

171. Organonickel(II) Complexes with Anionic N-Donor Ligands. Hydration of Coordinated Nitriles at a Nickel(II) Site

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The hydroxo complex $(\text{Bu}_4\text{N})_2[\text{Ni}_2(\text{C}_6\text{F}_5)_4(\mu\text{-OH})_2]$ reacts with 2,3,4,5,6-pentafluoro benzenamine ($\text{C}_6\text{F}_5\text{-NH}_2$), 1,3-diaryltriazen-1-enes (ArNH-N=N-Ar , $\text{Ar} = \text{Ph}$, 4-Me C_6H_4 , 4-MeOC $_6\text{H}_4$), 7-aza-1*H*-indole (= 1*H*-pyrrolo[2,3-*b*]pyridine; Hazind), *N*-phenylpyridin-2-amine (pyNHPH), and *N*-phenylpyridine-2-carboxamide (pyCONHPH) at room temperature in acetone to give the binuclear complexes $(\text{Bu}_4\text{N})_2[\text{Ni}_2(\text{C}_6\text{F}_5)_4(\mu\text{-C}_6\text{F}_5\text{NH})_2]$ (1) and $(\text{Bu}_4\text{N})_2\{[\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})(\mu\text{-azind})]\}_2$ (2) and the mononuclear complexes $\text{Bu}_4\text{N}[\text{Ni}(\text{C}_6\text{F}_5)_2(\text{ArN}_3\text{Ar})]$ (3–5), $\text{Bu}_4\text{N}[\text{Ni}(\text{C}_6\text{F}_5)_2(\text{pyNHPH})]$ (6), and $\text{Bu}_4\text{N}[\text{Ni}(\text{C}_6\text{F}_5)_2(\text{pyCONHPH})]$ (7). The hydroxo complex $(\text{Bu}_4\text{N})_2\{[\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})]\}_2$ promotes the nucleophilic addition of water to pyridine-2-carbonitrile, 2-aminoacetonitrile, and 2-(dimethylamino)acetonitrile, and complexes 8–10 containing pyridine-2-carboxamidato, 2-aminoacetamidato and 2-(dimethylamino)acetamidato ligands are formed. Analytical (C, H, N) and spectroscopic (IR, ^1H and ^{19}F -NMR, and FAB-MS) data were used for structural assignments. A single-crystal X-ray diffraction study of $(\text{Bu}_4\text{N})_2\{[\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})(\mu\text{-azind})]\}_2$ (2) established the binuclear nature of the anion; the two Ni-atoms are bridged by an OH group and a 7-aza-7*H*-indol-7-yl group, but the central Ni–O–Ni–N–C–N ring is not planar, the dihedral angle between the Ni–O–Ni and Ni–N–C–N–Ni planes being 84.4°.

Introduction. – Organometallic binuclear nickel, palladium, and platinum complexes of the types $[\text{M}_2\text{R}_4(\mu\text{-OH})_2]^{2-}$ ($\text{R} = \text{C}_6\text{F}_5$, $\text{M} = \text{Ni}$ [1], Pd [2], or Pt [3]; $\text{R} = \text{C}_6\text{Cl}_5$, $\text{M} = \text{Pd}$ [4] or Pt [3]; $\text{R} = \text{C}_6\text{H}_2\text{F}_3$, $\text{M} = \text{Pd}$ [5]) and $\{[\text{MR}(\text{L})(\mu\text{-OH})]\}_2$ ($\text{M} = \text{Ni}$, $\text{L} = \text{PMe}_3$, $\text{R} = \text{Me}$ [6], 2-Me $\text{C}_6\text{H}_4\text{CH}_2$ [7], Me_3SiCH_2 , $\text{PhC}(\text{Me})_2\text{CH}_2$ or PhCH_2 [8]; $\text{L} = \text{PPh}_3$, $\text{R} = \text{CCl}_2=\text{CCl}$ [9]; $\text{M} = \text{Pd}$, $\text{L} = \text{PPh}_3$, $\text{R} = \text{Ph}$ [10], C_6F_5 , or C_6Cl_5 [11]) have been reported. The basic character of these hydroxo complexes allows the preparation of new binuclear complexes $[(\text{MR}_2)_2(\mu\text{-X})(\mu\text{-Y})]^{2-}$ ($\text{X} = \text{OH}$, $\text{HY} = \text{azoles}$ [1][2][4][12]) and $[(\text{MR}_2)_2(\mu\text{-Y})]^{2-}$ ($\text{HY} = \text{azoles}$ [1][2][4][12], thiols [13] aromatic alcohols [14], or malononitrile [15]) and mononuclear anionic complexes $[\text{MR}_2\text{X}]^-$ ($\text{HX} = \beta$ -diketones, heterocyclic thiones [16] or β -ketoimines [17]) by reaction with the corresponding protic electrophile. The nickel complex $[\text{Ni}_2(\text{C}_6\text{F}_5)_4(\mu\text{-OH})_2]^{2-}$ is an efficient catalyst for the cyclotrimerization of malononitrile to 4,6-diamino-2-(cyanomethyl)pyridine-3,5-dicarbonitrile [15].

The hydroxo complexes $[\text{M}_2(\text{C}_6\text{F}_5)_4(\mu\text{-OH})_2]^{2-}$ ($\text{M} = \text{Ni}$, Pd , Pt) react with primary and secondary amines in the presence of carbon disulfide to give dithiocarbamate complexes [18][19] and β -iminoenolato complexes have been prepared from the di- μ -hydroxo-palladium and -platinum complexes and primary amines in the presence of dimethyl acetylenedicarboxylate [20].

