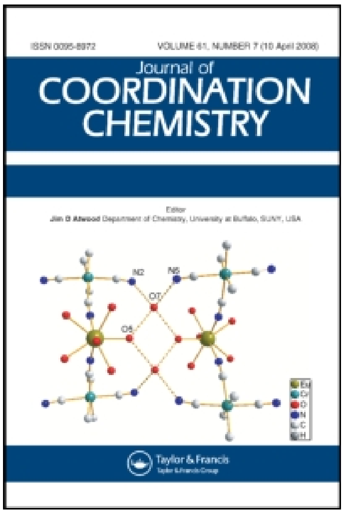

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TRANSITION METAL COMPLEXES WITH THIOSEMICARBAZIDE-BASED LIGANDS. PART 24.[1] SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF [PENTANE-2,4-DIONEBIS(THIOSEMICARBAZONATO(1-)]NICKEL(II) THIOCYANATE

Vukadin M. Leovac[a]; Valerija I. Češljević[a]; Gyula Argay[b]; Alajos Kálmán[b]; BÉLa Ribár[c]
[a] Faculty Of Sciences, Institute of Chemistry, Novi Sad, Yugoslavia [b] Central Research Institute of Chemistry, Hungarian Academy of Sciences, Budapest, Hungary [c] Faculty of Sciences, Institute of Physics, Novi Sad, Yugoslavia

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TRANSITION METAL COMPLEXES WITH THIOSEMICARBAZIDE-BASED LIGANDS. PART 24.[1] SYNTHESIS AND X-RAY CRYSTAL STRUCTURE OF [PENTANE-2,4-DIONEBIS(THIOSEMICARBAZONATO(1-)] NICKEL(II) THIOCYANATE

VUKADIN M. LEOVAC,* VALERIJA I. ČEŠLJEVIĆ

Institute of Chemistry, Faculty of Sciences, Trg D. Obradovića 3, 21000 Novi Sad, Yugoslavia

GYULA ARGAY, ALAJOS KÁLMÁN

Central Research Institute of Chemistry, Hungarian Academy of Sciences, H-1525 Budapest, P.O. Box 17, Hungary

and BÉLA RIBÁR

Institute of Physics, Faculty of Sciences, Trg D. Obradovića 4, 21000 Novi Sad, Yugoslavia

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The syntheses of dark-green diamagnetic complexes $[Ni(H_2L)]X$ (H_2L = the monoanion of pentane-2,4-dionebis(thiosemicarbazone) and X is either NO_3 or NCS) and the crystal structure of the NCS complex is described. Crystals of the NCS complex are monoclinic, space group *C2/c*, with $a = 11.867(1)$, $b = 10.715(1)$, $c = 22.319(1)$Å, $\beta = 90.11(1)°$, $V = 2838.0(4)$ Å^3, $Z = 8$. The crystal structure was refined using 2491 independent reflections to $R = 0.051$. The structure consists of well separated $[Ni(H_2L)]^+$ cations and NCS^- anions. Ni^{II} has a slightly distorted square-planar geometry formed with two nitrogen (Ni-N = 1.863(4) and 1.856(4) Å) and two sulphur atoms (Ni-S = 2.153(2) and 2.163(1) Å) of the monodeprotonated tetradentate ligand.

KEYWORDS: Pentane-2,4-dione bis(thiosemicarbazone), nickel(II), thiocyanate, complex, X-ray structure

INTRODUCTION

Several articles[2–8] have dealt with complexes of 3d-metals with pentane-2,4-dione bis(thioalkylisothiosemicarbazones). In contrast to the tetradentate NNNN S-alkyl derivatives (H_3LR_2), which stabilize unusually high oxidation states of some metals (*e.g.*, +4 and +3 of iron and copper respectively[5–8]), the tetradentate SNNS

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* Author for correspondence.

pentane-2,4-dione bis(thiosemicarbazone), (H_3L) ligand, stabilizes metals[2,3] in their common oxidation states. Recently, a number of complexes with H_3LR_2 have been characterized by X-ray analysis, among them being the square-planar nickel(II) complex, [Ni(H_2LMe_2)]I.[4] Although nickel(II) complexes with H_3L were synthesized some time ago,[2] there are X-ray crystallographic data in the literature neither on the nickel nor on any other metal complexes with the mentioned ligand.

