Synthesis and *X*-Ray Crystal Structure of the Asymmetric Trinuclear Complex $[Ni_3(\mu_3\text{-}S)_2(H_2O)(PPh_3)_5][PF_6]_2$ *

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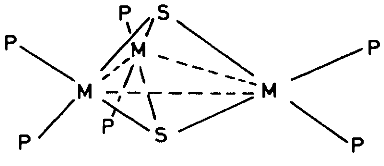
By reaction of H_2S and PPh_3 with $[Ni(H_2O)_6]^{2+}$ the trinuclear complex cation $[Ni_3(\mu_3\text{-}S)_2(H_2O)(PPh_3)_5]^{2+}$ is formed. The molecular structure of $[Ni_3(\mu_3\text{-}S)_2(H_2O)(PPh_3)_5][PF_6]_2$ was determined from three-dimensional *X*-ray data collected by counter methods. The crystals are monoclinic, space group *Pn*, with $a = 24.235(14)$, $b = 13.892(8)$, $c = 14.141(8)$ Å, $\beta = 91.45(7)°$, and $Z = 2$. The inner core of the cation consists of a triangle of nickel atoms capped above and below by two triply bridging sulphur atoms. Two nickel atoms are co-ordinated by two triphenylphosphine ligands, whereas the third is linked to a triphenylphosphine and to one water molecule. The mean value of the nickel–nickel bond distances, 2.95(5) Å, seems to exclude any direct metal–metal interaction; the geometry may be therefore described as three square-planar nickel(II) moieties sharing two triply bridging sulphur ligands.

Recently we have shown that hydrogen sulphide reacts with bivalent transition-metal ions in the presence of an excess of PMe_3 or PEt_3, to yield metal–sulphur clusters.[1] In the case of nickel and palladium, the propensity of unsubstituted sulphur atoms to co-ordinate three metal centres[2] and the high stability of d^8 square-planar complexes favour the formation of the trinuclear cations $[M_3(\mu_3\text{-}S)_2(PR_3)_6]^{2+}$.[3] Indeed in these compounds the three bivalent atoms, due to the absence of significant metal–metal interactions, display a square-planar co-ordination (I).



(I)

Now we have found that hydrogen sulphide reacts with $[Ni(H_2O)_6]^{2+}$ and an excess of PPh_3 to form the complex cation $[Ni_3(\mu_3\text{-}S)_2(H_2O)(PPh_3)_5]^{2+}$. In this complex one of the three metal centres is bound to a water molecule in the place of a triphenylphosphine, resulting in an asymmetric trinuclear unit. The *X*-ray crystal structure of $[Ni_3(\mu_3\text{-}S)_2(H_2O)(PPh_3)_5][PF_6]_2$ has been carried out in order to investigate the geometric changes in the cluster structure and possibly to understand the reasons for the formation of such an asymmetric structure.

Experimental

The magnetic, conductometric, and i.r. measurements were carried out as described previously.[4] The ^1H and ^{31}P n.m.r. spectra were recorded on a Varian CFT20 spectrometer equipped with ^1H and ^{31}P probes.

Preparation of $[Ni_3(\mu_3\text{-}S)_2(H_2O)(PPh_3)_5][BF_4]_2$ (1).—Triphenylphosphine (7.86 g, 30 mmol) dissolved in methylene chloride (30 cm³) was added to a solution of $[Ni(H_2O)_6][BF_4]_2$ (3.40 g, 10 mmol) in absolute ethanol (30 cm³). Upon bubbling H_2S through the solution for *ca.* 5 min, at room temperature, the colour of the solution turned from green to deep brown. By evaporation of the solvent in air, at room temperature, red-brown crystals precipitated together with colourless crystals. The precipitate was filtered off and washed with benzene until all the colourless crystals had dissolved. Then the brown crystals were washed with light petroleum and dried under vacuum at 80 °C. The complex was recrystallized from methylene chloride–benzene, yield 3.95 g (68% based on nickel tetrafluoroborate) (Found: C, 61.85; H, 4.45; Ni, 9.75; P, 9.15; S, 3.60. Calc. for $C_{90}H_{77}B_2F_8Ni_3OP_5S_2$: C, 62.0; H, 4.45; Ni, 10.1; P, 8.90; S, 3.70%).

