Synthesis, Spectroscopic and Structural Studies of Alkali Metal–Nickel Periodates $MNiIO_6$ (M = Na, K, Rb, Cs or NH_4) *

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The dark red-purple nickel(IV) periodates $MNiIO_6$ (M = Na, K, Rb, Cs or NH_4) have been prepared by peroxohexaoxodisulfate oxidation of mixtures of nickel(II) salts, MNO_3 and periodate ions in hot aqueous solution. Powder X-ray diffraction studies showed that the structures adopted the space group *P*312, with hexagonal close-packed layers of oxide ions. One-third of the octahedral holes in every second layer contained M ions, and in the other layers one-third of the octahedral holes contained I and one-third Ni. The Ni–O, I–O, Ni ⋯ I and Ni ⋯ Ni distances have been determined by a combination of nickel and iodine K-edge extended X-ray absorption fine structure (EXAFS) data. IR, Raman and UV/VIS spectroscopic data for $MNiIO_6$ were obtained. Iodine K-edge EXAFS data have also been obtained for the related periodates $M'M''IO_6$ (M′ = K or Rb; M″ = Ge, Sn, Pb or Mn).

A variety of metal ions may be incorporated into mixed-metal periodates of the type $M'MIO_6{\cdot}nH_2O$ (M′ = Na, K, Rb, Cs or NH_4; M = tetravalent metal ion including Ge,[1,2] Sn,[2,3] Pb[2,4] or Mn[5]). All of these contain double layers of close-packed oxide ions with one-third of the octahedral holes occupied by I, and one-third by M^{IV}, with the alkali metal occupying one-third of the octahedral holes between the layers. Two complexes of similar formula, $NaNiIO_6{\cdot}0.5H_2O$ and $KNiIO_6{\cdot}0.5H_2O$ have been reported,[6–8] but although formulated as nickel(IV) complexes, their properties suggest some nickel(III) is present. In a continuation of our studies of metal periodate complexes[2,5,9] we report here new examples of these complexes, and detailed structural and spectroscopic data. A bis(periodato)nickelate(IV) complex has also been reported.[10,11]

Experimental

The complexes were made by the same general method exemplified below. The samples were stored at −20 °C in the dark, and measurements were made on freshly prepared samples except where indicated otherwise.

Preparation of $NaNiIO_6$.—Nickel(II) sulfate heptahydrate (2.0 g, 7.1 mmol) was dissolved in distilled water (200 cm^3) and treated with sodium periodate ($Na_3H_2IO_6$, 5.0 g, 17 mmol) and dilute sulfuric acid (0.5 cm^3, 1 mol dm^{-3}), and the mixture heated to *ca.* 80 °C, more water being added if necessary to completely dissolve the periodate. Disodium μ-peroxo-hexaoxodisulfate(2−) (8.0 g, 34 mmol) was added in small portions to the hot solution, which slowly darkened in colour. A fine black solid slowly separated, and after *ca.* 4 h the solution was cooled and allowed to stand overnight. The precipitate was filtered off, rinsed with hot dilute disodium μ-peroxo-hexaoxodisulfate(2−) solution, and with a small quantity of hot water, and dried *in vacuo*. Yields are rather variable, but typically 40–50% on Ni (Found: I, 41.0; Na, 7.6; Ni, 19.7. $INaNiO_6$ requires I, 41.7; Na, 7.55; Ni, 19.3%).

The periodates $MNiIO_6$ (M = K, Rb or Cs) were made similarly from MIO_4 (instead of $M_3H_2IO_6$) and $K_2S_2O_8$ (M = K) or $(NH_4)_2S_2O_8$ (M = Rb or Cs) as oxidant (Found: I, 39.1; K, 12.2; Ni, 18.2. $IKNiO_6$ requires I, 39.6; K, 12.2; Ni, 18.3. Found: I, 34.7; Ni, 15.7; Rb, 23.1. $INiO_6Rb$ requires I, 34.6; Ni, 16.0; Rb, 23.3. Found: Cs, 31.8; I, 30.3; Ni, 14.1. $CsINiO_6$ requires Cs, 32.0; I, 30.6; Ni, 14.2%).

