Inorganica Chimica Acta, *128* (1987) 231–237

Cyclic Voltammetric and Infrared Spectral Studies on the Interaction of Ni(II) Dithiocarbamates with Triphenylphosphine and the Crystal and Molecular Structure of Diethyldithiocarbamatobis(triphenylphosphine)nickel(II)perchlorate, $[Ni(dedtc)(PPh_3)_2]ClO_4$

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(Received September 18, 1986)

Abstract

Ni(II) dithiocarbamates ($Ni(dtc)_2$) with various substituents on dtc were allowed to react with triphenylphosphine (PPh_3). Mixed ligand complexes of the general formulae $Ni(dtc)Cl(PPh_3)$ and $[Ni(dtc)(PPh_3)_2]ClO_4$ were prepared. The complexes were analysed by high resolution IR spectra. Comparison of the ν(C–N) frequencies of different complexes *viz.*, $Ni(dtc)_2$, $Ni(dtc)Cl(PPh_3)$ and $[Ni(dtc)(PPh_3)_2]ClO_4$, showed the following order of decreasing ν(C–N) values: $[Ni(dtc)(PPh_3)_2]^+ > Ni(dtc)Cl(PPh_3) > Ni(dtc)_2$. The observation showed the extent of contribution of the thiouride form in describing the structure of the complexes. The higher the contribution, larger is the value of ν(C–N). Cyclic voltammetric studies on the complexes showed the one electron reduction potentials to decrease in the following order: $Ni(dtc)Cl(PPh_3) > Ni(dtc)_2 > [Ni(dtc)(PPh_3)_2]^+$. The observations are explained with the nature of the substituents on the dtc moiety and other ligands present around Ni(II). Crystal structure of $[Ni(dedtc)(PPh_3)_2]ClO_4$ (dedtc = diethyldithiocarbamate) was determined to study the effect of the introduction of PPh_3 in place of Cl in the $Ni(dtc)Cl(PPh_3)$ complex. The complex is planar with NiS_2P_2 chromophore. The Ni–S distances are 2.190(2) and 2.239(2) Å and the Ni–P distances are 2.230(2) and 2.200(2) Å. The asymmetry in the Ni–S and Ni–P distances is ascribed to the steric effect due to bulky PPh_3. The structural aspects are compared with those of the $Ni(dtc)Cl(PPh_3)$ complex.

Introduction

Group VIII dithiolates of MS_4 chromophore react with Lewis bases to give adducts or substitution products [1–4]. In general, Pd(II) and Pt(II) dithiolates react with excess tertiary phosphines to give substitution products [5, 6]. In the case of Ni(II) dithiolates, nickel dithiocarbamates, ($Ni(dtc)_2$), exhibit an interesting intermediate reactivity towards Lewis bases compared to highly reactive xanthates and almost inert 1,2-dithiolates [7]. This difference in reactivity has been attributed to the varying extents of the contribution of the thiouride form (**I**) in describing the structure of the dithiolate which in turn depends on the nature of the substituents. It has been well established that bis((diethyl)dithiocarbamato)nickel(II), ($Ni(dedtc)_2$), is inert to hard nitrogenous bases even if they are strong chelating agents like ethylenediamine [8]. On the contrary, $Ni(dedtc)_2$ interacts with a soft Lewis base, PPh_3, with ease to give the mixed ligand complex, $Ni(dedtc)Cl(PPh_3)$ and recently we reported the crystal structure of this complex [9, 10]. Chan *et al.* reported the crystal structure of the complex $Ni(dedtc)Cl(PEt_3)$ and proposed that the electron density on the nickel atom is more than that in the corresponding dithiocarbamate complex based on IR evidences [11]. $Ni(dedtc)Cl(PR_3)$ also interacts with excess PR_3' to give the complex $[Ni(dedtc)(PPh_3)_2]^+$ which has not been subjected to crystal structure determination so far.

