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Synthesis, NMR spectral and single crystal X-ray structural studies on Ni(II) dithiocarbamates with NiS₂PN, NiS₂PC, NiS₂P₂ chromophores: Crystal structures of (4-methylpiperazinecarbodithioato)(thiocyanato-N) (triphenylphosphine)nickel(II) and bis(triphenylphosphine) (4-methylpiperazinecarbodithioato)nickel(II) perchlorate monohydrate

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Abstract

Four Ni(II) dithiocarbamates with NiS₂PX (X = NCS or CN or P) chromophores have been synthesized [[Ni(4-mpzdtc)(PPh₃)(CNS)] (1), [Ni(4-mpzdtc)(PPh₃)(CN)] (2), [Ni(4-mpzdtc)(PPh₃)₂]ClO₄ · H₂O (3) and [Ni(4-mpzdtc)(dppe)]ClO₄ (4) (where 4-mpzdtc = 4-methylpiperazinecarbodithioato anion, PPh₃ = triphenylphosphine and dppe = 1,2-bis((diphenylphosphino)ethane))] from [Ni(4-mpzdtc)₂]. Electronic spectra of the complexes show bands corresponding to $d_{z^2}/d_{xy} \rightarrow d_{x^2-y^2}$ transitions. IR spectra of all the compounds showed characteristic bands due to the dithiocarbamate ligand around 1500 cm⁻¹ and 990 cm⁻¹. CV studies showed a higher reduction potential for the parent complex indicating the reluctance to add more electron density to the already electron rich metal centre. ¹H NMR spectra of the complexes showed the deshielding of α -CH₂ protons on complexation. The ¹³C signals show interesting variations for the S₂-¹³C N< carbon signals between the neutral [1 and 2] and ionic complexes [3 and 4]. The S₂-¹³C N< chemical shifts of the three complexes with PPh₃ follow the order: 3 < 1 < 2 indicating the influence of PPh₃, NCS, CN respectively on the mesomeric drift of electron density towards nickel. The PPh₃ complexes show the following order of increasing ³¹P chemical shifts: 3 (30.9 ppm) > 2 (22.1 ppm) > 1 (20.5 ppm). The observed order clearly establishes the ease with which the back bonding interaction takes place. The back bonding is best observed in the case of the NiS₂P₂ chromophore. Single crystal X-ray structures of [Ni(4-mpzdtc)(PPh₃)(NCS)] and [Ni(4-mpzdtc)(PPh₃)₂]ClO₄ indicate that the central metal atom is in a planar environment for both complexes. The planarity of the molecules is supported by the observed diamagnetism of the complexes. The short S₂-C N< bonds indicate the partial double bond character in both cases.

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1. Introduction

The diversity in applications inherent to nickel(II) complexes with simple and chelating phosphines as catalysts [1-3] and in the medicinal field [4], combined with their

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structural novelty has resulted in the synthesis of a series of compounds with NiP_nX (X = halogens or N or C or S) chromophores. Dithiocarbamates have proven to be versatile metal chelates and in particular nickel(II) dithiocarbamates with a planar NiS₄ chromophore are found to show interesting variations in reactivity towards soft Lewis bases such as phosphines and hard bases such as nitrogenous ligands. As a continuation of our interest [5,6] in exploring the synthetic and structural chemistry of transition metal dithiocarbamates and to understand the influence of phosphines and nitrogenous ligands on the NiS₂PX (X = Cor N or P) chromophore and on the S_2 -C N \leq bond we investigated the following compounds: [Ni(4-mpzdtc)- $(PPh_3)(NCS)$] (1), $[Ni(4-mpzdtc)(PPh_3)(CN)]$ (2), [Ni- $(4-mpzdtc)(PPh_3)_2$ ClO₄ · H₂O (3) and [Ni(4-mpzdtc)-(dppe)]ClO₄ (4), where 4-mpzdtc = 4-methylpiperazinecarbodithioato anion, PPh₃ = triphenylphosphine and dppe = 1,2-bis((diphenylphosphino)ethane). In this paper, we report the synthesis, spectral and electrochemical properties of the compounds 1-4 along with the single crystal X-ray structures of 1 and 3 which crystallized out as single crystals.

