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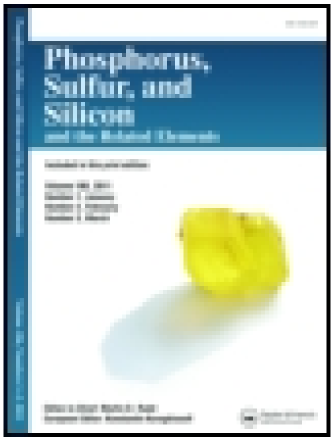

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EFFECT OF N-BOUND ORGANIC MOIETY IN DITHIOCARBAMATE ($RNCS_2^-$) AND trans INFLUENCE OF TRIPHENYLPHOSPHINE ON NiS_2PN CHROMOPHORE

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EFFECT OF N-BOUND ORGANIC MOIETY IN DITHIOCARBAMATE ($RNCS_2^-$) AND *trans* INFLUENCE OF TRIPHENYLPHOSPHINE ON NiS_2PN CHROMOPHORE

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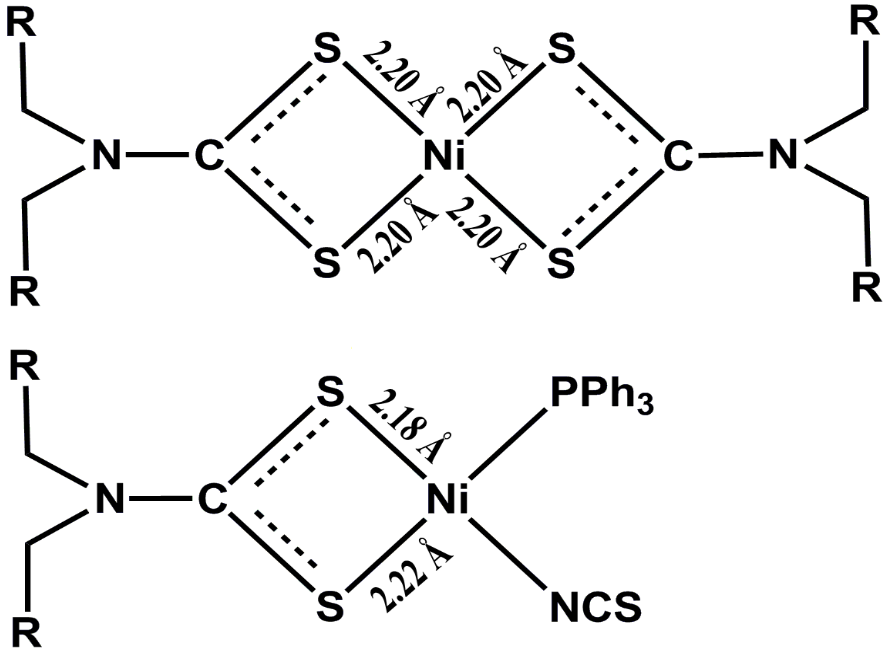
Abstract

Three square planar Ni(II) complexes of the composition [Ni(bzcprdtc)$_2$](**1**), [Ni(bzcprdtc)(NCS)(PPh$_3$)](**2**) and [Ni(bzcprdtc)(PPh$_3$)$_2$]ClO$_4$ (**3**)[(where bzcprdtc=N-benzyl-N-cyclopropyl-dithiocarbamate)] have been synthesized and characterized by ^{1}H and ^{13}C NMR, UV-Vis and FT-IR spectroscopy. ^{13}C NMR spectra show interesting differences between the $N^{13}CS_2$ carbon signals of the parent complex **1** and heteroleptic complex **2**. The $N^{13}CS_2$ carbon signal for **2** is observed at 209.3 ppm with an upfield shift of about 3.5 ppm compared with that found for **1** (212.8 ppm). The observed shielding in **2** indicates the effect of PPh_3 on the mesomeric drift of electron density toward nickel through the thioureide C-N bond of $[Ni(dtc)(NCS)(PPh_3)]$. Single crystal X-ray analysis of **2** and $[Ni(dbpdtc)(NCS)(PPh_3)]$(**4**) (dbpdtc = benzyl(4-(benzylamino)phenyl)dithiocarbamate) confirmed distorted square planar arrangement in the vicinity of the nickel atom with a S_2NP donor set. Comparative analysis of bond parameters of $[Ni(dtc)_2]$ and $[Ni(dtc)(NCS)(PPh_3)]$ has also been studied.



Keywords: dithiocarbamate; Nickel(II); thiocyanate; single-crystal X-ray analysis

