AN X-RAY STRUCTURAL STUDY OF NONVALENCE INTERACTIONS AND COORDINATION IN ORGANOMETALLIC COMPOUNDS. XXI.* THE CRYSTAL STRUCTURES OF 2-PHENYLSULFONYLIMINO-1.2-DIHYDROTHIAZOLE AND ITS N-PHENYLMERCURY DERIVATIVE

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X-ray diffraction (recording at -120° , $\lambda \operatorname{MoK}_{\alpha}$, $\theta/2\theta$ scanning) has been used to determine the crystal structures of 2-phenylsulfonyl-imino-1,2-dihydrothiazole (I) (R = 0.026 from 1931 reflections) and its N-phenylmercury derivative (II) (R = 0.057 from 8624 reflections). The molecules of compounds I and II are present in the crystal in the imino-form, that is both the hydrogen atom in compound I and the PhHg substituent in compound II are joined to the heterocyclic nitrogen atom N(1). In the crystal of compound I, the molecules are joined to give centrosymmetric dimers, formed by a pair of hydrogen bonds of the type N(1)-H...N(2). In the crystal of compound II, the Hg atom, in addition to forming covalent bonds with the N(1) and C atoms, is also involved in weak coordinative interactions with the O and N(2) atoms of neighboring molecules.

INTRODUCTION

Many heterocyclic N-acylamines can exist in the solid state in one of two tautomeric forms: amine or imine. In solutions of these compounds, a dynamic equilibrium is established between the limiting amino (A) and imino (B) forms:

$$\begin{array}{c} R \\ N(2) \\ \vdots \\ N(1) \\ (A) \end{array} \begin{array}{c} R \\ N(2) \\ \vdots \\ N(1) \\ (B) \end{array} \begin{array}{c} R = COOCH_3, COCHCl_2, COCF_3, \\ COCH_3, SO_2Ph, NO_2 etc. \end{array}$$

The position of this equilibrium can be influenced by changing the ratio of the basic strengths of the atoms N(1) and N(2). Sheinker and co-workers [2] previously showed that when the less electronegative acyl group on the exocyclic nitrogen atom N(2) is replaced by a more electronegative atom, the above equilibrium is displaced towards the imine form B. If this group is the benzenesulfonic acid residue PhSO₂-, most heterocyclic phenyl-sulfonylamines (aminopyridine, aminothiazole, aminothiodiazole, aminopyrimidine, aminoquinoline, amino-acridine, etc.) exist almost exclusively in the imine form both in the solid state and in solution.

The structure of acylamino-N-heterocyclic compounds in solution and in the crystal has been studied in detail by ultraviolet and infrared spectroscopy [2]. At the same time, their structure in the crystalline state has apparently not been studied by x-ray structural analysis. It was previously found that in agreement with data from the ultraviolet spectra, in solutions of the phenylmercury derivatives of 2- and 4-arylsulfonylamino-pyridines, a tautomeric equilibrium is established between the aminopyridine and pyridone-imine forms [3, 4]. No x-ray structural analysis of the structure of organomercury derivatives of acyl-amino-N-heterocyclic compounds has been carried out, however. At the same time, a parallel x-ray structural study of potentially tautomeric prototropic and metallotropic systems makes it possible to investigate the comparative regular fea-

*See [1] for communication XX.

