

Synthesis, crystal structure, infrared spectrum, and thermal properties of $[\text{Ni}(\text{1,10-phenanthroline})_3](\text{fumarate})\cdot 9\text{H}_2\text{O}$ complex with hydrogen bonded supramolecular layers involving fumarate anions

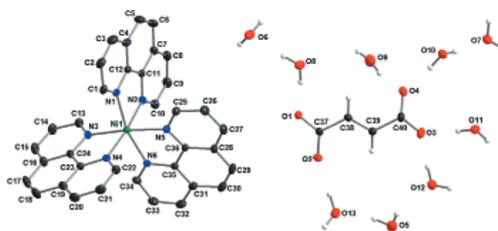
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Abstract: From the aqueous-ethanolic system $\text{Ni}(\text{OH})_2\text{--H}_2\text{fum--phen}$ (H_2fum = fumaric acid, phen = 1,10-phenanthroline), novel complex $[\text{Ni}(\text{phen})_3](\text{fum})\cdot 9\text{H}_2\text{O}$ (**1**) was isolated and characterized by chemical analyses and FT-IR spectroscopy. Results of single crystal X-ray structure analysis have shown that the ionic crystal structure of **1** is built of $[\text{Ni}(\text{phen})_3]^{2+}$ complex cations, fumarate dianions and nine crystallographically independent water molecules of crystallization. The Ni(II) atom exhibits hexa-coordination by three phen ligands with mean Ni-N bond length of 2.090 Å. Water molecules form hydrophilic supramolecular layers with fumarate dianions via extended network of O—H...O type hydrogen bonds with O...O distances from the range of 2.676(2)–2.916(2) Å; hydrophobic complex cations are embedded between these layers. Thermal study of **1** has shown that endothermic dehydration in the temperature range of 95–195 °C takes at least two steps of the process.

Graphical Abstract: Crystal structure of $[\text{Ni}(\text{phen})_3]\text{fum}\cdot 9\text{H}_2\text{O}$ (phen = 1,10-phenanthroline; H_2fum = fumaric acid) which is built of supramolecular layers formed by hydrogen bonded water solvate molecules and fumarate dianions and between the supramolecular layers embedded $[\text{Ni}(\text{phen})_3]^{2+}$ complex cations is described here.



Keywords: Nickel(II), fumarate ligand, crystal structure, hydrogen bond, thermal analysis

Introduction

Fumarate dianion is a versatile ligand exhibiting, due to four potentially donor oxygen atoms, a large number of bonding possibilities ranging from terminal to various bridging modes of coordination. However, it can also act simply as a counter ion (Oldham, 1987; Zheng et al., 2003; Devereux et al., 2000, Bora and Das, 2012; Téllez-López et al., 2015; Zhang et al., 2009). The ability of fumarate dianion to link magnetically active central atoms was used in synthetic design of magnetically interesting low-dimensional complexes (Téllez-López et al., 2015; Neuman et al., 2014; Téllez-López et al., 2014); in order to obtain low-dimensional systems, it is necessary to block some coordination sites of the central atom with suitable blocking ligands, e.g. with aromatic N,N-chelates like phen or bpy (phen = 1,10-phenanthroline;

bpy = 2,2'-bipyridine). Previously, using this approach, $[\text{Ni}(\text{phen})(\text{fum})]$ (Černák et al., 2009) and $[\text{Ni}(\text{H}_2\text{O})(\text{phen})(\text{fum})]_n$ complexes were isolated from systems $\text{Ni}(\text{II})\text{--phen--fum}$ (H_2fum = fumaric acid) and characterized (Uhrinová et al., 2012). Surprisingly, to our knowledge, only two complexes from these systems have been structurally characterized up to now, namely $[\text{Ni}_2(\text{phen})_4(\text{fum})(\text{H}_2\text{O})_2](\text{fum})\cdot 16\text{H}_2\text{O}$ containing a dinuclear complex cation (Ma et al., 2003) and ionic $[\text{Ni}(\text{phen})_3](\text{fum})\cdot 2\text{H}_2\text{fum}\cdot 4\text{H}_2\text{O}$ with solvate molecules of fumaric acid (Lin and Zheng, 2004). Within a deeper study of low-dimensional Ni(II) complexes (Černák et al., 2009; Čerák et al., 2015; Vráblová et al., 2016), system $\text{Ni}(\text{II})\text{--phen--fum}$ was added to our research. As the result of our experiments, the title complex **1** was isolated in single crystal form in case of full occupancy of the coordination sites around the Ni(II) central atom by blocking ligand (3x phen)

and its synthesis, IR spectroscopic characterization and crystal structure as well as its thermal properties are reported here.

