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Synthesis, structure and spectroscopic properties of nickel(II) macrocyclic and open-chain complexes resulted from 1-phenyl-butane-1,3-dione mono-*S*-methylisothiosemicarbazone template self-condensation

Julieta I. Gradinaru[a], Yurii A. Simonov[b], Vladimir B. Arion*[a,1], Polina N. Bourosh[b], Maria A. Popovici[a], Vitalii K. Bel'skii[c], Nicolai V. Gerbeleu*[a,2]

[a] *Institute of Chemistry of the Academy of Sciences of Moldova, Str. Academiei, 3, MD-2028 Chishinau, Moldova*
[b] *Institute of Applied Physics of the Academy of Sciences of Moldova, Str. Academiei, 5, MD-2028 Chishinau, Moldova*
[c] *L.Ya. Karpov's Institute of Physical Chemistry, 103064 Moscow, Russia*

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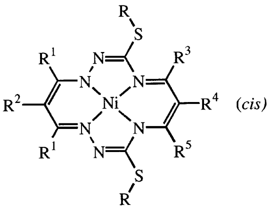
Abstract

Self-condensation of 1-phenyl-butane-1,3-dione mono-*S*-methylisothiosemicarbazone (**6**) in the presence of nickel(II) acetate in methanol gives rise to a mixture of two complexes: [2,9-bis(methylthio)-5,13-dimethyl-7,14-diphenyl-1,3,4,8,10,11-hexaazacyclotetradeca-2,4,6,9,11,13-hexaenato(2-)N^1,N^4,N^8,N^{11}]nickel(II) (**7**) and [1-amino-1,6-bis(methylthio)-4,9-dimethyl-11-phenyl-2,3,4,7,8-pentaazaundeca-1,3,6,8,10-pentaenato(-)-11-olato(-)N^2,N^4,N^8,*O*]nickel(II) (**8**). Both the macrocyclic complex **7** and the open-chain chelate **8** are characterised by X-ray diffraction methods, which reveal their square-planar structure. Electronic, IR, NMR, electron impact mass spectra and cyclic voltammograms of new compounds are also reported. © 2001 Elsevier Science B.V. All rights reserved.

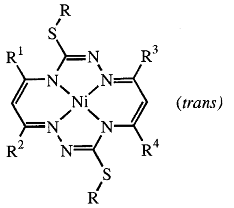
Keywords: Nickel(II) complexes; Isothiosemicarbazide-based ligands; Crystal structures

1. Introduction

Metal-directed condensation of 1, *n*-diamines with aldehydes or ketones produces mainly symmetric polyazamacrocyclic compounds [1–4]. The use of the *S*-alkylisothiosemicarbazide hydroiodide (NH_2–N=C(SR)–NH_2HI) as a building block in such reactions is particularly interesting. This leads to various macrocyclic systems containing two different β-dicarbonyl residues, as well as differently arranged *S*-alkylisothiosemicarbazide fragments around the metal ion.



$R = R^1 = R^3 = CH_3, R^2 = R^5 = H, R^4 = CH_3CO$ **(1)**
$R = R^1 = CH_3, R^2 = R^3 = R^5 = H, R^4 = NO_2$ **(2)**
$R = R^1 = CH_3, R^2 = R^3 = R^4 = R^5 = H$ **(3)**



$R = R^1 = R^2 = R^3 = R^4 = CH_3$ **(4)**
$R = CH_3, R^1 = R^2 = R^3 = R^4 = H$ **(5)**

Previously, it has been found that [1 + 2] condensation of pentane-2,4-dione with *S*-alkylisothiosemicarbazide hydroiodide in the presence of nickel(II) affords the complex [Ni(H_2L)]I, where H_3L = pentane-2,4-dione bis(*S*-alkylisothiosemicarbazone) [5]. The latter can successfully be used as a precursor for building up the macrocylic species **1**–**4** [6–10]. The unexpected formation of macrocyclic compounds with symmetri-

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[1] *Corresponding author. Present address: Laboratoire de Chimie de Coordination du CNRS, 205 route de Narbonne, F-31077 Toulouse Cedex 04, France. Tel.: + 33-5-6133 3159; fax: + 33-6155 3003; arion@lcc-toulouse.fr

[2] *Corresponding author

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cally disposed *S*-alkylisothiosemicarbazide groups (described as trans) around the nickel atom (regarded here as an inversion centre) from a precursor, in which the corresponding residues are arranged non-symmetrically around the same centre (described as cis), needs a series of successive transformations: (i) hydrolytic breaking of one C=N bond with liberation of the free *S*-alkylisothiosemicarbazide; (ii) reaction of the latter with *Hacac*, providing the formation of the tridentate ligand – pentane-2,4-dione mono-*S*-alkylisothiosemicarbazone; (iii) the self-condensation of the tridentate ligand in the presence of nickel(II), yielding the trans-macrocyclic species.

