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Steric and Electronic Effects of Substituents on Planar Nickel(II) Complexes: Synthesis, NMR Spectral and Single Crystal X-ray Structural Studies on Nickel(II) Dithiocarbamates with NiS_2PN, NiS_2PC, and NiS_2P_2 Chromophores

Balasubramaniam Arul Prakasam,[1] Kuppukkannu Ramalingam,*[1]
Gabriele Bocelli,[2] and Andrea Cantoni[2]

[1]Department of Chemistry, Annamalai University, Annamalainagar - 608002, India

[2]IMEM, Casella Postale, Parma, Italy

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Four new dithiocarbamatonickel(II) complexes [Ni(dchdtc)(NCS)(PPh_3)] (**1**), [Ni(dchdtc)(CN)(PPh_3)] (**2**), [Ni(dchdtc)(PPh_3)$_2$]ClO_4 (**3**), and [Ni(dchdtc)(dppe)]ClO_4 (**4**) (dchdtc = *N*,*N*-dicyclohexyldithiocarbamate anion, PPh_3 = triphenylphosphine, and dppe = 1,2-bis(diphenylphosphino)ethane) were prepared from the parent [Ni(dchdtc)$_2$]. All four complexes were analyzed by CV, UV–vis, IR, and NMR (^{1}H, ^{13}C, and ^{31}P) spectra. ^{13}C NMR spectra of the complexes (**1**–**4**) show the most notable $>N\overset{..}{-}{}^{13}CS_2$ signals at around 200 ppm. In the cyclohexyl ring, the α-CH carbon is deshielded to a greater extent on complexation. Extraordinary deshielding was observed for the ^{31}P signal in all of the cases, indicating the effective bonding of phosphorus to the metal center. Single crystal X-ray structural analysis of the mixed ligand complexes (**1**–**3**) indicates a decrease in S–Ni–S bite angle when compared to that of the parent bis(dithiocarbamate), due to an increase in steric crowding around the central metal by the introduction of a bulky PPh_3. The *trans* effects on Ni–S bonds can be arranged in the following order: $NCS^- < PPh_3 < CN^-$. The $S_2C\overset{..}{-}N<$ bond is very short for complex **3**, (1.306(3) Å), because of the steric effect exerted by two PPh_3 groups and dchdtc. The observed negative reduction potentials follow the order: **1** > **2** > **3**, indicating the presence of a higher relative electron density on **1** compared to **2** and **3**.

Group 10 dithiocarbamato complexes with phosphines and nitrogenous ligands have been in the lime light on account of their structural novelty and their biological profiles.[1] Variations in the reactivity of nickel(II) dithiocarbamates with Lewis acids is a well documented phenomenon.[2,3] The steric and electronic nature of the dithiocarbamato ligands has a pronounced effect on the reactivity of bis(dithiocarbamates) with phosphines (both simple and chelating) and nitrogenous ligands.[4,5] The symbiotically induced softness of substituents on the dithiocarbamato ligands was also found to be important when determining the reactivity.[4,5] Divalent nickel complexes of dithiocarbamates contain a planar diamagnetic MS_4 chromophore. Nickel(II) dithiocarbamates in their reaction with PR_3 form planar NiS_2P_2 chromophores, which are again diamagnetic in nature.[6] In our continuous efforts to investigate the synthetic and structural chemistry of dithiocarbamates,[6,7] we herein report on four complexes [Ni(dchdtc)(NCS)(PPh_3)] (**1**), [Ni(dchdtc)(CN)(PPh_3)] (**2**), [Ni(dchdtc)(PPh_3)$_2$]ClO_4 (**3**), and [Ni(dchdtc)(dppe)]ClO_4 (**4**) (dchdtc = *N*,*N*-dicyclohexyldithiocarbamate anion, PPh_3 = triphenylphosphine, and dppe = 1,2-bis(diphenylphosphino)ethane, corresponding with NiS_2PN, NiS_2PC, and NiS_2P_2 chromophores).

