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Synthesis, crystal structure and characterization of 3-thiophene aldehyde thiosemicarbazone and its complexes with cobalt(II), nickel(II) and copper(II)

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ABSTRACT

The reaction of cobalt(II), nickel(II), copper(II) chlorides and bromides with 3-thiophene aldehyde thiosemicarbazone (3TTSCH) leads to the formation of a series of new complexes: $[\text{Co}(3\text{TTSC})_2]$, $[\text{Ni}(3\text{TTSC})_2]$, $[\text{CuCl}(3\text{TTSC})_2]$, $[\text{CuBr}(3\text{TTSC})_2]$ and $[\text{CuBr}_2(3\text{TTSCH})]$. The crystal structures of the free ligand and of the compound $[\text{Ni}(3\text{TTSC})_2]$ have been determined by X-ray diffraction methods. For all these complexes, the central ion is coordinated through the sulfur and the azomethine nitrogen atom of the thiosemicarbazone. $[\text{Co}(3\text{TTSC})_2]$, $[\text{Ni}(3\text{TTSC})_2]$ and $[\text{CuBr}_2(3\text{TTSCH})]$ are mononuclear species, while $[\text{CuCl}(3\text{TTSC})_2]$ and $[\text{CuBr}(3\text{TTSC})_2]$ are binuclear complexes.

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1. Introduction

Thiosemicarbazones and their metal complexes have been extensively studied during recent years mainly because of their various biological properties [1,2]. Thiosemicarbazones usually act as chelating ligands with transition metal ions, bonding through the sulfur and hydrazine nitrogen atoms [3].

Heterocyclic thiosemicarbazones with a functional group attached at the 2-position have been the subject of extensive investigation. A review was recently published by Lobana et al. [4]. Changing the attachment of the thiosemicarbazone moiety to the 3-position on the heteroaromatic ring often causes a decrease in activity, presumably due to a lesser ability for coordination [5], and very few papers deal with 3-monosubstituted or 2,5-disubstituted thiophenes as ligands.

Chemically speaking, the heterocyclic thiosemicarbazones are of high interest because of their great versatility as ligands. This is due to the presence of several potential donor atoms, their flexibility and their ability to coordinate in either the neutral or deprotonated forms. However, in many papers, only 2-thiophene aldehyde derivatives have been investigated [4,6–8].

We have already described the furanic thiosemicarbazones: 3-furaldehyde thiosemicarbazone, 5-methyl 2-furfural thiosemicarbazone and 3-(2-furyl)prop-2-enal thiosemicarbazone [9–11]. As part of our continuous research work pertaining to the synthesis, characterization and the biological activity of metal complexes from semicarbazones [12,13] and thiosemicarbazones of furalde-

hyde [11,14], we describe here some new transition metal complexes obtained from 3-thiophenaldehyde thiosemicarbazone (3TTSCH) (Fig. 1) as a ligand and cobalt(II), nickel(II) and copper(II) chlorides and bromides. In addition, the crystal structures of the ligand 3TTSCH and its nickel complex $[\text{Ni}(3\text{TTSC})_2]$ are described.

2. Experimental

2.1. Reactants

All reactants and solvents were analytical grade. Thiosemicarbazide and thiophene-3-carboxaldehyde were purchased from Alfa Aesar. Cobalt, nickel and copper hydrated salts (Prolabo) were used as received.

2.2. Measurements

Elemental analyses were carried out by the service central of analyses (C.N.R.S. Vernaison, France). DSC diagrams were recorded in the 25–400 °C range with a Mettler DSC 822e unit, with the help of Mettler Toledo STAR[®] SW 8.10 System software (Laboratoire de Physique, Faculté de Pharmacie, Angers); the heating rate was 10 °C per min. All measurements were made in 40 mm³ closed Al crucibles. The IR spectra were recorded with a Bruker FTIR Vector 22 spectrometer between 4400 and 400 cm⁻¹ (KBr disks). The magnetic measurements were carried out using a SQUID magnetometer Quantum Design MPMS 5 and the EPR spectra were recorded using Bruker ELEXSYS 500 equipment. (Equipe Chimie Inorganique, ICMMO, Université Paris-Sud, Orsay, France) in the 200–300 K range with a 10000 G applied field, diamagnetic correc-

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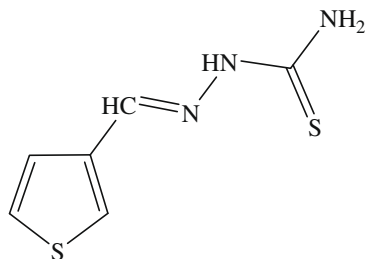


Fig. 1. Chemical structure of the ligand.

tions were estimated from Pascal's constants and magnetic data were corrected for diamagnetic contributions of the sample holder.

