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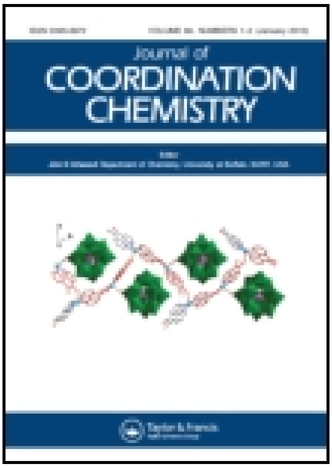

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Syntheses, crystal structures, and IR spectra of isonicotinamide-isonicotinamidium bis(isonicotinamide)-tetrakis(isothiocyanato)ferrate(III) and isonicotinamidium chloride

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Syntheses, crystal structures, and IR spectra of isonicotinamide-isonicotinamidium bis(isonicotinamide)-tetrakis(isothiocyanato)ferrate(III) and isonicotinamidium chloride

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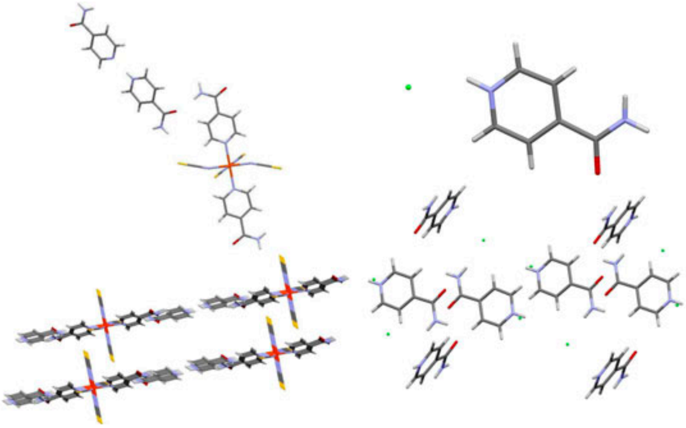

Reaction of iron(III) thiocyanate with isonicotinamide (*inia*) in ethanol leads to formation of a dark red, air stabile crystalline iron(III) compound of composition [*inia*H·*inia*][Fe(*inia*)$_2$(NCS-*N*)$_4$]. Single-crystal X-ray diffraction analysis shows the triclinic *P–1* space group with unit cell parameters: $a = 8.2440(4)$ Å, $b = 9.5540(3)$ Å, $c = 11.2590(5)$ Å, $\alpha = 93.945(4)°$, $\beta = 95.554(4)°$, $\gamma = 96.285(3)°$, and $Z = 1$. The iron compound contains [*inia*H·*inia*]$^+$ cations and [Fe(*inia*)$_2$(NCS-*N*)$_4$]$^-$ anions, which are held together by ionic interactions and hydrogen bonding. The Fe(III) is octahedrally coordinated by six nitrogens, four from NCS$^-$ in the equatorial plane and two from *inia* occupying axial positions. The [*inia*H]Cl has been formed by reaction of *inia* with hydrochloric acid. [*inia*H]Cl crystallized in the monoclinic *C2/c* space group with unit cell parameters: $a = 25.156(5)$ Å, $b = 5.095(1)$ Å, $c = 12.747(3)$ Å, and $Z = 8$. Both compounds have also been characterized by elemental analyses and infrared spectroscopy. Structural and infrared spectral data are compared with data of similar compounds in the literature.

Keywords: Fe(III) complex; Isonicotinamide; Crystal structure; Hydrogen bonds; IR spectra

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1. Introduction

Many heterocyclic nitrogen compounds play an active role in biological systems. Derivatives of pyridine such as nicotinamide (*nia*) and isonicotinamide (*inia*) have been extensively studied because of their potential pharmaceutical applications. Therefore, pyridine derivatives, their pyridinium salts, and metal complexes are attracting attention of many scientists.

Inia is a component of several drugs and has found exploitation in cosmetics too [1–9]. *Inia* possesses strong antitubercular, antipyretic, fibrinolytic, and antibacterial properties [2–8]. Several metal complexes of *inia* are more effective than the free ligand [4–7]. For instance, Pd(II) complexes with *inia* show antimycobacterial and antitumor activities [9]. Isonicotinamidium ($[\textit{inia}\mathrm{H}]^+$) also occurs in many drugs, for example, in drugs for the treatment of acute myeloid leukemia or for the treatment of pancreatic cancer [14, 15]. $[\textit{Inia}\mathrm{H}]^+$ may also be one of the components of a near-infrared ray absorption material [16]. There is possibility to use isonicotinamidium salts as precursors for preparation of ionic coordination compounds. We believe that compounds, which contain *inia* and $\textit{inia}\mathrm{H}^+$ may find application in the fortification of foods like nicotinamide [17].

In addition to importance of *inia* in biological systems, it is also an interesting ligand in coordination chemistry. *Inia* has three potential donor sites; (I) the nitrogen of amide, (II) the nitrogen of pyridine, and (III) the oxygen of carbonyl [2, 6].