The ammonium salt was more difficult to obtain pure, but was made using NH_4IO_4, $(NH_4)_2S_2O_8$ and the nickel(II) salt (Found: I, 43.0; N, 4.6; Ni, 19.5. H_4INNiO_6 requires I, 42.35; N, 4.7; Ni, 19.6%). The analyses were performed by dissolving known weights of the compounds in dilute sulfuric acid (2 mol dm^{-3}) saturated with SO_2. Alkali metals were determined by atomic absorption or emission, iodine gravimetrically as AgI, and nickel spectrophotometrically (445 nm) as the nickel dimethylglyoxime bromine complex.

Energy-dispersive X-ray (EDX) data were obtained using a JEOL JSM6400 scanning electron microscope operating with a 20 keV (*ca.* 3.2 × 10^{-15} J) electron energy, and fitted with a Tracor Northern series 2 X-ray and image analyser. Raman spectra were measured from powdered samples using a Perkin-Elmer PE 1700 FTIR instrument fitted with a Fourier-transform Raman adaptor, and using a Nd–YAG laser (9396 cm^{-1}). IR spectra were obtained from Nujol-mulled samples on a Perkin-Elmer 983G spectrometer and UV/VIS spectra from samples diluted with $BaSO_4$ using the diffuse-reflectance attachment of a Perkin-Elmer Lambda 19 spectrometer. Powder X-ray diffraction data were collected using a Siemens D5000 θ–2θ diffractometer employing Cu-Kα₁ radiation (1.5406 Å). Extended X-ray absorption fine structure (EXAFS) spectroscopic measurements were made at the Daresbury Synchrotron Radiation Source. Nickel K-edge and iodine L_{III}-edge data were obtained on station 7.1 using an order-sorting silicon(111) monochromator, and iodine K-edge data on station 9.2 using a channel-cut silicon(220) monochromator. Data were collected in transmission mode from samples diluted with boron nitride and mounted between Sellotape in 1 mm aluminium holders. Data analyses used the programs PAXAS[12a] and EXCURVE 92,[12b] and were carried out as described previously. For the iodine-edge studies KIO_4 was used as a model compound, and the EXAFS data refined to give *d*(I–O) = 1.77 Å compared with the X-ray crystallographic bond length of 1.775 Å.

Results and Discussion

The periodates $MNiIO_6$ (M = Na or K) were made by oxidising a mixture of a nickel(II) salt (nitrate or sulfate are both suitable), $Na_3H_2IO_6$ or KIO_4 in hot (80 °C) mildly acidic aqueous solution with the appropriate peroxohexaoxodisulfate

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* *Non-SI unit employed:* $\mu_B \approx 9.274 \times 10^{-24}$ J T^{-1}.

$M_2S_2O_8$. The compounds do not form in strongly acid solution. The new rubidium and caesium analogues were made similarly using the appropriate peroxohexaoxodisulfate, or $(NH_4)_2S_2O_8$ in the presence of $M'IO_4$ ($M' = Rb$ or Cs). An attempt to make the lithium salt, using $LiNO_3$ and $(NH_4)_2S_2O_8$ resulted only in NH_4NiIO_6, which was best obtained using $(NH_4)_2S_2O_8$ and NH_4NO_3. Attempts to incorporate NR_4^+ (R = alkyl) cations were unsuccessful. The $NaNiIO_6$ complex was also made at ambient temperatures by passing ozonised oxygen (*ca.* 3% ozone) through an aqueous solution of $NaIO_4$ and nickel(II) nitrate. All the $MNiIO_6$ are dark red-purple powders insoluble in water, dilute acids or alkalis. Several batches of the compounds were prepared during the course of this study. Some samples were analysed by conventional wet methods (Experimental section), but since these required relatively large amounts of sample, EDX was routinely used to check the heavy-atom ratios. The M:Ni:I ratios were found to be invariant (1:1:1) within experimental error. Although previously formulated [6,7] as containing some water, the 'water' content was determined only by difference, and our IR spectra show no evidence for significant amounts of water. It is possible that in some samples small amounts of water are trapped in vacant sites in the lattice, but are not essential constituents. The samples decompose slowly at room temperature and more rapidly on gentle heating, or on treatment with boiling water. The decomposition is not evident on visual inspection, but is readily detected spectroscopically (see below). Measurements were made on fresh samples which had been stored in the dark at −20 °C until required.