1. Introduction

The physicochemical properties of dithiocarbamate compounds allow for wide applications in different areas. These compounds were found to be useful as accelerators of vulcanization[1], fungicides[2] and pesticides[3]. Several thousands of transition metal complexes with the dithiocarbamate moiety have been prepared and reported to date and some of them are very promising from the biological activity point of view. The Pt^{II} complex of composition [Pt(esdtc)(Py)Cl] [esdtc = ethylsarcosinedithiocarbamate and Py = pyridine] is highly cytotoxic against several human cancer cell lines and more over, this substance was not found to be nephrotoxic in contrast to the cis platin[4]. Attention has been focused on nickel dithiocarbmate complexes for the large variety of the reactions in which they are involved as catalysts and are used for the preparation of semiconducting metal sulfide thin film by single source MOCVD techniques[5,6]. A number of bis(dithiocarbamato)nickel(II), $[Ni(dtc)_2]$ and $[Ni(dtc)(NCS)(PPh_3)]$ complexes have been synthesized, several of them have been characterized by single crystal X-ray diffraction[7-13]. The Ni-S bond distances are in the range 2.19-2.21Å and are symmetric with Δ(Ni-S), defined as $Ni\text{-}S_{long} – Ni\text{-}S_{short}$, being usually less than 0.02Å for all the $[Ni(dtc)_2]$ complexes except $[Ni(dbpdtc)_2]$[8] which is reported from our laboratory. In all the $[Ni(dtc)(PPh_3)(NCS)]$ complexes, the Ni-S bond *trans* to PPh_3 is longer than the other Ni-S bond. The aim of the present work is to study the *trans* effect of triphenylphosphine in $[Ni(dbpdtc)(NCS)(PPh_3)]$ and to compare the structural parameters of $[Ni(dtc)_2]$ and $[Ni(dtc)(NCS)(PPh_3)]$. In this paper, we report synthesis and spectral studies on $[Ni(bzcprdtc)_2]$(**1**), $[Ni(bzcprdtc)(NCS)(PPh_3)]$(**2**) and $[Ni(bzcprdtc)(PPh_3)]ClO_4$(**3**).

In addition to this, single crystal X-ray structural analysis of [Ni(bzcprdtc)(NCS)(PPh$_3$)] (**2**) and [Ni(dbpdtc)(NCS)(PPh$_3$)] (**4**) are also reported.

2. RESULTS AND DISSCUSION

Complexes **1-3** were prepared according to the synthetic procedure shown in Scheme 1. Benzaldehyde was condensed with cyclopropylamine to form the imine. Sodium borohydride reduction of imine in methanol-dichloromethane yielded secondary amine. Complex **1** was prepared from secondary amine in ethanol by reaction with CS_2 and $NiCl_2.6H_2O$. Complex **2** was prepared by refluxing **1,** $NiCl_2.6H_2O$, NH_4SCN and PPh_3 in acetonitrile-methanol and the reaction under reflux (3 h) between **1,** $NiCl_2.6H_2O$, $NaClO_4$ and PPh_3 yielded **3**.

[Insert Scheme 1]

2.1 *FT-IR spectral studies*

Important bands in the IR spectra of dithiocarbamate complexes are due to the C-N and C-S stretching modes. In the FT-IR spectra of the complexes **1-3**, the thioureide ν_{C-N} bands are observed at 1472, 1497 and 1478 cm^{-1}, respectively. These bands indicate that the C-N bond order is intermediate between a single bond (1350-1250 cm^{-1}) and double bond (1690-1650 cm^{-1}) (**Scheme 2**) [14]. The ν_{C-N} (thioureide) band of heteroleptic complexes observed at higher wave number compared with parent homoleptic complex **1** is due to the mesomeric drift of electron density from the bzcprdtc ligand towards nickel, increasing the contribution of polar thioureide. The ν_{C-S} stretching vibrations are observed around 1025 cm^{-1} without any splitting, supporting the bidentate coordination of the dithiocarbamate moiety [15]. The observed stretching frequency at 2084 cm^{-1} for **2** is assigned to the N-coordinated thiocyanate. The intense signal observed at 1090cm^{-1} for **3** is attributed to ClO_4.

[Insert Scheme 2]

2.2. *^{1}H NMR spectral studies*

In the complex **1**, two singlets observed at 0.89 and 4.79 ppm are due to the methylene protons of the cyclopropyl and benzyl groups, respectively. The methyne proton of cyclopropyl group shows a broad signal at 2.61 ppm. The signals of methylene protons in the ring are observed in the upfield region compared to the signals of methylene protons outside the ring (methylene protons of benzyl group). The chemical shifts of methyne proton of cyclopropyl and methylene protons of benzyl group are observed in the downfield region due to the release of electron density on the nitrogen of NR_2 groups, forcing high electron density towards the sulfur or metal via the thioureide π-system. The aliphatic protons of dithiocarbamate in **2** and **3** are observed as broad signals. This is due to the $\mathrm{C}\overset{\cdots\cdots}{\text{——}}\mathrm{N}$ bond rotation as observed in phosphine complexes. In all the complexes, the aromatic protons resonate in the region 7.16-7.80 ppm.

2.3. *^{13}C NMR spectral studies*

The chemical shift of the thioureide carbon atoms ($N^{13}CS_2$) are observed at 212.8 and 209.3 ppm for the complexes **1** and **2** respectively. This indicates the partial double bond character of C-N (thioureide) and C-S bonds. The $N^{13}CS_2$ chemical shift of dithiocarbamate is affected by the coordination of the PPh_3 to the nickel atom. The $N^{13}CS_2$ carbon site of the **2** is shielded by 3.5

ppm compared to the parent **1**. The presence of a triphenylphosphine (π-acceptor) in **2** increases the mesomeric drift of electron density from the dithiocarbamate moiety towards the metal atom[16]. This causes an increase in N-C partial double bond character of dithiocarbamate in **2**.

2.4. *Electronic spectral studies*

The electronic spectra of the complexes $[Ni(bzcprdtc)_2]$, $[Ni(bzcprdtc)(NCS)(PPh_3)]$ and $[Ni(bzcprdtc)(PPh_3)_2]ClO_4$were recorded in chloroform. In the case of **1**, two d-d transition bonds are observed at 624 ($d_{xy} \rightarrow d_{x^2-y^2}$) and 458 nm ($d_{z^2} \rightarrow d_{x^2-y^2}$)[17] transitions, respectively and are suggestive of the square planar geometry around Ni(II) metal ion. The bands observed at 490 and 455 nm for the complexes **2** and **3** respectively are due to the d-d transitions. These bands are assigned to $d_{z^2} / d_{xy} \rightarrow d_{x^2-y^2}$ transitions. In all the complexes **1-3**, bands observed in the UV region are due to the intraligand π-π* transitions, mainly associated with the intramolecular intraligand transitions corresponding to π-π* transitions of the N-C=S and S-C=S groups and n–π* transition located on the sulfur atom[18].

