Synthesis and properties of alkali-metal lithium periodatoferrate(III) and periodatocobaltate(III) complexes

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The pale-yellow $LiMFeIO_6$ (M = K, Rb or Cs) have been prepared by reaction of MIO_4, Li^+ and $[Fe(H_2O)_6]^{3+}$ in hot aqueous solution at pH 9. Olive-green $LiMCoIO_6$ were prepared from MIO_4, Li^+ and $[Co(H_2O)_6]^{2+}$ in hot alkaline solution using ozonised oxygen as oxidant. These insoluble powders have been characterised by analysis, IR and Raman, UV–VIS and EPR spectroscopy and magnetic measurements. PXRD studies revealed that they are amorphous, but structural data have been obtained *via* Fe or Co and I K-edge EXAFS, and are consistent with a layered periodate structure type similar to that found previously in $MM'IO_6$ (M′ = Mn, Ni, Ge, *etc*). ^{57}Fe Mössbauer data are reported for $LiKFeIO_6$.

Orthoperiodate groups, $[IO_6H_{5-n}]^{n-}$ function as strong O-donor ligands towards many metal ions. Two basic types of complexes may be isolated from syntheses in aqueous solution, discrete anions such as $Na_7[Mn\{IO_5(OH)\}_2\{IO_4(OH)_2\}]\cdot 18H_2O$ or $H_3[Co_4I_3O_{18}(OH_2)_6]$, and those containing extended layer structures.[1] The latter type $M[M'IO_6]$ where M is an alkali metal (M ≠ Li) have been characterised with several tetravalent metals (M′ = Mn, Ni, Ge, Sn or Pb).[2–4] They have structures which can be described either as M′ bound to three bidentate periodate $[IO_6]^{5-}$ groups, each periodate binding three M′ ions to form an extended layer, or as a close-packed double layer of oxide ions with M′ and I each filling 1/3 of the octahedral holes within the layer in a regular manner. The alkali metal ions lie between the layers. The radius of M′ is important in the formation of these species since neither Si^{4+} nor Ce^{4+} form similar structures, presumably being too small and too large respectively.[2,5] In principle trivalent ions could form similar compounds with either H^+ or a second M^+ ion balancing the charge. One possible example of this type is $LiKFeIO_6$ reported by Procke and Slouf[6] in 1939 as a complex for the gravimetric determination of lithium. Apart from a brief account of its IR spectrum[7] no characterisation of this complex is available. We have reported elsewhere[8] the characterisation of other iron(III) periodates, $M_n[Fe_4I_3O_{24}H_{15-n}]$ (M = K, Rb or Cs, $n = 4$; M = Na, $n = 5$; M = Li, $n = 6$) which contain an Anderson type polyanion composed of seven edge-linked octahedra. A bis(periodate) $Na_5[Fe(H_2IO_6)_2(OH)_2]$ has been claimed,[9] although we have suggested[8] that this may be a mixture. The cobalt(III) Anderson polyanion $H_3[Co_4I_3O_{18}(OH_2)_6]$ is well characterised[10–12] and a green $Na_5[Co(H_2IO_6)_2(OH)_2]$ of unknown structure has been reported.[10]

Results and Discussion

Iron complexes

Procke and Slouf[6] prepared $LiKFeIO_6$ by adding a solution of a lithium salt to a hot aqueous alkaline solution containing KOH, KIO_4 and $FeCl_3$ under carefully controlled conditions. We found it was easier to add a solution of iron(III) nitrate in water to a hot (95 °C) aqueous alkaline solution containing K^+, Li^+ and $[IO_4]^-$ ions in a 1 : 1 : 1 mol ratio. A fawn-yellow solid precipitated immediately, which was filtered from the hot solution. It is important to keep the pH $\geqslant 9$, otherwise darker materials co-precipitated probably containing the Anderson type anions. Rubidium and caesium salts were prepared similarly, but attempts to isolate a pure sample of $LiNaFeIO_6$ were unsuccessful, analysis and the IR spectrum of the product suggesting substantial contamination with the poorly soluble $Na_3H_2IO_6$. Indeed reaction of $NaIO_4$ with NaOH in hot aqueous solution precipitates either $Na_3H_2IO_6$ or $Na_2H_3IO_6$ depending upon the conditions.[13] Attempts to prepare Li_2FeIO_6 or $BaFeIO_6$ from similar reactions containing appropriate mixtures of ions were unsuccessful.

