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A Trinuclear Disulphido Complex of Nickel(II) with Triethylphosphine

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It is well-known that H_2S reacts with solutions of transition metal salts giving insoluble metal sulfides even in the presence of strongly coordinating ligands. We have recently found that by the reaction of H_2S with iron(II), cobalt(II) and nickel(II) tetrafluoroborate in the presence of poly(tertiary phosphines), stable and soluble mercapto or thio complexes can be obtained [1–3]. The mercapto derivatives are mononuclear compounds with a trigonal bipyramidal [1] or a square planar geometry [3]. The thio complexes so far isolated have a dinuclear structure with a sulfur atom bridging two metal atoms which are tetrahedrally coordinated [2].

In the course of this study we have carried out the above reaction in the presence of mono-tertiary phosphines and have found that the reaction of H_2S with $Ni(BF_4)_2 \cdot 6H_2O$ in the presence of triethylphosphine gives a polynuclear sulfur complex which was isolated as its tetraphenylborate salt and has the composition $[Ni_3S_2(P(C_2H_5)_3)_6](BPh_4)_2$.

The compound is air stable and soluble in organic solvents such as methylene chloride, acetone and nitroethane. It is diamagnetic and a 2:1 electrolyte in nitroethane solution. Its electronic spectrum which is substantially the same for a solution as for the solid state, shows a band at 27,800 cm^{-1}.

The molecular structure of the complex, determined by a single crystal X-ray diffraction study, consists of discrete $[Ni_3S_2(P(C_2H_5)_3)_6]^{2+}$ cations and BPh_4^- anions. Figure 1 shows a perspective view of the cation: selected bond distances and angles are reported in Table I. The central unit Ni_3S_2 consists of an equilateral triangle of nickel atoms capped above and below by two sulfur atoms thus forming an almost regular trigonal bipyramid. Furthermore each metal atom is coordinated to two phosphorus atoms lying approximately in the appropriate NiS_2 plane. Important bond lengths are: Ni–Ni(av) = 2.91(2) Å, Ni–S(av) = 2.15(2) Å, Ni–P(av) = 2.27(4) Å, S–S = 2.70(4) Å; the mean Ni–S–Ni and S–Ni–S angles are 84.9(1.0) and 77.4(1.1)°, respectively [4]. The length of the Ni–Ni distance and the diamagnetism of the complex indicate that there is no significant metal–metal interaction. Thus the overall geometry may be regarded as three square planar $Ni(II)S_2P_2$ moieties sharing two sulfur atoms. A similar bonding was proposed for the isoelectronic complex $[Pt_3S_2L_6]^{2+}$ where L = $P(CH_3)_2(C_6H_5)$ [5]. The structure of $[Ni_3S_2(P(C_2H_5)_3)_6]^{2+}$ may be compared with that of the complex $[Ni_3S_2(C_5H_5)_3]$ having the same trigonal bipyramidal Ni_3S_2 core and a Ni–Ni distance of 2.801(5) Å [6]. The magnetic moment of 1.7 μ_B found for this compound was accounted for by assuming the existence of a weak metal–metal interaction. The longer Ni–Ni distance of the complex described here is accompanied by a shortening of the intramolecular S–S distance, 2.70(4) Å compared with 2.90(2) Å reported for $[Ni_3S_2(C_5H_5)_3]$, and a consequent compression of the Ni_3S_2 core.

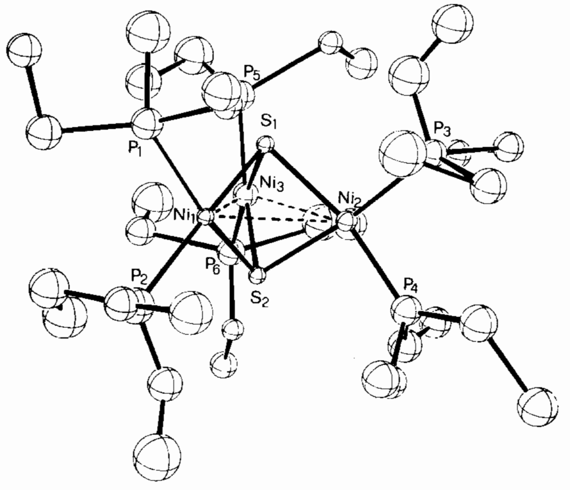

Figure 1. Perspective view of the $[Ni_3S_2(P(C_2H_5)_3)_6]^{2+}$ cation.