There is a recent interest on late transition-metal amide complexes because of their potential use to facilitate the formation of C–N bonds by insertion of unsaturated organic molecules into the metal–N bond [21][22]. Some amido complexes of Pd

and Pt have been prepared by us [23–25]. We have now investigated the reactions of $[\text{Ni}_2(\text{C}_6\text{F}_5)_3(\mu\text{-OH})_2]^{2-}$ with 2,3,4,5,6-pentafluorobenzeneamine, 7-aza-1*H*-indole (= 1*H*-pyrrolo[2,3-*b*]pyridine), 1,3-diaryltriaz-1-enes, *N*-phenylpyridin-2-amine, and *N*-phenylpyridine-2-carboxamide. The addition of water to pyridine-2-carbonitrile, 2-aminoacetonitrile and 2-(dimethylamino)acetonitrile in the presence of the above hydroxo nickel complex has also been studied.

Experimental. – 1. *General.* All the solvents were dried by conventional methods. The complex $(\text{Bu}_4\text{N})_2\{[\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})]_2\}$ [1], 1,3-diaryltriaz-1-enes [26] and *N*-phenylpyridine-2-carboxamide [27] were prepared as described elsewhere. Conductance measurements were performed with a *Criscon-525* conductimeter (in acetone soln., $c \approx 5 \cdot 10^{-4}$ mol/l). Decomposition temperatures: *Reichert* microscope. IR Spectra: *Perkin-Elmer-16F-PC-FT* spectrophotometer; nujol mulls between polyethylene sheets; $\bar{\nu}$ in cm^{-1} . ^1H - and ^{19}F -NMR Spectra: *Bruker-AC-200E* or *Varian-300* instrument, $(\text{CD}_3)_2\text{CO}$ as solvent and SiMe_4 and CFCl_3 as ref., resp.; δ in ppm, *J* in Hz. C, H, N Analyses were carried out with a *Carlo Erba* instrument.

2. *Bis(tetrabutylammonium) Bis{μ-[(pentafluorophenyl)amido- κN^1]}bis[bis(pentafluorophenyl)nickel]ate(2-)} $(\text{Bu}_4\text{N})_2\{[\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-C}_6\text{F}_5\text{NH})]_2\}$; **1**). 2,3,4,5,6-Pentafluorobenzeneamine (28.1 mg, 0.154 mmol) was added to an acetone (15 ml) soln. of bis(tetrabutylammonium) di- μ -hydroxobis[bis(pentafluorophenyl)nickel]ate(2-) $(\text{Bu}_4\text{N})_2\{[\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})]_2\}$ (100 mg, 0.077 mmol), and the mixture was stirred for 24 h. It was concentrated under reduced pressure to ca. 1 ml, and propan-2-ol was added to precipitate the complex, which was filtered off and recrystallized from $\text{CH}_2\text{Cl}_2/\text{hexane}$: 65% of **1**. M.p. 192° (dec). A_M 174 $\text{S cm}^2 \text{mol}^{-1}$. ^1H -NMR $(\text{CD}_3)_2\text{CO}$: 0.4 (s, 2 NH). ^{19}F -NMR $(\text{CD}_3)_2\text{CO}$: –116.6 (d, $J(o,m)$ = 32.2, 4F_o); –117.5 (d, $J(o,m)$ = 32.2, 4F_m); –144.1 (d, $J(o,m)$ = 22.0, 2F_o); –164.5 (d, $J(o,m)$ = 22.0, 2F_m); –166.8 (t, $J(m,p)$ 19.8, 4F_p); –167.9 (m, 4F_m); –168.3 (m, 4F_m); –169.3 (m, 2F_m); –172.0 (m, 2F_m); –177.5 (m, 2F_p). Anal. calc. for $\text{C}_{68}\text{H}_{74}\text{F}_{30}\text{N}_4\text{Ni}_2$: C 50.0, H 4.6, N 3.4; found: C 50.0, H 4.5, N 3.3.*

3. *Bis(tetrabutylammonium) μ-Hydroxo-[\mu-(1H-pyrrolo[2,3-b]pyridin-1-yl- κN^1 , κN^7)]bis[bis(pentafluorophenyl)nickel]ate(2-)} $(\text{Bu}_4\text{N})_2\{[\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})(\mu\text{-azind})]_2\}$; **2**). As described for **1**, with 1*H*-pyrrolo[2,3-*b*]pyridine (= 7-aza-1*H*-indole = Hazind; 9.1 mg, 0.077 mol), acetone (10 ml), and $(\text{Bu}_4\text{N})_2\{[\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})]_2\}$ (100 mg, 0.077 mmol; 1 h): 77% of yellow **2**. M.p. 177° (dec.). A_M 182 $\text{S cm}^2 \text{mol}^{-1}$. ^1H -NMR $(\text{CD}_3)_2\text{CO}$: –4.1 (s, OH); 6.0 (d, J = 2.6, 1 arom. H); 6.4 (m, 2 arom. H); 7.2 (d, J = 5.5, 1 arom. H); 7.5 (d, J = 5.5, 1 arom. H). ^{19}F -NMR $(\text{CD}_3)_2\text{CO}$: –113.5 (d, $J(o,m)$ = 30.5, 2F_o); –114.2 (d, $J(o,m)$ = 30.5, 4F_m); –114.8 (d, $J(o,m)$ = 30.5, 2F_m); –167.1 (m, 3F_p); –167.7 (t, $J(m,p)$ 19.8, 1F_p). Anal. calc. for $\text{C}_{63}\text{H}_{80}\text{F}_{20}\text{N}_4\text{Ni}_2$: C 53.8, H 5.7, N 4.0; found: C 53.8, H 5.5, N 4.1.*

4. *Bu₄N[Ni(C₆F₅)₂(ArN₃Ar)] Complexes 3–5.* The appropriate 1,3-diaryltriaz-1-ene (ArNHNNAr ; 0.154 mmol) was added to an acetone (15 ml) soln. of $(\text{Bu}_4\text{N})_2\{[\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})]_2\}$ (100 mg, 0.077 mmol), and the mixture was boiled under reflux for 2 h. The solvent was then partly evaporated to half the original volume. Addition of Et_2O resulted in the precipitation of the red complexes which were filtered off and recrystallized from $\text{CH}_2\text{Cl}_2/\text{hexane}$.

