Co-ordination Chemistry of Higher Oxidation States. Part 17.[1] Synthesis and Properties of Nickel(IV) Complexes with Neutral Ligands, and Structures of $[Ni\{o\text{-}C_6H_4(EMe_2)_2\}_2Cl_2][ClO_4]_n$ (E = P or As; *n* = 1 or 2) by Nickel *K*-edge Extended *X*-Ray Absorption Fine Structure†

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Pseudo-octahedral nickel(IV) complexes $[Ni(L\text{-}L)_2X_2][ClO_4]_2$ [X = Cl or Br; L–L = $o\text{-}C_6H_4(PMe_2)_2$, $o\text{-}C_6F_4(PMe_2)_2$, $o\text{-}C_6H_4(PMe_2)(AsMe_2)$, or $o\text{-}C_6H_4(AsMe_2)_2$] have been prepared by HNO_3–HX oxidation of $[Ni(L\text{-}L)_2X_2]$, followed by treatment with $HClO_4$, and $[Ni(Me_2PCH_2CH_2PMe_2)_2Cl_2][BF_4]_2$ by Cl_2–CCl_4 oxidation of $[Ni(Me_2PCH_2CH_2PMe_2)_2][BF_4]_2$. The complexes have been characterised by elemental analysis, i.r., u.v.–visible, and e.s.r. spectroscopy and magnetic measurements. Cyclic voltammetry has been used to study the Ni^{II}–Ni^{III}–Ni^{IV} redox potentials as a function of L–L. Extended *X*-ray absorption fine structure of the nickel *K*-edge has led to the first co-ordination sphere bond lengths for the title complexes: $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2]^+$ (Ni–P = 2.25, Ni–Cl = 2.41 Å), $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2]^+$ (Ni–As = 2.34, Ni–Cl = 2.42 Å), $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2]^{2+}$ (Ni–P = 2.225, Ni–Cl = 2.275 Å), $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2]^{2+}$ (Ni–As = 2.39, Ni–Cl = 2.27 Å), which are interpreted as evidence for metal centred oxidation $\{n = 1 \longrightarrow n = 2$ in $[Ni(L\text{-}L)_2X_2]^{n+}\}$.

Nickel(IV) is a rare oxidation state,[2] well characterised simple compounds being limited to M_2NiF_6 (M = Na, K, Rb, or Cs)[3] and oxoanions, *e.g.* $BaNiO_3$[4] and $[NiNb_{12}O_{38}]^{12-}$.[5] Complexes with anionic ligands include those with dithio-[6] and diseleno-carbamates,[7] and a variety of bi- and multi-dentate oximes.[8–13] Nickel(IV) bound to neutral ligands is particularly rare, the only examples being $[Ni(L\text{-}L)_2Cl_2][ClO_4]_2$ [L–L = $o\text{-}C_6H_4(AsMe_2)_2$,[14] or $o\text{-}C_6H_4(PMe_2)_2$[15]] and $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2Br_2][ClO_4]_2$,[14] which have not been studied in any detail. As an extension of our studies of Ni^{III},[16] Pd^{IV},[17] and Pt^{IV}[18] we report here a detailed characterisation of Ni^{IV} complexes with neutral ligands, and structural data on the title complexes. A preliminary communication of some aspects of this work has appeared.[19]

Results and Discussion

$[Ni(L\text{-}L)_2X_2][ClO_4]_2$ [L–L = $o\text{-}C_6H_4(PMe_2)_2$, $o\text{-}C_6H_4(AsMe_2)_2$, $o\text{-}C_6H_4(PMe_2)(AsMe_2)$, *or* $o\text{-}C_6F_4(PMe_2)_2$; X = Cl *or* Br].—Oxidation of $[Ni(L\text{-}L)_2][ClO_4]_2$ with concentrated HNO_3 in the presence of a few drops of concentrated HX at 0 °C gave deep red or green solutions from which 70% perchloric acid (**CARE:** explosion hazard) precipitated the $[Ni(L\text{-}L)_2X_2][ClO_4]_2$ complexes. Isolation of pure samples is critically dependent upon the method of isolation used. For example, the literature[14] synthesis of $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2][ClO_4]_2$ (which involves dilution of a conc. HNO_3–conc. $HClO_4$ solution of the Ni^{IV} complex with water to precipitate the product) gave products which often incorporated nitrogen, and containing significant amounts of the Ni^{III} analogue (e.s.r. evidence). Attempts to obviate the use of the potentially explosive ClO_4^- salts were not successful; HPF_6 or HBF_4 precipitated the Ni^{IV} complexes from HNO_3 solution, but these products were less pure (analytically and by e.s.r.) than the perchlorates, whilst addition of CF_3SO_3H failed to produce any precipitates. Oxidation of $[Ni(Me_2PCH_2CH_2PMe_2)_2][ClO_4]_2$ by conc. HNO_3–conc. HCl produced a deep purple solution, but the product could not be precipitated even by 70% $HClO_4$. The extremely hygroscopic purple $[Ni(Me_2PCH_2CH_2PMe_2)_2Cl_2][BF_4]_2$ was eventually isolated by chlorination of $[Ni(Me_2PCH_2CH_2PMe_2)_2][BF_4]_2$ suspended in dry CCl_4. Bromine however is an insufficiently strong oxidant to produce the bromo-analogue, and only the known[16] Ni^{III} complex $[Ni(Me_2PCH_2CH_2PMe_2)_2Br_2]BF_4$ was produced. Nitric acid decomposed the nickel(II) complexes of $o\text{-}C_6H_4(SbMe_2)_2$, $o\text{-}C_6H_4(PPh_2)_2$, and $Ph_2PCH_2CH_2PPh_2$, and also those of $o\text{-}C_6H_4(PMe_2)(SbMe_2)$ and $o\text{-}C_6H_4(PMe_2)(SMe)$. The case of the last two ligands is interesting since a similar strategy, incorporation of an $o\text{-}C_6H_4(PMe_2)$ group, *was* successful in yielding the first Ni^{III}–stibine and –thioether linkages.[16]

