Ligand Substitution Reactions of the Nickel–Sulphur Cluster $[Ni_3S_2(PEt_3)_6]^{2+}$. Phosphorus-31 Nuclear Magnetic Resonance Characterization of Mono- and Di-substituted Species and *X*-Ray Crystal Structure of $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_5Cl]BPh_4$*

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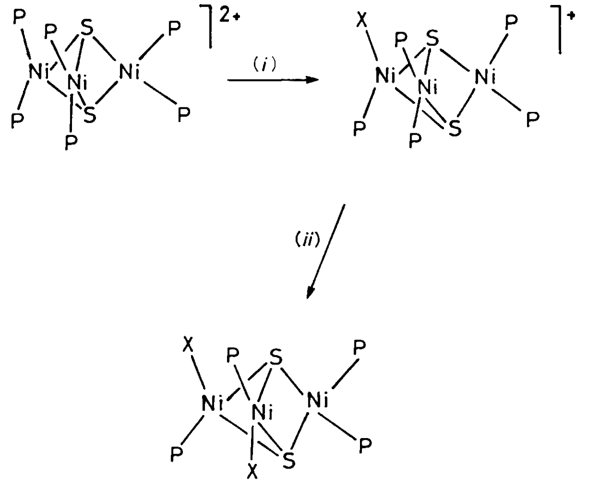
The complexes $[Ni_3Y_2(PEt_3)_6]^{2+}$, Y = S or Se, undergo metathetical reactions with halides and pseudohalides yielding both asymmetric, monosubstituted $[Ni_3Y_2(PEt_3)_5X]^+$ and disubstituted $[Ni_3Y_2(PEt_3)_4X_2]$ derivatives. The cationic trimetallic species react with donor molecules, such as CO and H_2S, only when the halide group is appropriately removed. All of the complexes have been characterized by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy. Computer simulation of the complicated second-order spectra allowed determination of the spectral parameters. The refined values of the coupling constants between phosphorus atoms in geminal, *trans*-vicinal, or *cis*-vicinal positions are quite similar within the two series of compounds. In contrast, the values of the ^{31}P chemical shifts depend remarkably on the nature of the substituting group. The molecular structure of $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_5Cl]BPh_4$ has been established by a single-crystal *X*-ray diffraction study. Crystal data are: $a = 17.496(12)$, $b = 17.087(12)$, $c = 11.027(9)$ Å, $\alpha = 98.95(8)$, $\beta = 90.58(8)$, $\gamma = 102.70(9)°$, space group $P\bar{1}$, $Z = 2$. Substitution of chloride ion for phosphine leaves unchanged the trigonal-bipyramidal skeleton, the only difference being some shortening of the M–S bond *trans* to the chlorine atom.

Heteronuclear clusters formed by transition-metal and main group atoms cemented together constitute an area of growing interest in modern co-ordination chemistry.[1] Some of this interest stems from the potential use of these complexes as models for biological systems.[2] In addition many transition-metal sulphides have been found to display intriguing catalytic properties[3] and transition-metal sulphur clusters constitute the basic structural units of several interesting conductor materials.[4]

In spite of continuous efforts to synthesize and characterize new cluster frameworks, little has been reported on their reactivities, apart from the iron–sulphur protein models.[2] Herein we report some ligand-exchange reactions of the $[Ni_3S_2(PEt_3)_6]^{2+}$ complex,[5] leading to a family of asymmetric substituted trigonal-bipyramidal species. These complexes are among the simplest metal-sulphur clusters and have been recently suggested to be a potential starting point in the synthesis of more highly condensed species.[1] The new complexes have been characterized by ^{31}P n.m.r. spectroscopy, and the structure of $[Ni_3S_2(PEt_3)_5Cl]BPh_4$ has been fully elucidated by *X*-ray analysis.



Scheme 1. (*i*) $+X^-$ in acetone (X = Cl, Br, I, or NCS); (*ii*) X^- in excess

Results and Discussion

The complex $[Ni_3S_2(PEt_3)_6][BPh_4]_2$ (**1**) reacts, at room temperature under a nitrogen atmosphere, in acetone solution with tetra-alkylammonium halides to form mono- and di-substituted derivatives (Scheme 1). The reactions have been monitored by $^{31}P\text{-}\{^1H\}$ n.m.r. spectroscopy. When (**1**) is treated with an equimolar amount of X^- (X = Cl, Br, or I), reaction takes place within minutes, with formation of the complex species $[Ni_3S_2(PEt_3)_5X]^+$ (X = Cl, Br, or I) and free PEt_3 (see below). Dark red crystals of formula $[Ni_3S_2(PEt_3)_5X]BPh_4$ can be isolated by addition of ethanol and solvent evaporation. When an excess of X^- is added the formation of new species occurs, as shown by the appearance of new n.m.r. signals. These new resonances have been assigned to the uncharged species $[Ni_3S_2(PEt_3)_4X_2]$, containing the two X^- anions in *trans*-vicinal† position (see below). The formation of the disubstituted species [step (*ii*) in Scheme 1] is not quantitative, even in the presence of a large excess of X^- or by use of long reaction times.

