

Available online at www.sciencedirect.com



Journal of MOLECULAR STRUCTURE

Journal of Molecular Structure 888 (2008) 394-400

www.elsevier.com/locate/molstruc

Synthesis, spectroscopic and structural investigation of two nickel(II) thiocyanate complexes with isonicotinic acid

Marijana Đaković, Zora Popović*, Neven Smrečki-Lolić

Laboratory of General and Inorganic Chemistry, Department of Chemistry, Faculty of Science, University of Zagreb, Horvatovac 102a, HR-10000 Zagreb, Croatia

Received 10 December 2007; received in revised form 3 January 2008; accepted 4 January 2008 Available online 12 January 2008

Abstract

Two co-crystals of *trans*-[Ni(NCS)₂(H₂O)₂(isonicH)₂] with isonicotinic acid and water molecules (isonicH = isonicotinic acid, i.e., pyridine-4-carboxylic acid) were obtained by reaction of Ni(NO₃)₂·6H₂O, isonicH and KSCN in 1:2:2 molar ratio in aqueous media. One cocrystal [Ni(NCS)₂(H₂O)₂(isonicH)₂]₂·4(isonicH)·3(H₂O) (**2**), is obtained from reaction which has been performed at room temperature while the other one, [Ni(NCS)₂(H₂O)₂(isonicH)₂]·(isonicH)·2(H₂O) (**1**), was obtained by refluxing the reaction mixture for a few hours. The complexes are characterized by IR-spectroscopy and thermal and X-ray crystallographic methods. The compounds crystallize in monoclinic C2/c (**1**) and $P2_1/c$ (**2**) space groups and in both complexes N₄O₂ nearly perfect octahedron around nickel is established. In both compounds molecules are linked into three-dimensional framework by O-H···O, N-H···O and O-H···S hydrogen bonds. The co-crystallized isonicotinic acid molecules are mutually linked forming $C^2_1(7)[R^2_1(4)](1)$ and in C(7) (**2**) hydrogen-bond motifs along *b* axis. The IR and thermal data correlate with the structures of the complexes in the solid state. © 2008 Elsevier B.V. All rights reserved.

Keywords: Nickel(II) thiocyanate complex; Isonicotinic acid; Co-crystals; X-ray crystal structure; IR-spectra; TGA/DTA analysis

1. Introduction

Pronounced interest has been recently focused on the crystal engineering of supramolecular architectures organised by coordinate covalent bonds or supramolecular non-covalent contacts such as hydrogen bonding or π - π stacking interactions. This approach requires a special knowledge of interactions in crystals as well as structure– property relationships in solids. The self-assembly of these frameworks is highly influenced by many factors such as solvent, template, pH, steric demands of counter ion. Using a "building block" methodology a combination of transition metals and pyridine-carboxylate ligands bearing both anionic and neutral donor atoms have been frequently employed as a successful tactic in construction of hybrid porous inorganic/organic materials. As a good bridging

* Corresponding author. Tel.: +385 1 4606 354.

E-mail address: zpopovic@chem.pmf.hr (Z. Popović).

ligand (Scheme 1) in the construction of metal-organic polymers, isonicotinic acid [1] is able to form various lattice species [2-16]. Regarding nickel(II) complexes with isonicotinic acid, Sekiya and coworkers [17-19] established that self-assembly of small components such as isonicH, Ni²⁺ and SCN⁻ in the presence of an aromatic guest gives a two-dimensional (2D) grid-type coordination framework (2D host layer) with relatively large rectangular cavities defined by two isonicH dimers and SCN-bridges. In this structure the isonicH dimers act as bridging ligands with more than 12 Å in length. The authors employed anionic ligand of SCN⁻ in order to prevent an interpenetrating network by shortening the width of the rectangular cavity and to cancel the positive charge on metal centers. In contrast, we have found that reaction product of isonicH, Ni²⁺ and SCN⁻ in the absence of any guest molecules and in aqueous solution is monomeric complex of formula trans-[Ni(NCS)₂(H₂O)₂(isonicH)₂] co-crystallized with water and uncoordinated isonicotinic acid molecules proving that



Scheme 1. The coordination modes of isonicotinic acid.

the prediction of crystal structure of a potential host is still difficult (vide infra). Moreover, 3D supramolecular network compound [Ni(isonic)₂(H₂O)₄], was obtained by mixing nickel(II) nitrate and isonicotinic acid in the presence of sodium dicyanoamide [20] and also hydrothermally by reacting of NiCl₂·6H₂O, CoCl₂·6H₂O, isonicH and NaOH in 1:1:1:1 molar ratio [21]. To the best of our knowledge, the only one nickel(II) compound crystallizes in a threedimensional framework consisting of three interpenetrating diamond-like nets that is *cis*-bis(pyridine-4-carboxylate)nickel(II) [22] obtained by hydrothermal reaction of NiCl₂·6H₂O, Eu₂O₃ and isonicH in 4:5:4 molar ratio. In complex Ni($C_{20}H_{32}N_8$)(isonicotinate)₂ isonicotinate anion, once again, proved its excellent potential in obtaining supramolecules which are constructed through its coordination to metal ion, but also by the π - π stacking interactions [23].

