Reactions of Polysulphide with Metal–Phosphine Species. Synthesis and *X*-Ray Crystal Structure of $[\{Ni(bppte)(\mu\text{-}OH)\}_2][ClO_4]_2\cdot(CH_3)_2CO$ *

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The reaction of $[Ni(H_2O)_6][ClO_4]_2$ in the presence of 1,1,1-tris(diphenylphosphinomethyl)-ethane, tppme, with $[S_n]^{2-}$ leads to the formation of the dimeric hydroxo-complex $[\{Ni(bppte)(\mu\text{-}OH)\}_2][ClO_4]_2\cdot(CH_3)_2CO$, bppte = $PPh_2SCH_2C(CH_3)(CH_2PPh_2)_2$, which was structurally characterized by *X*-ray diffraction. Crystal data are: *a* = 19.046(7), *b* = 18.195(6), *c* = 13.349(5) Å, β = 97.76(4)°, space group $P2_1/a$, and *Z* = 2. In the centrosymmetric dimeric hydroxo-bridged cation each metal atom displays square-planar co-ordination, the third arm of the ligand, PPh_2SCH_2, being unco-ordinated. The unexpected formation of hydroxo complexes is discussed.

The formation of metal sulphide complexes generally follows from self-assembly processes in which sulphur sources and organometallic substrata are involved.[1] A systematic investigation of the reactivity of different sulphur sources towards organometallic systems could contribute to clarifying the factors determining the reaction pathways.

We have recently reported that the reaction of H_2S with $[Ni(H_2O)_6][BF_4]_2$ or $[Co(H_2O)_6][BF_4]_2$, in the presence of the tripodal phosphine 1,1,1-tris(diphenylphosphinomethyl)-ethane, $CH_3C(CH_2PPh_2)_3$, tppme, under mild conditions, allows the facile synthesis of dimeric sulphide or disulphide derivatives.[2] Now we have treated the above metal–phosphine systems with ammonium polysulphide solutions. Unexpectedly, there is no attack of any $[S_n]^{2-}$ species on the metals, instead dimeric hydroxo-derivatives are formed: the previously reported complex $[\{Co(tppme)(\mu\text{-}OH)\}_2]^{2+}$ in the case of the cobalt,[3] and the new unusual planar species $[\{Ni(bppte)(\mu\text{-}OH)\}_2]^{2+}$, where bppte is $PPh_2SCH_2C(CH_3)(CH_2PPh_2)_2$. The latter complex, as its perchlorate salt, (**1**), has been completely characterized by an *X*-ray analysis.

Experimental

Infrared and electronic spectra, conductivity measurements, magnetic susceptibilities, and $^{31}P\text{-}\{^1H\}$ n.m.r. spectra were recorded by previously described methods.[1c] The methanolic ammonium polysulphide solution was prepared as described, by using the same quantity of reagent and solvent.[4]

Preparation of $[Ni(tppme)_2][ClO_4]_2$, (**2**).—The ligand tppme (1.25 g, 2 mmol) dissolved in acetone (10 cm³) was added to a solution of $[Ni(H_2O)_6][ClO_4]_2$ (0.365 g, 1 mmol) in acetone (5 cm³), at room temperature. After 10 min orange-yellow crystals separated; they were filtered off, washed with cold acetone, then with light petroleum (b.p. 40—70 °C) and dried *in vacuo*. Yield: 60%.

Preparation of $[\{Ni(bppte)(\mu\text{-}OH)\}_2][ClO_4]_2\cdot(CH_3)_2CO$, (**1**).—All the operations were carried out under a nitrogen atmosphere. The ligand tppme (0.624 g, 1 mmol) dissolved in acetone (15 cm³) was added to a solution of $[Ni(H_2O)_6][ClO_4]_2$ (0.365 g, 1 mmol) in acetone (10 cm³). Then a solution of ammonium polysulphide in methanol (5 cm³) was added at room temperature. By evaporation under a current of nitrogen, brown crystals precipitated. These were filtered off, washed with acetone, then with light petroleum (b.p. 40—70 °C) and dried in a stream of nitrogen. Yield: 72%.

