Bis(pentafluorophenyl)nickel(II) Thio-molybdates and -tungstates. Crystal Structure of $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}WS_4)]$†

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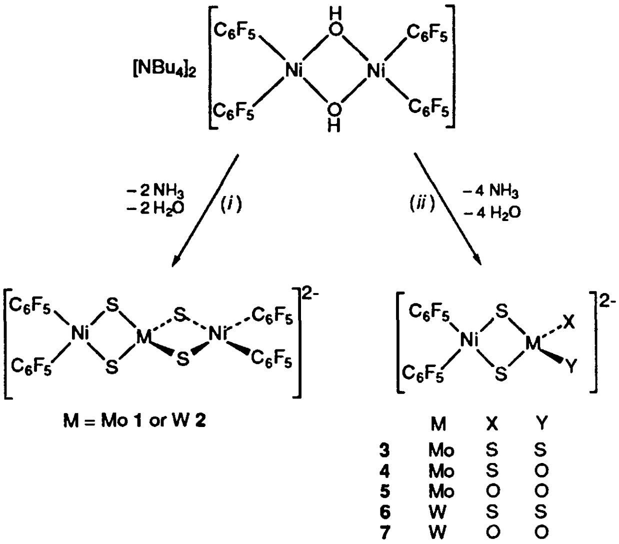
The complexes $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}MS_4)]$ (M = Mo **1** or W **2**) have been prepared by reaction of $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2]$ with $[NH_4]_2[MS_4]$ in ethanol in 1:1 molar ratio. When the bis(hydroxo) complex was treated with $[NH_4]_2[MO_{4-n}S_n]$ and NBu_4OH the complexes $[NBu_4]_2[Ni(C_6F_5)_2(\mu\text{-}MO_{4-n}S_n)]$ (M = Mo, n = 4 **3**, 3 **4**, or 2 **5**; M = W, n = 4 **6** or 2 **7**) were obtained. Conductance and spectroscopic (IR and ^{19}F NMR) measurements have been made. In complexes **1** and **2** two $Ni(C_6F_5)_2$ subunits are bridged by a tetradentate bridging MS_4^{2-} anion, whereas a bidentate terminal S-bonded $MO_{4-n}S_n^{2-}$ anion is present in **3–7**. A single-crystal X-ray diffraction study has established that the anion of complex **2** consists of a central S_2WS_2 tetrahedral subunit bridging two terminal square-planar $Ni(C_6F_5)_2$ subunits.

The tetrathiometalates $[MS_4]^{2-}$ (M = Mo or W)[1,2] are known to act as multidentate ligands towards a wide variety of transition-metal ions.[3–10] They have been shown to co-ordinate either in a bi- or tetra-dentate manner. Recent interest in this area follows from evidence that certain thiometalate complexes are structurally related to catalytic sites in both nitrogen-fixing enzymes[11,12] and industrial hydrodesulfurization and hydrodenitrogenation catalysts.[13]

Tetrathiometalate adducts of organometallic compounds are a relatively new class of compounds.[4,14–16] Since suitable organometallic halides are available, the metathesis of halide by a thiometalate anion is a common method for the synthesis of such derivatives. The dinuclear bis(μ-hydroxo) complexes $[M_2R_4(\mu\text{-}OH)_2]^{2-}$ (M = Ni,[17] Pd,[18] or Pt;[19] R = C_6F_5, C_6Cl_5 or $C_6H_2F_3$-2,4,6) have been shown to be useful and versatile reagents for the preparation of $[M_2R_4(\mu\text{-}X)_2]^{2-}$- or $[MR_2X]^-$-type complexes (X = exo- or endo-bidentate ligand, respectively) by reaction with the corresponding protic electrophile HX (azoles, malononitrile, β-diketones, 8-hydroxyquinoline, heterocycle-2-thiones).[17–22] The method is essentially based on the acid–base reaction $M(\mu\text{-}OH)_2M + 2HX \longrightarrow M(\mu\text{-}X)_2M + 2H_2O$ (or $2MX + 2H_2O$). Owing to current interest in the chemistry of organometallic derivatives of thiometalates, we turned our attention to reaction systems containing $[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-}$ and thiometalates $[MO_{4-n}S_n]^{2-}$ (M = Mo or W; n = 2, 3 or 4) in order to obtain adducts of the $Ni(C_6F_5)_2$ moiety with thiometalate. Since two protons are required by the bis(hydroxo)nickel complex to liberate two $Ni(C_6F_5)_2$ subunits the strategy was to use the ammonium thiometalate. Here we describe in detail the synthetic procedure and characterization of some bis(pentafluorophenyl)nickel(II) thiometalates.



Scheme 1 (*i*) $[NH_4]_2[MS_4]$; (*ii*) 2 $[NH_4]_2[MS_2X(Y)]$, 2 NBu_4OH

Results and Discussion

The complex $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2]$ has shown to be a useful precursor in synthetic work.[17,20–23] By reaction of it with $[NH_4]_2[MS_4]$ (M = Mo or W) in a 1:1 ratio in ethanol solution, crystals of $[NBu_4]_2[\{Ni(C_6F_5)_2\}_2(\mu\text{-}MS_4)]$ are formed. When the same reaction is carried out with the thiometalates $[NH_4]_2[MO_{4-n}S_n]$ (M = Mo, n = 2–4; M = W, n = 2 or 4) in the presence of NBu_4OH (1:2:2 molar ratio respectively) the bimetallic complexes $[Ni(C_6F_5)_2(MO_{4-n}S_n)]^{2-}$ are obtained. The experimental results are summarized in Scheme 1. In both reactions the OH bridges of the hydroxo complex are protonated by the NH_4^+ ions and the resulting $Ni(C_6F_5)_2$

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1994, Issue 1, pp. xxiii–xxviii.