Here, we report synthesis, spectroscopic and thermal characterization of two new monomeric complexes of trans-[Ni(NCS)₂(H₂O)₂(isonicH)₂] (isonicH = isonicotinic acid) with co-crystallized water and isonicotinic acid molecules, as well as their crystal structures determined by X-ray diffraction.

2. Experimental

2.1. Materials and physical measurements

All reagents were supplied by Aldrich Chemical Co. and were used as received without further purification. The CHNS-microanalyses were performed by the Chemical Analytical Service of the Ruđer Bošković Institute, Zagreb.

Infrared spectra were recorded as KBr pellets within the range 4000-400 cm⁻¹ on the Perkin-Elmer FTIR spectrometer 1600 Series.

Thermal measurements were performed using a simultaneous TGA–DTA analyzer (Mettler-Toledo TGA/SDTA 850^e). The TGA and DTA curves were obtained by placing the samples (approximately 10 mg in mass) in small closed alumina pans, with heating rate of 10 °C/min and oxygen and nitrogen (purity above 99.996%) at flowing a rate of 20 ml/min. All samples were heated from the room temperature up to 600 $^{\circ}$ C.

2.2. Preparation of compound 1

Warm aqueous solution of isonicotinic acid (0.25 g, 2 mmol in 30 mL) was added to an aqueous solution of nickel nitrate hexahydrate (0.29 g, 1 mmol in 15 mL). The resulting solution was then treated with an aqueous solution of potassium thiocyanate (0.18 g, 2 mmol in 15 mL) and refluxed for 2 h. After few days blue crystals of 1, suitable for X-ray experiment, were obtained from mother liquor. Yield: 0.32 g (78%). Anal. Calcd based on Ni for $C_{20}H_{23}NiN_5O_{10}S_2$ 1: C, 38.98; H, 3.76; N, 11.37; S, 10.41. Found: C, 39.34; H, 3.94; N, 11.03; S, 10.26%. IR data (cm⁻¹, KBr pellets): 3455s, 3101m, 3070m, 2809w, 2490m, 2091vs, 1690s, 1658s, 1616s, 1560s, 1500m, 1447s, 1413s, 1384vs, 1332s, 1304s, 1229s, 1149m, 1065m, 1021m, 974m, 861s, 825s, 777s, 706m, 692m, 677s, 534m, 484w.

2.3. Preparation of compound 2

The compound **2** was prepared in similar way to **1**; only the reaction mixture is left to stand on quiet place for few days. Blue crystals of **2** suitable for X-ray diffraction were collected from the mother liquor. Yield: 0.26 g (72%). Anal. Calcd based on Ni for $C_{52}H_{54}Ni_2N_{12}O_{23}S_4$ **2**: C, 42.76; H, 3.73; N, 11.51; S, 8.76. Found: C, 42.64; H, 3.94; N, 11.13; S, 8.76%. IR data (cm⁻¹, KBr pellets): 3578s, 3444s, 3106m, 3070m, 2804m, 2506m–s, 2090vs, 1699s, 1662s, 1594s, 1561s, 1500s, 1447s, 1415s, 1387vs, 1332vs, 1302vs, 1229s, 1138m, 1065s, 1019m, 974s, 862s, 825s, 777vs, 706m, 692s, 675s, 531s.

2.4. X-ray structural analysis

The general and crystal data and summary of intensity data collection and structure refinement for compounds 1 and 2 are collected in Table 1.

