Synthesis, Spectroscopic and Structural Characterisation of Periodate Complexes of Iron(III)†

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The reaction of $Fe(NO_3)_3{\cdot}9H_2O$ with $NaIO_4$ in aqueous acid solution gave brown $[Fe_4I_3O_{24}H_{15}]$ and subsequent reaction with concentrated alkalis formed $M_n[Fe_4I_3O_{24}H_{15-n}]$ (M = Li, Na, K, Rb or Cs). The crystal structure of $K_6Na_2[Fe_4I_3O_{24}H_7]{\cdot}14H_2O$ has been determined and shown to contain an Anderson-type anion composed of seven edge-linked octahedra. In the crystal studied a central FeO_6 group is surrounded by six disordered FeO_6 and IO_6 groups. All the prepared salts have been shown to contain a similar anion based upon spectroscopic data, iron and iodine K-edge extended X-ray absorption fine structure data, and the ^{57}Fe Mössbauer spectra.

Periodate $[H_{5-n}IO_6]^{n-}$ groups are strongly co-ordinating towards many transition-metal ions, producing stable complexes often containing unusually high oxidation states of the metal. The formulae and structures vary in an irregular manner across the Periodic Table: extended layer lattices $M'MIO_6$ (M′ = alkali metal, M = Mn^{IV} or Ni^{IV});[1,2] discrete bis(periodate) anions $[MY_2(HIO_6)_2]^{n-}$ (M = Ru^{VI} or Os^{VI}, Y = O; M = Pt^{IV} or Pd^{IV}, Y = OH)[3–5] and $[M(HIO_6)_2]^{5-}$ (M = Cu^{III}, Ag^{III}, or Au^{III});[6–8] a tris(periodate) species $[Mn^{IV}(HIO_6)_2(H_2IO_6)]^{7-}$;[1] and an Anderson-type heteropolyanion $[Co^{III}{}_4I_3O_{24}H_{12}]^{3-}$.[9,10] Two iron periodates, formulated $H_3[Fe_4I_3O_{24}H_{12}]$ and $Na_5[Fe(H_2IO_6)_2(OH)_2]$ on the basis of analytical data were reported some years ago,[11] but their intractable nature seems to have prevented further study. Here we report a detailed reinvestigation of the periodate complexes of iron. There is great current interest in the structures and properties of oxoiron cluster complexes.[12]

Results and Discussion

The reaction of iron(III) nitrate with $NaIO_4$ in hot weakly acidified (HNO_3) aqueous solution results in the formation of a yellow-brown insoluble solid, identified[11] as the acid $H_3[Fe_4I_3O_{24}H_{12}]$. Our analytical data from several samples are fully consistent with the formula $[Fe_4I_3O_{24}H_{15}]$, and an EDX (energy dispersive X-ray analysis) study confirmed both the absence of any other elements such as alkali metals and the sample homogeneity (from an examination of different areas in the samples). Treatment of the reaction mixture containing the freshly prepared yellow-brown complex with concentrated aqueous NaOH converts it into a greenish yellow insoluble material, formulated[11] as $Na_5[Fe(H_2IO_6)_2(OH)_2]$. However, although we too have obtained this material and the analyses for Fe, Na and I conform approximately to those expected, all our samples proved to be inhomogeneous when studied by EDX, and we believe on the basis of spectroscopic data discussed below that the material is a mixture. In contrast, freshly isolated $[Fe_4I_3O_{24}H_{15}]$ dissolved in concentrated aqueous solutions of KOH, RbOH or CsOH to give deep brownish solutions, from which red-brown powders of composition $M_x[Fe_4I_3O_{24}H_{15-x}]$ (M = K, Rb or Cs) can be precipitated by addition of acetone or ethanol. Although $[Fe_4I_3O_{24}H_{15}]$ did not dissolve in concentrated sodium or lithium hydroxide solutions, on stirring the suspensions for several hours, the solid turned darker brown and analysis showed substantial amounts of alkali metal had been incorporated. The analytical data, and the weight loss on heating to *ca.* 200 °C which approximates to that expected for the loss of the H_2O ligands, indicate that in contrast to many periodato-complexes these powdered materials do not contain significant amounts of lattice water. Slow evaporation (several weeks) of a concentrated solution of the potassium complex in aqueous KOH in a desiccator over $CaCl_2$ produced small dark brown crystals which were identified by EDX as containing K, Fe, I and Na, the latter arising from attack on the glass container by the strong alkali. The structure was determined and as this provides the most convenient starting point for a discussion of these complexes, it is described first.

Structure of $K_6Na_2[Fe_4I_3O_{24}H_7]{\cdot}14H_2O$.—The structure contains discrete anions '$[Fe_4I_3O_{24}]$' (see Fig. 1) in which a central Fe atom is surrounded by a ring of three I and three Fe atoms. Owing to the three-fold symmetry of the central atom, alternating Fe and I atoms are required in an ordered model for these peripheral atoms. However, a disordered model for these peripheral atoms provides a much better fit to the data. Each Fe and I is surrounded by six O atoms in an approximately octahedral arrangement, the octahedra being linked *via* edges, and the anion has crystallographic D_3 (32) symmetry. Owing to the disorder, the bond lengths (Table 1) are of limited value but nevertheless they fall in the range expected. The structural type found in the anion has been identified in several species including the heteropolyanions of Mo, $[XMo_6O_{24}]^{n-}$ (X = I or Te), but more pertinent to the present compound is the cobalt(III) analogue where two species ($[Co_4I_3O_{24}H_{12}]^{3-}$ and $[Co_4I_3O_{24}H_{14}]^{-}$) with varying degrees of protonation have been described.[9,10] In the present compound the charge on the anion is balanced by K and Na cations. The Na is surrounded by six O atoms from H_2O molecules in an approximate octahedron (Na ··· O 2.356–2.397 Å) and the K by seven O atoms closer than 3.0 Å [K ··· O minimum 2.71(2) Å] and an eighth at a little over 3.0 Å, these being drawn from both anion O atoms and water molecules. Many attempts were made to obtain other crystals (hopefully without the disorder) suitable

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1995, Issue 1, pp. xxv–xxx.