The colourless crystals obtained by evaporation of the benzene washing solution were identified as triphenylphosphine sulphide, their i.r. spectrum being identical to that of an authentic sample.

Preparation of $[Ni_3(\mu_3\text{-}S)_2(H_2O)(PPh_3)_5][PF_6]_2$ (2).—This complex was prepared since the crystals of the analogous tetrafluoroborate were not suitable for *X*-ray studies. A solution of the tetrafluoroborate complex in CH_2Cl_2 was added to an equimolar solution of $NBu^n{}_4PF_6$ in absolute ethanol followed by evaporation in air (Found: C, 57.4; H, 4.30. Calc. for $C_{90}H_{77}F_{12}Ni_3OP_7S_2$: C, 58.15; H, 4.15%).

Crystallography.—Crystal data. $C_{90}H_{77}F_{12}Ni_3OP_7S_2$, $M = 1\,859.67$, monoclinic, $a = 24.235(14)$, $b = 13.892(8)$, $c = 14.141(8)$ Å, $\beta = 91.45(7)°$, $U = 4\,759.4$ Å³, space group *Pn* (non-standard setting of *Pc*, no. 7), $Z = 2$, $D_c = 1.297$ g cm⁻³, $F(000) = 1\,908$, Mo-K_α radiation, $\lambda = 0.7107$ Å, μ(Mo-K_α) = 8.11 cm⁻¹.

A red-brown irregularly shaped crystal of dimensions *ca.* 0.05 × 0.35 × 0.40 mm was mounted on a Philips PW 1100 automatic computer-controlled diffractometer. Cell constants were determined by least-squares refinement of the setting angles of 20 carefully centred reflections. Intensity data were

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* 1-Aqua-di-μ_3-sulphido-1,2,2,3,3-pentakis(triphenylphosphine)-*cyclo*-trinickel(II) bis(hexafluorophosphate).

Supplementary data available (No. SUP 56279, 5 pp.): thermal parameters. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1985, Issue 1, pp. xvii—xix. Structure factors are available from the editorial office.

Table 1. Positional parameters (× 10^4) for complex (**2**)