Experimental

Materials

Nickel(II) hydroxide, Ni(OH)₂, fumaric acid, C₄H₄O₄ (H₂fum), 1,10-phenantroline, aqueous ammonia (25 %) and ethanol (96 %) were purchased from commercial sources and used as received.

Synthesis of [Ni(phen)₃](fum)·9H₂O (**1**)

Fumaric acid, 232 mg (2 mmol), was dissolved in 15 cm³ of ethanol (96 % vv). To the formed solution, 2 mmol of freshly prepared precipitate of Ni(OH)₂ and 1180 mg (6 mmol) of solid 1,10-phenantroline (*phen*) were added under stirring. The resulting red solution was filtered and left aside for crystallization at room temperature. Within a few days, red platelets formed on the surface of the mother liquor, these were collected and dried in air. Yield: 6 %

Anal. Calc. for C₄₀H₄₄Ni₁N₆O₁₃ (Mr = 875.51) (%): C, 54.88; H, 5.07; N, 9.60; Ni, 6.70. Found: C, 54.64; H, 4.98; N, 9.55; Ni, 6.69.

IR (cm⁻¹; s = strong, m = medium, w = weak, vs = very strong, sh = shoulder): 3405vs, 3037w, 2990w, 1639w, 1625w, 1578vs, 1516s, 1495wsh, 1425vs, 1397s, 1340wsh, 1306w, 1257vw, 1225m, 1143m, 1104m, 1010m, 955w, 868sh, 846s, 812m, 774w, 725s, 667w, 643w, 576w.

Physical measurements

Elemental analyses (C, H, N) were performed on a CHNS Elemental Analyzer Flash EA 1112 Thermo Finnigan. Nickel content was estimated using the AAS method (Varian Spectr AA-30).

Infrared spectra were recorded on a FT-IR Avatar 330 Thermo-Nicolet instrument using the KBr pellets technique (2 : 200) in the range of 4000–400 cm⁻¹.

Thermal analysis was performed on a NETZSCH STA 409 PC instrument using ceramic crucibles. Measurements were carried out under dynamic conditions (heating rate was 9 deg/min) in air atmosphere in the temperature range of 25–900 °C.

X-ray Crystallography

Single crystal X-ray experiments on **1** were carried out on an IPDS Stoe diffractometer equipped with an imaging plate area detector system with graphite-monochromatized MoK α radiation ($\lambda = 0.71073$ Å) at 100 K. Rotation method data acquisition using ω scans was used. Structure was solved by direct methods and further refined

using the SHELXS-97 (Sheldrick, 2008) and SHELXL-2014/7 programs (Sheldrick, 2015) incorporated in the WinGX program package (Farrugia, 2012). Hydrogen atoms in the *phen* ligands and *fum* dianion were placed in the calculated positions and allowed to ride on the parent atoms with isotropic thermal parameters tied with the thermal motion of the parent atoms ($U(\text{H}) = 1.2U(\text{CH})$). Isotropic thermal parameters of water hydrogen atoms were tied with thermal parameters of the parent oxygen atom ($U(\text{H}) = 1.5U(\text{O})$), other positional parameters of these hydrogen atoms were allowed to refine freely. Structural figures were drawn using the Diamond software (Brandenburg and Putz, 2008). Crystal data and final parameters of the structure refinement are summarized in Table 1, selected geometric parameters are presented in Table 2 while possible hydrogen bonds are given in Table 3.

Tab. 1. Crystal data and structure refinement for **1**.