2. Experimental

All the reagents and solvents employed were commercially available analytical grade materials and were used as supplied, without further purification. IR spectra were recorded on an ABB Bomem MB 104 spectrophotometer (range 4000–400 cm⁻¹) as KBr pellets. The UV–Vis spectra were recorded in CH₂Cl₂ on a HITACHI U-2001 spectrophotometer. Cyclic voltammetric studies were carried out using an ECDA-001, Basic Electrochemistry system. A three-electrode configuration was used, comprising of glassy carbon as the working electrode, a platinum wire as the counter electrode and Ag|AgCl as the reference electrode. Experiments were carried out at room temperature using 0.01 M tetrabutylammonium perchlorate as the supporting electrolyte under a nitrogen atmosphere. NMR spectra were recorded on a Bruker 400 MHz spectrometer at room temperature, using CDCl₃ as solvent. ¹³C NMR spectra were recorded in the proton decoupled mode.

2.1. Preparation of the complexes

2.1.1. Bis(4-methylpiperazinecarbodithioato) nickel(II)

2.1.1.1. [Ni(4-mpzdtc)₂]. A mixture of 1-methylpiperazine (100 mg, 1 mmol) and CS₂ (76 mg, 1 mmol) in ethanol (50 mL) was kept under ice cold conditions ($-5 \,^{\circ}$ C) for 10 min and to this pale yellow solution NiCl₂ \cdot 6H₂O (120 mg, 0.5 mmol) in water (25 mL) was added slowly with vigorous stirring. The dark green precipitate obtained was filtered, washed with ether and water. It was kept for evaporation and dried over anhydrous calcium chloride (Yield: 95%, dec.: >250 °C).

2.1.2. (4-Methylpiperazinecarbodithioato)(thiocyanato-N)-(triphenylphosphine) nickel(II)

2.1.2.1. $[Ni(4-mpzdtc)(PPh_3)(NCS)]$ (1). A mixture of Ni(4-mpzdtc)₂ (205 mg, 0.5 mmol), PPh₃ (260 mg, 1 mmol), NiCl₂ · 6H₂O (120 mg, 0.5 mmol) and NH₄SCN (75 mg, 1 mmol) was refluxed for 3 h in an acetonitrile-methanol solvent mixture (2:1, 75 cm³) and was then concentrated to ca. 25 cm³. The dark purple-red solution obtained was filtered and was kept for evaporation. After 2 days, a solid separated out, was filtered, and then dried over anhydrous calcium chloride. Single crystals suitable for X-ray analysis were obtained by recrystallization from the same solvent mixture (Yield: 75%, dec.: 189 °C). Anal. Calc. for C₂₅H₂₆N₃NiPS₃: C, 54.16; H, 4.72; N, 7.58. Found: C, 54.01; H, 4.59; N, 7.44%.

2.1.3. (Cyano)(4-methylpiperazinecarbodithioato)-(triphenylphosphine) nickel(II)

2.1.3.1. $[Ni(4-mpzdtc)(PPh_3)(CN)]$ (2). A mixture of Ni(4-mpzdtc)₂ (205 mg, 0.5 mmol), PPh₃ (260 mg, 1 mmol), NiCl₂ · 6H₂O (120 mg, 0.5 mmol) and KCN (65 mg, 1 mmol) was refluxed for 3 h in an acetonitrile-methanol solvent mixture (2:1, 75 cm³) and then concentrated to ca. 25 cm³. The pale orange-red solution obtained was filtered and kept for evaporation. After 2 days, an orange-red solid separated out. It was dried over anhydrous calcium chloride and recrystallized from the same solvent mixture (Yield: 65%, dec.: 180 °C). *Anal.* Calc. for C₂₅H₂₆N₃NiPS₂: C, 57.49; H, 5.01; N, 8.04. Found: C, 57.38; H, 4.90; N, 7.94%.