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Atom	x	, Y	. z	Atom	. x	y .	z
				1		· · ·	
S(1)	79333(9)	39026(6)	3677(2)	C(31)	35226(36)	21421(24)	-22606(10)
S(2)	90060(8)	15770(5)	-8259(2)	C(41)	44253(38)	32920(26)	-26330(10)
0(1)	107881 (23)	27249(16)	6043(6)	C(51)	66312(39)	39915(25)	-24260(11)
O(2)	98914(25)	1447(16)	-10552(7)	C(61)	79813(35)	35260(23)	-18560(10)
N(1)	48873(29)	18135(19)	5235(8)	H(1)	3981(41)	965(28)	451(11)
N(2)	72089(28)	11432(18)	-2984(7)	H(2)	3099(37)	2730(25)	1242(11)
C(1)	66581(32)	21353(21)	1508(9)	H(3)	6003(37)	5033(26)	1226(11)
C(2)	44612(35)	29230(23)	9748(10)	H(21)	4324(35)	901(24)	-1420(10)
C(3)	59387(36)	41302(24)	9560(10)	H(31)	1830(38)	1668(25)	-2407(11)
C(11)	71056(33)	23531(21)	-14947(9)	H(41)	3494(38)	3620(26)	-3052(11)
C(21)	48649(34)	16715(23)		H(51)	7152(38)	4797(25)	
				H(61)	9499(36)	3959(23)	1731(10)

TABLE 1. Coordinates of the Atoms ($\times 10^5,$ or $\times 10^4$ for H) in the Structure of Compound I

tures in the structures of structurally related prototropic and metallotropic systems in the crystal, and also in a number of cases to put forward suggestions regarding the possible mechanism of tautomeric rearrangements in solution and the structure of the transition state.

The present paper gives the results of an x-ray structural analysis of 2-phenylsulfonylimino-1,2-dihydro-thiazole (I) and its N-phenylmercury derivative (II).

EXPERIMENTAL

2-Phenylsulfonylaminothiazole was obtained by the acylation of 2-aminothiazole with benzenesulfonyl chloride in pyridine solution and recrystallized from alcohol. The melting point was 169-170°, compared with the published figure [2] of 170°. The phenylmercury derivative of 2-phenylsulfonylaminothiazole was obtained by the action of phenylmercury hydroxide on 2-phenylsulfonylaminothiazole in alcohol solution and recrystallized from propanol. The colorless crystals melted at 182-183°.

The crystals of C₉H₈N₂O₂S (I) are monoclinic; at -120°, $\alpha = 5.510(3)$, b = 8.766(3), c = 20.681(9) Å, $\beta = 96.23(4)^\circ$, V = 993.0(7) Å³, d_{calc} = 1.61 g/cm³, Z = 4, space group P2₁/n.

The crystals of $C_{15}H_{12}N_2O_2SHg$ (II) are monoclinic; at -120°, a = 15.516(2), b = 10.534(1), c = 22.877(3) Å, $\beta = 105.294(9)$ °, V = 3606.5(8) Å³, $d_{calc} = 1.90 \text{ g/cm}^3$, $\mu(\lambda \text{MoK}_{\alpha}) = 89.4 \text{ cm}^{-1}$, Z = 8, space group $P2_1/c$, two crystallographically independent molecules.

The unit cell parameters and the intensities of 1961 reflections for compound I and 8676 reflections for compound II with $I > 2\sigma$ were measured on a Syntex $P2_1$ four-circle automatic diffractometer (recording at -120°, λMoK_{α} , graphite monochromator, $\theta/2\theta$ scanning, $2\theta_{max}$ 52° for compound I, 56° for compound II). For compound II, a correction for absorption was introduced with allowance for the actual shape of the crystal, using the published method [5].

The structure of compound I was determined by the direct method using the program MULTAN. The refinement was carried out by the method of least squares initially in the full-matrix isotropic approximation, and then in the anisotropic approximation. The positions of the H atoms of the benzene and thiazole rings were calculated geometrically; the H atom on the N(1) atom was located in a difference synthesis. The final refinement of the structure of compound I was carried out in the anisotropic approximation for the atoms other than hydrogen, and in the isotropic approximation for the H atoms, from 1931 reflections with $F > 5\sigma$ as far as R = 0.026 and R_C = 0.0303. The positional parameters are given in Table 1.

The structure of compound II was determined by the heavy-atom method and refined by the method of least squares first in the isotropic approximation and then in the anisotropic approximation with allowance for the contribution of the hydrogen atoms with fixed temperature parameters ($B_{iso} = 3.5 \text{ Å}^2$) and positional parameters (calculated geometrically). The final divergence factors were R = 0.0518 and $R_G = 0.0859$ from 8624 reflections with F > 6 σ . The coordinates of the atoms are given in Tables 2 and 3.

