

# Periodates and periodato-complexes of aluminium, gallium and indium

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Crystallisation of aluminium or gallium salts with periodic acid at low pH forms  $[M(H_2O)_6][IO_2(OH)_4]_3$  ( $M = Al$  or  $Ga$ ) which have been characterised by elemental analysis, IR, MAS NMR spectroscopy and X-ray crystallography. Single crystal studies on both revealed disordered structures. The compound  $[Ga(H_2O)_6][IO_2(OH)_4]_3$  has also been characterised by gallium and iodine K-edge EXAFS studies. Indium(III) nitrate and  $H_5IO_6$  at  $pH < 1$  produced crystalline  $H_{11}I_2InO_{14}$  which contains indium(III) bound to two *trans*  $H_2O$  ligands and two chelating  $[H_2I_2O_{10}]^{4-}$  groups, the latter bridging neighbouring indiums to produce an infinite chain. This is the first example of  $I_2O_{10}$  groups functioning as chelates and co-ordination is *via* vertex- rather than the usual edge-linking. At higher pH, gallium and indium produced amorphous insoluble materials of composition  $M_3(IO_6)_3 \cdot nH_2O$  ( $M = Ga$  or  $In$ ) and  $H_3In_4(IO_6)_3 \cdot nH_2O$ . Multi-edge EXAFS studies showed that these have structures based upon edge-shared  $MO_6$  and  $IO_6$  groups and it is proposed that they are Anderson type heteropolyanions  $A[M_4(IO_6)_3(H_2O)_6] \cdot nH_2O$  ( $A = H_3$ ,  $M = In$ ;  $A$  and  $M = Ga$  or  $In$ ). The solution behaviour of these three metals in periodate media has been probed by  $^{27}Al$ ,  $^{71}Ga$  and  $^{115}In$  NMR spectroscopy, and thermal decomposition of the solid periodate compounds explored by a combination of TGA, IR spectroscopy and PXRD.

Perchlorate ion  $[ClO_4]^-$  is the archetypal weakly co-ordinating anion, but in marked contrast periodate ions  $[IO_6H_{5-n}]^{n-}$  function as strong O-donor ligands towards many transition metals. The commonest co-ordination mode is as a chelate *via* edge-linking ( $\eta^2$ ) although rare examples of  $\eta^1$  and  $\eta^3$  binding are known.<sup>1</sup> Group 1 and 2 metal periodates contain simple anions, usually  $[IO_4]^-$  or  $[IO_6H_{5-n}]^{n-}$  ( $n = 1-5$ ), although dinuclear anions  $[O_3I(\mu-O)_3IO_3]^{4-}$  and  $[(HO)O_3I(\mu-O)_2IO_3(OH)]^{4-}$  are also found. The beryllium complex  $[Be(H_2O)_4][IO_2(OH)_4]_2$  has been characterised recently,<sup>2</sup> and there is some evidence that other beryllium complexes exist.<sup>3</sup> Much less is known about p-block metal periodates. The Group 14 metals form  $M'[MIO_6]$  ( $M' =$  alkali metal,  $M = Ge, Sn$  or  $Pb$ ) which precipitate on mixing  $H_5IO_6$ ,  $M'NO_3$  and  $GeCl_4$ ,  $SnCl_4$  or  $Pb(OAc)_4$  in aqueous acetic acid.<sup>4</sup> They have structures based upon layers of edge-sharing  $IO_6$  and  $MO_6$  octahedra with  $M'$  ions between the layers. There are scattered reports of Group 13 metal periodates,<sup>5-10</sup> but little recent work, and the structures and in most cases even the stoichiometries are uncertain.

## Results

The compounds obtained depend markedly on the pH of the solutions, those formed in strong acid are well defined, whilst at higher pH amorphous and less easily characterised products result.

### Compounds formed at low pH

**Aluminium.** Evaporation of strongly acid ( $pH < 3$ ) aqueous solutions of aluminium(III) salts (nitrate, sulfate or chloride are all suitable) with an excess of periodic acid produces colourless octahedral crystals, analysing as  $Al(IO_4)_3 \cdot 12H_2O$ .<sup>5</sup> The same complex is obtained on dissolving  $Al_2O_3$  in refluxing aqueous  $H_5IO_6$  (1:4,  $Al:H_5IO_6$ ), followed by crystallisation. On the basis of the IR spectrum, Siebert and Wieghardt<sup>7</sup> formulated the compound as  $[Al(H_2O)_6][IO_2(OH)_4]_3$ . The IR spectra of our samples are in excellent agreement with that reported, and confirmation of the presence of  $[Al(H_2O)_6]^{3+}$  cations was obtained

from the  $^{27}Al$  MAS NMR spectrum which showed a single sharp line at  $\delta 0$ .

The crystal system, lattice type and unit cell dimension of the aluminium compound agree well with that found by Ferrari *et al.*<sup>5</sup> [ $a = 15.418(3) \text{ \AA}$ ] from powder and single crystal X-ray data. From Weissenberg photographs they concluded that the space group was 226 (*Fm3c*) or 219 (*F43c*) and our data whilst not unambiguous showed the very weak *hhl* ( $l = \text{odd}$ ) reflections which would probably have been taken as an absence from the film record. The I and Al could be positioned to give the same atomic arrangement in several cubic space groups having an *F* lattice and belonging to the same Laue group, and the correct choice of space group requires the positions of the O atoms. A similar problem with the choice of space group was found<sup>11</sup> in  $M(ClO_4)_3 \cdot 6H_2O$  ( $M = La, Tb, Er$  or  $Tl$ ). An ordered structure is inconsistent with the data and a plausible disordered structure was obtained for the aluminium derivative in space group 226 (*Fm3c*) based on six-co-ordinate I and Al atoms. The Al–O distance [ $1.90(5) \text{ \AA}$ ] is in agreement with that in the alums<sup>12</sup> [ $1.877(3) \text{ \AA}$ ] and the I–O distances [ $1.95(3), 1.97(5) \text{ \AA}$ ] are also plausible.<sup>13</sup> The structure is thus described as  $[Al(H_2O)_6][IO_2(OH)_4]_3$  (for details see Experimental section).

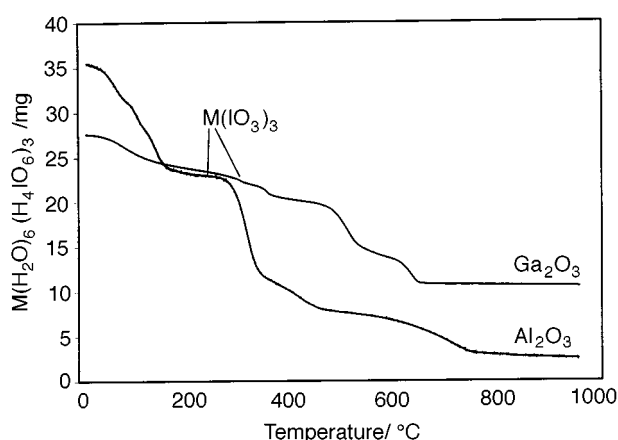
The compound  $[Al(H_2O)_6][IO_2(OH)_4]_3$  dissolved in water to give a clear solution, which had a sharp  $^{27}Al$  NMR resonance at  $\delta 0$ , showing that co-ordination of the periodate does not occur. Since the radius of  $Al^{3+}$  ( $0.57 \text{ \AA}$ ) is of similar size to those of  $Fe^{3+}$  ( $0.67 \text{ \AA}$ ) and  $Ge^{4+}$  ( $0.52 \text{ \AA}$ ) which form (insoluble) layered periodates,<sup>4,14</sup> attempts were made to make the layered periodate  $LiKAlIO_6$  by reaction of  $[Al(H_2O)_6]^{3+}$  with  $LiNO_3$  and  $KIO_4$  at various pH, but these were unsuccessful.

The thermal decomposition of  $[Al(H_2O)_6][IO_2(OH)_4]_3$  has been discussed previously<sup>6</sup> although there is some doubt about the products;  $Al(IO_4)_3$ ,  $Al(IO_3)_3$ , and iodine(VI) compounds such as  $Al_2(I_2O_7)_3$  having been suggested based upon the weight losses supplemented by wet analyses of the residues. Our TGA studies (heating rate  $3 \text{ }^\circ\text{C min}^{-1}$  in air) show weight losses of *ca.* 14% at  $< 140 \text{ }^\circ\text{C}$  and *ca.* 32% at  $200 \text{ }^\circ\text{C}$ , and eventually *ca.* 94% at  $750 \text{ }^\circ\text{C}$  (see Fig. 1). The first two correspond approximately to the loss of  $6H_2O$  (13.2%) and  $12H_2O$  plus 3 O (32.5%), and

**Table 1** Selected EXAFS data

Compound		$d(\text{M-O})/\text{\AA}$	$2\sigma^2/\text{\AA}^2$	$d(\text{I-O})/\text{\AA}$	$2\sigma^2/\text{\AA}^2$	$d(\text{M}\cdots\text{I})^b/\text{\AA}$	$2\sigma^2/\text{\AA}^2$	$R(\%)^c$
[Ga(H <sub>2</sub> O) <sub>6</sub> ][H <sub>4</sub> IO <sub>6</sub> ] <sub>3</sub>	<sup>d</sup>	1.9398(20)	0.0054(3)			5.392(23)	0.0390(65)	22.6
	<sup>e</sup>			1.8769(16)	0.0077(3)			24.3
Aluminium compound A	<sup>e</sup>			1.8784(20)	0.0032(3)			21.1
Gallium compound B	<sup>ef</sup>			1.8641(32)	0.0077(5)	3.005(8)	0.0176(18)	30.0
Ga <sub>5</sub> (IO <sub>6</sub> ) <sub>3</sub> · <i>n</i> H <sub>2</sub> O	<sup>d</sup>	1.9428(23)	0.0135(3)			2.998(3)	0.0229(6)	19.9
						3.019(11) <sup>g</sup>	0.0204(28)	
	<sup>e</sup>			1.8651(15)	0.0053(2)	2.993(3)	0.0111(20)	20.7
In <sub>2</sub> (IO <sub>6</sub> ) <sub>3</sub> · <i>n</i> H <sub>2</sub> O	<sup>d</sup>	2.1309(19)	0.0140(5)			3.225(3)	0.0128(5)	18.9
						3.407(5) <sup>h</sup>	0.0121(9)	
	<sup>e</sup>			1.8581(12)	0.0036(2)	3.192(7)	0.0191(13)	22.1
H <sub>3</sub> In <sub>4</sub> (IO <sub>6</sub> ) <sub>3</sub> · <i>n</i> H <sub>2</sub> O	<sup>d</sup>	2.1251(20)	0.0143(4)			3.225(3)	0.0115(5)	21.3
						3.398(4) <sup>h</sup>	0.0089(6)	
	<sup>e</sup>			1.8700(16)	0.0005(2)	3.217(4)	0.0208(29)	25.0