2.3. Crystal data collection and processing

Crystals of the ligand 3TTSCH and $[\text{Ni}(\text{3TTSC})_2]$ are monoclinic with the space group $P2_1/c$. The crystal and instrumental parameters used in the unit-cell determination and data collection are summarized in Table 1. X-ray single-crystal diffraction data were collected at 293 K on a STOE-IPDS diffractometer, equipped with a graphite monochromator using Mo $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) (CIMA, UMR CNRS 6200, Université d'Angers). The structures were solved by full-matrix least-squares techniques using the SHELX-97 package [15]. Positions of H-atoms were calculated geometrically and the distances N1–H1A and N1–H1B for $[\text{Ni}(\text{3TTSC})_2]$ were refined. Gaussian absorption corrections were applied.

2.4. Synthesis of the ligand 3TTSCH

The ligand was obtained from thiophene-3-carboxaldehyde and thiosemicarbazide (1:1 molar ratio) in absolute ethanol with the addition of two drops of sulfuric acid [16]. The mixture was refluxed for 1 h and then cooled, filtered and recrystallized from ethanol. Yellow single crystals suitable for X-ray analysis were grown

Table 1
Crystallographic data.

Formula	$\text{C}_6\text{H}_7\text{N}_3\text{S}_2$	$\text{C}_{12}\text{H}_{12}\text{N}_6\text{NiS}_4$
Name	3TTSCH	$[\text{Ni}(\text{3TTSC})_2]$
Formula weight	185.27	427.23
Crystal system	monoclinic	monoclinic
Space group	$P2_1/c$	$P2_1/c$
<i>a</i> (Å)	18.951(1)	7.4810(9)
<i>b</i> (Å)	5.7911(5)	7.5187(6)
<i>c</i> (Å)	23.551(2)	15.212(2)
α (°)	90	90
β (°)	99.914(8)	101.75(1)
γ (°)	90	90
<i>V</i> (Å ³)	2546.1(3)	837.7(2)
<i>Z</i>	12	2
Color	yellow	yellow-brown
<i>D</i> _{calc} (g cm ⁻³)	1.450	1.694
<i>F</i> (000)	1152	436
Crystal size (mm)	0.73 × 0.31 × 0.08	0.69 × 0.23 × 0.08
μ (mm ⁻¹)	0.564	1.662
<i>hkl</i> limits	−22 ≤ <i>h</i> ≤ 23 −7 ≤ <i>k</i> ≤ 7 −29 ≤ <i>l</i> ≤ 28	−9 ≤ <i>h</i> ≤ 9 −9 ≤ <i>k</i> ≤ 9 −18 ≤ <i>l</i> ≤ 18
θ_{min} , θ_{max} (°)	2, 26	3, 26
Reflections collected/unique	23584/4955	7898/1616
Number of data with <i>I</i> > 2σ(<i>I</i>)	3708	1317
Number of variables	299	126
<i>R</i> ₁ for <i>I</i> > 2σ(<i>I</i>)	0.0583	0.0295
<i>wR</i> ₂ for <i>I</i> > 2σ(<i>I</i>)	0.1670	0.0744

$$w = 1/[\sigma^2(F_o^2) + (0.1414P)^2 + 0.00000P] \text{ where } P = (F_o^2 + 2F_c^2)/3 \text{ for 3TTSCH.}$$

$$w = 1/[\sigma^2(F_o^2) + (0.0440P)^2 + 0.22020P] \text{ where } P = (F_o^2 + 2F_c^2)/3 \text{ for } [\text{Ni}(\text{3TTSC})_2].$$

at room temperature by slow evaporation of solution of the ligand in a mixture of ethanol (75%) and water (25%).

2.5. Preparation of the complexes

All the complexes were prepared starting from 5 mmol (1 g) of 3TTSCH dissolved in EtOH. An ethanolic solution of the metal halide was added slowly while stirring. The complexes were removed by filtration, washed with MeOH and finally dried in vacuum over silica gel.

2.5.1. Bis(3-thiophenylaldehyde thiosemicarbazone) cobalt(II)

$[\text{Co}(\text{3TTSC})_2]$

$\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.64 g; 2.5 mmol, 10 cm³) or CoBr_2 (0.59 g; 2.5 mmol, 10 cm³) was added to the 3TTSCH ethanolic solution (20 cm³) under refluxing conditions. The reflux was maintained for 24 h. The resulting solution was concentrated and a dark-brown precipitate was filtered off.

2.5.2. Bis(3-thiophenylaldehyde thiosemicarbazone) nickel(II)

$[\text{Ni}(\text{3TTSC})_2]$

$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.64 g; 2.5 mmol, 10 cm³) or $\text{NiBr}_2 \cdot x\text{H}_2\text{O}$ (0.59 g; 2.5 mmol, 10 cm³) was added to the ethanolic solution of 3TTSCH (20 cm³) under refluxing conditions. An aqueous solution of sodium hydroxide was added dropwise to reach a pH value in the range 6–7 [17]. The reflux was maintained for 3 h.