This paper describes the crystal and molecular structure of the newly synthesized nickel(II) complex with the monoanion of H_3L and the charge compensating anion NCS^-, [Ni(H_2L)]NCS. Spectroscopic characteristics of this complex, as well as those of the analogous nitrate salt from which [Ni(H_2L)]NCS was prepared, are presented as well.

EXPERIMENTAL

H_3L

To a 44 mmol (4.00 g) solution of thiosemicarbazide in EtOH (20 cm^3) was added 50 mmol (5.2 cm^3) of acetylacetone. The mixture heated to boiling and to it was added in portions a warm solution of NaOH (2.40 g) in H_2O (20 cm^3). The obtained mixture was heated for a few minutes. After 10 h, the resulting white glimmering crystals were separated by filtration from the brown solution and washed with H_2O. Yield: 2.35 g (43%). *Anal.*: calcd. for $C_7H_{14}N_6S_2$: C, 34.13; H, 5.73; N, 33.53; S, 26.03%. Found: C, 35.34; H, 6.22; N, 34.11; S, 26.45%.

[Ni(H_2L)]NO_3

This complex was prepared by dissolving 4 mmol (1.00 g) of H_3L in EtOH (50 cm^3) and adding to the warm mixture a solution of 5 mmol (1.50 g) $Ni(NO_3)_2 \cdot 6H_2O$ in small portions. The obtained mixture was heated until complete dissolution of the reactants was observed. The resulting dark-green crystals were filtered off after 2 h and washed with EtOH and Et_2O. Yield: 1.23 g (84%). *Anal.*: calcd. for $NiC_7H_{13}N_7O_3S_2$: C, 22.95; H, 3.58; N, 26.78%. Found: C, 22.99; H, 4.19; N, 27.03%.

[Ni(H_2L)]NCS

This complex was prepared by dissolving 1 mmol (0.37 g) of [Ni(H_2L)]NO_3 in MeOH (20 cm^3) and adding to the warm solution a further solution containing 5 mmol (0.39 g) NH_4NCS. In case of need, the resulting solution was filtered. After 24 h, dark green crystals were filtered off and washed with MeOH and Et_2O. Yield: 0.16 g (44%). *Anal.*: calcd. for $NiC_8H_{13}N_7S_3$: C, 26.53; H, 3.62; N, 27.08%. Found: C, 26.77; H, 4.62; N, 27.69%.

Measurements

Magnetic susceptibilities were verified by Gouy's method. Molar conductivities of freshly prepared 10^{-3} mol dm^{-3} EtOH solutions were measured at room temperature using a digital conductivity meter (Jenway 4010). Infrared spectra (KBr disc) were recorded on a Perkin-Elmer Infracord 457 spectrophotometer. Electronic absorption spectra of 5×10^{-4} mol dm^{-3} EtOH solutions were recorded on a Cary 219 spectrophotometer. Melting points were determined on a Boetius HPMK 05 apparatus without correction.

Data collection and structure determination of [Ni(H_2L)]NCS

Table 1 lists crystal data, data collection parameters and a summary of the structure determination. H-atom positions were generated geometrically, and refined isotropically. Atomic scattering factors were taken from SHELX76[9] and International Tables for X-ray Crystallography.[10] Non-hydrogen fractional atomic coordinates and equivalent temperature factors are given in Table 2. Bond lengths, bond angles and hydrogen bonds are presented in Table 3.

RESULTS AND DISCUSSION

Synthesis and General Physico-chemical Properties

Although some metal complexes with pentane-2,4-dionebis(thiosemicarbazone)

Table 1 Summary of crystal data, intensity collection and structure refinement.

