# Synthesis, Spectral, Cyclic Voltammetric Studies, and Single Crystal X-Ray Structure Determination of the Planar NiS<sub>2</sub>P<sub>2</sub>, NiS<sub>2</sub>PN, and NiS<sub>2</sub>PC Chromophores

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Abstract. Synthesis, spectral and cyclic voltammetric characterization of  $[Ni(dedtc)(4-MP)_2](ClO_4)$  (1), [Ni(dedtc)(4-MP)(NCS)](2),  $[Ni(dedtc)(PPh_3)(NCS)]$  (3) and  $[Ni(dedtc)(PPh_3)(CN)]$  (4) (dedtc = diethyldithiocarbamate, 4-MP = tri(4-methylphenyl)phosphine, PPh<sub>3</sub> = triphenylphophine) are reported. IR spectra of complexes 1- 4 show the characteristic thioureide (C-N) bands at higher wave numbers compared to that of the parent dithiocarbamate complex [Ni(dedtc)<sub>2</sub>]. The d-d transitions are observed in the region 452-482 nm. The CV studies clearly show the presence of reduced electron density on the nickel ions in mixed ligand complexes **1-4** compared to the parent dithiocarbamate. Single crystal X-ray structure studies show all the complexes to containplanar NiS<sub>2</sub>P<sub>2</sub>, NiS<sub>2</sub>PN, and NiS<sub>2</sub>PC chromophores in keeping with the observed diamagnetism. In all the complexes the Ni-S distances are asymmetric. The thioureide C-N distance of the complexes **1-4** are less thanthe C-N distance observed in the parent [Ni(dedtc)<sub>2</sub>].

Keywords: Nickel; Dithiocarbamates; Cyanide; Crystal structures

## Synthese, Spektroskopie, Cyclovoltammetrie und Einkristall-Strukturanalysen von planaren $NiS_2P_2$ -, $NiS_2PN$ - und $NiS_2PC$ -Chromophoren

Inhaltsübersicht. Es wird über die Synthese, die spektroskopische und cyclovoltammetrische Charakterisierung von [Ni(dedtc)-(4-MP)<sub>2</sub>](ClO<sub>4</sub>) (1), [Ni(dedtc)(4-MP)(NCS)] (2), [Ni(dedtc)(PPh<sub>3</sub>)-(NCS)] (3) und [Ni(dedtc)(PPh<sub>3</sub>)(CN)] (4) (dedtc = diethyldithiocarbamat, 4-MP = Tri(4-methylphenyl)phosphin, PPh<sub>3</sub> = Triphenylphosphin) berichtet. Die IR-Spektren der Komplexe 1-4 zeigen die charakteristische Thioharnstoff-(CN)-Bande bei größeren Wellenzahlen verglichen mit dem homoleptischen Dithiocarbamat-Komplex [Ni(dedtc)<sub>2</sub>]. Die d-d-Übergänge werden im Bereich von 452-482 nm beobachtet. Die CV-Untersuchungen zeigen eine deutlich reduzierte Elektronendichte der Nickelionen in den Gemischtligand-Komplexen 1-4 im Vergleich zu [Ni(dedtc)<sub>2</sub>]. Nach den Einkristallstrukturanalysen enthalten alle Komplexe planare NiS<sub>2</sub>P<sub>2</sub>-, NiS<sub>2</sub>PN- und NiS<sub>2</sub>PC-Chromophore, entsprechend ihrem Diamagnetismus. In allen Komplexen sind die Ni-S-Bindungen asymmetrisch. Die Thioharnstoff-CN-Abstände sind in 1-4 kürzer als im Ausgangskomplex [Ni(dedtc)<sub>2</sub>].

