

Short Note

A Ternary Nickel(II) Schiff Base Complex Containing Di-anionic and Neutral Forms of a Dithiocarbazate Schiff Base

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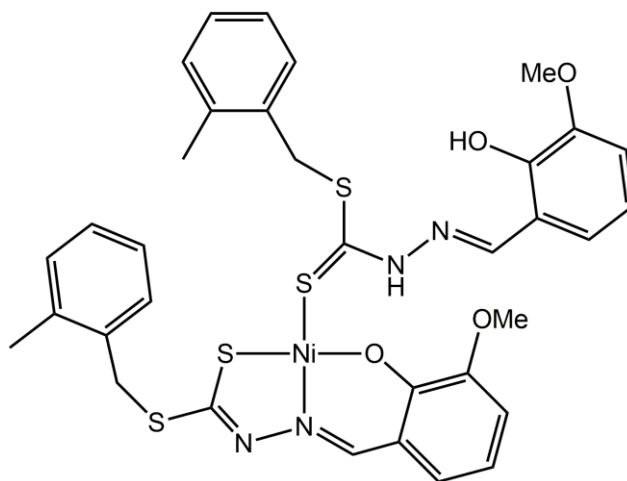
Abstract: The title Ni^{II} complex, Ni(L)(LH₂) (**1**), where LH₂ is *S*-2-methylbenzyl-β-*N*-(2-hydroxy-3-methoxybenzylmethylene) dithiocarbazate, was isolated from the reaction of Ni(acetate)₂·4H₂O and two molar equivalents of LH₂. The complex was characterized by elemental analysis, spectroscopy (IR and UV) as well as by a single-crystal X-ray structure determination. The nickel(II) center is coordinated within a *cis*-NOS₂ donor set that defines a square planar geometry. Three donor atoms, i.e., N, O, and S, are provided by a doubly deprotonated *S*-2-methylbenzyl-β-*N*-(2-hydroxy-3-methoxybenzylmethylene) dithiocarbazate ligand while the fourth donor, i.e., a thione-S, comes from the neutral form of the dithiocarbazate ligand. In the LH₂ ligand, an intramolecular hydroxy-O-H···N(imine) hydrogen bond is found. There is also an intra-ligand, charge assisted amine-N-H···O(phenoxide) hydrogen bond. A notable feature of the molecular packing is the formation of supramolecular chains sustained by π...π stacking interactions whereby the interacting rings are the five- and six-membered chelate and methoxybenzene rings. The chains are connected into a three-dimensional architecture by methyl-C-H···O(methoxy), methoxy-C-H···S(ester), and tolyl-C-H···π(tolyl) interactions.

Keywords: nickel(II); dithiocarbazate; hydrogen bonding; π(chelate)···π(chelate) interactions; X-ray crystallography

1. Introduction

S-Alkyl dithiocarbazates comprise an important member of the Schiff base class of compound. They are potential sulfur-nitrogen donor ligands for metals and have been investigated since 1971 [1,2]. *S*-Alkyl dithiocarbazates are generally formed by the condensation reaction of aldehydes or ketones with dithiocarbazate derivatives [3]. The presence of the mixed hard-soft nitrogen-sulfur donor atoms makes them multifaceted ligands capable of coordinating a metal ion through these, as well as additional donor atoms, when present [4–6]. These Schiff bases can be modified by incorporating various types of substituents to moderate/enhance their biological and pharmacological activities [7–9]. Relevant to the present study, recent investigations of the Schiff

base derived from the condensation of *S*-2-methylbenzylthiocarbamate and 2-hydroxy-3-methoxybenzaldehyde showed these molecules, when complexed to diorganotin centers, to exhibit good potency against a panel of cancer cells [10]. The bioactivities of the Schiff bases have also been reported to be enhanced by the coordination with transition metal ions such as nickel, possibly due to their reduced polarity and increased lipophilicity required for easier entry into the permeable membranes of cells and microbes [11]. In view of ongoing interest in the structures and biological activities of this class of Schiff base and their coordination complexes, the synthesis, spectroscopic characterization, and X-ray crystal structure determination of the title Ni^{II} complex, Ni(L)(LH₂) (**1**), and Scheme 1, are described; the systematic name for LH₂ is: 2-methoxy-6-[(1*E*)-{[(2-methylphenyl)methyl]sulfanyl}methanethioyl]amino]imino]methyl]phenol.