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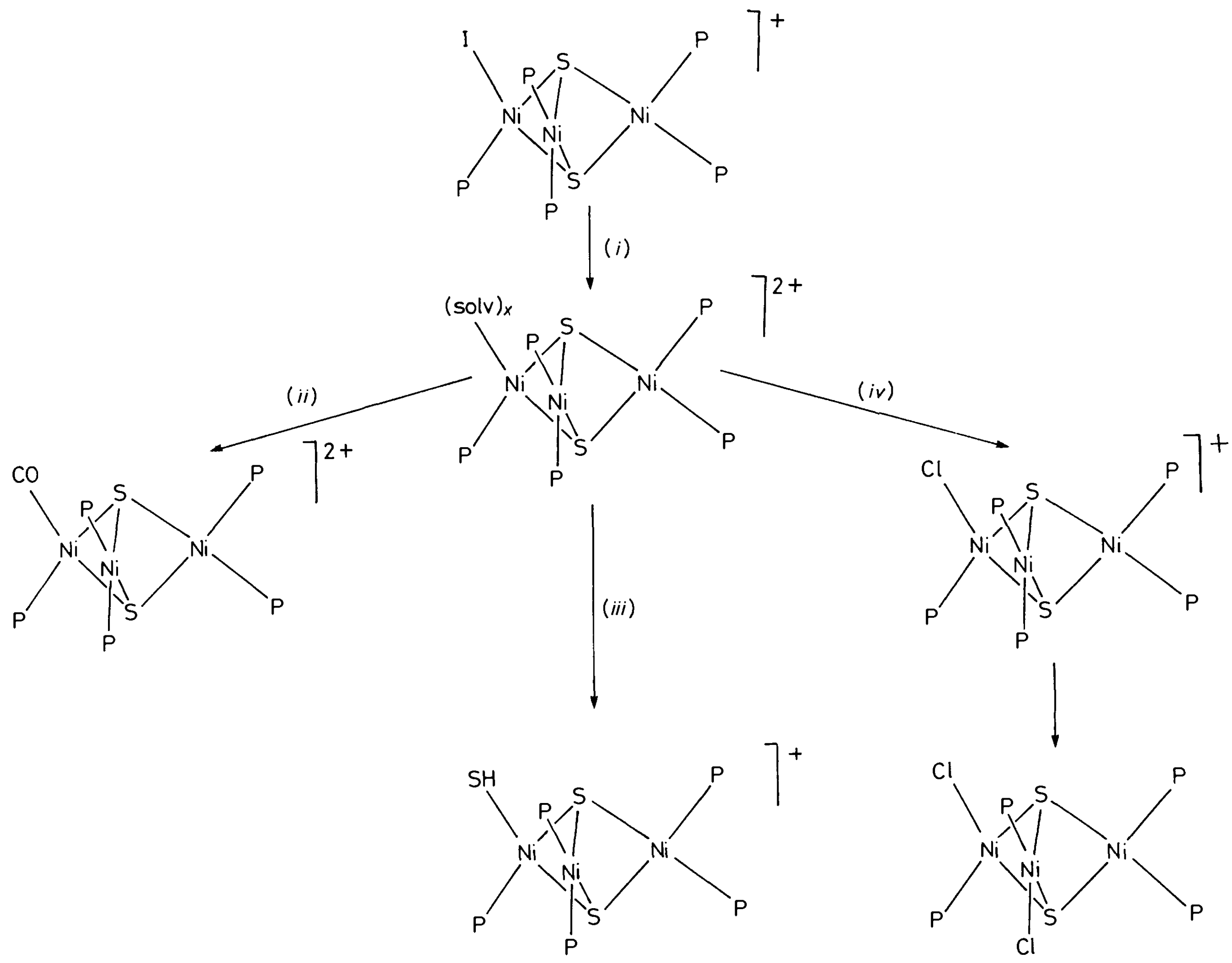
* 1-Chloro-di-μ_3-sulphido-1,2,2,3,3-pentakis/triethyl phosphine)trinickel(II) tetraphenylborate.

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1990, Issue 1, pp. xix–xxii.

† The 'vicinal' term has been adopted by analogy with the cyclopropane system, even though *X*-ray data do not provide evidence of any direct metal–metal bond.



Scheme 2. (i) Tl^+, acetone, -TlI; (ii) CO; (iii) H_2S; (iv) $CHCl_3$

However, we note that the metathetical reaction is favoured in the order Cl > Br > I. No formation of any further species was observed. The reaction with NCS^- essentially follows an analogous pathway. However, in this case there is a strong propensity to the formation of disubstituted derivatives. Indeed the clean formation of $[Ni_3S_2(PEt_3)_4(NCS)_2]$ occurs by using a stoicheiometric ratio of the reagents. The monosubstituted complexes can be alternatively prepared by reaction of $[Ni(PEt_3)_2X_2]$ (X = Cl, Br, or I) with $S(SiMe_3)_2$ according to the method developed by Fenske *et al.*[1b] The formation in low yield of the *trans*-vicinal disubstituted species $[Ni_3S_2(PPh_3)_4Cl_2]$ from $[Ni(PPh_3)_2Cl_2]$ has already been reported.[1b] We have been successful in the high-yield preparation of monosubstituted complexes, using $[Ni(PEt_3)_2X_2]$ (X = Cl, Br, or I). A determinant factor for the preparation of the PEt_3 derivatives appears to be the reaction time, which, in turn, depends on the nature of the halide ion. The formation of the complexes, indicated by the deep brown colour of the solution, is completed, at room temperature, in *ca.* 3, 5, and 7 d for X = Cl, Br, and I, respectively. For longer reaction times and for X = Cl or Br, the solutions turn dark and yield unidentified black products.

The halide ligand can be removed from $[Ni_3S_2(PEt_3)_5X]^+$ (X = Cl, Br, or I), in acetone solution, using thallium(I) salts, to form a reactive species, probably $[Ni_3S_2(PEt_3)_5(solv)_x]^{2+}$ (Scheme 2), the room-temperature $^{31}P-\{^1H\}$ n.m.r. spectrum of which shows complicated broad signals, probably due to fluxional behaviour, and has not been resolved. The above species slowly reacts with $CHCl_3$, at room temperature initially to give over a period of hours the monochloride complex and successively the *trans*-vicinal dichloride. The reaction with a typical π-donor molecule, such as CO, affords the monocarbonyl complex $[Ni_3S_2(PEt_3)_5(CO)]^{2+}$, which can be isolated as the tetraphenylborate salt. The CO stretching vibration at 2 080 cm^{-1} is consistent with weak co-ordination of the CO ligand. This carbonyl group can be readily displaced in solution by bubbling nitrogen. By treatment of $[Ni_3S_2(PEt_3)_5(solv)_x]^{2+}$ with H_2S, the previously described mercapto-complex[6] $[Ni_3S_2(PEt_3)_5(SH)]^+$ is obtained. The chemical behaviour of the selenium derivative $[Ni_3Se_2(PEt_3)_6]^{2+}$[5b] closely resembles that of (**1**) (see, for example, the Br and I derivatives). In contrast the analogous tellurium complex $[Ni_3Te_2(PEt_3)_6][BPh_4]_2$ rapidly decomposes on reaction with halides in acetone solution.