Table 1 Analytical data, yields and physical properties for the nickel complexes

Complex	Yield (%)	M.p.[a] (θ/°C)	Analysis (%)[b] C	H	N	S	Λ_M/Ω^{-1} cm^2 mol^{-1}
1	76	177	44.7 (44.9)	5.0 (4.9)	1.8 (1.8)	8.9 (8.9)	250
2	65	140	42.1 (42.5)	4.6 (4.6)	1.8 (1.8)	7.9 (8.1)	228
3	66	125	47.6 (47.9)	6.8 (6.6)	2.5 (2.5)	11.1 (11.6)	214
4	58	115	48.2 (48.7)	6.7 (6.7)	2.5 (2.6)	9.0 (8.9)	214
5	53	128	49.0 (49.4)	6.9 (6.7)	2.6 (2.6)	5.5 (5.9)	268
6	68	129	44.4 (44.4)	6.3 (6.1)	2.4 (2.3)	10.4 (10.7)	203
7	48	126	45.2 (45.6)	6.5 (6.3)	2.5 (2.4)	5.8 (5.5)	216

[a] With decomposition. [b] Calculated values in parentheses.

Table 2 Spectroscopic data for the nickel complexes

Complex	Selected IR bands (cm^{-1})	UV/VIS (cm^{-1})[a]	^{19}F NMR (δ)[b]
1	485, 475 ν(MoS)	16 000 (6476)[c] 19 500 (sh)	$-$114.2 [dd, 8F$_o$, J(H$_o$H$_m$) 23.1] $-$164.9 [t, 4F$_p$, J(H$_p$H$_m$) 19.2] $-$166.4 (m, 8F$_m$)
2	475, 465 ν(WS)	20 000 (7389)[d] 25 400 (sh)	$-$114.4 [dd, 8F$_o$, J(H$_o$H$_m$) 27.4] $-$165.1 [t, 4F$_p$, J(H$_p$H$_m$) 19.7] $-$166.5 (m, 8F$_m$)
3	485 ν(MoS$_t$), 465 ν(MoS$_b$)	18 100 (5130)[c] 23 100 (sh)	$-$112.9 [d, 4F$_o$, J(H$_o$H$_m$) 24.2] $-$167.0 [t, 2F$_p$, J(H$_p$H$_m$) 19.7] $-$167.7 (m, 4F$_m$)
4	490 ν(MoS$_t$), 470 ν(MoS$_b$) 875 ν(MoO)	19 200 (sh)[d] 21 800 (1886)	$-$112.9 (m, 4F$_o$) $-$167.4 [t, 2F$_p$, J(H$_p$H$_m$) 19.5] $-$167.8 (m, 4F$_m$)
5	470, 450 ν(MoS$_b$) 880, 855 ν(MoO)	21 500 (sh)[d] 25 400 (1302) 29 600 (1815)	$-$112.8 [d, 4F$_o$, J(H$_o$H$_m$) 28.2] $-$167.8 [t, 2F$_p$, J(H$_p$H$_m$) 19.2] $-$168.1 (m, 4F$_m$)
6	470 ν(WS$_t$), 450 ν(WS$_b$)	22 400 (5217)[d] 26 100 (sh)	$-$113.0 [d, 4F$_o$, J(H$_o$H$_m$) 27.6] $-$167.0 [t, 2F$_p$, J(H$_p$H$_m$) 19.7] $-$167.7 (m, 4F$_m$)
7	460, 450 ν(WS$_b$) 900, 860 ν(WO)	21 300 (sh)[d] 24 600 (2916)	$-$113.0 [d, 4F$_o$, J(H$_o$H$_m$) 29.9] $-$167.7 [t, 2F$_p$, J(H$_p$H$_m$) 19.7] $-$168.1 (m, 4F$_m$)

[a] Values in parentheses are for ε_{max}/dm^3 mol^{-1} cm^{-1}. [b] In (CD$_3$)$_2$CO; referenced to CFCl$_3$; J in Hz. [c] In CH$_2$Cl$_2$. [d] In Me$_2$CO.

fragment is trapped by the thiometalate ligand in either 2:1 or 1:1 ratio respectively.

