Synthesis, Spectroscopic, and Structural Studies of Diarsine Complexes of Nickel(III) Iodide

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Introduction

The formation of nickel(III) and nickel(IV) complexes $[Ni(L\text{-}L)_2X_2]^{+/2+}$ (X = Cl or Br) with alkyl-substituted diphosphine and diarsine ligands including $o\text{-}C_6H_4(AsMe_2)_2$, $o\text{-}C_6H_4(PMe_2)_2$, $o\text{-}C_6F_4(AsMe_2)_2$, and $o\text{-}C_6F_4(PMe_2)_2$ has long been known,[1−3] and more recently detailed spectroscopic[4−8] and structural[8−11] studies have confirmed the high oxidation states of nickel present. While the stabilities appear to vary little between the corresponding chloro and bromo complexes, no iodo analogues have been reported, and the combination of strongly oxidising metal centers with soft reducing iodide ligands seems unfavorable. Indeed we[12] demonstrated that reaction of $[Ni(L\text{-}L)_2Cl_2]^{+/2+}$ with I^- or of $[Ni(L\text{-}L)_2I_2]$ with I_2 afforded nickel(II) polyiodides such as $[Ni(L\text{-}L)_2](I_3)_2$ or $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2]I_{10}$. However two nickel(III) iodo complexes with tertiary phosphines have been obtained, which contain the only known examples of nickel(III)−iodine bonds. $[Ni(PMe_3)_2I_3]$ which was crystallographically characterized, was made by reaction of $[\{Ni(\mu\text{-}Bu_2As)(PMe_3)\}_2]$ with I_2,[13] and both it and $[Ni(PMe_2Ph)_2I_3]$ are formed from the appropriate R_3PI_2 and nickel powder.[14] In view of this we have re-examined the oxidation of some iodonickel(II) diarsine and diphosphine complexes, and report the results below.

Results and Discussion

Brown $[Ni(L\text{-}L)_2I_2]$ (L-L = $o\text{-}C_6H_4(AsMe_2)_2$ or $o\text{-}C_6F_4(AsMe_2)_2$),[1,11] suspended in 40% HBF_4 at 0 °C, turned bright green on dropwise treatment with concentrated HNO_3. The green solids were identified as the nickel(III) complexes $[Ni(L\text{-}L)_2I_2]BF_4$ by analysis and IR spectroscopy (Experimental Section). The solids were stable at room temperature for some days but decomposed slowly in solution in chlorocarbons and MeCN. The complexes are paramagnetic with $\mu_{eff} = 1.95 \pm 0.2$ μ_B as expected for low-spin d^7 complexes of this type,[1−3] and have rhombic EPR spectra, similar to those[4,5] of $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2]^+$. Figure 1 shows a typical example. The complexes exhibit irreversible reductions in CH_2Cl_2 solution at +0.64 V (L-L = $o\text{-}C_6H_4(AsMe_2)_2$) and +0.52 V ($o\text{-}C_6F_4(AsMe_2)_2$) vs the Fc/Fc^+ couple at +0.57V, but in contrast to the chloride and bromide analogues[2,8,11] there was no evidence for reversible Ni^{III}/Ni^{IV} couples at more positive potentials. The UV−visible spectra in CH_2Cl_2 (Figure 2) are similar in profile to those[3,7,11] of other $[Ni(L\text{-}L)_2X_2]^+$ complexes, which confirms the *trans* (D_{2h}) geometry.

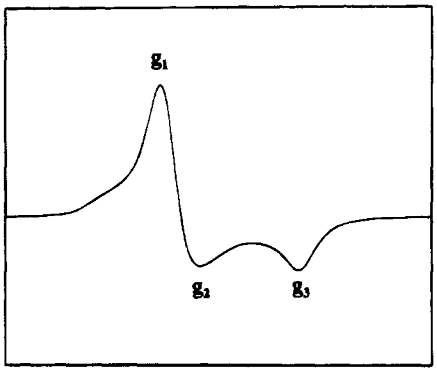

Figure 1. EPR spectrum of powdered $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2I_2]BF_4$ at room temperature. $g_1 = 2.194$, $g_2 = 2.131$, and $g_3 = 2.016$.