Vibrational Spectra.—The IR and Raman spectra of the compounds are listed in Table 1 and Fig. 1 shows typical examples. The spectra show only small shifts with change of cation, and although specific assignment of the bands does not seem possible, it is clear that the features are mostly vibrations of the IO_6 and NiO_6 octahedra.[2,13] The higher frequency regions of the IR spectra showed the absence of other than traces of water, and despite careful examination no weak bands in the region 1000–1200 cm^{-1} corresponding to δ(IOH) modes [14] were found, indicating that the periodate groups are not protonated in these compounds.

UV/VIS Spectra.—All the compounds appear black in bulk, and dark red-purple in thin films. The diffuse reflectance spectra of freshly prepared samples are characterised by a broad feature of rather ill-defined maximum at *ca.* 540 nm (18 500 cm^{-1}); Fig. 2 shows a typical example. For a low-spin d^6 nickel(IV) centre, the first spin-allowed d–d transition in O_h symmetry is $^1A_{1g} \longrightarrow {}^1T_{1g}$. In the present complexes the metal-centre symmetry is D_3 which will cause splitting of the band into $^1A_1 \longrightarrow {}^1E$ and $^1A_1 \longrightarrow {}^1A_2$, although separate transitions were not resolved. The energy of the transition is very similar to that observed [15] in the nonamolybdonickelate(IV) anion $[NiMo_9O_{32}]^{6-}$ which contains a distorted NiO_6 octahedron ($E_{max} = 17\,600\ cm^{-1}$). Further ill-defined absorptions to higher energy may be due to $O(\pi) \longrightarrow Ni(e_g)$ charge transfer, and to internal transitions of the hexaoxoiodate(5−) group.[2]

Magnetism and ESR Spectra.—The freshly prepared $MNiIO_6$ compounds were reported to be weakly paramagnetic [6,7] with magnetic moments *ca.* 1 μ_B. Our samples had magnetic moments in the range 0.7–1.1 μ_B which varied slightly from sample to sample. Low-spin nickel(IV) complexes should [16] have diamagnetic ground states with perhaps a small temperature-independent component of $\leqslant 0.5\ \mu_B$, and the higher values observed and their variation from sample to sample are probably due to nickel(II) or nickel(III) impurities.

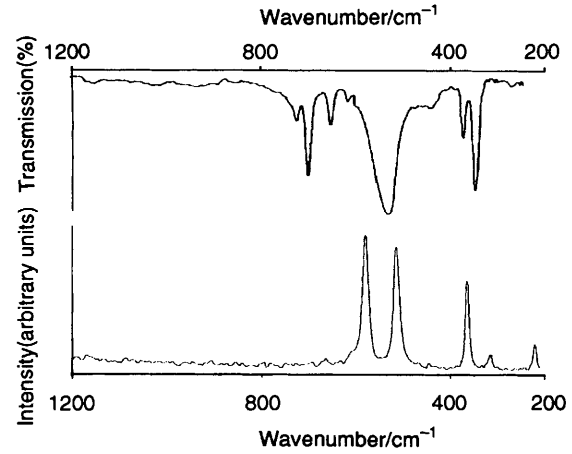

Fig. 1 IR (upper) and Raman (lower) spectra of $KNiIO_6$

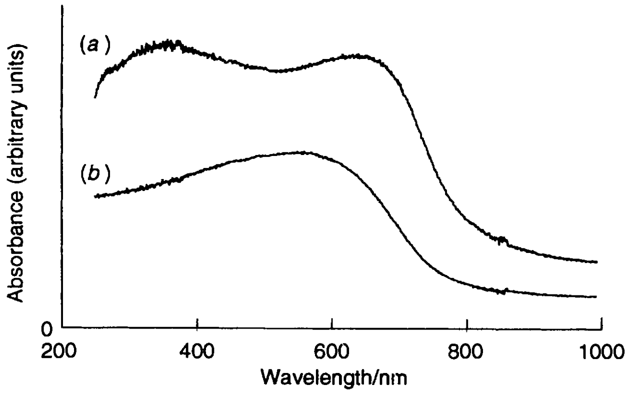

Fig. 2 Diffuse reflectance spectra of $NaNiIO_6$; (*a*) sample after 12 months storage and (*b*) freshly prepared

