

Short Note

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

Enis Nadia Md Yusof ^{1,2}, Nazhirah Muhammad Nasri ¹, Thahira B. S. A. Ravooft ^{1,3,*} and Edward R.T. Tiekink ^{4,*}

¹ Department of Chemistry, Faculty of Science, Universiti Putra Malaysia, UPM Serdang 43400, Selangor Darul Ehsan, Malaysia; enisnadia89@gmail.com (E.N.M.Y.); nazhirahnasri@gmail.com (N.M.N.)

² Discipline of Chemistry, School of Environmental and Life Sciences, University of Newcastle, University Drive, Callaghan, NSW 2308, Australia

³ Materials Synthesis and Characterization Laboratory, Institute of Advanced Technology, Universiti Putra Malaysia, Serdang 43400, Selangor, Malaysia

⁴ Research Centre for Crystalline Materials, School of Science and Technology, Sunway University, No. 5 Jalan Universiti, Bandar Sunway 47500, Selangor Darul Ehsan, Malaysia

* Correspondence: thahira@upm.edu.my (T.B.S.A.R.); edwardt@sunway.edu.my (E.R.T.T.); Tel.: +60-3-8946-6804 (T.B.S.A.R.); +60-3-7491-7181 (E.R.T.T.)

Received: 9 April 2019; Accepted: 22 April 2019; Published: 23 April 2019



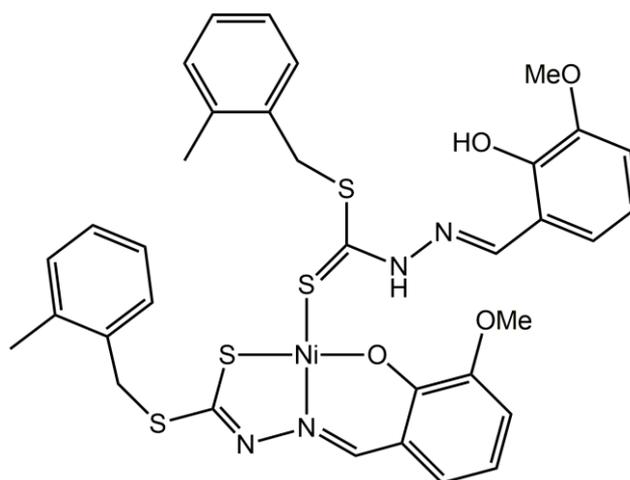
Abstract: The title Ni^{II} complex, Ni(L)(LH₂) (1), where LH₂ is *S*-2-methylbenzyl-β-*N*-(2-hydroxy-3-methoxybenzylmethylene) dithiocarbazate, was isolated from the reaction of Ni(acetate)₂·4H₂O and two molar equivalents of LH₂. The complex was characterized by elemental analysis, spectroscopy (IR 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-methylbenzylidithiocarbamate 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-methylbenzylidithiocarbamate 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.