Non-SI units employed: $\mu_B = 9.27 \times 10^{-24}$ J T^{-1}, G = 10^{-4} T, eV ≈ 1.60×10^{-19} J, Ci = 3.7×10^{10} Bq.

for an X-ray study, using mixtures of alkali-metal ions, but these were unsuccessful.

EXAFS Data.—We have shown elsewhere[4] that a combination of iodine and metal-edge EXAFS (extended X-ray absorption fine structure) data can provide reliable structural data in periodato-complexes, and notably for the Anderson polyanion [$Co_4I_3O_{24}H_{15}$] we obtained good agreement with the single-crystal X-ray data. Iodine and iron K-edge EXAFS data were collected from the acid form [$Fe_4I_3O_{24}H_{15}$] and the M_n[$Fe_4I_3O_{24}H_{15-n}$] and were found to be essentially the same for each compound, confirming the presence of the same basic structural unit in all (Table 2, Fig. 2). Refinement of the iodine-edge data placed a first shell of six oxygens at *ca.* 1.87 Å, an average value typical for co-ordinated periodate groups,[4] and a second shell of three irons at *ca.* 3.06 Å. Attempts to split the first (6O) shell into two, corresponding to bridging and terminal oxygens, failed the statistical significance test (*cf.* ref. 4). The iron K-edge data for [$Fe_4I_3O_{24}H_{15}$] placed six oxygens at *ca.* 1.98 Å and a second shell of iodines at *ca.* 3.07 Å. Attempts to fit a third shell corresponding to the non-bonded iron–iron distance failed due to high correlations with the iodine shell, except in the case of the lithium derivative where a shell of 1.5 Fe atoms at 3.0 Å was satisfactorily modelled. The iron-edge data also revealed a further oxygen shell at *ca.* 3.6 Å. The heavier alkali-metal salts gave similar iron-edge data, but suffered considerably from high mass absorption from the iodine and the alkali metals, resulting in large fit indices and *R* factors. The EXAFS data overall however confirm the Anderson-type structure with the central FeO_6 unit surrounded by alternating edge-linked IO_6 and FeO_6 groups.

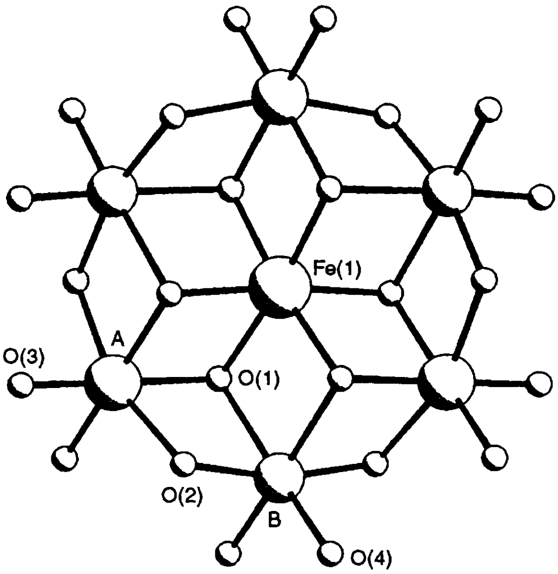

Fig. 1 View of the anion in $K_6Na_2[Fe_4I_3O_{24}H_7]\cdot14H_2O$ looking down the *c* axis: A and B indicate the disordered atoms I(1A), Fe(2A) (0.35, 0.65) and I(1B), Fe(2B) (0.65, 0.35)

Spectroscopic Data.—From the analytical and structural data and by analogy with the cobalt analogue, [$Fe_4I_3O_{24}H_{15}$] can be provisionally formulated as [$Fe_4(HIO_6)_3(H_2O)_6$]. The IR spectrum contains medium-intensity features at *ca.* 3300 and 1650 cm^{-1} assignable as ν(OH) and δ(HOH) of the water ligands, and several intense overlapping features between 800 and 400 cm^{-1} due to I–O and Fe–O vibrations. The region 1000–1300 cm^{-1} was examined for evidence of δ(IOH) modes which would confirm the protonation of terminal oxygens of the periodate groups. However, although some very weak features do occur in this region, none could be definitely

Table 1 Selected bond lengths (Å) and angles (°) for $K_6Na_2[Fe_4I_3O_{24}H_7]\cdot14H_2O$

Fe(1)–O(1)	2.040(6)		
I(1A),Fe(2A)–O(1)	1.96(1)	I(1B),Fe(2B)–O(1^{III})	2.15(1)
I(1A),Fe(2A)–O(2)	2.02(1)	I(1B),Fe(2B)–O(2^{III})	1.89(1)
I(1A),Fe(2A)–O(3)	1.88(1)	I(1B),Fe(2B)–O(4)	1.90(1)
I(1A),Fe(2A) ··· I(1B),Fe(2B^{I})	3.087(1)	Fe(1) ··· I(1A),Fe(2A)	3.075(2)
I(1A),Fe(2A) ··· I(1B),Fe(2B)	3.087(1)	Fe(1) ··· I(1B),Fe(2B)	3.100(2)
Minimum K(1) ··· O	2.71(2)	Minimum Na(1) ··· O	2.356(8)
O(1)–Fe(1)–O(1^{I})	97.7(2)	O(1)–Fe(1)–O(1^{III})	77.7(5)
O(1)–Fe(1)–O(1^{II})	87.2(5)		
Fe(1)–O(1)–I(1A),Fe(2A)	100.4(4)	I(1A),Fe(2A)–O(1)–I(1B),Fe(2B^{I})	97.3(2)
Fe(1)–O(1)–I(1B),Fe(2B^{I})	95.6(3)		

Symmetry operations: I $-y, x-y, z$; II $-x, -x+y, -z$; III $y, x, -z$. Atoms I(1A),Fe(2A) occupy the same site [populations 0.35(1) and 0.65(1) respectively], as do I(1B),Fe(2B) [populations 0.65(1) and 0.35(1) respectively].

