Di- and Tri-nuclear Nickel(II) Complexes with Bridging Thiolato Groups. Crystal Structure of $[NBu_4]_2[Ni_3(C_6F_5)_4(\mu\text{-}SEt)_4]$†

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The hydroxo complex $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2]$ reacts with H_2S or a thiol at room temperature in methanol to give the binuclear complexes $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}SR)_2]$ (R = H, Me, Et, Pr^i, Ph or C_6H_4Me-*p*). The trinuclear complex $[NBu_4]_2[Ni_3(C_6F_5)_4(\mu\text{-}SEt)_4]$ has been obtained by reaction of an excess of EtSH with the same hydroxo complex in refluxing methanol. The μ-azolato–μ-thiolato complexes $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}L)(\mu\text{-}SR)]$ (HL = pyrazole or 1,2,4-triazole; R = H, Ph or C_6H_4Me-*p*) can be prepared either by treating the μ-hydroxo–μ-azolato complexes $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}OH)(\mu\text{-}L)]$ with H_2S or a thiol (1:1 molar ratio) or $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2]$ with the corresponding thiol and azole (1:1:1 molar ratio). Analytical (C, H, N, S), conductance and spectroscopic (IR, ^1H and ^{19}F NMR) data have been used for structural assignments. An X-ray crystal structure determination of $[NBu_4]_2[Ni_3(C_6F_5)_4(\mu\text{-}SEt)_4]$ has established the trinuclear nature of the anion. The structure has been solved and refined to *R* = 0.052 and *R'* = 0.062 based on 3398 observed reflections. The Ni atoms are four-co-ordinated and show approximate square-planar arrangements. The bridge conformation could be determined by S ··· S repulsions.

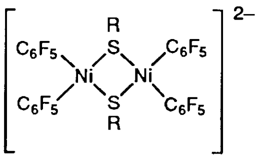
The relevance of transition-metal complexes with S-donor ligands as models of biologically redox-active metalloproteins[1] has stimulated interest in the chemistry of metal thiolates.[2,3] Nickel complexes with S-donor ligands are present in many hydrogenases.[4] Nickel(II) thiolates are generally square-planar species with a strong tendency to form dimers[5–7] and oligomers.[5–12] This tendency, which is also prevalent for hydroxide and amide complexes, has been an obstruction to the synthesis of mononuclear compounds. The simplest method for incorporation of thiolate (RS^-) into transition-metal complexes involves the displacement of a halide by a thiolate anion from an alkali-metal thiolate but thiolate may also be generated in solution by addition of base to the reaction mixture containing thiol.

Binuclear anionic complexes of the type $[M_2(C_6F_5)_4(\mu\text{-}OH)_2]^2$ (M = Ni, Pd or Pt)[13–15] have been reported recently. Their reactivity towards weak protic electrophiles (HX) is consistent with the high-field proton resonances [δ −5.74 (Ni), −2.84 (Pd) and −1.21 (Pt)] exhibited by the bridging OH groups and complexes of the type $[M_2(C_6F_5)_4(\mu\text{-}X)_2]^{2-}$ are formed, with the concomitant release of water. We report here the reactions of $[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-}$ with H_2S and some thiols RSH which lead to the formation of the corresponding di-μ-thiolato complexes $[Ni_2(C_6F_5)_4(\mu\text{-}SR)_2]^{2-}$ (R = H, alkyl or aryl). Complexes $[Ni_2(C_6F_5)_4(\mu\text{-}L)(\mu\text{-}SR)]^{2-}$ [HL = pyrazole (Hpz) or 1,2,4-triazole (Htz)] are similarly prepared by reaction of $[Ni_2(C_6F_5)_4(\mu\text{-}OH)(\mu\text{-}L)]^{2-}$ with a thiol.

Results and Discussion

Di-μ-thiolato Complexes.—Previous work demonstrated that $[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2]^{2-}$ is a useful precursor for the preparation of β-diketonate, heterocyclic 2-thiolate,[16] dithiocarbonate and dithiocarbamate[17] complexes and it is an efficient catalyst for the cyclotrimerization of malononitrile.[18] When $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2]$ is treated with H_2S or a thiol, the di-μ-hydrogensulfido or bis(μ-thiolato) complexes **1**–**6** are formed, according to equation (1) (R = H **1**, Me **2**, Et **3**, Pr^i **4**, Ph **5** or C_6H_4Me-*p* **6**).

$$[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2] + 2\,RSH \xrightarrow{-2H_2O}$$



(1)

The reaction implies protonation of the hydroxo groups and replacement by μ-hydrogensulfido or μ-thiolato ligands.

