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Facile synthesis of a rare example of an iron(III) iodide complex, [FeI₃(AsMe₃)₂], from the reaction of Me₃AsI₂ with unactivated iron powder

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Dedicated to the memory of the late Dr. Steve Godfrey (1966–2011), and Prof. Noel McAuliffe (1941–2002).

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1. Introduction

Iron(III) iodide stands out amongst the binary halides of iron due to its low stability. Indeed, for many years FeI₃ was believed to be non-existant, since iron(III) is reduced by $[I]^-$ to iron(II), with formation of I₂ (especially in aqeuous media) [1]. Only as recently as 1988 Yoon and Kochi reported the first preparation of FeI₃, which was obtained as a black solid via the photochemical reaction of [Fe(CO)₄I₂] with I₂ in hexane [2,3]. In the solid-state, FeI₃ shows moderate stability, but can only be synthesised in small quantities, and is highly unstable in solution. It is clear that the paucity of reports on neutral complexes of FeI₃ is a consequence of the instability of the parent halide.

There are only a few reports of iron(III) iodide coordination complexes, usually obtained via oxidation of an iron(II) complex, or utilising a combination of Fel₂ and I₂. Salts containing the tetrahedral [FeI₄]⁻ anion may be prepared, either from the reaction of [FeCI₄]⁻ with anhydrous HI [4], or via oxidation of FeI₂ with I₂ in the presence of an iodide salt [5–7]. The structures of a number of salts featuring the [FeI₄]⁻ anion have been reported [6–14], with Fe–I bonds typically varying between 2.51 and 2.57 Å. The related [FeI₃(THF)]⁻ anion has also been crystallographically characterised in the mixed iron(II)/(III) salt [Fe(THF)₆][FeI₃(THF)]₂ [7]. The only neutral iron(III) iodide complexes to have been reported are the

ABSTRACT

The reaction of Me₃AsI₂ with unactivated iron powder provides a synthetic entry into the coordination chemistry of iron(III) iodide, which is inaccessible by traditional routes due to the low stability of the parent halide FeI₃. The reaction of iron powder with Me₃AsI₂ results in the formation of a trigonal bipyramidal complex, [FeI₃(AsMe₃)₂], which features the iodide ligands in the equatorial positions, and the Me₃As groups occupying the axial positions. This complex is a rare example of an iron(III) iodide complex, and is the first iron(III) complex of a monodentate tertiary arsine ligand. The preparation of [FeI₃(AsMe₃)₂] via the direct oxidation of iron powder further demonstrates that complexes of "soft" donor ligands can be prepared with "hard" transition metal centres, such as iron(III), in direct contravention of the HSAB principle. The structure of [FeI₃(AsMe₃)₂] is isomorphous with all previously reported [MX₃(EMe₃)₂] (M = main group or transition metal, X = halide, E = N, P, As) trigonal bipyramidal structures.

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complexes [FeI₃{S=C(NMe₂)₂}] and [FeI₃{O=C(NMe₂)₂}], [15,16] both of which have been crystallographically characterised and feature the iron atom in a tetrahedral geometry. A small number of ionic iron(III) iodide complexes of chelating phosphines and arsines have been reported via the oxidation of iron(II) iodide complexes with concentrated HNO₃. The reactions of [FeI₂(L-L)₂], L-L = o-C₆H₄(PMe₂)₂, o-C₆H₄(AsMe₂)₂, o-C₆F₄(AsMe₂)₂, with HNO₃ in the presence of HBF₄ results in the formation of [FeI₂(L-L)₂][BF₄] [17]. Subsequently, the [FeI₂{o-C₆H₄(AsMe₂)₂]⁺ cation has been crystallographically characterised as the [I₃]⁻ salt, and contains octahedral iron(III) with mutually *trans* iodide ligands [18].