In the present study, complexes of the formulae $Ni(dtc)Cl(PPh_3)$ and $[Ni(dtc)(PPh_3)_2]ClO_4$ with different substituents on dtc such as, $(HOH_4C_2)NHCS_2^-$, (meadtc); $(HOH_4C_2)_2NCS_2^-$, (deadtc); $(H_{10}C_5)NCS_2^-$, (pipdtc); $(OH_8C_4)NCS_2^-$ (morphdtc) have been prepared. The electronic effects of the substituents, the extent of contribution of resonance structure (**II**) have been studied by IR spectroscopy and cyclic voltammetry. The crystal structure of $[Ni(dedtc)(PPh_3)_2]ClO_4$ is also reported in this paper and the effect of the introduction of another PPh_3 in the place of Cl in $Ni(dedtc)Cl(PPh_3)$ is explained.

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0020-1693/87/$3.50

TABLE I. C–N Stretching Frequencies Observed in Different Complexes (cm^{-1})

	dedtc	pipdtc	deadtc	meadtc	morphdtc
$Ni(dtc)_2$	1518	1513	1500	1540	1495
$Ni(dtc)Cl(PPh_3)$	1524	1515	–	1530	1505
$[Ni(dtc)(PPh_3)_2]^+$	1530	1525	1510	1545	1530

All spectra were recorded as KBr pellets of the complexes.

Experimental

Preparation of (Dialkyldithiocarbamato)bis(triphenylphosphine)nickel(II)perchlorate, [Ni(dtc)(PPh$_3$)$_2$]ClO$_4$

$Ni(dtc)Cl(PPh_3)$ complexes were prepared by an earlier method [9]. To a mixture of $Ni(dtc)Cl(PPh_3)$ (5 mmol), PPh_3 (10 mmol) and $LiClO_4$ (10 mmol), 25 ml of methanol was added and stirred for 3 h. A dark red crystalline product formed after sometime was filtered and washed several times with methanol and dried in vacuum over anhydrous calcium chloride. $Ni(deadtc)Cl(PPh_3)$ alone could not be prepared in the solid form since it was quite unstable. In the preparation of $[Ni(deadtc)(PPh_3)_2]ClO_4$, the purple solution of $Ni(deadtc)Cl(PPh_3)$ itself was used as the starting material. The composition of the complexes was established by chemical analysis.

IR Studies

Vibrational spectra of the complexes were taken as KBr pellets on a high resolution IR spectrophotometer (Perkin-Elmer 983G).

Cyclic Voltammetric Studies

Cyclic voltammetric (CVM) studies were carried out on a series of $Ni(dtc)_2$, $Ni(dtc)Cl(PPh_3)$ and $[Ni(dtc)(PPh_3)_2]ClO_4$ complexes. Recrystallised samples were used for the studies. The solvents, acetone and dichloromethane were purified [12] prior to use in the measurements.

CVM measurements were carried out using PAR 173, 175 and 179 units (Princeton Applied Research Corporation, USA) in conjunction with an x–y recorder (Digital Electronics, Bombay). The sweep rate employed in the present work ranged from 0.002 V s^{-1} to 0.300 V s^{-1}. A three electrode system was used in the measurement of potentials. Pt wire and foil were used as the working and counter electrodes respectively. The reference electrode was Ag/AgCl in 0.1 M LiCl in acetone or dichloromethane, separated from the cell by a salt bridge containing the supporting electrolyte. $(Bu_4N)ClO_4$ or $(Bu_4N)I$, 0.1 M, was used as the supporting electrolyte. In cases where a Ag wire was used as the reference electrode, the potentials were corrected to Ag/AgCl in 0.1 M LiCl reference using the measured conversion factor –0.46 V. In all the measurements the concentration of the compounds was 1×10^{-3} mol l^{-1} and in the cases where excess PPh_3 was added, the concentration of the added PPh_3 was to the extent of 100 fold excess (10, 50 mmols l^{-1}). In the course of the study the platinum wire electrode was cleaned with the solvent and heated to a red hot condition over a blue flame to remove the adsorbed compounds after each cycle.

Results and Discussion

IR Spectral Studies

The IR spectra of $Ni(dtc)_2$, $Ni(dtc)Cl(PPh_3)$ and $[Ni(dtc)(PPh_3)_2]ClO_4$ complexes show peaks due to C–N stretching and C–S vibration modes in the regions 1500 and 990 cm^{-1} respectively. The ν(C–N) has been used as a measure of the contribution of the thiouride form (I) of the ligands to the complexes [11]. A comparison of the ν(C–N) values in the complexes is given in Table I.

