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## Reactivity of the $[\{\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})\}_2]^{2-}$ ion towards $\beta$ -diketones, 8-hydroxyquinoline and heterocyclic thiones. Crystal structure of $[\text{NBu}_4][\text{Ni}(\text{C}_6\text{F}_5)_2(\text{C}_5\text{H}_4\text{NS-2})]$

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### Abstract

The di- $\mu$ -hydroxo-complex  $[\text{NBu}_4]_2[\{\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})\}_2]$  reacts with protic electrophiles  $\text{H}(\text{LL})$  in the 1/2 molar ratio to give  $(\text{NBu}_4)[\text{Ni}(\text{C}_6\text{F}_5)_2(\text{LL})]$  [ $(\text{LL}) = \text{acetylacetonate (acac)}$  (I),  $\text{benzoylacetate (bzac)}$  (II),  $\text{8-hydroxyquinolate (oxin)}$  (III),  $\text{pyridine-2-thiolate (pyt)}$  (IV),  $\text{pyrimidine-2-thiolate (pymt)}$  (V),  $\text{2,6-dimethyl-5-oxo-1,2,4-triazine-3-thiolate (tazt)}$  (VI),  $\text{N-methylimidazole-2-thiolate (mimt)}$  (VII),  $\text{thiazolidine-2-thiolate (tzt)}$  (VIII),  $\text{benzimidazole-2-thiolate (bimt)}$  (IX) or  $\text{benzothiazole-2-thiolate (btzt)}$  (X)]. The new compounds have been characterized by analysis, conductivity measurements, and spectroscopic (IR, UV-VIS,  $^1\text{H}$ , and  $^{19}\text{F}$ ) methods. The crystal structure of compound IV has been determined by X-ray diffraction. It crystallizes in the monoclinic space group  $P2_1/n$  with  $a$  11.7076(4),  $b$  22.183(1),  $c$  14.0280(6) Å,  $\beta$  105.012(3)°. Final  $R = 0.075$  and  $R_w = 0.067$  based on 3815 reflections.

### Introduction

The synthesis of binuclear anionic complexes of general formula  $[\text{R}_2\text{M}(\mu\text{-OH})_2\text{MR}_2]^{2-}$  [ $\text{M} = \text{Ni}$ ,  $\text{R} = \text{C}_6\text{F}_5$  [1],  $\text{M} = \text{Pd}$ ,  $\text{R} = \text{C}_6\text{F}_5$  [1,2],  $\text{C}_6\text{H}_2\text{F}_3\text{-2,4,6}$  [3] or  $\text{C}_6\text{Cl}_5$  [4], or  $\text{Pt}$ ,  $\text{R} = \text{C}_6\text{F}_5$  [1,5] or  $\text{C}_6\text{Cl}_5$  [4]] has been reported. Their use as precursors in synthetic work is based on the considerable nucleophilicity of the bridging OH groups, which is consistent with their high-field proton resonances. Thus these hydroxo complexes react with weak protic acids  $\text{H}(\text{L-L})$  to give mono- or bi-nuclear anionic species [1,2,5] depending on whether the deprotonated acid,

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(L-L)<sup>-</sup> is *exo*- or *endo*-bidentate. Mononuclear neutral complexes are obtained by reaction of the hydroxo complex with a neutral ligand in the presence of acid [4,5] and deprotonation of amines or alcohols by the hydroxo complex in the presence of carbon disulfide leads to the formation of the corresponding dithiocarbamate or xanthate complexes, respectively [6].

Following our systematic study of the reactivity of hydroxo complexes of the nickel group elements towards weak protic acids, we have now investigated the reactions of  $[\{\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})\}_2]^{2-}$  with acids H(L-L) specified in the abstract, in order to obtain the complexes  $[\text{Ni}(\text{C}_6\text{F}_5)_2(\text{L-L})]^-$ , where L-L is an *O,O*-, *O,N*- or *N,S*-donor *endo*-bidentate ligand.

