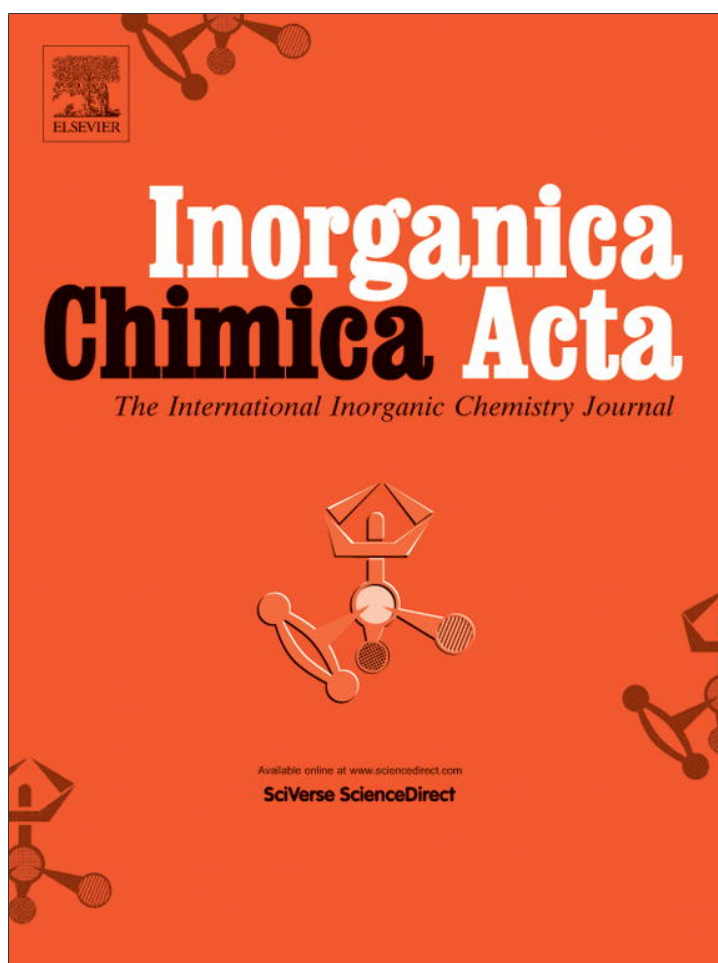


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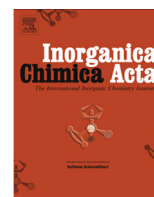
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Ring to open-chain transformation induced by selective metal coordination in a new dithiocarbazate ligand


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ABSTRACT

By unsymmetrical derivatization of acetylacetonone with S-ethyl-dithiocarbazide, a new tetradentate chelate ligand (N, N, S, S) has been prepared and studied. The compound can exist in two isomeric forms: an open tetradentate chelating form and a cyclic dihydropyrazole form. The cyclic form is obtained in the solid state and is the only one detected even in solution. However, in the presence of metal ions, a competition between intramolecular cyclization and metal complexation of the open form is active, and monochelate square planar complexes can be obtained through transformation of the cyclized into the open ligand form. We have proved this with metal ions prone to square planar coordination such as Ni(II) and Pd(II). On the other hand, with VO(II), Pb(II), UO₂(II), La(III), Ce(III), no complex was obtained and the cyclized form was recovered from the reaction mixture. This indicates some selectivity of the ligand towards specific metal ions.

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1. Introduction

Dithiocarbazate compounds can be obtained by reaction of dithiocarbazides with aldehydes or ketones. The presence of nitrogen and sulfur atoms as, respectively, medium and low crystal-field donors (hard–soft ligands), gives dithiocarbazates good ability to coordinate metal ions, yielding metal complexes with interesting structural and electronic properties. These compounds generally behave as bidentate (N,S) ligands forming five-membered chelate rings [1], but condensation with aldehydes or ketones having donor atoms such as nitrogen or oxygen in suitable position can lead to tridentate ligands [2] forming neutral and cationic complexes with different structural properties.

Dithiocarbazates and related metal complexes are well known because of their applications in biology and medicine. Bio-applications of metal-dithiocarbazate complexes include antibacterial (Gram-positive and Gram-negative) [3], antifungal [4], anticancer (SK-N-MC neuroepithelioma) [5], DNA cleavage activity [6], anti-hypertensive and antidepressant properties [1b]. Recently, dithiocarbazate complexes have found applications also in heterogeneous catalysis, and have been used in some catalytic reactions such as selective oxidation of thiols and alcohols [6] and Heck and Sonogashira cross-coupling reactions [7]. Applications of dithiocarbaz-

ato complexes in material science as nano-materials [6], solar cell components [8] and nonlinear optical (NLO) materials [9] have also been reported.

As a prosecution of our studies on such type of ligands and related metal complexes [10], we were interested in developing dithiocarbazate compounds having new ligand features. In particular, we were interested in developing tetradentate dithiocarbazate ligands in order to get monochelate complexes in square planar geometry. On these grounds, we have planned the synthesis of the new ligand shown in the Scheme 1, hereafter compound **1**, through derivatization of acetylacetonone with dithiocarbazate units, exploiting the reaction of carbonyl groups with amino function of S-ethyl-dithiocarbazide.

