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Synthesis and Crystal Structures of $[(\text{Nicotinic Acid})_2\text{H}]^+\text{I}^-$, $[(\text{2-Amino-6-methylpyridine})\text{H}]^+(\text{NO}_3)^-$, and the 1:1 Complex Between 1-Isoquinoline Carboxylic Acid (Zwitter Ion) and *L*-Ascorbic Acid Assembled *via* Hydrogen Bonds

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Summary. Three new complexes, namely $[(\text{nicotinic acid})_2\text{H}]^+\text{I}^-$, $[(\text{2-amino-6-methylpyridine})\text{H}]^+(\text{NO}_3)^-$, and the 1:1 complex between 1-isoquinoline carboxylic acid (zwitter ion form) and *L*-ascorbic acid were synthesized. The IR spectra revealed different types of hydrogen bonds in these compounds. The X-ray structure determination has shown the first compound to consist of a packing of $[(\text{nicotinic acid})_2\text{H}]^+$ cations and I^- anions. In the dimeric cation the two nicotinic acid molecules (zwitter ions) are connected through hydrogen bonds (O–H···O). Each dimer is further engaged in other hydrogen bonds with adjacent dimers giving 2D layers. The I^- ion is located at the inversion center. In the second compound the cation and anion are connected *via* hydrogen bonds formed between oxygen atoms of the NO_3^- anion and NH and NH_2 of the cation generating a layer structure. All atoms are coplanar on mirror planes. In the 1:1 complex the two molecules are connected through hydrogen bonds formed between the two oxygen atoms of the carboxylate group of 1-isoquinoline carboxylic acid (zwitter ion) and the oxygen atoms of the two adjacent hydrogen groups of the *L*-ascorbic acid molecule. These complex molecules are engaged in other hydrogen bonds with each other forming a 2D system normal to the long *b*-axis of the unit cell.

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Keywords. Isoquinoline carboxylic acid – *L*-ascorbic acid complexes; IR spectroscopy; Pyridine derivative complexes; X-Ray structure determination; Zwitter ion.

Introduction

Crystal engineering is the planning and synthesis of a crystal from the molecular constituents [1]. In recent years crystal engineering of metal-organic framework materials has evolved rapidly because this kind of materials may have interesting properties and applications such as adsorption, ion exchange, catalysis, and non linear optical and magnetic materials [2–7]. Generally, the construction of frameworks can be achieved by using either covalent bonds or weaker intermolecular forces, *e.g.* hydrogen bonds, aryl–aryl interactions, *etc.* [8–11].

During the last two decades we have been interested in the study of copper(I) complexes derived from pyridine ligands [12–14]. With 4-benzoylpyridine (4-*Bzpy*), however, we isolated a new yellow compound whose elemental analysis revealed that it contains no copper and should be formulated as $[(4\text{-}Bzpy)_2H]I$ [15]. The crystal structure determination has shown this compound to consist of a packing of $[(4\text{-}Bzpy)_2H]^+$ cations and I^- anions. In the cation the two 4-*Bzpy* molecules are connected by a hydrogen bond of the type N–H···N between the heterocyclic nitrogens. Because there is no possibility for other hydrogen bonds to exist, these cations remain as they are and do not extend in a one- or two-dimensional framework [15]. Now, we isolated three new colored compounds, namely $[(\text{nicotinic acid})_2H]^+I^-$ (**1**), $[(\text{2-amino-6-methylpyridine})H]^+(NO_3)^-$ (**2**), and the 1:1 complex between 1-isoquinoline carboxylic acid (zwitter ion form) and *L*-ascorbic acid (**3**). The X-ray structure determination of these compounds is presented in this paper.

Results and Discussions

Three charged non-metal complexes have been obtained from reactions intended to prepare copper(I) complexes (**1** and **3**) or by direct interaction between the components (**2**), either because the desired complex is very unstable as **1** or because it is not formed by such procedures as for **3**. These compounds are colored, sufficiently stable for long time, and soluble in many polar solvents, *e.g.* water, *Et*OH, *etc*. Compounds **1** and **2** gave conducting solutions in water and *Et*OH corresponding to 1:1 electrolytes.