#### Introduction

Group X dithiolates containing planar  $MS_4$  chromophores show interestingvariations in their reactions with Lewis bases [1, 2]. Soft Pd<sup>II</sup> and Pt<sup>II</sup> dithiolates preferably interact with soft phosphines to give rise to planar  $MS_2P_2$  chromophores [3, 4]. Unlike its congeners, Ni<sup>II</sup> is a border line acceptor. Ni<sup>II</sup> complexes of dithiocarbamates are typical complexes containing planar NiS<sub>4</sub> chromophores. The planar dithiocarbamates prefer to react with soft Lewis bases such as phosphines and border line bases like isothiocyanate and cyanide rather than hard nitrogenous bases such as NH<sub>3</sub> and pyridine, due to symbiotically induced softness [5, 6]. On reaction with  $PR_3$ , they form complexes with chromophore  $NiS_2P_2$  which are diamagnetic in nature [7 - 9].Mixed ligand complexes of the type  $[Ni(dtc)(PR_3)(X)]$  were obtained by reacting NiX<sub>2</sub> with dithiocarbamate and PR<sub>3</sub> [10]. Complexes of the type  $[Ni(dtc)(PPh_3)Cl]$  and  $[Ni(dtc)(PPh_3)_2](ClO_4)$  (dtc =  $(H_5C_2)_2NCS_2^-$ ,  $(H_{10}C_5)NCS_2^ (Pr^i)_2NCS_2^-$ ,  $HOH_4C_2^ (CH_3)NCS_2^{-}$ ) have also been reported from our laboratory [11-16]. Recently, single crystal X-ray structural study of  $[Ni(dnpdtc)(PPh_3)_2](ClO_4)$  (dnpdtc = di-*n*-propyldithiocarbamate anion) complex has also been reported [17]. In this paper, we report the synthesis, spectral, CV studies and single crystal X-ray structure analysis of the complexes 1 - 4.

#### **Results and Discussion**

#### IR and electronic spectra

IR spectra of the complexes 1 - 4 show thioureide (C-N) bands at 1538, 1532, 1537 and 1525 cm<sup>-1</sup>, respectively. The

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shift in  $v_{C-N}$  bands to higher frequencies compared to the parent [Ni(dedtc)<sub>2</sub>] (1519 cm<sup>-1</sup>) is due to the mesomeric drift of electron density from the dithiocarbamate moiety towards the nickel ions. The  $v_{C-N}$  bands appear at around 995 cm<sup>-1</sup>, without any splitting, supporting the isobidentate coordination of the dithiocarbamate moiety [18]. IR spectra also show strong bands around 2100, and 2098 cm<sup>-1</sup> in complex **2** and **3**, respectively, which correspond to the N-coordinated thiocyanate [19]. In complex **4**, a band of medium intensity at 2112 cm<sup>-1</sup> indicate the presence of C-coordinated cyanide ion [19]. The electronic absorption bands at 482, 478and 480 nm in complexes **1-3**, respectively, are due to d-d transitions [20]. The yellow orange complex **4** gives d-d band at 452 nm.

#### Cyclic voltammetry

All the complexes show metal centered one-electron reduction processes [20]. Parent [Ni(dedtc)<sub>2</sub>] showes a large irreversible reduction potential relatively in keeping with its reluctance to add electron density to already electron rich metalcenter. Complex 1 with two phosphine groups shows a relatively higher potential than the complexes 2, 3, and 4. Following is the increasing order of reduction potentials(mV): -1506(2) < -1510(4) < -1515(3) < -1522(1) < -1584 [Ni(dedtc)<sub>2</sub>].

#### Nuclear magnetic resonance spectra

The <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR chemical shift values are given in Table 1 with splitting patterns.

#### $^{1}H NMR$

For the ionic complex 1, ethyl groups are equivalent and hence only one triplet for methyl and a quartet for methyl-

Table 1 Chemical shift values / ppm

ene are obtained at 1.2 and 3.5 ppm, respectively. For the neutral complexes **2**, **3 and 4**, the ethyl groups are nonequivalent and hence methyl and methylene protons are split into a doublet of triplet and a doublet of quartet, respectively, indicating a substantial barrier to C-N bond rotation. The methylene protons adjacent to nitrogen atom undergo strong deshielding to give signal at 3.5 ppm. A multiplet in the region of 7.20 - 7.60 ppm is due to aromatic protons. Methyl protons attached to phenyl rings appear at 2.3 ppm.

