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THE TRIS(TELLURATO)MANGANATE(IV) ANION: SPECTROSCOPIC AND STRUCTURAL STUDIES OF $Na_7K[Mn\{TeO_4(OH)_2\}_3]\cdot 3H_2O$

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Abstract—The deep red manganese(IV) complex $Na_7K[Mn\{TeO_4(OH)_2\}_3]\cdot 3H_2O$ has been prepared by $S_2O_8^{2-}$ oxidation of a mixture of manganese(II) salt and telluric acid in aqueous alkali. It has been characterized by analysis, IR and UV–vis spectroscopy and magnetic measurements. The structure of the anion has been established by a combination of manganese and tellurium K-edge EXAFS studies. Attempts to obtain a nickel(IV) tellurate have been unsuccessful.

We have recently reported detailed spectroscopic and structural characterizations of two types of periodato complex of manganese(IV).[1] Sodium hypochlorite oxidation of a mixture of a manganese(II) salt and sodium periodate in alkaline solution produced the water-soluble red $Na_7[Mn(H_2IO_6)(HIO_6)_2]\cdot 18H_2O$, whilst alkali-metal periodates oxidize manganese(II) salts in acid solution to red insoluble $MMnIO_6\cdot nH_2O$ (M = Na–Cs). For many 4*d* and 5*d* transition metals, analogous periodate and tellurate complexes have been described,[2–6] but for 3*d* metals few tellurates are known,[7–11] and only the copper(III) complex $Na_5[Cu(H_2TeO_6)_2]\cdot nH_2O$ has been structurally characterized.[7] Here we describe detailed studies of a manganese(IV) tellurate complex.

EXPERIMENTAL

Physical measurements were made as described previously.[12] The heavy elements present in the complexes were identified by EDX.[12] For conventional analyses, known weights of the samples were dissolved in hot 2 mol dm^{-3} sulphuric acid saturated with SO_2, and then the excess SO_2 boiled off. Alkali metals were determined by atomic emission, manganese spectrophotometrically as permanganate after oxidation with periodate,[1] and tellurium gravimetrically as the element after reduction with hydrazine.[13]

Preparation of $Na_7K[Mn\{TeO_4(OH)_2\}_3]\cdot 3H_2O$

The preparation described here is quite lengthy, but is necessary to obtain a pure sample, as discussed further in the next section.

Manganese(II) chloride, $MnCl_2\cdot 4H_2O$ (2.0 g, 0.01 mol), telluric acid (8.2 g, 0.036 mol) and potassium peroxodisulphate (5.4 g, 0.02 mol) were added to 75 cm^3 water and heated to *ca* 50°C. To this solution 4 M KOH (50 cm^3) was slowly added with constant stirring. At first, a pale cream precipitate appeared which soon dissolved to give a deep red solution. This was filtered after 30 min to remove any solid impurities, and the filtrate was left in a refrigerator overnight. A pale red solid was formed which was removed by filtration and discarded, and filtrate was treated with 40 cm^3 of 50% NaOH. After 10 min of stirring, the red-coloured solid produced was filtered off and ethanol (50 cm^3) was slowly added to the filtrate under constant stirring. This produced a rather sticky red solid which was centrifuged off and redissolved in 1 M KOH (100 cm^3). A saturated solution of $NaNO_3$ (50 ml) was added and the solution was left overnight in a refrigerator. A red solid deposited and was filtered off, washed with water (30 cm^3)

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and dried *in vacuo*. Yield: 1.67 g (17% based on manganese). Found: Mn, 5.9; Te, 38.5; K, 4.0; Na, 16.0; H_2O (by difference), 5.5. Calc. for $H_{12}KMnNa_7O_{21}Te_3$: Mn, 5.6; Te, 38.8; K, 4.0; Na, 16.3; H_2O, 5.5%.