We have previously shown that metal complexes can be synthsised from the reaction of R_3EX_2 compounds (E = P, As, Sb; X = Br, I) directly with unactivated metal powders [19]. A number of complexes prepared by this synthetic route cannot be synthesised via conventional routes, and some, such as $[Col_3(SbPh_3)_2]$ [20], defy Pearsons HSAB principle [21].

The reaction of unactivated iron powder has been employed in a number of these reactions. For example, Me_2PhPBr_2 reacts with iron powder to produce a white solid, which when exposed to trace amounts of O_2 forms a deep-purple iron(III) complex [FeBr₃{-PPhMe_2}_2] [22]. The structure of this complex has been determined and shown to be trigonal bipyramidal at iron, with the phosphine ligands occupying the axial positions. Alternatively, the iron(0) carbonyl [Fe₂(CO)₉] could be oxidised by R_3EX_2 (E = P, As; X = Br, I) [8], to yield either either iron(II) species, [R_3EX][FeX₄]. The latter were only observed when X = Br.





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We have noticed the tendency of Me_3EX_2 adducts to behave differently towards metal powders than other R_3EX_2 systems [19]. The reaction generally does not produce ionic complexes (which are often formed with larger R groups). Instead, trigonal bipyramidal complexes of formula $[MX_3(EMe_3)_2]$ are formed, even when the +3 oxidation state is uncommon for phosphine/arsine complexes, as in the case of $[Col_3(EMe_3)_2]$ [23,24], or $[Nil_3(EMe_3)_2]$ [22,24], (E = P, As), or when the CFSE strongly favours a different geometry, as in the case of $[Aul_3(PMe_3)_2]$, where a square–planar geometry would have been expected [25]. We now report the reaction of Me_3Asl_2 with elemental iron powder to see if this synthetic route provides an entry into neutral Fel₃ complexes.

2. Results and discussion

2.1. Synthesis of $[FeI_3(AsMe_3)_2]$

The reaction of Me_3Asl_2 and iron powder was performed in a 2:1 ratio in anhydrous diethyl ether. After stirring at ambient temperature for *ca.* four days all the iron powder had been consumed, and a dark green precipitate was formed which was slightly soluble in diethyl ether. The solid was isolated and analysed as $[Fel_3(-AsMe_3)_2]$, although the overall reaction also produces half an equivalent of iodine, see Eq. (1). The iodine can be removed from the product by washing with anhydrous hexane.

$$2\mathrm{Me}_{3}\mathrm{AsI}_{2} + \mathrm{Fe} \stackrel{\mathrm{El}_{2}\mathrm{U}}{\rightarrow} [\mathrm{FeI}_{3}(\mathrm{AsMe}_{3})_{2}] + 1/2\mathrm{I}_{2} \tag{1}$$

The presence of iodine was confirmed from the electronic spectrum of the filtrate, which, in addition to peaks due to the iron complex, exhibited a band at 525 nm, typical for diiodine in diethyl ether [26]. The electronic spectrum of the black–green iron complex displayed two prominent bands, one at 461 nm ($\varepsilon_{max} = 9100 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$), and the other at 671 nm ($\varepsilon_{max} = 6900 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The former band is attributed to an iodine ligand-to-metal charge-transfer transition, $I(\pi) \rightarrow \text{Fe}$, whilst the latter is assigned as As(σ) \rightarrow Fe, by comparison with reported data for other iron(III) arsine complexes [17,27]. Additionally, the spectrum also displays two shoulder peaks at 542 and 600 nm, which may arise due to d–d transitions.

The formation of an iron arsine complex in a high oxidation state (+3) is unexpected. (on the basis of the HSAB principle) [21], as is formation of a five-coordinate complex for a d⁵ iron(III) configuration. A search of the CSD database (Dec. 2012) shows that the vast majority of reported iron(III) complexes exhibit a six-coordinate octahedral geometry. There are far fewer reports of neutral five-coordinate [FeX₃(L)₂] structures, (ten in total, eight of which are FeCl₃ complexes, [28] and two are FeBr₃ complexes). $[29]^1$ The structure of $[FeI_3(AsMe_3)_2]$ thus represents the first example of this geometry when X = I. All of the five-coordinate structures have a trigonal bipyramidal geometry, with the halide atoms in the equatorial positions, and the neutral ligands occupying the axial positions, as is the case in [FeI₃(AsMe₃)₂]. Additionally, there are two crystallographically characterised examples of [FeCl₃(L-L)] complexes with chelating ligands, where the five-coordinate geometry is distorted between trigonal bipyramidal and square pyramidal by the chelating ligand [30].