All the complexes slowly decompose in air; the analytical data and the molar conductivities in nitroethane solution are in good agreement with the given formulation.

X-*Ray Crystal Structure of* $[Ni_3S_2(PEt_3)_5Cl]BPh_4$, (**2**).—The molecular structure of (**2**) consists of discrete $[Ni_3(\mu_3-S)_2(PEt_3)_5Cl]^+$ cations and BPh_4^- anions. Figure 1 shows a perspective view of the cation and Table 1 reports selected bond distances and angles. In the cation a triangle of nickel atoms is capped above and below by two triply bridging sulphur ligands

Table 1. Selected bond distances (Å) and angles (°) with estimated standard deviations (e.s.d.s) in parentheses for complex (**2**)

Ni(1)–Ni(2)	3.028(3)	Ni(2)–S(2)	2.194(4)
Ni(1)–Ni(3)	2.874(3)	Ni(2)–P(3)	2.223(5)
Ni(2)–Ni(3)	2.867(3)	Ni(2)–P(4)	2.213(5)
Ni(1)–S(1)	2.197(4)	Ni(3)–S(1)	2.135(4)
Ni(1)–S(2)	2.195(4)	Ni(3)–S(2)	2.200(5)
Ni(1)–P(1)	2.200(5)	Ni(3)–P(5)	2.196(6)
Ni(1)–P(2)	2.222(5)	Ni(3)–Cl	2.191(5)
Ni(2)–S(1)	2.199(4)	S(1)–S(2)	2.779(6)
Ni(2)–Ni(1)–Ni(3)	58.1(1)	S(2)–Ni(3)–Cl	93.3(2)
Ni(1)–Ni(2)–Ni(3)	58.3(1)	P(5)–Ni(3)–Cl	90.9(2)
Ni(1)–Ni(3)–Ni(2)	63.7(1)	Ni(1)–S(1)–Ni(2)	87.1(2)
S(1)–Ni(1)–S(2)	78.5(2)	Ni(1)–S(1)–Ni(3)	83.1(2)
S(1)–Ni(1)–P(1)	93.8(2)	Ni(2)–S(1)–Ni(3)	82.8(2)
S(1)–Ni(1)–P(2)	160.3(2)	Ni(1)–S(2)–Ni(2)	87.2(2)
S(2)–Ni(1)–P(1)	169.0(2)	Ni(1)–S(2)–Ni(3)	81.6(2)
S(2)–Ni(1)–P(2)	88.6(2)	Ni(2)–S(2)–Ni(3)	81.5(2)
P(1)–Ni(1)–P(2)	100.8(2)	P(1)–Ni(1)–Ni(2)	122.7(1)
S(1)–Ni(2)–S(2)	78.5(2)	P(1)–Ni(1)–Ni(3)	129.6(1)
S(1)–Ni(2)–P(3)	163.0(2)	P(2)–Ni(1)–Ni(2)	130.1(1)
S(1)–Ni(2)–P(4)	93.7(2)	P(2)–Ni(1)–Ni(3)	112.9(2)
S(2)–Ni(2)–P(3)	86.4(2)	P(3)–Ni(2)–Ni(1)	125.0(1)
S(2)–Ni(2)–P(4)	169.7(2)	P(3)–Ni(2)–Ni(3)	116.0(1)
P(3)–Ni(2)–P(4)	102.2(2)	P(4)–Ni(2)–Ni(1)	123.3(2)
S(1)–Ni(3)–S(2)	79.7(2)	P(4)–Ni(2)–Ni(3)	128.8(2)
S(1)–Ni(3)–P(5)	95.9(2)	P(5)–Ni(3)–Ni(1)	128.5(2)
S(1)–Ni(3)–Cl	172.7(2)	P(5)–Ni(3)–Ni(2)	126.9(2)
S(2)–Ni(3)–P(5)	175.5(2)	Cl–Ni(3)–Ni(1)	127.1(2)
		Cl–Ni(3)–Ni(2)	123.7(2)

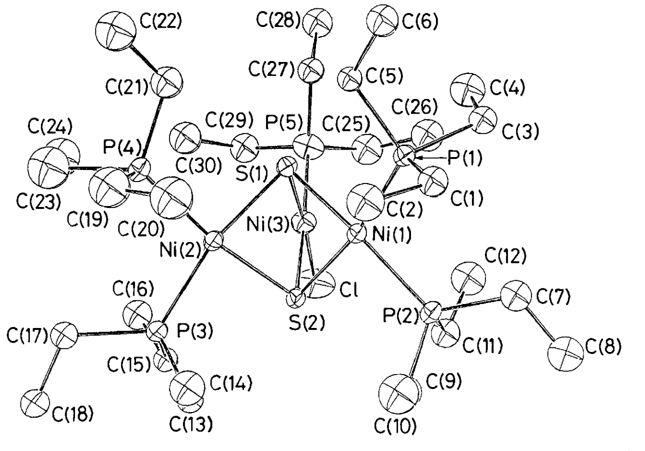


Figure 1. Perspective view of the cluster cation $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_5Cl]^+$ ORTEP drawing with 30% probability ellipsoids

forming a trigonal bipyramid. Moreover each metal atom is additionally co-ordinated in the appropriate NiS_2 plane by two other ligands: Ni(1) and Ni(2) by two triethylphosphine groups, Ni(3) by a phosphine and by a chlorine ligand.