## Experimental

C, H, and N analyses were obtained with a Perkin-Elmer 240C microanalyzer. Melting points were determined on a Reichert microscope. Molar conductivities were measured in acetone solution ( $c \approx 5 \cdot 10^{-4} \text{ M}$ ) with a Crison 525 conductimeter. The spectroscopic instruments used were Perkin-Elmer 1430 for IR spectra (Nujol mulls), Hitachi 2000U for UV-VIS spectra and Bruker AC 200E (<sup>1</sup>H) or Varian FT 80A (<sup>19</sup>F) for NMR spectra. SiMe<sub>4</sub> and CFCl<sub>3</sub> were used as internal standards, respectively.

The precursor (NBu<sub>4</sub>)<sub>2</sub>[\{\text{Ni}(\text{C}\_6\text{F}\_5)\_2(\mu\text{-OH})\}\_2] was prepared as described elsewhere [1] and 2,6-dimethyl-5-oxo-3-thioxo-1,2,4-triazine was synthesised as described in ref. 7. Solvents were dried by standard methods before use.

(NBu<sub>4</sub>)[Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(LL)] [LL = *acac* (I), *bzac* (II), or *oxin* (III)]

H(LL) (0.154 mmol) was added to a solution of (NBu<sub>4</sub>)<sub>2</sub>[\{\text{Ni}(\text{C}\_6\text{F}\_5)\_2(\mu\text{-OH})\}\_2] (0.1 g, 0.077 mmol) in acetone (10 ml). The solution was stirred at room temperature for 30 min, then concentrated under reduced pressure. Addition of n-hexane caused precipitation of the yellow complexes I-III, which were filtered off and air-dried.

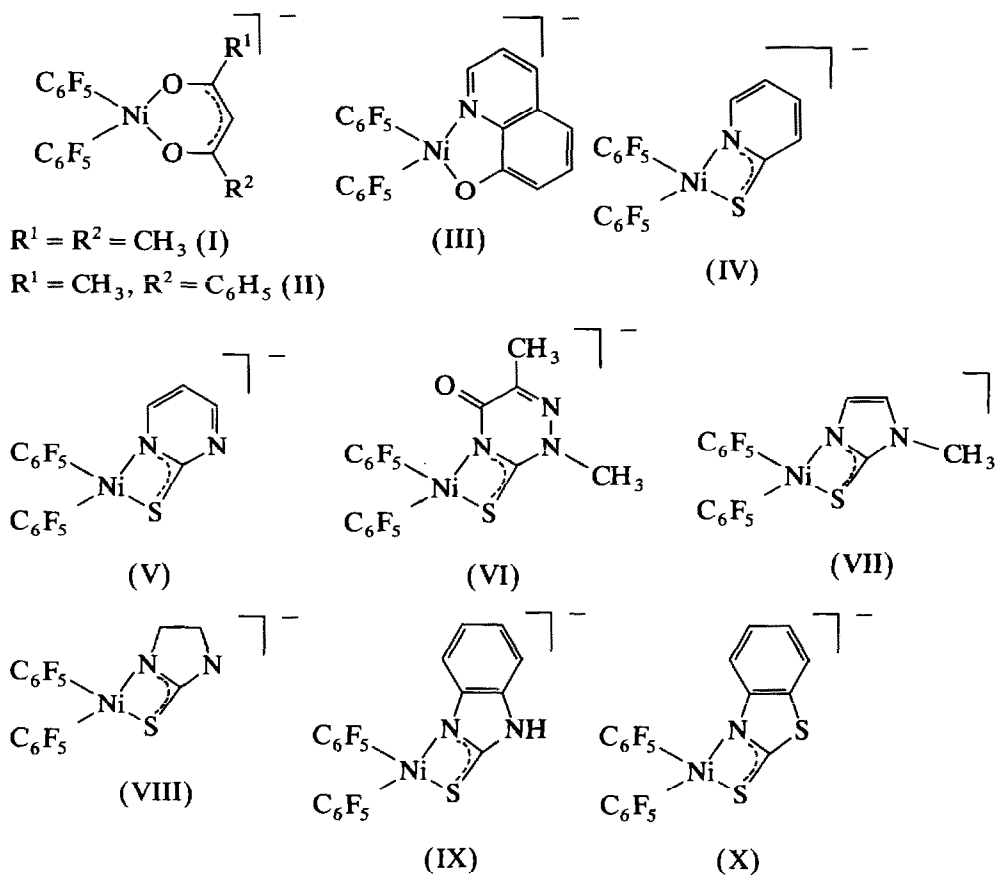
(NBu<sub>4</sub>)[Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>(LL)] [LL = *pvt* (IV), *pymt* (V), *tazt* (VI), *mimt* (VII), *tzt* (VIII), *bimt* (IX), or *btzt* (X)]

