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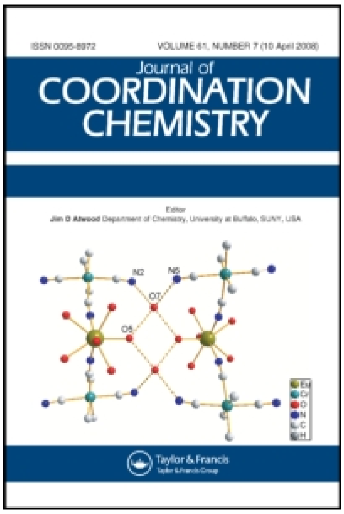

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Syntheses and structures of Zn(II) and Ni(II) complexes of 4-N-(acetylacetone amine)acetophenone thiosemicarbazone

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A new ligand, 4-N-(acetylacetone amine)acetophenone thiosemicarbazone (HL, **1**), was synthesized by condensation of *p*-aminoacetophenone with thiosemicarbazide and acetylacetone. Treatment of HL with zinc acetate and nickel acetate afforded ZnL_2 (**2**) and $NiL_2 \cdot DMF$ (**3**). The crystal structures of **1**, **2** and **3** have been determined by single-crystal X-ray diffraction. **2** and **3** have similar structures, in which metal atom is coordinated in a distorted tetrahedral configuration, and L^- coordinates to zinc(II) or nickel(II) through the azomethine nitrogen and the thiolato sulfur atom.

Keywords: Zinc; Nickel; Thiosemicarbazone; Schiff base

1. Introduction

Research on the reactions of thiosemicarbazones with transition metals which show a wide variety of biological activities such as antitumoral [1–3], antiviral [4], fungicidal [5, 6] or bactericidal [7], has increased steadily for many years. Thus much attention has been devoted to syntheses of new thiosemicarbazone ligands and their metal complexes [8–12]. In this work, a new thiosemicarbazone ligand, 4-N-(acetylacetone amine)acetophenone thiosemicarbazone (HL, **1**), and two complexes ZnL_2 (**2**) and $NiL_2 \cdot DMF$ (**3**) were synthesized. Crystal structures of **1**, **2** and **3** have been determined by single-crystal X-ray diffraction. The characterization of **1–3** in the solid state has also been carried out by elemental analysis and IR spectroscopy.

2. Experimental

2.1. *Preparation*

4-Aminoacetophenone thiosemicarbazone. Thiosemicarbazide (0.911 g; 10 mmol) dissolved in hot ethanol (20 mL) was added to a solution of 4-aminoacetophenone (1.352 g; 10 mmol) in hot water (30 mL). Two drops of acetic acid was added to the

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reaction mixture. After refluxing for 2 h on an oil bath, the mixture was cooled to room temperature. The product was collected by filtration, washed with ethanol and dried in air. (1.772 g, yield: 85.1%); m.p. 174–175°C.

HL (1). A mixture of aminoacetophenone thiosemicarbazone (1.042 g, 5 mmol) and acetylacetone (0.501 g, 5 mmol) in absolute methanol (40 mL) was stirred at 60°C for 2 h. After standing overnight, the crystalline solid was collected by filtration, washed with ethanol and dried in air. Crystals suitable for X-ray diffraction were obtained by recrystallization from methanol. (1.016 g, yield: 70%); m.p. 168–170°C. Calcd for $C_{14}H_{18}N_4OS$: C, 57.89; H, 6.26; N, 19.29; found: C, 57.71; H, 6.14; N, 19.47%.

ZnL_2 (2). A solution of **1** (0.290 g, 1 mmol) in 20 mL of hot methanol was treated with a solution of $Zn(OAc)_2 \cdot 2H_2O$ (0.110 g, 0.5 mmol) in methanol. The mixture was heated under reflux for 4 h. After evaporating the solution at room temperature for several days, pale yellow crystals of **2** were obtained. (0.180 g, yield: 56%); Calcd for $Zn(C_{14}H_{17}N_4OS)_2$: C, 52.20; H, 5.33; N, 17.40; found: C, 52.07; H, 5.24; N, 17.62%.