In comparison with bis(dithiocarbazate) ligands obtained by symmetric derivatization of β -diketones [11,12], for the less symmetric ligand **1**, containing one dithiocarbazate group and one dithiomethylidenehydrazono group, the formation of stable neutral monochelate complexes with bivalent metals should be favoured. In this paper we report on the noteworthy structural features of the free ligand and of its metal complexes.

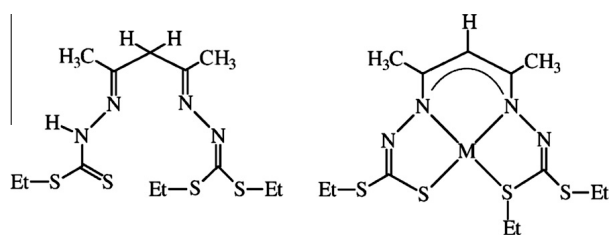
2. Experimental

2.1. Materials and methods

All reagents were analytical grade and were used without further purification. All experiments were carried out in air. IR spectra

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Scheme 1. Chemical diagrams of the ligand (left) and complexes (right).

were recorded on a FT-IR 8400-SHIMADZU spectrophotometer using KBr pellets, in the 400–4000 cm^{-1} . Elemental analyses were carried out with a Thermo Finnigan Flash Elemental Analyzer 1112EA. ^1H NMR and ^{13}C NMR spectra were obtained at 25 $^\circ\text{C}$ with a Bruker BRX 250 AVANCE spectrometer. The molar conductance of $1.0 \cdot 10^{-3}$ M solutions of the metal complexes in DMF were measured at 25 $^\circ\text{C}$ using a Metrohm 712. Electronic absorption spectra (DMF solution) were recorded with a SHIMADZU model 2550 UV-Vis spectrophotometer in the 240–900 nm region. An Electrothermal digital melting point apparatus was used to determine the melting points.

2.2. Ethyl 5-(2-(bis(ethylthio)methylidene)hydrazino)-3,5-dimethyl-2-pyrazoline-1-carbodithioate (**1**)

S-ethyl dithiocarbazine was synthesized by dropwise addition of CS_2 (0.21 mL, 3 mmol) to a solution of hydrazine hydrate (0.15 g, 3 mmol) in 20 mL ethanol at ca. 5 $^\circ\text{C}$, in the presence of KOH (0.18 g, 153 mmol) in 1 h. Ethyl bromide (0.33 g, 3 mmol) was added to the above mixture with continuous stirring. Acetylacetone (0.12 g, 1.2 mmol) diluted in 10 mL ethanol was mixed with the solution. The mixture was heated for 30 min at 40 $^\circ\text{C}$. The crystalline white product was separated by filtration, washed with cold ethanol and dried in vacuo over silica gel. The product was recrystallized from warm ethanol.

White crystals. Yield: 0.21 g, 57.6%. m.p.: 108 $^\circ\text{C}$. *Anal.* Calc. for $\text{C}_{13}\text{H}_{24}\text{N}_4\text{S}_4$ (364.62 g mol^{-1}): C, 42.82; H, 6.63; N, 15.37; S, 35.18. Found: C, 42.69; H, 6.59; N, 15.26; S, 35.27%. IR (KBr), cm^{-1} : $\nu(\text{NH})$ 3175m, $\nu(\text{C}=\text{C})$ 1660w, $\delta(\text{N}-\text{H}) + \nu(\text{C}=\text{N}) + \delta(\text{C}-\text{H})$ 1609s, $[\beta(\text{NH}) + \nu(\text{CN})]$ (thioamide I) 1550m, $[\nu(\text{CN}) + \beta(\text{NH})]$ (thioamide II) 1375s, $\nu(\text{C}=\text{S})$ 1325s, $\nu(\text{C}=\text{C}) + \nu(\text{C}-\text{H})$ 1265m, $\nu(\text{N}-\text{N})$ 1035s, $[\nu(\text{C}=\text{S}) + \nu(\text{C}-\text{S})]$ (thioamide IV) 971w, $\delta(\text{C}-\text{S})$ 868w. UV-Vis (DMF), λ_{max} , nm ($\log \epsilon$, $\text{L mol}^{-1} \text{cm}^{-1}$): 278 (4.62), 302 (4.69), 350 (3.57)sh. ^1H NMR (250 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ = 7.88 (s, 1H, N^2H ; exchanges with D_2O), 3.62 (d, 1H, C^8H), 2.95–3.11 (m, 3H, C^{10}H_3), 2.81–2.92 (m, 3H, C^7H_3), 2.67–2.78 (m, 1H, C^8H), 2.05 (d, 6H, C^{12}H_2 , C^5H_2 , C^2H_2), 1.25 (m, 9H, C^1H_3 , C^4H_3 , C^{13}H_3). ^{13}C NMR (62.90 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ = 13.45 (C^{13}), 14.47 (C^4), 15.45 (C^1), 16.16 (C^7), 23.83 (C^{10}), 26.76 (C^5), 27.31 (C^2), 28.38 (C^{12}), 50.66 (C^8), 86.39 (C^6), 142.37 (C^9), 157.74 (C^3), 190.00 (C^{11}).

