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SYNTHESIS AND SINGLE-CRYSTAL STRUCTURE DETERMINATION OF BIS(TRIPHENYLPHOSPHINE) (DIISOPROPYLDITHIOCARBAMATO)NICKEL(II) PERCHLORATE CHLOROFORM SOLVATE AND [1,2-BIS(DIPHENYLPHOSPHINO-k.*P*,*P*′)ETHANE] (DIISOPROPYLDITHIOCARBAMATO)NICKEL(II) PERCHLORATE CHLOROFORM SOLVATE: STERIC EFFECT OF BULKY ALKYL SUBSTITUENTS ON THE DITHIOCARBAMATE, FREE AND CHELATING PHOSPHINES ON THE NiS_2P_2 CHROMOPHORE

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Abstract—The complexes $[Ni(dipdtc)(PPh_3)_2]ClO_4\cdot CHCl_3$ (**1**) and $[Ni(dipdtc)dppe]ClO_4\cdot CHCl_3$ (**2**) (dipdtc = diisopropyldithiocarbamate, dppe = 1,2-bis(diphenylphosphino)ethane) have been prepared from the reaction between $Ni(dipdtc)_2$ (**3**) and phosphines (PPh_3 and dppe) in $CHCl_3$–CH_3OH. The crystal structures of **1** and **2** have been determined, showing that both complexes have planar NiS_2P_2 chromophores. Increased bulkiness of the alkyl substituent on the dithiocarbamate increases the span volume of the molecule and forces the lengthening of the C—N distance due to its puckering. Chelating dppe in complex **2** forces a lower P—Ni—P angle and increased S—Ni—S angle compared to complex **1**.

Group VIII dithiolates containing planar MS_4 chromophores show interesting variations in their reactions with Lewis bases.[1,2] Soft Pd^{II} and Pt^{II} dithiolates preferably interact with soft phosphines to give rise to planar MS_2P_2 chromophores.[3,4] In solution, an MS_2P_2 chromophore with square pyramidal geometry has also been reported for M = Pd^{II} and Pt^{II}. Detailed structural studies on a variety of MS_2P_2 chromophores have also been made.[5,6] Unlike its congeners, Ni^{II} is a border line acceptor. Ni^{II} complexes of dithiocarbamates are typical planar complexes containing NiS_4 chromophores. The planar dithiocarbamates prefer to react with soft Lewis bases such as phosphines rather than hard nitrogenous bases such as NH_3 and pyridine, due to the symbiotically induced softness.[7,8] On reaction with PR_3 or dppe, they form complexes of the chromophore NiS_2P_2 which are diamagnetic in nature.[9–11] Mixed ligand complexes of the type $[Ni(S_2CNR_2)X(PR_3)]$ have been prepared by the interaction of dithiocarbamate with PR_3 in the presence of NiX_2.[12] Complexes of the type $Ni(dtc)Cl(PPh_3)$ and $[Ni(dtc)(PPh_3)_2]ClO_4$

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{dtc = $[S_2CN(C_2H_5)_2]^-$, $[S_2CNH(C_2H_4OH)]^-$, $[S_2CN(C_2H_4OH)_2]^-$, $[S_2CN(C_4H_8O)]^-$ and $[S_2CN(C_5H_{10})]^-$} have also been reported from our laboratory.[13] Recently, a single-crystal study of [1,2-bis(diphenylphosphino - k.*P*,*P′*)ethane](4 - morpholinecarbodithioato) nickel(II) perchlorate dichloromethane solvate (**4**) showed an interesting thioureide bond distance.[14] In continuation of our interest in planar NiS_2P_2 chromophores, the present study was undertaken to understand (i) the influence of increased bulkiness of the dithiocarbamate ligand and (ii) the coordination of free and chelating phosphines on the structure of the chromophore. We report the preparation and single-crystal structure determination of $[Ni(dipdtc)(PPh_3)_2]ClO_4 \cdot CHCl_3$ (**1**) and $[Ni(dipdtc)(dppe)]ClO_4 \cdot CHCl_3$ (**2**) (dipdtc = diisopropyldithiocarbamate) in this paper.