$NiL_2 \cdot$ DMF (3). A solution of $Ni(OAc)_2 \cdot 4H_2O$ (0.124 g, 0.5 mmol) in methanol (10 mL) was added slowly into a solution of **1** (0.290 g, 1 mmol) in DMF (4 mL). The mixture was stirred at room temperature for 2 h. After evaporating the solution at room temperature for several days, crystals of **3** were obtained (0.220 g, yield: 62%); Calcd for $Ni(C_{14}H_{17}N_4OS)_2(C_3NO)$: C, 52.47; H, 5.69; N, 17.77; found: C, 52.58; H, 5.54; N, 17.56%.

2.2. *Physical measurements and X-ray crystallography*

All materials were commercially available and used as received. The FT-IR spectra were recorded from KBr pellets from 4000–400 cm^{-1} on a Mattson Alpha-Centauri spectrometer. Elemental analyses were carried out with a Carlo Erba 1106 elemental analyzer. Magnetic susceptibility data for polycrystalline compound **3** were obtained on a Quantum Design MPMSXL SQUID magnetometer at room temperature.

Experimental details of the X-ray analyses are provided in table 1. Diffraction intensities for **1**–**3** were collected on a Bruker Apex CCD diffractometer using ω scan technique with graphite-monochromated Mo-Kα radiation ($\lambda = 0.71069$ Å). Absorption corrections were applied using the multi-scan technique [13]. The structures were solved with the direct method of SHELXS-97 [14] and refined with full-matrix least-squares techniques using SHELXL-97 [15] within WINGX [16]. Non-hydrogen atoms were refined anisotropically. The hydrogen atoms on carbon atoms were generated geometrically. Analytical expressions of neutral-atom scattering factors were employed, and anomalous dispersion corrections incorporated [17]. Drawings were produced with SHELXTL-PLUS [18].

Table 1. Crystal data and structure refinement for **1**, **2** and **3**.

	1	**2**	**3**
Formula	$C_{14}H_{18}N_4OS$	$C_{28}H_{34}ZnN_8O_2S_2$	$C_{31}H_{40}NiN_9O_3S_2$
Formula weight	290.38	644.12	709.55
Crystal system	Orthorhombic	Orthorhombic	Monoclinic
Space group	*Pbca*	*Pbca*	$P2_1/c$
a (Å)	8.757(5)	11.115(5)	11.776(5)
b (Å)	16.241(5)	17.701(5)	13.156(5)
c (Å)	20.885(5)	30.310(5)	22.480(5)
α (°)	90	90	90
β (°)	90	90	102.427(5)
γ (°)	90	90	90
V (Å^3)	2970(2)	5963(3)	3401(2)
Z	8	8	4
R_{int}	0.0403	0.0863	0.0537
R_1 ($I>2\sigma(I)$)	0.0462	0.0468	0.0554
wR_2 ($I>2\sigma(I)$)	0.1173	0.0848	0.1290
D_c (g cm^{-3})	1.299	1.435	1.386
Goodness-of-fit	1.026	0.879	0.945
θ Range for data collection (°)	1.95–26.07	2.27–25.03	1.77–26.42
$F(000)$	1232	2688	1492
μ (mm^{-1})	0.220	1.005	0.740
Reflections collected	15700	29614	19107
Unique reflections	2939	5264	6916
Observed reflections ($I>2\sigma(I)$)	2197	2977	4310

3. Results and discussion

As reported in the literature, Schiff-base ligands formed from acetylacetone have chelating properties with two –N and –O donors [19]. Our work has concentrated on developing new potentially tetradentate ligands from condensation of this kind of Schiff base and thiosemicarbazide. The synthesis of ligand **1** by the two-step condensation of thiosemicarbazide with aminoacetophenone and acetylacetone is described. Our investigations on the coordination ability of **1** toward Zn^{2+} and Ni^{2+} show that the ligand is bidentate with the thiosemicarbazone fragment possessing better coordination ability than the Schiff-base fragment.