The formation of trans-hexaazamacrocylic products in [2 + 2] condensation of *S*-alkylisothiosemicarbazide with β-dicarbonyl compounds appears to be more preferable than that of cis-species. This was confirmed by template reaction of *S*-alkylisothiosemicarbazide hydroiodide with 1,1,3,3-tetraethoxypropane, which provided the formation of the trans-product **5** [11].

Efforts to explore this chemistry further were directed to extension of the range of β-dicarbonyl building blocks, which can lead to new macrocyclic systems. Only a few coordination compounds, e.g. [Fe(HL^1)Cl$_2$] [12], [Ni(HL^1)NH$_3$]I [13] and [Ni(HL^1)Py] [14], where H_2L^1 = 1-phenyl-butane-1,3-dione mono-*S*-methylisothiosemicarbazone (**6**), were synthesised starting from 1-phenyl-butane-1,3-dione.

Herein we report on the synthesis, structure and physico-chemical properties of new products (**7**) and (**8**) of nickel(II)-controlled self-condensation of 1-phenyl-butane-1,3-dione mono-*S*-methylisothiosemicarbazone (**6**) (Scheme 1).

2. Experimental

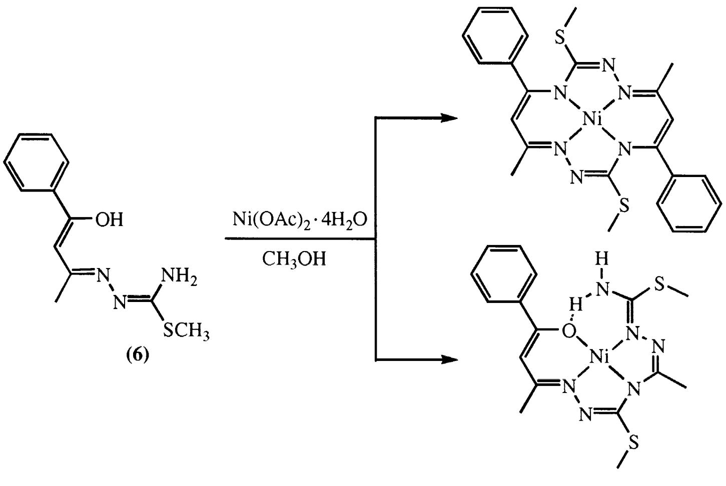
2.1. Chemicals

All chemicals used were analytical reagent grade. *S*-Methylisothiosemicarbazide hydroiodide and 1-phenyl-butane-1,3-dione mono-*S*-methylisothiosemicarbazone were prepared as described elsewhere [12,15].

2.2. Syntheses

2.2.1. Complexes 7 and 8

1-Phenyl-butane-1,3-dione mono-*S*-methylisothiosemicarbazone (0.50 g, 20 mmol) in methanol (10 cm^3) was added to $Ni(OAc)_2 \cdot 4H_2O$ (0.25 g, 10 mmol) in methanol (10 cm^3) and the reaction mixture was heated under reflux for 2 h. The brown rhombic crystals formed (**7**) were separated by filtration, washed with methanol and ether. Yield 0.20 g, 38.5%. *Anal.* Found: C, 54.91; H, 4.82; N, 15.73; Ni, 11.05. Calc. for $C_{24}H_{24}N_6NiS_2$ (fw 519.33): C, 55.51; H, 4.66; N, 16.18; Ni, 11.31. Molecular peak in the electron impact (EI) mass spectrum: m/z 518 (see supplementary data). ^{1}H and ^{13}C NMR spectra for **7** (see supplementary data): δ_H (300 MHz, CDCl$_3$) 7.37–7.29 (m, 10H, Ph), 4.69 (s, 2H, –CH=), 2.17 (s, 6H, SCH$_3$), 2.10 (s, 6H, CH$_3$); δ_C (75.5 MHz, CDCl$_3$) 162.5, 158.4, 154.0, 139.3, 129.5, 129.3, 128.4, 109.1, 19.70, 19.69. Electronic spectrum (CHCl$_3$), λ/nm (ε/l cm^{-1} mol^{-1}): 620 (820), 494 (5950), 416 (7370), 347 (26 040), 277 (19 970). The filtrate was left to stand for 2 days and the orange precipitate containing **8** that formed was collected and purified by chromatography on a silica column using as eluent a 2:1 mixture hexane–chloroform. Yield 0.06 g, 13.8%.



Scheme 1.