2.5.3. Bis(chloro (3-thiophenylaldehyde thiosemicarbazone) copper(II))

$[\text{CuCl}(\text{3TTSC})_2]$

$\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.91 g; 5 mmol, 10 cm³) was added to 3TTSCH in EtOH (15 cm³). Although the complex appeared instantaneously, the reflux was maintained for 1 h in order to complete the reaction. The same compound was obtained when operating at room temperature.

2.5.4. Dibromo (3-thiophenylaldehyde thiosemicarbazone) copper(II)

$[\text{CuBr}_2(\text{3TTSC})_2]$

CuBr_2 (1.2 g; 5 mmol, 10 cm³) was added to 3TTSCH in EtOH (15 cm³) at room temperature. The complex appeared instantaneously, however, the reaction was maintained for 3 h.

2.5.5. Bis(bromo (3-thiophenylaldehyde thiosemicarbazone) copper(II))

$[\text{CuBr}(\text{3TTSC})_2]$

CuBr_2 (1.2 g; 5 mmol, 10 cm³) was added to 3TTSCH in EtOH (15 cm³). Although the complex appeared instantaneously, the reflux was maintained for 2 h.

3. Results and discussion

3.1. Crystal structure of the ligand 3TTSCH

The main crystal parameters are reported in Table 1. The monoclinic unit cell (space group $P2_1/c$) contains twelve molecules in four groups of three independent molecules. The three independent molecules, with the numbering scheme, are given in Fig. 2. Each of the three independent molecules is quite planar and the most important deviations are observed for the thiosemicarbazone sulfur atoms as follows: S(1): 0.1838 Å, S(3): 0.1867 Å and S(5): 0.7895 Å. The first and the second molecules lie in quite parallel planes, while the third one is located in a plane forming angles of 54.17(6)° with the first molecule and 53.69(6)° with the second one. The sulfur atom S(1) and the hydrazone nitrogen N(3) are in the *E* position with respect to the C(1)–N(2) bond, the same configuration is observed for S(3) and S(5) with respect to the C(7)–N(5) and C(13)–N(8) bonds, respectively. This configuration is often ob-

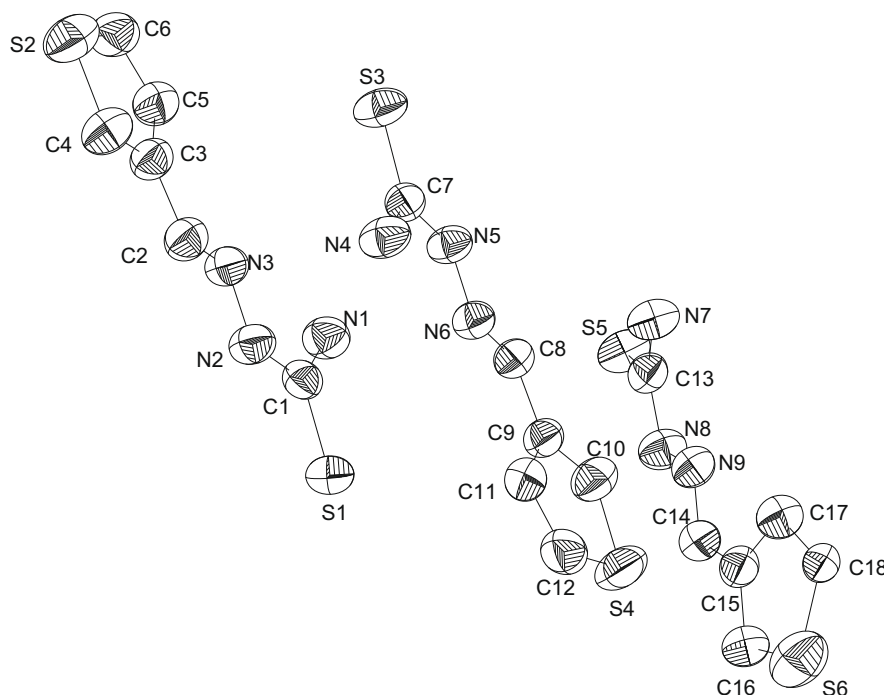


Fig. 2. ORTEP view (50% displacement ellipsoids) of the three independent molecules of the ligand with the numbering scheme.

served in thiosemicarbazones and its stability is due to the presence of an intramolecular hydrogen bond between the N-imino atom and H from NH_2 [5]. In the case of 3TTSC, the distances $\text{N}(3)\text{--H}$, $\text{N}(6)\text{--H}$ and $\text{N}(9)\text{--H}$ are 2.358(2), 2.248(2) and 2.290(3) Å, respectively, and consequently these interactions are weak, but sufficient to stabilise the *E* configuration.