RESULTS AND DISCUSSION

The structure of the molecule of compound I with the bond lengths is shown in Fig. 1, and Fig. 2 gives the structure of one of the crystallographically independent molecules (IIa) and the bond lengths in both independent molecules (in square brackets for the second of these, IIb). The valence angles are given in Tables 4 and 5.

			<u></u>				
Atom	x	V	z	Atom	x	V	z
Ha(1)	12444(3)	3754(4)		CIGD	5206(7)	1610(11)	1844(6)
$H_{\sigma}(2)$	33032(3)	-6631(4)	-4881(2)	C(12)	847(7)	-819(11)	-1104(5)
S(1)	2586(2)	3111(3)	1138(1)	CON	1084(7)		
S(1)	3207(2)	-37(19(3))	918(4)	C(32)	783(9)	-2924(11)	-1551(6)
S(2)	4145(2)	1728(3)	677(1)	C(42)	288(8)	-2467(14)	
S(2')	4464(2)		793(1)	C(52)	62(9)	-4482(14)	-2164(6)
0(1)	4326(5)	3080/8)	733(4)	C(62)	352(8)	-358(11)	-1662(6)
0(1)	4314(5)	-3308(7)	787(4)	C(1)	2918(7)	-2318(10)	496(5)
nex :	1011(0)		220(4)		4181(7)	2001(10)	944(G)
O(2)	-1010(3)	1024(7)	550(4) 298(7)	0(2)	4101(7)		638(6)
V(2)	1 704(3)		350(4)		4120(8)		(579(5)
N(1)	1613(5)	1075(9)	328(4)	G(11)	1845(7)		1072(0)
N(1')	3514(6)		1 5 (5)	C(21')	2141(8)	-2482(12)	2002(6)
N(2)	3124(5)	1373(8)	379(4)	C(31')	2418(8)	-2162(13)	2608(6)
N(2')	2228(6)		471 (4)	C(41')	2410(8)		2780(6)
C(1)	2490(7)	1960(10)	573(5)	C(51')	2099(8)	51(12)	2337(6)
C(2)	1034(7)	2330(12)	581(6)	C(61')	1826(8)	-260(11)	1747(6)
C(3)	1428(8)	3114(12)	1035(6)	C(12')	3329(7)	470(11)	
C(11)	4443(7)	1091(10)	1414(5)	C(22')	2630(8)	461(11)	-1741(6)
C(2f)	3966(7)	92(14)	1570(6)	C(32)	2654(8)	1254(13)	
C(31)	4238(8)	-427(14)	2145(6)	C(42)	3375(8)	2035(11)	-2198(5)
C(41)	4990(8)	54(13)	2574(8)	C(52)	4072(7)	2047(12)	
C(54)	5475(0)	40/7/(9)	2071(0)	0(02)	4040(7)	498/(14)	-1207(6)
0(01)	1 9419(0)	1047(15)	2400(0)	C(02)	4040(1)	1204(11)	-1=07(0)

TABLE 2. Coordinates of the Atoms ($\times 10^4,$ or $\times 10^5$ for Hg) in the Structure of Compound II

TABLE 3. Coordinates of the Hydrogen Atoms ($\times 10^3$) in the Structure of Compound II

Atom	x.	V	z	Atom	x	ν	z
H(2)	32	224	49	H(2')	470		2
H(3)	109	370	130	H(3')	458	470	76
H(21)	337	-28	124	H(21')	219	349	187
H(31)	385	-123	225	H(31')	266	-286	297
H(41)	520		302	H(41')	263	-60	326
H(51)	610	137	273	H(51')	211	107	250
H(61)	555	245	173	H(61')	162	50	142
H(22)	149	-248	62	H(22')	203	-12	-178
H(32)	99	-394	-148	H(32')	208	124	-264
H(42)	7	313	-247	H(42')	335	265	-260
H(52)	34	83	-259	H(52')	465	264	168
H(62)	23	68	-170	H(62')	461	133	80



Fig. 1. Structure of the molecule of compound I.