The $LiMFeIO_6$ complexes (M = K, Rb or Cs) are pale yellow powders, insoluble in water or aqueous alkali but soluble with decomposition in mineral acids. The IR spectra (Table 1) are essentially independent of the alkali metal present, and show the absence of ν(OH), δ(HOH), δ(IOH) modes indicating the complexes are anhydrous and the periodate groups are not protonated. The absence of a feature at *ca.* 840 cm^{-1} also excludes the presence of tetrahedral $[IO_4]^-$ groups.[7,14] The spectra are similar to those of $M[M'IO_6]$[3,15] and thus support the presence of $FeIO_6$ groups. The UV–VIS spectra are also independent of the cation and show a strong very broad

Table 1 Vibrational spectra of $LiMFeIO_6$ and $LiMCoIO_6$ (cm^{-1})[a]

$LiKFeIO_6$[b]	$LiRbFeIO_6$[b]	$LiCsFeIO_6$[b]	$LiKCoIO_6$		$LiRbCoIO_6$		$LiCsCoIO_6$	
IR	IR	IR	IR	Raman	IR	Raman	IR	Raman
760	760	760	780		775		775	
682	680	683	640	682	640	684	645	680
503	505	505	542	497	545	498	541	500
430	433	428	405	423	400	432	400	423
305	301	303	368	349	366	350	368	350w
205	203	200	199	223		224		236

[a]IR as Nujol mulls, Raman powdered solid samples. [b]The iron samples decomposed in the laser beam preventing Raman studies.

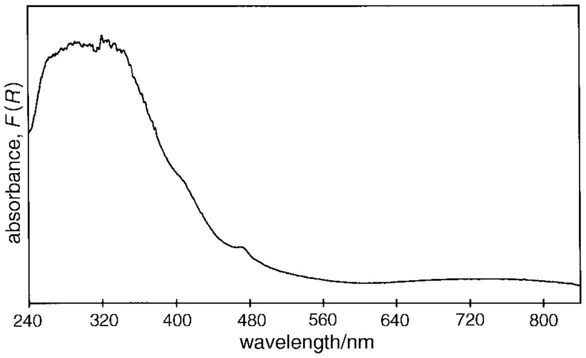

Fig. 1 UV–VIS (diffuse reflectance) spectrum of $LiRbFeIO_6$

absorption over the range 35 000–25 000 cm^{-1}, which is assigned as $IO_6(\pi) \rightarrow Fe(d)$ charge transfer, with very much weaker features at 25 000(sh), 21 300 and 13 900 cm^{-1} assignable as spin-forbidden d–d bands, in O_h symmetry respectively as ${}^6A_{1g} \rightarrow {}^4A_{1g}$, ${}^4E_g$, ${}^6A_{1g} \rightarrow {}^4T_{2g}$, ${}^6A_{1g} \rightarrow {}^4T_{1g}$. A typical example is shown in Fig. 1. The room-temperature magnetic moments ($\mu = 4.95 \pm 0.05\ \mu_B$) are consistent with high-spin d^5 iron(III) although lower than the spin-only formula predicts (5.9 μ_B). Iron(III) oxo species are often not magnetically dilute.[16] The EPR spectra show broad featureless resonances at *g ca.* 2, typical of high-spin Fe^{III}.[17]