Empirical formula	C40 H44 N6 Ni O13
Formula weight	875.52
Crystal system	monoclinic
Space group	$P2_1/c$
Unit cell dimensions:	
a (Å)	10.9212(12)
b (Å)	20.6837(17)
c (Å)	18.348(2)
β (°)	96.505(13)
Z	4
V (Å ³)	4118.0(7)
D_{calc} (g·cm ⁻³)	1.412
T (K)	100(2)
μ (mm ⁻¹)	0.544
Index ranges for data collection	$-13 \leq h \leq 13$ $-23 \leq k \leq 26$ $-23 \leq l \leq 23$
θ range for data collection	2.12–27.00
Reflections collected	31894
Independent reflections (R_{int})	8975 (0.0341)
Observed reflections [$I > 2\sigma(I)$]	6475
Data/restraints/parameters	8975/0/595
Goodness-of-fit on F^2	0.938
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0344$, $wR_2 = 0.0782$
R indices (all data)	$R_1 = 0.0548$, $wR_2 = 0.0840$
Data completeness	0.999
Largest peak and hole (e·Å ⁻³)	0.39(5) and -0.39(5)

Results and Discussion

Synthesis and identification

From the aqueous-ethanolic system Ni²⁺–*phen*–*fum*, under mild conditions, single crystals of [Ni(*phen*)₃]*fum*·9H₂O (**1**) were isolated and chemically characterized. Similar experimental conditions were used

to prepare $[\text{Ni}_2(\text{phen})_4(\text{fum})(\text{H}_2\text{O})_2]\text{fum} \cdot 16\text{H}_2\text{O}$ (Ma et al., 2003) and $[\text{Ni}(\text{phen})_3](\text{fum}) \cdot 2\text{H}_2\text{fum} \cdot 4\text{H}_2\text{O}$ (Lin and Zheng, 2004). The formed mother liquor exhibited a tendency towards jellification, so the formed crystals were separated immediately after their appearance which led to low yield of the product.

Spectroscopic characterization

Characteristic absorption bands in the IR spectrum of **1** (Fig. 1) were observed at 1578 and 1397 cm^{-1} ; these were ascribed to the asymmetric and symmetric carboxylate stretching vibrations $\nu(\text{COO})$ according to literature (Nakamoto, 1997). In the IR spectrum of the analogous complex $[\text{Ni}(\text{en})_3](\text{fum}) \cdot 3\text{H}_2\text{O}$ with ionic bonding of the fum^{2-} dianion, the corresponding absorption bands were found at very similar values of 1583 and 1395 cm^{-1} (Padmanabhan et al., 2008). The calculated value of $\Delta = 181 \text{ cm}^{-1}$ ($\Delta = \nu_{\text{as}}(\text{COO}) - \nu_{\text{s}}(\text{COO})$) for **1** is in line with the corresponding value of 188 cm^{-1} found for $[\text{Ni}(\text{en})_3](\text{fum}) \cdot 3\text{H}_2\text{O}$ (Padmanabhan et al., 2008), suggesting that the dicarboxylate dianion acts only as a counter ion; this was later corroborated by the results of X-ray structure analyses (see below). The well identifiable shoulder positioned at 3037 cm^{-1} can be assigned to $\nu(\text{C}_{\text{ar}}-\text{H})$ stretching vibrations due to the presence of aromatic rings. In the analogous complex $[\text{Ni}(\text{phen})_2]_2[\text{Ni}(\text{mnt})_2]_3 \cdot 2\text{DMF}$ ($\text{mnt} = 1,2\text{-dicyanovinylene-1,2-dithiolato}$, $\text{DMF} = \text{N,N-dimethylformamide}$), the corresponding weak band was observed at 3063 cm^{-1} (Wang et al., 2004). The broad strong absorption band observed around 3405 cm^{-1} corresponds well to $\nu(\text{OH})$ stretching vibrations for hydrogen bonded solvate water

molecules. The IR spectrum of **1** below 1300 cm^{-1} is rich mainly due to the presence of *phen* ligands and unambiguous assignment of the observed bands to various types of vibrations is difficult.