Table 1
Crystal data and details of data collection for **7** and **8**

	7	**8**
Chemical formula	$C_{24}H_{24}NiN_6S_2$	$C_{16}H_{20}NiN_6OS_2$
M (g mol^{-1})	519.33	435.21
Crystal size (mm)	$0.2\times0.2\times0.2$	$0.4\times0.3\times0.3$
Crystal colour, habit	dark brown, prism	orange, prism
Crystal system	monoclinic	monoclinic
Space group	$P2_1/n$ (no. 14)	$P2_1$ (no. 4)
a (Å)	8.915(2)	14.083(3)
b (Å)	13.835(3)	9.535(2)
c (Å)	10.106(2)	7.2060(10)
β (°)	107.26(3)	79.84(3)
V (Å^3)	1190.3(4)	952.5(3)
Z	2	2
T (K)	293	293
D_c (g cm^{-3})	1.449	1.518
Radiation	Mo Kα	Mo Kα
λ (Å)	0.71073	0.71073
μ (cm^{-1})	10.15	12.56
F(000)	540	452
$(\sin\theta/\lambda)_{max}$ (Å^{-1})	0.60	0.65
h range	$-9/10$	$-16/18$
k range	$-16/0$	$0/12$
l range	$-12/0$	$0/9$
No. measured reflections	1403	1824
No. reflections used in refinement	1388	1824
No. parameters	154	229
R_1 (obs.)	0.0281	0.0416
wR_2 (all data)	0.0743	0.1130
S	1.085	1.071
Final diff. density (e$^-$ Å^{-3})	0.220	0.389

Anal. Found: C, 43.91; H, 4.58; N, 19.18; Ni, 13.34. Calc. for $C_{16}H_{20}N_6NiOS_2$ (fw 435.21): C, 44.16; H, 4.63; N, 19.31; Ni, 13,49. Base peak in the EI mass spectrum: m/z 434. ^{1}H and ^{13}C NMR spectra for **8**: δ_H (300 MHz, $CDCl_3$) 7.49–7.46 (m, 2H, Ph), 7.34–7.31 (m, 3H, Ph), 6.2–6.8 (br s, 2H, NH), 5.61 (s, 1H, –CH=), 2.53 (s, 3H, CH_3), 2.30 (s, 3H, CH_3), 2.29 (s, 3H, CH_3), 2.27 (s, 3H, CH_3); δ_C (75.5 MHz, $CDCl_3$) 168.9, 166.9, 157.7, 153.3, 152.9, 140.4, 129.1, 128.8, 126.6, 98.0, 19.7, 17.3, 15.9, 13.3.

2.3. Analyses and physical measurements

Nickel was determined gravimetrically as $Ni(DMG)_2$, where H_2DMG = dimethylglyoxime. C, H, N contents were determined by standard micromethods. IR spectra were recorded on a Perkin–Elmer 2000FT-IR spectrophotometer using KBr disks (4000–400 cm^{-1}). Mass-spectrometric analysis was performed with a Finningan MAT 95 (Finningan GmbH, Bremen, Germany) doubly focusing (BE) mass spectrometer using EI ionisation (70 eV) and standard resolution conditions, $m/\Delta m = 2300$. Solution ^{1}H and ^{13}C NMR spectra were recorded on Bruker AC 270 and AM 300 spectrometers. Absorption spectra were recorded on a Perkin–Elmer Lambda 19 spectrophotometer. Cyclic voltammetric measurements were performed using an EG&G Model 273A potentiostat. The three-electrode cell consisted of a platinum working electrode, a platinum counter-electrode, and an Ag/AgCl/saturated LiCl (EtOH) reference electrode. Ferrocene was used as an internal standard. Deaeration of all solutions was accomplished by passing a stream of high-purity argon through the solution for 10 min prior to the measurements and then maintaining a blanketing atmosphere of argon over the solution during the measurements. Cyclic voltammograms in CH_2Cl_2 containing 0.10 M tetra-n-butylammonium hexafluorophosphate as the supporting electrolyte and ~ 10^{-3} M complex were recorded at scan rates ranging from 100 to 500 mV s $-^{-1}$.

2.3.1. Crystal structure determination of 7 and 8

X-ray diffraction measurements were performed on Enraf–Nonius CAD4 (**7**) and DAR-UMB (**8**) diffractometers. Crystal data, data collection, and structure refinement details are given in Table 1. Lattice parameters were determined by a least-squares procedure from 25 (θ range 13.0–20.5°) (**7**) and 24 (θ range 12.8–23.2°) (**8**) reflections. The structures were solved by direct methods and refined by full-matrix least-squares techniques. The non-H atoms were refined with anisotropic displacement parameters. In both cases, H atoms were calculated and allowed to ride. A Pentium II computer and the programs SHELXS-86 (for structure solution) [16] and SHELXL-93 (for refinement) [17] were used.

3. Results and discussion

Self-condensation of 1-phenyl-butane-1,3-dione mono-S-methylisothiosemicarbazone (**6**) in the presence of nickel(II) acetate results in a mixture of two, easily separated products: the hexaazamacrocyclic complex **7** and the open-chain species **8**. Both are diamagnetic substances, soluble in chloroform, less soluble in methanol and ethanol, and insoluble in hexane, diethyl ether and water.