The ^{57}Fe Mössbauer spectra of powdered $LiKFeIO_6$ were recorded at 300 and 4.2 K. At both temperatures a doublet was observed with isomer shifts of 0.37 and 0.49 mm s^{-1} respectively, typical[18] of six-coordinate high-spin Fe^{III}. The spectrum at 4.2 K is shown in Fig. 2. The quadrupole splittings (mm s^{-1}) of 0.74 (300 K) and 0.77 (4.2 K) confirm that the iron site has lower than cubic symmetry, consistent with the D_3 environment expected. The spectra were modelled to one and two components, and for the latter, with the abundance ratios varied from 1 : 1 to 1 : 9. Overall the fit to the two sites was better than the single site fit, but the fit was insensitive to the relative abundance of the two components. The very similar parameters of the two sites indicate that the difference is not in the first coordination sphere, but is a more subtle effect and may be due to different alkali metal positions with respect to the iron centres. The 4.2 K spectrum shows magnetic ordering is absent in these complexes, in contrast to the behaviour of the Anderson polyanion,[8] which is magnetically ordered at the low temperature.

Cobalt complexes

Olive-green cobalt(III) complexes $LiMCoIO_6$ (M = K, Rb or Cs) precipitate on slowly adding $[Co(H_2O)_6]^{2+}$ to a hot, dilute, strongly alkaline solution containing Li^+ and MIO_4 through which ozonised oxygen is passed. Ozone was used in preference to other oxidants such as OCl^- or $[S_2O_8]^{2-}$, since these tend to introduce Cl^- or $[SO_4]^{2-}$ impurities. It is essential to add the Co^{II} solution slowly, otherwise oxidation to Co^{III} is incomplete, and the products are distinctly paramagnetic (below) owing to incorporation of Co^{II}. The $LiMCoIO_6$ are completely insoluble in water or alkali, although when freshly prepared they tend to form fine suspensions which are difficult to filter. The previously reported $H_3[Co_4I_3O_{18}(OH_2)_6]$ and $Na_5[Co(H_2IO_6)_2(OH)_2]$ are soluble in aqueous alkali. The only previous mention of a 1 : 1 cobalt(III)–periodate was by Malaprade,[19] who described an impure green material with Co^{III} : I ratio of 1 : 1 but which incorporated variable amounts of Na^+ and Co^{II}.

As in the iron analogues described above, the spectroscopic properties of the $LiMCoIO_6$ (M = K, Rb or Cs) are essentially independent of M, for example the vibrational spectra (Table 1). The diffuse reflectance UV–VIS spectra (Fig. 3 shows a typical example) contain bands at *ca.* 15 750, 27 250(sh) and 36 000 cm^{-1}. The first two bands can be assigned as the d–d transitions of low-spin Co^{III}, ${}^1A_{1g} \rightarrow {}^1T_{1g}$ and ${}^1A_{1g} \rightarrow {}^1T_{2g}$ in O_h symmetry (the actual symmetry cannot be higher than D_3 but no splittings were resolved). The bands occur at similar energies to those in $[Co(H_2O)_6]^{3+}$.[20] Low-spin six-coordinate cobalt(III) complexes are expected to be diamagnetic, possibly with a small contribution from temperature independent paramagnetism.[20] The $LiMCoIO_6$ samples were weakly paramagnetic ($\mu \leqslant 0.7\ \mu_B$) which we attribute to TIP and probably some small amounts of cobalt(II) contamination. The magnetic susceptibility varied slightly from sample to sample, and samples prepared from concentrated solutions or by rapid addition of the $[Co(H_2O)_6]^{2+}$ solution were significantly more paramagnetic ($\mu \geq 1.5\ \mu_B$), no doubt due to co-precipitation of