Analytical data, colours, yields and decomposition temperatures of the new complexes are collected in Table 1. They exhibit conductance values corresponding to 2:1 electrolytes in acetone.[19] The infrared spectra show the bands attributed to the C_6F_5 group[20] at *ca.* 1630m, 1490vs, 1050vs and 950vs cm^{-1}, as well as a broad or split band at 780 cm^{-1} for the so-called 'X-sensitive' mode of C_6F_5 which is characteristic of the *cis*-$M(C_6F_5)_2$ fragment.[21]

The ^1H NMR spectra of the binuclear thiolato complexes indicate that both thiolate ligands are equivalent (Table 2). The presence of the SH ligand in complex **1** is manifested by the observation of a high-field proton resonance at δ −3.05 [the corresponding value for δ(OH) of the precursor hydroxo complex is −5.74]. The ^{19}F NMR spectra (Table 2) exhibit the three signals (intensity ratio of 2:1:2) corresponding to the *ortho*-, *para*- and *meta*-fluorine atoms of four equivalent freely rotating C_6F_5 rings.

We have found that the reaction of an excess of EtSH with

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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 and physical data for the new complexes

Complex	Colour	Yield (%)	Analysis (%)[a] C	H	N	S	M.p. (θ/°C)	Λ_M[b]/S cm^2 mol^{-1}
1	Yellow-orange	71	49.9 (50.3)	5.8 (5.6)	2.4 (2.1)	4.7 (4.8)	171	177
2	Orange	65	50.9 (51.0)	6.1 (5.8)	2.4 (2.1)	4.4 (4.7)	174	201
3	Red	81	51.4 (51.7)	6.1 (5.9)	2.2 (2.0)	4.5 (4.6)	170	161
4	Red-brown	61	52.3 (52.4)	6.3 (6.1)	2.0 (2.0)	4.3 (4.5)	181	145
5	Dark red	75	55.0 (54.9)	5.7 (5.6)	1.9 (1.9)	4.6 (4.3)	160	203
6	Dark red	81	55.1 (55.4)	5.9 (5.7)	1.8 (1.9)	4.2 (4.2)	165	190
7	Red	20	49.5 (48.8)	6.1 (5.9)	2.2 (1.8)	8.2 (8.1)	165	155
8	Yellow	75	52.0 (51.7)	5.7 (5.5)	4.0 (4.1)	2.3 (2.3)	120	181
9	Brown	80	53.6 (53.8)	5.9 (5.6)	3.6 (3.8)	2.5 (2.3)	173	185
10	Yellow	73	53.1 (53.4)	5.3 (5.5)	4.4 (4.7)	1.8 (2.1)	176	170
11	Yellow	72	50.5 (50.7)	5.2 (5.5)	5.1 (5.1)	2.7 (2.3)	119	177
12	Yellow	70	53.1 (53.0)	5.6 (5.5)	4.9 (4.8)	1.9 (2.2)	177	190
13	Yellow	82	53.2 (53.4)	5.2 (5.5)	4.5 (4.7)	1.8 (2.1)	180	193

[a] Calculated values are given in parentheses. [b] In acetone.