*Tetrabutylammonium (1,3-Diphenyltriazenido- κN^1 , κN^3)bis(pentafluorophenyl)nickelate(1-)} (Ar = Ph; **3**): Yield 80%. M.p. 173° (dec). A_M 112 $\text{S cm}^2 \text{mol}^{-1}$. ^1H -NMR $(\text{CD}_3)_2\text{CO}$: 6.6 (d, J = 7.7, 4 arom. H); 6.8 (t, J = 8.0, 2 arom. H); 7.0 (m, 4 arom. H). ^{19}F -NMR $(\text{CD}_3)_2\text{CO}$: –115.9 (d, $J(o,m)$ = 28.2, 4F_o); –164.4 (t, $J(m,p)$ = 19.8, 4F_p); –166.9 (m, 8F_m). Anal. calc. for $\text{C}_{40}\text{H}_{46}\text{F}_{10}\text{N}_4\text{Ni}$: C 57.8, H 5.6, N 6.7; found: C 57.6, H 5.5, N 6.7.*

*Tetrabutylammonium [1,3-Bis(4-methylphenyl)triazenido- κN^1 , κN^3]bis(pentafluorophenyl)nickelate(1-)} (Ar = 4-MeC₆H₄; **4**): Yield 82%. M.p. 174° (dec). A_M 105 $\text{S cm}^2 \text{mol}^{-1}$. ^1H -NMR $(\text{CD}_3)_2\text{CO}$: 2.1 (s, 2 Me); 6.5 (d, J = 8.0, 4 arom. H); 6.8 (d, J = 8.0, 4 arom. H). ^{19}F -NMR $(\text{CD}_3)_2\text{CO}$: –115.8 (d, $J(o,m)$ = 28.2, 4F_o); –164.4 (t, $J(m,p)$ = 19.8, 4F_p); –166.9 (m, 8F_m). Anal. calc. for $\text{C}_{42}\text{H}_{50}\text{F}_{10}\text{N}_4\text{Ni}$: C 58.7, H 5.9, N 6.5; found: C 58.5, H 5.8, N 6.4.*

*Tetrabutylammonium [1,3-Bis(4-methoxyphenyl)triazenido- κN^1 , κN^3]bis(pentafluorophenyl)nickelate(1-)} (Ar = 4-MeOC₆H₄; **5**): Yield 83%. M.p. 165° (dec). A_M 110 $\text{S cm}^2 \text{mol}^{-1}$. ^1H -NMR $(\text{CD}_3)_2\text{CO}$: 3.7 (s, 2 MeO); 6.5 (m, 8 arom. H). ^{19}F -NMR $(\text{CD}_3)_2\text{CO}$: –115.8 (d, $J(o,m)$ = 28.2, 4F_o); –164.4 (t, $J(m,p)$ = 19.8, 4F_p); –166.9 (m, 8F_m). Anal. calc. for $\text{C}_{42}\text{H}_{50}\text{F}_{10}\text{N}_4\text{NiO}_2$: C 56.6, H 5.6, N 6.3; found: C 56.6, H 5.4, N 6.3.*

5. *Bu₄N[Ni(C₆F₅)₂(pyNPh)] Complex 6 and Bu₄[Ni(C₆F₅)₂(pyCONPh)] Complex 7.* In separate experiments, the stoichiometric amount (0.154 mmol) of *N*-phenylpyridin-2-amine or *N*-phenylpyridine-2-carboxamide

was added to an acetone (15 ml) soln. of $(\text{Bu}_4\text{N})_2[\{\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})_2\}]_2$ (100 mg, 0.077 mmol). After stirring for 1 h, the soln. was concentrated to ca. 1 ml, and Et_2O was added to precipitate a yellow-orange solid, which was filtered off and recrystallized from $\text{CH}_2\text{Cl}_2/\text{hexane}$.

Tetrabutylammonium [Phenyl(pyridin-2-yl- κN^1)amido- κN]bis(pentafluorophenyl)nickelate(1-) (6): Yield 68%. M.p. 125° (dec.). A_M 100 $\text{S cm}^2 \text{ mol}^{-1}$. $^1\text{H-NMR}$ ($(\text{CD}_3)_2\text{CO}$): 5.9 (*t*, $J = 6.5$, 1 H); 6.4 (*d*, $J = 8.5$, 1 H); 6.5 (*m*, 3 H); 6.6 (*d*, $J = 7.0$, 1 H); 6.9 (*t*, $J = 8.5$, 2 H); 7.2 (*t*, $J = 7.0$, 1 H). $^{19}\text{F-NMR}$ ($(\text{CD}_3)_2\text{CO}$): -115.0 (*d*, $J(o,m) = 30.8$, 2F_o); -115.6 (*d*, $J(o,m) = 30.8$, 2F_o); -165.6 (*t*, $J(m,p) = 19.8$, 1F_p); -166.1 (*t*, $J(m,p) = 19.8$, 1F_p); -167.5 (*m*, 2F_m); -167.9 (*m*, 2F_m). Anal. calc. for $\text{C}_{39}\text{H}_{45}\text{F}_{10}\text{N}_3\text{Ni}$: C 58.2, H 5.6, N 5.2; found: C 58.3, H 5.6, N 5.2.

