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# Nickel(IV) dithiocarbamato complexes of the [Ni(*n*dtc)<sub>3</sub>]X type: X-ray structure of [Ni(*hmi*dtc)<sub>3</sub>][FeCl<sub>4</sub>]

Richard Pastorek<sup>a</sup>, Pavel Štarha<sup>b</sup>, Tomáš Peterek<sup>a</sup>, Zdeněk Trávníček<sup>b,\*</sup>

<sup>a</sup> Department of Inorganic Chemistry, Faculty of Science, Palacký University, 17. listopadu 12, CZ-771 46 Olomouc, Czech Republic <sup>b</sup> Regional Centre of Advanced Technologies and Materials, Department of Inorganic Chemistry, Faculty of Science, Palacký University, 17. listopadu 12, CZ-771 46 Olomouc, Czech Republic

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## ABSTRACT

A series of fourteen octahedral nickel(IV) dithiocarbamato complexes of the general formula  $[Ni(ndtc)_3]XyH_2O$  {*n*dtc stands for the appropriate dithiocarbamate anion, *X* stands for  $ClO_4^-$  (**1–8**; y = 0) or  $[FeCl_4]^-$  (**9–14**; y = 0 for **9–12**, 1 for **13** and 0.5 for **14**} was prepared by the oxidation of the corresponding nickel(II) complexes, i.e.  $[Ni(ndtc)_2]$ , with NOCIO<sub>4</sub> or FeCl<sub>3</sub>. The complexes, involving a high-valent Ni<sup>IV</sup>S<sub>6</sub> core, were characterized by elemental analysis (C, H, N, Cl and Ni), UV–Vis and FTIR spectroscopy, thermal analysis and magnetochemical and conductivity measurements. The X-ray structure of  $[Ni(hmidtc)_3][FeCl_4]$  (**9**) was determined {it consists of covalently discrete complex  $[Ni(hmidtc)_3]^+$  cations and  $[FeCl_4]^-$  anions} and this revealed slightly distorted octahedral and tetrahedral geometries within the complex cations, and anions, respectively. The Ni(IV) atom is six-coordinated by three bidentate S-donor hexamethyleneiminedithiocarbamate anions (*hmidtc*), with Ni–S bond lengths ranging from 2.2597(5) to 2.2652(5)Å, while the shortest Ni…Cl and Ni…Fe distances equal 4.1043(12), and 6.2862(6)Å, respectively. Moreover, the formal oxidation state of iron in  $[FeCl_4]^-$  as well as the coordination geometry in its vicinity was also proved by <sup>57</sup>Fe Mössbauer spectroscopy in the case of **9**.

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## 1. Introduction

Compounds involving nickel in its higher formal oxidation states, such as Ni(III)/Ni(IV), play an important role in many branches of industry (e.g., several representatives of nickel(IV) complexes bearing three bidentate-coordinated dithiocarbamate anions were used as a part of mineral or synthetic oil-based lubricants or lubricant concentrates [1]) and in biological systems (e.g., methanogenic bacteria [2]). Nevertheless, a systematic literature search of worldwide chemical (e.g., Web of Science) and crystallographic (e.g., Cambridge Structural Database) databases revealed few works dealing with nickel(IV) complexes (see e.g., [3-5]). In particular, although nickel(IV) complexes involving three bidentate-coordinated dithiocarbamate-based S-donor ligands (which is the subject of this work) have been known for more than 40 years, the total number of these compounds is not very large, as it is briefly reviewed below. The first of these compounds, a group of [Ni(ndtc)<sub>3</sub>]Br complexes, were prepared in 1969 by the oxidation of the appropriate  $[Ni(ndtc)_2]$  complex by bromine in CCl<sub>4</sub> {ndtc stands for N,N-diethyldithiocarbamate (et<sub>2</sub>dtc), N,N-dibutyldithiocarbamate (but<sub>2</sub>dtc) and N,N-dibenzyldithiocarbamate  $(bz_2dtc)$  [6]. The X-ray molecular structure