In separate experiments, the stoichiometric amount (0.282 mmol) of the required base was added to a solution of (NBu<sub>4</sub>)<sub>2</sub>[\{\text{Ni}(\text{C}\_6\text{F}\_5)\_2(\mu\text{-OH})\}\_2] (0.15 g, 0.141 mmol) in dichloromethane (10 ml). The solution was stirred at room temperature for 30 min, then concentrated under reduced pressure to half the original volume. Addition of diethyl ether resulted in the precipitation of the complex as a yellow (IV, V) or orange (VI-X) solid. These were filtered off and air-dried.

### Crystal structure of compound IV

Crystal data: NiSN<sub>2</sub>C<sub>33</sub>H<sub>45</sub>F<sub>10</sub>, monoclinic,  $P2_1/n$ ,  $a$  11.7076(4),  $b$  22.183(1),  $c$  14.0280(6) Å,  $\beta$  105.012(3)°,  $V$  3518.6(3) Å<sup>3</sup>,  $D_c$  1.417 g cm<sup>-3</sup>,  $M$  = 750.49,  $F(000)$  = 1564,  $\mu$  6.859 cm<sup>-1</sup>,  $Z$  = 4.

6304 reflections up to  $\theta = 65^\circ$  (5859 independent) were measured on a Philips PW1100 diffractometer with graphite monochromated Cu-K<sub>α</sub> radiation, using the  $\omega/2\theta$  scan mode. 3815 reflections were considered as observed, using the criterion  $I > 3\sigma(I)$ . Scattering factors and anomalous dispersion coefficients were taken



Scheme 1. The anions of compounds I-X.

from ref. 8. The heavy-atom (Ni) method and DIRDIF [9] system were followed by normal Fourier synthesis. Most of the H atoms were found on a difference map; others were located at the calculated positions [10].

Full-matrix least-squares refinements [11], 496 variables, 321 degrees of freedom, ratio of freedom 1.65, non-H atoms anisotropic, H atoms isotropic. Least-squares weights were applied so as to give no trends in  $\langle w\Delta^2F \rangle$  vs.  $\langle F_o \rangle$  and  $\langle \sin \theta/\lambda \rangle$  with  $w = K/(\sigma_1^2 \cdot \sigma_2^2)$  where  $K = 1$ ,  $\sigma_1 = f(F_o)$  and  $\sigma_2 = g(\sin \theta/\lambda)$  [12]. Final  $R$  and  $R_w$  were 0.075 and 0.067, respectively. Geometrical calculations were performed with PARST [13] on a VAX 6410. Tables of structure factors, full distances and angles and hydrogen atom positions, are available from the authors.

## Results and discussion

The proton resonance at  $\delta -5.7$  ppm for the OH bridges in  $[\{\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})\}_2]^{2-}$  is consistent with its chemical reactivity towards protic acids [1,14]. The reaction was carried out either in acetone (for I-III) or dichloromethane (for

