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Transition-Metal Complexes with Sulfur Atoms as Ligands. 6.[1] Synthesis, Properties, and Structure of the Nickel Chalcogenide Complexes $[Ni_3(\mu_3\text{-}X)_2(PR_3)_6]^{2+}$ (R = Me, X = S; R = Et, X = S, Se) and $[Ni_9(\mu_4\text{-}S)_3(\mu_3\text{-}S)_6(PEt_3)_6]^{2+}$

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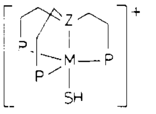
By reaction of hydrogen sulfide or hydrogen selenide with nickel(II) aquo ions and trimethyl- or triethylphosphine, the polynuclear diamagnetic sulfides $[Ni_3(\mu_3\text{-}X)_2(PR_3)_6]Y_2$ (R = Me, Y = ClO_4, X = S (**1**); R = Et, Y = BPh_4, X = S (**2**), Se (**3**)) and $[Ni_9(\mu_4\text{-}S)_3(\mu_3\text{-}S)_6(PEt_3)_6](BPh_4)_2$ (**4**) have been synthesized. The molecular structure of **3** and **4** has been established by single-crystal X-ray diffraction methods. Crystal data: **3**, space group $P2_1/n$, a = 29.466 (9) Å, b = 21.580 (8) Å, c = 13.748 (4) Å, β = 95.35 (5)°, Z = 4; **4**, space group $P2_1/a$, a = 19.784 (5) Å, b = 34.139 (9) Å, c = 14.595 (4) Å, β = 92.47 (5)°, Z = 4. Both structures were solved by the heavy-atom method and refined to the conventional R factor of 0.087 for **3** and 0.068 for **4** on the basis of 1874 and 4837 observed reflections, respectively. The inner core of the trinuclear complex cation consists of a triangle of nickel atoms capped above and below by two triply bridging selenium atoms forming an almost regular trigonal bipyramid. Furthermore, each metal atom is coordinated by two phosphorus atoms lying in the appropriate $NiSe_2$ plane. The value of the average Ni–Ni distance of 3.16 (2) Å seems to exclude a significant direct metal to metal interaction so that the overall geometry may be described as three d^8 square-planar $NiSe_2P_2$ moieties sharing two bridging ligands. The enneanuclear cation is built up of a cofacial-bioctahedral cluster of metal atoms held together by triply and quadruply bridging sulfur ligands. Furthermore, each metal atom belonging to the two octahedral faces parallel to the shared one is terminally bonded to a triethylphosphine group. The values of the Ni–Ni distances ranging from 2.953 (4) to 2.678 (4) Å indicate that only weak direct metal–metal interactions are operative and that the main interactions holding the cluster together are those between the nickel and sulfur species. The fractional formal oxidation number of the nickel atoms as well as the high symmetry of the metal framework, idealized D_{3h}, suggests a delocalized electronic structure. The lack of two electrons with respect to the hypothetic uncharged nickel(II) species (70 valence electrons vs. 72) appears to be essential in the stabilization of the cluster cation.

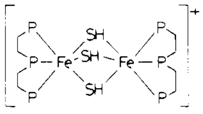
Introduction

Until a few years ago, soluble metal complexes with unsubstituted sulfur as ligand were comparatively rare; they tend to revert to binary sulfides.[2] However, an increasing interest in these compounds has been stimulated by studies on functional models of metal–sulfur redox proteins[3] and in general by synthetic, structural, and theoretical[4] or catalytic[5] research in the field of organometallic cluster chemistry.

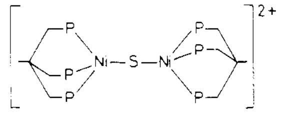
With the aim to prepare transition-metal complexes containing unsubstituted sulfur atoms as ligands, we have been systematically investigating the reactions between hydrogen sulfide and iron, cobalt, and nickel salts in the presence of tertiary phosphines or closely related ligands. When tripod tetradentate phosphines are used, only monomeric trigonal-bypiramidal mercapto complexes $[LM(SH)]^+$ (a)[6] are obtained. On the other hand, binuclear complexes containing SH (b),[7] S (c[8] and d[1]), or S_2 (e)[9] bridging groups can be isolated with tridentate phosphines. It is evident that the geometry of the polydentate phosphine ligands is very important in determining the geometry and the nuclearity of the derivative species. Therefore, it seemed of interest to carry out these reactions in the presence of simple mono(tertiary phosphines) so that the assembly of the complex species was spontaneous or was scarcely affected by the steric requirements of the ancillary ligands. Thus by reaction of H_2S (or H_2Se) with $[Ni(H_2O)_6]^{2+}$, in the presence of an excess of mono(tertiary phosphines), we succeeded in isolating the trinuclear species $[Ni_3(\mu_3\text{-}X)_2(PR_3)_6]Y_2$ (R = Me, Y = ClO_4, X = S (**1**); R = Et, Y = BPh_4, X = S (**2**), Se (**3**)) and the novel enneanuclear cluster $[Ni_9(\mu_4\text{-}S)_3(\mu_3\text{-}S)_6(PEt_3)_6](BPh_4)_2$ (**4**).



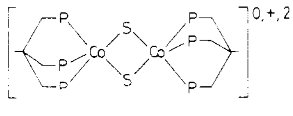
(a) Z = N, P M = Fe, Co, Ni



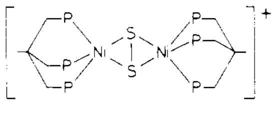
(b)



(c)



(d)



(e)

All of the complexes have been characterized by appropriate physical methods; the complete X-ray structural analyses of the complexes $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_6](BPh_4)_2$ (**2**) and $[Ni_9(\mu_4\text{-}S)_3(\mu_3\text{-}S)_6(PEt_3)_6](BPh_4)_2$ (**4**) have been carried out. The X-ray structure determination of **2** gave poor results owing to the quality of the data, consisting of low-angle and low-intensity reflections. We have thus carried out the molecular structure determination of the corresponding selenium derivative **3**. Because the two compounds are isostructural, we

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report the crystallographic results of the selenium derivative in detail. However, only the main features of the sulfur derivative will be discussed here.

Preliminary reports of this work have been published.[10]

Other high-nuclearity transition-metal sulfur clusters have recently been prepared both by analogous reactions, $[Fe_6(\mu_3\text{-}S)_8(PEt_3)_6]^{2+}$[11] and $[Co_6(\mu_3\text{-}S)_8(PEt_3)_6]^+$,[12] or by different means, $Co_6(\mu_3\text{-}S)_8(PEt_3)_6$,[13] $Co_6(\mu_3\text{-}S)_8(CO)_6$,[14] $[Co_8(\mu_4\text{-}S)_6(SPh)_8]^{4-}$,[3b] and $[Fe_6S_9(S\text{-}t\text{-}Bu)_2]^{4-}$;[3a] it thus seems that a new metal–sulfur cluster chemistry is rising.

Experimental Section

The complexes described in this paper all appear to be air stable. The reactions were nevertheless carried out, initially, under a nitrogen atmosphere, in order to prevent oxidation of the phosphines and especially to protect the operators from the hazards associated with the use of PMe_3, PEt_3, H_2S, and H_2Se. Trimethylphosphine and triethylphosphine were obtained from Strem Chemical Co. ^1H-decoupled ^{31}P NMR spectra were carried out by using a Varian CFT-20 spectrometer equipped with a ^{31}P probe. All reactions were carried out at room temperature.

