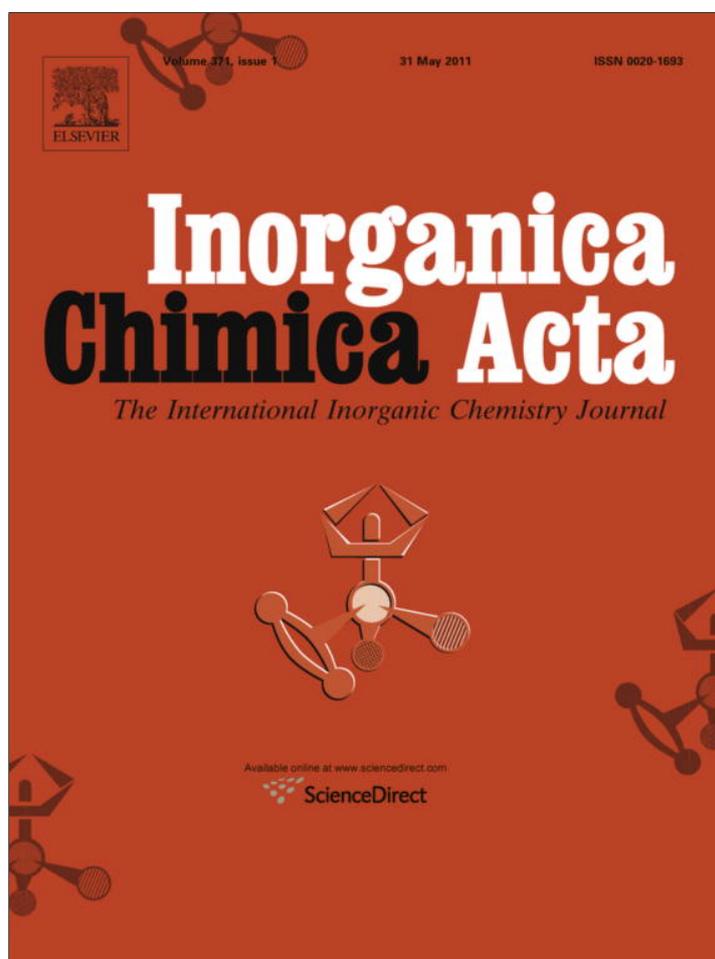


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S-allyl-3-(2-pyridyl-methylene)dithiocarbazate ligand and its manganese(II), cobalt(III) and nickel(II) complexes

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ABSTRACT

A new NNS tridentate ligand, S-allyl-3-(2-pyridyl-methylene)dithiocarbazate (HL) has been prepared. Three coordination complexes, Mn(L)₂ (**1**), [Co(L)₂]NO₃ (**2**) and Ni(L)₂ (**3**) (L⁻ is the deprotonated mono-anionic form of HL) have been synthesized and characterized by elemental analysis, molar conductivity, FT-IR, ¹H NMR and UV–Vis spectroscopy. **1** and **3** are neutral complexes, while **2** is cationic with nitrate as the counter ion. Single crystal X-ray diffraction analysis shows that bis-chelate complexes have a distorted octahedral geometry in which two ligands in thiolate tautomeric form coordinate to the metal center through N atoms of the pyridine and imino moieties and one S atom. Molecular geometry from X-ray analysis, molecular geometry optimization, atomic charges distribution and bond analysis of the ligand and complexes have been performed using the density functional theory (DFT) with the B3LYP functional.

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1. Introduction

It is more than one century from the first synthesis of dithiocarbazic acid by Curtius [1]. A considerable number of S-alkyl/aryl-esters and the Schiff base of such compounds have been prepared [2–12] with interesting applications as antibacterial [2], antifungal [3], antitumor [4,5] or insecticidal [6] compounds, nano-materials [7], solar cell components [8] and non-linear optical (NLO) materials [9,10]. Hydrazine carbodithioate ligands are typically bidentate-chelate, acting through one S and one N donor atom and the presence of hard N and soft S donor atoms enables these ligands to react with both transition and main group metals. Moreover, Schiff base functionalization with suitable aldehydes, for instance salicylaldehyde or pyridine-2-carboxaldehyde, can introduce an additional oxygen or nitrogen donor atom, the corresponding ligand acting as tridentate, with the pyridine ring that can provide more significant biological activities [11,13]. In this work, we report the synthesis, spectroscopic and X-ray analysis of the complexes of Mn(II), Co(III) and Ni(II) with the tridentate Schiff base ligand S-allyl-3-[(2-pyridyl-methylene)]dithiocarbazate (HL), Scheme 1, obtained by condensation of pyridine-2-carboxaldehyde with S-allyl-dithiocarbazate. Energy and geometry optimi-

zation of HL tautomers, L⁻, MnL₂ and NiL₂ complexes, carried out using DFT methods is also described in the paper.