The complex $[Ni(en)_2Cl_2]Cl_2$ (en = $H_2NCH_2CH_2NH_2$) could not be isolated although this moiety is present[20] in the mixed-valence material $[Ni^{II}(en)_2][Ni^{IV}(en)_2Cl_2]Cl_4$. Palladium(IV) is also more stable in mixed-valence materials[21] than in simple complexes.[17] No nickel(IV) complexes of the type $[Ni(L\text{-}L)Cl_4]$ could be obtained (L–L = various diphosphines and diarsines), as the compounds $[Ni(L\text{-}L)Cl_3]$[16] decompose with oxidation of the neutral ligand on further chlorination or in conc. HNO_3.

Properties. The $[Ni(L\text{-}L)_2X_2][ClO_4]_2$ complexes (Table 1) range in colour from dark violet to dark green, and are diamagnetic ($\mu \leqslant 0.6$ B.M.) as expected for a d^6 metal ion. Freshly-prepared pure samples of the complexes with L–L = $o\text{-}C_6H_4(PMe_2)_2$, $o\text{-}C_6H_4(PMe_2)(AsMe_2)$, or $o\text{-}C_6F_4(PMe_2)_2$ exhibited no e.s.r. signals, but those of $o\text{-}C_6H_4(AsMe_2)_2$ always gave weak e.s.r. signals indicative of trace Ni^{III} impurities.‡ Interestingly the $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2]^+$ 'impurity' in the

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† *Non-S.I. units employed:* B.M. = 0.927×10^{-23} A m², eV ≈ 1.60×10^{-19} J.

‡ The $[Ni(L\text{-}L)_2X_2]^+$ complexes give highly characteristic e.s.r. spectra at room temperature at low microwave power and receiver gain settings (ref. 16 and refs. therein).

Table 1. Analytical and physical data

Complex	Colour	Analysis[a] (%) C	H	X	ν(Ni–X)/ cm^{-1} [b]	Electronic spectra $10^{-3}E_{max.}/cm^{-1}$ [c]	$10^{-3}E_{max.}/cm^{-1}$ ($\varepsilon_{mol}/dm^3\ mol^{-1}\ cm^{-1}$)[d]
$[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2][ClO_4]_2$	Dark violet	33.0 (33.1)	4.4 (4.5)	9.8 (9.8)	425 (236)	16.8(sh), 17.8, 23.25, 26.2	18.25 (500), 27.78 (14 700)
$[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2Br_2][ClO_4]_2$	Dark green	29.3 (29.5)	4.2 (4.0)	—	306 (180)	14.6(sh), 16.85, 23.15, 26.45	17.18 (1 470), 27.03 (11 600)
$[Ni\{o\text{-}C_6F_4(PMe_2)_2\}_2Cl_2][ClO_4]_2$	Violet	27.3 (27.7)	2.8 (3.0)	7.9 (8.2)	425 (235)	16.9(sh), 18.0, 24.6, 26.7	18.59 (—)
$[Ni\{o\text{-}C_6F_4(PMe_2)_2\}_2Br_2][ClO_4]_2$	Dark green	25.1 (25.0)	2.5 (2.6)	16.4 (16.7)	315 (183)	16.7, 24.5	17.24 (—)
$[Ni\{o\text{-}C_6H_4(PMe_2)(AsMe_2)\}_2Cl_2][ClO_4]_2$	Dark green	30.0 (29.6)	4.2 (4.0)	8.5 (8.7)	416 (248)	15.9(sh), 17.5(br), 24.9	17.12 (970)
$[Ni\{o\text{-}C_6H_4(PMe_2)(AsMe_2)\}_2Br_2][ClO_4]_2$	Dark green	26.2 (26.6)	3.7 (3.6)	—	306 (189)	16.3, 24.6, 29.9	16.45 (1 550)
$[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2][ClO_4]_2$	Dark blue	26.9 (26.7)	3.6 (3.6)	—	418 (260)	15.7(sh), 16.5, 24.4, 26.6	16.90 (2 850), 26.88 (13 700)
$[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2Br_2][ClO_4]_2$	Green	23.8 (24.3)	3.0 (3.2)	—	311 (193)	16.2, 24.2, 26.2	Decomposes
$[Ni\{Me_2PCH_2CH_2PMe_2\}_2Cl_2][BF_4]_2$[e]	Violet	22.0 (23.9)	5.5 (5.3)	—	—	16.95 (sh), 17.6, 24.3	Decomposes
$[Co\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2]PF_6$	Light violet	35.7 (35.8)	4.8 (4.8)		398	—	17.79 (63), 26.88 (3 530)[f]
$[Co\{o\text{-}C_6F_4(PMe_2)_2\}_2Cl_2]Cl$	Light violet	34.3 (34.1)	3.4 (3.4)		399	—	17.86 (102), 27.17 (3 240)[f]