of the previously reported [Ni(but<sub>2</sub>dtc)<sub>3</sub>]Br revealed a distorted octahedral geometry, and moreover it was found that the compound, and its analogs of the compositions [Ni(bz<sub>2</sub>dtc)<sub>3</sub>]Br, [Ni (but<sub>2</sub>dtc)<sub>3</sub>](BF<sub>3</sub>Br), [Ni(but<sub>2</sub>dtc)<sub>3</sub>]NO<sub>3</sub> and [Ni(et<sub>2</sub>dtc)<sub>3</sub>]Br, behave as diamagnetics, thus proving that they have the oxidation state +IV [7,8]. Hendrickson et al., followed the synthetic strategies described in the above-mentioned papers and prepared several new  $[Ni(ndtc)_3]^+$  complexes, specifically  $[Ni(et_2dtc)_3]BF_4$  and [Ni $(bu_2dtc)_3$ ]BF<sub>4</sub> [9]. Golding et al. used iron(III) perchlorate and iron(III) chloride for the oxidation of nickel(II) dithiocarbamato complexes to the nickel(IV) analogs, preparing  $[Ni(et_2dtc)_3]CIO_4$ ,  $[Ni(et_2dtc)_3]$ [FeCl<sub>4</sub>],  $[Ni(etphdtc)_3]$ ClO<sub>4</sub> and  $[Ni(pipdtc)_3]$ [FeCl<sub>4</sub>], where *etph*dtc = ethylphenyldithiocarbamate and *pip*dtc = piperidinedithiocarbamate [10]. The complexes  $[Ni(et_2dtc)_3]PF_6$  and [Ni(but<sub>2</sub>dtc)<sub>3</sub>]PF<sub>6</sub> were used for the preparation of [Ni (R-CN)<sub>2</sub>(*et*<sub>2</sub>dtc)<sub>2</sub>]PF<sub>6</sub>, where R stands for *iso*-propyl, *tert*-butyl, *p*-chlorophenyl, methyldiphenylphosphine or ½ of 1,2-bis(diphen ylphosphino)ethane [11]. Larionov et al., reported the preparation and characterization of the octahedral and diamagnetic [Ni (ndtc)<sub>3</sub>]Br and [Ni(ndtc)<sub>3</sub>]I<sub>5</sub> (ndtc symbolizes N,N-dipropyldithiocarbamate and N,N-diisopropyldithiocarbamate anions) [12]. Other nickel(IV) dithiocarbamato complexes, specifically [Ni(pipdtc)3]-ClO<sub>4</sub>, [Ni(*pipdtc*)<sub>3</sub>]NO<sub>3</sub>, [Ni(*plddtc*)<sub>3</sub>]NO<sub>3</sub> and [Ni(*plddtc*)<sub>3</sub>][FeCl<sub>4</sub>], were also prepared and described by Pastorek et al. (plddtc stands for pyrrolidindithiocarbamate) [13,14]. The X-ray structure of





<sup>\*</sup> Corresponding author. Tel.: +420 585 634 352; fax: +420 585 634 954. *E-mail address:* zdenek.travnicek@upol.cz (Z. Trávníček).

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 $[Ni(et_2dtc)_3]$ PCNP was determined by a single crystal X-ray analysis as the second crystallographically studied nickel(IV) dithiocarbamato complex of the NiS<sub>6</sub> donor set so far; PCNP = pentacyanopropenide [15]. The heterobimetallic nickel(IV) dithiocarbamato complex with a ferrocenyl group bound to each of three dithiocarbamato moieties, having a composition of  $[Ni(etferdtc)_3][BF_4]$  with etferdtc = N,N-ethyl-ferrocenecarboxaldehydeethylimine dithiocarbamate anion, was prepared using electro-oxidation of the appropriate nickel(II) complex, i.e.  $[Ni(etferdtc)_2]$  [16].

#### 2. Experimental

#### 2.1. Starting materials

All chemicals and solvents used in this work were purchased from Sigma–Aldrich Co., Lachema Co., and Fluka Co., and they were used as received. The starting Ni(II) complexes, i.e. [Ni(*hmi*dtc)<sub>2</sub>] (**a**), [Ni(*in*dtc)<sub>2</sub>] (**b**), [Ni(*bzppz*dtc)<sub>2</sub>] (**c**), [Ni(*bz*<sub>2</sub>dtc)<sub>2</sub>] (**d**), [Ni(*pe*<sub>2</sub>dtc)<sub>2</sub>] (**e**), [Ni(*bzipr*dtc)<sub>2</sub>] (**f**), [Ni(*bzme*dtc)<sub>2</sub>] (**g**) and [Ni(*chet*dtc)<sub>2</sub>] (**h**) were prepared according to a previously described procedure [17]: *hmi*dtc, hexamethyleneiminedithiocarbamate anion; *in*dtc, indolinedithiocarbamate anion; *bzppz*dtc, benzylpiperazinedithiocarbamate anion; *pe*<sub>2</sub>dtc, *N*,*N*-dipentyldithiocarbamate anion; *bzipr*dtc, *N*,*N*-benzyl-*iso*propyldithiocarbamate anion; *bzme*dtc, *N*,*N*-benzylmethyldithiocarbamate anion; *chet*dtc, *N*,*N*-cyclohexyl-ethyldithiocarbamate anion.