Experimental

Preparation of Complexes. **[Ni(dchdtc)(NCS)(PPh_3)] (1):** A mixture of [Ni(dchdtc)$_2$] (285 mg, 0.5 mmol), PPh_3 (260 mg, 1 mmol), $NiCl_2 \cdot 6H_2O$ (120 mg, 0.5 mmol), and NH_4SCN (75 mg, 1 mmol) was refluxed for 2 h in an acetonitrile–methanol solvent mixture (2:1, 75 mL) and was then concentrated to ca. 50 mL. After two days, a purple-red solid separated out from the solution. The solid was filtered and then dried over anhydrous calcium chloride. Single crystals suitable for X-ray diffraction were obtained by repeated recrystallization of the sample from acetonitrile (Yield 65%, dec. 192 °C). Anal. Found: C, 59.94; H, 5.67; N, 4.15%. Calcd for $C_{32}H_{37}N_2NiPS_3$: C, 60.47; H, 5.86; N, 4.40%.

[Ni(dchdtc)(CN)(PPh_3)] (2): A mixture of [Ni(dchdtc)$_2$] (285 mg, 0.5 mmol), PPh_3 (260 mg, 1 mmol), $NiCl_2 \cdot 6H_2O$ (120 mg, 0.5 mmol), and KCN (65 mg, 1 mmol) in an acetonitrile–methanol (2:1, 75 mL) solvent mixture was refluxed for 3 h. The resulting orange-red solution was filtered and the filtrate was left undisturbed for two days. After two days, an orange-red solid separated out. Single crystals suitable for X-ray analysis were obtained by recrystallization of the sample from the same solvent mixture (Yield 65%, dec. 198 °C). Anal. Found: C, 62.99; H, 6.01; N, 4.44%. Calcd for $C_{32}H_{37}N_2NiPS_2$: C, 63.68; H, 6.17; N, 4.63%.

[Ni(dchdtc)(PPh_3)$_2$]ClO_4 (3): A mixture of [Ni(dchdtc)$_2$] (285 mg, 0.5 mmol), PPh_3 (520 mg, 2 mmol), $NiCl_2 \cdot 6H_2O$ (120 mg, 0.5 mmol), and NH_4ClO_4 (115 mg, 1 mmol) was refluxed for about 2 h in an acetonitrile–dichloromethane solvent mixture (1:1, 50 mL), and was then concentrated to ca. 25 mL. After two days, a purple-red solid separated out from the solution. The solid was filtered and then dried over anhydrous calcium chloride. Single crystals suitable for X-ray diffraction were obtained by recrys-

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Table 1. NMR Spectral Data (Chemical Shifts in ppm)

Complex	NMR	α-CH	β-CH_2	γ-CH_2	δ-CH_2	PPh_x[a)]	$>N^{13}CS_2$
	^1H		1.14–1.85			7.45–7.72	—
1	^{13}C	60.5	29.6	24.9	25.8	128.7–134.2	201.9[b)]
	^{31}P	—	—	—	—	22.8	—
	^1H		1.17–1.82			7.40–7.72	—
2	^{13}C	60.8	29.7	24.9	25.9	128.5–134.3	203.5[b)]
	^{31}P	—	—	—	—	30.3	—
	^1H		1.16–1.78			7.28–7.46	
3	^{13}C	61.2	29.8	24.7	25.6	127.5–134.2	197.8
	^{31}P	—	—	—	—	31.5	—
	^1H		1.22–3.08			7.52–8.24	—
4	^{13}C	54.0	24.0	24.6	24.8	127.2–133.6	201.0
	^{31}P	—	—	—	—	59.9	—

a) Where $x = 3$ for **1**, **2**, and **3** and 2 for **4**. b) S–^{13}C–N signal of **1** and ^{13}CN signal of **2** are observed respectively at 143.3 and 130 ppm.

tallization of the sample from acetonitrile (Yield 70%, dec. 187 °C). Anal. Found: C, 62.19; H, 5.48; N, 1.41%. Calcd for $C_{49}H_{52}ClNNiO_4P_2S_2$: C, 62.65; H, 5.58; N, 1.49%.