Atom	*x*	*y*	*z*
Ni(1)	0	1 148(5)	−946(3)
Ni(2)	665(3)	−390(5)	947(6)
Ni(3)	958(4)	145(4)	390(11)
S(1)	199(6)	−350(11)	−317(11)
S(2)	863(6)	985(11)	458(11)
P(1)	−871(6)	921(10)	−94(14)
P(2)	39(8)	2 797(12)	−1 185(11)
P(3)	564(6)	−1 967(11)	−2 271(10)
P(4)	1 080(6)	39(11)	2 372(11)
P(5)	958(7)	−674(11)	6 324(13)
P(6)	8 158(8)	398(14)	5 146(18)
P(7)	1 975(11)	4 275(16)	5 578(20)
F(1)	7 687(11)	588(24)	6 225(24)
F(2)	8 061(14)	−704(15)	7 074(20)
F(3)	8 626(11)	208(25)	7 124(19)
F(4)	7 730(11)	439(26)	5 524(19)
F(5)	8 584(12)	353(26)	6 421(24)
F(6)	8 256(14)	1 499(15)	4 165(25)
F(7)	1 711(21)	4 015(38)	6 126(25)
F(8)	2 238(21)	4 540(38)	5 173(40)
F(9)	1 616(21)	5 205(26)	5 644(36)
F(10)	1 512(18)	3 707(35)	5 117(39)
F(11)	2 332(20)	3 348(26)	4 647(35)
F(12)	2 436(19)	4 845(36)	1 230(25)
O	1 721(15)	623(27)	56(23)
C(11)	−1 435(13)	1 703(20)	−780(23)
C(21)	−1 741(13)	1 548(20)	−1 116(23)
C(31)	−2 107(13)	2 252(20)	−618(23)
C(41)	−2 166(13)	3 111(20)	217(23)
C(51)	−1 860(13)	3 266(20)	554(23)
C(61)	−1 495(13)	2 562(20)	1 737(22)
C(12)	−938(10)	1 004(21)	2 286(22)
C(22)	−465(10)	1 201(21)	3 247(22)
C(32)	−510(10)	1 408(21)	3 658(22)
C(42)	−1 027(10)	1 417(21)	3 109(22)
C(52)	−1 499(10)	1 220(21)	2 148(22)
C(62)	−1 455(10)	1 013(21)	161(23)
C(13)	−1 140(13)	−284(23)	−799(23)
C(23)	−1 141(13)	−518(23)	−1 118(23)
C(33)	−1 398(13)	−1 360(23)	−478(23)
C(43)	−1 654(13)	−1 967(23)	482(23)
C(53)	−1 653(13)	−1 733(23)	801(23)
C(63)	−1 396(13)	−891(23)	1 089(31)
C(14)	148(16)	3 218(26)	1 560(31)
C(24)	642(16)	2 981(26)	2 506(31)
C(34)	725(16)	3 240(26)	2 980(31)
C(44)	315(16)	3 736(26)	2 509(31)
C(54)	−179(16)	3 972(26)	1 563(31)
C(64)	−262(16)	3 714(26)	−760(21)
C(15)	613(16)	3 357(27)	−401(21)
C(25)	963(16)	4 073(27)	−990(21)
C(35)	1 339(16)	4 520(27)	−1 938(21)
C(45)	1 364(16)	4 251(27)	−2 298(21)
C(55)	1 014(16)	3 535(27)	−1 708(21)
C(65)	638(16)	3 088(27)	−696(27)
C(16)	−497(16)	3 487(23)	−1 429(27)
C(26)	−807(16)	3 064(23)	−1 957(27)
C(36)	−1 185(16)	3 615(23)	
C(46)	−1 252(16)	4 590(23)	−1 752(27)
C(56)	−941(16)	5 013(23)	−1 019(27)
C(66)	−564(16)	4 462(23)	−491(27)
C(17)	70(14)	−2 363(20)	−2 111(24)
C(27)	−221(14)	−1 644(20)	−2 599(24)
C(37)	−603(14)	−1 891(20)	−3 312(24)
C(47)	−694(14)	−2 857(20)	−3 538(24)
C(57)	−403(14)	−3 575(20)	−3 050(24)
C(67)	−21(14)	−3 328(20)	−2 336(24)
C(18)	360(12)	−2 723(27)	−158(28)
C(28)	697(12)	−3 343(27)	375(28)
C(38)	476(12)	−3 879(27)	1 108(28)
C(48)	−83(12)	−3 793(27)	1 310(28)
C(58)	−420(12)	−3 172(27)	777(28)
C(68)	−198(12)	−2 637(27)	43(28)
C(19)	1 233(18)	−2 466(25)	−1 407(24)
C(29)	1 654(18)	−2 140(25)	−796(24)
C(39)	2 194(18)	−2 457(25)	−910(24)
C(49)	2 314(18)	−3 100(25)	−1 635(24)
C(59)	1 893(18)	−3 426(25)	−2 245(24)
C(69)	1 353(18)	−3 109(25)	−2 132(24)
C(110)	625(11)	771(24)	−2 998(24)
C(210)	763(11)	1 102(24)	−3 894(24)
C(310)	375(11)	1 609(24)	−4 444(24)
C(410)	−149(11)	1 786(24)	−4 099(24)
C(510)	−287(11)	1 456(24)	−3 204(24)
C(610)	100(11)	948(24)	−2 654(24)
C(111)	1 309(12)	−825(24)	−3 120(23)
C(211)	1 863(12)	−1 078(24)	−3 196(23)
C(311)	2 017(12)	−1 773(24)	−3 851(23)
C(411)	1 617(12)	−2 215(24)	−4 429(23)
C(511)	1 063(12)	−1 962(24)	−4 353(23)
C(611)	909(12)	−1 267(24)	−3 698(23)
C(112)	1 701(13)	739(19)	−2 054(20)
C(212)	2 081(13)	416(19)	−1 367(20)
C(312)	2 575(13)	912(19)	−1 209(20)
C(412)	2 690(13)	1 732(19)	−1 739(20)
C(512)	2 310(13)	2 056(19)	−2 426(20)
C(612)	1 816(13)	1 559(19)	−2 583(20)
C(113)	1 311(14)	−1 868(31)	2 361(25)
C(213)	1 155(14)	−2 604(31)	2 970(25)
C(313)	1 428(14)	−3 488(31)	2 955(25)
C(413)	1 857(14)	−3 636(31)	2 331(25)
C(513)	2 013(14)	−2 900(31)	1 722(25)
C(613)	1 740(14)	−2 016(31)	1 737(25)
C(114)	320(14)	−868(22)	2 942(18)
C(214)	−93(14)	−1 393(22)	2 469(18)
C(314)	−581(14)	−1 614(22)	2 925(18)
C(414)	−655(14)	−1 310(22)	3 854(18)
C(514)	−242(14)	−786(22)	4 326(18)
C(614)	246(14)	−565(22)	3 870(18)
C(115)	1 381(12)	8(18)	3 240(22)
C(215)	1 806(12)	−384(18)	3 799(22)
C(315)	2 097(12)	195(18)	4 446(22)
C(415)	1 961(12)	1 166(18)	4 534(22)
C(515)	1 535(12)	1 558(18)	3 974(22)
C(615)	1 245(12)	979(18)	3 327(22)