3.1. *Crystal structure*

Selected bond distances and angles of **1**, **2** and **3** are given in table 2. As shown in figure 1, **1** exists in the *E* configuration with S1 *trans* to the azomethine N2 atom (scheme 1, I). The ligand consists of two nearly planar moieties: the thiosemicarbazone fragment with maximum deviation of 0.048 Å for S1 from the mean plane of N2–N4, C14 and S1, and the acetylacetone imine fragment with the maximum deviation of 0.055 Å for C5 from the mean plane of C1–C5, O1 and N1.

Previous work shows thiosemicarbazones are extensively delocalized, especially when aromatic groups are bound to the azomethine carbon. Scheme 1 (**I** and **II**) shows the thione-thiol tautomerism of the thioamide –NH–C=S functional group [20]. The distances of C14–S1 and C14–N3 are 1.687(2) and 1.352(3) Å, respectively, similar to

Table 2. Selected bond distances (in Å) and angles (in °) for **1**, **2** and **3**.

HL (**1**)			
N2–N3	1.386(2)	C14–S1	1.687(2)
C14–N3	1.352(3)	C14–N4	1.322(3)
N3–C14–N4	117.30(18)	N3–C14–S1	120.46(15)
N4–C14–S1	122.23(15)	C14–N3–N2	118.11(16)
N3–C14–N4	117.30(18)	N3–C14–S1	120.46(15)
N4–C14–S1	122.23(15)	C14–N3–N2	118.11(16)
ZnL_2 (**2**)			
Zn–N2	2.054(3)	Zn–N6	2.078(3)
Zn–S1	2.290(13)	Zn–S2	2.279(13)
N2–N3	1.401(4)	C14–S1	1.741(4)
C14–N3	1.291(4)	C14–N4	1.359(4)
N6–N7	1.402(4)	C28–S2	1.714(4)
C28–N7	1.300(5)	C28–N8	1.374(4)
N2–Zn–N6	112.96(12)	S1–Zn–S2	111.82(5)
N2–Zn–S1	86.36(9)	N2–Zn–S2	132.99(9)
N6–Zn–S1	134.13(9)	N6–Zn–S2	85.61(9)
C14–S1–Zn	92.97(14)	C12–N2–Zn	128.7(3)
C28–S2–Zn	93.70(15)	C26–N6–Zn	126.6(3)
N3–N2–Zn	116.6(2)	N7–N6–Zn	116.6(2)
N2–C12–C9	119.9(4)	N6–C26–C23	117.6(4)
N3–C14–N4	116.1(4)	N3–C14–S1	128.7(3)
N4–C14–S1	115.1(3)	C14–N3–N2	115.2(3)
N7–C28–N8	114.9(4)	N7–C28–S2	129.8(3)
N8–C28–S2	115.4(3)	C28–N7–N6	113.9(3)
$NiL_2 \cdot DMF$ (**3**)			
Ni–N2	1.922(3)	Ni–N6	1.919(3)
Ni–S1	2.148(12)	Ni–S2	2.152(12)
N2–N3	1.389(4)	C14–S1	1.748(4)
C14–N3	1.306(4)	C14–N4	1.339(5)
N6–N7	1.401(4)	C28–S2	1.737(4)
C28–N7	1.307(5)	C28–N8	1.351(5)
N2–Ni–N6	99.28(12)	S1–Ni–S2	93.91(5)
N2–Ni–S1	84.28(9)	N2–Ni–S2	165.46(9)
N6–Ni–S1	168.59(9)	N6–Ni–S2	85.30(9)
C14–S1–Ni	94.00(13)	C12–N2–Ni	127.8(3)
C28–S2–Ni	93.85(14)	C26–N6–Ni	126.0(3)
N3–N2–Ni	116.9(2)	N7–N6–Ni	117.9(2)
N2–C12–C9	119.3(3)	N6–C26–C23	118.0(3)
N3–C14–N4	119.9(3)	N3–C14–S1	122.4(3)
N4–C14–S1	117.6(3)	C14–N3–N2	110.3(3)
N7–C28–N8	117.9(4)	N7–C28–S2	124.2(3)
N8–C28–S2	117.9(3)	C28–N7–N6	110.0(3)