The new bis(pentafluorophenyl)nickel derivatives are air-stable solids and the conductances of their acetone solutions (Table 1) are consistent with 2:1 electrolytes.[24] The IR spectra exhibit the following bands attributed[25] to the C_6F_5 group: 1630m, 1490vs, 1050s and 950vs cm^{-1}, as well as a broad or split band at 780 cm^{-1} for the so-called 'X-sensitive' mode which is characteristic of the *cis*-M(C_6F_5)$_2$ fragment.[26] The most relevant IR bands of the thiometalate ligands and tentative assignments[1,27,28] are presented in Table 2. The spectra of the metallic complexes **1** and **2** exhibit in the ν(MS) region a split band assignable to the M–S bridging vibration. The two bands observed in the spectra of complexes **3** and **6** are consistent with the presence of both M–S bridging (b) and terminal (t) vibrations. Complex **4** gives the expected three bands for ν(MoS$_t$), ν(MoS$_b$) and ν(MoO$_t$), the observed wavenumbers being similar to those found[1] for $[Ni(MoOS_3)_2]^{2-}$. The dioxodithiometalate complexes **5** and **7** show two split bands due to M–S$_b$ and M–O$_t$ vibrations.

The ^{19}F NMR data for the nickel complexes are collected in Table 2. The spectra of complexes **3** and **5**–**7** show three resonances with relative intensities of 2:1:2 corresponding to the *o*-, *p*- and *m*-fluorine atoms, respectively, of two equivalent, freely rotating C_6F_5 groups. The asymmetric $MoOS_3^{2-}$ ligand causes non-equivalence of the two C_6F_5 groups in complex **4** and the multiplet observed in the *o*-fluorine region is interpreted as arising from overlapping of two distinct signals. A similar situation is found in the spectra of complexes **1** and **2** containing two organometallic square-planar subunits linked by the tetrahedral bridging tetrathiometalate (D_{2d} symmetry), and the resonance observed in the *o*-fluorine region is a doublet of doublets due to the closely spaced signals from two pairs of equivalent C_6F_5 rings.

The electronic spectra of the complexes in the visible region show the absorptions presented in Table 2 which tentatively are assigned[1,29] to charge-transfer transitions of the type L⟶3d (Ni), L being a non-bonding molecular orbital with a predominantly 3p (S) character. The spectra of complexes **1** and **3** in dichloromethane solution are presented in Fig. 1. As illustrated in Fig. 2, the visible spectrum of complex **3** varies with the electron-donor ability of the solvent: the spectrum of the methanolic solution is time-dependent and **3** is progressively converted into the corresponding trimetallic complex **1**. Scheme 2 shows a suggested mechanism for this conversion. It is likely that the driving force is the partial solvolysis of free $[MoS_4]^{2-}$, but we have been unable to identify any molybdenum species other than **1** and **3**. The tendency of MS_4^{2-} ligands to

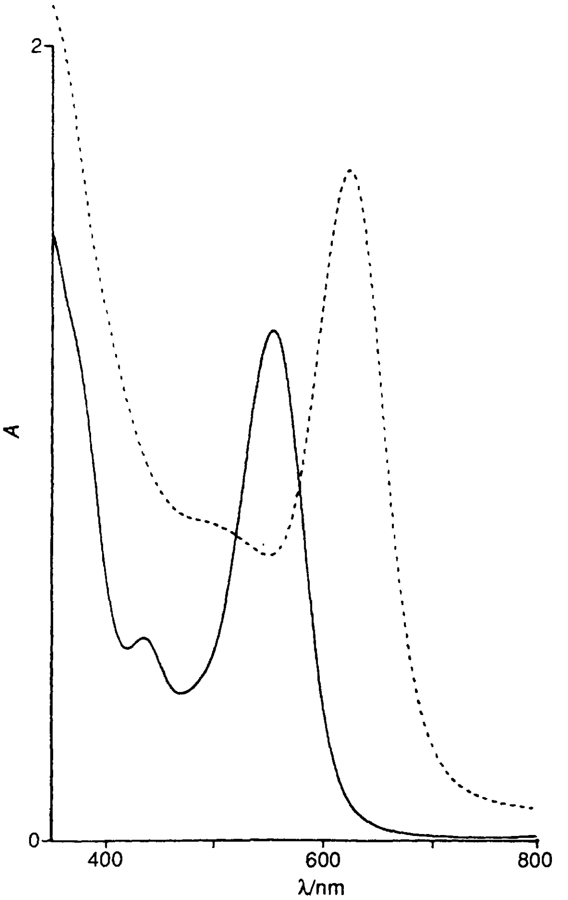


Fig. 1 Visible absorption spectra of $[NBu_4]_2[Ni(C_6F_5)_2(MoS_4)]$ **3** (——) and $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}MoS_4)]$ **1** (– – –) in dichloromethane solution ($c \approx 2.5 \times 10^{-4}$ mol dm^{-3})

form bridges has been attributed[1] to the higher transition metal $\longrightarrow MS_4^{2-}$ electron delocalization in the trimetallic complex. The analogous tungsten complex **6** undergoes a similar process in methanol but the conversion into **2** is completed only after 5 d.