Recently, we have reviewed the structural chemistry of 127 *inia* coordination compounds [10] and analyzed coordination modes of *inia* ligands. In the known crystal structures of metal complexes, *inia* molecules occur most frequently as monodentate ligands bonded to the metal through the nitrogen of pyridine [10]. In mononuclear complexes, the coordination of *inia* through the oxygen of the amide (*O*–coordination) was found only in two cases, $[\mathrm{Ca(H_2O)_4}(\textit{inia})_2]\mathrm{Cl_2}$ [11] and $[\mathrm{Ag}(\textit{inia})]\mathrm{BF_4}^-$ [12]. *Inia* molecules also rarely are bidentate bridges (*O,N*-coordination). In this case, the nitrogen of pyridine and the amide oxygen bridge two metal centers, e.g. Ag, Cu, and Mg [10, 13]. From the structural analysis, Cu complexes form the most numerous group (about one-third), followed by Co, Ag, Cd, and Ni complexes (about two-fifths). Other complexes containing Pb, Pd, Mn, Mg, Mo, Ru, Ca, Rh, Re, Tl, and Ir are rare [10]. However, to the best of our knowledge, iron complexes with coordinated molecules of *inia* have not yet been characterized by X-ray diffraction analysis [10].

In the crystallographic database are listed 15 salts and 9 coordination compounds which contain isonicotinamidium. $[\textit{inia}\mathrm{H}]^+$ serves as a counter ion in coordination compounds of Pd, Mo, Cu, Ni, Mn, and Fe [8, 10]. There are only two examples of salts which contain $[\textit{inia}\mathrm{H}\cdot\textit{inia}]^+$. In our laboratory the new iron(III) complex with $[\textit{inia}\mathrm{H}]^+$ cation and $[\mathrm{Fe(dipicolinate)_2}]^-$ [8] was recently prepared and characterized.

This article is a continuation of our previously reported studies on iron complexes with pyridine derivatives [18–22]. Herein, we report the synthesis, crystal and molecular structure, and IR spectral data of the new isonicotinamide Fe(III) complex, $[\textit{inia}\mathrm{H}\cdot\textit{inia}][\mathrm{Fe}(\textit{inia})_2(\mathrm{NCS}\text{-}N)_4]$, and for comparison also of isonicotinamidium salt, $[\textit{inia}\mathrm{H}]\mathrm{Cl}$. The results are compared with those which have been found for similar compounds.

2. Experimental

2.1. *Materials and physical measurements*

All chemicals were purchased commercially and used without purification. Ethanol of 96% vol. was used as a solvent. Elemental analyses (C, H, N and S) were accomplished by means of a Flash EA 1112 analyzer. Infrared spectra (4000–100 cm^{-1}) were measured in the solid state by KBr technique and recorded on a Nicolet 5700 FTIR spectrophotometer. Melting points were measured by Stuart SMP30 Melting Point Apparatus.

2.2. *Synthesis*

2.2.1. Synthesis of [*inia*H·*inia*][Fe*(inia)*$_2$(NCS-*N*)$_4$] (1). At first, a solution of iron(III) thiocyanate by mixing ethanol solution of iron(III) chloride (0.27 g $FeCl_3·6H_2O$, 1.0 mM in 20 mL ethanol) with solution of KSCN (0.29 g, 3.0 mM in 20 mL ethanol) was prepared. The resulting mixture was chilled and the insoluble KCl formed during the reaction was filtered off. Then the prepared solution of iron(III) thiocyanate (1.0 mM in 40 mL ethanol) was mixed with solution of *inia* (0.37 g, 3.0 mM in 25 mL ethanol) and the resulting mixture was stirred for 20 min at room temperature. A small amount of a brown–red powder as a by-product was filtered out. Then the obtained solution was diluted with ethanol to 80 mL and the resulting solution was allowed slowly to evaporate at room temperature until dark red crystals appeared (generally several weeks). The crystals were suitable for X-ray diffraction analysis. Yield: 27.5% (0.162 g). Anal. Calcd for $C_{28}H_{25}FeN_{12}O_4S_4$ (777.70) (%): C, 43.25; H, 3.20; N, 21.61; S, 16.49. Found (%): C, 42.78; H, 3.10; N, 21.11; S, 16.05. m.p. 200.7 °C. This compound has also been obtained from the reaction mixture containing methanol instead ethanol.

2.2.2. Synthesis of [*inia*H]Cl (2). Crystalline [*inia*H]Cl was obtained as a by-product during the synthesis of $(NH_4)_2[FeCl_5(H_2O)]$ [23]. The solution of $FeCl_3·6H_2O$ (4.2 g, 0.015 M in 35 mL of ethanol) was added to the mixture, which was prepared by mixing of 30 mL ethanol solution of *inia* (1.84 g, 0.015 M) with concentrated hydrochloric acid (1.3 mL, 0.015 M). Resulting orange solution was let stand for several days at room temperature. After 3 days, white crystals of [*inia*H]Cl were filtered out. These crystals were suitable for X-ray diffraction analysis. [*inia*H]Cl was also obtained as a powder which was precipitated from the solution prepared by mixing concentrated hydrochloric acid with ethanol solution of *inia* at room temperature. Anal. Calcd for $C_6H_6N_2OCl$ (158.59) (%): C, 45.44; H, 4.45; N, 17.66. Found (%): C, 45.70; H, 4.64; N, 17.95. m.p. 262.2 °C.