Table 2 Iron and iodine K-edge EXAFS data

Compound	Edge	d(I–O)^a/Å	$2\sigma^{2\,b}$	d(I ··· Fe)^c/Å	$2\sigma^2$	d(Fe–O)/Å	$2\sigma^2$	f.i.^{d}	R^e
[$Fe_4I_3O_{24}H_{15}$]	I	1.865(2)	0.0052(3)	3.029(5)	0.0126(9)			4.5	20.0
	Fe			3.067(8)	0.0248(23)	1.978(3)	0.0183(6)	5.8	22.9
$Cs_4[Fe_4I_3O_{24}H_{11}]$	I	1.872(2)	0.0061(3)	3.068(4)	0.0116(9)			4.8	20.5
	Fe			3.065(9)	0.0154(24)	1.998(6)	0.0275(13)	10.8	32.3
$Rb_4[Fe_4I_3O_{24}H_{11}]^f$	I	1.872(2)	0.0055(2)	3.082(4)	0.0127(8)			2.5	14.7
$K_4[Fe_4I_3O_{24}H_{11}]$	I	1.876(2)	0.0056(3)	3.073(5)	0.0142(10)			3.8	19.0
	Fe			3.075(9)	0.0164(16)	1.952(5)	0.0224(10)	12.4	34.4
$Na_5[Fe_4I_3O_{24}H_{10}]$	I	1.877(5)	0.0051(2)	3.070(5)	0.0142(10)			3.0	23.1
	Fe			3.104(8)	0.0166(14)	1.975(5)	0.0232(9)	9.0	30.1
$Li_6[Fe_4I_3O_{24}H_9]$	I	1.869(9)	0.0043(9)	3.062(3)	0.0133(5)			1.1	15.4
	Fe^g			3.061(5)	0.0156(1)	1.989(5)	0.0272(10)	7.8	30.5

[a] Standard deviations in parentheses. Note that the systematic errors in bond distances arising from the data-collection and analysis procedures are *ca.* ±0.02–0.03 Å for well defined co-ordination shells. [b] Debye–Waller factor. [c] Non-bonded distance. [d] Fit index defined as $\Sigma_i[(\chi^T - \chi^E)\,k_i^3]^2$. [e] R factor defined as $[\int(\chi^T - \chi^E)k^3dk/\int\chi^E k^3dk] \times 100\%$. [f] Good quality iron-edge data not obtained. [g] Iron shell at 3.006(14) Å, $2\sigma^2$ 0.0245(4).

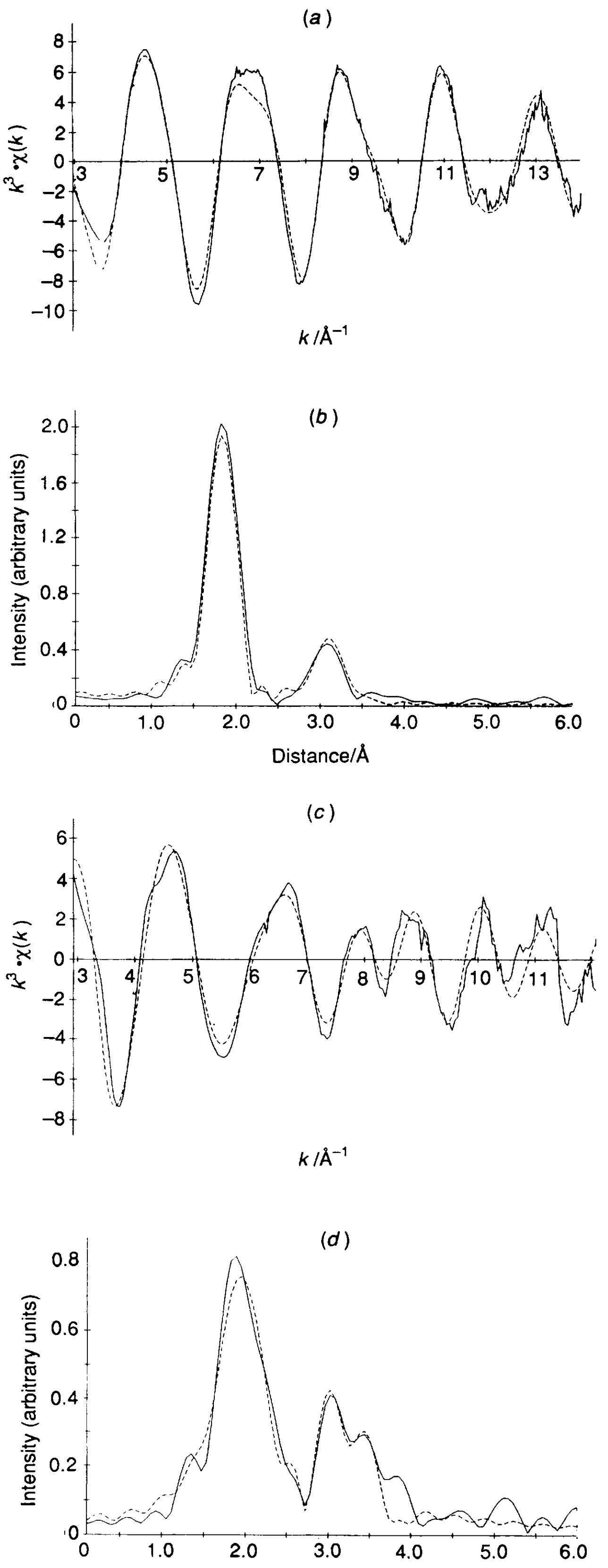

Fig. 2 K-Edge EXAFS data and the corresponding Fourier transforms for $Li_6[Fe_4I_3O_{24}H_9]$: (*a*), (*b*) iodine edge; (*c*), (*d*) iron edge

assigned. Deuteriation of $[Fe_4I_3O_{24}H_{15}]$ by treatment with D_2O for 24 h caused the expected shifts in the water vibrations, but no change in the weak features between 1000 and 1300 cm^{-1}. Since there is no lattice water to be protonated as suggested[9] for $[Co_4I_3O_{24}H_{15}]$, the protonation may be at the bridging oxygens, and the vibration obscured by other modes at lower frequency.