Crystallography.—Crystal data. $C_{85}H_{86}Cl_2Ni_2O_{11}P_6S_2$, *M* = 1 721.92, monoclinic, space group $P2_1/a$, *a* = 19.046(7), *b* = 18.195(6), *c* = 13.349(5) Å, β = 97.76(4)°, *U* = 4 583.6 Å³, D_c = 1.247 g cm⁻³, *Z* = 2, λ(Mo-K_α) = 0.7107 Å, μ(Mo-K_α) = 6.69 cm⁻¹, *F*(000) = 1 792.

Data collection. The crystal selected for data collection was a parallelepiped of dimensions 0.22 × 0.29 × 0.32 mm delimited by the faces 001,110,1$\bar{1}$0, and the centrosymmetric ones. The crystal was coated in paraffin to prevent decomposition and mounted on a Philips PW 1100 diffractometer. The cell dimensions were determined by least-squares refinement of the angular settings of 25 carefully centred reflections using the graphite-monochromated Mo-K_α radiation.

Intensity data within $2\theta < 50°$ were collected at room temperature with a scan speed of 0.08° s⁻¹ by using the ω—2θ scan technique, with a scan range calculated according to the expression $A + B\tan\theta$, where $A = 0.8°$ and $B = 0.3$. Stationary background measurements were taken before and after each scan for a time equal to half the scan time. The intensities of three standard reflections were measured every 2 h and showed no systematic trend. The intensities were corrected for background and assigned standard deviations calculated by using the value of 0.03 for the instability factor *k*.[5] The intensity data were corrected for Lorentz and polarization effects and an absorption correction (μ = 6.69 cm⁻¹) was applied,[6] the transmission coefficients ranging from 0.97 to 0.99.

Solution and refinement of the structure. All the calculations were carried out on a SEL 32/77 computer by using the SHELX 76[6] and ORTEP[7] programs. Atomic scattering factors for the appropriate neutral atoms were taken from ref. 8. Both the $\Delta f'$ and $\Delta f''$ components of the anomalous dispersion were included for all non-hydrogen atoms.[9] The refinement was based on F_o, the function minimized being $\Sigma w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. The structure was solved by the heavy-atom method; a series of Fourier maps showed all the non-hydrogen atoms. The bridging atom was first considered to be sulphur. However this hypothesis was rapidly rejected due to the unrealistic bond distances and thermal parameter. It was therefore attributed to a OH group (see below). Full-matrix least-squares refinement was undertaken assigning isotropic thermal parameters to all the atoms. Throughout the refinement the phenyl rings were treated as rigid groups of D_{6h} symmetry (C–C 1.395 Å), each

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* Di-μ-hydroxo-bis{[1,1-bis(diphenylphosphinomethyl)-1-(diphenylphosphinothioylmethyl)ethane-*PP'*]nickel} diperchlorate–acetone (1/1).

Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1988, Issue 1, pp. xvii—xx.

Table 1. Atomic co-ordinates (× 10^4)