IR Spectra

The IR bands between 1700–2800 cm^{-1} observed for free nicotinic acid [16] disappeared for **1**. Instead, the bands of nicotinic acid appeared as a very strong band with different satellites in the region 2860–3200 cm^{-1} due to $\bar{\nu}^{N-H}$. Further, the $\bar{\nu}^{C=O}$ appears at 1680 ($\Delta\bar{\nu} = -28\,cm^{-1}$) and the CC, CN vibrations appear at $\bar{\nu} = 1625, 1542, 1459\,cm^{-1}$. These results suggest strongly H–N bonded nicotinic acid molecules with a carboxylate group rather than a –COOH group, *i.e.* zwitter ionic form [17, 18]. The CC, CN shifts to higher frequencies in the spectrum of **1** are greater than corresponding shifts reported in copper(I) complexes of nicotinic

acid binding *via* the nitrogen atom [19], which is consistent with what has been reported earlier [20] for pyridine.

The IR data of 2-amino-6-methylpyridine are reported in Ref. [21]. The IR spectra of **2** exhibits the medium bands at $\bar{\nu} = 3366$, 3333, 3164 cm^{-1} due to hydrogen bonded NH_2 and NH [22, 23]. The NH_2 vibration mode is shifted to $\bar{\nu} = 1669\,cm^{-1}$, with $\Delta\bar{\nu}$ larger than those reported for metal complexes of 2-aminopyridine [24]. The ring vibrations appear at $\bar{\nu} = 1610$ sh, 1478 w, 1405 ms, 1340 ms in the IR spectrum of **2**. The shift to larger frequencies of some bands may reflect the formation of NH^+ in **2**, as found for protonation of pyridine itself [20]. The vibration modes of the hydrogen bonded nitrate anion appear at $\bar{\nu} = 1384$ vs, 819 wm.

The IR spectrum of **3** exhibits a very strong band in the $\bar{\nu} = 2900$–$3150\,cm^{-1}$ range with several satellites due to $\bar{\nu}^{N-H}$, similar to that observed for **1**. The broad medium to strong bands at $\bar{\nu} = 2455$ and $1915\,cm^{-1}$ in the spectrum of free 1-isoquinoline carboxylic acid are very similar to those reported in the spectrum of free nicotinic acid [19] and are attributed to $\bar{\nu}^{O-H\cdots N}$ between the heterocycle N atom and the O atom of the –COOH group of another molecule. These bands disappeared from the spectra of **3**. The medium broad band at $\bar{\nu} = 3444\,cm^{-1}$ is due to OH groups of *L*-ascorbic acid, which appeared at $\bar{\nu} = 3526$ and $3410\,cm^{-1}$ in the spectrum of the free acid.

Crystal Structures

Figure 1 illustrates the principal structural features of **1**. The compound consists of a packing of dimeric cations $[(\text{nicotinic acid})_2H]^+$ and I^- anions. In the cation the nitrogen atom of each nicotinic acid molecule is protonated due to the migration of the carboxy proton giving a zwitter ion. The two zwitter ions in the dimer are linked by a hydrogen bond (O···H···O) between oxygen atoms O(1) and O(1A) of the two carboxy groups [O···O = 243.7(4) pm]. Each dimer is further engaged in hydrogen bonds of the type N–H···O with adjacent dimer molecules