2.5 . *Single crystal X-ray structural analysis*

The $[Ni(bzcprdtc)(NCS)(PPh_3)]$ **(2)** and $[Ni(dbpdtc)(NCS)(PPh_3)]$ **(4)** complexes crystalized in triclinic and monoclinic systems with the space groups $P\bar{1}$ and Cc, respectively. The crystal data and refinement parameters are given in the Table 1**.** Selected bond distances and angles are listed in Table 2 and 3. The ORTEP diagrams of **2** and **4** are shown in Figures **1** and **2**, respectively. The central Ni^{II} ion of the both complexes **2** and **4** are tetracoordinated by PPh_3, isothiocyanate and bidentate coordinated dithiocarbamate anion. The atoms of NiS_2NP

chromophore arranged in the distorted square planar geometry around the metal centre. The distortion from the normal geometry arises from the bidentate ligand (S1-Ni-S2 of 78.97(3)° and 78.90(5)° for the **2** and **4**, respectively). Which causes the *trans* S-Ni-N and S-Ni-P angles to be between 172.08° and178.3°, smaller than the expected value of 180°. The other angles [N2-Ni-P1=91.96 (8)°, S1-Ni-P1= 95.56 (3)° for **2** and N3-Ni-P1=93.70 (15)°, S1-Ni-P1=94.22(5)° for **4**)] are slightly deviated from the ideal *cis* angle 90°. Selected bond lengths and angles are presented in Tables 2 and 3

[Insert Table 1]

[Insert Figure 1]

[Insert Figure 2]

The structure adopted by these complexes are characterized using $\boldsymbol{\tau_4}$ descriptor for four coordination ions suggested by Yang *et.al*[19]. The distortion index is defined as τ_4 = 360-(α+ß)/141. The τ_4 values for perfect, see saw structure, trigonal pyramid and tetrahedral are 0.00, 0.07-0.64, 0.85 and 1.00 respectively. τ_4 values for the complexes **2** and **4** are 0.102 and 0.106 respectively, which indicate that the coordination geometry of both the complexes is a seesaw structure. In both the complexes, the dithiocarbamate ligands are bidentate giving four membered chelate rings [NiS_2C]. Their planar geometry is supported by the corresponding torsion angles which are close to 0 and 180°. The C-S bond lengths in complexes **2** and **4** (*ca*.1.72Å) are characteristic of the partial double bonds (typical bond lengths: 1.81Å for C-S and 1.69Å for C=S). The C-N bond distances in both the complexes are shorter than the C=N bond length (*ca* 1.35Å). This behavior indicates that the electron density is delocalized over the NCS_2 moiety.

The Ni-N distances 1.866(2)Å and 1.856(5)Å for **2** and **4,** respectively, are significantly short which shows the effective bonding between the nickel atom and NCS^{-}. The N-C-S bond angle in thiocyanate is 178.3 and 178.9° for **2** and **4**, respectively and is almost linear. Ni-P distances are 2.1854(8)Å and 2.2032(14)Å for complexes **2** and **4**. These short Ni-P distances indicate a better bonding and back bonding interaction between Ni and P in [Ni(dtc)(NCS)(PPh_3)] complexes[20].

[Insert Table 2]

[Insert Table 3]

2.6. Comparative analysis of Ni–S, C–N and C–S distances and related angles in Ni(dtc)$_2$ and [Ni(dtc)(NCS)(PPh$_3$)]

Of particular interest with respect to the dithiocarbamate- metal bonding are the M–S, C–S and C–N distances and the related angles. A comparison of the bond parameters is given Table 4. Table 4 shows that the Ni–S bond distances are symmetric with Δ(Ni–S), defined as Ni–S_{long} – Ni–S_{short}, being usually less than 0.02Å for all the [Ni(dtc)$_2$] complexes except [Ni(dbpdtc)$_2$]. For all the [Ni(dtc)(NCS)(PPh_3)] complexes except [Ni(dbpdtc)(NCS)(pph_3)], the differences in Ni–S bond distances [Δ(Ni–S)] are about 0.036-0.056 Å indicating the significant asymmetry in Ni–S bonds. This observed difference in Ni–S distances is attributed to the difference in the *trans* influencing properties of PPh_3 and NCS^{-}. PPh_3 being a good π-acceptor has greater influence and hence the Ni–S bond *trans* to PPh_3 is longer than the other Ni–S bond. The Ni–S bond distances are slightly asymmetric in [Ni(dbpdtc)$_2$] (Δ(Ni–S) = 0.023 Å) and symmetric in [Ni(dbpdtc)(NCS)(PPh_3)] (Δ(Ni–S) = 0.018 Å). This may be due to the resonance effect and steric bulk of the dithiocarbamate ligand.

The Ni–S–C and S–Ni–S bond angles are also slightly affected by the π back bonding effect of the triphenylphosphine in [Ni(dtc)(NCS)(PPh_3)]. No significant changes in C–N and C–S bond lengths and S–C–S and N–C–S bond angles are observed. This study confirms that Ni-S bonds are affected by the *trans* effect of triphenylphosphine and N-bound organic moiety of dithiocarbamate ligand.