In general dedtc and pipdtc complexes show higher ν(C–N) values whereas the morphdtc complexes show lower ν(C–N) values because the heterocyclic ring system shows less tendency to release electrons to the N–C bond [13]. The substitution of one dtc by Cl and PPh_3 is expected to result in a greater drift of electrons from the dtc group to the metal with a resultant increase in ν(C–N). As expected ν(C–N) values of $Ni(dtc)Cl(PPh_3)$ complexes increase but the increase is found to be very small in dedtc and meadtc complexes. Replacement of Cl in $Ni(dtc)Cl(PPh_3)$ by PPh_3 increases the drift of electrons from dtc resulting in still higher ν(C–N) values as shown in Table I. Inclusion of better π-acceptor ligands like isocyanides has been shown to increase the ν(C–N) values [14]. Therefore ν(C–N) values decrease in the following order: $[Ni(dtc)(PPh_3)_2]^+ > Ni(dtc)Cl(PPh_3) > Ni(dtc)_2$.

Cyclic Voltammetric Studies

Reduction of Ni(dtc)(PPh$_3$)$_2$ClO$_4$

All these compounds are found to undergo a single electron reduction process in the potential range 0 to –2 V. The reductions are irreversible and

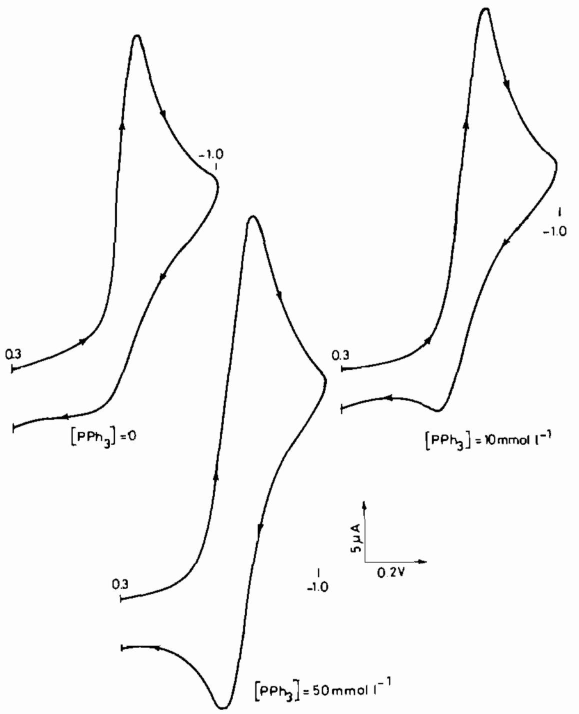

Fig. 1. Cyclic voltammograms of $[Ni(morphdtc)(PPh_3)_2]ClO_4$ (1×10^{-3} mol l^{-1}) in CH_2Cl_2 for various concentrations of added PPh_3. Scan rate = 100 mV s^{-1}.

are diffusion controlled as shown by the constant $i_p^c/v^{1/2}$ values [15]. On adding PPh_3 to a solution of the complex, an anodic peak appears in the CVM indicating the reversibility of the reduction process. The ratio of the anodic to cathodic peak currents increases and approaches unity at higher concentrations of added PPh_3. The peak separation potentials (ΔE_p) for the reduction processes after the addition of excess PPh_3 are above 150 mV indicating the quasi-reversible nature of the reduction [16]. Typical CVMs for the reduction of $[Ni(dtc)(PPh_3)_2]ClO_4$ with various added concentrations of PPh_3 are shown in Fig. 1. Similar studies on $[Ni((CN)_2C_2S_2)(PPh_3)_2]$ and $[Ni(dtc)(diphos)]^+$ supported by ESR evidences have shown that the reductions are metal based and Ni(I) complexes are produced by the reduction of parent Ni(II) complexes [17, 18].

As observed earlier [18], in the present case the reductions also show scan rate dependence indicative of an electrochemical reduction followed by a chemical reaction. The chemical reaction in the present case is the loss of PPh_3 and the addition of excess PPh_3 reverts the equilibrium and the anodic peak is observed.

Reduction of Ni(dtc)Cl(PPh$_3$)

The CVMs of these complexes show a cathodic peak in the forward scan and an anodic peak corresponding to the cathodic peak in the reverse scans.

