Nickel-(II), -(III) and -(IV) Complexes of 1,2-Bis(dimethylarsino)tetrafluorobenzene and X-Ray Crystallographic and Extended X-Ray Absorption Fine Structure Studies of Nickel-(III) and -(IV) Bromo Complexes†

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1,2-Bis(dimethylarsino)tetrafluorobenzene, o-$C_6F_4(AsMe_2)_2$, forms high-spin tetragonal nickel(II) complexes $[Ni(L-L)_2X_2]$ (X = Cl or Br), which remain six-co-ordinate in non-polar solvents, and planar diamagnetic $[Ni(L-L)_2]I_2$. Pseudo-octahedral nickel-(III) and -(IV) complexes $[Ni(L-L)_2X_2]^{n+}$ are formed on oxidation, and their properties are compared with those of the fluorine-free ligand o-$C_6H_4(AsMe_2)_2$. The X-ray crystal structure of *trans*-$[Ni\{o\text{-}C_6F_4(AsMe_2)_2\}_2Br_2]BF_4$ has been determined, and revealed a tetragonal cation with Ni–Br 2.543(1) and Ni–As 2.336(1), 2.339(1) Å. Nickel and bromine K-edge extended X-ray absorption fine structure data are reported for a variety of complexes of Ni^{II}, Ni^{III} and Ni^{IV} with o-$C_6F_4(AsMe_2)_2$, o-$C_6H_4(AsMe_2)_2$ and o-$C_6H_4(PMe_2)_2$, and the results compared with existing data on the chloride analogues.

The chemistry of nickel in oxidation states greater than two has developed rapidly in recent years, and that of nickel(III) is now extensive.[1,2] In contrast nickel(IV) is rarely found in co-ordination complexes, and the only examples with neutral donor ligands are with the bidentates o-$C_6H_4(PMe_2)_2$, o-$C_6H_4(AsMe_2)_2$, o-$C_6H_4(PMe_2)(AsMe_2)$ and o-$C_6F_4(PMe_2)_2$.[3,4] Interestingly Ni^{IV} is present[5] in the mixed-valence linear-chain diamines $[\{Ni^{II}(diamine)_2\text{–}Ni^{IV}(diamine)_2Cl_2\}_n]Cl_{4n}$, although simple diamine complexes have not been prepared. The present paper reports a study of the nickel complexes of the fluorophenyldiarsine o-$C_6F_4(AsMe_2)_2$ in order further[6] to explore the effect of the tetrafluorophenyl backbone. Structural data on a range of bromo complexes of Ni^{II}, Ni^{III} and Ni^{IV} obtained by the EXAFS (extended X-ray absorption fine structure) technique supplemented by an X-ray crystal structure determination are reported. Some complexes of the fluorophenyldiarsine were mentioned in a preliminary publication[7] 25 years ago, but no details have subsequently appeared.

Experimental

Physical measurements were made as described previously.[4,8] Nickel and bromine K-edge EXAFS data were collected in transmission mode on station 7.1 of the Daresbury Synchrotron Radiation Source, operating at 2 GeV (*ca.* 3.2×10^{-10} J) with an average current of 150–200 mA, using an order-sorting Si(111) monochromator, offset to 50% of the peak of the rocking curve for harmonic rejection. Samples were diluted with boron nitride (*ca.* 10% w/w Ni), and mounted in aluminium holders (1 mm) between Sellotape strips. Data analyses were carried out as described previously.[9]

Syntheses.—o-$C_6F_4(AsMe_2)_2$. To a three-necked flask fitted with a pressure-equalizing dropping funnel, Suba-seal septum cap and reflux condenser flushed with nitrogen was added dry nitrogen-purged diethyl ether (200 cm^3) and 1,2-dibromotetrafluorobenzene (10.0 g, 0.032 mol). The mixture was cooled to −97 °C (CH_2Cl_2 slush) and $LiBu^n$ (14 cm^3 of a 2.35 mol dm^{-3} solution) added dropwise over 40 min. Stirring was continued for 10 min, and then the deep yellow mixture warmed to −23 °C (CCl_4 slush) for 5 min. The mixture was cooled again to −97 °C and $AsMe_2I$ (7.6 g, 0.033 mol) added slowly *via* a syringe over *ca.* 30 min, the mixture becoming red. After stirring for 30 min the mixture was allowed to warm to room temperature. It was recooled to −97 °C and $LiBu^n$ (14 cm^3) and $AsMe_2I$ (7.6 g) added, and allowed to warm to room temperature overnight. The solution was hydrolysed with deoxygenated aqueous ammonium chloride (100 cm^3), the organic layer separated and dried (Na_2SO_4). The ether was distilled off, and the residue fractionated in vacuum to give a single fraction b.p. 70–77 °C (0.2 mmHg, *ca.* 27 Pa). Yield 8.8 g, 76%. NMR ($CDCl_3$): ^1H, δ 1.424 (d), J_{HF} = 3 Hz; ^{19}F, δ 34.4 (d, 2F) and 7.75 (d, 2F), $^3J_{FF}$ = 19 Hz (ref. to C_6F_6).