There is also very little structural data known for complexes with Fe–As bonds. A number of structures of organometallic complexes with iron in a low oxidation state are known. These include the iron(0) complex [Fe(CO)₄(AsMe₃)], which is trigonal bipyramidal with the Me₃As ligand occupying one of the axial positions [31], and a number of cluster complexes with difluorocarbene, CO and AsMe₃ ligands. [32] The only iron–halide complexes containing ar-

sine ligands to have been crystallographically characterised are the iron(II) complex $[FeI_2{o-C_6H_4(AsMe_2)_2}_2]$ and the cationic iron(III) species in $[FeI_2{o-C_6H_4(AsMe_2)_2}_2][I_3] \cdot 2CH_2CI_2$ [18].

In view of the limited structural data for iron-halide complexes with arsenic donors we sought to obtain crystals of [FeI₃(AsMe₃)₂].

2.2. Structural features of [Fel₃(AsMe₃)₂]

Crystals were obtained by dissolving the complex in warm dichloromethane:ether (50:50), followed by cooling to *ca*. 2 °C. Dark black–green crystals formed after several days. An ORTEP representation of the crystal structure of $[Fel_3(AsMe_3)_2]$ is shown in Fig. 1, along with selected bond lengths and angles.

Strikingly, $[FeI_3(AsMe_3)_2]$ is isomorphous with all 14 previously reported trigonal bipyramidal $[MX_3(EMe_3)_2]$ (E = N, P, As) structures, all of which crystallise in the orthorhombic space group *Pnma*, with similar cell dimensions, [23-25,28b,28h,33-41], see Table 1.

The iodide ligands in $[FeI_3(AsMe_3)_2]$ occupy the equatorial positions of the trigonal bipyramid, whilst the Me₃As ligands are located in the axial positions. The structure has a crystallographically imposed mirror plane running through atoms Fe(1), As(1), As(2), I(2), C(2) and C(4). This type of symmetry is identical to that observed throughout the isomorphous $[MX_3(EMe_3)_2]$ (E = N, P, As) series of structures. The distortion from an idealised D_{3h} trigonal bipyramidal symmetry is low, with both Fe–As bonds being similar in magnitude to each other, 2.414(3) and 2.419(3) Å, as are the Fe–I bonds which vary between 2.571(3) to 2.5828(14) Å. The angles around the iron atom are also close to the expected for a trigonal bipyramidal geometry, with the As–Fe–As angle close to linear at 178.46(11)°, whilst the As–Fe–I angles are close to 90°, as they vary between 88.48(8) and 90.79(6)°.

The Fe–As bonds in [FeI₃(AsMe₃)₂] are considerably longer than those observed in low oxidation state complexes with the AsMe₃ ligand, such as [Fe(CO)₄(AsMe₃)], *d*(Fe–As): 2.30(3) Å [31], and [Fe₂(CO)₆(μ –CF₂)(AsMe₃)₂], *d*(Fe–As): 2.3713(5) to 2.3782(6) Å [32]. These bonds are also longer than those observed for the iron(II)/iron(III) redox pair, [FeI₂{o-C₆H₄(AsMe₂)₂}]/[FeI₂{o-C₆H₄(AsMe₂)₂}]⁺ [18]. In the neutral iron(II) complex the Fe–As bonds are 2.3372(5) and 2.3388(5) Å, whilst in the iron(III) cation the Fe–