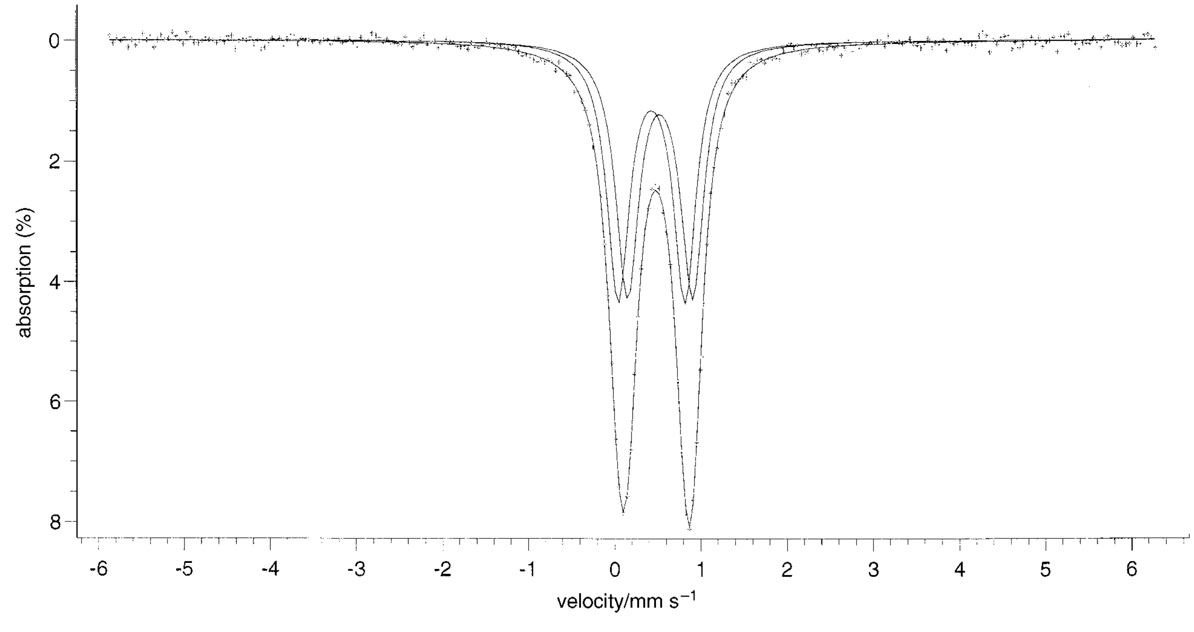

Fig. 2 ^{57}Fe Mössbauer spectrum of $LiKFeIO_6$ at 4.2 K showing the two-site fit with a 1 : 1 ratio of the components

Table 2 EXAFS data[a]

compound	K-edge	d(Fe/Co—O)/Å	$2\sigma^2$/Å^2[b]	d(Fe/Co···I)/Å	$2\sigma^2$/Å^2	d(I—O)/Å	$2\sigma^2$/Å^2	d(Fe···Fe) or d(I···I)/Å	$2\sigma^2$/Å^2
LiKFeIO$_6$[c]	Fe	2.008(3)	0.0075(6)	2.999(2)	0.0044(2)			5.187(14)	0.0157(30)
[d]	I			3.006(3)	0.0078(4)	1.877(2)	0.0056(2)	5.194(10)	0.0098(10)
LiRbFeIO$_6$[e]	Fe	2.019(3)	0.0080(5)	3.011(2)	0.0061(2)			5.208(15)	0.0196(34)
[f]	I			3.008(3)	0.0075(5)	1.878(2)	0.0047(3)	5.212(8)	0.0116(12)
LiCsFeIO$_6$[g]	Fe	2.017(3)	0.0066(6)	3.010(2)	0.0064(3)				
[h]	I			3.006(3)	0.0078(4)	1.877(2)	0.0056(2)	5.195(6)	0.0096(10)
LiKCoIO$_6$[i]	Co	1.873(3)	0.0095(5)	2.932(2)	0.0066(3)				
[j]	I			2.951(2)	0.0073(3)	1.854(2)	0.0110(3)		
LiRbCoIO$_6$[k]	Co	1.871(3)	0.0077(5)	2.930(3)	0.0055(3)				
[l]	I			2.946(2)	0.0057(3)	1.848(3)	0.0135(5)		
LiCsCoIO$_6$[m]	Co	1.863(3)	0.0126(5)	2.916(2)	0.0080(3)				
[n]	I			2.943(2)	0.0062(3)	1.851(3)	0.0130(4)		

