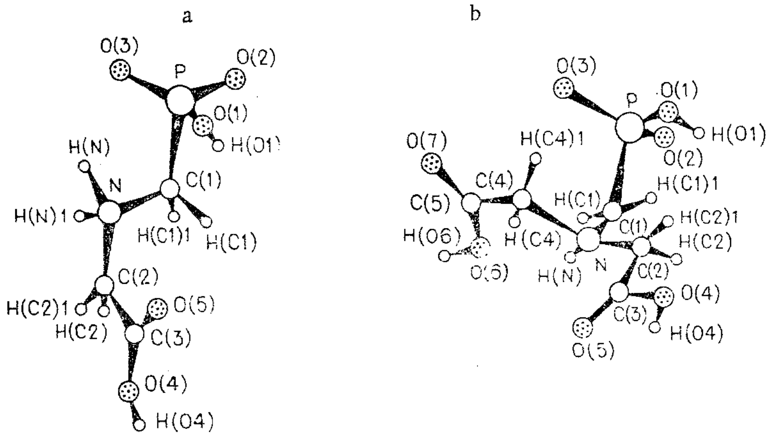


Fig. 1. Conformations of the molecules of compounds I and II.

in solution and for the deuterated derivative in the solid state, showed that the N atoms is protonated by the proton of the phosphonic acid group [7]. We have obtained structural proof of this result for compounds I and II in the crystalline state.

The geometry of the deprotonated phosphonic acid group shows characteristic freatures which are also detected in other related compounds, for example in aminoethylphosphonic acid [8]. The P—O(H) bond length is appreciably greater than the length of the other two equalized P—O bonds: P—O(1) 1.575(1) and 1.574(4) in compounds I and II respectively; P—O(2) 1.502(1) and 1.500(3); P—O(3) 1.500(1) and 1.500(3) Å. The O(2)PO(3) valence angle is correspondingly greater than the five other angles in the polyhedron of the P atom, as a result of the mutual repulsion of the O(2) and O(3) atoms carrying the excess negative charge: 118.61(6) in compound I and 116.9(2)° in compound II.

The other bond lengths and valence angles in compounds I and II coincide to within 2-3(σ). The C—N bonds are longer than the sum of the covalent radii (1.47 Å) by ∿0.02 Å; this is typical of protonated nitrogen [5].

The geometry of the carboxyl group corresponds to the results of the statistical treatment of data on compounds containing this group [9].

Table 5 gives the values of the torsional angles in the molecules of compounds I and II characterizing their conformation. Table 5 also gives the values of the corresponding angles for the two independent molecules (IIIA and IIIB in Table 5) in one (the most stable) of the three crystalline modifications of iminodiacetic acid (IDA-2) [1, 2], whose conformation has features similar to those of the conformation of the molecule of compound I. For the latter also, apparently, the possibility of the appearance of a similar conformational flexibility, responsible for the existence of different conformers depending on the crystallization conditions, is not excluded.

It can be seen from Fig. 1 that the relative positions of the functional groups is different for the molecules of compounds I and II. At the same time it can be seen from Table 5 that their conformations also show certain similarities. The oxygen atoms of the phosphonic acid groups are arranged in analogous fashion relative to the nitrogen atoms: the O(2) atoms have the trans-conformation, and the O(1) and O(3) atoms the gauche conformation. Thus the conformations of the NC(1)PO(1)O(2)O(3) fragments are similar. Analysis of the torsional angles around the C(1)—N bonds shows that when compound I is obtained from compound II, the removal of one of the acetate groups and its replacement by the H(N) atom is accompanied by the rotation of three bonds of the tetrahedral N atom about the fourth C(1)—N. As a result of this rotation, the tetrahedron of the N atom retains approximately its orientation relative to the P—C(1) bond, but its apices C(2), C(4), and H(N) (in structure II) are occupied by the atoms H(N), H(N)1, and C(2) respectively (in structure I) (see Table 5). At the same time the C(2) atom in compound I and the H(N) atom in compound II occupy the trans-position relative to the P atoms, and the other atoms — H(N) and H(N)1 in compound I, and C(2) and C(4) in compound II — occupy the gauche position.