[Insert Table 4]

3. Conclusions

Three new nickel(II) complexes have been prepared and characterized using IR, NMR and UV-Vis spectroscopy. The spectroscopic data reveal that all the compounds have square planar geometry. Single crystal X-ray structural studies on **2** and **4** show that the geometry of both complexes are not of the perfect square planar, because of the small bite angle (S-Ni-S) associated with the dithiocarbamate ligands. Comparative analysis is of bond parameters of [Ni($dtc)_2$] and [Ni(dtc)(PPh_3)(NCS)] complexes reveals the *trans* effect triphenylphosphine and the effect of N-bound organic moiety in dithiocarbamate ligands on bond parameters of nickel complexes.

4. Experimental

4.1. *Chemicals, Instrumentations*

All reagents and solvents were pure and used as purchased Merck, Sigma, Spectrochem) without further purifications. Melting points were determined using an electro thermal IA 9300 apparatus and were not corrected. Elemental analysis (C,H,N) were performed on Perkin Elmer 2400 series(II) CHN analyzer. FT-IR spectra (600-4000cm^{-1} region; KBr) was recorded on Thermo Nicolet Avatar 330. ^{1}H and ^{13}C NMR spectra of $CDCl_3$ solution were recorded on a Bruker 400/100 MHz. UV-Vis spectra were obtained on a Shimadzu UV-1650 PC spectrometer.

4.2. *X-ray crystallography*

Single Crystal x-ray diffraction data for **2** and **4** were recorded on an ‘Xcalibur, Sapphire 3’ diffractometer equipped with graphite monochromated MoKα radiation (λ = 0.71069Å) at ambient temperature. The structure was solved by direct methods SHELXS-97[21] and refined on F^2 with full matrix least-squares method in SHELXL-97[22]. Non-hydrogen atoms were refined anisotropically and the hydrogen atoms were refined isotropically.

4.3. *Synthesis of metal complexes*

4.3.1. *Preparation of N-benzyl-N-cyclopropylamine*

Cyclopropylamine (4.6 mmol, 0.5 mL) and benzaldehyde (5.1 mmol, 0.4 mL) were dissolved in methanol (40 mL) and the solution was stirred for 2 h at room temperature. The solvent was removed by evaporation. The resulting colourless oil was dissolved in methanol-dichloromethane solvent mixture (1:1, 20 mL) and sodium borohydride (13.8 mmol, 0.5 g) was added slowly and stirred for 2 h at 5°C. The reaction mixture was stirred at room temperature for 20 h. After evaporation of the solvent, the resulting viscous liquid was washed with water and dichloromethane was added in order to extract the product. Evaporation of the organic layer gave N-benzyl-N-cyclopropylamine as pale yellow oil.

4.3.2. *Preparation of 1*

An ethanolic solution of N-benzyl-N-cyclopropylamine (4mmol, 0.64g) was treated with carbon disulfide (4mmol, 0.3mL) and stirred for 30min at 5°C; yellow dithiocarbamic acid was obtained. $NiCl_2.6H_2O$ was dissolved in 50ml of water and was added to the solution drop wise leading to the formation of olive green precipitate. The precipitate was then filtered off, washed with distilled water and then dried. (**Scheme 1).** Yield: 68%; Dec. 186-188°C; Anal.calc. for C,54.04 H,5.67 N,5.25 (MW= 532.06); found C,53.72 H,5.54 N,5.17. IR (KBr, cm^{-1}): ν = 1472 (ν_{C-N}), 1020 (ν_{C-S}). UV-Vis ($CHCl_3$, nm): λ = 624, 458, 419, 397, 339, 276. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 4.79 (s, CH_2), 2.61 [br, CH (cyclopropyl)], 0.88 [br, CH_2 (cyclopropyl)], 7.33 (br, aromatic protons). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 53.1 ($N–\underline{C}H_2–C_6H_5$), 31.8 [CH (cyclopropyl)], 7.8 [CH_2 (cyclopropyl)], 127.9, 128.1, 128.4, 134.9 (phenyl ring carbons), 212.8 (NCS_2).

4.3.3. *Preparation of 2*

A mixture of $[Ni(bzcprdtc)_2]$ (0.533g, 1.0 mmol), PPh_3 (0.52g, 2mmol), $NiCl_2.6H_2O$ (0.327g, 1.0 mmol) and NH_4SCN (0.152g, 2.0 mmol) was refluxed in acetonitrile-methanol solvent mixture (1:1, 50 mL) for 3 h. The purple red solution obtained was filtered and left for evaporation. After 5 d, a purple red solid separated out, which was recrystallized from chloroform (**Scheme 1**). Suitable crystals for X-ray structural analysis were obtained by repeated recrystallization from dichlromethane-methanol solvent mixture. Yield:63% ; Dec. 98-100°C; Anal.calc.for C,59.91 H,4.53 N,4.66 (MW=601.41); found C,59.68 H,4.45 N,4.58. IR (KBr, cm^{-1}): ν = 2084 (NCS), 1478 (ν_{C-N}), 1025 (ν_{C-S}). UV-Vis ($CHCl_3$, nm): λ = 490, 451,397,331, 261. ^1H NMR (400 MHz, $CDCl_3$, ppm): δ = 4.45–4.78 (two broad signals overlapped to appear as a three signals, CH_2), 2.50, 2.67 [two broad signals, CH (cyclopropyl)], 0.73-0.90 [m, CH_2 (cyclopropyl)], 7.16-7.73 (aromatic protons). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ = 53.1, 53.4 (N–$\underline{C}H_2$–C_6H_5), 31.8 [CH (cyclopropyl)], 7.4, 7.8 [CH_2 (cyclopropyl)], 127.9, 128.0, 128.1, 128.2, 128.4, 128.8, 128.9, 129.0, 129.1, 131.1, 132.0, 134.1, 134.2, 135.0 (phenyl ring carbons), 209.3 (NCS_2).