2. Experimental

2.1. Materials and instrumentation

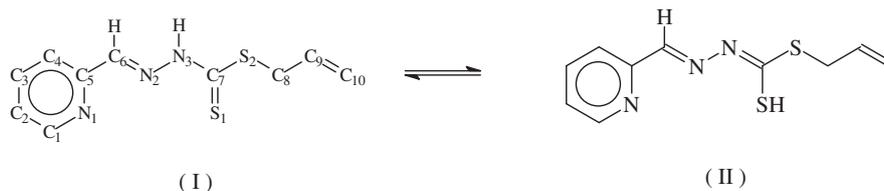
All chemicals were analytical grade and, unless otherwise specified, were used as received. Elemental analyses (C, H, N, S) were performed with a Thermo Finnigan Flash Elemental Analyzer 1112EA. The molar conductance values of 1.0×10^{-3} M DMF solutions of the complexes were measured with a Metrohm 712 Conductometer. IR spectra (KBr pellets) were recorded with a FT-IR 8400-SHIMADZU spectrophotometer (4000–400 cm⁻¹). ¹H NMR spectra were recorded at 25 °C with a Bruker BRX 100 AVANCE spectrometer. The electronic spectra were recorded in DMF with a SHIMADZU model 2550 UV–Vis spectrophotometer (250–1100 nm).

2.2. S-allyl-3-[(2-pyridyl-methylene)]dithiocarbazate (HL)

A solution of fresh S-allyl dithiocarbazate [14] (1.48 g, 10 mmol) in 15 mL hot ethanol was added to a boiling solution of the 2-pyridinecarbaldehyde (1.07 g, 10 mmol) in the same solvent (15 mL). The mixture was refluxed for 1 h on a water bath and then

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Scheme 1. Thione (I) and thiol (II) forms of S-allyl-3-[(2-pyridyl-methylene)]dithiocarbazate (HL).

left to stand overnight. A yellow microcrystalline compound separated. It was filtered off, washed several times with cold ethanol and dried in vacuo over silicagel.

Yield: 2 g, 84%. m.p.: 178 °C. *Anal. Calc.* for $C_{10}H_{11}N_3S_2$ (237.34 g mol⁻¹): C, 50.60; H, 4.67; N, 17.70; S, 27.02. Found: C, 49.09; H, 4.52; N, 16.81; S, 26.56%. IR (KBr), cm⁻¹: $\nu(\text{NH})$ 3096w, $\nu(\text{C}=\text{C})$ 1634w, $\nu(\text{C}=\text{N}_{\text{py}})$ 1585w, $\nu(\text{C}=\text{N})$ 1535s, $\nu(\text{C}=\text{S})$ 1283s, $\nu(\text{N}-\text{N})$ 1038s, $\nu(\text{CSS})$ 995m, $\rho(\text{py})$ 683w. UV-Vis (DMF), λ_{max} , nm (log ϵ , L mol⁻¹ cm⁻¹): 297 (3.85)sh, 335 (4.23). ¹H NMR (100 MHz, CDCl₃): δ = 15.55 (s, 1H, N³H; exchanges with D₂O), 7.53(d, 1H, C⁶H), 8.79 (d, 1H, C¹_{py}), 8.17–7.85 (m, 2H, C⁴_{py}, C⁵_{py}), 7.39 (t, 1H, C²_{py}), 5.81–6.1 (m, 1H, C⁹), 5.27 (t, 2H, C¹⁰), 4.00 (d, 2H, C⁸).

2.3. General method of synthesis of the complexes

The compounds **1–3** were synthesized by 2-h refluxing of an ethanolic (95%) solution of the ligand with Mn(CH₃COO)₂ · 4H₂O, Co(NO₃)₂ · 6H₂O and Ni(CH₃COO)₂ · 4H₂O, respectively, with a 1:2 molar ratio. The formed precipitate was filtered, washed with cold ethanol and dried in vacuo over silicagel.

The crude products **1–3** were recrystallized by a slow evaporation technique from solutions of methanol, DMF/water and DMF, respectively.

2.3.1. Mn(L)₂ (**1**)

Violet, Yield: 63%. m.p.: 187.5 °C. Molar conductivity (1.0 × 10⁻³ M; DMF): 1.6 Ω⁻¹ cm² mol⁻¹. Calc. for C₂₀H₂₀MnN₆S₄ (527.61 g mol⁻¹): C, 45.53; H, 3.82; N, 15.93; S, 24.31. Found: C, 44.48; H, 3.26; N, 15.92; S, 23.68%. IR (KBr), cm⁻¹: $\nu(\text{C}=\text{C})$ 1634w, $\nu(\text{C}=\text{N}_{\text{py}})$ 1595w, $\nu(\text{C}=\text{N})$ 1551m, $\nu(\text{N}-\text{N})$ 1065s, $\nu(\text{CSS})$ 966m, $\rho(\text{py})$ 656w. UV-Vis (DMF), λ_{max} , nm (log ϵ , L mol⁻¹ cm⁻¹): 291 (3.29)sh, 333 (4.64), 399 (4.35).