[Ni(dchdtc)(dppe)]ClO_4 (4): A mixture of [Ni(dchdtc)$_2$] (570 mg, 1 mmol), dppe (790 mg, 2 mmol), $NiCl_2 \cdot 6H_2O$ (240 mg, 1 mmol), and NH_4ClO_4 (230 mg, 2 mmol) was refluxed for about 4 h in a methanol–dichloromethane solvent mixture (1:1, 50 mL), followed by concentration to ca. 25 mL. After 2 days, a purple-red solid separated out and was dried over anhydrous calcium chloride. The solid was recrystallized from the same solvent mixture (Yield 65%, dec. 183 °C). Anal. Found: C, 57.25; H, 5.59; N, 1.62%. Calcd for $C_{39}H_{46}ClNNiO_4P_2S_2$: C, 57.60; H, 5.70; N, 1.72%.

Instrumentation and Methods. All of the reagents and solvents employed were commercially available analytical grade materials and were used as supplied without further purification. Electronic spectra of the complexes were recorded on a HITACHI U-2001 spectrophotometer using CH_2Cl_2 as the solvent. IR spectra were recorded on an ABB Bomem MB 104 spectrophotometer (range 4000–400 cm^{-1}) as KBr pellets. Cyclic voltammograms were recorded in CH_2Cl_2 (10^{-3} M) on an ECDA basic electrochemical system comprising of glassy carbon as the working electrode, Ag/Ag^+ as the reference electrode, and Pt wire as the counter electrode. NMR spectra of all four complexes were recorded on a Bruker AMX 400 spectrometer at room temperature, using $CDCl_3$ as the solvent and TMS as the internal reference. The ^{13}C NMR spectra were recorded in proton decoupled mode. The ^{1}H, ^{13}C, and ^{31}P chemical shifts and their corresponding assignments are given in Table 1.

X-ray Crystallography. Details of crystal data, data collection, and refinement parameters for complexes **1**, **2**, and **3** are summarized in Table 2. Intensity data were collected at ambient temperature (295 K) on a Bruker AXS (with CCD) diffractometer using graphite monochromated Mo Kα radiation. Absorption correction was performed with a method inserted into SHELXL-NT V.5.1.[8] The Bruker AXS software was used for solving structures. All of the non-hydrogen atoms were refined anisotropically and all of the hydrogen atoms were refined isotropically. Selected bond lengths and bond angles are given in Table 3.

Crystallographic data have been deposited with the Cambridge Crystallographic Data Collection Centre: Deposition numbers CCDC-263871, -263872, and -263873 for complexes **1**, **2**, and **3**, respectively. Copies of the data can be obtained free of charge by request quoting the deposition number from, The Director, CCDC, 12, Union Road, Cambridge, CB2 1EZ, UK (fax: +44 1223 336033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk/conts/retrieving.html).

Results and Discussion

Electronic Spectra. Electronic spectra show bands at 475, 439, 510, and 471 nm for complexes **1**, **2**, **3**, and **4**, respectively, due to d–d transitions. Based on the single crystal electronic spectral studies of similar complexes, the band around 470 nm for complexes **1** and **4** is attributed to the $d_{z^2} \rightarrow d_{x^2-y^2}$ transition[9] and the cyanide ion exerting a larger LFSE, resulting in the least λ_{max} being associated with **2**. In all of the cases the charge-transfer bands were observed below 400 nm.[9] Electronic spectral data of the complexes support the assumption of a square planar geometry around the nickel atom in all of the complexes.

IR Spectral Studies. The parent [Ni(dchdtc)$_2$] shows a $\nu_{C\text{–}N}$ band at 1462 cm^{-1}, whereas the same band appears at 1503, 1506, 1510, and 1499 cm^{-1} for complexes **1**, **2**, **3**, and **4**, respectively. This is because of the significant contribution made by the polar $S_2C^{-}\overset{..}{=}N^{+}<$ structure in all of the cases. Increasing drift of electron density from the dithiocarbamate towards the metal center moves the $\nu_{C\text{–}N}$ ($S_2C\overset{..}{=}N<$) stretching bands progressively to higher frequencies. The band resulting from the "N"-coordination of the thiocyanato-*N* ligand in **1** appears at 2092 cm^{-1}. Similarly for compound **2**, the band at 2108 cm^{-1} is evidence of the coordination of the cyanide ion and the metal center through carbon. In the present study, the occurrence of a single $\nu_{C\text{–}S}$ band in the region of 990–1000 cm^{-1} for all of the complexes indicates the uninegative bidentate behavior of the dithiocarbamato ligand.

