Co-ordination Chemistry of Higher Oxidation States. Part 11.[1] The Reaction of Nickel(II) Iodo-complexes with Molecular Iodine; Crystal and Molecular Structure of $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2][I_3]_2\cdot 2I_2$ †

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The reaction of excess of elemental iodine with the nickel(II) iodo-complexes $[Ni(L\text{-}L)_2I_2]$ [L-L = $H_2NCH_2CH_2NH_2$, $o\text{-}C_6H_4(PMe_2)_2$, $o\text{-}C_6H_4(AsMe_2)(PMe_2)$, or $o\text{-}C_6H_4(AsMe_2)_2$] in $CH_3CN\text{-}CH_2Cl_2$ solution produces diamagnetic $Ni(L\text{-}L)_2I_6$ materials formulated as $[Ni^{II}(L\text{-}L)_2][I_3]_2$ and containing tri-iodide(1−) anions. From neat CH_2Cl_2 solution the complex $Ni[o\text{-}C_6H_4(PMe_2)_2]_2I_{10}$ was obtained, and has been shown by single-crystal *X*-ray studies to be triclinic, space group $P\bar{1}$, with unit-cell dimensions $a = 9.672(2)$, $b = 12.369(2)$, $c = 9.574(3)$ Å, $\alpha = 106.55(2)$, $\beta = 107.70(2)$, $\gamma = 99.48(1)°$, and $Z = 1$. 2 914 Observed reflections [$F \geqslant 4\sigma(F)$] refined to R 0.032. The complex contains planar $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2]^{2+}$cations [Ni-P 2.210(2) and 2.200(2) Å], linear I_3^- anions [I-I 2.910(1) and 2.932(1) Å], and di-iodine [I-I 2.728(1) Å]. Weak secondary interactions between the iodine atoms of I_3^- and I_2 [$I \cdots I$ 3.442(1) and 3.576(1) Å] lead to the formation of bifurcated chains. Other nickel(II) polyiodides obtained include the paramagnetic $[Ni(L\text{-}L)_2(I_3)_2]$ (L-L = $MeSCH_2CH_2SMe$ or $MeSeCH_2CH_2SeMe$) and the diamagnetic $[Ni(L\text{-}L)I_4]$ [L-L = $o\text{-}C_6H_4(AsMe_2)_2$ or $o\text{-}C_6H_4(AsPh_2)_2$] and $[Ni(Ph_2PCH_2CH_2PPh_2)I_6]$. The reaction of the nickel-(III) and -(IV) species $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2]^{n+}$ (n = 1 or 2) with I^- gives a compound of composition $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2I_3]$ which is considered to be a nickel(II) derivative. The complexes have been characterised by electronic and e.s.r. spectroscopy, magnetic and conductance measurements. No evidence for the formation of nickel(III) iodo-complexes has been obtained.

Many nickel(II) phosphine and arsine complexes are oxidised by chlorine or bromine to nickel(III),[2,3] whilst diprimary amine compounds produce either nickel(III) or mixed-valence nickel(II)-nickel(IV) materials.[4,5] Here we describe a study of the reactions of various nickel(II) complexes with di-iodine, which was undertaken to establish whether nickel(III) iodo-complexes or nickel(II) polyiodides were produced. A number of nickel(II) polyiodides, mostly containing nitrogen-donor ligands, have been described previously,[6] and there has been intense recent interest [7] in the reactions of I_2 with 'stacked' nickel(II) complexes, *e.g.* bis(diphenylglyoximato)- or phthalocyaninato-nickel(II), which produce 'partially oxidised' materials. We have shown elsewhere [8] that various palladium(II) complexes and molecular iodine form palladium(II) polyiodides, *e.g.* $[Pd(Ph_2PCHCHPPh_2)I_4]$ and $[Pd\{o\text{-}C_6H_4(AsMe_2)_2\}_2][I_3]_2$.

Results and Discussion

$Ni(L\text{-}L)_2I_6$ (L-L = *bidentate ligand*).—The reaction of $[Ni(MeSCH_2CH_2SMe)_2I_2]$ with excess of di-iodine has been reported to give $[Ni(MeSCH_2CH_2SMe)_2I_n]$ (n = 4 [9] or 6 [10]) or possibly [10] $[Ni(MeSCH_2CH_2SMe)_2(H_2O)_2]I_6$. In our hands the product was brown-black $[Ni(MeSCH_2CH_2SMe)_2I_6]$, and we have obtained the 2,5-diselenahexane analogue $[Ni(MeSeCH_2CH_2SeMe)_2I_6]$. These complexes have magnetic moments corresponding to two unpaired electrons, and the presence of weak absorptions in the diffuse reflectance spectra (Table 1) at *ca.* 8 000—11 000 and *ca.* 17 000 cm^{-1} show these contain pseudo-octahedral nickel(II). The higher-energy absorptions are rather ill defined in the solid-state spectra, but broad maxima at *ca.* 29 000 and 33 000—35 000 cm^{-1} are present corresponding to the allowed transitions ($\pi_g \rightarrow \sigma_u^*$, $\sigma_g \rightarrow \sigma_u$, $D_{\infty h}$ symmetry) of the tri-iodide group.[11] The diselenahexane complex is unstable in air, and partially decomposed in hydroxylic solvents.‡ On the basis of the above data these two complexes are formulated as $[Ni(L\text{-}L)_2(I_3)_2]$ (L-L = $MeSeCH_2CH_2SeMe$ or $MeSCH_2CH_2SMe$). In contrast, black $Ni(H_2NCH_2CH_2NH_2)_2I_6$ [13,14] is diamagnetic, and has no electronic spectral absorption $< 17\,000$ cm^{-1}, consistent with essentially planar nickel(II), $[Ni(H_2NCH_2CH_2NH_2)_2][I_3]_2$.