2.3. *X-ray crystallographic data collection and refinement*

Intensity data for [*inia*H·*inia*][Fe(*inia*)$_2$(NCS-*N*)$_4$] (**1**) at 293 K were collected using an Oxford Cryostream room temperature device on a Nonius KappaCCD diffractometer with graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). Absorption correction was applied using SADABS [24]. Data reductions were performed with EVALCCD [25]. The structure was solved by direct method using the program SIR2011 [26] and refined by the full-matrix least-squares on all F^2 data using SHELXL-97 [27].

Intensity data for [*inia*H]Cl (**2**) at 293 K were obtained using a Siemens P4 diffractometer with graphite monochromated Mo Kα radiation [28]. The diffraction intensities were corrected for Lorentz and polarization effects with XSCANS [29]. Absorption correction was applied using the program XEMP [29]. The structure was solved by direct methods using SHELXS-86 [30] and refined by the full-matrix least-squares on all F^2 data using SHELXL-97 [27].

Geometrical analyses were performed by using SHELXL-97. The structures were drawn by ORTEP-3 [31] and Mercury software [32]. The single-crystal suite WINGX was used as an integrated system for all crystallographic programs and software for preparing the material for publication [33].

3. Results and discussion

3.1. *Synthesis and structure*

3.1.1. [*inia*H·*inia*][Fe(*inia*)$_2$(NCS-*N*)$_4$] (1). Compound **1** has been prepared by reaction of iron(III) thiocyanate with *inia* in ethanol solution as a dark red, air stable crystalline product. Part of *inia* molecules were protonated to [*inia*H]$^+$, although the reaction was carried out without addition of an acid. We suppose that the proton needed for formation of [*inia*H]$^+$ is produced by hydrolysis of $[Fe(H_2O)_6]^{3+}$, which occurs in $FeCl_3 \cdot 6H_2O$:

$$[Fe(H_2O)_6]^{3+} + H_2O \rightleftarrows [Fe(H_2O)_5(OH)]^{2+} + H_3O^+$$

Similar protonation was also observed in the systems which contain hydrates of other iron(III) salts and pyridine derivatives [18, 19]. Compounds which contain [*inia*H]$^+$ are usually formed in the presence of appropriate acid [8, 34–36].

Structure refinement and crystal data of **1** are given in table 1. Hydrogen bonds and angles are listed in table 2 and selected bond distances and angles are given in table 3. In figure 1, an ORTEP diagram of **1** is shown.

Compound **1** consists of [Fe(*inia*)$_2$(NCS-*N*)$_4$]$^-$ and [*inia*H·*inia*]$^+$ which are held together by ionic interactions and hydrogen bonding (N4–H41···O2) (figure 1, table 2). The hydrogen bond is formed by O2 of the amide group of [*inia*H]$^+$ in the cation and N4 of the amide group from coordinated *inia* in the anion (N4–H41 of 0.801 Å with H41···O2 of 2.109 Å with N4···O2 of 8.902 Å and angle N4–H41···O2 of 170.55°).

Table 1. Crystallographic and structural refinement parameters for **1** and **2**.

Complex	**1**	**2**
Empirical formula	$C_{28}H_{25}FeN_{12}O_4S_4$	$C_6H_7N_2OCl$
Formula weight	777.70	158.59
Crystal system	Triclinic	Monoclinic
Space group	*P–1*	*C2/c*
Temperature (K)	293(2)	293(2)
Until cell dimensions (Å, °)		
a	8.2440(4)	25.156(5)
b	9.5540(3)	5.095(1)
c	11.2590(5)	12.747(3)
α	93.945(4)	90
β	95.554(4)	90
γ	96.285(3)	90
Volume (Å^3), *Z*	874.50(6), 1	1436.7(5), 8
Crystal size (mm)	0.433 × 0.326 × 0.104	0.160 × 0.170 × 0.440
Absorption correction	Multi-scan, SADABS	*Ψ*-scan, XEMP
$[I > 2\sigma(I)]$ reflections	11,153	1828, 1393, 1227
R_{int}	0.0317	0.0355
$R[F^2 > 2\sigma(F^2)]$, $wR(F^2)$, S	0.0795, 0.0861, 1.120	0.0871, 0.0830, 1.076
No. of parameters	243	103
Largest diff. peak and hole (e Å^{-3})	0.490/–0.548	0.404/–0.279

Table 2. Comparison of some parameters in (Å) and (°) of hydrogen bonds for **1** and for **3** [18].

D–H···A	d(D–H)	d(H···A)	⟨D–H···A	d(D···A)	Compound
N5–H51···N5′	0.747	1.904	171.67	2.645	**1**
N7–H7···N8	1.00	1.68	175	2.675	**3**
N4–H41···O2	0.801	2.109	170.55	2.902	**1**
O68–H68···O78	0.860	1.86	170	2.710	**3**

Note: [3*pm*H·3*pm*][Fe(NCS)$_4$(3*pm*)$_2$] (**3**), where 3*pm* = 3-(hydroxymethyl)pyridine.