EXPERIMENTAL

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

Physical measurements

IR spectra were recorded on a JASCOIR-700 spectrophotometer (range 4000–400 cm^{-1}) as KBr pellets. The UV–vis spectra in $CHCl_3$ were recorded on a JASCO UVIDEC double-beam spectrophotometer.

Preparation of the complexes

Bis (triphenylphosphine) (diisopropyldithiocarbamato)nickel(II) perchlorate chloroform solvate, $[Ni(dipdtc)(PPh_3)_2]ClO_4 \cdot CHCl_3$ (**1**). A mixture of $Ni(dipdtc)_2$[15] (410 mg, 1 mmol), PPh_3 (520 mg, 2 mmol), $NiCl_2 \cdot 6H_2O$ (120 mg, 0.5 mmol) and $NaClO_4$ (125 mg, 1 mmol) in methanol–chloroform (50 cm^3) was refluxed for about 3 h, followed by concentration to *ca* 25 cm^3, and then allowed to settle for 2 days. The precipitated purple–red compound was filtered and dried over anhydrous calcium chloride. Single crystals suitable for X-ray work were obtained after recrystallization from chloroform–ethanol (yield 70%, m.p. 220°C).

[1,2 - Bis(diphenylphosphino - k.*P*,*P′*)ethane]-(diisopropyldithiocarbamato)nickel(II) perchlorate chloroform solvate, $[Ni(dipdtc)(dppe)]ClO_4 \cdot CHCl_3$ (**2**). A mixture of $Ni(dipdtc)_2$ (410 mg, 1 mmol), dppe (400 mg, 1 mmol) and $NaClO_4$ (125 mg, 1 mmol) was refluxed in methanol–chloroform (50 cm^3) for about 3 h, followed by concentration to *ca* 25 cm^3, and then allowed to settle for 2 days. An orange–yellow coloured solid was filtered off and dried over anhydrous calcium chloride. Crystals suitable for X-ray structural analysis were obtained by recrystallization from methanol–chloroform (yield 70%, m.p. 170°C).

X-ray crystallography

Details of the crystal data, data collection and refinement parameters for complexes **1** and **2** are summarized in Table 1. The intensity data were collected at ambient temperature on a Siemens R3m/V diffractometer using graphite monochromated Mo-K_α radiation ($\lambda = 0.71073$ Å). The lattice parameters were obtained from least-squares refinement using 25 reflections. Intensities of two standard reflections, recorded for every 123 reflections, showed no significant change. Lorentz and polarization corrections were made. A semi-empirical absorption correction was applied. The structures **1** and **2** were solved by direct methods and refined by full-matrix least-squares. All the non-hydrogen atoms were refined anisotropically and the hydrogen atoms were fixed isotropically using a riding model. Calculations were performed using SHELXTL PLUS PC version.[16] Selected bond distances and angles are presented in Tables 2 and 3.

RESULTS AND DISCUSSION

IR spectra of complexes **1** and **2** show ν(C—N) bands at 1532 and 1512 cm^{-1}, respectively. The shift in ν(C—N) values to higher wavenumber compared with the parent Ni(dipdtc) (**3**) is due to the mesomeric drift of electrons from the dithiocarbamate moiety to the metal centre, thereby increasing the contribution of the thioureide form. The ν(C—S) bands appear around 995 cm^{-1} without any splitting, supporting the bidentate coordination of the dithiocarbamate moiety.[17] The electronic absorption spectrum of complex **1** shows bands at 400, 460, 550 and 570 nm. The strong band at 400 nm is attributed to the metal → ligand charge transfer process.[13] The other bands are due to *d–d* transitions arising from $d_{yz} \rightarrow d_{xy}$ (460 nm), $d_{xz} \rightarrow d_{xy}$ (550 nm) and $d_{x^2-y^2} \rightarrow d_{xy}$ (570 nm) orbitals. Similar transitions were reported for the $[Ni(dedtc)(PPh_3)_2]^+$ complex,[13] based on a single-crystal polarized spectral study.[18] Two absorption bands clearly appear around 450 and 480 nm in

