# Synthesis and Structure of the Mercaptodithiotrinickel Complex $[Ni_3(\mu_3\text{-}S)_2(SH)(PEt_3)_5]BPh_4$ *

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Reaction of $H_2S$ and $PEt_3$ with $[Ni(C_2H_4)(PPh_3)_2]$ gives the mercaptodithiotrinickel complex $[Ni_3(\mu_3\text{-}S)_2(SH)(PEt_3)_5]BPh_4$, whose molecular structure has been established by three-dimensional *X*-ray data collected by the counter method. The crystals are triclinic, space group $P\bar{1}$, with $a = 17.461(8)$, $b = 17.048(7)$, $c = 11.112(6)$ Å, $\alpha = 99.21(7)$, $\beta = 90.76(8)$, $\gamma = 102.57(7)°$, and $Z = 2$. Full-matrix least-squares refinement converged at the conventional $R$ factor of 0.070 for 2 990 observed reflections. The cation consists of a triangle of nickel atoms capped above and below by two triply bridging sulphur atoms. Moreover, Ni(1) and Ni(2) are co-ordinated by two triethylphosphine ligands and Ni(3) by a triethylphosphine and by a mercapto-group. The average Ni–Ni distance of 2.93(5) Å is indicative of no significant direct metal–metal interaction so that the geometry may be described as three square-planar $d^8$ moieties sharing two bridging ligands. An *X*-ray photoelectron spectroscopic characterisation of the electronic structure of the title compound is presented.

Transition metal complexes with $H_2S$, $SH^-$, $S^{2-}$, and $S_2^{2-}$ ligands have recently attracted considerable interest because of the novelty of these compounds, their unusual stereochemistries, their potential for serving as models for biological systems, and finally the reactivity of the sulphur groups contained.[1]

We have found in recent years that simple reaction of hydrogen sulphide with unsaturated metal complexes, having tritertiary phosphines as ancillary ligands, constitutes a favourable route to the synthesis of such compounds.[2]

Here we report that the reaction of hydrogen sulphide with a solution of $[Ni(C_2H_4)(PPh_3)_2]$, containing an excess of $PEt_3$ and $NaBPh_4$, results in the formation of a mercaptodithiotrinickel complex of formula $[Ni_3S_2(SH)(PEt_3)_5]BPh_4$.

Recently we have reported that the analogous reaction of $H_2S$ with $[Ni(H_2O)_4]^{2+}$ and $PEt_3$ (excess) allows the simultaneous synthesis of two thio-clusters of formula $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_6]^{2+}$ [2a] and $[Ni_9(\mu\text{-}S)_3(\mu_3\text{-}S)_6(PEt_3)_6]^{2+}$.[2b]

The title complex has been characterized by magnetic, conductometric, n.m.r., i.r., and electron spin correlation analysis (ESCA) measurements. A complete *X*-ray analysis has been carried out by diffractometric methods.

## Experimental

Reactions were performed under an atmosphere of nitrogen in solvents that were purified by standard methods. The complex $[Ni(C_2H_4)(PPh_3)_2]$ was prepared as previously described.[3] $^1H$ N.m.r. spectra were recorded on a Varian CFT20 spectrometer at 80 MHz. Peak positions are relative to $SiMe_4$ with upfield values reported as negative.

*Preparation of* $[Ni_3(\mu_3\text{-}S)_2(SH)(PEt_3)_5]BPh_4$.—Triethylphosphine (0.350 g, 3 mmol) was added to a solution of $[Ni(C_2H_4)(PPh_3)_2]$ (0.610 g, 1 mmol) in tetrahydrofuran (thf) (50 $cm^3$). Upon bubbling $H_2S$ through the solution for 5 min, at room temperature, the colour of the solution turned from yellow to deep brown. A solution of $NaBPh_4$ (0.340 g, 1 mmol) in $Bu^nOH$ (20 $cm^3$) was added and the solvent was evaporated at room temperature under a current of nitrogen. Deep brown crystals precipitated; they were collected by filtration, washed with $Bu^nOH$ and then light petroleum and dried under vacuum. The compound was recrystallized from $CH_2Cl_2$—$Bu^nOH$. The yield was 64% based on $[Ni(C_2H_4)(PPh_3)_2]$ (Found: C, 54.6; H, 8.35; Ni, 14.7; S, 8.1. Calc. for $C_{54}H_{96}BNi_3P_5S_3$: C, 54.8; H, 8.20; Ni, 14.9; S, 8.15%).