The IR spectrum of **7** shows no absorption in the 3100–3400 cm^{-1} region or at 1700 cm^{-1}, indicating the absence of any unreacted NH_2 or C=O groups. Intense and very intense bands that can be attributed to charge-transfer and intraligand transitions dominate the electronic spectrum of **7** in chloroform. A broad band with a maximum at ~ 625 nm can be attributed to the d–d transition. The EI mass spectrum of **7** is rather simple and provides a direct confirmation of the macrocycle formation (see supplementary data). The most intense peak is that of the molecular ion $[M]^{+\cdot}$, the further fragmentation of which under EI is insignificant. The presence of the doubly-charged ion $[M]^{2+}$, which is the second most abundant ion in the spectrum (9% relative intensity), indicates the high stability of the molecular ion. Its further fragmentation under EI is almost negligible. The fragment ions mainly arise by losses from the side groups and could easily be related to the structure of the complex (see supplementary data). Their relative intensities do not exceed 6%. The ^{1}H NMR spectrum offers further evidence for the formation of the trans-macrocycle. Four distinct absorption regions were observed at 7.37–7.29 (m), 4.69 (s), 2.17 (s), and 2.10 ppm (s). The relative intensities were in accordance with the expected ratio of 5:1:3:3 between the resonance signals of phenyl, methine, thiomethyl and methyl protons. The number of signals indicates the presence of the inversion centre in the macrocyclic molecule. The ^{1}H NMR data for two closely related trans-macrocyclic complexes **4** and **5** are available as supplementary data. All these data, in addition to the previous results [6–11], suggest the building up the trans-hexaazamacrocyclic complex **7** through the nickel(II)-controlled self-condensation of **6**.

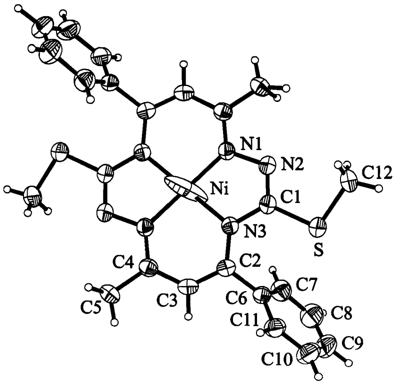


Fig. 1. ORTEP representation of the complex **7**, showing 50% probability thermal ellipsoids.

Table 2
Selected interatomic bond distances (Å) and angles (°) for **7**

Distances			
Ni–N1	1.821(2)	C3–C4	1.410(4)
Ni–N3	1.861(2)	C4–C5	1.501(4)
S–C1	1.764(3)	C2–C6	1.491(4)
S–C12	1.800(3)	C6–C7	1.383(4)
N1–C4*	1.318(4)	C6–C11	1.393(4)
N1–N2	1.400(3)	C7–C8	1.385(5)
N2–C1	1.287(4)	C8–C9	1.375(6)
N3–C2	1.376(3)	C9–C10	1.372(5)
N3–C1	1.397(4)	C10–C11	1.380(4)
C2–C3	1.372(4)		
Angles			
N1–Ni–N3	84.09(10)	N1*–C4–C5	119.9(3)
N1*–Ni–N3	95.91(10)	C3–C4–C5	119.6(3)
C1–S–C12	99.6(2)	C2–C3–C4	127.8(3)
C4*–N1–N2	115.4(2)	C3–C2–N3	121.4(3)
C4*–N1–Ni	128.8(2)	C3–C2–C6	116.9(2)
N2–N1–Ni	115.8(2)	N3–C2–C6	121.6(2)
C1–N2–N1	110.4(2)	C7–C6–C11	118.6(3)
C2–N3–C1	125.4(2)	C7–C6–C2	120.9(3)
C2–N3–Ni	124.9(2)	C11–C6–C2	120.3(3)
C1–N3–Ni	109.7(2)	C6–C7–C8	120.7(3)
N2–C1–N3	119.5(3)	C7–C8–C9	119.6(4)
N2–C1–S	116.2(2)	C8–C9–C10	120.6(3)
N3–C1–S	124.0(2)	C9–C10–C11	119.9(4)
N1*–C4–C3	120.5(3)	C10–C11–C6	120.5(3)