2.3.2. [Co(L)₂]/NO₃ (**2**)

Brown, Yield: 50%. m.p.: 210 °C. Molar conductivity (1.0 × 10⁻³ M; DMF): 60 Ω⁻¹ cm² mol⁻¹. Calc. for C₂₀H₂₀CoN₇O₃S₄ (593.61 g mol⁻¹): C, 40.47; H, 3.40; N, 16.52; S, 21.61. Found: C, 40.11; H, 3.37; N, 16.43; S, 21.23%. IR (KBr), cm⁻¹: $\nu(\text{C}=\text{C})$ 1632w, $\nu(\text{C}=\text{N}_{\text{py}})$ 1589w, $\nu(\text{C}=\text{N})$ 1547m, $\nu(\text{NO}_3)$ 1381s, $\nu(\text{N}-\text{N})$ 1053s, $\nu(\text{CSS})$ 962m, $\rho(\text{py})$ 660w. UV-Vis (DMF), λ_{max} , nm (log ϵ , L mol⁻¹ cm⁻¹): 287 (3.42)sh, 314 (4.30), 352 (4.40). ¹H NMR (100 MHz, CDCl₃): 7.55 (s, 1H, C⁶H), 8.85 (s, 1H, C¹_{py}), 7.7–8.4 (m, 3H, C⁴_{py}, C⁵_{py}, C²_{py}), 5.65–6.15 (m, 1H, C⁹), 5.24 (t, 2H, C¹⁰), 3.91 (d, 2H, C⁸).

2.3.3. Ni(L)₂ (**3**)

Brown, Yield: 65%. m.p.: 247 °C. Molar conductivity (1.0 × 10⁻³ M; DMF): 2 Ω⁻¹ cm² mol⁻¹. Calc. for C₂₀H₂₀NiN₆S₄ (531.37 g mol⁻¹): C, 45.21; H, 3.79; N, 15.82; S, 24.14. Found: C, 44.01; H, 3.72; N, 15.66; S, 23.93%. IR (KBr), cm⁻¹: $\nu(\text{C}=\text{C})$ 1632w, $\nu(\text{C}=\text{N}_{\text{py}})$ 1595w, $\nu(\text{C}=\text{N})$ 1547m, $\nu(\text{N}-\text{N})$ 1074s, $\nu(\text{CSS})$ 974m, $\rho(\text{py})$ 663w. UV-Vis (DMF), λ_{max} , nm (log ϵ , L mol⁻¹ cm⁻¹): 290 (3.96)sh, 316 (4.30)sh, 343 (4.40), 420 (4.37), 818 (1.59).

2.4. X-ray crystal structure determination

Single crystals of **1**, **2** and **3** suitable for X-ray analysis were grown from methanol, DMF/water and DMF, respectively. Data were collected on a Bruker-Nonius Kappa-CCD diffractometer using graphite monochromated Mo K α radiation (λ = 0.71073 Å) at 293 K for **1** and 173 K for **2** and **3**. Unit cell parameters were determined by least squares refinement [15] of the θ angles of, respectively, 132, 132 and 146 strong reflections in the range 3.161° < θ < 21.167°. Data were corrected for Lp and absorption using multi-scan method [16]. Structures were solved by direct methods [17] and refined by the full matrix least squares method [18] on F^2 against all reflections, using anisotropic displacement parameters for non-H atoms. H atoms, whose positions were determined stereochemically, were refined by the riding model with U_{eq} = 1.2U_{eq} of the carrier atom. In complexes **1** and **3** and in one crystallographically independent complex molecule of **2**, one allyl tail is disordered over two sites. The two split positions were refined with isotropic displacement parameters for the C atoms involved, without restraints for **3** and with few restraints for **1** and **2** (the three bond lengths S2–C8, C8–C9 and C9–C10 of the two split positions were restrained to be equal within 0.02 Å with SADI instructions of SHELXL). In the case of **2**, disorder is also found in one nitrate ion and in one water molecule. H atoms of the two water molecules contained in the independent unit were not considered in the refinement. A summary of crystal, collection and refinement data is shown in Table 1.