2.3. General method of synthesis of the complexes

To a solution of **1** (1 mmol) in 10 mL warm ethanol was added a solution (10 mL) of the appropriate salt (PdCl_2 and $\text{Ni}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$) (1 mmol) in the same solvent (10 mL); the mixture was heated at reflux under magnetic stirring for 1 h at 90 $^\circ\text{C}$ on a water bath. The resulting solution was left at room temperature and after 3–4 days, by slow evaporation, it yielded suitable crystals of the complexes which were filtered off, washed with ethanol and dried in a desiccator over silica gel. The above method was used with some other metal salts (VOSO_4 , $\text{Pb}(\text{OAc})_2 \cdot 3\text{H}_2\text{O}$, $\text{UO}_2(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$, $\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, $\text{Ce}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$). All the reactions led to pale yel-

low solutions from which, by slow evaporation at room temperature, white crystals of **1** were obtained.

2.3.1. Ethyl 2-(3-(2-(bis(ethylthio)methylidene)hydrazono)methylbutylidene)hydrazinecarbo-dithioato-nickel(II) (**2**)

Green crystals. Yield: 0.19 g, 46%. m.p.: 102 $^\circ\text{C}$. Molar conductivity ($1.0 \cdot 10^{-3}$ M; DMF): $29 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. *Anal.* Calc. for $\text{C}_{13}\text{H}_{22}\text{N}_4\text{NiS}_4$ (421.30 g mol^{-1}): C, 37.06; H, 5.26; N, 13.30; S, 30.44. Found: C, 36.66; H, 5.17; N, 13.05; S, 30.97%. IR (KBr), cm^{-1} : $\nu(\text{C}=\text{C})$ 1656w, $\delta(\text{N}-\text{H}) + \nu(\text{C}=\text{N}) + \delta(\text{C}-\text{H})$ 1610s, $[\beta(\text{NH}) + \nu(\text{CN})]$ (thioamide I) 1537m, $[\nu(\text{CN}) + \beta(\text{NH})]$ (thioamide II) 1392s, $\nu(\text{CSS})$ 1198w, $\nu(\text{C}=\text{C}) + \nu(\text{C}-\text{H})$ 1252m, $\nu(\text{N}-\text{N})$ 1026s, $[\nu(\text{C}=\text{S}) + \nu(\text{C}-\text{S})]$ (thioamide IV) 974w, $\delta(\text{C}-\text{S})$ 903w. UV-Vis (DMF), λ_{max} , nm ($\log \epsilon$, $\text{L mol}^{-1} \text{cm}^{-1}$): 250 (4.61), 330 (3.78), 450 (4.02), 582 (2.44). ^1H NMR (250 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ = 5.13 (s, 1H, C^8H), 3.10 (m, 6H, C^2H_2 , C^5H_2 , C^{12}H_2), 2.38–2.44 (s, 6H, C^7H_3 , C^{10}H_3), 1.43 (m, 9H, C^1H_3 , C^4H_3 , C^{13}H_3). ^{13}C NMR (62.90 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ = 14.35 (C^5), 14.66 (C^4), 14.72 (C^{13}), 22.53 (C^1), 22.80 (C^7), 29.80 (C^{10}), 29.94 (C^{12}), 36.96 (C^2), 96.95 (C^8), 136.51 (C^6), 155.40 (C^3), 157.79 (C^{11}), 158.89 (C^9).

2.3.2. Ethyl 2-(3-(2-(bis(ethylthio)methylidene)hydrazono)methylbutylidene)hydrazinecarbo-dithioato-palladium(II) (**3**)

Red crystals. Yield: 0.24 g, 53%. m.p.: 114 $^\circ\text{C}$. Molar conductivity ($1.0 \cdot 10^{-3}$ M; DMF): $27 \Omega^{-1} \text{cm}^2 \text{mol}^{-1}$. *Anal.* Calc. for $\text{C}_{13}\text{H}_{22}\text{N}_4\text{PdS}_4$ (469.03 g mol^{-1}): C, 33.29; H, 4.73; N, 11.95; S, 27.35. Found: C, 33.15; H, 4.71; N, 11.89; S, 27.16%. IR (KBr), cm^{-1} : $\nu(\text{C}=\text{C})$ 1658w, $\delta(\text{N}-\text{H}) + \nu(\text{C}=\text{N}) + \delta(\text{C}-\text{H})$ 1612s, $[\beta(\text{NH}) + \nu(\text{CN})]$ (thioamide I) 1530m, $[\nu(\text{CN}) + \beta(\text{NH})]$ (thioamide II) 1395s, $\nu(\text{C}=\text{C}) + \nu(\text{C}-\text{H})$ 1257m, $\nu(\text{N}-\text{N})$ 1029s, $[\nu(\text{C}=\text{S}) + \nu(\text{C}-\text{S})]$ (thioamide IV) 972w, $\delta(\text{C}-\text{S})$ 902w. UV-Vis (DMF), λ_{max} , nm ($\log \epsilon$, $\text{L mol}^{-1} \text{cm}^{-1}$): 252 (4.37), 330 (3.78), 448 (4.02). ^1H NMR (250 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ = 5.05 (s, 1H, C^8H), 2.85–3.31 (m, 6H, C^2H_2 , C^5H_2 , C^{12}H_2), 2.66–2.27 (m, 6H, C^7H_3 , C^{10}H_3), 1.30 (m, 9H, C^1H_3 , C^4H_3 , C^{13}H_3). ^{13}C NMR (62.90 MHz, CDCl_3 , 25 $^\circ\text{C}$): δ = 14.47 (C^5), 14.60 (C^4), 15.29 (C^{13}), 21.68 (C^1), 22.09 (C^7), 30.40 (C^{10}), 30.62 (C^{12}), 36.62 (C^2), 96.10 (C^8), 134.30 (C^6), 152.44 (C^3), 154.68 (C^{11}), 157.77 (C^9).