Scheme 1. Chemical diagram for Ni(L)(LH₂) (**1**).

2. Results and Discussion

The Schiff base, LH₂, was prepared by reacting *S*-2-methylbenzylthiocarbamate with *o*-vanillin [10]. The Ni^{II} complex was isolated as brown crystals in a good yield from the 1:2 reaction of nickel(II) acetate and LH₂. Complex **1** is stable at room temperature and soluble in common organic solvents such as acetonitrile, chloroform, dimethylsulfoxide (DMSO), and dimethylformamide. The room temperature molar conductance analysis of **1** in DMSO was 0.14 Ω⁻¹ cm² mol⁻¹, indicating **1** is nonelectrolytic. Complex **1** was also characterized by elemental analysis, FTIR and UV-Vis spectroscopy. LH₂ can exist as thione or thiol tautomers or as a mixture of both tautomers. In the solid state, the FTIR indicated that LH₂ was primarily in the thione tautomer form owing to the presence of a ν(NH) band at 3089 cm⁻¹ [10]. The sharp bands at 1600 cm⁻¹, assigned to ν(C=N), and at 1117 cm⁻¹ due to ν(N-N), in the spectrum of LH₂ [10] were shifted to lower frequencies at 1590 and 971 cm⁻¹, respectively, in the spectrum of **1**. This result is consistent with coordination via the azomethine nitrogen atom. The ν(CSS) splitting band found at 700 cm⁻¹ provides strong evidence for coordination by the thiolate sulfur. In the UV-Vis spectrum of **1** in the DMSO solution, three important bands were observed at 344, 438, and 614 nm, which are ascribed to π-π*, ligand-metal charge transfer, and *d-d* transitions, respectively. Definitive structure determination was afforded by an X-ray crystallographic investigation of **1**.

The molecular structure of **1** is shown in Figure 1 and comprises a square planar Ni^{II} center coordinated in a N, O, S fashion by the di-negative, tridentate ligand (L) and by the thione-S atom of the neutral LH₂ molecule. The significant elongation of the C1-S1 bond [1.7289(15) Å] compared with the C18-S3 bond [1.7039(15) Å], along with the disparity in the Ni-S1 [2.1512(4) Å] and Ni-S3 [2.2290(4)] bond lengths confirm the presence of a thiolate-S1 and thione-S3 atoms. In the same way, the reduction of the C1-N1 bond [1.294(2) Å] compared with the C18-N3 bond [1.3229(19) Å] confirms the formation of an imine-C1-N1 bond in the di-anion. Allowing for differences in

Ni-donor atom bond lengths, the deviations from the ideal square planar geometry are rather small; see the caption to Figure 1 for selected geometric data.

