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Synthesis, spectral (IR, UV–Vis and variable temperature NMR) characterization and crystal structure of (N-benzyl-N-furfuryldithicarbamato-S,S') (thiocyanato-N)(triphenylphosphine)nickel(II)



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HIGHLIGHTS

- Ni(bzfdtc)(NCS)(PPh₃) (1) (bzfdtc = Nbenzyl-N-furfuryldithiocarbamate) was prepared.
- 1 was characterized by IR, UV-Vis, CV, variable temp. NMR and X-ray diffraction.
- Ni²⁺ in 1 exists within a S₂PN donor set that defines a square planar geometry.
- In CHCl₃ solution of 1, thiocyanate exchange process occurs at room temperature.
- Ni—S bonds in **1** are asymmetric due to the difference in trans effect of PPh₃ and NCS⁻.

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ABSTRACT

Planar (N-benzyl-N-furfuryldithiocarbamato-S,S')(thiocyanato-N)(triphenylphospine)nickel(II), [Ni (bfdtc)(NCS)(PPh₃)], (1) was prepared from bis(N-benzyl-N-furfuryldithiocarbamato-S,S')nickel(II), [Ni(bfdtc)₂], (2) and characterized by elemental analysis, cyclic voltammetry, electronic, IR and variable temperature ¹H and ¹³C NMR spectra. For complex **1**, the thioureide vC-N value is shifted to higher wavenumber compared to 2 and N¹³CS₂ carbon signal observed for 1 is additionally shielded compared to the parent complex **2**, suggesting increased strength of the thioureide bond due to the presence of the π -accepting phosphine. In the room temperature ¹³C NMR spectrum of **1**, two pseudo doublets are observed in the aliphatic region. Variable temperature ¹³C NMR spectral studies suggest that the fast thiocyanate exchange appears to be responsible for the appearance of pseudo doublets. Single crystal X-ray structural analysis of 1 and 2 confirm the presence of four coordinated nickel in a distorted square planar arrangement with the NiS₂PN and NiS₄ chromophores, respectively. The Ni–S bonds are symmetric in 2 (2.1914(14) and 2.2073(13) Å). But significant asymmetry in Ni–S bond distances was observed in 1 (2.2202(8) Å and 2.1841 Å). This observation clearly supports the less effective trans effect of SCN⁻ over PPh₃. Cyclic voltammetric studies revealed easier reduction of nickel(II) to nickel(I) in complex 1 compared to 2.

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Introduction

Dithiocarbamate complexes of various metal ions are used in analytical chemistry [1,2], organic synthesis [3], medicine [4], biology [5], as oxidants of organic molecules [6], polymer photostabilizers [7], and precursors for preparing metal sulfide nanoparticles [8,9]. Optical and electrochemical properties of metal-dithiocarbamate complexes favour the creation of cation, anion and neutral molecule sensors [10-13]. Nickel(II) complexes of the type Ni(dtc)₂ have a mononuclear square planar structure [14]. Ni(dtc)₂ complexes are found to show interesting variations in reactivity towards soft Lewis bases such as phosphines [15] and hard bases such as nitrogenous ligands [16]. Complexes containing the NiXS₂P chromophore have shown catalytic activity, especially for oligomerization of olefins [17,18]. In the dithiocarbamate complexes, the R^1 , R^2 groups in the S₂CNR¹R² moiety influence the stability, structure, physico-chemical and biological properties of the complexes [19]. Suitable changes in substituents at the nitrogen of dithiocarbamate can markedly affect the properties of the complexes [20]. At room temperature, no ligand exchange process was observed in [Ni(dtc)(NCS)(PPh₃)] [4]. In the case of $[Ni(S_2CNR_2)(PPh_3)X]$ (R = Et and X = Cl, I, SCN), the ligand (X) exchange process was observed at low temperature (-60 °C) [21]. The aim of the present work was a detailed study of the coordination complex 1 to investigate the ligand exchange process and to determine the effect of P-donor atom on the structure. In this paper, we report synthesis, cyclic voltammetry, spectral and structural studies on complexes 1 and 2. The study of ligand exchange process using variable temperature NMR spectra is also presented.