* Symmetry transformations used to generate equivalent atoms: $-x$, $-y+1$, $-z$

Inspection of the results for **8** showed its considerable difference from **7**. In particular, the IR spectrum of **8** contains a band at 3130–3370 cm^{-1} attributable to ν_{NH} stretching vibrations. The number of signals in the ^{1}H and ^{13}C NMR spectra indicates the absence of an inversion centre in the molecule. The deuterochloroform ^{1}H NMR spectrum of **8** consists of seven signals at 7.49–7.31 (m), 6.2–6.8 (br s), 5.61 (s), 2.53 (s), 2.30 (s), 2.29 (s), and 2.27 ppm (s), assigned to Ph, NH_2, $=CH-$, two SCH_3 and two CH_3 groups respectively. The proton-decoupled ^{13}C NMR spectrum showed the presence of 16 carbon atoms in the molecule. These data are in agreement with the non-symmetric structure of **8**. The EI mass spectrum of the latter reveals its reasonable stability under these conditions. The most abundant ion is that of $[M]^{+\cdot}$, the further fragmentation of which is more extensive than for **7**, with increased relative amounts of the fragment ions formed (see supplementary data). Note also the presence of the doubly-charged molecular ion $[M]^{2+}$ in the spectrum. But the peak of the latter is overlapped with the peak due to the $[Ni(C_6H_5COCHC(CH_3)N]^+$ ion. From the above observations we concluded that **8** has an open-chain square-planar structure.

3.1. X-ray diffraction structures of 7 and 8

Fig. 1 reveals the structure of the centrosymmetric complex **7**. Selected bond lengths and angles are given in Table 2. As in **4** and **5**, a trans-arrangement of the $-SCH_3$ groups has been found in **7**. In the coordination of the macrocycle with the nickel atom there are four chelate rings formed: two six-membered NiN_2C_3 and two five-membered NiN_3C in the sequence 5, 6, 5, 6. The square-planar coordination of the ligand to nickel(II) occurs through four nitrogen atoms at 1.821(2) Å (Ni–N1) and 1.861(2) Å (Ni–N3). The corresponding distances in **4** are at 1.835(2) and 1.882(4) Å [7], whereas they are at 1.827(19), 1.829(19) and 1.818(18), 1.826(19) Å in two independent molecules of **5** [11]. The non-significant differences in the Ni–N distances can be explained by the influence of the substituent R on the electron density distribution over the macrocyclic ligand.

The 14-membered skeleton of the macrocycle in **7** is practically planar. The dihedral angle between the five- and six-membered chelate rings is 4.8°. The phenyl ring at C2 forms an angle of 111.6° with the plane through

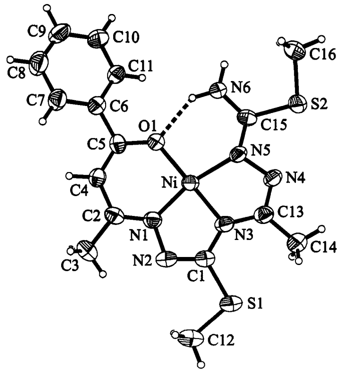


Fig. 2. ORTEP representation of the complex **8**, showing 50% probability thermal ellipsoids.

Table 3
Selected interatomic bond distances (Å) and angles (°) for **8**

Distances			
Ni–N1	1.825(5)	N4–N5	1.437(7)
Ni–O1	1.838(4)	N5–C15	1.298(6)
Ni–N3	1.834(5)	N6–C15	1.349(7)
Ni–N5	1.901(5)	C2–C4	1.428(9)
S1–C1	1.763(6)	C2–C3	1.514(8)
S1–C12	1.800(8)	C4–C5	1.358(5)
S2–C15	1.759(4)	C5–C6	1.505(9)
S2–C16	1.803(4)	C6–C7	1.388(10)
O1–C5	1.305(7)	C6–C11	1.399(9)
N1–C2	1.312(9)	C7–C8	1.385(10)
N1–N2	1.427(7)	C8–C9	1.371(11)
N2–C1	1.307(9)	C9–C10	1.367(12)
N3–C1	1.365(8)	C10–C11	1.382(9)
N3–C13	1.374(9)	C13–C14	1.385(10)
N4–C13	1.303(8)		
Angles			
N1–Ni–O1	95.3(2)		
N1–Ni–N3	84.1(2)	C2–N1–N2	116.1(5)
O1–Ni–N3	178.6(2)	N1–N2–C1	108.8(5)
N1–Ni–N5	166.5(2)	N2–C1–N3	119.8(5)
O1–Ni–N5	98.1(2)	C1–N3–C13	132.9(5)
N3–Ni–N5	82.4(2)	N3–C13–N4	117.6(6)
O1–C5–C6	115.0(5)	C13–N4–N5	111.1(5)
C5–C4–C2	125.7(6)	N4–N5–C15	112.1(5)
C4–C2–N1	120.2(6)	N5–C15–N6	120.7(4)

the NiN_4 core. Sulfur and carbon atoms of thiomethyl groups deviate out from the mean plane of **7** by 0.564 Å and 1.048 Å respectively. In the macrocycle the interatomic distances are very close to those found in its nearest analogues **4** and **5** [7,11]. Note that the N2–C1 distance of 1.287(4) Å is shorter than N3–C1 at 1.397(4) Å; both five- and six-membered metallocycles are characterised by π-electron delocalisation.