The reactions of excess of di-iodine with the planar $[Ni(L\text{-}L)_2]^{2+}$ ions [L-L = $o\text{-}C_6H_4(PMe_2)_2$, $o\text{-}C_6H_4(AsMe_2)_2$, or $o\text{-}C_6H_4(AsMe_2)(PMe_2)$] were especially of interest since these ligands are particularly effective at producing nickel(III) complexes with Cl or Br co-ligands.[3,15,16] The addition of a five-fold excess of I_2 in CH_2Cl_2 to acetonitrile solutions of $Ni(L\text{-}L)_2I_2$ and cooling to *ca.* −20 °C gave reflective green-black needle crystals of composition $Ni(L\text{-}L)_2I_6$. Crystallisation of a mixture of $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2I_2]$ and I_2 (1 : 5 molar ratio) from neat CH_2Cl_2 produced triclinic black crystals of composition $Ni[o\text{-}C_6H_4(PMe_2)_2]_2I_{10}$, the structure of which was determined (below) by an *X*-ray study as $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2][I_3]_2\cdot 2I_2$. Preliminary *X*-ray data on $Ni[o\text{-}C_6H_4(PMe_2)_2]_2I_6$ showed it to be monoclinic, but when the presence of I_3^- groups in the decaiodide was established, the full *X*-ray examination of the hexaiodide was not proceeded with, since it is clearly $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2][I_3]_2$. Chemical evidence supports a similar formula for all three hexaiodides. In particular, they are diamagnetic ($\mu_{eff.} \leqslant 0.3$ B.M.), and their diffuse reflectance spectra contain strong broad absorptions (Table 1) at *ca.* 28 000 and 34 000 cm^{-1} characteristic of the I_3^- ion.[11] Other absorptions to lower energy could not be clearly assigned since both the planar nickel(II) cation

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† Bis[*o*-phenylenebis(dimethylphosphine)]nickel(II) tri-iodide(1−)-di-iodine (1/2).

Supplementary data available (No. SUP 23908, 21 pp.): H-atom co-ordinates, thermal parameters, structure factors. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1984, Issue 1, pp. xvii—xix.

Non-S.I. unit employed: B.M. ≈ 9.27 × 10^{-24} A m^2.

‡ The complexes $[Ni(MeSeCH_2CH_2SeMe)_2X_2]$ (X = Cl, Br, or I) also decompose slowly in moist air, and dissociate in donor solvents.[12]

Table 1. Electronic spectra of nickel(II) polyiodides

Complex	$10^{-3}E_{max.}$/cm^{-1}	
	a	*b*
$[Ni(MeSCH_2CH_2SMe)_2(I_3)_2]$	9.3, 11.9, 16.9 (br), 24.8, 29.2, 33.1 (sh)	19.2 (sh) (124), 27.9 (28 150), 34.7 (53 500)
$[Ni(MeSeCH_2CH_2SeMe)_2(I_3)_2]$	8.0, 12.3 (w), 17.1, 24.9, 29.4 (sh), 34.7	Decomposes
$[Ni(H_2NCH_2CH_2NH_2)_2][I_3]_2$	18.2 (w), 24.9, 29.2, 34.5	17.7 (sh) (110), 27.9 (24 570), 34.7 (48 340)
$[Ni\{o-C_6H_4(PMe_2)_2\}_2][I_3]_2$	18.2 (br), 20.1 (br), 23.9, 26.5, 27.9, 34.3	18.9 (sh), 20.9 (sh) (1 840), 27.8 (16 400), 34.3 (42 000)
$[Ni\{o-C_6H_4(AsMe_2)(PMe_2)\}_2][I_3]_2$	18.1, 24.7, 28.4, 36.0	18.1 (sh), 27.8 (15 400), 34.7 (41 900) 21.3 (sh), 28.1, 34.5 [c]
$[Ni\{o-C_6H_4(AsMe_2)_2\}_2][I_3]_2$	17.4 (w), 25.3, 27.5, 34.5	20.7 (1 350), 26.2 (sh), 27.9 (5 600), 30.7 (5 600), 35.7 (14 700) 17.5 (sh), 20.7 (sh), 27.9, 34.7 [c]
$Ni[o-C_6H_4(AsMe_2)_2]_2I_3$	17.1, 24.9 (sh), 29.9, 36.2	17.5 (sh), 21.5 (475), 30.9 (1 900) [c]
$Ni[o-C_6H_4(AsMe_2)(PMe_2)]_2I_3$	16.9 (sh), 23.3 (sh), 27.8, 35.7	Insoluble
$[Ni\{o-C_6H_4(AsPh_2)_2\}I_4]$	18.5 (sh), 26.7, 33.8	Decomposes 18.9 (sh), 30.1, 33.3 [c]
$[Ni\{o-C_6H_4(AsMe_2)_2\}I_4]$	26.5, 28.2 (sh), 34.2	Decomposes
$Ni(Ph_2PCH_2CH_2PPh_2)I_6$	18.4, 27.2 (sh), 28.7, 35.0	Decomposes

[a] Diffuse reflectance spectra. [b] Acetonitrile solution except where indicated; ε/dm³ mol⁻¹ cm⁻¹ given in parentheses. [c] In CH_2Cl_2 solution.

absorptions [15,17,18] and the singlet–triplet [11] transitions of the I_3^- are expected in this region. Attempts to confirm the presence of I_3^- ions by Raman spectroscopy were unsuccessful since the compounds decomposed in the laser beam. In 10^{-3} mol dm^{-3} solution in acetonitrile the complexes are 1 : 1 electrolytes, suggesting the presence of five-co-ordinate $[Ni(L-L)_2(I_3)]^+$ although dissociation of the cation to $[Ni(L-L)_2I]^+ + I_2$ cannot be ruled out.

The complexes $[Ni(L-L)_2X_2]$ (X = Cl, Br, or I) behave similarly in that $[Ni(L-L)_2X]^+$ ions are present in solution, but the solids contain essentially planar $Ni(L-L)_2^{2+}$ units with weak association of the X^- groups in axial positions.[15,19] Hence these $Ni(L-L)_2I_6$ complexes are formulated as nickel(II) polyiodides, rather than nickel(III) complexes. Pure samples * also lack the characteristic e.s.r. spectra given by $[Ni(L-L)_2X_2]^+$ (X = Cl or Br).[3,21] On heating *in vacuo* these complexes lose some di-iodine, but decompose to black tars concurrently.