#### 2.2. Syntheses of nickel(IV) complexes (1-14)

#### 2.2.1. [Ni(ndtc)<sub>3</sub>]ClO<sub>4</sub> (1-8)

2.5 mmol of pulverized  $[Ni(ndtc)_2](\mathbf{a-h})$  was dissolved in 20 mL of CHCl<sub>3</sub> and NOClO<sub>4</sub> (3.2 mmol), as an oxidant, was added to this solution with constant stirring. The reaction mixture was stirred with charcoal at room temperature for 2–3 h, and consequently filtered. 50 mL of diethyl ether (or hexane) were added to the filtrate which led to the formation of a brown (or dark brown) precipitate. The product was filtered off, washed with diethyl ether (or hexane) and dried at 40 °C under an infrared lamp. *Caution:* the prepared compounds need to be handled carefully because the some of **1** exploded on the fritted funnel while it was being scraped off.

#### 2.2.2. [Ni(ndtc)<sub>3</sub>][FeCl<sub>4</sub>]·yH<sub>2</sub>O (**9–14**)

FeCl<sub>3</sub> (2 mmol) was added to a solution of the starting  $[Ni(ndtc)_2]$  complex (**a**, **b**, **d**, **f**-**h**; 1 mmol) in 20 mL of CHCl<sub>3</sub>. The reaction mixture was stirred for 1–5 h, and after that it was filtered (together with charcoal). Diethyl ether, hexane or a mixture of benzene and diethyl ether (1:1, v/v) was added to the filtrate. A brown or dark brown product precipitated and it was filtered off, washed (diethyl ether) and dried at 40 °C (infrared lamp). In the case of 9, dark brown crystals formed in the benzene/diethyl ether mixture (1:1, v/v), some of which were found to be suitable for a single crystal X-ray analysis.

#### 2.3. Physical measurements

Elemental analyses (C, H, N) were performed on a Flash 2000 CHNS Elemental Analyzer (Thermo Fisher Scientific). Chlorine contents were determined using the Schöniger method and the nickel content was determined by 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

#### Table 1

Crystal data and structure refinement for [Ni(hmidtc)<sub>3</sub>][FeCl<sub>4</sub>] (9).

Empirical formula	C <sub>21</sub> H <sub>36</sub> N <sub>3</sub> Cl <sub>4</sub> FeNiS <sub>6</sub>
Formula weight	779.25
Temperature (K)	115(2)
Wavelength (Å)	0.71073
Crystal system, space group	Rhombohedral, <i>R</i> 3
Unit cell dimensions	
a = b (Å)	15.7605(3)
<i>c</i> (Å)	22.5351(8)
$\alpha = \beta$ (°)	90.00
γ (°)	120.00
V (Å <sup>3</sup> )	4847.6(2)
Z, $D_{\text{calc}}$ (g cm <sup>-3</sup> )	6, 1.602
Absorption coefficient $(mm^{-1})$	1.768
Crystal size (mm)	$0.40\times0.35\times0.25$
F (000)	2406
$\theta$ range for data collection (°)	$3.12 \leqslant  heta \leqslant 24.98$
Index ranges (h, k, l)	$-18\leqslant h\leqslant 18$
	$-18\leqslant k\leqslant 18$
	$-26 \leqslant l \leqslant 19$
Reflections collected/unique $(R_{int})$	12181/1888 (0.0138)
Data/restraints/parameters	1888/0/128
Goodness-of-fit on $F^2$	1.112
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0250, wR_2 = 0.0637$
R indices (all data)	$R_1 = 0.0270, wR_2 = 0.0644$
Largest peak and hole (e Å <sup>-3</sup> )	0.577, -0.542
-	

[18]. The molar conductivity of  $10^{-3}$  M acetone solutions was measured by an LF 330/SET conductometer (WTW GmbH) at 25 °C. Electronic absorption spectra of  $1.67 \times 10^{-4}$  M DMF solutions of 8-14 and solid state (diffuse-reflectance, nujol technique) spectra of 1-14 were recorded on a Specord M40 device. FTIR spectra (450–4000 cm<sup>-1</sup> region) were recorded on a Perkin–Elmer Spectrum one FTIR spectrometer using the KBr technique. Simultaneous thermogravimetric (TG) and differential thermal (DTA) analysis was performed 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 with a 2.5 °C min<sup>-1</sup> heating rate. Complex 13 was also studied by simultaneous thermogravimetry and differential scanning calorimetry (DSC) from laboratory temperature to 800 °C (5.0 °C min<sup>-1</sup> gradient) in a dynamic argon atmosphere, which was carried out by a STA 449 C Jupiter (Netzsch) coupled with a quadrupole mass spectrometer QMS 403 Aëolos (Netzsch). The transmission 57Fe Mössbauer spectrum was measured at 300 K in zero applied magnetic field using a spectrometer working in a constant acceleration mode with a <sup>57</sup>Co(Rh) radioactive source; iron foil was used as a calibration standard. X-ray powder diffraction experiments were performed with a PANalytical X'Pert PRO instrument (CoK $\alpha$  radiation) equipped with an X'Celerator detector. Samples were placed on a zero-background Si slide and scanned in the  $2\theta$  range of 5–90° in steps of 0.017°. Evaluation was made using HighScore Plus software and a PDF-4 database.