2.4. X-ray analysis

All data for crystal structure determinations were measured on a Bruker-Nonius KappaCCD diffractometer equipped with Oxford Cryostream 700 apparatus, using graphite monochromated $\text{MoK}\alpha$ radiation (0.71073 Å). Reduction of data and semiempirical absorption correction were done using *SADABS* program [13]. The structures were solved by direct methods (*SIR97* program [14]) and refined by the full-matrix least-squares method on F^2 using *SHELXL-97* program [15] with the aid of the program *WINGX* [16]. H atoms bonded to C were generated stereochemically, that bonded to N in **1** was found in a difference Fourier map; all H atoms were refined by the riding model. Crystal and refinement data are summarized in Table 1.

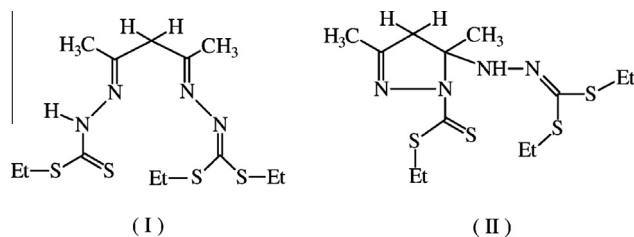
The analysis of the crystal packing was performed using the program *MERCURY* [17], which was also used for the calculation of the X-ray powder diffraction patterns.

2.5. Computational details

An initial conformational analysis was carried out for both the linear and the cyclic forms of the ligand (Scheme 2). This is a highly advisable procedure because important molecular properties such as charge distribution can significantly depend on conformations [18]. The MMFF94 force field implemented in Spartan [19] was used. Equilibrium geometries of all the lowest energy conformers were then refined by full geometry optimization at DFT level of computation. We adopted the B3LYP functional, which is known to give excellent relative energies and geometries, except for the

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

	1	2	3
Empirical formula	C ₁₃ H ₂₄ N ₄ S ₄	C ₁₃ H ₂₂ N ₄ S ₄ Ni	C ₁₃ H ₂₂ N ₄ S ₄ Pd
<i>M</i>	364.62	421.3	469.03
System	triclinic	triclinic	triclinic
Space group	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$	<i>P</i> $\bar{1}$
<i>a</i> (Å)	9.818(3)	9.226(1)	9.1870(9)
<i>b</i> (Å)	9.927(1)	10.8870(9)	10.6440(9)
<i>c</i> (Å)	10.167(2)	10.889(1)	11.1770(5)
α (°)	95.33(1)	101.860(8)	101.178(5)
β (°)	107.36(2)	103.053(8)	103.003(4)
γ (°)	91.174(15)	112.758(7)	112.164(7)
<i>V</i> (Å ³)	940.5(3)	928.8(2)	938.0(1)
<i>Z</i>	2	2	2
<i>T</i> (K)	173	293	293
ρ_{calc} (g cm ⁻³)	1.288	1.506	1.660
Reflections collected	11397	11137	11780
Unique reflections (<i>R</i> _{int})	4248 (0.0452)	4222(0.0309)	4275 (0.0371)
<i>R</i> 1 [<i>I</i> > 2 σ (<i>I</i>)]	0.0453	0.0317	0.0286
<i>wR</i> 2 [all data]	0.1272	0.0672	0.0699
Maximum peak/hole (e Å ⁻³)	0.459/−0.491	0.262/−0.251	0.360/−0.553



Scheme 2. The two isomeric forms of the free ligand.

cases where the self-interaction error prevents its use [20]. The 6-31+G** was adopted throughout.

The geometries of the Ni(II) and VO(II) complexes were optimized by DFT computations. Effects due to the polarization of the solvent (ethanol) were taken into account by using the polarizable continuum model (PCM) [21]. UV–Vis absorption spectra were computed by using time dependent DFT (TDDFT) computations; PCM standard parameters for DMF were used. The unrestricted formalism was used for electron unpaired species. DFT and TDDFT calculations were carried out by using the GAUSSIAN09 package [22].

3. Results and discussion

3.1. Structure of the ligand

It was early suggested [12] that reaction of β -diketones with hydrazine derivatives can lead to the formation of 2-pyrazolinic cyclic structures. Our results give a direct proof of that. In fact, the X-ray single crystal analysis revealed that the molecular structure of the ligand in the solid state, shown in Fig. 1, is quite different from that reported in Scheme 1. Indeed, an intramolecular cyclization has taken place with formation of a 4,5-dihydropyrazole ring unit.

Actually, the transformation of the open form into the cyclic one is an isomerization process since the two species have the same chemical formula, Scheme 2.