$[Ni\{o\text{-}C_6F_4(AsMe_2)_2\}_2Cl_2]$. The ligand (0.72 g, 2.0 mmol) was dissolved in deoxygenated ethanol (5 cm^3) and added to a solution of $[Ni(H_2O)_6]Cl_2$ (0.24 g, 1.0 mmol) in ethanol (5 cm^3). The solution turned red and an immediate green precipitate appeared. The solution was filtered and the green solid washed with cold ethanol (3 cm^3) and diethyl ether (5 cm^3) and dried *in vacuo*. Yield 0.51 g, 60% (Found: C, 28.3; H, 2.9. $C_{20}H_{24}As_4Cl_2F_8Ni$ requires C, 28.4; H, 2.9%).

The compounds $[Ni\{o\text{-}C_6F_4(AsMe_2)_2\}_2Br_2]$, yield 60% (Found: C, 26.0; H, 2.7. $C_{20}H_{24}As_4Br_2F_8Ni$ requires C, 25.7; H, 2.6%), and $[Ni\{o\text{-}C_6F_4(AsMe_2)_2\}_2]I_2$, yield 45% (Found: C, 22.1; H, 2.1. $C_{20}H_{24}As_4F_8I_2Ni$ requires C, 23.4; H, 2.4%), were made similarly.

$[Ni\{o\text{-}C_6F_4(AsMe_2)_2\}_2Cl_2]BF_4$. All solvents were deoxygenated before use. To a red solution of $[Ni\{o\text{-}C_6F_4(AsMe_2)_2\}_2Cl_2]$ (0.42 g, 0.5 mmol) in CH_2Cl_2 (3 cm^3) was added NEt_4BF_4 (0.11 g, 0.5 mmol) dissolved in ethanol (3 cm^3). The solution was treated immediately with a chlorine-saturated $CHCl_3$ solution (*ca.* 10 cm^3), and a yellow precipitate formed immediately. The solution was concentrated by blowing nitrogen gas over it, and the precipitate filtered off, washed with cold diethyl ether (10

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Non-SI unit employed: B.M. ≈ 0.927×10^{-23} A m^2.

cm^3) and dried *in vacuo*. Yield 0.18 g, 39% (Found: C, 25.9; H, 2.7. $C_{20}H_{24}As_4BCl_2F_{12}Ni$ requires C, 25.8; H, 2.6%).

$[Ni\{o\text{-}C_6F_4(AsMe_2)_2\}_2Br_2]BF_4$. To a red solution of $[Ni\{o\text{-}C_6F_4(AsMe_2)_2\}_2Br_2]$ (0.45 g, 0.5 mmol) in CH_2Cl_2 (3 cm^3) was added NEt_4BF_4 (0.11 g, 0.5 mmol) in ethanol (3 cm^3), and the solution treated with bromine–ethanol solution [1.9 cm^3 of Br_2 (1 g) in ethanol (50 cm^3)] and an orange-brown precipitate formed immediately. The solution was concentrated in a stream of nitrogen gas, the precipitate filtered off, washed with diethyl ether (5 cm^3) and dried *in vacuo*. Yield 0.31 g, 63% (Found: C, 23.8; H, 2.4. $C_{20}H_{24}As_4BBr_2F_{12}Ni$ requires C, 23.5; H, 2.4%).

$[Ni\{o\text{-}C_6F_4(AsMe_2)_2\}_2Cl_2][ClO_4]_2$. Finely powdered $[Ni\{o\text{-}C_6F_4(AsMe_2)_2\}_2Cl_2]$ (0.3 g, 0.35 mmol) was moistened with concentrated hydrochloric acid (three drops), cooled to 0 °C, and concentrated nitric acid (5 cm^3) added dropwise. The mixture was stirred at 0 °C for 5 min to produce a deep blue solution, and then treated dropwise with 70% perchloric acid (2 cm^3). **CAUTION:** Metal perchlorate complexes are often unpredictably explosive, and due precautions should be taken. No explosions were experienced in this study. The resulting mixture was centrifuged, the supernatant liquid removed, the residue washed with 5% $HClO_4$ solution at 0 °C, centrifuged, and the solid dried *in vacuo*. Yield *ca.* 90% (Found: C, 22.9; H, 2.1. $C_{20}H_{24}As_4Cl_4F_8NiO_8$ requires C, 23.0; H, 2.3%).

The compound $[Ni\{o\text{-}C_6F_4(AsMe_2)_2\}_2Br_2][ClO_4]_2$ was made similarly (Found: C, 21.1; H, 2.3. $C_{20}H_{24}As_4Br_2Cl_2F_8NiO_8$ requires C, 21.2; H, 2.1%). Other complexes of Ni^{II}, Ni^{III} and Ni^{IV} were made as described previously.[4,8]

X-Ray Structure Determination on $[Ni\{o\text{-}C_6F_4(AsMe_2)_2\}_2Br_2]BF_4$.—Dark brown air-stable crystals of approximately octahedral shape were obtained by vapour diffusion of diethyl ether into a MeCN solution of the complex. The crystals were mounted in thin-walled glass capillaries and secured by a trace of silicone grease. Preliminary photographic X-ray examination established the crystal system and the suitable crystal quality. The crystal density was measured by flotation (CCl_4–$C_2H_4Br_2$).