*Crystal Data*.—$C_{54}H_{96}BNi_3P_5S_3$, $M = 1\,183.37$, triclinic, space group $P\bar{1}$, $a = 17.461(8)$, $b = 17.048(7)$, $c = 11.112(6)$ Å, $\alpha = 99.21(7)$, $\beta = 90.76(8)$, $\gamma = 102.57(7)°$, $U = 3\,182.89$ Å$^3$, $D_c = 1.234$ g $cm^{-3}$, $Z = 2$, $\lambda$(Mo-$K_\alpha$ radiation) = 0.7107 Å, $\mu$(Mo-$K_\alpha$) = 11.3 $cm^{-1}$, $F(000) = 1\,263.9$.

*Data Collection*.—A deep brown crystal, of dimensions $0.25 \times 0.15 \times 0.10$ mm was mounted in a random orientation on a Philips PW 1100 automatic diffractometer. Lattice constants were determined by the least-squares refinement of the angles defining 22 reflections, carefully centred on the diffractometer. Intensity data were collected within $2\theta \leqslant 40°$ using Mo-$K_\alpha$ radiation monochromated with a flat graphite crystal. The $\omega$—$2\theta$ scan technique was used with a scan speed of 0.07° $s^{-1}$ and a scan width calculated according to the formula $A + B \tan \theta$, where $A = 0.7°$ and $B = 0.69$. Backgrounds were measured at the end of each scan for a time equal to half the scan time. The intensities of three standard reflections were measured every 120 min during the data collection, but no significant trend was noticed. The intensity data were processed as already described;[4] the intensity $I$ was attributed a standard deviation calculated as reported elsewhere,[5] by using the value of 0.03 for the instability factor $k$. Intensity data were corrected for Lorentz-polarization effects but not for absorption. Of 5 919 total reflections, 2 990 having $I \geqslant 3\sigma(I)$ were considered observed.

*Structure Solution and Refinement*.—All the calculations were performed using the SHELX 76 crystallographic programs on a SEL 32/70 computer.[6] Atomic scattering factors for non-hydrogen atoms were taken from ref. 7 and those for hydrogen from ref 8. Both the $\Delta f'$ and $\Delta f''$ compo-

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* 1-Mercapto-di-$\mu_3$-sulphido-1,2,2,3,3-pentakis(triethylphosphine)-trinickel(II) tetraphenylborate.

*Supplementary data available* (No. SUP 23871, 22 pp.): thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

*Non-S.I. unit employed:* 1 eV ≈ $1.60 \times 10^{-19}$ J.