In the solid state only the cyclic isomer is obtained. The formation of the cyclic isomer should be energetically favoured, as the form (II) contains one σ bond more and one π bond less than (I). Theoretical calculations support this picture. The calculated energy difference between the most stable conformers of the two forms is 10.3 kcal/mol in the gas-phase, and 7.2 kcal/mol in ethanol solu-

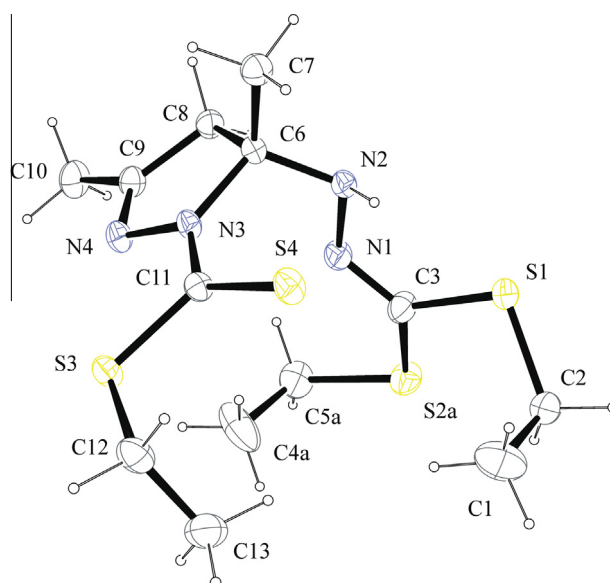


Fig. 1. Ortep diagram of **1** in the solid state. Thermal ellipsoids are drawn at 30% probability level. Only one orientation of the split S2–C5–C4 tail is shown for clarity.

tion, with the cyclic form (II) being always more stable than the open one. Yet, the formation of the cycle is favoured also entropically, since the intramolecular process leads to a five membered ring. So it is expected that in solution the cyclic form (II) is predominant. The computed room temperature equilibrium constants for the process (II) \leftrightarrow (I), including vibrational zero point energies, are $1.7 \cdot 10^{-7}$ in the gas phase and $6.8 \cdot 10^{-5}$ in ethanol solution.

NMR data of the ligand, reported in the Experimental Part and in the Supplementary Material (SM), confirm that hypothesis, as they indicate that only one form, in particular the most stable (II), is detected both in polar (D6-DMSO) and in less polar solvents (CDCl₃). Of particular relevance for drawing that conclusion are the ¹³C NMR resonance signals of atoms C6 (δ = 86.39) and C9 (δ = 142.37) and, to a lesser extent, of C7 (δ = 16.16) and C10 (δ = 23.83). The significantly different chemical shifts of those atoms are indicative of a different chemical environment which is in agreement with the cyclic form (II) and not with the open form (I).

3.2. Structure and packing of the complexes

Although some examples of metal complexes with pyrazole or dihydropyrazole based ligands are reported in literature [23], it is evident that in the form (II) the compound is expected to have a far lesser chelating ability than (I). We have tried to obtain complexes with a variety of metal ions, such as Ni(II), Pd(II), Pb(II), VO(II), UO₂(II), La(III), Ce(III), and only in the first two cases a metal complex has been actually obtained; in the other cases the unreacted compound in the form (II) was obtained after recrystallization from the reaction mixture. The crystal structures of the nickel and palladium complexes, hereafter **2** and **3**, are isomorphous. The X-ray structure of **3** is shown in Fig. 2 as a representative example, while that of **2** is given in the SM. It is evident that the two complexes are obtained from the open form (I) of the ligand. So, metal chelation provides a tool for opening the cyclic (II) into the ligand form (I); the formation of the complex shows some selectivity, taking place only for two of the tested metal ions. Actually, examples of tautomeric switching upon metal coordination, though not frequent, are described in literature [24], but to our knowledge, this is the first example in which the non-coordinating form is a highly stable heterocyclic ring. Upon coordination, the ligand, form (I), loses the amido hydrogen and one methylene

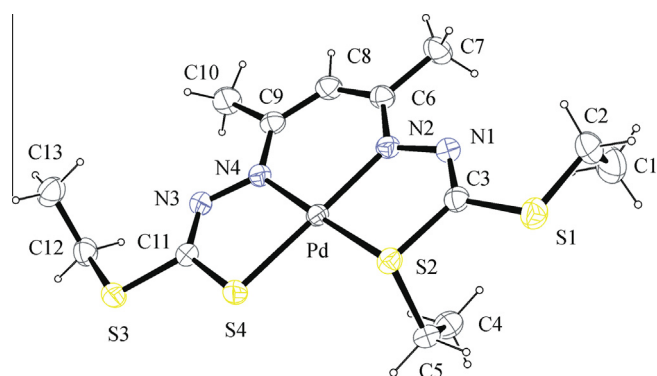


Fig. 2. X-ray molecular structure of **3**. Thermal ellipsoids are drawn at 30% probability level.

hydrogen, taken up by the metal counterions, assuming a π -conjugated planar structure with two negative charges; the complexes are therefore neutral as also confirmed by conductance measurements. This is a significant difference with respect to similar complexes early proposed or even structurally characterized in literature, but based on symmetric bis(dithiocarbazate) ligands [11,12]; in those cases, in fact, the complexes bear acidic protons and are obtained either in anionic or in dipolar form, and they can be easily oxidized. Also the synthetic procedures are different. In fact, they were prepared by reaction of metal-diketonate complexes with large excess of S-alkylhydrazinocarbothioate [11,12], while we have reacted the free ligand with the metal salt in mild conditions (*vide supra*).