Tetrabutylammonium [N-Phenyl(pyridine- κN^1)-2-carboxamidato- κN]bis(pentafluorophenyl)nickelate(1-) (7): Yield 85%. M.p. 112° (dec.). A_M 115 $\text{S cm}^2 \text{ mol}^{-1}$. IR (nujol): 1620 (CO). $^1\text{H-NMR}$ ($(\text{CD}_3)_2\text{CO}$): 6.7 (*m*, 1 H, Ph); 6.8 (*m*, 4 H, Ph); 7.4 (*m*, 2 H, py); 7.8 (*d*, $J = 7.4$, 1 H, py); 8.0 (*m*, 1 H, py). $^{13}\text{C-NMR}$ (CDCl_3): 168.4 (CO). $^{19}\text{F-NMR}$ ($(\text{CD}_3)_2\text{CO}$): -115.3 (*t*, 2F_o); -116.4 (*t*, 2F_o); -165.0 (*t*, $J(m,p) = 19.8$, 1F_p); -166.5 (*m*, 2F_m); -167.2 (*t*, $J(m,p) = 19.8$, 1F_p); -168.4 (*m*, 2F_m). Anal. calc. for $\text{C}_{40}\text{H}_{46}\text{F}_{10}\text{N}_3\text{NiO}$: C 57.6, H 5.6, N 5.0; found: C 57.4, H 5.2, N 5.0.

6. Hydration of Coordinated Aminonitriles: Complexes 8–10. In separate experiments, the corresponding aminonitrile (pyridine-2-carbonitrile, 2-aminoacetonitrile, or 2-(dimethylamino)acetonitrile; 0.154 mmol) was added to a soln. of $(\text{Bu}_4\text{N})_2[\{\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-OH})_2\}]_2$ (100 mg, 0.077 mmol) in acetone/ H_2O 15:1 (16 ml). The mixture was boiled under reflux for 2 h and then evaporated to ca. 1 ml. Addition of Et_2O resulted in the precipitation of a yellow complex, which was filtered off and recrystallized from $\text{CH}_2\text{Cl}_2/\text{hexane}$.

Tetrabutylammonium [(Pyridine- κN^1)-2-carboxamidato- κN]bis(pentafluorophenyl)nickelate(1-) (8): Yield 75%. M.p. 105° (dec.). A_M 132 $\text{S cm}^2 \text{ mol}^{-1}$. IR (nujol): 1634 (CO). $^1\text{H-NMR}$ ($(\text{CD}_3)_2\text{CO}$): 7.3 (*m*, 2 H, py); 7.7 (*d*, $J = 6.5$, 1 H, py); 8.0 (*t*, $J = 6.5$, 1 H, py). $^{13}\text{C-NMR}$ ($(\text{CD}_3)_2\text{CO}$): 172.1 (CO). $^{19}\text{F-NMR}$ ($(\text{CD}_3)_2\text{CO}$): -114.8 (*d*, $J(o,m) = 32.2$, 2F_o); -115.5 (*d*, $J(o,m) = 32.2$, 2F_o); -164.7 (*t*, $J(m,p) = 19.9$, 1F_p); -165.9 (*t*, $J(m,p) = 19.9$, 1F_p); -166.2 (*m*, 2F_m); -167.3 (*m*, 2F_m). Anal. calc. for $\text{C}_{34}\text{H}_{41}\text{F}_{10}\text{N}_3\text{NiO}$: C 54.0, H 5.5, N 5.6; found: C 53.5, H 5.5, N 5.4.

Tetrabutylammonium [2-(Amino- κN)-acetamidato- κN]bis(pentafluorophenyl)nickelate(1-) (9): Yield 65%. M.p. 110° (dec.). A_M 125 $\text{S cm}^2 \text{ mol}^{-1}$. IR (nujol): 1630 (CO). $^1\text{H-NMR}$ ($(\text{CD}_3)_2\text{CO}$): 2.8 (*s*, CH_3). $^{13}\text{C-NMR}$ ($(\text{CD}_3)_2\text{CO}$): 178.5 (CO). $^{19}\text{F-NMR}$ ($(\text{CD}_3)_2\text{CO}$): -115.4 (*m*, 4F_o); -166.2 (*t*, $J(m,p) = 19.9$, 1F_p); -166.9 (*t*, $J(m,p) = 19.9$, 1F_p); -167.6 (*m*, 2F_m); -168.1 (*m*, 2F_m). Anal. calc. for $\text{C}_{30}\text{H}_{41}\text{F}_{10}\text{N}_3\text{NiO}$: C 50.9, H 5.8, N 5.9; found: C 51.0, H 5.8, N 5.9.

Tetrabutylammonium [2-(Dimethylamino- κN)acetamidato- κN]bis(pentafluorophenyl)nickelate(1-) (10): Yield 65%. M.p. 110° (dec.). A_M 130 $\text{S cm}^2 \text{ mol}^{-1}$. IR (nujol): 1630 (CO). $^1\text{H-NMR}$ ($(\text{CD}_3)_2\text{CO}$): 2.1 (*s*, 6 H). $^{13}\text{C-NMR}$ ($(\text{CD}_3)_2\text{CO}$): 179.2 (CO). $^{19}\text{F-NMR}$ ($(\text{CD}_3)_2\text{CO}$): -115.3 (*d*, $J(o,m) = 30.5$, 2F_o); -116.1 (*d*, $J(o,m) = 30.5$, 2F_o); -168.1 (*t*, $J(m,p) = 19.8$, 1F_p); -168.6 (*m*, 1F_p, 2F_m); -169.2 (*m*, 2F_m). Anal. calc. for $\text{C}_{32}\text{H}_{45}\text{F}_{10}\text{N}_3\text{NiO}$: C 52.2, H 6.2, N 5.7; found: C 52.0, H 6.1, N 5.6.