**Table 1.** Atomic co-ordinates ( $\times 10^3$ for H, $\times 10^4$ for other atoms)

| Atom | $x$ | $y$ | $z$ | Atom | $x$ | $y$ | $z$ |
|---|---|---|---|---|---|---|---|
| Ni(1) | 1 385(1) | 2 862(1) | 3 447(2) | C(24) | 4 245(14) | 1 283(14) | 3 390(20) |
| Ni(2) | 2 054(1) | 1 353(1) | 3 248(2) | C(25) | 4 208(11) | 3 612(12) | 5 214(17) |
| Ni(3) | 2 316(1) | 2 572(1) | 5 419(2) | C(26) | 5 030(12) | 4 140(12) | 5 864(17) |
| S(1) | 1 222(3) | 1 840(3) | 4 463(4) | C(27) | 3 921(13) | 2 949(13) | 7 415(19) |
| S(2) | 2 585(3) | 2 661(3) | 3 540(4) | C(28) | 4 198(13) | 2 173(14) | 6 875(19) |
| S(3) | 1 883(4) | 2 426(5) | 7 234(5) | C(29) | 3 255(13) | 4 358(13) | 7 061(19) |
| P(1) | 145(3) | 2 899(3) | 3 804(4) | C(30) | 2 938(13) | 4 856(14) | 6 186(20) |
| P(2) | 1 700(3) | 3 780(3) | 2 219(5) | C(31) | 3 949(7) | −3 065(7) | −377(8) |
| P(3) | 1 507(3) | 117(3) | 3 616(5) | C(32) | 4 328(7) | −3 490(7) | 325(8) |
| P(4) | 2 880(3) | 1 061(3) | 1 849(4) | C(33) | 4 863(7) | −3 926(7) | −204(8) |
| P(5) | 3 421(3) | 3 343(4) | 6 247(4) | C(34) | 5 019(7) | −3 937(7) | −1 434(8) |
| C(1) | −372(10) | 3 615(11) | 3 232(16) | C(35) | 4 639(7) | −3 512(7) | −2 135(8) |
| C(2) | −1 237(12) | 3 581(12) | 3 612(17) | C(36) | 4 105(7) | −3 076(7) | −1 607(8) |
| C(3) | −536(10) | 1 931(10) | 3 314(15) | C(37) | 2 407(7) | −3 143(8) | −15(10) |
| C(4) | −572(12) | 1 615(12) | 1 924(19) | C(38) | 2 296(7) | −3 930(8) | −678(10) |
| C(5) | 30(11) | 3 092(11) | 5 464(15) | C(39) | 1 546(7) | −4 437(8) | −836(10) |
| C(6) | 497(12) | 3 947(13) | 6 132(18) | C(40) | 907(7) | −4 157(8) | −331(10) |
| C(7) | 2 718(12) | 4 067(13) | 1 887(19) | C(41) | 1 019(7) | −3 371(8) | 332(10) |
| C(8) | 2 930(16) | 4 577(16) | 830(24) | C(42) | 1 769(7) | −2 863(8) | 490(10) |
| C(9) | 1 169(17) | 3 335(18) | 666(25) | C(43) | 3 355(6) | −1 753(6) | −550(11) |
| C(10) | 1 174(16) | 2 546(18) | 179(25) | C(44) | 2 740(6) | −1 715(6) | −1 339(11) |
| C(11) | 1 411(18) | 4 820(18) | 2 447(27) | C(45) | 2 841(6) | −1 114(6) | −2 075(11) |
| C(12) | 1 722(18) | 5 201(18) | 3 538(28) | C(46) | 3 557(6) | −550(6) | −2 023(11) |
| C(13) | 1 898(12) | −759(12) | 3 060(17) | C(47) | 4 171(6) | −587(6) | −1 234(11) |
| C(14) | 1 537(14) | −1 593(14) | 3 526(20) | C(48) | 4 071(6) | −1 189(6) | −498(11) |
| C(15) | 453(11) | −201(12) | 3 288(18) | C(49) | 3 462(7) | −2 264(7) | 1 736(12) |
| C(16) | 223(14) | −427(15) | 1 923(22) | C(50) | 3 845(7) | −1 479(7) | 2 281(12) |
| C(17) | 1 581(12) | 127(12) | 5 261(17) | C(51) | 3 956(7) | −1 286(7) | 3 549(12) |
| C(18) | 2 446(14) | 343(13) | 5 776(19) | C(52) | 3 685(7) | −1 878(7) | 4 270(12) |
| C(19) | 3 382(10) | 1 930(10) | 1 158(15) | C(53) | 3 302(7) | −2 663(7) | 3 725(12) |
| C(20) | 3 922(11) | 1 731(11) | 72(16) | C(54) | 3 191(7) | −2 856(7) | 2 458(12) |
| C(21) | 2 458(11) | 317(11) | 526(16) | B | 3 302(12) | −2 547(13) | 175(18) |
| C(22) | 1 837(13) | 590(13) | −189(19) | H | 119(9) | 220(9) | 728(13) |
| C(23) | 3 686(11) | 666(11) | 2 380(16) | | | | |