A number of low-spin square-planar nickel(II) complexes pack in stacks with intermolecular Ni···Ni or Ni···N contacts. According to the Ref. [18], the metal–metal interactions are possible at distances up to 5.0 Å. In **4** the molecules also form stacks via Ni···Ni interaction at 4.915 Å. The shortest intermolecular Ni···Ni contact at 3.180(2) Å [19] was found in bis(dimethylglyoximato)nickel(II). In **7** the phenyl ring at C2 impedes the stacking of the molecules. Instead, a short C10···Ni contact at 3.957 Å with the corresponding H···Ni separation at 3.07 Å has been found. Such contacts have also been mentioned for NiL^1Py (L^1 = dianion of the 1-phenyl-butane-1,3-dione mono-*S*-methylisothiosemicarbazone), where the carbon atom of the adjacent pyridine molecule is shown to be at 3.421(3) Å from the nickel(II) atom [14]. All other intermolecular contacts can be regarded as van der Waals interactions.

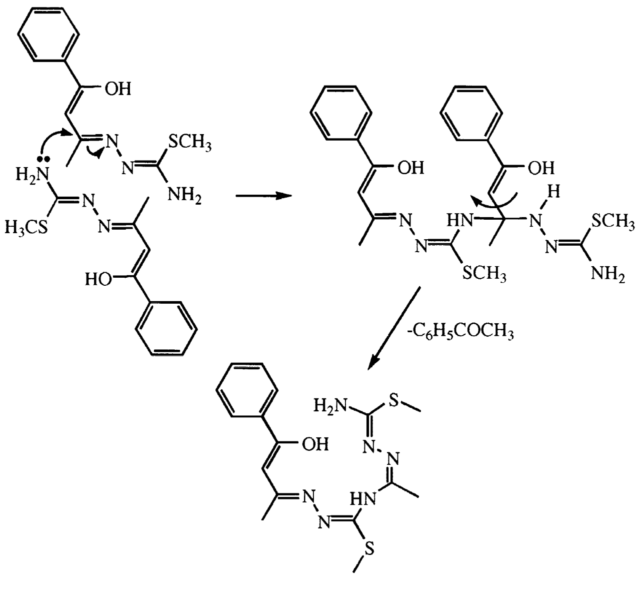
A view of the molecule of **8**, along with the atom numbering scheme, is shown in Fig. 2. Selected bond lengths and angles are given in Table 3. A square-planar coordination of the ligand to the nickel(II) occurs through three nitrogen and one oxygen atoms with the corresponding bond distances (Ni–O1 = 1.838(4), Ni–N1 = 1.825(5), Ni–N3 = 1.834(5), Ni–N5 = 1.901(5) Å) similar to those in some *S*-alkylisothiosemicarbazide-based analogues. The tetradentate ligand forms three chelate rings, one being six-membered and the two other five-membered, in the sequence 6, 5, 5. This is a common feature for a number of complexes with pentane-2,4-dione bis(*S*-alkylisothiosemicarbazones) [1,5,10,20]. It is worth noting the additional pseudo metal ring formation in them via the H-bonding between the terminal NH groups and the I^- anion. In **8** the pseudo ring is formed by the N6–H···O1 intramolecular H-bond (Fig. 2). Finally, the complex can be described as pseudo-macrocyclic with a 6, 5, 5, 6 sequence of chelate cycles. The same alternation of chelate rings has previously been found in [(1,9-dihydroxyimino-5-ethylthio-1,2-di(α-furyl)-8-methyl-3,4,6,7-tetraazanona - 2,4,7 - trienato(2-)*N*,N^3,N^6,N^1)]nickel(II) [21].

Here, the similarity with the other *S*-alkylisothiosemicarbazide-based ligands ends. The two *S*-methylisothiosemicarbazide residues in the template-assembled ligand of **8** are arranged 'tail-to-head'. They adopt two different conformations: *Z* for N1N2C1N3 and *E* for N4N5C15N6 moieties. Only one of the isothiosemicarbazide residues is bound to the metal via two terminal nitrogen atoms to form a chelate ring. The second shows unusual monodentate behaviour, being coordinated to the metal through the N5 atom. This is due to the stereochemical demands of the nickel(II) template and the ability of the ligand product formed to meet them. Involvement of the non-terminal hydrazine nitrogen in coordination to the metal has been revealed for (*p*-anisaldehyde thiosemicarbazonato)dimethylthallium(III) by X-ray diffraction methods [22]. The binding mode of the second *S*-methylisothiosemicarbazide fragment does not strongly influence the distribution of the electron density over the whole ligand. The noticeable changes are only observed in the N5–C15–N6 moiety, and the reason might be the coordination of N5 to nickel(II).