Chemical formula	[Ni($C_7H_{13}N_6S_2$)]NCS
Formula weight	362.14
Crystal system	monoclinic
Space group	$C2/c$ (No. 15)
a/Å	11.867(1)
b/Å	10.715(1)
c/Å	22.319(1)
β/°	90.11(1)
V/Å^3	2838.0(4)
Z	8
Dc/g cm^{-3}	1.70
Crystal dimensions/mm	0.10 × 0.15 × 0.15
μ/cm^{-1}	60.28
F(000)	1488
Radiation Cukα/Å	1.54184
Diffractometer	CAD-4
Number of reflection used in unit cell determination	25
Range of reflection used in unit cell determination/°	30.00–34.61
Data collection method	2Θ-ω
Scan speed/min	1.65–16.50
Scan width	$0.51 + 0.19\tan(\Theta)$
h range	0–14
k range	0–13
l range	−28–28
Number of reflections collected	3285
Number of unique reflections	2963
Number of refined reflections with $Fo > 3\sigma(Fo)$	2491
Number of variables	224
w	1
R	0.051
Maximum (eÅ^{-3}) in final difference map	1.12

Table 2 Non-hydrogen fractional atomic coordinates ($\times 10^4$) and equivalent temperature factors ($Å^2 \times 10^3$) with e.s.d.'s in parentheses.

	x/a	*y/b*	*z/c*	*Ueq*
Ni	2289(1)	883(1)	4837(1)	39(1)
S1	3913(1)	297(1)	4513(1)	50(1)
C2	3691(4)	615(5)	3782(2)	52(1)
N3	4489(5)	379(7)	3364(3)	86(2)
N4	2730(3)	1101(4)	3613(2)	54(1)
N5	1891(3)	1271(4)	4051(2)	47(1)
C6	922(4)	1737(5)	3847(2)	55(1)
C7	763(7)	2043(8)	3193(3)	79(2)
C8	39(4)	1981(5)	4234(3)	59(1)
C9	18(4)	1813(4)	4851(3)	55(1)
C10	- 1033(5)	2174(6)	5181(4)	71(2)
N11	907(3)	1362(3)	5150(2)	47(1)
N12	790(4)	1239(4)	5768(2)	56(1)
C13	1616(4)	761(5)	6088(2)	54(1)
N14	1518(6)	640(6)	6685(2)	80(2)
S15	2810(1)	334(1)	5728(1)	52(1)
S16	8612(2)	1460(2)	6790(1)	127(1)
C17	8370(6)	2807(8)	7076(2)	86(2)
N18	8127(5)	3682(6)	7264(2)	98(2)

(H_3L) are known, there is no report on the preparation of the ligand itself. Our attempts to synthesize H_3L by the method[11] in which the analogous pentane-2,4-dione bis(4-phenylthiosemicarbazone) was prepared, by refluxing stoichiometric amounts of reactants in EtOH was fruitless. Therefore the ligand was prepared by the reaction of warm alkaline EtOH-H_2O solutions of the reactants.

The initial [Ni(H_2L)]NO_3 complex, which used to prepare the [Ni(H_2L)]NCS by metathesis (NH_4NCS), was obtained by reacting warm EtOH solutions of the ligand and Ni$(NO_3)_2$. Both the NCS- and NO_3-complexes are dark-green, and are stable to 250 and 350°C, respectively. They are soluble in polar organic solvents. Their diamagnetism suggests a square-planar configuration. This means that only the tetradentate SNNS ligand takes part in coordination. The presence of characteristic bands at 1380 cm^{-1} (NO_3) and 2020 cm^{-1} (NCS)[12] in the i.r. spectra, as well as the λ_M of EtOH solutions of the complexes (37.1 and 31.7 S cm^2 mol^{-1}, respectively)[13] indicate also that the NO_3 and NCS groups are not coordinated.