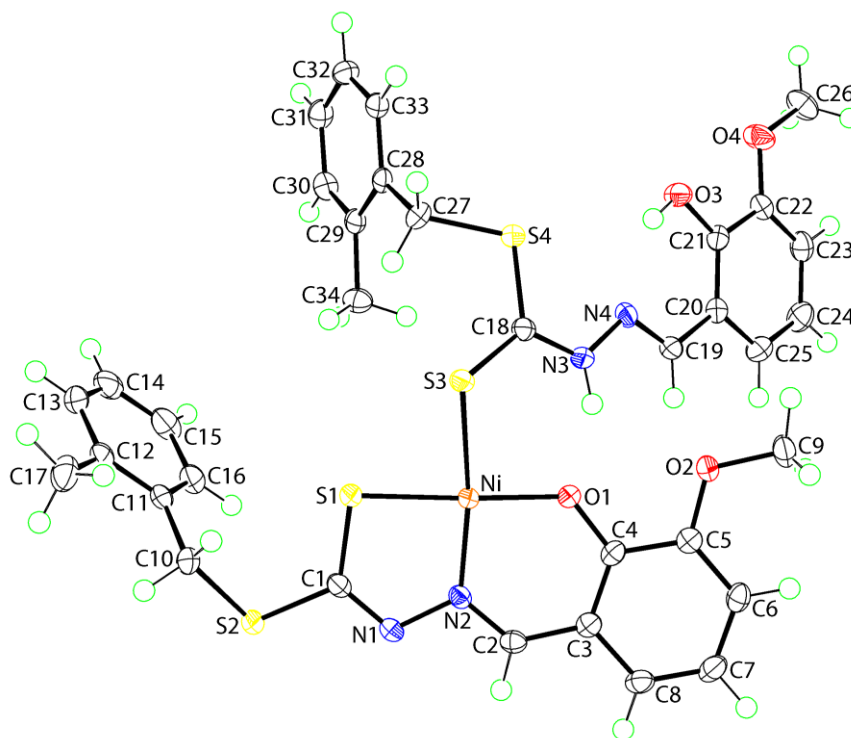


Figure 1. The molecular structure of **1** showing atom labeling and displacement ellipsoids at the 70% probability level. Selected geometric parameters: Ni-S1 = 2.1512(4) Å, Ni-S3 = 2.2290(4) Å, Ni-O1 = 1.8615(11) Å, and Ni-N2 = 1.8728(12) Å; S1-Ni-S3 = 84.523(16)°, S1-Ni-O1 = 176.63(4)°, S1-Ni-N2 = 87.40(4)°, S3-Ni-O1 = 93.99(3)°, S3-Ni-N2 = 171.02(4)°, and O1-Ni-N2 = 94.28(5)°.

The tridentate mode of coordination of L gives rise to five- and six-membered chelate rings. To a first approximation, the five-membered ring is planar with the r.m.s. deviation of the five fitted atoms, i.e., Ni, S1, N1, N2, and C1, being 0.0186 Å with maximum deviations to either side of the plane being $-0.0215(5)$ and $0.0247(7)$ Å for the Ni and N2 atoms, respectively. By contrast, the six-membered ring is less planar, having an r.m.s. deviation for the Ni, O1, N2, and C2-C4 atoms of 0.0591 Å with maximum deviations to either side of the plane being 0.0801(6) for the Ni atom and $-0.0928(8)$ for the O1 atom. The dihedral angle between the two chelate rings amounts to a relatively small $5.26(4)^\circ$. This planarity extends the C3-C8 ring which forms a dihedral angle of $5.76(5)^\circ$ with the adjacent chelate ring. In the LH₂ molecule, an intramolecular hydroxy-O3-H3o...N4(imine) hydrogen bond which closes an S(6) loop is noted [H3o...N4 = 1.95(2) Å, O3...N4 = 2.670(2) Å with angle at H3o = $144.9(19)^\circ$]. There is also an intra-ligand, charge assisted amine-N3-H3n...O1(phenoxide) hydrogen bond [H3n...O1 = 1.813(14) Å, N3...O1 = 2.6269(19) Å with angle at H3n = $152.8(15)^\circ$]. Overall, the LH₂ ligand has a curved shape, as seen in the dihedral angle of $76.80(8)^\circ$ formed between the peripheral rings.

The most prominent feature of the molecular packing of **1** is the formation of a series of $\pi\cdots\pi$ stacking interactions, propagated by inversion symmetry and leading to twisted supramolecular chains oriented along the *a*-axis. Of particular interest is that the interacting rings are the chelate rings, as has been commented upon in recent reviews [12,13]. In the crystal of **1**, interactions occur between each of the five- and six-membered chelate rings and the methoxyphenyl ring as well as between six-membered chelate rings, as highlighted in the images of Figure 2a and 2b; see the caption to Figure 2 for geometric parameters characterizing these interactions. The dihedral angles between the respective planes of the three interactions are $9.99(6)$, $5.76(6)$ and $0.02(5)^\circ$, respectively, and are consistent with stacking interactions; the closest atom-to-atom contacts for each $\pi\cdots\pi$ interactions are also collated in the caption to Figure 2. The resulting chains are connected into a

supramolecular layer in the *ab*-plane by methyl-C-H \cdots O(methoxy) and methoxy-C-H \cdots S(ester) interactions. The connections between layers to consolidate the three-dimensional architecture are of the type methylene- and tolyl-C-H \cdots π (tolyl).