Crystal structure of $[\text{Ni}(\text{phen})_3](\text{fum}) \cdot 9\text{H}_2\text{O}$

Ionic crystal structure of $[\text{Ni}(\text{phen})_3](\text{fum}) \cdot 9\text{H}_2\text{O}$ (**1**) consists of $[\text{Ni}(\text{phen})_3]^{2+}$ complex cation, fumarate dianion and nine crystallographically independent molecules of crystal water (Fig. 2). Within the complex cation,

Tab. 2. Selected geometric parameters [\AA , $^\circ$] for $[\text{Ni}(\text{phen})_3](\text{fum}) \cdot 9\text{H}_2\text{O}$.

Ni1—N1	2.0822(14)	O4—C40	1.249(2)
Ni1—N2	2.0888(14)	C38—C37	1.499(2)
Ni1—N3	2.0965(14)	C38—C39	1.317(2)
Ni1—N4	2.0782(14)	C39—C40	1.502(2)
Ni1—N5	2.1167(14)	N1—Ni1—N2	80.09(6)
Ni1—N6	2.0802(14)	N3—Ni1—N4	79.78(5)
O1—C37	1.253(2)	N5—Ni1—N6	79.61(5)
O2—C37	1.250(2)	O1—C37—O2	124.66(16)
O3—C40	1.253(2)	O3—C40—O4	125.52(17)

the Ni(II) central atom is hexacoordinated by six nitrogen atoms from three chelate bonded *phen* molecules. Although the complex cation is chiral, both enantiomers are present in the crystal structure due to its centrosymmetric character. The same complex cation was found in analogous complexes $[\text{Ni}(\text{phen})_3](\text{succBr}_2) \cdot 7\text{H}_2\text{O}$ ($\text{H}_2(\text{succBr}_2) = 2,3\text{-dibromosuccinic acid}$) (Li et al., 2005) or $[\text{Ni}(\text{phen})_2(\text{phen-dione})][\text{Ni}(\text{phen})_3]$

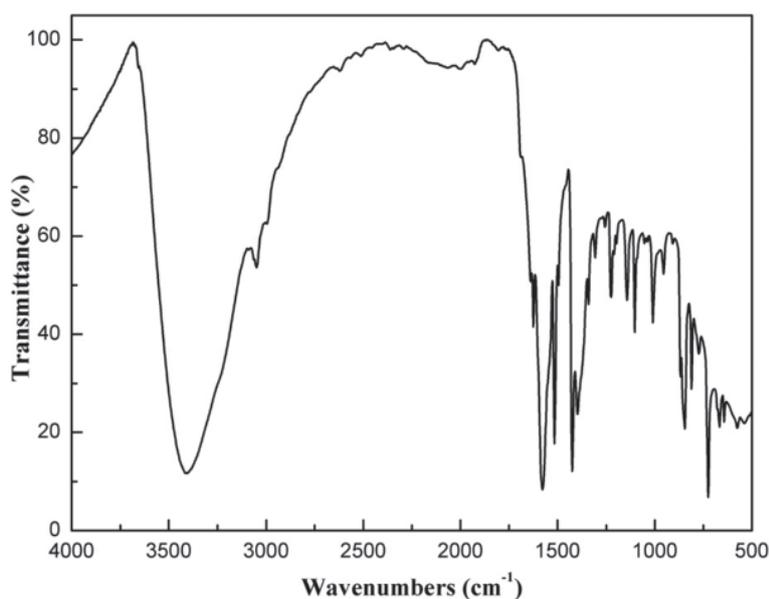


Fig. 1. FT-IR spectrum of $[\text{Ni}(\text{phen})_3](\text{fum}) \cdot 9\text{H}_2\text{O}$.