Table 1 IR and Raman data (wavenumber/cm^{-1})* for $MNiIO_6$

$NaNiIO_6$		$KNiIO_6$		$RbNiIO_6$		$CsNiIO_6$		NH_4NiIO_6	
IR	Raman	IR	Raman	IR	Raman	IR	Raman	IR	Raman
702		696		693		687		692	
653		647		647		643	655w	647	
	586		582		588		578		582
532		528		524		514		524	
	523		516		512		508		516
374	374	368	368	367	365	365	363	368	367
344		342		342		339		341	
	322		320		317		315		318
278		268		271					
235	237	224	225	222	223	221	222	221	224

* IR spectra from Nujol mulls, Raman spectra from powdered samples.

All samples of $NaNiIO_6$ exhibited weak ESR signals at room temperature, consisting of a single broad isotropic feature at $g = 2.18$. The ESR spectra obtained from $KNiIO_6$ were similar, although very weak, but the NH_4, rubidium and caesium salts were ESR silent when freshly prepared. On cooling the sodium and potassium salts to 77 K the spectra develop the characteristic features of a rhombic d^7 spectrum.[7] The spectra are consistent with the presence of very small amounts of low-spin d^7 nickel(III) in the sodium and potassium salts, but apparently not in the other three examples. Weak ESR signals were found in old samples of all the compounds.

Powder X-Ray Diffraction Spectra.—Examination of the powder X-ray diffraction patterns did not indicate the presence of impurity phases, but did show a variation in crystallinity and *hkl*-dependent peak broadening. That is, samples exhibited significantly larger peakwidths and anisotropic broadening of the 00*l* diffraction lines. This is clearly a manifestation of the particle size and shape or an indication of disorder along the *c* direction.

As has been peviously described[8] and investigated by us,[2] mixed-metal periodates with layered structures can exist in two space groups, *P*312 and *P*6$_3$22. Both contain ordering of the M^{IV} and I ions within the oxide layers, but the latter has further ordering between the stacked oxide layers and a subsequent doubling of the *c* axis. In order to assess which structure was adopted by the nickel system, high quality data sets were collected over a period of approximately 1000 min on the potassium and rubidium samples and Rietveld profile refinements, using DBW9006pc software,[17] were attempted for both structural models. Incorrect peak-position assignment in the *P*6$_3$22 model clearly indicated that the *P*312 space group was preferred and this structure, with no ordering of the Ni and I ions along the *c* axis was deemed to be correct. Cell parameters for all samples could now be determined and showed *a* and *c* to increase linearly with the size of the M ion (Fig. 3); the *c* parameter clearly increases quite markedly as the Ni–I–O layers are separated by the M ions, the *a* parameter showing a comparatively small increase.

Previous attempts[2] to refine the oxygen position, and thus the difference in magnitude between the I–O and M^{IV}–O bonds, have shown that powder X-ray diffraction is not the most useful technique for such differentiation. In this structure the oxygen position is a 6*l*, *x,y,z* site. The *x*- and *z*-coordinates refined smoothly to approximate values of 0.6 and 0.4 respectively, but the *y* coordinate refined to within an estimated standard deviation of zero. This implies that the Ni–O and I–O bond distances are identical, a description which is not chemically sensible and which stems from the two-dimensional nature of powder X-ray diffraction data and the coincidence of *h*0*l* and 0*kl* diffraction lines. The Rietveld refinement did, however, provide a close starting model for the EXAFS data analysis.

EXAFS Studies.—The nickel K-edge EXAFS data were recorded for several samples of the five nickel periodate complexes, and typical results are listed in Table 2. The results from different samples were consistent within experimental error. The data treatment was carried out as described previously[3,5] with the co-ordination numbers fixed as required by the lattice type. As expected from the layer structures, the Ni–O distances at *ca.* 1.87 Å and the *d*(Ni ··· I) separations at *ca.* 2.86 Å, are independent of the monovalent cation present, within the usual precision of *ca.* ± 0.02–0.03 Å. The unit-cell *a* parameters, as measured by the *d*(Ni ··· Ni) separation were established as *ca.* 4.97 Å, in good agreement with the values determined by powder diffraction.