#### $^{13}C NMR$

From the <sup>13</sup>C NMR spectra of complexes, the chemical shifts of the thioureide carbon atom are correlated to the  $\pi$ -bonding in the NCS<sub>2</sub><sup>-</sup> fragment [20]. Generally higher  $v_{C-N}$  values correlate with lower NCS<sub>2</sub><sup>-</sup> ppm values for dblock element [20]. The thioureide carbon atom  $(N^{13}CS_2^{-})$ chemical shifts are observed at 203.0, 202.9 and 203.6 ppm for neutral complexes 2-4, respectively. For ionic complex 1, the  $N^{13}CS_2^{-}$  signal appeared significantly upfield at 198.2 ppm. The alleviation of excess electron density on nickel by phosphine, cyanide and isothiocyanate results in a drift of electron density towards the metal atom through thioureide bond from nitrogen atom and hence a significant shift is observed. Among phosphines, cyanide, and isothiocyanate, phosphines have a maximum back bonding ability. Hence, ionic complex (1) containing two phosphine groups shows signal at 198.2 ppm in the upfield. The isothiocvanate carbon atom shifts in complexes 2 and 3 appear at 143.4 and 143.8 ppm, respectively. Complex 4 gives the cyanide carbon atom shift at 130.5 ppm. Cyanide carbon atom signal merged with the phenyl ring signals in the region of 128-135 ppm. The 4-methyl carbon atom attached to phenyl rings appears at 21 ppm.

Complex	NMR	CH <sub>3</sub>	CH <sub>2</sub>	PPh <sub>3</sub> /4-MP	Phenyl-CH <sub>3</sub>	$NCS_2^-$	NCS <sup>-</sup> /CN <sup>-</sup>
Ni(dedtc) <sub>2</sub>	<sup>1</sup> H <sup>13</sup> C	1.23 12.2	3.65 43.6			206.4	
1	<sup>1</sup> H <sup>13</sup> C <sup>31</sup> P	1.15 12.5	3.56 44.3	7.05-7.37 134.9-124.8 30.91	2.35 21.4	198.2	
2	<sup>1</sup> H <sup>13</sup> C <sup>31</sup> P	1.12, 1.22 12.5, 12.3	3.37, 3.43 43.9, 43.7	7.26-7.76 134.2-128.8 21.72	2.34 21.6	202.9	143.8
3	<sup>1</sup> H <sup>13</sup> C <sup>31</sup> P	1.11, 1.23 12.6, 12.4	3.43, 3.59 43.8, 43.6	7.21-7.62 134.2-125.1 20.03		203.0	143.4
4	<sup>1</sup> H <sup>13</sup> C <sup>31</sup> P	1.13, 1.23 12.6, 12.3	3.55, 3.40 44.0, 43.7	7.26-7.66 134.2-128.6 20.97		203.6	130.5

<sup>1</sup>H and <sup>31</sup>P nmr chemical shifts are listed to  $\pm 0.01$  ppm accuracy and the <sup>13</sup>C nmr chemical shifts to  $\pm 0.1$  ppm accuracy



Fig. 1 ORTEP diagram of [Ni(dedtc)(4-MP)<sub>2</sub>](ClO<sub>4</sub>)

#### C16 C27 C 20 C24 C17 C25 C23 S12 C14 C22 C26 C19 C21 P13 N10 C28 C33 Ni1ı C29 C30 S2ı S3I 🗑 C34 C4

#### $^{31}P NMR$

<sup>31</sup>P NMR show signals at 30.9, 20.3, 21.7 and 21.0 ppm for complexes **1–4**, respectively. The free PPh<sub>3</sub> phosphorus resonates at the more upfield region of -5.8 ppm [21]. A very high deshielding observed in the case of complex **1** indicates the most effective coordination of phosphine to nickel atom. The minimum value observed for NiS<sub>2</sub>PN chromophore with 4-methylphenylphosphine indicates a steric influence on the stability of the compound.

#### X-ray crystal structure analyses

ORTEP diagram of complex 1 is shown in Figure 1. The cation is mononuclear with no significant interionic contacts. Four formula units are present in the unit cell. The nickel atom is coordinated approximately planar in keeping with the observed diamagnetism. It is not of perfect square geometry because of small bite angle  $(78.24(4)^{\circ})$  associated with the dithiocarbamate. The Ni-S bonds, 2.200(1) Å and 2.228(1) Å show clear asymmetry, as reported earlier for similar compounds [11-15]. The bulkiness of phosphine groups is responsible for the asymmetry in the Ni-P distances (2.214(1) Å and 2.236(1) Å) and also an increase in the P-Ni-P angle (98.64(4)°). The asymmetry in the Ni-P bonds reflects on the Ni-S bonds. The thioureide C-N distance is observed to be 1.300(5) A, which is significantly different from the distancein the parent dithiocarbamate [Ni(dedtc)<sub>2</sub>], 1.33(1) A, indicating a mesomeric drift of electron density from the dithiocarbamate moiety towards the nickel atom. The short C-N bond distance observed in the mixed ligand complex agrees very well with IR spectral observations. The C-N bond distances (mean 1.473 A) of Nethyl groups are in the range of clear single bond distances.