Table 2 Proton and ^{19}F NMR data (J in Hz) for the complexes

Complex	δ(SiMe$_4$)*	δ(CFCl$_3$)
1	−3.05 (s, 2 H, SH)	−112.41 [d, 8F$_o$, J(F$_o$F$_m$) 29.3] −167.68 [t, 4F$_p$, J(F$_m$F$_p$) 19.2] −167.99 (m, 8F$_m$)
2	0.35 (s, 6H, CH$_3$)	−112.42 [d, 8F$_o$, J(F$_o$F$_m$) 32.2] −167.69 [t, 4F$_p$, J(F$_m$F$_p$) 19.6] −168.00 (m, 8F$_m$)
3	0.21 (t, 6H, CH$_3$, J_{HH} 7.3) 0.88 (q, 4H, CH$_2$)	−111.80 [d, 8F$_o$, J(F$_o$F$_m$) 30.2] −167.72 [t, 4F$_p$, J(F$_m$F$_p$) 19.5] −167.99 (m, 8F$_m$)
4	0.75 (d, 12H, CH$_3$, J_{HH} 7.5) 0.94 (spt, 2H, CH)	−112.26 [d, 8F$_o$, J(F$_o$F$_m$) 30.5] −168.32 (m, 4F$_p$ + 8 F$_m$)
5	6.65 (m, 2H$_p$ + 4H$_m$, Ph) 7.46 [d, 4H$_o$, J(H$_o$H$_m$) 7.5]	−118.47 [d, 8F$_o$, J(F$_o$F$_m$) 29.6] −168.09 (m, 4F$_o$ + 8F$_p$)
6	1.99 (s, 6H, CH$_3$) 6.46 [d, 4H$_m$, J(H$_o$H$_m$) 7.5] 7.31 [d, 4H$_o$, J(H$_o$H$_m$) 7.5]	−112.26 [d, 8F$_o$, J(F$_o$F$_m$) 30.5] −168.40 (m, 4F$_p$ + 8F$_m$)
7	1.20 (t, 12H, CH$_3$, J_{HH} 7.3) 1.66 (q, 8H, CH$_2$)	−113.51 [d, 8F$_o$, J(F$_o$F$_m$) 31.8] −167.00 [t, 4F$_p$, J(F$_m$F$_p$) 19.8] −167.43 (m, 8F$_m$)
8	−2.04 (s, 1H, SH) 5.47 (t, 1H, pz, J_{HH} 7.5) 6.34 (d, 2H, pz)	−113.56 (m, 8F$_o$) −166.52 [t, 2F$_p$, J(F$_m$F$_p$) 19.2] −167.01 (m, 4F$_m$) −167.77 [t, 2F$_p$, J(F$_m$F$_p$) 19.7] −168.10 (m, 4F$_m$)
9	5.48 (t, 1H, pz, J_{HH} 7.5) 6.28 (d, 2H, pz) 6.50 (m, 3H, Ph) 7.16 [d, 2H, Ph, J(H$_o$H$_m$) 7.1]	−113.40 (m, 4F$_o$) −113.95 (m, 4F$_o$) −166.70 [t ,2F$_p$, J(F$_m$F$_p$) 19.8] −167.22 (m, 4F$_m$) −168.80 (m, 2F$_p$ + 4F$_m$)
10	1.92 (s, 3H, CH$_3$) 5.46 (t, 1H, pz, J_{HH} 7.5) 6.27 [d, 2H, C$_6$H$_4$, J(H$_o$H$_m$) 7.8] 6.30 (d, 2H, C$_6$H$_4$) 7.02 (d, 2H, pz)	−113.32 (m, 4F$_o$) −113.90 (m, 4F$_o$) −166.69 [t, 2F$_p$, J(F$_m$F$_p$) 19.8] −167.20 (m, 4F$_m$) −168.94 (m, 2F$_p$ + 4F$_m$)
11	−2.23 (s, 1H, SH) 6.75 (s, 2H, tz)	−114.10 (m, 8F$_o$) −165.62 [t, 2F$_p$, J(F$_m$F$_p$) 19.8] −166.52 (m, 4F$_m$) −167.29 [t, 2F$_p$, J(F$_m$F$_p$) 19.8] −167.88 (m, 4F$_m$)
12	6.52 (m, 3H, Ph) 6.68 (s, 2H, tz) 7.17 [d, 2H, Ph, J(H$_o$H$_m$) 7.0]	−113.76 (m, 4F$_o$) −114.34 (m, 4F$_o$) −165.77 (m, 2F$_p$) −166.72 (m, 4F$_m$) −168.26 (m, 2F$_p$) −168.57 (m, 4F$_m$)
13	1.61 (s, 3H, CH$_3$) 5.08 (s, 2H, tz) 6.16 [d, 2H, C$_6$H$_4$, J(H$_o$H$_m$) 7.8] 6.63 (d, 2H, C$_6$H$_4$)	−113.70 (m, 4F$_o$) −114.37 (m, 4F$_o$) −165.82 [t, 2F$_p$, J(F$_m$F$_p$)] −166.75 (m, 4F$_m$) −168.59 (m, 2F$_p$ + 4F$_m$)

* Additional peaks of [NBu$_4$]$^+$ are found at δ *ca.* 3.7 (t, NCH$_2$), 1.8 (m, NCH$_2$C*H*$_2$), 1.5 (m, C*H*$_2$CH$_3$) and 1.0 (t, CH$_3$).