nents of anomalous dispersion corrections were applied to the non-hydrogen atoms.[9] The structure was solved by the heavy-atom technique. Successive Fourier syntheses revealed all the non-hydrogen atoms. A full-matrix least-squares refinement was undertaken, by assigning isotropic temperature factors to all the atoms, then anisotropic thermal vibration was allowed for nickel, phosphorus, and sulphur atoms. During the refinements the function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w$ was set equal to $1/\sigma^2(F_o)$. The phenyl rings were treated as rigid groups with $d$(C–C) = 1.395 Å, each carbon atom being assigned an individual thermal parameter. Hydrogen atoms were introduced in their calculated positions, but not refined. A difference-Fourier map, calculated by using either all the data or the data within $(\sin\theta)/\lambda < 0.3$ Å$^{-1}$, showed a peak at a bond distance from the S(3) atom, which was attributed to a mercapto-hydrogen atom. Its positional and thermal parameters were included in the refinement and successfully refined without constraints, the largest shift/error of the mercapto-hydrogen parameters in the last cycle being 0.04. A final difference-Fourier map showed no particular features apart from some residual electron density (<0.6 e Å$^{-3}$) in the region of the ethylenic chains. Although some conformational disorder was observed, it was impossible to resolve the electron density into separate components. The convergence was reached at $R$ and $R'$ factors of 0.070 and 0.067 respectively. The final atomic co-ordinates are given in Table 1.

*ESCA Measurements*.—Photoelectron spectra have been run on a VG ESCA III Mk.2 spectrometer using Al-$K_\alpha$ radiation. Samples were dusted as thin films onto gold sample plates. The C(1*s*) line [binding energy (b.e.) = 285.0 eV] from residual pump-line oil contamination was used as internal standard for spectral calibration. The binding energies reported were measured at the full-width of the half-maximum of the bands (f.w.h.m.). Possible changes in the products under the action of the *X*-ray radiation were monitored by repeated scans, the spectra being recorded at liquid-nitrogen temperature. No significant changes in the spectra were observed. Measurements of the average of three different values from different deposited samples are considered accurate to ±0.2 eV. Peak deconvolution has been performed by means of a Dupont 310 curve resolver using a Gaussian shape fit.

## Results and Discussion

The reaction between the complex $[Ni(C_2H_4)(PPh_3)_2]$ and $H_2S$, in the presence of $PEt_3$ (3 : 1) and $NaBPh_4$ (1 : 1) in thf solution, affords a deep brown, crystalline diamagnetic product.

Spectroscopic and conductivity data, together with the analytical results, are in agreement with the formula $[Ni_3S_2(SH)(PEt_3)_5]BPh_4$. Indeed, (*i*) the complex behaves as a 1 : 1 electrolyte in nitroethane solution; (*ii*) the $^1$H n.m.r. spectrum ($CD_2Cl_2$) shows a proton resonance at δ −1.85 (d), which is attributable to an SH proton,[10] split into a doublet by a phosphorus nucleus [$^3J$(P–H) = 15.4 Hz]. The absence of an S–H stretching vibration in the i.r. spectrum of the compound is not unexpected.[10]

The molecular structure of the title compound consists of discrete $[Ni_3(\mu_3\text{-}S)_2(SH)(PEt_3)_5]^+$ cations and $BPh_4^-$ anions.

**Table 2.** Selected bond distances (Å) and angles (°)

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ni(1)–Ni(2) | 3.027(3) | Ni(1)–P(1) | 2.219(5) | Ni(2)–P(3) | 2.219(5) | Ni(3)–S(3) | 2.196(6) |
| Ni(1)–Ni(3) | 2.878(3) | Ni(1)–P(2) | 2.223(5) | Ni(2)–P(4) | 2.206(5) | Ni(3)–P(5) | 2.182(6) |
| Ni(2)–Ni(3) | 2.882(3) | Ni(2)–S(1) | 2.201(5) | Ni(3)–S(1) | 2.194(5) | S(1) · · · S(2) | 2.784(6) |
| Ni(1)–S(1) | 2.193(5) | Ni(2)–S(2) | 2.190(5) | Ni(3)–S(2) | 2.168(5) | S(3)–H | 1.20(15) |
| Ni(1)–S(2) | 2.199(5) | | | | | | |