Table 1 Crystal data and structure refinement for complexes $1 \mbox{ and } 2$

omplex 1		2				
Empirical formula	C20H23NiN5O10S2	C ₅₂ H ₅₄ Ni ₂ N ₁₂ O ₂₃ S ₄				
Formula weight	616.26	1460.73				
Temperature [K]	200	200				
Wavelength [Å]	0.71073	0.71073				
Crystal system	Monoclinic	Monoclinic				
Space group	C2/c	P21/c				
a [Å]	24.900(1)	14.355(1)				
<i>b</i> [Å]	7.4757(3)	7.4349(8)				
<i>c</i> [Å]	14.4352(5)	14.355(1)				
β [°]	108.579(4)	93.989(1)				
Volume [Å ³]	2547.0(2)	1528.3(3)				
Ζ	4	1				
ρ Calcd [g/cm ³]	1.607	1.587				
<i>F</i> (000)	1272	754				
Crystal size [mm]	$0.109 \times 0.240 \times 0.376$	$0.043\times0.176\times0.298$				
Reflections collected	10980	13563				
Unique reflections	3698	3235				
Parameters	196	234				
R_1 , all data,	0.0532; 0.0352	0.0924; 0.0588				
$R_1^{a}[I \leq 2\sigma(I)]$						
wR_2 , all data,	0.0973; 0.0921	0.1743; 0.1612				
$wR_2^{b}[I \leq 2\sigma(I)]$						
g_1, g_2 in w^c	0.0549, 0.000	0.1035, 0.1354				
S^{d} on F^{2}	1.061	1.029				
$\Delta \min/\max [e \ A^{-3}]^e$	-0.31/0.94	-0.35/1.07				

^a $R = \sum ||F_{o}| - |F_{c}|| / \sum |F_{o}|.$

^b $wR = [\sum (F_o^2 - F_c^2)^2 / \sum w (F_o^2)^2]^{1/2}.$

^c $w = 1/[\sigma^2(F_{\alpha}^2) + (g_1P)^2 + g_2P]$ where $P = (F_{\alpha}^2 + 2F_{\alpha}^2)/3$.

^d $S = \sum \left[w(F_0^2 - F_c^2)^2 / (N_{obs} - N_{param}) \right]^{1/2}$.

Data were collected at 200 K on an Oxford Diffraction Xcalibur four-circle kappa geometry single-crystal diffractometer with Sapphire-3 CCD detector, by applying CrysAlisPro Software system [24]. A crystal-detector distance was 60 mm for 1 and 50 mm for 2. Data reduction, including absorption correction, was done by CrysAlice RED application of the CrysAlicePro Software system [24].

The structures were solved by direct methods implemented in the SHELXS-97 program [25]. The coordinates and the anisotropic thermal parameters for all non-hydrogen atoms were refined by the least-squares methods based on F^2 using SHELXL-97 program [26].

The carboxylic acid hydrogen atoms and hydrogen atoms belonging to water molecules of 1 were placed at the positions indicated by difference electron-density map and refined freely. Hydrogen atom of the co-crystallized isonicotinic acid molecule was found to be attached on pyridinic nitrogen from difference electron-density map and refined semi-freely with $U_{iso}(H) = 1.2 U_{eq}(N)$. The carboxylic, water as well as co-crystallized isonicotinic acid molecule hydrogens of 2 were all located in difference maps and then treated as riding atoms in geometrically idealized distances O-H = 0.84 Å and positions, with N– H = 0.88 Å, and with $U_{iso}(H) = 1.2U_{eq}$ of the parent atoms. All other (aromatic) hydrogen atoms were placed in geometrically idealized positions and constrained to ride

on their parent C atom at distances of 0.93 Å and with $U_{\rm iso}({\rm H}) = 1.2 U_{\rm eq}({\rm C})$. Graphical work has been performed by the programs ORTEP-3 *for Windows* [27] and Mercury 1.4.1 [28]. The thermal ellipsoids are drawn at the 50% probability level.

3. Results and discussion

3.1. Preparation of the complexes

Both crystals were grown by slow evaporation of the reaction mixture under ambient condition in a period from 2 days to 1 week. They are light blue air-stable substances.

3.2. Structural description of 1

Selected bond distances and bond angles are listed in Table 2, as well as hydrogen-bond geometry in Table 3. The ORTEP-3 drawing of molecular structure of 1 along with the atomic numbering scheme is given in Fig. 1(a). The structure consists of mononuclear nickel complex molecules, [Ni(NCS)₂(H₂O)₂(isonicH)₂], and co-crystallized one molecule of isonicotinic acid and two water molecules per each complex molecule. The octahedrally coordinated nickel(II) ion lies on crystallographic centre of inversion. Nickel coordination environment consists of two isonicotinic acids-N, two isothiocyanate ligands and two water molecules all in trans-positions. The coordination polyhedron is almost a perfect octahedron, with angular deviations being less than 1.7°. Coordinated as well as co-crystallized isonicotinic acids are found in protonated form, but the co-crystallized isonicH is present in zwitterionic form and thus protonated at pyridinic N-atom.