The metal–metal separation averaging 2.92(5) Å is fully comparable with the values reported for the isostructural cations $[Ni_3S_2(PEt_3)_6]^{2+}$ [2.91(2)],[5a] $[Ni_3S_2(PEt_3)_5(SH)]^+$ [2.93(5)],[6] and $[Ni_3S_2(PPh_3)_5(H_2O)]^{2+}$ [2.95(5) Å],[7] and is indicative of absence of a significant direct nickel–nickel interaction. Moreover the three metals atoms are asymmetrically arranged with two shorter [2.867(3), 2.874(3)], and one larger [3.028(3) Å] Ni–Ni distances. As we have previously found for the related trinickel compounds, the metal–metal distances are influenced by the bulkiness of the triply bridging ligands (S or Se) and by the steric requirements of the phosphine ligands (PPh_3 or PEt_3). In this context it is interesting that the species containing six triphenylphosphine groups has never been synthesized.

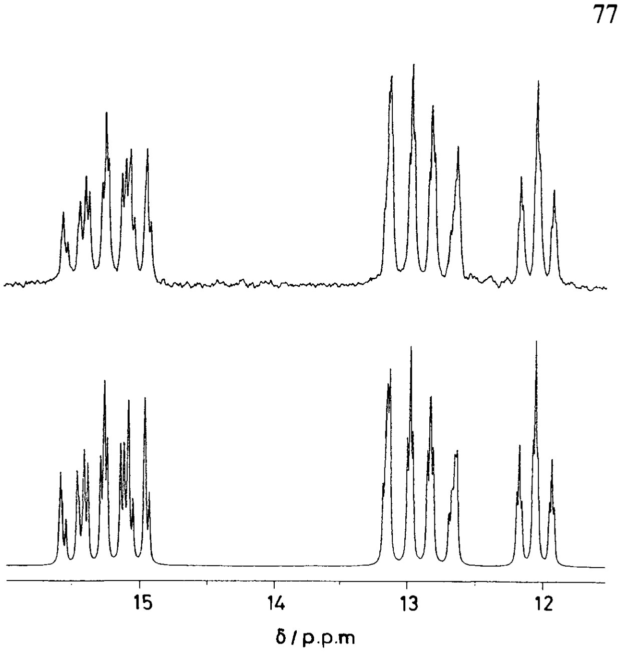


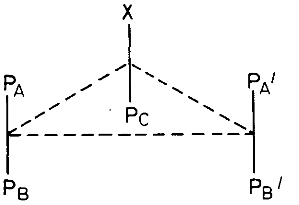
Figure 2. Experimental (upper) and calculated (lower) $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of $[Ni_3S_2(PEt_3)_5Cl]BPh_4$

Similarly to $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_5(SH)]^+$,[6] in compound (**2**) the reduced steric requirement of the chlorine with respect to a triethylphosphine group induces a rearrangement in order to minimize the contacts between the ethylenic chain so that the two $Ni(PEt_3)_2$ fragments are bent towards the $Ni(PEt_3)Cl$ moiety. It follows that the metal atom linked to the chlorine ligand displays Ni–Ni distances of 2.874(3) and 2.867(3) Å significantly shorter than that of 3.028(3) Å between the two $Ni(PEt_3)_2$ fragments. Evidence of this bending is provided by the values of the P–Ni–Ni angles.

The values of the Ni–P distances ranging from 2.196(6) to 2.223(5) Å are within the range given in literature. The Ni–S *trans* to the chlorine ligand shows a significant shortening [2.135(4) Å] with respect to the other ones averaging 2.197(1) Å, the last value being fully comparable with those reported for the series of trinickel compounds.[5–7]

$^{31}P\text{-}\{^1H\}$ *N.M.R. Spectra.*—All of the $^{31}P\text{-}\{^1H\}$ n.m.r. spectra for the complexes here reported display a marked second-order character and have been simulated by computer analysis. The spectrum of the related complex $[Ni_3S_2(PPh_3)_5(H_2O)][PF_6]_2$[7] has also been simulated for comparative purposes. The refined spectral parameters are reported in Table 2. The spectra of the monosubstituted species have been simulated according to the spin system AA′BB′C. The experimental and calculated spectra of the monochloro derivative are reported in Figure 2. The spectrum essentially consists of three multiplets with intensities corresponding to two, two, and one phosphorus atom, respectively. The assignment of the low-field pseudo-triplet of triplets (1P) to P_C is straightforward. The chemical shifts $\delta(P_A)$ and $\delta(P_B)$ can be assigned only by taking into account the coupling constants. Values of −38.9, 21.0, and −1.9 Hz are obtained for the geminal $^2J(P_AP_B) = {}^2J(P_{A'}P_{B'})$, *trans*-vicinal $^4J(P_AP_{B'}) = {}^4J(P_{A'}P_B)$, and *cis*-vicinal $^4J(P_AP_{A'}) = {}^4J(P_BP_{B'})$ coupling constants, respectively. The sign cannot be unequivocally determined; however, negative values for the coupling constants of phosphorus atoms *cis*-co-ordinated to a metal are strongly suggested by theoretical considerations and commonly reported in the literature.[8] Accordingly, it appears reasonable to

Table 2. ^{31}P N.m.r. data for the monosubstituted complexes[a]