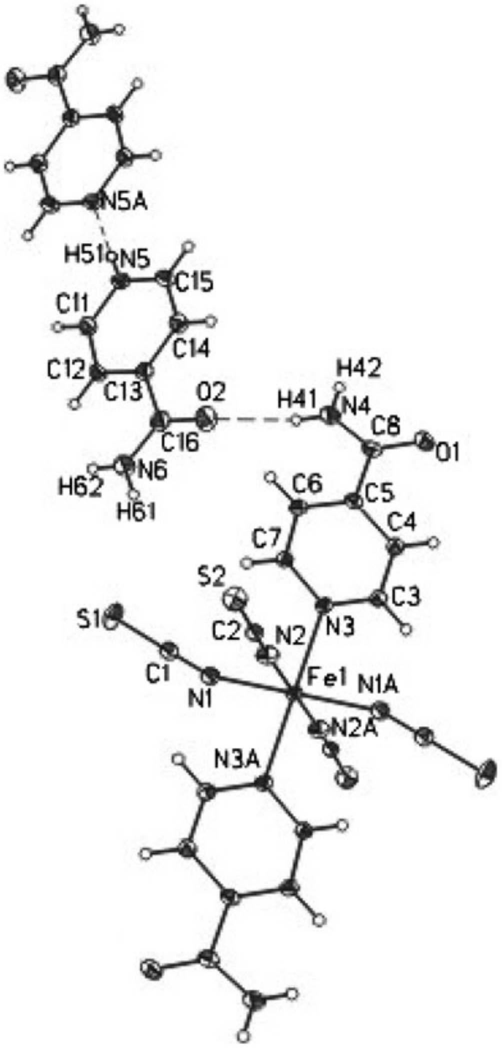

Figure 1. An ORTEP plot of **1**.

The cation [*inia*H·*inia*]$^+$ of **1** consists of one *inia* molecule and one protonated *inia* ([*inia*H]$^+$) linked by a hydrogen bond (figure 1, table 2). The hydrogen bond occurs between pyridine N5 of [*inia*H]$^+$ and pyridine ring N5A of *inia* (N5–H51 of 1.00 Å with

Table 3. Comparison of some selected bond distances (Å) and angles (°) for **1** and **3** [18].

	1	**3**		**1**	**3**
Fe–N1	2.037(2)	2.037(2)	Fe–N3	2.159(1)	2.155(2)
Fe–N1′	2.037(2)	2.047(2)	Fe–N3′	2.159(1)	2.152(2)
Fe–N2	2.017(2)	2.026(2)	N5–H51	0.750	1.00(4)
Fe–N2′	2.017(2)	2.031(2)	N4–H41	0.801	1.00(4)
N2–Fe–N1	90.85(5)	90.37(9)	N2–Fe–N1	90.85(7)	90.83(1)
N2–Fe–N1′	90.04(6)	90.07(9)	N2–Fe–N1′	89.15(7)	88.74(1)
N1–Fe–N1′	180.00	178.71(8)	N3–Fe–N3′	180.00	178.15(1)
N1–Fe–N3	90.04(5)	91.22(8)	N3–Fe–N1	90.04(6)	91.22(1)
N1–Fe–N3′	89.96(6)	89.87(8)	N3′–Fe–N1′	89.96(6)	89.65(1)
N2′–Fe–N2	180.00	178.94(8)	N3′–Fe–N2′	89.55(6)	89.63(1)

H51···N5A of 1.68 Å with N5···N5A of 2.675 Å and angle N5–H51···N5A of 175°). Similarly, hydrogen bonds also occur in the Fe(III) ionic coordination compound with 3-(hydroxymethyl)pyridine (3*pm*), [3*pm*H·3*pm*][Fe(NCS-*N*)$_4$(3*pm*)$_2$] (**3**) [18]. There are hydrogen bonds between [3*pm*H·3*pm*]$^+$ and [Fe(NCS-*N*)$_4$(3*pm*)$_2$]$^-$ and also in the [3*pm*H·3*pm*]$^+$ cation between one [3*pm*H]$^+$ and 3*pm*. The comparison of some hydrogen bond parameters for **1** and **3** is listed in table 2.

The [Fe(*inia*)$_2$(NCS-*N*)$_4$]$^-$ forms a slightly distorted octahedron (figure 1). The iron(III) in the anion is coordinated by six nitrogens, four from NCS$^-$ in the equatorial plane and two from *inia* molecules occupying axial positions. The Fe–N (of *inia*) axial distances (average is 2.159 Å) are slightly longer than the Fe–N (of NCS) equatorial distances (average is 2.027 Å). Similar distortion of FeN$_6$ octahedron was also observed for **3** (table 3), where the Fe–N (of 3*pm*) axial distances (average is 2.154 Å) are slightly longer than Fe–N (of NCS) equatorial distances (average is 2.035 Å).