The numbers in parentheses are the statistical errors in the calculations. Errors in the EXAFS determined bond lengths due to systematic errors in data collection and treatment are usually taken as  $\pm 0.02$  Å for well defined shells, and rather larger for more distant shells. <sup>a</sup> Debye–Waller factor. <sup>b</sup> Non-bonded distances. For the Anderson type structures the occupation numbers were fixed as in the text. <sup>c</sup> Defined as  $[\int(\chi^T - \chi^E)k^3 dk / \int \chi^E k^3 dk] \times 100\%$ . <sup>d</sup> Metal K-edge data. <sup>e</sup> Iodine K-edge data. <sup>f</sup> Usable gallium K-edge data for this complex were not obtained (see text). <sup>g</sup>  $d(\text{Ga}\cdots\text{Ga})/\text{\AA}$ . <sup>h</sup>  $d(\text{In}\cdots\text{In})/\text{\AA}$ .



**Fig. 1** Thermogravimetric analysis (TGA) results for [Al(H<sub>2</sub>O)<sub>6</sub>][IO<sub>2</sub>(OH)<sub>4</sub>]<sub>3</sub> and [Ga(H<sub>2</sub>O)<sub>6</sub>][IO<sub>2</sub>(OH)<sub>4</sub>]<sub>3</sub>.

the last to the formation of Al<sub>2</sub>O<sub>3</sub>. The IR spectra and the PXRD pattern of samples heated to 200 °C identified the product as Al(IO<sub>3</sub>)<sub>3</sub> by comparison with literature data.<sup>15</sup> Infrared spectra of samples heated to *ca.* 150 °C showed no evidence of the  $\nu_3$  mode (*ca.* 850 cm<sup>-1</sup>) of tetrahedral IO<sub>4</sub><sup>-</sup> groups and thus intermediate formation of Al(IO<sub>4</sub>)<sub>3</sub> is discounted. The further decomposition of Al(IO<sub>3</sub>)<sub>3</sub> to Al<sub>2</sub>O<sub>3</sub> has been described previously.<sup>15</sup> The properties of [Al(H<sub>2</sub>O)<sub>6</sub>][IO<sub>2</sub>(OH)<sub>4</sub>]<sub>3</sub> closely resemble those of the recently characterised<sup>2,3</sup> [Be(H<sub>2</sub>O)<sub>4</sub>][IO<sub>2</sub>(OH)<sub>4</sub>]<sub>2</sub>, which similarly decomposes on heating to Be(IO<sub>3</sub>)<sub>2</sub>.

**Gallium.** Evaporation to small volume of a mixture of Ga(NO<sub>3</sub>)<sub>3</sub>·*x*H<sub>2</sub>O and H<sub>5</sub>IO<sub>6</sub> in water at pH < 2 gave colourless octahedral crystals. Analysis identified these as [Ga(H<sub>2</sub>O)<sub>6</sub>][IO<sub>2</sub>(OH)<sub>4</sub>]<sub>3</sub>. The formulation is supported by the IR spectrum which is consistent with the presence of a heavily protonated pseudo-octahedral periodate group, and the <sup>71</sup>Ga MAS NMR spectrum which shows a single resonance at  $\delta$  *ca.* 0 ( $w_{1/2}$  = 4000 Hz). Crystallographically the gallium derivative is very similar to [Al(H<sub>2</sub>O)<sub>6</sub>][IO<sub>2</sub>(OH)<sub>4</sub>]<sub>3</sub>: both are cubic ( $Z = 8$ ) with the Ga and I being located convincingly, but no structure was obtained which modelled the disorder of the O atoms (see Experimental section). For both the gallium and aluminium compounds a relationship to cubic close packing is apparent: taking a subcell with half the cell edge (1/8 the volume) and containing one M (M = Ga or Al) and three I atoms. The four atoms form a face-centred cubic arrangement with M at the corner and I at the face centres. Each M is surrounded by 12 I, and each I is sur-

rounded by 4 M and 8 I atoms all at the same distance. First co-ordination sphere bond lengths (to oxygen) were obtained *via* gallium and iodine K-edge EXAFS data. The gallium K-edge EXAFS (Table 1) of [Ga(H<sub>2</sub>O)<sub>6</sub>][IO<sub>2</sub>(OH)<sub>4</sub>]<sub>3</sub> was modelled by a single shell of six oxygen atoms at 1.93 Å which is in excellent agreement with the Ga–OH<sub>2</sub> bond length of 1.944(3) Å in [Ga(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> [in CsGa(SO<sub>4</sub>)<sub>2</sub>·12H<sub>2</sub>O].<sup>12</sup> A weak feature in the Fourier transform at 5.4 Å was satisfactorily modelled as the non-bonded shell of 12 iodine atoms consistent with the crystal structure. Incorporation of this shell was statistically significant, resulting in a 3% decrease in the *R* factor. The iodine K-edge data on this compound were fitted by a single shell of six oxygens at 1.87 Å. In the crystal structure of Li[IO<sub>2</sub>(OH)<sub>4</sub>] there are two short I–O distances [1.800(2), 1.812(2)] and four longer I–OH bonds [1.906(2)–1.918(2) Å].<sup>13</sup> Attempts to model the iodine edge EXAFS data to two shells failed due to unacceptably high correlations, a problem often encountered in periodates,<sup>16</sup> but the single (averaged) distance of 1.87 Å is in good agreement with the averaged I–O/OH bond lengths in the lithium salt (1.87 Å). Thus the EXAFS data complement the single crystal X-ray work, and provide the bond length information lacking in the latter due to the disorder problem.

The TGA studies on [Ga(H<sub>2</sub>O)<sub>6</sub>][IO<sub>2</sub>(OH)<sub>4</sub>]<sub>3</sub> gave results very similar to those obtained with the aluminium analogue (see Fig. 1), the major steps in the mass loss corresponding to the loss of 6H<sub>2</sub>O, the loss of 12H<sub>2</sub>O plus 3 O [formation of Ga(IO<sub>3</sub>)<sub>3</sub>], and finally the formation of Ga<sub>2</sub>O<sub>3</sub>. The intermediate formation of Ga(IO<sub>3</sub>)<sub>3</sub> at *ca.* 200 °C was confirmed by comparison of its IR spectrum and PXRD pattern with literature data.<sup>15</sup>

In contrast to the aluminium complex, [Ga(H<sub>2</sub>O)<sub>6</sub>][IO<sub>2</sub>(OH)<sub>4</sub>]<sub>3</sub> dissolves in water to give a milky solution, which on boiling deposits an insoluble white powder (see below). The solution chemistry has been partially explored using <sup>71</sup>Ga NMR spectroscopy; <sup>71</sup>Ga ( $I = 3/2$ , 40%,  $\mathcal{E} = 30.5$  MHz,  $D_c = 319$ ,  $Q = 0.112 \times 10^{-28}$  m<sup>2</sup>)<sup>17</sup> is a sensitive NMR nucleus but, due to the line-broadening caused by the moderate quadrupole moment, resonances are only observable in relatively high symmetry environments. The <sup>71</sup>Ga reference, [Ga(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> in HNO<sub>3</sub> at pH 1, gives a sharp line ( $\delta$  0,  $w_{1/2}$  = 130 Hz), and no change occurred to this resonance on adding H<sub>5</sub>IO<sub>6</sub> to this solution, showing no co-ordination of the periodate. The milky solution produced on dissolving [Ga(H<sub>2</sub>O)<sub>6</sub>][IO<sub>2</sub>(OH)<sub>4</sub>]<sub>3</sub> in water did not exhibit a gallium resonance, although on addition of an excess of H<sub>5</sub>IO<sub>6</sub> a weak broad ( $w_{1/2}$  *ca.* 4000 Hz) resonance at  $\delta$  *ca.* 0 was apparent, and if further acidified with HNO<sub>3</sub> the sharp [Ga(H<sub>2</sub>O)<sub>6</sub>]<sup>3+</sup> resonance appeared. On boiling Ga<sub>2</sub>O<sub>3</sub>

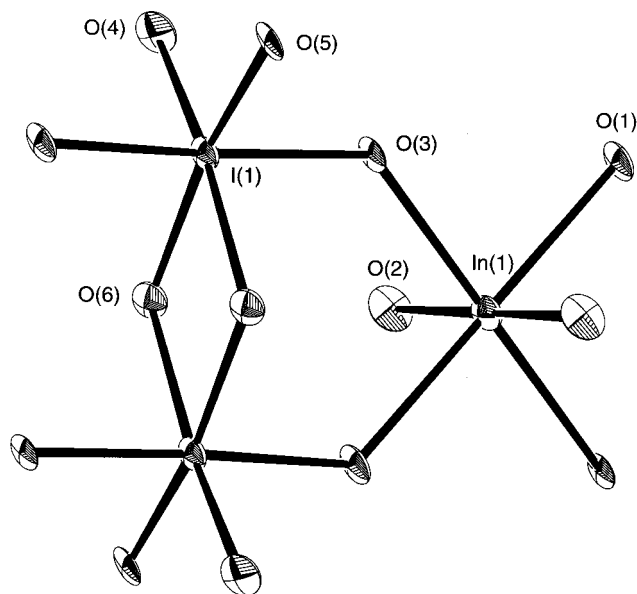


Fig. 2 Structure of  $H_{11}I_2InO_{14}$  showing the environment about I(1) and In(1) and the atom labelling scheme. Ellipsoids are drawn at the 50% probability level.