Compound	$\delta(P_A)$ $\delta(P_{A'})$	$\delta(P_B)$ $\delta(P_{B'})$	δP_C	$^2J(P_AP_B)$ $^2J(P_{A'}P_{B'})$	$^4J(P_AP_{B'})$ $^4J(P_{A'}P_B)$	$^4J(P_AP_C)$ $^4J(P_{A'}P_C)$	$^4J(P_BP_C)$ $^4J(P_{B'}P_C)$	$^4J(P_AP_{A'})$ $^4J(P_BP_{B'})$
$[Ni_3S_2(PEt_3)_5Cl]BPh_4$[b]	15.2	12.9	12.1	−38.9	21.0	14.8	−2.3	−1.9
$[Ni_3S_2(PEt_3)_5Br]BPh_4$[b]	15.3	13.4	12.4	−38.6	21.4	14.5	−2.3	−1.6
$[Ni_3S_2(PEt_3)_5I]BPh_4$[b]	15.8	14.2	14.5	−38.5	20.8	13.4	−2.3	−1.0
$[Ni_3S_2(PEt_3)_5(NCS)]BPh_4$[b]	16.4	14.0	16.7	−40.5	20.6	15.9	−1.4	−2.5
$[Ni_3S_2(PEt_3)_5(SH)]BPh_4$[b]	17.0	14.5	17.3	−37.8	22.8	12.6	−2.4	−3.0
$[Ni_3Se_2(PEt_3)_5Br]BPh_4$[c]	15.6	15.0	16.4	−30.8	21.5	14.0	−3.3	−2.1
$[Ni_3Se_2(PEt_3)_5I]BPh_4$[c]	15.5	14.6	16.6	−31.0	21.7	13.7	−2.8	−0.6
$[Ni_3S_2(PEt_3)_5(CO)][PF_6]_2$[c]	17.3	16.2	28.9	−49.8	16.5	16.3	0	−0.8
$[Ni_3S_2(PPh_3)_5(H_2O)][PF_6]_2$[b]	24.1	22.4	13.0	−35.4	24.2	17.6	0	−1.8

[a] At room temperature; data (p.p.m.) referenced to H_3PO_4; coupling constants in Hz. ^{31}P N.m.r. spectra of $[Ni_3Y_2(PEt_3)_6]^{2+}$ in $(CD_3)_2CO$ show singlets at δ 11.8, 10.5, and 7.7 p.p.m. for Y = S, Se, or Te respectively. [b] In $CDCl_3$ solution. [c] In $(CD_3)_2CO$ solution.

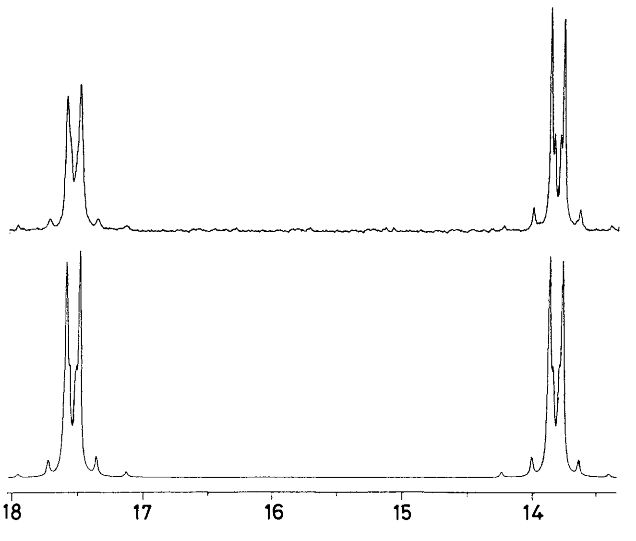


Figure 3. Experimental (upper) and calculated (lower) $^{31}P\text{-}\{^1H\}$ n.m.r. spectra of $[Ni_3S_2(PEt_3)_4Br_2]$

attribute the values of 14.8 and −2.3 Hz to the *trans*-vicinal $^4J(P_AP_C)$ and *cis*-vicinal $^4J(P_BP_C)$ coupling constants, respectively (see the drawing in Table 2). The spectra of the other monosubstituted complexes have been analogously resolved. These results are comparable with the n.m.r. data reported for the related complex $[Rh_3(\mu_3\text{-}S)_2(\mu\text{-}S)(\mu\text{-}Cl)_2(PEt_3)_6]PF_6$.[9]

The disubstituted complexes may adopt disubstituted geminal, *cis*-vicinal, or *trans*-vicinal structures, corresponding to the spin systems A_4, ABCC′, and AA′BB′, respectively. The spectra of the dihalogeno derivatives are quite similar to each other. Therefore, the spectral analysis has been limited to the dibromo species. Since two ^{31}P chemical shifts are clearly present in the spectrum of $[Ni_3S_2(PEt_3)_4Br_2]$, Figure 3, we have considered the system AA′BB′ (Table 3).* On the other hand, a *trans*-vicinal disubstituted geometry has been found for $[Ni_3S_2(PPh_3)_4Cl_2]$, by an *X*-ray analysis.[1b] The spectrum has been well simulated according to this structure. As shown in Table 3, the values of the coupling constants are consistent with those found for the monosubstituted derivatives. For the reaction of complex (1) with NCS^- (molar ratio = 1:2.05) the ^{31}P n.m.r. spectrum of the resulting solution appears different, as it shows a unique symmetrical multiplet centred at *ca.* 18.15 p.p.m. (4P) together with the signal of the displaced PEt_3 (2P, − 18.4 p.p.m.). However, the computer analysis has shown that also this spectrum, which is due to the isolable complex $[Ni_3S_2(PEt_3)_4(NCS)_2]$, can be interpreted on the basis of the same *trans*-disubstituted geometry (scheme in Table 3, Figure 4). The quite different aspect of this spectrum as compared to that of the corresponding halogeno derivatives is due to the very small difference in the chemical shifts of $P_AP_{A'}$ and $P_BP_{B'}$. The coupling constants show again a similar trend.

Tables 2 and 3 clearly show that the values of the corresponding coupling constants are scarcely affected by changing the substituent group. By contrast, the chemical shifts of the phosphorus atoms are remarkably dependent on the nature of the substituent. In this case, however, one has to consider the differing charge of the resulting cluster. As expected the phosphorus atom in geminal position to X is the one that is most affected upon varying the substituent. Interestingly, the phosphorus chemical shifts for corresponding nuclei in the series of the isocharged and isostructural compounds $[Ni_3S_2(PEt_3)_5X]^+$ (X = Cl, Br, I, SH, or NCS) are gradually shifted to lower field in the order SH, NCS, I, Br, Cl, reflecting the increase in electronegativity of the substituents (Figure 5).