[a] Calculated values in parentheses. [b] Nujol mulls, values in parentheses are ν(Ni–X) for the Ni^{III} analogues from ref. 16. [c] Diffuse reflectance. [d] CF_3CO_2H solution unless otherwise indicated. [e] Compound is highly unstable and the analysis reflects this. [f] MeCN solution.

bulk Ni^{IV} material gave an axial e.s.r. spectrum ($g_1 = 2.133$, $g_2 = 2.016$), whereas the bulk Ni^{III} material gives a rhombic spectrum. Previous studies of the Ni^{III} complex in the Co^{III} host $[Co\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2]^+$ reported rhombic spectra at concentrations > ~10% Ni^{III} and axial spectra ($g_1 = 2.14, g_2 = 2.08$) at the ~5% Ni^{III} concentration level.[22]

All the Ni^{IV} complexes develop the characteristic rhombic[16] e.s.r. spectra of the Ni^{III} analogues on storage for a few days at room temperature. The complexes are insoluble in halocarbons and decomposed by the common organic solvents, but are soluble in anhydrous trifluoroacetic acid although the solutions decompose on standing. All attempts to grow crystals *in situ* from $[Ni(L\text{-}L)_2][ClO_4]_2$–HX–$HNO_3$–$HClO_4$ mixtures for an *X*-ray study were unsuccessful, but the Ni–ligand bond lengths were measured for two examples by the extended *X*-ray absorption fine structure (EXAFS) technique (see below).

Careful comparison of the far-i.r. spectra of corresponding chloro- and bromo-complexes reveals the presence of single medium intensity bands at *ca.* 420 cm^{-1} (Cl) and *ca.* 310 cm^{-1} (Br) assignable as ν(Ni–X) stretches B_{1u}, consistent with *trans* D_{2h} structures for the cations. The Ni^{III} analogues have ν(Ni–X) at *ca.* 250 cm^{-1} (Cl) and *ca.* 190 cm^{-1} (Br) (Table 1). The large high-frequency shifts in the Ni^{IV} complexes are consistent[23] with the removal of the antibonding electron ($t_{2g}^6e_g^1$ $Ni^{III} \longrightarrow t_{2g}^6e_g^0$ Ni^{IV}), and correlate with the short Ni^{IV}–X bonds found in the EXAFS study.

Electronic spectra were recorded both by diffuse reflectance (d.r.) and in freshly-prepared solutions in anhydrous trifluoroacetic acid, although even in the latter decomposition is rapid, and the absorption coefficients in Table 1 are only approximate. The spectra (Figure 1) are very similar in profile to those of the corresponding *trans*-$[Co(L\text{-}L)_2X_2]^+$ complexes, again supporting the presence of isoelectronic Ni^{IV}, and consist of one moderate intensity band at *ca.* (16—19) × 10^3 cm^{-1}, and more intense bands >25 × 10^3 cm^{-1}. In D_{4h} symmetry the first band can be assigned as the first spin-allowed transition of a d^6 ion, $^1A_1 \longrightarrow {}^1E$, and the remainder to L $\longrightarrow$ Ni e_g charge-transfer bands. The $^1A_1 \longrightarrow {}^1E$ transition shifts to higher energy in the order Br < Cl and $o\text{-}C_6H_4(AsMe_2)_2 < o\text{-}C_6H_4(PMe_2)(AsMe_2) < o\text{-}C_6H_4(PMe_2)_2 \leqslant o\text{-}C_6F_4(PMe_2)_2$. However this transition energy in ligand-field theory corresponds to $10Dq - C - 35/4Dt$,[24] involving the Racah parameter *C*, and the tetragonality parameter *Dt* in addition to *Dq*, and since the higher energy *d–d* bands were obscured by the charge-transfer transitions, any analysis of the relative importance of these terms as a function of changes in the ligands is precluded. The $Ni^{II} \longleftrightarrow Ni^{III} \longleftrightarrow Ni^{IV}$ redox reactions were examined by cyclic voltammetry, and representative data are given in Table 2. The Ni^{II}–Ni^{III} couples involve a change in co-ordination number (6 for Ni^{III}, 4 or 5 for Ni^{II}) and are not electrochemically reversible. The couples are influenced by whether NEt_4Cl or