There are no significant differences for bond distances and angles in the thiosemicarbazone moiety between the three independent molecules. Representative bond distances and angles for the three independent molecules are shown in Table 2. The C–S bond lengths (1.683(3)–1.691(3) Å) and the dihedral angles around C(1), C(7) and C(13) are typical of a delocalised π electron system [10,18]. The bond length of the C(2)–N(3) bond is 1.268(4) Å, that of N(2)–N(3) is 1.389(4) Å, and these distances are typical of a C=N double bond and an N–N single bond, respectively, and similar values are observed for the two other independent molecules.

The packing arrangement in the unit cell is given in Fig. 3. The third independent molecules in parallel planes are located along the *c* edges and are common to two unit cells. The first and the sec-

ond independent molecules are grouped in two rows between the planes of the third molecule. The packing of a group of independent molecules is governed by hydrogen bonds (Table 4). Their lengths are consistent with those observed in the case of the furanic analogue thiosemicarbazone [9,19].

3.2. Crystal structure of the nickel complex $[\text{Ni}(\text{3TTSC})_2]$

The main crystal parameters are reported in Table 1. The bond distances and angles for the thiosemicarbazone moiety are listed in Table 3 and the structure and the numbering scheme are given in Fig. 4. The centrosymmetric structure consists in the neutral complex species $[\text{Ni}(\text{3TTSC})_2]$, with the nickel at the centre of symmetry. The coordination results in a square-planar geometry involving the thiolato sulfur atoms and the N(3) nitrogen atoms in a *Z* configuration around the C(1)–N(2) bond (Fig. 4). As the ligand is deprotonated, the resulting negative charge is delocalized along the thiosemicarbazone moiety. Due to the free rotation around the C(2)–C(3) bond there are two possible configurations for the thiophene ring, with an almost 50% probability for each one. This phenomenon was not observed in the case of the furan analogue [10]. The complex molecule is quite planar, the highest deviations are due to the S(1) and N(2) atoms, with 0.5477 and -0.2654 Å deviations, respectively (Fig. 5).

The molecular arrangement inside the unit cell is given in Fig. 6. All the nickel ions are located at the midpoint of the *b* and *c* edges (Fig. 6a). The neutral molecules $\text{Ni}(\text{3TTSC})_2$ lie in two sets of parallel planes (Fig. 6b) with a 60° angle between them. The packing is governed by hydrogen bonds between S(1) and H(1A), and N(2) and H(1B) (Table 4). Though these interactions are weak, they have already been observed and described for similar compounds [5].

3.3. Structures of the cobalt and copper complexes

3.3.1. Analytical data

The elemental analysis of the ligand and its complexes is summarized in Table 5. A good harmony between the experimental and

Table 2
Selected bond lengths (Å) and angles ($^\circ$) of the three independent molecules for the ligand 3TTSC.

Bond lengths		Bond angles	
C(1)–N(1)	1.330(4)	N(1)–C(1)–N(2)	118.2(3)
C(1)–N(2)	1.350(4)	N(1)–C(1)–S(1)	123.0(2)
C(1)–S(1)	1.687(3)	N(2)–C(1)–S(1)	118.8(2)
C(2)–N(3)	1.268(4)	N(3)–C(2)–C(3)	122.2(3)
N(2)–N(3)	1.389(4)	C(1)–N(2)–N(3)	121.2(3)
C(7)–N(4)	1.320(4)	N(4)–C(7)–N(5)	117.2(3)
C(7)–N(5)	1.344(4)	N(4)–C(7)–S(3)	123.6(2)
C(7)–S(3)	1.683(3)	N(5)–C(7)–S(3)	119.2(2)
C(8)–N(6)	1.276(4)	N(6)–C(8)–C(9)	119.0(3)
N(5)–N(6)	1.379(3)	C(7)–N(5)–N(6)	118.6(2)
C(13)–N(7)	1.304(4)	N(7)–C(13)–N(8)	117.4(3)
C(13)–N(8)	1.348(4)	N(7)–C(13)–S(5)	123.5(2)
C(13)–S(5)	1.691(3)	N(8)–C(13)–S(5)	119.1(2)
C(14)–N(9)	1.270(4)	N(9)–C(14)–C(15)	120.8(3)
N(8)–N(9)	1.371(4)	C(13)–N(8)–N(9)	119.9(3)