RESULTS AND DISCUSSION

Lister and Yoshino[8,9] obtained manganese(IV) tellurate anions with a 1 : 3 Mn : Te ratio by hypochlorite oxidation of a mixture of manganese(II) salt and alkali-metal tellurate in alkaline solution, but did not describe their properties in detail. We prepared similar materials by OCl^- oxidation, but found the products were impure, usually being contaminated with varying amounts of manganese oxides. Use of peroxodisulphate as oxidant overcame this problem, but resulted in contamination of the products with alkali sulphates unless carefully controlled. The choice of alkali-metal counterion was also important. The potassium salt is highly soluble and difficult to separate from the other salts present, whilst the sodium salt is much less soluble but tends to co-precipitate with a poorly soluble sodium tellurate. The tris(tellurato)manganate(IV) anion is less stable in solution than the corresponding periodate,[1] which also complicates isolation of pure samples. After many attempts varying the reaction conditions and using different alkali-metal combinations, the title complex containing both Na^+ and K^+ cations was isolated as described in the Experimental section. Spectroscopic (IR and UV–vis) data suggest all salts we have obtained contain the same anion, and therefore we need describe only the single example.

Conventional analyses indicated a Na : K : Mn : Te : H_2O ratio of 7 : 1 : 1 : 3 : *ca* 3. Assuming that the tellurium is present in an octahedral TeO_6 group and the manganese as Mn^{IV}, charge balance requires six protons, leading to a provisional formulation $Na_7KH_6[Mn(TeO_6)_3]\cdot 3H_2O$. This complex is a red powder, poorly soluble in water to give a red solution, which slowly decomposes on standing depositing colourless crystals of sodium tellurate. The presence of manganese(IV) was established by the magnetic moment of 3.88 B. M., which is very close to the expected value for a d^3 ion in an octahedral environment.[14] The diffuse reflectance UV–vis spectrum is shown in Fig. 1, and contains features at 14,800 (sh), 20,000, 28,000(sh) and 33,000 cm^{-1}, which are very similar to those observed[1] in the $[Mn(H_2IO_6)(HIO_6)_2]^{7-}$ anion. On this basis the strong features at 33,000 and 28,000 cm^{-1} are assigned as $\pi(O) \rightarrow Mn(t_{2g})$ charge transfer bands, the 20,000 cm^{-1} feature is the lowest energy spin allowed *d–d* transition ($^4A_{2g} \rightarrow {}^4T_{2g}$), and the very weak shoulder at 14,800 cm^{-1} is the spin forbidden $^4A_{2g} \rightarrow {}^2E_g$. The spectrum of the neutral aqueous solution is similar, with the $^4A_{2g} \rightarrow {}^4T_{2g}$ transition occurring at 20,400 cm^{-1}. Addition of saturated sodium tellurate solution causes this band to increase in intensity, showing that the complex partially dissociates tellurate in solution. The IR spectrum (Nujol mull) shows strong features at *ca* 3300, and 1650 cm^{-1} due to water, a medium intensity band at 1145 cm^{-1} assignable as δ (TeOH),[15] and several very strong broad bands between 800 and 450 cm^{-1} due to the coordinated tellurate groups. The Raman spectrum was very similar, although the bands were generally sharper. The presence of δ(TeOH) vibrations shows that the tellurate groups are protonated to some degree, and it is very likely in view of the six protons required for charge balance that three $[TeO_4(OH)_2]^{4-}$ groups are present. The $[TeO_4(OH)_2]^{4-}$ group has been identified previously as the form present in the copper(III), and osmium(VI) complexes by X-ray crystallographic studies.[7,16] The basic geometry proposed for the anion is shown in Fig. 2.

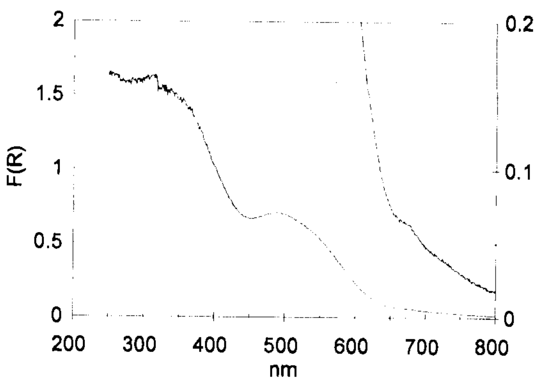

Fig. 1. The diffuse reflectance spectrum of the title complex diluted with $BaSO_4$.

