

Scientific paper

Synthesis, Crystal Structure and Electrochemical Behavior of Two New Ni-based Complexes: $[\text{Ni}_2(\text{ttpy})_2(\text{SCN})_4]$ and $[\text{Ni}(\text{ttpy})_2](\text{CH}_3\text{OH})_2$ (**2I**)

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Abstract

A simple synthetic procedure has been used to prepare two new nickel(II) complexes $[\text{Ni}_2(\text{ttpy})_2(\text{SCN})_4]$, (**1**) and $[\text{Ni}(\text{ttpy})_2](\text{CH}_3\text{OH})_2$ (**2I**), (**2**) from 4'-p-tolyl-2,2':6',2''-terpyridine (ttpy) ligand, potassium thiocyanate, and potassium iodide in good yields. The single crystal X-ray analyses reveal that the metals in these complexes are sixfold coordinated with M:L ratio of 1:1 and 1:2 for (**1**) and (**2**), respectively. In both complexes, the Ni(II) has distorted octahedral geometry including N_5S and N_6 environments. Versatile interactions in supramolecular level containing coordinative bonding, I...H, and N...H hydrogen bonding, π - π stacking play considerable roles in forming crystal packing of (**1**) and (**2**). From obtained data it is concluded that differences in coordination abilities, of used counterions, cause the formation of complexes with 1:1 or 1:2 ratio of metal and ligand. Electrochemical behaviors of the both complexes were investigated.

Keywords: Ni(II) complexes, 2,2':6',2''-terpyridine, Single crystal structure.

1. Introduction

The terpyridine molecule contains three nitrogen atoms and can therefore act as a tridentate ligand. It has been extensively studied as an outstanding complexing ligand for a wide range of transition metal ions.¹⁻² Many 2,2':6',2''-terpyridine derivatives have been used as tridentate ligands in combination with bipyridine derivatives for dye sensitized solar cells. Polydentate ligands, containing N-donor heterocyclic rings, have covered extra dimension in the realm of coordination chemistry. Terpyridine transition metal complexes have wide ranges of utilities in the field of photochemistry, biological activities and often have unusual electronic, photophysical and/or structural properties.¹⁻⁹ The 4'-position on terpyridine offers a

broad range of substituents that allows us to change the inductive influence to a great extent.³ Therefore, in recent decades, the metal coordination chemistry of 2,2':6',2''-terpyridine and its substituted derivatives, such as 4'-p-tolyl-2,2':6',2''-terpyridine (ttpy) have received a great deal of attention.⁴⁻⁷ In the case of nickel(II) adducts of tpy, the lability of the d^8 metal centre leads to additional complications, although a number of general features emerge.⁸⁻⁹ The thermal decomposition of $[\text{Ni}(\text{tpy})_2]\text{X}_2$ (X=halide) leads to five coordinate complexes $[\text{Ni}(\text{tpy})\text{X}_2]$,¹⁰⁻¹³ which may also be obtained directly from NiX_2 and tpy under a variety of conditions.¹⁰⁻¹⁵ In contrast, the $\{\text{Ni}(\text{tpy})\text{X}_2\}$ specie obtained from the reaction of tpy with $[\text{NiX}_4]^{2-}$ is correctly formulated as $[\text{Ni}(\text{tpy})_2][\text{NiX}_4]$.¹⁶⁻¹⁷ Under the other conditions, hydrated six-coordinate spe-

cies such as $[\text{Ni}(\text{tpy})\text{Cl}(\text{H}_2\text{O})_2]\text{Cl} \cdot n\text{H}_2\text{O}$, have been isolated and structurally characterized.¹⁸ Because of their redox or photophysical properties, many of the metal complexes developed through the use of the ligands tpy and 4'-substituted-tpy are of importance.^{8–10,17 and 19–23}

This article stems from our interest in the coordination chemistry of 4'-p-tolyl-2,2':6',2''-terpyridine (ttpy).²⁴ We report on the synthesis, structure and characterization of two new Ni(II) complexes with the ttpy ligand: $[\text{Ni}_2(\text{ttpy})_2(\text{SCN})_4]$ (**1**) and $[\text{Ni}(\text{ttpy})_2](\text{CH}_3\text{OH})_2$ (**2**). Cyclic voltammetry of complexes **1** and **2** were studied.

2. Experimental

2.1. Reagents and Instrumentation

4'-p-tolyl-2,2',6',2''-terpyridine ligand (ttpy) is commercially available from Aldrich. All other solvents and reagents were of analytical grade and used without further purification. Infrared (FTIR) spectra were recorded using KBr discs on a Shimadzu FT-IR model Prestige 21 spectrometer. Melting points were determined using an electrothermal apparatus and were uncorrected. The UV-Vis spectra in 200–900 nm range were obtained in CH_3CN on a Perkin-Elmer lambda 25 spectrophotometer. Cyclic voltammograms (CVs) were obtained using an Autolab modular electrochemical system (Ecochimie, Utrecht, The Netherlands) equipped with a PGSTAT 20 module and driven by GPES (Ecochimie) in conjunction with a three-electrode system and a personal computer for data storage and processing. An Ag/Ag Cl (Saturated KCl)/3M KCl reference electrode, a Pt wire (counter electrode) and a glassy carbon working electrode, (Metrohm 0.0314 cm^2) were employed for the electrochemical studies. Voltammetric measurements were performed at room temperature in acetonitrile solution with 0.1 M tetrabutylammonium perchlorate as a supporting electrolyte.