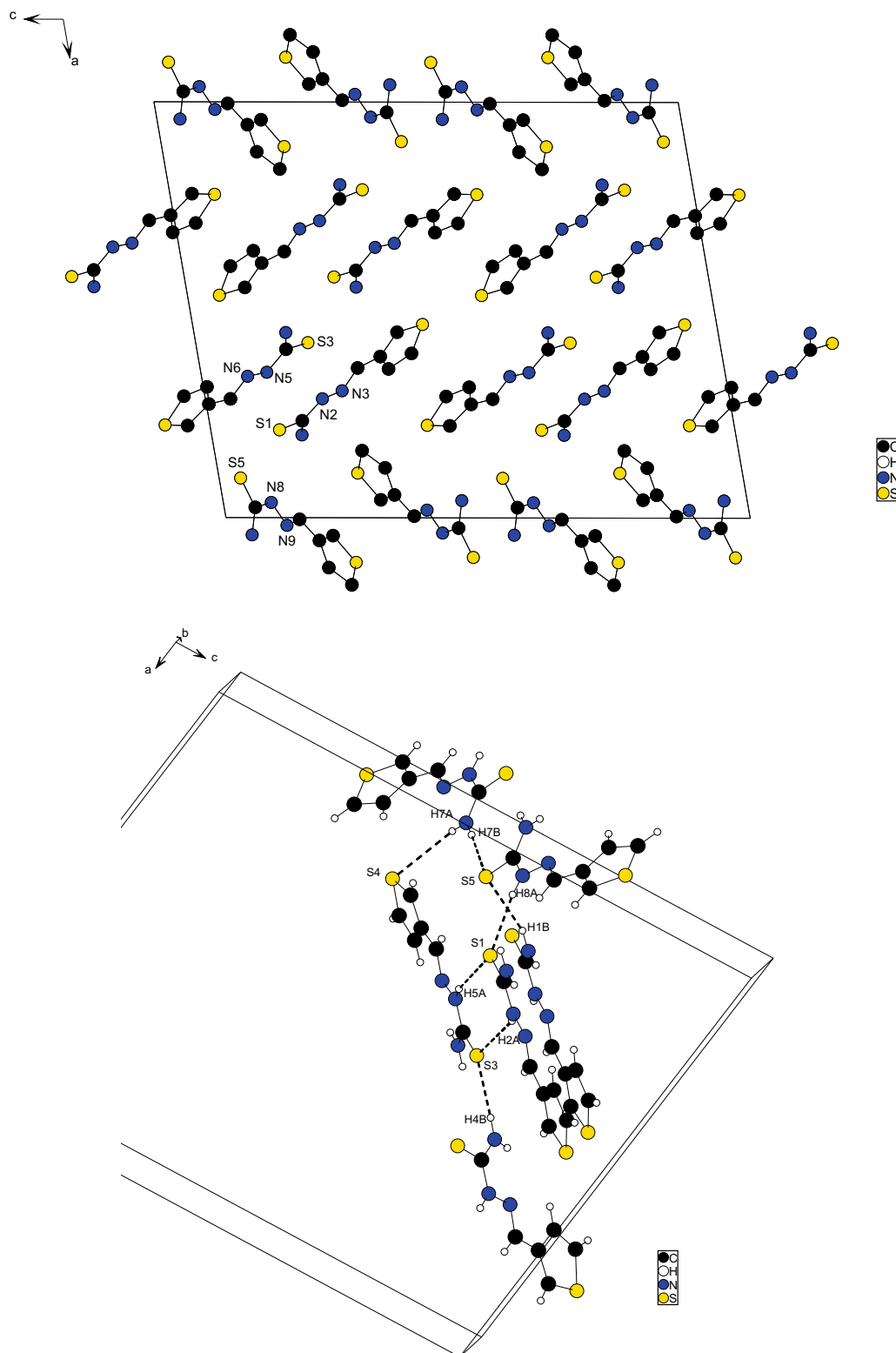


Fig. 3. Packing arrangement and intermolecular hydrogen bonds for the ligand.

calculated values is observed and the formulae of the complexes are $[\text{Co}(\text{3TTSC})_2]$, $[\text{Ni}(\text{3TTSC})_2]$, $[\text{CuCl}(\text{3TTSC})_2]$, $[\text{CuBr}(\text{3TTSC})_2]$ and $[\text{CuBr}_2(\text{3TTSCH})]$.

The melting points were determined using DSC. In all complexes, decomposition follows the beginning of the melting process.

3.3.2. Infrared spectra

The main infrared vibration bands are reported in Table 6. In principle, since the ligand contains a thioamide $-\text{NH}-\text{C}=\text{S}$ functional group, it can exhibit thione–thiol tautomerism [20]. The $\nu(\text{S}-\text{H})$ band around 2570 cm^{-1} [21] is absent from IR spectra of the ligand but the $\nu(\text{N}-\text{H})$ band at 3149 cm^{-1} is present, indicating

Table 3

Bond lengths (Å) and angles (°) for the nickel complex.