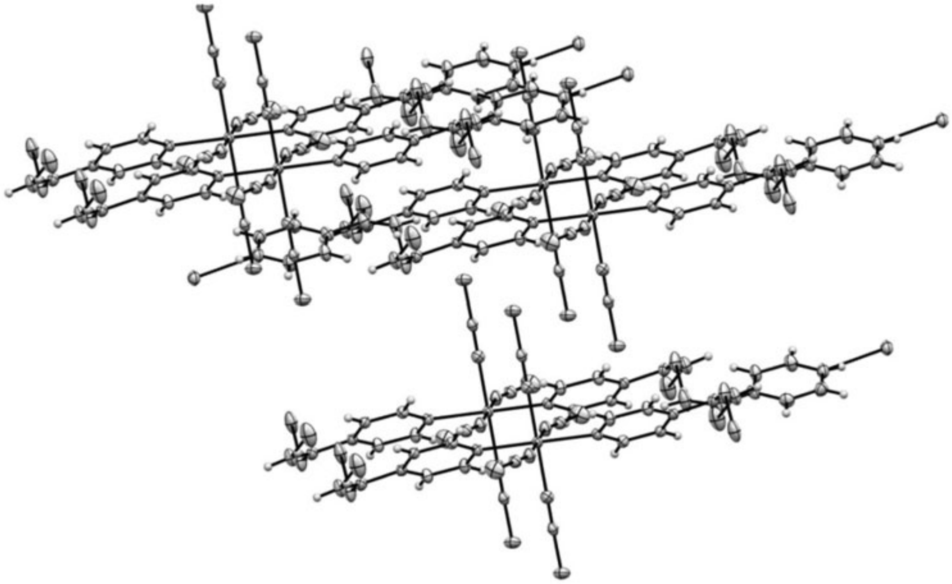

Figure 2. The packing diagram in **1**.

The packing diagram of **1** is shown in figure 2. In **1**, [*inia*H·*inia*]$^+$ and [Fe(*inia*)$_2$(NCS-*N*)$_4$]$^-$ are joined into a 3-D supramolecular network (figure 3). The cations and anions which are bonded together by hydrogen bonds form layers which are connected by van der Waal's forces. The distance between the layers is 7.323 Å (figure 3).

Similar composition as **1** has been observed not only for **3**, but also for (L_2H)[Mo(NCS)$_4L_2$] (*L* = pyridine (*py*) or 4-methylpyridine (*pic*)) [37, 38], (*py*H)[Mo(NCS)$_4$*py*$_2$] [38], (*pic*H)$_2$[M(NCS)$_4$*pic*$_2$]·2*pic* (*M* = Mn or Fe) [39], and (*inia*H)[Fe(dipicolinate)$_2$]·3H$_2$O [8].

3.1.2. [*inia*H]Cl (2). Generally, isonicotinamidium salts can by prepared by reaction of *inia* with appropriate inorganic or organic acids [8, 10, 17, 34–40]. [*inia*H]Cl has been prepared by reaction of *inia* with hydrochloric acid. However, [*inia*H]Cl crystals suitable for X-ray diffraction analysis were obtained as a side product during preparation of

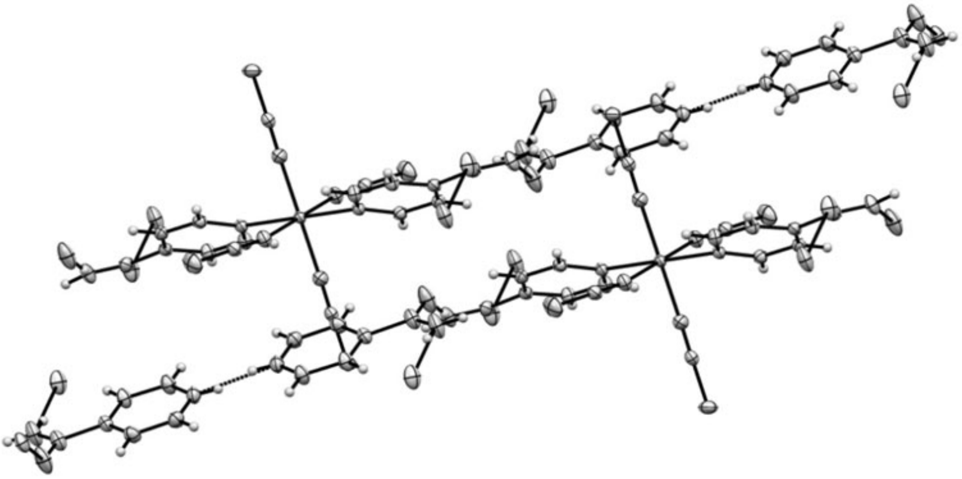

Figure 3. Hydrogen bonds in **1**.

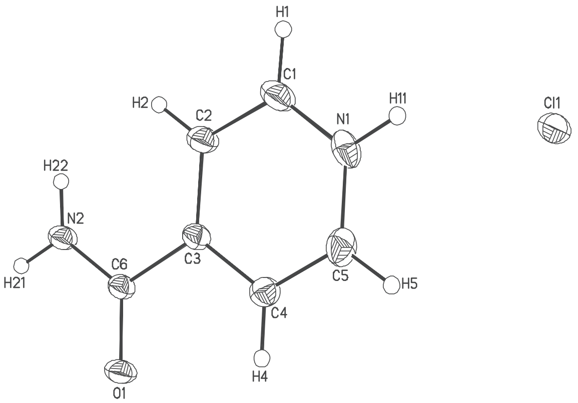

Figure 4. An ORTEP plot of **2a**.