The oxygen atoms of the  $(ClO_4)^-$  ion show large thermal vibrations, due to disorder. The Cl–O distances are in the

Fig. 2 ORTEP diagram of [Ni(dedtc)(4-MP)(NCS)]

range: 1.375-1.413 Å. The O-Cl-O angles vary from  $103.2(4)^{\circ}$  to  $112.2(4)^{\circ}$ , indicating distortion from the tetrahedral geometry as observed in many complexes of similar nature reported from our laboratory [11-15].

ORTEP diagram of complex 2 is shown in Figure 2. The complex is monomeric and discrete. It does not show significant intermolecular contacts. Four formula units are present in the unit cell. The complex contains planar NiS<sub>2</sub>PN chromophore in keeping the observed diamagnetism of the compound. The Ni-S bond distances, 2.170(1) Å and 2.225(1) Å are quite different, in contrast to the parent dithiocarbamate, [Ni(dedtc)<sub>2</sub>] (2.195(2) Å and 2.207(2) Å). This is ascribed to the different trans influences exerted by phosphine and NCS<sup>-</sup> ligand. The bond parameters of the dithiocarbamate moiety are found to be normal. The thioureide C-N distance, 1.311(4) Å observed in the present compound is shorter than that observed in the corresponding parent dithiocarbamate viz., 1.33(1) A, indicating mesomeric drift of electron density from the dithiocarbamate towards the metal centre. The Ni-P distance observed in the complex 2.207(1) A is the shortest distance reported for divalent Ni-phosphorus complexes [23]. The shorter Ni-P distance may be the result of strong back donation from nickel atom. The Ni-N distance is 1.865(3) Å, which is also significantly short. The P-Ni-Nangle (92.47 (9)° is slightly different from the right angle and Ni-N-C(-S) angle (174.1(3)° shows a small deviation from linearity. The C-N and C-S distances viz., 1.148(4) and 1.613(4) Å show the double bonded nature as expected.



Fig. 3 ORTEP diagram of [Ni(dedtc)(PPh<sub>3</sub>)(NCS)]



Fig. 4 ORTEP diagram of [Ni(dedtc)(PPh<sub>3</sub>)(CN)]

ORTEP diagram of complex 3 is shown in Figure 3. The molecule contains discrete mononuclear units, which have no significant intermolecular contacts. Four formula units are present in the unit cell. The complex contains planar NiS<sub>2</sub>PN chromophore in keeping the observed diamagnetism of the compound. The two Ni-S bonds, 2.167(1) and 2.224(1) Å are quite different, as a contrast to the parent dithiocarbamate (2.195(2) and 2.207(2) Å). Phosphine being a good  $\pi$ -acceptor has a greater trans influence and hence the Ni-S bond trans to P is longer than that trans to NCS<sup>-</sup>. Asymmetry in the Ni-S bonds leads to an increase in Ni-S-C angle and decrease in S-C-S angle when compared to the parent dithiocarbamate complex. The Ni-S-C angle is  $86.9(1)^{\circ}(85.3(4)^{\circ}$  for [Ni(dedtc)<sub>2</sub>]) and S-C-S angle is 108.8(1)° (110.5(4)° for [Ni(dedtc)<sub>2</sub>]). The thioureide C–N distance is 1.304(3) Å, which is lower than the distance 1.33(1) Å observed in the parent [Ni(dedtc)<sub>2</sub>] [24]. Similar trend was observed in  $[Ni(dedtc)(PPh_3)_2]^+$  [20] and in  $[NiCl(dedtc)(PPh_3)]$  [16].

90.56,(6)° which supports the planar coordination of the nickel atom. The Ni–N–C(–S) angle is 176.2(2)°, which indicates the deviation from linearity due to steric effect of the bulky phosphine. The short N–C and C–S bond distances 1.153(3) Å, 1615(3) Å respectively show characteristic double bondednature of N=C=S<sup>-</sup>ion. The N–C–S angle is 179.1(2)°, which indicates the near linearity of the isothiocyanate moiety.