Bond lengths		Bond angles	
C(1)–N(2)	1.300(3)	N(2)–C(1)–N(1)	118.9(2)
C(1)–N(1)	1.341(3)	N(2)–C(1)–S(1)	123.29(2)
C(1)–S(1)	1.739(2)	N(1)–C(1)–S(1)	117.83(2)
C(2)–N(3)	1.298(3)	C(1)–N(2)–N(3)	111.97(3)
C(2)–C(3)	1.444(4)	C(2)–N(3)–N(2)	114.7(2)
N(2)–N(3)	1.396(3)	C(2)–N(3)–Ni(1)	125.59(2)
N(3)–Ni(1)	1.912(2)	N(2)–N(3)–Ni(1)	119.67(2)
S(1)–Ni(1)	2.1714(7)	C(1)–S(1)–Ni(1)	95.05(9)

Table 4

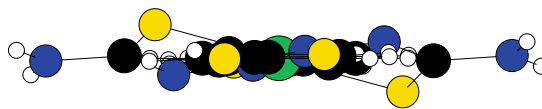
Bond lengths (Å), angles (°) and positions of intermolecular hydrogen bonds for the ligand and the Ni(II) complex.

Compound	Hydrogen bonds	Distance (Å)	Angle (°)
3TTSCH	S(1)⋯H(5A)	2.63	160.2(2)
	S(1)⋯H(8A)	2.53	162.4(2)
	S(3)⋯H(2A)	2.55	145.5(2)
	S(3)⋯H(4B)	2.48	173.7(2)
	S(4)⋯H(7A)	3.00	144.1(2)
	S(5)⋯H(1B)	2.61	162.5(2)
	S(5)⋯H(7B)	2.53	172.5(2)
[Ni(3TTSC) ₂]	S(1)⋯H(1A)	2.69	162(1)
	N(2)⋯H(1B)	2.64	127(1)

that in the solid state the ligand remains as the thione tautomer. The spectrum of the ligand exhibits a strong band at 1603 cm⁻¹ due to the C=N stretching vibration.

In the case of the nickel complex, the ν(NH₂) vibration band is slightly shifted to lower wavenumbers, whereas ν(N–H) is shifted to higher values. The ring breathing remains quite unchanged when passing from ligands to complexes at ca. 830 cm⁻¹ [22] and ν(C=N) is not significantly modified. There is no significant influence of complexation upon the two bands corresponding to ν(CS), situated at 1165 and 786 cm⁻¹ in the ligand spectrum.

In addition, the spectrum of the nickel complex shows the two vibration bands, ν(M–S) and ν(M–N), at 519 and 420 cm⁻¹, respectively, which correspond to coordination bonds [23]. In the spectra of the other complexes, we find the same bands shifts as in the case of the nickel complex. The respiration band of the cycle at ca. 830 cm⁻¹ remained unchanged.

**Fig. 5.** Atoms deviation with respect to the plane of the molecule of [Ni(3TTSC)₂].

The spectra of all the complexes show the presence of ν(M–S) and ν(M–N) bands, again like in the case of the nickel complex. Thus, in all the complexes the coordination occurs through the sulfur and the nitrogen atom of the imino moiety of the molecule. According to these results, the proposed structures for these new complexes are given in Fig. 6.

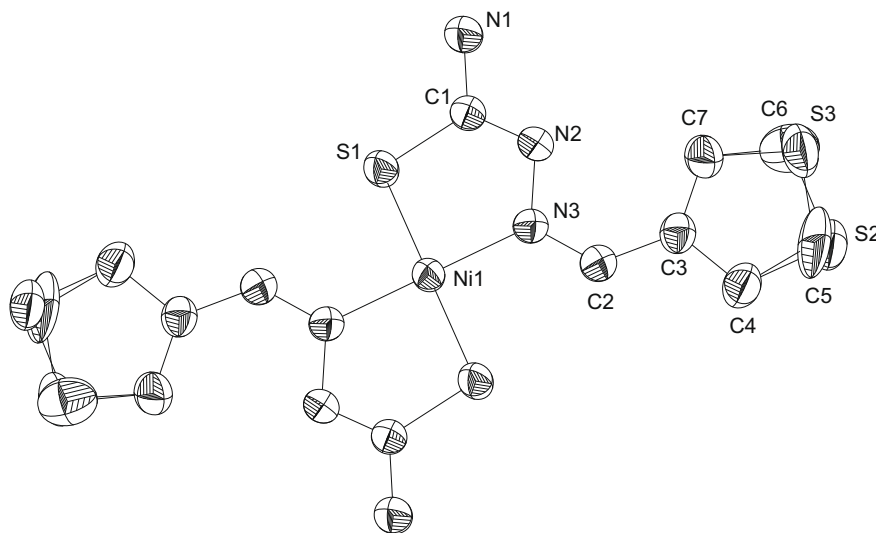
3.3.3. Structures of the complexes

The structures of the cobalt(II) and copper(II) complexes are given in Fig. 7. They were determined on the basis of the crystal structure of [Ni(3FTSC)₂] and from their spectroscopic data. In all the species, the coordination occurs through the sulfur (thiosemicarbazone) atom and the N (imino) atom, as in all cases the vibration bands relative to these atoms are identically shifted (Table 5). In addition, the nickel complex was found to be a diamagnetic species.