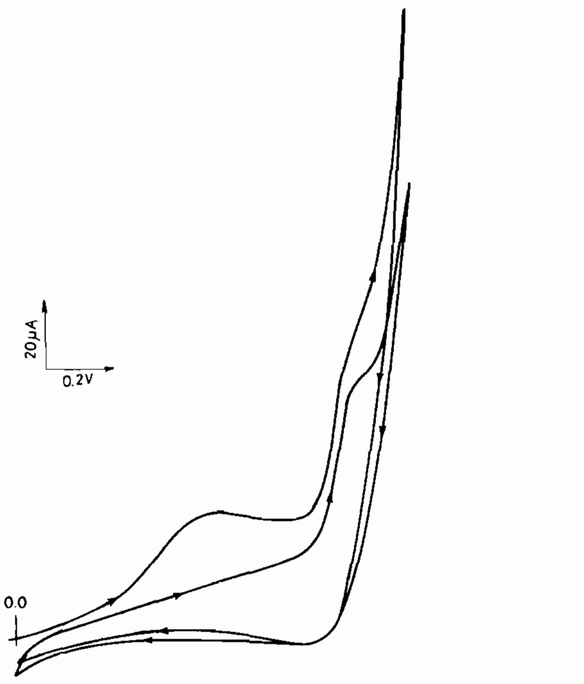

Fig. 2. Cyclic voltammogram of $Ni(dedtc)ClPPh_3$ (1×10^{-3} mol l^{-1}). Sweep rate = 100 mV s^{-1}.

The cathodic peak is preceded by adsorption prepeaks which disappear in the continuous cycles [19]. A typical CVM is shown in Fig. 2. The ΔE_p values are more than 150 mV indicating the quasi-reversible nature of the reduction process. In the case of $Ni(morphdtc)Cl(PPh_3)$ and $Ni(pipdtc)Cl(PPh_3)$, to avoid the decomposition to the corresponding bisdithiocarbamates, addition of PPh_3 was necessary prior to examination. The addition of excess PPh_3 to the solution containing the complexes did not alter the course of the electrochemical processes in these complexes and $[Ni(dtc)(PPh_3)_2]^+$ is formed only in the presence of counter ion such as ClO_4^-.

Reduction of Ni(dtc)$_2$

For better comparison of the reduction potentials, the CVMs of dithiocarbamates were recorded under identical conditions. As observed aerlier, the complexes undergo a quasi-reversible one electron reduction in the potential range 0 to -2 V [20]. The ratio of the anodic to cathodic peak currents is 0.8.

The cathodic peak potentials for different complexes at 200 mV s^{-1} scan rate are listed in Table II. In all the three general cases, dedtc and pipdtc complexes occupy the higher negative potential end, those with meadtc and morphdtc the lower negative potential end. The complexes with deadtc show an intermediate potential. Another important observation which can be made is that the $Ni(dtc)Cl(PPh_3)$ complexes get reduced at a higher potential than the

TABLE II. Reduction Potentials[a] (V) for the Nickel Complexes

Complex	dedtc	pipdtc	deadtc	meadtc	morphdtc
$Ni(dtc)_2$[b]	−1.40	−1.41	−1.38	−1.29	−1.28
$Ni(dtc)Cl(PPh_3)$[b]	−1.51	−1.50	–	−1.48	−1.47
$[Ni(dtc)(PPh_3)_2]^+$[c]	−0.80	−0.78	−0.74	−0.72	−0.73

[a] One electron reduction potentials are relative to Ag/AgCl, 0.1 mol l^{-1} LiCl, and the concentration of the complexes in all the cases is 1×10^{-3} mol l^{-1}. [b] Pure acetone was used as solvent and tetrabutylammonium iodide as the supporting electrolyte. [c] Pure dichloromethane was used as solvent and tetrabutylammonium perchlorate as the supporting electrolyte.

corresponding $Ni(dtc)_2$ complexes. Since the reduction has been proved to be metal based, it can be concluded that the negative charge on nickel in $Ni(dtc)Cl(PPh_3)$ is more than that in $Ni(dtc)_2$.