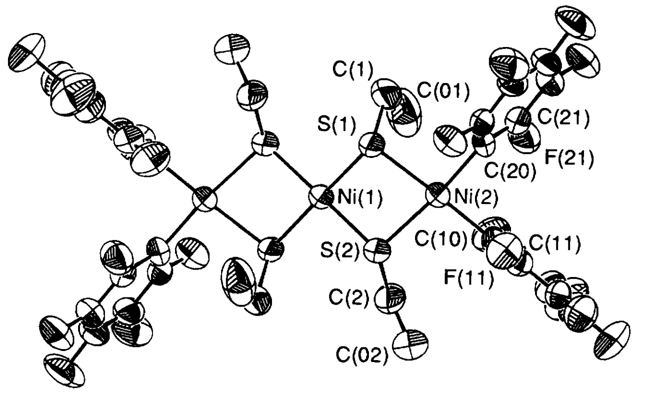
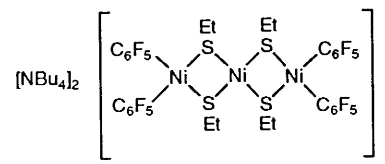


Fig. 1 An ORTEP[24] drawing of the anion of complex 7



7

$[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2]$ in refluxing methanol (5 h) produces the di-µ-thiolato-dinickel complex together with the new tetra-µ-thiolato-trinickel complex 7 (20% yield). The analytical, conductance (Table 1) and ^1H NMR ($2[NBu_4]^+ : 4\ ^-SEt$) data for 7 are consistent with the proposed formula. This reaction implies cleavage of two Ni–C_6F_5 bonds leading to the likely formation of the homoleptic thiolato complex $[Ni(SEt)_4]^2$, which in turn acts as a ligand to two $Ni(C_6F_5)_2$ fragments. The neutral trinuclear palladium complex *trans*-$([Pd_3(\mu\text{-}SC_6H_{11})_4(PMe_3)_2Cl_2]$ has been reported recently[22] and the anionic complex $[Ni_3\{\mu\text{-}C_6H_4(SCH_2)_2\text{-}o\}_4]^{2-}$ is also known.[23] The ^1H NMR spectrum of complex 7 indicates that the SEt groups are equivalent and the SEt resonances are found at lower field than in the spectrum of the binuclear complex 3, whereas the *ortho*-fluorine resonance of the C_6F_5 groups in complex 7 are shifted to higher field (δ − 113.51 for 7 *versus* − 111.80 for 3).

The X-ray crystal structure determination carried out for complex 7 shows a centrosymmetrical trinuclear $[(C_6F_5)_2Ni(\mu\text{-}SEt)_2Ni(\mu\text{-}SEt)_2Ni(C_6F_5)_2]^{2-}$ anion (Fig. 1) and two $[NBu_4]^+$ cations held together by electrostatic interactions. Positional parameters are given in Table 3 and selected geometrical features in Table 4. The nickel atom has approximately square-planar co-ordination, the deviations from the ideal geometry being revealed by the S–Ni–S angles. The values Ni(1)–S(1)–Ni(2) 94.1(1) and Ni(1)–S(2)–Ni(2) 94.0(1)° *vs.* 85.5(17)° reported by Watson *et al.*,[5] in a trinuclear compound with bridging (S_b) and terminal (S_t) thiolates, and *vs.* 85.5(17)° (standard deviation of the sample 5°) in compounds with S_b, S_t and chelating ligands,[8,9,23,25–28] seem to indicate that the equilibrium positions of the sulfur atoms in the bridge are determined by S ··· S repulsions, as suggested by Tremel *et al.*[8] On the other hand, the NiS_4 portion is planar, but the entire $Ni_3S_4C_4$ core is not, there being a dihedral angle of 31° between the NiS_4 and NiS_2C_2 subunits. The two pentafluorophenyl rings are planar and rotated from each other by 92.5(3)°. The C_6F_5 rings show distortions in their endocyclic bond angles, especially at the *ipso* carbon [113.1(9) and 113.7(9)°] and the two adjacent carbon atoms [125(1) and 125.5(9)°]. This type of distortion has been observed in other substituted-benzene derivatives[29] and for pentafluorophenyl groups in metal complexes.[30]

