

Scientific paper

Preparation and Characterization of a New Example of a Double Salt of Nickel(II) Complexes

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Abstract

A new double salt of nickel(II) complexes, formulated as, $[\text{Ni}(\text{bipy})(\text{H}_2\text{O})_4][\text{Ni}(\text{H}_2\text{O})_6][\text{Ni}(\text{pydc})_2]_2 \cdot 6\text{H}_2\text{O}$ (**1**), (pydc = pyridine-2,6-dicarboxylate anion, bipy = 2,2'-bipyridine) has been hydrothermally synthesized. Complex was characterized by FT-IR spectroscopy, elemental analysis and X-ray diffraction studies. The compound **1** consists of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, $[\text{Ni}(\text{bipy})(\text{H}_2\text{O})_4]^{2+}$, two symmetry-independent anionic complexes $[\text{Ni}(\text{pydc})_2]^{2-}$ and six co-crystallized water molecules. In the crystal structure of compound **1**, the formation of extensive O–H...O hydrogen bonds between uncoordinated water molecules and cationic or anionic complexes play important roles in stabilizing the corresponding lattice and formation of 3-dimensional networks.

Keywords: Nickel(II) Complexes, Supramolecular, Hydrothermal Synthesis, Crystal Structure,

1. Introduction

Several types of non-covalent forces, such as hydrogen bonding,^{1–4} π - π stacking⁵ and electrostatic⁶ interactions are of great interest in constructing extended supramolecular networks. Such non-covalent interactions play key roles in the construction of various architectures for molecular self assembly and aggregation.^{7–9} In the past decade metallosupramolecular species, containing transition metals and organic ligands with novel structures and properties have been rapidly developed due to their fascinating molecular structure and potential applications as functional materials.^{10,11} Aggregation of organic molecules and metal ions can lead to formation of multi-dimensional networks which contain channels or cavities of various sizes and shapes.^{12,13} The coordination geometry of the metal ion, solvent molecules, the counter ions and the method of synthesis are influenced in final metallosupramolecular architectures.¹⁴ As known, ligands containing oxygen or hybrid oxygen-nitrogen atoms, especially multicarboxylate ligands can act as hydrogen-bond donor or acceptor and aromatic systems such as those of 2,2'-bipyridine and 1,10-phenanthroline can be stabilized by stacking

interactions involving the π systems. Recently we reported some transition metal supramolecular structure with polycarboxylate ligands^{15–17} and in this communication, we wish to report the hydrothermal synthesis and characterization of a supramolecular double salt Ni^{II} complex, $[\text{Ni}(\text{bipy})(\text{H}_2\text{O})_4][\text{Ni}(\text{H}_2\text{O})_6][\text{Ni}(\text{pydc})_2]_2 \cdot 6\text{H}_2\text{O}$ (**1**). In the solid state, complex forms a novel three-dimensional (3D) network resulting due to intermolecular hydrogen-bonding interactions.

2. Experimental

2.1. Materials and Instrumentations

The starting materials $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, pyridine-2,6-dicarboxylic acid and 2,2'-bipyridine were all purchased from Merck, Germany. IR spectra were recorded using FT-IR Spectra Bruker Tensor 27 spectrometer (KBr pellets, 4000–400 cm^{-1}). Elemental analyses were performed using a Costech ECS 4010 CHNS-O analyzer.

2.2. Synthesis of the Complex

Pyridine-2,6-dicarboxylic acid (0.167 g, 1 mmol)

was dissolved in 10 ml deionized water containing NaOH (0.08 g, 2 mmol) and stirred for 30 min at room temperature. Then an aqueous solution of $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (0.29 g, 1 mmol) and 2,2'-bipyridine (0.078 g, 0.5 mmol) was added to above-mentioned solution. Reaction mixture was placed in a Parr-Teflon lined stainless steel vessel. It was sealed and heated to 120 °C for 14 h. Blue crystalline complex was obtained upon slow cooling (Yield 79% based on dipicolinic acid).