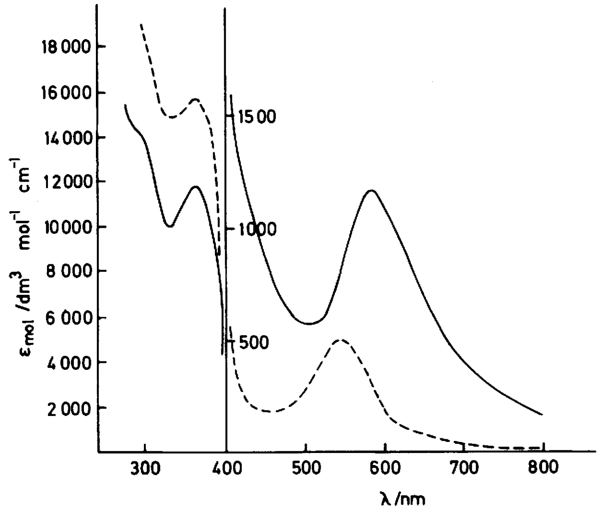

Figure 1. Electronic spectra of $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2X_2][ClO_4]_2$ [(——) X = Br, (- - -) X = Cl] in trifluoroacetic acid solution

Table 2. Electrochemical data

	Ni^{II}–Ni^{III}			Ni^{III}–Ni^{IV}			
Complex	I_p(av.)[a]	I_{pa}/I_{pc}	ΔE_p/mV	I_p(av.)[a]	I_{pa}/I_{pc}	ΔE_p/mV	Ref.
$[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2][ClO_4]_2$[b]	0.29	1.04	80	—	—	—	This work
$[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2]$[c]	0.36	1.10	110	1.18	1.04	75	This work
$[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2]$[d]	0.35	—	—	1.26	—	—	15
$[Ni\{o\text{-}C_6F_4(PMe_2)_2\}_2][ClO_4]_2$[b]	0.41	1.01	70	—	—	—	This work
$[Ni\{o\text{-}C_6F_4(PMe_2)_2\}_2Cl_2]$[c]	0.47	1.08	70	1.40	1.02	65	This work
$[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2]$[d]	0.21	—	—	1.30	—	—	15
$[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2Br_2]$[d]	0.49	—	—	1.23	—	—	15
$[Ni(Me_2PCH_2CH_2PMe_2)_2][BF_4]_2$[b]	0.22	1.04	100	—	—	—	This work

[a] In volts (±0.01). [b] 0.1 mol dm^{-3} NEt_4Cl in CH_3CN as supporting electrolyte; carbon electrode, potentials *versus* standard calomel electrode (s.c.e.). [c] 0.1 mol dm^{-3} $NBu^n{}_4BF_4$ in CH_3CN as electrolyte; carbon electrode, potentials *versus* s.c.e. [d] 0.1 mol dm^{-3} NEt_4ClO_4 in CH_3CN as electrolyte; Pt electrode *versus* Ag–$AgClO_4$, literature values converted to s.c.e. by adding +0.46.

NEt_4BF_4 is used as supporting electrolyte, due to the equilibrium $[Ni(L\text{-}L)_2]^{2+} + Cl^- \rightleftharpoons [Ni(L\text{-}L)_2Cl]^+$ in the Ni^{II} systems.[15,25] The Ni^{III}–Ni^{IV} couples which are reversible could only be measured with NEt_4BF_4 as supporting electrolyte, since the potentials are similar to that of $Cl^- \longrightarrow \frac{1}{2}Cl_2 + e^-$. In spite of these limitations two significant features emerge from the data. First, the oxidation of the nickel(II) complex of $Me_2PCH_2CH_2PMe_2$ occurs at a similar potential to those of $o\text{-}C_6H_4(PMe_2)_2$ or $o\text{-}C_6H_4(AsMe_2)_2$, but unlike the latter, no evidence for a further *reversible* oxidation to Ni^{IV} was observed with the aliphatic diphosphine complex, only several ill defined oxidation peaks and no corresponding reduction peaks. This correlates with the immediate decomposition in solution of the chemically prepared $[Ni(Me_2PCH_2CH_2PMe_2)_2Cl_2][BF_4]_2$. Secondly, in both the Ni^{II}–Ni^{III} and Ni^{III}–Ni^{IV} couples oxidation is considerably harder for complexes of $o\text{-}C_6F_4(PMe_2)_2$ than for those of $o\text{-}C_6H_4(PMe_2)_2$.

The instability of the Ni^{IV} complexes in solution prevents ligand exchange reactions, *e.g.* $[Ni(L\text{-}L)_2Cl_2]^{2+}$–LiBr or conversion of *trans*-$[Ni(L\text{-}L)_2X_2]^{2+}$ to (the unknown) *cis*-$[Ni(L\text{-}L)_2X_2]^{2+}$ *via* $Ag(O_2CMe)$ [*cf.* Co^{III} *trans* ⟶ *cis* conversions[26]].

EXAFS: Data Collection and Analysis.—The EXAFS measurements were carried out at room temperature on undiluted powdered samples (approx. 1 mm in thickness) which were contained between strips of 'sellotape'. The procedure was sufficient to prevent any hydrolysis of the hygroscopic samples for the duration of two scans (each 30 min). The absence of any sample deterioration/changes in the EXAFS showed that no radiation damage had occurred.