As mentioned earlier, Chan *et al.* proposed that the contribution of the canonical form **II** with higher negative charge on the metal is more in $Ni(dtc)Cl(PPh_3)$ than in $Ni(dtc)_2$. Even though no crystal structure evidence could be given for the proposal, IR studies supported the idea. The reduction potentials observed in the present study serve as an additional evidence. Comparison of the reduction potentials $[Ni(dtc)(PPh_3)_2]^+$ with other types of complexes shows that the reduction potentials decrease in the following order: $Ni(dtc)Cl(PPh_3) > Ni(dtc)_2 > Ni(dtc)(PPh_3)_2$.

Based on IR studies, C–N in $[Ni(dtc)(PPh_3)_2]ClO_4$ has the maximum double bond character and hence this complex is expected to be more difficult to reduce. However, in reality it is the most easily reduced of all. The reason propably is the extensive π-back bonding with the phosphorus atoms which drain the excess negative charge on the metal and hence the low reduction potential.

Crystal Structure of $Ni(dedtc)(PPh_3)_2ClO_4$

Plate like crystals of the complex were obtained by the repeated crystallisation from the dichloromethane solutions. Good crystals were selected by an examination under polarizing microscope. One such crystal of dimensions $0.40 \times 0.3 \times 0.33$ mm^3 was used in the present data collection and the complete crystal data are presented in Table III. The data were collected on an Enraf Nonius CAD 4 diffractometer. Lorentz and polarization corrections were applied. No absorption correction was applied, μ(Mo Kα) being 7.0 mm^{-1}. A Patterson map on the data using SHELX-76 program [21] revealed the nickel position as 0.20, 0.18, 0.23 and the successive difference Fourier maps revealed all the positions of the non-hydrogen atoms. Of the 40 hydrogens, 13 hydrogens appeared themselves and others were geometrically fixed. All the non-hydrogens were refined anisotropically and hydrogens isotropically.

TABLE III. Crystal Data of (Diethyldithiocarbamato)bis(triphenylphosphine)nickel(II)perchlorate, $[Ni(dedtc)(PPh_3)_2]ClO_4$

Molecular formula	$C_{41}H_{40}ClNNiO_4P_2S_2$
Molecular weight	831.01
Space group	$P\bar{1}$
a (Å)	9.917(2)
b (Å)	12.630(3)
c (Å)	17.415(3)
α (°)	83.43(2)
β (°)	87.76(2)
γ (°)	71.07(2)
V (Å^3)	2049.8
Z	2
D_x (g cm^{-3})	1.34
λ(Mo Kα) (Å)	0.71069
μ (mm^{-1})	7.00
Final R	0.0632
R_w	0.0649
No. unique reflections ($I > 3\sigma(I)$)	4104

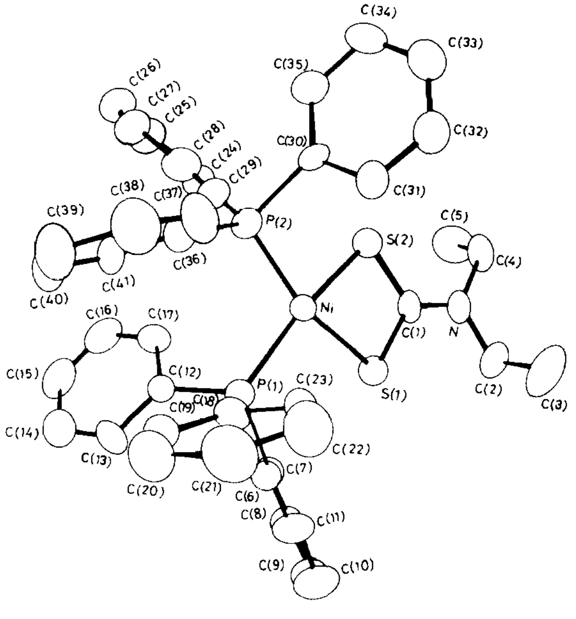

Fig. 3. ORTEP plot of the molecule.