The elemental analysis for the cobalt(II) complex shows unambiguously that the ligand acts as the deprotonated thiol tautomer. The χ_T value at 300 K is 0.5 cm³ mol⁻¹, corresponding to a low spin Co(II) complex and the magnetic moment is 2.13 B.M. This value, much lower than expected for Co(II) tetrahedral complexes, is typical of Co^{II} in a strongly distorted tetrahedral geometry, almost square-planar [24,25]. In addition, there no signal in the EPR spectrum, which is typical of low spin cobalt(II) species.

The two binuclear complexes [CuX(3TTSC)₂] (X = Cl or Br) exhibit the same binuclear structure in which the copper(II) shows a square-planar geometry and bridging halogenides, as has already been reported for 3-furaldehyde thiosemicarbazone [10]. These complexes revealed antiferromagnetic coupling, as is usually observed in binuclear copper(II) complexes with bridging halides [26].

The mononuclear [CuBr₂(3TTSC)] complex is a square-planar species and the copper is coordinated through the sulfur thione atom and the N-imino atom. In this case, the ligand remains protonated and remains as the thione tautomer, like in Ref. [10]. The

**Fig. 4.** ORTEP view (50% displacement ellipsoids) and atom numbering for [Ni(3TTSC)₂].

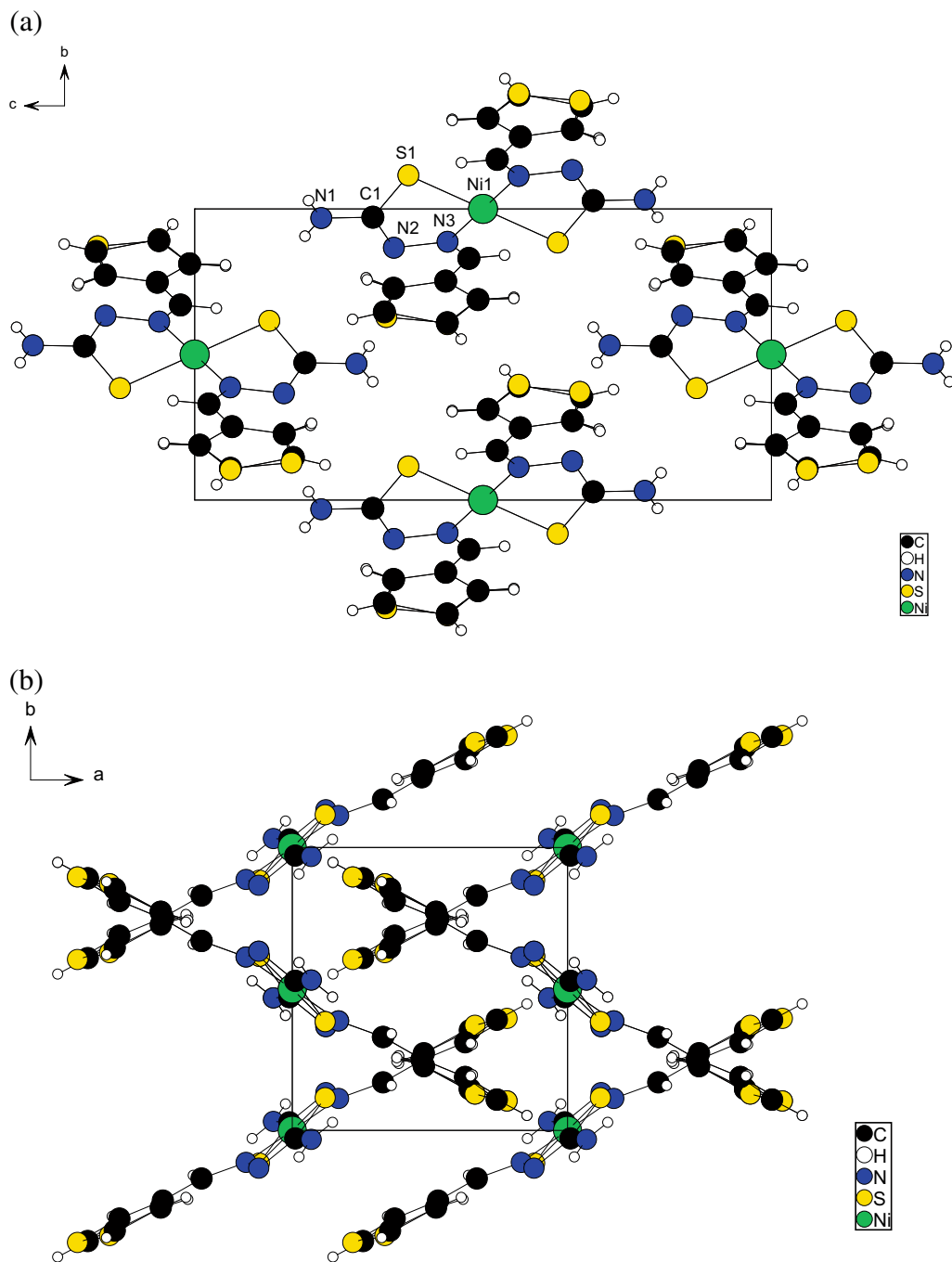


Fig. 6. Packing arrangement for the nickel complex viewed from the *a* axis (a) and *c* axis (b).