4.3.4 *Preparation of 3*

A mixture of [Ni(bzcprdtc)$_2$] (0.533g, 1.0 mmol), PPh_3 (0.52g, 2mmol), $NiCl_2.6H_2O$ (0.327g,1.0mmol) and $NaClO_4$ (0.152g, 2.0 mmol) was refluxed in chloroform- methanol solvent mixture (3;2 50 mL) for 3 h. The purple red solution obtained was filtered and left for evaporation. After 2 d, a purple red solid separated out, which was recrystallized from chloroform (**Scheme 1**). Yield: 63%; Dec. 96-98°C; Anal. Calc .for C,62.66 H,4.93 N,1.52 (MW=920.00); found C,62.42 H,4.85 N,1.48. IR (KBr, cm^{-1}): ν = 1090 (ClO_4), 1478 (ν_{C-N}), 1025 (ν_{C-S}). UV-Vis ($CHCl_3$, nm): λ = 455, 397, 331, 295, 270. ^{1}H NMR (400 MHz, $CDCl_3$, ppm): δ = 4.63–4.69 (broad doublet, CH_2), 2.55, 2.60 [broad doublet, CH (cyclopropyl)], 0.82, 0.88 [br, CH_2 (cyclopropyl)], 7.19-7.81 (aromatic protons). ^{13}C NMR (100 MHz, $CDCl_3$, ppm): δ =53.1, 53.4 (N–$\underline{C}H_2$–C_6H_5), 31.9, 32.0[CH (cyclopropyl)], 7.4, 7.6[CH_2 (cyclopropyl)], 128.0, 128.5, 128.6, 128.7, 129.0, 129.9, 130.5, 130.7, 131.6, 131.9, 132.0, 132.2, 132.3, 132.9, 133.0, 133.1, 133.3, 133.8, 133.9, 135.3 (phenyl ring carbons).

4.3.5 *Preparation of 4*

Complex **4** was prepared by the method reported in the literature [8]. Purple colour crystals were obtained from the slow evaporation of chloroform-ethanol (2:1) solution of **4**.

5. Supplementary materials

CCDC 1013960 and 1013879 contain the supplementary crystallographic data for the complexes **2** and **4**. Copies of the data can be obtained free of charge *via* http://www.ccdc.cam.ac.uk/conts/retrieving.html or from the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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References

1. Nieuwenhuizen, P.J.; Ehlers, A.W.; Haasnoot, J.G.; Janse, S.R.; Reedijk, J.; Baerends, E.J. *Am. Chem. Soc*. **1999**, *121*, 163-168.

2. Coucouvanius, D. *Prog. Inorg. Chem*. **1970,** *11*, 233-371.

3. Muskett, A.E.; Colhoun, j. *Nature* **1940,** *146*, 32-32.

4.Marzano, C.; Bettio, F.; Baccichetti, F.; Trevisan, A.; Giovagnini, L.; Fregona, D. *Chem. Bio. Inter*. **2004,** *148,* 37-48.

5 Brien, P.O.; Park, J.H.; Waters, J. *Thin Solid Films* **2003,** *431*, 502-505.

6.Nomura, R.; Nakai, N.; *Trans. Mater. Res. Soc. JPN* **2003,** *28*, 1287-1290.