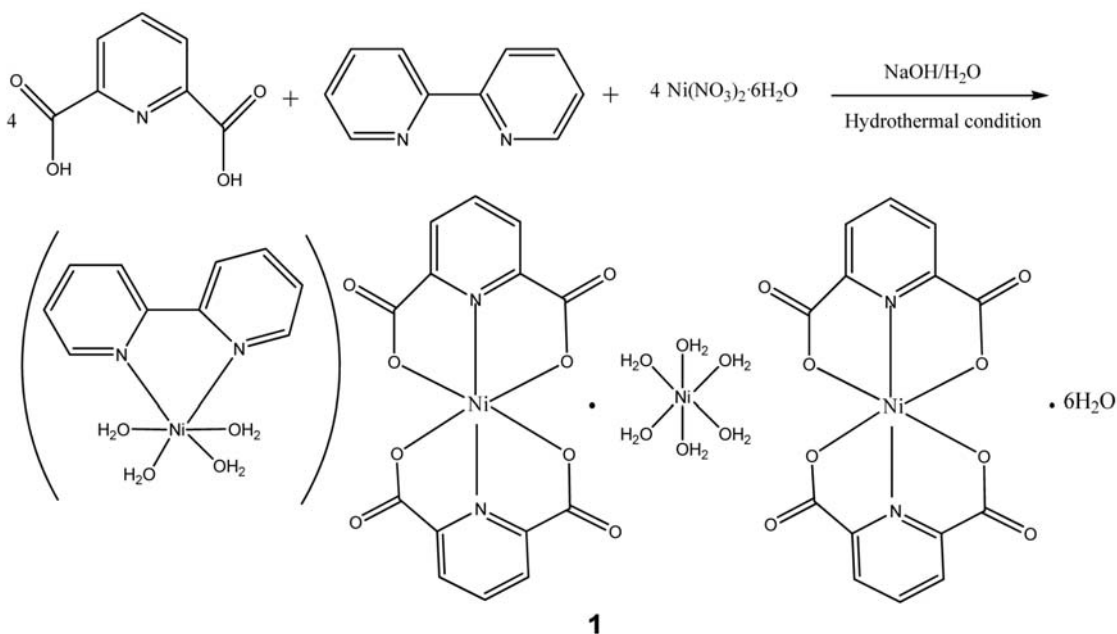
IR (KBr) $\tilde{\nu}$ (cm^{-1}): 3398 (b), 1602 (s), 1436 (s), 1385 (s), 1278 (m), 1183 (w), 1021(w), 839 (m), 764 (s), 692 (w). Anal. For $\text{C}_{38}\text{H}_{52}\text{N}_6\text{Ni}_4\text{O}_{32}$ (1339.70): Calcd. C 34.04, H 3.88, N 6.27; Found C 34.08, H 3.78, N 6.19.

2. 3. X-Ray Crystallography

X-ray structure analysis of suitable single crystal was carried out on a Bruker Smart 1000 CCD area detector (MoK α radiation, graphite monochromator, $\lambda = 0.71073\text{\AA}$, at 120(2) K). The semi-empirical absorption correction was applied for **1**. The crystal structure of **1** was solved by direct methods and refined by a full-matrix least-squares based on F^2 using the program SHELXTL 5.1.¹⁸ Hydrogen atoms were refined in the isotropic approximation according to a riding model with U_{iso} equal to 1.5 U_{eq} of the carrier atoms. Programs used were SHELXS 97,¹⁹ SHELXL 97²⁰ and PLATON 98.²¹ The molecular graphics were done with PLATON 98 and MERCURY (Version 2.3).²¹ Details of the crystal structure analysis are shown in Table 1.

3. Results and Discussion

Compound **1** was prepared according to equation 1.