Initially we recorded iodine L_{III}-edge data (*cf.* ref. 2), which although of limited accuracy due to the short data sets resulting from the proximity of the L_{II}-edge, placed the *d*(I–O) at *ca.* 1.84 Å. However, using a different monochromator, we were subsequently able to obtain iodine K-edge data out to $k = 15$ Å^{-1}, and this more reliable data (Table 2) gave *d*(I–O) as *ca.* 1.86 Å and *d*(Ni ··· I) and unit-cell *a* parameters in excellent agreement with those determined from the nickel K-edge data. Typical examples of the background-subtracted EXAFS and their Fourier transforms are shown in Fig. 4. We also recorded iodine K-edge data for related periodato compounds $M'M''IO_6$ (M′ = K or Rb; M″ = Ge, Sn, Pb or Mn) which complement our previous EXAFS and powder diffraction studies.[2,5] For the two tin compounds the tin K-edge data were obtained. The results of these studies are summarised in Table 3.

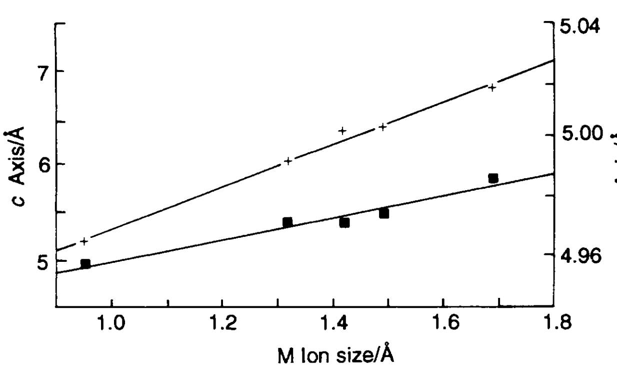

Fig. 3 Cell parameters, *a* (■) and *c* (+), for $MNiIO_6$

Decomposition.—The samples of $MNiIO_6$ decompose slowly at room temperature. Diffuse reflectance spectra of old samples ('old' meaning 3–12 months after preparation) show the maximum of the first absorption band, initially *ca.* 540 nm, shifts progressively to lower energy to *ca.* 590–640 nm. However, powder diffraction and Ni K-edge EXAFS data on 'old' samples show that no pronounced change in the structures has occurred. In the EXAFS data treatment, attempts to split the Ni–O shells into two to allow for different nickel environments failed, two-shell models producing small and erratic changes in the f.i. and *R* factors, and with high correlations between the shells. The shells merged on iteration. This behaviour may be due to the progressive formation of mixed-valence materials with the same basic lattice structure, the lower energy transitions corresponding to an intervalance charge-transfer band. Further studies are required to clarify the nature of these aged samples.

Partial decomposition of the compounds also occurs in boiling in water, with the formation of alkali-metal periodate and iodate, and a black residue. A previous study[7] indicated that $KNiIO_6$ decomposed on heating to form a green product identified as $K_2Ni^{II}{}_2I^{VI}{}_2O_9$. We confirm that a light green product is formed on heating to *ca.* 500 °C, but powder diffraction data and the IR spectrum show the presence of KIO_3 and KIO_4. The diffuse reflectance spectrum is consistent with octahedral nickel(II), but the form present was not identified; the powder pattern did not correspond to that of NiO. Reduction occurred even on heating under high pressure oxygen. Thus, $CsNiIO_6$ decomposed at 450 °C, 480 atmospheres (48 636 kPa), to form a grey-green solid, which contained $CsIO_3$ and other unidentified products.

Conclusion

These studies have shown that the uncommon nickel(IV) oxidation state is readily stabilised by periodate ligands in these layer structures. The value of combining powder X-ray diffraction and multi-edge EXAFS spectroscopy to obtain detailed structural characterisation of materials not obtainable as single crystals is clearly demonstrated. The compounds are very similar to those of other tetravalent metals including Ge, Sn, Pb and Mn, which might suggest that other M^{IV} ions of similar size could be incorporated. However our attempts to prepare Co^{IV} or Fe^{IV} compounds have been unsuccessful. We