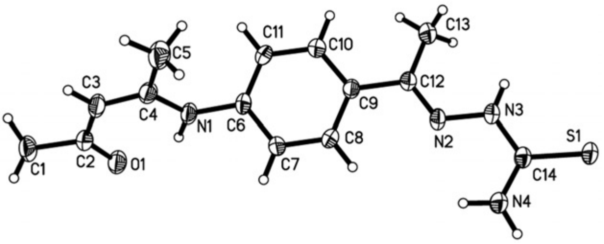
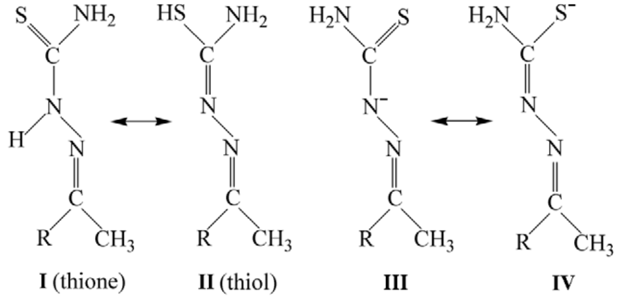


Figure 1. View of the structure of HL (**1**).



Scheme 1. Thione and thiol tautomerism forms of the compounds.

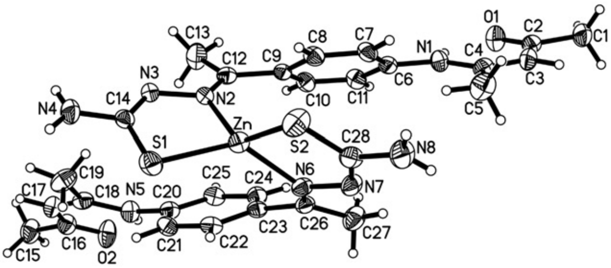


Figure 2. View of the structure of ZnL_2 **2**.

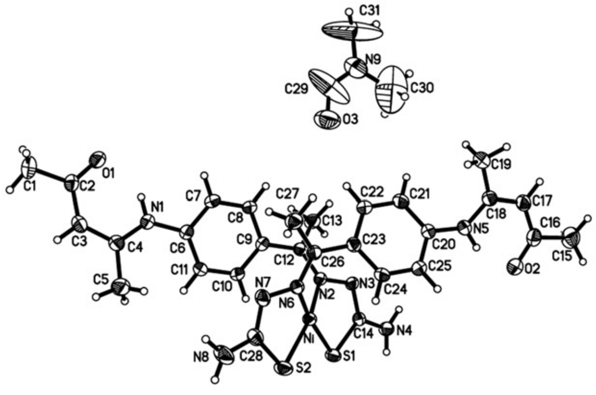


Figure 3. View of the structure of $NiL_2 \cdot DMF$ (**3**).

those found in the analogous thiosemicarbazone compounds with thioketo tautomeric form [21].

The structures of **2** and **3** are shown in figures 2 and 3. Compounds **2** and **3** are formed by two monodeprotonated ligands and one metal cation, leading to mononuclear noncentrosymmertric (ZnL_2) of **2** and (NiL_2) of **3** species. One dimethylformamide is also present in the lattice of **3**. In these compounds, the ligands are bidentate coordinating to metal ions through the azomethine nitrogen and the thiolato sulfur atom in a Z-configuration (scheme 1, **IV**), indicating that the coordination occurs after a 180° rotation around the C14–N3 bond of the free ligand [22].

As expected, obvious changes occur for the bond distances of the thiosemicarbazone moiety upon formation of **2** and **3**. Deprotonation of N3 causes a negative charge delocalized over the thiosemicarbazone moiety (scheme 1, **III** and **IV**). The thione form in HL decreases, and the thiol and thiolate forms increase in complexes [23, 24]. This is consistent with the shorter C14–N3 and larger C14–S1 bond distances in the complexes [C14–N3, S1: 1.291(4), 1.741(4) and 1.306(4), 1.748(4) Å, for **2** and **3**, respectively]. The deprotonation of HL takes place before coordination through the sulfur anion and the formation of a C–S single bond [25]. All C–N single bonds (C4–N1, C12–N2, C14–N3, C14–N4, C18–N5, C26–N6, or C28–N8) in the compounds are shorter than a reported C–N single bond [1.47 Å] due to delocalization of electron density through the thiosemicarbazone moiety [24].