Experimental

The compound was prepared by adding triethylphosphine (3 mmol) to $Ni(BF_4)_2 \cdot 6H_2O$ (1 mmol) in 25 ml of ethanol and by bubbling H_2S through the solution for 3 min. The black crystals [7] which had precipitated after three days were filtered off and the filtrate was added to a solution of $NaBPh_4$ (0.5 mmol) in 10 ml of ethanol. After 2 days brown crystals had separated. These were filtered off and recrystallized from a solution of methylene chloride and ethanol. *Anal.* Calcd. for $C_{84}H_{130}B_2Ni_3P_6S_2$: C, 63.55; H, 8.25; Ni, 11.09; P, 11.71; S, 4.04. Found: C, 63.76; H, 8.52; Ni, 11.39; P, 12.01; S, 4.28.

The crystals are monoclinic space group $P2_1/a$ with a = 22.10(2), b = 29.10(2), c = 13.30(1) Å, β =

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TABLE I. Selected Bond Distances (Å) and Angles (deg) with Estimated Standard Deviations in Parentheses.

Ni(1)–Ni(2)	2.88(2)	Ni(2)–S(1)	2.16(3)
Ni(1)–Ni(3)	2.96(2)	Ni(2)–S(2)	2.23(3)
Ni(2)–Ni(3)	2.89(3)	Ni(2)–P(3)	2.23(5)
S(1)–S(2)	2.70(4)	Ni(2)–P(4)	2.14(5)
Ni(1)–S(1)	2.11(3)	Ni(3)–S(1)	2.20(3)
Ni(1)–S(2)	2.11(3)	Ni(3)–S(2)	2.11(3)
Ni(1)–P(1)	2.35(5)	Ni(3)–P(5)	2.24(5)
Ni(1)–P(2)	2.25(6)	Ni(3)–P(6)	2.39(6)
Ni(2)–Ni(1)–Ni(3)	59.1(6)	P(3)–Ni(2)–P(4)	95.4(1.8)
Ni(1)–Ni(2)–Ni(3)	62.0(6)	S(1)–Ni(3)–S(2)	77.3(1.2)
Ni(1)–Ni(3)–Ni(2)	58.9(5)	S(1)–Ni(3)–P(5)	164.7(1.8)
S(1)–Ni(1)–S(2)	79.4(1.2)	S(1)–Ni(3)–P(6)	96.1(1.6)
S(1)–Ni(1)–P(1)	165.4(1.5)	S(2)–Ni(3)–P(5)	87.4(1.7)
S(1)–Ni(1)–P(2)	92.4(1.7)	S(2)–Ni(3)–P(6)	173.2(1.8)
S(2)–Ni(1)–P(1)	87.9(1.5)	P(5)–Ni(3)–P(6)	99.2(2.0)
S(2)–Ni(1)–P(2)	169.5(1.9)	Ni(1)–S(1)–Ni(2)	84.6(1.1)
P(1)–Ni(1)–P(2)	99.4(1.9)	Ni(1)–S(1)–Ni(3)	86.9(1.1)
S(1)–Ni(2)–S(2)	75.6(1.1)	Ni(2)–S(1)–Ni(3)	82.7(1.2)
S(1)–Ni(2)–P(3)	170.7(1.6)	Ni(1)–S(2)–Ni(2)	82.9(1.1)
S(1)–Ni(2)–P(4)	91.1(1.6)	Ni(1)–S(2)–Ni(3)	89.3(1.2)
S(2)–Ni(2)–P(3)	97.7(1.4)	Ni(2)–S(2)–Ni(3)	83.2(1.2)
S(2)–Ni(2)–P(4)	166.7(1.7)		

94.3(1)°, D_c = 1.24 g cm^{-3} for Z = 4. Three-dimensional intensity data were collected with Mo-Kα radiation on a Philips computer controlled PW 1100 diffractometer. Crystals are very small and fragile and the intensities showed a rapid attenuation with θ so that very few reflections could be collected up to 2θ = 30°. As a consequence only 1145 reflections having $I \geqslant 3\sigma(I)$ were used in the calculations. The structure was solved by the heavy atom technique and many Fourier maps were necessary owing to the difficulties caused by disorder in locating the lighter atoms. Owing to the unfavorable ratio number of reflections/number of variables (94 non-hydrogen atoms) least squares refinements were carried out using isotropic thermal parameters and treating the eight phenyl rings as rigid bodies. Few cycles of refinement yielded an R factor of 0.18. Since a successive difference Fourier map did not suggest any improvement to the model in which three carbon atoms of the disordered ethylenic chains are still missing, calculations were concluded at this stage. In spite of the values of R and σ, attributable to the poor quality of the data consisting of a small number of low intensity and low angle reflections, and to the difficulties produced by disorder, the main features of the structure are considered to be reliable.

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7 This compound is another polynuclear sulfur complex of nickel whose characterization is in progress.