collected using the ω—2θ scan technique within 2θ = 40°. The scan speed was 0.05° s^{-1} and the scan width was calculated according to the formula $A + B\tan\theta$, where $A = 0.74°$ 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 reflections measured every 2 h were used to rescale the observed intensities which at the end of the data collection showed a decay of *ca.* 25%. The intensities were assigned standard deviations $\sigma(I)$ calculated by using a value of 0.03 for the instability factor *p*.[5] Of the total 4 900 reflections, 1 919 were considered observed with $I \geqslant 3\sigma(I)$. The intensities were corrected for Lorentz-polarization and for absorption effects.[6]

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 programs.[7] Neutral atom scattering factors were taken from ref. 8 for the non-hydrogen atoms and from ref. 9 for hydrogen atoms. Both the $\Delta f'$ and $\Delta f''$ components

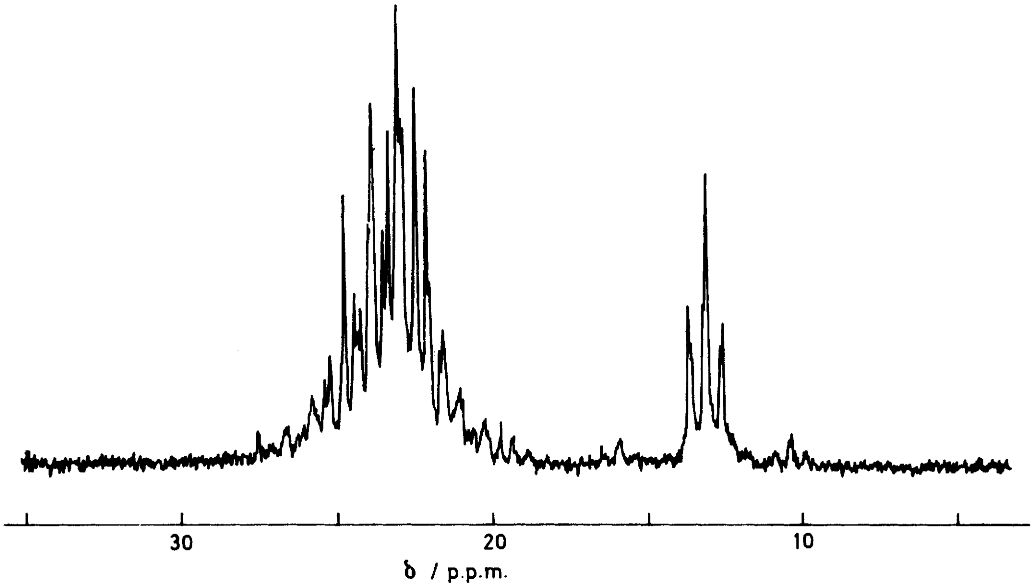

Figure 1. $^{31}P-\{^1H\}$ N.m.r. spectrum of complex (**1**) in CH_2Cl_2 (positive chemical shifts are downfield from the H_3PO_4 standard)

of anomalous dispersion were included for all non-hydrogen atoms.[10] 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 heavy-atom method was used to determine the positions of the three nickel atoms. Successive Fourier syntheses showed all the non-hydrogen atoms. Full-matrix least-squares refinements were carried out, assigning anisotropic thermal parameters to the nickel, sulphur, and phosphorus atoms. During the refinement the phenyl rings were treated as rigid bodies of D_{6h} symmetry. The hydrogen atoms were introduced in their calculated positions, but not refined. A final Fourier difference synthesis showed no particular features except some residual electron density in the region of the PF_6 anions. Indeed the two PF_6^- appeared highly disordered and rigid-group refinement was used. The final values of the discrepancy indices R and R' were 0.094 and 0.091 respectively. Final positional parameters are reported in Table 1.