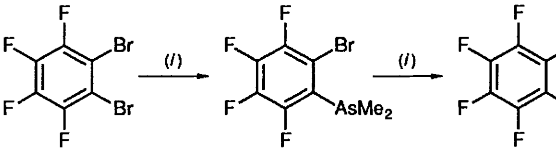
Crystal data. $C_{20}H_{24}As_4BBr_2F_{12}Ni$, $M = 1021.4$, monoclinic, space group *A*2/*a* (no. 15), $a = 13.005(3)$, $b = 12.687(7)$, $c = 19.300(6)$ Å, $\beta = 99.43(2)°$, $U = 3141.4(21)$ Å^3, $D_m = 2.13(2)$ g cm^{-3}, $Z = 4$, $D_c = 2.159$ g cm^{-3}, $F(000) = 1948$, Mo-Kα radiation, $\lambda = 0.710\ 69$ Å, μ(Mo-Kα) = 73.4 cm^{-1}.

Accurate cell dimensions were obtained from 25 centred reflections using a room-temperature crystal (0.6 × 0.3 × 0.3 mm) mounted on an Enraf-Nonius CAD4 diffractometer. Using the same crystal, 3052 data were recorded ($1.5 < \theta < 25°$; *h* −15 to 15, *k* 0–15, *l* 0–22) using graphite-monochromated Mo-Kα radiation. A small amount of decay (3%) was observed in the two check reflections and this was allowed for in the data-reduction process, along with the Lorentz and polarization factors. An empirical ψ-scan absorption correction based on three reflections was applied (transmission: minimum 71.84, maximum 99.92%). After data reduction there remained 2763 unique reflections ($R_{int} = 0.008$) of which 2101 with $F > 2\sigma(F)$ were used in the solution and refinement. The systematic absences indicated the space group *Aa* or *A*2/*a* of which the latter was established from the structure solution. The normalized structure factors (*E*) favoured the centrosymmetric space group and the direct-methods routine available in SHELX 76[10] (EEES) located the Ni, As and Br atoms. Subsequent structure-factor and difference electron-density syntheses yielded the remaining non-H atoms. The boron atom is located on a two-fold axis and the BF_4^- anion exhibited disorder, a feature which is commonly encountered. Atom F(5) appeared prominently in the difference map and was included with a site population of 1.0. Several other smaller peaks were apparent as part of the disordered anion. Three were included [F(6), F(7), F(8)] with refined site populations, all of the F atoms being given a common refined isotropic thermal parameter. The populations account for the four F atoms required for the B(1), and F(5) appears to be involved in several BF_4^- anions, thus accounting for its enhanced site occupation. The methyl H atoms were not included in the model and one reflection thought to be subject to extinction (020) was excluded. Full-matrix least-squares refinement minimizing $\Sigma w\Delta^2$ converged to $R = 0.055$ {178 parameters, 2100 reflections, anisotropic [Br, As, Ni, F (cation), C] and isotropic [B, F (anion)] atoms, $w = 1/[\sigma^2(F) + 0.000\ 5\ F^2]$, maximum $\Delta/\sigma = 0.1$, $R' = 0.053$, $S = 1.59$}. The final difference electron-density synthesis showed all features in the range 0.67 to −1.18 e Å^{-3}. Neutral atom scattering factors and anomalous dispersion corrections were taken from ref. 11 (As, Ni) and SHELX 76 (Br, F, C, B). All calculations were carried out on an IBM 3090 computer using the programs SHELX 76,[10] ORTEP II[12] and XANADU.[13] The atomic coordinates are given in Table 3, and Table 4 presents selected bond lengths and angles.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

Results and Discussion

Complexes of $o\text{-}C_6F_4(AsMe_2)_2$.—The ligand was made by stepwise replacement of the bromine in $o\text{-}C_6F_4Br_2$ by treatment with $LiBu^n$ and $AsMe_2I$, in a similar manner to that of the diphosphine analogue[6] (Scheme 1). The ligand is an oily, air-sensitive [less so than $o\text{-}C_6H_4(AsMe_2)_2$] liquid.



Scheme 1 (*i*) (*a*) $LiBu^n$, (*b*) $AsMe_2I$

The reaction of nickel(II) halides with the ligand in a 1:2 molar ratio in ethanol gave green $[Ni\{o\text{-}C_6F_4(AsMe_2)_2\}_2X_2]$ (X = Cl or Br) and brown $[Ni\{o\text{-}C_6F_4(AsMe_2)_2\}_2]I_2$. The latter is diamagnetic and its diffuse reflectance spectrum (Table 1) suggests an essentially planar (As_4) co-ordination sphere, similar to the halogeno complexes of $o\text{-}C_6H_4(AsMe_2)_2$.[16] However in marked contrast to the complexes of $o\text{-}C_6H_4(AsMe_2)_2$, the green $[Ni\{o\text{-}C_6F_4(AsMe_2)_2\}_2X_2]$ are paramagnetic (μ *ca.* 3 B.M.) with electronic spectra in the solid state consistent with a tetragonal-octahedral geometry.[6] This is unusual behaviour for nickel(II) complexes of bidentate Group 15 ligands,[17] but is reminiscent of $[Ni\{o\text{-}C_6F_4(PMe_2)_2\}_2Cl_2]$ for which both planar and octahedral forms are known,[6] although the corresponding bromide is exclusively planar. In benzene these two complexes form green solutions, in which the six-co-ordinate geometry is retained, but in dichloromethane red-brown solutions are formed which seem to contain both five-and six-co-ordinate species. In support of this they have molar conductances in CH_2Cl_2 which are much less than those of 1:1 electrolytes (Table 1), and even in the more polar $MeNO_2$ the ionization is incomplete. The nickel(III) complexes $[Ni\{o\text{-}C_6F_4(AsMe_2)_2\}_2X_2]BF_4$ (X = Cl or Br) were easily made by treatment of the nickel(II) complexes in ethanol with the appropriate halogen and NEt_4BF_4. Their formulation as tetragonal-octahedral complexes follows from comparison of the spectroscopic properties with those of other diphosphines and diarsines,[8] and from the X-ray structure of the bromo complex (below). Oxidation of $[Ni\{o\text{-}C_6F_4(AsMe_2)_2\}_2X_2]$ with concentrated nitric acid gave dark blue (X = Cl) or green (X = Br) solutions, from which 70% perchloric acid precipitated the diamagnetic nickel(IV) complexes $[Ni\{o\text{-}C_6F_4(AsMe_2)_2\}_2X_2][ClO_4]_2$. These are highly unstable decomposing to the nickel(III) complexes in about 1 d at room temperature, and more slowly at −10 °C in the dark. Decomposition is instantaneous in most organic solvents, although spectra can be obtained from CF_3CO_2H solution. Even in this medium,