Synthesis of the Complexes. $[Ni_3(\mu_3\text{-}S)_2(PMe_3)_6](ClO_4)_2$. A solution of PMe_3 (0.46 g, 6 mmol) in 50 mL of methylene chloride was added to a solution of $[Ni(H_2O)_6](ClO_4)_2$ (0.73 g, 2 mmol) in 10 mL of ethanol. Hydrogen sulfide was bubbled for ca 3 min through the above mixture, which turned dark red. After filtration 25 mL of ethanol was added and red crystals precipitated (0.45 g, yield 76% with respect to the starting nickel perchlorate). ^{31}P NMR (CD_2Cl_2): δ 13.87 s (positive shifts are upfield to H_3PO_4). Anal. Calcd for $C_{18}H_{54}Cl_2O_8Ni_3P_6S_2$: C, 24.14; H, 6.08; Ni, 19.66; P, 20.75; S, 7.16. Found: C, 23.89; H, 6.37; Ni, 19.12; P, 21.23; S, 7.01.

$[Ni_9(\mu_4\text{-}S)_3(\mu_3\text{-}S)_6(PEt_3)_6](BPh_4)_2$. A solution of PEt_3 (0.70 g, 6 mmol) in 50 mL of methylene chloride was added to a solution of $[Ni(H_2O)_6](ClO_4)_2$ (0.73 g, 2 mmol) in 20 mL of ethanol. Hydrogen sulfide was bubbled through for ca. 3 min, the suspension filtered, and the resulting black solution evaporated in air. After ca. 5 days black crystals together with a dark powder separated. This material was filtered and dissolved in methylene chloride, the insoluble dark powder being again filtered off. Sodium tetraphenylborate (0.68 g, 2 mmol) in 20 mL of ethanol was added and the resulting black solution evaporated in air. After ca. 2 days black crystals separated, which were recrystallized from methylene chloride–ethanol (0.11 g, yield 23%). ^{31}P NMR (CD_3COCD_3): δ −32.96 s. Anal. Calcd for $C_{84}H_{130}B_2Ni_9P_6S_9$: C, 46.61; H, 6.05; Ni, 24.41; S, 13.33. Found: C, 45.40; H, 5.97; Ni, 23.59; S, 13.68.

$[Ni_3(\mu_3\text{-}S)_2(PEt_3)_6](BPh_4)_2$. Sodium tetraphenylborate (0.68 g, 2 mmol) in 10 mL of ethanol was added to the filtrate from which, in the previous preparation, black crystals and a dark powder were separated. A red compound precipitated, which was recrystallized from methylene chloride–*n*-butanol to yield 0.14 g of red crystals (yield 13%). ^{31}P NMR (CD_3COCD_3): δ −9.17 s. 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.

$[Ni_3(\mu_3\text{-}Se)_2(PEt_3)_6](BPh_4)_2$. A solution of PEt_3 (0.70 g, 6 mmol) in 30 mL of methylene chloride was added to a solution of $[Ni(H_2O)_6](ClO_4)_2$ (0.73 g, 2 mmol) in 20 mL of ethanol. Hydrogen selenide was bubbled through for ca. 5 min, and the resulting red solution concentrated under a stream of nitrogen until red crystals precipitated. They were filtered and dissolved in 50 mL of acetone. Sodium tetraphenylborate (0.68 g, 2 mmol) dissolved in 25 mL of ethanol was added and the solution filtered. After concentration under a stream of nitrogen red crystals precipitated (0.62 g, yield 56%). ^{31}P NMR (CD_3COCD_3): δ −8.55 s. Anal. Calcd for $C_{84}H_{130}B_2Ni_3P_6Se_2$: C, 60.00; H, 7.79; Ni, 10.47; P, 11.05. Found: C, 59.46; H, 7.61; Ni, 9.88; P, 11.24.

Table I. Crystal Data and Data Collection Details

	$[Ni_3(\mu_3\text{-}Se)_2(PEt_3)_6](BPh_4)_2$	$[Ni_9(\mu_4\text{-}S)_3(\mu_3\text{-}S)_6(PEt_3)_6](BPh_4)_2$
mol formula	$C_{84}H_{130}B_2Ni_3P_6Se_2$	$C_{84}H_{130}B_2Ni_9P_6S_9$
mol wt	1681.5	2164.4
a, Å	29.466 (9)	19.784 (5)
b, Å	21.580 (8)	34.139 (9)
c, Å	13.748 (4)	14.595 (4)
β, deg	95.35 (5)	92.47 (5)
d_{calcd}, g cm^{-3}	1.283	1.459
d_{obsd}(by flot), g cm^{-3}	1.27	1.41
V, Å^3	8703.9	9848.4
Z	4	4
space group	$P2_1/n$	$P2_1/a$
abs coeff, μ(Mo Kα), cm^{-1}	16.2	20.1
color	red	black
habit	parallelepiped	parallelepiped
dimens, mm	0.07 × 0.09 × 0.22	0.22 × 0.22 × 0.25
diffractometer	Philips PW 1100	Philips PW 1100
λ(Mo Kα), Å	0.7107	0.7107
monochromator	graphite	graphite
method	ω–2θ scan	ω–2θ scan
scan speed, deg/s	0.04	0.08
scan width, deg	$0.64 + 0.69 \tan \theta$	$0.66 + 0.3 \tan \theta$
bkgd time	half the scan time	half the scan time
stds	3 every 120 min	3 every 120 min
% max dev std	2	3
2θ limits, deg	$5 \leqslant 2\theta \leqslant 40$	$5 \leqslant 2\theta \leqslant 45$
no. of data used ($I \geqslant 3\sigma(I)$)	1874	4837
final no. of variables	332	465

X-ray Data Collection. Crystallographic structural determinations were carried out for three compounds, viz. $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_6](BPh_4)_2$ (**2**), $[Ni_3(\mu_3\text{-}Se)_2(PEt_3)_6](BPh_4)_2$ (**3**), and $[Ni_9(\mu_4\text{-}S)_3(\mu_3\text{-}S)_6](BPh_4)_2$ (**4**). The X-ray study of **3** was performed because the structure determination of **2** owing to the quality of the data, consisting of low-angle and low-intensity reflections, gave poor results.[10a] For this reason and because the two compounds are isostructural, we report here the crystallographic data of **3**. For compound **4** mentioned in the preliminary communication[10b] a new data collection has been carried out.

Diffraction data were collected on a Philips PW1100 automatic diffractometer. Unit cell parameters for compounds **3** and **4** were determined at room temperature from the least-squares refinement of 22 and 23 reflections, respectively. Systematic absences for **3** ($h0l$ for $h + l = 2n + 1$ and $0k0$ for $k = 2n + 1$) and **4** ($h0l$ for $h = 2n + 1$ and $0k0$ for $k = 2n + 1$) indicate the space groups $P2_1/n$ and $P2_1/a$, respectively. Details of crystal data and data collection for the two compounds are given in Table I. After correction for background the intensities were assigned standard deviations calculated by using for the instability factor k the value of 0.03.[15] Intensity data were corrected for Lorentz and polarization effects and for absorption.