The diffuse reflectance UV/VIS spectra of the acid form and the alkali-metal salts were superimposable consisting of a broad feature at 320 nm and a weak shoulder at 475 nm. The spectrum of the caesium salt dissolved in dilute aqueous CsOH was similar with a band at 320 nm (ε_{mol} = 4800 dm^3 mol^{-1} cm^{-1}) and a shoulder at 480 nm (ε_{mol} *ca.* 500 dm^3 mol^{-1} cm^{-1}) which are probably charge transfer O$\longrightarrow$Fe in character. The ESR spectra of the powdered solids at 295 K were broad featureless resonances at *g ca.* 2 consistent with high-spin d^5 Fe^{III},[13] and the presence of high-spin iron was confirmed by the room-temperature magnetic susceptibilities which were *ca.* 5.3 μ_B for the alkali-metal salts, and 4.6 μ_B for the acid (Experimental section). These values are markedly lower than the spin-only value (5.9 μ_B) indicating the materials are not magnetically dilute, a common feature of oxo-bridged iron(III) compounds.[12]

Mössbauer Spectroscopy.—Samples of $[Fe_4I_3O_{24}H_{15}]$ and $Na_5[Fe_4I_3O_{24}H_{10}]$ were studied at room temperature (300 K) and 4.2 K, with the aims of establishing the oxidation state of the iron and gaining information about the iron environments and any magnetic ordering that may be present. Spectra of the samples at 300 and 4.2 K are shown in Figs. 3 and 4 respectively and the parameters used in the fits are listed in Table 3.

All the spectra were fitted with two components corresponding to the two different iron sites. Fits to the acid form at 300 and 4.2 K and to the sodium salt at 300 K were satisfactorily modelled with just two components, but there is some evidence that the sodium sample at 4.2 K required additional parameters for a good fit. All components of both samples showed isomer shift values characteristic of high-spin iron(III).[14] Isomer shift values typical of high-spin Fe^{III} in oxide environments are 0.3–0.4 mm s^{-1} at 300 K and 0.45–0.55 mm s^{-1} at 4.2 K, the temperature dependence arising from the reduced vibrations at lower temperature. For iron(II) typical isomer shifts lie above 1.0 mm s^{-1}, which establishes the iron oxidation state in these periodates as III in all sites. Two components were required for satisfactory fits of the 300 and 4.2 K spectra of the $[Fe_4I_3O_{24}H_{15}]$ sample. Each component represents a distinct iron site and the ratio of the components was fixed as 1 : 3 corresponding to the central and peripheral iron sites. Figs. 3 and 4 show that the fits are consistent with this model, although they do not uniquely establish the ratio as 1 : 3 since different parameter sets can lead to equally good fits with different intensity ratios. The spectrum fits of the sodium salt at 4.2 K were performed as a function of the area ratio 1 : X with the linewidths constrained to be equal. A plot of the goodness-of-fit parameter χ^2 *versus* X was relatively insensitive to the ratio as shown by a shallow minimum, which however occurred at X *ca.* 3.8. It should be noted that the recoil-free fraction which is combined with the site abundance in giving the component area may not be the same for different iron sites, and thus the area ratio may deviate from 1 : 3.

The finite quadrupole splittings at 300 K show that the iron(III) does not occupy regular octahedral sites which would lead to zero splitting. The 4.2 K spectra are composed of sextet components arising from a defined hyperfine field acting on the iron centres and implying magnetic order.[14] The large magnitude of the hyperfine fields (> 450 kG) confirms the iron(III) oxidation state. In the acid form the two sextet components give rise to a satisfactory fit, but in the sodium salt the two-component fit would be improved by additional components with smaller hyperfine fields.

Other Compounds.—Although nickel(IV) and manganese(IV) are stabilised by periodate ligands,[1,2] attempts to prepare iron(IV) compounds have failed. In particular boiling an aqueous solution of $[Fe(H_2O)_6]^{3+}$ with IO_4^- and peroxodisulfate produced only the $[Fe_4I_3O_{24}H_{15}]$, and a saturated