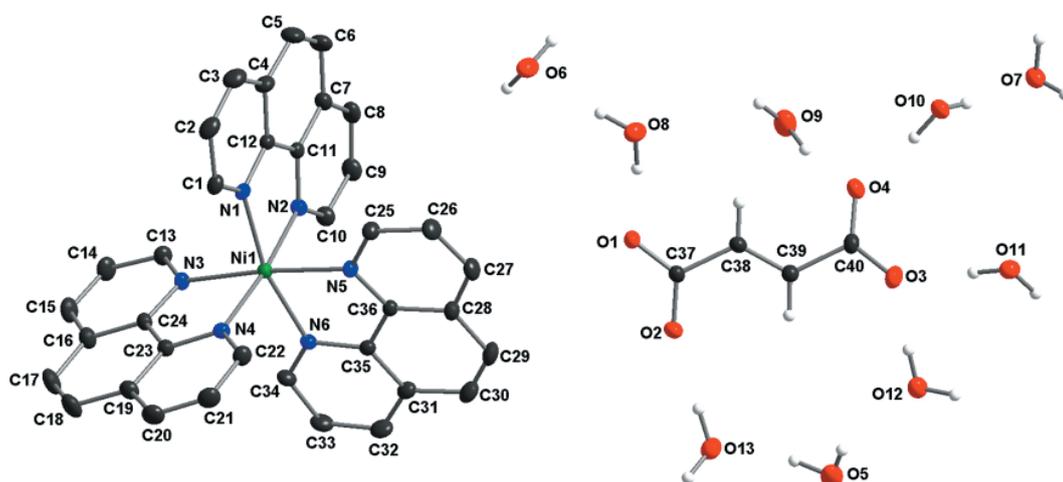


Fig. 2. Structure of $[\text{Ni}(\text{phen})_3](\text{fum}) \cdot 9\text{H}_2\text{O}$ with atoms numbering scheme. Thermal ellipsoids are drawn at the 30 % probability level. Hydrogen atoms from *phen* ligand are omitted for clarity.

$(\text{PF}_6)_4 \cdot \text{CH}_3\text{CN}$ (*phen-dione* = 1,10-phenanthroline-5,6-dione) (Hadadzadeh et al., 2012). The Ni—N bonds in **1** are within the range of 2.0782(14)–2.1167(14) Å (Table 2). Similar ranges for Ni—N bonds, 2.082(4)–2.194(5) Å and 2.081(6)–2.137(7), were reported for the already mentioned $[\text{Ni}(\text{phen})_3](\text{succBr}_2) \cdot 7\text{H}_2\text{O}$ (Li et al., 2005) and $[\text{Ni}(\text{phen})_2(\text{phen-dione})][\text{Ni}(\text{phen})_3](\text{PF}_6)_4 \cdot \text{CH}_3\text{CN}$ (Hadadzadeh et al., 2012), respectively. Fumarate dianion acts as a counter ion and its carboxylate groups are somewhat twisted out of the plane formed by the four carbon atoms C37—C40 as it can be seen from the values of the torsion angles O1—C37—C38—C39 and O3—C40—C39—C38, $-172.93(1)$ and $-159.45(1)^\circ$, respectively; this deviation from the planarity may reflect the tendency

to maximize the formation of hydrogen bonds (see below). The remaining geometric parameters of **1** correspond well to those observed of $[\text{Ni}(\text{phen})_3](\text{fum}) \cdot 2\text{H}_2\text{fum} \cdot 4\text{H}_2\text{O}$ (Lin and Zheng, 2004).

An outstanding feature of the presented structure **1** is the formation of a 2D supramolecular structure perpendicular to the *a* axis built of O—H...O type hydrogen bonds; fumarate dianions together with nine crystallographically independent solvate water molecules are involved in this structure (Figs. 3 and 4, Table 3). Within the hydrogen bonded layers, ten different hydrogen bonded ring systems can be distinguished and these can be described using the graph-set analysis (Bernstein et al., 1995); descriptors for the respective ring systems are (see also Fig. 3) : *R1*: $R_4^4(13)$, *R2*: $R_3^3(10)$, *R3*: $R_4^3(10)$,