The electronic absorption spectra of EtOH solutions of both complexes are practically identical. In the visible spectra there are two weak bands at $\lambda_{max} = 680$ and 525 nm (ε 260 and 500 $M^{-1}cm^{-1}$, respectively) which are probably due to d-d transitions. The other two strong absorption bands at $\lambda_{max} = 412$ and 394 (sh) nm (ε 12000 and 9500 M^{-1} cm^{-1}, respectively) may presumably be assigned to charge transfer, possibly d-π^* transition.[14] Finally, the band at $\lambda_{max} = 310$ nm, (ε 8200 M^{-1} cm^{-1}) arises from a ligand $\pi \rightarrow \pi^*$ transition. It should be mentioned that very similar properties have been observed for square-planar complexes of nickel(II) with bis(thiosemicarbazones) of other diketones.[14]

An important question thus arises as to which group in the ligand molecule has been deprotonated. As can be seen from Scheme 1, the ligand can exist in two tautomeric forms, thione (1) and thiol (2). X-ray analyses of thiosemicarbazide[15]

Table 3 Bond lengths (Å) and angles (°) with e.s.d.'s in parentheses.

Ni-S1	2.153(2)	Ni-S1-C2	97.3(2)
Ni-N5	1.863(4)	S1-C2-N3	121.4(4)
Ni-N11	1.856(4)	S1-C2-N4	119.6(4)
Ni-S15	2.163(1)	N3-C2-N4	119.1(5)
S1-C2	1.687(5)	C2-N4-N5	117.9(4)
C2-N3	1.354(8)	Ni-N5-N4	116.5(3)
C2-N4	1.309(6)	Ni-N5-C6	128.5(3)
N4-N5	1.408(6)	N4-N5-C6	115.0(4)
N5-C6	1.333(6)	N5-C6-C7	121.2(5)
C6-C7	1.508(8)	N5-C6-C8	120.7(5)
C6-C8	1.384(7)	C7-C6-C8	118.0(5)
C8-C9	1.389(9)	C6-C8-C9	127.5(5)
C9-C10	1.500(9)	C8-C9-C10	118.0(5)
C9-N11	1.338(6)	C8-C9-N11	121.7(5)
N11-N12	1.393(6)	C10-C9-N11	120.3(5)
N12-C13	1.315(7)	Ni-N11-C9	127.5(3)
C13-N14	1.344(6)	Ni-N11-N12	115.9(3)
C13-S15	1.693(5)	C9-N11-N12	116.6(4)
S16-C17	1.604(8)	N11-N12-C13	119.9(4)
C17-N18	1.067(10)	N12-C13-N14	120.7(5)
S1-Ni-N5	88.5(1)	N12-C13-S15	118.1(4)
S1-Ni-N11	177.4(1)	N14-C13-S15	121.2(4)
S1-Ni-S15	88.6(1)	Ni-S15-C13	97.2(2)
N5-Ni-N11	94.0(2)	S16-C17-N18	174.6(7)
N5-Ni-S15	176.4(1)		
N11-Ni-S15	88.9(1)		