2.2. Synthesis of Ni(II) Complexes

2.2.1. Synthesis of complex $[\text{Ni}_2(\text{ttpy})_2(\text{SCN})_4]$ (**1**)

The Ni(II) complex was prepared by branch tube method: ttpy (0.132 g, 0.5 mmol) and potassium thiocyanate (0.0996 g, 1.0 mmol) were placed in one arm of a branched tube and nickel acetate tetrahydrate (0.124 g, 0.5 mmol) in the other. Methanol was carefully added to fill both arms, then the tube was sealed and the ligand-containing arm immersed in a bath at 60 °C while the other was at ambient temperature. After eight days, brown crystals had deposited in the cooler arm which were filtered off, washed with acetone and air dried (yield 50%), m.p. 278 °C. *Anal. Calc.* for calculated $\text{C}_{44}\text{H}_{34}\text{N}_{10}\text{S}_4\text{Ni}_2$: C, 58.75; H, 3.45; N, 14.06. Found: C, 58.46; H, 3.38; N, 14.13%. IR (KBr) (ν_{max} , cm^{-1}): 3032 (C-H, arom); 2875 (C-H, aliph); 1470–1601 (C=C, arom); 1543 (C=N, Py); 2090 (SCN⁻).

2.2.2. Synthesis of complex

$[\text{Ni}(\text{ttpy})_2](\text{CH}_3\text{OH})_2$ (**2**) (**2**)

Complex **2** was prepared in the same way as complex **1** using potassium iodide in place of potassium thiocyanate. After five days, light brown crystals had deposited in the cooler arm which were filtered off, washed with acetone and air dried (yield 68%), m.p. 232 °C (dec.). *Anal. Calc.* for calculated $\text{C}_{46}\text{H}_{42}\text{I}_2\text{N}_6\text{NiO}_2$: C, 53.98; H, 4.14; N, 8.21. Found: C, 53.64; H, 4.27; N, 8.23%. IR (KBr) (ν_{max} , cm^{-1}): 3036 (C-H, arom); 2925 (C-H, aliph); 1467–1611 (C=C, arom); 1548 (C=N, Py).

2.3. X-Ray Crystallography

2.3.1. Structure Determination

Data collection for X-ray crystal structure determinations was performed on a Bruker Kappa Apex II diffractometer using graphite-monochromated Mo- $\text{K}\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$). The data were corrected for Lorentz and polarization effects. An empirical absorption correction based on crystal-shape optimization was applied for all data. The programs used in this work are Bruker Saint Plus, including X-RED and X-Shape for data reduction and absorption correction, and the WinGX suite of programs, including, SIR-92 and SHELXL-97 for structure solution and refinement.²⁵ The position and isotropic thermal parameters for hydrogen atoms were fixed. Materials for publication were prepared using Diamond, Mercury and ORTEP-3^{26–28} The summary of the crystal data, experimental details and refinement results of **1**, **2** are listed in Table 1.

3. Results and Discussion

The reaction of nickel acetate tetrahydrate with 4'-p-tolyl-2,2':6',2''-terpyridine (ttpy), Fig. 1., in the presence of potassium thiocyanate or potassium iodide in methanol yielded crystalline materials formulated as $[\text{Ni}_2(\text{ttpy})_2(\text{SCN})_4]$ (**1**), and $[\text{Ni}(\text{ttpy})_2](\text{CH}_3\text{OH})_2$ (**2**) (**2**), respectively. Crystals of complex **2** were air sensitive and should remain within solvent.

The IR spectra of both complexes show absorption bands resulting from the skeletal vibrations of aromatic rings in the 1400–1601 cm^{-1} range.^{29–30} A relatively weak absorption band around 3038–3056 cm^{-1} is due to the C-H

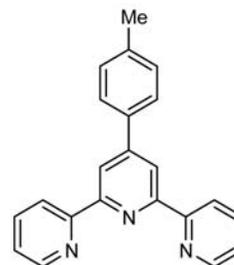


Fig. 1. Structure of 4'-p-tolyl-2,2':6',2''-terpyridine

modes of aromatic rings bonds and in the region 505–1093 cm^{-1} is due to the bending vibration of C-H group in or out the aromatic plane, and ring deformation absorptions of ligands in the complex. The strong peak in 2090 cm^{-1} for **1** assigned to 1,3- μ -thiocyanate anion and 2038 cm^{-1} is indicative of N-terminal coordination to the Ni(II) center.^{29–32}