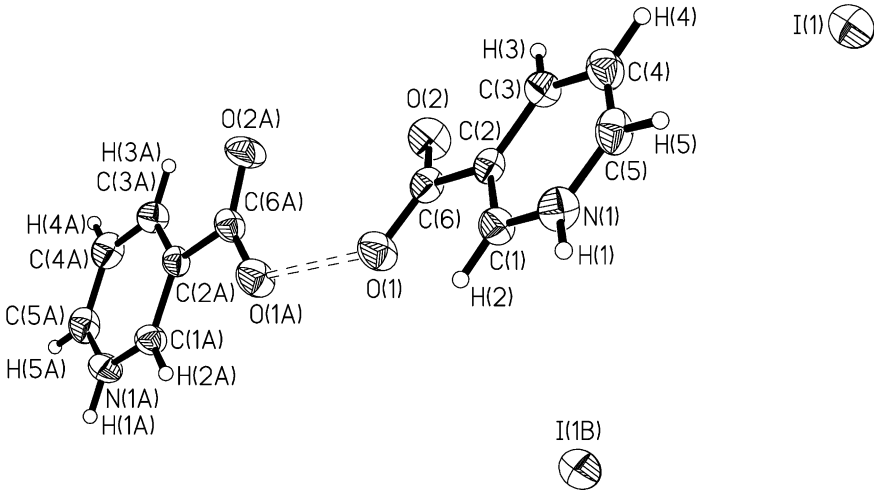

Fig. 1. Perspective view of **1**

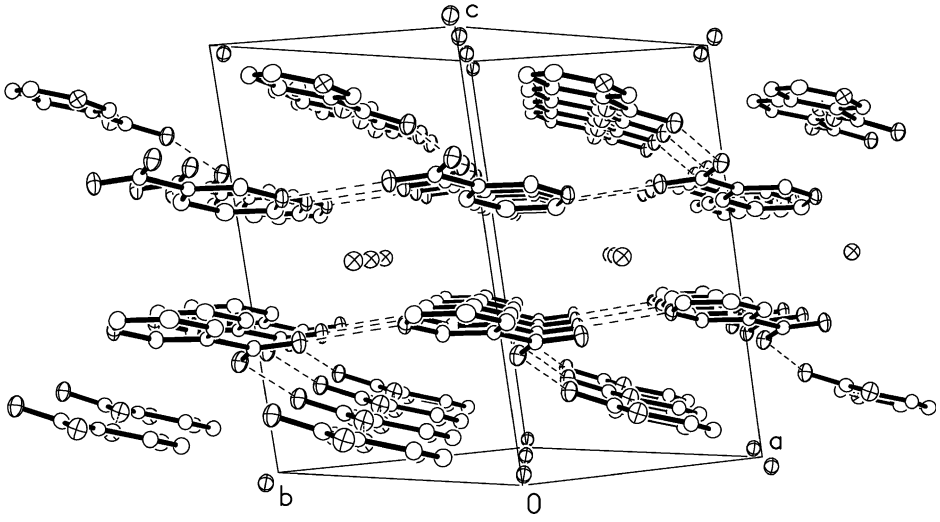

Fig. 2. Packing plot of **1**; broken lines indicate hydrogen bonds between O(1)···O(1) and N(1)···O(2)

[N(1)···O(2B) = 272.9(5) pm]. Thus a 1D network (Fig. 2) results and is extended along the *b*-axis of the unit cell.

In this respect the structure of the dimer in **1** differs from those found in [4-benzoylpyridine)$_2$H]I [15] and [(methylquinaldate)$_2$H][AuBr4] [25]. In these the dimers exist as they are in crystals without any extension due to lack of hydrogen bonding between the dimers. Comparing the bond distances of the zwitter ion in **1** with that of the *N*-coordinated nicotinic acid in its copper(I) chloride complex **4** [19b], we observe that only one of the two C–O bonds [C(6)–O(1)] is a little longer [117.3(9) pm] whereas all other C–C, C–N, and C–O bond lengths are shorter in **1** than the corresponding values in **4**. These bond lengths in **4** are: C(6)–O(2) = 128.9(8), C(6)–C(2) = 156.0(11), C(4)–C(5) = 138.2(3) pm] [19b]. This may explain the earlier observation [20] that the shifts of CC, CN vibrations to higher frequencies caused by complex formation of pyridine are smaller for transition metal ions than for protons.