1

3. 1. Crystal Structure

Figure 1 illustrates the principle structural features of **1** and selected bond lengths and angles are given in table 2. **1** consists of two symmetric-independent $[\text{Ni}(\text{pydc})_2]^{2-}$ complexes (Fig. 2a), one $[\text{Ni}(\text{bipy})(\text{H}_2\text{O})_4]^{2+}$ (Fig. 2b) and one $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ (Fig. 2c) cationic complexes. Two independent $[\text{Ni}(\text{pydc})_2]^{2-}$ complexes are different only in relevant bond lengths and angles (important data are listed in Table 2 for comparison). The nickel(II) ions in $[\text{Ni}(\text{pydc})_2]^{2-}$ complexes are six-coordinated by two tridentate pydc^{2-} anions and the geometry of the resulting NiN_2O_4 coordination can be described as a distorted octahedral. The bond angles around Ni1 and Ni2 involving *trans* pairs of donor atoms are in the range of 155.08(10)–177.98(14)° and 154.86(10)–176.55(14)° respectively and deviate from linearity. For the *cis* pairs of donor atoms this range is 77.44(12)–103.52(12)° for Ni1 and 77.51(12)–104.23(12)° for Ni2. As is shown in table 1, compound crystallizes in the monoclinic $P 2_1$ space group. While all molecular species present are apparently achiral, the crystal packing is chiral and it is a less-common case of achiral compound crystallizing in a chiral space group.

In the $[\text{Ni}(\text{bipy})(\text{H}_2\text{O})_4]^{2+}$ cationic complex, Ni(II) atom is coordinated by four oxygen atoms of water molecules and two nitrogen atoms of bidentate 2,2'-bipyridine ligand. The environment of the metal center in $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ can be described as octahedral. Uncoordinated water molecules occupy general positions in the cell. The most important features of the crystal structure of compound **1** are a number of O–H...O hydrogen bonds between cationic and anionic fragments, uncoordinated water molecules and carboxylate groups (table 3). These hydrogen bonds play important role for the formation of

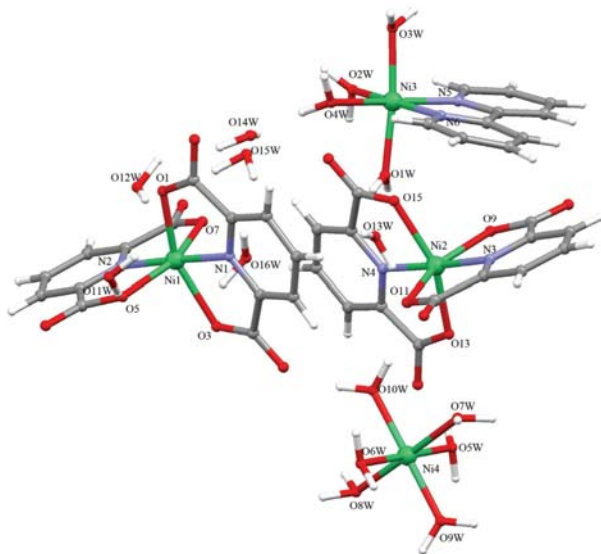


Fig. 1. A general view of compound **1**.

double salt Ni(II) complexes and an interesting supramolecular structure (Fig. 3).

All Ni–N and Ni–O distances in **1** are comparable with the corresponding values reported for nickel(II) species having the same coordinating atoms.^{22–24}

3. 2. IR Spectra

The pattern of IR spectra of complex shows two sets of vibrations due to the aqua and dipicolinate ligands. The carboxylate ion may coordinate to a metal atom in one of the unidentate, bidentate or bridging mode.²⁵ In the spectrum of **1**, the band associated to the antisymmetric stretching vibrational mode, $\nu_{as}(-\text{COO})$, appears at 1602 cm^{-1} (1700 cm^{-1} in the spectrum of free pydcH_2), together with the $\nu_s(-\text{COO})$ band at 1385 cm^{-1} (1326 cm^{-1} in the spectrum of free pydcH_2). The value of $\Delta(\nu_{as}(-\text{COO}) - \nu_s(-\text{COO}))$ amounts 217 cm^{-1} , indicating the presence of carboxylate group coordinated to nickel(II) ion in unidentate mode^{25–27} which is in agreement with the crystal structure of **1**. The IR spectra of **1** shows broad strong bands at the region $3400\text{--}3000\text{ cm}^{-1}$, which could be related to the existence of O–HO hydrogen bonding between water molecules.²⁸ Absorptions typical of coordinated 2,2'-bipyridine can be observed at $700\text{--}840$ and $1400\text{--}1600\text{ cm}^{-1}$.^{29,30}