The crystals of complex **2** consist of $[W\{NiS_2(C_6F_5)_2\}_2]^{2-}$ anions and $[NBu_4]^+$ cations held together by electrostatic interactions. Fig. 3 shows an ORTEP[30] perspective of the anion which includes the atom numbering scheme. Positional parameters are given in Table 3 and selected interatomic bond distances and angles in Table 4. The central S_2WS_2 tetrahedral subunit bridges the two terminal $Ni(C_6F_5)_2$ subunits. The W–S distances are slightly longer than those found in $[NH_4]_2[WS_4]$ (2.165 Å average).[31] In comparison, $[AsPh_4]_2[Ni(WS_4)_2]$ exhibits terminal W–S distances of 2.150(5) and 2.151(4) Å and bridging W–S distances of 2.234(3) and 2.229(4) Å.[32] The complexes $[Fe_2Cl_4(WS_4)]$,[29] $[Ru_2(\eta^5\text{-}C_5H_5)_2(MeNC)_2(WS_4)]$,[4] and $[Rh_2(cod)_2(WS_4)]$ (cod = cycloocta-1,5-diene)[14] all contain a bridging tetradentate WS_4 group and the average W–S distances are 2.209, 2.212 and 2.20 Å, respectively. The Ni atoms show practically square-planar co-ordination, with average deviations of 0.10 and 0.11 Å for the Ni(1) and Ni(2) planes respectively.[33] The Ni–C_6F_5 distances are similar to those found in $[Ni_2(C_6F_5)_4(\mu\text{-}Cl)_2]$[34] and $[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2]$.[17] The two pentafluorophenyl rings bonded to Ni are planar and rotated with respect to each other by 98.6(6) and 105(1)° for rings bonded to Ni(1) and Ni(2) respectively. There are distortions of the internal angles at the *ipso* positions of the C_6F_5 ring, as in related compounds.[35] The W···Ni(1) and W···Ni(2) distances are 2.739(3) and 2.732(3) Å, respectively, and the angle between the Ni(1) and Ni(2) is 91.0(2)°.

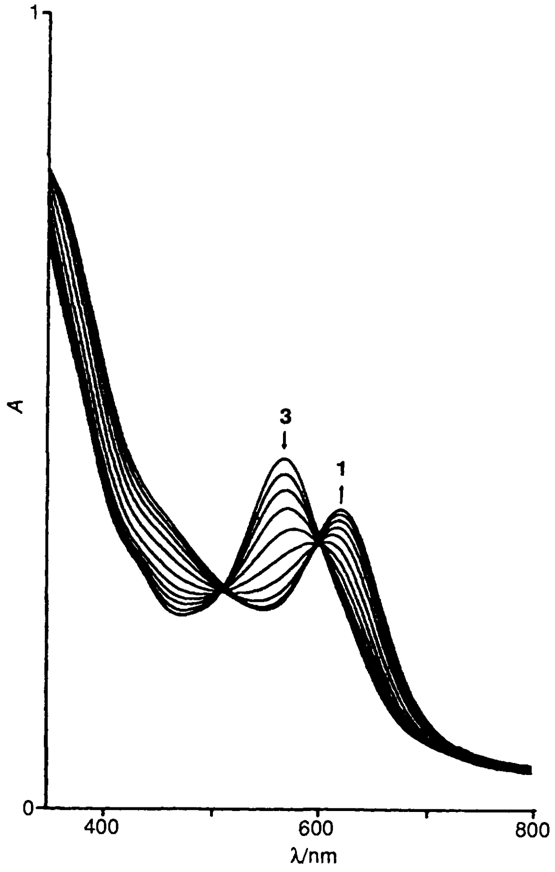
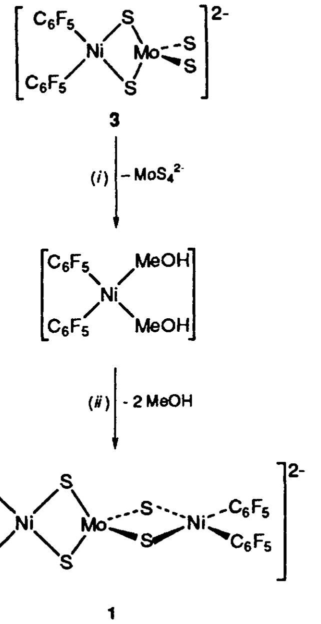


Fig. 2 Visible absorption spectra of $[NBu_4]_2[Ni(C_6F_5)_2(MoS_4)]$ **3** in methanol solution ($c \approx 2.5 \times 10^{-4}$ mol dm^{-3}), as a function of time (at 1 h intervals). The presence of the isosbestic point near 600 nm indicates the progressive transformation of **3** into **1** (compare with Fig. 1)



Scheme 2 (*i*) 2MeOH; (*ii*) **3**

Experimental

Carbon, H and N analyses were carried out with a Carlos Erba instrument. The spectroscopic instruments used were Perkin-Elmer 1430 for IR spectra (Nujol mulls), Hitachi 2000U for electronic spectra and Bruker AC 200E or Varian 300 for ^{19}F NMR spectra. Conductance measurements were

Table 3 Atomic parameters for complex **2** with estimated standard deviations (e.s.d.s) in parentheses