The atom labeling scheme for compound **2** is shown in Fig. 3. The structure consists of a packing of protonated 2-amino-6-methylpyridine cations and NO_3^- anions. These cations and anions are connected by the following hydrogen bonds, (i) N–H···O between protonated nitrogen N(1) and an oxygen atom of the NO_3^- anion [N(1)–O(3C) = 290.6(5) pm], (ii) an almost parallel hydrogen bond (N–H···O) to the former, between NH_2 group and another oxygen atom of the same NO_3^- anion [N(2)–O(2C) = 298.6(5) pm], (iii) N–H···O bond between the NH_2 group and an oxygen atom of another NO_3^- anion [N(2)–O(1) = 306.4(5) pm]. These hydrogen bonds give a zigzag chain of the cations and NO_3^- anions. The complex ions are located on mirror planes with special positions (x, $1/4$, z). Additional C–H···O contacts form a 2D layer normal to the *b*-axis of unit cell (Fig. 4).

The principle structural features of **3** are shown in Fig. 5. The structure determination showed the complex to be a collection of two molecules. It consists of 1-isoquinoline carboxylic acid as zwitter ion formed by migration of the carboxylic

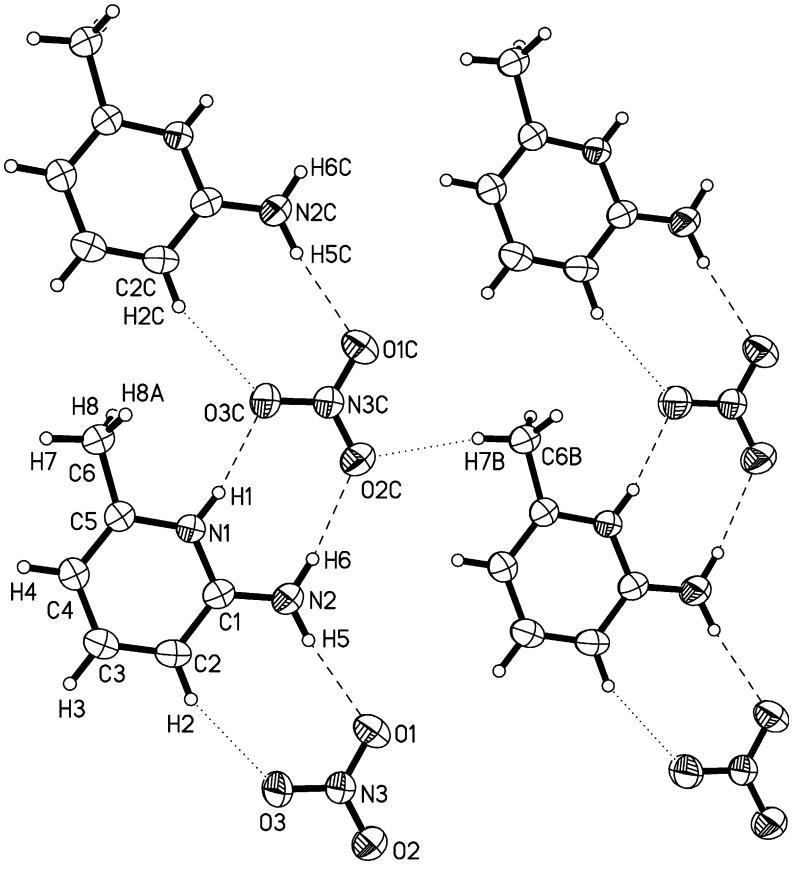

Fig. 3. Hydrogen bonding system in the layers of **2**

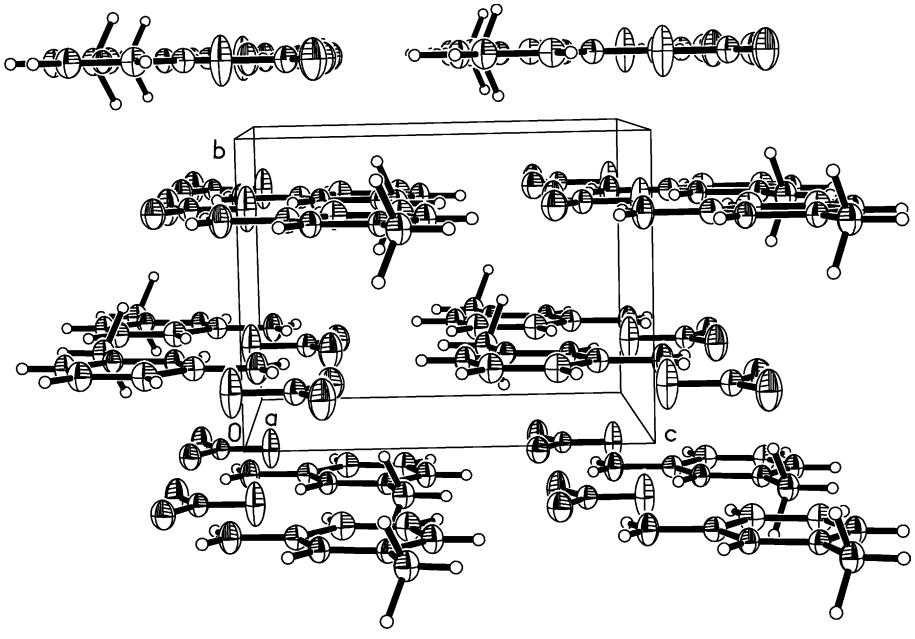

Fig. 4. Packing view of **2**

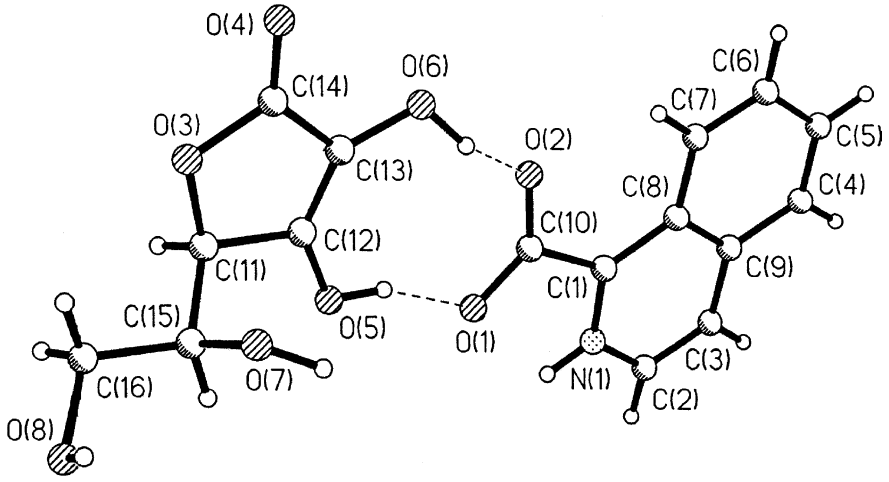

Fig. 5. Perspective view of **3**

proton to the heterocycle nitrogen and *L*-ascorbic acid. This connection takes place *via* two O–H···O hydrogen bonds between O(1) and O(2) of the carboxylic group of 1-isoquinolinium acid and oxygen atoms O(5) and O(6) of the two adjacent hydroxy groups of *L*-ascorbic acid [O(1)···O(5) = 256.1(3) and O(2)···O(6) = 260.6(3) pm]. As can be seen from Fig. 6 additional hydrogen bonds are formed, (i) O–H···O between oxygen atom O(7) of *L*-ascorbic acid and an oxygen atom O(3A) (A = x, y, $z-1$) of another *L*-ascorbic acid of another complex molecule, (ii) O–H···O hydrogen bond between oxygen atom O(8) of *L*-ascorbic acid and an oxygen atom O(7B) (B = $2-x$, $1-y$, z) of *L*-ascorbic acid of a third complex molecule, and (iii) a hydrogen bond N–H···O between oxygen atom O(8) and the nitrogen atom N(1C) (C = $1-x$, $1-y$, $1+z$) of a zwitter ion, with bond distances of