Solution and Refinement of the Structures. All the calculation were carried out on a SEL 32/70 computer by using the SHELX 76[16] and ORTEP[17] programs. Atomic scattering factors of the appropriate neutral atoms were taken from ref 18 for the non-hydrogen atoms and from ref 19 for hydrogen atoms. Both the $\Delta f'$ and $\Delta f''$ components of anomalous dispersion were included for all non-hydrogen atoms.[20]

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Table II. Atomic Parameters for $[Ni_3(\mu_3\text{-}Se)_2(PEt_3)_6](BPh_4)_2$[a]

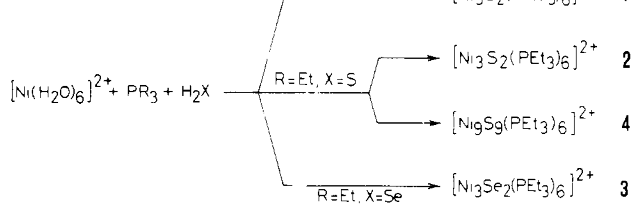
atom	*x*	*y*	*z*	atom	*x*	*y*	*z*
Se1	3793 (2)	3158 (3)	−2119 (4)	C39	459 (1)	49 (1)	374 (2)
Se2	3728 (2)	1903 (3)	−2815 (4)	C40	431 (1)	52 (1)	287 (2)
Ni1	3312 (2)	2388 (3)	−1670 (5)	C41	447 (1)	78 (1)	204 (2)
Ni2	3587 (2)	2821 (3)	−3687 (5)	C42	492 (1)	100 (1)	208 (2)
Ni3	4364 (2)	2414 (4)	−2039 (5)	C43	566 (1)	201 (2)	336 (2)
P1	2959 (5)	1536 (7)	−1234 (12)	C44	526 (1)	232 (2)	306 (2)
P2	2958 (5)	3110 (7)	−859 (11)	C45	520 (1)	294 (2)	333 (2)
P3	3320 (5)	2263 (7)	−5010 (12)	C46	555 (1)	324 (2)	390 (2)
P4	3609 (5)	3763 (7)	−4341 (12)	C47	595 (1)	293 (2)	420 (2)
P5	4788 (5)	1576 (8)	−2293 (13)	C48	601 (1)	231 (2)	393 (2)
P6	4845 (5)	2993 (8)	−1051 (15)	C49	604 (1)	86 (2)	386 (2)
C1	316 (2)	83 (3)	−185 (4)	C50	628 (1)	36 (2)	352 (2)
C2	292 (2)	18 (2)	−155 (4)	C51	653 (1)	−2 (2)	418 (2)
C3	227 (2)	147 (3)	−141 (4)	C52	655 (1)	10 (2)	518 (2)
C4	213 (5)	188 (6)	−183 (9)	C53	631 (1)	60 (2)	552 (2)
C5	301 (2)	135 (3)	10 (5)	C54	606 (1)	98 (2)	486 (2)
C6	348 (2)	131 (3)	50 (4)	C55	593 (1)	133 (2)	199 (3)
C7	247 (2)	289 (2)	−15 (4)	C56	616 (1)	186 (2)	172 (3)
C8	224 (2)	348 (2)	28 (4)	C57	635 (1)	188 (2)	82 (3)
C9	335 (2)	359 (2)	−1 (4)	C58	631 (1)	137 (2)	20 (3)
C10	348 (2)	318 (3)	87 (5)	C59	607 (1)	84 (2)	47 (3)
C11	270 (1)	369 (2)	−174 (3)	C60	589 (1)	82 (2)	136 (3)
C12	229 (1)	345 (2)	−240 (3)	C61	211 (1)	13 (2)	261 (2)
C13	284 (2)	169 (2)	−469 (3)	C62	210 (1)	−52 (2)	253 (2)
C14	242 (2)	208 (2)	−438 (3)	C63	248 (1)	−83 (2)	228 (2)
C15	376 (2)	169 (2)	−547 (3)	C64	288 (1)	−51 (2)	212 (2)
C16	411 (2)	209 (3)	−608 (4)	C65	289 (1)	14 (2)	220 (2)
C17	305 (2)	266 (3)	−605 (4)	C66	250 (1)	46 (2)	245 (2)
C18	288 (2)	217 (3)	−700 (4)	C67	172 (1)	43 (1)	424 (3)
C19	407 (2)	381 (2)	−519 (3)	C68	214 (1)	30 (1)	477 (3)
C20	452 (2)	368 (3)	−465 (4)	C69	216 (1)	25 (1)	579 (3)
C21	378 (2)	436 (2)	−349 (4)	C70	176 (1)	32 (1)	627 (3)
C22	386 (2)	501 (3)	−390 (4)	C71	135 (1)	45 (1)	573 (3)
C23	311 (2)	410 (3)	−502 (5)	C72	133 (1)	51 (1)	472 (3)
C24	267 (2)	398 (3)	−457 (4)	C73	169 (1)	125 (2)	278 (2)
C25	470 (2)	124 (3)	−360 (5)	C74	161 (1)	171 (2)	347 (2)
C26	493 (3)	182 (4)	−416 (6)	C75	159 (1)	233 (2)	320 (2)
C27	466 (3)	88 (4)	−149 (6)	C76	165 (1)	250 (2)	225 (2)
C28	417 (3)	45 (5)	−164 (7)	C77	173 (1)	205 (2)	156 (2)
C29	539 (3)	161 (4)	−222 (5)	C78	175 (1)	143 (2)	182 (2)
C30	544 (3)	153 (5)	−147 (6)	C79	117 (1)	20 (1)	254 (3)
C31	466 (2)	384 (3)	−90 (5)	C80	94 (1)	44 (1)	170 (3)
C32	490 (4)	420 (6)	−29 (8)	C81	52 (1)	20 (1)	134 (3)
C33	519 (3)	273 (4)	18 (6)	C82	33 (1)	−29 (1)	183 (3)
C34	472 (3)	257 (4)	59 (6)	C83	56 (1)	−53 (1)	267 (3)
C35	543 (3)	321 (4)	−174 (6)	C84	98 (1)	−29 (1)	303 (3)
C36	540 (3)	328 (4)	−298 (6)	B1	573 (2)	127 (3)	303 (4)
C37	520 (1)	97 (1)	295 (2)	B2	168 (2)	47 (2)	299 (4)
C38	503 (1)	71 (1)	378 (2)				

[a] Coordinates of Se, Ni, and P multiplied by 10^4, the remaining by 10^3.

The refinement was based on F_o, the function minimized being $\sum w(|F_o| - |F_c|)^2$, where $w = 1/\sigma^2(F_o)$. The structures of both compounds were solved by the heavy-atom method, and in the case of **4** the determination required many efforts. A series of Fourier maps was necessary in order to locate the atoms of the ethylenic chains, which in both compounds appeared as diffuse electron density regions. Owing to the difficulty of locating distinct positions, no attempt was made to treat the disorder. Refinements were carried out with use of anisotropic thermal parameters for the nickel, sulfur (or selenium), and phosphorus atoms only. In both compounds the eight phenyl rings of the tetraphenylborate anions were treated as rigid groups. Hydrogen atoms were not included in the calculations. Refinements converged at the R and R_w factors of 0.087 and 0.082 for compound **3** and 0.068 and 0.069 for compound **4**. R and R_w factors are defined as $\sum||F_o| - |F_c||/\sum|F_o|$ and $[\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2}$. The final difference Fourier maps showed no peak higher than 0.70 e Å^{-3} in the region of the ethylenic chains. Final positional and thermal parameters are reported in Tables II–V (Tables IV and V are supplementary material).