The Ni–Ow bond distance in 1 [Ni1–O1 = 2.083(2) Å] are in agreement with those reported for [Ni(H₂O)₄(isonic)₂] [2.0669(11) and 2.0932(11) Å] [20,21]. The Ni– N1(NCS) and Ni–N2(py) bond distances (2.043(2) and 2.122(1) Å, respectively) are also comparable with analogous observed in octahedral nickel(II) thiocyanate complexes with *p*-substituted pyridine ligands [17–19]. All

Table 2

Selected bond distances	(Å)	and	angles	(°)	for	complexes	1	and	2
-------------------------	-----	-----	--------	-----	-----	-----------	---	-----	---

		•	
Complex 1		Complex 2	
Ni(1)–O(1)	2.083(2)	Ni(1)-O(1)	2.075(3)
Ni(1) - N(1)	2.043(2)	Ni(1) - N(1)	2.063(3)
Ni(1)-N(2)	2.122(1)	Ni(1) - N(2)	2.109(3)
S(1)-C(1)	1.635(2)	S(1) - C(1)	1.642(4)
N(1)-C(1)	1.160(3)	N(1)-C(1)	1.152(5)
O(2)–C(7)	1.307(3)	O(2)–C(7)	1.317(5)
O(3)–C(7)	1.218(2)	O(3)–C(7)	1.212(5)
O(4)–C(11)	1.241(2)	O(4)–C(13)	1.229(5)
		O(5)–C(13)	1.250(5)
O(1)-Ni(1)-N(1)	91.65(6)	O(1)-Ni(1)-N(1)	92.1(1)
O(1)–Ni(1)–N(2)	90.56(6)	O(1)-Ni(1)-N(2)	89.3(1)
N(1)-Ni(1)-N(2)	89.62(6)	N(1)-Ni(1)-N(2)	90.4(1)
Ni(1)-N(1)-C(1)	164.5(2)	Ni(1)-N(1)-C(1)	164.2(3)
S(1)-C(1)-N(1)	179.3(2)	S(1)-C(1)-N(1)	178.7(4)

Table 3 Hydrogen bonds (Å and °) for compounds 1 and 2

D–H···A	D–H	$H{\cdots}A$	D····A <dha< th=""><th colspan="3">H···A D···A <dha< th=""></dha<></th></dha<>		H···A D···A <dha< th=""></dha<>		
Compound 1							
$O(5)-H(15O)\cdots S(1)$	0.94(4)	2.37(4)	3.309(2)	179(5)	x, -1 + y, z		
$N(3)-H(13N)\cdots O(4)$	0.89(4)	2.07 (3)	2.864(3)	148.0(5)	1-x, -1+y, 3/2-z		
$O(2)-H(12O)\cdots O(4)$	0.87(3)	1.79(3)	2.636(2)	163(3)	$\frac{1}{2} - x, -\frac{1}{2} + y, \frac{1}{2} - z$		
$N(3)-H(13N)\cdots O(4)$	0.89(4)	2.07(3)	2.864(3)	148.0(5)	x, -1 + y, z		
O(1) - H(11O) - O(3)	0.87(3)	1.98(3)	2.849(2)	172(2)	$\frac{1}{2} - x$, $-\frac{1}{2} + y$, $\frac{1}{2} - z$		
$O(1)-H(21O)\cdots O(5)$	0.81(3)	1.91(3)	2.717(2)	173(3)	1-x, 3/2-y, 1-z		
$O(5)-H(25O)\cdots O(3)$	0.82(3)	2.09(3)	2.761(2)	138(3)	$\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} - z$		
$C(2)-H(2)\cdots O(3)$	0.95	2.57	3.424(2)	151	x, -1 + y, z		
$C(8)-H(8)\cdots S(1)$	0.95	2.87	3.596(3)	134	-		
Compound 2							
$O(1) - H(11O) \cdots O(6)$	0.84(3)	1.93(4)	2.761(6)	167(4)	_		
N(3) - H(13) - O(5)	0.88	1.72	2.597(6)	175	x, 1 + y, z		
O(1) - H(21O) - O(3)	0.84(3)	1.97(3)	2.810(4)	173(4)	1 - x, $-1/2 + y$, $1/2 - z$		
$O(6)-H(16O)\cdots S(1)$	0.85(14)	2.77(14)	3.430(6)	135(10)	1 - x, $-1/2 + y$, $1/2 - z$		
$O(2)-H(2O)\cdots O(4)$	0.85(4)	1.82(4)	2.554(4)	143(6)	x, 1/2 - y, -1/2 + z		
$O(6)-H(26O)\cdots O(3)$	0.86(8)	2.06(6)	2.716(6)	132(8)	x, 1/2 - y, -1/2 + z		