2.1.4. Bis(triphenylphosphine)(4-methylpiperazinecarbodithioato)nickel(II) perchlorate monohydrate

2.1.4.1. $[Ni(4-mpzdtc)(PPh_3)_2]ClO_4 \cdot H_2O(3)$. A mixture of Ni(4-mpzdtc)_2 (205 mg, 0.5 mmo1), PPh₃ (520 mg, 2 mmol), NiCl₂ · 6H₂O (120 mg, 0.5 mmol) and NH₄ClO₄ (115 mg, 1 mmol) was refluxed for about 2 h in a methanol-dichloromethane solvent mixture (1:1, 50 cm³), and then concentrated to ca. 25 cm³. The purple-red solution obtained was filtered and left for evaporation. The separated solid was filtered and dried, and single crystals suitable for X-ray analysis were obtained by repeated recrystallization from the same solvent mixture (Yield: 65%, dec.: 183 °C). Anal. Calc. for C₄₂H₄₃ClN₂NiO₅P₂S₂: C, 57.58; H, 4.94; N, 3.19. Found: C, 57.42; H, 4.84; N, 3.10%.

2.1.5. 1,2-Bis((diphenylphosphino)ethane)(4-methylpiperazinecarbodithioato) nickel(II) perchlorate

2.1.5.1. $[Ni(4-mpzdtc)(dppe)]ClO_4$ (4). A mixture of Ni(4-mpzdtc)₂ (410 mg, 1 mmol), dppe (790 mg, 2 mmol), NiCl₂ · 6H₂O (240 mg, 1 mmol) and NH₄ClO₄ (230 mg, 2 mmol) was refluxed for about 4 h in a methanol-dichloromethane solvent mixture (1:1, 50 cm³). The solution was then concentrated to ca. 25 cm³. The purple-red solution obtained was filtered and kept for evaporation. After 2 days, a purple-red solid separated out and it was recrystallized from the same solvent mixture (Yield: 65%,

Table 1 Crystal data, data collection and refinement parameters for **1** and **3**

Complex	1	3
Empirical formula	C ₂₅ H ₂₆ N ₃ NiPS ₃	$C_{84}H_{86}Cl_2N_4Ni_2O_{10}P_4S_4$
FW	554.3	1752.0
Crystal dimensions (mm)	$0.19 \times 0.23 \times 0.24$	$0.22 \times 0.25 \times 0.29$
Crystal system	monoclinic	monoclinic
Colour	purple red	orange red
Habit	needle	column, irregular
Space group	$P2_1/c$	$P2_1/c$
a (Å)	7.86(2)	31.819(3)
b (Å)	31.011(3)	11.323(3)
c (Å)	11.033(2)	24.464(3)
α (°)	90	90
β (°)	90.31 (2)	105.31(3)
γ (°)	90	90
$U(\text{\AA}^3)$	2689(7)	8501(3)
Ζ	4	8
$D_{\rm c}~({\rm g~cm^{-3}})$	1.290	1.367
$\mu (\mathrm{cm}^{-1})$	9.53	7.38
<i>F</i> (000)	1088	3640
λ (Å)	Μο Κα (0.71073)	Μο Κα (0.71069)
θ Range (°)	1.31–27.53	3.03-28.01
Scan type	ω –2 θ	ω –2 $ heta$
Index ranges	$-3 \leq h \leq 3, -40 \leq k \leq 40, -1 \leq l \leq 14$	$0 \le h \le 42, \ 0 \le k \le 14, \ -32 \le l \le 31$
Reflections collected	2649	20311
Observed reflections $F_{\rm o} > 4\sigma(F_{\rm o})$	1474	6357
Weighting scheme	$W = 1/[\sigma^2(F_0^2) + (0.0470P)^2 + 0.00P]$, where	$W = 1/[\sigma^2(F_o^2) + (0.0051P)^2 + 0.00P]$, where
	$P = (F_{0}^{2} + 2F_{c}^{2})/3$	$P = (F_0^2 + 2F_c^2)/3$
Number of parameters refined	402	1355
Final R , R_w (observed, data)	0.0354, 0.1033	0.0660, 0.0598
Goodness-of-fit	1.009	0.877