The *X*-ray absorption measurements were recorded in the transmission mode at the Daresbury Synchrotron Radiation Source operating at an energy of 1.8 GeV and an average current of 150 mA. A channel cut Si (111) crystal was used as monochromator.[27] Each scan was extended above the edge until all EXAFS oscillations had damped out. For most of the compounds analysed one scan was sufficient for data analysis, however in one case, $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2]^+$, the average of two scans was used. Data analysis employed single-scattering spherical-wave theory for calculating EXAFS with phase shifts derived from *ab initio* calculations as described previously.[28,29] The EXAFS is plotted in *K*-space where $K = \sqrt{0.263(E - E_0)}$ [K (Å^{-1}) = photoelectron wave vector, E (eV) = energy of the beam, and E_0 (eV) = energy zero of the photoelectron wave]. The EXAFS amplitude is multiplied by K^2 to 'highlight' the amplitude at higher *K*, where single scattering theory is most accurate. The quality of fit was assessed using criteria described elsewhere,[29] by means of a non-linear least-squares minimisation program, and is quoted for $K^2/3.57$ weighted spectra. Minimisation was performed for distance and Debye–Waller parameters.*

The model compounds (*i.e.* those for which *X*-ray crystallographic data were available) were used to assess the transferability of the calculated phase shifts. It was found that calculated phase shifts using neutral atoms within the 'muffin-tin' approximation were completely satisfactory for the nickel–phosphorus–chlorine systems. However, similarly calculated phase shifts for the nickel–arsenic–chlorine systems were unsatisfactory in that there was a considerable departure from the known *X*-ray crystallographic values for *d*(Ni–As) and *d*(Ni–Cl) in $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2]ClO_4$ [EXAFS calculation (I) in Table 3]. This problem may arise from a number of factors, resulting from the similar co-ordination distances of arsenic and chlorine atoms with greatly different back-scattering power. In order to overcome this, the calculated phase shifts were refined on the Ni^{III} complex using the known crystallographic bond distances, and then transferred to the other compounds [Table 3, EXAFS calculation (II)]. An attempt to mimic these refined phase shifts required the use of a three-positive charge on the central nickel atom in the phase-shift calculation. In view of the good correlation between the *X*-ray crystallographic data and the EXAFS determined bond lengths using the refined phase shifts [calculation (II)] for the nickel(II) and (necessarily) the nickel(III)–diarsine complexes, we believe that the data from calculation (II) are the most reliable for $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2][ClO_4]_2$. It is also encouraging to note that these data and those for $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2][ClO_4]_2$ give internally consistent *d*(Ni–Cl) bond lengths. A full listing of the bond distances is given in Table 3, and the EXAFS and their Fourier transforms are shown in Figure 2.

For $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2]^+$ the two overlapping shells can be seen in the Fourier transform where the difference in Ni–P and Ni–Cl is approximately 0.16 Å. For the analogous Ni^{IV} complex both distances are reduced, the Ni–Cl very considerably. With the two distances being so similar (Table 3) and the atoms having similar back scattering one might consider reversing the assignments or quoting a single shell with average Ni–L at 2.245 (±0.03) Å. However reversing the radii and subsequent refinement affords less satisfactory fits, and causes the Debye–Waller factor of the chlorine to become so high as to deny its presence. An attempted fit with only phosphorus atom (4 P) co-ordination gave a distance of 2.25 Å but a far worse fit (f.i. = 0.50). In the Fourier transforms of the diphosphine complexes a small peak can be seen at approximately 4.5 Å. This cannot be assigned to the nearest carbon atoms (either methyl or *ipso*-carbon) but may result from the *ortho*-carbons of the phenyl rings.

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* Debye–Waller factor σ involves both static and thermal disorder.[27]