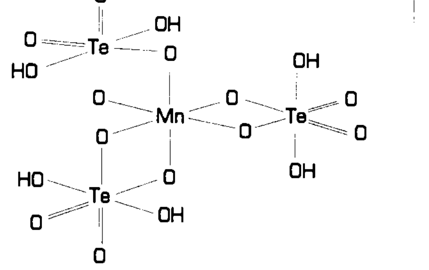

Fig. 2. Proposed structure of the tris(tellurato) manganate(IV) anion. The Te=O and Te—OH positions may be interchanged, although in other X-ray characterized examples the Te=O are usually *trans* to Te—O—M.

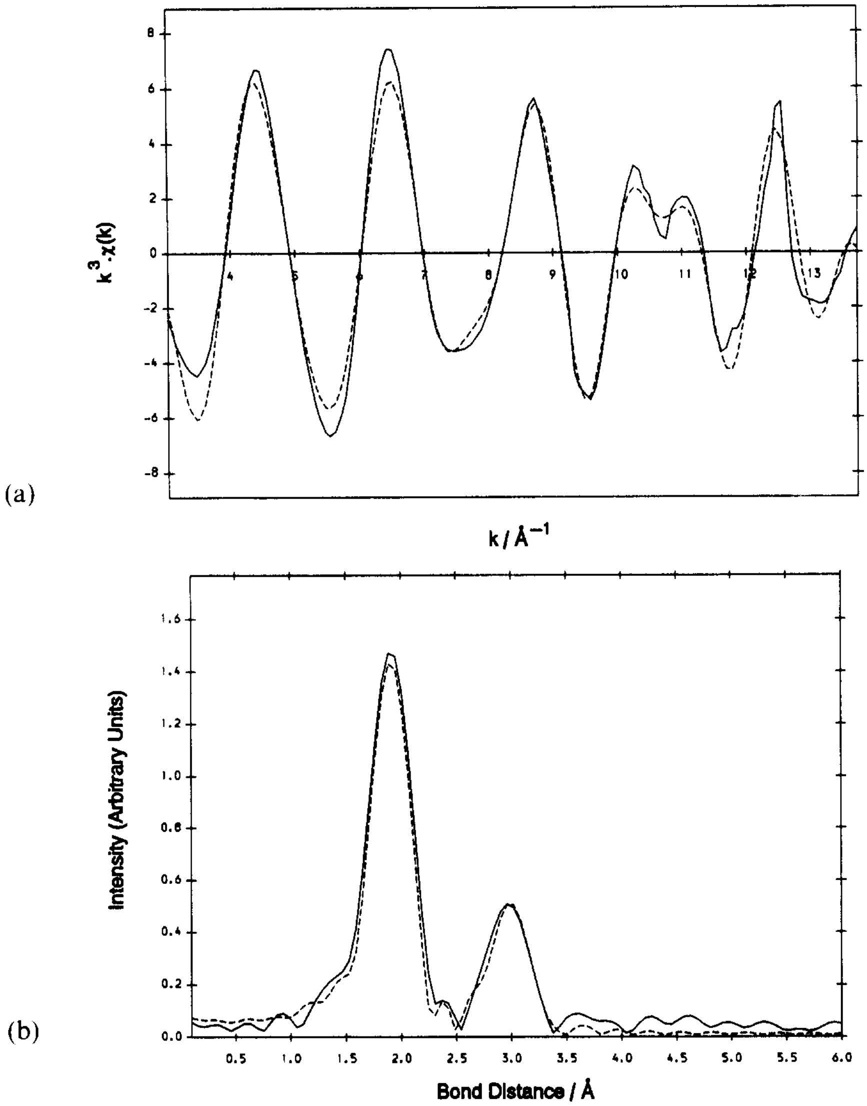

Fig. 3. (a) Background subtracted tellurium K-edge EXAFS data. (b) The resulting Fourier transform (broken line, calculated data; full line, experimental data).