#### 2.4. Single crystal X-ray analysis of [Ni(hmidtc)<sub>3</sub>][FeCl<sub>4</sub>] (9)

The single crystal X-ray analysis of a selected crystal of **9** was collected on an Xcalibur<sup>TM</sup>2 diffractometer (Oxford Diffraction Ltd.) with a Sapphire2 CCD detector and with MoK $\alpha$  radiation (Monochromator Enhance, Oxford Diffraction Ltd.). Data collection and reduction were performed using CrysAlis software [19]. The same software was used for data correction for an absorption effect by empirical absorption correction using spherical harmonics, implemented in the 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) [20]. Nonhydrogen atoms were refined anisotropically and hydrogen atoms were located in a difference map and refined by using the riding



Complex	ndtc	R <sub>1</sub>	R <sub>2</sub>	<i>N</i> – <i>R</i> ₁ <i>R</i> ₂
1, 9	<i>hmi</i> dtc ( <b>a</b> )	-	-	hexamethyleneimine
2, 10	<i>in</i> dtc ( <b>b</b> )	-	-	indoline
3	bzppzdtc (c)	benzyl	piperazine	-
4, 11	<i>bz₂</i> dtc ( <b>d</b> )	benzyl	benzyl	-
5	<i>pe₂</i> dtc ( <b>e</b> )	pentyl	pentyl	-
6, 13	<i>bzipr</i> dtc ( <b>f</b> )	benzyl	<i>iso</i> propyl	-
7, 12	<i>bzme</i> dtc ( <b>g</b> )	benzyl	methyl	-
8, 14	<i>chet</i> dtc ( <b>h</b> )	cyclohexyl	ethyl	-

**Scheme 1.** The schematic representation of the  $[Ni(ndtc)_3]^+$  complex cation of the nickel(IV) complexes 1–14 given with the list of substituents of the appropriate dithiocarbamate.

model with C–H = 0.99 Å, and  $U_{iso}(H) = 1.2U_{eq}(CH_2)$ . The crystal data and structure refinements are given in Table 1. Molecular graphics as well as additional structural calculations were drawn and interpreted using DIAMOND [21] and Mercury [22].

#### 3. Results and discussion

#### 3.1. General properties

Nickel(IV) complexes of the general formulas  $[Ni(ndtc)_3][ClO_4 (1-8) and [Ni(ndtc)_3][FeCl_4]·yH_2O (9-14) were prepared (see Scheme 1) by oxidation of the starting nickel(II) complexes <math>[Ni(ndtc)_2]$  (**a**-**h**; see Section 2.1) by NOClO<sub>4</sub> (1-8) or FeCl\_3 (9-14). All the reactions were performed in chloroform and the molar ratios of the starting complexes and oxidants equaled 1:1.3 (1-8) or 1:2 (9-14). The obtained results of the elemental analysis (C, H, N) and determinations of chlorine (only for 9-14) and nickel contents correlated well with the calculated ones (Table 2). The molar conductivity values of 1-14 (see Table 3) are typical for 1:1 electrolytes in acetone [23], which was used for dissolving the prepared complexes. The complexes **1-8** are diamagnetic, while paramagnetic behavior, specifically 6.01, 6.03, 6.00, 6.15, 6.14 and 6.14  $\mu_{eff}/\mu_B$ , was detected in the case of **9-14**, respectively, due to the presence of the [FeCl\_4]<sup>-</sup> anion in the

Table 2					
Results of elemental	analysis	performed	for	complexes	1-14

#### 3.2. Single crystal X-ray analysis of [Ni(hmidtc)<sub>3</sub>][FeCl<sub>4</sub>] (9)

Complex **9** was prepared in the crystalline form and some crystals were found to be suitable for a crystallographic study. The molecular structure of **9** is depicted in Fig. 1. The crystal data and structure refinements are given in Table 1, while Table 4 summarizes selected bond lengths and angles.