7. Valarmathi, P.; Thirumaran, S.; Sarmal, L; Kant, R. *Spectrochim. Acta Part A* **2014,** *129*, 285-292.

8. Srinivasan, N.; Valarmathi, P.; Thirumaran, S.; Ciattini, S. *Trans. Metal Chem.* **2010,** *35,* 815-819.

9. Valarmathi, P.; Srinivasan, N.; Thirumaran, S.; *J. Sulfur Chem*. **2011**, *32,* 583-591.

10. Anastasiadis, C.; Hogarth, G.; Wilton-Ely, J. D. E. T. *Inorg. Chim. Acta* , **2010**, *363*, 3222-3228.

11. Valarmathi, P.; Thirumaran, S.; Selvanayagam, S. *Acta Cryst.* **2011**, *E67*, m1882.

12. Srinivasan, S.; Ramalingam, K.; Rizzoli, C. *Z. Anorgallg. Chem.* **2012**, 638, 1356-1361.

13. Sheldrick, G.M. *SHELXL-97*, University of Gottingen, Gottingen, Germany **1997**.

14. Oliveira, M. R. L. De Bellis, V. M. *Trans. Metal Chem*. **1999**, *24*, 127-130.

15. Bonati, F.; Ugo, R. *J. organomet. Chem.* **1967**, *10*, 257-268.

16. Fackler, Jr. J.P.; Lin, I. J. B.; Andrews, J. *Inorg. Chem*. **1977**, *16*, 450.

17. Jorgensen, C. K. *J. Inorg. Nucl. Chem*. **1962**, *24*, 1571-1581.

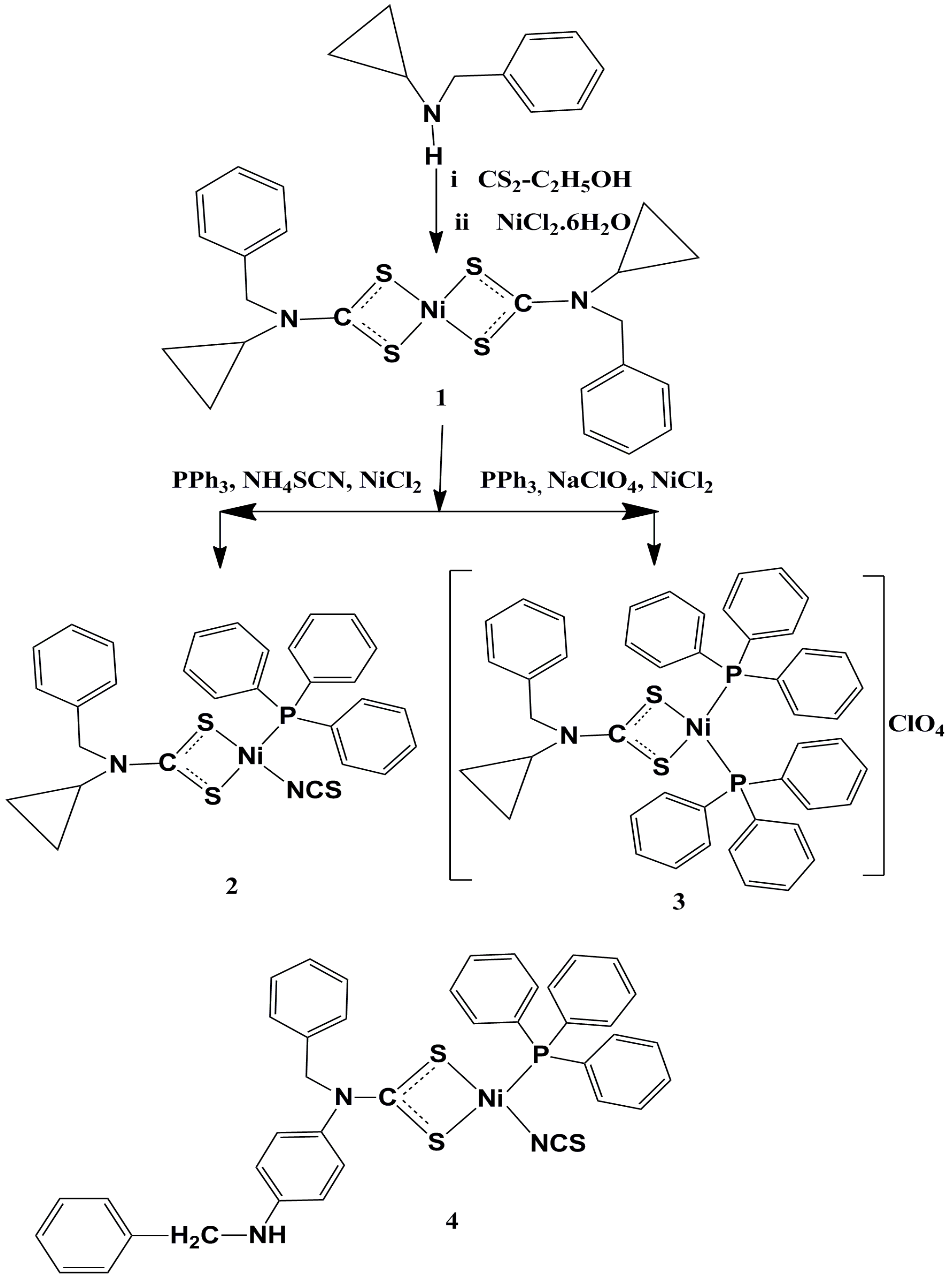
18. Manav, N.; Mishra, A.K.; Kaushik, N.K. *Spectrochim. Acta Part A*, **2006**, *65*, 32-35.

19. Yang, L.; Powell, D.R.; Houser, R.P. *Dalton Trans*. **2007**, 955-964.

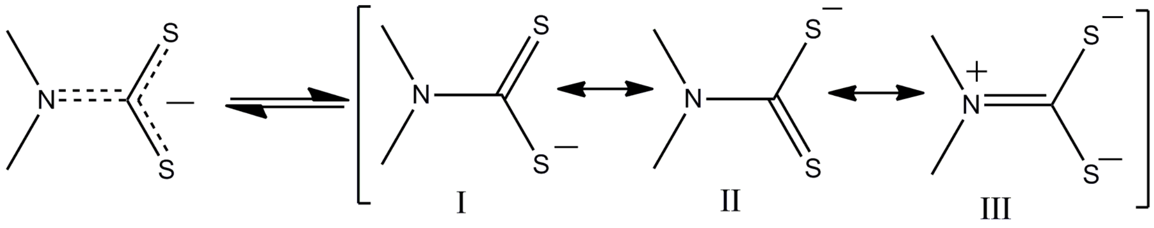
20. Srinivasan, N.; Sathyaselvabala, V.; Kuppulakshmy, K.; Valarmathi, P.; Thirumaran, S. *Monatsh Chem.* **2009**, *140*, 1431-1436.