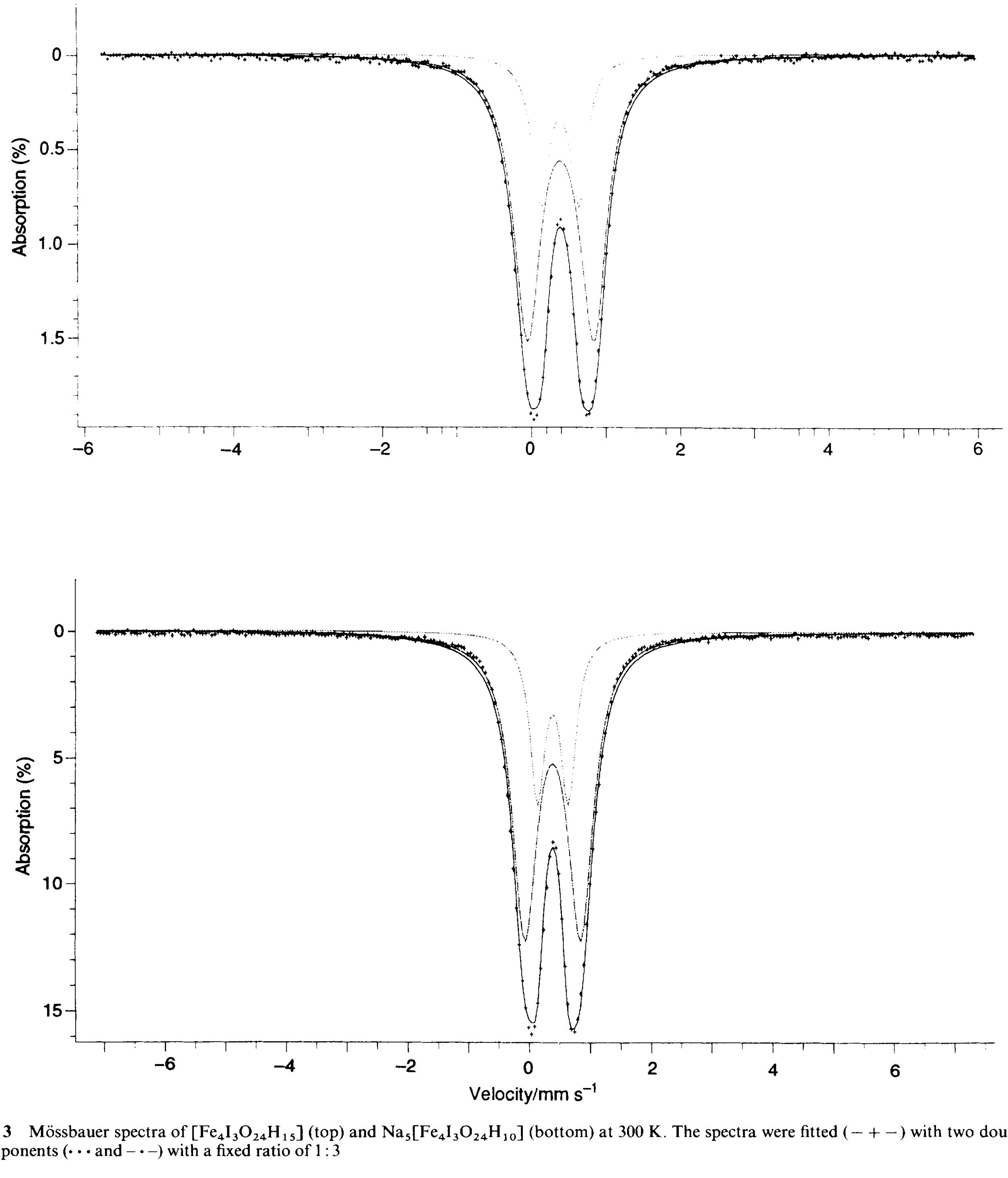

Fig. 3 Mössbauer spectra of [$Fe_4I_3O_{24}H_{15}$] (top) and Na_5[$Fe_4I_3O_{24}H_{10}$] (bottom) at 300 K. The spectra were fitted (— + —) with two doublet components (· · · and — · —) with a fixed ratio of 1 : 3

solution of [$Fe_4I_3O_{24}H_{15}$] in concentrated aqueous CsOH was unchanged on treatment with ozone. Both reagents easily generate Ni^{IV} in the corresponding systems.

'$Na_5[Fe(H_2IO_6)_2(OH)_2]$'. The yellow-green material is formed[11] by addition of aqueous sodium hydroxide to the *reaction mixture* containing freshly made [$Fe_4I_3O_{24}H_{15}$]. Acid (H_2SO_4 or HNO_3) converts the yellow-green material into brown [$Fe_4I_3O_{24}H_{15}$] and the supernatant solution contains periodate ions.[11] We prepared several samples of the yellow-green material and confirm the reaction with acid (the *isolated acid form* reacts with NaOH to produce the brown Na_5[$Fe_4I_3O_{24}H_{10}$] already described), but found that the composition was rather variable, and examination of different regions of the samples by EDX showed them to be inhomogeneous. The K-edge EXAFS for Fe and I were similar to those of the Na_5[$Fe_4I_3O_{24}H_{10}$] and provide some evidence that the Anderson-type polyanion is present. Notably the iodine K-edge EXAFS data fit shell one as six oxygens, but the second shell of three irons was unsatisfactory, which would be consistent with a mixture of the cluster anion and a sodium periodate. The IR spectrum of the yellow-green complex showed strong water bands (3300, 1660 cm^{-1}), δ(IOH) at 1170 cm^{-1} and was complex below 800 cm^{-1}. The Mössbauer spectrum at 300 K revealed two components with isomer shifts of 0.43 and 0.31 mm s^{-1} and at 4.2 K it was not magnetically ordered.