The molecular structure of the ionic-pair complex 9 involves the [Ni(hmidtc)<sub>3</sub>]<sup>+</sup> cation and [FeCl<sub>4</sub>]<sup>-</sup> anion (Fig. 1). The Ni(IV) atom of [Ni(hmidtc)<sub>3</sub>]<sup>+</sup> is hexacoordinated by three bidentate S-donor ligands (*hmi*dtc anions) arranged in a slightly distorted octahedral geometry around the metal center. A comparison of the parameters of **9** with both nickel(IV) complexes having the NiS<sub>6</sub> donor set in the Cambridge Structural Database (CSD ver. 5.32) [24] shows that the average value of the Ni-S bond lengths [2.262(3) Å] is in good agreement with that of  $[Ni(but_2dtc)_3]Br[2.2608(4)Å]$ , however, they are a bit longer as compared with  $[Ni(et_2dtc)_3]C_3(CN)_5$ , whose average value equals 2.252(4) Å. The octahedral distortion can be outlined by the values of the three axial S-Ni-S angles, whose values significantly differ from 180° (see Table 4). For comparison, the corresponding angles equal 167.472(6) in Ni(but<sub>2</sub>dtc)<sub>3</sub>]Br and 167.14(8), 164.87(8) and 164.20(7)° in [Ni(*et*<sub>2</sub>dtc)<sub>3</sub>]C<sub>3</sub>(CN)<sub>5</sub>. The dihedral angles formed by the least-square planes fitted through the NiS<sub>2</sub>C atoms of a particular hmidtc ligand are 84.74(2)° for NiS1-S2<sup>i</sup>C1 and NiS1<sup>i</sup>S2<sup>ii</sup>C1<sup>i</sup>, and 84.75(2)° for NiS1S2<sup>i</sup>C1 and NiS1<sup>ii</sup>S2C1<sup>ii</sup> (symmetry codes: (i) x - y - 1, 1 - y, z; (ii) 1 - x, 2 - x + y, z).

The Fe–Cl bond lengths found within  $[FeCl_4]^-$  of **9** range from 2.1818(2) to 2.1881(6) Å, while the shortest Ni…Cl and Ni…Fe distances are equal to 4.1043(12) and 6.2862(6) Å, respectively. Its tetrahedral geometry is slightly distorted, as can be seen from the bond angle values (Table 4). Moreover, the distortion can be quantified using a four-coordinated geometry index  $\tau_4 = [360^\circ - (\alpha + \beta)]/141^\circ$  ( $\alpha$  and  $\beta$  being the largest angles in the four-coordinate species), which equals 0.991 (the value of 1.000 represents an ideal tetrahedral geometry) [25].

The crystal structure (Fig. 2) of complex **9** contains several types of van der Waals non-covalent contacts, namely intramolecular  $S \cdots Cl$  and intermolecular  $C-H \cdots C$ ,  $C-H \cdots Cl$  and  $S \cdots S$  types of contacts, with the shortest donor  $\cdots$  acceptor distances of 3.4907(10), 3.493(5), 3.716(3), and 3.4867(7) Å, respectively.