Structure of $Ni[o-C_6H_4(PMe_2)_2]_2I_{10}$.—The environment of the nickel atom is shown in Figure 1, the molecular packing diagram in Figure 2, whilst Figure 3 displays the iodine-atom arrangement. Selected bond lengths and angles are in Table 2.

The structure determination revealed a square-planar arrangement about the nickel atom, comprising the four phosphorus atoms of the chelated diphosphines. The NiP_4 unit is necessarily planar, with the benzene-ring backbones lying at 14.4° to the NiP_4 plane. The planar geometry is characteristic of d^8 Ni^{II}, consistent with the chemical evidence, rather than of Ni^{III} or Ni^{IV} which are usually octahedrally co-ordinated.[2] The Ni–P bond lengths [2.210(2) and 2.200(2) Å] are normal for Ni^{II}–P(*trans* to P) in planar complexes and can be compared with 2.206(7) Å in *trans*-$[Ni(PMe_3)_2Cl(CH_2SiMe_3)]$,[22] or 2.200(2) Å in *trans*-$[Ni(PMe_3)_2Cl(COMe)]$.[23] The rather longer M–P bond lengths [24] in the square-pyramidal $[Cu^{III}\{o-C_6H_4(PMe_2)_2\}_2Cl][ClO_4]_2$ (mean 2.263 Å) and in the six-co-ordinate $[Co\{o-C_6H_4(PMe_2)_2\}_2Cl_2]ClO_4$ (mean 2.251 Å) are probably mainly a consequence of the higher co-ordination numbers of the metals. The internal dimensions of the diphosphine are unexceptional (Table 2).

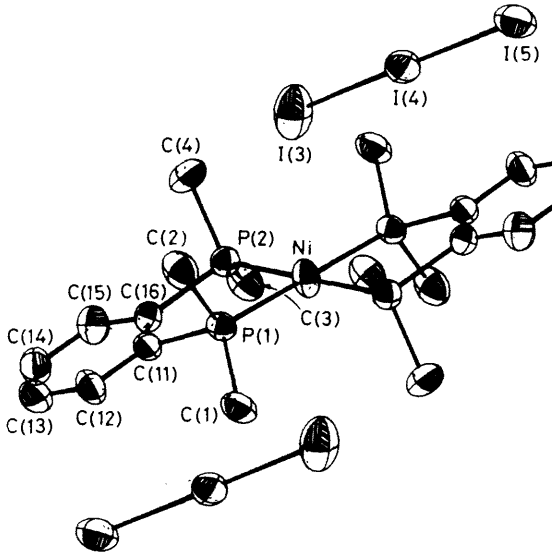

Figure 1. View of $[Ni\{o-C_6H_4(PMe_2)_2\}_2][I_3]_2 \cdot 2I_2$ showing the phosphine ligands and the nearest I_3 groups around the nickel atom. Hydrogen atoms have been excluded for clarity, and atoms are drawn with 50% probability ellipsoids

The closest approach of an iodine atom [I(3)] to the nickel is 3.491(1) Å suggesting negligible binding. For comparison, normal Ni^{II}–I σ bonds lie in the range *ca.* 2.4—2.8 Å depending upon the *trans* ligand and the co-ordination number of the metal,[25–28] whilst even the weakly associated iodides in $[Ni\{o-C_6H_4(AsMe_2)_2\}_2I_2]$ are at 3.215(2) Å.[19]

Particular interest lies in the nature of the polyiodide unit.

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* A few $Ni(L-L)_2I_6$ samples gave very weak e.s.r. signals at $g \approx$ 2.0—2.2 characteristic of nickel(III) centres, although the intensities indicated <1% of the nickel was involved. The signals were very similar to those of $[Ni(L-L)_2Br_2]^+$,[3] and subsequently we established the presence of small amounts of bromine in the samples and in the di-iodine (as IBr?) used in the preparation (positive fuchsin-bisulphite test[20]). Samples prepared from di-iodine from a different source gave no e.s.r. signals.

Table 2. Selected bond lengths (Å) and angles (°) for $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2][I_3]_2\cdot2I_2$

I(1)–I(2)	2.728(1)	Ni–P(1)	2.210(2)	C(11)–C(12)	1.397(9)	C(14)–C(15)	1.394(10)
I(3)–I(4)	2.910(1)	Ni–P(2)	2.200(2)	C(12)–C(13)	1.384(11)	C(15)–C(16)	1.379(10)
I(4)–I(5)	2.932(1)			C(13)–C(14)	1.370(11)	C(16)–C(11)	1.362(9)
P(1)–C(1)	1.819(7)	P(2)–C(3)	1.808(7)	$I(5^{IV}) \cdots I(1^{II})$	3.576(1)	$P(1) \cdots P(2)$	3.02
P(1)–C(2)	1.816(7)	P(2)–C(4)	1.801(7)	$I(5) \cdots I(2^{II})$	3.442(1)	$P(1) \cdots P(2^{I})$	3.22
P(1)–C(11)	1.818(7)	P(2)–C(16)	1.839(7)	$I(5) \cdots I(5^{III})$	3.871(1)	$Ni \cdots I(3)$	3.491(1)
$P(1)–Ni \cdots I(3)$	96.6(1)	P(1)–Ni–P(2)	86.3(1)	P(1)–C(11)–C(12)	123.0(5)	P(2)–C(16)–C(15)	121.9(5)
$P(2)–Ni \cdots I(3)$	95.8(1)			P(1)–C(11)–C(16)	117.2(5)	P(2)–C(16)–C(11)	116.6(5)
Ni–P(1)–C(1)	120.0(3)	Ni–P(2)–C(3)	119.6(3)	$Ni \cdots I(3)–I(4)$	118.5(1)	$I(5) \cdots I(2^{II})–I(1^{II})$	169.3(1)
Ni–P(1)–C(2)	115.8(3)	Ni–P(2)–C(4)	115.9(3)	I(3)–I(4)–I(5)	178.8(1)	$I(2^{II})–I(1^{II}) \cdots I(5^{IV})$	164.7(1)
Ni–P(1)–C(11)	108.4(2)	Ni–P(2)–C(16)	108.3(2)	$I(4)–I(5) \cdots I(2^{II})$	104.0(1)	$I(1^{II}) \cdots I(5^{IV})–I(4^{IV})$	82.6(1)
C(1)–P(1)–C(2)	103.5(4)	C(3)–P(2)–C(4)	103.8(4)	$I(4)–I(5) \cdots I(5^{III})$	161.1(1)		
C(1)–P(1)–C(11)	105.2(3)	C(3)–P(2)–C(16)	104.6(3)				
C(2)–P(1)–C(11)	102.1(3)	C(4)–P(2)–C(16)	102.9(4)				