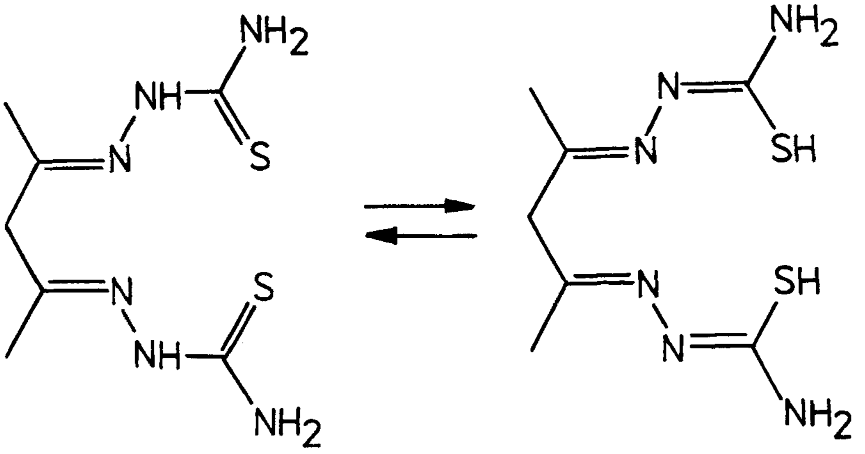
Hydrogen bonds

	N-H(Å)	H...N(Å)	N...N(Å)	<N-H...N(°)
N3-H3B...N18[i]	1.04(4)	2.11(7)	3.104(8)	160(6)
N4-H4...N18[i]	1.02(7)	2.13(7)	3.057(6)	151(5)
N14-H14A...N18[ii]	1.04(7)	2.12(7)	3.116(9)	160(6)

i: *x*-1/2, 1/2-*y*, *z*-1/2; ii: *x*-1/2, *y*-1/2, *z*.

and thiosemicarbazones[16] have shown that these ligands, in the solid state, exist in the thione form. The presence of a strong ν(C=S) band at 792 cm^{-1} and the absence of the ν(S—H) band in the range 2590–2530 cm^{-1} in the i.r. spectrum of free H_3L indicates that the ligand in the solid state exists also in the thioketo form.[17] On the other hand, during the complexing process in the presence of a proton acceptor, the SH-group of the thiol form of the ligand present in equilibrium[18] can easily be deprotonated in solution. The H_3L complexes reported earlier involve the ligand in its neutral, mono- and di-anionic forms; the last can be ascribed to deprotonation of both SH-groups, whereas for the monoanionic form it has not been stated which group was deprotonated.[2,3]

X-ray analysis of our [Ni(H_2L)]NCS complex shows unambiguously that the monoanionic form of the ligand is formed by deprotonation of the CH_2-group of the pentane-2,4-dione residue. It is worth noting that complexes with similar tetradentate *S*-alkyl-derivatives (H_3LR_2) may utilize the ligand in its trianionic form, *i.e.*, CH_2^-, and both NH_2-groups deprotonated.[5-8]



(1) (2)

Scheme 1

Structure of [Ni(H_2L)]NCS

The structure consists of well separated pentane-2,4-dionebis(thiosemicarbazonato) (1 –)nickel(II) cations and thiocyanate anions (Fig. 1). The square-planar coordination of the nickel atom suggested by the magnetic measurements involves two sulphur and two nitrogen atoms of the tetradentate pentane 2,4-dionebis(thiosemicarbazonato) ligand. The *cis* bond angles range from 88.5(2) to 93.9(3)° and the *trans* bond angles are 176.5(2) and 177.5(2)° (Table 3). Maximum deviation from the best plane of fit of the square-planar NiS_2N_2 chromophore is 0.055(4)Å (N5). A search in the Cambridge Structural Database (1993) for planar coordinated Ni(II) ions resulted in 484 entries possessing Ni-S distances with a grand mean of 2.232Å and in 1614 compounds incorporating Ni—N distances with a grand mean of 2.049Å. The Ni—S = 2.158Å (av) and Ni—N = 1.861Å (av) distances of the title compound are shorter from these mean values but they can be compared with those found for other square-planar thiosemicarbazide-based ligand complexes of nickel(II).[19] The Ni—Ni separation is only 3.5767(3)Å, which is shorter than found in bis (dimethyltetrathio- malonato)nickel(II)[20] and reported as the shortest Ni—Ni contact (4.0633(5)Å) for this kind of compound.

The nearly planar cation (the non-H atoms do not deviate from the best plane by more than 0.1 Å) exhibits near C_s symmetry with a *pseudo*-mirror plane bisecting the C8 and Ni atoms.

