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# Octahedral nickel(II) hexamethyleneimine-dithiocarbamato complexes involving bidentate N,N-donor ligands

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### ABSTRACT

The nickel(II) complexes of the compositions [Ni(hmidtc)(bpy)<sub>2</sub>]ClO<sub>4</sub> (I), [Ni(hmidtc)(phen)<sub>2</sub>]ClO<sub>4</sub> (II), [Ni(hmidtc)(phen)<sub>2</sub>]SCN (III), [Ni(hmidtc)(phen)<sub>2</sub>]PF<sub>6</sub> (IV), [Ni(hmidtc)(phen)<sub>2</sub>]BPh<sub>4</sub> (V), [Ni(hmidtc) (phen)<sub>2</sub>]AcO·2H<sub>2</sub>O (VI) and [Ni(hmidtc)(phen)<sub>2</sub>]Br·H<sub>2</sub>O (VII), involving a combination of one hexamethyleneimine-dithiocarbamate anion (hmidtc) and two bidentate N,N-donor ligands (2,2'-bipyridine (bpy) for I or 1,10-phenanthroline (phen) for II-VII), have been prepared. The compounds were characterized by elemental analysis, molar conductivity measurements, UV-Vis and IR spectroscopy, magnetochemical measurements and thermal analysis. A single-crystal X-ray analysis of the complex I revealed a distorted octahedral geometry with the nickel(II) ion coordinated by four nitrogen atoms (from two bidentate-coordinated bpy molecules) and two sulfur atoms (from one bidentate-coordinated hmidtc anion), together giving an NiN<sub>4</sub>S<sub>2</sub> donor set.

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#### 1. Introduction

A large number of nickel complexes involving various dithiocarbamate anions as ligands in the inner coordination sphere have been described in the literature to date. Focusing on the hexamethyleneimine-dithiocarbamato (hmidtc) complexes of nickel, the following substances have been reported: [Ni(X)(hmidtc)(Y)], where  $X = Cl^-$ ,  $Br^-$ ,  $I^-$  or NCS<sup>-</sup> and  $Y = PPh_3$  or  $PBu_3$  [1]; [Ni( $\mu$ -SR)  $(hmidtc)]_2$ , where *SR* = thiophenol, 4-methylthiophenol, 2-thionaphthol, thiosalicylic acid, 1-hexanethiol or 1-butanethiol [2]; [Ni(hmidtc)(dppf)]ClO<sub>4</sub>, where dppf = 1,1'-bis(diphenylphosphino)ferrocene [3];  $[Ni_2(\mu-dpph)(hmidtc)_2X_2]$ , where dpph = 1,6bis(diphenylphosphino)hexane and  $X = Cl^{-}$ ,  $Br^{-}$ ,  $I^{-}$  or NCS<sup>-</sup> [4];  $[Ni(hmidtc)_2X]$  and  $[Ni(hmidtc)_2X_2]$ , where  $X = SbI_3$  or  $AsI_3$  [5]. As for the octahedral nickel(II) complexes involving a different dithiocarbamato ligand from hmidtc, we have to mention the [Ni(*n*dtc)  $(phen)_2 X$  and  $[Ni(ndtc)(bpy)_2]ClO_4$  complexes [ndtc = N,N'-benzyl-methyldithiocarbamate (bzmedtc), N,N'-dipentyldithiocarbamate (pe<sub>2</sub>dtc) and 4-benzylpiperazinedithiocarbamate anions (bzppzdtc);  $X = ClO_4^-$  or SCN<sup>-</sup>] [6,7]. These complexes are structurally analogical to the nickel(II) complexes I-VII reported herein, i.e. the central Ni(II) ion is hexacoordinated by two bidentate N-donor ligand and by one bidentate dithiocarbamate-based S-donor ligand forming the  $[Ni(dtc)(N-N)_2]^+$  type of complex. Two X-ray structures of such complexes have been determined and deposited within the Cambridge Structural Database (CSD ver. 5.31, May 2010 update [8]) to date, namely [Ni(bzppzdtc)(phen)<sub>2</sub>]ClO<sub>4</sub>·CHCl<sub>3</sub> [6] and [Ni(-pe<sub>2</sub>dtc)(phen)<sub>2</sub>]ClO<sub>4</sub> [7]. Thus, only the third X-ray structure of a nickel(II) complex of the above-mentioned [Ni(dtc)(N-N)<sub>2</sub>]<sup>+</sup> type is described herein, together with a series of the complexes **I**-**VII** involving a dithiocarbamato ligand (hmidtc anion) different from the mentioned complexes in combination with the bidentate N-do-nor ligands (bpy in the case of **I** and phen in the case of **II**-**VII**) coordinated to the metal center. The outer coordination sphere contains various anions, concretely  $ClO_4^-$  (**I**, **II**),  $SCN^-$  (**III**),  $PF_6^-$  (**IV**),  $BPh_4^-$  (**V**),  $AcO^-$  (**VI**) and  $Br^-$  (**VI**).