21. Srinivasan, S.; Ramalingam, K.; Rizzoli, C. *Polyhedron* **2012**, *33*, 60-66.

22. Sheldrick, G. M. *Acta Cryst*. **2008**, *A64*, 112-122.



Scheme 1 Preparation of complexes



Scheme 2

Scheme 2 The resonance structures of dtc ligands

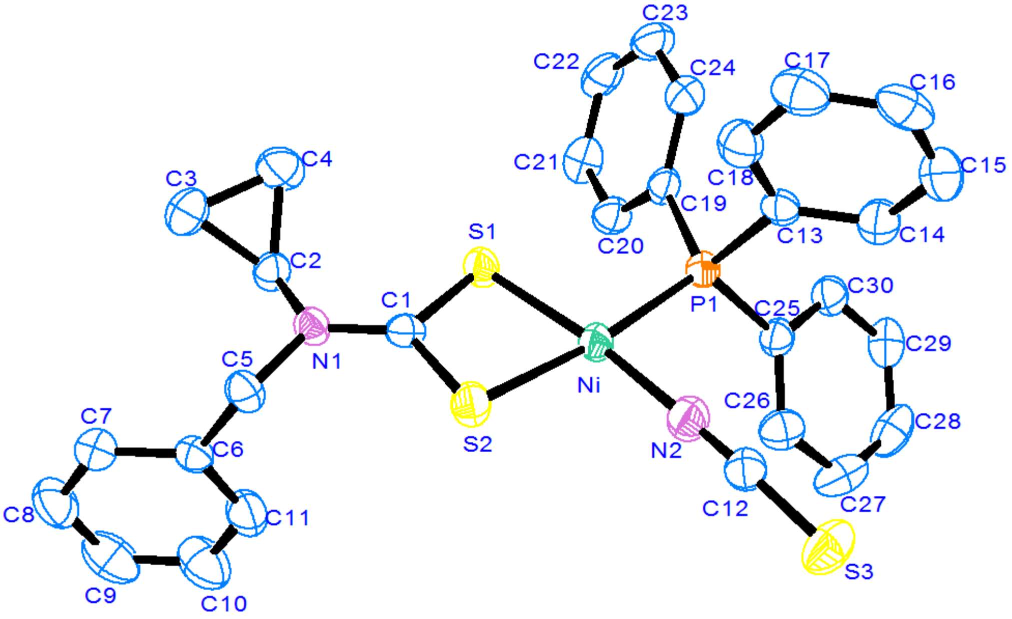


Figure 1: ORTEP diagram of **2**

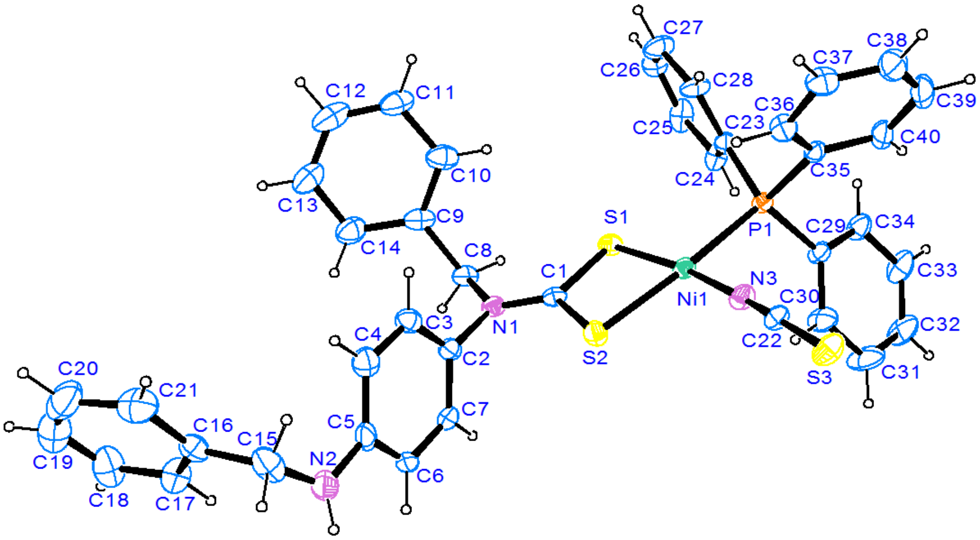


Figure 2 ORTEP diagram of **4**

Table 1 Crystal Structure and Data Refinement Parameters for **2** and **4**

Compound	**2**	**4**
Empirical formula	$C_{30}H_{27}N_2NiPS_3$	$C_{40}H_{34}N_3NiPS_3$
Formula Weight	601.40	742.56
Crystal system / Space group	Triclinic / $P\bar{1}$	Monoclinic / Cc
a/Å	10.3295(5)	18.167(5)
b/Å	11.2565(6)	11.948(5)
c/Å	13.9232(7)	20.977(5)
α/°	100.845 (4)	90.000(5)
β/°	101.311(4)	123.590(5)
γ/°	109.455(4)	90.000(5)
V/Å^3	1439.47(13)	3793(2)
Z	2	4
Dcalc (g/cm^3)	1.388	1.300
μ (cm^{-1})	0.969	0.750
Crystal size (mm)	0.35× 0.25× 0.20	0.25 × 0.20 × 0.20
Color / Shape	Brown / prismatic	Brown/ block

Temp (K)	100(2)	293(2)
Theta range for collections	4.23-29.47	3.41-32.32
Reflections collected	6541	8190
Independent reflections	4724	4278
Data / restraints / parameters	6541/0/ 442	8190/2/ 438
Goodness of fit on F^2	1.135	0.854
Final R indicates I> 2σ(I)	4724	4278
R indicates (all data)	0.0431, 0.0908	0.0546, 0.1419
Largest difference peak / hole	0.478, -0.411	0.556,-0.547