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

Compound	1	2	3
Chem. formula	(C ₁₀ H ₁₀ N ₃ S ₂) ₂ Mn	[(C ₁₀ H ₁₀ N ₃ S ₂) ₂ Co]NO ₃ · H ₂ O	(C ₁₀ H ₁₀ N ₃ S ₂) ₂ Ni
Formula weight	527.60	611.62	531.37
T/K	293(2)	173(2)	173(2)
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	c2 ₁ /c	c2/c	p2 ₁ /c
a (Å)	12.420(4)	36.062(8)	12.229(5)
b (Å)	14.931(4)	8.810(4)	14.994(7)
c (Å)	15.640(5)	32.300(8)	14.626(6)
β (°)	123.26(2)	98.22(3)	121.72(4)
V (Å ³), Z	2425.2(13), 4	10156(6), 16	2281(2), 4
Density (g/cm ³)	1.445	1.600	1.547
μ (mm ⁻¹)	0.908	1.047	1.238
Reflections collected, maximum θ	19872, 27.51°	36554, 27.51°	19314, 27.51°
Independent reflections (R _{int} = 0.0568)	5546	11191 (R _{int} = 0.0649)	5215 (R _{int} = 0.0893)
Data/restraints/param.	5546/3/278	11191/5/657	5215/0/279
R, wR (I > 2(I))	0.0555, 0.1227	0.0693, 0.1526	0.0406, 0.0713
R, wR (all data)	0.1184, 0.1560	0.1420, 0.1800	0.0915, 0.0834
Maximum peak and hole (e/Å ³)	1.15, -0.765	1.00, -0.689	0.385, -0.456

2.5. Theoretical methodology

All calculations have been performed using gradient-corrected density functional theory with the B3LYP functional [19] as implemented in the GAUSSIAN 98 program package [20]. The standard Pople's split valence 6-311G(*d, p*) basis set was employed except for the metal atoms, in which the LANL2DZ [21] basis set was used including effective core potential functions. Geometries of HL tautomers, and of its deprotonated form (L^-) together with Mn(II) and Ni(II) complexes were fully optimized (calculations were not performed on the cobalt complex because of its ionic nature, see below). At the same level and basis sets, calculations of natural electron population, natural charge for each atom and frontier molecular orbitals of the L^- ligand and of metal complexes have been performed by natural bond orbital (NBO) analysis [22] on the gas phase optimized structures. Multiplicities of the Ni(II) and Mn(II) central metals are considered as 3 and 6, respectively. The Polarized Continuum Model (PCM) [23] has been used for investigation of solute–solvent interactions. On the gas phase optimized geometries, the PCM energies were evaluated by neglecting the thermal corrections.

3. Results and discussion

The tridentate ligand HL, having NNS donor atoms, was prepared by the 1:1 condensation reaction of *S*-allyl dithiocarbamate with pyridine-2-carboxaldehyde in ethanol. Like other dithiocarbamates, HL can undergo thione–thiol tautomerism (Scheme 1). Furthermore, because of the presence of C=N moiety, *E* and *Z* isomeric forms can be considered for the free ligand [24]. The complexes (1–3) were characterized by elemental analysis, solution electrical conductivity, IR and UV–Vis spectra. The complexes were found to be fairly soluble in organic solvents such as DMF, DMSO, methanol, ethanol and acetonitrile. Molar conductivity values of complexes 1 and 3 show non-electrolytic behaviors, while the molar conductivity value of 2 is in accord with 1:1 electrolyte behavior in DMF solution. During preparation of the complex, the cobalt(II) salt presumably undergoes aerial oxidation in the presence of the ligand in the solution [25].

3.1. Spectroscopic characterization of the ligand and complexes

The IR spectrum of the free ligand shows a weak band at 3096 cm^{-1} for $\nu(\text{N–H})$ and does not exhibit any band around 2600 cm^{-1} corresponding to S–H stretching, indicating that the free ligand exists as the thione tautomer in the solid state [26]. In the spectra of the complexes, the $\nu(\text{N–H})$ band is absent, indicating that the ligand is coordinated in its deprotonated form [27]. The IR spectrum of the free ligand exhibits the $\nu(\text{C=N})$ and $\nu(\text{N–N})$ bands at ca. 1540 and 1036 cm^{-1} , respectively. The coordination of the azomethine nitrogen to the metal ion is indicated by the shift of the $\nu(\text{C=N})$ and $\nu(\text{N–N})$ bands to higher frequencies, 1547 – 1558 cm^{-1} and 1053 – 1076 cm^{-1} , respectively [28]. In HL, the $\nu(\text{CSS})$ band is observed at 995 cm^{-1} . The lower frequency $\nu(\text{CSS})$ (959 – 974 cm^{-1}) in the spectra of the complexes indicates coordination through one of the sulfur atoms [28]. The $\nu(\text{C=S})$ band of the free ligand (1283 cm^{-1}), disappears upon coordination, indicating that sulfur atom is bound to the metal as thiolate. The pyridine ring deformation mode of the free ligand at 683 cm^{-1} is decreased in the spectra of the complexes (650 – 663 cm^{-1}), indicating coordination of the N atom of pyridine ring to the metal ion [29,30].