# 2. Experimental

# 2.1. Starting materials

Chemicals and solvents employed in this work were purchased from commercial sources (Sigma–Aldrich Co., Lachema Co., and Fluka Co.). [Ni(hmidtc)<sub>2</sub>] was prepared according to a previously described procedure [9].

# 2.2. Syntheses of nickel(II) complexes I-VII

The ethanolic (30 mL) suspension of powdered  $[Ni(hmidtc)_2]$  (1 mmol) was mixed with 4 molar equivalents of 2,2'-bipyridyl (I) or 1,10-phenanthroline (II) dissolved in 20 mL of ethanol. The



Note



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mixture was stirred for 10 min at laboratory temperature. After that, pulverized NiCl<sub>2</sub>· $GH_2O$  (1 mmol) and LiClO<sub>4</sub>· $3H_2O$  (2 mmol) were poured into the reaction mixture which was afterwards refluxed for 10 h. In the case of I, the clear red solution was cooled down, filtered, and the filtrate was left to crystallize at laboratory temperature. The product, which formed in 5 days, was filtered off, washed with diethyl ether and dried at 40 °C under an infrared lamp. Some of the obtained crystals were suitable for a single crystal X-ray analysis. As for II, the hot solution was cooling down. It was filtered off, washed with hot distilled water, ethanol and diethyl ether and dried at 40 °C under an infrared lamp. The syntheses of III–VII are similar to that of II, but KSCN (for III), K[PF<sub>6</sub>] (for IV) or Na[BPh<sub>4</sub>] (for V) was used instead of LiClO<sub>4</sub>·3H<sub>2</sub>O.

**VI** and **VII** were prepared by the reactions of  $[Ni(hmidtc)_2]$ (1 mmol), 1,10-phenanthroline (4 mmol) and Ni(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O (1 mmol; **VI**) or NiBr<sub>2</sub>·3H<sub>2</sub>O (1 mmol; **VII**) which were suspended in 30 mL of ethanol and the suspension was refluxed for 4 h.