Table 4. Comparison of some selected bond lengths (Å) and angles (°) for the cations in [*inia*H·*inia*][Fe *(inia)*$_2$(NCS)$_4$] (**1**), [*inia*H]Cl (**2**), [*nia*H]Cl (**4**) [41], and [*inia*H]ClO$_4$ (**5**) [40].

Compound	**1**	**2**	**4**	**5**		**1**	**2**	**4**	**5**
N1−C1	1.336(3)	1.331(3)	1.332(3)	1.327(4)	C2−C3	1.385(3)	1.392(2)	1.396(3)	1.389(4)
N1−C5	1.336(3)	1.336(2)	1.335(3)	1.334(4)	C3−C4	1.384(3)	1.392(2)	1.372(4)	1.385(4)
N2−C6	1.325(3)	1.321(2)	1.326(2)	1.310(4)	C3−C6	1.510(2)	1.515(2)	1.498(3)	1.507(4)
O1−C6	1.229(3)	1.241(2)	1.224(2)	1.231(3)	C4−C5	1.376(3)	1.380(2)	1.368(3)	1.369(5)
C1−C2	1.377(3)	1.383(2)	1.380(3)	1.377(4)	N1−H1	0.80(3)	0.90	0.93(3)	0.8600
C1−N1−C5	120.1(2)	122.7(2)	122.9(2)	123.0(3)	C3−C4−C5	118.8(2)	119.3(2)	119.3(2)	120.0(3)
N1−C1−C2	121.2(2)	120.0(2)	119.6(2)	119.7(3)	N1−C5−C4	121.7(8)	119.7(2)	119.7(3)	119.3(3)
C1−C2−C3	119.3(2)	119.0(2)	118.3(2)	118.9(3)	O1−C6−N2	123.1(2)	123.6(1)	123.9(3)	123.2(3)
C2−C3−C4	119.0(2)	119.2(1)	120.1(2)	119.0(3)	O1−C6−C3	119.2(2)	118.6(1)	119.3(2)	118.9(3)
C4−C3−C6	117.4(2)	117.3(1)	118.8(2)	117.9(3)	N2−C6−C3	117.7(2)	117.9(1)	116.8(2)	117.8(3)
C2−C3−C6	123.6(2)	123.5(1)	122.9(2)	123.1(3)					

(NH$_4$)$_2$[FeCl$_5$(H$_2$O)] [23]. Reaction of *inia* with conc. HCl led to the formation of **2** only as white powder.

The molecular structure of the ionic salt **2** (figure 4, table 1) consists of [*inia*H]$^+$ cations and Cl$^-$ anions. These ions are held together by a hydrogen bond between chloride (Cl1) and N1 of pyridine in [*inia*H]$^+$ (table 4).

All important distances and angles for **2** are listed in table 5. Geometrical parameters for [*inia*H]$^+$ cations in **1**, in [*inia*H]ClO$_4$ (**5**) [41], and for [*nia*H]$^+$ cation in [*nia*H]Cl (**4**) [40] are also presented. [*inia*H]$^+$ cations have very similar structures despite the fact that they contain different anions. The cations [*inia*H]$^+$ in **2** and [*nia*H]$^+$ in **4** have also similar structures. Only small variations of distances and angles are observed which can be caused by different positions of –CONH$_2$ groups in the cations.

The packing diagram of **2** is shown in figure 5. Figure 6 shows hydrogen bonds in the crystal structure of **2**. The [*inia*H]$^+$ cations and Cl$^-$ anions are linked in supramolecular networks (3-D) through hydrogen bonds, N1–H11···Cl1, N2–H22···Cl1B, N2–H21···O1A, and N2A–H21A···O1 (table 4). The N1–H11···Cl1 hydrogen bond is located between N1 of pyridine and chloride (Cl1) and another N2–H22···Cl1B hydrogen bond is between the N2 of the amide group and the chloride (Cl1B). Two neighboring cations are connected by two hydrogen bonds (N2–H21···O1A and N2A–H21A···O1) formed by amide oxygen and amide nitrogen of both cations (figure 6). The cations and anions are arranged into layers.

Table 5. Comparison of some parameters of hydrogen bonds (Å, °) for selected compounds.

Compound	D–H···A	d(D–H)	d(H···A)	⟨D–H···A	d(D···A)	Ref.
2	N1–H11···Cl1	0.895	2.277	145.31	3.056	This work
4	N1–H11···Cl1	0.93(2)	2.12(2)	164(3)	3.019(2)	[40]
5	N1–H11···O3	0.860	2.10	162	2.932(4)	[41]
2	N2–H21···O1	0.898	2.020	176.350	2.917	This work
4	N2–H21···O1	0.88(4)	2.04(3)	176(3)	2.920(2)	[40]
5	N2–H21···O1	0.860	2.32	168	3.162(4)	[41]
2	N2–H21···Cl1	0.850	2.357	171.91	3.200	This work
4	N2–H21···Cl1	0.94(3)	2.29(2)	163(2)	3.203(2)	[40]
5	N2–H21···O5	0.860	2.17	164	3.004(4)	[41]

Note: O3 – oxygen from perchlorate, O5 – oxygen from –CONH$_2$ group.