The nickel and palladium complexes have a very similar geometry, Table 2. The coordination around the metal is square planar with the ligand acting as tetradentate chelate. The metal and the four atoms to which it is bonded are coplanar within 0.0032(6) Å in **2** and 0.0039(7) Å in **3**. The metal to sulfur distances are, on average, 0.4 Å longer than the metal to nitrogen distances and bond lengths involving palladium are, on average, 0.12 Å longer than the corresponding distances involving nickel.

The four bond angles around the metal are all close to the expected value of 90°. In particular, the angles corresponding to the two five-membered chelate rings are close to each other and smaller than the angle corresponding to the six-membered chelate ring. The π -conjugation along the chain N2, C6, C8, C9, N4 is clearly evidenced by the pattern of the bond lengths. In particular, the bonds C6–N2 and C9–N4 are significantly longer than double bonds and the bond lengths C6–C8 and C8–C9 have values typical of benzene rings. Inspection of the bond lengths also indicates that in both

complexes the dithiocarbazate moiety is in the thiolato form. This is evidenced by the bond lengths C11–N3 which take values typical of a double bond. In summary, the X-ray analysis indicates that the solid state structure of complexes **2** and **3** corresponds to the chemical diagram shown in Scheme 1. The solution NMR data support the results of the X-ray analysis. In particular, in the two complexes, the ^{13}C NMR resonance peaks of C6 ($\delta = 136.51$ for **2**, $\delta = 134.30$ for **3**) and C9 ($\delta = 158.89$ for **2**, $\delta = 157.77$ for **3**) and of C7 ($\delta = 22.80$ for **2**, $\delta = 22.09$ for **3**) and C10 ($\delta = 29.80$ for **2**, $\delta = 30.40$ for **3**) are much more similar to each other than in the free ligand (*vide supra*) indicating a much more similar electronic environment.

3.3. Electronic spectra

The electronic spectrum of the ligand (see Experimental part and SM) exhibits $L \rightarrow L^*$ bands at 278 nm and 302 nm in DMF solution. These can be ascribed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions of the thioamide portion of the dithiocarbazate moiety. The metal complexes (see Experimental Part and SM) display a blue shift in the $\pi \rightarrow \pi^*$ band and a red shift in the $n \rightarrow \pi^*$ transition as compared with the free ligand. The strong band at ca. 450 nm is assignable to $d \rightarrow \pi^*$ metal-to-ligand charge transfer transition. The presence of this band is a strong evidence of sulfur coordinated to the metal center. The square planar Ni-complex with d^8 configuration shows just the low energy $^1A_1 \rightarrow ^1E$ spin-allowed transition at 592 nm, the other d-d bands are covered by the CT transition band. Compound **3** does not show any absorption peak in the visible region.

3.4. Theoretical analysis

The selectivity of the ligand toward complexation with specific metal cations has also been investigated by theoretical computations in the two selected cases of Ni(II) and VO(II), by comparing the stability of the two complexes with respect to unassociated Ni^{2+} , VO^{2+} , and L^{2-} in ethanol solution. B3LYP computations predict association energy of 238 kcal/mol for the Ni complex, and of only 188 kcal/mol for the VO^{2+} one. The high energy difference can be traced back to the significantly lower energy of the Kohn–Sham LUMO level of Ni^{2+} with respect to that of VO^{2+} , thus indicating that σ donation is much more effective in the former than in the latter. The analysis of the atomic charges, carried out according to the atomic polar tensor procedure [25], confirms the above picture: the Ni ATP charge is nearly zero, whereas the vanadyl group still holds a positive charge amounting to +0.7 atomic units.

The computed UV–Vis spectrum of the free ligand in DMF is reported in Table 3.

Three strong absorptions are predicted in the region 290–270 nm, in good agreement with the observed spectrum, showing an absorption maximum at 302 nm with a shoulder at 278 nm. The lowest energy strong absorption, computed at $\lambda = 289$ nm, is essentially due to a HOMO \rightarrow LUMO transition. The HOMO is mainly localized on the diethylthiomethylidenehydrazino moiety, with

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

	1	2	3
M–N2		1.867(2)	1.999(2)
M–N4		1.857(2)	1.989(2)
M–S2		2.1516(7)	2.2568(8)
M–S4		2.1554(7)	2.2656(7)
C3–N1	1.269(3)	1.271(3)	1.272(4)
N1–N2	1.399(2)	1.401(2)	1.380(3)
N2–C6	1.449(3)	1.351(3)	1.339(4)
C6–C8	1.534(3)	1.371(3)	1.373(4)
C8–C9	1.486(3)	1.390(3)	1.403(4)
C9–N4	1.277(3)	1.336(3)	1.322(4)
N3–N4	1.406(2)	1.396(3)	1.394(3)
N3–C11	1.335(3)	1.281(3)	1.275(4)
C11–S4	1.669(2)	1.733(2)	1.738(3)
N2–M–N4		95.11(8)	93.68(9)
N2–M–S2		87.64(6)	84.71(7)
N4–M–S4		88.03(6)	85.31(7)
S2–M–S4		89.22(2)	96.30(3)

Table 3
Predicted (PCM/TD-B3LYP) transitions of the free ligand in DMF.