The metal ions in **2** and **3** are coordinated in a distorted tetrahedral configuration [M–N2, N6, S1, S2 = 2.054(3), 2.078(3), 2.29(1), 2.28(1) and 1.922(3), 1.919(3), 2.15(1), 2.15(1) Å for **2** and **3**], with sulfurs and nitrogens of two L^- ligands forming two five-membered chelate rings. In **2**, the atoms of the two five-membered rings exhibit high planarity. As a consequence, the sums of the respective internal angles 539.86° and 539.61° are in good agreement with the ideal value of 540°. The dihedral angle between the planes of the two five-membered rings is 110.6°.

It is important to note that the pentagonal rings are highly twisted in complex **3** [with the maximum deviation of 0.85 Å for Ni from the mean plane of Ni–C14–N2–N3–S1 ring, and the maximum deviation of 0.72 Å for Ni from the mean plane of the Ni–C28–N6–N7–S2 ring]. This may be caused by steric hindrance between two L^- ligands. According to previous reports, the chelating coordination of thiosemicarbazone moiety usually results in a planar configuration [23, 26, 27]. Highly twisted five-membered rings are seldom reported.

3.2. *Infrared spectrum*

Selected vibration bands of the IR spectra of **1**, **2** and **3** are presented in table 3. There is no IR band at 2500–2600 cm^{-1} in the spectrum of **1**, indicating the absence of S–H. However, there is a band in the region of 854 cm^{-1} characteristic of ν(C=S), indicating that the ligand is the thione tautomer, consistent with the crystal structure of the ligand. In contrast to **1**, red shifts of ν(C=S) are observed for **2** [845 cm^{-1}] and **3** [839 cm^{-1}] as reported in related studies [10].

As reported earlier [28], ν_s and ν_{as} of $-NH_2$ at 3398–3292 cm^{-1} of **1** undergo slight change due to coordination of sulfur from the $C{=}S(NH_2)$ group in **2** and **3**. This is also confirmed by the presence of ν(Zn–S) and ν(Ni–S) vibrations at 388 (**1**) and 384 cm^{-1}(**2**), respectively [10, 29].

Table 3. Main IR spectral vibrations (cm^{-1}) for **1**, **2** and **3**.

	ν(C=O)	$\nu(NH_2)$	ν(C=S)	ν(C=N)	ν(M–N)	ν(M–S)
1	1714	3398a, 3292s	854	1595		
2	1718	3404a, 3292s	845	1578	442	388
3	1717	3445a, 3288s	839	1572	451	384

In ligand spectra, the strong band observed at $1595\,\mathrm{cm}^{-1}$ corresponds to ν(C=N) vibration [28]. This band shifts higher in the spectra of **2** and **3** [1578 and $1572\,\mathrm{cm}^{-1}$, respectively], indicating coordination of nitrogen of the azomethine to the central metal atoms in both of the complexes. The presence of a new band in the region 442 and $451\,\mathrm{cm}^{-1}$ due to ν(Zn–N) and ν(Ni–N) is another indication of coordination through nitrogen of the azomethine group [29, 30]. The ν(C=O) band at $1714\,\mathrm{cm}^{-1}$ for the free ligands does not exhibit any change after complexation.

3.3. *Magnetic study*

The magnetic moment of compound **3** has been measured. Experimental value revealed that compound **3** is diamagnetic compound.

Supplementary data

X-ray crystallographic files in CIF format for the complexes **1–3** have been deposited at the Cambridge Crystallographic Data Center with the deposition number CCDC-603402 for **1**, CCDC-603403 for **2** and CCDC603404 for **3**. Copies of the data can be obtained free of charge from The Director, CCDC, 12 Union Road, Cambridge, CB2 IEZ, UK (Fax: +44-1223-336033; Email: deposit@ccdc.cam.ac.uk).

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