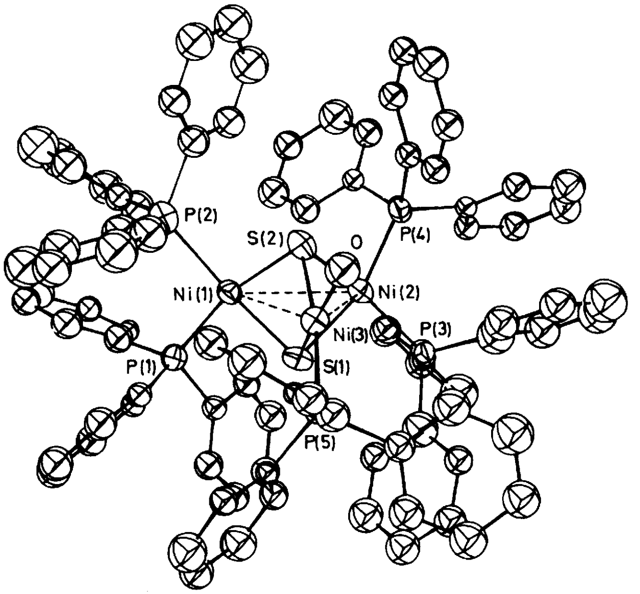

Figure 2. Perspective view of the complex $[Ni_3(\mu-S)_2(H_2O)(PPh_3)_5]^{2+}$. ORTEP drawing with 30% probability ellipsoids

Results and Discussion

Hydrogen sulphide reacts rapidly, at room temperature, with $[Ni(H_2O)_6][BF_4]_2$ in the presence of an excess of PPh_3 (molar ratio 1:3) to form the diamagnetic complex $[Ni_3(\mu_3-S)_2(H_2O)(PPh_3)_5][BF_4]_2$ (**1**). The corresponding hexafluorophosphate derivative (**2**) can easily be prepared by a simple methathetical reaction of (**1**) with $NBu^n_4PF_6$. The complex is moderately air stable and soluble in polar organic solvents such as methylene chloride, tetrahydrofuran, nitroethane, and acetonitrile. The above formulation, which is indicated by elemental analysis, is supported by the following data: (*i*) electrical conductance measurements show that the complex behaves as a 1:2 electrolyte in nitroethane solution; (*ii*) the i.r. spectrum shows a broad absorption centred at 3 570m cm^{-1} and a band at 1 630s cm^{-1} which must be attributed to the O–H stretching and to the H–O–H bending vibrations respectively of the H_2O ligand; (*iii*) the $^{31}P-\{^1H\}$ n.m.r. spectrum (Figure 1) is not first order, indicating the magnetic non-equivalence of the phosphine phosphorus atoms;* the ^1H n.m.r. spectrum shows a multiplet centred at δ 7.33 p.p.m. due to the C_6H_5 hydrogens and a broad singlet at 1.60 p.p.m.† which must be attributed to the hydrogens of co-ordinated water. Finally an *X*-ray structure determination of complex (**2**) has confirmed that the molecular structure consists of discrete cations $[Ni_3(\mu_3-S)_2(H_2O)(PPh_3)_5]^{2+}$ and PF_6^- anions. Figure 2 shows a perspective view of the complex cation, selected bond distances and angles being reported 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 atoms, which complete a trigonal bipyramid. Each metal atom, besides the two sulphur atoms, is linked in the appropriate NiS_2 plane to two other ligands: Ni(1) and Ni(2) to two triphenylphosphine ligands, Ni(3) to a triphenylphosphine group and to the oxygen atom of a water molecule. The average

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* A similar pattern was previously observed in the ^{31}P n.m.r. spectrum of the asymmetric trinuclear cluster $[Ni_3(\mu_3-S)_2(SH)(PEt_3)_5]BPh_4$.[11]

† Peak positions are relative to $SiMe_4$ with downfield values reported as positive.