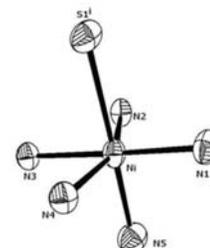
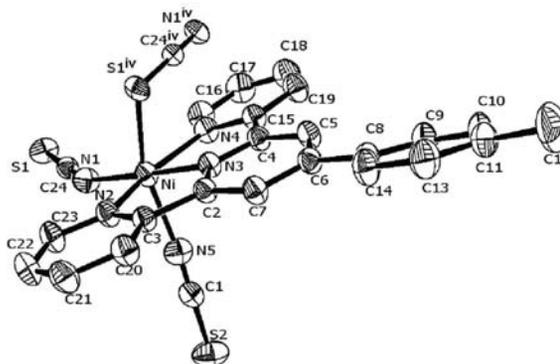
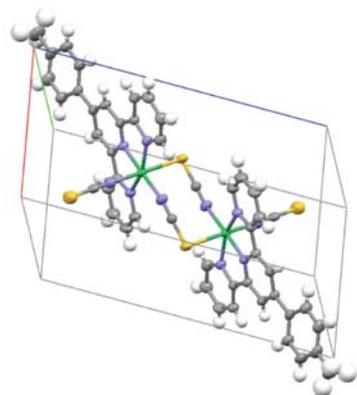


Fig. 2. Crystal structure of complex 1

Table 1. Crystallographic Data of **1** and **2**

Identification code	$[\text{Ni}_2(\text{tppy})_2(\text{SCN})_4](\mathbf{1})$	$[\text{Ni}(\text{tppy})_2](\text{CH}_3\text{OH})_2 \cdot 2(\mathbf{2})$
Empirical formula	$\text{C}_{48}\text{H}_{34}\text{N}_{10}\text{Ni}_2\text{S}_4$	$\text{C}_{46}\text{H}_{42}\text{I}_2\text{N}_6\text{NiO}_2$
Formula weight	996.51	1023.37
Temperature	298(2) K	150(2) K
Wavelength	0.71073 Å	0.71073 Å
Crystal system	Triclinic	Triclinic
Space group	P-1	P-1
Unit cell dimensions	a = 8.1087(7) Å b = 9.1801(8) Å c = 16.6607(14) Å $\alpha = 86.175(5)^\circ$ $\beta = 78.630(3)^\circ$ $\gamma = 70.628(4)^\circ$	a = 9.337(19) Å b = 12.436(13) Å c = 36.972(8) Å $\alpha = 92.428(11)^\circ$ $\beta = 92.076(10)^\circ$ $\gamma = 91.330(10)^\circ$
Volume	1147.02(17) Å ³	485.6(15) Å ³
Z	1	4
Density (calculated)	1.443 g cm ⁻³	1.586 g cm ⁻³
Absorption coefficient	1.049 mm ⁻¹	1.938 mm ⁻¹
F(000)	512	2040
Crystal size	0.35 × 0.22 × 0.16 mm ³	0.411 × 0.207 × 0.158 mm ³
Theta range for data collection	2.66 to 33.03 °	1.1 to 32.93 °
Index ranges	-12 ≤ h ≤ 12 -13 ≤ k ≤ 13 -25 ≤ l ≤ 25	-13 ≤ h ≤ 14 -18 ≤ k ≤ 18 -55 ≤ l ≤ 55
Reflections collected	56096	120325
Independent reflections	8326	30668
Absorption correction	Empirical	Empirical
Max. and min. transmission	0.7463 and 0.6763	0.7466 and 0.604
Refinement method	Full-matrix least-squares on F ²	Full-matrix least-squares on F ²
Data / restraints / parameters	8326 / 0 / 290	30668 / 0 / 1015
Goodness-of-fit on F ²	1.035	1.040
Final R indices [I > 2σ(I)]	R ₁ = 0.0326 wR ₂ = 0.0789	R ₁ = 0.0541 wR ₂ = 0.1499
R Indices (all data)	R ₁ = 0.0462 wR ₂ = 0.0859	R ₁ = 0.0804 wR ₂ = 0.1668
Largest diff. Peak, hole	0.717 and -0.544 e.Å ⁻³	3.725 and -1.709 e.Å ⁻³

3. 2. Structural Analysis

3. 2. 1. Crystal Structure of $[\text{Ni}_2(\text{tppy})_2(\text{SCN})_4](\mathbf{1})$