Fig. 1. ORTEP representation of the molecular structure of $[Fel_3(AsMe_3)_2]$. Thermal ellipsoids are shown at the 30% probability level. Selected bond lengths [Å] and angles [°]: Fe(1)–I(1): 2.5828(14), Fe(1)–I(2): 2.571(3), Fe(1)–As(1): 2.414(3), Fe(1)–As(2): 2.419(3), As(1)–C(1): 1.912(13), As(1)–C(2): 1.94(2), As(2)–C(3): 1.911(14), As(2)–C(4): 1.928(16), As(1)–Fe(1)–As(2): 178.46(11), I(1)–Fe(1)–I(2): 120.93(4), I(1)–Fe(1)–I(1ⁱ): 118.11(8), I(1)–Fe(1)–As(1): 90.79(6), I(1)–Fe(1)–As(2): 90.00(6), I(2)–Fe(1)–As(1): 89.98(8), I(2)–Fe(1)–As(2): 88.48(8). Symmetry operations to generate equivalent atoms: (i): x, $\frac{1}{2} - y$, z.

¹ JODFOX: See Ref. [22].

Table 1

Comparison of crystal data for the isomorphous series of [MX ₃ (EMe ₃) ₂	2] trigonal bipyramidal structures which crystallise in the orthorhombic Pn	ma spacegroup: CSD database
search (Dec. 2012).		

Complex	CCDC code	Cell parameters, a, b, c (Å)	Cell volume (Å ³)	Refs.
[TiBr ₃ (NMe ₃) ₂]	TMATBI	10.23(2), 10.28(2), 13.46(3)	1415(1)	[33]
$[VCl_3(NMe_3)_2]$	CLTAMV	9.817(20), 10.127(14), 13.152(14)	1307.5	[34]
$[CrCl_3(NMe_3)_2]$	TMAMCR	9.69(1), 10.12(1), 13.05(2)	1268(1)	[33]
[FeCl ₃ (NMe ₃) ₂]	FINJIV	9.753(9), 10.150(11), 13.156(12)	1302.4(9)	[28b]
[AlCl ₃ (NMe ₃) ₂]	QQQCMP	9.645(8), 9.994(2), 12.918(6)	1245.2(12)	[35], [36]
[InCl ₃ (NMe ₃) ₂]	DOHBAD	9.99(1), 10.09(1), 13.08(1)	1318.7	[37]
$[MnI_3(PMe_3)_2]$	CEVTEC	10.509(1), 11.167(8), 14.398(2)	1689.7	[38], [39]
[FeCl ₃ (PMe ₃) ₂]	SAVHOM	9.846(2), 10.680(3), 13.439(7)	1413(1)	[28g]
$[CoI_3(PMe_3)_2]$	VUHZIH	10.217(4), 11.184(2), 14.252(4)	1629(1)	[23]
$[NiI_3(PMe_3)_2]$	GAPYAX	10.197(3), 11.155(8), 14.213(3)	1616.7(5)	[40]
$[AuI_3(PMe_3)_2]$	TURBOH	10.488(4), 11.122(3), 14.279(3)	1148(1)	[25]
$[InCl_3(PMe_3)_2]$	VOXBUF	10.418(8), 10.769(9), 13.808(9)	1549(2)	[41]
[FeI ₃ (AsMe ₂) ₂]	this work	10.412(2), 11.3617(10), 14.543(3)	1720.4(5)	this work
$[CoI_3(AsMe_3)_2]$	ZOJMEQ	10.142(3), 11.210(3), 14.291(4)	1625(1)	[24]
$[NiI_3(AsMe_3)_2]$	ZOJMIV	10.298(5), 11.363(3), 14.440(5)	1690(2)	[24]

As bonds are longer, at 2.3792(4) and 2.3822(5) Å. The Me₃As ligands in [FeI₃(AsMe₃)₂] are therefore more weakly bound than in these previously reported examples, which is consistent with the expected weaker nature of the Fe–As bond due to the increased mismatch of the soft arsenic donor and the harder iron(III) metal centre, and the reduction in the contribution of π -backbonding for the higher oxidation state, as recognised by Levason and coworkers for the redox pair above [18].

