

mounted as described above. Unit cell parameters were determined by least-squares refinement of 13 reflections with  $6.1^\circ < 2\theta < 18.4^\circ$ . The two check reflections show only random fluctuations ( $<2\%$ ) throughout the data collection. The data were corrected for Lorentz and polarization effects. Crystal data are given in Table III.

Based on the observed condition  $0k0$ ,  $k = 2n$ , two space groups,  $P2_1$  (No. 4) and  $P2_1/m$  (No. 11) were possible. The chiral space group  $P2_1$  (No. 4), was chosen based on the absence of a crystallographic mirror plane. The structure was solved using direct methods and refinement followed procedures outlined above. The absolute configuration was determined by adding the parameter,  $\eta$ , to the atomic scattering factors.<sup>24</sup> Subsequent refinement led to an  $\eta$  of 1.01 (6). An absorption correction was applied.<sup>22</sup> Final refinement was carried out with anisotropic thermal parameters for all non-hydrogen atoms of the cation except O(1) and the carbon atoms. Hydrogens were fixed to the methylene carbons of the two dpmp ligands and to the  $\text{CHCl}_3$  in a fashion previously outlined. The largest peak in the final difference map had density equal to 1.13 electrons/ $\text{\AA}^3$ . This peak is 0.924  $\text{\AA}$  from F(8).

$[\text{PtIr}(\text{CO})\text{Cl}(\mu\text{-dpmp})_2](\text{PF}_6)_2 \cdot 0.75\text{CH}_2\text{Cl}_2$  (4). Yellow pyramids were obtained by slow diffusion of diethyl ether into a dichloromethane solution of  $[\text{PtIr}(\text{CO})\text{ClPd}(\mu\text{-dpmp})_2](\text{PF}_6)_2$ . The crystals were handled and mounted as previously described. Unit cell parameters were determined by least-squares refinement of 23 reflections with  $7.5^\circ < 2\theta < 22.4^\circ$ . The monoclinic crystal system and the cell parameters were verified by ex-

amination of axial photo data. The two check reflections showed only random fluctuations ( $<2\%$ ) during the data collection. The data were corrected for Lorentz and polarization effects. Crystal data are given in Table III.

The structure was solved in the centrosymmetric space group,  $P2_1/n$  (No. 14). Platinum and iridium atomic positions were determined from a Patterson map. Refinement and calculations were performed as described above. There exists a heavily disordered dichloromethane molecule in the structure at 75% occupancy. This was best modeled with one carbon atom, C(66), sharing a position with a chlorine at 25% occupancy and five other chlorines each at 25% occupancy. The largest peak in the final difference map is equivalent to 3.60 electrons/ $\text{\AA}^3$ . This peak is 1.119  $\text{\AA}$  from Pt(1).

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**Supplementary Material Available:**  $^1\text{H}$  NMR spectrum of 3 and tables of atomic coordinates, bond distances, bond angles, anisotropic thermal parameters, hydrogen atom positions, and crystal data for 1, 1', 3, and 4 (55 pages); listings of observed and calculated structure factors (103 pages). Ordering information is given on any current masthead page.

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## Coordination Chemistry of Higher Oxidation States. 39.<sup>1</sup> Structural and Spectroscopic Studies on Manganese(IV) Periodato Complexes. Crystal Structure of $\text{Na}_7[\text{Mn}(\text{HIO}_6)_2(\text{H}_2\text{IO}_6)] \cdot 18\text{H}_2\text{O}$

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The reaction of  $\text{MIO}_4$  ( $\text{M} = \text{Na}, \text{K}, \text{Rb}, \text{or Cs}$ ) with a manganese(II) salt in acidic aqueous solution at  $40^\circ\text{C}$  produces insoluble dark red-brown manganese(IV) complexes  $\text{MMnIO}_6 \cdot n\text{H}_2\text{O}$ . In contrast  $\text{NaOCl}$  oxidation of a manganese(II) salt in alkaline solution in the presence of  $\text{NaIO}_4$  affords soluble red crystals of  $\text{Na}_7[\text{Mn}(\text{H}_2\text{IO}_6)(\text{HIO}_6)_2] \cdot 18\text{H}_2\text{O}$ . This crystallizes in the orthorhombic system, space group  $Pnca$  ( $a = 10.281$  (7)  $\text{\AA}$ ,  $b = 15.971$  (2)  $\text{\AA}$ ,  $c = 19.564$  (2)  $\text{\AA}$ ,  $Z = 4$ ,  $V = 3212$   $\text{\AA}^3$ ). The structure of the anion reveals octahedrally coordinated Mn, chelated by two  $\text{O}_2\text{IO}_3(\text{OH})^{4-}$  and one *trans*- $\text{O}_2\text{IO}_2(\text{OH})_2^{3-}$  groups, and is the first structurally characterized example of a coordinated  $\text{H}_2\text{IO}_6^{3-}$  group. EXAFS (Mn K- and  $\text{L}_{\text{III}}$  edge) studies on the  $\text{MMnIO}_6 \cdot n\text{H}_2\text{O}$  gave  $\text{Mn}-\text{O} = 1.89$   $\text{\AA}$ ,  $\text{I}-\text{O} = 1.92$   $\text{\AA}$ , and  $\text{Mn} \cdots \text{I} = 2.89$   $\text{\AA}$ . UV-visible spectroscopy and magnetic data are reported and confirm all the complexes contain Mn(IV). Attempts to obtain periodate complexes of Mn(III) or of oxidation states  $\text{Mn}(\geq 5)$  have been unsuccessful. Spectroscopic and EXAFS data are also reported for the hexakis(iodate) complex  $\text{K}_2[\text{Mn}(\text{IO}_3)_6]$ .