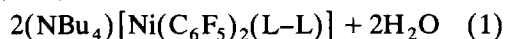
Table 1

Analytical data, yields, decomposition temperatures, and conductivities

Compound	Yield (%)	Analysis (%) <sup>a</sup>			Decomp. Temp. (°C)	$\Lambda_M^b$ ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )
		C	H	N		
I	85	53.8 (54.0)	5.9 (5.9)	1.7 (1.9)	165	95
II	74	57.5 (57.3)	5.6 (5.7)	1.8 (1.8)	240	90
III	73	57.0 (57.1)	5.4 (5.4)	3.7 (3.7)	208	93
IV	89	53.4 (53.2)	5.5 (5.4)	3.8 (3.7)	113	98
V	73	51.7 (51.5)	5.5 (5.3)	5.5 (5.5)	115	102
VI	83	49.7 (49.5)	5.4 (5.3)	6.7 (7.0)	128	94
VII	87	51.6 (51.4)	5.8 (5.5)	5.6 (5.6)	176	104
VIII	88	49.1 (49.4)	5.7 (5.4)	3.9 (3.7)	118	110
IX	72	53.5 (53.6)	5.3 (5.2)	5.1 (5.4)	90	109
X	67	52.5 (52.5)	5.2 (5.0)	3.4 (3.5)	113	110

<sup>a</sup> Calculated values in parentheses. <sup>b</sup> In  $(\text{CH}_3)_2\text{CO}$  ( $c = 5 \cdot 10^{-4} \text{ M}$ ).

IV–X) with formation of the mononuclear anionic complex  $[\text{Ni}(\text{C}_6\text{F}_5)_2(\text{L-L})]^-$ , according to eq. 1. The isolated complexes are sketched in Scheme 1. The slightly

$$(\text{NBu}_4)_2[\{\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})\}_2] + 2\text{H}(\text{L-L}) \rightarrow$$


[L-L = acac (I), bzac (II), oxin (III), pyt (IV), pymt (V), tazz (VI), mimt (VII), tzt (VIII), bimt (IX), or btzt (X)]

Table 2

Important IR (in Nujol) and UV–VIS (in acetone) data

Complex	IR bands ( $\text{cm}^{-1}$ )	UV–VIS <sup>a</sup> ( $\text{cm}^{-1} \times 10^{-3}$ )
I	1570, 1515, 1395, 450	22.4 (481)
II	1560, 1505, 1395, 460	22.6 sh
III	1565, 1390, 820	22.5 sh
IV	1570, 1420, 1135, 760	22.4 sh
V	1565, 1550, 1250, 1210, 1170, 1000, 750, 680, 310, 225	22.9 sh
VI	1650, 1350, 1005, 870	22.2 (292)
VII	1520, 1280, 1020, 690, 310	22.1 (296)
VIII	1525, 1350, 1280, 1150, 975, 740, 690	21.4 (436)
IX	3460, 1340, 1270, 1010, 735, 320	21.4 (334)
X	1490 sh, 1350, 1010, 850, 700, 310, 290	21.5 (358)

<sup>a</sup> Values in parentheses are for  $\epsilon_{\text{max}}$  ( $\text{cm}^{-1} \text{ mol}^{-1} \text{ L}$ ).

acidic proton of H(LL) is abstracted by the hydroxo-nickel complex, forming (L-L)<sup>-</sup> and providing the metal substrate (the Ni(C<sub>6</sub>F<sub>5</sub>)<sub>2</sub>-moiety) which is trapped by the anion to form the new nickel complex with the concomitant release of water. The palladium [2] and platinum [5] analogues of compounds I-III were prepared by a similar experimental procedure.

The coordination chemistry of heterocyclic thiones has received considerable attention in recent years [15] because thiolate coordination occurs in many metal-

Table 3

NMR data (solvent acetone-*d*<sub>6</sub>; *J* in Hz)