I: Red crystals. Yield: 77%. Anal. Calc. for C27H28N5ClO4S2Ni (*M<sub>r</sub>* = 644.8): C, 50.3; H, 4.4; N, 10.8; Cl, 5.5; Ni, 9.1. Found: C, 50.1; H, 4.6; N, 11.1; Cl, 5.8; Ni, 9.0%. II: Light brown powder. Yield: 77%. Anal. Calc. for  $C_{31}H_{28}N_5O_4S_2CINi$  ( $M_r = 692.9$ ): C, 53.7; H, 4.1; N, 10.1; Cl, 5.1; Ni, 8.5. Found: C, 53.4; H, 4.2; N, 9.8; Cl, 4.8; Ni, 9.1%. III: Red crystals. Yield: 85%. Anal. Calc. for C<sub>32</sub>H<sub>28</sub>N<sub>6</sub>S<sub>3</sub>Ni (*M<sub>r</sub>* = 651.5): C, 59.0; H, 4.3; N, 12.6; Ni, 9.0. Found: C, 58.6; H, 4.7; N, 12.9; Ni, 8.8%. IV: Red-brown powder. Yield: 68%. Anal. Calc. for  $C_{31}H_{28}N_5F_6PS_2Ni$  ( $M_r = 738.4$ ): C, 50.4; H, 3.8; N, 9.5; Ni, 7.9. Found: C, 50.0; H, 3.7; N, 9.3; Ni, 7.7%. V: Orange-brown powder. Yield: 73%. Anal. Calc. for C<sub>55</sub>H<sub>48</sub>N<sub>5</sub>BS<sub>2</sub>Ni (M<sub>r</sub> = 912.6): C, 72.4; H, 5.3; N, 7.7; Ni, 6.4. Found: C, 72.1; H, 4.9; N, 7.3; Ni, 6.6%. VI: Brown powder. Yield: 81%. Anal. Calc. for C<sub>33</sub>H<sub>31</sub>N<sub>5</sub>O<sub>2</sub>S<sub>2</sub>Ni·2H<sub>2</sub>O (*M<sub>r</sub>* = 688.5): C, 57.3; H, 5.1; N, 10.2; Ni, 8.5. Found: C, 57.6; H, 5.3; N, 10.1; Ni, 8.2%. VII: Light-brown powder. Yield: 76%. Anal. Calc. for  $C_{31}H_{28}N_5BrS_2Ni \cdot H_2O$  ( $M_r = 691.3$ ): C, 53.9; H, 4.4; N, 10.1; Cl, 11.6; Ni, 8.5. Found: C, 53.5; H, 4.5; N, 10.2; Cl, 11.1; Ni, 8.5%. A schematic representation of the composition of the complexes I-VII is depicted in Scheme 1.

## 2.3. Methods

Elemental analyses (C, H, N) were performed on a Fisons EA-1108 CHNS-O Elemental Analyzer (Thermo Scientific). Chlorine



 $Y = CIO_4^{-} (I, II), SCN^{-} (III), PF_6^{-} (IV), BPh_4^{-} (V), AcO^{-} (VI), Br^{-} (VII)$ 

Scheme 1. Composition of the prepared nickel(II) complexes I-VII.

and bromine contents were determined using the Schöniger method. The nickel content was determined by the chelatometric titration with murexide as an indicator. The measurements of the room temperature magnetic susceptibilities were performed using the Faraday method with a laboratory designed instrument with a Sartorius 4434 MP-8 microbalance; Co[Hg(NCS)<sub>4</sub>] was used as a calibrant and the correction for diamagnetism was performed using Pascal constants [10]. The molar conductivity of the 10<sup>-3</sup> M nitromethane solutions was measured by an LF 330/SET conductometer (WTW GmbH) at 25 °C. Electronic absorption spectra (10<sup>-3</sup> M DMF solutions) and diffuse-reflectance spectra were recorded on a Specord M40 device (nujol technique). IR spectra (450–4000 cm<sup>-1</sup> region; KBr pellets) were recorded on a Perkin-Elmer Spectrum one FT-IR spectrometer. Thermogravimetric (TG) and differential thermal (DTA) analyses were performed simultaneously by an Exstar TG/DTA 6200 (Seiko Instruments Inc.) in a dynamic air atmosphere (100 mL min<sup>-1</sup>) from laboratory temperature to 1050 °C  $(2.5 \circ C \min^{-1} \text{gradient}).$ 