$^1\text{H NMR}$ spectrum of HL shows a NH signal at 14.55 ppm, which disappears upon adding D_2O . This signal, which is shifted relatively downfield as compared to the usual values of δ 8–9 [31], strongly

suggests that N–H is involved in intramolecular H bonding, very likely with the N atom of the 2-pyridyl moiety as the acceptor with *Z* configuration for the C=N bond (*vide ultra*) [32]. Furthermore, the absence of any signal close to 4 ppm, which is the typical resonance of S–H proton, indicates that the thione tautomer is also present in solution [33,34]. Since Co(III), unlike Mn(II) and Ni(II) which are paramagnetic in octahedral geometry, is diamagnetic, we acquired $^1\text{H NMR}$ spectra for the Co-complex. The spectrum of the cobalt complex, on the other hand, does not contain NH signal resonance and this supports that ligand coordination to the Co(III) ion takes place in its deprotonated thiolate form.

The electronic spectrum of the free ligand exhibits bands at 297 nm and 335 nm corresponding to the $\pi \rightarrow \pi^*$ transition of the imine portion and $n \rightarrow \pi^*$ transitions of the aromatic ring, respectively. The electronic spectra of the complexes show intra-ligand bands in the range 287–343 nm, corresponding to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions [35,36]. The band at approximately 400 nm can be assigned to S \rightarrow M charge transfer. The appearance of this LMCT band in the complexes strongly indicates that the metal ion is coordinated to sulfur through the thiolate sulfur atom. The electronic spectrum of Ni(L) $_2$ shows only one *d–d* band at 818 nm. Octahedral

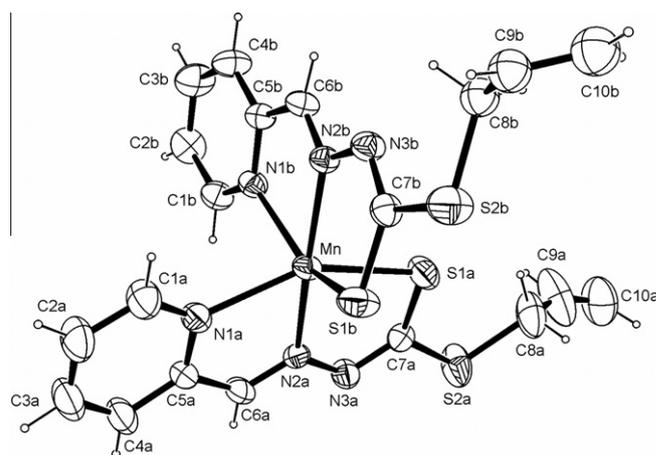


Fig. 1. ORTEP drawing of 1 with atom numbering. Thermal ellipsoids are shown at 30% probability level. Only one position is shown for the disordered *S*-allyl tail.

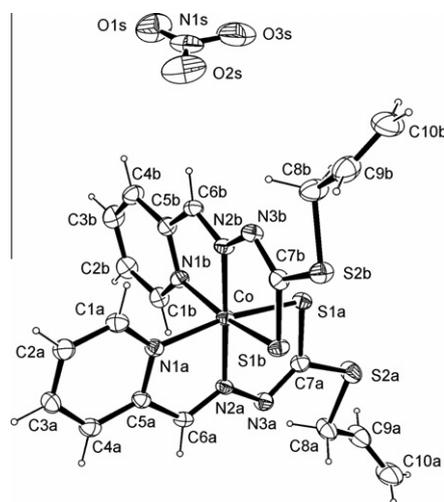


Fig. 2. ORTEP drawing with atom numbering of one of the two crystallographically independent units of the salt complex 2. Thermal ellipsoids are drawn at 30% probability level. The water molecule is not shown for clarity.

nickel(II) complexes are expected to exhibit three bands corresponding to the ${}^3A_2 \rightarrow {}^3T_2$, ${}^3A_2 \rightarrow {}^3T_1(F)$ and ${}^3A_2 \rightarrow {}^3T_1(P)$ transitions, but in the presence of sulfur donors, the high energy transitions are hidden by the CT absorption (~ 400 nm) [37]. The CT tails into the visible region obscure the very weak $d-d$ absorption bands of the manganese(II) and cobalt(III) complexes [38].

3.2. Discussion of the X-ray molecular structures of the complexes

ORTEP drawings of the three complexes are shown in Figs. 1–3. Selected bond lengths and bond angles are given in Table 2.

In **1** and **3** the crystallographically independent unit contains one complex molecule, while in **2** it contains two salt formula units (i.e. two complex molecules and two nitrate ions) plus two water molecules. The dithiocarbazate moiety of the ligand is in the thiolate tautomeric form in the three complexes. This is suggested by the observation that the average value of bond distances C7–N3, 1.311(3) Å, is only 0.033 Å longer than the average value of double bonds C6–N2, 1.278(4) Å, and by the similar observation that the average value of bond distances C7–S1, 1.708(6) Å, is only 0.035 Å shorter than the average value of single bonds C7–S2, 1.743(4) Å. In the three complexes, the pyridyl ring is almost coplanar with the hydrazinecarbodithioate fragment so, with the exclusion of the S-allyl tail, the remaining part of the ligand takes an almost planar conformation: the maximum distance from the least