Results and Discussion

By the bubbling of hydrogen sulfide through methylene chloride–ethanol solutions of $[Ni(H_2O)_6](ClO_4)_2$ and mono(tertiary phosphines) such as PMe_3 and PEt_3 (molar ratio $Ni/PR_3 = 1/3$) the color of the solutions darkens without or with only small precipitation of the binary sulfide NiS:



The trinuclear compound of formula $[Ni_3(\mu_3\text{-}S)_2(PMe_3)_6]$ crystallizes from these solutions. When R = Et, two complexes, which can be separated by exploiting their different solubilities, are simultaneously obtained: the red species $[Ni_3(\mu_3\text{-}S)_2(PEt_3)_6](BPh_4)_2$ and the black unusual species $[Ni_9(\mu_4\text{-}S)_3(\mu_3\text{-}S)_6(PEt_3)_6](BPh_4)_2$. Although the mechanism of these reactions is unknown, we think that the formation of the trinuclear derivatives is a general process, while that of the enneanuclear cluster is a quite peculiar case. In fact

Table III. Atomic Parameters for $[Ni_9(\mu_4\text{-}S)_3(\mu_3\text{-}S)_6(PEt_3)_6](BPh_4)_2$[a]

atom	x	y	z	atom	x	y	z
Ni1	−3746 (1)	3888 (1)	−3737 (2)	C32	−721 (29)	3601 (16)	−4896 (43)
Ni2	−3959 (1)	3767 (1)	−1771 (2)	C33	−1274 (18)	4501 (10)	−4116 (24)
Ni3	−2987 (1)	3271 (1)	−2717 (2)	C34	−653 (18)	4619 (10)	−4831 (25)
Ni4	−3948 (1)	3115 (1)	−4012 (2)	C35	−1759 (25)	4054 (14)	−5452 (34)
Ni5	−4158 (1)	2999 (1)	−2107 (2)	C36	−2291 (15)	4049 (8)	−5987 (19)
Ni6	−4895 (1)	3597 (1)	−3097 (2)	C37	3204 (6)	2958 (4)	517 (10)
Ni7	−2405 (1)	3927 (1)	−3371 (2)	C38	3229 (6)	2578 (4)	162 (10)
Ni8	−2617 (1)	3813 (1)	−1460 (2)	C39	3000 (6)	2505 (4)	−740 (10)
Ni9	−3358 (1)	4413 (1)	−2432 (2)	C40	2746 (6)	2812 (4)	−1287 (10)
S1	−4411 (3)	4186 (2)	−2775 (4)	C41	2721 (6)	3191 (4)	−933 (10)
S2	−3286 (3)	3283 (2)	−1279 (4)	C42	2950 (6)	3264 (4)	−31 (10)
S3	−2979 (3)	3458 (2)	−4166 (4)	C43	3705 (7)	2651 (5)	2120 (9)
S4	−3511 (3)	2705 (2)	−3031 (4)	C44	4364 (7)	2519 (5)	2008 (9)
S5	−4892 (3)	3415 (2)	−1677 (4)	C45	4573 (7)	2160 (5)	2378 (9)
S6	−4587 (3)	3588 (2)	−4506 (4)	C46	4122 (7)	1932 (5)	2861 (9)
S7	−1974 (3)	3516 (2)	−2389 (4)	C47	3464 (7)	2064 (5)	2973 (9)
S8	−3375 (3)	4225 (2)	−1020 (4)	C48	3255 (7)	2423 (5)	2603 (9)
S9	−3053 (3)	4399 (2)	−3848 (4)	C49	2747 (13)	3240 (5)	2123 (11)
P1	−4534 (3)	2508 (2)	−1315 (5)	C50	2109 (13)	3123 (5)	1781 (11)
P2	−3969 (4)	2750 (2)	−5239 (4)	C51	1529 (13)	3266 (5)	2179 (11)
P3	−5960 (3)	3762 (2)	−3303 (5)	C52	1588 (13)	3524 (5)	2919 (11)
P4	−1925 (3)	3889 (2)	−266 (4)	C53	2226 (13)	3641 (5)	3261 (11)
P5	−3483 (4)	5049 (2)	−2250 (5)	C54	2806 (13)	3498 (5)	2863 (11)
P6	−1548 (3)	4024 (2)	−4242 (4)	C55	4088 (8)	3381 (5)	1673 (9)
C1	−5426 (13)	2374 (7)	−1678 (19)	C56	4378 (8)	3507 (5)	869 (9)
C2	−5472 (18)	2276 (10)	−2634 (26)	C57	4950 (8)	3746 (5)	917 (9)
C3	−4695 (16)	2623 (9)	−64 (22)	C58	5233 (8)	3859 (5)	1769 (9)
C4	−4031 (20)	2688 (11)	462 (27)	C59	4944 (8)	3733 (5)	2573 (9)
C5	−4041 (14)	2063 (8)	−1456 (20)	C60	4371 (8)	3494 (5)	2525 (9)
C6	−4296 (15)	1682 (9)	−856 (22)	C61	3563 (7)	−661 (6)	3059 (8)
C7	−3307 (15)	2342 (8)	−5228 (20)	C62	3456 (7)	−1050 (6)	2796 (8)
C8	−2617 (18)	2473 (10)	−5174 (24)	C63	3505 (7)	−1348 (6)	3450 (8)
C9	−3803 (17)	3115 (10)	−6256 (25)	C64	3661 (7)	−1257 (6)	4368 (8)
C10	−3836 (23)	2889 (14)	−6968 (34)	C65	3767 (7)	−868 (6)	4631 (8)
C11	−4708 (19)	2378 (11)	−5258 (25)	C66	3718 (7)	−570 (6)	3977 (8)
C12	−5335 (20)	2613 (11)	−5300 (26)	C67	2689 (9)	−110 (5)	2356 (11)
C13	−6054 (20)	4112 (11)	−4311 (26)	C68	2429 (9)	−56 (5)	3221 (11)
C14	−6782 (26)	4124 (14)	−4590 (34)	C69	1808 (9)	131 (5)	3305 (11)
C15	−6492 (20)	3223 (10)	−3405 (30)	C70	1448 (9)	266 (5)	2524 (11)
C16	−6473 (34)	3263 (17)	−4495 (42)	C71	1708 (9)	213 (5)	1659 (11)
C17	−6353 (22)	3993 (12)	−2290 (31)	C72	2329 (9)	25 (5)	1575 (11)
C18	−6067 (16)	4192 (9)	−1603 (22)	C73	3616 (7)	−447 (4)	1195 (12)
C19	−2308 (12)	3880 (7)	846 (17)	C74	4221 (7)	−358 (4)	782 (12)
C20	−2675 (16)	3506 (9)	1069 (22)	C75	4350 (7)	−513 (4)	−78 (12)
C21	−1200 (12)	3544 (7)	−264 (16)	C76	3875 (7)	−756 (4)	−526 (12)
C22	−703 (13)	3604 (7)	573 (17)	C77	3270 (7)	−845 (4)	−113 (12)
C23	−1588 (12)	4408 (7)	−200 (17)	C78	3141 (7)	−690 (4)	747 (12)
C24	−1179 (15)	4493 (9)	−1098 (21)	C79	4028 (6)	75 (5)	2510 (9)
C25	−3825 (24)	5222 (13)	−1093 (30)	C80	3827 (6)	465 (5)	2414 (9)
C26	−4559 (22)	5048 (12)	−1211 (28)	C81	4294 (6)	766 (5)	2585 (9)
C27	−2722 (20)	5315 (11)	−1872 (30)	C82	4962 (6)	676 (5)	2852 (9)
C28	−2193 (19)	5262 (11)	−2750 (28)	C83	5163 (6)	286 (5)	2948 (9)
C29	−3830 (22)	5340 (12)	−3127 (31)	C84	4696 (6)	−15 (5)	2777 (9)
C30	−4470 (20)	5151 (11)	−3751 (27)	B1	3450 (12)	3066 (7)	1591 (17)
C31	−775 (19)	3710 (11)	−3888 (28)	B2	3499 (15)	−305 (8)	2195 (21)