Table 1. X-ray crystal data collection, solution and refinement details for complexes **1** and **2**

Compound	**1**	**2**
Empirical formula	$C_{44}H_{45}Cl_4NO_4P_2S_2Ni$	$C_{34}H_{39}Cl_4NO_4P_2S_2Ni$
M	978.4	852.2
Crystal dimensions (mm)	0.30 × 0.35 × 0.40	0.15 × 0.20 × 0.20
Crystal system	Monoclinic	Triclinic
Space group	$P2_1/c$	$P\bar{1}$
a (Å)	9.829(3)	11.015(2)
b (Å)	34.786(9)	13.325(3)
c (Å)	14.009(4)	14.211(4)
α (°)	90	91.81(2)
β (°)	100.40(2)	106.06(2)
γ (°)	90	100.73(2)
U (Å^3)	4711(2)	1961.7(8)
Z	4	2
D_c (g cm^{-3})	1.379	1.443
μ (mm^{-1})	0.84	0.992
F (000)	2024	880
T (K)	294	293
2θ range/°	3–45	3–45
Scan type, speed (°min^{-1} in ω);	ω, variable; 4.0–29.30	ω–2θ, variable; 3.0–29.30
range (°)	0.80	0.60
Index ranges	$0 \leqslant h \leqslant 10$, $0 \leqslant k \leqslant 37$, $-15 \leqslant l \leqslant 14$	$0 \leqslant h \leqslant 11$, $-14 \leqslant k \leqslant 14$, $-16 \leqslant l \leqslant 16$
Reflections collected	6953	5168
Independent reflections (R_{int})	6188	5168
Observed reflections [$F > 6\sigma(F)$]	3695	3446
Min./max. transmission	0.7190/0.7582	0.776/0.855
Weighting scheme	$w^{-1} = \sigma^2(F)+0.0008F^2$	$w^{-1} = \sigma^2(F)+0.0006F^2$
Number of parameters refined	267	317
Final R, R_w (obs. data)	0.0652, 0.0825	0.0583, 0.0764
Goodness-of-fit	1.96	2.12
Data-to-parameter ratio	13.8 : 1	10.9 : 1
Largest and mean Δ/σ	0.239, 0.011	0.099, 0.005
Largest difference peak, hole (e Å^{-3})	0.85, −0.59	0.66, −0.76

complex 2; these bands are attributed to the *d–d* transitions.

Structure analysis

The crystal structure, along with the numbering scheme, of complex **1** is shown in Fig. 1. The crystal contains discrete mononuclear [Ni(dipdtc)$(PPh_3)_2]^+$ units with no significant intermolecular contacts. Four formula units are present in the unit cell. The Ni, S(1), S(2), P(1) and P(2) atoms are coplanar. The planarity of the molecule is in keeping with the observed diamagnetism of the complex. The molecule is not of perfect square geometry because of the small bite angle [77.7(1)°] associated with the dithiocarbamate ligand. A similar geometry is also found in the complex [Ni(dedtc)$(PPh_3)_2]^+$. The two Ni—S bonds [2.209(3) and 2.201(3) Å] are not significantly different, though the two Ni—P distances are [2.215(2) and 2.224(3) Å]. The related C—S distances [1.717(9) and 1.713(3) Å] are also symmetric. The bond parameters of the dithiocarbamate moiety are normal, as observed in the earlier studies.[19] There is a very significant lengthening of the Ni—S bond in complex **1** compared to the parent complex (**3**).