ORTEP diagram of the complex **4** is shown in Figure 4. It is monomeric with no significant intermolecular contacts. Four molecules are present in the unit cell. Ni, S(1), S(2), P and C of the cyanide are coplanar. The planarity of the coordination around Ni<sup>II</sup> is also supported bythe observed diamagnetism of the compound. The deviation of this plane from a perfect square is caused by the small bite angle (79.08(4)° of the dithiocarbamate. The two Ni-S bonds 2.193(1) Å, 2.207(1) Å are significantly different. The Ni-S bond trans to P is longer than that trans to CN<sup>-</sup> due to different trans influences of phosphine and cyanide. Asymmetry in the Ni-S bonds leads to an increase in Ni-S-C angle and decrease in S-C-S angle when compared to parent dithiocarbamate complex. The thioureide C-N distance is 1.305(4) Å, which is significantly different from the distance 1.33(1) Å observed in the parent [Ni(dedtc)<sub>2</sub>] [24].

Complex	Ni-S(1)	Ni-S(2)	Ni-P(1)	Ni-P(2)	Ni–N/ Ni–C	C-N	S-Ni-S	P-Ni-P/ P-Ni-N/ P-Ni-C	Ref.
[Ni(dedtc) <sub>2</sub> ]	2.195(2)	2.207(2)	_	_	_	1.33(1)	79.3(1)	_	[24]
[Ni(dedtc)(PPh <sub>3</sub> ) <sub>2</sub> ] <sup>+</sup>	2.190(2)	2.239(2)	2.200(2)	2.230(3)	-	1.307(1)	78.2(1)	99.7(1)	[20]
[Ni(dedtc)(4-MP)2] <sup>+</sup>	2.200(1)	2.228(1)	2.214(1)	2.236(1)	-	1.300(5)	78.24(4)	98.64(4)	This work
[Ni(dedtc)(PPh <sub>3</sub> )Cl]	2.170(4)	2.232(3)	2.204(3)	-	2.187(3) (Ni-Cl)	1.323(16)	78.4(1)	93.7(1) (Pi-Ni-Cl)	[16]
[Ni(dedtc)(4-MP)(NCS)]	2.170(1)	2.225(1)	2.207(1)	_	1.865(3)	1.311(4)	78.87(4)	92.8(1)	This work
[Ni(dedtc)(PPh3)(NCS)]	2.167(1)	2.224(1)	2.188(1)	_	1.863(2)	1.304(3)	79.04(3)	90.6(1)	This work
[Ni(dedtc)(PPh <sub>3</sub> )(CN)]	2.193(1)	2.207(1)	2.175(1)	—	1.863(4)	1.305(4)	79.08(4)	91.0(1)	This work

Table 2 Comparison of bond distances/Å and bond angles/°

Other bond parameters of the dithiocarbamate moiety are

normal. The Ni-N distance, 1.863(2) Å is also short. Short

Ni-P and Ni-N distances are as a result of strong back

bonding effects from nickel atom. The P-Ni-N angle is

This clearly indicates the mesomeric drift of electron density from dithiocarbamate moiety towards the metal atom. The other bond parameters of the dithiocarbamate moiety are normal. Ni-P and Ni-C distances in the compound are 2.175(4) Å and 1.863(4) Å, respectively. The observation is as a result of a highly favourable steric environment in addition to effective back bonding effects. The P-Ni-C angle is  $91.03(10)^\circ$ , which shows the planar coordination of the nickel atom. The Ni-C-N angle is  $179.0(3)^{\circ}$  which indicates the slight deviation from linearity due to steric effect of phosphine ligand. The short C-N distance, 1.144(4) À indicates the characteristic triple bonded nature. Phenyl rings show normal bond parameters. The observed average P-C distance is 1.826 Å. The C-P-C angles deviate appreciably from the normal tetrahedral angle and the resultant crowding of the phenyl rings causes the P-C-C angles to be asymmetric.

Comparative structural parameters are given in Table 2. All the complexes are asymmetric with respect to Ni-S distances. This is attributed to the difference in trans influences exerted byphosphines, NCS<sup>-</sup> and CN<sup>-</sup>. The thioureide C-N distances in the present complexes 1, 2, 3, and 4 are relatively short compared tothat in the parent compound.