Table 1 Selected spectroscopic data

Compound	Colour	ν(Ni–X)[a]/cm^{-1}	μ[b]/B.M.	Ultraviolet–visible $E_{max}/10^3$ cm^{-1} (ε/dm^3 mol^{-1} cm^{-1})[c]		Λ$_M$[d]/ohm^{-1} cm^2 mol^{-1}	
						CH_2Cl_2	$MeNO_2$
$[Ni\{o-C_6F_4(AsMe_2)_2\}_2Cl_2]$	Green	261	3.0	8.29(sh), 10.40, 14.60(sh), 17.92, 25.51 (sh), 30.9	(d.r.)	1.2	44
				10.41(sh), 14.60(sh), 17.95(30), 25.51 (sh)	(C_6H_6)		
				10.26(24), 14.75(sh), 19.31(130), 25.5 (sh)	(CH_2Cl_2)		
$[Ni\{o-C_6F_4(AsMe_2)_2\}_2Br_2]$	Green	208	3.2	10.11, 15.11(sh), 17.76, 23.35(sh), 28.01, 29.59(sh)	(d.r.)	1.6	67
				10.21(18), 15.13(sh), 17.54(47)	(C_6H_6)		
				10.09(15), 15.34(sh), 19.61(112), 28.57(6150)	(CH_2Cl_2)		
$[Ni\{o-C_6F_4(AsMe_2)_2\}_2]I_2$	Brown	n.o.[e]	diam	17.12(sh), 19.88(sh), 26.60, 29.00, 33.44	(d.r.)		115
				19.96(sh) (*ca.* 350)	($MeNO_2$)		
$[Ni\{o-C_6F_4(AsMe_2)_2\}_2Cl_2]BF_4$	Orange	263	1.95	10.81, 13.68, 23.26(sh), 25.58	(d.r.)	30.1	120
				10.25(48), 23.26(sh), 25.51(8130)	(MeCN)		
$[Ni\{o-C_6F_4(AsMe_2)_2\}_2Br_2]BF_4$	Brown	n.o.	1.98	10.31, 13.77, 22.88, 27.70, 34.60	(d.r.)	27.6	125
				10.53(22), 22.27(sh), 22.83(2800), 28.82(sh)	(MeCN)		
$[Ni\{o-C_6F_4(AsMe_2)_2\}_2Cl_2][ClO_4]_2$	Dark blue	418	diam	17.0, 24.5	(d.r.)		
				17.45, 25.77, 32.0(sh)	(CF_3CO_2H)[f]		
$[Ni\{o-C_6F_4(AsMe_2)_2\}_2Br_2][ClO_4]_2$	Dark green	312	diam	16.0, 22.0	(d.r.)		
				16.34, 23.09	(CF_3CO_2H)[f]		

[a] Nujol mull. [b] Solid state ±0.05 B.M.; diam = diamagnetic. [c] d.r. = Diffuse reflectance. [d] In CH_2Cl_2 solution 1:1 electrolytes have Λ$_M$ in the range 20–30 ohm^{-1} cm^2 mol^{-1};[14] in $MeNO_2$ 1:1 electrolytes have Λ$_M$ 70–95 ohm^{-1} cm^2 mol^{-1} and 1:2 electrolytes Λ$_M$ 150–180 ohm^{-1} cm^2 mol^{-1}.[15] [e] n.o. = Not observed. [f] Solution too unstable to measure ε.

Table 2 Electrochemical data[a]

Complex	E (Ni^{II}–Ni^{III})/V	E (Ni^{III}–Ni^{IV})/V
$[Ni\{o-C_6F_4(AsMe_2)_2\}_2Cl_2]BF_4$	0.28	1.35
$[Ni\{o-C_6F_4(AsMe_2)_2\}_2Br_2]BF_4$	0.36	1.29
$[Ni\{o-C_6H_4(AsMe_2)_2\}_2Cl_2]BF_4$	0.21[b]	1.30
$[Ni\{o-C_6H_4(AsMe_2)_2\}_2Br_2]BF_4$	0.25[b]	1.10

[a] For 10^{-3} mol dm^{-3} solutions in MeCN containing 0.1 mol dm^{-3} of $[NBu^n_4][BF_4]$ at a vitreous carbon electrode. Potentials *versus* the saturated calomel electrode. All couples are electrochemically reversible with ΔE_p in the range 65–80 mV except where marked *b*. [b] Quasi-reversible couple.