Table 2 Selected bond distances and bond angles for 1 and 3

1		3	
Bond distances			
Ni(1)–N(31)	1.859(6)	Ni(1A)-S(2A)	2.1937(15)
Ni(1)–S(2)	2.1809(19)	Ni(1A)–P(11A)	2.2149(16)
Ni(1)–P(12)	2.207(3)	Ni(1A)-P(30A)	2.2333(16)
Ni(1)-S(3)	2.213(4)	Ni(1A)-S(1A)	2.2272(16)
S(2)–C(4)	1.714(8)	S(1A)-C(3A)	1.710(5)
S(3)–C(4)	1.706(7)	S(2A)-C(3A)	1.707(5)
C(4)–N(5)	1.316(8)	C(3A)-N(4A)	1.306(5)
N(8)–C(11)	1.477(13)	N(7A)-C(10A)	1.471(8)
N(31)-C(32)	1.152(7)	N(4A)-C(9A)	1.493(6)
C(32)-S(33)	1.619(7)	N(4A)-C(5A)	1.486(6)
Bond angles			
N(31)-Ni(1)-	92.15(19)	S(2A)-Ni(1A)-P(11A)	91.02(6)
P(12)			
S(2)-Ni(1)-P(12)	97.35(8)	P(11A)-Ni(1A)-	99.82(6)
		P(30A)	
N(31)-Ni(1)-S(3)	92.2(2)	S(2A)-Ni(1A)-S(1A)	78.44(5)
S(2)-Ni(1)-S(3)	78.86(8)	P(30A)-Ni(1A)-S(1A)	90.72(6)
C(4)-S(2)-Ni(1)	86.3(2)	C(3A)-S(1A)-Ni(1A)	85.31(18)
C(4)-S(3)-Ni(1)	85.5(3)	C(3A)-S(2A)-Ni(1A)	86.42(17)
N(5)-C(4)-S(3)	125.3(6)	N(4A)-C(3A)-S(1A)	123.7(4)
N(5)-C(4)-S(2)	125.4(6)	N(4A)-C(3A)-S(2A)	126.5(4)
S(3)-C(4)-S(2)	109.3(4)	S(1A)-C(3A)-S(2A)	109.8(3)
C(32)-N(31)-	168.6(6)	C(3A)-N(4A)-C(9A)	122.5(5)
Ni(1)			
N(31)-C(32)-	179.5(9)	C(3A)-N(4A)-C(5A)	124.1(5)
S(33)			

dec.: 193 °C). *Anal.* Calc. for C₃₂H₃₅ClN₂NiO₄P₂S₂: C, 52.51; H, 4.82; N, 3.82. Found: C, 52.41; H, 4.70; N, 3.71%.

2.2. X-ray crystallography

Details of the crystal data, data collection and refinement parameters for 1 and 3 are summarized in Table 1. Intensity data were collected at ambient temperature (295 K) on Bruker AXS (with CCD) (for 1) [7] and Philips PW 1100 (for 3) diffractometers [8], using graphite monochromated Mo K α radiation ($\lambda = 0.71073$ Å and 0.71069 Å for 1 and 3, respectively). All the non-hydrogen atoms were refined anisotropically and all the hydrogen atoms were refined isotropically. The absorption corrections were performed with the method in SHELXTL-NT V5.1 [7] for 1 and with the North, Phillips and Mathews method for 3 [9]. The ORTEP diagram was drawn with the ORTEP-3 program [10]. Selected bond distances and bond angles are given in Table 2.

3. Results and discussion

3.1. Electronic spectra

The d-d transition bands are observed at 483, 465, 483 and 467 nm for complexes 1, 2, 3 and 4, respectively. The

bands are assigned to $d_{z^2}/d_{xy} \rightarrow d_{x^2-y^2}$ transitions [11]. The cyanide ion exerts a larger LFSE and hence the lowest λ_{max} value is associated with **2**. The observed red shift in **2** when compared to similar complexes with a NiS₂PN chromophore [6] is significant.