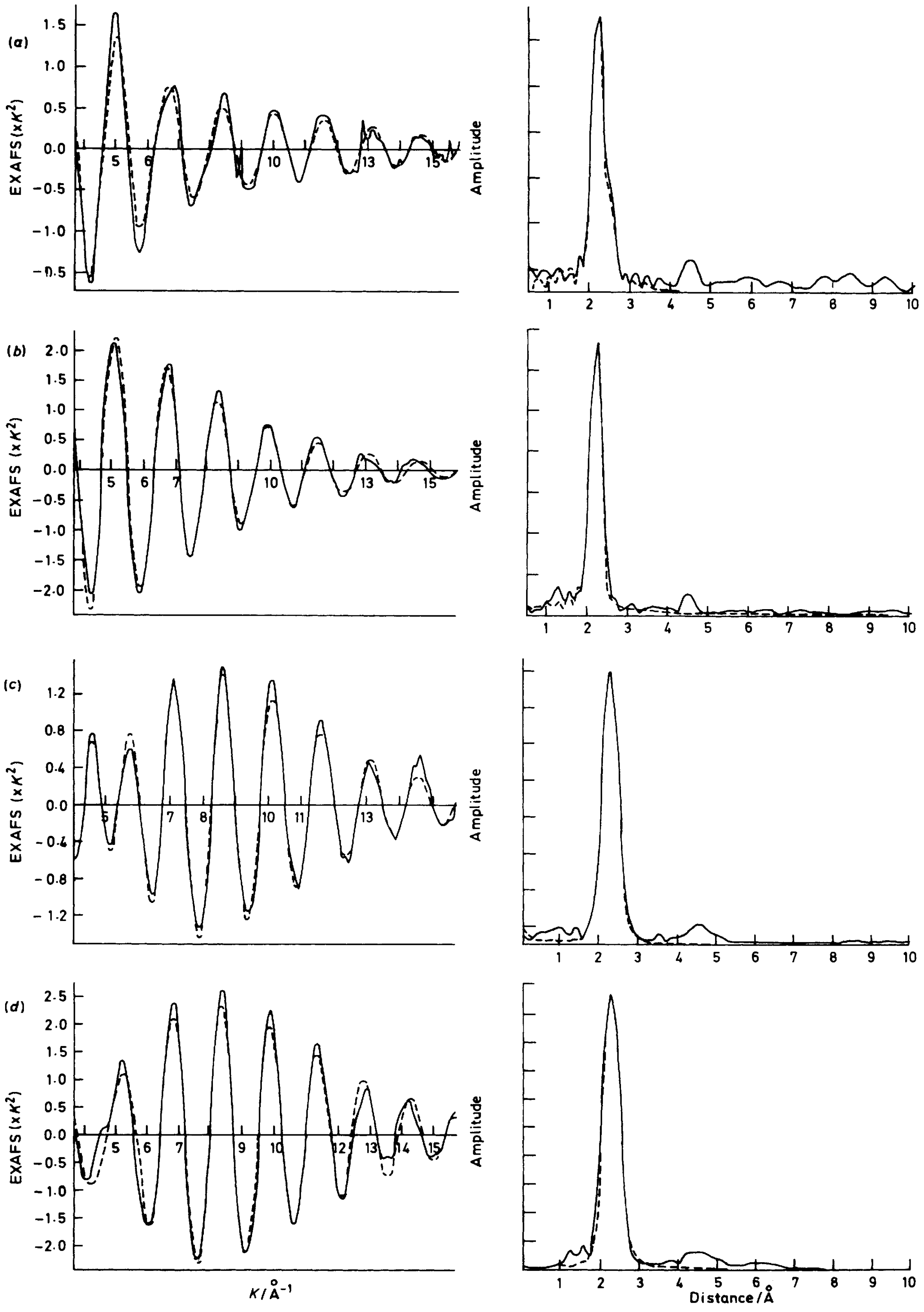

Figure 2. K^2 Weighted EXAFS (left) and their Fourier transforms (right): (*a*) $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2]ClO_4$, (*b*) $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2][ClO_4]_2$, (*c*) $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2]ClO_4$ [calculation (II)], and (*d*) $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2][ClO_4]_2$ [calculation (II)]. (——) Experimental data, (- - -) calculated

Table 3. Selected nickel–ligand bond lengths (Å)

Compound	Technique	d(Ni–E)[a]	d(Ni–Cl)	σ/Å^2	E_0/eV	Fit index (f.i.)	Ref.
$[PMePh_3][NiCl_4]$	EXAFS	—	2.25	0.010	24.68	0.18	This work
$[AsMePh_3][NiCl_4]$	*X*-Ray	—	2.27(1)				*b*
$[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2][ClO_4]_2$	EXAFS	2.19	—	0.007	27.34	0.20	This work
$[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2]I_{10}$	*X*-Ray	2.205(av.)	—				*c*
$[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2]ClO_4$	EXAFS	2.25	2.41	0.007, 0.008	27.59	0.12	This work
	X-Ray	2.255(3)	2.424(4)				*d*
$[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2][ClO_4]_2$	EXAFS	2.225	2.275	0.006, 0.008	27.59	0.19	This work
$[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2][ClO_4]_2$	EXAFS Calc. (I)	2.28	—	0.008	22.18	0.24	This work
	Calc. (II)	2.30		0.007	22.18	0.25	This work
$[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2]I_2$	*X*-Ray	2.29(av.)	—				*e*
$[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2]ClO_4$	*X*-Ray	2.342(2)	2.425(5)				*f*
	EXAFS Calc. (I)	2.31	2.33	0.008, 0.012	22.23	0.076	This work
	Calc.(II)	2.34	2.42	0.009, 0.009	21.47	0.086	This work
$[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2][ClO_4]_2$	EXAFS Calc. (I)	2.36	2.21	0.004, 0.007	22.47	0.23	This work
	Calc. (II)	2.39	2.275	0.007, 0.004	22.47	0.36	This work
$[Co\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2]ClO_4$	*X*-Ray	2.241(av.)[g]	2.253(av.)[h]				*i*
$[Co\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2]Cl$	*X*-Ray	2.334(av.)[g]	2.256(3)[h]				*f*

[a] E = P or As; using current data analysis packages EXAFS distances are accurate to ±0.01—0.02 Å. [b] P. Pauling, *Inorg. Chem.*, 1966, **5**, 1498. [c] L. R. Gray, S. J. Higgins, W. Levason, and M. Webster, *J. Chem. Soc., Dalton Trans.*, 1984, 1433. [d] C. Mahadevan, M. Seshasayee, B. L. Ramakrishna, and P. T. Manoharan, *Acta Crystallogr., Sect. C*, 1985, **41**, 38. [e] N. C. Stephenson, *Acta Crystallogr.*, 1964, **17**, 592. [f] P. Kreisman, G. A. Rodley, R. Marsh, and H. B. Gray, *Inorg. Chem.*, 1972, **11**, 3040. [g] Co–E. [h] Co–Cl. [i] Unpublished data quoted in L. F. Warren and M. A. Bennett, *Inorg. Chem.*, 1976, **15**, 3126.