4. Acknowledgements

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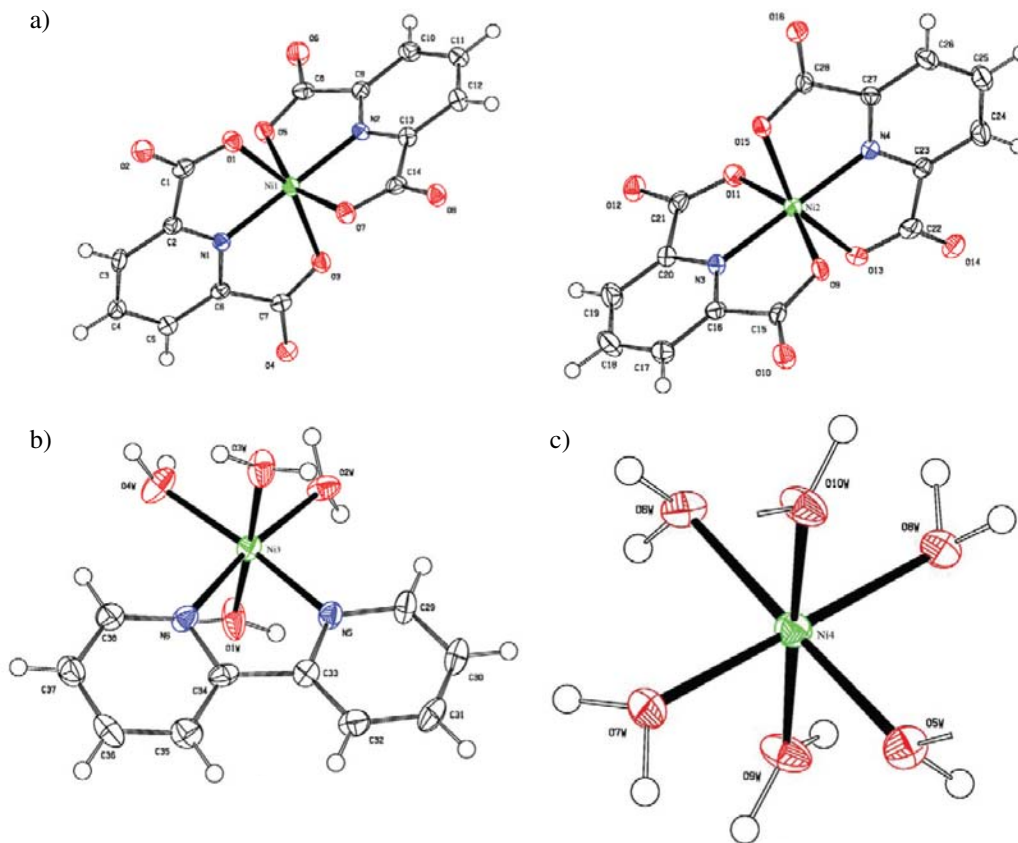


Fig. 2. a) A view of two symmetry-independent $[\text{Ni}(\text{pydc})_2]^{2-}$, b) Molecular structure of the $[\text{Ni}(\text{bipy})(\text{H}_2\text{O})_4]^{2+}$ cationic complex showing the atom-numbering scheme c) Molecular structure of $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$, in representation of atoms by thermal ellipsoid at the 50% probability level.

Table 1. Crystal data of $[\text{Ni}(\text{bipy})(\text{H}_2\text{O})_4][\text{Ni}(\text{H}_2\text{O})_6][\text{Ni}(\text{pydc})_2] \cdot 6\text{H}_2\text{O}$.