Table 2 Nickel and iodine K-edge EXAFS data for $MNiIO_6$

Compound[a]	d(Ni–O)[b]/Å	$2\sigma^{2c}$/Å^2	d(I–O)/Å	$2\sigma^2$/Å^2	d(Ni···I)/Å	$2\sigma^2$/Å^2	d^d/Å	$2\sigma^2$/Å^2	F.i.[e]	R^f
$NaNiIO_6$	1.863(2)	0.0025(2)			2.863(1)	0.0034(1)	4.969(5)	0.0084(10)	2.6	21.3
			1.868(1)	0.0024(2)	2.849(1)	0.0025(2)	4.950(6)	0.0114(9)	2.0	16.3
$KNiIO_6$	1.873(2)	0.0029(3)			2.876(1)	0.0029(2)	4.985(7)	0.0100(14)	3.2	22.0
			1.862(2)	0.0022(3)	2.849(2)	0.0019(3)	4.957(8)	0.0108(13)	4.1	22.2
$RbNiIO_6$	1.869(2)	0.0070(3)			2.867(1)	0.0058(2)	4.964(9)	0.0153(17)	3.0	21.8
			1.869(2)	0.0014(2)	2.859(2)	0.0032(3)	4.955(7)	0.0107(12)	2.3	15.1
$CsNiIO_6$	1.875(2)	0.0055(3)			2.874(1)	0.0048(2)	4.990(8)	0.0133(15)	3.0	21.7
			1.860(2)	0.0017(2)	2.859(2)	0.0035(3)	4.939(7)	0.0113(12)	3.1	19.1
NH_4NiIO_6	1.867(2)	0.0075(4)			2.870(2)	0.0053(2)	4.964(7)	0.0123(13)	3.2	21.8
			1.830(3)	0.0025(4)	2.880(4)	0.0051(7)			8.3	24.1

[a] For each compound the first line reports nickel and the second iodine K-edge data. Standard deviations are given in parentheses. [b] The systematic errors in the bond distances arising from the data collection and analysis procedures are *ca.* ± 0.02–0.03 Å for well defined co-ordination shells, and ± 0.04 Å for more remote shells. [c] Debye–Waller factor. [d] Repeat distance within the layers. [e] Fit index defined as $\Sigma_i[(\chi^T - \chi^E)k_i^3]^2$. [f] R defined as $[\int(\chi^T - \chi^E)k^3dk/\int\chi^E k^3dk] \times 100\%$.

Table 3 Iodine and tin K-edge EXAFS data for other $MM'IO_6$ compounds

Compound	K-edge (X)	d(X–O)[a]/Å	$2\sigma^{2a}$/Å^2	d(M'···X)/Å	$2\sigma^2$/Å^2	F.i.[a]	R^a
$KMnIO_6$	I	1.861(2)	0.0042(2)	2.886(2)[b]	0.0043(3)	3.3	18.9
$KGeIO_6$	I	1.862(3)	0.0016(3)	2.877(3)[c]	0.0014(3)	6.8	26.3
$RbGeIO_6$	I	1.867(2)	0.0015(2)	2.879(2)[c]	0.0017(2)	3.9	21.3
$KSnIO_6$	I	1.865(2)	0.0015(2)	3.043(3)	0.0076(4)	4.2	20.9
$RbSnIO_6$	I	1.863(2)	0.0016(2)	3.035(2)	0.0039(3)	3.1	17.1
$KPbIO_6$	I	1.866(2)	0.0030(3)	3.116(2)[d]	0.0020(2)	4.5	22.0
$KSnIO_6$	Sn	2.048(3)	0.0057(4)	3.064(3)	0.0105(4)	7.8	27.3
$RbSnIO_6$	Sn	2.051(3)	0.0046(4)	3.056(2)	0.0039(2)	6.5	23.0

[a] Systematic errors and definitions as in Table 2. [b] 2.89 Å from manganese K-edge data, ref. 5. [c] 2.90 Å from germanium K-edge data, ref. 3. [d] 3.13 Å from lead L_{III}-edge data, ref. 3.