Complex	$\delta(^1\text{H})$ (ppm) (SiMe <sub>4</sub> ) <sup>a</sup>	$\delta(^{19}\text{F})$ (ppm) (CFCl <sub>3</sub> )
I	5.21 (1H, s, CH)	-115.9 (4F <sub>o</sub> , d, <i>J</i> <sub>om</sub> 26.2)
	1.59 (6H, s, CH <sub>3</sub> )	-166.0 (2F <sub>p</sub> , t, <i>J</i> <sub>mp</sub> 19.5) -167.8 (4F <sub>m</sub> , m)
II	7.56 (2H, m, Ph)	-116.2 (4F <sub>o</sub> , m)
	7.25 (3H, m, Ph)	-165.8 (2F <sub>p</sub> , t, <i>J</i> <sub>mp</sub> 19.3)
	6.01 (1H, s, CH)	-167.7 (4F <sub>m</sub> , m)
	1.78 (3H, s, CH <sub>3</sub> )	
III	8.16 (1H, d, <i>J</i> 7.9)	-114.3 (2F <sub>o</sub> , d, <i>J</i> <sub>om</sub> 33.0)
	7.32-7.13 (3H, m)	-115.3 (2F <sub>o</sub> , d, <i>J</i> <sub>om</sub> 30.1)
	6.74 (1H, d, <i>J</i> 7.9)	-164.2 (1F <sub>p</sub> , t, <i>J</i> <sub>mp</sub> 19.8)
	6.50 (1H, d, <i>J</i> 7.7)	-166.4 (4F <sub>m</sub> + 1F <sub>p</sub> , m)
IV	7.31 (1H, m, H <sup>6</sup> )	-113.8 (4F <sub>o</sub> , m)
	6.65 (1H, m, H <sup>3</sup> )	-164.5 (1F <sub>p</sub> , t, <i>J</i> <sub>mp</sub> 19.3)
	6.47 (2H, m, H <sup>4</sup> and H <sup>5</sup> )	-166.9 (4F <sub>m</sub> + 1F <sub>p</sub> , m)
V	8.23 (1H, dd, H <sup>6</sup> , <i>J</i> <sub>56</sub> 5.0, <i>J</i> <sub>46</sub> 2.3)	-113.8 (2F <sub>o</sub> , d, <i>J</i> <sub>om</sub> 33.1)
	6.99 (1H, dd, H <sup>4</sup> , <i>J</i> <sub>45</sub> 5.0, <i>J</i> <sub>46</sub> 2.3)	-114.7 (2F <sub>o</sub> , d, <i>J</i> <sub>om</sub> 32.2)
	6.60 (1H, pseudotriplet, H <sup>5</sup> , <i>J</i> <sub>45</sub> = <i>J</i> <sub>56</sub> = 5.0)	-164.3 (1F <sub>p</sub> , t, <i>J</i> <sub>mp</sub> 20.0)
		-166.0 (1F <sub>p</sub> + 2F <sub>m</sub> , m) -167.5 (2F <sub>m</sub> , m)
VI	3.54 (3H, s, CH <sub>3</sub> -N)	-114.2 (2F <sub>o</sub> , d, <i>J</i> <sub>om</sub> 33.2)
	2.03 (3H, s, CH <sub>3</sub> -C)	-115.1 (2F <sub>o</sub> , d, <i>J</i> <sub>om</sub> 30.7)
		-165.7 (1F <sub>p</sub> , t, <i>J</i> <sub>mp</sub> 19.0) -166.6 (1F <sub>p</sub> , t, <i>J</i> <sub>mp</sub> 19.6) -168.0 (4F <sub>m</sub> , m)
VII	6.61 (1H, d, H <sup>4</sup> , <i>J</i> <sub>45</sub> 1.6)	-112.9 (4F <sub>o</sub> , m)
	6.32 (1H, d, H <sup>5</sup> , <i>J</i> <sub>54</sub> 1.6)	-167.4 (2F <sub>p</sub> + 4F <sub>m</sub> , m)
VIII	3.79 (3H, s, CH <sub>3</sub> )	
	3.15 (4H, m, H <sup>5</sup> and H <sup>6</sup> )	-113.4 (2F <sub>o</sub> , d, <i>J</i> <sub>om</sub> 32.9)
		-114.8 (2F <sub>o</sub> , d, <i>J</i> <sub>om</sub> 31.6)
		-165.1 (1F <sub>p</sub> , t, <i>J</i> <sub>mp</sub> 19.6)
		-165.9 (1F <sub>p</sub> , t, <i>J</i> <sub>mp</sub> 18.9) -167.3 (4F <sub>m</sub> , m)
IX	11.0 (1H, br, NH)	-113.6 (4F <sub>o</sub> , m)
	7.21 (1H, d, <i>J</i> 7.0)	-165.1 (1F <sub>p</sub> , <i>J</i> <sub>mp</sub> 19.9)
	6.83 (2H, m, H <sup>5</sup> and H <sup>6</sup> )	-166.0 (1F <sub>p</sub> , t, <i>J</i> <sub>mp</sub> 19.9)
	6.00 (1H, d, <i>J</i> 7.3)	-167.6 (4F <sub>m</sub> , m)
X	7.66 (1H, m, H <sup>7</sup> )	-114.1 (4F <sub>o</sub> , m)
	7.05 (2H, m, H <sup>5</sup> and H <sup>6</sup> )	-164.0 (1F <sub>p</sub> , t, <i>J</i> <sub>mp</sub> 19.6)
	6.05 (1H, m, H <sup>4</sup> )	-165.3 (1F <sub>p</sub> , t, <i>J</i> <sub>mp</sub> 19.5) -166.8 (4F <sub>m</sub> , m)