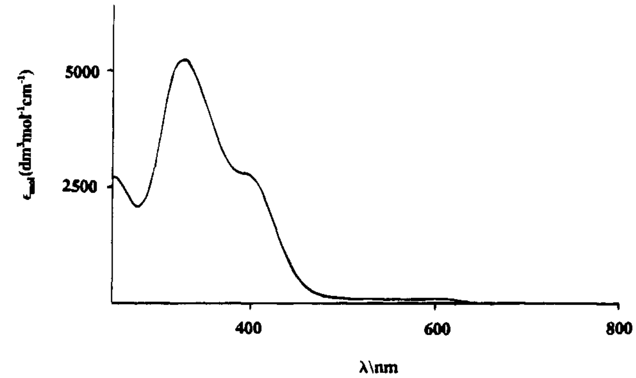

Figure 2. UV−visible spectrum of $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2I_2]BF_4$ in CH_2Cl_2 solution.

Surprisingly, attempts to make the diphosphine analogues $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2I_2]BF_4$ or $[Ni(Me_2PCH_2CH_2PMe_2)_2I_2]BF_4$ were unsuccessful. When the corresponding orange nickel(II) complexes[12] were suspended in aqueous HBF_4, they rapidly turned yellow, the products being identified as $[Ni(L\text{-}L)_2][BF_4]_2$ by comparison of their spectra with those of genuine samples. Addition of nitric acid to this mixture resulted in the formation of diiodine and polyiodides of nickel(II).[12] Addition of a 1:1 mixture of concentrated $HNO_3−H_2O$ to powdered $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2I_2]$ at 0 °C produced a transient green color, which changed in seconds to brown-black. It seems that the diphosphine complexes are more soluble in the aqueous acids with some liberation of iodide ions which prevents the isolation of the nickel(III) complexes, whereas the diarsine complexes are essentially insoluble in aqueous HBF_4, and the iodide remains associated with the nickel center allowing oxidation to nickel(III).[15] In support of this hypothesis an MeCN solution of $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2I_2]BF_4$ immediately turned brown on addi-

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(1) Nyholm, R. S. *J. Chem. Soc.* **1950**, 2061. Harris, C. M.; Nyholm, R. S.; Phillips, D. J. *J. Chem. Soc.* **1960**, 4370.

(2) Warren, L. F.; Bennett, M. A. *Inorg. Chem.* **1976**, *15*, 3126.

(3) Higgins, S. J.; Levason, W. *Inorg. Chem.* **1985**, *24*, 1105. Gray, L. R.; Higgins, S. J.; Levason, W.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1984**, 459.

(4) Manoharan, P. T.; Rogers, M. T. *J. Chem. Phys.* **1970**, *53*, 1682.

(5) Bernstein, P. K.; Gray, H. B. *Inorg. Chem.* **1972**, *11*, 3035.

(6) Sethulakshmi, C. N.; Subramainan, S.; Bennett, M. A.; Manoharan, P. T. *Inorg. Chem.* **1979**, *18*, 2520.

(7) Chandramouli, G. V. R.; Manoharan, P. T. *Inorg. Chem.* **1987**, *26*, 3291.

(8) Higgins, S. J.; Levason, W.; Feiters, M. C.; Steel, A. T. *J. Chem. Soc., Dalton Trans.* **1986**, 317.

(9) Kreisman, P. K.; Rodley, G. A.; Marsh, R.; Gray, H. B. *Inorg. Chem.* **1972**, *11*, 3040.

(10) Mahadevan, C.; Seshasayee, M.; Ramakrishna, B. L.; Manoharan, P. T. *Acta Crystallogr., Sect. C* **1985**, *41*, 38.

(11) Hanton, L. R.; Evans, J.; Levason, W.; Perry, R. J.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1991**, 2039.