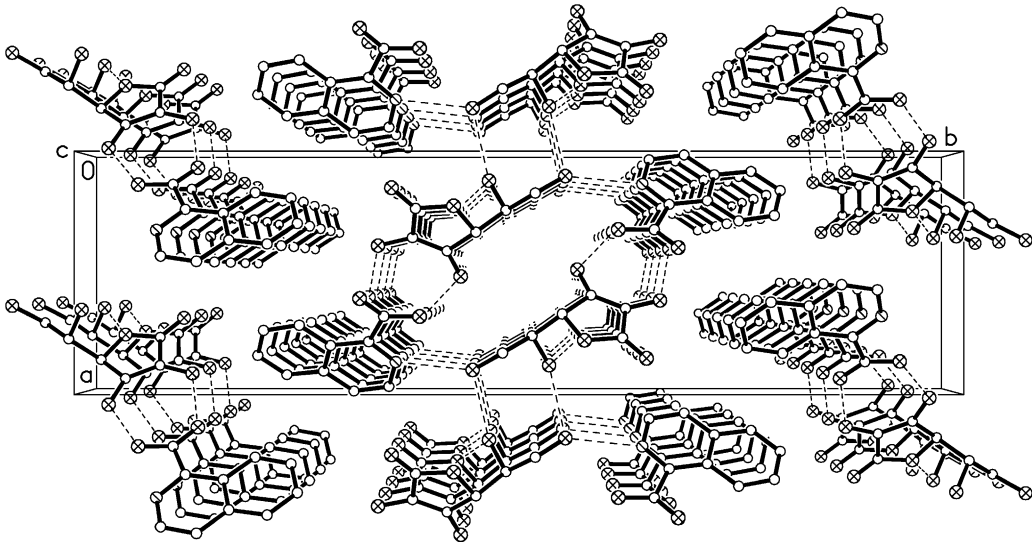

Fig. 6. Packing plot of **3** along the *c*-axis of the unit cell; broken lines indicate hydrogen bond system

286.3(4), 276.3(4), 276.5(6), and 273.0(4) pm, respectively. These hydrogen bonds extend the structure to have a 2D system normal to the long *b*-axis of the unit cell (Fig. 6). The five-membered ring, *i.e.* C(11)–C(12)–C(13)–C(14)–O(3) and O(4), O(5), O(6) are coplanar to the carboxylic acid molecule.

Experimental

The experimental procedures and instruments used for physical measurements were described previously [26]. Nicotinic acid, 2-amino-6-methylpyridine, and 1-isoquinoline carboxylic acid were obtained from Aldrich, other chemicals are of analytical grade quality.

[(Nicotinic Acid)$_2$H]$^+$I$^-$ (**1**, $C_{12}H_{11}N_2O_4$)

A stoichiometric amount of an aqueous solution of $CuSO_4 \cdot 5H_2O$ was mixed with an aqueous solution of NaI in the presence of *L*-(+)-ascorbic acid. The precipitated CuI was washed several times with H_2O, then dissolved by slow addition of NaI under stirring and filtered. To the filtrate, a hot ethanolic solution of nicotinic acid (4 to 1 molar ratio to copper) was added and the final mixture was allowed to stand in open air over several days upon which very few red-brown needle-like crystals along with good quality yellow crystals are separated. Analysis: calcd. (%): C 38.52, H 2.97, N 7.48; found (%): C 38.4, H 3.7, N 7.7; IR (KBr): $\bar{\nu} = 3189, 3077, 2985, 2860, 1680, 1625, 1542, 1459\,cm^{-1}$.

[(2-Amino-6-methylpyridine)H]$^+$(NO$_3$)$^-$ (**2**, $C_6H_9N_3O_3$)

This compound was prepared by dropwise addition of an equimolar amount of conc. HNO_3 to a solution of 3.24 g of 2-amino-6-methylpyridine in 60 cm^3 of MeOH. Transparent light brown crystals were obtained by allowing the final mixture to stand over several days in open air. Analysis: calcd. (%): C 42.11, H 5.31, N 24.54; found (%): C 42.0, H 5.3, N 24.5; IR (KBr): $\bar{\nu} = 3366, 3333, 3164, 1669, 1610, 1478, 1405, 1384, 1340, 819\,cm^{-1}$.