From Table 3 it can be seen that there is an increase in d(Ni–E) (E = P or As) between the four-co-ordinate $[Ni\{o\text{-}C_6H_4(EMe_2)_2\}_2]^{2+}$ and the six-co-ordinate $[Ni\{o\text{-}C_6H_4(EMe_2)_2\}_2Cl_2]^{n+}$ (n = 1 or 2); similar changes were found in the corresponding Pd^{II}–Pd^{IV} diarsine compounds,[17] and are partly due to the increase in co-ordination number of the metal centre. Further changes in d(Ni–P) in the six-co-ordinate diphosphine compound between n = 1 and n = 2 are small, but there is a more marked lengthening in d(Ni–As) ($Ni^{III} < Ni^{IV}$), which may reflect poorer overlap of the arsenic and nickel orbitals as the metal orbitals contract with increasing oxidation state. There is a dramatic shortening in d(Ni–Cl) between n = 1 and n = 2, which correlates with the removal of the σ-antibonding $(3d_{z^2})^1$ electron on oxidation.

The large changes in d(Ni–Cl) and small variations in d(Ni–E) between $[Ni\{o\text{-}C_6H_4(EMe_2)_2\}_2Cl_2]^+$ and $[Ni\{o\text{-}C_6H_4(EMe_2)_2\}_2Cl_2]^{2+}$ is unequivocal evidence for metal centred oxidation. It is inconsistent with the cation–radical ligand description sometimes suggested (*e.g.* ref. 8) in that a dithiolene like system would not show such a large reduction in d(Ni–Cl). Data on two isoelectronic Co^{III} complexes is also given in Table 3 for comparison with the Ni^{IV} systems.

Conclusions

Nickel(IV) complexes of the type $[Ni(L\text{–}L)_2X_2][ClO_4]_2$ (X = Cl or Br) were obtained only with the ligands $o\text{-}C_6H_4(PMe_2)_2$, $o\text{-}C_6H_4(AsMe_2)_2$, $o\text{-}C_6H_4(PMe_2)(AsMe_2)$, $o\text{-}C_6F_4(PMe_2)_2$, and (X = Cl) with $Me_2PCH_2CH_2PMe_2$, which combine strong σ donor power with small steric demands. Strong σ bonding (a π-acceptor component is unlikely to be important in view of the high metal oxidation state) will maximise the ligand field stabilisation energy (l.s.f.e.) contribution to the stability, particularly important for a d^6 ion $(t_{2g}^6e_g^0)$ in a pseudo-octahedral field. The formation of the stable complexes by ligands with $o\text{-}C_6H_4$ backbones is probably a further[15,16] example of the ability of this rigid backbone to resist ligand dissociation, and conversely its absence may be the main reason for the instability of $Me_2PCH_2CH_2PMe_2$ complexes of Ni^{IV}, since in lower oxidation states (including Ni^{III}) there is often little difference in stability between complexes of $o\text{-}C_6H_4(PMe_2)_2$ and $Me_2PCH_2CH_2PMe_2$. Evidence for the presence of electronic effects is clearest in the electrochemical data, where oxidation of the Ni^{II} complexes of $o\text{-}C_6F_4(PMe_2)_2$ is considerably more difficult than for those of $o\text{-}C_6H_4(PMe_2)_2$ although the steric properties are very similar. This is consistent with the expected weaker σ donor power of the fluorodiphosphine, which will bind less strongly to hard metals.[30]

The failure to prepare any examples of $[Ni(L\text{–}L)X_4]$ may be due to the reduced l.f.s.e. on replacement of L–L by weak field halides. However the *cis* X groups in $[Ni(L\text{–}L)X_4]$ make reductive elimination of X_2 a facile decomposition route, and from previous work[17,18] where it was shown that $[Pt(L\text{–}L)X_4]$ are stable thermally to *ca.* 300 °C, whereas $[Pd(L\text{–}L)X_4]$ decompose to *ca.* 100—150 °C, thermal instability of $[Ni(L\text{–}L)X_4]$ at ambient temperatures appears not unlikely.