7. Crystal-Structure Determination of Complex 2. The pertinent crystallographic data are summarized in Table 1. A $0.58 \times 0.21 \times 0.14$ mm yellow prism of complex 2, obtained by diffusion of hexane in a CH_2Cl_2 soln., was mounted on a glass fibre and transferred to a Siemens-P4 diffractometer. An ω -scan was applied to collect a set of 12762 reflections ($2\theta_{\text{max}} 50^\circ$, 10742 unique, $R_{\text{int}} 0.061$) using graphite monochromated MoK_α radiation. Unit-cell parameters were determined from a least-squares fit of 59 accurately centered reflections ($4 < 2\theta < 25$). An absorption correction based on ψ -scans was applied, with transmission factors 0.74–0.77. The structure was solved by direct methods and refined anisotropically on F^2 [28]. The bridging hydroxo H-atom position was determined from the difference Fourier map. All the other H-atoms were included using a riding model. Three of the butyl groups in the cations are disordered over two sites. The final $R1$ ($I > 2\sigma I$) is 0.0658 for 484 parameters ($wR2 = 0.1236$). Maximum $\Delta/\sigma = 0.025$, maximum and minimum $\Delta\rho$ 0.29 and $-0.29 \text{ e}\text{\AA}^{-3}$.

Results and Discussion. – *Synthesis and Characterization of Complexes 1–7.* By reaction of $(\text{Bu}_4\text{N})_2[\text{Ni}_2(\text{C}_6\text{F}_5)_4(\mu\text{-OH})_2]$ with pentafluorobenzeneamine (1:2 molar ratio) and 7-aza-1*H*-indole (1:1 molar ratio) in acetone the corresponding bis [μ -(penta-

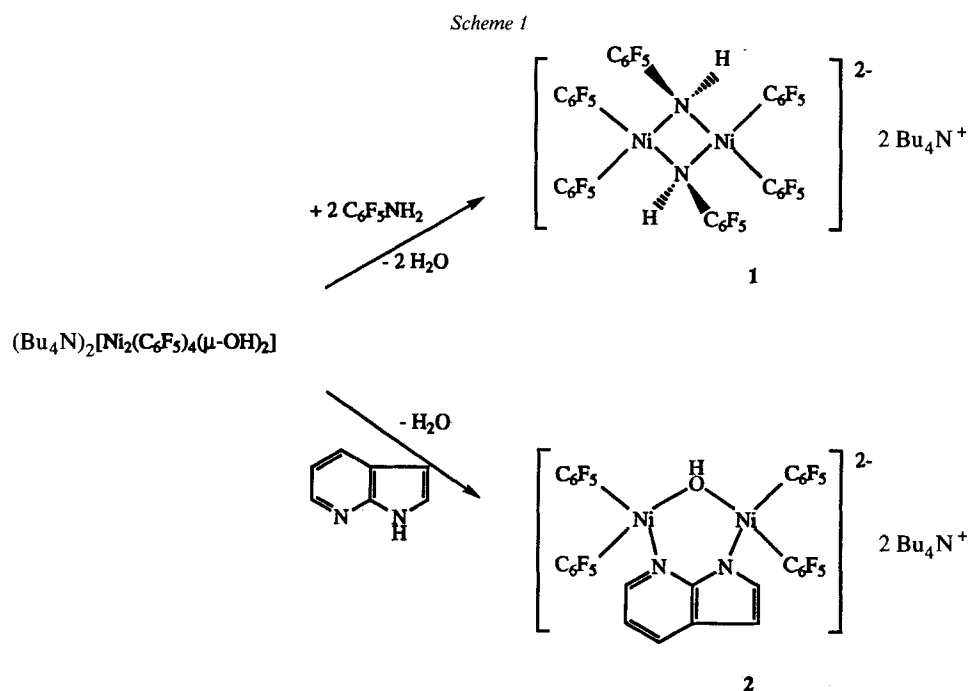
¹) Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication No. CCDC-10/61. Copies of the data can be obtained, free of charge, on application to the Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: + 44-(0)1223-336033 or e-mail: teched@chemcrs.cam.ac.uk).

Table 1. Crystal Data and Parameter of Data Collection for Complex 2

Mol. formula	$C_{63}H_{78}F_{20}N_4Ni_2O$	β [deg]	90.803(5)
Rel. mol. mass M	1404.71	Z ; V [\AA^3]	8; 13712(3)
Temp. [K]	173(2)	Calc. density [g cm^{-3}]	1.361
Absorption coeff. [cm^{-1}]	6.45	Radiation	$\text{MoK}\alpha$ ($\lambda = 0.71073 \text{\AA}$)
Crystal system	monoclinic	$F(000)$	5824
Space group	$C 2/c$ (No. 15)	No. of indep. refl.	10742
a [\AA]	30.032(4)	Parameters	398
b [\AA]	11.051(2)	$R1^a$)	0.0658
c [\AA]	41.319(5)	$wR2^b$)	0.1236

^a) $R1 = \sigma \|F_o\| - |F_c| / \sigma |F_o|$ for reflections with $I > 2\sigma I$. ^b) $wR2 = [\sigma[w(F_o - F_c)^2] / \sigma[w(F_o^2)^2]]^{1/2}$ for all reflections; $w^{-1} = \sigma^2(F^2) + (aP)^2 + bP$, where $P = (2F_c^2 + F_o^2)/3$ and a and b are constants set by the program.

fluorophenyl)amido- κN] and μ -hydroxo-(μ -7-aza-1*H*-indol-1-yl)CN¹, κN^7) binuclear complexes **1** and **2**, respectively, are obtained (Scheme 1; for yields and microanalysis, see *Exper. Part*). Both **1** and **2** are isolated as the tetrabutylammonium salts, and they behave as 2:1 electrolytes in acetone solution [28]. Attempts made to prepare the di(μ -7-aza-1*H*-indol-1-yl- $\kappa N^1, \kappa N^7$) complex by reacting the di- μ -hydroxo complex with 7-aza-1*H*-indole in 1:2 molar ratio were unsuccessful.