A comparison of the Fe–I bonds in [FeI₃(AsMe₃)₂] with the small number of crystallographically characterised iron(III) iodide complexes is shown in Table 2. The Fe–I bonds of 2.571(3) to 2.5828(14) Å are significantly longer than those observed for the tetrahedral neutral iron(III) iodide complexes, [FeI₃{S=C(NMe₂)₂}] and [FeI₃{O=C(NMe₂)₂}], [15,16] but are not as elongated as the Fe–I bonds of 2.6009(3) Å in the cationic [FeI₂{o-C₆H₄(AsMe₂)₂}]⁺ species [18].

A comparison of bond lengths and angles within the isomorphous series of $[MX_3(EMe_3)_2]$ structures shows that some of the complexes display some distortion from an ideal trigonal bipyramidal geometry. This distortion is mainly observed in the M–X bonds to the equatorial halide ligands, and in the X–M–X angles between the equatorial ligands, see Table 3. In contrast, the angles between the axial EMe₃ ligands are close to the expected linear geometry, (in all the structures the angles are between 176° and 180°).

Table 2

Comparison of Fe-I bond lengths in iron(III) iodide complexes.

Complex	Fe–I (Å)	Refs.
$[FeI_3(AsMe_3)_2]$	2.571(3)-	this
	2.5828(14)	work
$[FeI_3{S=C(NMe_2)_2}]$	2.530(1)-2.553(1)	[15]
$[FeI_3{O=C(NMe_2)_2}]$	2.526(1)-2.532(1)	[16]
$[FeI_2{o-C_6H_4(AsMe_2)_2}_2][I_3]$	2.6009(3)	[18]
[Et ₄ N][FeI ₄]	2.531(3)-2.540(3)	[6]
$[Fe(OCH_2)_6][FeI_4]$	2.517(4)-2.567(4)	[7]
[Ph ₄ Sb][FeI ₄].Ph ₃ SbI ₂	2.525(7)-2.553(7)	[8]
$[{Cp_2Cr_2(\mu-SCMe_3)-(\mu_3-S)_2}_2Fe][FeI_4]$	2.518(2)-2.548(2)	[9]
[Cp ₂ Co][FeI ₄]	2.5369(11)-	[10]
	2.5511(11)	
$[{(C_2H_5)_4C_4P}_2Fe][FeI_4]$	2.5451(7)-	[11]
	2.5468(8)	
[{(o-C ₆ H ₄ SMe)S(CH ₂) ₂ S(o-	2.519(2)-2.548(2)	[12]
C ₆ H ₄ SMe)}Fe(CO)I][FeI ₄]		
$[(Cp*)_2Mo_2(\mu-I)_4][FeI_4]$	2.510(3)-2.546(3)	[13]
$[(Me_2N)_2C=S-S=C(NMe_2)_2][FeI_4]$	2.526(5)-2.569(4)	[14]
[Fe(THF) ₆][FeI ₃ (THF)] ₂	2.611(2)	[7]