TABLE IV. Fractional Atomic Coordinates (×10^4) for the Non-hydrogen Atoms (e.s.d.s in parentheses)

	x	*y*	*z*
Ni	2027(1)	1841(1)	2330(1)
S(1)	2570(2)	3057(2)	2955(1)
S(2)	3017(2)	2719(2)	1395(1)
P(1)	1242(2)	981(2)	1482(1)
P(2)	1371(2)	1063(2)	3413(1)
C(1)	3138(7)	3544(6)	2079(4)
N	3573(6)	4421(5)	1953(4)
C(2)	3521(9)	5123(7)	2577(5)
C(3)	2096(11)	6129(9)	2509(7)
C(4)	4099(10)	4725(7)	1204(5)
C(5)	5699(10)	4105(10)	1126(6)
C(6)	1809(8)	1540(6)	4290(4)
C(7)	3245(8)	1223(7)	4494(4)
C(8)	3641(10)	1603(8)	5136(5)
C(9)	2612(11)	2265	5613(5)
C(10)	1202(12)	2543(9)	5418(6)
C(11)	793(9)	2196(8)	4759(5)
C(12)	2306(7)	−434(6)	3588(4)
C(13)	2065(8)	−1102(7)	4221(4)
C(14)	2875(10)	−2241(7)	4340(6)
C(15)	3940(10)	−2680(7)	3815(6)
C(16)	4225(9)	−2047(7)	3202(5)
C(17)	3409(8)	−903(7)	3079(4)
C(18)	−542(7)	1350(6)	3473(4)
C(19)	−1238(8)	591(6)	3731(4)
C(20)	−2712(8)	931(7)	3779(5)
C(21)	−3485(8)	1997(8)	3561(5)
C(22)	−2851(8)	2808(7)	3295(5)
C(23)	−1541(8)	2463(6)	3246(4)
C(24)	2587(7)	−158(6)	1050(4)
C(25)	2194(9)	−914(7)	677(5)
C(26)	3234(12)	−1806(8)	381(5)
C(27)	4690(11)	−1926(9)	464(6)
C(28)	5063(9)	−1126(9)	799(5)
C(29)	4029(8)	−259(7)	1107(5)
C(30)	503(7)	2064(6)	678(4)
C(31)	−358(8)	3112(6)	859(4)
C(32)	−849(8)	3997(7)	270(5)
C(33)	−466(9)	3830(7)	−477(5)
C(34)	406(9)	2778(8)	−660(4)
C(35)	885(8)	1885(6)	−80(4)
C(36)	−168(7)	368(6)	1760(4)
C(37)	−1582(8)	973(6)	1597(5)
C(38)	−2645(8)	497(8)	1797(5)
C(39)	−2319(9)	−557(7)	2158(5)
C(40)	−904(9)	−1169(7)	2342(5)
C(41)	154(8)	−694(6)	2129(4)
C(1)	2211(3)	4209(2)	7558(2)
O(1)	3120(11)	4518(7)	7049(7)
O(2)	2126(13)	3180(8)	7528(7)
O(3)	1132(11)	5020(6)	7873(6)
O(4)	3119(22)	3872(23)	8251(12)

Description of the Structure

The complex is monomeric and discrete. ORTEP plot and a plot of packing of the molecules in the unit cell are shown in Figs. 3 and 4 respectively. The fractional coordinates of all the non-hydrogen atoms are given in Table IV. The bond lengths and angles are listed in Table V (see also 'Supplementary Material'). Ni, S(1), S(2), P(1) and P(2) are nearly planar, the maximum deviation from the plane being 0.17 Å and the sum of the angles subtended at the metal centre is ~360°.

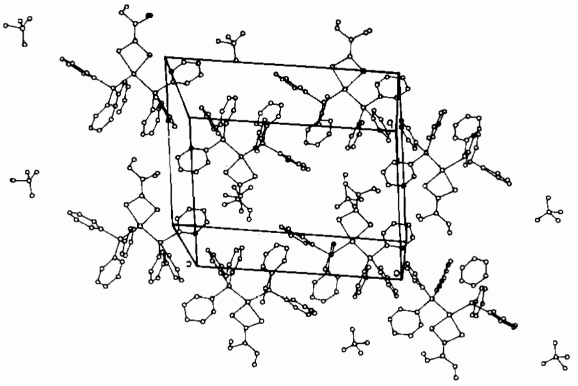

Fig. 4. Packing of molecules in the unit cell.