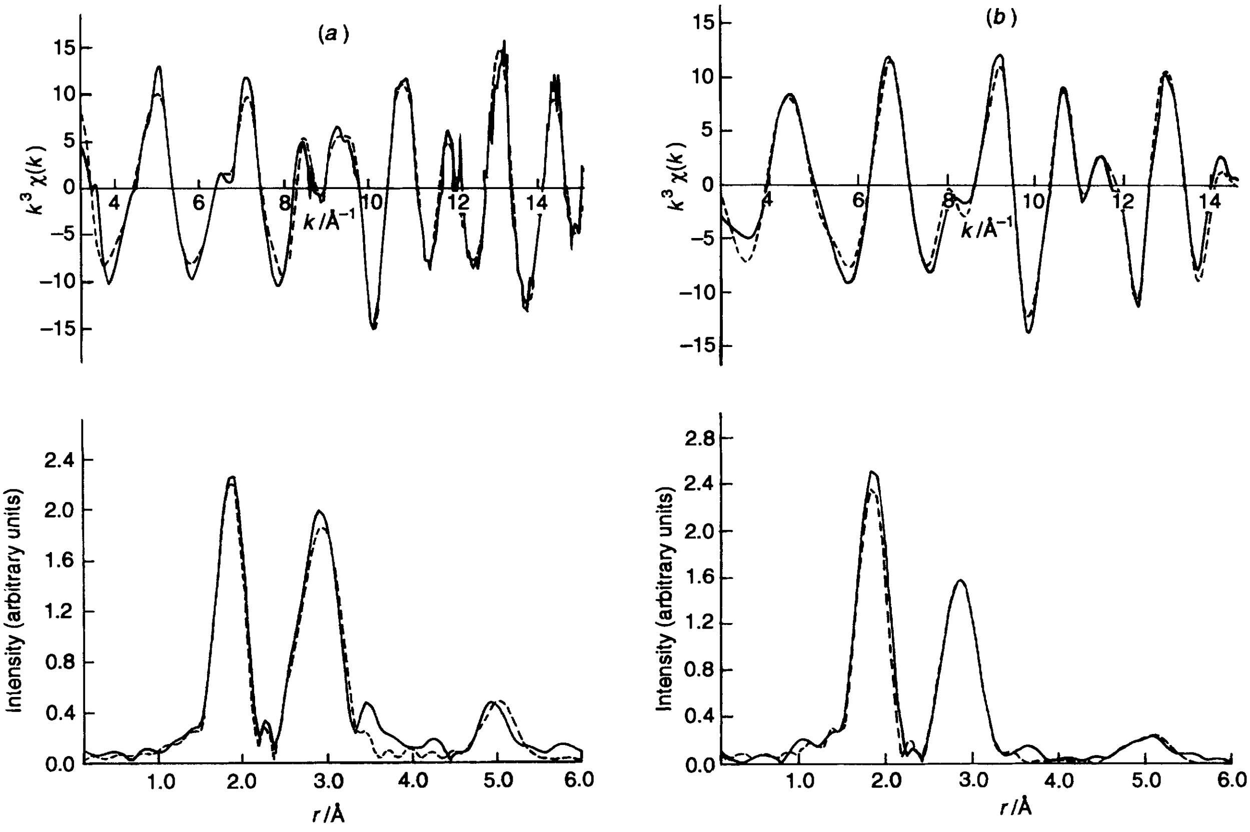

Fig. 4 Background-subtracted (*a*) nickel and (*b*) iodine K-edge EXAFS and Fourier transform of $NaNiIO_6$

have so far been unable to obtain $MM'IO_6$ (M' = Pd or Pt), although $[M'(OH)_2(HIO_6)_2]^{6-}$ which contains discrete anions can be obtained under different conditions.[9] In several cases comparable tellurate and periodate compounds with discrete anions have been described, *e.g.* $[RuO_2L_2]^{6-}$ or $[CuL_2]^{5-}$ ($L = HIO_6$ or H_2TeO_6),[18,19] but attempts to obtain tellurate species, *e.g.* $MM^{IV}HTeO_6$ or $M_2M^{IV}TeO_6$ analogous to the periodates with extended layer structures have failed for M = Ge, Sn, Pb, Mn or Ni.[20] From these results it is clear that although p-block oxo anions such as tellurate or periodate are effective ligands for stabilising unusual high oxidation states of a variety of metals, the factors which control the stoichiometry and oxidation states achieved with particular metals are quite subtle and are being further investigated.

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