### Introduction

Periodate ( $\text{H}_5\text{-}_n\text{IO}_6$ ) <sup>$n-$</sup>  and tellurate ( $\text{H}_6\text{-}_n\text{TeO}_6$ ) <sup>$n-$</sup>  anions are highly effective ligands for stabilizing high oxidation states of the transition metals, often as water-soluble anions, which in addition to their inherent interest have found uses as multielectron oxidants and in chemical analysis.<sup>3-7</sup> A number of manganese periodate complexes have been reported previously,<sup>8</sup> and we report here some

new examples and a detailed structural (X-ray and EXAFS) and spectroscopic reinvestigation of known complexes. The high oxidation state chemistry of manganese has been reviewed several times,<sup>9</sup> and particular recent interest attaches to complexes with N and/or O donor ligands which may function as models for the manganese site in photosystem II.<sup>9c</sup>

### Experimental Section

Spectroscopic measurements were made as described previously.<sup>1,4,5</sup> IR spectra were obtained from Nujol mulls, and samples for diffuse reflectance spectra were diluted with barium sulfate. Samples were dried in vacuo ( $10^{-3}$  Torr) at room temperature for 24 h. The approximate composition of the complexes was established by energy dispersive X-ray fluorescence spectroscopy. For conventional analyses, known weights of the complexes were dissolved/suspended in hot 2 mol  $\text{dm}^{-3}$  sulfuric acid, and sulfur dioxide was bubbled in until a colorless solution was formed.

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The excess  $\text{SO}_2$  was boiled off. Manganese was determined spectrophotometrically at 545 nm as permanganate after reoxidation with periodate, iodine was determined gravimetrically as  $\text{AgI}$ , and alkali metals were determined by flame photometry. The water content was estimated from the weight loss  $<200^\circ\text{C}$  (by thermal gravimetric analysis). The reported analyses refer to a single batch of each compound. Several batches of the compounds were prepared and analyzed. The water content varied slightly with the batch but the heavy atom ratios were constant.

Manganese K-edge and iodine  $\text{L}_{\text{III}}$ -edge EXAFS data were recorded at the Daresbury Synchrotron Radiation Source operating at an average energy of 2 GeV and current of 200 mA. Data were collected in transmission mode on beam line 7, using a silicon 111 monochromator offset to 50% of the rocking curve for harmonic rejection. Samples were finely powdered and diluted with dry boron nitride. Due to the high mass absorption of iodine (and also Cs and Rb), the dilution had to be carefully controlled to maximize the signal/noise at the manganese K-edge. The same sample was then used for the iodine  $\text{L}_{\text{III}}$ -edge data collection. Data treatment used the programs PAXAS<sup>10</sup> and EXCURVE90<sup>11</sup> and was carried out as described elsewhere.<sup>5,12</sup>  $\text{Na}_7[\text{Mn}(\text{HIO}_6)_2(\text{H}_2\text{IO}_6)] \cdot 18\text{H}_2\text{O}$  was used as a model compound for assessing the reliability of phase shifts in these systems.

**$\text{Na}_7[\text{Mn}(\text{HIO}_6)_2(\text{H}_2\text{IO}_6)] \cdot 18\text{H}_2\text{O}$ .** This complex was prepared as described by Lister and Yoshino.<sup>13</sup> (It was formulated by them as  $\text{Na}_4\text{H}_4\text{Mn}(\text{IO}_6)_3 \cdot 17\text{H}_2\text{O}$ .) After purification, the red powder was dissolved in water, which was allowed to evaporate in the dark. Long deep red needles were formed, which were separated by filtration and dried in vacuo. Yield 30%. Anal. Calcd for  $\text{H}_{40}\text{I}_3\text{MnNa}_7\text{O}_{36}$ : Na, 13.3; Mn, 4.5; I, 31.4;  $\text{H}_2\text{O}$  26.7. Found: Na, 13.8; Mn, 4.6; I, 31.6;  $\text{H}_2\text{O}$ , 26.0.  $\mu = 3.84 \mu_{\text{B}}$ .