The reaction of tppy with $\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ and KSCN in methanol gave colorless solids that were suitable for X-ray diffraction analysis. Crystal data and structure

re determination details for **1** are given in Table 1. Some selected interatomic bond distances and angles are listed in Tables 2 and 3. ORTEP-3 view of the molecular structure of compound **1** is depicted in Fig. 2. The complex **1** crystallizes in a triclinic system with space group P-1. The structure determination reveals that six-coordinated dinuclear species are present in the unit cell. The structure of the dinuclear unit is shown in Fig. 2. In this case, there are two six-coordinated nickel(II) centers, each of them is bonded to a tridentate N₃ tpy metal binding domain of ligand. The remaining coordination sites on each metal are occupied by a terminal and two bridging SCN⁻ ligands. Ni(II) adopts a distorted octahedral geometry in a NiN₅S fashion (Figs. 2–3). The {Ni(μ-SCN-μ-NCS)Ni} motif is symmetrical with Ni-S and Ni-N bond lengths of 2.642(1) and 2.088(1)–2.134(1) Å, respectively. The Ni-N and Ni-S distances, falling in the range of 2.032–2.134 Å, and 2.642 Å, are in a good agreement with the literature.^{33–42}

The tpy metal-binding domain is approximately planar with interplanar angles between bonded pyridine rings being less than 6. The 4'-phenyl substituent is twisted with respect to the central pyridine ring of the tpy domain, with a torsion angle of 17.09°. The Ni–Ni distance within the dimer is 5.560 Å which is longer than the intermetallic distances observed in {(tpy)Ni(μ-X)₂Ni(tpy)} species with azide, cyanate or chloride bridges.^{38–42} The S1–S1 distance between the two discrete dimers is 3.647 Å. The SCN⁻ anions are nearly linear: the N-C-S bond angles lie in the range 178.71–179.12°. The C-N-Ni and C-S-Ni linkages are bent and the related bond angles are in accordance with similar types of reported complexes.³²

There are three crystallographic independent sets of quasi-linear thiocyanate bridges, two in the end-to-end (EE) mode and one in the end-on-N (EO-N) mode. Two Ni atoms are bridged by two equivalent EE-SCN⁻ ions to give a binuclear centrosymmetric eight-membered ring [Ni(NCS)₂Ni] which adopts a quasi-rectangular shape, with Ni–N–C–S (Ni–N–C, 151.92) being quasi-linear and Ni–S–C (Ni–S–C, 97.34) being close to 90. The quasi-rectangular shape (Ni, S1, Ni, S1) forms a dihedral angle of 89.16° with the metal cycle plane (NiN2C3C2N3) and an angle of 87.40° with the other plane (NiN4C15C4N3), showing that the planes are perpendicular. The configuration of the ligand closely resembles those observed in other complexes of 2,2':6',2''-terpyridine.

Intermolecular and intramolecular hydrogen bonding and π–π stacking interactions are observed in complex **1**, and seem to be responsible for the arrangement of complexes in the crystal packing that are summarized in Table 3.

3. 2. 2. Crystal structure of [Ni(tppy)₂](CH₃OH)₂ (**2I**) (**2**)

According to the X-ray single-crystal diffraction analysis, **2** crystallizes in triclinic system with P-1 space group. The molecular structure of **2** is shown in Fig. 4. The asymmetric unit contains two independent molecules (**2A** & **2B**). Both compounds have ML₂ structures. A six coordinate nickel(II) center is found and two free iodine anions serve as counterions. Two methanol solvent molecules are present in crystal. In both independent molecules, each nickel atom is located in a distorted octahedral

Table 2. Selected bond lengths/Å and angles/° for **1** and **2** (A, B)

	(1)	(2)A	(2)B
Ni–N1	2.032(1)	Ni1–N1	2.136(3)
Ni–N3	2.111(1)	Ni1–N3	2.006(3)
Ni–N2	2.008(1)	Ni1–N2	2.127(3)
Ni–N4	2.134(1)	Ni1–N4	2.002(3)
Ni–N5	2.088(1)	Ni1–N5	2.124(3)
Ni–S1	2.642(1)	Ni1–N6	2.131(3)
N1–Ni–N2	102.56(5)	N1–Ni1–N2	77.6(1)
N1–Ni–N3	177.74(5)	N1–Ni1–N3	155.9(1)
N1–Ni–N4	100.78(5)	N1–Ni1–N4	101.7(1)
N1–Ni–N5	90.77(6)	N1–Ni1–N5	88.4(1)
N1–Ni–S1	90.49(4)	N1–Ni1–N6	96.6(1)
N2–Ni–N3	78.22(5)	N2–Ni1–N3	78.31(1)
N2–Ni–N4	156.40(5)	N2–Ni1–N4	178.5(1)
N2–Ni–N5	90.67(5)	N2–Ni1–N5	100.6(1)
N2–Ni–S1	88.82(3)	N2–Ni1–N6	103.2(1)
N3–Ni–N4	78.33(5)	N3–Ni1–N4	102.3(1)
N3–Ni–N5	91.35(5)	N3–Ni1–N5	95.8(1)
N3–Ni–S1	87.40(3)	N3–Ni1–N6	89.01(1)
N4–Ni–N5	92.52(5)	N4–Ni1–N5	78.1(1)
N4–Ni–S1	87.49(4)	N4–Ni1–N6	78.2(1)
N5–Ni–S1	178.72(4)	N5–Ni1–N6	156.2(1)
		Ni2–N7	2.131(3)
		Ni2–N8	2.000(3)
		Ni2–N9	2.129(3)
		Ni2–N10	2.125(3)
		Ni2–N11	1.998(3)
		Ni2–N12	2.136(3)
		N7–Ni2–N8	77.9(1)
		N7–Ni2–N9	156.3(1)
		N7–Ni2–N10	88.9(1)
		N7–Ni2–N11	101.9(1)
		N7–Ni2–N12	95.4(1)
		N8–Ni2–N9	78.5(1)
		N8–Ni2–N10	101.8(1)
		N8–Ni2–N11	178.8(1)
		N8–Ni2–N12	101.6(1)
		N9–Ni2–N10	96.3(1)
		N9–Ni2–N11	101.8(1)
		N9–Ni2–N12	89.01(1)
		N10–Ni2–N11	78.2(1)
		N10–Ni2–N12	156.6(1)
		N11–Ni2–N12	78.4(1)