Angle	۵. ۵۵۰ ۲	Angle	ω.
C(1)S(1)C(4)	90,82(2)	S(2)N(2)C(1)	121,8(1)
O(1)S(2)O(2)	117,83(8)	S(1)C(1)N(2)	130,2(1)
O(1)S(2)N(2)	113,54(8)	N(1)C(1)N(2)	120,0(2)
O(2)S(2)N(2)	105,88(8)	S(2)C(11)C(21)	119,1(1)
O(1)S(2)C(11)	107,63(8)	S(2)C(11)C(61)	119,5(1)
O(2)S(2)C(11)	105,58(8)	C(11)C(21)C(31)	119,2(2)
N(2)S(2)C(11)	105,44(9)	C(21)C(31)C(41)	119,9(2)
S(1)C(1)N(1)	109,8(1)	C(31)C(41)C(51)	120,2(2)
C(1)N(1)C(2)	115,3(2)	C(41)C(51)C(61)	120,3(2)
N(1)C(2)C(3)	112,8(2)	C(51)C(61)C(11)	119,4(2)
C(2)C(3)S(1)	111,3(2)	C(21)C(11)C(61)	121.0(2)

TABLE 4. Valence Angles ω (deg) in the Molecule of Compound I



Fig. 2. Structure of the molecule IIa (the bond lengths in molecule IIb are given in square brackets).

The lengths of the corresponding bonds in the molecules I, IIa, and IIb coincide within the limits of accuracy. Both the phenylmercury group in compound II and the hydrogen atom H(1) in compound I are attached to the N(1) nitrogen atom of the thiazole heterocyclic ring, indicating that the molecules of both compounds are in the imine form in the crystal,



At the same time, this canonical formula does not describe all the characteristic features of the structures studied. In fact, the imide bond C(1)-N(2) (1.331(2) Å in I and 1.33(1) Å in II a and IIb) is much longer than the standard length of the C=N double bond, 1.255 Å [6], whereas the C(1)-N(1) bond (1.337(2) Å in I, 1.36(1) and 1.37(2) Å in II a and IIb) is shorter than the standard length of the $C(sp^2)-N(sp^2)$ single bond, 1.43 Å [7]. Moreover, the length of the S(2)-N(2) bond (1.597(2) Å in I, 1.60(1) and 1.61(1) Å in IIa and IIb) is shorter than the usual value for an S-N single bond, 1.67 Å [7]. Thus, to describe the nature of the electron density distribution in the molecules studied, it is necessary to take account of the contributions of the following forms with separated charges:



Angle	8	Angle	3	Angle	3	Angle	3
molecule	IIa	molecule I	Ib	molecule	IIa	m olecule	dII
N(1)Hg(1)C(12)	176,6(4)	N(1')Hg(2)C(12')	170,3(4)	S(2)C(11)C(21)	120,9(9)	S(2')C(11')C(21')	120,1(9)
C(1)S(1)C(3)	91,0(6)	C(1')S(1')C(3')	91,3(6)	S(2)C(11)C(61)	118,2(8)	S(2')C(11')C(61')	119,3(9)
O(1)S(2)O(2)	115,5(5)	O(1')S(2')O(2')	117,5(5)	C(11)C(21)C(31)	120(1)	C(11')C(21')C(31')	120(1)
O(1)S(2)N(1)	114,4(5)	O(1')S(2')N(1')	113,0(5)	C(21)C(31)C(41)	120(1)	C(21')C(31')C(41')	119(1)
O(2)S(2)N(1)	105,3(5)	0(2')S(2')N(1')	106,3(5)	C(31)C(41)C(51)	120(1)	C(31')C(41')C(51')	120(1)
U(1)S(2)C(11)	107,2(5)	O(1')S(2')C(11')	105,0(5)	C(41)C(51)C(61)	121(1)	C(41')C(51')C(61')	121(1)
O(2)S(2)C(11)	106,6(5)	0(2')S(2')C(11')	106.7(5)	C(51)C(61)C(11)	118(1)	C(51')C(61')C(11')	120(1)
N(1)S(2)G(11)	107,4(5)	N(1')S(2')G(11')	107,9(5)	C(21)C(11)C(61)	121(1)	C(21')C(11')C(61')	121(1)
S(1)C(1)N(1)	109.7(8)	S(1')C(1')N(1')	111,2(8)	IIg(1)C(12)C(22)	119,5(8)	IIg(2)C(12')C(22')	124,2(9)
C(1)N(1)C(2)	114(1)	C(1')N(1')C(2')	111,5(9)	Hg(t)C(12)C(62)	120.5(9)	IIg(2)C(12')C(62')	118.6(9)
N(1)C(2)C(3)	115(1)	N(1')C(2')C(3')	115(1)	C(12)C(22)C(32)	118(1)	C(12')C(22')C(32')	120(1)
C(2)C(3)S(1)	110(1)	C(2')C(3')S(1')	111(1)	C(22)C(32)C(42)	124(1)	C(22')C(32')C(42')	120(1)
Hg(1)N(1)C(1)	120,3(7)	IIg(2)N(1')C(1')	126,7(8)	C(32)C(42)C(52)	121(1)	C(32')C(42')C(52')	120(1)
Hg(1)N(1)C(2)	125,5(8)	Hg(2)N(1')C(2')	121,1(8)	C(42)C(52)C(62)	119(1)	C(42')C(52')C(62')	120(1)
S(2)N(2)C(1)	119.1(8)	S(2')N(2')C(1')	120,4(8)	C(52)C(62)C(12)	121(1)	C(52')C(62')C(12')	122(1)
N(2)C(1)S(1)	129.9(9)	N(2')C(1')S(1')	128,2(9)	C(22)C(12)C(62)	120(1)	C(22')C(12')C(62')	117(1)
N(2)C(1)N(1)	120(1)	N(2')C(1')N(1')	120,6(9)				

TABLE 5. Valence Angles ω (deg) in Molecules IIa and IIb

A similar increase in the length of the imide bond C(9)-N(2) and decrease in the length of the N(2)-S bond were found in the previously studied structure of phenylsulfonyl-iminoacridone-9 (III) [8], where the lengths of these bonds are 1.328(3) and 1.589(2) Å:



In contrast to molecules I and II, however, in molecule III there is a marked increase [to $131.4(2)^{\circ}$] in the angle at the N(2) nitrogen atom [in molecules I, IIa, and IIb this angle is 121.8(1), 119.1(8), and $120.4(8)^{\circ}$ respectively]. This increase in the angle at the imide nitrogen atom was previously observed in phosphimines [9], where it is attributed to the contribution to the N-P bond from the π_s -component, that is to $p_{\pi}(N) - d_{\pi}(P)$ interaction [10]. The formation of this bond involves a hybrid sp orbital of the unshared pair of electrons of the trigonal nitrogen atom and the unoccupied d_{xy} and $d_{x^2-y^2}$ orbitals of the phosphorus atom. If the angle at the N atom is close to 120° , the π_s -overlap is slight, but it increases with increase in the s-character of the bonds formed by the N atom, that is with increase in the angle at the nitrogen atom. This approach can apparently also be extended to sulfonimides. This means that for compound III a contribution from the following form with separated charges may be proposed:



This is confirmed by the nature of the intermolecular H bonds in the structure of compound III. The molecules are joined to form centrosymmetric dimers by a pair of hydrogen bonds N(1) - H...O(1) and N(1) - H...O(1), that is the excess of electron density required for the formation of the H bond is situated on the O(1) atom, and not the N(2) atom. It should be noted that the S-O bond with the O(1) atom, involved in the H bond, is much longer [1.459(1) Å] than the bond with the second oxygen atom O(2) [1.443(1) Å].