**$\text{NaMnIO}_6 \cdot \text{H}_2\text{O}$ .** Manganese(II) sulfate hydrate,  $\text{MnSO}_4 \cdot 7\text{H}_2\text{O}$  (5.5 g, 20 mmol), was dissolved in water (300  $\text{cm}^3$ ), sulfuric acid (0.5  $\text{cm}^3$  of 2 mol  $\text{dm}^{-3}$ ) and sodium periodate,  $\text{Na}_2\text{H}_2\text{IO}_6$  (11.7 g, 40 mmol), were added, and the mixture heated to  $40^\circ\text{C}$  for 4 h. The dark-red precipitate was filtered off, washed well with water, and dried in vacuo. Yield: 3.8 g (60%). Anal. Calcd for  $\text{H}_2\text{IMnNaO}_7$ : Na, 7.2; Mn, 17.2; I, 39.8;  $\text{H}_2\text{O}$  5.6. Found: Na, 7.0; Mn, 17.2; I, 39.7;  $\text{H}_2\text{O}$ , 5.1.  $\mu = 4.13 \mu_{\text{B}}$ .

**$\text{KMnIO}_6 \cdot 1.5\text{H}_2\text{O}$ .** This compound was made similarly by using  $\text{KIO}_4$ . Yield 55%. Anal. Calcd for  $\text{H}_3\text{IKMnO}_{7.5}$ : K, 11.4; Mn, 16.0; I, 36.9;  $\text{H}_2\text{O}$ , 7.8. Found: K, 11.4; Mn, 16.5; I, 36.8;  $\text{H}_2\text{O}$ , 7.3.  $\mu = 4.01 \mu_{\text{B}}$ .

**$\text{RbMnIO}_6 \cdot \text{H}_2\text{O}$ .**  $\text{RbIO}_4$  was made in situ by mixing  $\text{RbOH}$  and  $\text{H}_2\text{IO}_6$  in a 1:1 mole ratio in water and then conducting the preparation as above. Yield 65%. Anal. Calcd for  $\text{H}_2\text{IMnO}_7\text{Rb}$ : Mn, 14.4; I, 33.3;  $\text{H}_2\text{O}$ , 4.5. Found: Mn, 14.1; I, 32.9;  $\text{H}_2\text{O}$ , 4.7.  $\mu = 4.16 \mu_{\text{B}}$ .

**$\text{CsMnIO}_6 \cdot 2\text{H}_2\text{O}$ .**  $\text{CsIO}_4$  was made in situ from  $\text{CsOH}$  and  $\text{H}_2\text{IO}_6$  in a 1:1 mole ratio, and the preparation continued as above. Yield 63%. Anal. Calcd for  $\text{CsH}_2\text{IMnO}_8$ : Mn, 12.3; I, 29.7;  $\text{H}_2\text{O}$ , 8.1. Found: Mn, 12.6; I, 29.7;  $\text{H}_2\text{O}$ , 7.7.  $\mu = 4.05 \mu_{\text{B}}$ .

**$\text{K}_2[\text{Mn}(\text{IO}_3)_6]$ .** This compound was made as described previously.<sup>14</sup> Anal. Calcd for  $\text{I}_6\text{K}_2\text{MnO}_{18}$ : Mn, 4.65; I, 64.4. Found: Mn, 4.4; I, 64.2.  $\mu = 3.87 \mu_{\text{B}}$ .

**X-ray Crystallography of  $\text{Na}_7[\text{Mn}(\text{HIO}_6)_2(\text{H}_2\text{IO}_6)] \cdot 18\text{H}_2\text{O}$ .** Dark red air-stable crystals were isolated from the synthesis and mounted in glass capillaries for the X-ray studies. Preliminary photographic X-ray examination established the crystal system and approximate cell dimensions. Accurate cell dimensions and intensity data were measured using an Enraf-Nonius CAD-4 diffractometer fitted with a graphite monochromator and  $\text{Mo K}\alpha$  radiation. Reflections (3272) were measured from a room temperature crystal; the check reflections showed no decay, and after data reduction there remained 2830 unique reflections. An empirical  $\psi$ -scan absorption correction based on three reflections was applied. The systematic absences uniquely established the space group as centrosymmetric *Pnca* (No. 60). Direct methods with SHELX-76<sup>15</sup> failed to yield a solution; however SHELXS-86<sup>16</sup> produced one solution with a low CFOM which gave the Mn, I, and one Na position. Subsequent structure factor and difference electron density syntheses located oxygen and sodium atoms. The oxygen atoms of the anion were quickly established and consideration of the distances surrounding an atom and the behavior of the thermal parameters on refinement enabled water oxygen

Table I. Crystallographic Data

formula	$\text{H}_{40}\text{I}_3\text{MnNa}_7\text{O}_{36}$	Z	4
fw	1212.87		
cryst syst	orthorhombic	$D_{\text{calc}}$ , g $\text{cm}^{-3}$	2.507
space group	<i>Pnca</i> (No. 60)	$D_{\text{obsd}}$ , g $\text{cm}^{-3}$	2.50 (1)
a, Å	10.281 (7)	$\mu(\text{Mo K}\alpha)$ , $\text{cm}^{-1}$	34.6
b, Å	15.971 (2)	$\lambda(\text{Mo K}\alpha)$ , Å	0.71069
c, Å	19.564 (2)	$R^a$	0.0291
$V$ , Å <sup>3</sup>	3212.4 (23)	$R_w^b$	0.0393