Thiolate–Azolate-bridged Complexes.—Binuclear complexes containing the central M(µ-L)(µ-SR)M [HL = pyrazole (Hpz) or 1,2,4-triazole (Htz)] core have been reported. In these complexes the bridging azolate group binds the metal atoms in an *exo*-bidentate fashion and the five-membered ring M(µ-L)-(µ-SR)M usually deviates from planarity by adopting a bent configuration.[31] Although complexes of this type have recently been reported for palladium and platinum,[32,33] similar nickel complexes have not been described. In dichloromethane or acetone $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}OH)(\mu\text{-}L)]$ complexes (L = pz or tz) react with H_2S or a thiol affording the corresponding

Table 3 Atomic parameters (× 10^4) for complex **7**

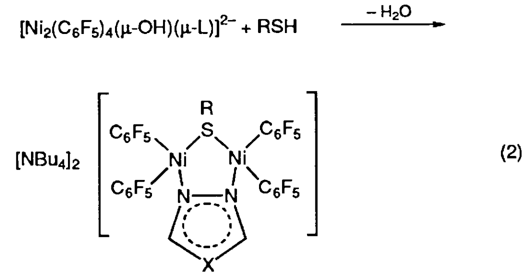
Atom	*x*	*y*	*z*
Ni(1)	0(0)	0(0)	0(0)
Ni(2)	1 711(1)	1 415(1)	1 786(1)
S(1)	1 816(2)	10(2)	836(1)
S(2)	−582(2)	649(2)	1 102(1)
C(10)	1 574(9)	2 716(9)	2 546(5)
C(11)	1 853(10)	3 908(9)	2 441(6)
F(11)	2 287(7)	4 235(5)	1 767(4)
C(12)	1 734(12)	4 826(9)	2 963(7)
F(12)	2 028(9)	5 977(6)	2 807(5)
C(13)	1 329(12)	4 575(11)	3 643(7)
F(13)	1 215(9)	5 458(7)	4 177(4)
C(14)	1 075(10)	3 409(11)	3 811(5)
F(14)	709(7)	3 147(7)	4 488(3)
C(15)	1 190(9)	2 522(9)	3 256(6)
F(15)	901(7)	1 375(6)	3 443(3)
C(20)	3 597(9)	1 731(8)	2 383(5)
C(21)	4 881(10)	2 790(9)	2 513(5)
F(21)	4 938(6)	3 824(5)	2 229(4)
C(22)	6 236(10)	2 968(10)	2 936(6)
F(22)	7 468(6)	4 041(6)	3 034(4)
C(23)	6 299(10)	1 980(11)	3 238(5)
F(23)	7 602(6)	2 100(7)	3 626(4)
C(24)	5 048(10)	881(10)	3 132(5)
F(24)	5 097(6)	−90(6)	3 437(3)
C(25)	3 728(9)	765(9)	2 712(5)
F(25)	2 529(6)	−349(5)	2 636(3)
N(1)	7 770(8)	7 509(6)	2 838(4)
C(30)	6 864(10)	6 721(8)	3 341(6)
C(31)	6 500(12)	7 401(10)	4 026(6)
C(32)	5 609(13)	6 457(11)	4 484(7)
C(33)	5 238(15)	7 049(13)	5 188(8)
C(40)	9 260(11)	8 521(9)	3 318(5)
C(41)	10 231(12)	8 031(11)	3 748(6)
C(42)	11 493(14)	9 153(13)	4 323(7)
C(43)	12 604(17)	8 829(16)	4 685(9)
C(50)	6 988(11)	8 230(9)	2 465(6)
C(51)	5 488(12)	7 403(11)	1 942(7)
C(52)	4 820(17)	8 162(14)	1 590(8)
C(53)	3 308(18)	7 415(18)	1 111(10)
C(60)	8 026(11)	6 647(9)	2 212(6)
C(61)	8 847(12)	7 218(13)	1 616(6)
C(62)	8 616(40)	5 934(33)	948(15)
C(63)	890(7)	607(6)	59(3)
C(1)	3 559(13)	859(17)	532(7)
C(01)	3 759(15)	2 156(17)	377(8)
C(2)	−1 183(12)	1 921(10)	987(6)
C(02)	−2 110(13)	2 014(13)	1 566(8)