Complex	Empirical formula	Molecular weight	Yield (%)	Elemental analysis (calc./found, %)				
				С	Н	Ν	Cl	Ni
$[Ni(hmidtc)_3]ClO_4(1)$	C <sub>21</sub> H <sub>36</sub> N <sub>3</sub> ClNiO <sub>4</sub> S <sub>6</sub>	681.07	44	37.03/37.32	5.33/5.29	6.17/6.09	nd	8.62/8.57
$[Ni(indtc)_3]ClO_4(2)$	C27H24N3ClNiO4S6	741.04	43	43.86/43.87	3.26/3.02	5.67/5.54	nd	7.92/7.86
$[Ni(bzppzdtc)_3]ClO_4$ ( <b>3</b> )	C <sub>36</sub> H <sub>45</sub> N <sub>6</sub> ClNiO <sub>4</sub> S <sub>6</sub>	912.32	69	47.39/46.95	4.97/4.32	9.21/8.74	nd	6.43/6.47
$[Ni(bz_2dtc)_3]ClO_4$ ( <b>4</b> )	C45H42N3CINiO4S6	975.37	47	55.41/54.96	4.34/4.30	4.30/4.07	nd	6.02/6.05
$[Ni(pe_2dtc)_3]ClO_4$ (5)	C33H66N3CINiO4S6	855.44	39	46.33/46.36	7.78/7.97	4.91/4.87	nd	6.86/6.81
$[Ni(bzipdtc)_3]ClO_4$ (6)	C33H42N3CINiO4S6	831.25	50	47.68/47.35	5.09/4.91	5.06/4.64	nd	7.06/7.18
$[Ni(bzmedtc)_3]ClO_4(7)$	C27H30N3CINiO4S6	747.09	45	43.41/43.78	4.05/4.07	5.62/5.17	nd	7.86/7.78
$[Ni(chetdtc)_3]ClO_4$ (8)	C27H48N3CINiO4S6	765.23	56	42.38/42.65	6.32/6.64	5.49/5.86	nd	7.67/7.55
$[Ni(hmidtc)_3][FeCl_4]$ (9)	C21H36N3Cl4FeNiS6	779.28	51	32.37/32.11	4.66/4.24	5.39/4.86	18.20/17.85	7.53/7.28
[Ni(indtc) <sub>3</sub> ][FeCl <sub>4</sub> ] (10)	C <sub>27</sub> H <sub>24</sub> N <sub>3</sub> Cl <sub>4</sub> FeNiS <sub>6</sub>	839.24	66	38.64/39.08	2.88/2.74	5.01/4.74	16.90/17.20	6.99/6.98
$[Ni(bz_2dtc)_3][FeCl_4]$ (11)	C45H42N3Cl4FeNiS6	1073.58	53	50.34/49.87	3.94/3.71	3.91/3.82	13.21/12.78	5.47/5.48
[Ni(bzmedtc)3][FeCl4] (12)	C27H30N3Cl4FeNiS6	845.29	58	38.36/38.86	3.58/3.71	4.97/4.84	16.78/16.95	6.94/6.88
$[Ni(bzipdtc)_3][FeCl_4] \cdot H_2O(13)$	C33H44N3Cl4FeNiOS6	947.47	45	41.83/42.19	4.68/4.29	4.44/4.32	14.97/14.87	6.19/6.23
[Ni(chetdtc) <sub>3</sub> ][FeCl <sub>4</sub> ] 0.5H <sub>2</sub> O (14)	$\mathrm{C}_{27}\mathrm{H}_{49}\mathrm{N}_{3}\mathrm{Cl}_{4}\mathrm{FeNiO}_{0.5}\mathrm{S}_{6}$	872.44	47	37.17/37.87	5.66/5.81	4.82/4.73	16.25/16.41	6.73/6.67

nd, not determined for safety reasons.

#### Table 3

The results of molar conductivity measurements (S cm<sup>2</sup> mol<sup>-1</sup>), UV–Vis ( $\times$  10<sup>3</sup> cm<sup>-1</sup>) and FTIR (cm<sup>-1</sup>) spectroscopy, and thermal analysis (TG/DTA) obtained for the nickel(IV) complexes 1–14.

	$\lambda_{\mathbf{M}}$	FTIR	UV-Vis <sup>a</sup>	Thermal analysis	
				TG <sup>b</sup>	DTA <sup>c</sup>
1	144.0	623vs, 1008w, 1086vs, 1519vs	22.0, 29.9	-	-
2	136.9	622m, 1008w, 1087vs, 1497vs	21.0, 27.6	-	-
3	125.6	623m, 1010m, 1091vs, 1529vs	23.0, 26.0	-	-
4	137.5	623m, 1001w, 1091vs, 1522vs	17.8, 20.7	-	-
5	141.0	624m, 1005w, 1088vs, 1536vs	19.4, 23.5	-	-
6	136.8	622m, 1005m, 1089m, 1501vs	20.7, 26.5	-	-
7	129.1	623m, 1002w, 1094vs, 1540vs	22.1, 27.2	-	-
8	126.0	623m, 1009m, 1099vs, 1508vs	22.4, 27.3	-	-
9	142.4	1006w, 1521vs	23.0	115-728	231, 243, 285, 363, 423, 528
10	145.6	1009w, 1496vs	16.0, 26.9	69-477	175, 193, 223, 244, 365, 464
11	127.2	1001w, 1513vs	17.9, 24.6	131-774	166en, 194, 354
12	139.5	1002w, 1536vs	16.8, 25.9	58-770	136, 207, 253, 374, 449
13	134.2	1009w, 1499vs	19.5, 24.0	29-796	40en, 146en, 204, 356, 434, 454
14	144.5	1007w, 1502vs	20.4	64-733	86en, 170, 220, 231, 359, 492

<sup>a</sup> Solid state (diffuse-reflectance) spectra.

<sup>b</sup> The temperature range of thermal decomposition (°C).

<sup>c</sup> The position of maxima of exothermic effects (°C) and minima of endothermic effects (°C; symbolized *en*).



**Fig. 1.** The molecular structure of  $[Ni(hmidtc)_3][FeCl_4]$  (**9**) with non-hydrogen atoms drawn as thermal ellipsoids at the 50% probability level; the hydrogen atoms are omitted for clarity. Symmetry codes: (i) x - y - 1, 1 - y, z; (ii) 1 - x, 2 - x + y, z.