Experimental

The complexes were prepared under an atmosphere of dinitrogen. The compound H_2Te[10] and the complexes (1) and $[Ni_3Se_2(PEt_3)_6][ClO_4]_2$[5] were prepared according to reported methods.

Preparation of Complexes.—$[Ni_3S_2(PEt_3)_5Cl]BPh_4$. *Method*

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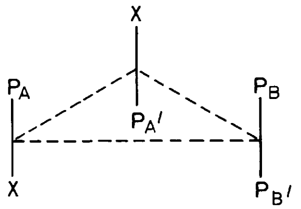
* The ^{31}P n.m.r. spectra of $[Ni_3S_2(PEt_3)_4Cl_2]$ and $[Ni_3S_2(PEt_3)_4I_2]$ in $(CD_3)_2CO$ show quite similar features with two signals at δ 12.1 and 15.8, and at 15.9 and 19.1 p.p.m. for the chloro and iodo derivatives respectively.

Table 3. ^{31}P N.m.r. data for the disubstituted complexes*



Compound	$\delta(P_A)$ $\delta(P_{A'})$	$\delta(P_B)$ $\delta(P_{B'})$	$^2J(P_BP_{B'})$	$^4J(P_AP_{A'})$	$^4J(P_AP_B)$ $^4J(P_{A'}P_{B'})$	$^4J(P_AP_{B'})$ $^4J(P_{A'}P_B)$
$[Ni_3S_2(PEt_3)_4Br_2]$	17.5	13.8	−31.9	15.9	−5.5	18.0
$[Ni_3S_2(PEt_3)_4(NCS)_2]$	18.5	17.8	−34.6	17.3	−4.5	17.8

* In $(CD_3)_2CO$ solutions at room temperature; data (p.p.m.) referenced to H_3PO_4; coupling constants in Hz.

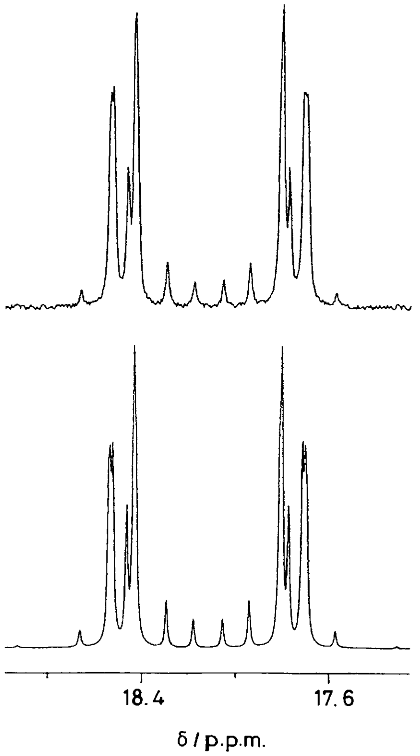


Figure 4. Experimental (upper) and calculated (lower) $^{31}P-\{^1H\}$ n.m.r. spectra of $[Ni_3S_2(PEt_3)_4(NCS)_2]$

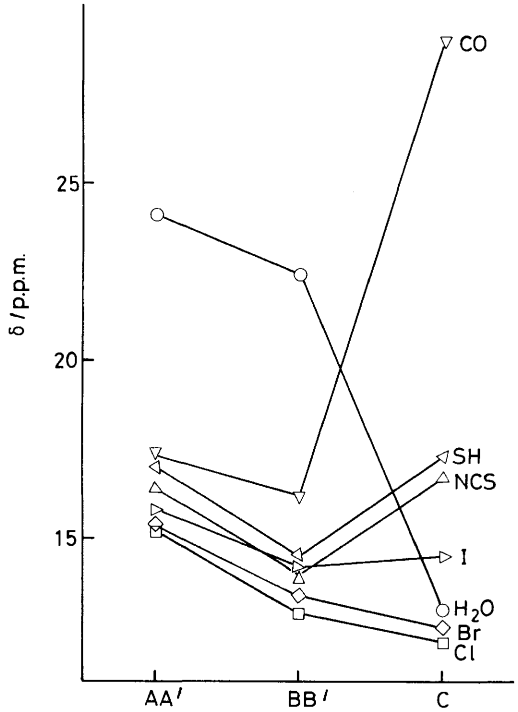


Figure 5. Variation of the ^{31}P chemical shifts within the series of monosubstituted derivatives $[Ni_3S_2(PEt_3)_5X]^+$, X = Cl, Br, I, NCS, or SH and $[Ni_3S_2(PR_3)_5X]^{2+}$, R = Et, X = CO; R = Ph, X = H_2O

(*a*). The salt $[NBu^n{}_4]Cl$ (0.292 g, 1.05 mmol) was added at room temperature to an acetone solution (15 cm^3) of complex (**1**) (1.59 g, 1 mmol). Ethanol (20 cm^3) was then added and the solvent was evaporated under a current of nitrogen until crystals precipitated. These were washed with ethanol, then with pentane and dried under a current of nitrogen. Yield, 0.8 g (Found: C, 54.55; H, 8.20. $C_{54}H_{95}BClNi_3P_5S_2$ requires C, 54.7; H, 8.10%).

The bromo- and iodo-derivatives were analogously prepared, and in a comparable yield.