Fig. 1. (a) The ORTEP-3 drawing of the structural unit of complex 1 with the atomic numbering scheme of the asymmetric unit viewed down the b axis; (b) crystal packing of complex 1 viewing down the b axis with hydrogen bonds indicated by dotted lines.

other bond lengths and angles are of usual values [29]. In comparison of Ni–N bond distances of **1** with those in the aforementioned structures of $[Ni(H_2O)_4(isonic)_2]$ [20,21] and $[Ni(NCS)_2(isonicH)_2 \cdot xG]_n$ (G = guest molecules) [17–19], it is obvious that introducing the thiocyanate ligand into the coordination sphere of Ni atom lengthen the Ni–N(py) bond length.

The monodentately bounded thiocyanate groups are usually slightly bent and the search of the 830 entries in CSD (Cambridge Structural Database, Version 5.28 of 2007) [30] for metal complexes with terminally bonded thiocyanate shows that the \angle (N–C–S) bond angle spans from 169 to 180°. In **1** the thiocyanate bond angle of 179.3(2)° approaches the upper value. The terminal Ni–NCS linkage is bent with Ni–N–C angle of 164.5(2)° which is in agreement with those found for Ni²⁺ having bent terminally bonded NCS-anions (141–174°) [31].

Fig. 1(b) shows the crystal packing of 1, viewed down the b axis. The crystal structure is characterized by *inter*molecular hydrogen bonds. There are three types of

strong hydrogen bonds (O-H···O, N-H···O and O- $H \cdots S$) and two of weak ones (C- $H \cdots O$ and C- $H \cdots S$) and their geometric parameters are displayed in Table 3. Although N-coordination of isonicotinic acid is established, the carboxylic acid dimers (CADs) were not found in the crystal structure of **1** as in the analogous polymeric structures [17–19]. The carboxylic oxygen atom O3 from ligand molecule acts as trifurcated acceptor. It accepts two hydrogens from two water molecules, the coordinated and co-crystallized ones, O1-H13N...O3 and O5-H25O ... O3, and one aromatic hydrogen atom in weak C2–H2···O3 hydrogen bond. The other carboxylic oxygen atom O2, which is protonated, takes part in $O2-H2\cdots O3$ hydrogen bonding as proton donor. As a consequence of participation of carboxylic group in abovementioned Hbond network, the carboxylic group is twisted from the plane of the pyridine moiety forming the angle between these two planes of 22.9(1)°. The co-crystallized isonicotinic acid is essentially planar with dihedral angle between pyridine ring and carboxylic group plane being 2.4(1)° and they are mutually connected into infinite chains in [010] direction by double N-H···O hydrogen bonds forming the $C_1^2(7)[R_1^2(4)]$ hydrogen-bond motif [32,33]. The co-crystallized water molecule which participates in aforementioned O5-H25O···O3 hydrogen bond, participates also in one much weaker, O5-H15O...S1, and connects every second complex molecule in the direction of caxis. Thus an extensive three-dimensional H-bond framework is formed.

3.3. Structural description of 2

Fig. 2(a) displays the ORTEP-3 diagram of 2 which crystallizes in $P2_1/c$ space group with two molecules of trans-[Ni(NCS)₂(H₂O)₂(isonicH)₂], four molecules of isonicH and three H₂O molecules per unit cell. Nickel ion sits in crystallographic center of inversion, and isonicotinic acid and thiocyanate coordinate to the metal ion via the nitrogen atoms, while the water molecules occupy the fifth and sixth coordination sites and complete an N_4O_2 nearly perfect octahedron around nickel. The differences in bond distances and bond angles in coordination environment of nickel(II) ion between two complexes 1 and 2 are very small and are all within 11σ (Table 2.). The isothiocyanate ligands approach the metal center in substantially non-linear manner with the Ni1-C1-N1 angle also being of the same value (164.5(2) in 1 and 164.2(3)° in 2) and bond angle, \angle (N–C–S) is also retained. The carboxylate group of coordinated isonicotinic acid is slightly less twisted out of pyridine plane and the dihedral angles between pyridine and carboxylic group planes are $22.9(1)^{\circ}$ and 19.1(2) in 1 and 2, respectively.