1:1 Complex of 1-Isoquinoline Carboxylic Acid (Zwitter Ion) and L-Ascorbic Acid (**3**, $C_{16}H_{15}NO_8$)

An excess of *L*-(+)-ascorbic acid was added to a mixture of $CuSO_4 \cdot 5H_2O$ (1 mmol) and NaI (1 mmol) in 15 cm^3 of H_2O. To the obtained heterogeneous mixture an ethanolic solution of 1-isoquinoline carboxylic acid (4 mmol) was added, then boiled until a clear solution resulted. To prevent oxydation an additional amount of *L*-ascorbic acid was added to the final hot solution mixture, which was allowed to stand in open air for several days producing good quality yellow crystals along with an undefined white compound. Analysis: calcd. (%): C 48.13, H 4.34, N 4.00; found (%): C 47.8, H 4.2, N 4.2; IR (KBr): $\bar{\nu} = 3444, 3142, 3088, 3013, 2927, 1602, 1477, 1412, 1342\,cm^{-1}$.

X-Ray Crystallography

Single crystal X-ray data were measured on a modified *STOE* four circle diffractometer for **1** and **2** and a *SIEMENS SMART* diffractometer for **3** using graphite crystal-monochromatized Mo-Kα radiation ($\lambda = 71.069$ pm). The intensities were corrected for *Lorentz*-polarisation effects and for absorption in case of **1** and **3** [range of normalized transmission factors: 1.000–0.248 and 1.000–0.897, respectively]. Crystallographic data and processing parameters are given in Table 1.

The structures were solved by direct methods and subsequent *Fourier* analyses. Anisotropic displacement parameters were applied to non-hydrogen atoms in full-matrix least-squares refinements based on F^2. The hydrogen atoms were assigned with isotropic displacement factors and included in

Table 1. Crystallographic data and processing parameters

Compound	**1**	**2**	**3**
Formula	$C_{12}H_{11}IN_2O_4$	$C_6H_9N_3O_3$	$C_{16}H_{15}NO_8$
Formula weight	374.13	171.16	349.29
Crystal system	Monoclinic	Monoclinic	Orthorhombic
Space group	$C2/c$	$P2_1/m$	$P2_12_12$
a/pm	1161.6(3)	738.3(2)	926.88(7)
b/pm	905.2(3)	637.1(2)	3381.4(3)
c/pm	1257.9(4)	838.0(3)	476.08(4)
$\alpha/^\circ$	90	90	90
$\beta/^\circ$	101.81(2)	91.82(2)	90
$\gamma/^\circ$	90	90	90
V/pm^3	$1294.7(7) \cdot 10^6$	$394.0(2) \cdot 10^6$	$1492.1(2) \cdot 10^6$
Z	4	2	4
μ(MoKα)/mm^{-1}	2.485	0.117	0.127
D_{calc}/Mg $\cdot$ m^{-3}	1.919	1.443	1.555
Crystal size/mm	$0.30 \times 0.25 \times 0.20$	$0.60 \times 0.28 \times 0.20$	$0.28 \times 0.21 \times 0.08$
Theta range/$^\circ$	2.88–29.99	2.76–29.99	1.20–28.33
Refl. collected	2328	2045	10461
Indep. refl./R_{int}	1877/0.0421	1242/0.0315	3725/0.0388
Parameters	92	87	227
GooF on F^2	1.130	1.000	0.912
$R1/wR2$	0.0435/0.1332	0.0544/0.1503	0.0422/0.1013
Residuals (e/Å^3)	0.957/−2.893	0.255/−0.210	0.193/−0.173

the final refinement cycles by use of geometrical restraints. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections were incorporated. The program DIFABS [27] and SHELXTL/PC program package [28] were used for computations.

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre, as supplementary publication Nos. CCDC-195282, CCDC-195283, and CCDC-121743. Copies of the data can be obtained free of charge upon application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (FAX: +44(1223)336-033; E-mail: deposit@ccdc.cam.ac.uk).

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