[a]Systematic errors in data collection and analysis result in bond lengths reliable to ±0.02 Å, standard deviations on the data listed above reflect statistical errors in the fitting. [b]Debye–Waller factor. [c]$R=25.2\%$. [d]$R=19.7\%$. [e]$R=19.1\%$. [f]$R=24.7\%$. [g]$R=30.4\%$. [h]$R=18.6\%$. [i]$R=26.2\%$. [j]$R=20.6\%$. [k]$R=27.6\%$. [l]$R=25.5\%$. [m]$R=24.9\%$. [n]$R=24.4\%$. R factor defined as $[\int(\chi^T-\chi^E)k^3\mathrm{d}k/\int\chi^E k^3\mathrm{d}k]\times 100\%$.

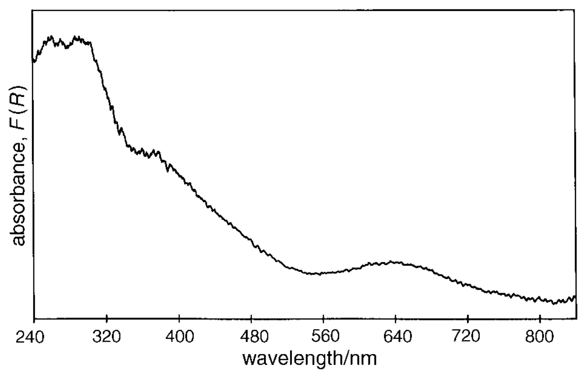

Fig. 3 UV–VIS (diffuse reflectance) spectrum of LiCsFeIO$_6$

cobalt(II). The isoelectronic MNiIO$_6$ are also weakly paramagnetic,[3] owing to lower oxidation state impurities. The ^{7}Li MAS NMR spectrum of KLiCoIO$_6$ showed a single resonance at δ 0.4 (relative to $[\mathrm{Li(H_2O)_4}]^+$) showing the compound contains a single lithium site. Although the lithium chemical shift range is very small (*ca.* 10 ppm),[21] the very similar shift to the $[\mathrm{Li(H_2O)_4}]^+$ reference probably indicates that lithium occupies a tetrahedral site. Since larger alkali metals will prefer an octahedral site, this probably explains the specificity of these systems for lithium. However in the absence of crystallographic data this cannot be confirmed.

EXAFS Data

PXRD showed that all the LiMFeIO$_6$ and LiMCoIO$_6$ samples obtained were amorphous, and attempts to obtain crystalline samples by, for example, prolonged heating of the reaction mixtures have been unsuccessful. However based upon the spectroscopic evidence of IO$_6$ and FeO$_6$/CoO$_6$ groups, iron or cobalt and iodine K-edge EXAFS (extended X-ray absorption fine structure) spectroscopy has been used to provide some structural information. EXAFS in combination with PXRD has been previously applied to the study of M[M′IO$_6$] compounds.[1–4] The structural information obtained from both the iron/cobalt and iodine edge data are independent of the alkali metal present (Table 2), and only one example needs to be discussed in each case. Refinement of the iron edge data on LiRbFeIO$_6$ (Fig. 4) shows a shell of six oxygens at 2.02 Å, a second shell of three iodines at 3.01 Å, and a further feature at 5.21 Å is tentatively attributed to the Fe···Fe repeat distance. The iodine-edge data show six oxygens at 1.88 Å and three irons at 3.01 Å, and d(I···I) at 5.21 Å. For LiKCoIO$_6$ the Co K-edge EXAFS data were fitted to a first shell of six oxygens at 1.87 Å and a second shell of three iodines at 2.93 Å. The iodine K-edge data on the same complex placed d(I—O) at 1.85 Å and d(Co···I) at 2.95 Å, the latter in good agreement with the same distance determined from the cobalt-edge data. In contrast to the iron complexes, neither the cobalt- nor the iodine-edge data on LiMCoIO$_6$ showed significant features at *ca.* 5 Å which would correspond to the repeat distance within the layers.