Experimental

General

All reagents and solvents were commercially available highgrade materials (Merck/sd Fine/Hi media) and used as received. A Shimadzu UV-1650 PC double beam UV-Vis spectrometer was used for recording the electronic spectra. The spectra were recorded in CHCl₃ and the pure solvent was used as the reference. Cyclic voltammograms were recorded on a CHI604C Electrochemical Analyzer. The working electrode was platinum. The counter electrode was platinum wire, and reference electrode was Ag/AgCl. Pure dichloromethane was used as the solvent and tetrabutylammonium perchlorate as the supporting electrolyte. The scan rate was 100 mVs⁻¹. All the measurements were recorded at room temperature (27 °C) in an oxygen free atmosphere, provided by bubbling purified nitrogen through the solution. IR spectra were recorded on a Thermo Nicolet Avatar 330 FT-IR spectrophotometer (range 400–4000 cm⁻¹) as KBr pellets. Elemental analysis was performed using Perkin Elmer 2400 series II CHN analyzer. The NMR spectra were recorded on AV-III 400 NMR spectrometer operating at 400 MHz.

Preparation of Complexes

Preparation of amine

N-Benzyl-N-furfurylamine was prepared by general methods reported earlier [22].

Preparation of [Ni(bfdtc)₂] (2)

N-Benzyl-N-furfurylamine (4.0 mmol, 0.75 g) in ethanol was mixed with carbon disulfide (4.0 mmol, 0.3 mL) under ice cold condition. To the resultant yellow dithiocarbamic acid solution, aqueous solution of NiCl₂·6H₂O (2.0 mmol, 0.47 g) was added with constant stirring. The solid which precipitated was washed several



Scheme 1. Preparation of 1.

times with cold water and then dried [23]. Single crystals suitable for X-ray structure analysis were obtained by the recrystallization from a solution of the substance in a mixture of dichloromethaneacetonitrile (1:1).

IR (KBr, cm⁻¹): $v = 1499 (v_{C-N})$, 1012 (v_{C-S}). UV–Vis (CHCl₃, nm): $\gamma = 642$, 489, 430, 390, 326, 256. ¹H NMR (400 MHz, CDCl₃, ppm): $\delta = 4.67$ (s, N–CH₂–C₆H₅), 4.82 [s, CH₂ (furfuryl)], 6.38–7.42 (aromatic protons). ¹³C NMR (101 MHz, CDCl₃, ppm): $\delta = 43.4$ (N– CH₂–C₆H₅), 51.3 [CH₂ (furfuryl)], 110.7, 110.8, 143.1, 147.5 (furyl ring carbons), 128.4–133.9 (phenyl ring carbons), 209.4 (NCS₂).

Preparation of complex [Ni(bfdtc)(NCS)(PPh₃)] (1)

A mixture of $[Ni(bfdtc)_2]$ (1.0 mmol, 0.583 g), PPh₃ (2.0 mmol, 0.524 g), NiCl₂·6H₂O (1.0 mmol, 0.238 g) and NH₄SCN (2.0 mmol, 0.152 g) was refluxed for 3 h in chloroform—methanol solvent mixture (1:1, 50 mL). The purple-red solution obtained was filtered and left for evaporation. After 2 days, a purple-red solid separated out. Single crystals suitable for X-ray structural analysis were obtained by the recrystallization from dichloromethane-acetonitrile (1:2) solvent mixture (Scheme 1).

Yield: 58%, mp 188 °C. IR (KBr, cm⁻¹): *ν* = 2094 (NCS), 1514 (*ν*_{C−N}), 1017 (*ν*_{C−S}). UV–Vis (CHCl₃, nm): *γ* = 485, 331, 251. ¹H NMR (400 MHz, CDCl₃, ppm): *δ* = 4.44–4.76 (four broad signals overlapped to appear as a triplet, CH₂), 6.17–7.78 (aromatic protons). ¹³C NMR (101 MHz, CDCl₃, ppm): *δ* = 43.2, 43.6 (N–CH₂–C₆H₅), 51.2, 51.7 [CH₂ (furfuryl)], 110.7, 111.3, 143.3, 146.7 (furyl ring carbons), 143.9 (NCS), 127.8–134.1 (phenyl ring carbons), 206.0 (NCS₂). ³¹P NMR (CDCl₃, ppm): *δ* = 22.2 (PPh₃). Anal. Calcd. for C₃₂H₂₇N₂S₃OPNi (%): C, 59.92; H, 4.24; N, 4.37. Found (%): C, 59.84; H, 4.16; N, 4.37.