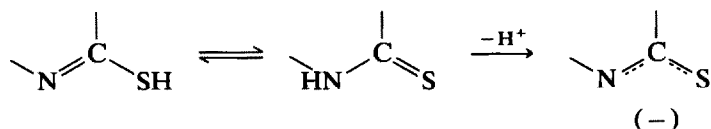
<sup>a</sup> Additional peaks of [NBu<sub>4</sub>]<sup>+</sup> are found at *ca.* 3.7 (t, N-CH<sub>2</sub>), 1.8 (m, N-CH<sub>2</sub>-CH<sub>2</sub>), 1.5 (m, CH<sub>2</sub>-CH<sub>3</sub>) and 1.0 (t, CH<sub>3</sub>), the relative intensities being 8/8/8/12.

Table 4

Atomic parameters ( $\times 10^4$ ) for compound IV. Coordinates and thermal parameters as  $U_{eq} = (1/3)\Sigma[U_{ij} \cdot a_i^* \cdot a_j^* \cdot \cos(a_i, a_j)] \cdot 10^3$

Atom	x	y	z	$U_{eq}$
Ni	1375(1)	-3543(0)	2716(1)	70(0)
S	1052(2)	-2889(1)	1443(1)	67(0)
N1	-179(4)	-3219(2)	2582(4)	53(1)
C1	-1078(6)	-3261(3)	2992(5)	63(2)
C2	-2099(6)	-2907(3)	2661(6)	75(2)
C3	-2158(6)	-2510(3)	1895(6)	75(2)
C4	-123(6)	-2464(3)	1459(5)	65(2)
C5	-242(5)	-2827(3)	1823(4)	54(1)
C10	2934(5)	-3758(3)	2705(4)	53(1)
C11	3204(6)	-4126(3)	2005(5)	62(2)
F11	2323(4)	-4360(2)	1281(3)	81(1)
C12	4336(7)	-4261(3)	1978(6)	78(2)
F12	4543(5)	-4618(2)	1250(4)	105(2)
C13	5269(7)	-4033(4)	2677(7)	78(2)
F13	6389(4)	-4164(3)	2654(5)	123(2)
C14	5059(6)	-3668(4)	3389(6)	75(2)
F14	5980(4)	-3429(3)	4083(4)	112(2)
C15	3914(5)	-3546(3)	3398(5)	61(2)
F15	3762(4)	-3172(2)	4128(3)	84(1)
C20	1433(5)	-4061(3)	3801(4)	52(1)
C21	1411(5)	-3853(3)	4724(5)	60(2)
F21	1380(4)	-3240(2)	4868(3)	81(1)
C22	1422(6)	-4206(4)	5516(5)	71(2)
F22	1414(5)	-3954(3)	6402(3)	105(2)
C23	1452(6)	-4810(4)	5436(5)	71(2)
F23	1454(4)	-5178(2)	6208(4)	105(1)
C24	1474(5)	-5056(3)	4543(6)	68(2)
F24	1487(4)	-5666(2)	4438(4)	99(1)
C25	1446(5)	-4683(3)	3767(4)	56(2)
F25	1472(4)	-4958(2)	2900(3)	76(1)
N2	2697(6)	3745(3)	1206(4)	75(2)
C30	3534(7)	3342(4)	826(6)	80(2)
C31	4654(8)	3610(5)	727(7)	101(3)
C32	5321(10)	3166(6)	275(10)	127(4)
C33	6567(11)	3314(8)	296(11)	151(5)
C40	2226(9)	4249(4)	479(7)	98(2)
C41	1614(11)	4061(5)	-540(8)	132(3)
C42	1094(17)	4608(7)	-1160(11)	176(5)
C43	1802(23)	5054(9)	-1309(10)	205(9)
C50	1731(7)	3333(4)	1350(7)	89(2)
C51	699(9)	3628(5)	1652(9)	116(3)
C52	-88(12)	3143(7)	1969(16)	129(5)
C53	452(15)	2855(9)	2887(16)	136(5)
C60	3311(9)	4103(4)	2132(6)	91(2)
C61	3804(14)	3732(6)	3001(8)	136(4)
C62	4474(16)	4130(8)	3833(9)	168(5)
C63	5481(15)	4333(10)	3775(14)	192(6)