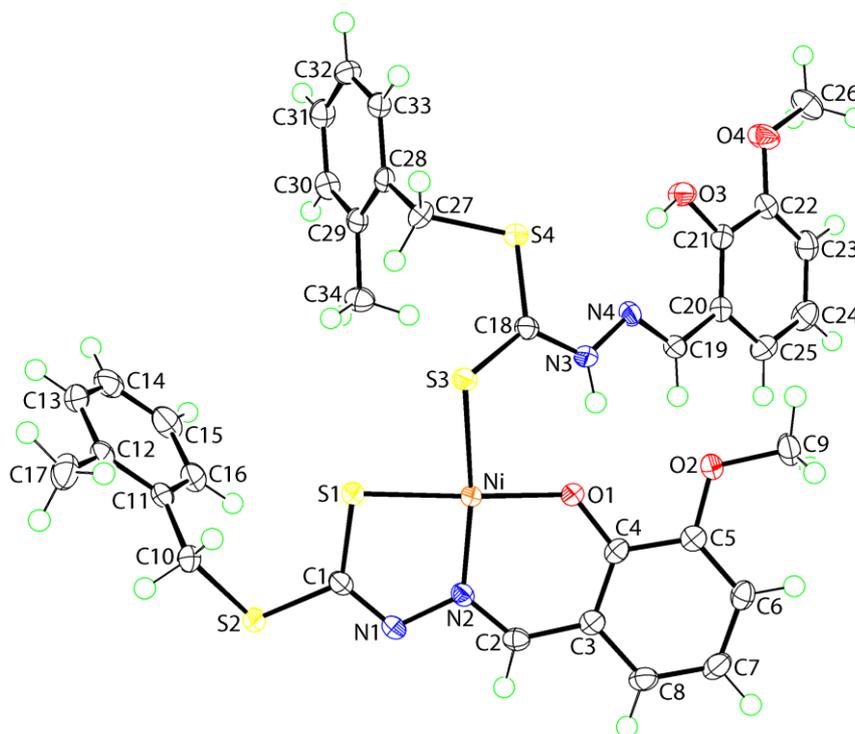


Figure 1. The molecular structure of **1** showing atom labeling and displacement ellipsoids at the 70% probability level. Selected geometric parameters: Ni-S1 = 2.1512(4) Å, Ni-S3 = 2.2290(4) Å, Ni-O1 = 1.8615(11) Å, and Ni-N2 = 1.8728(12) Å; S1-Ni-S3 = 84.523(16)°, S1-Ni-O1 = 176.63(4)°, S1-Ni-N2 =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