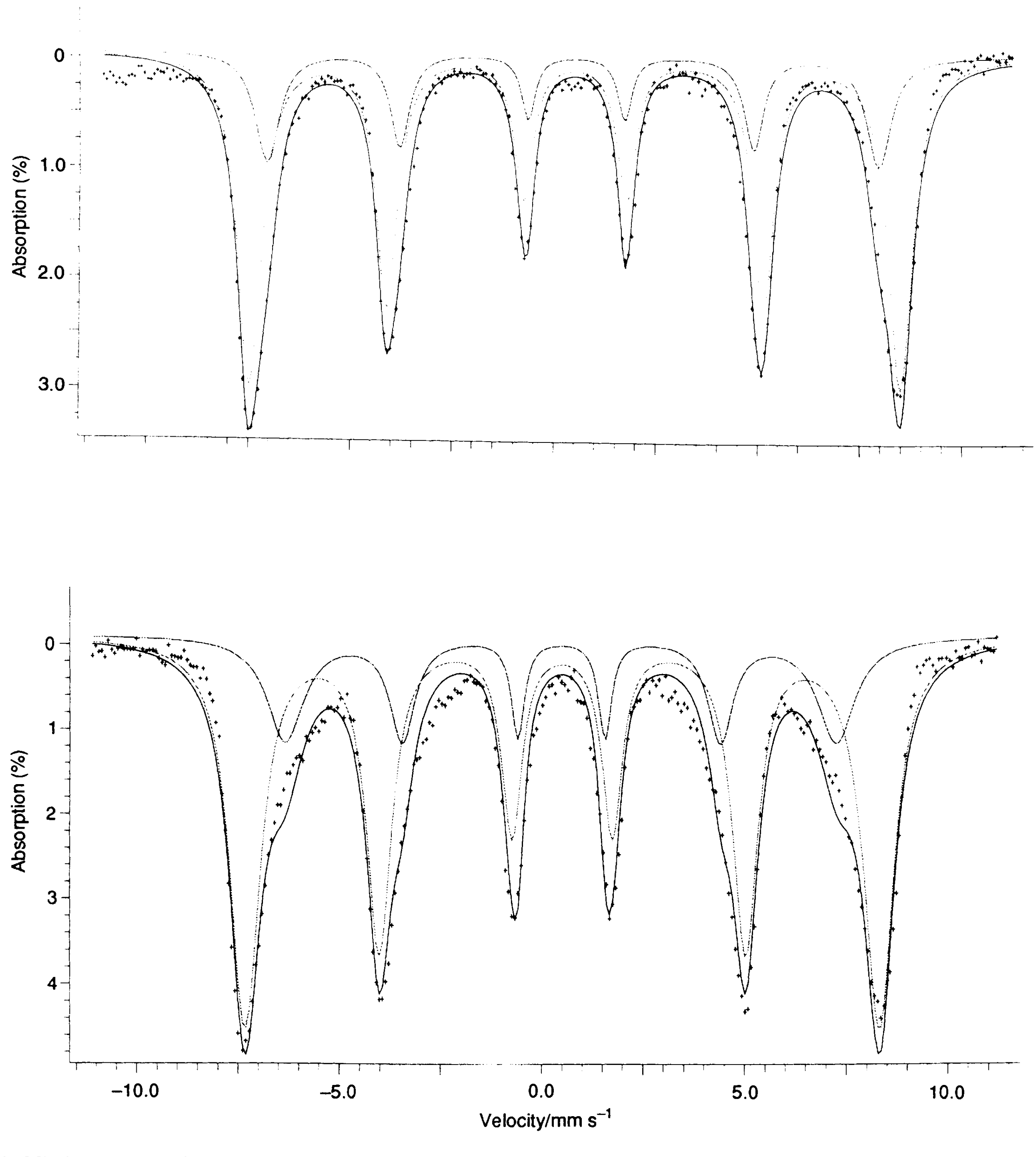

Fig. 4 Mössbauer spectra of $[Fe_4I_3O_{24}H_{15}]$ (top) and $Na_5[Fe_4I_3O_{24}H_{10}]$ (bottom) at 4.2 K. The spectra were fitted with two sextet components as in Fig. 3

Although the nature of this yellow-green material is not definitely established, our data suggest that it is a mixture and not a discrete complex.

'$Na_5[Co(HIO_6)_2]{\cdot}nH_2O$'. A green cobalt(III) bis(periodate) of this formulation is reported to form from OCl^- or $S_2O_8^{2-}$ oxidation of a mixture of Co^{II} and periodate ions in alkaline solution.[15,16] On treatment with acid it is converted into the well characterised $H_3[Co_4I_3O_{24}H_{12}]{\cdot}nH_2O$. In view of the possible analogy with the yellow-green sodium iron periodate, we prepared several samples of this material. Whilst our data are similar to those in the literature, there are several anomalous properties of these samples. The EDX analysis conformed with the approximate atom ratios reported, but again showed the samples to be inhomogeneous. All samples were also significantly paramagnetic (noted before[16] but attributed to impurities), inconsistent with $t_{2g}{}^6$ Co^{III}, and a spin cross-over or high-spin form is unlikely since both the Anderson anion and $[Co(H_2O)_6]^{3+}$ are low spin. The solubility in water is not high, but a ^{59}Co NMR spectrum revealed two cobalt resonances at δ 13 100 and 12 700 {relative to $[Co(CN)_6]^{3-}$} very similar to those reported[17] for $[Co_4I_3O_{24}H_{12}]^{3-}$ (δ 13 200, 12 560). Treatment of the material with acid gave a pink solution containing $[Co(H_2O)_6]^{2+}$ identified by its UV/VIS spectrum, and the solid green Anderson polyanion. Attempts to model the cobalt K-edge spectra of the 'bis(periodate)' material failed; the EXAFS were not simply those[4] of $[Co_4I_3O_{24}H_{12}]^{3-}$. A possible constitution is a mixture of a sodium periodate and a cobalt(II) salt of the Anderson

Table 3 Mössbauer spectral data *

Sample		8p9h9.3l0I mm s^{-1}	Quadrupole splitting/ mm s^{-1}	Line width/ mm s^{-1}	Hyperfine field/ kG	Relative intensity
$[Fe_4I_3O_{24}H_{15}]$	(300 K)	0.40	0.89	0.43		3
		0.40	0.51	0.28		1
	(4.2 K)	0.50	0.0	0.64	495	3
		0.50	−0.09	0.57	466	1
$Na_5[Fe_4I_3O_{24}H_{10}]$	(300 K)	0.38	0.91	0.50		3
		0.38	0.51	0.30		1
	(4.2 K)	0.50	−0.01	0.75	485	3
		0.49	−0.01	0.75	422	1

* Hyperfine parameters used in the fits to the spectra in Figs. 3 and 4. The relative intensities of the components were fixed as 1 : 3; other parameters were optimised values, freely varied. The errors are ±0.01 mm s^{-1} and ±1 kG.

polyanion. It may be that the Co^{II} is co-ordinated to the anion; there are literature precedents for metal ions linking polyanions into chains, notably the recently characterised[18] $K_6[Co(H_2O)_4]_2[H_2W_{12}O_{24}]\cdot14H_2O$.