Method (*b*). The compound PEt_3 (0.236 g, 2 mmol) was added to a tetrahydrofuran (20 cm^3) suspension of anhydrous $NiCl_2$ (0.130 g, 1 mmol). The mixture was stirred for 24 h at room temperature until the solid completely dissolved. The compound $S(SiMe_3)_2$ (0.178 g, 1 mmol) was added and the solution was stirred at room temperature until a deep red colour appeared (*ca.* 2 d). Sodium tetraphenylborate (0.171 g, 0.5 mmol) in n-butanol (20 cm^3) was added to the above filtered solution and the solvent was evaporated in a current of nitrogen. Deep red crystals precipitated together with pale yellow ones. The mixture was filtered and the red material was dissolved in a mixture of acetone (4 cm^3) and benzene (30 cm^3). The filtered solution, after addition of butanol (20 cm^3), was evaporated in a current of nitrogen to yield well shaped dark red crystals (0.270 g).

The bromo- and iodo-derivatives were prepared analogously, with comparable yield, but the reaction mixture has to be stirred for 5 and 7 d in the case of X = Br and I respectively, in order to obtain the corresponding deep red solutions.

$[Ni_3S_2(PEt_3)_5(NCS)]BPh_4$. The complex was prepared according to method (*a*) used for the monosubstituted halogeno derivatives, by treating (**1**) and NaNCS in a rigorous equimolar ratio [for 1.59 g of (**1**), yield = 0.90 g] (Found: C, 53.8; H, 8.0; N,

Table 4. Positional parameters (× 10^4) for complex (**2**)

Atom	*x*	*y*	*z*
Ni(1)	7 953(1)	3 653(1)	1 767(1)
Ni(2)	8 614(1)	2 145(1)	1 581(1)
Ni(3)	7 708(1)	2 443(1)	−409(1)
P(1)	7 120(2)	3 939(2)	3 158(3)
P(2)	8 501(2)	4 889(2)	1 395(4)
P(3)	9 852(2)	2 102(2)	1 212(3)
P(4)	8 289(2)	1 222(2)	2 800(4)
P(5)	6 597(2)	1 676(3)	−1 251(3)
Cl	8 162(3)	2 587(3)	−2 225(4)
S(1)	7 418(2)	2 344(2)	1 446(3)
S(2)	8 796(2)	3 174(2)	569(3)
C(1)	7 556(8)	4 695(8)	4 493(12)
C(2)	8 164(10)	4 397(10)	5 232(16)
C(3)	6 309(8)	4 331(8)	2 596(12)
C(4)	5 778(11)	3 743(11)	1 601(16)
C(5)	6 610(7)	3 059(7)	3 855(11)
C(6)	6 061(8)	3 262(9)	4 933(13)
C(7)	8 066(9)	5 750(9)	1 897(14)
C(8)	8 444(10)	6 576(11)	1 453(16)
C(9)	9 539(9)	5 243(10)	1 756(15)
C(10)	9 750(11)	5 447(12)	3 113(19)
C(11)	8 431(9)	4 850(9)	−302(13)
C(12)	7 590(11)	4 616(11)	−830(17)
C(13)	526(7)	3 054(7)	1 712(11)
C(14)	542(9)	3 336(10)	3 131(15)
C(15)	−9(7)	1 948(7)	−437(11)
C(16)	9 497(9)	1 082(10)	−1 139(14)
C(17)	363(8)	1 356(8)	1 781(12)
C(18)	1 220(8)	1 407(8)	1 391(13)
C(19)	8 802(13)	1 607(13)	4 355(19)
C(20)	8 777(12)	2 437(13)	4 861(20)
C(21)	7 248(9)	952(10)	3 130(15)
C(22)	7 023(11)	380(12)	4 136(18)
C(23)	8 583(14)	193(13)	2 576(22)
C(24)	8 263(13)	−156(13)	1 473(22)
C(25)	6 137(10)	2 094(11)	−2 409(16)
C(26)	5 810(11)	2 833(11)	−1 876(17)
C(27)	5 807(8)	1 383(8)	−254(12)
C(28)	4 996(10)	859(10)	−911(15)
C(29)	6 765(10)	697(10)	−2 093(15)
C(30)	7 067(10)	177(11)	−1 224(16)
B	3 299(9)	2 473(9)	5 218(14)
C(111)	3 942(5)	1 940(5)	4 613(6)
C(211)	4 320(5)	1 522(5)	5 331(6)
C(311)	4 850(5)	1 081(5)	4 805(6)
C(411)	5 002(5)	1 058(5)	3 562(6)
C(511)	4 624(5)	1 475(5)	2 845(6)
C(611)	4 094(5)	1 916(5)	3 370(6)
C(121)	3 351(4)	3 256(5)	4 458(7)
C(221)	4 069(4)	3 814(5)	4 506(7)
C(321)	4 177(4)	4 415(5)	3 759(7)
C(421)	3 567(4)	4 456(5)	2 964(7)
C(521)	2 849(4)	3 897(5)	2 915(7)
C(621)	2 742(4)	3 297(5)	3 662(7)
C(131)	3 471(5)	2 738(5)	6 744(10)
C(231)	3 200(5)	2 143(5)	7 471(10)
C(331)	3 310(5)	2 332(5)	8 747(10)
C(431)	3 690(5)	3 114(5)	9 296(10)
C(531)	3 960(5)	3 708(5)	8 569(10)
C(631)	3 851(5)	3 520(5)	7 294(10)
C(141)	2 397(6)	1 873(5)	4 995(8)
C(241)	1 768(6)	2 158(5)	5 524(8)
C(341)	1 016(6)	1 658(5)	5 385(8)
C(441)	893(6)	874(5)	4 717(8)
C(541)	1 521(6)	590(5)	4 188(8)
C(641)	2 273(6)	1 089(5)	4 327(8)

1.2. $C_{55}H_{95}BNNi_3P_5S_3$ requires C, 54.70; H, 7.90; N, 1.15%). ν_{NCS} (Nujol mull) 2 100 cm^{-1}.