The crystal packing of **2** is presented in Fig. 2(b) and the hydrogen-bond geometry is listed in Table 3. In the crystal structure of **2** there are three types of H-bonds are found: $O-H\cdots O$, $N-H\cdots O$ and $O-H\cdots S$. The carboxylic oxygen atom O3 acts as trifurcated hydrogen-bond acceptor in three $O-H\cdots O$ hydrogen bonds. It accepts three hydrogen atoms of three water molecules: two from



Fig. 2. (a) The ORTEP-3 drawing of the structural unit of complex 2 with the atomic numbering scheme of the asymmetric unit viewed down the *b* axis; (b) crystal packing of complex 2 viewing down the *b* axis with hydrogen bonds indicated by dotted lines.

399

ligated water molecules thus connecting two adjacent complex molecules in the direction of b axis and forming an infinitive zig-zag hydrogen-bond chains, and one from co-crystallized water molecule. The other carboxylic oxygen atom O2 participates together with co-crystallized isonicH in an extensive three-dimensional H-bond framework by O-H···O type of hydrogen bonding and therefore causes the twisting of carboxylic group out of pyridine plane by 10.5(5)°. The molecules of uncoordinated isonicH are present in zwitterionic and mutually linked by single N-H···O hydrogen bonds in the infinite C(7) chains in [010] direction. There are two short contacts in the crystal structure of 2 which involve aromatic π -system. The hydrogen atom belonging to co-crystallized water molecule is directed toward the pyridine ring aromatic system of isonicH with the O6–H(16O) $\cdot \cdot \cdot$ Cg(N2, C2–C6) angle of $128(1)^{\circ}$ and contact distance H···Cg of 3.0(1) Å, while the thiocyanate sulfur atom is directed toward the pyridine ring of the co-crystallized isonicH molecule with the C1–S1···Cg(N3, C8–C12) and H···Cg value of $160.6(2)^{\circ}$ and 3.692(2) Å. The incorporation of thiocyanate S atom into the hydrogen-bond network as well as in the interactions with π -system reduces its thermal motions. Therefore, the smaller values of its displacement parameters are found as compared with 1. In thiocyanate complexes where sulfur atom is not involved in H-bonding frameworks large values of its displacement parameters are established [34,35].

3.4. IR spectra

Complexes 1 and 2 exhibit very similar solid state infrared spectrum, what makes these compounds undistinguishable by this method.

Concerning the C–N stretching frequencies of thiocyanates in general, v(CN) are lower in *N*-bonded than in *S*-bonded complexes, while for bridging complexes (M–SCN–M) the CN stretching frequencies are found at still higher wave numbers [36]. In Ni complexes with terminally N-bound NCS⁻ ligands, the v(CN) stretching frequencies are usually found at ~2100 cm⁻¹ [37,38]. In the spectra of both compounds a sharp absorption band at 2090 cm⁻¹ suggests the *N*-coordination of SCN⁻ group. The absorption band corresponding to C–S stretching is usually employed for differentiating *S*- from *N*-bonded terminal thiocyanates. The v(CS) modes are in spectra of **1** and **2** overlapped by pyridine stretching and deformation bands, making the assignment of the C–S stretches quite uncertain.

Unfortunately, due to overlapping of maxima and vibrational coupling, the observed shifts of absorption bands sensitive to metal coordination relatively to those of free ligands could not be unambiguously assigned in the IR spectra of the title compounds. A broad band observed in the range of $2300-3500 \text{ cm}^{-1}$ for both compounds indicates complex hydrogen-bond framework confirmed by X-ray structure analysis.

3.5. Thermal analysis

The TGA–DTA measurements of complexes 1 and 2 were performed in the temperature range of 25–600 °C under flowing nitrogen and oxygen atmosphere. The thermal gravimetric analyses were performed on the crystalline samples. At common temperatures and pressure the crystals possess good stability and do not show any hygroscopic effect.

The TG data in nitrogen atmosphere show the thermal stability of 1 up to 70 °C. The compound decomposes in four consecutive steps in temperature range between 70 and 520 °C but could not be unambiguously described because several simultaneous processes could take place but all of these steps associated with corresponding endothermic peaks in DTA curve. Measured solid residue of (47.61%) at 524 °C, is of heterogeneous consistency, i.e., it consists of green and black solid. Therefore, it can be concluded that it is incompletely decomposed compound of formula Ni(NCS)₂(isonicotinic acid) in mixture with carbonized matter (calculated 48.35%). The compound 2 in nitrogen is stable up to 110 °C. Decomposition processes of complex 2 investigated in temperature range between 110 and 480 °C consists of five stages. To all of decomposition steps corresponding broad endothermic DTA peaks are observed. Similarly, we found that the residual solid of 23.98% after 480 °C could be described as the mixture of Ni(NCS)₂ and undefined carbonized solid due to our visual observation of sample and recorded IR (calculated 23.94%).