[a] Coordinates multiplied by 10^4.

analogous trinuclear sulfides of palladium[21] and platinum[22] have been prepared and when one of the reagents that allows the synthesis of the Ni_9 cluster is replaced by a closely related one (i.e. PEt_3 by PMe_3, $[Ni(H_2O)_6]^{2+}$ by $[Pd(CH_3CN)_4]^{2+}$, or H_2S by H_2Se) only the trinuclear sulfide species is obtained.

Use in these reactions of some other mono(tertiary phosphines) such as tricyclohexylphosphine, triisopropylphosphine, and triisobutylphosphine gave only unidentified, intractable materials.

All the complexes isolated are diamagnetic, air stable, and soluble in common polar organic solvents such as methylene chloride, acetone, and nitroethane, in which they behave as 1:2 electrolytes.

The complexes **2** and **4**, when reacted at 50 °C with a solution of hydrogen chloride in tetrahydrofuran, do not evolve hydrogen sulfide. The same complexes do not form adducts by reaction with $(CO)_5Cr(THF)$.

The ^{31}P NMR spectra of the complexes at room temperature exhibit singlets at δ 13.87, −9.17, −8.55, and −32.96 for **1–4**, respectively, which are indicative of six equivalent PR_3 groups in the complex cations.

The molecular structure of **3** consists of discrete $[Ni_3(\mu_3\text{-}Se)_2(PEt_3)_6]^{2+}$ cations and BPh_4^- anions. Figure 1 shows a perspective view of the cation. Selected bond distances and angles are reported in Table VI. The inner core of the cation consists of a triangle of nickel atoms capped above and below by two triply bridging selenium atoms, thus forming an almost

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(21) (a) Ghilardi, C. A.; Midollini, S.; Nuzzi, F.; Orlandini, A. *Transition Met. Chem.* (*Weinheim, Ger.*) **1983**, *8*, 73. (b) Werner, H.; Bertleff, W.; Shubert, U. *Inorg. Chim. Acta* **1980**, *43*, 199.

(22) Chatt, J.; Mingos, D. M. P. *J. Chem. Soc. A* **1970**, 1243.

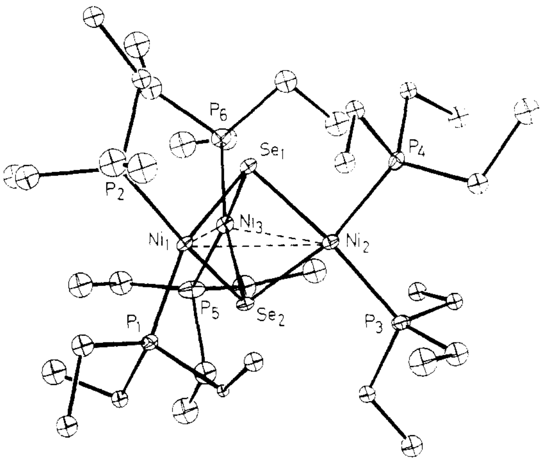

Figure 1. Perspective view of the $[Ni_3(\mu_3\text{-}Se)_2(PEt_3)_6]^{2+}$ with 30% probability ellipsoids. For the sake of clarity the thermal parameters of some carbon atoms have been arbitrarily reduced.

Table VI. Selected Bond Lengths (Å) and Angles (deg) with Estimated Standard Deviations for $[Ni_3(\mu_3\text{-}Se)_2(PEt_3)_6](BPh_4)_2$

Ni1-Ni2	3.11 (1)	Se2-Ni2	2.333 (8)
Ni1-Ni3	3.19 (1)	Se2-Ni3	2.344 (8)
Ni2-Ni3	3.19 (1)	Ni1-P1	2.22 (2)
Se1-Se2	2.873 (7)	Ni1-P2	2.23 (2)
Se1-Ni1	2.304 (8)	Ni2-P3	2.26 (2)
Se1-Ni2	2.302 (9)	Ni2-P4	2.23 (2)
Se1-Ni3	2.319 (8)	Ni3-P5	2.24 (2)
Se2-Ni1	2.331 (9)	Ni3-P6	2.25 (2)
Ni2-Ni1-Ni3	60.9 (2)	P3-Ni2-P4	100.5 (6)
Ni1-Ni2-Ni3	60.8 (2)	Se1-Ni3-Se2	76.1 (2)
Ni1-Ni3-Ni2	58.3 (2)	Se1-Ni3-P5	164.2 (5)
Se1-Ni1-Se2	76.6 (3)	Se1-Ni3-P6	93.3 (5)
Se1-Ni1-P1	169.6 (5)	Se2-Ni3-P5	89.0 (5)
Se1-Ni1-P2	87.6 (5)	Se2-Ni3-P6	165.6 (6)
Se2-Ni1-P1	95.6 (5)	P5-Ni3-P6	102.3 (6)
Se2-Ni1-P2	162.0 (5)	Ni1-Se1-Ni2	84.7 (3)
P1-Ni1-P2	101.0 (6)	Ni1-Se1-Ni3	87.1 (3)
Se1-Ni2-Se2	76.6 (3)	Ni2-Se1-Ni3	87.3 (3)
Se1-Ni2-P3	164.5 (5)	Ni1-Se2-Ni2	83.4 (3)
Se1-Ni2-P4	94.3 (5)	Ni1-Se2-Ni3	85.9 (3)
Se2-Ni2-P3	89.6 (5)	Ni2-Se2-Ni3	86.0 (3)
Se2-Ni2-P4	166.5 (5)		