X-ray data of the selected crystal of [Ni(hmidtc)(bpy)<sub>2</sub>](ClO<sub>4</sub>) (I) was collected on an Xcalibur™2 diffractometer (Oxford Diffraction Ltd.) with a Sapphire2 CCD detector, and with Mo Ka radiation (Monochromator Enhance, Oxford Diffraction Ltd.). Data collection and reduction were performed using the CrysAlis software [11]. The same software was used for data correction for an absorption effect by the empirical absorption correction using spherical harmonics, implemented in SCALE3 ABSPACK scaling algorithm. The structure was solved by direct methods using SHELXS-97 and refined on  $F^2$  using the full-matrix least-squares procedure (SHELXL-97) [12]. Non-hydrogen atoms were refined anisotropically and hydrogen atoms were located in a difference map and refined using the riding model with C-H = 0.95 and 0.99 Å, N-H = 0.88 Å and  $U_{iso}(-$ H) =  $1.2U_{eq}$ (CH, CH<sub>2</sub>, NH) or  $1.5U_{eq}$ (CH<sub>3</sub>). The crystal data and structure refinement are given in Table 1. The molecular graphics as well as additional structural calculations were drawn and interpreted using DIAMOND [13].

#### 3. Results and discussion

The values of molar conductivity of nitromethane solutions of **I**– **VII** range from 79.6 to 93.4 S cm<sup>2</sup> mol<sup>-1</sup> (Table 2), which are typical

Table 1
Crystal data and structure refinement for $[Ni(hmidtc)(bpy)_2]ClO_4$ (I).

Formula	C27H28N5ClO4S2Ni
Formula weight	644.82
T (K)	100(2)
λ (Å)	0.71073
Crystal system, space group	monoclinic, C2/c
Unit cell dimensions	
a (Å)	15.3888(3)
b (Å)	23.8055(5)
<i>c</i> (Å)	15.7739(3)
α (°)	90.00
β(°)	103.630(2)
γ (°)	90.00
V (Å <sup>3</sup> )	5615.9(2)
Z, $D_{calc}$ (g cm <sup>-3</sup> )	8, 1.525
Absorption coefficient (mm <sup>-1</sup> )	0.978
Crystal size (mm)	$0.30 \times 0.20 \times 0.20$
F (0 0 0)	2672
$\theta$ range for data collection (°)	$2.91 \leqslant  heta \leqslant 25.00$
Index ranges (h, k, l)	$-18\leqslant h\leqslant 18$
	$-28\leqslant k\leqslant 28$
	$-15\leqslant l\leqslant 18$
Reflections collected/unique $(R_{int})$	26 391/4947 (0.0249)
Data/restraints/parameters	4947/0/361
Goodness-of-fit (GOF) on F <sup>2</sup>	1.001
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0266, wR_2 = 0.0770$
R indices (all data)	$R_1 = 0.0318$ , $wR_2 = 0.0786$
Largest peak and hole ( $e Å^{-3}$ )	0.855, -0.293

Table 2	
Magnetic, molar conductivity, UV-Vis and IR data for	complexes I-VII.