| | | | | | | | |
|---|---|---|---|---|---|---|---|
| Ni(2)–Ni(1)–Ni(3) | 58.4(1) | S(1)–Ni(2)–P(3) | 88.6(2) | S(3)–Ni(3)–P(5) | 90.5(3) | P(2)–Ni(1)–Ni(2) | 122.9(2) |
| Ni(1)–Ni(2)–Ni(3) | 58.2(1) | S(1)–Ni(2)–P(4) | 169.1(2) | Ni(1)–S(1)–Ni(2) | 87.1(2) | P(2)–Ni(1)–Ni(3) | 128.8(2) |
| Ni(1)–Ni(3)–Ni(2) | 63.4(1) | S(2)–Ni(2)–P(3) | 161.0(2) | Ni(1)–S(1)–Ni(3) | 82.0(2) | P(3)–Ni(2)–Ni(1) | 129.8(2) |
| S(1)–Ni(1)–S(2) | 78.7(2) | S(2)–Ni(2)–P(4) | 93.4(2) | Ni(2)–S(1)–Ni(3) | 81.9(2) | P(3)–Ni(2)–Ni(3) | 112.8(2) |
| S(1)–Ni(1)–P(1) | 86.8(2) | P(3)–Ni(2)–P(4) | 100.9(2) | Ni(1)–S(2)–Ni(2) | 87.2(2) | P(4)–Ni(2)–Ni(1) | 122.8(2) |
| S(1)–Ni(1)–P(2) | 169.5(2) | S(1)–Ni(3)–S(2) | 79.3(2) | Ni(1)–S(2)–Ni(3) | 82.5(2) | P(4)–Ni(2)–Ni(3) | 129.6(2) |
| S(2)–Ni(1)–P(1) | 164.2(2) | S(1)–Ni(3)–S(3) | 93.5(2) | Ni(2)–S(2)–Ni(3) | 82.8(2) | P(5)–Ni(3)–Ni(1) | 127.0(2) |
| S(2)–Ni(1)–P(2) | 93.1(2) | S(1)–Ni(3)–P(5) | 175.7(2) | Ni(3)–S(3)–H | 116(6) | P(5)–Ni(3)–Ni(2) | 128.9(2) |
| P(1)–Ni(1)–P(2) | 102.0(2) | S(2)–Ni(3)–S(3) | 172.5(3) | P(1)–Ni(1)–Ni(2) | 125.0(2) | S(3)–Ni(3)–Ni(1) | 124.1(2) |
| S(1)–Ni(2)–S(2) | 78.7(2) | S(2)–Ni(3)–P(5) | 96.6(2) | P(1)–Ni(1)–Ni(3) | 116.7(1) | S(3)–Ni(3)–Ni(2) | 127.0(2) |

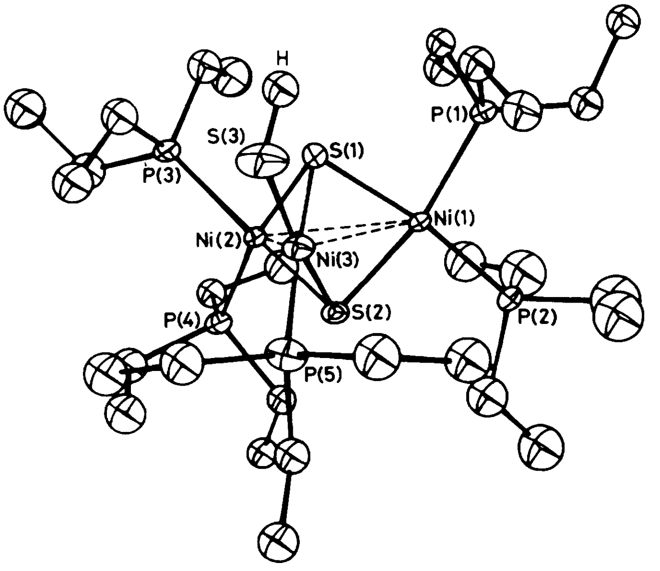

**Figure.** Perspective view of the complex cation $[Ni_3(\mu_3\text{-}S)_2(SH)(PEt_3)_5]^+$: ORTEP drawing with 30% probability ellipsoids

A perspective view of the cation is shown in the Figure. Selected bond distances and angles are given in Table 2.