Table 3 Atomic coordinates for $[Ni\{o-C_6F_4(AsMe_2)_2\}_2Br_2]BF_4$

Atom	*x*	*y*	*z*
Ni	0.000 0	0.250 0	0.250 0
As(1)	0.105 72(6)	0.139 52(6)	0.195 05(4)
As(2)	−0.042 72(6)	0.339 29(6)	0.143 13(4)
Br(1)	0.148 85(6)	0.374 24(6)	0.296 52(5)
C(1)	0.255 5(6)	0.168 0(8)	0.205 4(5)
C(2)	0.095 1(7)	−0.010 8(6)	0.212 2(5)
C(3)	0.061 1(6)	0.159 2(6)	0.094 8(4)
C(4)	0.097 2(7)	0.098 2(8)	0.046 2(5)
C(5)	0.069 7(7)	0.122 9(8)	−0.025 4(5)
C(6)	0.010 1(8)	0.204 6(8)	−0.046 0(5)
C(7)	−0.025 7(7)	0.268 0(7)	0.002 0(5)
C(8)	−0.001 4(6)	0.246 4(6)	0.073 2(4)
C(9)	−0.189 4(6)	0.368 4(8)	0.110 1(5)
C(10)	0.028 3(7)	0.470 8(7)	0.129 4(5)
F(1)	0.159 7(4)	0.014 6(5)	0.065 5(3)
F(2)	0.105 7(5)	0.058 7(5)	−0.072 3(3)
F(3)	−0.015 3(5)	0.226 8(5)	−0.114 5(3)
F(4)	−0.082 5(5)	0.351 1(5)	−0.020 5(3)
B(1)	0.250 0	0.363 8(14)	0.000 0
F(5)	0.163 1(6)	0.419 3(6)	−0.001 1(4)
F(6)	0.240 8(17)	0.299 1(27)	−0.059 0(19) *
F(7)	0.254 5(22)	0.265 1(20)	0.023 5(18) *
F(8)	0.225 1(21)	0.366 5(27)	−0.083 4(15) *

* Partial atom occupancy [F(6) 0.39(2), F(7) 0.33(3), F(8) 0.29(2)].

decomposition was sufficiently rapid to prevent absorption coefficients being obtained, although the profiles are characteristic[4] of a low-spin d^6 ion and confirm the nickel(IV) formulation.

Cyclic voltammetry was used to probe the effect of the $o-C_6F_4$ backbone upon the redox potentials. The results are shown in Table 2, along with data on the $o-C_6H_4(AsMe_2)_2$ analogues. First of note is the fact that the Ni^{II}–Ni^{III} couples for the $o-C_6F_4(AsMe_2)_2$ compounds are electrochemically reversible, whereas for other diphosphine and diarsine complexes the couples are irreversible.[4] This is rationalized by the tendency of the nickel(II)–$o-C_6F_4(AsMe_2)_2$ complexes to retain the six-co-ordinate structure in solution, whereas with other ligands four- or five-co-ordinate species are present. Since the nickel(III) compounds are all pseudo-octahedral, the change in co-ordination number accounts for the irreversibility of the couples with the other ligands. Secondly the comparison of the Ni^{III}–Ni^{IV} couples for the complexes of the fluorophenyldiarsine and its hydrocarbon analogue reveal that the potentials are more positive for the former compounds, reflecting the −I effect of the C_6F_4 backbone which makes oxidation harder. This effect confirms the previous observations on the corresponding diphosphines $o-C_6H_4(PMe_2)_2$ and $o-C_6F_4(PMe_2)_2$.[6]

X-Ray Structure of $[Ni\{o-C_6F_4(AsMe_2)_2\}_2Br_2]BF_4$.—The structure consists of discrete anions and cations with the nickel atom located on a crystallographic centre of symmetry (Fig. 1). The two Ni–As distances are nearly equal (Table 4) and agree with the Ni–As distance in the $[Ni\{o-C_6H_4(AsMe_2)_2\}_2Cl_2]^+$ cation.[18] The structure is isomorphous with $[Fe\{o-C_6F_4(PMe_2)_2\}_2Cl_2]BF_4$.[19] As is normally found[18–20] with these bis diphosphine and diarsine complexes they form a 'stepped' structure with in the present case an angle of 15.0° between the $NiAs_4$ plane and the plane through the ligand C_6As_2 atoms. As expected the C_6As_2 group is close to planar with the two arsenic atoms displaced from the C_6 plane by 0.15 (av.) Å and both lying on the same side of the ring.