with an excess of  $H_5IO_6$  in water the oxide partially dissolved, but again this solution showed no  $^{71}Ga$  NMR resonance unless acidified. The gallium present in these solutions not observable by  $^{71}Ga$  NMR spectroscopy is presumably present as low symmetry oligomers which are found in other gallium solutions at similar pH, although the species are poorly understood.<sup>18</sup>

**Indium.** A clear solution is formed by addition of an aqueous solution of  $H_5IO_6$  to a solution of  $In(NO_3)_3$  in concentrated  $HNO_3$ , but on boiling down to small volume or dilution with water a white amorphous insoluble material separated. The same material precipitates immediately on mixing the solutions at  $pH > 2$ . In contrast to aluminium or gallium oxide,  $In_2O_3$  does not dissolve in boiling aqueous solutions of  $H_5IO_6$ , although EDX (EDX = energy dispersive X-ray spectroscopy) of the "oxide" recovered from such reactions shows incorporation of some iodine, presumably as an insoluble surface coating of the periodato-complex described below. Indium-115 ( $I = 9/2$ , 95.7%,  $\mathcal{E} = 21.91$  MHz,  $D_c = 1890$ ,  $Q = 1.16 \times 10^{-28}$  m<sup>2</sup>) is not well suited to NMR studies due to the large quadrupole moment which often results in unobservably broad lines.<sup>17</sup> However a solution of indium nitrate in aqueous nitric acid (1:1 v/v water- $HNO_3$ ) shows a relatively sharp line ( $\delta 0$ ,  $w_{1/2} = 500$  Hz). Addition of  $H_5IO_6$  to this solution did not change either the chemical shift or the linewidth, and hence at this pH  $[In(H_2O)_6]^{3+}$  exists even in the presence of periodate. However dilution of the solution or increasing pH caused immediate loss of the resonance. Slow evaporation of a solution of  $In(NO_3)_3 \cdot nH_2O$  and  $H_5IO_6$  (1:3 mol ratio) in nitric acid solution over KOH in a desiccator produced small colourless crystals, identified as  $H_{11}I_2InO_{14}$  by a single crystal X-ray study. The structure consists of chains of composition  $I_2InO_{12}$  running in the  $a$  direction. Both I and In are six-co-ordinate with the In positioned on a centre of symmetry and within the structure can be recognised  $I_2O_{10}$  units based on two edge-linked 'IO<sub>6</sub>' octahedra. The oxygen co-ordination about In is made up from two terminal O(H<sub>2</sub>) and four bridging In-O-I bonds from two  $I_2O_{10}$  units (see Fig. 2). The co-ordination is unusual in that the bridging oxygen atoms come from O atoms bonded to different I's in the  $I_2O_{10}$  unit and the chains are clearly shown in the packing diagram (Fig. 3). The H atoms were not located in the X-ray analysis and the composition is based on charge balance. Both  $K_4[H_2I_2O_{10}] \cdot 8H_2O$ <sup>19</sup> and  $Na_5HI_2O_{10} \cdot 14H_2O$ <sup>20</sup> contain the centrosymmetric  $[H_2I_2O_{10}]^{4-}$  anion and only in the latter com-

Table 2 Selected bond lengths (Å) and angles (°) for  $H_{11}I_2InO_{14}$

I(1)-O(1 <sup>I</sup> )	1.823(7)	In(1)-O(1)	2.118(7)
I(1)-O(3)	1.821(6)	In(1)-O(2)	2.227(7)
I(1)-O(4)	1.829(6)	In(1)-O(3)	2.111(6)
I(1)-O(5)	1.876(7)		
I(1)-O(6)	1.961(6)	I(1)⋯I(1 <sup>III</sup> )	3.074(2)
I(1)-O(6 <sup>II</sup> )	1.983(7)	O(7)⋯O(2 <sup>V</sup> )	2.683(11)
		O(7)⋯O(5 <sup>III</sup> )	2.718(9)
		O(7)⋯O(2 <sup>VI</sup> )	2.849(10)
O(3)-I(1)-O(4)	89.6(3)	O(1 <sup>I</sup> )-I(1)-O(6 <sup>II</sup> )	89.6(3)
O(1 <sup>I</sup> )-I(1)-O(4)	91.1(3)	O(5)-I(1)-O(6 <sup>II</sup> )	90.0(2)
O(3)-I(1)-O(5)	86.7(3)	O(6)-I(1)-O(6 <sup>II</sup> )	77.6(3)
O(1 <sup>I</sup> )-I(1)-O(5)	88.5(3)	O(3)-In(1)-O(1)	82.7(3)
O(4)-I(1)-O(5)	100.0(3)	O(3)-In(1)-O(2)	91.6(3)
O(3)-I(1)-O(6)	92.5(3)	O(1)-In(1)-O(2)	90.9(3)
O(1 <sup>I</sup> )-I(1)-O(6)	92.1(3)	I(1 <sup>IV</sup> )-O(1)-In(1)	130.0(4)
O(4)-I(1)-O(6)	92.4(3)	I(1)-O(3)-In(1)	129.4(3)
O(3)-I(1)-O(6 <sup>II</sup> )	90.5(3)	I(1)-O(6)-I(1 <sup>II</sup> )	102.4(3)

Symmetry transformations used to generate equivalent atoms: I  $x - 1, y, z$ ; II  $-x, -y + 1, -z$ ; III  $x + 1, \frac{1}{2} - y, \frac{1}{2} + z$ ; IV  $x + 1, y, z$ ; V  $1 - x, 1 - y, 1 - z$ ; VI  $1 - x, y - \frac{1}{2}, \frac{1}{2} - z$ .

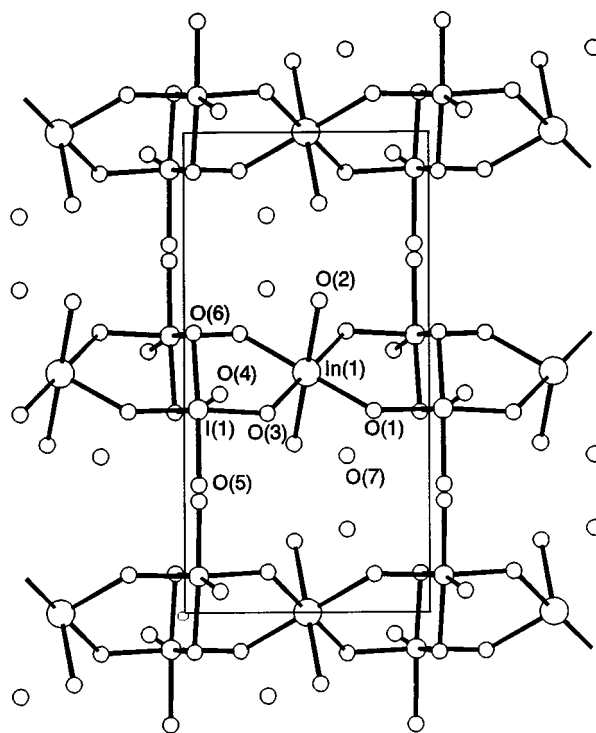


Fig. 3 Packing diagram for  $H_{11}I_2InO_{14}$  viewed down the  $c$  direction.

pound were the H atoms located in the X-ray analysis. In both examples the bridging I-O bonds are longer than the terminal and are close to the values found in the present compound (Table 2). For the present compound there is IR spectroscopic evidence for I-OH groups and on the basis of bond lengths the most likely candidate is O(5) [I-O 1.876(7) Å] and again the ' $I_2O_{10}$ ' residue is centrosymmetric. The In-O bonds involved in the bridging are shorter (0.1 Å) than the terminal In-O which presumably involves a co-ordinated water molecule *cf.* In-O(H<sub>2</sub>) 2.112(4) Å in  $CsIn[SO_4]_2 \cdot 12H_2O$ .<sup>12</sup> Atom O(7) is a suitable distance from other O atoms to form hydrogen bonds and the three shortest distances are given in Table 2. If we regard O(7) as water, the model proposed accounts for 20 of the 22 H atoms in the unit cell. However since the crystals grow from a solution at  $pH < 1$  it is plausible that O(7) is partially protonated to  $H_3O^+$  which would complete the charge balance. A similar problem with formally balancing the charges was seen in  $Na_5HI_2O_{10} \cdot 14H_2O$ .<sup>20</sup>

## Compounds formed at higher pH

**Aluminium.** When alkali (2 M NaOH) is added slowly to a solution of  $[\text{Al}(\text{H}_2\text{O})_6][\text{IO}_2(\text{OH})_4]_3$  in water turbidity appears *ca.* pH 4 and then a white powder precipitates (compound A). After drying in air at 40 °C this material has a composition close to  $\text{Al}:\text{IO}_6:\text{H}_2\text{O}$  of 3.2:1:*ca.* 9 (“ $\text{H}_2\text{O}$ ” estimated by difference and by TGA could include O/OH/OH<sub>2</sub> groups), does not contain any Na, and is amorphous to PXRD. The IR spectrum shows strong  $\nu(\text{OH})$  and  $\delta(\text{HOH})$  modes, and whilst the lower frequency region is poorly resolved, broad features at *ca.* 730 and 590  $\text{cm}^{-1}$  are attributable to  $\text{IO}_6$  groups. Perhaps surprisingly, no  $\delta(\text{IOH})$  modes were observed, weak features in the region 1000–1300  $\text{cm}^{-1}$  were unchanged after deuteration, which would suggest that the periodate is present as  $[\text{IO}_6]^{5-}$ . In other systems,<sup>21</sup> hydrolysis products of  $[\text{Al}(\text{H}_2\text{O})_6]^{3+}$  include dimers and trimers and two terdecimers  $[\text{Al}_{13}\text{O}_4(\text{OH})_{24}(\text{H}_2\text{O})_{12}]^{7+}$  and  $[\text{Al}_{13}(\text{OH})_{24}(\text{H}_2\text{O})_{24}]^{15+}$ . The iodine K-edge EXAFS of this material showed a single shell of six oxygens at 1.88 Å in the Fourier transform, and a very weak feature at *ca.* 2.95 Å. The latter feature cannot be modelled satisfactorily as a (non-bonded) I or O, but modelling it as Al results in a 4% reduction in the *R* factor, although the fits are insensitive to the occupation number of the shell. From the composition and the EXAFS data, we conclude that this material is oligomeric possibly with periodate co-ordination to the aluminium.