The relationship described between the conformations of molecules I and II is apparently determined by the requirements of close packing of the molecules in the crystal and

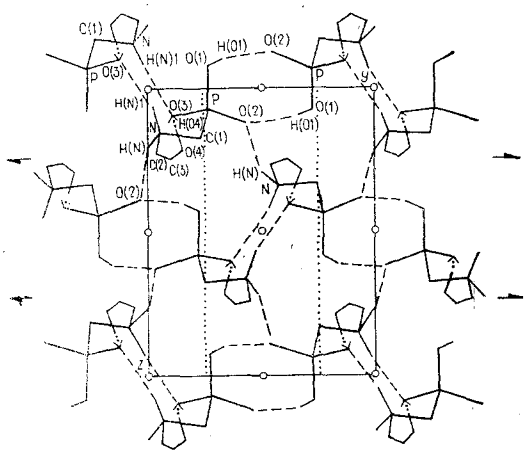


Fig. 2. Diagram of the hydrogen bonds in structure I (projection on the (100) plane, the carboxyl group is given schematically, and the O(5) atom is omitted).

TABLE 5. Torsional Angles in Compounds I-III, deg

Torsional angle	I	Torsional angle	II	Torsional angle	IIIA	IIIB
O(1)PC(1)N	75,2	O(3)PC(1)N	—54,7	O(1)C(2)C(1)N	—16	12
O(2)PC(1)N	—166,5	PC(1)NH(N)	—170,4	O(2)C(2)C(1)N	166	—169
O(3)PC(1)N	—37,7	PC(1)NC(2)	73,3			
PC(1)NC(2)	—174.9	PC(1)NC(4)	—53,7	C(2)C(1)NC(3)	—178	—175
PC(1)NH(N)	71,9	H(N)NC(2)C(3)	35,0			
PC(1)NH(N)1	—49.4	H(N)NC(4)C(5)	56,7			
H(N)NC(2)C(3)	170,3					
H(N)1NC(2)C(3)	51,3	NC(2)C(3)O(4)	179,1			
C(1)NC(2)C(3)	—74,9	NC(4)C(5)O(6)	—26,1	C(1)NC(3)C(4)	76	—73
NC(2)C(3)O(4)	177,8	NC(2)C(3)O(5)	—1.1			
		NC(4)C(5)O(7)	154,7			
NC(2)C(3)O(5)	—1,5	C(1)NC(2)C(3)	150,9			
C(2)C(3)O(4)H(O4)	163,0	C(1)NC(4)C(5)	—59,9			
O(1)PC(1)N	61,0	C(2)C(3)O(4)H(O4)	173,5			
O(2)PC(1)N	—172,4	C(4)C(5)O(4)H(O6)	177,1			

the formation of a convenient system of intermolecular hydrogen bonds (HB). Figures 2 and 3 give schematic representations of the systems of HB in the structures being compared, projected on the (100) plane.

It can be seen from Figs. 2 and 3 and Table 6 that the overall organization of structures I and II (in spite of the above-mentioned differences in the structure of the molecules and the significant differences in the lattice parameters and symmetry of the crystals) is on the whole the same.

In both cases the functions of proton acceptors in the intermolecular HB are fulfilled only by the deprotonated O(2) and O(3) atoms of the phosphonic acid groups (but not the carboxyl or hydroxyl oxygen atoms of the COOH groups). In both structures, the HB denoted as Nos. 1 and 2 in Table 6a form centrosymmetric dimeric rings containing 8 and 10 members in compound I and 8 and 16 members in compound II respectively. The dimers form ribbons extending along the y and z axes in compounds I and II respectively. The ribbons are arranged in networks lying parallel to the (100) plane in structure I and parallel to the (110) plane in structure II.

The packing of the ribbons in the network is simpler in the triclinic crystal of compound II than in the monoclinic crystal of compound I. In compound II, the HB join trans-

TABLE 6. a) Geometry of the Intermolecular Hydrogen Bond

No.	Bond A-H...B	Position of the atom B	Distance, Å			Angle AHB,°	Bond A-H...B	Position of the atom B	Distance, Å			Angle AHB,°
			A—H	H...B	A—B				A—H	H...B	A—B	
1	O(1)—H(O1) ... O(2)	$\bar{x}, 1-y, \bar{z}$	0,79(3)	1,84(3)	2,618(1)	171(2)	O(1)—H(O1) ... O(2)	$\bar{x}, \bar{y}, \bar{z}$	0,71(6)	1,89(6)	2,606(4)	175(6)
2	N—H(N)1 ... O(3)	$\bar{x}, \bar{y}, \bar{z}$	0,94(2)	1,95(2)	2,818(1)	158(2)	O(6)—H(O6) ... O(3)	$\bar{x}, \bar{y}, 1-z$	0,92(6)	1,71(7)	2,627(5)	175(6)
3	N—H(N) ... O(2)	$\bar{x}, 1/2+y, 1/2-z$	0,86(2)	1,93(2)	2,733(1)	154(2)	O(4)—H(O4) ... O(2)	$x-1, y+1, z$	0,84(6)	1,79(6)	2,598(4)	159(6)
4	O(4)—H(O4) ... O(3)	$x+1, y, z$	0,98(3)	1,62(3)	2,571(1)	163(2)	N—H(N) ... O(3)	$x-1, y, z$	0,85(6)	1,99(6)	2,763(4)	151(6)
	b) Shortest intramolecular contacts N-H...O											
1	N—H(N)1 ... O(5)		0,94(2)	2,59(2)	2,761(1)	90(1)	N—H(N) ... O(5)		0,85(6)	2,38(6)	2,737(5)	106(5)
2							N—H(N) ... O(6)		0,85(6)	2,44(6)	2,709(5)	100(5)