These data provide strong support for the presence of the layered structure proposed (Fig. 5) and may be compared with the data on K[NiIO$_6$] [d(Ni—O) = 1.87 Å, d(Ni···I) = 2.86 Å][3] and K[MnIO$_6$] [d(Mn—O) = 1.89 Å, d(Mn···I) = 2.89 Å].[4] The difference in the d(M—O) distances correlate well with the ionic radii of the transition metal [$\mathrm{Fe^{3+}}$ (high spin) 0.65 Å, $\mathrm{Co^{3+}}$ (low spin) 0.55 Å, $\mathrm{Ni^{4+}}$ 0.54 Å and $\mathrm{Mn^{4+}}$ 0.58 Å].[22] The d(Fe—O) and d(Co—O) are also in excellent agreement with those found in $\mathrm{M_n[Fe_4I_3O_{24}H_{15-n}]}$ (1.97–1.99 Å)[8] and $\mathrm{H_3[Co_4I_3O_{24}H_{12}]}$ (1.88–1.92 Å).[11,12] The absence of any dependence of the EXAFS data on the alkali metal is also a characteristic of this structure type.[2]

Other compounds

Attempts were made to incorporate other trivalent 3d transition-metal ions. Ozonisation of a hot alkaline solution containing $\mathrm{Li^+}$, $\mathrm{KIO_4}$ and $[\mathrm{Ni(H_2O)_6}]^{2+}$ did not lead to any oxidation of the nickel, whilst heating a weakly acid solution containing the same ions with peroxodisulfate, $\mathrm{K_2S_2O_8}$, slowly produced a black precipitate. The latter was identified as the known nickel(IV) complex KNiIO$_6$.[3] Similarly warming a weakly acidic solution containing $\mathrm{Li^+}$, $\mathrm{KIO_4}$ and $[\mathrm{Mn(H_2O)_6}]^{2+}$ produced the known red manganese(IV) complex KMnIO$_6$.[4] Addition of a solution of $[\mathrm{Cr(H_2O)_6}]^{3+}$ to a warm alkaline solution containing $\mathrm{Li^+}$ and $\mathrm{KIO_4}$ rapidly gave a deep yellow solution, identified as containing $[\mathrm{CrO_4}]^{2-}$ by its UV–VIS spectrum. As discussed previously,[1] periodate appears to favour one oxidation state of each metal which is surprising in comparison to similar π donors like oxide or halide which form stable compounds with a range of oxidation states of most transition metals.

Conclusion

The compounds LiMFeIO$_6$ and LiMCoIO$_6$ have been isolated and characterised. The structures are related to those of MM′IO$_6$, but with a trivalent metal and Li instead of a tetravalent M′. These are the first examples of this type of compound to incorporate a trivalent metal. Attempts to form analogues with $\mathrm{Cr^{3+}}$, $\mathrm{Ni^{3+}}$ or $\mathrm{Mn^{3+}}$ have failed.