loenzymes. Complexes IV–X all have in common the N–C–S structural group generated by deprotonation of a heterocyclic thione (represented below by its thione and thiol tautomers). This group may coordinate as monodentate through



the S donor or bidentate through the S and N donors [16]. In the latter case, the bridging or the chelating mode may be adopted [16–21], although for first-row transition-metal ions a four-membered chelate ring is generally formed in spite of its small bite [20,21]. This coordination mode has been confirmed by X-ray diffraction for the pyt complex IV.

The new bis(pentafluorophenyl)nickel derivatives are air-stable solids with the decomposition temperatures listed in Table 1. Their molar conductivities (Table 1) indicate that they are 1:1 electrolytes [22] in acetone solution, consistent with the proposed structure. The IR spectra show absorptions attributed to the  $\text{C}_6\text{F}_5$  group [23] at *ca.* 1630m, 1490vs, 1050s and 950vs  $\text{cm}^{-1}$ , as well as a broad or split band at *ca.* 780  $\text{cm}^{-1}$  for the so-called 'X-sensitive' mode of  $\text{C}_6\text{F}_5$ , which is characteristic of the *cis*- $\text{Ni}(\text{C}_6\text{F}_5)_2$  fragment [24]. The most relevant IR bands of the anionic ligands are presented in Table 2. The electronic spectra show an absorption band (Table 2) which may be assigned to the  ${}^1\text{A}_{1g} \rightarrow {}^1\text{A}_{2g}$  transition in a square-planar ligand field [25].

The  ${}^1\text{H}$  and  ${}^{19}\text{F}$  NMR data for complexes I–X are listed in Table 3. The  ${}^{19}\text{F}$  spectrum of complex I is consistent with the presence of two equivalent  $\text{C}_6\text{F}_5$  groups rotating freely around the Ni–C bond and the expected three 4/2/4 signals

Table 5

Selected bond distances (Å) and angles (deg) with e.s.d.s in parentheses

Ni–S	2.257(2)	C10–C15	1.38(8)
Ni–N1	1.919(5)	C11–C12	1.369(11)
Ni–C10	1.891(6)	C12–C13	1.362(11)
Ni–C20	1.894(6)	C13–C14	1.357(13)
S–C5	1.737(7)	C14–C15	1.371(10)
N1–C1	1.327(10)	C20–C21	1.381(9)
N1–C5	1.362(8)	C20–C25	1.381(9)
C1–C2	1.405(9)	C21–C22	1.357(11)
C2–C3	1.377(11)	C22–C23	1.346(13)
C3–C4	1.381(11)	C23–C24	1.373(11)
C4–C5	1.394(9)	C24–C25	1.361(10)
C10–C11	1.375(10)		
C10–Ni–C20	91.2(3)	C1–N1–C5	119.7(5)
N1–Ni–S	73.8(2)	N1–C1–C2	121.3(6)
N1–Ni–C20	98.2(2)	C1–C2–C3	118.8(7)
N1–Ni–C10	170.4(2)	C2–C3–C4	120.4(7)
S–Ni–C10	96.8(2)	C3–C4–C5	117.9(6)
S–Ni–C20	172.0(2)	S–C5–N1	108.3(4)
C11–C10–C15	113.7(6)	N1–C5–C4	121.8(6)
C21–C20–C25	111.7(5)		