Experimental

Physical measurements were made as described in previous parts of this series. The nickel(II) and nickel(III) complexes were made by literature methods.[15,16,30]

Dichlorobis[(o-*methylthiophenyl*)*dimethylphosphine*]-*nickel*(II), $[Ni\{o\text{-}C_6H_4(PMe_2)(SMe)\}_2Cl_2]$.—The ligand (0.39 g, 2 mmol) was syringed into a warm solution of $NiCl_2\cdot6H_2O$ (0.24 g, 1 mmol) in ethanol (25 cm^3). After stirring for 20 min the solvent volume was reduced to *ca.* 10 cm^3 and the product precipitated by addition of diethyl ether. It was recrystallised from CH_2Cl_2–diethyl ether. Yield: 0.5 g, 80% (Found: C, 43.2; H, 5.2. Calc. for $C_{16}H_{26}Cl_2NiP_2S_2$: C, 43.4; H, 5.4%). $10^{-3}E_{max.}$/cm^{-1} (d.r.), 12.9(sh), 14.1, 15.0, 26.6, 32.3; $10^{-3}E_{max.}$/cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1}), 20.25(290), 32.9(sh)(5 750).

Dibromobis[(o-methylthiophenyl)dimethylphosphine]-nickel(II) was made similarly. $10^{-3}E_{max.}$/cm^{-1} (d.r.), 16.8(br), 21.55, 24.4, 29.9; $10^{-3}E_{max.}$/cm^{-1} (ε_{mol}/dm^3 mol^{-1} cm^{-1}), 15.15(sh) (110), 19.16 (345), 28.6(sh) (6 200).

$[Ni(L\text{–}L)_2X_2][ClO_4]_2$ [L–L = $o\text{-}C_6H_4(PMe_2)_2$, $o\text{-}C_6H_4(AsMe_2)_2$, $o\text{-}C_6F_4(PMe_2)_2$, *or* $o\text{-}C_6H_4(PMe_2)(AsMe_2)$; X = Cl *or* Br]: *General Method.*—Concentrated nitric acid was added dropwise to a mixture of $[Ni(L-L)_2][ClO_4]_2$* (0.5 mmol) and the appropriate conc. HX (2—3 drops) at 0 °C until all the complex had dissolved. The deep red or green solutions were stirred at 0 °C whilst 70% perchloric acid was added dropwise to precipitate the product. (**CARE**: explosion hazard. No explosions were experienced in this study, but high-valent metal perchlorates are often unpredictably explosive.) The solid was filtered off, rinsed quickly with 10% $HClO_4$ (distilled water appears to cause some minor decomposition), and dried *in vacuo* for 48 h at room temperature.

The nickel(IV) complexes were stored in sealed ampoules at −20 °C. All measurements were made on freshly prepared samples ($\leqslant$3 days old) whenever possible.

$[Ni(Me_2PCH_2CH_2PMe_2)_2Cl_2][BF_4]_2$.—Finely powdered $[Ni(Me_2PCH_2CH_2PMe_2)_2][BF_4]_2$ (0.53 g, 1 mmol) in a Schlenk apparatus was treated with an excess of Cl_2–CCl_4 (*ca.* 1.2 mmol Cl_2) under dry nitrogen with stirring. The purple product was filtered off after 2 h and dried *in vacuo* (*ca.* 90%). The complex is deliquescent and becomes green (Ni^{III}) and sticky after less than 1 min on exposure to air.

Bis[1,2-*bis*(*dimethylphosphino*)*benzene*]*dichlorocobalt*(III) *Hexafluorophosphate*, $[Co\{o\text{-}C_6H_4(PMe_2)_2\}_2Cl_2]PF_6$.—The ligand (0.2 g, 1 mmol) was added with stirring to a solution of $[Co(H_2O)_6]Cl_2$ (0.12 g, 0.5 mmol) and $NaPF_6$ (0.84 g, 5 mmol) in ethanol–water (*ca.* 8:1, *ca.* 25 cm^3) under nitrogen. After warming for 5 min, the dark green solution was stirred in air for 3 h. The solution changed to purple-green, and was concentrated *in vacuo* to a small volume, whereupon a violet powder precipitated. This was washed with cold ethanol (5 cm^3) and diethyl ether (5 cm^3) and dried *in vacuo*. Yield: 0.15 g, 45%.

Bis[1,2-*bis*(*dimethylphosphino*)*tetrafluorobenzene*]-*dichlorocobalt*(III) *Chloride*, $[Co\{o\text{-}C_6F_4(PMe_2)_2\}_2Cl_2]Cl$.—The ligand (0.27 g, 1 mmol) was added to $[Co(H_2O)_6]Cl_2$ (0.12 g, 0.5 mmol) in warm propan-2-ol (20 cm^3) and on cooling to room temperature pale green crystals separated. These were rinsed with diethyl ether and dried *in vacuo*. They were powdered, suspended in CCl_4 (*ca.* 5 cm^3) and treated with chlorine. After standing for 2 h the light purple powder was filtered off and dried. Yield: 0.2 g, 50%.

Acknowledgements

We thank the S.E.R.C. for support of this work in the forms of a postgraduate studentship (to S. J. H.), and for an allocation on the S.R.S. EXAFS service. We thank the Director of the Daresbury Laboratory for the provision of facilities, and Dr. D. Pletcher and Mr. D. J. Pearce for assistance with the electrochemical studies. We also acknowledge helpful discussions with Professor C. D. Garner and Drs. J. Evans, S. S. Hasnain, and S. L. Cook.

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Received 22nd April 1985; *Paper* 5/665

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* The compounds $[Ni(L-L)_2X_2]$ or $[Ni(L-L)_2X_2]ClO_4$ can also be used.