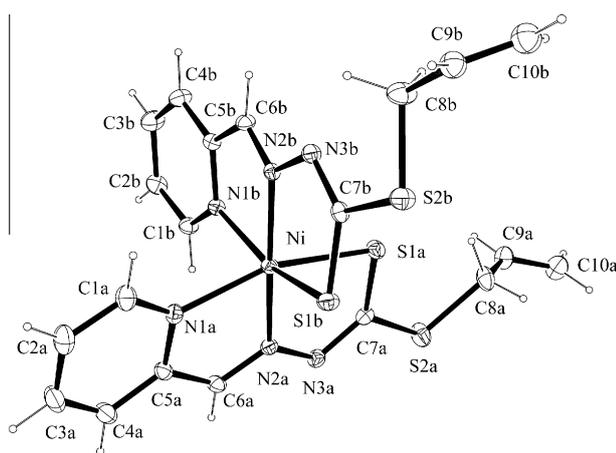


Fig. 3. ORTEP drawing of **3** with atom numbering. Thermal ellipsoids are drawn at 30% probability level. Only one position is shown for the disordered S-allyl tail.

Table 2
Selected bond lengths (Å) and bond angles (°) for **1**, **2** and **3**, with esd's in parentheses.

Compound	1	2	3
M–N1	2.260(4), 2.285(3)	1.954(4), 1.965(4), 1.952(4), 1.961(4)	2.114(3), 2.121(2)
M–N2	2.202(3), 2.205(3)	1.883(4), 1.878(4), 1.872(4), 1.872(4)	2.004(2), 2.009(2)
M–S1	2.523(2), 2.524(2)	2.224(2), 2.234(1), 2.220(2), 2.215(2)	2.388(1), 2.424(1)
C7–S1	1.693(4), 1.712(4)	1.729(5), 1.721(5), 1.677(7), 1.719(6)	1.703(3), 1.716(3)
C7–S2	1.755(4), 1.735(4)	1.733(6), 1.744(5), 1.746(6), 1.731(5)	1.764(3), 1.750(3)
C7–N3	1.304(5), 1.302(5)	1.313(6), 1.305(6), 1.323(7), 1.307(6)	1.321(4), 1.311(3)
C6–N2	1.271(5), 1.275(5)	1.269(6), 1.285(6), 1.263(7), 1.295(6)	1.288(4), 1.286(3)
N2a–M–N2b	167.8(1)	178.4(2), 179.0(2)	170.4(1)
S1–M–N1	148.5(1), 145.8(1)	168.0(1), 167.8(1), 169.1(1), 169.5(1)	160.37(7), 159.10(6)

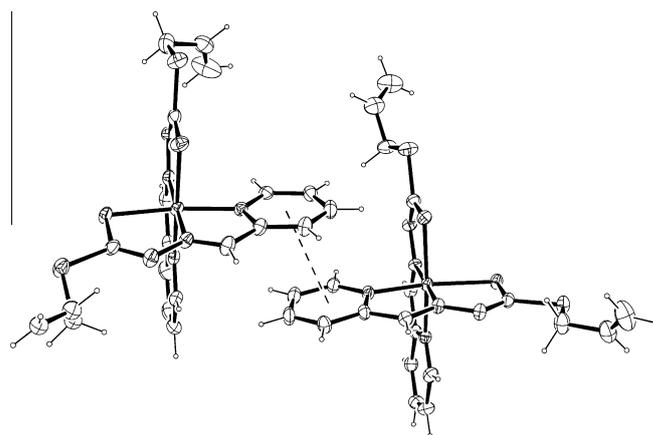


Fig. 4. The two crystallographically independent complex molecules of **2**. The dashed distance between the centroids of the two pyridyl rings is 3.656(8) Å.

squares plane is 0.191(2) Å for S1b atom in **1**. Each ligand acts as tridentate through nitrogen atoms of pyridine (N1) and imine (N2) and through the thioenolate S atom (S1). Two ligand units, placed approximately perpendicular to each other, are coordinated to the metal, giving rise to mononuclear octahedral complexes: the dihedral angles between the least-squares planes of the two coordinated ligands are 88.63(8)° in **1**, 86.38(5)° and 85.54(5)° in **2** and 89.39(6)° in **3**. Each metal atom is at the center of a distorted octahedron whose vertices are occupied by two imino N atoms in *trans* configuration with respect to each other, two pyridine N atoms and two thiolate S atoms in *cis* (or *facial*) configuration. The distortion of the octahedral geometry is mainly due to the bond angles S1a–M–N1a and S1b–M–N1b which differ from the ideal value of 180° by more than 20°; the distortion is more pronounced in the Mn(II) complex (see Table 2). The average bite angle of the five-membered chelate rings is 91.6° for **1**, 90.2° for **2** and 90.6° for **3**. The bond lengths from the metal to the coordinated atoms are systematically longer in **1** as compared with **3**; this is related to the ionic radius of Mn(II), which is the largest among bivalent cations of the first transition row and with the fact that for Mn(II), which is a d^5 ion, no stabilization is gained in a high-spin octahedral ligand field [39]. In complex **2** the crystallographic analysis clearly shows the presence in the unit cell of a nitrate ion and a water molecule for each independent molecule, so the oxidation state of the metal is +3; actually, metal to ligand bond lengths in complex **2** are systematically shorter than **1** and **3**, and this is consistent with the higher oxidation state of cobalt. The two independent complex molecules of **2** are arranged in such a way that the planes of the pyridyl rings (C1, C2, C3, C4, N1) are parallel to each other and in close contact (the distance between the centroids of the two rings is 3.656(8) Å), Fig. 4. That arrangement of the molecules in the independent unit, gives rise to a crystal packing containing parallel displaced and perpendicular T-shaped (i.e. face-to-edge) contacts [40] between the pyridyl rings, Fig. 5.