The phenyl rings show normal bond parameters. Two of the phenyl rings in PPh_3 are pitched to the same extent, whereas the third one is almost

Table 2. Selected bond distances (Å) and angles (°) for [Ni(dipdtc)(PPh$_3$)$_2$]ClO$_4$·CHCl$_3$ (1)

Ni(1)—P(1)	2.215(2)	Ni(1)—P(2)	2.224(3)
Ni(1)—S(1)	2.209(3)	Ni(1)—S(2)	2.201(3)
P(1)—C(13)	1.826(5)	P(1)—C(19)	1.803(5)
P(1)—C(25)	1.804(5)	P(2)—C(31)	1.818(5)
P(2)—C(37)	1.818(4)	P(2)—C(43)	1.823(5)
S(1)—C(1)	1.717(9)	S(2)—C(1)	1.713(9)
C(1)—N(1)	1.321(11)	N(1)—(2)	1.500(13)
N(1)—C(5)	1.485(13)	C(2)—C(3)	1.517(15)
C(2)—C(4)	1.494(15)	C(5)—C(6)	1.487(12)
C(5)—C(7)	1.507(13)		
P(1)—Ni(1)—P(2)	99.4(1)	P(1)—Ni(1)—S(1)	169.0(1)
P(2)—Ni(1)—S(1)	89.4(1)	P(1)—Ni(1)—S(2)	94.1(1)
P(1)—Ni(1)—S(2)	166.0(1)	S(1)—Ni(1)—S(2)	77.7(1)
Ni(1)—P(1)—C(13)	113.9(2)	Ni(1)—P(1)—C(19)	107.1(2)
C(13)—P(1)—C(19)	104.1(2)	Ni(1)—P(1)—C(25)	118.7(2)
C(13)—P(1)—C(25)	100.9(2)	C(19)—P(1)—C(25)	111.2(2)
Ni(1)—P(2)—C(31)	112.1(2)	Ni(1)—P(2)—C(37)	108.2(2)
C(31)—P(2)—C(37)	107.6(2)	Ni(1)—P(2)—C(43)	122.2(2)
C(31)—P(2)—C(43)	102.2(2)	C(37)—P(2)—C(43)	103.4(2)
Ni(1)—S(1)—C(1)	87.2(3)	Ni(1)—S(2)—C(1)	87.6(3)
S(1)—C(1)—S(2)	107.5(5)	S(1)—C(1)—N(1)	123.1(7)
S(2)—C(1)—N(1)	129.4(7)	C(1)—N(1)—C(2)	120.1(8)
C(1)—N(1)—C(5)	122.7(8)	C(2)—N(1)—C(5)	117.2(7)
N(1)—C(2)—C(3)	108.1(9)	N(1)—C(2)—C(4)	112.4(9)
C(3)—C(2)—C(4)	113.3(9)	N(1)—C(5)—C(6)	113.0(8)
N(1)—C(5)—C(7)	114.7(8)	C(6)—C(5)—C(7)	113.8(9)
P(1)—C(13)—C(8)	122.5(1)	P(1)—C(13)—C(12)	117.4(1)
P(1)—C(19)—C(14)	113.7(2)	P(1)—C(19)—C(18)	126.0(2)
P(1)—C(25)—C(20)	118.7(2)	P(1)—C(25)—C(24)	121.3(2)
P(2)—C(31)—C(26)	117.5(1)	P(2)—C(31)—C(30)	122.2(1)
P(2)—C(37)—C(32)	121.6(1)	P(2)—C(37)—C(36)	118.1(1)
P(2)—C(43)—C(38)	120.2(1)	P(2)—C(43)—C(42)	119.8(1)

perpendicular to the Ni—P—C—C plane as a requirement for the packing of the molecules in the unit cell. The oxygen atoms of the ClO$_4^-$ ion show large thermal parameters, even though there are no short contacts, suggesting the presence of disorder.