λ (nm) ^a	Osc. Str. ^b
362	0.007
316	0.017
289	0.307
277	0.194
273	0.177
259	0.004

^a Observed λ_{max} (nm): 278, 302, 350.

^b Oscillator strength.

Table 4
Predicted (PCM/TD-B3LYP) transitions of the Ni–L complex in DMF.

λ (nm) ^{a,b}	Osc. Str. ^c
622	0.0005
590	0.0003
465	0.0019
430	0.2408
422	0.0989
294	0.1069
269	0.1329
261	0.2666

^a Observed λ_{max} (nm): 250, 330, 450, 592.

^b Only the most intense transitions have been reported in the shorter wavelength region.

^c Oscillator strength.

contributions from the lone pairs of sulfur atoms and those of the exocyclic nitrogens. The LUMO is a π^* orbital localized on the thioamide part of the thiocarbamate moiety, so that the observed band can be interpreted as an $n \rightarrow \pi^*$ transition. Computations also predict intense transitions at 277 and 273 nm. They involve essentially the HOMO-3 and the LUMO+1 orbitals, both having π character; therefore the band observed at 278 nm in the experimental spectrum can be interpreted as a $\pi \rightarrow \pi^*$ transition.

The UV–Vis spectrum of the Ni complex in DMF features two intense absorptions peaked at 315 and 450 nm; moreover in the region of longer wavelengths, a much less intense band, peaked at 592 nm, is observed (see SM). TD-B3LYP computations predict two intense transitions, falling at 294 and 430 nm, respectively, see Table 4. The transition at 294 nm does not involve contribution from the metal cation, being essentially the $n \rightarrow \pi^*$ of the free ligand, which is red-shifted in the complex, whereas the absorption at 430 nm is mainly due to a metal-to-ligand $d \rightarrow \pi^*$ transition (*vide supra*). Finally TD computations predict two very weak transitions, at 622 and 590 nm, which involve orbitals localized on the Ni atom ($d \rightarrow d^*$), corresponding to the $^1A_1 \rightarrow ^1E$ spin-allowed band observed at 592 nm.

4. Conclusion

We have synthesized a new dithiocarbamate compound, which exhibits two isomeric forms: an open form in which the compound can behave as tetradentate chelate ligand and a cyclic dihydropyrazole form. Because the cyclized form is by far more stable than the open form, both in solution and in the solid state, a high metal selectivity turns out: only if the metal complex is very stable, the cyclic form can be converted in the open form, leading to formation of the metal complex. As a matter of fact, within the metal ions that we have tested, that happened only for Ni(II) and Pd(II).

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Appendix A. Supplementary material

CCDC numbers 888354–888356 contains the supplementary crystallographic data for compounds 1–3, respectively. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.ica.2013.04.030>.