NMR Spectral Studies. **^{1}H NMR:** Since the α, β, and γ (a, e) protons of the cyclohexyl ring give only a multiplet, in the table only the region in which cyclohexyl ring proton signals were observed is given, and no individual assignments were made. For all four (**1**–**4**) complexes, the aromatic protons from triphenylphosphine and chelating dppe resonate in the region of 7.28–8.24 ppm. In the case of complex **4**, the signal for the CH_2 in dppe also merged with the cyclohexyl ring proton signals.

Table 2. Crystal Data, Data Collection, and Refinement Parameters for **1**, **2**, and **3**

Complex	**1**	**2**	**3**
Empirical formula	$C_{32}H_{37}N_2NiPS_3$	$C_{32}H_{37}N_2NiPS_2$	$C_{49}H_{52}ClNNiO_4P_2S_2$
FW	635.5	603.5	939.2
Crystal dimensions/mm^3	0.23 × 0.31 × 0.39	0.17 × 0.19 × 0.21	0.15 × 0.30 × 0.36
Crystal system	Monoclinic	Hexagonal	Orthorhombic
Colour	Purple-red	Orange-red	Purple
Space group	$P2_1/c$	$P3_1$	*Pbca*
a/Å	12.745(2)	16.124(2)	15.488(3)
b/Å	10.474(2)	16.124(2)	37.392(4)
c/Å	25.765(3)	10.185(2)	16.571(3)
α/°	90	90	90
β/°	98.67(2)	90	90
γ/°	90	120	90
U/Å^3	3400.1(9)	2293.2(6)	9596.7(3)
Z	4	3	8
D_{calcd}/g cm^{-3}	1.241	1.311	1.297
μ/cm^{-1}	8.24	8.47	6.57
$F(000)$	1336	954	3936
λ/Å	Mo Kα (0.71069)	Mo Kα (0.71073)	Mo Kα (0.71073)
θ range/°	1.62–28.61	2.48–23.99	1.09–28.56
Scan type	$\omega - 2\theta$	$\omega - 2\theta$	$\omega - 2\theta$
Index ranges	$-15 \le h \le 16$, $-10 \le k \le 13$, $-33 \le l \le 32$	$-11 \le h \le 10$, $-4 \le k \le 11$, $-7 \le l \le 9$	$0 \le h \le 20$, $0 \le k \le 49$, $0 \le l \le 22$
Reflections collected	6644	1463	11273
Observed reflections $F_0 > 4\sigma(F_0)$	1985	1384	7484
Weighting scheme	$W = 1/[\sigma^2(F_0{}^2) + (0.0302P)^2 + 0.000P]$ where $P = (F_0{}^2 + 2F_c{}^2)/3$	$W = 1/[\sigma^2(F_0{}^2) + (0.0334P)^2 + 0.00P]$ where $P = (F_0{}^2 + 2F_c{}^2)/3$	$W = 1/[\sigma^2(F_0{}^2) + (0.0867P)^2 + 0.000P]$ where $P = (F_0{}^2 + 2F_c{}^2)/3$
Number of parameters refined	478	467	749
Final R, R_w (obs, data)	0.0567, 0.0841	0.0185, 0.0431	0.0322, 0.1068
GOOF	0.721	0.973	0.860