Atom	*x*	*y*	*z*
W	0.157 73(1)	0.069 12(1)	0.258 24(1)
Ni(1)	0.153 7(3)	−0.054 4(2)	0.167 7(1)
Ni(2)	0.152 6(3)	0.221 0(2)	0.341 9(1)
S(1)	0.320 4(5)	−0.079 4(5)	0.225 0(2)
S(2)	−0.018 2(5)	0.082 1(5)	0.204 8(2)
S(3)	0.217 3(6)	0.227 3(5)	0.273 2(2)
S(4)	0.114 2(6)	0.052 3(5)	0.328 7(2)
C(1)	0.292 1(20)	−0.151 1(17)	0.127 0(7)
C(2)	0.343 7(21)	−0.099 7(18)	0.097 2(9)
C(3)	0.436 7(25)	−0.162 0(27)	0.065 0(8)
C(4)	0.488 9(24)	−0.275 1(27)	0.061 5(9)
C(5)	0.445 9(27)	−0.333 0(20)	0.089 2(11)
C(6)	0.349 9(21)	−0.267 4(20)	0.121 5(8)
C(7)	0.020 8(17)	−0.064 3(16)	0.114 1(7)
C(8)	−0.024 0(19)	−0.159 8(16)	0.102 6(7)
C(9)	−0.114 5(22)	−0.175 1(19)	0.064 1(9)
C(10)	−0.160 5(22)	−0.096 7(23)	0.033 8(7)
C(11)	−0.116 5(23)	−0.001 2(20)	0.044 4(8)
C(12)	−0.027 8(21)	0.012 4(16)	0.082 7(8)
C(13)	0.150 0(23)	0.376 8(18)	0.358 3(8)
C(14)	0.257 0(31)	0.409 1(21)	0.384 1(10)
C(15)	0.251 0(24)	0.524 4(30)	0.396 0(10)
C(16)	0.148 2(40)	0.601 0(22)	0.380 8(10)
C(17)	0.039 2(30)	0.580 9(22)	0.353 9(11)
C(18)	0.044 9(23)	0.464 9(18)	0.342 3(8)
C(19)	0.131 4(23)	0.232 6(19)	0.408 6(8)
C(20)	0.012 6(25)	0.299 7(21)	0.428 8(9)
C(21)	0.009 6(27)	0.313 4(25)	0.478 6(12)
C(22)	0.118 8(48)	0.261 4(37)	0.501 9(14)
C(23)	0.226 5(28)	0.193 6(25)	0.485 3(13)
C(24)	0.237 5(27)	0.178 1(21)	0.438 2(9)
C(25)	−0.004 8(23)	0.392 5(17)	0.173 3(8)
C(26)	−0.133 7(29)	0.492 1(23)	0.185 3(10)
C(27)	−0.235 8(34)	0.451 1(32)	0.201 7(12)
C(28)	−0.354 9(46)	0.549 7(37)	0.215 4(15)
C(29)	0.143 7(27)	0.517 6(21)	0.181 0(9)
C(30)	0.202 2(27)	0.502 3(22)	0.229 6(10)
C(31)	0.249 8(28)	0.604 3(28)	0.256 1(12)
C(32)	0.145 5(33)	0.711 3(24)	0.259 8(11)
C(33)	0.037 5(29)	0.456 6(21)	0.101 2(9)
C(34)	−0.033 3(38)	0.378 5(24)	0.068 1(11)
C(35)	−0.113 7(42)	0.427 2(30)	0.029 6(14)
C(36)	−0.193 3(34)	0.368 4(26)	−0.004 2(12)
C(37)	0.223 2(24)	0.308 8(19)	0.141 6(10)
C(38)	0.338 1(30)	0.319 8(27)	0.120 3(13)
C(39)	0.454 5(48)	0.212 2(38)	0.118 2(15)
C(40)	0.576 0(53)	0.210 6(43)	0.105 8(18)
C(41)	−0.386 2(23)	0.141 1(20)	0.326 4(10)
C(42)	−0.289 1(29)	0.207 7(25)	0.321 7(12)
C(43)	−0.390 1(38)	0.343 9(32)	0.311 3(13)
C(44)	−0.390 0(0)	0.292 6(0)	0.260 0(0)
C(45)	−0.230 8(23)	−0.057 6(21)	0.293 4(9)
C(46)	−0.312 7(28)	−0.057 5(27)	0.245 0(11)
C(47)	−0.229 3(27)	−0.150 9(28)	0.208 7(11)
C(48)	−0.313 7(29)	−0.155 0(35)	0.164 3(12)
C(49)	−0.428 0(21)	−0.029 9(22)	0.342 6(9)
C(50)	−0.379 6(25)	−0.153 9(21)	0.352 4(10)
C(51)	−0.503 8(31)	−0.187 1(27)	0.358 1(13)
C(52)	−0.469 0(40)	−0.302 1(36)	0.367 6(14)
C(53)	−0.210 3(23)	0.009 8(22)	0.380 8(9)
C(54)	−0.278 3(31)	0.073 7(27)	0.426 3(10)
C(55)	−0.169 9(42)	0.067 3(33)	0.464 7(13)
C(56)	−0.227 0(51)	0.120 9(43)	0.512 8(19)
F(2)	0.295 8(15)	0.015 6(11)	0.100 7(5)
F(3)	0.484 1(15)	−0.107 2(15)	0.038 9(6)
F(4)	0.585 5(16)	−0.340 7(16)	0.029 7(6)
F(5)	0.501 9(15)	−0.453 0(12)	0.086 0(7)
F(6)	0.312 9(13)	−0.331 2(10)	0.148 6(6)
F(8)	0.020 6(12)	−0.246 1(10)	0.129 4(4)
F(9)	−0.152 9(14)	−0.273 2(11)	0.054 2(5)
F(10)	−0.246 2(14)	−1.113 2(14)	−0.005 1(5)
F(11)	−0.164 5(15)	0.080 4(13)	0.015 6(6)
F(12)	0.003 9(13)	0.110 8(11)	0.091 6(5)
F(14)	0.369 5(13)	0.333 3(12)	0.401 9(5)
F(15)	0.356 7(19)	0.556 2(16)	0.422 1(7)
F(16)	0.135 5(20)	0.724 0(16)	0.390 2(7)
F(17)	−0.071 8(18)	0.664 4(13)	0.336 7(7)
F(18)	−0.061 4(15)	0.441 4(13)	0.315 4(6)
F(20)	−0.101 5(14)	0.359 0(13)	0.403 9(5)
F(21)	−0.111 9(21)	0.387 3(17)	0.497 8(7)
F(22)	0.103 8(21)	0.281 0(17)	0.553 6(7)
F(23)	0.340 3(19)	0.138 8(16)	0.515 7(7)
F(24)	0.356 0(15)	0.107 6(13)	0.421 5(5)
N(1)	0.098 9(18)	0.419 5(14)	0.148 0(7)
N(2)	−0.313 3(17)	0.017 6(15)	0.337 1(7)