In contrast to compound III, for compounds I and II the contribution from a form with a positive charge on the N(2) atom is not significant, since, as noted above, the valence angles at the N(2) atom are not increased in these compounds. Moreover, the crystal of compound I contains centrosymmetric dimers formed by H-bonds of the type N(1)-H...N(2):



This character of the H bonds indicates a slight excess of negative charge on the N(2) atom. The parameters of the H bond are as follows: N(1)...N(2) 2.856(2), N(1)-H(1) 0.90(2), H(1)...N(2) 1.98(3) Å, angle at the H(1) atom 166(2)°.

The results of the x-ray structural analysis of compound I make it possible to put forward various predictions regarding the mechanism of the prototropic tautomerism of 2-acylaminothiazoles in solution in inert solvents with a low polarity. The dimer present in the crystal acts as a "blank" for the transition state in these tautomeric transformations and indicates the possibility that they take place by a bimolecular mechanism.

In the crystal of compound II, the Hg atoms of the two independent molecules have extremely similar coordination environments. The Hg(1) and Hg(2) atoms form two covalent almost collinear bonds of the usual length [11] with the atoms N(1) and N(1') [2.08(1) Å in IIa, 2.07(1) Å in IIb], and also C(12) and C(12') [2.05(1) Å in IIa, 2.03(1) Å in IIb] and three secondary coordinate bonds. The Hg(1) atom of molecule IIa forms coordinate



Fig. 3. Arrangement of the heteroatoms in the equatorial plane of the Hg(1) and Hg(2) atoms in the structure of compound II.

bonds with the atoms N(2') [at a distance of 2.942(9) Å] and O(2') [2.922(8) Å] of molecule IIb and the atom O(2'i) [3.057(8) Å] of the molecule related to the basis molecule IIb by the center of symmetry at 000. The Hg(2) atom of molecule IIb forms coordinate bonds with the atoms N(2) [3.025(9) Å] and O(2) [2.921(8) Å] of the molecule IIa, and also with the atom O(2^{j}) [2.989(8) Å] of the molecule related to the basis molecule IIa by a center of symmetry at 1/200. All these secondary-coordinated heteroatoms X, as usual [11], are situated in the equatorial planes of the Hg atoms, that is, in planes at right angles to their covalent bonds [the angles C-Hg...X and N-Hg...X vary in the ranges 83.1(3)-99.3(3)° in IIa and 85.8(3)-97.8(3)° in IIb; Fig. 3]. These secondary bonds are formed at distances commensurate with the sums of the van der Waals radii (VR) of the corresponding atoms (VR of the atoms 1.5-1.6 for mercury [11], 1.52 for oxygen [12], and 1.55 Å for nitrogen [12]) and are apparently mainly electrostatic in character.

The molecules of compound II are joined in dimers by interactions of the type Hg...N(2). This indicates the existence of favorable geometric conditions for metallotropic processes to take place by a bimolecular mechanism, in spite of the difference in the geometric requirements for the hydrogen bonds N-H...N and the secondary bonds Hg...N.

A detailed analysis of the geometry of molecules IIa and IIb and a comparison with published data indicate, however, that this is not the only possible path for the metallotropic process. The geometries of the molecules IIa and IIb show appreciable differences which lie outside the range of errors. Thus in molecule IIa the valence angle C(1)N(1)Hg(1) [120.3(7)°] is smaller than the valence angle C(2)N(1)Hg(1) [125.5(8)°]; in molecule IIb, on the other hand, the angle C(1')N(1')Hg(2) is larger [126.7(8)°] than the angle C(2')N(1')Hg(2) [121.1(8)°]. The fact that the valence angles are not equal at the N(1) atom forming the covalent bond with the Hg atom was previously observed in the two crystallographically independent molecules of N-phenylmercury-N,N'-di-ptolylformamidine [13]. One of the molecules was found to contain an intramolecular secondary bond Hg...N(2) (2.68 Å), and this molecule represents a model of the intermediate stage of the metallotropic rearrangement, taking place in solution by an intramolecular mechanism. This coordination does not take place in the second independent molecule.