#### 3.3. FTIR, UV-Vis and Mössbauer spectroscopy

The v(C=S) and v(C=N) vibrations, known as very characteristic for dithiocarbamate-based organic ligands, showed their maxima at 1001–1010 cm<sup>-1</sup> of weak to middle intensity [for v(C=S)] and 1496–1540 cm<sup>-1</sup> of very strong intensity [for v(C=N)] (Table 3). The vibrations detected at 622–624 and 1086–1099 cm<sup>-1</sup> demonstrated the presence of the perchlorate anion [ $v_4(ClO_4^-)$  and  $v_3(ClO_4^-)$ , respectively] in the structure of the [Ni(ndtc)<sub>3</sub>]ClO<sub>4</sub> complexes (**1–8**).

The diffuse-reflectance UV–Vis spectra showed two maxima (only one maximum in the case of **9** and **14**) assignable to the d-d transitions of the prepared octahedral nickel(IV) dithiocarbamato complexes between 16000 and 30000 cm<sup>-1</sup> (Table 3). With the aim to better understand spectral properties of the studied complexes, mainly complexes **9–14** which are influenced by the simultaneous presence of nickel(IV) and iron(III) species, some addi-

Table 4	
Selected bond lengths	Å) and angles (°) of $Ni(hmidtc)_3]$ [FeCl <sub>4</sub> ] (9).

Rond longths		Pond angles	
Boliu leligilis		Boliu aligies	
Ni1-S1	2.2652(5)	S1-Ni1-S2 <sup>i</sup>	76.46(2)
Ni1-S2	2.2597(5)	S1-Ni1-S1 <sup>i</sup>	94.57(2)
S1-C1	1.719(2)	S1-Ni1-S2 <sup>ii</sup>	95.51(2)
S2 <sup>i</sup> -C1	1.715(2)	S1-Ni1-S2	167.00(2)
C1-N1	1.308(3)	S2-Ni1-S2 <sup>i</sup>	94.82(2)
Fe1-Cl1	2.1881(6)	Ni1-S1-C1	86.96(7)
Fe1-Cl2	2.1818(12)	Ni1-S2 <sup>i</sup> -C1	87.24(8)
		Cl1-Fe1-Cl2	108.79(2)
		Cl1-Fe1-C11 <sup>i</sup>	110.14(2)

Symmetry codes: (i) x - y - 1, 1 - y, z; (ii) 1 - x, 2 - x + y, z

tional experiments have been performed. We measured DMF solution UV-Vis spectra of the representative complexes involving the  $[FeCl_4]^-$  anion (9–14) as well as the CHCl<sub>3</sub> spectrum of complex 8 in an effort to find whether the stereochemistry (i.e., coordination geometry) of the complexes is changed in a solution as compared to the solid state. As for the representative complex 8 (see Fig. 3), it may be concluded that the DMF and CHCl<sub>3</sub> spectra are nearly identical and quite comparable with the solid state spectrum with main maxima at about 27 500 and 22 500  $\text{cm}^{-1}$ , thus showing that no significant geometric changes proceed in the vicinity of the central atoms among the mentioned phases. We also strived to interpret the spectra of complexes 9-14, involving Ni(IV) and Fe(III) species, which are influenced by a superposition of both components. For that reason, we prepared (PhMe<sub>3</sub>N)[FeCl<sub>4</sub>] [26], a simple compound involving the [FeCl<sub>4</sub>]<sup>-</sup> anion, and measured its DMF and solid state (diffuse-reflectance) UV-Vis spectra. The solid state spectrum of the compound showed a weak shoulder at 22 300 cm<sup>-1</sup> and a weak maximum at 18750 cm<sup>-1</sup>, while no typical maximum (shoulder) was observed in the DMF solution spectrum. A comparison of the DMF spectra of  $[Ni(bzipdtc)_3](ClO_4)$  (6),  $[Ni(bzipdtc)_3][FeCl_4] \cdot H_2O$ (13), and DMF and solid state spectra of (PhMe<sub>3</sub>N)[FeCl<sub>4</sub>] is shown in Fig. 3. Based on the obtained results, we are not able to make an univocal conclusion explaining how the simultaneous presence of nickel(IV) and iron(III) species may affect the electronic spectra of compounds 9-14. Nevertheless, we may draw the conclusion that the maxima (shoulders) observed at about 22300 and 18700 cm<sup>-1</sup> may be ascribed to both the  $[Ni(ndtc)_3]^+$  complex cations and the [FeCl<sub>4</sub>]<sup>-</sup> anions, while the maxima (shoulders) at about 20500 cm<sup>-1</sup> may be associated with the d-d transitions of the  $[Ni(ndtc)_3]^+$  complex cations.