Table 4 Selected bond distances (Å) and angles (°) for complex **2**

W–S(1)	2.178(5)	Ni(1)–C(1)	1.89(2)
W–S(2)	2.178(6)	Ni(1)–C(7)	1.92(2)
W–S(3)	2.187(7)	Ni(2)–S(3)	2.190(7)
W–S(4)	2.193(3)	Ni(2)–S(4)	2.200(7)
Ni(1)–S(1)	2.181(6)	Ni(2)–C(13)	1.88(2)
Ni(1)–S(2)	2.213(6)	Ni(2)–C(19)	1.93(2)
S(3)–W–S(4)	102.8(2)	S(1)–Ni(1)–S(2)	101.5(3)
S(2)–W–S(4)	113.5(3)	C(13)–Ni(2)–C(19)	85(1)
S(2)–W–S(3)	112.3(2)	S(4)–Ni(2)–C(19)	88.8(7)
S(1)–W–S(4)	114.6(2)	S(4)–Ni(2)–C(13)	168.3(8)
S(1)–W–S(3)	111.2(3)	S(3)–Ni(2)–C(19)	165.7(8)
S(1)–W–S(2)	102.8(2)	S(3)–Ni(2)–C(13)	85.4(7)
C(1)–Ni(1)–C(7)	87.1(8)	S(3)–Ni(2)–S(4)	102.5(3)
S(2)–Ni(1)–C(7)	87.0(6)	W–S(1)–Ni(1)	77.9(2)
S(2)–Ni(1)–C(1)	168.7(6)	W–S(2)–Ni(1)	77.2(2)
S(1)–Ni(1)–C(7)	169.0(6)	W–S(3)–Ni(2)	77.2(2)
S(1)–Ni(1)–C(1)	85.6(7)	W–S(4)–Ni(2)	76.9(2)

performed with a Crison 525 conductimeter (in acetone, $c \approx 5 \times 10^{-4}$ mol dm^{-3}). Decomposition temperatures were determined on a Reichert microscope. All the solvents were dried by conventional methods. The ammonium thiometalates[2] and $[NBu_4]_2[\{Ni(C_6F_5)_2(\mu\text{-}OH)\}_2]$[17] were prepared as described elsewhere.

Preparations.—$[Ni_2(C_6F_5)_4(\mu\text{-}MoS_4)]$ **1**. The salt $[NH_4]_2[MoS_4]$ (30 mg, 0.115 mmol) was added to a solution of $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2]$ (150 mg, 0.115 mmol) in ethanol (5 cm^3). After stirring at room temperatue for 30 min the solution was concentrated under reduced pressure. Addition of diethyl ether resulted in the precipitation of complex **1** as a blue-violet solid, which was filtered off and recrystallized from ethanol–diethyl ether.

$[Ni_2(C_6F_5)_4(\mu\text{-}WS_4)]$ **2**. The salt $[NH_4]_2[WS_4]$ (40 mg, 0.115 mmol) was added to an ethanolic solution (5 cm^3) of $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2]$ (150 mg, 0.115 mmol). The solution was stirred for 30 min, during which time a red solid separated. The solvent was then partly evaporated under reduced pressure and an additional amount of complex **2** was formed. The solid was filtered off and recrystallized from ethanol–diethyl ether.

$[Ni(C_6F_5)_2(MS_4)]$ (M = Mo **3** *or* W **6**). A 20% solution of NBu_4OH(aq) (0.3 cm^3, 0.230 mmol) was added to an ethanolic (5 cm^3) solution of $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2]$ (150 mg, 0.115 mmol). After stirring for 15 min, $[NH_4]_2[MS_4]$ (0.230 mmol) was added. The solution was stirred at room temperature for 30 min, during which time a red (Mo) or orange (W) solid separated. Partial evaporation of the solvent under reduced pressure caused the complete precipitation of the complex, which was filtered off and recrystallized from dichloromethane–diethyl ether.

