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Preparation and *X*-Ray Structure of a Dimeric Diamagnetic Complex of Nickel(II) with Distorted Tetrahedral Co-ordination

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Summary The diamagnetic dimeric complex $[Ni_2S\{MeC(CH_2PPh_2)_3\}_2][BPh_4]_2$ is shown by *X*-ray diffraction to contain two nickel(II) atoms with a distorted tetrahedral co-ordination, joined by a linearly bridging sulphur atom.

UNPOLYMERIZED transition-metal complexes with unsubstituted sulphur as ligand are rare on account of their high tendency to revert to binary sulphides.[1] Thus the formation of dark green crystals of $[Ni_2S\{MeC(CH_2PPh_2)_3\}_2][BPh_4]_2,1·5HCONMe_2$ on bubbling H_2S through a solution of $[Ni(H_2O)_6][BF_4]_2$ (1 mmol), $NaBPh_4$ (1 mmol), and 1,1,1-tris(diphenylphosphinomethyl)ethane (1 mmol) in 20 ml of ethanol and 10 ml of $HCONMe_2$ was unexpected. The compound is diamagnetic, the X_g values being *ca.* $-0·6 \times 10^{-6}$ (c.g.s. units) in the temperature range 85—296 K. The electronic spectrum shows bands at 9100, 10,500, 15,400, 20,600, and 25,000 cm^{-1}. An analogous selenium derivative $[Ni_2Se\{MeC(CH_2PPh_2)_3\}_2][BPh_4]_2,1·5HCONMe_2$ can be obtained by reaction with H_2Se.

The molecular stereochemistry of the sulphur derivative has been determined through three dimensional *X*-ray analysis. *Crystal data:* triclinic, $a = 17·754(4)$, $b = 13·972(3)$, $c = 12·658(3)$ Å, $\alpha = 93·09(2)°$, $\beta = 106·41(2)°$, $\gamma = 106·89(2)°$, $U = 2850·09$ Å^3, $D_m = 1·18$ g cm^{-3}, $D_c = 1·194$ g cm^{-3}, $Z = 1$, space group $P\bar{1}$.

Intensity data were collected using a Philips PW 1100 automated diffractometer and the structure was solved by standard Patterson and Fourier methods. It was refined to a conventional *R* index of 0·066 for 1807 observations above background.

The structure of the complex cation (Figure) is a centrosymmetric dimer where each nickel atom is in a distorted tetrahedral environment provided by three phosphorous atoms from the phosphine ligand and by a shared sulphur atom which gives rise to crystallographically co-linear Ni–S–Ni linkages. This type of sulphur bridge seems to be unique in transition-metal complexes.[1] Each Ni–S distance [2·034(2) Å] is considerably shorter than any analogous distance reported in the literature.[2,3] Other bond distances and angles of interest are: Ni–P(1) = 2·235(6), Ni–P(2) = 2·232(6), Ni–P(3) = 2·242(5) Å, ∠P(1)–Ni–P(2) = 92·37(22)°, P(2)–Ni–P(3) = 91·24(21)°, P(1)–Ni–P(3) = 93·52(21)°, S–Ni–P(1) = 120·42(16)°, S–Ni–P(2) = 121·64(18)°, S–Ni–P(3) = 128·39(18)°. The Ni atom is 1·24 Å from the plane of the three phosphorus atoms.

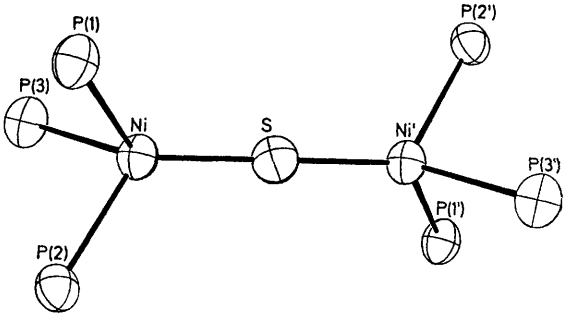

FIGURE. ORTEP drawing of the skeleton of the dimeric $[Ni_2S\{MeC(CH_2PPh_2)_3\}_2]^{2+}$

This seems to be the first example of a tetrahedral diamagnetic nickel(II) complex; the compound [Ni_4(tep)NO]-BPh_4 [tep = 1,1,1-tris(diethylphosphinomethyl)ethane],[4] in spite of doubts raised by recent ESCA studies,[5] is considered to contain Ni^0.

The electronic spectrum of the compound is not easily interpreted in the absence of more detailed studies but the diamagnetism can be rationalized by a qualitative MO approach similar to that proposed for $[Ru_2OCl_{10}]^{4-}$.[6] In the D_{3d} symmetry of the dimer two E_u non-σ-bonding orbitals on each nickel atom can mix with two sulphur p-orbitals to give π-type bonding, non-bonding, and antibonding MOs. Since the energy of the antibonding orbitals is presumably too high for them to be populated, the valence electrons can be accommodated within a closed-shell configuration. The model predicts a shortening of the Ni–S single bond distance which is in agreement with that observed.

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