**Fig. 2.** A part of the crystal structure of  $[Ni(hmidtc)_3][FeCl_4]$  (9), as viewed along the *c* axis, showing the packing of the molecules within the unit cell and selected non-covalent contacts (dashed lines) of the C-H···Cl, C-H···C, S···Cl and S···S type; the hydrogen atoms not involved in the depicted contacts are omitted for clarity.



**Fig. 3.** A comparison of solution and solid state UV–Vis spectra of [Ni(*chet*dtc)<sub>3</sub>]ClO<sub>4</sub> (**6**) (*on top*), and spectra of [Ni(*bzip*dtc)<sub>3</sub>](ClO<sub>4</sub>) (**6**), [Ni(*bzip*dtc)<sub>3</sub>][FeCl<sub>4</sub>]·H<sub>2</sub>O (**13**) and (PhMe<sub>3</sub>N)[FeCl<sub>4</sub>] (*down*).



**Fig. 4.** The results of simultaneous TG/DTA analyses of complex **13** performed in a dynamic air atmosphere (*up*), simultaneous TG/DSC curves of **13** performed in a dynamic argon atmosphere (*middle*), and TG curve together with the *in situ* mass spectrometry with  $H_2O$  (*m*/*z* = 18) elimination (*down*). Insets show XRD patterns of the thermal degradation products.

The room temperature Mössbauer spectrum of **9** consists of one singlet with an isomer shift of 0.24 mm s<sup>-1</sup>, which is consistent with the results of the crystallographic study and it proves the presence of the tetrahedral [FeCl<sub>4</sub>]<sup>-</sup> anion involving the Fe(III) ion in the high-spin state.

#### 3.4. Thermal analysis (TG/DTA)

The thermal properties of the complexes **9–14** were studied by means of simultaneous TG/DTA analyses (the thermal properties of 1-8 were not studied because of the presence of the explosive perchlorate anion in their structure). All the complexes 9-14 decomposed in one step without the formation of thermally stably intermediates and the process of thermal decomposition is connected with several endo- and exo-effects (see Table 3). Interestingly, the decay of **10** finished at 477 °C, which differs significantly from other complexes, whose degradation proceeded to 728-796 °C. Thermal studies also showed that complexes 9-12 are non-solvated, while 13 and 14 were found to be hydrated. The weight losses detected at the beginning of the TG curves of [Ni(bzipdtc)<sub>3</sub>][FeCl<sub>4</sub>]·H<sub>2</sub>O (13) and [Ni(chetdtc)<sub>3</sub>][FeCl<sub>4</sub>]·0.5H<sub>2</sub>O (14) equal 1.7% (1.9% calc. for H<sub>2</sub>O), and 1.1% (1.0% calc. for 0.5H<sub>2</sub>O), respectively, and they were caused by the water molecules elimination, as proved by the mass spectrometry of the thermal degradation products, where the fragment corresponding to water molecule was unambiguously identified in the case of **13** (see Fig. 4). The final product of the thermal decay of 13 performed in air was identified by XRD as a mixture of NiFe<sub>2</sub>O<sub>4</sub> (PDF-4 No. 01-074-2081; ca 63%) and Fe<sub>2</sub>O<sub>3</sub> (PDF-4 No. 01-086-2368; ca 37%), while the residue of the analysis carried out in a dynamic argon atmosphere consists of Fe<sub>5</sub>Ni<sub>4</sub>S<sub>8</sub> (PDF-4 No. 01-086-2470; ca 86%) and FeS (PDF-4 No. 03-065-6841; ca 14%).

#### 4. Conclusions

Octahedral nickel(IV) dithiocarbamato complexes of two types, i.e.  $[Ni(ndtc)_3]ClO_4$  (1–8) and  $[Ni(ndtc)_3][FeCl_4]\cdot yH_2O$  (y = 0 for 9–12, 1 for 13 and 0.5 for 14), have been prepared and characterized. The series involves the complex  $[Ni(h-midtc)_3][FeCl_4]$  (9), whose crystallographically determined structure represents only the third example of a nickel(IV) complex involving the  $[Ni(ndtc)_3]^+$  moiety with three bidentate S,S'-donor dithiocarbamate anions (*n*dtc) arranged in a distorted octahedral geometry.

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#### Appendix A. Supplementary data

CCDC 827947 contains the supplementary crystallographic data for  $[Ni(hmidtc)_3]$ [FeCl<sub>4</sub>]. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: +44 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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