Complex **1** gives a single ¹H-NMR signal at δ 0.4 due to the NH proton. In the ¹⁹F-NMR spectrum (see *Exper. Part*), the F_o and F_m resonances of both Ni- and N-bonded C_6F_5 groups are duplicated, but the F_p -atoms of the Ni-bonded C_6F_5 groups give a single resonance signal. This NMR pattern is inconsistent with the presence

of 'syn'/'anti' isomers or a mixture of both isomers. The experimental data suggest that there is frozen rotation of the N-bonded C_6F_5 moiety around the C–N bond, and the resulting anisotropy produces two separate resonances (in the ratio 1:1) for the F_o and F_m atoms of both types of C_6F_5 groups. This effect has also been observed in some bis(pentafluorophenyl) derivatives of nickel(II) with salicylaldimine ligands [17]. Unconcluded investigations of the analogous palladium complex $[Pd_2(C_6F_5)_4(\mu-C_6F_5NH)_2]^{2-}$ demonstrate that this complex shows a temperature-dependent ^{19}F -NMR spectrum, and the F_o -atoms of the Pd-bonded C_6F_5 moieties give only one signal at 20° but two signals at –50°. However, the solvent used for complex **1** did not allow to reach the coalescence temperature.

The presence of the μ -OH ligand in complex **2** is demonstrated by a high-field 1H -NMR signal $\delta = 4.1$. The ^{19}F -NMR spectrum consists of deceptive t (intensity ratio 1:2:1) of d 's in the F_o region. The expected for d 's for four nonequivalent C_6F_5 groups are partly overlapped, and the accidental coincidence of the two central d 's produces a central d of double intensity.

The dinuclearity of complex **2** was established by single-crystal X-ray diffraction. Selected geometrical features are given in Table 2. The structure consists of binuclear $[\{Ni(C_6F_5)_2\}_2(\mu-OH)(\mu-azind)]^{2-}$ anions (Fig. 1) joining Bu_4N^+ cations by electrostatic interactions and CH_2Cl_2 molecules of crystallization. The two Ni-atoms are bridged by one hydroxo group (Ni(1)–O 1.892(6) Å, Ni(2)–O 1.887(6) Å, angle Ni(1)–O–Ni(2) 112.1°), and one 7-aza-1*H*-indol-1-yl ligand (Ni(1)–N(1) 1.944(6) Å, Ni(2)–N(2) = 1.943(6) Å). The six-membered ring containing the Ni-atoms is not planar, there being a dihedral angle of 84.4° between the Ni–O–Ni and Ni–N–C–N–Ni planes. A similar puckered central ring was found in the $[\{Ni(C_6F_5)_2\}_2(\mu-OH)(\mu-pyrazolyl)]^{2-}$ anion [1].

Table 2. Selected Bond Lengths [Å] and Angles [°] for Complex **2**. For numbering, see Fig. 1.

Ni(1)–C(11)	1.890(9)	C(11)–Ni(1)–O	175.4(4)
Ni(1)–C(21)	1.925(8)	C(11)–N(1)–C(21)	87.8(3)
Ni(2)–C(41)	1.886(8)	O–Ni(1)–C(21)	92.1(3)
Ni(2)–C(31)	1.916(8)	C(11)–Ni(1)–N(2)	93.9(3)
Ni(1)–O	1.892(6)	O–Ni(1)–N(2)	86.6(3)
Ni(1)–N(2)	1.944(6)	C(21)–Ni(1)–N(2)	175.8(3)
Ni(2)–O	1.887(6)	O–Ni(2)–N(1)	87.9(3)
Ni(2)–N(1)	1.943(6)	Ni(2)–O–Ni(1)	112.1(3)
		C(41)–Ni(2)–O	177.0(3)
		C(41)–Ni(2)–C(31)	88.0(3)
		O–Ni(2)–C(31)	89.6(3)
		C(41)–Ni(2)–N(1)	94.4(3)
		C(31)–Ni(2)–N(1)	177.5(3)

The reaction of the di- μ -hydroxo complex with 1,3-diaryltriaz-1-enes, *N*-phenylpyridin-2-amine and *N*-phenylpyridine-2-carboxamide (Scheme 2) leads to the formation of anionic mononuclear complexes, i.e., to $Bu_4N[Ni(C_6F_5)_2(ArN_3Ar)]$ (Ar = Ph, **3**; Ar = 4-MeC₆H₄, **4**, Ar = 4-MeOC₆H₄, **5**, to $Bu_4N[Ni(C_6F_5)_2(pyNPh)]$ (**6**), and to $Bu_4N[Ni(C_6F_5)_2(pyCONPh)]$ (**7**), respectively. The deprotonated amino moiety acts here as an endobidentate ligand. In acetone solution, these complexes behave as 1:1 electrolytes [29].

The IR spectra of the triazenido complexes **3–5** display bands in the 1600 cm^{-1} region which are characteristic of the triazene skeleton [30], and the ^{19}F -NMR spectra are consistent with the presence of two equivalent C_6F_5 groups. However, the ^{19}F -NMR data of complexes **6** and **7**, which contain asymmetric *N,N'*-donor ligands, indicate the presence of two nonequivalent C_6F_5 groups. Moreover, in the spectrum of **7**, there appear two pseudo- t in the F_o region indicating the anisotropy derived from the presence of the *N*-phenyl substituent; the