Note that the *E*-conformation has been documented for the S-methylisothiosemicarbazidium nitrate [23] and some metal-free tetradentate isothiosemicarbazide-based ligand products [24,25].

The skeleton of the molecule of **8** is almost planar, the dihedral angle between the five-membered rings being at only 0.9°. The corresponding angle between the six- and five-membered rings is 2.5°. The phenyl ring forms an angle of 22.5° with the mean plane of the six-membered ring NiN_2C_3.

The above-mentioned intramolecular H-bond is characterised by the following parameters: $N6\cdots O1 = 2.751(7)$, $H\cdots O1 = 1.96$ Å, the angle at the H atom being 146°. The second hydrogen of the $-NH_2$ group joins the symmetry-related molecule $(2-x,\ 0.5+y,\ 1-z)$ by weak H-bonding. The corresponding parameters are as follows: $N6\cdots N4^* = 3.163(8)$, $N4^*\cdots H = 2.47$ Å, the angle at H being 135°. We also mention the intermolecular contact $Ni\cdots S1$ $(x,\ y,\ -1+z) = 3.982(2)$ Å. All other contacts correspond to van der Waals interactions.



Scheme 2.

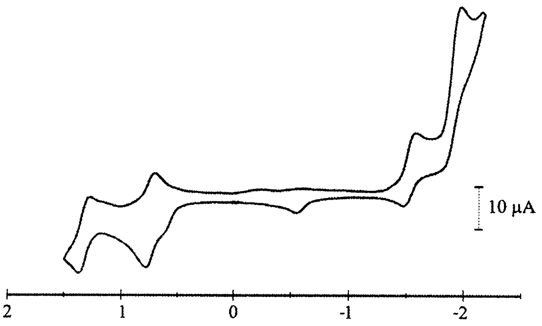


Fig. 3. Cyclic voltammogram of **7** in CH_2Cl_2 (0.10 M $[N(C_4H_9)_4][PF_6]$; platinum working electrode; scan rate 100 mV s^{-1}).

One of the possible routes to **8** is supposed to be the intermolecular nucleophilic addition of **6** at the C=N bond of the second molecule of **6** with subsequent elimination of phenyl-methyl-ketone (Scheme 2). The metal ion presumably exerts a degree of control over the reaction. The essential driving force of the reaction is supposedly the match between the steric and electronic requirements of the matrix and the ability of the final ligand product to meet them.

3.2. Electrochemical behaviour

The electrochemical behaviour of the trans-complexes **4**, **7** and the open-chain product **8** were studied by cyclic voltammetry. The cyclic voltammogram of **4** displays two reversible one-electron oxidation transfer waves at 0.217 and 0.821 V versus the ferrocenium/ferrocene couple (Fc^+/Fc). The cyclic voltammogram of **7** is shown in Fig. 3. This displays three quasi-reversible one-electron transfer waves at 0.746, 1.332 and −1.539 V, and one irreversible cathodic peak at −1.974 V versus Ag^+/Ag. Complex **8** shows one quasi-reversible, one irreversible anodic, and one irreversible cathodic peak at 0.814, 1.367 and −1.932 V versus Ag^+/Ag. Conversions from the Ag^+/Ag scale to Fc^+/Fc can easily be performed by adding +0.454 V and +0.493 V respectively to the values given above for **7** and **8**. We conclude that the two consecutive one-electron oxidation steps for **4**, **7** and **8** are metal-centred, and can be represented as shown in Eq. (1):

$$Ni^{2+} - e^- = Ni^{3+}$$

$$Ni^{3+} - e^- = Ni^{4+} \qquad (1)$$

The peak at −1.539 V for **7** we conclude is a one-electron metal-centred reduction, as shown in Eq. (2):

$$Ni^{2+} + e^- = Ni^+ \qquad (2)$$

The corresponding irreversible cathodic peaks at −1.974 and −1.932 V for **7** and **8** are supposed to be ligand-centred. The higher electrochemical flexibility of **7** compared with **8** is due to the macrocyclic nature of the ligand in **7**.

4. Conclusions

Nickel(II)-controlled self-condensation of **6** affords two different products, the macrocyclic complex **7** and the open-chain species **8**. Complex **7** is presumably formed by bimolecular nickel(II)-assisted self-condensation of **6**, whereas **8** by intermolecular nucleophilic addition of **6** at the C=N bond of the second molecule of **6** with subsequent elimination of phenyl-methyl-ketone.

5. Supplementary material

Complete tables of atomic coordinates, anisotropic thermal parameters, bond lengths and angles may be obtained from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1 EZ, UK, on quoting the depository numbers CCDC 143057 (for **7**), 143058 (for **8**), the names of the authors and the journal citation. Structure factors of **7** and **8**, Table S1 showing the relative intensities of the identified ions in the EI mass spectra of **7** and **8**, and Table S2 with the ^{1}H NMR data of trans-hexaazamacrocyclic complexes **4**, **5** and **7** are available from the authors on request.