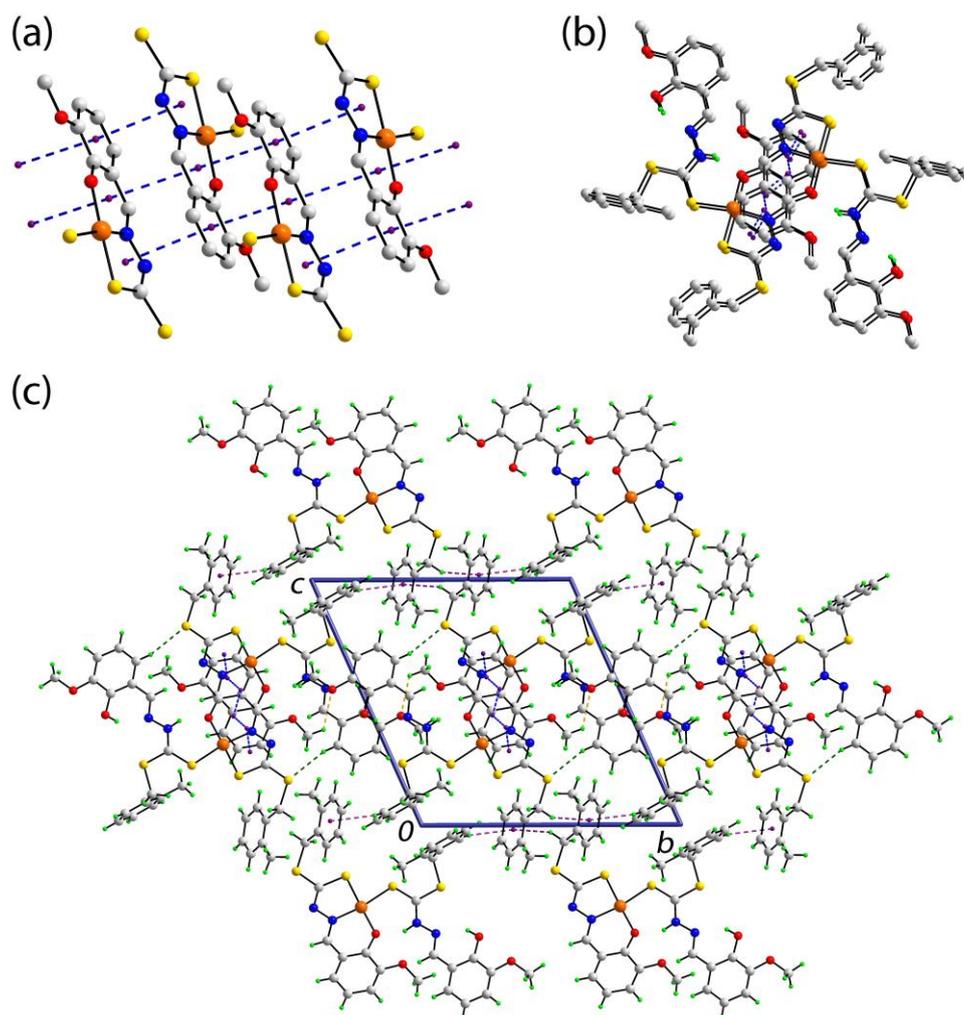


Figure 2. The molecular packing in the crystal of **1**: (a) a simplified view of the supramolecular chain sustained by $\pi\cdots\pi$ interactions [inter-centroid separations: $\text{Cg}(\text{Ni},\text{S}1,\text{N}1,\text{N}2,\text{C}1)\cdots\text{Cg}(\text{C}3-\text{C}8)^{\text{i}}$ = 3.5231(8) Å (closest atom-to-atom contact between rings occurs between the N1 and C5ⁱ atoms and is 3.370(2) Å), $\text{Cg}(\text{Ni},\text{O}1,\text{N}2,\text{C}2-\text{C}4)\cdots\text{Cg}(\text{C}3-\text{C}8)^{\text{ii}}$ = 3.4748(8) Å ($\text{Ni}\cdots\text{C}7^{\text{ii}}$ = 3.3449(16) Å) and $\text{Cg}(\text{Ni},\text{O}1,\text{N}2,\text{C}2-\text{C}4)\cdots\text{Cg}(\text{Ni},\text{O}1,\text{N}2,\text{C}2-\text{C}4)^{\text{i}}$ = 3.4718(8) Å ($\text{O}1\cdots\text{C}2^{\text{i}}$ = 3.339(2) Å) 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 [$\text{C}9-\text{H}9\text{b}\cdots\text{O}4^{\text{iii}}$; $\text{H}9\text{b}\cdots\text{O}4^{\text{iii}}$ = 2.52 Å, $\text{C}9\cdots\text{O}4^{\text{iii}}$ = 3.126(2) Å with angle at H9b = 120° and $\text{C}25-\text{H}25\cdots\text{S}2^{\text{i}}$; $\text{H}25\cdots\text{S}2^{\text{i}}$ = 2.86 Å, $\text{C}25\cdots\text{S}2^{\text{i}}$ = 3.7783(19) Å 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) [$\text{C}10-\text{H}10\text{a}\cdots\text{Cg}(\text{C}11-\text{C}16)^{\text{iv}}$ = 2.95 Å and angle at H10a = 122° and $\text{C}33-\text{H}33\cdots\text{Cg}(\text{C}11-\text{C}16)^{\text{v}}$ = 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.

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.

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).

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.

Funding: This research received funding from Universiti Putra Malaysia (UPM) under the Putra Group Initiative (IPB No. 9581001), Research University Grant Scheme (RUGS No. 9548700), and the Malaysian Fundamental Research Grant Scheme (FRGS No. 01-01-16-1833FR). The APC was funded by Sunway University.

Acknowledgments: The Department of Chemistry, Universiti Putra Malaysia, is thanked for X-ray diffraction facilities.

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

References

1. Ali, M.A.; Livingstone, S.E. Metal complexes of sulphur-nitrogen chelating agents. *Inorg. Chim. Acta* **1971**, *5*, 119–123. [[CrossRef](#)]
2. Ali, M.A.; Livingstone, S.E. Metal chelates of dithiocarbazic acid and its derivatives. II. Complexes of the schiff base formed by condensation of *S*-methyldithiocarbazate with acetone and pyridine-2-aldehyde. *Inorg. Chim. Acta* **1971**, *5*, 493–498. [[CrossRef](#)]
3. Mokhtaruddin, N.S.M.; Yusof, E.N.M.; Ravoof, T.B.S.A.; Tiekink, E.R.T.; Veerakumarasivam, A.; Tahir, M.I.M. Unusual saccharin-N,O (carbonyl) coordination in mixed-ligand copper(II) complexes: Synthesis, X-ray crystallography and biological activity. *J. Mol. Struct.* **2017**, *1139*, 1–9. [[CrossRef](#)]
4. How, F.N.-F.; Crouse, K.A.; Tahir, M.I.M.; Tarafder, M.T.H.; Cowley, A.R. Synthesis, characterization and biological studies of *S*-benzyl- β -*N*-(benzoyl) dithiocarbazate and its metal complexes. *Polyhedron* **2008**, *27*, 3325–3329. [[CrossRef](#)]
5. Akbar Ali, M.; Huq Mirza, A.; Wei, L.K.; Bernhardt, P.V.; Atchade, O.; Song, X.; Eng, G.; May, L. Synthesis and characterization of pentagonal bipyramidal organotin(IV) complexes of 2,6-diacetylpyridine Schiff bases of *S*-alkyl- and arylthiocarbazates. *J. Coord. Chem.* **2010**, *63*, 1194–1206. [[CrossRef](#)]
6. Ravoof, T.B.S.A.; Crouse, K.A.; Tahir, M.I.M.; How, F.N.F.; Rosli, R.; Watkins, D.J. Synthesis, characterization and biological activities of 3-methylbenzyl 2-(6-methylpyridin-2-ylmethylene)hydrazine carbodithioate and its transition metal complexes. *Transit. Met. Chem.* **2010**, *35*, 871–876. [[CrossRef](#)]
7. Omar, S.A.; Ravoof, T.B.S.A.; Tahir, M.I.M.; Crouse, K.A. Synthesis and characterization of mixed-ligand copper(II) saccharinate complexes containing tridentate NNS Schiff bases. X-ray crystallographic analysis of the free ligands and one complex. *Transit. Met. Chem.* **2013**, *39*, 119–126. [[CrossRef](#)]
8. Low, M.L.; Maigre, L.; Tahir, M.I.M.; Tiekink, E.R.T.; Dorlet, P.; Guillot, R.; Crouse, K.A. New insight into the structural, electrochemical and biological aspects of macrocyclic Cu(II) complexes derived from *S*-substituted dithiocarbazate schiff bases. *Eur. J. Med. Chem.* **2016**, *120*, 1–12. [[CrossRef](#)] [[PubMed](#)]
9. Tarafder, M.T.H.; Ali, A.M.; Wong, Y.W.; Wong, S.H.; Crouse, K.A. Complexes of transition and nontransition metals of dithiocarbazate ion and their biological activities. *Inorg. Met. Org. Chem.* **2001**, *31*, 115–125. [[CrossRef](#)]
10. Yusof, E.N.M.; Latif, M.A.M.; Tahir, M.I.M.; Sakoff, J.A.; Simone, M.I.; Page, A.J.; Veerakumarasivam, A.; Tiekink, E.R.T.; Ravoof, T.B.S.A. *o*-Vanillin derived Schiff bases and their organotin(IV) compounds: Synthesis, structural characterisation, in-silico studies and cytotoxicity. *Int. J. Mol. Sci.* **2019**, *20*, 854. [[CrossRef](#)] [[PubMed](#)]
11. Rocha, F.V.; Barra, C.V.; Mauro, A.E.; Carlos, I.Z.; Nauton, L.; El Ghozzi, M.; Gautier, A.; Morel, L.; Netto, A.V.G. Synthesis, characterization, X-ray structure, DNA cleavage, and cytotoxic activities of palladium(II) complexes of 4-phenyl-3-thiosemicarbazide and triphenylphosphane. *Eur. J. Inorg. Chem.* **2013**, 4499–4505. [[CrossRef](#)]
12. Malenov, D.P.; Janjić, G.V.; Medaković, V.B.; Hall, M.B.; Zarić, S.D. Noncovalent bonding: Stacking interactions of chelate rings of transition metal complexes. *Coord. Chem. Rev.* **2017**, *345*, 318–341. [[CrossRef](#)]
13. Tiekink, E.R.T. Supramolecular assembly based on “emerging” intermolecular interactions of particular interest to coordination chemists. *Coord. Chem. Rev.* **2017**, *345*, 209–228. [[CrossRef](#)]