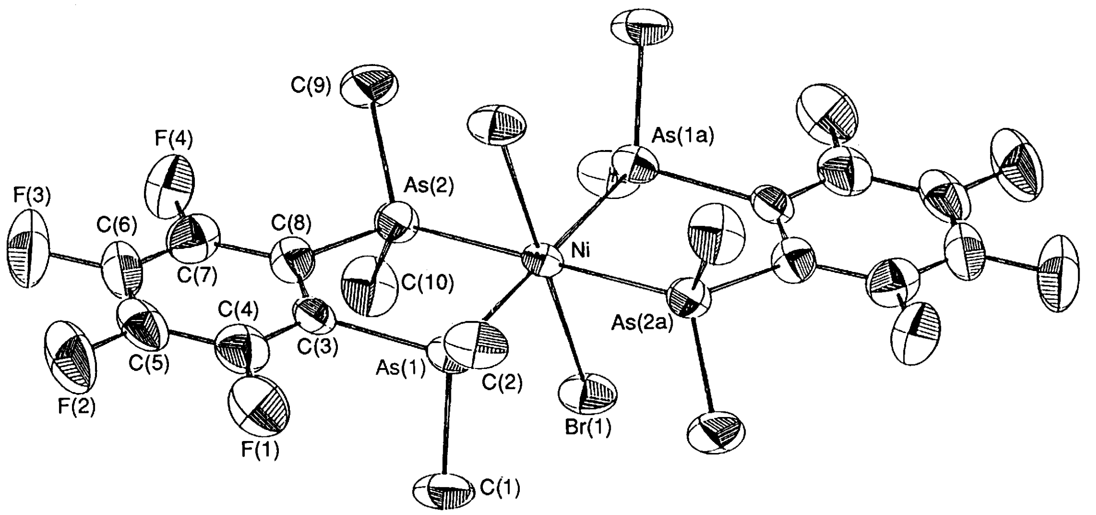


Fig. 1 View of the cation showing the atom-labelling scheme. The thermal ellipsoids are drawn with boundary surfaces at the 50% level

Table 4 Selected bond lengths (Å) and angles (°) for $[\mathrm{Ni}\{o\text{-}\mathrm{C_6F_4(AsMe_2)_2}\}_2\mathrm{Br_2}]\mathrm{BF_4}$

Ni–As(1)	2.336(1)	Ni–Br(1)	2.543(1)
Ni–As(2)	2.339(1)		
As(1)–C(1)	1.959(8)	As(2)–C(8)	1.932(8)
As(1)–C(2)	1.945(8)	As(2)–C(9)	1.945(8)
As(1)–C(3)	1.943(8)	As(2)–C(10)	1.946(8)
	Minimum	Maximum	
C–F	1.32(1)	1.36(1)	
C–C	1.32(1)	1.40(1)	
B–F	1.33(2)	1.59(3)	
As(1) ··· As(2)	3.243(1)	Br(1) ··· As(1a)	3.346(1)
As(1) ··· As(2a)	3.367(1)	Br(1) ··· As(2)	3.571(1)
Br(1) ··· As(1)	3.558(1)	Br(1) ··· As(2a)	3.336(1)
As(1)–Ni–As(2)	87.9(1)	As(1)–Ni–Br(1)	93.5(1)
As(1)–Ni–As(2a)	92.1(1)	As(2)–Ni–Br(1)	93.9(1)
Ni–As(1)–C(1)	119.5(3)	Ni–As(2)–C(8)	105.5(2)
Ni–As(1)–C(2)	116.6(2)	Ni–As(2)–C(9)	117.3(3)
Ni–As(1)–C(3)	105.8(2)	Ni–As(2)–C(10)	119.0(3)
As(1)–C(3)–C(4)	122.3(7)	As(2)–C(8)–C(3)	119.4(6)
As(1)–C(3)–C(8)	117.6(6)	As(2)–C(8)–C(7)	121.9(7)
	Minimum	Maximum	
C–As–C	102.0(4)	106.1(4)	
C–C–C	118.6(8)	121.0(9)	

Symmetry code: a $-x, \frac{1}{2} - y, \frac{1}{2} - z$.

In summary $o\text{-}\mathrm{C_6F_4(AsMe_2)_2}$ is a strongly co-ordinating ligand, lying high in the spectrochemical series, and able to stabilize high oxidation states of the transition elements. More detailed comparison with the complexes of $o\text{-}\mathrm{C_6H_4(AsMe_2)_2}$ reveals that, despite very similar steric properties, the electronic properties, specifically the reduced donor power of $o\text{-}\mathrm{C_6F_4(AsMe_2)_2}$ makes its complexes somewhat less stable. This is particularly evident in the most demanding cases such as the nickel(IV) compounds. Like the corresponding complexes[21] of $o\text{-}\mathrm{C_6F_4(PMe_2)_2}$ those of $o\text{-}\mathrm{C_6F_4(AsMe_2)_2}$ are often less soluble than those of the fluorine-free analogues.

EXAFS Studies.—The instability of nickel(IV) complexes prevents X-ray crystallographic studies, but as shown previously[4] for related chloronickel(IV) complexes the EXAFS technique provides an alternative source of structural data. Nickel and bromine K-edge data were collected for bromo complexes of $\mathrm{Ni^{II}}$, $\mathrm{Ni^{III}}$ and $\mathrm{Ni^{IV}}$ with $o\text{-}\mathrm{C_6H_4(PMe_2)_2}$, $o\text{-}\mathrm{C_6H_4(AsMe_2)_2}$ and $o\text{-}\mathrm{C_6F_4(AsMe_2)_2}$, and for the chloro complexes of the last ligand. The refined EXAFS data are given in Table 5 and examples of the background-subtracted EXAFS and the Fourier transforms are presented in Fig. 2. The nickel K-edge EXAFS data were dominated by back scattering from the donor atoms; only very weak features ascribable to the carbon atoms of the ligand were evident in the Fourier transforms, and attempts to fit further shells for these carbon atoms showed that these were not statistically significant. Two of the complexes, $[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(PMe_2)_2}\}_2]\mathrm{Br_2}$ and $[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(AsMe_2)_2}\}_2]\mathrm{Br_2}$, are effectively planar, and for these a single shell of four P or As atoms gave a good fit to the data, with the refined bond lengths in excellent agreement with data for the same cations in other salts.[4] For the other complexes the data treatment was based upon a two-shell model of four P or As and two halide donors. For the tetragonal nickel(II) complexes of $o\text{-}\mathrm{C_6F_4(AsMe_2)_2}$ the *d*(Ni–As) are long in comparison with those in the planar $[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(AsMe_2)_2}\}_2]^{2+}$ reflecting the increase in co-ordination number, and the effect of the antibonding e_g electrons. The *d*(Ni–X) are also long, consistent with the high-spin d^8 configuration. Oxidation to $\mathrm{Ni^{III}}$ and $\mathrm{Ni^{IV}}$ removes the σ-antibonding electron in the $d_{x^2-y^2}$ orbital and the Ni–As bond shortens to *ca.* 2.35 Å, but differs little between the d^7 and d^6 ions. However the $t_{2g}{}^6e_g{}^1$ configuration in the nickel(III) complexes with the σ-antibonding electron in d_{z^2} produces long Ni–Br bonds (*ca.* 2.54 Å), whilst oxidation to $\mathrm{Ni^{IV}}$, $t_{2g}{}^6$, results in a marked shortening to *ca.* 2.34 Å. These changes parallel those reported previously for the corresponding chloro complexes.[4]