Table 3. Selected Bond Distances and Bond Angles for **1**, **2**, and **3**

1		**2**		**3**	
Bond distances/Å					
Ni1–N18	1.878(6)	Ni–C1	1.878(9)	Ni1–S3	2.1914(7)
Ni1–S2	2.1751(17)	Ni–S3	2.189(2)	Ni1–P18	2.2110(7)
Ni1–P21	2.196(2)	Ni–P2	2.205(2)	Ni1–S2	2.2141(7)
Ni1–S3	2.2041(19)	Ni–S4	2.211(2)	Ni1–P37	2.2525(7)
S2–C4	1.705(6)	S3–C20	1.722(7)	S2–C4	1.736(2)
S3–C4	1.724(6)	S4–C20	1.745(7)	S3–C4	1.717(3)
C4–N5	1.350(7)	C20–N2	1.320(8)	C4–N5	1.306(3)
N5–C12	1.493(7)	N2–C21	1.478(9)	N5–C6	1.495(3)
N5–C6	1.476(7)	N2–C27	1.499(8)	N5–C12	1.526(4)
Bond angles/°					
N18–Ni1–S2	172.43(17)	C1–Ni–S3	90.0(2)	S3–Ni1–P18	170.38(3)
N18–Ni1–P21	91.87(17)	C1–Ni–P2	95.3(2)	S3–Ni1–S2	77.71(3)
S2–Ni1–P21	95.62(7)	S3–Ni–P2	169.28(9)	P18–Ni1–S2	93.11(3)
N18–Ni1–S3	94.36(17)	C1–Ni–S4	168.2(2)	S3–Ni1–P37	89.05(3)
S2–Ni1–S3	78.23(7)	S3–Ni–S4	78.56(7)	P18–Ni1–P37	100.20(2)
P21–Ni1–S3	173.14(7)	P2–Ni–S4	96.47(8)	S2–Ni1–P37	166.63(3)
C4–S2–Ni1	87.9(2)	C20–S4–Ni	86.6(3)	C4–S2–Ni1	87.06(8)
C4–S3–Ni1	86.5(2)	C20–S3–Ni	87.9(3)	C4–S3–Ni1	88.26(8)
N5–C4–S2	127.9(5)	N2–C20–S3	126.6(5)	N5–C4–S3	127.23(19)
N5–C4–S3	124.7(5)	N2–C20–S4	126.4(5)	N5–C4–S2	126.43(19)
S2–C4–S3	107.3(3)	S3–C20–S4	106.9(5)	S3–C4–S2	106.33(14)

^{13}C NMR: As observed earlier,[10] the dithiocarbamates that show high $\nu_{C–N}$ ($S_2C\overset{\cdots}{-}N<$) band values in IR spectrum have a corresponding low $>N^{13}CS_2$ chemical shifts in ^{13}C NMR spectrum and vice versa. In the cyclohexyl ring, the α-CH carbon appears to be deshielded to a greater extent and signals are observed at 60.5, 60.8, 61.2, and 54.0 ppm for complexes **1**, **2**, **3**, and **4**, respectively. Among the γ-CH_2 and δ-CH_2 carbons, the δ-CH_2 carbon signals are observed in the up field region (of around 1 ppm) relative to that of γ-CH_2 carbon signals with comparatively low intensity. An up field shift is generally observed for any carbon that exists in *gauche* orientation with respect to another carbon or hetero atom, relative to the shielding of its *anti* counterpart.[11]

^{31}P NMR: Generally, free triphenylphosphine shows a signal at -5 ppm[11] and a coordinated phosphine shows a signal at around 20 ppm. Similarly, free chelating dppe shows a signal at -13 ppm[12] and a coordinated chelating phosphine shows a signal at around 60 ppm. The complex with chelating dppe gives a signal at 59.9 ppm for the coordinated phosphorus. An increase in negative charge on phosphorus by the direct bonding of the electron donating methylene group may force the alleviation of excess electron density (from the chelating dppe) to the metal center, in contrast to those of complexes with free PPh_3 (**1**–**3**) where phosphorus is attached to electron withdrawing phenyl groups. Similarly, there is an interesting correlation between the λ_{max} of d–d bands observed in the complexes with the nature of phosphine involved in the complex. The presence of two PPh_3 groups in complex **3** shows a larger λ_{max} value compared to that of the chelating dppe analogue **4**. The observation is in line with the observed ^{31}P NMR chemical shift values. More than the binding ability, two molecules of PPh_3 in the place of dppe destabilize the complex due to their steric demand. Higher relative deshielding is observed in the case of complexes with NiS_2P_2 and NiS_2PC chromophores. Very high deshielding is observed for the ^{31}P signal in all of the cases, indicating the drift of electron density from phosphorus on complexation.