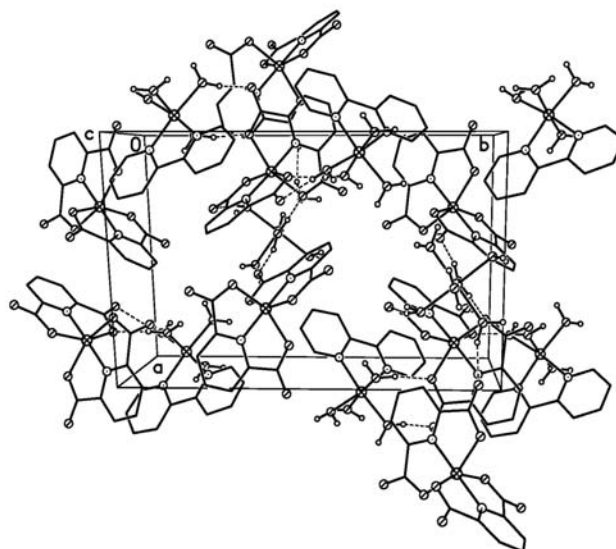
Compound	1
Empirical formula	$\text{C}_{38}\text{H}_{52}\text{N}_6\text{Ni}_4\text{O}_{32}$
Formula mass	1339.70
Crystal size (mm)	$0.35 \times 0.25 \times 0.25$
Crystal system	Monoclinic
Space group	$P 2_1$
a [Å]	12.2114(8)
b [Å]	18.0287(13)
c [Å]	12.3438(9)
β [°]	109.317(5)
Volume Å ³	2564.6(3)
Z	2
$D_{\text{calcd.}}$ [g cm ⁻³]	1.735
Absorption correction	Semi-empirical from equivalents
$F(000)$	1380
Temperature [K]	120(2)
Index range	h -16→16
	k -24→24
	l -16→16
Reflections collected	24694
Unique reflections (R_{int})	13128 (0.0362)
Reflections with $F_o > 4\sigma(F_o)$	9117
Parameters	726
R_1	0.0430
wR_2 (all data)	0.0930 ^a

$$^a w = 1/[\sigma^2(F_o^2) + (0.0327P)^2 + 0.3100P],$$

$$P = [\max(F_o^2, 0) + 2F_c^2]/3$$

Table 2. Selected bond lengths (Å) and bond angles (°) for $[\text{Ni}(\text{bipy})(\text{H}_2\text{O})_4][\text{Ni}(\text{H}_2\text{O})_6][\text{Ni}(\text{pydc})_2] \cdot 6\text{H}_2\text{O}$

Ni1-N2	1.960(3)	Ni(3)-O(3W)	2.041(3)
Ni1-N1	1.960(3)	Ni(3)-O(2W)	2.049(3)
Ni1-O1	2.116(3)	Ni(3)-O(4W)	2.065(3)
Ni1-O5	2.116(3)	Ni(3)-O(1W)	2.052(3)
Ni1-O7	2.144(3)	Ni(4)-O(5W)	2.048(3)
Ni1-O3	2.172(3)	Ni(4)-O(10W)	2.051(3)
Ni2-N3	1.969(3)	Ni(4)-O(9W)	2.051(3)
Ni2-N4	1.967(3)	Ni(4)-O(6W)	2.054(3)
Ni2-O13	2.114(3)	Ni(4)-O(7W)	2.054(3)
Ni2-O9	2.118(3)	Ni(4)-O(8W)	2.061(3)
Ni2-O11	2.125(3)	N1-Ni1-N2	177.98(14)
Ni2-O15	2.146(3)	O7-Ni1-O5	156.18(10)
Ni3-N5	2.038(3)	O1-Ni1-O3	155.08(10)
Ni3-N6	2.067(3)	N4-Ni2-N3	176.55(14)
		O9-Ni2-O11	155.36(10)
		O13-Ni2-O15	154.86(10)
		N5-Ni3-O4W	173.43(13)
		O2W-Ni3-N6	172.37(12)
		O3W-Ni3-O1W	174.11(14)
		O10W-Ni4-O9W	179.01(14)
		O5W-Ni4-O6W	178.67(12)
		O7W-Ni4-O8W	178.89(13)

**Fig. 3.** Crystal packing fragment along c crystal axes. Only Ni-containing species are depicted for clarity. Hydrogen bonds are shown with dashed lines.**Table 3.** Selected hydrogen bonds for $[\text{Ni}(\text{bipy})(\text{H}_2\text{O})_4][\text{Ni}(\text{H}_2\text{O})_6][\text{Ni}(\text{pydc})_2] \cdot 6\text{H}_2\text{O}$ [Å and °].