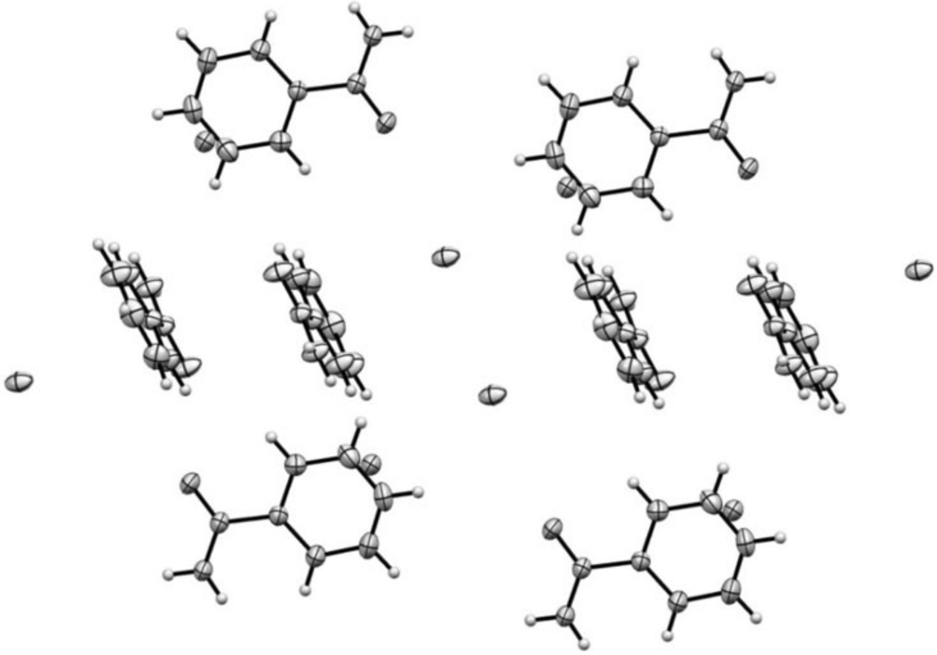

Figure 5. The packing diagram in **2a**.

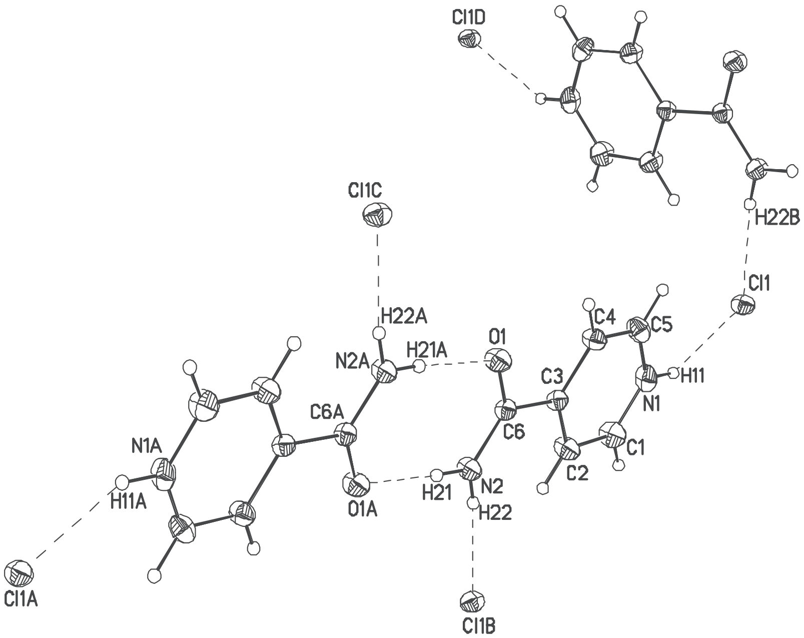

Figure 6. Hydrogen bonds of **2a**.

The distance between the layers is 2.349 Å and they are connected by van der Waal's forces. In each layer, the cations form *zig–zag* chains.

3.2. *IR spectra*

The IR spectrum of **1** shows typical bands for N–bonded thiocyanate complexes [42], peaks at 2062 and 2041 cm^{-1} (ν(CN)), at 857 cm^{-1} (ν(CS)), at 490 and 476 cm^{-1} (δ(NCS)) (table 6). Typical bands for –NH_2 occur at 3327 cm^{-1} for $\nu_{as}(NH_2)$, at 3199 cm^{-1} for $\nu_s(NH_2)$, and at 1609 cm^{-1} for δ(NH). Vibration at 1668 cm^{-1} is characteristic for ν(CO), at 1556 cm^{-1} for ν(ring), and at 626 cm^{-1} for γ(CCC). Other bands for pyridine ring are listed in table 7. The peak at 244 cm^{-1} can be assigned to ν(Fe–N) from *inia* and at 299 cm^{-1} to ν(Fe–N) from NCS [18, 37, 43]. The spectral data of **1** are in agreement with published data of thiocyanate and isonicotinamide complexes (tables 6 and 7).