X-ray crystallography

Details of the crystal data, data collection and refinement parameters for **1** and **2** are summarized in Table 1. Intensity data were collected at ambient temperature (293(2) K) on Oxford diffraction 'Xcalibur, Sapphire3' using graphite monochromated Mo K α radiation (γ = 0.71073 Å). The structures of **1** and **2** were solved by SIR-92 [24] and SHELXS-97 [25] respectively and refined by full matrix least square with SHELXL-97 [24]. All the non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. Selected bond distances and angles are given in Table 2.

3. Results and discussion

3.1. Infrared spectral studies

As concerns the dithiocarbamate moiety, two main regions of the IR are of interest: first the 1450–1580 cm⁻¹ region, which is primarily associated with the "thioureide" band due to the $v(N-CS_2)$ vibration; second, the 940–1060 cm⁻¹ region which is associated with the v(C-S) vibrations. Dithiocarbamate compounds exhibit a characteristic band at around 1500 cm⁻¹ assignable to $v(N-CS_2)$, this band defines a carbon-nitrogen bond order between a single bond (1250–1350 cm⁻¹) and a double bond (1640–1690 cm⁻¹) [26] (Scheme 2 [27,28]). IR spectra of the complexes **1** and **2** show $v(N-CS_2)$ bands at 1514 and 1499 cm⁻¹, respectively, indicating the partial double bond character. The mesomeric drift of electrons from the dithiocarbamate moiety towards the metal increases the contribution of the canonical form (c). This is reflected in the shift in $v(N-CS_2)$ value of **1** to higher wavenumber when compared with that observed in 2. The v(C-S) bands appear around 1000 cm⁻¹ without any splitting, supporting the bidentate coordination of the dithiocarbamte moiety [29]. The observed stretching frequency at 2094 cm^{-1} for complex **1** is attributed to the 'N' coordinated thiocyanate anion.

Electronic spectral studies

The observed band at 485 nm for complex **1** can be attributed to the d-d electron transitions for nickel(II) complexes that contain the NiS₂PN chromophore [30]. The electronic spectrum of **2** shows two bands (489 and 642 nm) that are typical for square planar Ni(dtc)₂ complexes and are assigned to d-d transition. The band

Table 1

Crystal data, data collection and refinement parameters for 1 and 2.

Table 2

Selected bond lengths (Å) and bond angles (°) of **1** and **2**.

1		2	
Bond lengths			
Ni—N2	1.861(3)	S1-Ni1	2.1914(14)
Ni—S1	2.1841(8)	S2-Ni1	2.2073(13)
Ni-P1	2.2135(8)	C13—S1	1.710(4)
Ni—S2	2.2202(8)	C13—S2	1.726(4)
S2-C19	1.702(3)	C13-N1	1.303(5)
S1-C19	1.714(3)	C7—N1	1.483(6)
S3-C32	1.617(3)	C8-N1	1.471(6)
C19–N1	1.322(3)	-	-
N2-C32	1.153(4)	-	-
Bond angles			
N2-Ni-S1	171.02(8)	S1-Ni1-S1 ⁱ	180.00(6)
N2-Ni-P1	95.39(8)	S1-Ni1-S2 ⁱ	100.75(4)
S1—Ni—P1	92.70(3)	S1-Ni1-S2	79.25(4)
N2-Ni-S2	93.21(8)	S2-Ni1-S2 ⁱ	180
S1—Ni—S2	78.51(3)	C13-S1-Ni1	86.04(15)
P1—Ni—S2	170.79(3)	C13-S2-Ni1	85.17(15)
S2-C19-S1	109.31(16)	S1-C13-S2	109.5(2)



Scheme 2. Resonance structures of dithiocarbamate (NCS₂) moiety.

at 390 nm is assigned to the charge transfer transition. This band is also observed in the spectra of square planar nickel(II) in the dithiocarbamate complexes. The bands below 350 nm are connected with intraligand transitions in the S_2CN^- group [31].