3.3. DFT calculations

DFT optimized geometries of thione (I) and thiol (II) tautomers of HL are shown in Fig. 6. Some structural parameters are presented in Table 3. DFT calculations indicate that the thione form is more stable than the thiol by 14.65 kcal/mol. Using solvent effects (PMC model), the energy difference slightly decreases to 14.24 kcal/mol (thione form still more stable), but this is still too high to allow a significant population of the thiol tautomer at room temperature to be formed. These results are consistent with the spectroscopic data discussed above, indicating the thione tautomer

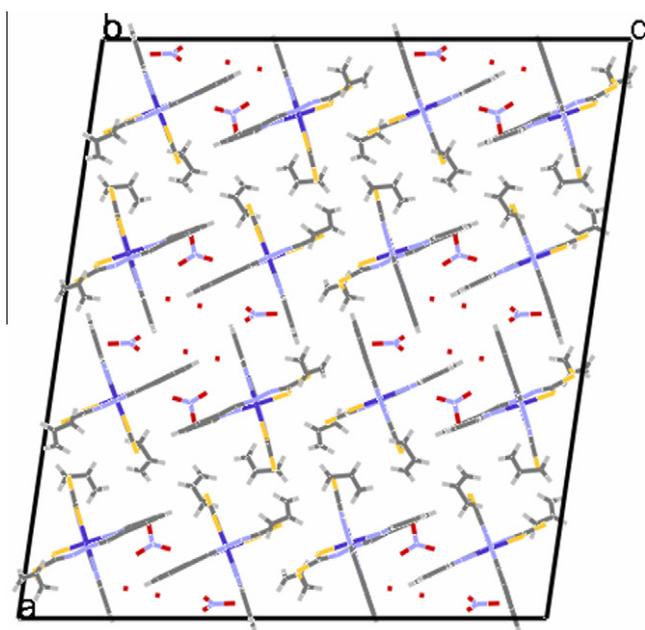


Fig. 5. Crystal packing of **2** viewed down *b*.

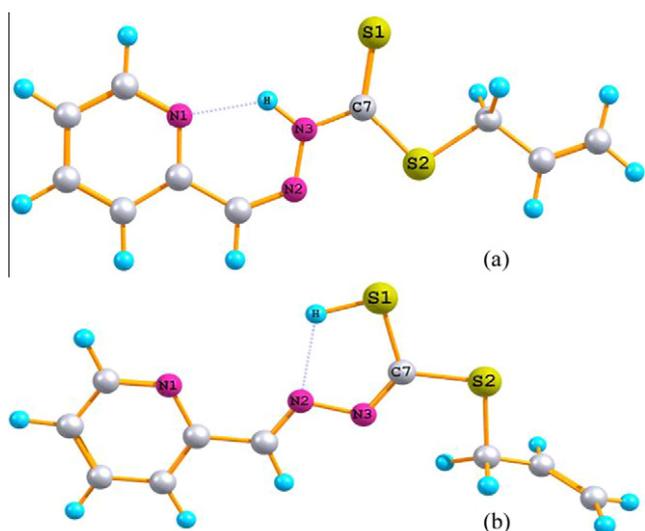


Fig. 6. Optimized structures of the HL ligand: (a) thione, (b) thiol.

as the species present both in solution and in the crystal phase. The theoretical analysis can also help to explain why the thione form is more stable than the thiol. In fact, as it is clearly shown in Fig. 4a, a strong intramolecular H bonding is present in the thione tautomer between N–H donor and pyridine N acceptor with *Z* configuration of C=N bond (N–H = 1.026 Å, H...N = 1.937, N...N = 2.719 Å, N–H...N = 130.69°), giving rise to a six membered ring. In the case of the thiol tautomer, Fig. 4b, the interaction is between S–H donor and imino N acceptor (five membered ring, S–H = 1.360 Å, H...N = 2.082 Å, N...S = 2.917 Å, S–H...N = 114.20°) but that is far less energetically favored. The intramolecular H bonding is probably responsible for the strong downfield chemical shift of the N–H proton observed in the ¹H NMR spectrum (δ 14.55). After deprotonation, several structural parameters of the ligand do change in the anionic form of the ligand (L[−]), Table 3. In this case, conjugation is established through the whole ligand but the allylic fragment.