The inner core of the cation may be described as a triangle of nickel atoms capped above and below by two triply bridging sulphur ligands which complete a trigonal bipyramid. Moreover, each metal atom is 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 mercapto-group. The $NiS_2X_2$ fragments are not strictly planar, the deviations from the $NiS_2$ planes ranging from 0.06 to 0.54 Å. This geometry is fully comparable with that described for $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_6]^{2+}$,[2a] as shown by the average * values of the Ni–S–Ni and S–Ni–S angles which are respectively 84.9(1.1) and 77.4(1.1)° in the latter and 83.9(1.0) and 78.9(2)° in the title compound. The value of the average Ni–Ni distance of 2.93(5) Å is indicative of no significant direct metal–metal interaction, and analogously to $[Ni_3(\mu_3\text{-}X)_2(PEt_3)_6]^{2+}$ (X = S or Se)[2d] and related compounds,[11,12] the overall geometry may be described as three square-planar $d^8$ moieties sharing two bridging ligands.

Although the average Ni–Ni distance compares well with that of 2.91(2) Å reported for $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_6]^{2+}$, the three distances show significant variations, two of these being shorter [2.882(3) and 2.878(3) Å] than the other [3.027(3) Å]. This difference, can be, in our opinion, attributed to the reduced steric hindrance of the mercapto-group with respect to the triethylphosphine ligands, which allows the two $Ni(PEt_3)_2$ fragments to approach the $Ni(SH)(PEt_3)$ moiety. As a matter of fact the replacement of a $PEt_3$ by a $SH^-$ group induces a general rearrangement, in order to minimize the contacts between the ethylenic chains. This arrangement is evidenced by the value of the S(3)–Ni(3)–P(5) angle compared to the P(1)–Ni(1)–P(2) and P(3)–Ni(2)–P(4) angles [90.5(3) *versus* 102.0(2) and 100.9(2)°] and by an examination of the P–Ni–Ni angles, whose values show that the P(1) and P(3) phosphine ligands take advantage of the reduced steric hindrance of the SH group, the P(1)–Ni(1)–Ni(3) and P(3)–Ni(2)–Ni(3) angles [116.7(1) and 112.8(2)°] being significantly smaller than the other P–Ni–Ni angles which range from 122.8(2) to 129.8(2)°.

The values of the Ni–P and Ni–S distances are within the normal range; only the Ni(3)–S(2) bond distance, with S(2) being *trans* to the mercapto-sulphur, shows a value [2.168(5) Å] significantly shorter than the others [average 2.195(2) Å]. The value of the S–H distance, 1.20(15) Å, matches those of 1.19(7) and 1.17(8) Å reported for $[W_2(CO)_{10}(\mu\text{-}SH)]^-$ [13] and $[Cr(CO)_5(SH)]^-$,[14] respectively. There are no unusual intermolecular contacts. No contacts involving the mercapto-hydrogen atom of <2.9 Å are observed.

*X*-Ray photoelectron spectra of the title compound, together with those of $[Ni(SH)(tdpep)]^+$[tdpep = tris(2-diphenylphosphinoethyl)phosphine] [15] and $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_6]^{2+}$ [2a] (in which a unique type of mercapto- and thio-group, respectively, are present), have been run in order to clarify the electronic structure of these compounds. Indeed, the x.p.s. technique is able, in principle, to give information about the oxidation states of the elements and of the variation of electronic density on an atom, as a consequence of the variations of the ligands.[16] Table 3 shows the Ni($2p\frac{3}{2}$), S(2*p*), and P(2*p*) b.e. values and f.w.h.m. for the title compound, together with values for reference compounds. Among these only the S(2*p*) spectra for $[Ni(SH)(tdpep)]^+$ have been previously reported in the literature.[17]

The P(2*p*) b.e. values for the three compounds are very similar (131.8—132.0 eV) and significantly higher than the value of that for P(2*p*) in the free ligand (131.1 eV). It is known that when the phosphine σ-co-ordination is accompanied by M ⟶ L back-donation, it results in a close

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* The estimated errors on the means were calculated using the formula $[\Sigma_n(d_n - \bar{d})^2/n(n - 1)]^{\frac{1}{2}}$.