Internal ring angles in the range 118.9(3)—121.5(6)°; torsion angle P(1)–C(11)–C(16)–P(2) 1.5°.
Symmetry codes: I $-x, -y, -z$; II $-x, -1 - y, 1 - z$; III $1 - x, -1 - y, 1 - z$; IV $x, y, 1 + z$.

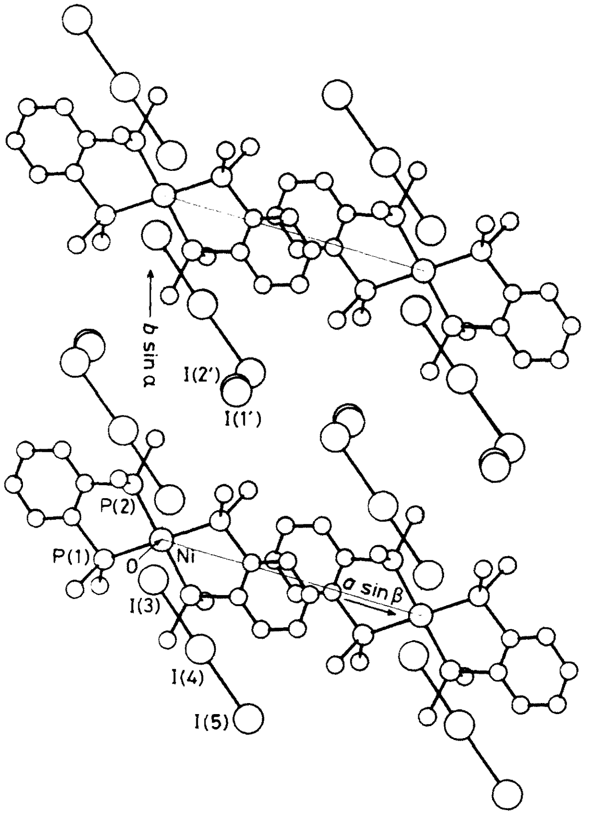


Figure 2. Packing diagram for $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2][I_3]_2\cdot2I_2$ viewed from the *c* direction and excluding H atoms for clarity

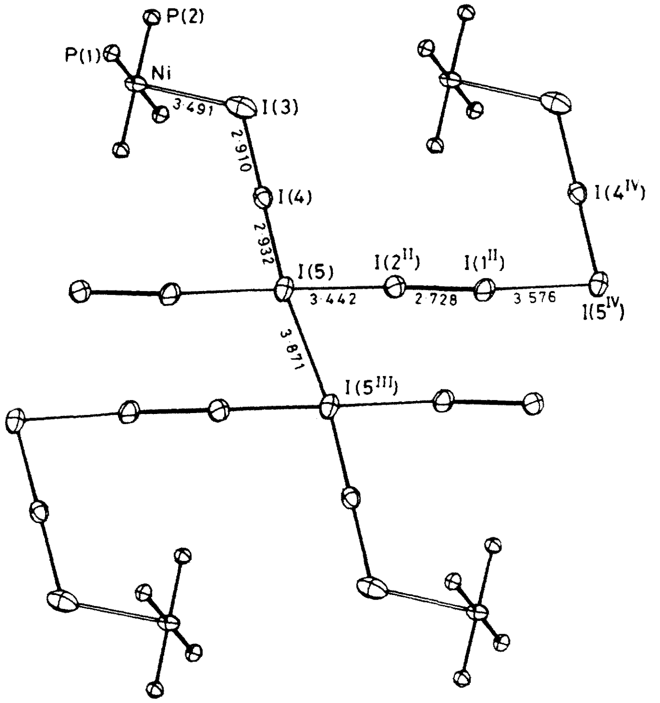
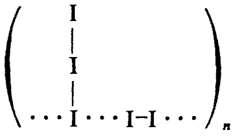


Figure 3. View of $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2][I_3]_2\cdot2I_2$ showing nickel, phosphorus, and iodine atoms only. Atoms drawn with 50% probability ellipsoids and viewed approximately perpendicular to the 110 plane. The symmetry labels correspond with those in Table 2

A considerable number of complexes containing tri-iodide (I_3^-) and tetraiodide (I_4^{2-}) groups have been structurally characterised,[6,7] but data on larger units are much rarer. Description of the structural units present is often ambiguous since the distinction between intra- and inter-molecular I–I distances is rarely clear. Coppens [7b] has proposed a limiting value of 3.30 Å, and if we adopt this value only three of the I–I bonds in Table 2 would be classified as intramolecular [I(1)–I(2), I(3)–I(4), and I(4)–I(5)]. On this basis the structure consists of approximately linear (178.8°), unsymmetrical I_3^- groups [I(3)–I(4) 2.910(1) and I(4)–I(5) 2.932(1) Å] lying at 21° to the NiP_4 plane, and di-iodine molecules [I(1)–I(2) 2.728(1) Å]. The latter is slightly longer (*ca.* 7σ) than in solid di-iodine [2.715(2) Å].[29] The I_2 molecules link neighbouring I_3^- units in a distinctly asymmetric manner as shown in Figure 3. All other I · · · I distances are >4.0 Å.