NMR spectral studies

NMR spectra were recorded using TMS as internal reference. $CDCl_3$ was used as solvent. The ¹³C NMR spectra were recorded in the proton decoupled mode.

	1	2
	1	2
Empirical formula	C ₃₂ H ₂₇ N ₂ NiOPS ₃	$C_{26}H_{24}N_2NiO_2S_4$
FW	641.45	583.42
Crystal dimensions (mm)	$0.30\times0.25\times0.20$	$0.22\times0.20\times0.20$
Crystal system	Triclinic	Monoclinic
Space group	P-1	C2/c
a (Å)	10.1501(6)	16.095(5)
b (Å)	12.2115(6)	9.431(5)
<i>c</i> (Å)	13.7059(9)	18.248(5)
α (°)	96.070(4)	90.000(5)
β (°)	105.169(5)	107.018(5)
γ (°)	109.093(4)	90.000(5)
V (Å ³)	1514.95(15)	2648.6(18)
Ζ	2	4
Dc (g cm ⁻³)	1.406	1.463
μ (cm ⁻¹)	0.928	1.075
F(000)	664	1208
γ (Å)	Μο Κα (0.71073)	Μο Κα (0.71073)
θ Range (°)	3.12-32.26	3.17-32.51
Index ranges	$-14 \leqslant h \leqslant 12$, $-13 \leqslant k \leqslant 18$, $-20 \leqslant l \leqslant 19$	$-23 \leqslant h \leqslant 21, -13 \leqslant k \leqslant 14, -26 \leqslant l \leqslant 26$
Reflections collected	16795	9176
Observed reflections $[I > 2\sigma(I)]$	9660	4189
Weighting scheme	Calc. $W = 1/(\sigma^2(F_o^2) + (0.1000p)^2 + 0.8337p)$ where $p = (F_o^2 + 2F_c^2)/3$	Calc. $W = 1/(\sigma^2(F_0^2) + (0.0931p)^2 + 0.0000p)$ where $p = (F_0^2 + 2F_c^2)/3$
Number of parameters refined	363	172
$R[F^2 > 2\sigma(F^2)], wR(F2)$	0.0548, 0.1178	0.0793, 0.2008
GOOF	0.817	0.953



Fig. 1. Variable temperature ¹H NMR spectra of 1 at (a) room temperature, (b) 35 °C (c) 45 °C and (d) 55 °C.

¹H, ¹³C and ³¹P NMR spectral studies ¹H NMR and ¹³C NMR analysis of the **1** and **2** show good agree-ment with other data to characteristize the structures of the complexes. The $N^{13}CS_2$ carbon signal for the **1** is observed at 209.4 ppm

with an upfield shift of about 3.4 ppm compared with that found in 2 (206.0 ppm). The observed shielding in 1 indicates the effect of PPh3 on the mesomeric drift of electron density toward nickel through the thioureide C-N bond. There is a strong empirical



correlation between δ (N¹³CS₂) values and the carbon–nitrogen stretching vibration in the infrared spectra: the higher $v(N-CS_2)$ values indicate an increased carbon–nitrogen double bond character, which well correlates with lower δ (N¹³CS₂) values because of a greater electron density on the NCS₂ moiety. In a semi empirical way, δ (N¹³CS₂) could be expressed as a linear function of the sum of CN, CS1 and CS2 π -bond orders, and $v(N-CS_2)$ as a linear function of the C–N π -bond order [32]. The sum of the π -bond order is derived to be maximal for equal π -bonds and to decrease with increasing in equality of the three π -bonds. Therefore, the compounds with high N–CS₂ values have low CS and low total π -bond order, thus leading to low δ (N¹³CS₂) values and *vice versa*.