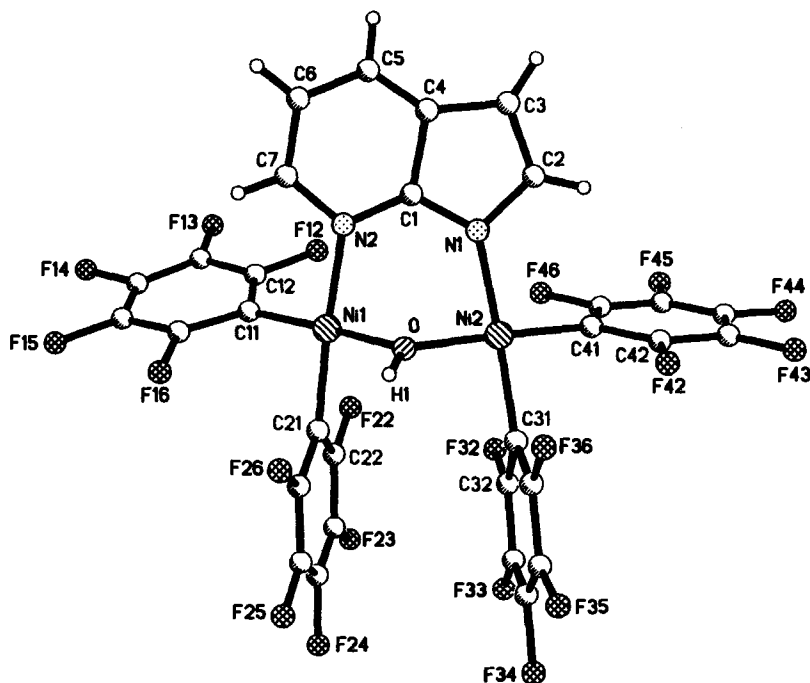


Fig. 1. Structure of the anion of complex **2** in the crystal. Counteranions are Bu_4N^+ (not shown). ORTEP representation showing 50% probability ellipsoids. Arbitrary numbering.

rotation is sufficiently sluggish to make the F_o -atoms distinguishable by their different chemical shifts and four 1:1:1:1 d 's should be seen, but partial overlapping produces the two observed pseudo- t . Complex **7** gives an IR absorption at 1620 cm^{-1} ($\nu(\text{CO})$) and a ^{13}C -NMR signal at δ 168.4 (CO). All the complexes show the characteristic IR absorptions of the C_6F_5 group [31] (ca. $1630m$, $1495vs$, $1050s$, $950vs$, and $780s\text{ cm}^{-1}$).

The negative FAB-MS data of complexes **1–5** with the m/z values for the expected fragments are listed in *Table 3*. The spectrum of **1** shows that the peak with the largest mass number corresponds to $[\{\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-C}_6\text{F}_5\text{NH})\}_2]^-$ (m/z 1148) and additional peaks to $[\{\text{Ni}_2(\text{C}_6\text{F}_5)_4(\mu\text{-C}_6\text{F}_5\text{NH})\}^-]$, $[\text{Ni}_2(\text{C}_6\text{F}_5)_3(\mu\text{-C}_6\text{F}_5\text{NH})]^-$, $[\text{Ni}_2(\text{C}_6\text{F}_5)_2(\text{C}_6\text{F}_5\text{NH})]^-$, and $[\text{Ni}(\text{C}_6\text{F}_5)_2]^-$. An isotopic distribution pattern was calculated (*Fig. 2*) for the peak with m/z 1148 which also justifies the assignment. The spectra of compounds **2–5** show their highest mass number at m/z 1159, 588, 616, and 648, which correspond to $\text{Bu}_4\text{N}[\{\text{Ni}(\text{C}_6\text{F}_5)_2\}_2(\mu\text{-OH})(\mu\text{-azind})]^-$ and $[\text{Ni}(\text{C}_6\text{F}_5)_2(\text{ArN}_3\text{Ar})]^-$ ($\text{Ar} = \text{Ph}$, $4\text{-MeC}_6\text{H}_4$ and $4\text{-MeOC}_6\text{H}_4$), respectively.

Hydration of Coordinated Aminonitriles: Complexes 8–10. The activation of nitriles with respect to attack by nucleophiles in the coordination sphere of metal ions has attracted considerable interest [32–34] and we have recently described the nucleophilic attack of OH^- and MeO^- on benzonitrile coordinated to Pt^{II} [3]. In acetone/ H_2O , the reaction between $(\text{Bu}_4\text{N})_2[\text{Ni}(\text{C}_6\text{F}_5)_4(\mu\text{-OH})_2]$ and pyridine-2-carbonitrile (pyCN), 2-aminoacetonitrile ($\text{NH}_2\text{CH}_2\text{CN}$), and 2-(dimethylamino)acetonitrile ($\text{Me}_2\text{NCH}_2\text{CN}$) leads to the formation of the bis(pentafluorophenyl)nickel anionic complexes containing