There are three closely related literature precedents that may be compared with **1**. These feature the same backbone as formed by the tridentate ligand in **1** with the fourth site in the square planar Ni^{II} coordination sphere occupied by pyridyl-*N* [14], 1*H*-imidazole-*N* [15], and triphenylphosphane-*P* [16] donor atoms.

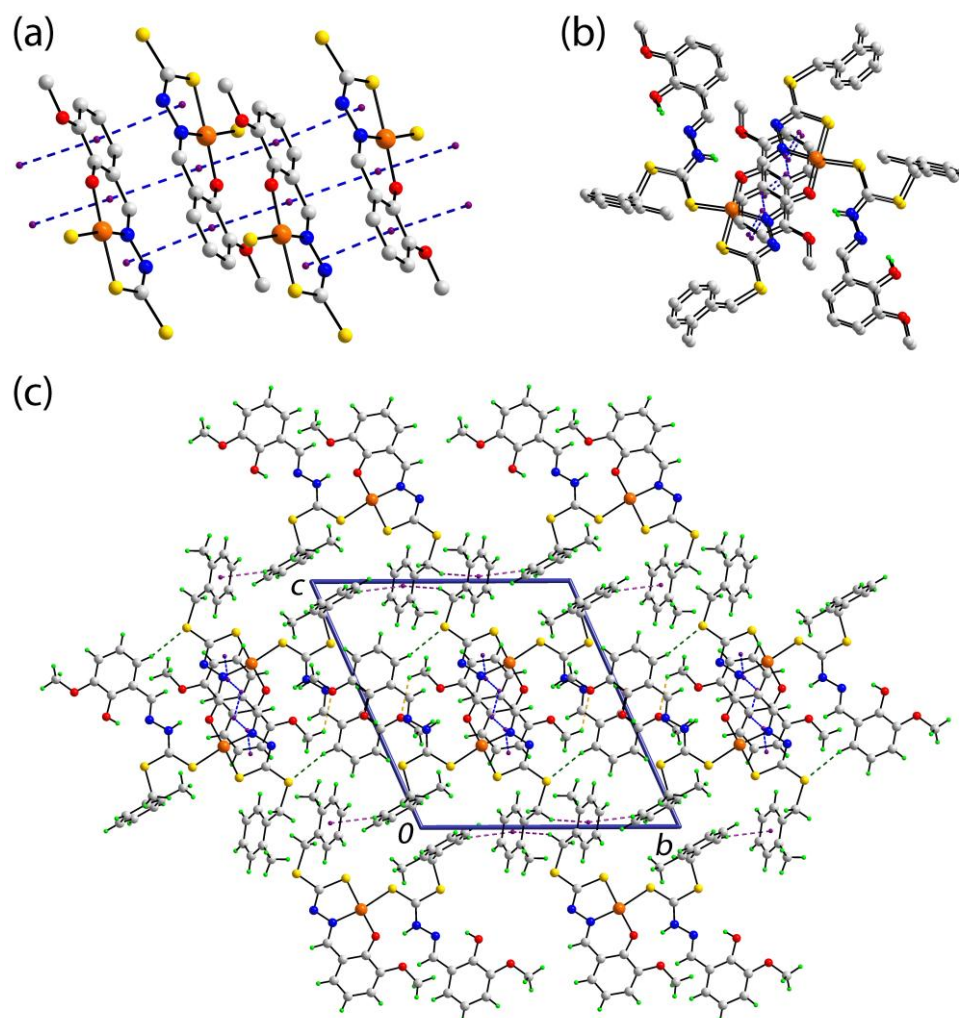


Figure 2. The molecular packing in the crystal of **1**: (a) a simplified view of the supramolecular chain sustained by $\pi\cdots\pi$ interactions [inter-centroid separations: $\text{Cg}(\text{Ni}, \text{S1}, \text{N1}, \text{N2}, \text{C1})\cdots\text{Cg}(\text{C3}-\text{C8})^i = 3.5231(8) \text{ \AA}$ (closest atom-to-atom contact between rings occurs between the N1 and C5ⁱ atoms and is $3.370(2) \text{ \AA}$), $\text{Cg}(\text{Ni}, \text{O1}, \text{N2}, \text{C2}-\text{C4})\cdots\text{Cg}(\text{C3}-\text{C8})^{ii} = 3.4748(8) \text{ \AA}$ ($\text{Ni}\cdots\text{C7}^{ii} = 3.3449(16) \text{ \AA}$) and $\text{Cg}(\text{Ni}, \text{O1}, \text{N2}, \text{C2}-\text{C4})\cdots\text{Cg}(\text{Ni}, \text{O1}, \text{N2}, \text{C2}-\text{C4})^i = 3.4718(8) \text{ \AA}$ ($\text{O1}\cdots\text{C2}^i = 3.339(2) \text{ \AA}$) for symmetry operations *i*: $2 - x, 1 - y, 1 - z$ and *ii*: $3 - x, 1 - y, 1 - z$] shown as blue dashed lines, (b) a view down the axis of the chain, and (c) a view of the unit cell contents shown in projection down the *a*-axis. The methyl-C-H \cdots O(methoxy) and methoxy-C-H \cdots S(ester) interactions [$\text{C9}-\text{H9b}\cdots\text{O4}^{iii}$: $\text{H9b}\cdots\text{O4}^{iii} = 2.52 \text{ \AA}$, $\text{C9}\cdots\text{O4}^{iii} = 3.126(2) \text{ \AA}$ with angle at H9b = 120° and $\text{C25}-\text{H25}\cdots\text{S2}^i$: $\text{H25}\cdots\text{S2}^i = 2.86 \text{ \AA}$, $\text{C25}\cdots\text{S2}^i = 3.7783(19) \text{ \AA}$ and angle at H25 = 162° for symmetry operations *iii*: $2 - x, -y, 1 - z$] are shown as orange and green dashed lines, respectively. The C-H \cdots π (2-tolyl) [$\text{C10}-\text{H10a}\cdots\text{Cg}(\text{C11}-\text{C16})^{iv} = 2.95 \text{ \AA}$ and angle at H10a = 122° and $\text{C33}-\text{H33}\cdots\text{Cg}(\text{C11}-\text{C16})^v = 2.84$ with angle at H33 = 149° for symmetry operations *iv*: $1 - x, 1 - y, -z$ and *v*: $1 - x, -y, -z$] interactions connecting layers along the *c*-axis are shown as purple dashed lines.

In conclusion, X-ray crystallography on **1** reveals the complex to comprise both the di-anionic form of LH₂, coordinating by the N, O, and S atoms, and the neutral thione tautomer of LH₂ which binds the Ni^{II} atom via the thione-S atom. The resulting NOS₂ coordination geometry is based on a square plane. The most prominent feature of the molecular packing is the formation of supramolecular chains sustained by $\pi(\text{chelate})\cdots\pi(\text{chelate})$ and $\pi(\text{chelate})\cdots\pi(\text{phenyl})$ interactions.

3. Materials and Methods

3.1. General Information

All chemicals and solvents were of analytical grade and used without any further purification. Chemical: nickel(II) acetate tetrahydrate (Sigma Aldrich, St. Louis, MO, USA). Solvents: acetonitrile (Fisher, Pittsburgh, PA, USA), ethanol (HmbG, Hamburg, Germany), methanol (Fisher, Pittsburgh, PA, USA), and dimethylsulfoxide (Scharlau, Barcelona, Spain). Instrumentation: The melting point was measured using an Electrochemical digital melting point apparatus (Cole-Parmer, Staffordshire, UK). Molar conductivities of 10⁻³ M solutions of (**1**) in DMSO was measured at 27 °C using a Jenway 4310 conductivity meter fitted with a dip-type cell with a platinised electrode (Cole-Parmer, Staffordshire, UK). The C, H, and N elemental analysis was carried out using a LECO CHNS-932 instrument (LECO, Saint Joseph, MI, USA). FTIR spectra were recorded using the Perkin Elmer Spectrum 100 with Universal ATR Polarization (PerkinElmer, Boston, MA, USA) in the range 4000–280 cm⁻¹. Electronic spectra were recorded on a Shimadzu UV-1650 PC recording spectrophotometer (1000–200 nm) (Shimadzu, Tokyo, Japan).