Complex	$\mu_{\rm eff}$	$\lambda_M^a$	UV–Vis (× $10^3$ cm <sup>-1</sup> )		$IR (cm^{-1})$	(cm <sup>-1</sup> )		
	$\mu_{ m B}$	$\mu_{ m B}$	lΒ	Diffuse-reflectance	Solution $(\varepsilon^{\rm b})$	$v(C \cdots S)$	$v(C \cdots N)$	Other
[Ni(hmidtc)(bpy) <sub>2</sub> ]ClO <sub>4</sub> (I)	3.07	93.4	11.7, 19.8, 27.8, 32.1	11.6 (23.7)	984m	1514m	623s $[(v_4 \text{ClO}_4^-)]$ , 1072s $[(v_3 \text{ClO}_4^-)]$	
[Ni(hmidtc)(phen) <sub>2</sub> ]ClO <sub>4</sub> (II)	3.10	88.4	11.8, 19.4, 29.7, 34.1, 36.3, 42.1, 44.7	11.5 (26.5)	982m	1515m	623s [v <sub>4</sub> (ClO <sub>4</sub> -)], 1088s [(v <sub>3</sub> ClO <sub>4</sub> <sup>-</sup> )]	
[Ni(hmidtc)(phen) <sub>2</sub> ]SCN (III)	3.07	89.2	11.6, 19.6, 29.2, 32.4	12.6 (13.2)	964m	1508m	740w [v(C-S)], 2048 m [v <sub>as</sub> (C=N)]	
[Ni(hmidtc)(phen) <sub>2</sub> ]PF <sub>6</sub> ( <b>IV</b> )	3.02	90.1	11.9, 19.6, 28.7, 33.4, 40.4	11.6 (19.2)	982m	1516m	839s [(vPF <sub>6</sub> <sup>-</sup> )]	
[Ni(hmidtc)(phen) <sub>2</sub> ]BPh <sub>4</sub> ( <b>V</b> )	3.13	79.6	11.6, 19.2, 26.9, 32.9, 40.0	11.6 (18.9)	982m	1515s		
[Ni(hmidtc)(phen) <sub>2</sub> ]AcO·2H <sub>2</sub> O	3.02	88.3	11.5, 19.4, 25.9, 29.7, 35.3, 36.2, 37.0	11.5 (15.2)	980m	1515s		
( <b>VI</b> )								
[Ni(hmidtc)(phen) <sub>2</sub> ]Br·H <sub>2</sub> O ( <b>VII</b> )	3.15	87.5	11.5, 19.3, 26.2, 30.4, 32.9, 34.9, 35.8, 39.9	11.5 (23.0)	982m	1514s		

<sup>a</sup> S cm<sup>2</sup> mol<sup>-1</sup>.

 $^{\rm b}~{\rm dm^3}~{\rm mol^{-1}}~{\rm cm^{-1}}$ 

values for the 1:1 electrolyte type in the solvent used [14]. The magnetochemical measurements proved paramagnetic behavior of the complexes **I–VII** with two unpaired electrons (3.02–3.15  $\mu_{eff}/\mu_{B}$ , see Table 2), thus indirectly showing on the presence of a hexacoordinated nickel(II) ion and octahedral geometry around the metal center [15].

Three maxima, characteristic for the *d*-*d* transitions of the octahedral nickel(II) complexes, were detected in the diffuse-reflectance UV–Vis spectra of the studied compounds at 11 500–11 900 cm<sup>-1</sup> for the electronic transition  ${}^{3}A_{2g} \rightarrow {}^{3}T_{2g}$  ( $v_1$ ), 19 200–19 800 cm<sup>-1</sup> for  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$  (F) ( $v_2$ ) and 25 900–29 700 cm<sup>-1</sup> for  ${}^{3}A_{2g} \rightarrow {}^{3}T_{1g}$  (P) ( $v_3$ ) [16–18]. The bands, whose maxima exceeded 30 000 cm<sup>-1</sup>, may be assigned to intraligand charge-transfer transitions. Table 3 also shows the position of the maxima observed in the electronic UV–Vis spectra of the 10<sup>-3</sup> DMF solutions of **I–VII** together with the appropriate molar absorption coefficient values. These bands are again assignable to the above-described *d*-*d* transitions.

The bands of the vibrations characteristic for dithiocarbamtes, i.e.  $v(C \cdots S)$  and  $v(C \cdots N)$ , were detected in the IR spectra of the prepared nickel(II) complexes (Table 2) [19,20]. The presence of the ClO<sub>4</sub><sup>-</sup> anion in the structure of I and II, SCN<sup>-</sup> anion in the structure

 Table 3

 Selected bond lengths (Å) and angles (°) of [Ni(hmidtc)(bpy)<sub>2</sub>]ClO<sub>4</sub> (I).