Table 4 Selected bond lengths (Å) and angles (°) for complex **7**

Ni(1)–S(1)	2.199(3)	Ni(2)–S(2)	2.211(3)
Ni(1)–S(2)	2.208(3)	Ni(2)–C(10)	1.93(1)
Ni(1)–S(2)	2.216(5)	Ni(2)–C(20)	1.914(8)
S(1)–Ni(1)–S(2)	81.09(9)	S(2)–Ni(2)–C(10)	96.6(3)
S(1)–Ni(1)–S(2′)	98.91(9)	S(1)–Ni(2)–C(20)	92.7(3)
C(10)–Ni(2)–C(20)	90.7(4)	S(1)–Ni(2)–C(10)	174.9(3)
S(2)–Ni(2)–C(20)	168.6(3)	S(1)–Ni(2)–S(2)	80.6(1)

The primed atom is generated by −*x*, −*y*, −*z*.

hetero-bridged complexes $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}L)(\mu\text{-}SR)]$ as shown in equation (2) (X = C, R = H **8**, Ph **9** or C_6H_4Me-*p* **10**; X = N, R = H **11**, Ph **12** or C_6H_4Me-*p* **13**). Alternatively, these complexes can be prepared by reaction of $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2]$ with a thiol and an azole in 1 : 1 : 1 molar ratio.



Some relevant data for the hetero-bridged complexes are presented in Table 1 and the infrared spectra show the characteristic bands of the pentafluorophenyl group.[20,21] The ^1H and ^{19}F NMR data are listed in Table 2. The ^1H NMR spectra of complexes **8** and **11** show the SH resonance at δ − 2.04 and −2.23, respectively, indicating larger electronic charge delocalization over the $Ni_2(N\text{–}N)S$ ring in comparison with the four-membered ring of complex **1**. The pz ligand in complexes **8**–**10** gives one triplet (H^4) and one doublet (H^3 and H^5), with relative intensities of 1 : 2, as expected for a bridging pz ligand.[13,34,35] The presence of a single tz resonance in the ^1H NMR spectra of **11**–**13** is also consistent with a bridging triazolate ligand.[13] The overall NMR patterns observed in the ^{19}F spectra of complexes **8**–**13** indicate the presence of two equivalent C_6F_5 rings *trans* to S and two equivalent C_6F_5 rings *trans* to N, although due to overlapping of some signals the number of observed resonances is smaller than the theoretically expected six resonances corresponding to four freely rotating C_6F_5 rings.

Experimental

Carbon, H and N analyses were carried out with a Carlos Erba instrument. Infrared spectra were recorded on a Perkin Elmer 1430 spectrophotometer using Nujol mulls between polyethylene sheets, and proton and ^{19}F NMR spectra on a Brucker AC 200E or a Varian 300 instrument. Conductance measurements were performed with a Crison 525 conductimeter (in acetone solution, $c \approx 5 \times 10^{-4}$ mol dm^{-3}). Decomposition temperatures were determined on a Reichert microscope. All the solvents were dried by conventional methods. The complexes $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2]$ and $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}OH)(\mu\text{-}L)]$ (L = pz or tz) were prepared as described elsewhere.[13]

Preparations.—Complex **1**. A stream of hydrogen sulfide was passed through a solution of $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2]$ (150 mg, 0.115 mmol) in methanol (15 cm^3) at room temperature for 1 min and the initially orange solution became dark red. The solution was then stirred at room temperature for 15 min. After reduction of the solvent to 1 cm^3 under reduced pressure, the addition of propan-2-ol caused the precipitation of complex **1** as a red-brown solid, which was filtered off, washed with hexane and air-dried.

Complex **2**. Methanethiol was bubbled for 1 min through a solution of $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}OH)_2]$ (150 mg, 0.115 mmol) in methanol (15 cm^3) at room temperature. The colour of the solution turned from orange to deep brown. After 15 min with constant stirring, the solution was concentrated under reduced pressure, and the addition of propan-2-ol caused the complete precipitation of a brown solid, which was filtered off, washed with hexane and air-dried.

Complexes **3**–**6**. The appropriate thiol (0.23 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 methanol (15 cm^3), and the solution was stirred at room temperature for 30 min. It was then concentrated under reduced pressure to *ca.* 1 cm^3, and propan-2-ol was added to precipitate the binuclear complexes, which were filtered off, washed with hexane and air-dried.