Atom	*x*	*y*	*z*	Atom	*x*	*y*	*z*
Ni	561(2)	373(2)	634(2)	C(13)	1 334(9)	1 439(9)	−829(18)
Cl	2 761(6)	3 802(7)	927(9)	C(23)	1 057(9)	1 982(9)	−1 508(18)
S	2 800(4)	889(4)	4 999(6)	C(33)	1 194(9)	1 962(9)	−2 508(18)
P(1)	1 057(3)	165(3)	2 148(4)	C(43)	1 608(9)	1 400(9)	−2 829(18)
P(2)	1 128(3)	1 371(4)	448(4)	C(53)	1 886(9)	857(9)	−2 150(18)
P(3)	3 076(3)	1 654(4)	4 146(5)	C(63)	1 748(9)	877(9)	−1 150(18)
O(1)	33(7)	467(8)	−659(9)	C(14)	574(8)	2 150(14)	598(13)
O(2)	2 336(16)	3 773(27)	130(22)	C(24)	870(8)	2 853(14)	645(13)
O(3)	2 876(24)	3 083(16)	1 251(37)	C(34)	441(8)	3 467(14)	721(13)
O(4)	2 423(17)	4 108(19)	1 679(26)	C(44)	−283(8)	3 378(14)	750(13)
O(5)	3 392(13)	4 102(12)	792(16)	C(54)	−579(8)	2 675(14)	702(13)
C(1)	1 523(11)	1 896(11)	2 855(15)	C(64)	−150(8)	2 061(14)	627(13)
C(2)	2 036(11)	1 362(12)	2 369(15)	C(15)	2 769(8)	2 550(8)	4 524(12)
C(3)	1 938(10)	496(11)	2 553(13)	C(25)	2 567(8)	2 614(8)	5 487(12)
C(4)	2 016(10)	1 513(11)	1 172(15)	C(35)	2 347(8)	3 292(8)	5 820(12)
C(5)	2 839(11)	1 562(11)	2 760(15)	C(45)	2 329(8)	3 906(8)	5 191(12)
C(11)	482(6)	461(7)	3 049(12)	C(55)	2 531(8)	3 842(8)	4 228(12)
C(21)	733(6)	600(7)	4 062(12)	C(65)	2 751(8)	3 164(8)	3 895(12)
C(31)	267(6)	838(7)	4 717(12)	C(16)	4 024(8)	1 769(11)	4 275(18)
C(41)	−449(6)	938(7)	4 358(12)	C(26)	4 451(8)	1 447(11)	5 088(18)
C(51)	−700(6)	799(7)	3 345(12)	C(36)	5 187(8)	1 504(11)	5 163(18)
C(61)	−234(6)	560(7)	2 691(12)	C(46)	5 495(8)	1 883(11)	4 425(18)
C(12)	1 153(7)	−816(10)	2 288(10)	C(56)	5 067(8)	2 206(11)	3 613(18)
C(22)	749(7)	−1 212(10)	2 899(10)	C(66)	4 331(8)	2 149(11)	3 537(18)
C(32)	791(7)	−1 977(10)	2 930(10)	C(7)*	4 921(41)	275(44)	7 722(56)
C(42)	1 236(7)	−2 346(10)	2 351(10)	C(8)*	4 222(39)	343(52)	7 951(69)
C(52)	1 640(7)	−1 950(10)	1 740(10)	C(9)*	5 461(44)	681(68)	8 178(86)
C(62)	1 599(7)	−1 185(10)	1 708(10)	C(10)*	4 987(67)	−33(82)	6 776(87)

Carbon atoms marked with an asterisk belong to the solvent molecule.

carbon atom being assigned an individual thermal parameter. At this point a Fourier difference map showed the solvating acetone molecule whose population parameter was fixed at 0.5. The solvent molecule appeared disordered and a rigid-group refinement was necessary, with the scattering factors of the carbon atom assigned to all the atoms. The final refinements performed, allowing anisotropic thermal motion to the nickel, phosphorus, sulphur, chlorine, and oxygen atoms, converged at *R* and *R′* values 0.095 and 0.092 respectively for 1 864 observed reflections $[I \geqslant 3\sigma(I)]$. The rather high value of *R* can be justified by considering the high disorder in the region of the perchlorate ion and of the solvent molecule. The final atomic co-ordinates are listed in Table 1.

Discussion

The ammonium polysulphide solution in methanol does not react with the solution of $[Co(H_2O)_6][ClO_4]_2$ and tppme in acetone, the only isolable product being the dimeric complex $[(tppme)Co(\mu\text{-}OH)_2Co(tppme)]^{2+}$,[3] which is easily formed also in the absence of the polysulphide reagent. On the contrary, when the $[Ni(H_2O)_6][ClO_4]_2$ salt is used in the place of the cobalt one a rapid reaction occurs with formation of brown crystals which analyse as $C_{41}H_{40}ClNiO_5S\cdot0.5(CH_3)_2(CO)$, (**1**). Complex (**1**) is diamagnetic and little soluble in common polar organic solvents. It decomposes in air but can be stored indefinitely under an inert gas atmosphere.