An alternative description of the polyiodide unit as I_5^- chains is possible if the intramolecular I · · · I distinction is set at *ca.* 3.5 Å. Four basic types of I_5^- group have been described: (*i*) isolated V-shaped ions, *e.g.* $[K(valinomycin)]_2I_5\cdot I_3$;[30] (*ii*) V-shaped ions which interact with neighbouring I_5^- ions as in $[NMe_4]I_5$;[31] (*iii*) linear ions also interacting as in $[10C_6H_3(CO_2H)_3\text{-}1,3,5\cdot H_2O\cdot I_5$;[32] (*iv*) zigzag chains, *e.g.* $2C_{10}H_{13}NO_2\cdot HI_5$ [$C_{10}H_{13}NO_2$ = *N*-(4-ethoxyphenyl)acetamide].[33] Types (*i*)—(*iii*) have internuclear distances suggesting $I_2 \cdots I^- \cdots I_2$, but type (*iv*) contain $I_3^- \cdots I_2$ units. Although there is considerable similarity between the I_5^- unit in the title complex and in $2C_{10}H_{13}NO_2\cdot HI_5$, the networks of 'secondary' bonds are different. In the latter they are zigzag ($\cdots$I–I–I $\cdots$I–I$\cdots$)$_n$ chains, whilst in the title complex the chains are as shown below.



Other Complexes.—Di-iodine in CH_2Cl_2 instantly decomposed the ditertiary stibine complex $[Ni\{Me_2Sb(CH_2)_3SbMe_2\}_2I_2]$,[34] the free ligand being converted into $Me_2Sb(I_2)(CH_2)_3Sb(I_2)Me_2$, identified by ^1H n.m.r. spectroscopy. The complex $[Ni(Me_2PCH_2CH_2PMe_2)_2I_2]$ has been reported [35] to give a nickel(III) complex $[Ni(Me_2PCH_2CH_2PMe_2)_2I_2]I$ on refluxing in ethanol–aqueous HI in the presence of air. However, the brown solid produced after about 30 min contains a very strong i.r. band at 1 120 cm^{-1} attributable to the presence of a phosphine oxide, whilst on prolonged reflux with excess of aqueous HI the material is completely decomposed and $Me_2P(O)CH_2CH_2P(O)Me_2$ [36] is produced. The reaction of $[Ni(Me_2PCH_2CH_2PMe_2)_2I_2]$ with I_2 in CH_2Cl_2 gave an unstable diamagnetic black substance of approximate composition '$Ni(Me_2PCH_2CH_2PMe_2)I_5$'. Black powders $Ni(L\text{–}L)_2I_3$ [L–L = $o\text{-}C_6H_4(AsMe_2)_2$ [16] or $o\text{-}C_6H_4(AsMe_2)(PMe_2)$] were produced by reaction of $[Ni^{III}(L\text{–}L)_2Cl_2]^+$ with excess of aqueous potassium iodide. Nyholm [37] suggested a similar material was also produced from $[Ni^{IV}\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2]^{2+}$, but due to the insolubility of the starting material and product, he could not obtain a pure sample. We have recently found [38] that the nickel(IV) complex dissolves in trifluoroacetic acid, and by treating this solution with aqueous KI have confirmed that $Ni[o\text{-}C_6H_4(AsMe_2)_2]_2I_3$ is the product, identical with the material obtained from the nickel(III) complex. These $Ni(L\text{–}L)_2I_3$ materials are diamagnetic, poorly soluble in, or decomposed by organic solvents, and exhibit no e.s.r. signals. Since crystals could not be obtained for an *X*-ray study, the structure remains unclear. The diffuse reflectance spectra do not support the presence of I_3^-, whilst the solution spectra (when they can be obtained) are not dissimilar to a superimposition of the spectra of $Ni(L\text{–}L)_2I_2 + I_2$.

Treatment of $[Ni(L\text{–}L)I_2]$ [L–L = $Ph_2PCH_2CH_2PPh_2$, $Ph_2P(CH_2)_3PPh_2$, *cis*-$Ph_2PCHCHPPh_2$, $Ph_2AsCH_2CH_2AsPh_2$, $Ph_2AsCHCHAsPh_2$, $o\text{-}C_6H_4(AsPh_2)_2$, or $o\text{-}C_6H_4(PPh_2)_2$] and $[Ni(PEt_3)_2I_2]$ with I_2 in CH_2Cl_2 under standardised conditions (I_2 : Ni 5 : 1 and cooling to −20 °C) was also studied. Two black diamagnetic polyiodides, $Ni[o\text{-}C_6H_4(AsPh_2)_2]I_4$ and $Ni(Ph_2PCH_2CH_2PPh_2)I_6$, were isolated, $[Ni\{Ph_2P(CH_2)_3PPh_2\}I_2]$ decomposed, and the other four nickel(II) complexes were recovered unchanged. The complex $Ni(Ph_2PCH_2CH_2PPh_2)I_6$ loses iodine rapidly at room temperature, and both polyiodides revert cleanly to the di-iodides on heating *in vacuo*, and seem to dissociate in solution to the di-iodides and di-iodine (electronic spectral data). It is probable that the structures consist of planar $[Ni(L\text{–}L)I_2]$ units linked by di-iodine I$\cdots$I–I$\cdots$I as in $Pd(Ph_2PCHCHPPh_2)I_4$.[8]

Finally we re-examined the brown-black $Ni[o\text{-}C_6H_4(AsMe_2)_2]I_4$ [39] formed from $[Ni(CO)_2\{o\text{-}C_6H_4(AsMe_2)_2\}]$ and excess of I_2. This moisture-sensitive, diamagnetic material dissolves in polar solvents (MeOH or acetone) with rearrangement into $Ni[o\text{-}C_6H_4(AsMe_2)_2]_2I_n$, similar behaviour to other 1 : 1 nickel(II) complexes of this ligand,[39] and supporting a $Ni(L\text{–}L)I_2{\cdot}I_2$ formulation.

Conclusions

This study has shown that the reaction of nickel(II) iodo-complexes with elemental iodine, and of nickel-(III) or -(IV) complexes with iodide ions, produces nickel(II) polyiodides, and no evidence for the formation of nickel iodo-complexes in higher oxidation states was obtained.