#### Experimental

All the reagents and solvents employed were commercially available high-grade purity materials (E-Merk) used as supplied without further purification.

**CAUTION!** Metal perchlorate with organic ligands are potentially explosive and Potassium cyanide is highly poisonous. Only, small amounts of complex should be prepared, and these should be handled with great caution.

IR spectra were recorded on a Avator Nicolet FT-IR spectrophotometer (range:  $4000 - 400 \text{ cm}^{-1}$ ) as KBr pellets. The uv-visible spectra in CH<sub>2</sub>Cl<sub>2</sub> were recorded in a Hitachi U-2001 double beam spectrophotometer. <sup>1</sup>H, <sup>13</sup>C and <sup>31</sup>P NMR spectra were recorded on a Bruker AMX-400 spectrophotometer at room temperature. CDCl<sub>3</sub> was used as solvent and TMS was used as reference.

#### Preparation

### Bis[tri(4-methylphenyl)phosphine)](diethyldithiocarbamato)nickel(II) perchlorate; [Ni(dedtc)(4-MP)<sub>2</sub>](ClO<sub>4</sub>) (1)

A mixture of  $[Ni(dedtc)_2]$  (0.36 g, 1 mmol), 4- MP (1.23 g, 4 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (0.24 g, 1 mmol) and NH<sub>4</sub>ClO<sub>4</sub> (0.23 g, 2 mmol) in acetonitrile-methanol (1:1, 50 cm<sup>3</sup>) was refluxed for about 3 hours followed by concentration to ca. 25 cm<sup>3</sup>. The red solution obtained was left undisturbed for two days. Red crystals suitable for X-ray structure analysis were obtained directly (yield 85 %; dec. 158 °C).

#### (Diethyldithiocarbamato)(isothiocyanato)(tri(4-methylphenyl)phosphine)nickel(II); [Ni(dedtc)(4-MP)(NCS)] (2)

A mixture of [Ni(dedtc)<sub>2</sub>] (0.36 g, 1 mmol),  $P(C_6H_4 \cdot Me-4)_3$  (0.61 g, 2 mmol),  $NiCl_2 \cdot 6H_2O$  (0.24 g, 1 mmol) and  $NH_4SCN$  (0.15 g, 2 mmol) in acetonitrile-methanol (2:1, 75 cm<sup>3</sup>) was refluxed for

 Table 3
 Crystal data, data collection and refinement parameters for 1, 2, 3 and 4

2 3 4 Compound 1 Empirical formula C47H53CINO4P2S2Ni C27H31N2PS3Ni C24H25N2PS3Ni C24H25N2PS2Ni 527.3 FW 916.1 569.4 606.3 Crystal dimensions/mm  $0.17 \times 0.20 \times 0.38$  $0.24 \times 0.31 \times 0.37$  $0.11 \times 0.19 \times 0.34$  $0.24 \times 0.26 \times 0.33$ Crystal system monoclinic monoclinic monoclinic monoclinic Space group  $P2_1/c$  $P2_1/n$  $P2_1/n$  $P2_1/c$ 11.974(1)7.611(1) 8.105(2) 11.348(2)a/Å 17.026(2) b/Å 23.892(1) 20.097(3) 30.728(2)c/Å 16.774(1) 12.380(1) 16.621(2) 12.826(2) 100.22(3) β/° 103.02(2)101.86(2) 91.02(2) U/Å<sup>3</sup> 4675 2895 2664.4(8) 2425.22 Z 4 4 4 4 1.302 1.306 1.356 Dc/gcm<sup>-3</sup> 1.315  $\mu/cm^{-1}$ 6.72 9.60 10.37 10.5 1096 F(000) 1924 1192 1032 λÀ Mo-Kα(0.71069) Mo-Kα(0.71069) Mo-Kα(0.71069) Mo-Kα(0.71069) θ range/° 2-27 2 - 282-28 2 - 30ω-2θ Scan type ω-2θ ω-2θ ω-2θ  $-13 \le h \le 15$ ,  $-10 \le h \le 10$ ,  $-10 \le h \le 10$ ,  $-15 \le h \le 15$ , Index ranges  $-26 \le k \le 26$ ,  $-29 \le k \le 30$ .  $-38 \le k \le 40$ .  $0 \le k \le 23$ .  $-21 \le l \le 13$  $-16 \le l \le 15$  $-21 \le l \le 21$  $0 \le l \le 18$ Reflections collected 10062 6822 6168 7057 Observed reflections 5011 2729 3235 3485  $[Fo > 4\sigma(F_o)]$  $W = 1 / [\sigma^{2}(F_{o}^{2}) + (0.1252P)^{2} W = 1 / [\sigma^{2}(F_{o}^{2}) + (0.0301P)^{2} W = 1 / [\sigma^{2}(F_{o}^{2}) + (0.0293P)^{2} W = 1 / [\sigma^{2}(F_{o}^{2}) + (0.1627P)^{2} W = 1 / [\sigma^{2}(F_{o}^{2}) + (0.162P)^{2} W$ Weighting scheme + 0.0000P+ 0.00P)+ 0.0000P] + 0.0000P]  $P = (max (F_o^2 + 2F_c^2)/3)$  $P = (\max (F_o^2 + 2F_c^2)/3)$  $P = \max(F_o^2 + 2F_c^2)/3$  $P = \max(F_o^2 + 2F_c^2)/3$ 735 432 373 381 Number of parameters refined Final R, R<sub>w</sub> (obs, data) 0.0456, 0.1172 0.0407, 0.0642 0.0302,0.0649 0.0463, 0.1687 GOOF 0.7240.910 0.766 0.594