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}.$$

Table II. Atomic Coordinates and Equivalent Isotropic Temperature Factors ( $\times 10^3$ )<sup>a</sup>

atom	x	y	z	$U$ , Å <sup>2</sup>
Mn(1)	0.2500	0.0000	0.29305 (4)	10.6 (4)
I(1)	0.23334 (2)	0.16340 (2)	0.36341 (1)	11.7 (2)
I(2)	0.2500	0.0000	0.14176 (2)	12.0 (2)
Na(1)	0.2536 (2)	-0.1741 (1)	0.6259 (1)	28.9 (10)
Na(2)	0.2599 (2)	0.1702 (1)	0.0047 (1)	37.9 (12)
Na(3)	0.2500	0.0000	-0.1104 (1)	26.8 (13)
Na(4)	0.2500	0.0000	0.4670 (1)	25.4 (12)
Na(5)	0.2500	0.0000	0.7250 (1)	26.0 (12)
O(1)	0.3429 (3)	0.2039 (2)	0.2859 (1)	22.0 (14)
O(2)	0.1304 (3)	0.2531 (2)	0.3475 (1)	21.0 (14)
O(3)	0.3484 (2)	0.2131 (2)	0.4211 (1)	19.5 (14)
O(4)	0.1369 (3)	0.1187 (2)	0.4330 (1)	18.6 (14)
O(5)	0.1426 (2)	0.0959 (1)	0.2967 (1)	14.1 (13)
O(6)	0.3414 (3)	0.0630 (2)	0.3585 (1)	14.4 (13)
O(7)	0.3582 (3)	0.0481 (2)	0.0801 (1)	19.2 (14)
O(8)	0.1401 (3)	0.0978 (2)	0.1403 (1)	21.6 (15)
O(9)	0.3466 (2)	0.0454 (2)	0.2163 (1)	16.3 (13)
O(10)	0.1200 (3)	-0.0976 (2)	0.5356 (1)	25.5 (15)
O(11)	0.3870 (3)	-0.0475 (2)	0.6318 (1)	28.6 (17)
O(12)	0.1245 (3)	-0.1253 (2)	0.7200 (1)	28.4 (16)
O(13)	0.3932 (3)	-0.2422 (2)	0.7017 (1)	31.5 (16)
O(14)	0.3950 (3)	0.2184 (2)	0.0995 (2)	31.7 (16)
O(15)	0.1154 (3)	0.2732 (2)	0.0386 (1)	25.9 (15)
O(16)	0.3832 (3)	0.1181 (2)	-0.0971 (2)	38.9 (19)
O(17)	0.1175 (3)	0.0652 (2)	-0.0276 (1)	24.4 (15)
O(18)	0.3793 (3)	-0.0705 (2)	-0.1926 (1)	25.4 (15)

$$^a U_{\text{eq}} = 1/3(\text{trace } U).$$

atoms and sodium atoms to be identified. Refinement with anisotropic atoms gave  $R$  of 0.034 at which time clear evidence for the H atoms was apparent in the difference electron-density map (20 of the largest 30 peaks were used (0.82–0.48  $\text{e } \text{\AA}^{-3}$ ). These were introduced into the model with fixed positions and with a fixed isotropic thermal parameter. For O(14) only one H atom was included because of an ambiguity in the choice of the second H atom position. Full-matrix least-squares refinement minimizing  $\sum w(|F_o| - |F_c|)^2$  converged to  $R = 0.029$  (215 parameters, 2538 reflections with  $F > 2\sigma(F)$ , max shift/error 0.29). The residual electron density was in the range 0.63 to  $-1.95 \text{ e } \text{\AA}^{-3}$ . Atomic scattering factors for neutral atoms and anomalous dispersion corrections were taken from SHELX-76 (O, H) and ref 17 (I, Mn, Na). Crystallographic data are given in Table I and the atomic coordinates are given in Table II. All calculations were performed on an IBM3090 computer using the programs SHELX-76,<sup>15</sup> SHELXS-86,<sup>16</sup> ORTEP-II,<sup>18</sup> and STRUPLO-84.<sup>19</sup>

## Results and Discussion

**$\text{MMnIO}_6 \cdot n\text{H}_2\text{O}$  ( $M = \text{Na, K, Rb, or Cs}$ ).** The reaction of a manganese(II) salt (nitrate, acetate, or sulfate are all suitable) with an alkali-metal periodate in neutral or slightly acid aqueous solution at  $40$ – $60^\circ\text{C}$  resulted in the slow precipitation of dark-red insoluble powders. The sodium and potassium salts have been reported previously,<sup>20–22</sup> and variously formulated as  $\text{M}_2\text{Mn}_2\text{I}_2\text{O}_{11}$  (or  $\text{M}_2\text{Mn}_2\text{I}_2\text{O}_{11} \cdot n\text{H}_2\text{O}$ ) or  $\text{MMnIO}_6$ , which contain Mn(III) or Mn(IV), respectively. We have carried out a large number of preparations and find that the correct composition is