³¹P chemical shift is observed at 22.2 ppm for complex **1**. A good extent of deshielding of 27 ppm is observed for the ³¹P signal of

complex **1** compared to the free PPh₃ signal observed at -5 ppm [33]. A very high deshielding of signal observed for **1** is attributed to the movement of electron density from the phosphorus towards the nickel atom on complexation.

Variable temperature ¹H NMR spectral studies on **1**

Variable temperature ¹H NMR spectra of [Ni(bfdtc)(NCS)(PPh₃)] are given in Fig. 1. In the case of [Ni(bfdtc)(NCS)(PPh₃)], two singlets are expected for methylene protons of benzyl and furfuryl groups of bfdtc in the aliphatic region. But at room temperature (21.9 °C) four lines are observed in the region 4.44–4.76 ppm, while when the temperature is increased, the spectral lines merged and at 55 °C two spectral lines (broad doublet) are observed. The fast isothiocyanate ligand exchange appears to be responsible for



Fig. 3. Cyclic voltammograms of (a) 1 and (b) 2.

this process. The aromatic protons are not discussed because of their complicated multiplets.

Similar ligand exchange was reported for $[Ni(S_2CNR_2)(PPh_3)X]$ (R = Et and X = Cl, I, SCN) complexes [21]. In these complexes, at -60 °C two different R resonances are observed. But at room temperature one *R* resonance is observed. In this complex, the fast ligand (*X*) exchange process occurs only at low temperature (-60 °C). But in the case of **1**, the fast isothiocyanate ligand exchange process occurs at room temperature. This indicates that the N-bound organic moiety in dithiocarbamate ligand affects the properties of the complex.

Variable temperature ¹³C NMR spectral studies on [Ni(bfdtc)(NCS)(PPh₃)]

¹³C NMR spectra of [Ni(bfdtc)(NCS)(PPh₃)] at room temperature and 55 °C are shown in Fig. 2. In the case of [Ni(bfdtc)(NCS)(PPh₃)], two signals are expected for methylene carbons of benzyl and furfuryl groups of bfdtc. But at room temperature (21.9 °C) two pseudo doublets are observed at 43.4 (43.6 and 43.2 ppm) and 51.5 ppm (51.7 and 51.2 ppm), while when the temperature is increased to 55 °C, the doublet merged and only two signals are observed. The fast isothiocyanate ligand exchange appears to be responsible for this process.

When ethanol was added to a chloroform solution of $[Ni(bfdtc)(NCS)(PPh_3)]$, the purple-red colour changed immediately to greenish yellow. After the mixture stood overnight, a deep green precipitate formed. The precipitate was identified as $[Ni(bfdtc)_2]$ by comparing its melting point with those of authentic sample. As expected for a ligand dissociation process, the compounds were sensitive to the nature of the solvents present.

Cyclic voltammetric studies

Both compounds are found to undergo a single electron reduction process in the potential range 0 to -1.6 V. Cyclic voltammograms are given in Fig. 3. The reductions are irreversible. The reduction potentials for **1** and **2** are observed at -931 and -1141 mV, respectively. The lower reduction potential observed for heteroleptic complex **1** indicates the ease of electron addition in the heteroleptic complex because of the presence of PPh₃ around the nickel atom [34]. Based on IR and ¹³C NMR spectral studies, C—N thioureide in **1** has maximum double bond character and hence, complex **1** is expected to be more difficult to reduce; in reality, however, complex **1** is more easily reduced than the parent complex **2**, probably because of the extensive π -back bonding with phosphorus atom which drains the excess negative charge on the metal and hence lowers the reduction potential.

Structural analysis

The ORTEP diagram of the **1** is shown in Fig. 4. Complex **1** is monomeric and discrete. In this complex, nickel cation is coordinated by two sulfur atom from N-benzyl-N-furfuryl dithiocarbamate, one nitrogen atom from the thiocyanate and one phosphorus atom from PPh₃ into a distorted square planar configuration. The angles S1–Ni–P1 [92.70(3)°]; N2–Ni–P1 [95.39(8)°] and N2–N1–S2 [93.21(8)°] are less distorted from the 90° than the angle S1–Ni–S2 [78.51(3)°]. The S1–Ni–S2 angle is smaller



Fig. 4. ORTEP diagram of 1.