References

- [1] (a) V. Fares, A.M. Giuliani, P. Imperatori, L. Suber, F. Tarli, J. Chem. Soc., Dalton Trans. (1987) 1035; (b) K. Tampouris, S. Coco, A. Yannopoulos, S. Koinis, Polyhedron 26 (2007) 4269; (c) M.-H.E. Chan, K.A. Crouse, M.I.M. Tahir, R. Rosli, N. Umar-Tsafe, A.R. Cowley, Polyhedron 27 (2008) 1141; (d) P. Bera, C.-H. Kim, S.I. Seok, Polyhedron 27 (2008) 3433; (e) S.K.S. Hazari, J. Kopf, D. Palit, S. Rakshit, D. Rehder, Inorg. Chim. Acta 362 (2009) 1343.
- [2] (a) A. Marchi, A. Duatti, R. Rossi, L. Magon, R. Pasqualini, V. Bertolasi, V. Ferretti, G. Gilli, J. Chem. Soc., Dalton Trans. (1988) 1743; (b) M.T.H. Tarafder, A. Kasbollah, K.A. Crouse, A.M. Ali, B.M. Yamin, H.-K. Fun, Polyhedron 20 (2001) 2363; (c) D.K. Sau, R.J. Butcher, S. Chaudhuri, N. Saha, Polyhedron 23 (2004) 5; (d) M.A. Ali, A.H. Mirza, F.H. Bujang, M.H.S.A. Hamid, P.V. Bernhardt, Polyhedron 25 (2006) 3245; (e) T.B.S.A. Ravoof, K.A. Crouse, M.I.M. Tahir, A.R. Cowley, M.A. Ali, Polyhedron 26 (2007) 1159; (f) M.A. Ali, H.J.H.A. Bakar, A.H. Mirza, S.J. Smith, L.R. Gahan, P.V. Bernhardt, Polyhedron 27 (2008) 71; (g) S. Roy, T.N. Mandal, A.K. Barik, S. Gupta, R.J. Butcher, M. Nethaji, S.K. Kar, Polyhedron 27 (2008) 593.
- [3] M.X. Li, L.Z. Zhang, C.L. Chen, J.Y. Niu, B.S. Ji, J. Inorg. Biochem. 106 (2012) 117.
- [4] L.Z. Zhang, T. Ding, C.L. Chen, M.X. Li, D. Zhang, J.Y. Niu, Russ. J. Coord. Chem. 37 (2011) 356.
- [5] M.T. Basha, J.D. Chartres, N. Pantarat, M.A. Ali, A.H. Mirza, D.S. Kalinowski, D.R. Richardson, P.V. Bernhardt, Dalton Trans. 41 (2012) 6536.
- [6] H. Eshtiagh-Hosseini, T. Tabari, R. Takjoo, H. Eshghi, Synth. React. Inorg. Met.-Org., Nano-Met. Chem. 43 (2013) 264.
- [7] M. Bakherad, A. Keivanloo, S. Samangooei, Tetrahedron Lett. 53 (2012) 5773.
- [8] P. Bera, C.-H. Kim, S.I. Seok, Solid State Sci. 12 (2010) 532.
- [9] P. Bera, C.H. Kim, S. I. Seok, Inorg. Chim. Acta 362 (2009) 2603.
- [10] (a) M. Yazdanbakhsh, R. Takjoo, Struct. Chem. 29 (2008) 895; (b) M. Yazdanbakhsh, M.M. Heravi, R. Takjoo, W. Frank, Z. Anorg. Allg. Chem. 634 (2008) 972; (c) M. Azdanbakhsh, R. Takjoo, W. Frank, A.A. Kaju, J. Coord. Chem. 62 (2009) 1569; (d) R. Takjoo, R. Centore, M. Hakimi, S.A. Beyramabadi, A. Morsali, Inorg. Chim. Acta 371 (2011) 36; (e) R. Takjoo, R. Centore, L. Rhyman, P. Ramasami, J. Coord. Chem. 65 (2012) 1569; (f) R. Takjoo, R. Centore, J. Mol. Struct. 1031 (2013) 180.
- [11] J. Gabel, V. Hasemann, H. Hendriksen, E. Larsen, S. Larsen, Inorg. Chem. 18 (1979) 1088.
- [12] M.F. Iskander, L. El-Sayed, A. El-Touky, M. Tawfik, Trans. Met. Chem. 7 (1982) 135.
- [13] Bruker-Nonius (2002) SADABS, Bruker-Nonius, Delft, The Netherlands.
- [14] A. Altomare, M.C. Burla, M. Camalli, G.L. Cascarano, C. Giacovazzo, A. Guagliardi, G.G. Moliterni, G. Polidori, R. Spagna, J. Appl. Crystallogr. 32 (1999) 115.
- [15] G.M. Sheldrick, Acta Crystallogr. A 64 (2008) 112.
- [16] L.J. Farrugia, J. Appl. Crystallogr. 32 (1999) 837.
- [17] C.F. Macrae, I.J. Bruno, J.A. Chisholm, P.R. Edgington, P. McCabe, E. Pidcock, L. Rodriguez-Monge, R. Taylor, J. van de Streek, P.A. Wood, J. Appl. Crystallogr. 41 (2008) 466.
- [18] A. Capobianco, R. Centore, C. Noce, A. Peluso, Chem. Phys. 411 (2013) 11.
- [19] Spartan'04; Wavefunction, Inc., Irvine, CA, 2004.
- [20] (a) A.J. Cohen, P. Mori-Sánchez, W. Yang, Chem. Rev. 112 (2012) 289; (b) A. Capobianco, A. Esposito, T. Caruso, F. Borbone, A. Carella, R. Centore, A. Peluso, Eur. J. Org. Chem. (2012) 2980.
- [21] J. Tomasi, B. Mennucci, R. Cammi, Chem. Rev. 105 (2005) 2999.
- [22] Gaussian 09, Revision A.02, M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G.A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H.P. Hratchian, A.F. Izmaylov, J. Bloino, G. Zheng, J.L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J.A. Montgomery, Jr., J.E. Peralta, F. Ogliaro, M. Bearpark, J.J. Heyd, E. Brothers, K.N. Kudin, V.N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J.M. Millam, M. Klene, J.E. Knox, J.B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R.E. Stratmann, O. Yazyev, A.J. Austin, R. Cammi, C. Pomelli, J.W. Ochterski, R.L. Martin, K. Morokuma, V.G. Zakrzewski, G.A. Voth, P. Salvador, J.J. Dannenberg, S. Dapprich, A.D. Daniels, Ö. Farkas, J.B. Foresman, J.V. Ortiz, J. Cioslowski, D.J. Fox, GAUSSIAN Inc., Wallingford CT, 2009.
- [23] (a) M.J. Bagley, D. Nicholls, B.A. Warburton, J. Chem. Soc. A (1970) 2694; (b) T.I.A. Gerber, E. Hosten, O. Knoesen, P. Mayer, J. Coord. Chem. 60 (2007) 2369.
- [24] (a) S.J. Angyal, Aust. J. Chem. 25 (1972) 1957; (b) A.R. Todorov, M. Nieger, J. Helaja, Chem. Eur. J. 18 (2012) 7269.
- [25] J. Cioslowski, J. Am. Chem. Soc. 111 (1989) 8333.