Experimental

Physical measurements were made as described previously.[3,5] Moisture-sensitive materials were prepared in Schlenk equipment and samples were manipulated in a dry-box (⩽ 10 p.p.m. water). Solvents were dried by conventional methods and distilled under dinitrogen. Nickel(II) iodide was prepared *in situ* in 1-butanol by reaction of $Ni(NO_3)_2{\cdot}6H_2O$ and 2NaI, the precipitated $NaNO_3$ being removed by filtration.

The following nickel(II) complexes were made by literature methods: $[Ni(CO)_2\{o\text{-}C_6H_4(AsMe_2)_2\}]$,[39] $[Ni(L\text{–}L)I_2]$ [L–L = $Ph_2AsCH_2CH_2AsPh_2$,[40] $Ph_2PCH_2CH_2PPh_2$,[41] $Ph_2P(CH_2)_3PPh_2$,[41] *cis*-$Ph_2AsCHCHAsPh_2$,[40] *cis*-$Ph_2PCHCHPPh_2$,[42] $o\text{-}C_6H_4(AsPh_2)_2$,[40] or $o\text{-}C_6H_4(PPh_2)_2$ [40]], $Ni(L\text{–}L)_2I_2$ [L–L = $o\text{-}C_6H_4(AsMe_2)_2$,[43] $o\text{-}C_6H_4(AsMe_2)(PMe_2)$,[17] or $MeSCH_2CH_2SMe$ [10]], and $[Ni(PEt_3)_2I_2]$.[44]

Di-iodobis[o-*phenylenebis*(*dimethylphosphine*)]*nickel*(II), $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2I_2]$.—A solution of $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2][ClO_4]_2$[15] (0.33 g, 0.5 mmol) in acetonitrile (50 cm^3) was treated with NaI (0.3 g, *ca.* 2 mmol) in methanol (10 cm^3). On reducing the volume of the solution, well formed orange crystals precipitated. Yield approximately quantitative (Found: C, 33.8; H, 4.6. $C_{20}H_{32}I_2NiP_4$ requires C, 33.9; H, 4.6%). $10^{-3}E_{max.}$ (CH_3CN): 22.2(sh) (ε 200), 24.8 (430), and 32.3 cm^{-1} (840 dm^3 mol^{-1} cm^{-1}).

Bis[1,3-*bis*(*dimethylstibino*)*propane*]*di-iodonickel*(II), $[Ni\{Me_2Sb(CH_2)_3SbMe_2\}_2I_2]$.—The ligand (0.35 g, 1 mmol) was added under dinitrogen to a freshly prepared degassed solution of nickel(II) iodide (0.6 mmol) in 1-butanol (15 cm^3). After stirring for 10 min the resulting dark purple solid was filtered off (Schlenk tube) and dried. It was recrystallised under dinitrogen from $MeNO_2$–Et_2O, but in the presence of oxygen some oxidation of the ligand occurs. Yield 0.35 g (70%) (Found: C, 16.9; H, 3.8. $C_{14}H_{36}I_2NiSb_4$ requires C, 16.75; H, 3.6%). $10^{-3}E_{max.}$ (CH_2Cl_2): 18.3 (ε 1 200) and 25.7 cm^{-1} (2 320 dm^3 mol^{-1} cm^{-1}).

Bis[1,2-*bis*(*dimethylphosphino*)*ethane*]*di-iodonickel*(II), $[Ni(Me_2PCH_2CH_2PMe_2)_2I_2]$.—The ligand (0.3 g, 2 mmol) was syringed into a degassed solution of nickel(II) iodide (1 mmol) in 1-butanol (50 cm^3), with stirring. After 15 min the bright orange precipitate was filtered off, rinsed with diethyl ether (2 × 15 cm^3), and dried *in vacuo*. Yield 0.53 g (83%) (Found: C, 23.3; H, 5.1. $C_{12}H_{32}I_2NiP_4$ requires C, 23.5; H, 5.3%). $10^{-3}E_{max.}$ (CH_2Cl_2): 21.7(sh) (ε 460), 25.5 (1 080), and 33.1 cm^{-1} (8 800 dm^3 mol^{-1} cm^{-1}).

Bis(2,5-*diselenahexane*)*di-iodonickel*(II), $[Ni(MeSeCH_2CH_2SeMe)_2I_2]$.—To nickel(II) iodide (1 mmol) in 1-butanol (12 cm^3) was added the ligand (0.43 g, 2 mmol) by syringe. After stirring for 30 min, precipitation was completed by slow addition of diethyl ether (10 cm^3), and the yellow malodorous solid filtered off and rinsed with ether (2 × 5 cm^3). The complex slowly decomposes in moist air and is best kept in sealed ampoules. Yield 0.59 g (79%) (Found: C, 13.0; H, 2.7. $C_8H_{10}I_2NiSe_4$ requires C, 12.9; H, 2.6%). $10^{-3}E_{max.}$ (Nujol mull): 9.7 and 11.3; diffuse reflectance, 14.3, 24.3, and 29.1 cm^{-1}. μ = 2.91 B.M. (Gouy method).

Di-iodobis[o-*phenylenebis*(*diphenylphosphine*)]*nickel*(II), $[Ni\{o\text{-}C_6H_4(PPh_2)_2\}_2I_2]$.—A warm ethanol solution (100 cm^3) of $[Ni\{o\text{-}C_6H_4(PPh_2)_2\}I_2]$ (0.75 g, 1 mmol) was treated with the ligand (0.44 g, 1 mmol) in CH_2Cl_2 (10 cm^3) and the mixture boiled. Water was then added slowly to the refluxing solution until a purple solid started to precipitate, whereupon the solution was cooled. The black-purple solid was washed with water (100 cm^3), diethyl ether (2×100 cm^3), and dried. Yield 0.90 g, (76%) (Found: C, 59.6; H, 4.0. $C_{60}H_{48}I_2NiP_4$ requires C, 59.8; H, 4.0%). 10^{-3} $E_{max.}$ (CH_2Cl_2): 18.9 (ε 1 300), 30.1 (7 300), and 33.3 cm^{-1} (31 000 dm^3 mol^{-1} cm^{-1}).