Conclusion

We have shown that $[Fe_4I_3O_{24}H_{15}]$ and its alkali-metal derivatives all contain an Anderson-type polyanion, and have provided structural and spectroscopic characterisation of these compounds. Our data also cast considerable doubt on the existence of bis(periodate) complexes of Fe^{III}, $[Fe(H_2IO_6)_2(OH)_2]^{5-}$ and the cobalt analogue. Whilst the analytical evidence of variable composition and inhomogeneity of these latter species could be due simply to our inability to obtain pure samples, the spectroscopic and structural probes have identified features characteristic of the Anderson polyanions in the materials.

Experimental

Physical measurements were made as described previously.[2] For chemical analyses the samples were decomposed by boiling with an aqueous solution of SO_2 and then the excess of SO_2 boiled off. Alkali metals were determined by atomic emission spectroscopy, iodide gravimetrically as AgI, and iron spectrophotometrically as the iron(II)–1,10-phenanthroline complex.[19] The weight loss on heating to 200 °C (by TGA) was used to obtain an estimate of the water content. Weight losses occurred over a broad temperature range. The calculated values (below) are based upon loss of all hydrogens as H_2O, although some oxygen loss may also be involved.

$[Fe_4I_3O_{24}H_{15}]$.—A solution of $Fe(NO_3)_3\cdot9H_2O$ (4.04 g, 0.01 mol) was dissolved in water (100 cm^3) and heated to 80 °C. A solution of $NaIO_4$ (2.14 g, 0.01 mol) in water (100 cm^3) and nitric acid (2 cm^3) pre-heated to 80 °C was added slowly with stirring, producing a yellow-brown precipitate. The precipitate was separated by centrifuging, washed twice with water (100 cm^3) and the washings discarded. The residue was dried *in vacuo* for 24 h. Yield 2.5 g (Found: Fe, 21.7; I, 38.6. $H_{15}Fe_4I_3O_{24}$ requires Fe, 22.8; I, 38.0%). $\mu = 4.6\ \mu_B$ per Fe.

$Li_6[Fe_4I_3O_{24}H_9]$.—A suspension of finely powdered $[Fe_4I_3O_{24}H_{15}]$ (0.5 g, 0.5 mmol) was stirred for 2 h with a saturated solution of LiOH in water (100 cm^3). The brown solid produced was separated by centrifuging, washed twice with distilled water (100 cm^3), again separated by centrifuging, and dried *in vacuo*. Yield approximately quantitative (Found: Fe, 21.9; I, 36.3; Li, 4.1%; weight loss 8.3%. $H_9Fe_4I_3Li_6O_{24}$ requires Fe, 21.5; I, 36.6; Li, 4.0%; weight loss 7.8%). $\mu = 5.2\ \mu_B$ per Fe.

The salt $Na_5[Fe_4I_3O_{24}H_{10}]$ was made analogously using 6 mol dm^{-3} NaOH (Found: Fe, 20.0; I, 34.5; Na, 10.4%; weight loss 8.1%. $H_{10}Fe_4I_3Na_5O_{24}$ requires Fe, 20.1; I, 34.2; Na, 10.3%; weight loss 8.0%). $\mu = 5.2\ \mu_B$ per Fe.

$K_4[Fe_4I_3O_{24}H_{11}]$.—Finely powdered $[Fe_4I_3O_{24}H_{15}]$ (0.5 g, 0.5 mmol) was dissolved with stirring in 10 mol dm^{-3} KOH in water (100 cm^3) to produce a yellowish brown solution. The solution was decanted from any undissolved solid, and ethanol (100 cm^3) added slowly with stirring. The brown precipitate was separated by centrifuging, washed with cold distilled water (2 × 50 cm^3) and dried *in vacuo*. Yield 75% (Found: Fe, 19.4; I 33.3: K, 13.6%; weight loss 9.4%. $H_{11}Fe_4I_3K_4O_{24}$ requires Fe, 19.3; I, 33.0; K, 13.5%; weight loss 8.6%). $\mu = 5.4\ \mu_B$ per Fe.

The salts $Rb_4[Fe_4I_3O_{24}H_{11}]$ and $Cs_4[Fe_4I_3O_{24}H_{11}]$ were made similarly, using the minimum quantity of MOH solution needed completely to dissolve the $[Fe_4I_3O_{24}H_{15}]$, since these salts are more soluble in the alkali solution, and correspondingly more difficult to reprecipitate in good yield: $Rb_4[Fe_4I_3O_{24}H_{11}]$ (Found: Fe, 16.5; I, 27.9; Rb, 24.9%; weight loss 8.7%. $H_{11}Fe_4I_3O_{24}Rb_4$ requires Fe, 16.7; I, 28.4; Rb, 25.5%, weight loss 7.4%), $\mu = 5.3(5)\ \mu_B$ per Fe; $Cs_4[Fe_4I_3O_{24}H_{11}]$ (Found: Cs, 35.6; Fe, 14.8; I, 24.6%; weight loss 7.9%. $H_{11}Cs_4Fe_4I_3O_{24}$ requires Cs, 34.7; Fe, 14.6; I, 24.9%; weight loss 6.5%), $\mu = 5.3\ \mu_B$ per Fe.

The yellow-green '$Na_5[Fe(H_2IO_6)_2(OH)_2]$' was made as described[11] (Found: Fe, 9.9; I, 37.3; Na, 17.0%; weight loss 15.6%. $H_6FeI_2Na_5O_{14}$ requires Fe, 8.6; I, 38.8; Na, 17.7%; weight loss 8.2%). The salt '$Na_5[Co(HIO_6)_2]\cdot nH_2O$' was made as described.[15]

Crystal Structure Determination.—Brown air-stable crystals of $K_6Na_2[Fe_4I_3O_{24}H_7]\cdot14H_2O$ were obtained by slow evaporation from concentrated aqueous alkali (KOH) and mounted on a glass fibre for X-ray examination.