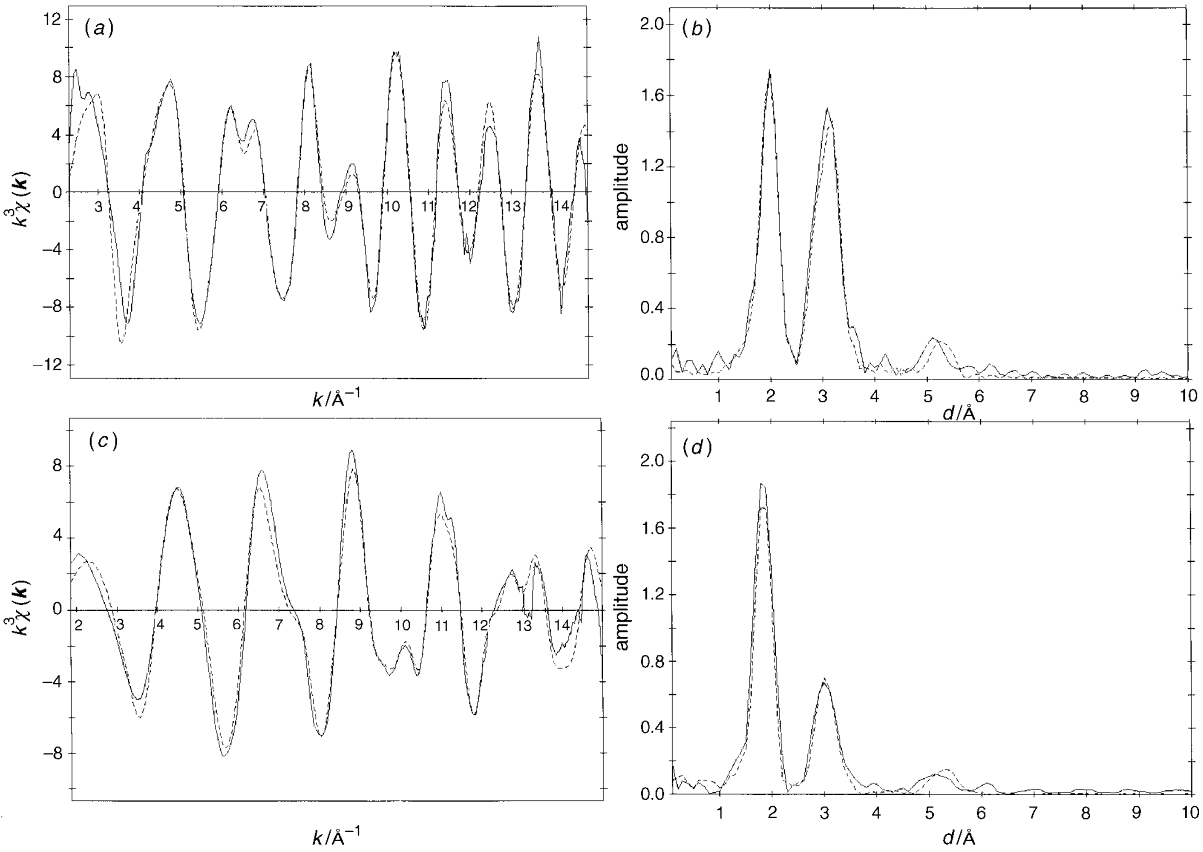

Fig. 4 (*a*) Background subtracted Fe K-edge EXAFS and (*b*) corresponding Fourier transform of $LiRbFeIO_6$, and (*c*) background subtracted iodine K-edge EXAFS and (*d*) corresponding Fourier transform of $LiKFeIO_6$ (broken line theoretical fit, full line experimental data)

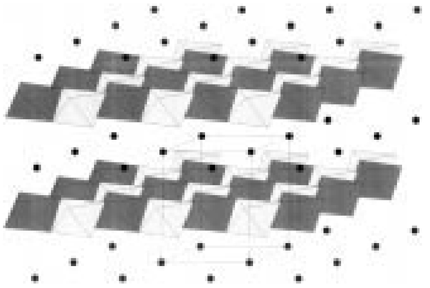

Fig. 5 Proposed structure of $LiMFeIO_6$ showing the IO_6 and $Fe(Co)O_6$ octahedra and M ions as spheres. The Li ions are not shown.