The thermal analysis of complexes 1 and 2 performed in oxygen do not show better resolved decomposition peaks. The decomposition process of 1 ended at 490 °C with NiO as final product (found 14.34%; calculated 12.12%) which is followed by strong and sharp exothermic peak at 421 °C. The thermal decomposition of 2 ended at 477 °C with end product NiO (found 13.04%; calculated 10.23%) which correspond to the sharp, strong exothermic peak at 396 °C.

4. Conclusion

Two monomeric nickel(II) isothiocyanate complexes with isonicotinic acid have been prepared in situ. $[Ni(NCS)_2(H_2O)_2(isonicH)_2] \cdot (isonicH) \cdot 2(H_2O)$ (1) and $[Ni(NCS)_2(H_2O)_2(isonicH)_2]_2 \cdot 4(isonicH) \cdot 3(H_2O)$ (2). The complex obtained by mixing an aqueous solution of components at room temperature 2 is more stable than complex 1 which have been obtained by refluxing the same reaction mixture for 2 h. Infrared spectra indicated N-coordination of thiocyanate ligands, while the coordination modes of carboxylic acid could not be unambiguously determined. The crystal structures were investigated by X-ray structure analysis. In both complexes Ni^{II} ion is six-coordinated with four nitrogen atoms, two from isonicotinic acid and two from isothiocyanate ligand, and two oxygen atoms from water molecules in almost perfect octahedral geometry.

Very small differences are found in molecular structure of two complexes, $[Ni(NCS)_2(H_2O)_2(isonicH)_2]$, in contrast to their crystal structures which differ significantly. In **1**, one molecule of isonicotinic acid and two water molecules are co-crystallized per one complex molecule, while in **2** two molecules of isonicotinic acid and 1.5 water molecules are co-crystallized per parent Ni complex. Although isonicotinic acid ligand molecule coordinate to Ni^{II} via pyridine *N*-atom, carboxylic acid dimers were not found in **1** and **2**. The co-crystallized isonicH molecules are mutually connected by two strong hydrogen N–H···O bonds in **1** and

by one of the same type in 2 forming the infinite hydro-

gen-bond chains in [010] direction with $C_{1}^{2}(7)[R_{1}^{2}(4)]$

Supplementary material

and C(7) hydrogen-bond motifs.

Crystallographic data for the structural analysis have been deposited with the Cambridge Crystallographic Data Centre, CCDC number 669793 for complex 1 and 669792 for complex 2. Copies of this information may be obtained from the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44 (0) 1223 336033; e-mail: deposit@ccdc.cam.ac.uk or website: http://www.ccdc.cam.ac.uk.

Acknowledgements

This research was supported by Ministry of Science, Education and Sports of the Republic of Croatia within the scientific project under the title "Chemistry of metal complexes in reactions of biological importance and new materials" (No. 119-1193079-1332) and in the framework of the scientific programme "Ligands, complexes, proteins synthesis and structure–properties relationship". The authors are grateful to Prof. Helen Stoeckli-Evans for valuable instructions and suggestions in structure refinement.

References

- [1] F. Takusagawa, A. Shimada, Acta Crystallogr. B32 (1976) 1925.
- [2] L.R. MacGillivray, R.H. Groeneman, J.L. Atwood, J. Am. Chem. Soc. 120 (1998) 2676.
- [3] A.D. Burrows, M.F. Mahon, M.T. Palmer, J. Chem. Soc. Dalton Trans. (1998) 1941.
- [4] R.-G. Xiong, S.R. Wilson, W. Lin, J. Chem. Soc. Dalton Trans. (1998) 4089.
- [5] J.Y. Lu, A.M. Babb, Chem. Commun. (2001) 821.
- [6] J.Y. Lu, A.M. Babb, Inorg. Chem. 40 (2001) 3261.