$[Ni_3S_2(PEt_3)_4(NCS)_2]$. Sodium thiocyanate (0.243 g, 3 mmol) in acetone (10 cm^3) was added to an acetone solution (15 cm^3) of complex (**1**). The resulting solution, after addition of butanol (20 cm^3), was evaporated under a current of nitrogen until brown crystals precipitated (0.60 g) (Found: C, 38.2; H, 7.45; N, 3.4. $C_{26}H_{60}N_2Ni_3P_4S_4$ requires C, 37.70; H, 7.30; N, 3.40%).

Solutions of $[Ni_3S_2(PEt_3)_4X_2]$, X = Cl, Br, *or* I. The salt $[NBu^n_4]X$ (X = Cl, Br, or I) (10 mmol) was added to an acetone solution (15 cm^3) of complex (**1**) (1.59 g, 1 mmol). The resulting solution was warmed at *ca.* 50 °C for 30 min under continuous stirring.

$[Ni_3S_2(PEt_3)_5(CO)][PF_6]_2$. The salt $TlPF_6$ (0.720 g, 2.05 mmol) was added to an acetone solution (15 cm^3) of $[Ni_3S_2(PEt_3)_5I]BPh_4$ (1.28 g, 1 mmol). The mixture was stirred for 30 min at 50 °C to yield a suspension. The salts $TlBPh_4$ and TlI were filtered off and CO was bubbled through the resulting solution. Butanol (20 cm^3) was added and the solvent was evaporated, at room temperature, under a current of nitrogen and carbon monoxide until a deep orange microcrystalline product precipitated (0.60 g) (Found: C, 32.4; H, 6.65. $C_{31}H_{75}F_{12}Ni_3OP_7S_2$ requires C, 32.40; H, 6.60%). ν_{CO} (Nujol mull) 2 080 cm^{-1}.

$[Ni_3S_2(PEt_3)_5(SH)]BPh_4$. An acetone solution (20 cm^3) of $[Ni_3S_2(PEt_3)_5I]BPh_4$ (1.28 g, 1 mmol) was treated with $TlPF_6$ (0.72 g, 2.05 mmol) as in the previous preparation. Hydrogen sulphide was bubbled through the resulting filtered solution for 5 min. After addition of ethanol (20 cm^3) and evaporation of the solvent in a current of nitrogen deep brown crystals were obtained (0.90 g) (Found: C, 55.1; H, 8.3. $C_{54}H_{96}BNi_3P_5S_3$ requires C, 54.80; H, 8.15%).

$[Ni_3Se_2(PEt_3)_5X]BPh_4$, X = Br *or* I. The compounds were prepared according to method (*a*) used for the corresponding sulphur derivatives, with $[Ni_3Se_2(PEt_3)_6][ClO_4]_2$ in place of (**1**).

$[Ni_3Te_2(PEt_3)_6][BPh_4]_2$. Triethylphosphine (0.354 g, 3 mmol) was added to an acetone–ethanol (1:1) (20 cm^3) solution of $Ni(ClO_4)_2 \cdot 6H_2O$ (0.370 g, 1 mmol). Hydrogen telluride was bubbled through the solution for 5 min. Sodium tetraphenylborate (0.684 g, 2 mmol) in n-butanol (20 cm^3) was added and the solvent was evaporated until dark brown crystals precipitated. The complex was recrystallized from acetone–butanol (0.350 g) (Found: C, 57.6; H, 7.7. $C_{84}H_{130}B_2Ni_3P_6Tl_2$ requires C, 56.70; H, 7.35%).

N.M.R. Measurements.—^{31}P N.m.r. spectra were recorded at 121.421 MHz on a Varian VXR 300 spectrometer. Simulation of the spectra was performed using a locally integrated package based on the LAOCN3[11] and DAVINS[12] programs from the literature.

Crystallography.—*Crystal data.* $C_{54}H_{95}BClNi_3P_5S_2$, M = 1 185.7, triclinic, space group $P\bar{1}$, a = 17.496(12), b = 17.087(12), c = 11.027(9) Å, α = 98.95(8), β = 90.58(8), γ = 102.70(9)°, U = 3 173.4 Å^3, Z = 2, D_c = 1.241 g cm^{-3}, λ = 0.7107 Å, μ(Mo-K_α) = 11.46 cm^1, F(000) = 1 264.

Philips PW 1100 diffractometer using a red-brown crystal of dimensions 0.13 × 0.30 × 0.32 mm, cell constants from 24 randomly selected reflections, ω—2θ mode with a scan speed of 0.07° s^{-1} and a scan width = 0.37 + 0.3 tan θ, graphitemonochromated Mo-$K\alpha$ radiation, background measurements equal to half the scan time, standard deviations $\sigma(I)$ calculated according to ref. 13. Of a total of 5 902 reflections, 4 314 having $I > 3\sigma(I)$ were considered observed. The intensities were corrected for Lorentz and polarization effects and for absorption.[14]

Solution and refinement of the structure. All the calculations were carried out on a SEL 32/77 computer by using the SHELX 76[15] and ORTEP[16] programs. Atomic scattering factors for the appropriate neutral atoms were taken from ref. 17 for non-hydrogen and from ref. 18 for hydrogen atoms. Both the $\Delta f'$ and $\Delta f''$ components of the anomalous dispersion were included for all non-hydrogen atoms.[19] On the assumption that the compound is isomorphous with $[Ni_3S_2(PEt_3)_5(SH)]^+$,[6] the final parameters of the structure were used as starting parameters. Full-matrix least-squares refinements were carried out using anisotropic thermal parameters for nickel, phosphorus, sulphur, and chlorine and isotropic for the remaining atoms, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$, where w was set equal to $1/\sigma^2(F_o)$. The phenyl rings were treated as rigid groups, each carbon atom being assigned an individual thermal parameter. The hydrogen atoms were introduced in their calculated positions but not refined. Convergence was reached at R and R' factors of 0.075 and 0.078. A difference map showed some peaks (0.7 e Å^{-3}) in the proximity of the ethylenic chains. Final positional parameters are given in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom co-ordinates, thermal parameters, and remaining bond lengths and angles.

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