regular trigonal bipyramid. Each metal atom in addition to the linkages to the selenium atoms is coordinated by two phosphorus atoms of the triethylphosphine ligand lying approximately in the appropriate $NiSe_2$ plane. The $NiSe_2P_2$ fragments are not strictly planar, the deviations of the phosphorus atoms from their $NiSe_2$ plane ranging from 0.21 to 0.38 Å. In the corresponding sulfur derivative **2** the cation has the same geometry;[10a] indeed the replacement of the sulfur with selenium leaves unchanged the geometry of the Ni_3X_2 core. As a matter of fact, the average Ni–X–Ni and X–Ni–X angles are 85.7 and 76.4° for the selenium and 84.9 and 77.4° for the sulfur derivative, respectively. However, owing to the bulkiness of the selenium with respect to the sulfur, the Ni_3X_2 core is expanded, the average[23] Ni–Ni distance going from 2.91 (2) to 3.16 (3) Å and the X–X distance from 2.70 (4) to 2.873 (7) Å. The values of the average Ni–Ni distances and the fact that the X–Ni–X angle remains almost constant are indicative that in these trinuclear compounds there is no significant direct metal–metal interaction. In the isostructural $Ni_3(\mu_3\text{-}S)_2Cp_3$ compound having a Ni–Ni distance of 2.801 (5) Å the existence of a weak metal–metal interaction was assumed.[4c] In the latter compound, owing to the shorter Ni–Ni distance, the X–Ni–X angle, which in **2** and **3** is 77.4 and 76.4°, reaches the value of 83.8°.

Table VII. Selected Bond Lengths (Å) with Estimated Standard Deviations for $[Ni_9(\mu_4\text{-}S)_3(\mu_3\text{-}S)_6(PEt_3)_6](BPh_4)_2$

Ni-Ni

Intralayer Equatorial

Ni1-Ni2	2.948 (4)	Ni2-Ni3	2.948 (4)
Ni1-Ni3	2.953 (4)		

Intralayer Basal

Ni4-Ni5	2.856 (4)	Ni7-Ni8	2.865 (4)
Ni4-Ni6	2.869 (4)	Ni7-Ni9	2.899 (4)
Ni5-Ni6	2.865 (4)	Ni8-Ni9	2.860 (4)

Interlayer

Ni1-Ni4	2.699 (4)	Ni2-Ni8	2.678 (4)
Ni1-Ni6	2.686 (4)	Ni2-Ni9	2.705 (4)
Ni1-Ni7	2.688 (4)	Ni3-Ni4	2.675 (4)
Ni1-Ni9	2.702 (4)	Ni3-Ni5	2.682 (4)
Ni2-Ni5	2.691 (4)	Ni3-Ni7	2.712 (4)
Ni2-Ni6	2.683 (4)	Ni3-Ni8	2.684 (4)

$(\mu_4\text{-}S)\text{-}Ni$

within layers		between layers	
S1-Ni1	2.212 (7)	S1-Ni6	2.265 (6)
S1-Ni2	2.209 (6)	S1-Ni9	2.260 (7)
S2-Ni2	2.222 (7)	S2-Ni5	2.279 (7)
S2-Ni3	2.205 (7)	S2-Ni8	2.264 (7)
S3-Ni1	2.220 (7)	S3-Ni4	2.267 (7)
S3-Ni3	2.210 (7)	S3-Ni7	2.256 (7)

$(\mu_3\text{-}S)\text{-}Ni$

within layers		between layers	
S4-Ni4	2.155 (6)	S4-Ni3	2.231 (7)
S4-Ni5	2.148 (7)		
S5-Ni5	2.145 (7)	S5-Ni2	2.211 (7)
S5-Ni6	2.163 (7)		
S6-Ni4	2.158 (7)	S6-Ni1	2.217 (7)
S6-Ni6	2.171 (7)		
S7-Ni7	2.156 (7)	S7-Ni3	2.206 (7)
S7-Ni8	2.153 (7)		
S8-Ni8	2.172 (7)	S8-Ni2	2.207 (7)
S8-Ni9	2.160 (7)		
S9-Ni7	2.154 (7)	S9-Ni1	2.227 (7)
S9-Ni9	2.178 (7)		

Ni-P

Ni5-P1	2.185 (7)	Ni8-P4	2.185 (7)
Ni4-P2	2.180 (7)	Ni9-P5	2.204 (7)
Ni6-P3	2.188 (7)	Ni7-P6	2.188 (7)

The values of the Ni–Se bond distances, 2.302 (8) –2.344 (8) Å, as well as those for Ni–P 2.22 (2) –2.26 (2) Å, appear to be normal.

An analogous structure must be attributed to the closely related PMe_3 derivative **1**.

The molecular structure of **4** consists of discrete $[Ni_9(\mu_4\text{-}S)_3(\mu_3\text{-}S)_6(PEt_3)_6]^{2+}$ cations and BPh_4^- anions. Figure 2 shows a perspective view of the inner core of the cation. Selected bond distances and angles are presented in Tables VII and VIII. The complex cation has no crystallographically imposed symmetry; however, the inner core may be considered to possess idealized D_{3h} symmetry. The cation is built of a cofacial bioctahedron of nickel atoms; the nine metal atoms are therefore on three parallel planes that are 2.1 Å apart. Moreover, each trinickel layer contains three sulfur atoms each symmetrically bridging a triangular edge so that the three sulfur atoms are at the vertices of a triangle that is coplanar with the nickel triangle and is rotated by ca. 60° with respect to it. The deviations of the sulfur atoms from the trinickel planes are very small, the largest deviation being less than 0.03

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[23] The estimated errors in the means were calculated by using the formual $[\sum_n(d_n - \bar{d})^2/n(n-1)]^{1/2}$.

Table VIII. Selected Bond Angles (deg) with Estimated Standard Deviations for $[Ni_9(\mu_4\text{-}S)_3(\mu_3\text{-}S)_6(PEt_3)_6](BPh_4)_2$