Table 3

Selected B3LYP calculated geometry parameters (Å, °) of the thione and thiol tautomers of HL, of the thiolate anion (L[−]) and of MnL₂ and NiL₂ complexes.

	Ligand			Complexes			
	Thione	Thiol	L [−]	Calculated		Experimental	
				Mn	Ni	Mn	Ni
M–S1	–	–	–	2.579	2.480	2.523(2)	2.388(1)
M–N1	–	–	–	2.338	2.174	2.285(3)	2.113(2)
M–N2	–	–	–	2.276	2.061	2.203(4)	2.004(3)
S1–H	2.769	1.360	–	–	–	–	–
N3–H	1.027	2.585	–	–	–	–	–
N2–H	2.054	2.082	–	–	–	–	–
C7–S1	1.664	1.780	1.692	1.718	1.712	1.713(5)	1.703(4)
C7–S2	1.774	1.764	1.877	1.770	1.777	1.736(5)	1.765(4)
C7–N3	1.366	1.291	1.332	1.325	1.332	1.301(6)	1.321(4)
N2–N3	1.347	1.379	1.346	1.352	1.345	1.377(4)	1.381(4)
C8–S2	1.846	1.853	1.842	1.779	1.845	1.819(6)	1.813(3)
S1–C7–S2	126.89	113.02	122.55	111.9(3)	122.92	111.9(3)	121.8(2)
N1–N2–N3	66.21	173.99	70.75	0.04	2.39	177.8(3)	176.1(2)
N2–N3–C7–S1	179.98	0.17	179.69	0.71	−0.28	3.9(6)	−1.7(4)
S1a–M–N2b	–	–	–	74.9	99.2	97.01(9)	93.16(8)
N2a–M–N2b	–	–	–	154.1	178.2	167.8(1)	170.4(1)

Table 4

The natural charges for selected atoms of the free L[−] ligand and its Mn(II) and Ni(II) complexes.

Atom	Natural charge		
	L [−]	MnL ₂	NiL ₂
M	–	1.38	1.19
S1	−0.29	−0.31	−0.23
S2	0.16	0.30	0.30
N1	−0.43	−0.56	−0.54
N2	−0.26	−0.36	−0.32
N3	−0.38	−0.41	−0.40
C1	0.066	0.10	0.099
C2	−0.28	−0.24	−0.25
C3	−0.19	−0.14	−0.14
C4	−0.23	−0.21	−0.22
C5	0.16	0.18	0.18
C6	−0.011	0.058	0.027
C7	−0.055	−0.079	−0.078

Structural parameters for DFT optimized geometries of Mn(II) and Ni(II) complexes are reported in Table 3; the calculated structural parameters are in good agreement with the X-ray experimental results.

The natural charges on the atoms of the complexes and of free L[−] ligand have been calculated by the (NBO) analysis and are gathered in Table 4. The negative charge of L[−] ligand is mainly localized on N1, N3 and S1 atoms, as expected on the basis of the resonance formulae of L[−]. Upon coordination of S1 to the metal center, the electron cloud of the C7–S1 bond is displaced towards the S1 atom. Electron deficiency of C7 is partially compensated by electron displacement from the C7–S2 bond. Hence, the positive charge on the S2 atom is higher in the complex than in the L[−] ligand (Table 4).

4. Conclusion

A new *S*-allyl dithiocarbazate Schiff base (*S*-allyl-3-(2-pyridylmethylene)dithiocarbazate) and its Mn(II), Co(III) and Ni(II) complexes were prepared. The complexes are soluble in several common organic solvents (DMF, DMSO, methanol, ethanol and acetonitrile). Based on the elemental analysis and spectroscopic studies of the ligand and its complexes, it can be concluded that the ligand is coordinated to the metal in a tridentate NNS donor fashion through sulfur, pyridine nitrogen and azomethine nitrogen.

This is confirmed by the X-ray molecular structures, indicating that complexes are bis-chelate, with distorted octahedral geometry. Accurate DFT calculations on the neutral ligand indicate that the thione tautomeric form is the most stable, because of a strong intramolecular H bonding.

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Appendix A. Supplementary material

CCDC Nos. 771934–771936 for **3**, **1** and **2**, respectively, contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif. Calculated HOMO and LUMO frontier orbitals of the Mn(II) and Ni(II) complexes are given as Supplementary publication. Supplementary data associated with this article can be found, in the online version, at [doi:10.1016/j.ica.2011.02.090](https://doi.org/10.1016/j.ica.2011.02.090).

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