Compound	I		
Bond lengths		N3-Ni1-S1	93.39(4)
Ni1-S1	2.4022(5)	N3-Ni1-S2	96.00(4)
Ni1-S2	2.4625(5)	N4-Ni1-N5	78.20(6)
Ni1-N2	2.073(2)	N4-Ni1-S1	172.91(5)
Ni1-N3	2.069(2)	N4-Ni1-S2	102.97(4)
Ni1-N4	2.101(2)	N5-Ni1-S1	95.37(4)
Ni1-N5	2.094(2)	N5-Ni1-S2	89.10(4)
N2-C10	1.341(2)	S1-Ni1-S2	73.69(2)
N2-C14	1.349(2)	Ni1-N2-C10	126.52(13)
N3-C15	1.351(2)	Ni1-N2-C14	114.23(12)
N3-C19	1.344(2)	Ni1-N3-C15	114.64(12)
N4-C20	1.345(3)	Ni1-N3-C19	126.92(13)
N4-C24	1.343(3)	Ni1-N4-C20	126.40(13)
N5-C25	1.350(2)	Ni1-N4-C24	114.74(13)
N5-C29	1.345(2)	Ni1-N5-C25	114.47(12)
S1-C1	1.719(2)	Ni1-N5-C29	126.31(13)
S2-C1	1.725(2)	Ni1-S1-C1	85.74(6)
Bond angles		Ni1-S2-C1	83.73(6)
N2-Ni1-N3	79.50(6)	C10-N2-C14	118.6(2)
N2-Ni1-N4	91.69(6)	C15-N3-C19	118.2(2)
N2-Ni1-N5	97.41(6)	C20-N4-C24	118.4(2)
N2-Ni1-S1	92.11(4)	C25-N5-C29	118.0(2)
N2-Ni1-S2	164.93(4)	S1-C1-N1	121.13(14)
N3-Ni1-N4	93.19(6)	S1-C1-S2	115.78(11)
N3-Ni1-N5	170.83(6)	S2-C1-N1	123.09(14)

of **III**, and  $PF_6^-$  anion in the structure of **IV** was also detected by IR spectroscopy (Table 2) [21–23].

The thermal analysis proved the complexes **I–V** to be non-solvated and **VI** and **VII** solvated (see Appendix A Supplementary material). The thermal decay of **VI** and **VII** started right after the beginning of the analyses as a consequence of the water molecules of crystallization elimination (two for **VII** and one for **VI**) from the structure of the mentioned complexes.

The X-ray crystal structure of [Ni(hmidtc)(bpy)<sub>2</sub>](ClO<sub>4</sub>) (I) contains the [Ni(hmidtc)(bpy)<sub>2</sub>]<sup>+</sup> cations and perchlorate anions with the shortest Ni1...Cl1 contact of 6.8902(5) Å (Fig. 1). The Ni(II) atom is coordinated by three bidentate ligands, i.e. by one S-donor hexamethyleneimine-dithiocarbamate anion (hmidtc) and two Ndonor 2,2'-bipyridine molecules (bpy<sup>A</sup> containing N2 and N3 atoms and bpy<sup>B</sup> containing N4 and N5 atoms), thus forming the distorted octahedral arrangement in the vicinity of the metal center. The bond lengths between the Ni(II) center and donor atoms S1, S2, N2, N3, N4 and N5 (see Table 3) did not exceed the interval found for nickel(II) complexes involving bidentate-coordinated dithiocarbamate (2.164–2.485 Å, an average value of 2.211 Å) and with the 2,2'-bipyridine molecule coordinated through both nitrogen atoms (1.963–2.153 Å, an average value of 2.083 Å), as it has been found for the compounds deposited in the Cambridge Structural Database (CSD ver. 5.31, May 2010 update) [8].

The dihedral angles formed by the planes created through the selected atoms of the mentioned ligands and central atom (Ni1–



**Fig. 1.** The molecular structure of [Ni(hmidtc)(bpy)<sub>2</sub>]ClO<sub>4</sub> (I) with non-hydrogen atoms drawn as thermal ellipsoids at the 50% probability level, the hydrogen atoms and perchlorate anion were omitted for clarity.