EXAFS studies

Numerous attempts were made to obtain crystals of a tris(tellurato)manganate(IV) complex suitable for an X-ray study, using Na, K, Rb and Cs cations, either singly or mixed,* but without success. In many cases colourless crystals of alkali metal tellurates separated, indicative of partial dissociation of the complex anion. However, we have shown elsewhere[16] that a combination of metal and tellurium edge EXAFS (extended X-ray absorption fine structure) data can be used to identify the basic structural unit in complex metal tellurates. For the present complex the manganese K-edge data were satisfactorily modelled to a first shell of six oxygens at 1.90 Å, and a second shell of three (non-bonded) telluriums at 2.98 Å (Fig. 3). Modelling the tellurium edge data was potentially more complex due to the different Te—O bond distances that occur in coordinated tellurate ligands. For $TeO_4(OH)_2$ groups, two short terminal Te═O bonds, two bridging Te—O(Mn) bonds and two protonated Te—O(H) bonds would be expected, giving a short : long bond ratio of 2 : 4. Previous studies[16] have shown that in some cases EXAFS can achieve this level of resolution. However, in the present case, the result of splitting the single shell of six oxygens to two shells with 2 : 4 (short : long) coordination was not statistically significant, and so the values given are for the single shell model. The value of 1.94 Å is intermediate between typical values for single and double Te—O bonds found in coor-

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* Previous studies have shown that mixtures of alkali cations are often needed to obtain crystals of this type of complex.[2,4,6,16]

Table 1. EXAFS data on $Na_7K[Mn\{TeO_4(OH)_2\}_3]\cdot 3H_2O$

K-Edge	d(Mn—O) (Å)[a]	$2\sigma^2$ (Å^2)[b]	d(Te—O) (Å)	$2\sigma^2$ (Å)^2	d(Mn···Te) (Å)[c]	$2\sigma^2$ (Å^2)	F.I.[d]	R[e]
Mn	1.901 (2)	0.0016 (3)			2.979 (2)	0.0048 (3)	5.8	30.5
Te			1.937 (2)	0.0069 (3)	2.991 (3)	0.0004 (4)[f]	3.9	17.4

[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 coordination shells, and ±0.03 Å for more remote 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 $[\int(\chi^T - \chi^E)k^3\,dk / \int \chi^E k^3\,dk] \times 100\%$.

[f] See text.

dinated tellurates.[16] The fitting of the second shell of a single manganese atom was less satisfactory, producing an anomalously small Debye–Waller factor, although the Te···Mn distance of 2.99 Å is the same as the value obtained from the manganese K-edge within experimental error. Details of the refined EXAFS data are given in Table 1.

Other complexes

Attempts to prepare 1 : 1 manganese tellurate complexes (e.g. M_2MnTeO_6 or $MHMnTeO_6$) analogous to the known[1] $MMnIO_6 \cdot nH_2O$ type were unsuccessful, no complexes being formed on reaction of mixtures of manganese(II) salts and telluric acid with peroxodisulphate in acid solution. Similarly, although two types of nickel(IV) periodates $\{MNiIO_6$ (M = alkali metal)[12] and $[Ni(HIO_6)_2(OH)_2]^{6-}$ [5]$\}$ have been characterized, all attempts to oxidize mixtures of nickel(II) salts and tellurate ions to nickel(IV), either in acid or basic solutions using peroxodisulphate or hypochlorite, failed. These results show that although periodate and tellurate ligands coordinate to many high oxidation state transition metal centres, tellurate is less effective than periodate in this role, resulting either in lower stability complexes as in the manganese(IV) case, or failure as in that of nickel(IV). Consistent with this trend, our attempts to prepare similar complexes in aqueous solution with antimonate $[SbO_6H_{7-n}]^{n-}$ or stannate $[SnO_6H_{8-n}]^{n-}$ have been unsuccessful.

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