Ni2-Ni1-Ni3	59.9 (1)	Ni1-Ni3-Ni4	57.1 (1)	S5-Ni5-P1	95.9 (3)	S1-Ni9-S8	93.2 (2)
Ni2-Ni1-Ni4	88.9 (1)	Ni1-Ni3-Ni5	89.3 (1)	Ni1-Ni6-Ni2	66.6 (1)	S1-Ni9-S9	94.2 (2)
Ni2-Ni1-Ni6	56.6 (1)	Ni1-Ni3-Ni7	56.5 (1)	Ni1-Ni6-Ni4	58.0 (1)	S1-Ni9-P5	105.0 (3)
Ni2-Ni1-Ni7	89.7 (1)	Ni1-Ni3-Ni8	88.3 (1)	Ni1-Ni6-Ni5	91.1 (1)	S8-Ni8-S9	156.1 (3)
Ni2-Ni1-Ni9	57.0 (1)	Ni2-Ni3-Ni4	89.3 (1)	Ni2-Ni6-Ni4	90.8 (1)	S8-Ni9-P5	99.9 (3)
Ni3-Ni1-Ni4	56.3 (1)	Ni2-Ni3-Ni5	56.9 (1)	Ni2-Ni6-Ni5	57.9 (1)	S9-Ni9-P5	100.0 (3)
Ni3-Ni1-Ni6	88.9 (1)	Ni2-Ni3-Ni7	89.2 (1)	Ni4-Ni6-Ni5	59.7 (1)	Ni1-S1-Ni2	83.6 (2)
Ni3-Ni1-Ni7	57.2 (1)	Ni2-Ni3-Ni8	56.6 (1)	S1-Ni6-S5	94.2 (2)	Ni1-S1-Ni6	73.7 (2)
Ni3-Ni1-Ni9	89.7 (1)	Ni4-Ni3-Ni5	64.4 (1)	S1-Ni6-S6	94.3 (2)	Ni1-S1-Ni9	74.4 (2)
Ni4-Ni1-Ni6	64.4 (1)	Ni4-Ni3-Ni7	102.5 (1)	S1-Ni6-P3	101.4 (3)	Ni2-S1-Ni6	73.7 (2)
Ni4-Ni1-Ni7	102.5 (1)	Ni4-Ni3-Ni8	141.7 (1)	S5-Ni6-S6	156.1 (3)	Ni2-S1-Ni9	74.5 (2)
Ni4-Ni1-Ni9	142.1 (1)	Ni5-Ni3-Ni7	142.1 (1)	S5-Ni6-P3	99.7 (3)	Ni6-S1-Ni9	136.7 (3)
Ni6-Ni1-Ni7	142.4 (1)	Ni5-Ni3-Ni8	103.0 (1)	S6-Ni6-P3	100.5 (3)	Ni2-S2-Ni3	83.5 (2)
Ni6-Ni1-Ni9	102.6 (1)	Ni7-Ni3-Ni8	64.1 (1)	Ni1-Ni7-Ni3	66.3 (1)	Ni2-S2-Ni5	73.4 (2)
Ni7-Ni1-Ni9	65.1 (1)	S2-Ni3-S3	156.8 (2)	Ni1-Ni7-Ni8	90.1 (1)	Ni2-S2-Ni8	73.3 (2)
S1-Ni1-S3	156.1 (2)	S2-Ni3-S4	94.0 (2)	Ni1-Ni7-Ni9	57.7 (1)	Ni3-S2-Ni5	73.4 (2)
S1-Ni1-S6	94.6 (2)	S2-Ni3-S7	93.7 (2)	Ni3-Ni7-Ni8	57.5 (1)	Ni3-S2-Ni8	73.8 (2)
S1-Ni1-S9	94.1 (2)	S3-Ni3-S4	94.4 (2)	Ni3-Ni7-Ni9	90.6 (1)	Ni5-S2-Ni8	135.2 (3)
S3-Ni1-S6	93.4 (2)	S3-Ni3-S7	93.1 (2)	Ni8-Ni7-Ni9	59.5 (1)	Ni1-S3-Ni3	83.6 (2)
S3-Ni1-S9	93.8 (2)	S4-Ni3-S2	141.5 (2)	S3-Ni7-S7	93.2 (2)	Ni1-S3-Ni4	73.9 (2)
S6-Ni1-S9	140.9 (3)	Ni1-Ni4-Ni3	66.7 (2)	S3-Ni7-S9	94.8 (2)	Ni1-S3-Ni7	73.8 (2)
Ni1-Ni2-Ni3	60.1 (1)	Ni1-Ni4-Ni5	91.0 (2)	S3-Ni7-P6	101.2 (2)	Ni3-S3-Ni4	73.4 (2)
Ni1-Ni2-Ni5	89.2 (1)	Ni1-Ni4-Ni6	57.6 (2)	S7-Ni7-S9	156.1 (3)	Ni3-S3-Ni7	74.8 (2)
Ni1-Ni2-Ni6	56.7 (1)	Ni3-Ni4-Ni5	57.9 (2)	S7-Ni7-P6	101.0 (2)	Ni4-S3-Ni7	136.5 (3)
Ni1-Ni2-Ni8	88.5 (1)	Ni3-Ni4-Ni6	90.8 (2)	S9-Ni7-P6	99.5 (3)	Ni3-S4-Ni4	75.2 (2)
Ni1-Ni2-Ni9	56.9 (1)	Ni5-Ni4-Ni6	60.1 (2)	Ni2-Ni8-Ni3	66.7 (1)	Ni3-S4-Ni5	75.5 (2)
Ni3-Ni2-Ni5	56.6 (1)	S3-Ni4-S4	94.9 (2)	Ni2-Ni8-Ni7	91.7 (1)	Ni4-S4-Ni5	83.2 (2)
Ni3-Ni2-Ni6	89.0 (1)	S3-Ni4-S6	93.7 (2)	Ni2-Ni8-Ni9	58.4 (1)	Ni2-S5-Ni5	76.3 (2)
Ni3-Ni2-Ni8	56.8 (1)	S3-Ni4-P2	101.6 (3)	Ni3-Ni8-Ni7	58.4 (1)	Ni2-S5-Ni6	75.7 (2)
Ni3-Ni2-Ni9	89.7 (1)	S4-Ni4-S6	157.0 (3)	Ni3-Ni8-Ni9	92.1 (1)	Ni5-S5-Ni6	83.4 (2)
Ni5-Ni2-Ni6	64.4 (1)	S4-Ni4-P2	99.7 (3)	Ni7-Ni8-Ni9	60.9 (1)	Ni1-S6-Ni4	76.2 (2)
Ni5-Ni2-Ni8	103.0 (1)	S6-Ni4-P2	99.4 (3)	S2-Ni8-S7	93.5 (2)	Ni1-S6-Ni6	75.5 (2)
Ni5-Ni2-Ni9	142.4 (1)	Ni2-Ni5-Ni3	66.5 (1)	S2-Ni8-S8	93.9 (2)	Ni4-S6-Ni6	83.0 (2)
Ni6-Ni2-Ni8	141.6 (1)	Ni2-Ni5-Ni4	91.0 (1)	S2-Ni8-P4	110.6 (2)	Ni3-S7-Ni7	76.9 (2)
Ni6-Ni2-Ni9	102.7 (1)	Ni2-Ni5-Ni6	57.6 (1)	S7-Ni8-S8	157.7 (3)	Ni3-S7-Ni8	76.0 (2)
Ni8-Ni2-Ni9	64.2 (1)	Ni3-Ni5-Ni4	57.7 (1)	S7-Ni8-P4	101.0 (2)	Ni7-S7-Ni8	83.3 (2)
S1-Ni2-S2	156.3 (3)	Ni3-Ni5-Ni6	90.8 (1)	S8-Ni8-P4	96.0 (2)	Ni2-S8-Ni8	75.4 (2)
S1-Ni2-S5	94.4 (2)	Ni4-Ni5-Ni6	60.2 (1)	Ni1-Ni9-Ni2	66.1 (1)	Ni2-S8-Ni9	76.5 (2)
S1-Ni2-S8	93.4 (2)	S2-Ni5-S4	94.2 (2)	Ni1-Ni9-Ni7	57.2 (1)	Ni8-S8-Ni9	82.6 (2)
S2-Ni2-S5	93.8 (2)	S2-Ni5-S5	94.1 (2)	Ni1-Ni9-Ni8	89.9 (1)	Ni1-S9-Ni7	75.7 (2)
S2-Ni2-S8	94.2 (2)	S2-Ni5-P1	108.2 (2)	Ni2-Ni9-Ni7	90.4 (1)	Ni1-S9-Ni9	75.7 (2)
S5-Ni2-S8	140.7 (3)	S4-Ni5-S5	157.3 (3)	Ni2-Ni9-Ni8	57.5 (1)	Ni7-S9-Ni9	84.0 (2)
Ni1-Ni3-Ni2	59.9 (1)	S4-Ni5-P1	101.5 (3)	Ni7-Ni9-Ni8	59.7 (1)		

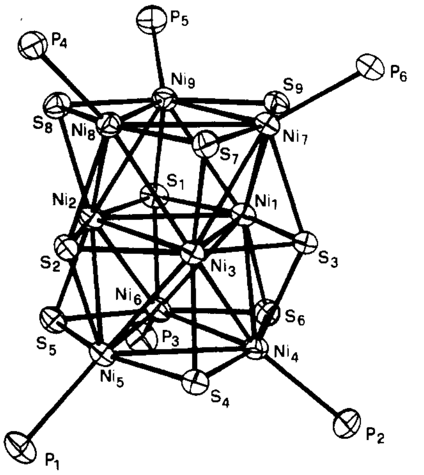

Figure 2. Inner core of the $[Ni_9(\mu_4\text{-}S)_3(\mu_3\text{-}S)_6(PEt_3)_6]^{2+}$ cation with 30% probability ellipsoids.