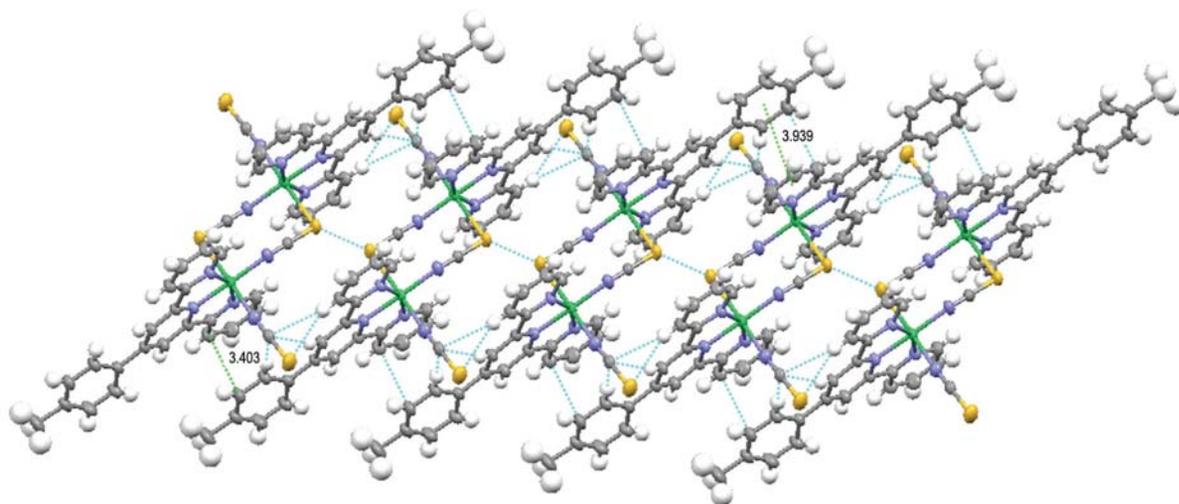


Fig. 3. Crystal packing of complex 1

coordination environment surrounded by six nitrogen atoms of two ttpy ligands. The Cd-N bond distances mostly match those observed in analogous NiN₆ chromophores.^{33–37} The iodine anions and solvent methanol molecules play important roles in forming a three dimensional network (Fig. 5). I1...H5A (methanol), I00...H91C (methanol), I00...H1 (methanol), I...H8 (methanol) intermolecular hydrogen contacts are observed.^{43–45} Furthermore, some weak I1...H78 (**2B**), I1...H23 (**2A**), and I4...H8 (**2A**) interactions are responsible for keeping two discrete molecules close. The ttpy metal-binding domains are not planar where interplanar angles between bonded pyridine rings of **2A** are ≤ 9.02 . This angle for **2B** is ≤ 10.89 . The 4'-phenyl substituent is twisted with respect to the central pyridine ring of **2A** ttpy domain, with torsion angles of 46.73 and 10.12. For **2B** corresponded torsion angles are 41.19 and 18.14.

Both the terpyridine rings of Ni(II) dication **2** are packed along parallel direction to the crystallographic axis (Fig. 6a), and there are some weak aryl-aryl and end to face stacking interactions between the adjacent aromatic rings (Fig. 6b and Table 3). As illustrated in Fig. 5 in the

crystal structure of **2**, there are two sets of Ni(II) dications which are packed alternately. Thus a three-dimensional hydrogen-bonded network of **2** is constituted.