All important vibrations of **2** (table 7) are compliant with the data cited in the literature [3, 9]. Characteristic amide bond vibrations occur at 3236 and 3105 cm^{-1} ($\nu_{as}(NH_2)$), at 3071 cm^{-1} ($\nu_s(NH_2)$), and at 1627 cm^{-1} (δ(NH)). Band for ν(CO) is at 1709 cm^{-1}. Pyridine ring vibrations occur at 1594 cm^{-1} for ν(ring) and at 654 and 639 cm^{-1} for γ(CCC). The band at 2752 cm^{-1} (ν(>N–H^+)) confirms the presence of isonicotinamidium cation [42, 44].

Table 6. Comparison of some IR spectral data for iron thiocyanate complexes and KSCN.

	Vibration (cm^{-1})			
Compound	ν(CN)	δ(CS)	δ(NCS)	Ref.
1	2062sh, 2041vs	857m	490m, 476m	This work
[3*pm*H·3*pm*][Fe$(NCS)_4$(3*pm*$)_2$]	2094sh, 2052vs	829m	484m, 476m	[18]
$(NEt_4)_3[Fe(NCS)_6]$	2098sh, 2052s	822w	479m	[42]
[Fe(*dena*$)_2(NCS)_2]_n$	2094s	823m	469m	[20]
$[Fe(NCS)_3(OPPh_3)_3]$	2081vs, 2041s	856w	476w	[35]
KSCN	2053s	748	471m, 486m	[42]

Note: s = strong, vs = very strong, m = medium, w = weak, sh = shoulder; 3*pm*H^+: 3-(hydroxymethyl)pyridinium(1+); 3*pm*: 3-(hydroxymethyl)pyridine; $OPPh_3$: triphenyl-phosphine oxide; NEt_4^+: tetraethylammonium(1+); *dena: N,N*-diethylnicotinamide.

Table 7. The characteristic IR bands of **1**, **2**, free *inia* (**10**), and *inia* complexes.

	Vibration (cm^{-1})						
Compound	$\nu_{as}(NH_2)$	$\nu_s(NH_2)$	ν(CO)	δ(NH)	ν(ring)	γ(CCC)	Ref.
1	3327	3199	1668	1609	1556	626	This work
2	3236s, 3105vs	3071vs	1709vs	1627s	1594s	654s, 639s	This work
10	3371vs	3188s	1666vs	1632s	1547m	631s	[2]
11	3417vs, 3308w	3171vs	1711vs	1627w	1556s	686sh	[3]
12	3370vs, 3294vw	3192vs	1716m	1628m	1615m, 1555m	689vw	[3]
13	3376s, 3300w	3180m	1703vs	1624m	1612m, 1555m	676vw	[3]
14	3369–3205s	–	1674s	1626	–	–	[9]
15	3412–3186	–	1705	–	1063	–	[9]
16	3406–3207	–	1670	–	1063	–	[9]
17	3381–3186	–	1707	–	1061	–	[9]

Note: Ni(*inia*$)_2Cl_2$ (**11**), Cu(*inia*$)_2Cl_2$ (**12**), Hg(*inia*$)_2Cl_2$ (**13**), $[Pd(SCN)_2$(*inia*$)_2]$ (**14**), $[PdCl_2$(*inia*$)_2]$ (**15**), $[Pd(N_3)_2$(*inia*$)_2]$ (**16**), and $[Pd(NCO)_2$(*inia*$)_2]$ (**17**); – not given.

4. Conclusion

Two ionic compounds $[\textit{inia}\mathrm{H}\cdot\textit{inia}][\mathrm{Fe}(\textit{inia})_2(\mathrm{NCS}\text{-}N)_4]$ (**1**) and $[\textit{inia}\mathrm{H}]\mathrm{Cl}$ (**2**) which contain isonicotinamidium(1+) have been prepared and characterized by single-crystal X-ray diffraction and IR spectra. The iron(III) compound has been prepared from $\mathrm{FeCl_3 \cdot 6H_2O}$, KSCN, and *inia* in ethanol without addition of an acid. The proton needed for protonation of *inia* may be produced by hydrolysis of $[\mathrm{Fe(H_2O)_6}]^{3+}$. $[\textit{inia}\mathrm{H}]\mathrm{Cl}$ has been formed by direct reaction of *inia* with hydrochloric acid.

In both compounds, cations and anions are joined into 3-D supramolecular networks by hydrogen bonds. The iron(III) in **1** is coordinated to six nitrogens; four from thiocyanate and two from *inia* molecules. All typical features of the IR spectra of **1** and **2** are in agreement with their determined structures and also with data from the literature.

Investigation of iron complexes with pyridine derivatives indicates that the preparation method of **1** can be used for preparation of ionic coordination compounds with related pyridinium cations.

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