**Gallium.** The gallium system is more complex. The white insoluble material formed by boiling  $[\text{Ga}(\text{H}_2\text{O})_6][\text{IO}_2(\text{OH})_4]_3$  in water has a  $\text{Ga}:\text{IO}_6:\text{H}_2\text{O}$  ratio of 1.55:1: $\approx$ 5. What seems to be the same product (compound B) is formed by slow addition of gallium nitrate solution to an excess of periodic acid solution at pH *ca.* 2.5 followed by digestion at 80 °C. Using  $\text{Na}_3\text{H}_2\text{IO}_6$  or  $\text{KIO}_4$  as the source of periodate does not lead to incorporation of alkali metal in the product. The various products are amorphous to PXRD, and the IR spectra which are superimposable show the presence of  $\text{H}_2\text{O}$  (3300, 1630  $\text{cm}^{-1}$ ) and  $\text{IO}_6$  (730, 580  $\text{cm}^{-1}$ ) modes and as with the aluminium complex no features in the  $\delta(\text{IOH})$  region which respond to deuteration. The identical IR spectra and essentially constant heavy atom ratios from several preparations using different initial  $\text{Ga}:\text{IO}_6$  ratios suggest a discrete complex rather than mixtures forms. The TGA trace is quite different from that of the  $\text{Ga}_5(\text{IO}_6)_3 \cdot n\text{H}_2\text{O}$  species described below, notably decomposition to  $\text{Ga}_2\text{O}_3$  is complete below 500 °C, a substantially lower temperature than for the latter.

The reaction of an excess of gallium nitrate with periodate ions in weakly acidic solution (pH  $\approx$ 3–4) results in precipitation of a white amorphous powder, which after drying in air at 40 °C has the analytical composition  $\text{Ga}:\text{I}:\text{H}_2\text{O}$  5:3: $\approx$ 6. The composition of the material is reproducible providing an excess of Ga is present in the reaction mixture, and if prepared in the presence of  $\text{Na}^+$  or  $\text{K}^+$  ions these are not incorporated (EDX evidence). The TGA studies show water loss begins <100 °C and decomposition to  $\text{Ga}_2\text{O}_3$  (identified by PXRD) is complete at *ca.* 650 °C. The water content in different samples seems to vary slightly between 6 and 8  $\text{H}_2\text{O}$  per  $\text{Ga}_5$  unit. The compound is insoluble in water, dissolves only slowly in nitric acid solutions on heating, and is decomposed by strong alkalis to  $\text{GaO}(\text{OH})$ . The IR spectrum shows water and  $\text{IO}_6$  groups, but no clear evidence for IOH groups. Attempts to record <sup>71</sup>Ga MAS NMR spectra of these gallium compounds were unsuccessful; presumably the gallium environments deviate sufficiently from cubic symmetry that unobservably broad resonances result. Possible structures based upon EXAFS studies are described below.

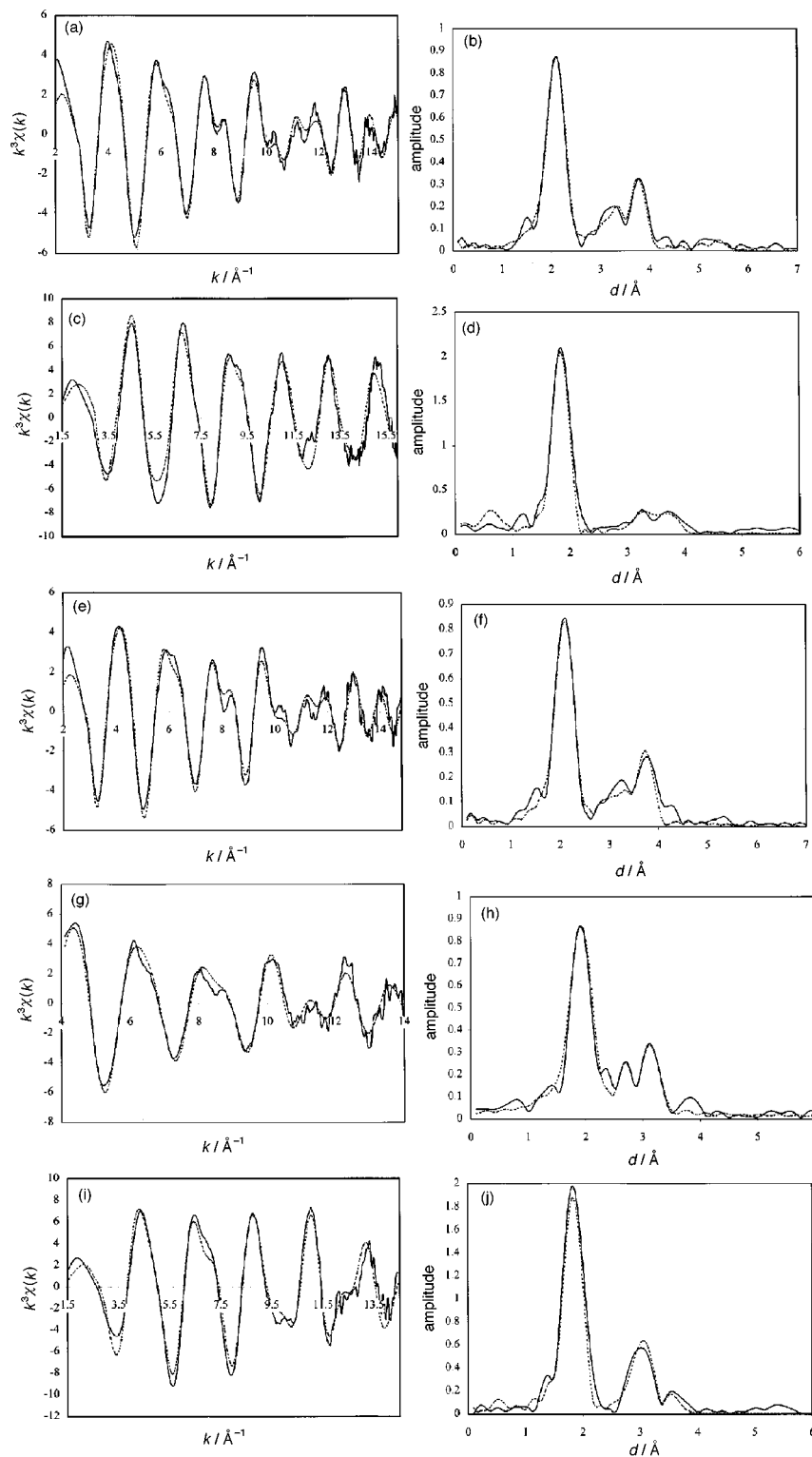
**Indium.** The reaction of indium nitrate with periodate ions in weakly acidic aqueous solution results in immediate precipi-

tation of white powders. Similar compounds were reported over 50 years ago by Ensslin<sup>10</sup> and formulated as “basic indium periodates”,  $x\text{InIO}_5 \cdot \text{In}(\text{OH})_3 \cdot y\text{H}_2\text{O}$  ( $x = 2, 3$  or 4). We experienced considerable initial difficulties in characterising our products, since they are insoluble in water, amorphous (by PXRD), have poorly resolved IR spectra and appeared to have variable composition. We eventually established that two similar compounds could be isolated. If the strongly acidified ( $\text{HNO}_3$ , pH < 1.5) solution of indium nitrate and periodic acid with an In:I ratio of 1:>4 used in attempts to prepare  $[\text{In}(\text{H}_2\text{O})_6][\text{IO}_2(\text{OH})_4]_3$  was diluted with water and the pH increased by slow addition of aqueous 2 M KOH, the white solid which precipitated, after thorough washing with water and drying in air at 40 °C, had an analytical composition  $\text{In}_4(\text{IO}_6)_3 \cdot n\text{H}_2\text{O}$  (as written the formula corresponds to an unreasonable oxidation state for the indium see below). The water content (*n*) as estimated (by difference) from the analysis or directly from the TGA studies lies in the range 6–8  $\text{H}_2\text{O}$  and may be slightly variable. In contrast, if an aqueous solution of  $\text{H}_5\text{IO}_6$  is added slowly to an excess of  $\text{In}(\text{NO}_3)_3$  solution at pH  $\approx$  3 the white precipitate after similar processing has the composition  $\text{In}_5(\text{IO}_6)_3 \cdot n\text{H}_2\text{O}$  (*n*  $\approx$  6–8). The key factors appear to be the ratio of In:I in the reaction mixtures and the pH. White solids obtained under conditions intermediate between those described are probably mixtures. If the reactions are conducted using  $\text{KIO}_4$  or  $\text{Na}_3\text{H}_2\text{IO}_6$  as a source of periodate, providing the In:I ratio and the pH are appropriate, the same compounds are formed, EDX measurements confirming the absence of alkali metal ions.