The Ni–S bonds in the complex, [Ni(dedtc)(PPh$_3$)$_2$]$^+$ **(III)** show asymmetry as also observed in Ni(dedtc)Cl(PPh$_3$) **(IV)** (2.190(2), 2.239(2) in **(III)**, 2.170(4), 2.232(3) in **(IV)**). The asymmetry in **IV** has been explained based on the differences in *trans* influences exerted by Cl and PPh$_3$. In **III** the bulkiness of the PPh$_3$ group does not allow another PPh$_3$ to proximate to the nickel atom and results in asymmetry in the Ni–P distances (2.230(2) and 2.200(2) Å). In turn Ni–S bonds also show asymmetry. The bond parameters of the dithiocarbamate moiety are normal. The C–N distance in the present compound does not vary from that observed in **IV**. The contribution of the thiouride structure to **III** is expected to be more and the C–N bond distance observed does not explicitly show this effect. But IR evidences support the above fact.

The replacement of Cl in **IV** by another PPh$_3$ leads to a P–Ni–P angle of 99.6(1)° whereas the P–Ni–Cl angle in **IV** is 93.7(1)°. This increase in the angle is a manifestation of the steric effect due to PPh$_3$. The phenyl rings show normal bond parameters (average C–C = 1.38(1) Å). Two of the phenyl rings in PPh$_3$ are pitched to the same extent whereas the third one is almost perpendicular to the Ni–P–C–C plane as a requirement for the packing of the molecules in the unit cell (65.45, 68.45, 90.61, 60.51, 69.58, 100.8, interplanar angles for the phenyl rings with NiS$_2$P$_2$ plane).

The perchlorate group is non-coordinating. Its oxygen atoms show large thermal parameters. The Cl–O distances are in the range 1.34–1.47 Å (average Cl–O = 1.38 Å) whereas for the free ClO$_4^-$ without

TABLE V. Bond Lengths (Å) and Angles (°)

Ni–S(1)	2.190(2)	Ni–P(1)	2.200(2)
Ni–S(2)	2.239(2)	Ni–P(2)	2.230(3)
C(1)–S(1)	1.722(7)	C(1)–S(2)	1.702(8)
C(1)–N	1.307(11)	N–C(2)	1.468(12)
C(2)–C(3)	1.568(12)	N–C(4)	1.443(11)
C(4)–C(5)	1.533(12)	P(1)–C(6)	1.821(8)
P(1)–C(12)	1.811(7)	P(1)–C(18)	1.813(7)
C(6)–C(7)	1.397(11)	C(7)–C(8)	1.384(13)
C(8)–C(9)	1.403(12)	C(9)–C(10)	1.373(16)
C(10)–C(11)	1.393(16)	C(6)–C(11)	1.385(11)
C(12)–C(13)	1.372(11)	C(13)–C(14)	1.397(11)
C(14)–C(15)	1.385(13)	C(15)–C(16)	1.337(13)
C(16–C(17)	1.404(11)	C(12)–C(17)	1.399(10)
C(18)–C(19)	1.380(12)	C(19)–C(20)	1.386(11)
C(20–C(21)	1.334(11)	C(21)–C(22)	1.395(14)
C(22)–C(23)	1.232(11)	P(2)–C(24)	1.827(7)
P(2)–C(30)	1.833(7)	P(2)–C(36)	1.831(8)
C(24)–C(25)	1.374(13)	C(25)–C(26)	1.391(12)
C(26)–C(27)	1.413(16)	C(27)–C(28)	1.376(17)
C(28)–C(29)	1.379(12)	C(24)–C(29)	1.400(11)
C(30)–C(31)	1.386(10)	C(31)–C(32)	1.401(10)
C(32)–C(33)	1.361(12)	C(33)–C(34)	1.395(12)
C(34)–C(35)	1.396(10)	C(30)–C(35)	1.382(10)
C(36)–C(37)	1.385(10)	C(37)–C(38)	1.389(13)
C(38)–C(39)	1.346(12)	C(39)–C(40)	1.395(11)
C(40)–C(41)	1.388(13)	C(36)–C(41)	1.362(10)
Cl–O(1)	1.355(11)	Cl–O(2)	1.336(12)
Cl–O(3)	1.366(9)	Cl–O(4)	1.472(21)