D-H...A	d(D-H)	d(H...A)	d(D...A)	<(DHA)
O(1W)-H(1WA)...O(15)#1	0.95	1.81	2.752(4)	170
O(2W)-H(2WB)...O(12W)#2	0.95	1.89	2.758(4)	151
O(3W)-H(3WA)...O(9)#3	0.95	1.83	2.748(4)	162
O(3W)-H(3WB)...O(11W)#4	0.95	1.85	2.701(7)	148
O(4W)-H(4WA)...O(10)#3	0.95	1.75	2.697(4)	173
O(6W)-H(6WA)...O(2)#5	0.95	1.92	2.867(4)	173
O(6W)-H(6WB)...O(16W)#6	0.95	1.76	2.704(4)	177
O(12W)-H(12W)...O(2)#7	0.95	1.84	2.786(4)	172
O(13W)-H(13W)...O(3)#6	0.95	1.84	2.794(4)	179
O(8W)-H(8WA)...O(15W)#9	0.95	1.81	2.758(4)	171
O(15W)-H(15V)...O(14)#6	0.95	1.90	2.841(4)	173

Symmetry transformations used to generate equivalent atoms:

#1 x, y, z #2 $-x+1, y+1/2, -z+2$ #3 $-x, y+1/2, -z+1$ #4 $x-1, y, z$ #5 $x, y, z-1$
 #6 $-x+1, y+1/2, -z+1$
 #7 $-x+1, y-1/2, -z+2$ #9 $-x+1, y-1/2, -z+1$ #10 $x+1, y, z$

5. Appendix A. Supplementary material

Further details can be obtained free of charge on application to the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, U. K. [Fax. (internat.) +44 (0)1223 336033; E-mail: deposit@ccdc.cam.ac.uk] quoting the depository number CCDC 742665 for **1**.