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Table III. Refined EXAFS Parameters for Manganese Periodate Species<sup>a</sup>

compound	$d(\text{Mn}-\text{O})/\text{\AA}$	$2\sigma^2/\text{\AA}^2$ <sup>b</sup>	$d(\text{Mn}\cdots\text{I})/\text{\AA}$	$2\sigma^2/\text{\AA}^2$ <sup>b</sup>	VPI <sup>c</sup>	$E_0$	FI <sup>d,e</sup>	$R$ <sup>d,f</sup>
NaMnIO <sub>6</sub> · <i>n</i> H <sub>2</sub> O	1.892 (2)	0.0018 (2)	2.884 (2)	0.0037 (1)	-7.5 (5)	26.7 (5)	16.9 (10.1)	24.8 (21.4)
KMnIO <sub>6</sub> · <i>n</i> H <sub>2</sub> O	1.892 (2)	0.0022 (3)	2.891 (2)	0.0050 (2)	-7.5 (4)	25.5 (5)	14.3 (9.7)	27.7 (20.1)
RbMnIO <sub>6</sub> · <i>n</i> H <sub>2</sub> O	1.895 (2)	0.0019 (3)	2.888 (1)	0.0034 (2)	-7.7 (5)	25.9 (6)	40.7 (7.7)	27.9 (21.2)
CsMnIO <sub>6</sub> · <i>n</i> H <sub>2</sub> O	1.910 (3)	0.0044 (7)	2.961 (6)	0.011 (1)	-8.0 (9)	24.7 (8)	48.3 (8.1)	61.0 (33.6)
Na <sub>7</sub> H <sub>4</sub> [Mn(IO <sub>6</sub> ) <sub>3</sub> ]	1.896 (3)	0.0047 (6)	2.946 (2)	0.0036 (4)	-6.1 (6)	24.6 (5)	9.3 (6.1)	22.7 (16.9)
K <sub>2</sub> Mn(IO <sub>3</sub> ) <sub>6</sub> <sup>g</sup>	1.901 (4)	0.0017 (4)	3.444 (3)	0.010 (2)	-5.8 (7)	24.3 (5)	41.9 (11.5)	31.3 (24.8)

<sup>a</sup>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. <sup>b</sup> $2\sigma^2$  is the Debye–Waller factor. <sup>c</sup>VPI is the constant imaginary potential describing the lifetime of the final state. <sup>d</sup>Values for Fourier filtered data in parentheses. <sup>e</sup>The fit index is defined as:  $\text{FI} = \sum_i [(\chi^T - \chi^E)k^3]^2$ . <sup>f</sup>The  $R$  factor is defined as:  $R = [\int (\chi^T - \chi^E)k^3 dk / \int \chi^E k^3 dk] \times 100\%$ . <sup>g</sup>An iodate (I(V)) species.

MMnIO<sub>6</sub>·*n*H<sub>2</sub>O, although the water content varies slightly with the conditions ( $0.5 \leq n \leq 2.0$ ). The new rubidium and cesium salts were prepared in an analogous manner, but an analytically pure lithium salt was not obtained. The reactions were also carried out with ratios of alkali-metal (M) periodate:Mn between 3:1 and 0.5:1, but in all cases only the MMnIO<sub>6</sub>·*n*H<sub>2</sub>O product stoichiometry was obtained. Care must be taken with the heavier alkali-metal periodates to conduct the reactions in dilute solution and wash the products thoroughly, otherwise contamination with the poorly soluble MIO<sub>4</sub> may occur. If the preparations were conducted in boiling water, the products were darker colored and had poor analyses, although spectroscopically they again appeared to be the same complex. It is likely in these cases that some hydrolysis to MnO<sub>2</sub> occurs, which contaminates the products.

The MMnIO<sub>6</sub>·*n*H<sub>2</sub>O compounds are insoluble in water, dilute acids, or alkalis but dissolve in acidified H<sub>2</sub>O<sub>2</sub> or aqueous SO<sub>2</sub> with reduction to Mn(II). The water is lost on heating below 200 °C, but further decomposition occurs only on strong heating. The magnetic moments are ca. 4  $\mu_B$ , slightly greater than the spin-only value for three unpaired electrons (3.87), and consistent with their formulation as Mn(IV) complexes. The IR spectra of all four compounds show only very small differences in band positions and relative intensities. Significant features may be assigned to water (ca. 3500 and 1630 cm<sup>-1</sup>), and coordinated IO<sub>6</sub> groups (ca. 695, 610, 520, 480, and 350 cm<sup>-1</sup>), and there are no features in the range 1000–1200 cm<sup>-1</sup> which would indicate protonation of the periodate (see below). The IR spectra thus rule out formulations such as MMn(HIO<sub>6</sub>)(OH)·(*n* – 1)H<sub>2</sub>O, which have an identical analytical composition. The diffuse reflectance UV–visible spectra were also independent of the cation and contain features at 14 290 (w, sh), 20 200, 26 000, and 35 700 cm<sup>-1</sup>. For a high oxidation state like Mn(IV), charge transfer (CT) bands are expected at relatively low energy.<sup>23</sup> Using the optical electronegativity model which relates the energy of the lowest energy allowed charge-transfer band to the electronegativity difference between metal acceptor and ligand donor orbitals, it is possible to predict the lowest energy O( $\pi$ ) → Mn(*t*<sub>2g</sub>) CT band. The optical electronegativity of Mn(IV),  $\chi_{\text{opt}}(\text{Mn})$ , was calculated as 2.75 from the spectrum of K<sub>2</sub>MnF<sub>6</sub>.<sup>24</sup> Theory<sup>23</sup> predicts the energy of the transition as