3.2. IR spectral studies

For complexes 1, 2, 3 and 4, the v_{C-N} (S₂-C==N \leq) bands are observed at 1547, 1529, 1534 and 1519 cm⁻¹, respectively. The increase in wavenumber for the mixed ligand complexes compared to that observed for the parent complex $[Ni(4-mpzdtc)_2]$ (1503 cm⁻¹) is attributed to the mesomeric drift of electron density towards the nickel atom through the S_2 -C==N \leq bond from the dithiocarbamate. The v_{C-S} stretching vibrations are observed around 1000 cm⁻¹ (1-4) without any splitting, supporting the bidentate coordination of the dithiocarbamate ligand. The observed stretching frequencies at 2093 cm⁻¹ for complex 1 and at 2115 cm⁻¹ for complex 2 are attributed to the 'N'-coordinated thiocyanate and 'C'-coordinated cyanide anions, respectively. The intense signals observed in the fingerprint region for complexes **3** and **4** [1095 cm⁻¹ for **3** and 1089 cm⁻¹ for 4] are due to the presence of v_{CIO_4-} stretching in both cases.

3.3. Cyclic voltammetric studies

The reduction potential for the parent $[Ni(4-mpzdtc)_2]$ complex is observed at -1548 mV. All the mixed ligand complexes showed lower one electron reduction potentials. (-1189, -972 and -754 mV for complexes **1**, **2** and **3** respectively). For the chelating phosphine complex **4**, quasi-reversible reduction potentials are observed at $-998(E_p^c)/-790(E_p^a)$ mV and it is due to the chelating nature of the phosphine, which is not completely delinked from the Ni¹-species formed as a result of the electrochem-

Table	3					
NMR	chemical	shifts	of the	complexe	es (in	ppm)

ical reduction. Lower reduction potentials observed for complexes 1-3 indicate the ease of electron addition in the mixed ligand complexes and this is because of the presence of PPh₃, NCS⁻ and CN⁻ around the nickel atom [5].

3.4. NMR spectral studies

NMR chemical shifts of the synthesized complexes are summarized in Table 3.

3.4.1. ¹H NMR

For all the four mixed ligand complexes (1–4), the aromatic protons resonate in the region 7.31–7.91 ppm. The α (methylene) protons are greatly deshielded and are observed in the downfield region due to complexation. However, the β -CH₂ and N–CH₃ proton signals are observed closely and the assignments are made on the basis of proton integral values obtained for the corresponding signals. For complex 4, the signal due to the methylene protons of the chelating phosphine appears at 2.67 ppm.

3.4.2. ¹³C NMR

For all the four complexes, the N-CH₃ carbon signal is observed around 45.0 ppm and this deshielding is due to the minor deshielding effect of the nearby electronegative nitrogen. The β -CH₂ carbon signals are observed around 53.0 ppm with a small upfield shift of about 3 ppm compared to that of the corresponding carbon signal in Nmethylpiperazine [56.4 ppm]. Signals due to α -carbons are only slightly deshielded. Aromatic carbon signals are observed in the downfield region of 126.9-137.3 ppm for all the four synthesized complexes. The $N^{-13}CS^{-1}$ and carbon signals are observed at 143.9 and $^{13}CN^{-}$ \sim 131 ppm for complexes 1 and 2, respectively (for complex 2, the ${}^{13}CN^{-}$ signal at 131 ppm, is merged with the aromatic carbon signals). For complex 4, the methylene carbon present in the chelating phosphine is observed at