## EXAFS Studies

The intractable nature of the amorphous and insoluble gallium and indium species described in the preceding sections precludes an unequivocal structural characterisation. However a combination of iodine and indium or gallium K-edge EXAFS data has identified the local environments of these elements and allows possible structures to be proposed. The EXAFS data treatment follows the methodology applied to periodate complexes previously,<sup>16</sup> as summarised in the Experimental section. The final fits are summarised in Table 1 and Fig. 4 shows examples of the background subtracted EXAFS and the corresponding Fourier transforms for  $\text{Ga}_5(\text{IO}_6)_3 \cdot n\text{H}_2\text{O}$ ,  $\text{In}_4(\text{IO}_6)_3 \cdot n\text{H}_2\text{O}$  and  $\text{In}_5(\text{IO}_6)_3 \cdot n\text{H}_2\text{O}$ . The iodine edge data for all three compounds showed a first shell of 6 oxygens at 1.87 Å, and the gallium or indium edge data corresponding first shells of 6 oxygens at 1.94 (Ga) or 2.13 Å (In). Further shells were then added stepwise, refined and tested for statistical significance. Most important are the second shell features in the iodine edge data which model satisfactorily as non-bonded Ga(In) atoms, and the second shells in the Ga(In) data which refine to give the same Ga(In)  $\cdots$  I distances within experimental error (Table 1). In the metal edge data the third shell was modelled as Ga  $\cdots$  Ga or In  $\cdots$  In non-bonded distances of *ca.* 3.0 Å (Ga) or *ca.* 3.4 Å (In), and in most cases a more distant feature, attributed to a further oxygen shell was evident. Also notable is that the EXAFS data at both indium and iodine K-edges of the “ $\text{In}_4$ ” and “ $\text{In}_5$ ” compounds are essentially superimposable (Fig. 4). The occupation number of shell 1 in all the fits as 6 (oxygens) is unequivocal, but refinement of the occupancies of more distant shells produced only small variations in the quality of fit. The multi-edge EXAFS data show that these three compounds are built up of edge-sharing  $\text{IO}_6$  and  $\text{MO}_6$  (M = Ga or In) octahedra, but cannot alone afford a complete description of the structures. As previously stated the compounds are amorphous as judged by PXRD and thus long range order is lacking.

Although the resulting conclusions are not beyond doubt, it is possible to combine the information about analytical composition, the available ligands ( $\text{IO}_6$ , O/OH/ $\text{H}_2\text{O}$ ) and the

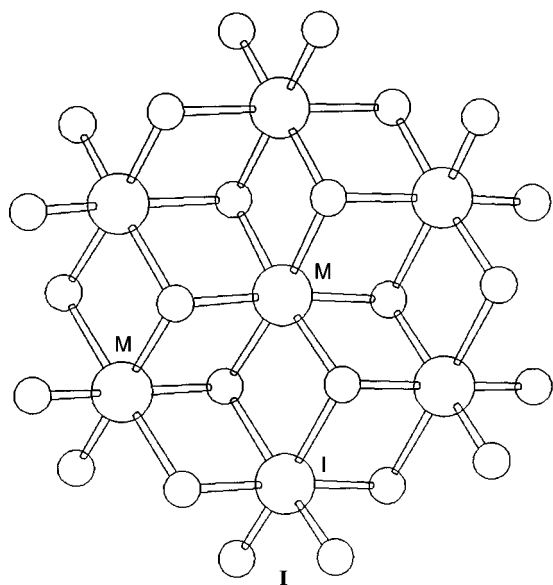


**Fig. 4** Background subtracted EXAFS and corresponding Fourier transforms for  $\text{In}_5(\text{IO}_6)_3 \cdot n\text{H}_2\text{O}$  indium K-edge (a,b),  $\text{In}_5(\text{IO}_6)_3 \cdot n\text{H}_2\text{O}$  iodine K-edge (c,d),  $\text{H}_3\text{In}_4(\text{IO}_6)_3 \cdot n\text{H}_2\text{O}$  indium K-edge (e,f),  $\text{Ga}_5(\text{IO}_6)_3 \cdot n\text{H}_2\text{O}$  gallium K-edge (g,h) and  $\text{Ga}_5(\text{IO}_6)_3 \cdot n\text{H}_2\text{O}$  iodine K-edge (i,j). The full lines are real data, the broken lines theoretical fits.

EXAFS data to arrive at plausible formulations. The 4:3 M:I ratio in "In<sub>4</sub>" suggested a possible analogy with the Anderson polyanions formed by  $\text{Co}^{\text{III}}$ <sup>22</sup> and  $\text{Fe}^{\text{III}}$ <sup>23</sup> where the basic unit consists of a central  $\text{MO}_6$  octahedron edge sharing with three  $\text{IO}_6$  and three  $\text{MO}_6$ , structure I. On this basis the "In<sub>4</sub>" compound is formulated as the free acid  $\text{H}_3[\text{In}_4(\text{IO}_6)_3(\text{H}_2\text{O})_6] \cdot x\text{H}_2\text{O}$ , whilst the "In<sub>5</sub>" is the corresponding indium(III) salt  $\text{In}[\text{In}_4(\text{IO}_6)_3(\text{H}_2\text{O})_6] \cdot x\text{H}_2\text{O}$ , and the "Ga<sub>5</sub>" compound is  $\text{Ga}[\text{Ga}_4(\text{IO}_6)_3(\text{H}_2\text{O})_6] \cdot x\text{H}_2\text{O}$ . The IR spectra whilst relatively uninformative are similar to that of  $\text{H}_3[\text{Fe}_4(\text{IO}_6)_3(\text{H}_2\text{O})_6]$ .<sup>23</sup> No  $\delta(\text{IOH})$

vibrations were identified in the "In<sub>4</sub>" acid form, even after deuteration, but this is inconclusive, since the sites of protonation remain unclear in the cobalt and iron salts.<sup>22,23</sup> The cobalt and iron compounds have been characterised by single crystal X-ray studies, and we have shown that a combination of metal and iodine EXAFS studies may also be used to provide structural data and to fingerprint the local environments about the primary absorbers.<sup>16,23</sup> We therefore remodelled the iodine and indium EXAFS data for the "In<sub>4</sub>" compound, fixing the co-ordination numbers of subsequent shells as required for the

structure **I** *i.e.* for the iodine edge data  $6 \times \text{O}$ ,  $3 \times \text{In}$ , and for indium  $6 \times \text{O}$ ,  $2.25 \times \text{I}$  and  $1.5 \times \text{In}$ . After refinement this produced the data in Table 1, with no unacceptably high correlations, reasonable Debye–Waller factors and internally consistent values for the same non-bonded distances, obtained from the different edge data. The fits of the data to this final model were as good as or marginally better than other fits (with slightly different occupation numbers for the remote shells) developed earlier, although as already indicated the fits are relatively insensitive to small variations in co-ordination numbers. The iodine and indium edge data on the “In<sub>5</sub>” compound were initially modelled using the same co-ordination numbers as used for the “In<sub>4</sub>” and the fit in Table 1 obtained. Attempts to add the fifth indium to the model produced no significant improvement in the fit. We tentatively interpret this as due to the fifth indium being disordered over several sites, and note that, although not an exact analogy, the EXAFS data on the iron(III) Anderson type heteropolyanion are insensitive to the counter cations (in this case alkali metals) present.<sup>23</sup> The “Ga<sub>5</sub>” complex modelled satisfactorily in a similar way as the gallium(III) salt of the Anderson anion  $[\text{Ga}_4(\text{IO}_6)_3(\text{H}_2\text{O})_6]^{3-}$ .



The iodine K-edge EXAFS data on the gallium compound **B** were modelled satisfactorily to 6 oxygens (1.86 Å) and 3 galliums (3.0 Å) suggesting a similar structural motif to the “Ga<sub>5</sub>”. Unfortunately, due to instrumental problems during data collection, the gallium K-edge data on this compound were of inadequate quality to provide any reliable information, and thus further discussion of the structure of **B** is not warranted.

## Discussion

The chemistry of these three metals in periodate containing media has proved to be complex and rather intractable. Several trends can however be established. From strongly acid media Al and Ga afford simple salts of the hexaqua cations  $[\text{M}(\text{H}_2\text{O})_6]^{3+}$ – $[\text{IO}_2(\text{OH})_4]_3$  which can be isolated in crystalline form. Thermal decomposition of these proceeds *via*  $\text{M}(\text{IO}_3)_3$  to  $\text{M}_2\text{O}_3$ . In the indium system, at very low pH,  $[\text{In}(\text{H}_2\text{O})_6]^{3+}$  ions coexist in solution with periodate ions, but crystallisation results in the co-ordination of  $[\text{H}_2\text{I}_2\text{O}_{10}]^{4-}$  ions to the indium in  $\text{H}_{11}\text{I}_2\text{InO}_{14}$ . This is both the first example of “I<sub>2</sub>O<sub>10</sub>” anions behaving as ligands, and also an unprecedented chelation mode in periodates *via* vertex linking (all other examples contain edge-linking).<sup>1</sup> At higher (but still acid) pH the aluminium and gallium systems produce insoluble amorphous materials. The structures of these remain unclear and despite much effort the

oligomeric hydrolysis products of these elements are not well understood.<sup>21,24</sup> Further increase in the pH for Ga and In results in insoluble amorphous materials for which a combination of gallium/indium and iodine EXAFS data provides clear evidence for periodate co-ordination, based upon edge-linked  $\text{IO}_6$  and  $\text{MO}_6$  octahedra. We propose that these materials are (or contain) Anderson type heteropolyanions, and the EXAFS have been satisfactorily modelled to the Anderson structure **I**. The  $\text{H}_3[\text{Fe}_4(\text{IO}_6)_3(\text{H}_2\text{O})_6]$  is also amorphous and insoluble in water but dissolves in very concentrated KOH, RbOH or CsOH, from which X-ray quality crystals were obtained.<sup>23</sup> Unfortunately concentrated alkalis decompose the gallium or indium compounds to the corresponding gelatinous hydroxides. Arguments which could call into question the Anderson type formulation are the observation that when the “In<sub>5</sub>” or “Ga<sub>5</sub>” compounds are prepared in the presence of alkali metals the latter are not incorporated, and our failure to prepare the gallium “acid form”  $[\text{H}_3\{\text{Ga}_4(\text{IO}_6)_3(\text{OH})_6\}]$ . However this may simply reflect the insolubility of the metal(III) salts of these anions. Our attempts to obtain any of these compounds in crystalline form for X-ray studies which are needed to confirm (or otherwise) the proposed structures have failed. Many attempts varying pH, concentrations, or by diffusion of solutions through sintered discs or gels failed to yield crystals.