Crystallographic data for the structures have been deposited with the Cambridge Crystallographic Data Centre (CCDC 183244(1), CCDC 183243(2), CCDC 183256(3) and CCDC 210916(4). Copies of the data can be obtained free of charge on application to the Director, CCDC 12 Union Road, Cambridge, CB2 1EZ, UK (fax: +44-1223-336033, e-mail: deposit@ccdc.ac.uk).

1		2		3		4	
Ni1-S3 Ni1-P4 Ni1-P5 S2-C6 S3-C6 C6-N7 N7-C8 N7-C10 P5-C12 P4-C22	2.228(1) 2.214(1) 2.236(1) 1.733(2) 1.713(4) 1.300(5) 1.480(2) 1.466(5) 1.832(4) 1.832(4)	Ni1-S3 Ni1-P13 Ni1-N10 S2-C4 S3-C4 C4-N5 N10-C11 C11-S12 N5-C6	2.170(1) 2.207(1) 1.865(3) 1.707(4) 1.716(4) 1.311(4) 1.148(4) 1.613(4) 1.482(5) 1.482(5)	Ni1-S3 Ni1-P13 Ni1-N10 S2-C4 S3-C4 C4-N5 N10-C11 C11-S12 N5-C6 N5-C6	2.167(1) 2.188(1) 1.863(2) 1.712(3) 1.725(2) 1.304(4) 1.153(3) 1.615(3) 1.471(3) 1.471(3)	Ni1-S3 Ni1-P10 Ni1-C29 S2-C4 S3-C4 C4-N5 C29-N30 N5-C6 N5-C8 N5-C8	2.207(1) 2.175(1) 1.863(4) 1.739(3) 1.706(4) 1.305(4) 1.144(5) 1.479(6) 1.488(5) 1.629(2)
$\begin{array}{c} P4-C33\\ S2-Ni1-S3\\ S2-Ni1-P4\\ S3-Ni1-P5\\ P4-Ni1-P5\\ S2-C6-S3\\ S2-C6-N7\\ S3-C6-N7\\ C6-N7-C8\\ Ni1-S2-C6\\ Ni1-S3-C6\\ \end{array}$	1.836(4) $78.24(40)$ $92.30(4)$ $90.88(4)$ $98.64(4)$ $108.4(2)$ $127.1(3)$ $124.5(3)$ $121.6(5)$ $86.9(1)$ $86.5(1)$	N5-C8 S2-Ni1-S3 S2-Ni1-N10 N10-Ni1-P13 S3-Ni1-P13 S2-C4-S3 S2-C4-N5 S3-C4-N5 C4-N5-C6 Ni1-N10-C11 N10-C11-S12	1.495(6) 79.04(3) 95.2(1) 90.6(1) 95.27(3) 108.8(1) 126.6(2) 124.7(2) 121.4(2) 176.2(2) 179.1(2)	N5-C8 S2-Ni1-S3 S2-Ni1-N10 N10-Ni1-P13 S2-C4-S3 S2-C4-N5 S3-C4-N5 C4-N5-C6 Ni1-N10-C11 N10-C11-S12	1.474(3) 79.04(3) 95.2(1) 90.6(1) 95.27(3) 108.8(1) 126.6(2) 124.7(2) 121.4(2) 176.2(2) 179.1(2)	$\begin{array}{c} P10-C11\\ S2-Ni1-S3\\ S3-Ni1-C29\\ C29-Ni1-P10\\ S2-Ni1-P10\\ S2-C4-S3\\ S2-C4-N5\\ S3-C4-N5\\ C4-N5-C6\\ C4-N5-C6\\ Ni1-C29-N30\\ \end{array}$	$\begin{array}{c} 1.829(3) \\ \hline 79.08(4) \\ 93.2(1) \\ 91.0(1) \\ 96.770(3) \\ 108.8(2) \\ 124.6(3) \\ 126.7(3) \\ 121.1(4) \\ 117.5(4) \\ 179.0(3) \end{array}$