Experimental

EXAFS measurements were made at the Daresbury Synchrotron Radiation Source on stations 7.1 and 9.2 and 9.3, data being collected from powdered samples at room temperature in transmission mode. Details of the data collection and analysis were similar to those described previously.[2,4] The compounds KIO_4 and the Anderson polyanions[2,8] were used as model compounds to check the EXAFS data collection and treatment. The coordination numbers of the shells were fixed, but all other parameters were refined. ^7Li MAS NMR spectra were obtained from powdered samples in a silicon nitride rotor, using a Bruker AM300 instrument at 116.65 MHz with spinning speeds of 4.5 and 6.2 KHz. The pulse was 1 μs and the relaxation delay 0.25 s, typically 200 transients being collected. The reference was aqueous 1 mol dm^{-3} LiCl. Other physical measurements were made as described previously.[2,3,8]

$LiKFeIO_6$

Potassium periodate, KIO_4 (2.3 g, 1 mmol), $LiNO_3$ (0.69 g, 1 mmol) and KOH (1.1 g, 1 mmol) were dissolved in water (200 cm^3) and the mixture heated with stirring to 95 °C. The pH was adjusted to 9 if necessary by addition of more KOH, and then a solution of $Fe(NO_3)_3{\cdot}9H_2O$ (4.0 g, 1 mmol) in water (25 cm^3) added dropwise. During this process the pH was monitored, more KOH being added as required to keep the pH $\geqslant 9$. An immediate fawn precipitate appeared, and the mixture was stirred at 95 °C for 30 min. The solution was filtered hot (G4 sinter), and the yellow solid washed with cold water (3×25 cm^3) and dried, first *in vacuo*, and then in air at 100 °C overnight. Yield *ca.* 3.0 g, 92%. Analysis: Found: Li, 2.0; Fe, 17.4; I, 39.6; K, 11.8. $LiKFeIO_6$ requires Li, 2.1; Fe, 17.2; I, 39.1; K, 12.0%. $LiRbFeIO_6$ and $LiCsFeIO_6$ were made similarly. Analysis: $LiRbFeIO_6$: Found: Li, 1.8, Fe, 15.2; I, 34.5. $LiRbFeIO_6$ requires Li, 1.9; Fe, 15.0; I, 34.2%. $LiCsFeIO_6$: Found: Li, 1.7; Fe, 13.5; I, 31.4. $LiCsFeIO_6$ requires Li, 1.7; Fe, 13.3; I, 30.3%.

$LiKCoIO_6$

Potassium periodate, KIO_4 (2.3 g, 1 mmol), $LiNO_3$ (0.69 g, 1 mmol) and KOH (1.1 g, 1 mmol) were dissolved in water (200 cm^3), the mixture heated with stirring to 80 °C, and a fast stream of ozonised oxygen (*ca.* 3% O_3 by volume) bubbled through it. The pH was adjusted to 9 if necessary by addition of more KOH, and then a solution of $Co(NO_3)_2{\cdot}7H_2O$ (3.8 g, 1 mmol) in water (100 cm^3) added slowly dropwise. During this process the pH was monitored, more KOH being added if required to keep the pH $\geqslant 9$. A deep green precipitate formed rapidly, and the mixture was stirred at 80 °C for 30 min maintaining the flow of ozone. The solution was filtered hot (G4 sinter), and the olive-green solid washed with hot water (3×25 cm^3) and dried *in vacuo* for 48 h. Yield *ca.* 2.6 g, 80%. Analysis: Found: Li, 2.0; Co, 18.2; I, 39.0; K, 11.5. $LiKCoIO_6$ requires Li, 2.1; Co, 18.0; I, 38.7; K, 11.9%. $LiRbCoIO_6$ and $LiCsCoIO_6$ were made similarly. Analysis: $LiRbCoIO_6$: Found: Li, 1.9; Co, 15.6; I, 33.4; $LiRbCoIO_6$ requires Li, 1.8; Co, 15.7; I, 33.9%. $LiCsCoIO_6$: Found: Li, 1.5; Co, 14.2; I, 29.8. $LiCsCoIO_6$ requires Li, 1.6; Co, 14.0; I, 30.1%.

We thank the EPSRC for support and the Director of the Daresbury Laboratory for provision of facilities for the EXAFS studies. We are grateful to Dr E. G. Hope for collection of some of the iodine edge EXAFS data, Dr S. E. Dann for the ^{7}Li NMR spectra and Mr A. J. Brookes for running Raman spectra.

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Paper 7/03445H; *Received* 19*th May*, 1997