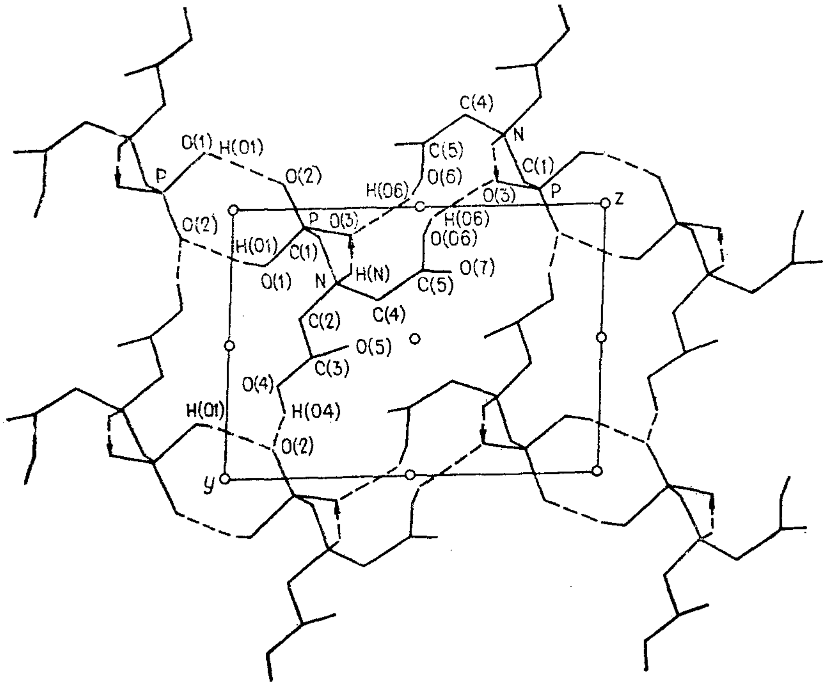


Fig. 3. Diagram of the hydrogen bonds in structure II (projection on the (100) plane).

lationally equivalent ribbons (HB No. 3 in Table 6a); in compound I, the networks are made up of ribbons related by 2_1 screw axes (HB No. 3 in Table 6a) (two ribbons per cell). The three-dimensional framework is formed from the networks by identical interactions in translation in the direction of the x axis (the HB No. 4 in Table 6a are marked by arrows in Figs. 2 and 3).

The fine differences in the nature of the crystal structures of compounds I and II are determined by the nature of the donor atoms taking part in the intermolecular interactions. It should be noted that all the HB O–H...O detected in compounds I and II lie in the range 2.57-2.63 Å and belong to the class of strong HB [10]. At the same time the HB N–H...O correspond to weaker interactions. Thus in the structure of compound II, the forces of interaction within the dimeric ribbons and between the ribbons in the networks are approximately identical and the interactions between the networks are slightly weaker. In the structure of compound I the situation is different; some of the interactions in the ribbons, and also the interactions between the ribbons (HB Nos. 2 and 3), are weakened. Thus the above description of the packing in compound I is somewhat formal in character, but it is convenient from the viewpoint of the comparison of the crystals being discussed.