There are clear trends in the chemistry of the Group 13 elements in periodate media. In addition to the usual<sup>21</sup> hydrolytic trends with pH, there is an increasing tendency to co-ordinate periodate anions as the group is descended, from little or no affinity in the case of Al, to preferred co-ordination at indium except in very acid media. Gallium is intermediate in behaviour, but closer to indium than aluminium.

## Experimental

The MAS NMR spectra were obtained from powdered samples in silicon nitride rotors on a Bruker AC300 spectrometer operating at 78.2 (<sup>27</sup>Al) or 91.6 MHz (<sup>71</sup>Ga) using 4.5 kHz spinning speeds, solution NMR spectra using a Bruker AM360 spectrometer operating at 93.8 (<sup>27</sup>Al), 109.9 (<sup>71</sup>Ga) and 78.95 MHz (<sup>115</sup>In) referenced in each case to the  $[\text{M}(\text{H}_2\text{O})_6]^{3+}$  ion in aqueous  $\text{HNO}_3$  ( $\delta$  0). The EDX measurements were routinely employed to determine the elements present and provided approximate heavy atom ratios. Other physical measurements were made as described previously.<sup>14,23</sup> For analysis, known weights of the complex were dissolved/suspended in 2 M  $\text{H}_2\text{SO}_4$ , an excess of aqueous  $\text{SO}_2$  solution added, and then the excess of  $\text{SO}_2$  boiled off. In the resulting solutions, iodine was determined gravimetrically as  $\text{AgI}$ , aluminium, gallium and indium gravimetrically as the tris(quinolin-8-olate). The TGA measurements were used to estimate the amounts of water present. Since water loss occurred over a wide temperature range, particularly for  $\text{M}_5(\text{IO}_6)_3 \cdot n\text{H}_2\text{O}$ , and may be accompanied by some oxygen loss, the values are approximate.

## Preparations

$[\text{Al}(\text{H}_2\text{O})_6][\text{IO}_2(\text{OH})_4]_3$ . Aluminium nitrate,  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (0.75 g, 2.0 mmol), was dissolved in water (50 cm<sup>3</sup>), a few drops of concentrated  $\text{HNO}_3$  were added to adjust the pH to *ca.* 3, and then  $\text{H}_5\text{IO}_6$  (2.28 g, 10.0 mmol) was added and the mixture evaporated to about 10 cm<sup>3</sup>. On standing in a desiccator over  $\text{CaCl}_2$  the solution deposited colourless octahedra, which were filtered off and dried *in vacuo* (0.98 g, 60%) (Found: Al, 3.1; I, 46.8. Calc. for  $\text{H}_{24}\text{AlI}_3\text{O}_{24}$ : Al, 3.3; I, 46.7%). IR (cm<sup>-1</sup>) (Nujol mull) 3300s (br), 3100 (sh), 2900s (br), 2300m (br), 1610m, 1230m, 1175m, 1145m, 955 (sh), 930w, 750s, 650s, 610s, 580s, 430w, 370m, 365m and 320s. The same compound was obtained using  $\text{Al}_2(\text{SO}_4)_3 \cdot 16\text{H}_2\text{O}$  or  $\text{AlCl}_3 \cdot 6\text{H}_2\text{O}$  again using concentrated  $\text{HNO}_3$  to adjust the pH.

Alternatively, Al<sub>2</sub>O<sub>3</sub> (0.20 g, 2.0 mmol) was added to a solution of H<sub>5</sub>IO<sub>6</sub> (1.8 g, 8.0 mmol) in water (50 cm<sup>3</sup>), and the mixture refluxed for 6 h. Unchanged Al<sub>2</sub>O<sub>3</sub> was removed by filtration, and the solution concentrated to 10 cm<sup>3</sup>. On standing over CaCl<sub>2</sub> in a desiccator colourless octahedra were deposited. These were identified as [Al(H<sub>2</sub>O)<sub>6</sub>][IO<sub>2</sub>(OH)<sub>4</sub>]<sub>3</sub> by single crystal X-ray diffraction (identical unit cell). On further concentration needle crystals of H<sub>5</sub>IO<sub>6</sub> deposited.

**[Ga(H<sub>2</sub>O)<sub>6</sub>][IO<sub>2</sub>(OH)<sub>4</sub>]<sub>3</sub>.** Gallium(III) nitrate, Ga(NO<sub>3</sub>)<sub>3</sub>·*x*H<sub>2</sub>O (0.69 g, 2.0 mmol, *x* ≈ 5), was dissolved in water (50 cm<sup>3</sup>), concentrated HNO<sub>3</sub> added to adjust the pH < 2, followed by a solution of H<sub>5</sub>IO<sub>6</sub> (2.28 g, 10.0 mmol) in water (20 cm<sup>3</sup>). The solution was evaporated on a hot plate to *ca.* 15 cm<sup>3</sup>, cooled and placed in a desiccator over anhydrous CaCl<sub>2</sub>. Over a few days colourless octahedra deposited which were removed periodically. When needles (H<sub>5</sub>IO<sub>6</sub>) started to deposit along with the octahedra the collection was stopped. The octahedra were dried *in vacuo* (1.2 g, 70%) (Found: Ga, 8.1; I, 44.6. Calc. for H<sub>24</sub>GaI<sub>3</sub>O<sub>24</sub>: Ga, 8.15; I, 44.35%). IR (cm<sup>-1</sup>) (Nujol mull) 3300s (br), 3100 (sh), 2900s (br), 1630m, 1230m, 1140m, 1120m, 1090 (sh), 930w, 765s, 650s, 615s, 577s, 357m and 330 m.

**H<sub>11</sub>I<sub>2</sub>InO<sub>14</sub>.** A solution of In(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.39 g, 1.0 mmol) in 10 cm<sup>3</sup> of 1:1 v/v concentrated HNO<sub>3</sub>–water was added to a solution of H<sub>5</sub>IO<sub>6</sub> (1.13 g, 5.0 mmol) in 20 cm<sup>3</sup> of the same acid–water mixture. The clear solution produced was evaporated to *ca.* 10 cm<sup>3</sup> on a hot-plate, cooled and placed in a desiccator over KOH pellets. After about 2 weeks some small colourless crystals had formed which were filtered off and dried in air (*ca.* 0.2 g) (Found: I, 41.8. Calc. for H<sub>11</sub>I<sub>2</sub>InO<sub>14</sub>: I, 42.05%). The quantity of material was too small for full gravimetric analysis, but the structure was established by single crystal X-ray study, and a PXRD pattern showed the bulk small crystals to be the same complex. IR (cm<sup>-1</sup>) (Nujol mull) 3300s (br), 2360 (br), 1600m, 1230m, 765s, 660s, 560s, 417s, 307m and 251m.

**Ga<sub>5</sub>(IO<sub>6</sub>)<sub>3</sub>·*n*H<sub>2</sub>O.** Gallium(III) nitrate (1.4 g, 4.0 mmol) and periodic acid (0.92 g, 4.0 mmol) were dissolved in water (50 cm<sup>3</sup>), and 2 M aqueous KOH solution added slowly to adjust the pH to 3. A white precipitate formed immediately and the solution was heated with stirring at 80 °C for 1 h to coagulate it. The solution was filtered hot, the residue washed with hot water (3 × 20 cm<sup>3</sup>) and dried in air at 40 °C (0.7 g, 60 %) [Found: Ga, 30.8; I, 34.4; H<sub>2</sub>O (by difference 6H<sub>2</sub>O; by TGA weight loss 7.5H<sub>2</sub>O). Calc. for H<sub>12</sub>Ga<sub>5</sub>I<sub>3</sub>O<sub>24</sub>: Ga, 31.0; I, 33.8%]. IR (cm<sup>-1</sup>) (Nujol mull) 3300s (br), 1630m (br), 760s, 560s, 460s (br) and 370 (sh).

**In<sub>5</sub>(IO<sub>6</sub>)<sub>3</sub>·*n*H<sub>2</sub>O.** A solution of periodic acid (0.92 g, 4.0 mmol) in water (25 cm<sup>3</sup>) was added slowly to a solution of In(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (2.34 g, 6.0 mmol) in water (25 cm<sup>3</sup>) containing sufficient HNO<sub>3</sub> to adjust the pH to *ca.* 3. A white precipitate formed immediately. The mixture was heated with stirring at 90 °C for 1 h, filtered hot, and the solid washed with water (3 × 25 cm<sup>3</sup>) and dried in air at 40 °C for 24 h (1.1 g, 70%) [Found: In, 41.8; I, 27.9; H<sub>2</sub>O (by difference 8H<sub>2</sub>O, by TGA weight loss 6H<sub>2</sub>O). Calc. for H<sub>12</sub>I<sub>3</sub>In<sub>5</sub>O<sub>24</sub>: In, 42.5; I, 28.1%]. IR (cm<sup>-1</sup>) (Nujol mull) 3300s (br), 1630m, 759s, 643s, 560s, 420m, 360m and 205 (sh).