Table 2 Selected bond distances (Å) and angles (°) for **2**

Bond distance (Å)		**Bond angle (°)**	
Ni–S1	2.1742(7)	N2–Ni–S1	172.47(8)
Ni–P1	2.1854(8)	N2–Ni–P1	91.96(8)
Ni–S2	2.6159(8)	S1–Ni–P1	95.56(3)
Ni–N2	1.866(2)	N2–Ni–S2	93.49(8)
N1–C1	1.314(3)	S1–Ni–S2	78.97(3)
N2–C12	1.152(3)	P1–Ni–S2	173.13(3)
S1–C1	1.720(3)	N2–C12–S3	178.3(3)
S2–C1	1.710(3)	S2–C1–S1	108.96(15)
S3–C12	1.625(3)	C1–S1–Ni	86.53(9)
		C1–S2–Ni	85.47(10)

Table 3 Selected bond distances (Å) and angles (°) for **4**

Bond distances (Å)		**Bond angles (°)**	
C1–N1	1.285(6)	N1–C1–S2	126.1(4)
C1–S2	1.721(5)	N1–C1–S1	126.0(4)
C1–S1	1.739(5)	S2–C1–S1	107.8(3)
C2–N1	1.458(7)	N3–C22–S3	178.9(4)
C5–N2	1.391(9)	C1–N1–C2	117.5(4)
C8–N1	1.474(6)	C1–N1–C8	123.5(4)
C15–N2	1.425(11)	C2–N1–C8	119.0(4)
C22–N3	1.160(6)	C5–N2–C15	124.4(7)
C22–S3	1.616(5)	C35–P1–C23	105.5(2)
C23–P1	1.822(5)	C35–P1–C29	107.3(2)
C29–P1	1.821(5)	C23–P1–C29	107.7(2)
C35–P1	1.818(5)	C35–P1–Ni1	113.55(16)
P1–Ni1	2.2032(14)	C23–P1–Ni1	111.75(16)
S1–Ni1	2.1914(15)	C29–P1–Ni1	110.74(17)
S2–Ni1	2.2095(15)	C1–S1– Ni1	86.64(17)
N3–Ni1	1.856(5)	C1–S2–Ni1	86.50(18)
		C22–N3–Ni1	175.7(4)
		N3–Ni1–S1	172.08(15)
		N3–Ni1–S2	93.19(15)
		S1–Ni1–S2	78.90(5)
		N3–Ni1–P1	93.70(15)
		S1–Ni1–P1	94.22(5)
		S2–Ni1–P1	173.04(6)

Table 4 Comparison of bond distances (Å) and angles (°)

S.No	Complex	Ni–S1	Ni–S2	**C–N**	C–S	**S–Ni–S**	**Ni–S–C**	**N–C–S**	S–C–S	Ref
1.	$[Ni(bfdtc)_2]$	2.1914(14)	2.2073(13)	1.303(5)	1.718(4)	79.25(4)	85.61(15)	125.3(3)	109.5(2)	7
2	$[Ni(bfdtc)(NCS)(PPh_3)]$	2.1841(8)	2.2202(10)	1.322(3)	1.708(3)	78.51(3)	86.08(10)	125.36(11)	109.31(16)	
3	$[Ni(dbpdtc)_2]$	2.1831(10)	2.2061(10)	1.316(4)	1.714(4)	79.48(3)	85.11(13)	125.05(3)	109.9(2)	8
4	$[Ni(dbpdtc)(NCS)(PPh_3)]$	2.1914(15)	2.2095(15)	1.285(6)	1.730(5)	78.90(5)	86.57(18)	126.05(4)	107.8(3)	This work
5	$[Ni(thqdtc)_2]$	2.1941(6)	2.1968(5)	1.326(3)	1.717(2)	79.34(2)	85.59(7)	125.26(16)	109.46(11)	9
6	$[Ni(thqdtc)(NCS)(PPh_3)]$	2.2068(5)	2.1648(5)	1.316(2)	1.7115(17)	78.58(2)	86.59(6)	126.0(13)	107.96(9)	
7	$[Ni(thiqdtc)_2]$	2.208(1)	2.198(1)	1.315(4)	1.716(3)	79.02(5)	85.73(2)	125.3(3)	109.52(18)	10
8	$[Ni(thiqdtc)(NCS)(PPh_3)]$	2.2183(7)	2.1620(7)	1.315(3)	1.712(3)	79.06(3)	85.90(9)	125.45(2)	109.07(14)	11
9	$[Ni(achdtc)_2]$	2.2081(10)	2.1897(10)	1.316(4)	1.723(4)	79.42(3)	85.58(12)	125.4(3)	109.22(19)	12
10	$[Ni(achdtc)(NCS)(PPh_3)]$	2.1674.(5)	2.2299(5)	1.316(2)	1.7196(16)	78.80(16)	86.29(6)	125.73(12)	108.53(9)	
11	$[Ni(echdtc)_2]$	2.2108(4)	2.2004(5)	1.319(2)	1.7242(17)	79.188(16)	85.77(6)	125.38(13)	109.23(9)	13
12	$[Ni(echdtc)(NCS)(PPh_3)]$	2.1779(7)	2.2127(7)	1.316(3)	1.717(3)	78.63(3)	86.58(9)	125.9(2)	108.21(4)	
13	$[Ni(bzcprdtc)(NCS)(PPh_3)]$	2.1742(7)	2.1854(8)	1.314(3)	1.715(3)	78.97(3)	86.00(10)	124.4(2)	108.96(15)	This work