The x-ray structural studies of the carboxyl-containing complexes indicate that the zwitterion structure of the Complexone is generally accompanied by the production of short intramolecular contacts N–H...O. Similar contacts, leading to the formation of five-membered H-rings, are observed for ethylenediaminetetra-acetic [11], nitrilotriacetic [3], ethylenediaminedisuccinic [12], mercaptoethylaminotriacetic [13], dihydroxybutanediaminetetra-acetic [14], cyclohexanediaminetetra-acetic [15], and diethylenetriaminepenta-acetic [16] acids. In the case of iminodiacetic acid, for which, as noted above, the structure of three crystalline modifications has been studied, the authors do not examine these relationships. Our calculations showed, however, that in this Complexone also, the formation of intramolecular contacts H...O shorter (to different extents) than the sums of the van der Waals radii is observed. It should be noted that the N...O distances in these cases usually lie in the range of values corresponding to generally accepted ideas about HB. The geometry of the fragment N–H...O, however, does not always correspond to the criteria for the existence of intramolecular HB.

According to the formal criterion proposed by Hamilton [17], interactions A–H...O with an H...O distance less than 2.4 Å should be regarded as HB. According to [18], the angle at the H atom in this case should be greater than 97°.

In the structure of compound I, the conformation of the molecule does not facilitate the formation of H-rings. In fact, Table 6b shows the absence of contacts allowed even according to the extremely soft criterion of Hamilton.*

The intramolecular contacts N—H...O detected in the structure of compound II have boundary values within this criterion. Although on the whole the choice of the conformation of the molecule in the structure of compound II, as in the structure of compound I, is determined by the requirements for the formation of a convenient system of intermolecular HB, it can be shown that the two comparatively weak intramolecular interactions N—H(N)...O(6) and N—H(N)...O(5) also make a contribution to the stabilization of the structure.

It should be noted that one of these contacts (with O(5)) is with the carbonyl oxygen atom of the COOH group and the other (with O(6)) is with the protonated (hydroxyl) oxygen atom of the same group. These contacts generally lead to weaker HB than the interactions with the protonated anionic group COO^-. On the other hand, the absence of an intramolecular bond N—H with the oxygen atom of the phosphonic acid group is due to steric factors. Our analysis of the structure of the molecules of compounds I and II using Stuart—Briegleb models showed that the closure of the H-rings by HB whose lengths satisfy Hamilton's criterion is impossible, because of the extremely large P—C distance.

The situation is different for the molecules of classical (purely carboxyl) Complexones. Here, the zwitterion structure implies the formation of one (or several, depending on the number of nitrogen atoms) deprotonated carboxyl branches COO^-, which tend to form strong HB and whose geometry permits the closure of intramolecular glycine H-rings. The fact that these rings are detected in the crystal structures of all classical Complexones, irrespective of their composition, proves that this structure is characteristic of purely carboxyl Complexones even outside the crystal structure. The inclusion in the Complexone of a phosphonic acid group, which has a higher acidity, not only excludes the deprotonation of the carboxyl groups, but also possibly leads to a further redistribution of electron density throughout the molecule, and hence to an additional decrease in the activity of the oxygen atoms of the COOH group and to the participation of these atoms in HB in the role of proton acceptors.

Overall, this study has shown that the chief factors determining the conformation of the stereochemically nonrigid molecules of compounds I and II are the intramolecular HB O—H...O and N—H...O involving the oxygen atoms of the phosphonic acid groups as proton acceptors. The formation of H-rings based on intramolecular interactions N—H...O with carboxyl oxygen atoms is a secondary feature.

Nevertheless, the existence of these weak interactions in the structure of compound II indicates the possibility of obtaining, in this case, more stable metal complexonates containing chelate rings, compared with Complexone I, for which the structural studies show a tendency to form only bridging bonds.

Studies in this direction are being continued.

The authors thank V. Ya. Temkina for interest in the work and for providing the specimen of compound II.

LITERATURE CITED

1. C. E. Boman, H. Herbertsson, and A. Oskarsson, Acta Crystallogr., B30, 378 (1974).
2. J. Bernstein, Acta Crystallogr., B35, 360 (1979).
3. R. H. Standford, Jr., Acta Crystallogr., 23, 825 (1967).
4. M. Darriet, J. Darriet, A. Cassaigne, and E. Nauzil, Acta Crystallogr., B31, 460 (1975).
5. J. J. Daly and P. J. Wheatley, J. Chem. Soc., A, 212 (1967).
6. W. S. Sheldrick and M. Morr, Acta, Crystallogr., B37, 733 (1981).
7. A. I. Grigor'ev, N. I. Voronezheva, and N. M. Dyatlova, Zh. Neorg. Khim., 25, 125 (1980).
8. Y. Okaya, Acta Crystallogr., 20, 712 (1966).
9. P. W. Borthwock, Acta Crystallogr., B36, 628 (1980).
10. I. D. Brown, Acta Crystallogr., A32, 24 (1976).
11. M. Cotrait, Acta Crystallogr., B28, 781 (1972).