Table 4 Selected bond distances /Å and angles /° for complexes 1, 2, 3, and 4.

about 3 hours followed by concentration to ca.  $25 \text{ cm}^3$ . Resultant purple red solution obtained was left for evaporation. After two days purple red crystals suitable for X-ray structure analysis were obtained directly (yield 85 %; dec. 159 °C).

#### (Diethyldithiocarbamato)(isothiocyanatio)(triphenylphosphine)nicekl(II); [Ni(dedtc)(PPh<sub>3</sub>)(NCS)] (3)

A mixture of [Ni(dedtc)<sub>2</sub>] (0.36 g, 1 mmol), PPh<sub>3</sub> (0.52 g, 2 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (0.24 g, 1 mmol) and NH<sub>4</sub>SCN (0.15 g, 2 mmol) in acetonitrile-methanol (2:1, 75 cm<sup>3</sup>) was refluxed for about 3 hours followed by concentration to ca. 25 cm<sup>3</sup>. Resultant purple red solution obtained was left for evaporation. After two days red solid separated from the solution which was filtered anddried over anhydrous calcium chloride. Single crystals suitable for X-ray structure analysis were obtained by recrystallization from acetonitrile (yield 80 %; dec. 161 °C).

#### (Cyano)(diethyldithiocarbamato)(triphenylphosphine)nickel(II); [Ni(dedtc)(PPh<sub>3</sub>)(CN)](4)

A mixture of  $[Ni(dedtc)_2]$  (0.36 g, 1 mmol), PPh<sub>3</sub> (0.52 g, 2 mmol), NiCl<sub>2</sub>·6H<sub>2</sub>O (0.24 g, 1 mmol) and KCN (0.13 g, 2 mmol) in acetonitrile – methanol (1:2, 50 cm<sup>3</sup>) was refluxed for about 3 hours. Orange yellow solution obtained was left for evaporation. After two days orange yellow solid was obtained. The solid was filtered and was dried over anhydrous calcium chloride. Single crystals suitable for X-ray analysis were obtained by recrystallization from CH<sub>3</sub>OH – CH<sub>3</sub>CN solvent mixture (yield 60 %; dec. 153 °C).

#### Cyclic voltammetry

ECDA-001 Basic Electrochemistry system was used for all measurements. Glassy carbon was used, as working electrode and the counter electrode was a platinum wire. The reference electrode was Ag/AgCl. Tetrabutylammonium perchlorate (0.01M) was used as the supporting electrolyte. The experiments were carried out under oxygen free atmosphereby bubbling purified nitrogen gas through the solution at room temperature.

#### X-ray data collection

Details of crystal data, data collection and refinement parameters for complexes 1-4 are summarized in Table 3. The intensity data

were collected at 295 K on Bruker AXS smart single crystal diffractometer with CCD (area detector)for complexes 1–4 using Mo-K $\alpha$  radiation ( $\lambda = 0.71069$  Å). The absorption correction was performed with the method inserted in SHELXTL-NT V 5.1 [25]. The structure was solved by direct method inserted in SHELXTL-NT V 5.1 [25]. NT V5.1 in the Bruker AXS software [25]. All the ORTEP diagrams were drawn with ORTEP-3 [26]. All the non-hydrogen atoms were refined anisotropically and hydrogen atoms were refined isotropically. Selected bond distances are presented in Table 4.

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