Scheme 2

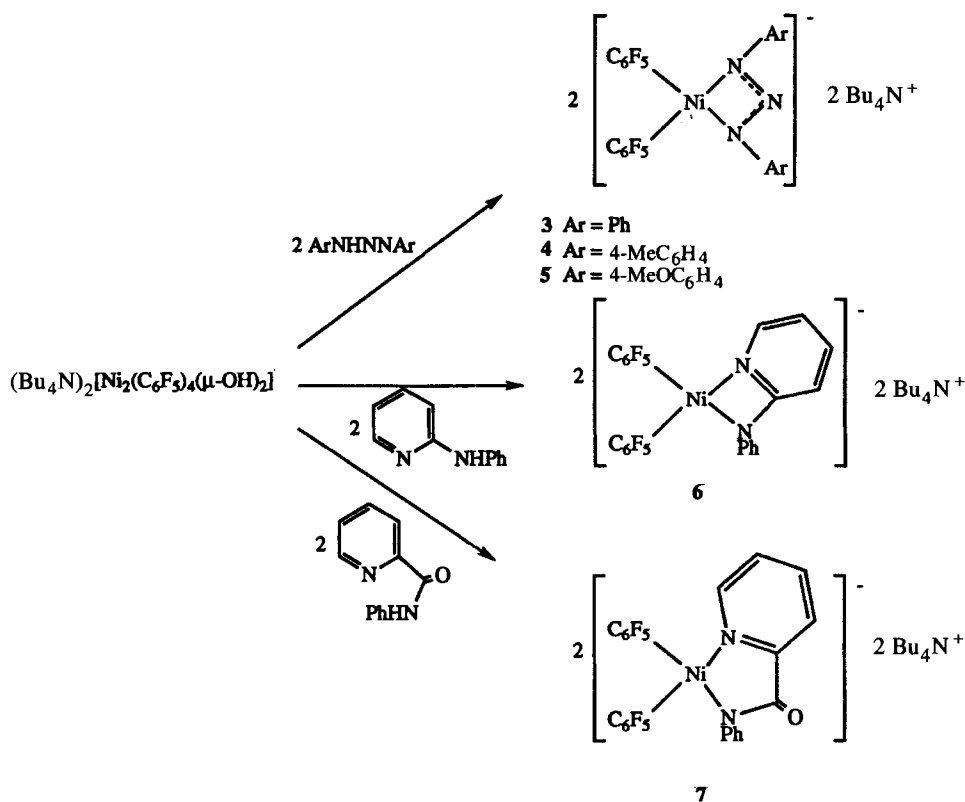


Table 3. FAB Mass Spectrometric Data (neg. mode) for the Complexes 1–5

Ions (<i>m/z</i>)	
1	$[\{\text{Ni}(\text{C}_6\text{F}_5)_2(\mu\text{-C}_6\text{F}_5\text{NH})\}_2]^-$ (1148), $[\text{Ni}_2(\text{C}_6\text{F}_5)_4(\mu\text{-C}_6\text{F}_5\text{NH})]^-$ (966), $[\text{Ni}_2(\text{C}_6\text{F}_5)_3(\mu\text{-C}_6\text{F}_5\text{NH})]^-$ (799), $[\text{Ni}_2(\text{C}_6\text{F}_5)_2(\text{C}_6\text{F}_5\text{NH})]^-$ (632), $[\text{Ni}(\text{C}_6\text{F}_5)_2]^-$ (392)
2	$[\text{Bu}_4\text{N}[\{\text{Ni}(\text{C}_6\text{F}_5)_2\}_2(\mu\text{-OH})(\mu\text{-azind})]]^-$ (1159), $[\text{Ni}_2(\text{C}_6\text{F}_5)_4(\text{azind})]^-$ (901), $[\text{Ni}_2(\text{C}_6\text{F}_5)_3(\text{OH})(\text{azind})]^-$ (751), $[\text{Ni}(\text{C}_6\text{F}_5)_3]^-$ (559), $[\text{Ni}(\text{C}_6\text{F}_5)_2]^-$ (392)
3	$[\text{Ni}(\text{C}_6\text{F}_5)_2(\text{PhN}_3\text{Ph})]^-$ (588), $[\text{Ni}(\text{C}_6\text{F}_5)_2]^-$ (392)
4	$[\text{Ni}(\text{C}_6\text{F}_5)_2(\text{MeC}_6\text{H}_4\text{N}_3\text{C}_6\text{H}_4\text{Me})]^-$ (616), $[\text{Ni}(\text{C}_6\text{F}_5)_2]^-$ (392)
5	$[\text{Ni}(\text{C}_6\text{F}_5)_2(\text{MeOC}_6\text{H}_4\text{N}_3\text{C}_6\text{H}_4\text{OMe})]^-$ (648), $[\text{Ni}(\text{C}_6\text{F}_5)_2]^-$ (392)

pyridine-2-carboxamidato, 2-aminoacetamidato, and 2-(dimethylamino)acetamidato ligands, respectively (Scheme 3). The new complexes 8–10 are air-stable solids, and the conductances of their acetone solutions are consistent with the presence of 1:1 electrolytes [29].

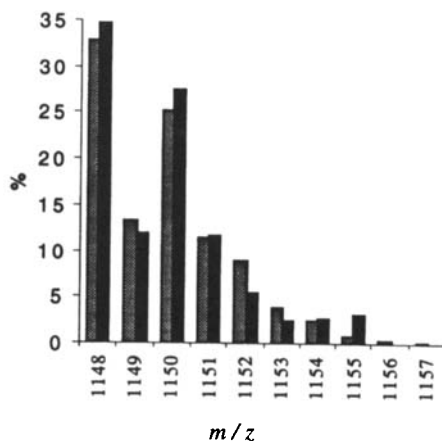
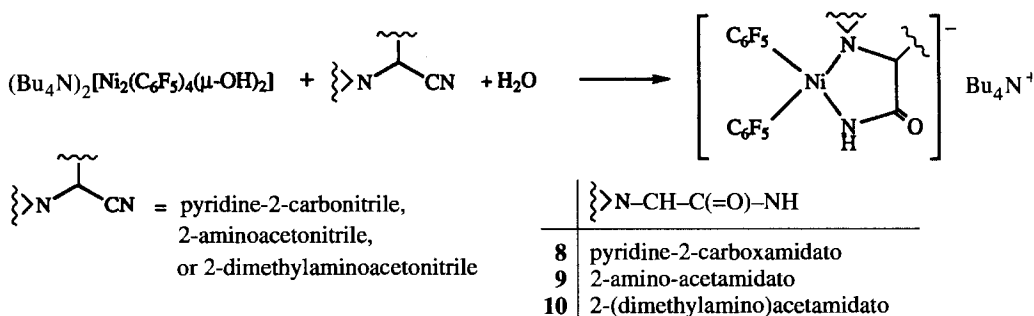


Fig. 2. Comparison of isotope abundance for the experimentally observed (black bars) and theoretically calculated peak with m/z 1148 of complex 1

Scheme 3



The compounds all show the characteristic IR absorptions of the pentafluorophenyl group [31]. The ^{19}F -NMR data are consistent with the presence of two different C_6F_5 groups, one *trans* to N (amino moiety) and one *trans* to NHCO (amide moiety). The presence of the carbonyl group in complexes **8–10** is manifested by an IR band at $1620\text{--}1635\text{ cm}^{-1}$ and a ^{13}C -NMR signal at δ 165–180.

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