In almost all of the complexes the M-X bonds to the two halide ligands related by the mirror plane are longer than the M-X bond to the third halide ligand. Only [FeCl₃(PMe₃)₂] is an exception to this, where the Fe-Cl bonds are equal within experimental error [28g]. In a number of cases, as in [Fel₃(AsMe₃)₂], the difference (Δ) between the two M-X distances is very small, but is much more marked in other complexes, such as [TiBr₃(NMe₃)₂]. Distortion in the M-X bond lengths and X-M-X angles in a number of these complexes has been attributed to Jahn-Teller effects. [40,42-43] In a trigonal bipyramidal field the d¹, d³, d⁵(LS), d⁶(HS), d⁷(LS) and d⁸(HS) configurations may be Jahn–Teller active. A relationship between distortions in the magnitude of the equatorial X-M-X angles and expected Jahn-Teller activity can be seen in Table 3, where $\Delta(X-M-X)$ varies considerably between different complexes in the series. For example, $\Delta(X-M-X)$ is only 2.4° for $[Col_3(AsMe_3)_2]$, but is 12.9° for $[CrCl_3(NMe_3)_2]$. The chromium complex has a d³ configuration and is expected to be Jahn-Teller active, [33,42] whereas the cobalt complex has been assigned a low-spin d⁶ configuration [43], and hence is Jahn–Teller inactive. The distortion in [TiBr₃(NMe₃)₂] (d¹) manifests itself in the variation observed between the equatorial M-X bond lengths [44], as the differences between the X-M-X angles is rather small. Distortions in the nickel complex [NiI₃(PMe₃)₂] have also previously been discussed in terms of Jahn-Teller effects [40]. The only complex to show unexpected marked distortions is [AuI₃(PMe₃)₂] [25], where Jahn-Teller activity would only be expected for a high-spin complex, however the strong field expected for a 5d⁸ system, coupled with the advantagous CFSE in pairing all the d electrons would strongly favour a low-spin configuration for this complex.

In the structure of $[FeI_3(AsMe_3)_2]$ the $\Delta(X-M-X)$ is small, with I–Fe–I angles of 118.11(8)° and 120.93(4)°. The smaller of these two angles is the angle between the symmetry related I(1) atoms, which is the smallest angle in all of the $[MX_3(EMe_3)_2]$ structures. The amine complex $[FeCI_3(NMe_3)_2]$ also shows similar features [28b], whilst there is more distortion in $[FeCI_3(PMe_3)_2]$, where $\Delta(X-M-X)$ is 7.4(2)°, compared to 2.9(5)° for $[FeCI_3(NMe_3)_2]$ and 2.82(8)° for $[FeI_3(AsMe_3)_2]$. The complex $[FeCI_3(PMe_3)_2]$ is known to be low-spin d⁵ [28g], which would be Jahn–Teller active in a trigonal bipyramidal field. The much lower distortion for the NMe₃ and AsMe₃ complexes may indicate that these are high-spin d⁵, and hence Jahn–Teller inactive.

Molecules of $[FeI_3(AsMe_3)_2]$ pack in a regular fashion at distances beyond van der Waals contacts, as shown in Fig. 2, viewed down the *a*-cell dimension. One of the methyl groups on the AsMe₃ ligand As(2) is oriented towards the two symmetry related I(1) atoms on a neighbouring molecule, although the H4(B) \cdots I(1) inter-

Table 3

Comparison of equatorial M–X bonds [Å] and X–M–X angles [°] around the metal centre for the isomorphous series of [MX3(EMe3)2] (E = N, P, As) trigonal bipyramidal structures.
The X–M–X angle of lowest magnitude is that between the two symmetry related halide ligands.