Cyclic Voltammetric Studies. From the CV studies, it was observed that all of the complexes undergo a one electron reduction process ($Ni^{II} \rightarrow Ni^{I}$). All four mixed ligand complexes have lower reduction potentials [-1310, -1246, -1180, and $-890/-801$ mV for **1**, **2**, **3**, and **4**, respectively] than the parent $Ni(dchdtc)_2$ [-1580 mV], which shows a reluctance to add more electron density to the already electron rich metal center in the parent complex. For complex **4**, a quasi-reversible reduction couple [$E_p{}^c = -890\,\text{mV}/E_p{}^a = -801\,\text{mV}$] is observed, and this observation is a phenomenon due to the chelating phosphine which stabilizes the reduced Ni^I complexes.[6] Gradation of the observed negative reduction potentials viz, **1** > **2** > **3**, indicates the presence of a higher relative electron density on **1** compared to **2** and **3**.

Structural Analysis. Single crystal X-ray structural analysis of complexes **1**, **2**, and **3** are discussed here, our attempts to crystallize complex **4** having been unsuccessful. The ORTEP diagram of $[Ni(dchdtc)(NCS)(PPh_3)]$ (**1**) is shown in Fig. 1 together with the atom numbering scheme. The structure consists of a distorted square planar metal coordination with the NiS_2PN chromophore. For **1**, the coordination sphere shows only minor deviations from planarity, but with angles that differ considerably from 90° [S(2)–Ni(1)–P(21) = 95.62(7); N(18)–Ni(1)–S(3) = 94.36(17); N(18)–Ni(1)–P(21) = 91.87(17); S(2)–Ni(1)–S(3) = 78.23(7)°]. The molecule is not perfectly square planar because of the small bite angle of 78.23(7)°. The two Ni–S [Ni(1)–S(2) = 2.1751(17) and Ni(1)–S(3) = 2.2041(19) Å] and C–S [C(4)–S(2) = 1.705(6) and C(4)–S(3) = 1.724(6) Å] distances are asymmetric due to the difference in the *trans* influencing property of the NCS^- and PPh_3 groups. The delocalization of the π electron density over the S_2CN moiety results in the strong double bond character of the [C(4)–N(5) = 1.350(7) Å] bond, which is also supported by the observed increase in S–C–N angles [124.7(5) and 127.9(5)°] over the S–C–S angle of 107.3(3)°. The N–C–S bond angle of the thiocyanato-*N* [177.3(7)°] exemplifies the linear nature of the N–C–S fragment. The packing diagram of the molecule shows that the cyclohexyl rings of the dithiocarbamate and the phenyl rings of the PPh_3 molecules are found well stacked, one over the other, along the OB axis of the unit cell, enabling an effective three-dimensional arrangement for the molecule. The two cyclohexyl rings appear to be bonded to the nitrogen equatorially and the phenyl rings in the triphenylphosphine show normal bond parameters.

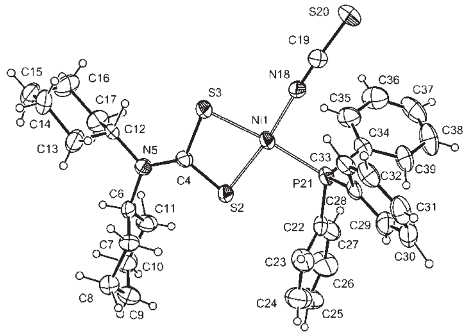

Fig. 1. ORTEP of $[Ni(dchdtc)(PPh_3)(NCS)]$.

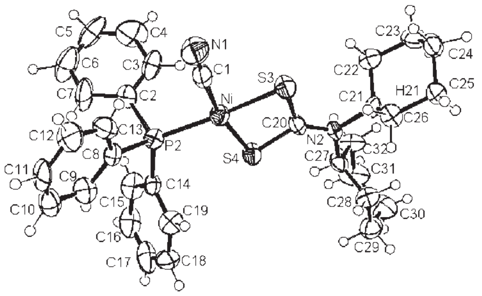

Fig. 2. ORTEP of $[Ni(dchdtc)(PPh_3)(CN)]$.