Complex **7**. Excess of ethanethiol (1 cm^3) 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 methanol (15 cm^3) and the mixture was boiled under reflux for 5 h. The solvent was then partly evaporated under reduced pressure to half the original volume, whereupon red crystals of the trinuclear complex **7** formed, which were filtered off, washed with hexane and air-dried (24.5 mg, 20% yield). The filtered solution was further concentrated to *ca.* 1 cm^3, and the addition of propan-2-ol resulted in the precipitation of the dinuclear complex **3** (73.1 mg, 59%).

Complexes **8** *and* **11**. Hydrogen sulfide was bubbled for 1 min through a solution of $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}OH)(\mu\text{-}L)]$ (0.11 mmol; L = pz or tz) in dichloromethane (10 cm^3). After stirring for 15 min, the solution was vacuum-concentrated to *ca.* 1 cm^3. The addition of isopropanol caused precipitation of the yellow complexes **8** and **11**, which were filtered off, washed with hexane and air-dried.

Complexes **9**, **10**, **12** *and* **13**. Method A. The appropriate thiol (0.115 mmol) was added to a solution of $[NBu_4]_2[Ni_2(C_6F_5)_4(\mu\text{-}OH)(\mu\text{-}L)]$ (150 mg, 0.115 mmol; L = pz or tz) in acetone (10 cm^3). The solution was stirred for 30 min, then concentrated under reduced pressure to *ca.* 1 cm^3. The addition of isopropanol precipitated the complexes, which were filtered off, washed with hexane and air-dried.

Method B. The appropriate thiol (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 acetone (10 cm^3). After stirring the solution for 30 min, the azole (0.115 mmol) was added and stirring was prolonged for 30 min. The solution was then concentrated under reduced pressure to *ca.* 1 cm^3. The addition of isopropanol caused the precipitation of the complexes, which were filtered off, washed with hexane and air-dried.

X-Ray Structure Determination of Complex **7**.—Crystallographic data and other parameters are given in Table 5. Measurements were made on an Enraf–Nonius CAD4 diffractometer, with bisecting geometry, a graphite orientated monochromator with Mo-Kα radiation (λ = 0.710 69 Å) and $\omega/2\theta$ scans up to 25°. Unit-cell parameters were refined from a least-squares fit from 25 reflections (θ < 25°). Two standard reflections measured every 60 min showed no variation. Solution was achieved using the heavy-atom (Ni) method followed by normal Fourier synthesis and full-matrix least-

Table 5 Crystal data and data collection parameters for complex **7**

Formula	$C_{64}H_{92}F_{20}N_2S_4Ni_3$
M	1573.78
Crystal habit	Rectangular prisms
Crystal size/mm	0.13 × 0.33 × 0.33
Symmetry, space group	Triclinic, $P\bar{1}$
Unit-cell dimensions	a = 10.029(4), b = 11.81(2), c = 17.610(8) Å α = 98.7(1), β = 96.71(4), γ = 114.0(2)°
U/Å^3, Z	1846(5), 1
D_c/g cm^{-3}, F(000)	1.415, 818
μ/cm^{-1}	9.55
Reflections measured	6955
Independent reflections	6466
Observed reflections	3398 [$I > 2\sigma(I)$]
Number of variables	548
Degrees of freedom	1880
Ratio of freedom	6.2
Final R, R'*	0.052, 0.062

* $R = (\Sigma|F_o| - |F_c|)/\Sigma|F_o|$, $R' = \{[\Sigma w(|F_o| - |F_c|)^2]/\Sigma w|F_o|^2\}^{\frac{1}{2}}$.

squares refinement (in 3 blocks), with H atoms located on a difference synthesis map,[36,37] carried out on a VAX 6410 machine. Scattering and anomalous dispersion factors were taken from ref. 38. All non-hydrogen atoms were refined anisotropically except C(63) (terminal atom of the chain in the cation) which was affected by severe thermal movement, and was refined isotropically. Most H atoms were refined isotropically but the thermal parameters of some of them were kept fixed. In the final cycles of refinement a weighting scheme[39] was applied so as to give no trends in $\langle w\Delta^2F\rangle$ *vs.* $\langle F_o\rangle$ and *vs.* $\langle \sin\theta/\lambda\rangle$ with $w = k/(\sigma_1^2 \times \sigma_2^2)$ where $k = 1$, $\sigma_1 = f(F_o)$ and $\sigma_2 = g(\sin\theta/\lambda)$.

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

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