Complex **2** is monomeric, with two molecules per unit cell. The crystal structure of complex **2**, along with the numbering scheme, is shown in Fig. 2. There is almost perfect symmetry with respect to the Ni—S distances [2.194(2) and 2.196(2) Å], indicating symmetric bidentate bonding to the nickel ion. The related C—S distances are also symmetric [1.733(7) and 1.721(7) Å]. The Ni—P distances are similar to those reported earlier in [1,2-bis(diisopropylphosphino)ethane]carbenenickel(0)[14] (**4**) [namely 2.165(2) and 2.160(2) Å]. The Ni—P distance is a relatively very short distance compared to the long Ni—P distance reported.[20] The P—Ni—P angle is 87.3(1)°, which is less than that observed in complex **4** (91.0°). In complexes **1** and **2**, the Cl—O average distance is 1.502 Å and angles are in the range 105–117°, indicating distortion from tetrahedral geometry. Similar distortions of the ClO$_4^-$ ion in complexes are well known.[13] The chloroform C—Cl bond shows an average distance of C—Cl = 1.717 Å. Table 4 gives a comparison of

Table 3. Selected bond distances (Å) and angles (°) for [Ni(dipdtc)(dppe)]$ClO_4 \cdot CHCl_3$ (**2**)

Ni(1)—P(1)	2.164(2)	Ni(1)—P(2)	2.160(2))
Ni(1)—S(1)	2.194(2)	Ni(1)—S(2)	2.196(2)
P(1)—C(8)	1.837(6)	P(1)—C(15)	1.802(7)
P(1)—C(21)	1.807(6)	P(2)—C(9)	1.827(6)
P(2)—C(27)	1.804(6)	P(2)—C(33)	1.800(7)
S(1)—C(1)	1.733(7)	S(2)—C(1)	1.721(7)
N(1)—C(2)	1.446(9)	N(1)—C(1)	1.316(8)
C(2)—C(3)	1.491(10)	N(1)—C(5)	1.497(10)
C(5)—C(6)	1.459(9)	C(2)—C(4)	1.509(12)
C(8)—C(9)	1.524(10)	C(5)—C(7)	1.471(12)
P(1)—Ni(1)—P(2)	87.3(1)	P(1)—Ni(1)—S(1)	98.3(1)
P(2)—Ni(1)—S(1)	174.3(1)	P(1)—Ni(1)—S(2)	175.3(1)
P(2)—Ni(1)—S(2)	95.4(1)	S(1)—Ni(1)—S(2)	79.0(1)
Ni(1)—P(1)—C(8)	107.9(2)	Ni(1)—P(1)—C(15)	115.1(2)
C(8)—P(1)—C(15)	107.1(3)	Ni(1)—P(1)—C(21)	114.1(2)
C(8)—P(1)—C(21)	105.2(3)	C(15)—P(1)—C(21)	106.8(3)
Ni(1)—P(2)—C(9)	108.1(2)	Ni(1)—P(2)—C(27)	113.5(2)
C(9)—P(2)—C(27)	104.1(3)	Ni(1)—P(2)—C(33)	113.5(2)
C(9)—P(2)—C(33)	108.7(3)	C(27)—P(2)—C(33)	108.5(3)
Ni(1)—S(1)—C(1)	86.1(2)	Ni(1)—S(2)—C(1)	86.3(2)
C(1)—N(1)—C(2)	124.5(6)	C(1)—N(1)—C(5)	120.1(6)
C(2)—N(1)—C(5)	115.4(6)	S(1)—C(1)—S(2)	107.9(3)
S(1)—C(1)—N(1)	127.3(5)	S(2)—C(1)—N(1)	124.7(6)
N(1)—C(2)—C(3)	115.0(5)	N(1)—C(2)—C(4)	112.7(6)
C(3)—C(2)—C(4)	113.2(7)	N(1)—C(5)—C(6)	111.9(7)
N(1)—C(5)—C(7)	112.0(6)	C(6)—C(5)—C(7)	114.0(7)
P(1)—C(8)—C(9)	106.3(4)	P(2)—C(9)—C(8)	107.0(4)
P(1)—C(15)—C(14)	121.3(5)	P(1)—C(15)—C(10)	119.0(5)
P(1)—C(21)—C(20)	120.2(5)	P(1)—C(21)—C(16)	120.8(5)
P(2)—C(27)—C(26)	119.5(5)	P(2)—C(27)—C(22)	121.6(4)
P(2)—C(33)—C(32)	117.3(5)	P(2)—C(33)—C(28)	124.0(5)