**H<sub>3</sub>In<sub>4</sub>(IO<sub>6</sub>)<sub>3</sub>·*n*H<sub>2</sub>O.** A solution of In(NO<sub>3</sub>)<sub>3</sub>·5H<sub>2</sub>O (0.78 g, 2.0 mmol) in 5 cm<sup>3</sup> 1:1 v/v concentrated HNO<sub>3</sub>–water was added to a solution of periodic acid (1.82 g, 8.0 mmol) in water (25 cm<sup>3</sup>). The clear solution was stirred and aqueous KOH (5 M) added slowly until a permanent dense white precipitate appeared. This was filtered off, rinsed with hot water (30 cm<sup>3</sup>) and dried in air at 40 °C (1.5 g, 60%) [Found: I, 31.3; In, 36.8; H<sub>2</sub>O (by difference 6H<sub>2</sub>O, by TGA weight loss 7H<sub>2</sub>O). Calc. for

H<sub>15</sub>I<sub>3</sub>In<sub>4</sub>O<sub>24</sub>: I, 30.8; In, 37.1%]. IR (cm<sup>-1</sup>) (Nujol mull) 3300s (br), 1625m, 780s, 645s, 577s, 450m, 360m and 220 (sh).

**Aluminium compound A.** A solution of [Al(H<sub>2</sub>O)<sub>6</sub>][IO<sub>2</sub>(OH)<sub>4</sub>]<sub>3</sub> (0.86 g, 1.0 mmol) in water was stirred vigorously and sodium hydroxide solution (2 M) added dropwise until the pH of the solution was *ca.* 4. The white precipitate formed was stirred in the mother-liquor for 1h, then filtered off, washed with hot water, and dried in air (Found: Al, 17.6; I, 25.65%, giving Al:IO<sub>6</sub>:“H<sub>2</sub>O” 3.2:1:10). IR (cm<sup>-1</sup>) (Nujol mull) 3400s (br), 1640s, 1040m, 940m, 760s (br), 580s (br), 478 (sh) and 380 (sh).

**Gallium compound B.** Powdered [Ga(H<sub>2</sub>O)<sub>6</sub>][IO<sub>2</sub>(OH)<sub>4</sub>]<sub>3</sub> (0.90 g, 1.03 mmol) was added to water (15 cm<sup>3</sup>) and the mixture heated to boiling for 30 min. The white product was filtered off, rinsed with water and dried in air at 40 °C (Found: Ga, 27.8; I, 31.3%, giving Ga:IO<sub>6</sub>:“H<sub>2</sub>O” 1.55:1:5). IR (cm<sup>-1</sup>) (Nujol mull) 3300s (br), 1630s, 1135w, 732s, 560s, 473m and 390 (sh). The same compound was also obtained by combination of Ga(NO<sub>3</sub>)<sub>3</sub>·*n*H<sub>2</sub>O and H<sub>5</sub>IO<sub>6</sub> in the mol ratio 1:3 in hot water at pH 2.5.

### Crystallography

Data were recorded using a Rigaku AFC7S diffractometer fitted with Mo-K $\alpha$  radiation and graphite monochromator. For both [M(H<sub>2</sub>O)<sub>6</sub>][IO<sub>2</sub>(OH)<sub>4</sub>]<sub>3</sub> compounds, crystals were obtained by slow evaporation of solutions held in open vials contained inside a desiccator containing drying agent. Initially the crystals (Al and Ga) appeared as octahedra ( $\{111\}$ ) but later other forms developed giving almost spherical crystals (Al) and truncated octahedra (Ga,  $\{111\} + \{100\}$ ). The crystals appeared to be indefinitely stable in air. Indexing of the 20 search reflections was straightforward and cell reduction pointed to a cubic system and *F* lattice. The Laue checks for aluminium and gallium compounds) convincingly supported the cubic *m3m* Laue group. The crystal of H<sub>11</sub>I<sub>2</sub>InO<sub>14</sub> was selected from a batch of rather small crystals formed during the reaction of indium nitrate with periodic acid (see above). Initial data processing was carried out using the TEXSAN package.<sup>25</sup>

**[Al(H<sub>2</sub>O)<sub>6</sub>][IO<sub>2</sub>(OH)<sub>4</sub>]<sub>3</sub>.** An approximately spherical crystal (diameter 0.7 mm) was glued to a glass fibre and examined at room temperature.

*Crystal data.* H<sub>24</sub>Al<sub>3</sub>O<sub>24</sub>, *M<sub>r</sub>* = 815.87, cubic, lattice *F*, Laue group *m3m*, *a* = 15.421(2) Å, *V* = 3667(1) Å<sup>3</sup>, *T* = 295 K, *Z* = 8, *D<sub>c</sub>* = 2.956 g cm<sup>-3</sup>, *F*(000) = 3104,  $\mu$ (Mo-K $\alpha$ ) = 52.8 cm<sup>-1</sup>,  $\lambda$ (Mo) = 0.71073 Å.

504 Reflections were recorded ( $2\theta_{\max} = 50^\circ$ ) which after data processing (in space group 226) yielded 159 unique reflections (*R<sub>int</sub>* = 0.023). No decay was observed in the check reflections and a spherical absorption correction was applied. There are eight cubic *F*-lattice space groups in the Laue group *m3m* of which three (nos. 210, 227 and 228) can be rejected by consideration of the special absences. The pattern of intensities showed *eee* reflections more intense than *ooo* and weaker still the *hhl* reflections (*l* odd). [The values of  $\langle I/\sigma(I) \rangle$  were: *eee*, 84.7; *ooo*, 19.5; *hhl* (*l* even), 143.6; *hhl* (*l* odd), 5.8.] The *N*(*z*) test showed a large fraction of weak reflections rather like the hypercentric distribution<sup>26</sup> and the distribution of *E*'s favoured a centrosymmetric space group but as pointed out several times this can be misleading particularly in the present circumstances.<sup>27</sup> Accepting the *hhl* (*l* odd) as a systematic absence gives space groups 219 (*F43c*), 226 (*Fm3c*) whereas rejecting the absence gives 209 (*F432*), 216 (*F43m*) and 225 (*Fm3m*). All five space groups have 24-fold positions to accommodate I and either 8- or 4-fold positions for the Al atoms. Structure solutions were attempted in all the space groups either by introducing I into a 24-fold site or allowing direct methods<sup>28</sup> to locate possible

heavy atom positions. The  $R$  was encouragingly low and Fourier-difference maps phased on the I showed peaks at about 1.9 Å from the I but not in the expected approximately octahedral arrangement; rather the co-ordination number was too large. The I positions were consistent with the Patterson map vectors. The 'best' solution that was obtained was in space group 226 ( $Fm\bar{3}c$ ) with I in 24c sites and Al in 8a sites. Assuming six-co-ordinate I and Al atoms, the total number of O atoms (192) was accounted for by changing the site occupation factor (s.o.f.) of the 192-fold general position O atoms that were located in difference electron-density maps. Thus the Al atoms require 48 O atoms in total and the general position O(1) found in the Fourier-difference map was given a s.o.f. of 0.25 (48/192). Similarly 144 O atoms surround the 24 I atoms and these were accounted for by O(2) and O(3) both of which were again located in the Fourier-difference map. The relative proportion of O(2) and O(3) was allowed to refine and the two atoms were given a common refined isotropic displacement parameter. Full-matrix least-squares refinement on  $F^2$  (17 parameters, 159 reflections)<sup>29</sup> converged to  $R1$  0.086 with reasonable anisotropic (I) and isotropic (Al, O) displacement parameters, no very large residual peaks in the electron density map (+1.8 to -3.0 e Å<sup>-3</sup>) and sensible Al-O (1.90(5) Å) and I-O distances [1.95(3), 1.97(5) Å] with the latter including I-O and I-O(H) distances.

Note that the I and Al atoms form a centrosymmetric arrangement and an equivalent solution using 24d and 8b sites exists but that these sites have different point group symmetries. The other space groups considered can also produce the same iodine and aluminium solution and although giving evidence for O atom positions did not yield in our hands a satisfactory solution. A set of data were measured on a second crystal with similar results.

**[Ga(H<sub>2</sub>O)<sub>6</sub>][IO<sub>2</sub>(OH)<sub>4</sub>]<sub>3</sub>.** The crystal showed both {111} and {100} forms and was examined at 150 K using the oil-film mounting technique. Some oscillation photographs were recorded on Polaroid film when the crystal was on the diffractometer and showed the expected layer line spacing with no evidence for additional weak reflections indicating a larger unit cell or satellite peaks adjacent to the main peaks seen in modulated structures.<sup>30</sup>

*Crystal data.* H<sub>24</sub>GaI<sub>3</sub>O<sub>24</sub>,  $M_r = 858.61$ , cubic, lattice  $F$ , Laue group  $m\bar{3}m$ ,  $a = 15.478(1)$  Å,  $V = 3708.6(6)$  Å<sup>3</sup>,  $T = 150$  K,  $Z = 8$ ,  $D_c = 3.076$  g cm<sup>-3</sup>,  $F(000) = 3248$ ,  $\mu(\text{Mo-K}\alpha) = 66.0$  cm<sup>-1</sup>,  $\lambda(\text{Mo}) = 0.71073$  Å.

205 Reflections were recorded ( $2\theta_{\text{max}} = 50^\circ$ ) which after data processing (in space group 226) yielded 159 unique reflections. No decay was observed in the check reflections and an empirical  $\psi$ -scan absorption correction was applied to the data (transmission: maximum 1.00; minimum 0.92).

The pattern of intensities in various parity groups was similar to that of the aluminium compound with eee reflections more intense than ooo and weaker still the hhl reflections ( $l$  odd). [The values of  $(I/\sigma(I))$  were: eee, 77.6; ooo, 20.0; hhl ( $l$  even), 114.9; hhl ( $l$  odd), 8.5.] The  $N(z)$  test again showed a distribution more like the hypercentric one<sup>26</sup> with a greater proportion of weak reflections present at low  $z$ . The arguments about the space group exactly parallel that for the aluminium compound above. The positions of I and Ga always emerged from direct methods or followed from the space group special positions, and were fully consistent with the Patterson function. Development of the model proved elusive and a structure factor calculation (I and Ga only) and electron-density map in space group 219 for example gave peaks 1.89 to 1.94 Å from I and 1.91 and 1.93 Å from Ga but with the same disorder problem as described for the aluminium compound repeating itself. For comparison, I-O distances in LiH<sub>4</sub>IO<sub>6</sub>·H<sub>2</sub>O are 1.800(2)–1.920(2) Å<sup>13</sup> and Ga-O(H<sub>2</sub>) distances in alums are 1.944(3) Å.<sup>12</sup> The 'best' model had  $R1$  ca. 0.10 in space group 219 (I at 24d, Ga at 8b) but with unsatisfactory isotropic displacement

parameters and bond lengths moving away from reasonable values on least-squares refinement. Attempts to introduce ordered O atom positions based on an octahedron where the site symmetry permitted and using typical Ga-O(H<sub>2</sub>) and I-O distances failed. The model developed for the aluminium compound was not a satisfactory fit for these data.