**Table 3.** $Ni(2p_{\frac{3}{2}})$, $S(2p)$, and $P(2p)$ binding energies (eV) and f.w.h.m. (eV) in parentheses

| Compound | $Ni(2p_{\frac{3}{2}})$ | $S(2p)$ | $P(2p)$ |
|---|---|---|---|
| $[Ni(SH)(tdpep)]^+$ | 856.0(2.1) | 162.8(2.4) | 132.0(2.2) |
| $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_6]^{2+}$ | 855.3(2.2) | 161.5(2.4) | 131.8(2.3) |
| $[Ni_3(\mu_3\text{-}S)_2(SH)(PEt_3)_5]^+$ | 855.7(2.7) [a] | 161.7(2.8) [b] | 131.8(2.3) |
| $PPh_3$ | | | 131.1(2.2) |

[a] Can be deconvoluted into two components: 855.2 and 856.0.
[b] Can be deconvoluted into two components: 161.4 and 162.6.

similarity between the binding energies of the free and the co-ordinated ligand, since the electron density on the phosphorus atom tends to be equal in both cases. Therefore the net increase of the $P(2p)$ b.e. values, with respect to the free ligand, seems to indicate that the P atoms are σ-co-ordinated to Ni and there is a very small degree of $Ni \longrightarrow P$ back-donation, if any.

The $S(2p)$ binding energies for $[Ni(SH)(tdpep)]^+$ and $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_6]^{2+}$ differ considerably: the higher b.e. value of the mercapto-group compared with the thio-ligand has been explained[17] by a greater covalency of the M–SH bond than the M–S bond in the $M_3S_2$ fragment. Indeed, the $S(2p)$ value for $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_6]^{2+}$ closely approaches the values found in the literature[16] for ionic sulphide groups, whilst the value for $[Ni(SH)(tdpep)]^+$ reflects the decrease of the charge density around the sulphur atom as a consequence of the formation of the S–H bond.

The $S(2p)$ f.w.h.m. for the title compound is larger than that of the other two (2.8 *versus* 2.4 eV). It is possible to find two components each with a f.w.h.m. of *ca.* 2.3 eV by deconvolution of the $S(2p)$ peak. The intensity ratio is 2 : 1 and the b.e. values are at 161.4 and 162.6 eV, which can be attributable to the presence of the thio- and mercapto-group, respectively.

As for the nickel atoms, the binding energies range from 855.3 eV for $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_6]^{2+}$ to 856.0 eV for $[Ni(SH)(tdpep)]^+$, through 855.7 eV for the title compound. Again, in the last compound, it is possible to deconvolute the peak (which has a f.w.h.m. value larger than the other two) into two components in the ratio 2 : 1. The first of these matches the binding energy value of $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_6]^{2+}$ (Ni bound to $S^{2-}$ ligand) and the second one has the position of the $Ni(2p_{\frac{3}{2}})$ peak in $[Ni(SH)(tdpep)]^+$ (Ni–SH bond).

It seems very difficult to rationalise these values in terms of formal oxidation number of the metal atom, the binding energies being, to the first approximation, a function of the overall spatial charge distribution around the atom due to the nature of the ligands and to the chemical bond. However, it is worthwhile noting that, on going from a Ni–S(sulphide) bond to a Ni–SH bond there is an increase of the b.e. of both nickel and sulphur atoms. The values of the deconvoluted Ni and S peaks of the title compound clearly show the presence of two nickel atoms only bonded to the $S^{2-}$ atoms and of a third nickel bonded also to one $SH^-$ group. The x.p.s. spectra can distinguish between the different ways in which the sulphur and nickel atoms can be bonded in the title compound.

The analysis of the $Ni(2p_{\frac{3}{2},\frac{1}{2}})$ photoelectronic doublet shows the absence of satellite peaks, indicative of a paramagnetic species (*i.e.* tetrahedral or octahedral co-ordination for nickel). The diamagnetism of these compounds and the square-planar co-ordination geometry for the nickel atoms in the compounds $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_6]^{2+}$ and $[Ni_3(\mu_3\text{-}S)_2(SH)(PEt_3)_5]^+$ are thus confirmed.

The reactivity of the $SH^-$ groups linked to metal complexes is of current interest. Unfortunately preliminary results seem to indicate that the title complex is very inert. Indeed deprotonation does not occur, even by using a large excess of NaOEt in thf. Moreover, the reactions with acetic anhydride or phenyl isothiocyanate, which recently have been found to occur with $[W(CO)_5(SH)]^-$ and $[W_2(CO)_{10}(\mu\text{-}SH)]^-$,[18] do not take place for the title compound.

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