$$E_{\text{max}}(\text{cm}^{-1}) = 30000\{\chi_{\text{opt}}(\text{O}) - \chi_{\text{opt}}(\text{Mn})\} + 2D$$

where  $\chi_{\text{opt}}(\text{O}) = 3.5$  and  $2D$  is the spin pairing correction. This gives  $E_{\text{max}}$  at ca. 27 000 cm<sup>-1</sup>, and thus the band observed at 26 000 cm<sup>-1</sup> is so assigned. For a d<sup>3</sup> ion in O<sub>h</sub> symmetry three spin-allowed d–d transitions are expected, and the feature at 20 200 cm<sup>-1</sup> is assigned to the lowest energy of these (<sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>2g</sub>), with the others obscured by the CT bands. The energy of this first band corresponds in ligand field theory to 10Dq, and the value seems reasonable when compared with that<sup>24</sup> in K<sub>2</sub>MnF<sub>6</sub> of 21 800 cm<sup>-1</sup>. The weak shoulder at 14 290 cm<sup>-1</sup> is then a spin-forbidden transition <sup>4</sup>A<sub>2g</sub> → <sup>2</sup>E<sub>g</sub>. The spectra are also similar to those reported for Mn(IV) in heteropoly molybdate and niobate complexes.<sup>25</sup> The satisfactory fit of the spectrum confirms the Mn(IV)

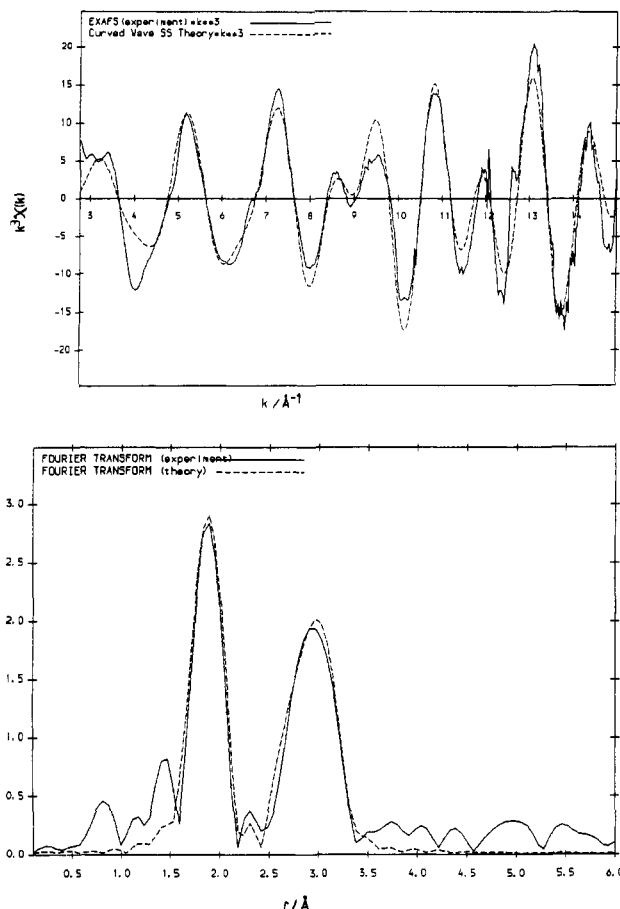


Figure 1. Background subtracted  $k^3$ -weighted EXAFS and associated Fourier transform for NaMnIO<sub>6</sub>·*n*H<sub>2</sub>O.

formulation, and rules out the presence of other Mn oxidation states, and a mixed valence formulation.

X-ray powder diffraction studies by Brown<sup>26</sup> found that the sodium and potassium salts had poor crystallinity, resulting in broad lines. Nonetheless it was concluded that the compounds were isomorphous with KNiIO<sub>6</sub>, with the compounds being regarded as anhydrous. The structure of KNiIO<sub>6</sub> is based on hexagonal close-packed oxygen atoms with Ni and I occupying 2/3 of the octahedral holes between two adjacent layers. The octahedral holes between the next two layers are only occupied by potassium atoms filling 1/3 of available sites.<sup>27</sup> Vacancies in the K-containing layers provide potential space for water molecules. Our powder X-ray pattern for KMnIO<sub>6</sub>·*n*H<sub>2</sub>O agreed with Brown<sup>26</sup> again showing very broad lines; heating the sample to remove H<sub>2</sub>O had no effect on the diffraction pattern.