The C—N bond distances in this ring are shorter than normally expected, while the C—C distances are very close to the distances found in aromatic systems. They are comparable with bond lengths found in the square-planar complex of nickel(II) with pentane-2,4-dione bis(*S*-methylisothiosemicarbazone), [Ni(H_2LMe_2)]I,[4] which is coordinated *via* the deprotonated diketonic residue. These values indicate strong delocalization in the six-membered ring, an observation which may be attributed to deprotonation of the CH_2-group of the diketonic residue. On the other hand, the

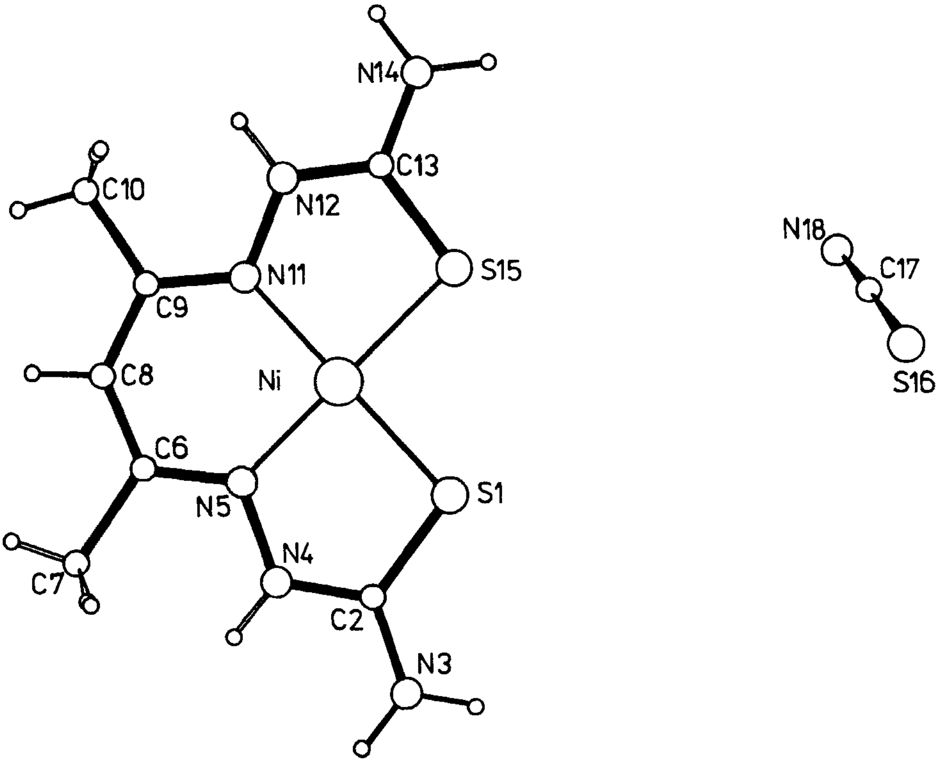


Figure 1 Molecular structure of $[Ni(H_2L)]NCS$ showing the atom numbering scheme.

C—S bond distances (1.687(5) and 1.693(5)Å) are similar to those found in non-coordinated thiosemicarbazide and thiosemicarbazones,[16] and this suggests their double-bond character, *i.e.*, that the sulphur is coordinated in the thionic form. Other bond lengths and angles in the ligand are similar to those found in other thiosemicarbazone complexes.[19]

The N—C bond distance of 1.067(10)Å in the linear thiocyanate anion is significantly shorter than those found in other thiocyanates. It can only be compared with the ionic thiocyanate of the γ-form of isothiocyanato-[1,7-bis-(2-pyridyl)-2,6-diazo-heptane]copper(II) thiocyanate (1.09 Å). However, this structure is disordered.[21] The N3, N4 and N14 atoms of the ligand form weak hydrogen bonds with the N atom of the NCS anion (Table 3).

Supplementary Material

Tables of bond distances and angles, atomic parameters, anisotropic thermal parameters and structure factors are available from Bêla Ribár upon request.

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