Bis[o-*phenylenebis*(*dimethylarsine*)]*nickel*(II) *Tri-iodide* (1 −), $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2][I_3]_2$.—A saturated solution of $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2I_2]$ in MeCN (20 cm^3) was treated with excess of I_2 (Ni : I_2 = 1 : 5) in CH_2Cl_2 (20 cm^3). On cooling slowly to −20 °C, greenish black crystals formed. These were filtered off, rinsed with diethyl ether (5 cm^3), and dried briefly *in vacuo*. Yield essentially quantitative (Found: C, 17.6; H, 2.4; I, 55.5. $C_{20}H_{32}As_4I_6Ni$ requires C, 17.3; H, 2.3; I, 54.7%). μ *ca.* 0.3 B.M. [Gouy and Evans ($CHCl_3$) methods]. Λ (10^{-3} mol dm^{-3} $MeNO_2$) = 95 ohm^{-1} cm^2 mol^{-1}. The complexes $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2][I_3]_2$ (Found: C, 19.7; H, 2.5. $C_{20}H_{32}I_6NiP_4$ requires C, 19.75; H, 2.65%) and $[Ni\{o\text{-}C_6H_4(AsMe_2)(PMe_2)\}_2][I_3]_2$ (Found: C, 18.4; H, 2.5. $C_{20}H_{32}As_2I_6NiP_2$ requires C, 18.5; H, 2.45%) were made analogously.

Bis(2,5-*diselenahexane*)*bis*(*tri-iodo*)*nickel*(II), $[Ni(MeSeCH_2CH_2SeMe)_2(I_3)_2]$.—To $[Ni(MeSeCH_2CH_2SeMe)_2I_2]$ (0.15 g, 0.2 mmol) in CH_2Cl_2 (25 cm^3) was added I_2 (0.254 g, 1 mmol) in CH_2Cl_2 (10 cm^3). On cooling to −25 °C for 48 h a black powder was obtained. This was collected, rinsed with diethyl ether, and dried *in vacuo*. Yield quantitative (Found: C, 8.0; H, 1.6; I, 60.8. $C_8H_{20}I_6NiSe_4$ requires C, 7.7; H 1.6; I, 60.0%). μ = 2.91 B.M. (Gouy).

Bis(2,5-dithiahexane)bis(tri-iodo)nickel(II) [10] was made analogously (Found: C, 9.0; H, 1.7. $C_8H_{20}I_6NiS_4$ requires C, 9.0; H, 1.9%); μ = 3.4 B.M.

$Ni[o\text{-}C_6H_4(AsPh_2)_2]I_4$.—A solution of $[Ni\{o\text{-}C_6H_4(AsPh_2)_2\}I_2]$ (0.17 g, 0.2 mmol) in CH_2Cl_2 (20 cm^3) was added to iodine (0.254 g, 1 mmol) in CH_2Cl_2 (10 cm^3). On standing at −20 °C for 2 d a black powder precipitated. This was filtered off, washed with n-pentane, and dried. Yield 0.175 g (80%) (Found: C, 32.4; H, 2.6; I, 44.9. $C_{30}H_{24}As_2I_4Ni$ requires C, 32.7; H, 2.2; I, 46.1%). μ = 0.5 B.M. (Gouy).

The complex $[Ni(H_2NCH_2CH_2NH_2)_2][I_3]_2$ was made by the method of Nyholm and co-workers [13] (Found: C, 5.3; H, 1.8; N, 6.1. $C_4H_{16}I_6N_4Ni$ requires C, 5.1; H, 1.7; N, 6.0%). μ = 0.0 B.M. (Gouy).

$Ni[o\text{-}C_6H_4(AsMe_2)_2]I_4$.—Dicarbonyl[*o*-phenylenebis(dimethylarsine)]nickel(0) (0.2 g, 0.5 mmol) was recrystallised under dinitrogen from cyclohexane and redissolved in CH_2Cl_2. Iodine (0.64 g, 2.5 mmol) in CH_2Cl_2 (20 cm^3) was added with vigorous stirring, and the resulting black solid filtered off in a Schlenk tube, rinsed with CH_2Cl_2, and dried *in vacuo* (Found: C, 13.8; H, 2.2. $C_{10}H_{16}As_2I_4Ni$ requires C, 14.1; H, 1.9%).

$Ni[o\text{-}C_6H_4(AsMe_2)_2]_2I_3$.—(*a*) A solution of $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2]ClO_4$ [16] (0.15 g, 0.19 mmol) in MeCN (35 cm^3) was added to excess of aqueous KI (40 cm^3, *ca.* 0.1 mol dm^{-3}) with stirring. The khaki-green precipitate was filtered off and dried to give a green-black solid. Yield 0.14 g, (73%) (Found: C, 23.6; H, 3.2. $C_{20}H_{32}As_4I_3Ni$ requires C, 23.7; H, 3.2%). μ = 0.0 B.M.

(*b*) A solution of $[Ni\{o\text{-}C_6H_4(AsMe_2)_2\}_2Cl_2][ClO_4]_2$ [39] (0.2 g, 0.22 mmol) in CF_3CO_2H (15 cm^3) was filtered into an excess of aqueous KI (40 cm^3). The precipitate was filtered off, rinsed well with water, and dried (Found: C, 23.6; H, 3.2%).

X-Ray Structure Determination.—The products obtained from the reaction between $[Ni\{o\text{-}C_6H_4(PMe_2)_2\}_2I_2]$ and I_2 depend on the choice of solvent and the problems associated with solving the structure arose because of not knowing which polyiodide species was present in the crystals examined. The 'I_6' material [density (flotation) 2.18(4) g cm^{-3}] prepared as described earlier (CH_2Cl_2–MeCN solvent) appears to be stoicheiometrically well defined. Attempts to grow crystals for *X*-ray examination yielded a few well formed examples over a longer period of time and these subsequently were shown to have the composition 'I_{10}'. Carrying out the reaction of the same complex with I_2 (1 : 5 mole ratio) in the solvent CH_2Cl_2 produced small amounts of the microcrystalline 'I_{10}' complex (Found: C, 13.5; H, 2.0. $C_{20}H_{32}I_{10}NiP_4$ requires C, 13.9; H, 1.9%) with an observed density (flotation) of *ca.* 2.77 g cm^{-3}. The rather variable density of crystals prepared for *X*-ray examination may indicate the possibility of producing a range of compounds containing varying amounts of iodine between the compositions 'I_6' and 'I_{10}' per nickel atom, however the 'I_6' compound was shown (single-crystal *X*-ray photographs) to be monoclinic.