Table 5
Analytical data.

Compound	Colour	Yield (%)	MP (°C)	Elemental analysis found (calc.)		
				C (%)	H (%)	N (%)
3TTSCH	yellow	93	165	38.98 (38.87)	3.81 (3.77)	22.68 (22.67)
[Co(3TTSC) ₂]	dark-brown	44	197d	33.33 (33.56)	3.41 (3.29)	19.35 (19.57)
[Ni(3TTSC) ₂]	yellow-brown	57	240d	33.89 (33.58)	3.26 (3.29)	19.57 (19.58)
[CuCl(3TTSC) ₂]	green	72	215d	25.46 (25.35)	2.61 (2.48)	14.36 (14.78)
[CuBr(3TTSC) ₂]	green	67	223d	20.78 (21.92)	2.31 (2.15)	11.82 (12.78)
[CuBr ₂ (3TTSCH)]	dark-green	58	215d	17.83 (17.64)	2.08 (1.73)	9.46 (10.28)

d, decomposition.

Table 6
Infrared data for the ligand and the complexes (cm^{-1}).

Compound	$\nu(\text{NH}_2)$	$\nu(\text{NH})$	$\nu(\text{C}=\text{N})$	$\nu(\text{CS})$	Ring breath	$\nu(\text{N}-\text{N})$	$\nu(\text{M}-\text{S})$	$\nu(\text{M}-\text{N})$
3TTSCH	3408	3149	1603	1165 786	831	944		
$[\text{Co}(\text{3TTSC})_2]$	3406	3150	1603	1164 783	833	944	519	420
$[\text{Ni}(\text{3TTSC})_2]$	3372	3168	1608	1163 780	830	945	533	440
$[\text{CuCl}(\text{3TTSC})_2]$	3408	3140	1600	1167 780	835	947	528	430
$[\text{CuBr}(\text{3TTSC})_2]$	3378	3143	1600sh	1166 784	830	949	525	422
$[\text{CuBr}_2(\text{3TTSCH})]$	3403	3138	1600sh	1166 783	831	946	525	420

sh, shoulder.

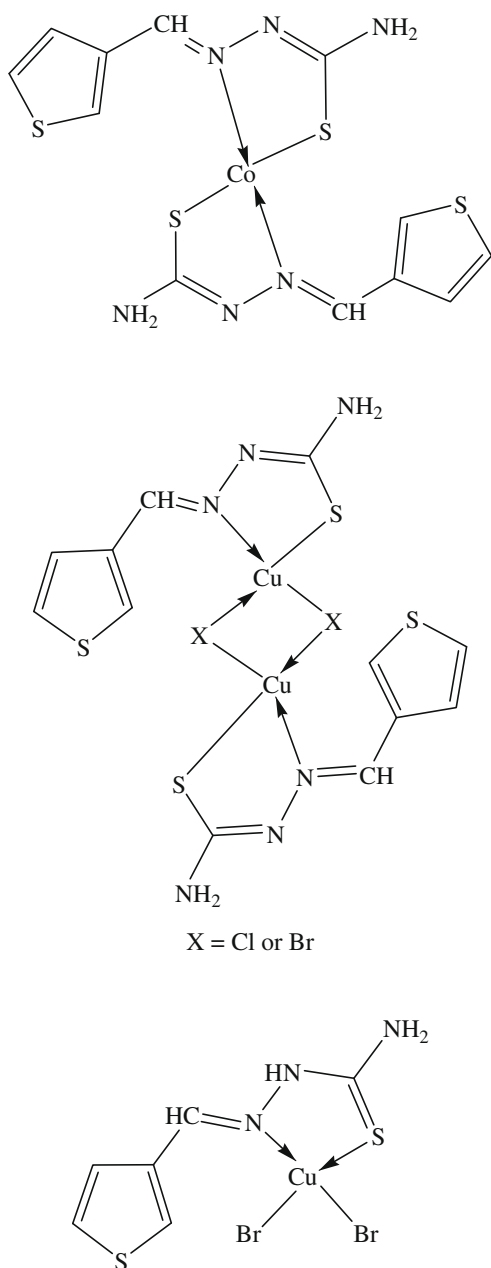


Fig. 7. Chemical structures of the cobalt(II) and copper(II) complexes.

EPR spectrum at room temperature showed typical signals corresponding to the Cu^{2+} ion.

These various structures for complex species have already been observed for other thiosemicarbazones [19,27].

Supplementary data

CCDC 710981 and 710982 contains the supplementary crystallographic data for this article. 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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