4. Electrochemical Study

The cyclic voltammogram of ttpy exhibits a quasi-reversible oxidation peak at -0.755 V, ($\Delta E_p=182$ mV). So, the free ligand is inactive in the potential range of -0.65 to 1.5 V. Electrochemical behavior of the [Ni(tpy)₂](CH₃OH)₂ (**2I**), (**2**) and [Ni₂(ttpy)₂(SCN)₄], (**1**) were investigated by cyclic voltammetry on the surface of glassy carbon (GC) electrode. On the GC surface, (**1**) and (**2**) were oxidized via one and two anodic peaks located at 752 for (**1**) and 693 and 784 mV for (**2**) (Fig. 7). These were followed by a decrease in the cathodic peak current in the reverse sweep. The appearance of one and two peaks in the voltammograms and the one and two-step electrooxidation reaction of (**1**) and (**2**) on the glassy carbon electrode, were further confirmed by representation of derivative voltammograms (Fig. 7, insets). Hence, the redox transi-

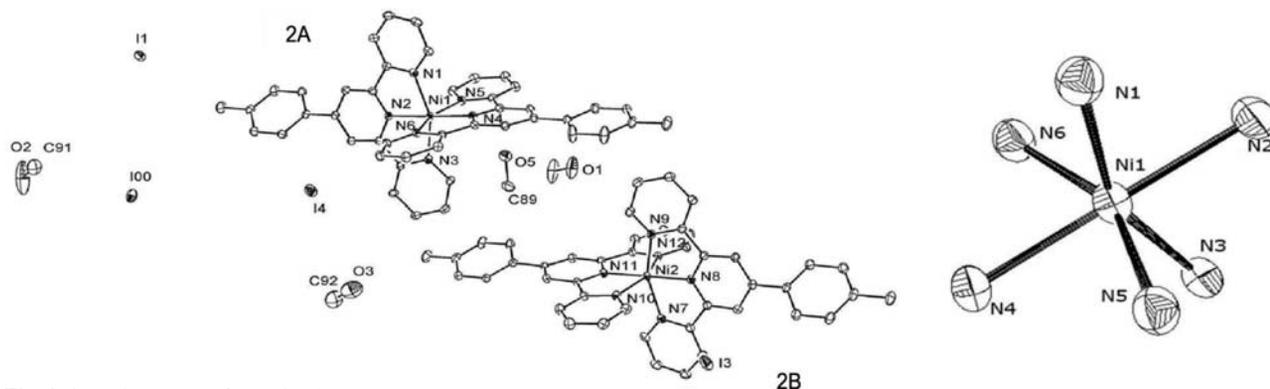


Fig. 4. Crystal structure of complex 2

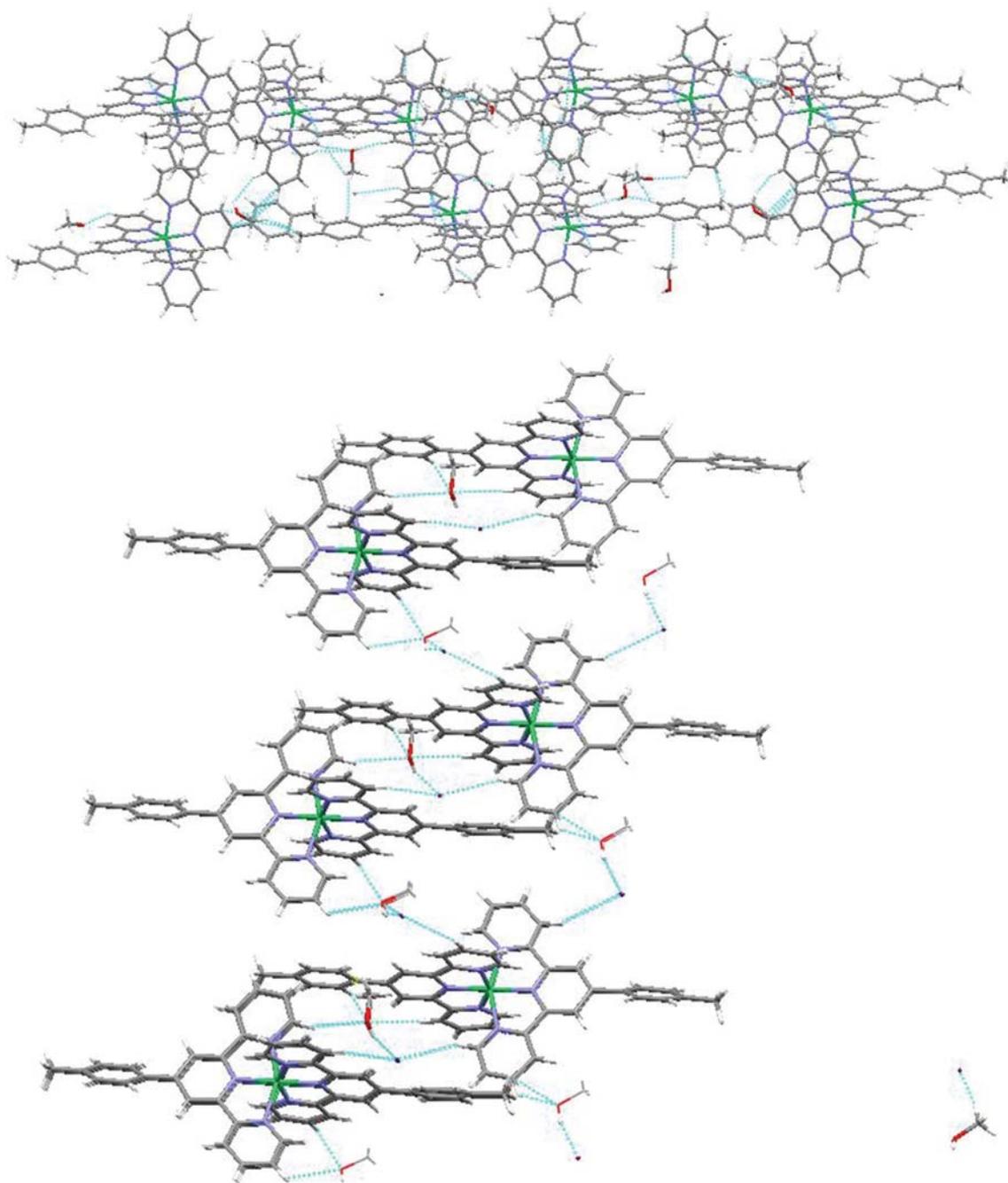
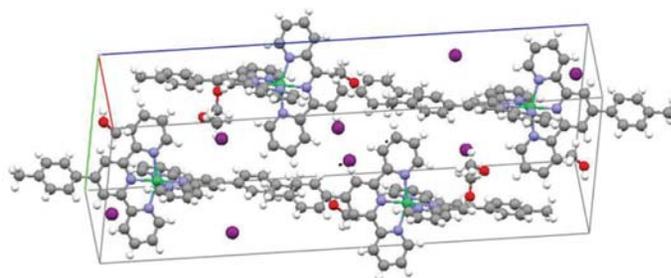