Manganese K-edge EXAFS data were obtained for the series of compounds MMnIO<sub>6</sub>·*n*H<sub>2</sub>O (M = Na – Cs) in the solid state

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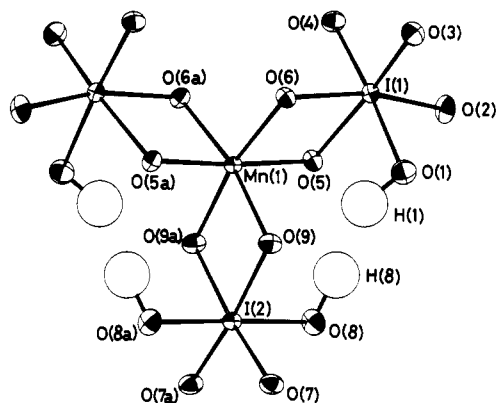


Figure 2. Anion in  $\text{Na}_7[\text{Mn}(\text{HIO}_6)_2(\text{H}_2\text{IO}_6)] \cdot 18\text{H}_2\text{O}$ . Thermal ellipsoids are drawn with surfaces at the 50% probability level.

and supporting iodine  $L_{\text{III}}$ -edge data were also recorded. As a result of the high absorption cross sections of iodine and the heavier group 1 metals, these compounds gave rather weak spectra with poor signal to noise statistics, and this is reflected in the rather high fit indices for non-Fourier filtered data. Calculated and experimental data for  $\text{NaMnIO}_6 \cdot n\text{H}_2\text{O}$  are shown as the  $k^3$  weighted EXAFS and resulting Fourier transform in Figure 1, while Table III displays the refined EXAFS parameters. It can be seen from the tabulated data that the Mn–O and Mn···I distances obtained from these compounds are essentially identical. Each has a shell at ca. 1.89 Å corresponding to six Mn–O distances and a second shell at ca. 2.89 Å arising from three periodate iodine atoms, one in the same unit cell as the manganese and two in adjoining cells, as is expected from the structure indicated by the powder patterns.<sup>27</sup> These distances are very similar to those found in the crystal structure of  $[\text{Mn}(\text{HIO}_6)_2(\text{H}_2\text{IO}_6)]^{7-}$  (see below) which suggests that this tris-chelated moiety is the dominant building block in manganese(IV) periodate compounds, 1:1 stoichiometry being accommodated by chelation of each periodate ligand to three manganese centers. The lack of variation in the refined distances is readily explained from the proposed structure, which consists of polymeric sheets of  $\text{MnIO}_6$  units with the alkali-metal ions filling holes between the layers. Thus parameters within the two-dimensional sheets are effectively invariant while the separation of these layers might be expected to increase with increasing metal ion radius. Unfortunately the powder X-ray diffraction data were not of sufficient quality to yield cell parameters and thus confirm this assertion. The deviation of the cesium salt is probably a reflection of the poor data quality rather than a genuine structural change. The iodine  $L_{\text{III}}$ -edge data sets are very short (ca. 300 eV) because of the proximity of the  $L_{\text{II}}$  absorption edge, and thus only a limited amount of information can be obtained. It is found that  $d(\text{I} \cdots \text{O}) = 1.92$  Å in each of the complexes, consistent with average I–O distances in other periodate complexes, and there is some evidence for the three nonbonded  $\text{I} \cdots \text{Mn}$  contacts at 2.90 Å.

$\text{Na}_7[\text{Mn}(\text{HIO}_6)_2(\text{H}_2\text{IO}_6)] \cdot 18\text{H}_2\text{O}$ . Oxidation of manganese(II) salts in the presence of periodate ions with alkaline hypochlorite gave the deep red tris(periodate) complexes. The sodium salt was described by Lister and Yoshino,<sup>13</sup> who formulated it as  $\text{Na}_7\text{H}_4[\text{Mn}(\text{IO}_6)_3] \cdot 17\text{H}_2\text{O}$ , and a subsequent partial X-ray study<sup>28</sup> indicated that the anion contained manganese in a six-coordinate environment provided by three chelating periodates. The low precision of the available X-ray data precluded a more detailed understanding of the structure, and hence it was redetermined. The structure consists of discrete  $[\text{Mn}(\text{HIO}_6)_2(\text{H}_2\text{IO}_6)]^{7-}$  anions together with hydrated sodium cations. The anion is shown in Figure 2; Figure 3 gives an alternative linked octahedral representation, and in Table IV selected bond distances and angles are presented. The anion has crystallographic 2-fold symmetry through Mn(1) and I(2), but Figure 3 shows clearly the ap-

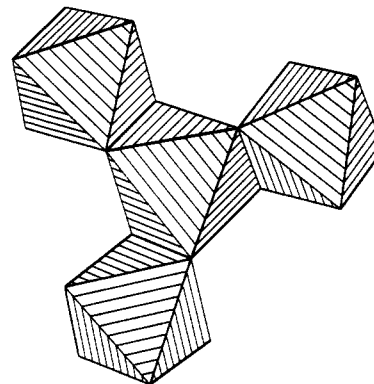


Figure 3. Edge-linked octahedral representation of the anion.