**H<sub>11</sub>I<sub>2</sub>InO<sub>14</sub>.** The selected crystal (0.27 × 0.20 × 0.15 mm) was examined at 150 K using the oil-film mounting technique.

*Crystal data.* H<sub>11</sub>I<sub>2</sub>InO<sub>14</sub>,  $M_r = 603.71$ , monoclinic, space group  $P2_1/c$  (no. 14),  $a = 6.434(3)$ ,  $b = 12.001(3)$ ,  $c = 7.246(5)$  Å,  $\beta = 105.98(4)^\circ$ ,  $V = 537.9(4)$  Å<sup>3</sup>,  $T = 150$  K,  $Z = 2$ ,  $D_c = 3.728$  g cm<sup>-3</sup>,  $F(000) = 556$ ,  $\mu(\text{Mo-K}\alpha) = 80.1$  cm<sup>-1</sup>,  $\lambda(\text{Mo}) = 0.71073$  Å.

1096 Reflections were recorded ( $2\theta_{\text{max}} = 50^\circ$ ,  $h$  0–7,  $k$  0–14,  $l$  -8 to 8) which after data processing yielded 948 unique reflections ( $R_{\text{int}} = 0.043$ ). No decay was observed in the check reflections and an empirical  $\psi$ -scan absorption correction was applied (transmission: maximum 1.00; minimum 0.70). The heavy atoms were located using the direct methods routines in SHELXS 97<sup>28</sup> and the O atoms found by structure factor and electron-density calculations. Full-matrix least-squares refinement<sup>29</sup> on  $F^2$  converged to  $R1$  0.040 for 865 reflections with  $F_o > 4\sigma(F_o)$  [79 parameters, all atoms with anisotropic displacement parameters,  $S = 1.051$ ,  $\Delta/\sigma$  (maximum) 0.03,  $R1$  (all data) 0.044,  $wR2$  0.116]. The residual electron density was in the range 1.33 to -3.38 e Å<sup>-3</sup> and no H atoms were included in the model.

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## EXAFS

Data were collected from powdered samples diluted with BN, and held in 1 mm aluminium holders between Sellotape. Transmission EXAFS data at the iodine, gallium and indium K-edges were obtained on station 9.2 of the Daresbury Synchrotron Radiation Source, operating at 2 GeV and with typical currents of 200 mA, and using a silicon 220 monochromator. Harmonic rejection was set at 50%. Two or three scans were recorded for each sample and averaged. The general data treatment methodology follows that used previously for periodate complexes.<sup>14,16,23</sup> The raw data were background subtracted using the program PAXAS,<sup>31</sup> by fitting a 6- or 8-order split polynomial to the pre-edge subtracted spectrum between  $k = 2$  and 15 Å<sup>-1</sup> in most cases, although in some cases data were truncated at  $k = 12$  due to high noise. Curve fitting was carried out using the program EXCURV 92.<sup>32</sup> Ground state potentials of the atoms were calculated using Von-Barth theory and phase shifts using Hedin-Lundqvist potentials. Shells were added stepwise to the models, the distances and the Debye-Waller factors refined, as well as the Fermi energy difference. The amplitude reduction factor (AFAC) was fixed as 0.8 from studies of model compounds.<sup>23</sup> As indicated in the Results section, in some cases the occupancy of the shells was varied stepwise to determine the best fit, in others occupation numbers were fixed as required by the composition. Attempts to split the iodine edge data into separate I=O and I-OH/I-OM shells failed due to high correlations and the consequences have been discussed elsewhere.<sup>23</sup> The addition of subsequent shells was tested for statistical significance.<sup>33</sup> The number of independent data points ( $N$ ) was greater in all cases than the number of variables refined ( $N = 2\Delta k\Delta R/\pi$ ).<sup>32</sup>

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## References

- 1 W. Levason, *Coord. Chem. Rev.*, 1997, **161**, 33.
- 2 Z. Zhang, H. D. Lutz, M. Georgiev and M. Maneva, *Acta Crystallogr., Sect C*, 1996, **52**, 2660.
- 3 M. Maneva, M. Georgiev, N. Lange and H. D. Lutz, *Z. Naturforsch., Teil B.*, 1991, **46**, 795; M. Maneva, M. Georgiev and A. Pavlova, *J. Therm. Anal.*, 1988, **33**, 589.
- 4 D. B. Currie, W. Levason, R. D. Oldroyd and M. T. Weller, *J. Mater. Chem.*, 1993, **3**, 447.
- 5 A. Ferrari, A. Briabanti and A. Tiripicchio, *Gazz. Chim. Ital.*, 1961, **91**, 77.
- 6 J. Matejcek and L. Pacesova, *Collect. Czech. Chem. Commun.*, 1966, **31**, 190 and refs. therein.
- 7 H. Siebert and G. Wieghardt, *Spectrochim. Acta, Part A*, 1971, **27**, 1677.
- 8 L. C. W. Baker, H. G. Mukherjee and S. B. Sarkar, *J. Indian Chem. Soc.*, 1983, **60**, 429.
- 9 A. I. Busev, S. M. Guseinzade and N. A. Verdizade, *Zh. Anal. Khim.*, 1969, **24**, 1144.
- 10 F. Ensslin, *Z. Anorg. Allg. Chem.*, 1947, **254**, 313.
- 11 J. Glaser and G. Johansson, *Acta Chem. Scand., Ser. A*, 1981, **35**, 639.
- 12 J. K. Beattie, S. P. Best, B. W. Skelton and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1981, 2105.
- 13 T. Kraft and M. Jansen, *Z. Anorg. Allg. Chem.*, 1994, **620**, 805.
- 14 D. B. Currie, A. L. Hector, W. Levason and M. Thomas, *J. Mater. Chem.*, 1997, **7**, 1871.
- 15 T. G. Balicheva, G. A. Petrova and S. S. Potemin, *Zh. Neorg. Khim.*, 1987, **32**, 1344; B. N. Ivanov-Emin, V. I. Rybina, N. U. Venskorskii, G. Z. Kaziev and B. E. Zaitsev, *Zh. Neorg. Khim.*, 1981, **26**, 3227; B. N. Ivanov-Emin, V. I. Rybina, B. E. Zaitsev, T. V. Ustyuzhinskaya and G. Z. Kaziev, *Koord. Khim.*, 1979, **5**, 515.
- 16 W. Levason, R. D. Oldroyd and M. Webster, *J. Chem. Soc., Dalton Trans.*, 1994, 2983.
- 17 J. Mason (Editor), *Multinuclear NMR*, Plenum, New York, 1987; M. J. Taylor, *Polyhedron*, 1990, **9**, 207.
- 18 S. M. Bradley, R. A. Kydd and R. Yamdagni, *J. Chem. Soc., Dalton Trans.*, 1990, 413, 2653 and refs. therein.
- 19 A. Ferrari, A. Braibanti and A. Tiripicchio, *Acta Crystallogr.*, 1965, **19**, 629.
- 20 K. M. Tobias and M. Jansen, *Z. Anorg. Allg. Chem.*, 1986, **538**, 159.
- 21 M. J. Taylor and P. J. Brothers, in *Chemistry of Aluminium, Gallium, Indium and Thallium*, ed. A. J. Downs, Blackie, London, 1993, ch. 3; W. Seichter, H.-J. Moegel, P. Brand and D. Salah, *Eur. J. Inorg. Chem.*, 1998, 795.
- 22 L. Lebioda, M. Ciechanowicz-Rutkowska, L. C. W. Baker and J. Grochowski, *Acta Crystallogr., Sect. B*, 1980, **36**, 2530; H. Kondo, A. Kobayashi and Y. Sasaki, *Bull. Chem. Soc. Jpn.*, 1982, **55**, 2113.
- 23 E. M. Jones, W. Levason, R. D. Oldroyd, M. Webster, M. Thomas and J. Hutchings, *J. Chem. Soc., Dalton Trans.*, 1995, 3367.
- 24 M. Henry, J. P. Jolivet and J. Livage, *Struct. Bonding (Berlin)*, 1992, **77**, 155.
- 25 TEXSAN, Single crystal structure analysis software, version 1.7-1, Molecular Structure Corporation, The Woodlands, TX, 1995.
- 26 H. Lipson and M. M. Woolfson, *Acta Crystallogr.*, 1952, **5**, 680.
- 27 R. E. Marsh, *Acta Crystallogr., Sect. B*, 1995, **51**, 897.
- 28 G. M. Sheldrick, SHELXS 97, Crystal structure solution program, University of Göttingen, 1997.
- 29 G. M. Sheldrick, SHELXL 97, Crystal structure refinement program, University of Göttingen, 1997.
- 30 C. Giacovazzo, H. L. Monaco, D. Viterbo, F. Scordari, G. Gilli, G. Zanotti and M. Catti, *Fundamentals of Crystallography*, IUCr/OUP, Oxford, 1992; see also W. Depmeier, *Acta Crystallogr., Sect. B*, 1981, **37**, 330, 1322 for some photographs.
- 31 N. Binsted, PAXAS, Program for the analysis of X-ray absorption spectra, University of Southampton, 1988.
- 32 EXCURV 92, SERC Daresbury Laboratory Program, 1992.
- 33 S. S. Hasnain (Editor), *XAFS*, Ellis Horwood, New York, 1991.

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