(12) Gray, L. R.; Higgins, S. J.; Levason, W.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1984**, 1433.

(13) Chandler, D. J.; Jones, R. A.; Whittlesey, B. R. *J. Coord. Chem.*, **1987**, *16*, 19.

(14) Godfrey, S. M.; McAuliffe, C. A.; Pritchard, R. G. *J. Chem. Soc., Dalton Trans.* **1993**, 2875.

(15) The X-ray structure of $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2I_2]$ reveals a square planar $NiAs_4$ unit with weakly associated iodides completing a very distorted octahedron d(Ni−I) = 3.21 Å. Stephenson, N. C. *Acta Crystallogr.* **1964**, *17*, 592.

0020-1669/95/1334-1626$09.00/0

Table 1. Ni K-Edge EXAFS and Relevant Crystallographic Data

compound	d(Ni−As)/Å[a]	$2\sigma^2$/Å^2 [b]	d(Ni−I)/Å	$2\sigma^2$/Å^2	FI[c]	R[d]
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(AsMe_2)_2}\}_2\mathrm{I_2}]$	2.301(2)	0.007(02)			5.1	28.7
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(AsMe_2)_2}\}_2\mathrm{I_2}]\mathrm{BF_4}$	2.369(2)	0.008(02)	2.745(7)	0.017(1)	4.5	28.0
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6F_4(AsMe_2)_2}\}_2\mathrm{I_2}]$	2.290(2)	0.004(01)			2.1	20.6
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6F_4(AsMe_2)_2}\}_2\mathrm{I_2}]\mathrm{BF_4}$	2.336(1)	0.008(01)	2.697(10)	0.034(3)	1.9	20.0
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(AsMe_2)_2}\}_2\mathrm{I_2}]$[e,f]	2.293(4)		3.215(2)			
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(AsMe_2)_2}\}_2\mathrm{Cl_2}]\mathrm{ClO_4}$[e,g]	2.342(2)		2.425(5) (Ni−Cl)			
$[\mathrm{Ni}\{o\text{-}\mathrm{C_6F_4(AsMe_2)_2}\}_2\mathrm{Br_2}]\mathrm{BF_4}$[e,h]	2.337(2)		2.543(1) (Ni−Br)			
$[\mathrm{Ni(PMe_3)_2I_3}]$[e,i]			2.543(10)			

[a] Standard deviations in parentheses. Note that systematic errors in bond distances arising from data collection and analysis procedures are *ca.* ±0.02 Å for well-defined shells.[17] [b] Debye−Waller factor. [c] Fit index defined as $\sum_i[(\chi^T - \chi^E)k^3{}_i]^2$. [d] R factors defined as $[\int(\chi^T - \chi^E)k^3\,dk/\int\chi^E k^3\,dk] \times 100\%$. The relatively high FI's and R factors are a reflection of the features >3 Å in the Fourier transforms which correspond to carbon shells in the ligand. These cannot be adequately modeled. [e] X-ray crystallographic data from reference given. [f] Reference 15. [g] Reference 9. [h] Reference 11. [i] Reference 13.