The ^{31}P n.m.r. spectrum of the complex in CD_2Cl_2 solution shows two singlets at 14.86 and 32.76 p.p.m. (intensity ratio 2:1), respectively attributable to the co-ordinated PPh_2 and the unco-ordinated $SPPh_2$ groups. The i.r. spectrum, Nujol mull, shows bands at 3 630 and 1 715 cm^{-1} attributable to an O–H stretching vibration and to the C–O stretching vibration of acetone respectively.

Table 2. Selected bond distances (Å) and angles (°) with estimated standard deviations*

Ni–P(1)	2.146(6)	P(2)–C(14)	1.80(2)
Ni–P(2)	2.144(7)	P(3)–S	1.92(1)
Ni–O(1)	1.884(12)	P(3)–C(5)	1.80(2)
Ni–O(1′)	1.904(14)	P(3)–C(15)	1.83(2)
Ni ··· Ni′	2.879(6)	P(3)–C(16)	1.80(3)
P(1)–C(3)	1.80(2)	C(1)–C(2)	1.58(3)
P(1)–C(11)	1.81(2)	C(2)–C(3)	1.61(3)
P(1)–C(12)	1.80(2)	C(2)–C(4)	1.62(3)
P(2)–C(4)	1.85(2)	C(2)–C(5)	1.59(3)
P(2)–C(13)	1.80(3)		

P(1)–Ni–P(2)	95.4(2)	C(4)–P(2)–C(14)	109.9(9)
P(1)–Ni–O(1)	172.4(4)	C(13)–P(2)–C(14)	104.9(9)
P(1)–Ni–O(1′)	91.7(4)	S–P(3)–C(5)	118.6(8)
P(2)–Ni–O(1)	91.8(5)	S–P(3)–C(15)	111.1(7)
P(2)–Ni–O(1′)	172.4(5)	S–P(3)–C(16)	112.2(8)
O(1)–Ni–O(1′)	81.0(6)	C(5)–P(3)–C(15)	108.3(9)
Ni–O(1)–Ni′	99.0(6)	C(5)–P(3)–C(16)	102.2(11)
Ni–P(1)–C(3)	119.9(7)	C(15)–P(3)–C(16)	102.9(9)
Ni–P(1)–C(11)	110.1(5)	C(1)–C(2)–C(3)	116.7(18)
Ni–P(1)–C(12)	107.3(5)	C(1)–C(2)–C(4)	111.6(17)
C(3)–P(1)–C(11)	108.9(8)	C(1)–C(2)–C(5)	110.2(17)
C(3)–P(1)–C(12)	102.9(9)	C(3)–C(2)–C(4)	109.2(16)
C(11)–P(1)–C(12)	106.7(7)	C(3)–C(2)–C(5)	107.5(16)
Ni–P(2)–C(4)	119.8(7)	C(4)–C(2)–C(5)	100.3(17)
Ni–P(2)–C(13)	110.2(6)	P(1)–C(3)–C(2)	113.9(14)
Ni–P(2)–C(14)	110.1(7)	P(2)–C(4)–C(2)	113.0(14)
C(4)–P(2)–C(13)	100.6(9)	P(3)–C(5)–C(2)	116.2(16)

* Primed atoms are related to the corresponding unprimed atoms by the centre of symmetry.

The molecular structure consists of discrete $[\{Ni(bppte)(OH)\}_2]^{2+}$ cations, ClO_4^- anions, and interspersed acetone molecules. The Figure shows a perspective view of the cation, and Table 2 reports selected bond distances and angles. In the