Fig. 5. ORTEP diagram of 2.

than 90° due to the chelation of the N-benzyl-N-furfuryldithiocarbamate. The Ni—S bonds in [Ni(bfdtc)(NCS)(PPh₃)] are asymmetric. The asymmetry has been explained based on the differences in the trans influence exerted by PPh₃ and NCS⁻. PPh₃, being a good π acceptor has a greater trans influence and hence the Ni—S bonds trans to PPh₃ is longer than the other Ni—S bond.

A short Ni—P distance [2.2135(8) Å], shows a better bonding and back bonding interaction between Ni and P in the complex. The other parameters of the phenyl rings are normal and observed average P—C distance is 1.815(3) Å. The C—P—C angles deviate appreciably from the tetrahedral angle and the crowding of the phenyl ring causes the P—C—C angles to be asymmetric. The Ni—N distance [1.816(3) Å] is siginificantly shorter than the distance reported for the octahedral [Ni(en)₂(NCS)₂] (2.15 Å) [35] which shows the effective bonding between the nickel atom and NCS⁻. In the isothiocynate part, the N—C—S bond angle is almost linear [N—C—S = 178.1(3)°]. The C—N bond distance in thiocyanate is [1.153(4) Å] which is shorter than that of thioureide N—C bond distance of 1.322(3) Å. The C—S bond length in the thiocyanate group is 1.617(3) Å, which is similar to the C=S distance of 1.69 Å.

The ORTEP diagram of **2** is shown in Fig. 5. Complex **2** is monomeric with eight molecules per unit cell. The Ni(II) cation is coordinated with the four sulfur atoms of the two N-benzyl-N-fur-furyldithiocarbamate ligands. The nickel lies on an inversion centre with a distorted square planar environment of the NiS₄ chromophore. Because of the small bite angles associated with the dithio-carbamate moiety [S–Ni–S = 79.25(4)°], the NiS₄ chromophore is not perfectly square planar arrangement. The torsion angles, S1–C13–N1–C89 [–174.9(3)°]; S2–C13–N1–C8 [5.3(6)°]; S1–C13–N1–C7 [2.8(6)°]; S2–C13–N1–C7 [–177.1(3)°] confirm the near planarity of the S₂CN moiety. The near equality of the two Ni–S distances confirms the isobidendate coordination of the dithiocarabamate group. The crystal structure of a triclinic polymorph of complex **2** has been reported recently [23].

In complexes **1** and **2**, the dithiocarbamate ligands are bidentate, giving four membered chelate rings [NiS₂C]. Their planar geometry is supported by the corresponding torsion angles which are close to 0 or 180°. The C—S bonds observed in **1** [1.708(3)Å] and **2** [1.718(4)Å] are similar to those observed in the other dithiocarbamate complexes, which confirms the considerable double bond character associated with C–S bonds. The short thioureide C–N distances, 1.322(3) and 1.303(5) Å of **1** and **2**, respectively, indicate the π electron density delocalized over the S₂CN moiety and this thioureide bond has a significant double bond character.

Conclusions

The crystalline compounds **1** and **2** were prepared and their structures and properties were characterized by cyclic voltammetry, IR, electronic, ¹H and ¹³C NMR spectroscopy. The Ni(II) ion in complex **1** is four coordinated with two sulfur, one phosphorus and one nitrogen atoms and giving to a distorted square planar arrangement. Variable temperature ¹H and ¹³C NMR spectral studies show that the ligand exchange process occurs at room temperature in **1**. This supports that N-bound organic moieties (R¹ and R²) in dithiocarbamate ligand (R¹R²NCS₂) influence the properties of the complexes.

Appendix A

Crystallographic data have been deposited with the Cambridge Crystallographic Centre as supplementary publication number CCDC-962918 and 962942 for **1** and **2**, respectively. Copies of the data can be obtained free of charge an application to CCDC, 12 Union Road, Cambridge CBZ 1FZ, UK.

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