- [7] G. Yang, H.-G. Zhu, B.-H. Liang, X.-M. Chen, J. Chem. Soc. Dalton Trans. (2001) 580.
- [8] C.Z.-J. Lin, S.S.-Y. Chui, S.M.-F. Lo, F.L.-Y. Shek, M. Wu, K. Suwinska, J. Lipkowski, I.D. Williams, Chem. Commun. (2002) 1642.
- [9] J.-H. Yu, J.-Q. Xu, L. Ye, H. Ding, W.-J. Jing, T.-G. Wang, J.-N. Xu, H.-B. Jiam, Z.-C. Mu, G.-D. Yang, Inorg. Chem. Commun. 5 (2002) 572.
- [10] S.W. Ng, V.G. Kumar Das, J. Crystallogr. Spectrosc. Res. 22 (1992) 371.
- [11] M. Biagini Cingi, A. Gaetani Manfredotti, C. Guastini, M. Nardelli, Gazz. Chim. Ital. 102 (1972) 1034.
- [12] R.-G. Xiong, J.-L. Zuo, X.-Z. You, H.-K. Fun, S.S.S. Sundra, New J. Chem. 23 (1999) 1051.
- [13] O.R. Evans, Z. Wang, R.-G. Xiong, B.M. Foxman, W. Lin, Inorg. Chem. 38 (1999) 2969.
- [14] F.F. Jian, C.L. Li, P.S. Zhao, L. Zhang, Struct. Chem. 16 (2005) 529.
- [15] O.R. Evans, W. Lin, Inorg. Chem. 39 (2000) 2189.
- [16] O.R. Evans, R.-G. Xiong, Z. Wang, G.K. Wong, W. Lin, Angew. Chem. Int. Ed. 38 (1999) 536.
- [17] R. Sekiya, S. Nishikiori, Chem. Commun. (2001) 2612.
- [18] R. Sekiya, S. Nishikiori, K. Ogura, J. Am. Chem. Soc. (2004) 16587.
- [19] R. Sekiya, S. Nishikiori, K. Ogura, Inorg. Chem. 45 (2006) 9233.
- [20] S.R. Batten, A.R. Harris, Acta Crystallogr. E57 (2001) m7.
- [21] T.-H. Ma, J.-H. Yu, L. Ye, J.-Q. Xu, T.-G. Wang, C.-H. Lu, J. Mol. Struct. 654 (2003) 47.
- [22] T.-B. Lu, R.L. Luck, Acta Crystallogr. C58 (2002) m152.
- [23] K.S. Min, M.P. Suh, Eur. J. Inorg. Chem. (2001) 449.
- [24] Oxford Diffraction, CrysAlisPro Version 171.32, Oxford Diffraction Ltd., Abingdon, Oxfordshire, England, 2007.
- [25] G.M. Sheldrick, SHELXS-97, Program for the Automatic Solution of Crystal Structures, University of Göttingen, Germany, 1997.
- [26] G.M. Sheldrick, SHELXL-97, Program for the Refinement of Crystal Structures, University of Göttingen, German, 1997.
- [27] L.J. Farrugia, ORTEP-3, J. Appl. Crystallogr. 30 (1997) 565.
- [28] I.J. Bruno, J.C. Cole, P.R. Edgington, M.K. Kessler, C.F. Macrae, P. McCabe, J. Pearson, R. Taylor, Acta Crystallogr. B58 (2002) 389.
- [29] H.F. Allen, O. Kennard, D.G. Watson, L. Brammer, A.G. Orpen, J. Chem. Soc. Perkin Trans. II (1987) S1.
- [30] F.H. Allen, Acta Crystallogr. B58 (2002) 380.
- [31] R. Kapoor, A. Kataria, A. Pathak, P. Venugopalan, G. Hundal, P. Kapoor, Polyhedron 24 (2005) 1221.
- [32] J. Bernstein, R.E. Davis, L. Shimoni, N.-L. Chang, Angew. Chem. Int. Ed. Engl. 34 (1995) 1555.
- [33] M.C. Etter, J.C. MacDonald, J. Bernstein, Acta Crystallogr. B46 (1990) 256.
- [34] M. Đaković, Z. Popović, G. Giester, M. Rajić-Linarić, Polyhedron (2007), doi:10.1016/j.poly.2007.09.014.
- [35] M. Đaković, Z. Popović, G. Giester, M. Rajić-Linarić, Polyhedron (2007), doi:10.1016/j.poly.2007.09.036.
- [36] R. Bala, R.P. Sarma, R. Sarma, B.M. Kariuki, Inorg. Chem. Comm. 9 (2006) 852.
- [37] J.-Y. Xu, H.-D. Bian, W. Gu, S.-P. Yan, P. Cheng, D.-Z. Liao, Z.-H. Jiang, P.-W. Shen, J. Mol. Struct. 646 (2003) 237.
- [38] P. Mukherjee, C. Biswas, M.G.B. Drew, A. Ghosh, Polyhedron 26 (2007) 3121.