3.2. Synthesis and Characterization of **1**

The Schiff base, HL₂, was prepared following a literature method [10]. HL₂ (2 mmol, 0.692 g) was dissolved in hot ethanol (50 mL) and added to nickel(II) acetate tetrahydrate (1 mmol, 0.200 g) in ethanol (30 mL). The mixture was heated with continuous stirring until the volume of the solution reduced to half. Precipitation occurred once the mixture cooled to room temperature. The precipitate was filtered and dried over anhydrous silica gel. Complex (**1**) was recrystallized from its methanol solution as dark brown crystals. Yield: 90%; M.pt: 289–290 °C. Anal. Calc. for C₃₄H₃₆NiN₂O₄S₄: C, 53.91; H, 4.62; N, 7.31%. Found C, 54.13; H, 4.54; N, 7.43%. IR (cm⁻¹): 1590 (m) $\nu(\text{C}=\text{N})$, 971 (m) $\nu(\text{N}-\text{N})$, 700 (s) $\nu(\text{C}=\text{S})$. UV-Vis (DMSO; nm, L.cm⁻¹.mol⁻¹) $\lambda_{\text{abs}} = 344$, $\epsilon = 476,000$, $\lambda_{\text{abs}} = 438$, $\epsilon = 355,000$, $\lambda_{\text{abs}} = 614$, $\epsilon = 157,000$.

3.3. Crystallography

Intensity data for **1** were measured at T = 100(2) K on an Oxford Diffraction Gemini E CCD diffractometer (Agilent Technologies, Santa Clara, CA) diffractometer fitted with Mo K α radiation ($\lambda = 0.71073$ Å) so that θ_{max} was 29.0°. Data reduction, including absorption correction, was accomplished with CrysAlis Pro [17]. Of the 42,853 reflections measured, 7,895 were unique ($R_{\text{int}} = 0.041$), and of these, 6,813 data satisfied the $I \geq 2\sigma(I)$ criterion of observability. The structure was solved by direct methods [18] and refined (anisotropic displacement parameters and C-bound H atoms in the riding model approximation) on F^2 [19]. The O- and N-bound H atoms were located from a difference map and refined with O-H and N-H distance restraints of 0.84 ± 0.01 Å and 0.88 ± 0.01 Å, respectively. A weighting scheme of the form $w = 1/[\sigma^2(F_o^2) + (0.031P)^2 + 0.995P]$ was introduced, where $P = (F_o^2 + 2F_c^2)/3$. Based on the refinement of 434 parameters, the final values of R and wR (all data) were 0.028 and 0.070, respectively. The molecular structure diagram was generated with ORTEP for Windows [20] and the packing diagram using DIAMOND [21].

Crystal data for C₃₄H₃₄N₄NiO₄S₄ (**1**): $M = 749.60$, triclinic, $P\bar{1}$, $a = 7.3219(3)$ Å, $b = 15.4319(7)$ Å, $c = 16.2478(6)$ Å, $\alpha = 111.406(4)^\circ$, $\beta = 100.879(3)^\circ$, $\gamma = 98.313(4)^\circ$, $V = 1632.10(13)$ Å³, $Z = 2$, $D_x = 1.525$ g cm⁻³, $F(000) = 780$, and $\mu = 0.897$ mm⁻¹. CCDC deposition number: 1908837.

Supplementary Materials: The following are available online: IR and UV spectra and crystallographic data for **1** in the crystallographic information file (CIF) format. CCDC 1908837 also contains the supplementary

crystallographic data for this paper. These data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>.

Author Contributions: Synthesis and characterization was carried out by E.N.M.Y and N.M.N. X-ray crystallography was analyzed by E.R.T.T. The manuscript was written by E.N.M.Y., T.B.S.A.R., N.M.N., and E.R.T.T.

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Conflicts of Interest: The authors declare no conflict of interest.

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Sample Availability: A sample of the complex is not available from the authors.



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