

**Tris[triphenylphosphinehexachloronaphthalene-1,8-dithiolato]nickel(II),
[Ni₃(PPh₃)₃(S₂C₁₀Cl₆)₃], a Ni₃S₆ Metal–Sulphur Cluster Compound;
Preparation and Crystal and Molecular Structure**

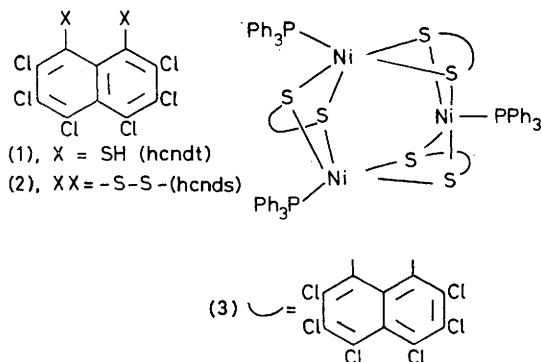
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Summary The trinuclear nickel complex [Ni₃(PPh₃)₃(S₂C₁₀Cl₆)₃] has been prepared by the reaction of equimolar amounts of [Ni(cyclo-octa-1,5-diene)₂], PPh₃, and hexachloronaphtho[1,8-*cd*]-1,2-dithiole; an *X*-ray study shows that the six sulphur atoms are situated in a trigonal prismatic arrangement with the nickel atom situated 0.60 Å above the prism faces, thus forming a unique Ni₃S₆ cluster.

HEXACHLORONAPHTHALENE-1,8-dithiol (**1**) (hcndt) has been shown to form bis complexes, [R₄N]₂[M(hcndt)₂] with M = Ni, Pd, Pt and Zn;¹ the Ni, Pd, and Pt complexes are assumed to be planar from their diamagnetism. We now report the preparation and crystal and molecular structure of a trinuclear nickel complex containing a remarkable Ni₃S₆ cluster. So far, there seems to be only one other known example of a trinuclear nickel-sulphur cluster compound, S₂Ni₃(C₅H₅)₃.²

The compound $[\text{Ni}_3(\text{PPh}_3)_3(\text{hcndt})_3]^\dagger$ (**3**) was prepared by adding an equimolar amount of solid $[\text{Ni}(\text{cyclo-octa-1,5-diene})_2]$ to a solution in benzene of triphenylphosphine and hexachloronaphtho[1,8-*cd*]-1,2-dithiole (**2**)[‡] with exclusion of dioxygen. A dark coloured solution results from which the compound was precipitated by addition of *n*-hexane. Air-stable dark brown needles were obtained by recrystallisation from benzene-hexane. The reaction of equimolar amounts of (**2**) with $\text{Pd}(\text{PPh}_3)_3$ or $\text{Pt}(\text{PPh}_3)_4$ in benzene under an inert atmosphere led, however, to red-orange products $[\text{M}(\text{PPh}_3)_2(\text{hcndt})]$ ($\text{M} = \text{Pd}$ or Pt).[†]



The i.r. spectra (CsI disc) of the newly prepared compounds apart from bands due to PPh_3 show bands at 1505m, 1400m, 1240s, 1160m, 960w, and 840w cm^{-1} , which can be attributed to co-ordinated hcndt. The absence of $\nu(\text{S-S})$ at 405 cm^{-1} found for hcnds and $\nu(\text{S-H})$ at 2650 cm^{-1} found for hcndt indicates strongly co-ordination of the dithiolato (2-) ligand.

Crystalline (**3**) consists of discrete molecules, and the details of the cluster are illustrated in the Figure. The remarkable feature of the structure is the trigonal prismatic arrangement of the sulphur atoms of the three dithiolato ligands, with the nickel ions situated 0.60(2) Å above the prism faces. In this way each nickel ion is five-co-ordinated by four sulphur atoms and an apical phosphorus atom forming a square pyramid.

In each dithiolato-ligand one of the sulphur atoms is situated in the plane of the carbon atoms of the ligand, while the other is displaced by about 0.5 Å from that plane.

The Ni-Ni distance of 2.641 Å is intermediate between the reported² large value of 2.801 Å in $[\text{S}_2\text{Ni}_3(\text{C}_5\text{H}_5)_3]$ and the very short one of 2.39 Å in the $[\text{Ni}_3(\text{C}_5\text{H}_5)_3(\text{CO})_2]$ complex. In other thiolato-bridged complexes of nickel⁴ the Ni-Ni distances are *ca.* 2.75 Å.