S(1)–Ni–S(2)	78.2(1)	P(1)–Ni–P(2)	99.7(1)
S(1)–Ni–P(1)	91.0(1)	S(2)–Ni–P(2)	92.1(1)
Ni–S(1)–C(1)	86.6(3)	S(1)–C(1)–N	125.5(5)
Ni–S(2)–C(1)	85.5(3)	S(2)–C(1)–N	125.1(5)
S(1)–C(1)–S(2)	109.4(4)	C(1)–N–C(2)	120.1(5)
C(1)–N–C(4)	121.2(5)	N–C(2)–C(3)	108.4(6)
N–C(4)–C(5)	111.1(6)	C(2)–N–C(4)	118.8(6)
Ni–P(1)–C(6)	115.0(3)	Ni–P(1)–C(12)	112.9(3)
Ni–P(1)–C(18)	112.5(3)	P(1)–C(6)–C(7)	117.8(5)
C(6)–C(7)–C(8)	120.1(4)	C(7)–C(8)–C(9)	120.9(7)
C(8)–C(9)–C(10)	118.3(7)	C(9)–C(10)–C(11)	121.3(8)
C(10)–C(11)–C(6)	120.4(7)	C(11)–C(6)–C(7)	118.9(6)
P(1)–C(12)–C(13)	123.5(5)	C(12)–C(13)–C(14)	120.5(6)
C(13)–C(14)–C(15)	118.9(7)	C(14)–C(15)–C(16)	122.1(7)
C(15)–C(16)–C(17)	119.1(7)	C(16)–C(17)–C(12)	120.4(6)
C(13)–C(12)–C(17)	118.8(5)	P(1)–C(18)–C(19)	126.5(5)
C(18)–C(19)–C(20)	120.8(6)	C(19)–C(20)–C(21)	120.4(5)
C(20)–C(21)–C(22)	121.8(6)	C(21)–C(22)–C(23)	115.5(6)
C(22)–C(23)–C(18)	129.7(6)	C(23)–C(18)–C(19)	111.6(5)
Ni–P(2)–C(24)	116.4(3)	Ni–P(2)–C(30)	105.5(3)
Ni–P(2)–C(36)	120.0(3)	P(2)–C(24)–C(25)	120.5(5)
C(24)–C(25)–C(26)	119.9(6)	C(25)–C(26)–C(27)	119.7(7)
C(26)–C(27)–C(28)	119.7(7)	C(27)–C(28)–C(29)	120.2(7)
C(28)–C(29)–C(24)	120.2(6)	C(25)–C(24)–C(29)	120.1(6)
P(2)–C(30)–C(31)	117.6(5)	C(30)–C(31)–C(32)	119.8(5)
C(31)–C(32)–C(33)	119.9(5)	C(32)–C(33)–C(34)	120.2(6)
C(33)–C(34)–C(35)	120.3(6)	C(34)–C(35)–C(30)	119.1(6)
C(31)–C(30)–C(35)	120.5(5)	P(2)–C(36)–C(37)	120.7(5)
C(36)–C(37)–C(38)	120.4(6)	C(37)–C(38)–C(39)	120.6(6)
C(38)–C(39)–C(40)	119.8(6)	C(39)–C(40)–C(41)	119.2(6)
C(40)–C(41)–C(36)	121.2(5)	C(37)–C(36)–C(41)	118.7(5)

(continued)

TABLE V. *(continued)*

O(1)–Cl–O(2)	116.1(5)	O(1)–Cl–O(3)	119.4(5)
O(1)–Cl–O(4)	99.4(9)	O(2)–Cl–O(3)	120.7(5)
O(2)–Cl–O(4)	94.0(9)	O(3)–Cl–O(4)	95.9(9)

disorder it is 1.44 Å [22]. The O–Cl–O angles are in the range 95–120° indicating distortion from tetrahedral geometry as observed in an earlier case [23].

The molecules in the unit cell are held together by van der Waals forces.

Supplementary Material

Lists of the anisotropic thermal parameters of the non-hydrogen atoms, fractional coordinates of the hydrogen atoms and structure factor tables are deposited with the Editor-in-Chief.

Acknowledgement

One of the authors (K.R.) thanks CSIR, New Delhi, for financial assistance.

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