Å. The six sulfur atoms belonging to the external layers are triply bridging two nickel atoms within the layer and one metal atom of the equatorial plane while the three sulfur atoms of the equatorial layer are quadruply bridging two nickel atoms of the central plane and two metal atoms of two opposite basal planes. In this way each octahedral face with the exception of those parallel to the shared one is capped by a sulfur ligand. It is interesting to note that the sulfur belonging to the equatorial plane bridges at the same time two octahedral faces. Finally each metal atom of the external planes is terminally bonded to a triethylphosphine group.

The average values of the intralayer Ni–Ni distances, 2.950 (2) Å within the equatorial layer and 2.869 (6) Å within the basal ones, as well as the value of the interlayer distances of 2.690 (3) Å are rather long compared with those observed in other polynuclear compounds containing nickel triangles.[24] Concerning the difference between equatorial and basal Ni–Ni intralayer distances, the different formal coordination number of the metal, 10 and 8 for equatorial and basal respectively, can probably account for this fact. The marked difference between the interlayer distances with respect to the intralayer ones results in a compression of the two trigonal antiprisms along their pseudothreefold axis. This distortion is just the opposite to what has been found for $[Ni_3(\mu\text{-}CO)_3(CO)_3]_2^{2-}$, having a trigonal-antiprismatic metal framework.[24b] In the latter compound however the layers are kept together only by metal–metal interactions, no bridging ligands between the layers being present.

In compound 4 the sulfur ligand plays an important role in bonding between the layers, the Ni–S linkages being in our opinion the more important. The sulfur ligand displays two different bonding modes; i.e., there are six triply bridging and three quadruply bridging sulfur atoms. The μ_4-S examples are still very rare and are of two types: the sulfur can be in

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a "tetrahedral hole" or can bridge, as in the title compound, four metals lying on a same side. This latter mode has been observed so far in very few cases.[3a,b,4g,25] As expected, the Ni–S bond distances associated with triply bridging sulfur are shorter than those associated with those quadruply bridging; moreover, within the linkages departing from the same sulfur the interlayer distances are significantly longer than the intralayer ones. All these values however fall in the range of values reported for 3d metal compounds containing triply or quadruply bridging sulfur ligands.[3a,b,e,4c,g–i,11–13,25]

In the trinuclear complexes $[Ni_3X_2(PR_3)_6]^{2+}$ direct metal to metal interactions can be excluded. Therefore each of these diamagnetic systems, and likewise the isostructural, previously reported $[Pd_3(\mu_3\text{-}S)_2(PR_3)_6]^{2+}$ (R = Me, Et)[21] and $[Pt_3(\mu_3\text{-}S)_2(PMe_2Ph)_6]^{2+}$[22] can be described as three d^8 square-planar complexes that all share two ligands, the bridging chalcogenides. However an equally straightforward description of the bonding is not possible in the case of the enneanickel cluster. This complex formally contains seven nickel(II) and two nickel(III) ions, but on account of the very high symmetry of the structural framework it seems likely to assume a delocalized electronic structure for the complex cation. The lack of two electrons with respect to the situation of nine nickel(II) ions (70 valence electrons vs. 72 for the hypothetical $[Ni_9S_9(PEt_3)_6]$ uncharged species) appears to be essential to stabilize the compound. In fact, the oxidation of the starting nickel(II) ions is spontaneous and all attempts to reduce the complex cation $[Ni_9S_9(PEt_3)_6]^{2+}$ with sodium tetrahydroborate or sodium naphthalenide invariably led to the breaking up of the compound.[26] On the other hand, the Ni–Ni distances can be considered indicative of weak direct metal to metal interactions, although caution is necessary in such an assessment because of the presence of strong Ni–S bridge bonds.

Analogous cofacial-bioctahedra units $\{Mo_9(\mu_4\text{-}Se)_3(\mu_3\text{-}Se)_8\}$ have been found, together with the octahedral ones $\{Mo_6(\mu_3\text{-}Se)_8\}$ in the ternary molybdenum chalcogenides of formula $In_xMo_{15}Se_{19}$ ($x = 2–3.3$).[27] These units are members of the structural series $M_{3n}X_{3n+2}$, $n = 1–\infty$. Even if only formally, both the complexes $[Ni_3X_2(PR_3)_6]^{2+}$ and $[Ni_9S_9(PEt_3)_6]^{2+}$ and the related octahedrally face-capped shaped $[Fe_6S_8(PEt_3)_6]^{2+}$[11] and $[Co_6S_8(PEt_3)_6]^{0,1+}$[12,13] can be considered to belong to the above structural series with $n = 1$, 3, and 2 respectively. In the case of the title complexes each metal–sulfur bond lacking with respect to the only chalcogenide ligand structures is substituted by one metal–phosphorus (from the phosphine) linkage. According to the bonding model of Hönle et al.,[28] which is an extension of the MO treatment of Cotton and Haas[29] for the clusters $\{Mo_6X_8\}$, there are $12n$ orbitals per $M_{3n}X_{3n+2}$ unit available for the formation of a metal to metal bond. Out of these, $6n$ orbitals have more or less bonding character. In compounds having more than $12n$ electrons per M_{3n} cluster the excess electrons will occupy antibonding orbitals, the metal to metal interactions being lowered. Therefore in the cations $[Ni_3X_2(PR_3)_6]^{2+}$ ($n = 1$), there are 24 electrons that fill the 6 bonding and the 6 antibonding orbitals. The net result is a situation of nonbonding between the metal atoms. In the case of the $[Ni_9S_9(PEt_3)_6]^{2+}$ cluster ($n = 3$) the two electrons lacking with respect to the nine nickel(II) atom situation (70 vs. 72 valence electrons) should determine the presence of a very weak metal–metal interaction. These considerations, although rising from only qualitative reasoning, seem in agreement with the experimental finding. However, the presence of a similar structural framework in compounds involving different metal ion and having quite different physical and chemical properties (the above molybdenum compounds are solid phases with metallic properties) suggests that the formation of these geometric figures is determined by the bonding requirements of the bridging chalcogenide rather than by electronic reasons concerning the metal cage.

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Supplementary Material Available: Listings of structure factor amplitudes and Tables IV and V giving thermal parameters (42 pages). Ordering information is given on any current masthead page.

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