The intra- and inter-ligand sulphur-sulphur distances observed are comparable with those found in several metal tris-dithiolene complexes.⁵ These relatively short inter-ligand S-S distances, centred around 3.1 Å, are taken as an

[†] Satisfactory analytical data were obtained.

[‡] Compound (**2**), m.p. 288–289 °C, was obtained by the procedure of J. H. Thelin (U.S.P. 2,905,695; *Chem. Abs.*, 1960, **54**, 5602) by exhaustive chlorination of naphthalene and reaction of the purified octachloronaphthalene with sodium polysulphide. Compound (**1**) can be obtained by the reduction of (**2**) with NaBH_4 in ethanol.

§ The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre University Chemical Laboratory, Lensfield Road, Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

¹ J. G. M. van der Linden, Proceedings, XVIth I.C.C. Conference, Toronto, 1972, p. 483; J. G. M. van der Linden, Thesis, University of Nijmegen, 1973.

² H. Vahrenkamp, V. A. Uchtman, and L. F. Dahl, *J. Amer. Chem. Soc.*, 1968, **90**, 3272.

³ A. A. Hock and O. S. Mills, 'Advances in the Chemistry of Coordination Compounds,' ed. S. Kirschner, McMillan, New York, 1961, p. 640.

⁴ J. P. Fackler, Jr., *Progr. Inorg. Chem.*, 1976, **21**, 55.

⁵ R. Eisenberg, *Progr. Inorg. Chem.*, 1970, **12**, 295.

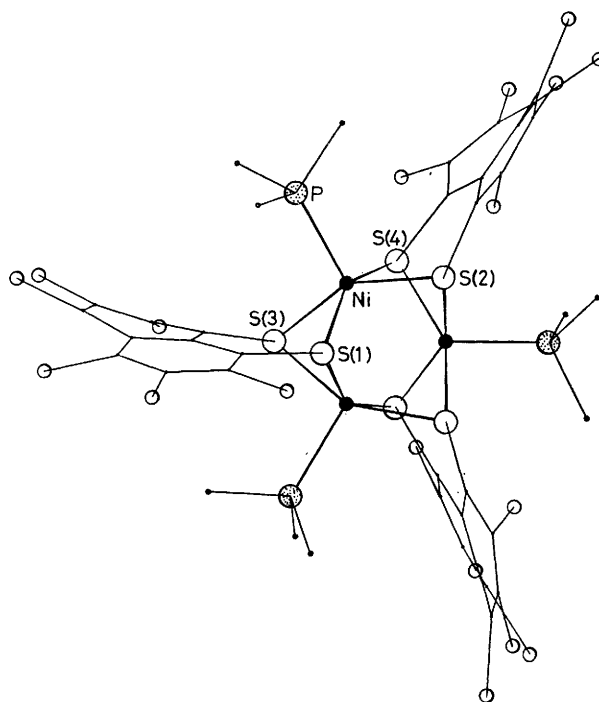


FIGURE. Structure of complex (**3**). Only the carbon atoms of the phenyl rings attached to the phosphorus atom are drawn. Important average bond lengths (Å) and angles (°) (with their e.s.d.'s based on r.m.s. deviation given in parentheses) are Ni-Ni 2.641(4), Ni-S 2.29(7) [ranging from 2.253(12) to 2.338(10)] Ni-P 2.339(7), S-S (intra-ligand) 3.05(2), S-S (inter-ligand) 3.21(2), \angle Ni-Ni-Ni 60.0(2), S(1)-Ni-S(2) 88.9(5), S(1)-Ni-S(3) 83.3(5), and S(1)-Ni-S(4) = 149.8(5).

indication for interligand sulphur-sulphur bonding. Thus the detailed geometry of $[\text{Ni}_3(\text{PPh}_3)_3(\text{hcndt})_3]$ suggests that Ni-Ni as well as S-S bonding interactions are operative in the prismatic Ni_3S_6 cluster.

Crystal data. $\text{C}_{84}\text{H}_{45}\text{Cl}_{18}\text{Ni}_3\text{P}_3\text{S}_6$, $M = 2153.9$, trigonal, space group $R\bar{3}$, $a = 66.57(2)$, $c = 11.075(3)$ Å, $D_c = 1.51$ g cm^{-3} , $D_m = 1.53$ g cm^{-3} for $Z = 18$. 8709 independent reflections with $\sin\theta/\lambda < 0.48$ Å⁻¹ were measured on a NONIUS CAD-4 single crystal diffractometer (θ -2 θ scan) employing monochromated Mo- K_α radiation. 2477 reflections with $I > 3\sigma_c(I)$ [$\sigma_c(I)$ based on counting statistics] were used in the refinement. The final conventional R -value is 0.082 for 2477 reflections. §

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