Fig. 5. Crystal packing of complex 2

b)



a)

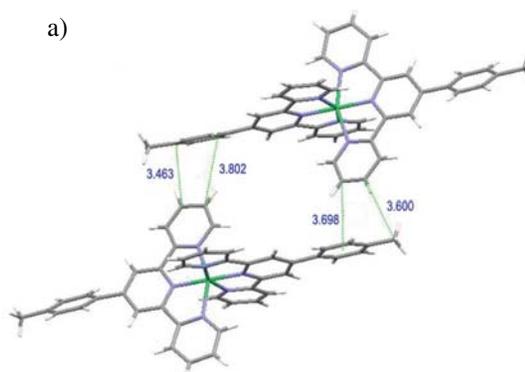


Fig. 6. Centroid ··· P interaction complex 2

Table 3. Intermolecular interactions in crystals of **1** and **2**

A...H-B	H...A/Å	B...A/Å	B-H...A/°
(1)			
(S2C1N5) C1...H20C20(-x, y, -z+1/2)	2.754	–	–
(S2C1N5) C1...H22C22(-x, y, -z+1/2)	2.810	–	–
(S2C1N5) C1...H14C14(-x, y, -z+1/2)	2.880	–	–
(S2C1N5) N5...H14C14(-x, y, -z+1/2)	2.928	3.835	165.17
(S2C1N5) N1...H22C22(-x, y, -z+1/2)	2.862	3.764	163.72
C19...C13(-x, -y, -z)		3.403	
(S2C1N5) S2...H10C10(-x, y, -z+1/2)	3.078	3.824	138.53
(S2C1N5) S2...H5C5(-x, y, -z+1/2)	3.013	3.724	134.49
(S2C1N5) S2...H20C20(-x, y, -z+1/2)	3.055	3.902	152.23
centroid...centroid (N4C15–C19)...(C8–C14)	–	3.939	–
(bridging SCN) S1...S1(bridging SCN)	–	3.647	–
Ni...Ni	–	5.560	–
(2A & 2B)			
I1...H23–C23(x+1/2, -y+1/2, z+1/2)	3.017	3.90(8)	140.96
I1...H78–C78(x+1/2, -y+1/2, z+1/2)	3.011	3.911(8)	157.93
I1...H5A(methanol)	2.814	3.595	155.29
I4...H8–C8(x+1/2, -y+1/2, z+1/2)	3.137	4.028(8)	156.78
I4...H3(methanol)	2.855	3.618(8)	151.96
I00...H32–C32(x+1/2, -y+1/2, z+1/2)	3.076	3.816(8)	136.02
I00...H1(methanol)	2.733	3.475	148.05
I3...H91C(methanol)	2.71	3.638	158.14
centroid...π (C34–C39)...C58	–	3.698	–
C83...C6		3.92	
C84...C7		3.463	
C37...C58		3.698	
C40...C59		3.60	

tion of the **(1)** is:



Also for **(2)** is:



The proposition of a two-step reaction for the electrooxidation of **(1)** and **(2)** on the GC surface (reaction 1) and (reactions 2&3) is based on the appearance of one and two anodic peaks in the corresponding voltammogram (Fig. 7A and B), respectively.⁴⁶ GC electrode represented a single anodic peak in the voltammograms for $[\text{Ni}_2(\text{tpp})_2(\text{SCN})_4]$, while GC generated two anodic peaks with the higher corresponding currents for electrooxidation of $[\text{Ni}(\text{tpp})_2](\text{CH}_3\text{OH})_2$ (**2I**). In addition, the anodic current densities compared to **(1)** at the same potentials and related to the electrooxidation of the **(2)** on the GC surface were higher. Compared to $[\text{Ni}_2(\text{tpp})_2(\text{SCN})_4]$, it can be related to the higher reactivity of $[\text{Ni}(\text{tpp})_2](\text{CH}_3\text{OH})_2$ (**2I**)

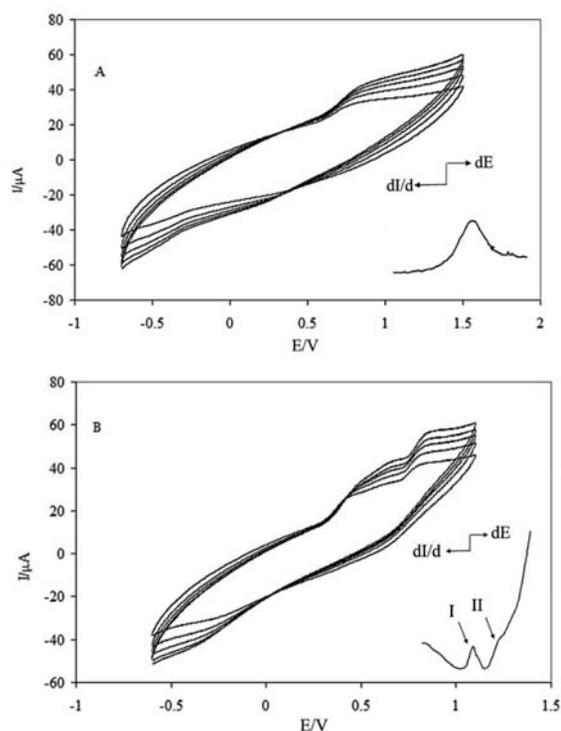


Fig. 7. Cyclic voltammograms of the GC electrode in the presence of $[\text{Ni}_2(\text{tpp})_2(\text{SCN})_4]$, **(1)** and $[\text{Ni}(\text{tpp})_2](\text{CH}_3\text{OH})_2$ (**2I**) **(2)** at different scan rate. The insets show the derivative voltammograms.

because the currents were normalized for the effective surface area of both complex. Therefore, the electrooxidation of $[\text{Ni}(\text{ttpy})_2](\text{CH}_3\text{OH})_2$ (2I) was performed by the GC with a higher rate.

5. Conclusion

Through a thermal gradient approach as suitable single crystals, two new Ni^{II} complexes, $[\text{Ni}_2(\text{ttpy})_2(\text{SCN})_4]$ (1) and $[\text{Ni}(\text{ttpy})_2](\text{CH}_3\text{OH})_2$ (2I) (2) have been prepared. 4'-p-tolyl-2,2':6',2''-terpyridine (ttpy) serves as a tridentate ligand and occupies the equatorial plane of complexes. The results convey the fact that with changing of the anion geometrical structure, packing system and stoichiometric ratio of formed complexes are changing too. This shows that with SCN^- , the metal to ligand ratio is 1:1 and with I^- this is 1:2. To sum up, in comparison with thiocyanate, iodine has low ability for coordination to nickel center. Electrochemical behavior (1) and (2) were investigated by cyclic voltammetry on the surface of glassy carbon (GC) electrode. On the GC surface complexes (1) and (2) were oxidized via one and two anodic peaks, respectively.

6. Acknowledgements

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7. Appendix A. Supplementary data

CCDC reference numbers 842181 and 842182 contain the supplementary crystallographic data for this paper. These data can be obtained free of charge at www.ccdc.cam.ac.uk/conts/retrieving.html.

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Povzetek

Nova nikeljeva (II) kompleksa $[\text{Ni}_2(\text{tpty})_2(\text{SCN})_4]$, (**1**) in $[\text{Ni}(\text{tpty})](\text{CH}_3\text{OH})_2 \cdot (2\text{I})$, (**2**) sta bila pripravljena z novim, enostavnim postopkom iz liganda (L) 4'-p-tolil-2,2':6',2''-terpiridin (tpty), kalijevega tiocianata in kalijevega jodida z velikim izkoristkom. Rentgenska strukturna analiza monokristalov je pokazala, da imajo kovinski atomi v obeh kompleksih šestštevno koordinacijo, pri čemer je v (**1**) razmerje M:L 1:1 in v (**2**) 1:2. Interakcije na supramolekularni ravni, (koordinacijske vezi, I...H, in N...H vodikove vezi, π - π) so ključnega pomena za nastanek kristalnih struktur (**1**) ain (**2**). V delu poročamo o elektrokemijskih lastnostih nikeljevih kompleksov.