Complex	M-X _{eq} (Å)	M–X (Å)	X–M–X (°)	(X-M-X) (°)	Refs.
[TiBr ₃ (NMe ₃) ₂]	2.400(8), 2.445(5) × 2	0.045(8)	117.5(3), 121.3(2) × 2	3.8(3)	[33]
$[VCl_3(NMe_3)_2]$	2.236(5), 2.241(5) × 2	0.005(5)	118.1(2), 121.0(1) × 2	2.9(3)	[34]
$[CrCl_3(NMe_3)_2]$	2.222(3), 2.253(5) × 2	0.031(5)	111.4(2), 124.3(1) × 2	12.9(1)	[33]
[FeCl ₃ (NMe ₃) ₂]	$2.207(2), 2.228(1) \times 2$	0.021(2)	118.0(5), 120.99(4) × 2	2.9(5)	[28b]
$[AlCl_3(NMe_3)_2]$	2.1676(10), 2.1725(5) × 2	0.0049(10)	117.85(3), 121.07(2) × 2	3.22(3)	[35,36]
[InCl ₃ (NMe ₃) ₂]	2.343(8), 2.376(4) × 2	0.033(8)	117.45(19), 121.27(14) × 2	3.82(19)	[37]
$[MnI_3(PMe_3)_2]$	2.605(6), 2.635(3) × 2	0.030(6)	117.5(1), 121.3(1) × 2	3.8(1)	[38,39]
[FeCl ₃ (PMe ₃) ₂]	2.232(5), 2.231(13) × 2	0.001(13)	115.1(2), 122.46(9) × 2	7.4(2)	[28g]
$[CoI_3(PMe_3)_2]$	2.543(2), 2.551(1) × 2	0.008(2)	118.17(8), 120.91(4) × 2	2.74(8)	[23]
$[NiI_3(PMe_3)_2]$	$2.530(1), 2.551(1) \times 2$	0.021(1)	114.70(4), 122.65(2) × 2	7.95(4)	[40]
$[AuI_3(PMe_3)_2]$	2.709(3), 2.761(2) × 2	0.052(3)	115.01(9), 122.49(4) × 2	7.48(9)	[25]
$[InCl_3(PMe_3)_2]$	2.453(4), 2.503(3) × 2	0.050(4)	116.1(1), 122.0(1) × 2	5.9(1)	[41]
[FeI ₃ (AsMe ₂) ₂]	2.571(3), 2.5828(14) × 2	0.0118(14)	118.11(8), 120.93(4) × 2	2.82(8)	this work
[CoI ₃ (AsMe ₃) ₂]	2.510(5), 2.530(3) × 2	0.020(5)	118.4(2), 120.8(1) × 2	2.4(2)	[24]
[Nil ₃ (AsMe ₃) ₂]	2.531(9), 2.550(5) × 2	0.019(9)	114.7(3), 122.6(1) × 2	7.9(3)	[24]



Fig. 2. Packing of molecules of [FeI₃(AsMe₃)₂] viewed down the crystallographic *a*-axis.

actions of 3.43 to 3.53 Å are notably longer than the sum of the van der Waals radii of hydrogen and iodine (3.18 Å).

The crystallographic cone angles for the Me₃As ligands in [FeI₃(-AsMe₃)₂] have been calculated directly from the structure, and are 116.7° for the As(1) ligand, and 116.3° for the As(2) ligand. These values are close to that of 121° calculated for Me₃As by Imyanitov [45]. An examination of other metal complexes with Me₃As ligands show that similar cone angles are observed. For example, the cone angles lie between 114.0° and 116.3° for the Me₃As ligands in the iron clusters [Fe₂(CO)₆(μ -CF₂)(AsMe₃)₂] and [Fe₂(CO)₅(μ -CF₂)(-AsMe₃)₃] [32], and between 115.9° and 118.0° in the series of tetrahedral [GaX₃(AsMe₃)] (X = Cl, Br, I) complexes [46].

3. Conclusion

The oxidation of unactivated iron powder with Me₃AsI₂ provides an entry route into the coordination chemistry of iron(III) iodide, which is inaccessible via traditional synthetic routes, due to the low stability of the parent halide. [FeI₃(AsMe₃)₂] is an example of a complex which defies the HSAB principle, as the hard iron(III) centre has a very soft As₂I₃ donor set. The adoption of a trigonal bipyramidal geometry is consistent with the isomorphous set of $[MX_3(EMe_3)_2]$ (M = TM or main group metal, X = any halogen, E = N, P, As) complexes, all of which crystallise in the orthorhombic *Pnma* space group, irrespective of the nature of M, X or E. A study of this series of complexes shows that some complexes exhibit deviations from an ideal trigonal bipyramidal geometry, and these deviations appear to be due to Jahn–Teller effects.