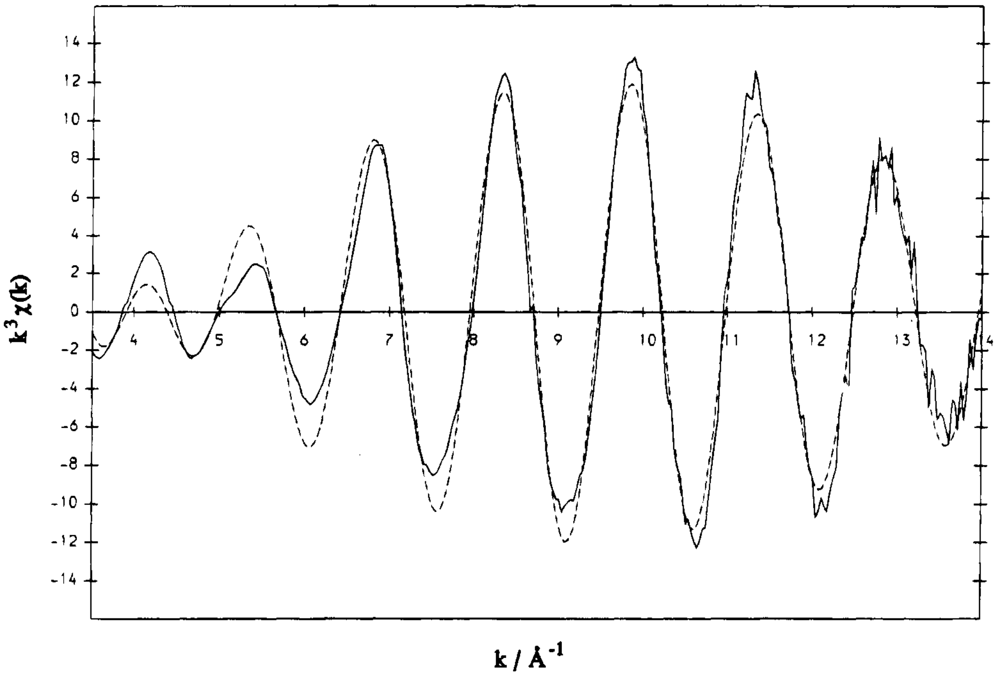

Figure 3. Background-subtracted nickel K-edge EXAFS of $[\mathrm{Ni}\{o\text{-}\mathrm{C_6F_4(AsMe_2)_2}\}_2\mathrm{I_2}]\mathrm{BF_4}$ (full line, experimental data; broken line, calculated data).

tion of a solution of $\mathrm{Bu_4NI}$, and the UV−visible spectrum of this solution resembled that[12] of $[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(AsMe_2)_2}\}_2][\mathrm{I_3}]_2$.

Attempts to grow crystals of the nickel(III) complexes were unsuccessful,[16] but the first coordination sphere bond-lengths were readily obtained via nickel K-edge EXAFS (extended X-ray absorption fine structure) data, as we have shown for other nickel(III) and nickel(IV) complexes.[8,11] Nickel K-edge data were collected for both nickel(III) complexes and for the nickel(II) precursors, the latter serving as model systems. The best fits are given in Table 1 along with relevant X-ray crystallographic data for comparison, and an example of the spectra is shown in Figure 3. For the nickel(II) complexes attempts to add a second shell corresponding to the long Ni··I contacts[15] failed. Statistically this second shell was not a significant component of the back-scattering,[17] and these two complexes were adequately modeled by a single shell of four arsenics. For the $[\mathrm{Ni(L\text{-}L)_2I_2}]\mathrm{BF_4}$ complexes a two-shell model of 4As and 2I gave a good fit to the data. The d(Ni−As) distances in the nickel(III) iodocomplexes (*ca.* 2.35 Å) are in excellent agreement with the corresponding bond lengths determined crystallographically in chloride or bromide analogues (Table 1). The only literature $\mathrm{Ni^{III}}$−I bond lengths are in the distorted trigonal bipyramidal $[\mathrm{Ni(PMe_3)_2I_3}]$ (2.54 Å average), whereas in the present *trans* octahedral complexes d(Ni−I) is *ca.* 2.73 Å. In D_{2h} symmetry the d-orbital occupancy is $(d_{xy},d_{xz},d_{yz})^6(d_{z^2})^1(d_{x^2-y^2})^0$, and the resulting Jahn−Teller distortion produced long axial Ni−X halide bonds in the corresponding chlorides (*ca.* 2.42 Å) and bromides (*ca.* 2.54 Å). On this basis the d(Ni−I) bonds of *ca.* 2.73 Å appear eminently reasonable and provide strong confirmatory evidence for the presence of a tetragonally distorted nickel(III) environment.[18]