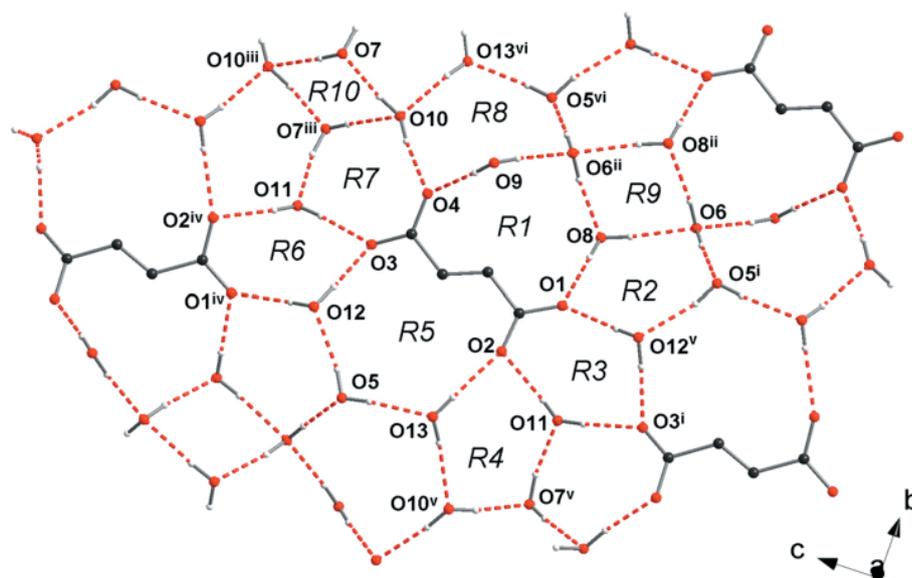


Fig. 3. A part of hydrogen bonded supramolecular layers in **1**. Symmetry codes: i: $x, 1/2 - y, z - 1/2$; ii: $1 - x, 1 - y, 1 - z$; iii: $1 - x, 1 - y, 2 - z$; iv: $x, 1/2 - y, 1/2 + z$; v: $1 - x, y - 1/2, 3/2 - z$; vi: $1 - x, y + 1/2, 3/2 - z$.

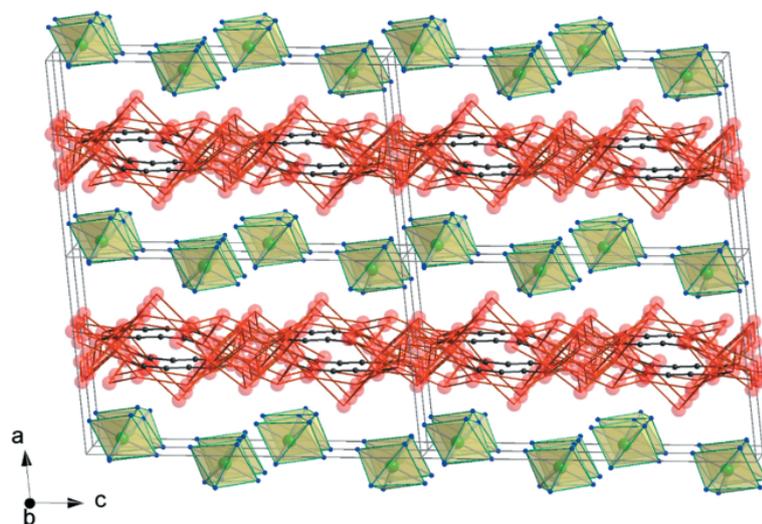


Fig. 4. Approximate crystal structure of **1** along *b* axis showing the hydrogen bonded hydrophilic host part of the structure (red balls are oxygen atoms, black balls are carbon atoms, brown lines are O—H...O hydrogen bonds) and embedded hydrophobic guest part of the structure formed by [Ni(phen)₃]²⁺ complex cations (light green octahedrons).

R4: $R_5^4(10)$, *R5*: $R_4^4(13)$, *R6*: $R_4^4(10)$, *R7*: $R_4^4(10)$, *R8*: $R_6^5(12)$, *R9*: $R_4^4(8)$, *R10*: $R_4^4(8)$. Similarly hydrogen bonded supramolecular layers with auxiliary anionic species were observed in [Ni(*bpy*)₃]Cl₂·5.5H₂O (*bpy*=2,2'-bipyridine; chloride anions are involved as anionic species) (Ruiz-Pérez et al., 2002), [Ni(*bpy*)₃] [Cu(CN)₃]·4.5H₂O (tricyanidocuprate(2-) anions are the anionic species) (Kočanová et al., 2010) or in [Ni(*phen*)₃](HB)₂·7H₂O (HB⁻ = diphenylglycolate; with HB⁻ anions as anionic species) (Covelo

et al., 2008). As a consequence of the formed supramolecular layers in **1**, the title compound can be viewed as a host-guest (HG) system in which the hydrophilic host part of the structure is built of hydrogen bonded water solvate molecules and fumarate dianions, while hydrophobic [Ni(*phen*)₃]²⁺ complex cations as guest species are enclosed between the formed layers (Fig. 4). The presented crystal structure thus displays some similarity with the well-know Hofmann-type clathrates in which