Preliminary photographic examination established the triclinic system and cell volume for the selected air-stable black crystals and precise cell dimensions were obtained from 25 accurately centred reflections on an Enraf–Nonius CAD-4 diffractometer which was also used for the data collection.

Crystal data. $C_{20}H_{32}I_{10}NiP_4$, M = 1 724.1, triclinic, a = 9.672(2), b = 12.369(2), c = 9.574(3) Å, α = 106.55(2), β = 107.70(2), γ = 99.48(1)°, U = 1 005.6 $Å^3$, D_m(flotation) = 2.77(3), Z = 1, D_c = 2.846 g cm^{-3}, $F(000)$ = 770, λ(Mo-K_α) = 0.7107 Å, μ(Mo-K_α) = 82.3 cm^{-1}, space group $P\bar{1}$ (no. 2) from the structure analysis.

Data collection. Using a room-temperature crystal ($0.5 \times 0.15 \times 0.25$ mm) mounted in a Lindemann capillary, 3 680 reflections were recorded ($1.5 \leqslant \theta \leqslant 25.0°$) using graphite-monochromated Mo-K_α radiation. The three check reflections showed no deterioration during the experiment and after averaging multiply measured reflections (merging R 0.0096) there remained 3 542 unique reflections. An empirical psi-scan absorption correction was applied to the data [% transmission: 99.9 (max.) to 70.4 (min.)]. Removing those reflections where $F < 4\sigma(F)$ (628) left 2 914 observations which were used in the structure solution and refinement.

Structure solution and refinement. The normalised structure factors (E's) favoured the centrosymmetric space group $P\bar{1}$ although this was based on the (incorrect) assumption of I_6 per cell. Using direct methods, both SHELX [45] and MULTAN [46] gave an identical solution with high figure of merit in this space group, but apart from a linear I_3 group no further chemically persuasive features emerged from this model on repeated structure-factor and electron-density calculations. Examination of the Patterson synthesis showed a number of vector triangles having in common one prominent vector of length *ca.* 2.8 Å presumed to be a bonded I–I vector. Using these related vectors an image of the structure was gradually built up in the space group $P\bar{1}$ by repeated structure-factor and electron-density calculations which contained solely iodine atoms. When 10 iodine atoms were in the unit cell (R *ca.* 0.23) a partial image of the $Ni[o\text{-}C_6H_4(PMe_2)_2]_2$ residue was recognised in the electron-density synthesis and the remaining atoms were readily located to give the composition $Ni[o\text{-}C_6H_4(PMe_2)_2]_2I_{10}$ (R *ca.* 0.08). In the space group $P\bar{1}$ the nickel atom must be located on one of the centres of symmetry and transforming the co-ordinates to place Ni at 0,0,0 showed that the atoms of the structure indeed conformed well with $P\bar{1}$ symmetry. Refinement was subsequently continued in this space group.

Table 3. Fractional atomic co-ordinates (× 10^4)

Atom	*X*/*a*	*Y*/*b*	*Z*/*c*	Atom	*X*/*a*	*Y*/*b*	*Z*/*c*
I(1)	−2 834(1)	−4 907(0)	27(1)	C(2)	−3 306(9)	−2 145(7)	−1 352(10)
I(2)	−2 794(1)	−5 020(0)	2 843(1)	C(3)	−245(8)	2 868(6)	1 046(9)
I(3)	−278(1)	−1 226(1)	2 802(1)	C(4)	−1 654(10)	1 425(8)	2 341(10)
I(4)	1 506(1)	−2 840(0)	3 395(1)	C(11)	−3 437(7)	−88(6)	−2 062(8)
I(5)	3 361(1)	−4 425(1)	4 020(1)	C(12)	−4 832(8)	−430(7)	−3 295(9)
Ni	0	0	0	C(13)	−5 706(8)	349(7)	−3 338(9)
P(1)	−2 226(2)	−1 055(1)	−1 830(2)	C(14)	−5 237(8)	1 431(7)	−2 178(10)
P(2)	−1 133(2)	1 355(1)	671(2)	C(15)	−3 843(8)	1 770(6)	−952(9)
C(1)	−2 367(9)	−1 854(7)	−3 806(8)	C(16)	−2 965(7)	997(6)	−927(8)

The introduction of anisotropic thermal parameters for I, Ni, and P atoms and empirical weights, $w = 1/[\sigma^2(F) + AF^2]$, where A is adjusted to make $w\Delta^2$ approximately constant when analysed in terms of F, reduced R by least-squares refinement to 0.039. There was evidence for some H atoms in the electron-density difference synthesis and all of these were introduced into the model in geometrically calculated positions [d(C−H) = 1.08 Å]. Methyl H atoms were given a common refined thermal parameter as were the phenyl H atoms. Introducing anisotropic carbon atoms produced a highly significant decrease in R [47] and refinement converged at $R = 0.0320$ ($R' = 0.0449$) {2 914 reflections, 174 parameters, anisotropic (I, Ni, P, and C) and isotropic (H) atoms, $w = 1/[\sigma^2(F) + 0.0002F^2]$, reflections/parameters = 16.7}. There was no evidence from the thermal parameters that the composition was less than I_{10} per Ni atom in the crystal selected. A final electron-density difference synthesis showed all features in the range −2.6 to +2.2 e Å^{-3} with the largest feature close to I(3).

The final atomic co-ordinates are presented in Table 3. Atomic scattering factors for neutral atoms and anomalous dispersion terms were taken from SHELX [45] (P, C, and H) and ref. 48 (I and Ni). All calculations were carried out using an ICL 2970 computer and the programs SHELX,[45] MULTAN,[46] ORTEP,[49] PLUTO,[50] XANADU,[51] and various local programs.

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