Experimental Section

Physical measurements were made as described previously.[19] EXAFS data at the Ni K-edge were collected in transmission mode on Station 7.1 at the Daresbury Synchrotron Source from samples diluted with BN. Details of the data collection and treatment are described elsewhere.[20,21] The Ni(III) samples were freshly prepared and stored below 0 °C before data collection. After data collection the samples

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(16) This is to be expected in view of the relative solution instability of the complexes. On one occassion brown crystals of $[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(AsMe_2)_2}\}_2\mathrm{I_2}]$ deposited from the green solution of $[\mathrm{Ni}\{o\text{-}\mathrm{C_6H_4(AsMe_2)_2}\}_2\mathrm{I_2}]\mathrm{BF_4}$ in MeCN/diethyl ether.

(17) The statistical tests, errors, and resolution limits are discussed in Hasnain, S. S., Ed. *XAFS*; Ellis Horwood: New York, 1991; Chapter 195.

(18) Steel, A. T.; Feiters, M. C.; Garner, C. D.; Hasnain, S. S.; Higgins, S. J.; Levason, W. *J. Chem. Soc., Chem. Commun.* **1985**, 484.

(19) Cipriano, R. A.; Levason, W.; Mould, R. A. S.; Pletcher, D.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1990**, 2609.

(20) Corker, J. M.; Evans, J.; Levason, W.; Spicer, M. D.; Andrews, P. *Inorg. Chem.* **1991**, *30*, 331.

were extracted from the BN with dry CH_2Cl_2 and their integrity checked by recording their UV–visible spectra.

Preparation of *trans*-[Ni{*o*-$C_6H_4(AsMe_2)_2\}_2I_2]BF_4$. The powdered [Ni{*o*-$C_6H_4(AsMe_2)_2\}_2I_2$][1] (0.18 g, 0.19 mmol) was suspended in 40% HBF_4 (15 cm^3) at 0 °C and concentrated HNO_3 (1 cm^3 in total) added dropwise with vigorous stirring. The color of the suspension changed from brown to green, and the product was filtered off, washed with diethyl ether (2 × 5 cm^3), and dried *in vacuo*. Yield: 80%. Anal. Calcd for [Ni{*o*-$C_6H_4(AsMe_2)_2\}_2I_2]BF_4$ ($C_{20}H_{32}As_4BF_4I_2Ni$): C, 24.7; H, 3.3. Found: C, 24.9; H, 3.5. IR (Nujol mull): 1080, 620 cm^{-1} (BF_4). $\mu = 1.94\ \mu_B$. Λ_M (10^{-3} mol dm^{-3} $MeNO_2$, 293 K) = 94 Ω^{-1} cm^2 mol^{-1}. $E_{max}/10^3$ cm^{-1} (ϵ_{mol}/dm^3 mol^{-1} cm^{-1}) in CH_2Cl_2: 30.8 (5100), 25.1 (2700), 16.7 (sh). EPR: g_1 2.194, g_2 2.131, g_3 2.016. *trans*-[Ni{*o*-$C_6F_4(AsMe_2)_2\}_2I_2]BF_4$ was made similarly. Anal. Calcd for $C_{20}H_{24}As_4BF_{12}I_2Ni$: C, 21.5; H, 2.2. Found: C, 21.8; H, 2.3. IR (Nujol mull): 1060, 616 cm^{-1} (BF_4). $\mu = 1.97\ \mu_B$. Λ_M (10^{-3} mol dm^{-3} $MeNO_2$, 293 K) = 73 Ω^{-1} cm^2 mol^{-1}. $E_{max}/10^3$ cm^{-1} (ϵ_{mol}/dm^3 mol^{-1} cm^{-1}) in CH_2Cl_2: 30.1 (1710), 25.2 (2210), 22.9(sh), 19.4 (290). EPR: g_1 2.132, g_2 2.086, g_3 2.064.

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(21) Champness, N. R.; Levason, W.; Pletcher, D.; Spicer, M. D.; Webster, M. *J. Chem. Soc., Dalton Trans.* **1992**, 2201.