$[Ni(dchdtc)(CN)(PPh_3)]$ (**2**) is monomeric with no significant intermolecular associations. ORTEP of the complex is shown in Fig. 2. Three formula units are present in the unit cell. The planar environment around the central metal atom is well supported by the small mean plane deviation of S(3) of 0.142 Å. The bite angle associated with the dithiocarbamate is very small [S–Ni–S = 78.56(7)°]. Ni–S [Ni–S(3) = 2.189(2) and Ni–S(4) = 2.211(2) Å] and C–S [C(20)–S(3) = 1.722(7) and C(20)–S(4) = 1.745(7) Å] distances are symmetrical. The C–N bond length [1.134(8) Å] in the cyanide moiety is shorter than the [$>N\overset{\cdots}{-}CS_2$] C–N distance of 1.320(8) Å, indicating its triple bonded nature. The increase in P–Ni–C [95.3(2)°] and

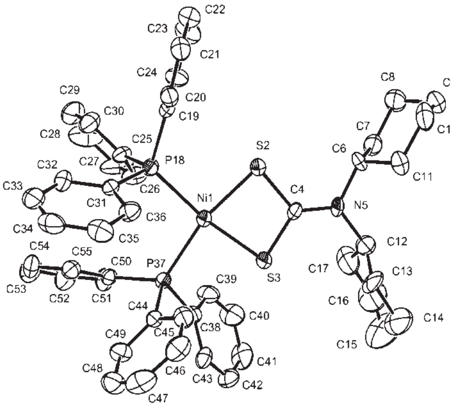

Fig. 3. ORTEP of [Ni(dchdtc)$(PPh_3)_2$]ClO_4 (hydrogen atoms and ClO_4 anion are omitted for clarity).

P–Ni–S [96.47(8)°] angles over the other two angles [C(1)–Ni–S(3) = 90.0(2)° and S(4)–Ni–S(3) = 78.56(7)°] around the metal center exemplifies the steric effect exerted by the bulkier PPh_3. The Ni–C–N angle [174.4(7)°] is slightly nonlinear because of the presence of bulky PPh_3 in the adjacent position.

ORTEP of complex **3** is shown in Fig. 3. The observed planarity of the NiS_2P_2 chromophore in this molecule is consistent with the diamagnetic nature of the complex. For nickel, the two sulfur atoms from the dithiocarbamate part and two phosphorus atoms from the triphenylphosphine ligand form an approximate square planar arrangement with the small bite angle associated with the dithiocarbamate moiety [77.71(3)°]. The observed reduction in bite angle is attributed to the very high steric effect caused by the two triphenylphosphine ligands and the two cyclohexyl rings of the dithiocarbamate. The Ni–P distances [2.2110(7) and 2.2525(7) Å] are asymmetric. As in **1**, **2**, and in the case of complex **3** also, two cyclohexyl rings are stacked in chair conformation. The Ni–S [2.1914(7) and 2.2141(7) Å] and C–S [1.736(2) and 1.717(3) Å] bonds are almost symmetrical, indicating delocalization of the negative charge on the dithiocarbamate ligand. The two S–C–N angles [127.23(19) and 126.43(19)°] are about 20° higher than the S–C–S angle [106.33(14)°]. The C–P–C angles in the triphenylphosphines are asymmetric [102.04(10) to 110.91(13)°] due to the steric crowding of the phenyl rings. In the counter anion, the Cl–O distances vary from 1.129(8) to 1.424(6) Å, and the O–Cl–O angles vary from 102.8(5) to 116.8(9)°, indicating a deviation from an ideal tetrahedral geometry. The perchlorate anion shows extensive thermal disorder as observed in many similar compounds.

Comparison of Bond Parameters. The decrease in the S–Ni–S bite angle for all of the mixed ligand complexes compared to that of the parent [79.06(5)°] bisdithiocarbamate[13] is due to the increase in steric crowding around the metal center by the introduction of bulky PPh_3 in the cases of complexes **1**, **2**, and **3**. The S–Ni–S bite angle and the [$>NCS_2$] C–N bond distance are very small for complex **3**, a clear manifestation of the steric crowding caused by the two bulky PPh_3 groups, and to some extent by the bulky nature of the two cyclohexyl rings attached to the dithiocarbamate. P–Ni–N (**1**) and P–Ni–C (**2**) angles are smaller than the P–Ni–P angle in **3** because of the sterically less demanding NCS^- and CN^- present in **1** and **2**, respectively, in the place of bulky PPh_3.

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