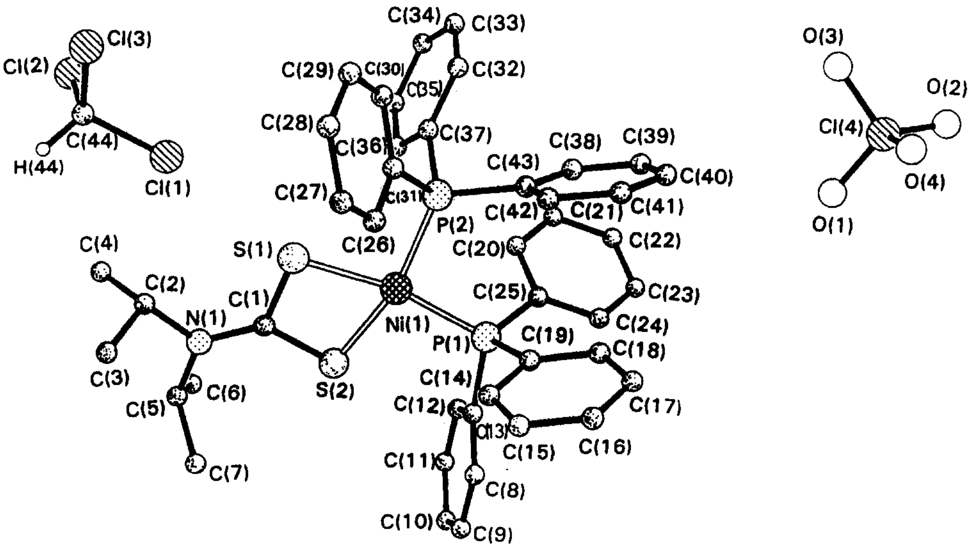

Fig. 1. Molecular structure of [Ni(dipdtc)$(PPh_3)_2$]$ClO_4 \cdot CHCl_3$ (**1**) showing the atom numbering scheme.

Table 4. Comparison of bond distances (Å) and angles (°) for complexes **1–3**

Complex	Ni—S(1)	Ni—S(2)	Ni—P(1)	Ni—P(2)	C—N	P(1)—Ni—P(2)	S(1)—Ni—S(2)	S(3)—Ni—S(4)
$Ni(dipdtc)_2$	2.183 (3)	2.182 (3)	—	—	1.307 (4)	—	79.6 (1)	78.9 (1)
$[Ni(dipdtc)(PPh_3)]^+$	2.209 (3)	2.201 (3)	2.215 (2)	2.224 (3)	99.4 (1)	1.321 (11)	77.7 (1)	—
$[Ni(dipdtc)(dppe)]^+$	2.194 (2)	2.196 (2)	2.165 (2)	2.160 (2)	1.316 (8)	87.3 (1)	79.0 (1)	—

Table 5.

Complex	Space group	Volume (Å^3)	No. of molecules per unit cell
$[Ni(dedte)(PPh_3)_2]ClO_4$	$P\bar{1}$	2049	2
$[Ni(dipdtc)(PPh_3)_2]ClO_4$	$P2_1/c$	4711	4
$[Ni(dipdtc)(dppe)]ClO_4$	$P\bar{1}$	1961	2
$[Ni(dipdtc)_2]$	$P2_1/c$	2128	4

bond distance and angles for the related complexes **1–3**.