**Fig. 2.** Part of the crystal structure of the complex I showing selected non-covalent interactions of the C-H···O, C-H···S, C-H···C and C···C types (dashed green lines); hydrogen atoms not involved in the depicted interactions were omitted for clarity. The d(D-H), d(H···A), d(D···A) and  $\angle$ (DHA) parameters are equaled to 0.990 Å, 2.876(2) Å, 3.726(3) Å and 144.40(14)° for C5-H5A···C16<sup>i</sup>, 0.950 Å, 2.8316(4) Å, 3.577(2) Å and 133.92(12)° for C12-H12A···S1<sup>ii</sup>, 0.950 Å, 2.6319(14) Å, 3.479(2) Å and 150.71(12)° for C13-H13A···O2<sup>iii</sup>, 0.950 Å, 2.639(14) Å, 3.315(2) Å and 126.21(12)° for C13-H13A···O4<sup>iii</sup>, 0.950 Å, 2.6016(13) Å, 3.547(2) Å and 173.07(12)° for C16-H16A···O2<sup>iii</sup>, 0.950 Å, 2.8373(5) Å, 3.743(2) Å and 159.69(13)° for C26-H26A···S2<sup>iv</sup>, 0.950 Å, 2.4490(14) Å, 3.224(3) Å and 138.76(13)° for C27-H27A···O2<sup>iv</sup> and C21···C21<sup>iv</sup> = 3.286(3) Å. Symmetry codes: i = 0.5 - *x*, *y* - 0.5, 0.5 - *z*; ii = 0.5 - *x*, *y* + 0.5, 0.5 - *z*; iv = 1 - *x*, *y*, 0.5 - *z*. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

S1–C1–S2 for hmidtc, Ni1–N2–C14–C15–N3 for bpy<sup>A</sup> and Ni1–N4–C24–C25–N5 for bpy<sup>B</sup>) equal 86.43(3)° (between hmidtc and bpy<sup>A</sup>), 85.34(4)° (between hmidtc and bpy<sup>B</sup>) and 86.77(5)° (between bpy<sup>A</sup> and bpy<sup>B</sup>). The deviations of the donor atoms from the mentioned planes were found to be -0.0082(5)Å (S1), -0.0080(5)Å (S2), 0.038(2)Å (N2), -0.001(2)Å (N3), 0.035(2)Å (N4) and 0.083(2)Å (N5). Two rings of each bpy molecule formed the dihedral angles of 11.88(5)° (for bpy<sup>A</sup>) and 15.83(6)° (for bpy<sup>B</sup>), which shows on the substantial deformation of the bpy ligands.

The C–H···O, C–H···S, C–H···C, C···O and C···C van der Waals non-covalent contacts stabilize the secondary structure of the complex I, a part of which is, together with the parameters of the detected non-covalent contacts, given in Fig. 2.

In summary, a series of seven octahedral nickel(II) dithiocarbamato complexes involving a combination of the hexamethyleneimine-dithiocarbamate anion (hmidtc) and 2,2'-bipyridine (I) or 1,10-phenanthroline (II–VII) were prepared and characterized by various techniques including the single-crystal X-ray analysis of the complex [Ni(hmidtc)(bpy)<sub>2</sub>]ClO<sub>4</sub> (I). The molecular structure of I represents a rare structural type among numerous nickel dithiocarbamato complexes. Concretely, it is only the third example of the complexes involving two bidentate-coordinated N-donor ligands and one bidentate-coordinated dithiocarbamate in a distorted octahedral NiN<sub>4</sub>S<sub>2</sub> donor set, whose X-ray structure has been determined to date.

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## Appendix A. Supplementary material

CCDC 796091 for  $[Ni(hmidtc)(bpy)_2](ClO_4)$  (I) contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data\_request/cif. TG and DTA data and curves of I–VII are given in Fig. S1. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ica.2011.03.010.

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