Tab. 3. Possible hydrogen bonds in **1** [Å, °].

D—H...A	D—H	H...A	D...A	D—H...A
O5—H51...O12	0.84(4)	1.93(4)	2.747(2)	162(4)
O5—H52...O13	0.84(4)	1.93(4)	2.771(2)	173(3)
O6—H61...O5 ⁱ	0.83(3)	1.86(3)	2.685(2)	177(3)
O6—H62...O8 ⁱⁱ	0.87(3)	1.91(3)	2.775(2)	172(3)
O7—H71...O10 ⁱⁱⁱ	0.79(3)	2.04(3)	2.824(2)	172(3)
O7—H72...O11 ⁱⁱⁱ	0.90(3)	1.79(3)	2.676(2)	168(2)
O8—H81...O1	0.84(3)	1.87(3)	2.710(2)	177(3)
O8—H82...O6	0.79(3)	2.03(3)	2.803(2)	171(3)
O9—H91...O4	0.79(3)	2.04(3)	2.828(2)	175(3)
O9—H92...O6 ⁱⁱ	0.90(3)	2.01(4)	2.900(3)	173(3)
O10—H101...O4	0.87(3)	1.87(3)	2.728(2)	170(3)
O10—H102...O7	0.86(3)	1.93(3)	2.776(2)	169(2)
O11—H112...O2 ^{iv}	0.79(3)	2.00(3)	2.788(2)	174(3)
O11—H111...O3	0.84(3)	1.93(3)	2.766(2)	175(3)
O12—H121...O3	0.88(3)	1.87(3)	2.741(2)	177(3)
O12—H122...O1 ^{iv}	0.78(3)	2.00(3)	2.781(2)	178(3)
O13—H131...O2	0.80(3)	2.01(3)	2.812(2)	177(3)
O13—H132...O10 ^v	0.84(3)	2.08(3)	2.916(2)	176(3)

Symmetry codes: i: $x, 1/2 - y, z - 1/2$; ii: $1 - x, 1 - y, 1 - z$; iii: $1 - x, 1 - y, 2 - z$; iv: $x, 1/2 - y, 1/2 + z$; v: $1 - x, y - 1/2, 3/2 - z$.

the aromatic guest molecules are enclosed between the cyanidometallate layers (Iwamoto, 1996). Additional much weaker hydrogen bonding interactions of the C—H···O type (C···O distances are from the range of 3.2040(4)–3.4555(4) Å and C—H···O angles are from the range of 138–166 °) link complex cations with the solvate water molecules.

Thermal analysis

Thermal curves of **1** are shown in Fig. 5. From the TG curve it follows that decomposition starts at 95 °C. The observed weight loss of 17.5 % in the temperature range of 95–195 °C corresponds well to the complete dehydration of **1** (calculated 18.5 % for nine water molecules from the formula unit). The DTA curve suggests that the observed dehydration is formed of three weak endothermic processes. Endothermic dehydration of the analogous complex $[\text{Ni}(\text{en})_3](\text{fum}) \cdot 3\text{H}_2\text{O}$ occurred in the similar temperature range of 90–165 °C (Padmanabhan et al., 2008) while $[\text{Ni}(\text{fum})] \cdot 4\text{H}_2\text{O}$ dehydrates at somewhat higher temperature from the range of 130–225 °C (Randhawa and Kaur, 2007). On the TG curve of **1** after its dehydration, a plateau in the temperature range of 195–220 °C can be seen; which is accompanied by a weak exothermic peak on the DTA curve at 210 °C suggesting a possible phase transition. The second mass loss of 21.7 % was observed in the temperature range of 200–290 °C; this weight loss corresponds well to the release of one *phen* ligand from the formula of **1** (calc. 20.6 %).