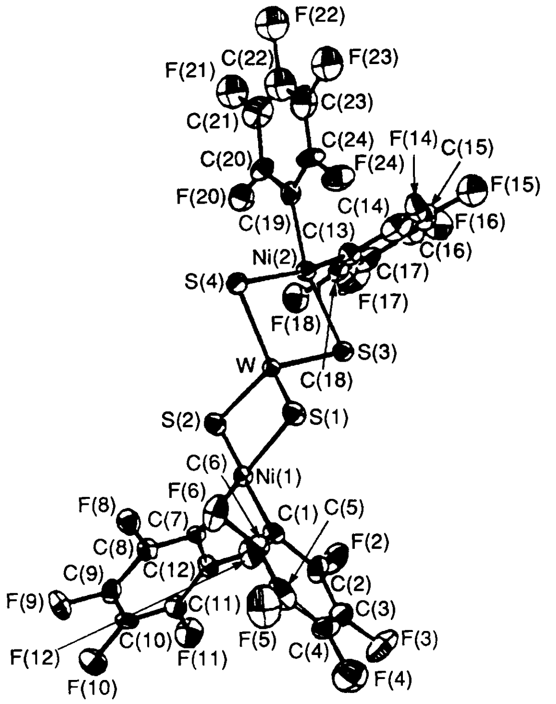


Fig. 3 An ORTEP drawing of the $[Ni_2(C_6F_5)_4(\mu\text{-}WS_4)]^{2-}$ anion, with atomic numbering scheme. Thermal ellipsoids are at the 20% probability level

$[Ni(C_6F_5)_2(MoOS_3)]$ **4**. A 20% solution of $NBu_4OH(aq)$ (0.3 cm^3, 0.230 mmol) was added to an EtOH (5 cm^3) solution of $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2]$ (150 mg, 0.115 mmol). After stirring for 15 min, $[NH_4]_2[MoOS_3]$ (76.2 mg, 0.230 mmol) was added and the solution was stirred at room temperature for 30 min. The solvent was then removed under vacuum and the residue was washed with Pr^iOH. Crystals of complex **4** were obtained by recrystallization from Me_2CO–Pr^iOH.

$[Ni(C_6F_5)_2(MoO_2S_2)]$ **5**. A 20% solution of $NBu_4OH(aq)$ (0.3 cm^3, 0.230 mmol) was added to an EtOH (5 cm^3) solution of $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2]$ (150 mg, 0.115 mmol), with constant stirring for 15 min. The salt $[NH_4]_2[MoO_2S_2]$ (52.4 mg, 0.230 mmol) was added and the resulting solution stirred for 30 min. The solvent was partly evaporated under reduced pressure and slow addition of water precipitated an orange solid which was filtered off, washed with water and air-dried.

$[Ni(C_6F_5)_2(WO_2S_2)]$ **7**. The procedure was similar to that used for complex **4** and the isolated solid was recrystallized from Me_2CO–Pr^iOH.

The analytical data and some physical properties of the complexes are listed in Table 1.

Structure Determination of Complex **2**.—Diffraction data were measured on an Enraf-Nonius CAD4 diffractometer operating in the ω–2θ mode with graphite-monochromated Mo-Kα radiation (λ = 0.710 69 Å) up to θ = 25° from crystals of size 0.4 × 0.3 × 0.3 mm. Three standard reflections were monitored periodically to check the stability of the system. 118 32 Unique reflections were scanned and 4456 with $I \geqslant 2\sigma(I)$ were considered observed and used in the analyses.

Crystal data. $C_{56}H_{72}F_{20}N_2Ni_2S_4W$, triclinic, space group $P1$, a = 10.296(6), b = 12.336(2), c = 28.643(5) Å, α = 101.35(2), β = 98.31(2), γ = 70.00(2)°, U = 3340(2) $Å^3$, Z = 2, D_c = 1.57 g cm^{-3}, μ(Mo-Kα) = 25.3 cm^{-1}, $F(000)$ = 1592.

The cell dimensions were refined by least-squares fitting of the θ values of 25 reflections. The intensities were corrected for Lorentz and polarization effects. Scattering factors for neutral atoms and anomalous dispersion corrections for W, Ni and S were taken from ref. 36. The structure was solved by Patterson and Fourier methods. An empirical absorption correction[37] was applied at the end of isotropic refinement and final refinement was carried out using fixed isotropic thermal parameters and coordinates for the hydrogen atoms. A slight non-resolvable disorder was found for a few atoms, and consequently these were refined isotropically. Most calculations were carried out with the X-RAY 80 system.[38] Final R = 0.065 and R' = 0.073 (unit weights).

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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References