14. Ali, M.A.; Guan, T.S.; Bhattacharjee, P.; Butcher, R.J.; Jasinski, J.P.; Li, Y. Nickel(II) and copper(II) complexes of ONS ligands formed from 2-hydroxyacetophenone and S-alkyldithiocarbazates and the X-ray crystal structure of the [Ni(Ap-SMe)py] complex (Ap-SMe = anion of the 2-hydroxyacetophenone Schiff base of S-methyl-dithiocarbazate). *Transit. Met. Chem.* **1996**, *21*, 351–357. [[CrossRef](#)]
15. Takjoo, R.; Centore, R. Synthesis, X-ray structure, spectroscopic properties and DFT studies of some dithiocarbazate complexes of nickel(II). *J. Mol. Struct.* **2013**, *1031*, 180–185. [[CrossRef](#)]
16. Ali, M.A.; Tan, A.L.; Mirza, A.H.; Santos, J.H.; Abdullah, A.H.H. Synthesis, structural characterization and electrochemical studies of nickel(II), copper(II) and cobalt(III) complexes of some ONS donor ligands derived from thiosemicarbazide and S-alkyl/aryl dithiocarbazates. *Transit. Met. Chem.* **2012**, *37*, 651–659. [[CrossRef](#)]
17. Agilent Technologies Inc. *CrysAlis PRO*; Agilent Technologies Inc.: Santa Clara, CA, USA, 2011.
18. Sheldrick, G.M. A short history of SHELX. *Acta Crystallogr. A* **2008**, *64*, 112–122. [[CrossRef](#)] [[PubMed](#)]
19. Sheldrick, G.M. Crystal structure refinement with SHELXL. *Acta Crystallogr. C* **2015**, *71*, 3–8. [[CrossRef](#)] [[PubMed](#)]
20. Farrugia, L.J. WinGX and ORTEP for Windows: An update. *J. Appl. Crystallogr.* **2012**, *45*, 849–854. [[CrossRef](#)]
21. Brandenburg, K.; Putz, H. *DIAMOND*; Crystal Impact GbR: Bonn, Germany, 2006.

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



© 2019 by the authors. Licensee MDPI, Basel, Switzerland. This article is an open access article distributed under the terms and conditions of the Creative Commons Attribution (CC BY) license (<http://creativecommons.org/licenses/by/4.0/>).