In the temperature range of 360–650 °C, a strongly exothermic process associated with the mass loss

of 52.4 % can be observed; the experimental mass loss corresponds well to the release (or decomposition) of the remaining organic part of the studied compound (calculated value is 54.2 %). The solid residue after thermal decomposition represents 8.4 % of the initial weight, which is in line with the assumed formation of NiO (calculated value is 8.5 %). The formation of NiO as the solid residue was also reported in case of thermal decomposition of $[\text{Ni}(\text{phen})(\text{fum})]$ (Černák et al., 2009), $[\text{Ni}(\text{fum})] \cdot 4\text{H}_2\text{O}$ (Randhawa and Kaur, 2007) and $[\text{Ni}(\text{en})_3](\text{fum}) \cdot 3\text{H}_2\text{O}$ (Padmanabhan et al., 2008).

Conclusions

Complex $[\text{Ni}(\text{phen})_3](\text{fum}) \cdot 9\text{H}_2\text{O}$ was synthesized and chemically and spectroscopically characterized. Crystal structure of **1** is ionic and it is formed of $[\text{Ni}(\text{phen})_3]^{2+}$ complex cations with a hexacoordinated Ni(II) atom, *fum* counter dianion and nine water molecules of crystallization. Water molecules and *fum*²⁻ dianions interact *via* hydrogen bonds forming a 2D supramolecular structure with complex cations embedded between the hydrophilic layers, which enables considering the presented crystal structure as a host-guest system built of hydrophilic hydrogen bonded host part and hydrophobic guest complex cations. A study of the thermal properties has shown that dehydration is the first step of thermal decomposition.

Supplementary materials

Crystallographic data for the compound have been deposited with the Cambridge Crystallo-

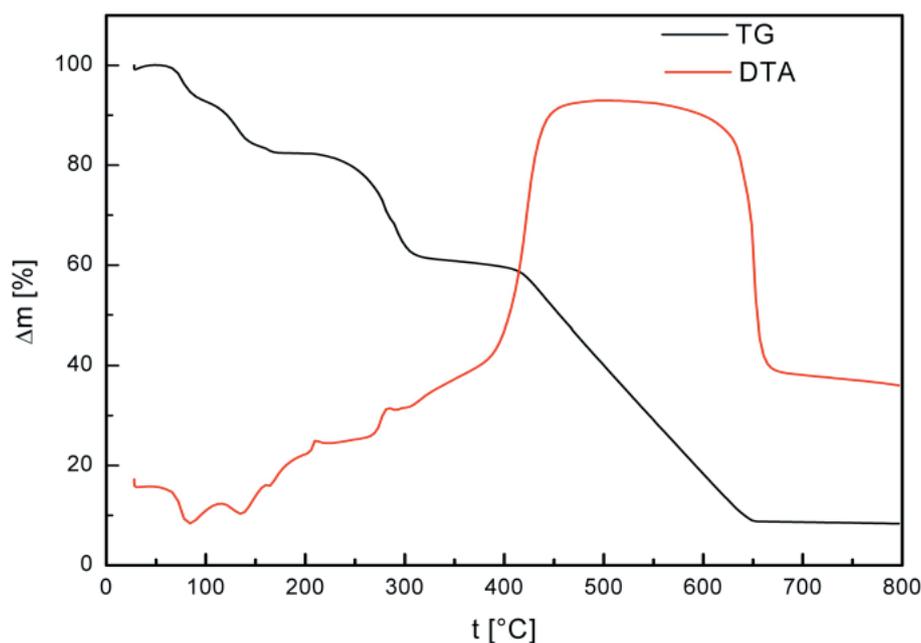


Fig. 5. Thermal curves for $[\text{Ni}(\text{phen})_3](\text{fum}) \cdot 9\text{H}_2\text{O}$.

graphic Data Centre, CCDC 1542632. Copies of the information may be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB21EZ, UK (fax: +44-1223-336033; e-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

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