4. Experimental

4.1. Reagents and physical measurements

The iron(III) complex [FeI₃(AsMe₃)₂] is highly sensitive to air and moisture, therefore standard Schlenk techniques were employed throughout, with all additions being performed under a stream of dry argon. Diethyl ether and hexane were purchased commercially (BDH) and freshly distilled from sodium/benzophenone ketyl before use. Dichloromethane was purchased (Aldrich) as anhydrous grade and stored over 4 Å molecular sieves. Me₃AsI₂ was prepared as previously described [47]. Iron powder (10– 40 mesh) was purchased commercially (Aldrich) and used as received. Elemental analyses were performed by the Chemistry Departmental Microanalytical service. Electronic spectra were prepared in anhydrous diethyl ether in 1 cm path quartz cells fitted with PTFE seals, and recorded on a Shimadzu UV-2101PC spectrophotometer.

4.2. Crystallographic details

Details of the structural analysis for [Fel₃(AsMe₃)₂] are summarised in Table 4. Diffraction data were recorded on a Rigaku AFC 6S four-circle diffractometer using graphite-monochromated Mo Ka radiation (λ = 0.71073 Å), at 293(2) K. Structural data were solved by direct methods, with full-matrix least squares refinement on F^2 using the shelx-97 program [48] Absorption corrections were applied by the psi-scan method [49]. Non-hydrogen atoms were refined with anisotropic thermal parameters. The hydrogen atom treatment was mixed, with all modeled in ideal positions, except for atoms H(2A)/(2B) and H(4A)/(4B). All thermal ellipsoid plots were generated using ORTEP-3 for Windows [50], and other pictures generated using the MERCURY program [51]. The crystallographic cone angles were calculated directly from the crystal structure, using the method of Immirzi and Musco [52].

4.3. Synthetic details

4.3.1. Reaction of Me₃AsI₂ with Fe powder

0.645 g (1.73×10^{-3} mol) of Me₃AsI₂ was suspended in 30 mL of anhydrous Et₂O. Under a stream of argon 0.048 g (8.63×10^{-4} mol) of iron powder was added. The solution was left to stir for ca. 7 days, after which time the dark black-green solid was isolated by standard Schlenk techniques, washed with 5 mL of anhydrous hexane to remove any remaining iodine, and dried in vacuo. The solid was then transferred in the glove box to pre-dried argon-filled ampoules. Yield = 0.376 g (64.4%). Anal. Calc. for C₆H₁₈As₂Fel₃: C, 10.6; H, 2.7; I, 56.3%; Found: C, 10.4; H, 2.6; I, 56.5%. UV–Vis, Et₂O, λ/nm $(\varepsilon_{\text{max}}/\text{dm}^3 \text{ mol}^{-1} \text{ cm}^{-1})$: 461(9100), 542(sh), 600(sh), 671(6900).

Table 4

Crystallographic parameters for [FeI₃(AsMe₃)₂].

	[FeI3(AsMe3)2]
Empirical formula	C6H18As2FeI3
Fw	676.59
Colour, habit	Green-black, needle
Crystal system	Orthorhombic
Space group	Pnma (No. 62)
Crystal size (mm)	$0.25\times0.15\times0.15$
Unit cell dimensions	
a (Å)	10.412(2)
b (Å)	11.3617(10)
<i>c</i> (Å)	14.543(3)
α (°)	90
β(°)	90
γ (°)	90
Volume (Å ³)	1720.4(5)
<i>T</i> (K)	293(2)
Ζ	4
$D_{\rm calc}({\rm mg}/{\rm m}^3)$	2.612
λ (Å)	0.71073
μ (Mo-K) (mm ⁻¹)	10.044
F(000)	1220
θ (°)	range 3.00–24.98
No. of reflections	1581 (1581 unique)
Final R indices (all data)	$R_1 = 0.0376, 0.0871$
	$wR_2 = 0.1132, 0.1134$
Largest diff. peak and hole (e Å ⁻³)	0.919 and -1.158
Goodness-of-fit (GOF)	1.002

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Appendix A. Supplementary material

CCDC 177337 contains the supplementary crystallographic data for [FeI₃(AsMe₃)₂]. This data can be obtained free of charge via www.ccdc.cam.ac.uk/conts/retrieving.html, or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge CB2 1EZ, UK; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk.

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