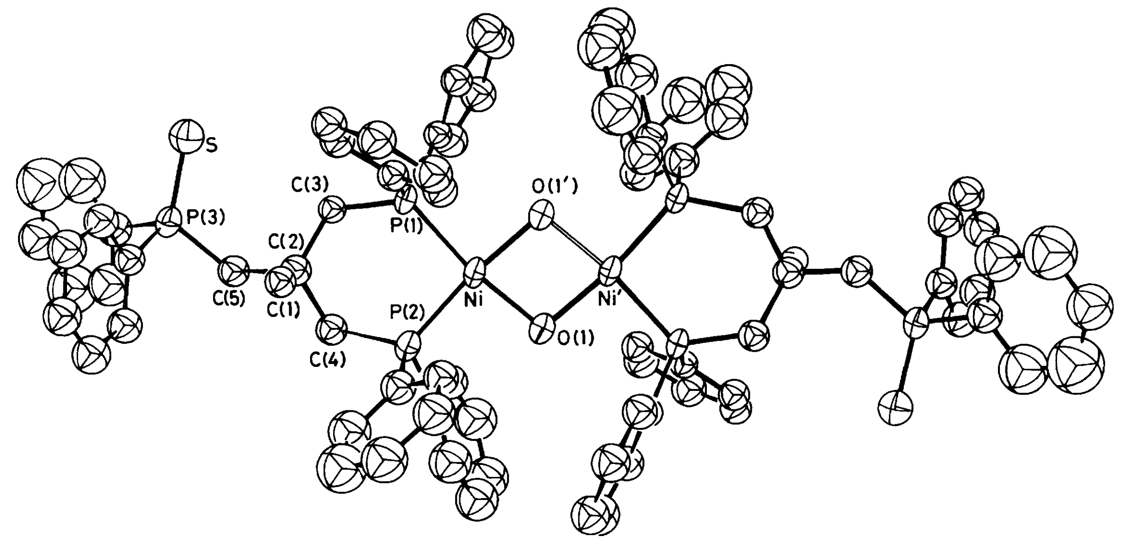
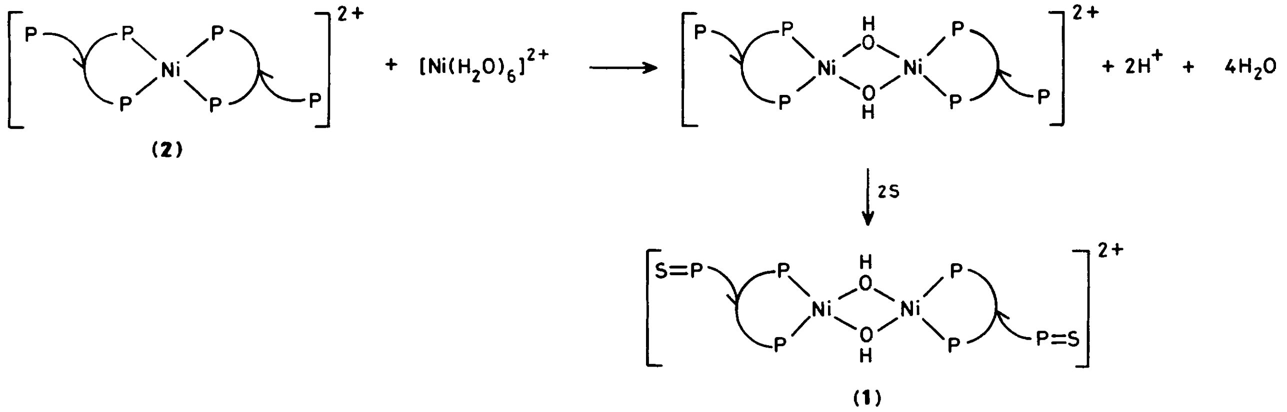


Figure. Perspective view of the cation $[\{Ni(tppme)(\mu\text{-}OH)\}_2]^{2+}$: ORTEP drawing with 30% probability ellipsoids

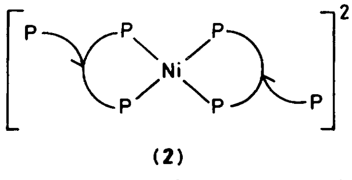


Scheme 1.