(in ppin)								
Compound	NMR	α -CH ₂ ^a	β -CH ₂ ^a	δ-CH ₃	PPh_x^{b}	>N ¹³ CS ₂	$S - {}^{13}C - N^{-}$	$^{13}CN^{-}$
1	¹ H ¹³ C ³¹ P	3.78 (t) 46.6	2.46 (t) 53.2	2.17 (s) 45.2	7.46–7.70 (m) 128.8–134.9 20.5	202.8	143.9	
2	¹ H ¹³ C ³¹ P	3.74 (t) 46.0	2.43 (t) 53.7	2.30 (s) 45.5	7.40–7.81 (m) 128.6–134.1 22.1	204.2		~131
3	¹ H ¹³ C ³¹ P	3.73 (t) 46.3	2.63 (t) 53.4	2.43 (s) 45.3	7.31–7.66 (m) 128.8–137.3 30.9	199.2		
4	¹ H ¹³ C ³¹ P	3.89 (t) 46.3	2.63(t) 53.3	2.40 (s) 45.1	7.52–7.91 (m) ^c 126.9–132.8 ^d 61.8	201.7		

^a Chemical shifts due to a, e protons.

^b Where x = 3 for **1**, **2** and **3** and 2 for **4**.

^c The ($P-CH_2-$)₂ signal is observed at 2.67 ppm.

^d The $(P^{-13}CH_2)_2$ signal is observed at 26.4 ppm.

26.4 ppm. Finally, the most important ¹³C NMR signals of the S₂–¹³C===N \leq carbons are observed at 202.8, 204.2, 199.2 and 201.7 ppm for complexes **1**, **2**, **3** and **4**, respectively with a very weak intensity characteristic of the quaternary carbon signals. The mesomeric shift of electron density from the dithiocarbamate moiety towards the metal centre contributes to the upfield shift from the normal chemical shift values of Ni(dtc)₂ complexes (206– 210 ppm) [12]. The S₂–¹³C===N \leq chemical shifts of the three complexes with PPh₃ follow the order: **3** < **1** < **2**, indicating the influence of PPh₃, NCS and CN, respectively on the mesomeric drift of electron density towards nickel.

3.4.3. ³¹P NMR

³¹P chemical shifts are observed at 20.5, 22.1, 30.9 and 61.8 ppm for complexes 1, 2, 3 and 4, respectively. A good extent of deshielding of about 75 ppm is observed for the ³¹P signal of complex 4, compared to the free chelating dppe 31 P signal observed at -13 ppm [13]. In the case of complexes 1, 2 and 3 signals are also observed in the deshielded region compared to the free PPh3 signal at -5 ppm [14]. A very high deshielding of signals observed in all the cases is attributed to the movement of electron density from the phosphorus towards the nickel atom on complexation. The PPh3 complexes show the following order of increasing ³¹P chemical shifts: 3 (30.9 ppm) ≥ 2 (22.1 ppm) > 1 (20.5 ppm). The observed order clearly establishes the ease with which the back bonding interaction takes place. The back bonding electron donation is the best in the case of 3, containing the NiP_2 chromophore.

3.5. Structural analysis

C23

C22

The single crystal X-ray structure of 1 contains four discrete molecules per unit cell. The ORTEP diagram of the molecule is shown in Fig. 1. The observed distortion of the square planar coordination around nickel is attributed to the small bite angle of $78.86(8)^\circ$. The planarity is sup-

S3

N5

ported by the observed diamagnetism of the complex. Delocalization of π electron density over the S₂CN moiety leads to a decrease in the C–N [S₂–C==N \leq] distance [1.316(8) Å] and also an increase in the S–C–N angles [125.3(6)° and 125.4(6)°] over the S–C–S angle [109.3(4)°]. The observed difference in Ni–S distances [2.213(4) and 2.1809(19) Å] is attributed to the difference in the *trans* influencing properties of PPh₃ and NCS⁻. PPh₃ being a good π acceptor has a greater *trans* influence and hence the Ni–S bond *trans* to PPh₃ is longer than the other Ni–S bond.

The Ni–N distance [1.859(6) Å] is quite short, showing the effective bonding between the nickel atom and the thiocyanate-N. The C–N bond distance in N–C–S [1.152(7) Å] is significantly shorter than the S₂–C==N \leq N–C bond distance of 1.316(8) Å. The C–S bond length in N–C–S is 1.619(7) Å, which is similar to the C=S distance of 1.69 Å. The N–C–S bond is [179.5(9)°] and is almost linear. In the dithiocarbamate part, the piperazine ring is in a sterically favoured chair conformation with the normal C–C and C–N bond lengths. The N-methyl group in the terminal position is equatorially oriented to avoid the 1,3-diaxial steric interactions with the axial hydrogens. Phenyl groups in triphenylphosphine show normal bond parameters.