Crystal data. $H_{35}Fe_4I_3K_6Na_2O_{38}$, $M = 1527.9$, trigonal, space group $R32$ (no. 155), $a = b = 13.097(2)$, $c = 18.518(3)$ Å, $\gamma = 120°$, $U = 2750.8(9)$ Å^3, $Z = 3$, $D_c = 2.766$ g cm^{-3}, λ(Mo-Kα) = 0.710 69 Å, μ(Mo-Kα) = 48.3 cm^{-1}, $F(000) = 2214$, $T = 298$ K.

Data were collected from a room-temperature crystal (0.2 × 0.2 × 0.15 mm) using a Rigaku AFC7S diffractometer equipped with Mo-Kα radiation and a graphite monochromator. Cell dimensions were obtained from 18 centred reflections (2θ 19.9–22.4°). The intensities of 1191 reflections were measured (ω–2θ scans, $5 < 2\theta < 50°$: h −13 to 13, k 0–15, l 0–21) and corrected for Lorentz and polarisation factors, decay (7%) and absorption using the ψ-scan method (three reflections; minimum, maximum transmission 0.72, 1.00). Data analysis gave 1043 unique reflections ($R_{int} = 0.050$). The preliminary data established a trigonal crystal system (referred to hexagonal axes in the analysis) with systematic absences consistent with space group $R\bar{3}m$ (166) or $R32$ (155). No satisfactory solution emerged with the favoured $R\bar{3}m$ whereas the direct-methods strategy in SHELXS 86[20] with the non-centrosymmetric space group $R32$ produced one solution with a low figure of merit and

Table 4 Atomic coordinates for $K_6Na_2[Fe_4I_3O_{24}H_7]\cdot 14H_2O$

Atom	*x*	*y*	*z*
Fe(1)	0	0	0
I(1A), Fe(2A)	−0.2348(2)	−0.2348(2)	0
I(1B), Fe(2B)	−0.2367(2)	0	0
K(1)	0.5285(6)	0.4798(6)	0.1420(1)
Na(1)	0.6667	0.3333	0.0750(3)
O(1)	−0.0865(9)	−0.1560(5)	−0.0544(3)
O(2)	−0.1372(11)	−0.2876(5)	0.0563(3)
O(3)	−0.3615(9)	−0.3015(12)	0.0654(7)
O(4)	−0.3675(10)	−0.0737(12)	0.0635(7)
O(5)	0.5802(17)	0.4193(17)	0.0002(4)
O(6)	0.4862(6)	0.2366(13)	0.1377(4)
O(7)	0.6667	0.3333	−0.0856(11)

Atoms I(1A), Fe(2A) occupy the same site [populations 0.35(1) and 0.65(1) respectively], as do I(1B), Fe(2B) [populations 0.65(1) and 0.35(1) respectively].

plausible positions for the heavy atoms (Fe,I). Repeated structure-factor and electron-density calculations revealed the O atoms of the anion, K(1) and several other possible atom sites. From the separations of possible water molecules it became apparent that one was a sodium cation and this was confirmed by subsequent EDX measurements. Least-squares refinement with two ordered models for the anion (central Fe with alternating Fe and I on the periphery) gave R *ca.* 0.08 (R' *ca.* 0.12) and non-definite positive anisotropic thermal parameters. However the disordered model for the peripheral Fe,I atoms gave satisfactory thermal parameters and a much better fit to the data. This model was adopted and full-matrix least-squares refinement minimising $\Sigma w\Delta^2$ converged to R = 0.0498 [51 parameters, 945 observations, $F > 3\sigma(F)$], $w^{-1} = \sigma^2(F) + AF^2$ (A = 0.0007), anisotropic (Fe, I, K) and isotropic (O, Na) atoms, maximum |shift/error| = 0.3, R' = 0.073). The residual electron density was in the range +2.18 to −2.49 e Å^{-3}. No H atoms were included in the model: the number of H atoms included in the formula arises from the need to balance the charge. The absolute configuration of the crystal examined could not be determined. Neutral atom complex scattering factors were taken from ref. 21 (Fe, I, K, Na) and SHELX 76[22] and calculations were performed on a personal computer using SHELX 76 and SHELXS 86. Final atomic coordinates are given in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and remaining bond lengths and angles.

EXAFS.—Measurements were made at the Daresbury Synchrotron Radiation Source, operating at 2 GeV with typical currents of 200 mA. Iodine K-edge data were collected on station 9.2 using a channel-cut silicon 220 monochromator and iron K-edge data on station 7.1 using a silicon 111 order-sorting monochromator. Data were collected in transmission mode from samples diluted with BN and mounted between Sellotape in 1 mm aluminium holders. Data analysis used the programs PAXAS and EXCURVE 92 and was carried out as described elsewhere.[4]

Mössbauer Spectroscopy.—Optimum masses of the periodate samples were calculated as *ca.* 60 mg cm^{-2}. The sample materials were finely ground, mixed with boron nitride to ensure random crystallite orientation and packed into nylon sample holders. Conventional Mössbauer absorption spectroscopy was performed with a double-ramp velocity scan so that folded spectra had a flat background. The spectrometer, using a source of ^{57}Co in Rh of strength *ca.* 50 mCi, was calibrated with a 25 μm foil of β-Fe at room temperature and isomer shift values are quoted relative to α-Fe at 300 K. Spectra were fitted with doublet or sextet components the isomer shifts, quadrupole splittings, linewidth, hyperfine fields and areas of which could be varied or constrained. Unless otherwise stated the parameters of fit in Table 3 have been allowed to vary freely.

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