cation two centrosymmetrically related Ni(bppte) fragments are bridged by two OH groups. Each metal atom is co-ordinated by two phosphorus atoms of the tripod ligand in a square-planar geometry. The third arm of the ligand, PPh_2SCH_2, remains unco-ordinated. Owing to the presence of the centre of symmetry the Ni_2O_2 fragment is strictly planar, and in the $P_2NiO_2NiP_2$ moiety the largest deviation from planarity is only 0.037 Å. The Ni–O–Ni′ angle of 99.0(6)° may be compared with the value of 102.8(3)° found in the hydroxo-bridged iron(III) complex $[\{FeL(OH)\}_2]\cdot 2H_2O\cdot 2py$, where L = *N,N′*-ethylenebis(salicylideneiminate)(2−) and py = pyridine.[10] The value of the nickel–nickel separation [2.879(6) Å] is indicative of no significant direct metal–metal bonding. The Ni–P and Ni–O distances are comparable with those reported for a variety of square-planar nickel complexes.[11]

In order to elucidate the formation of the complex we have investigated the reaction of $Ni(ClO_4)_2\cdot 6H_2O$ with tppme. It is known that NiX_2 (X = Cl or Br) reacts with tppme to form square-planar complexes of formula $[Ni(tppme)X_2]$[12] with the tripodal phosphine acting as a bidentate ligand. In the case of NiI_2 the reaction yields tetrahedral [Ni(tppme)I] spontaneously.[13]

We have now found that $Ni(ClO_4)_2\cdot 6H_2O$ [or $Ni(BF_4)_2\cdot 6H_2O$] reacts in acetone with tppme to give a red-brown solution from which the complex $[Ni(tppme)_2][ClO_4]_2$, (**2**), can easily be isolated. The reflectance spectrum with no absorptions below 20 000 cm^{-1} is indicative of square-planar co-ordination. The i.r. spectrum does not show any absorption attributable to O–H stretching. The $^{31}P\text{-}\{^1H\}$ n.m.r. spectrum in CH_2Cl_2, with singlets at 2.7 and −31.2 p.p.m. (intensity ratio 2:1), clearly shows that only two PPh_2 groups of tppme are co-ordinated.[14] Thus the complex could have the structure shown.



(**2**)

The ^{31}P n.m.r. spectra of acetone solutions containing $Ni(ClO_4)_2\cdot 6H_2O$ and tppme in molar ratios 1:0.5, 1:1, 1:1.5, and 1:2 have been recorded: these all are practically identical to those of (**2**), the two signals being only slightly shifted because of the different solvent (δ 2.8 and −29.8 p.p.m).* Since the solution

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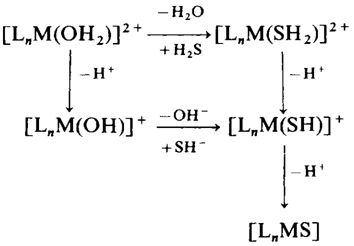
* It was not possible to record the spectra of complex (**2**) in acetone because of its low solubility in this solvent.

of $Ni(ClO_4)_2{\cdot}6H_2O$ and tppme (molar ratio 1:1) contains (**2**) as the only species, we must admit that the hydroxo-bridged species is formed by addition of the methanolic ammonium polysulphide solution. Thus we suggest the pathway shown in Scheme 1, which is promoted by the basicity of the polysulphide solution. The concomitant sulphurization of the non-co-ordinated PPh_2 groups finally produces complex (**1**).

The unsuccessful formation, in the above reaction, of the metal sulphido derivatives $[(tppme)Ni{-}S{-}Ni(tppme)]^{2+}$, $[(tppme)Ni(S)_2Ni(tppme)]^{+}$, and $[(tppme)Co(S_2)Co(tppme)]^{0,1+,2+}$,[2] otherwise easily prepared by reaction with H_2S, is noteworthy. The formation of these sulphides probably occurs through a reaction pathway involving the substitution of OH^- by SH^- and successive H^+ elimination (see Scheme 2). The synthesis of mercapto species by this route has already been reported.[2]



$$\begin{tikzcd}
{[L_nM(OH_2)]^{2+}} \arrow[r, "-H_2O", "+H_2S"'] \arrow[d, "-H^+"] & {[L_nM(SH_2)]^{2+}} \arrow[d, "-H^+"] \\
{[L_nM(OH)]^{+}} \arrow[r, "-OH^-", "+SH^-"'] & {[L_nM(SH)]^{+}} \arrow[d, "-H^+"] \\
 & {[L_nMS]}
\end{tikzcd}$$

Scheme 2.

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