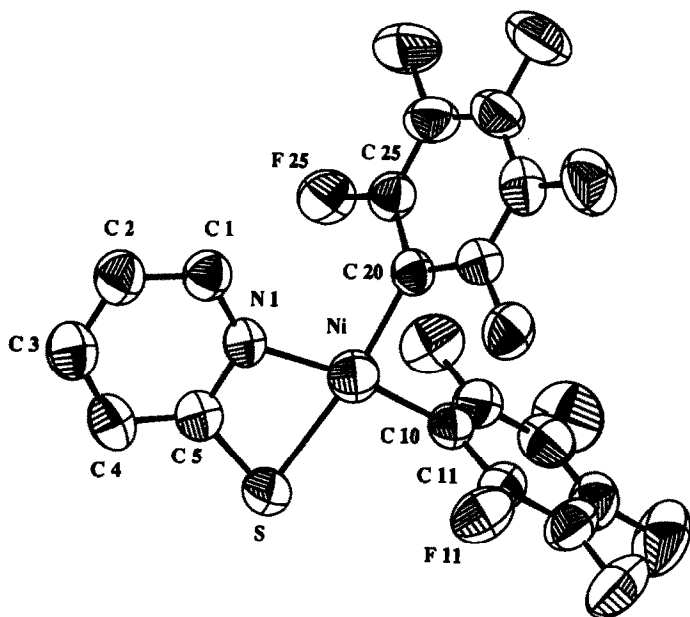


Fig. 1. ORTEP drawing [26] of the  $[\text{Ni}(\text{C}_6\text{F}_5)_2(\text{pyt})]^-$  anion showing 50% probability ellipsoids and the atom-labeling scheme. Hydrogen atoms are omitted for clarity.

are observed for the *o*-, *p*- and *m*-fluorine atoms, respectively. Complex III gives two 2/2 resonances in the *o*-fluorine region, indicating that there are two inequivalent  $\text{C}_6\text{F}_5$  groups, one *trans* to O and one *trans* to N. However, complex II, which contains the asymmetric ligand bzac, gives two unresolved multiplet resonances in the same spectral region. The  $^{19}\text{F}$  NMR patterns exhibited by all the other complexes are similar to those of complexes II (compounds IV and VII–IX) and III (compounds V, VI and X).

#### Crystal structure of $[\text{NBu}_4][\text{Ni}(\text{C}_6\text{F}_5)_2(\text{pyt})]$ (IV)

The structure contains  $[\text{Ni}(\text{C}_6\text{F}_5)_2(\text{pyt})]^-$  anions and  $[\text{NBu}_4]^+$  cations held together by electrostatic interactions. A view of the anion is depicted in Fig. 1. Table 4 lists the atomic coordinates, and relevant bond distances and angles are shown in Table 5.

The Ni atom and the four atoms coordinated to it deviate slightly from the mean plane defined by them, with the largest deviation from the least-squares plane being 0.020(5) Å for the N1 atom. The angles around Ni deviate from the square-planar coordination (see Table 5) due to the small “bite” of the bidentate ligand. However, the S–Ni–N1 “bite” angle, 73.8(2)°, is greater than that found in other pyridine–thiolate  $\text{Ni}^{\text{II}}$  complexes [27,28] whose mean value is 67.8(2)°. The Ni–N1 bond distance, 1.919(5) Å, is significantly shorter than the reported mean value of 2.056(9) Å [27,28]. Similarly, there is a shortening of the Ni–S bond distance, 2.257(2) *vs.* 2.51(1) Å (mean value).

The pyridine ring is planar, with normal N–C and S–C bond distances, 1.328(9) and 1.737(7) Å, respectively. The two pentafluorophenyl rings are planar and



rotated  $91.6(2)^\circ$  with respect to each other. There are severe distortions of the internal angles at the *ipso* positions of the ring, as occur in related compounds [29,30].

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