---

*Zefirov [19] suggests that H...O interactions having a length $\leqslant$ 2.10 Å should be regarded as HB.

12. F. E. Scarbrough and D. Voet, Acta Crystallogr., B32, 2715 (1976).
13. L. M. Shkol'nikova, V. Ya. Temkina, and N. M. Dyatlova, Zh. Strukt. Khim., 23, No. 1, 135 (1982).
14. A. E. Obodovskaya, L. M. Shkol'nikova, L. O. Atovmyan, et al., Zh. Strukt. Khim. (in the press).
15. L. M. Shkol'nikova, G. V. Polyanchuk, M. A. Porai-Koshits, et al., Zh. Strukt. Khim. (in press).
16. L. M. Shkol'nikova, G. V. Polyanchuk, I. A. Polyakova, and N. M. Dyatlova, Zh. Strukt. Khim. (in press).
17. W. C. Hamilton, "On hydrogen bonding in inorganic crystals: some generalizations, some recent results, and some new techniques," in: Structural Chemistry and Molecular Biology, W. H. Freeman, ed., San Francisco (1968), pp. 466-483.
18. T. F. Koetzle, W. C. Hamilton, and R. Tarthasavathy, Acta Crystallogr., B28, 2083 (1972).
19. Yu. V. Zefirov, Zh. Obshch. Khim., 44, 1105 (1974).
20. M. Cotrait, M. Avignon, J. Prigent, and C. Carrigou-Lagrange, J. Mol. Struct., 32, 45 (1976).

CRYSTAL STRUCTURE OF o-PHTHALATO(AQUO)BIS(ETHYLENEDIAMINE)NICKEL(II) HEMIHYDRATE

N. P. Kozlova, V. M. Agre,
V. K. Trunov, S. S. Makarevich,
and N. N. Barkhanova

UDC 539.26+54.386+547.584

An x-ray structural study of $[Ni(C_2H_8N_2)_2(C_8H_4O_4)(H_2O)]\cdot 0.5H_2O$ has been carried out (automatic diffractometer, λMo, 2146 reflections, heavy-atom method, all H atoms located, anisotropic-isotropic(H) refinement, $R = 0.039$). The crystals are monoclinic, $a = 15.979$, $b = 10.185$, $c = 21.896$ Å, $\beta = 109.34°$, $d_{calc} = 1.501$ g/cm³, $Z = 8$, space group C2/c. The four N atoms of two bidentate-cyclic ethylenediamine ligands, the $O(H_2O)$ atom, and an O(phthalate) atom are coordinated octahedrally to the Ni atom; the O atoms are in the cis-position. The octahedron is distorted as a result of the formation of nonplanar (gauche conformation) five-membered metal-containing rings with an intrachelate angle NNiN 82.5°. The distances are Ni—N (H_2O) 2.154, Ni—O(phthalate) 2.094, Ni—O 2.081-2.108 Å. The carboxyl groups form angles of 42.2 and 113.6° with the planar benzene ring, and an angle of 126.5° with one another. The molecules of the complex are joined in the crystal by van der Waals forces and also by H-bonds N—H...O and O—H...O. The shortest of these is formed by the oxygen atoms of the coordinated water (O...O 2.718 and 2.716 Å) and the water of crystallization (2.742 Å).

The structures of compounds containing the ligands ethylenediamine (en) and the o-phthalate anion (Pht) have not been studied. The only published data relate to the synthesis and lattice parameters of the complex compound $[Cu(en)_2][Cu(Pht)_2]$ [1].

The present paper describes an x-ray structural study of a complex compound of nickel(II) containing these ligands, but in a different ratio, $Ni(en)_2(Pht)\cdot 1.5H_2O$.

EXPERIMENTAL AND STRUCTURE DETERMINATION

The blue crystals of $Ni(C_2H_8N_2)_2(C_8H_4O_4)\cdot 1.5H_2O$ are monoclinic; $a = 15.979(5)$, $b = 10.185(5)$, $c = 21.896(6)$ Å, $\beta = 109.34(1)°$, $V = 3362(4)$ Å³, $M = 370.12$, $d_{calc} = 1.501$ g/cm³, $Z = 8$, space group C2/c.

All-Union Scientific-Research Institute for Chemical Reagents and Ultrapure Chemical Substances (IREA). Translated from Zhurnal Strukturnoi Khimii, Vol. 23, No. 5, pp. 108-113, September-October, 1982. Original article submitted June 12, 1981.

0022-4766/82/2305-0746$07.50