1 A. Müller, E. Diemann, R. Jostes and H. Bögge, *Angew. Chem., Int. Ed. Engl.*, 1981, **20**, 934.
2 J. W. McDonald, G. D. Friesen, L. D. Rosenheim and W. D. Newton, *Inorg. Chim. Acta*, 1983, **72**, 205.
3 A. Müller and E. Diemann, *Comprehensive Coordination Chemistry*, 1987, vol. 2, p. 559 and refs. therein.
4 K. E. Howard, T. B. Rauchfuss and S. R. Wilson, *Inorg. Chem.*, 1988, **27**, 1710.
5 M. A. Greaney, C. L. Coyle, M. A. Harmer, A. Jordan and E. I. Stiefel, *Inorg. Chem.*, 1989, **28**, 912.
6 F. Bonomi, S. Iametti and D. M. Kurtz, jun., *Inorg. Chim. Acta*, 1992, **193**, L125.
7 S. Bernès, F. Sécheresse and Y. Jeannin, *Inorg. Chim. Acta*, 1992, **191**, 11.
8 D. Shaown, Z. Nianyong, C. Pengcheng, W. Xintao and L. Jiaxi, *J. Chem. Soc., Dalton Trans.*, 1992, 339; *Polyhedron*, 1992, **11**, 109.
9 T. Matsumoto, K. Matsumoto and T. Sato, *Inorg. Chim. Acta*, 1992, **202**, 31.
10 E. Bencini, F. Cecconi, C. A. Ghilardi, S. Midollini, F. Nuzzi and A. Orlandini, *Inorg. Chem.*, 1992, **31**, 5339.
11 R. H. Holm, *Chem. Soc. Rev.*, 1981, **10**, 455.
12 D. Coucouvanis, *Acc. Chem. Res.*, 1981, **14**, 201.
13 T. R. Halbert, S. A. Cohen and E. I. Stiefel, *Organometallics*, 1985, **4**, 1689.
14 K. E. Howard, T. B. Rauchfuss and A. L. Rheingold, *J. Am. Chem. Soc.*, 1986, **108**, 297.
15 K. E. Howard, J. R. Lockemeyer, M. A. Massa, T. B. Rauchfuss, S. R. Wilson and Xiaoguang Yang, *Inorg. Chem.*, 1990, **29**, 4385 and refs. therein.
16 A. R. Siedle, C. R. Hubbard, A. D. Mighell, R. M. Doherty and J. M. Stewart, *Inorg. Chim. Acta*, 1980, **38**, 197.
17 G. López, G. García, G. Sánchez, J. García, J. Ruiz, J. A. Hermoso, A. Vegas and M. Martínez-Ripoll, *Inorg. Chem.*, 1992, **31**, 1518.
18 G. López, J. Ruiz, G. García, C. Vicente, J. Casabó, E. Molins and C. Miravitlles, *Inorg. Chem.*, 1991, **30**, 2607.
19 G. López, J. Ruiz, G. García, C. Vicente, J. M. Martí, J. A. Hermoso, A. Vegas and M. Martínez-Ripoll, *J. Chem. Soc., Dalton Trans.*, 1992, 53.
20 G. López, G. Sánchez, G. García, J. García, A. Martínez, J. A. Hermoso and M. Martínez-Ripoll, *J. Organomet. Chem.*, 1992, **435**, 193.
21 G. López, G. Sánchez, G. García, M. Martinez-Ripoll, A. Vegas and J. A. Hermoso, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 716.
22 G. Sánchez, F. Ruiz, M. D. Santana, G. García, G. López, J. A. Hermoso and M. Martínez-Ripoll, *J. Chem. Soc., Dalton Trans.*, 1994, 19.
23 G. López, G. Sánchez, G. García, J. García, A. Sanmartín and M. D. Santana, *Polyhedron*, 1991, **10**, 2821.
24 W. J. Geary, *Coord. Chem. Rev.*, 1971, **7**, 81.
25 E. Maslowsky, *Vibrational Spectra of Organometallic Compounds*, Wiley, New York, 1977, p. 437.
26 M. M. Brezinski and K. J. Klabunde, *Organometallics*, 1983, **2**, 1116.
27 D. Coucouvanis, P. Stremple, E. D. Simhon, D. Swenson, N. C. Baenziger, M. Draganjac, L. T. Chan, A. Simopoulos, V. Papaefthymou, A. Kostikas and V. Petrouleas, *Inorg. Chem.*, 1983, **22**, 293.

28 I. Paulat-Böschen, B. Krebs, A. Müller, E. Kpniger-Ahlborn, H. Dornfeld and H. Schultz, *Inorg. Chem.*, 1978, **17**, 1440.

29 D. Coucouvanis, E. D. Simhon, P. Stremple, M. Ryan, D. Swenson, N. C. Baenziger, A. Simopoulos, V. Papaefthymiou, A. Kostikas and V. Petrouleas, *Inorg. Chem.*, 1984, **23**, 741.

30 C. K. Johnson, ORTEP, Report ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, TN, 1965.

31 K. Sasvary, *Acta Crystallogr., Sect. B*, 1983, **36**, 3090.

32 J. D. Dunitz, H. C. Mez, O. S. Mills and H. M. M. Shearer, *Helv. Chim. Acta*, 1962, **45**, 647.

33 M. Nardelli, A. Musatti, P. Domiano and G. D. Andreetti, *Ric. Sci.*, Parte 2, Sez. A, 1965, 8, 807.

34 M. M. Brezinski, J. Schneider, L. J. Radonovich and K. J. Klabunde, *Inorg. Chem.*, 1989, **28**, 2414.

35 P. G. Jones, *J. Organomet. Chem.*, 1988, **345**, 405.

36 *International Tables for X-Ray Crystallography*, Kynoch Press, Birmingham, 1974, vol. 4.

37 N. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

38 J. M. Stewart, F. A. Kundell and J. C. Baldwin, The X-RAY 80 system of crystallographic programs, Computer Science Centre, University of Maryland, College Park, MD, 1980.

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