There is a significant increase in the Ni—S distances of the complexes **1** and **2** compared to the parent complex **3**. However, in both complexes **1** and **2** the Ni—S distances are symmetrical. In the structure of $Ni(dedtc)Cl(PPh_3)$ (dedtc = diethyldithiocarbamate) and $[Ni(dedtc)(PPh_3)_2]^+$ complexes reported from our laboratory,[13,21] the Ni—S bonds were found to be asymmetric. There was also a similar asymmetry in the Ni—P distances. Because of the chelating nature of dppe when compared to PPh_3, the corresponding P—Ni—P angle is close to 90° [87.2(1)°], whereas in complex **1** the P—Ni—P angle is 99.4(1)°. Reduction in the span volume of the phenyl groups attached to dppe makes the S—Ni—S bite open up considerably relative to the PPh_3 analogue.

Complexes **1** and **2** show an increasing trend in the C—N distances, though the increase is highly significant in complex **1** compared to that in the parent complex **3**. Apparently this increase in C—N distance is due to the puckering of the bulky alkyl groups attached to the nitrogen, forcing the C—N—C bonds to deviate much away from 120° in the lengthening of the C—N bond distances in both the complexes. This is supported by the fact that, of the two phosphines, the compact dppe has a relatively shorter C—N distance than that containing PPh_3. The increase in C—N distances is not in line with the small increase in ν(C—N) values observed in the present study. Span volume for a single molecule calculated from unit cell volumes for the complexes **1**, **2** and **3** increases in the following order: $Ni(dipdtc)_2 < [Ni(dipdtc)(dppe)]^+ < [Ni(dipdtc)(PPh_3)_2]^+$ (Table 5).

Therefore, an increase in the bulkiness of the alkyl group forces a lengthening of C—N distances and an increase in total span volume for each molecule, in addition to the effects due to the hydrogen-bonded interactions envisaged earlier.[22] Also, a chelating phosphine, dppe, induces a higher stability by forcing a regular square planar geometry

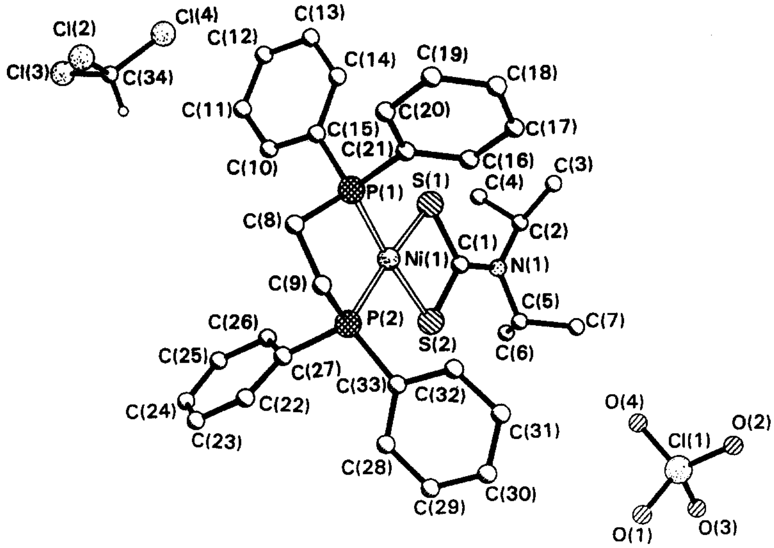

Fig. 2. Molecular structure of [Ni(dipdtc)(dppe)]$ClO_4 \cdot CHCl_3$ (**2**) showing the atom numbering scheme.

and compactness in complex **2**. This effect in turn increases the S—Ni—S bite angle for the complex.

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