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

Ni(1)···Ni(2)	3.01(1)	Ni(2)–S(2)	2.16(2)
Ni(1)···Ni(3)	2.99(1)	Ni(2)–P(3)	2.23(2)
Ni(2)···Ni(3)	2.85(1)	Ni(2)–P(4)	2.23(2)
Ni(1)–S(1)	2.20(2)	Ni(3)–S(1)	2.10(2)
Ni(1)–S(2)	2.16(1)	Ni(3)–S(2)	2.14(2)
Ni(1)–P(1)	2.25(2)	Ni(3)–P(5)	2.31(2)
Ni(1)–P(2)	2.30(2)	Ni(3)–O	2.00(4)
Ni(2)–S(1)	2.23(2)	S(1)···S(2)	2.67(2)

Ni(2)–Ni(1)–Ni(3)	56.7(2)	P(3)–Ni(2)–P(4)	100.7(6)
Ni(1)–Ni(2)–Ni(3)	61.4(2)	S(1)–Ni(3)–S(2)	77.9(6)
Ni(1)–Ni(3)–Ni(2)	61.9(2)	S(1)–Ni(3)–P(5)	98.4(6)
S(1)–Ni(1)–S(2)	75.3(6)	S(1)–Ni(3)–O	169.5(12)
S(1)–Ni(1)–P(1)	89.8(6)	S(2)–Ni(3)–P(5)	172.8(7)
S(1)–Ni(1)–P(2)	161.3(6)	S(2)–Ni(3)–O	93.8(11)
S(2)–Ni(1)–P(1)	165.1(6)	P(5)–Ni(3)–O	90.6(12)
S(2)–Ni(1)–P(2)	92.9(6)	Ni(1)–S(1)–Ni(2)	85.6(6)
P(1)–Ni(1)–P(2)	101.4(6)	Ni(1)–S(1)–Ni(3)	88.2(6)
S(1)–Ni(2)–S(2)	74.9(6)	Ni(2)–S(1)–Ni(3)	82.4(6)
S(1)–Ni(2)–P(3)	95.6(6)	Ni(1)–S(2)–Ni(2)	88.4(6)
S(1)–Ni(2)–P(4)	162.9(6)	Ni(1)–S(2)–Ni(3)	88.2(6)
S(2)–Ni(2)–P(3)	162.9(6)	Ni(2)–S(2)–Ni(3)	83.1(6)
S(2)–Ni(2)–P(4)	90.6(6)		

Ni–Ni bond distance [2.95(5) Å] is only slightly longer than the corresponding values reported for the isostructural cations $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_6]^{2+}$ [2.91(2) Å][3a] and $[Ni_3(\mu_3\text{-}S)_2(SH)(PEt_3)_5]^{+}$ [2.93(5) Å].[11] However, one Ni–Ni bond is significantly shorter than the other two. A similar asymmetric arrangement has also been found in $[Ni_3(\mu_3\text{-}S)_2(SH)(PEt_3)_5]^{+}$ [11] and $[Rh_3(\mu_3\text{-}E)_2(CO)_6]^{-}$ (E = S or Se).[12] Indeed, as pointed out earlier,[3a] these compounds may be considered to be formed by three square-planar nickel(II) moieties sharing the bridging ligands: for this reason the M–M distances depend on the bulkiness of the bridging atom (E = S or Se) [1c] and on the steric requirements of the terminal ligands.[11] In this context an examination of the contact distances shows some crowding of the 15 phenyl rings around the inner core. This fact seems to be responsible also for not obtaining the species with six phosphines, when the bulky triphenylphosphine ligand is used in the place of triethylphosphine.

Taking into account the large standard deviations, the Ni–S and Ni–P bond distances appear to be normal. Moreover it is noteworthy that the Ni–S bond *trans* to the water molecule is significantly shorter than the others. On the other hand the Ni–O distance is slightly elongated with respect to the sum of covalent radii (1.88 Å).

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