In view of the similarity of the $\mathrm{Ni^{IV}}$–Br and $\mathrm{Ni^{IV}}$–As bond lengths the data for the nickel(IV) bromo complexes were also fitted to a single shell of six As or six Br atoms. Comparison of the two models showed significantly lower *R* factors for the two-shell model and this model also passed the Joyner test.[22] The highest correlations (*ca.* 0.8) were between the two distances, but these fell within acceptable levels, and we conclude that the two-shell fit is justified. Bromine K-edge data for these complexes proved to be of lower quality. Fits to a single nickel shell gave bond lengths in acceptable agreement with the Ni-edge data results (Table 5). Models were also developed based upon two (Ni and remote Br) and three (Ni, remote Br and four As) shells resulting in improved fits but no significant change in *d*(Ni–Br); these were not pursued due to the relatively poor quality of the original data.

Nickel K-edge data for the $o\text{-}\mathrm{C_6F_4(AsMe_2)_2}$ chloro complexes were also obtained (Table 5) and the Ni–As bond lengths are generally consistent with previous data.[4] Curiously the *d*(Ni–Cl) are slightly shorter for both the nickel-(III) and -(IV) complexes than for the complexes of related ligands. The

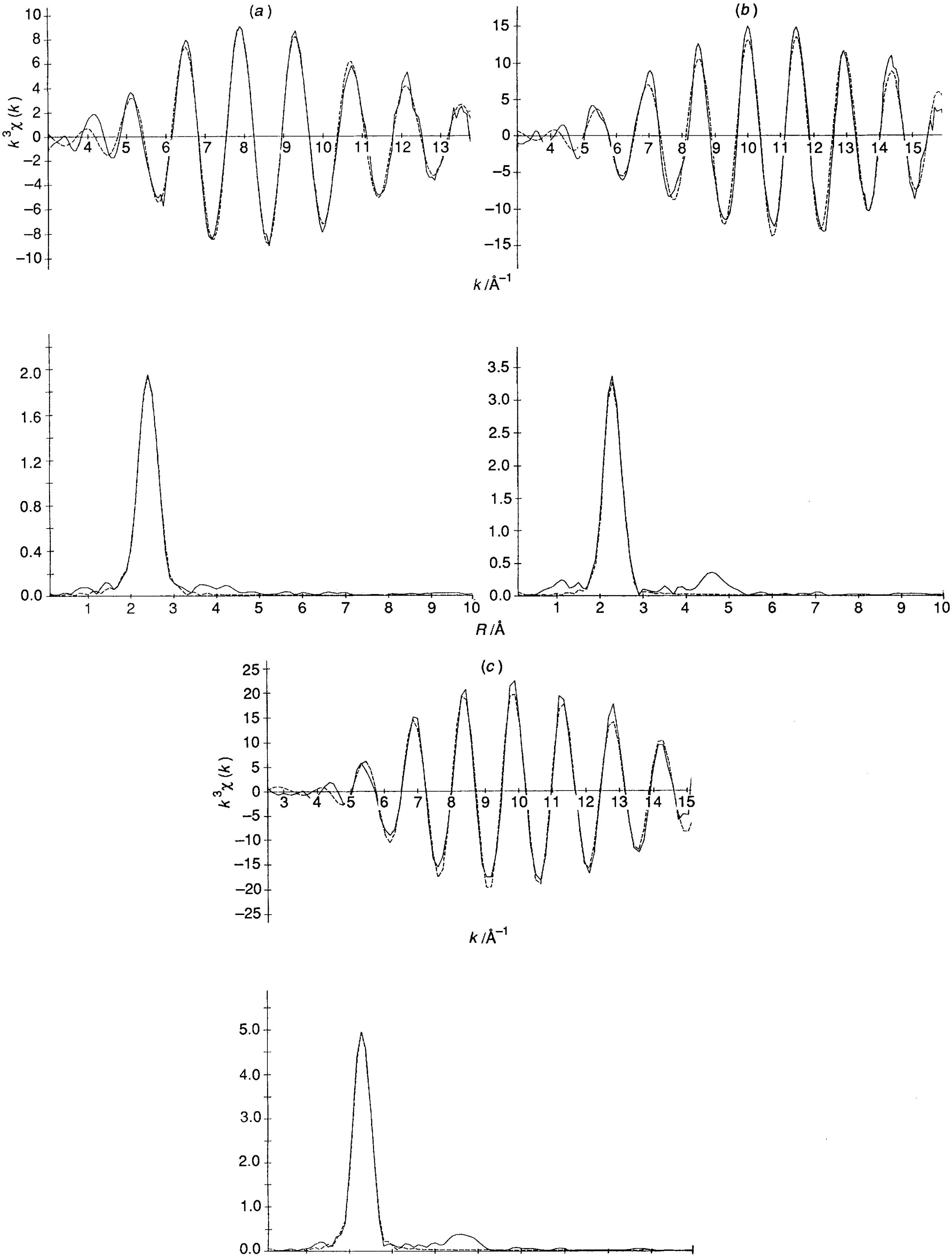


Fig. 2 The background-subtracted nickel K-edge EXAFS (——, experimental × k^3; – – –, curved-wave theory × k^3) and the Fourier transforms (—, experimental; – – –, theoretical) for (*a*) [Ni{*o*-$C_6F_4(AsMe_2)_2$}$_2$Br$_2$], (*b*) [Ni{*o*-$C_6F_4(AsMe_2)_2$}$_2$Br$_2$]BF$_4$ and (*c*) [Ni{*o*-$C_6F_4(AsMe_2)_2$}$_2$Br$_2$][ClO$_4$]$_2$

Table 5 EXAFS data

	d(Ni–X)[a]/Å	$2\sigma^2$[b]/Å^2	d(Ni–E)/Å	$2\sigma^2$/Å^2	R(%)[c]	Fit index[d]
Nickel K-edge data						
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(AsMe_2)_2}\}_2]\mathrm{Br_2}$	—	—	2.29	0.007	18.4	4.13
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6F_4(AsMe_2)_2}\}_2\mathrm{Br_2}]$	2.55	0.014	2.46	0.012	14.0	1.07
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(PMe_2)_2}\}_2]\mathrm{Br_2}$	—	—	2.18	0.007	20.6	2.99
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(AsMe_2)_2}\}_2\mathrm{Br_2}]\mathrm{BF_4}$	2.54	0.014	2.33	0.007	22.1	7.32
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6F_4(AsMe_2)_2}\}_2\mathrm{Br_2}]\mathrm{BF_4}$	2.53	0.011	2.34	0.007	19.4	3.14
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(PMe_2)_2}\}_2\mathrm{Br_2}]\mathrm{BF_4}$	2.56	0.016	2.24	0.007	22.6	3.09