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References

[1] N.V. Gerbeleu, V.B. Arion, J. Burgess, Template Synthesis of Macrocyclic Compounds, Wiley–VCH, Weinheim, 1999.

[2] D.H. Busch, Helv. Chim. Acta, Fasciculus Extraordinarius, A. Werner (1967) 174.

[3] L.F. Lindoy, D.H. Busch, in: W.L. Jolly (Ed.), Preparative Inorganic Chemistry, vol. 6, Interscience, New York, 1971, p. 1.

[4] N.F. Curtis, Coord. Chem. Rev. 3 (1968) 3.

[5] Yu.A. Simonov, V.K. Bel'sky, N.V. Gerbeleu, S.G. Shova, V.B. Arion, Dokl. Akad. Nauk SSSR 282 (1985) 620.

[6] N.V. Gerbeleu, Yu.A. Simonov, V.B. Arion, S.G. Shova, T.I. Malinovsky, Dokl. Akad. Nauk SSSR 282 (1985) 633.

[7] Yu.A. Simonov, P.N. Bourosh, V.B. Arion, M.D. Mazus, N.V. Gerbeleu, Kristallografiya 33 (1988) 1535.

[8] N.V. Gerbeleu, J.I. Gradinaru, V.B. Arion, K.M. Indrichan, Zh. Neorg. Khim. 36 (1991) 100.

[9] A.A. Dvorkin, P.N. Bourosh, Yu.A. Simonov, V.B. Arion, J.I. Gradinaru, N.V. Gerbeleu, Polyhedron 14 (1995) 571.

[10] V.B.Arion, Ph.D. Thesis, Institute of Physical Chemistry of the Academy of Sciences of Ukraine, Kiev, 1985.

[11] N.V. Gerbeleu, Yu.A. Simonov, V.B. Arion, J.I. Gradinaru, V.E. Zavodnik, K.M. Indrichan, T.I. Malinovskii, Zh. Neorg. Khim. 36 (1991) 96; Russ. J. Inorg. Chem. 36 (1991) 52.

[12] V.M. Leovac, L.S. Jovanovic, V.J. Cesljevic, L.J. Bjelica, V.B. Arion, N.V. Gerbeleu, Polyhedron 13 (1994) 3005.

[13] N. Galesic, V.M. Leovac, Acta Crystallogr., Sect. C 45 (1989) 745.

[14] G.A. Bogdanovici, A. Spasojevici-de-Bire, V.M. Leovac, V.I. Cesljevic, Acta Crystallogr., Sect. C 55 (1999) 1656.

[15] M. Freund, Th. Paradies, Ber. Dtsch. Chem. Ges. 34 (1901) 3110.

[16] G.M. Sheldrick, Acta Crystallogr., Sect. A 46 (1990) 467.

[17] G.M. Sheldrick, SHELXL-93, University Göttingen, Germany, 1993.

[18] B.M. Hoffman, J. Martinsen, L.J. Pace, L.A. Ibers, in: J.S. Miller (Ed.), Extended Linear Chain Compounds, vol. 3, Plenum, New York, 1983, p. 561.

[19] L.E. Godycki, R.E. Rundle, Acta Crystallogr. 6 (1953) 487.

[20] Yu.A. Simonov, J.I. Gradinaru, A.A. Dvorkin, P.N. Bourosh, N.V. Gerbeleu, Koord. Khim. 21 (1995) 214.

[21] Yu.A. Simonov, N.V. Gerbeleu, L.A. Nemchinova, S.G. Baka, A.N. Sobolev, T.I. Malinovskii, Zh. Neorg. Khim. 36 (1991) 2520; Russ. J. Inorg. Chem. 36 (1991) 1416.

[22] J.S. Casas, E.E. Castellano, A. Macias, M.C. Rodriguez-Argüelles, A. Sánchez, J. Sordo, J. Chem. Soc., Dalton Trans. (1993) 353.

[23] S.G. Shova, Yu.A. Simonov, V.B. Arion, M.D. Revenco, T.I. Malinovskii, Dokl. Akad. Nauk SSSR 282 (1985) 1142.

[24] Yu.A. Simonov, N.V. Gerbeleu, M.D. Revenco, S.G. Shova, V.E. Zavodnik, V.G. Rusu, Kristallografiya 30 (1985) 1090.

[25] P.N. Bourosh, Yu.A. Simonov, V.B. Arion, A.N. Sobolev, N.V. Gerbeleu, V.S. Pakhopol, Kristallografiya 34 (1989) 637; Sov. Phys. Crystallogr. 34 (1989) 38.