6. References

1. C. M. R. Juan, B. Lee, *Coord. Chem. Rev.* **1999**, *183*, 43–80.
2. T. N. Guru Row, *Coord. Chem. Rev.* **1999**, *183*, 81–100.
3. G. R. Desiraju, *Acc. Chem. Res.* **1996**, *29*, 441–449.
4. S. S. Kuduva, D. C. Craig, A. Nangia, G. R. Desiraju, *J. Am. Chem. Soc.* **1999**, *121*, 1936–1944.
5. I. Unamuno, J. M. Gutiérrez-Zorrilla, A. Luque, P. Román, L. Lezama, R. Calvo, T. Rojo, *Inorg. Chem.* **1998**, *37*, 6452–6460.
6. D. S. Reddy, K. Panneerselvam, T. Pilati, G. R. Desiraju, *J. Chem. Soc., Chem. Commun.* **1993**, 661–720.
7. J. M. Lehn, *Supramolecular Chemistry*, VCH, Weinheim, **1995**.
8. G. M. Whitesides, J. P. Mathias, C.T. Seto, *Science*, **1991**, *254*, 1312–1319.
9. G. M. Whitesides, B. Grzybowski, *science*, **2002**, *295*, 2418–2421.
10. R-Q. Zou, X.-H. Bu, M. Du, Y.-X. Sui, *J. Mol. Struct.* **2004**, *707*, 11–15.
11. L. J. Zhang, J. Q. Xu, Z. Shi, W. Xu, T. G. Wang, *Dalton Trans.* **2003**, 1148–1152.
12. P. J. Hagrman, D. Hagrman, J. Zubieta, *Angew. Chem., Int. Ed.*, **1999**, *38*, 2639–2684.
13. S. R. Batten, R. Robson, *Angew. Chem., Int. Ed.*, **1998**, *37*, 1460–1494.
14. B. Moumita, D. M. Jason, M. Samiran, *Struct. Chem.* **2007**, *18*, 9–13.
15. M. Tabatabaee, M. A. Sharif, F. Vakili, S. Saheli, *J. Rare Earth.* **2009**, *27*, 356–361.
16. M. Tabatabaee, F. Abbasi, B.-M. Kukovec, N. Nasirizadeh, *J. Coord. Chem.* **2011**, *64*, 1718–1728.
17. M. Tabatabaee, V. Razavimahmoudabadi, B.-M. Kukovec, M. Ghassemzadeh, B. Neumüller, *J. Inorg. Organomet. Polym.* **2011**, *21*, 450–457.
18. G. M. Sheldrick, SHELXTL v. 5.10, Structure Determination Software Suite, Bruker AXS, Madison, Wisconsin, USA (1998b).
19. G. M. Sheldrick, *Acta Crystallogr.*, **2003**, A64, 112.
20. A. L. Spek *PLATON 98*, Utrecht, **1998**.
21. C. F. Macrae, I. J. Bruno, J. A. Chisholm, P. R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P. A. Wood. *J. Appl. Crystallogr.*, **2008**, *41*, 466–445.
22. H. Aghabozorg, Z. Bahrami, M. Tabatabaie M. Ghadermazi, J. Attar Gharamaleki, *Acta Crystallogr.*, **2007**, E63, m2022.
23. M. Tabatabaee, *Acta Crystallogr.*, **2010**, E66, m647–m648.
24. Y. G. Li, D. H. Shi, H. L. Zhu, H. Yan, S. W. Ng, *Inorg. Chim. Acta*, **2007**, *360*, 2881–2889.
25. K. Nakamoto “Infrared and Raman Spectra of Inorganic and Coordination Compounds”, 3rd edn. Interscience-Wiley, New York, **1978**, 233.
26. G. B. Deacon, R. J. Philips, *Coord. Chem. Rev.* **1980**, *33*, 227–250.
27. M. Tabatabaee, M. Tahriri, M. Tahriri, Y. Ozawab, B. Neumüller, H. Fujioka, K. Toriumi, *Polyhedron*, **2012**, *33*, 336–340.
28. H. Aghabozorg, E. Sadrkhanlou, A. Shokrollahi, M. Ghaedi, M. Shamsipur, *J. Iran. Chem. Soc.* **2009**, *6*, 55–70.
29. A. A. Schilt, R. C. Taylor, *J. Inorg. Nucl. Chem.* **1959**, *9*, 211–221.
30. R. G. Inskeep, *J. Inorg. Nucl. Chem.* **1963**, *24*, 763–776.

Povzetek

S hidrotermalno sintezo smo pripravili dvojno sol dvovalentnega niklja s formulo $[\text{Ni}(\text{bipy})(\text{H}_2\text{O})_4][\text{Ni}(\text{H}_2\text{O})_6][\text{Ni}(\text{pydc})_2] \cdot 6\text{H}_2\text{O}$, (**1**), (pydc = piridin-2,6-dikarboksilatni anion, bipy = 2,2'-bipiridin). Spojino smo okarakterizirali s FT-IR spektroskopijo, elementno analizo in rentgensko strukturno analizo na monokristalu. Spojino **1** tvorijo kationi $[\text{Ni}(\text{H}_2\text{O})_6]^{2+}$ in $[\text{Ni}(\text{bipy})(\text{H}_2\text{O})_4]^{2+}$, dva simetrijsko neodvisna kompleksna aniona $[\text{Ni}(\text{pydc})_2]^{2-}$ in šest molekul kristalne vode. V kristalni strukturi spojine **1** so prisotne številne vodikove vezi tipa O–H...O med nekoordiniranimi molekulami vode ter kompleksnimi kationi in anioni, ki imajo pomembno vlogo pri stabilizaciji kristalne strukture in nastanku 3-dimenzionalne mreže.