[Ni(4-mpzdtc)(PPh₃)₂]ClO₄ · H₂O is discrete and monomeric. One molecule of water is co-crystallized with the complex. Eight formula units are present in the unit cell. Each asymmetric unit has two molecules and the bond parameters of one molecule are listed. The ORTEP diagram of **3** is shown in Fig. 2. Distortions with respect to the idealized geometry are observed in the coordination angles: the P–Ni–P angle is very large [99.82(6)°] due to steric interactions between two PPh₃ groups, while the S–Ni–S bite angle is low, 78.44(5)° as observed in similar compounds [6]. The observed shortening of the >N–CS₂ C–N distance is in line with the bond parameters observed for [Ni(dtc)(PPh₃)₂]⁺ (where, dtc = dmdtc or dedtc or pipdtc) complexes [6]. Among the mixed ligand complexes, those



P12

C13

Fig. 1. Thermal ellipsoid plot of [Ni(4-mpzdtc)(PPh₃)(NCS)] (30% probability).



Fig. 2. Thermal ellipsoid plot of $[Ni(4-mpzdtc)(PPh_3)_2]ClO_4 \cdot H_2O$ (30% probability) (H₂O and the ClO₄⁻ ion are omitted for clarity).

of the NiS₂P₂([Ni(dtc)(PPh₃)₂]⁺) chromophore show very short S₂–C===N \leq distances due to the π -acidic nature of the triphenylphosphine. The two S–C–N angles $[123.7(4)^{\circ}]$ and 126.5(4)°] are observed to be larger than the S-C-S angle [109.8(3)°]. Ni–P distances are very similar [2.2333(16) and 2.2149(16) Å]. The two Ni-S and S-C distances are comparable, showing that the negative charge of the bidentate ligand is equally distributed over the two donor atoms. The perchlorate ion shows thermal disorder as reported earlier [5]. The disordered perchlorate ion shows extensive short contacts ranging from 2.5 to 2.9 Å with H atoms of the piperazine ring and similarly with the oxygen atom of the water molecule O1W in the same range. Two hydrogen atoms of the water molecule attached to O2W could not be located in the Fourier map. Also, the disorder associated with ClO4- has been modelled such that each oxygen atom is positioned at two coordinate positions of 50% site occupancy at distances of 0.552, 0.336, 0.465, 0.391 Å (for molecule A) and 0.912, 0.815, 0.778, 1.223 Å. (for molecule B). Probable contacts indicating H-bonded interactions in the distance range of 2.4-2.8 Å are observed. Approximately 32 such interactions were noted [15,16]. The very large number of short contacts observed is a result of the modelled oxygen atoms of the perchlorate ion (eight oxygens of 50% site occupancy for every perchlorate ion). The triphenylphosphine and piperazine ring in the dithiocarbamate ligand show normal bond parameters. As observed in complex 1, the methyl group in the terminal position prefers the equatorial orientation.

Comparison of bond parameters of **1** and **3** indicates a similarity in shortening of the N–CS₂ (N–C) distance for both complexes. The Ni–P distance in the NiS₂PN chromophore [2.207(3) for **1**] is slightly shorter than that of the NiS₂P₂ chromophore [the mean value is 2.2241(16) Å for **3**]. The observed decrease in P–Ni–N angle of about 8° for **1** [92.15(19) versus 99.82(6)] compared to that of the P–Ni–P angle in **3** is due to the decrease in steric crowding around metal centre by the replacement of bulky PPh₃ with NCS⁻. The S–C–S and S–Ni–S angles are however similar.

Appendix A. Supplementary material

CCDC 263874 and 263875 contain the supplementary crystallographic data for 1 and 3. These 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. Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.poly.2006.10.006.

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