In the molecules IIa and IIb the intramolecular distances Hg(1)...N(2) 3.151(9) Å and Hg(2)...N(2') 3.325(9) Å are too large for a secondary interaction. In solution, however, where the intermolecular coordination breaks down, the production of intramolecular coordination is possible.

Thus the flexibility of the angles at the N(1) atom is important for the dynamics of the metallotropic system studied, since it allows metallotropic processes to take place by an intramolecular mechanism with the formation of intramolecular secondary bonds with the N(2) atom.

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A CRYSTAL-STRUCTURAL STUDY OF THE PRODUCTS OF THE ATTACHMENT OF AROMATIC AMINES TO NICKEL TRICHLOROACETATE

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A complete x-ray structural study (DRON-1.5) has been carried out for crystals of the products of the reaction of nickel trichloroacetate with aniline $(Cl_3CCOO)_2Ni \cdot 4H_2NC_6H_5$ (I) (a = 18.72(4),b = 10.59(2), c = 9.80(2) Å, $\alpha = 117.2(1)$, $\beta = 89.3(1)$, $\gamma = 105.5(1)^\circ$, space group PI, Z = 2, R = 0.05), para-toluidine $(Cl_3CCOO)_2Ni \cdot 4p-H_2NC_6H_4CH_3$ (II) (a = 11.75(2), b = 15.49(2), c = 12.33(2) Å, $\alpha = 94.4(1), \beta = 104.8(1), \gamma = 113.5(1)^\circ, Z = 2$, space group PI, R = 0.04), and para-anisidine $(Cl_3CCOO)_2Ni \cdot 4p-H_2NC_6H_4OCH_3$ (III) (a = 10.17(2), b = 12.13(2), c = 10.35(2) Å, $\alpha = 113.6(1),$ $\beta = 64.5(1), \gamma = 118.4(1)^\circ, Z = 1$, space group PI, R = 0.05). The structures are molecular. The central nickel atom has distorted trans-octahedral coordination: The nitrogen atoms of the aminogroups are arranged around the metal atom almost at the corners of a square, and the oxygen atoms of the monodentate acetate groups occupy the other two (apical) sites in the coordination polyhedron. The distances are Ni = O 2.08-2.10(2) Å, Ni=N 2.14-2.19(2) Å.* Some results of an x-ray study of the compounds of nickel trichloroacetate with bromoaniline $(Cl_3CCOO)_2Ni \cdot 6p-H_2NC_6H_4Cl$ (V) have also been given.

The adducts formed by nickel trichloroacetate with aniline and its derivatives containing a single substituent in the benzene ring were first synthesized and described by A. V. Ablov in 1935 [1]. Like the adducts formed by aniline and its derivatives with cobalt trichloroacetate [2], they have extremely varied compositions: The number of attached amines may be 2, 3, 4, 5, or 6, depending on the substituent. To explain this variety, A. V. Ablov proposed the determination of the crystal structures of a series of compounds of nickel trichloroacetate with aromatic amines.

Table 1 gives the unit cell parameters and other characteristics of the crystals studied. The experimental material was obtained on a modified DRON-1.5 diffractometer with layer recording of the reflections $(\lambda \operatorname{MoK}_{\alpha}, \operatorname{graphite\ monochromator})$; no allowance was made for absorption ($\mu \simeq 10 \text{ cm}^{-1}$). The insufficiently high accuracy in the determination of the unit cell parameters was due to the instability of the crystals.

The refinement of models of the structures by the method of least squares was carried out in the isotropic approximation using the Rentgen-70 and Kristall programs [3, 4]. The hydrogen atoms were not fixed at this stage [5]. Subsequently, the refinement of the anisotropic parameters of the thermal factors was carried out (Rentgen-75, modified by Yu. F. Shepelev and Yu. I. Smolin [6, 7]), and the positions of all the hy-

*Data on the structures of compounds I-III, determined without the hydrogen atom, were given in [5]. In the present work, the determination was completed and a full analysis of the structures carried out.

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