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(AsMe_2)_2}\}_2\mathrm{Br_2}][\mathrm{ClO_4}]_2$	2.32	0.011	2.36	0.006	18.5	13.14
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6F_4(AsMe_2)_2}\}_2\mathrm{Br_2}][\mathrm{ClO_4}]_2$	2.36	0.007	2.35	0.007	16.1	8.21
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(PMe_2)_2}\}_2\mathrm{Br_2}][\mathrm{ClO_4}]_2$	2.32	0.007	2.26	0.008	18.1	6.52
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6F_4(AsMe_2)_2}\}_2\mathrm{Cl_2}]$	2.34	0.005	2.44	0.016	24.4	3.00
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6F_4(AsMe_2)_2}\}_2\mathrm{Cl_2}]\mathrm{BF_4}$	2.35	0.020	2.33	0.007	18.3	5.63
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6F_4(AsMe_2)_2}\}_2\mathrm{Cl_2}][\mathrm{ClO_4}]_2$	2.19	0.004	2.35	0.009	25.3	12.90
Bromine K-edge data						
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(AsMe_2)_2}\}_2\mathrm{Br_2}]\mathrm{BF_4}$	2.56	0.011			28.9	0.28
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6F_4(AsMe_2)_2}\}_2\mathrm{Br_2}]\mathrm{BF_4}$	2.51	0.013			45.0	0.56
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(PMe_2)_2}\}_2\mathrm{Br_2}]\mathrm{BF_4}$	2.57	0.010			36.3	0.48
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(AsMe_2)_2}\}_2\mathrm{Br_2}][\mathrm{ClO_4}]_2$	2.34	0.006			29.0	1.46
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6F_4(AsMe_2)_2}\}_2\mathrm{Br_2}][\mathrm{ClO_4}]_2$	2.33	0.006			35.1	1.02
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(PMe_2)_2}\}_2\mathrm{Br_2}][\mathrm{ClO_4}]_2$	2.34	0.005			34.1	2.08

[a] With current data-analysis packages EXAFS-determined bond lengths are accurate to ±0.02 Å. [b] Debye–Waller parameter. [c] R factor defined as $\int|\chi^T - \chi^E|k^3\mathrm{d}k/\int|\chi^E|k^3\mathrm{d}k \times 100$. [d] Fit index defined as $(1/100n)\Sigma_i[(\chi_i^T - \chi_i^E)k_i^3]^2$ where the summation is over the n data points.[22]

apparent shortening is *ca.* 0.08 Å, which is larger than the error limits expected in the EXAFS data (*ca.* 0.02–0.03 Å), even allowing for the fact that the arsenics are responsible for the major back-scattering component. It is possible that the weaker donor power of o-$\mathrm{C_6F_4(AsMe_2)_2}$ results in tighter binding of the chlorines, although it should be noted that a similar effect does not seem to be present in the bromo complexes. The data for the nickel(IV) bromo complexes are the first structural data on these systems, and will be of value for comparison with data from the mixed-valence diamine systems.

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