Table IV. Selected Bond Distances (Å) and Angles (deg)

Bond Distances			
I(1)–O(1)	1.996 (3)	I(2)–O(7)	1.811 (2)
I(1)–O(2)	1.808 (2)	I(2)–O(8)	1.928 (3)
I(1)–O(3)	1.817 (2)	I(2)–O(9)	1.908 (2)
I(1)–O(4)	1.830 (2)	Mn(1)–O(5)	1.889 (2)
I(1)–O(5)	1.934 (2)	Mn(1)–O(6)	1.880 (2)
I(1)–O(6)	1.954 (2)	Mn(1)–O(9)	1.941 (2)
I(1)···Mn(1)	2.955 (1)	I(2)···Mn(1)	2.960 (1)
O(1)–H(1)	0.96	O(8)–H(8)	1.01
Na···O(H <sub>2</sub> ) min 2.314 (3) max 2.550 (3)			
Bond Angles			
O(1)–I(1)–O(2)	86.7 (1)	O(2)–I(1)–O(6)	167.1 (1)
O(1)–I(1)–O(3)	87.9 (1)	O(3)–I(1)–O(4)	93.5 (1)
O(1)–I(1)–O(4)	175.9 (1)	O(3)–I(1)–O(5)	167.7 (1)
O(1)–I(1)–O(5)	86.6 (1)	O(3)–I(1)–O(6)	91.1 (1)
O(1)–I(1)–O(6)	84.7 (1)	O(4)–I(1)–O(5)	91.4 (1)
O(2)–I(1)–O(3)	98.2 (1)	O(4)–I(1)–O(6)	91.4 (1)
O(2)–I(1)–O(4)	96.9 (1)	O(5)–I(1)–O(6)	77.5 (1)
O(2)–I(1)–O(5)	92.5 (1)		
O(7)–I(2)–O(8)	90.4 (1)	O(5)–Mn(1)–O(6)	80.4 (1)
O(7)–I(2)–O(9)	91.6 (1)	O(5)–Mn(1)–O(9)	91.4 (1)
O(8)–I(2)–O(9)	90.5 (1)	O(6)–Mn(1)–O(9)	94.1 (1)
O(7)–I(2)–O(7a)	96.6 (1)	O(5)–Mn(1)–O(5a)	175.7 (1)
O(7)–I(2)–O(8a)	88.5 (1)	O(5)–Mn(1)–O(6a)	96.7 (1)
O(7)–I(2)–O(9a)	171.8 (1)	O(5)–Mn(1)–O(9a)	91.9 (1)
O(8)–I(2)–O(8a)	178.3 (1)	O(6)–Mn(1)–O(6a)	94.1 (1)
O(8)–I(2)–O(9a)	90.8 (1)	O(6)–Mn(1)–O(9a)	169.3 (1)
O(9)–I(2)–O(9a)	80.3 (1)	O(9)–Mn(1)–O(9a)	78.6 (1)
I(1)–O(1)–H(1)	108	I(2)–O(8)–H(8)	104

Symmetry:  $a = \frac{1}{2} - x, -y, z$

proximate  $D_3$  symmetry of the heavy atoms. Frequently in such studies it is difficult to know where to place the H atoms and their location is inferred from bond length data. However in the present case there was good evidence for the H-atom positions, and these form a consistent picture when the bond lengths are examined (Table IV). Thus I(1)–O(1) is the longest I(1)–O distance (1.996 (3) Å) and as expected O(1) is bonded to H(1). The I–O terminal bonds (1.82 (av) Å) are shorter than the bridging I–O bonds to Mn. The I(2) centered octahedron is required by symmetry to contain two OH groups having identified H(8) bonded to O(8). The evidence that this is *not* a disordered  $[\text{HIO}_6]^{4-}$  group is provided by the height of H(8) in the difference electron density map, the I(2)–O(8) bond length (1.928 (3) Å), and the form of the anisotropic thermal ellipsoid of O(8). The remaining I(2)–O bonds appear normal. Although the two Mn···I distances are similar, O(9) has a longer Mn–O distance and correspondingly shorter I(2)–O distance than related bonds involving I(1). Each sodium atom is surrounded by six oxygen atoms drawn from water molecules or terminal I–O bonds and arranged in distorted octahedra.

The  $[\text{HIO}_6]^{4-}$  ligand is known in several compounds, for example,<sup>5</sup>  $[\text{Pt}(\text{OH})_2(\text{HIO}_6)_2]^{6-}$ , where edge-linking is encountered. A discrete  $[\text{H}_2\text{IO}_6]^{3-}$  anion containing two cis OH groups has been recently described,<sup>29</sup> and the present structure is the first char-

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acterized compound containing this coordinated group although with the trans OH geometry. Manganese(IV) has been found in several salts of heteropolyniobates<sup>30</sup> in which Mn is octahedrally coordinated (Mn–O, 1.87 (av) Å); this distance is similar to the value found in the present structure.

The IR spectrum shows, in addition to bands at ca. 3400 and 1640 cm<sup>-1</sup> (H<sub>2</sub>O) and 770, 725, 600, 525, 420, and 385 cm<sup>-1</sup> ("IO<sub>6</sub>"), medium intensity features at 1050–1200 cm<sup>-1</sup> which are assignable<sup>29,31</sup> as δ(IOH), consistent with the presence of protonated periodate groups, and contrasting with the absence of such features in the spectra of the MMnIO<sub>6</sub> complexes. The diffuse reflectance UV–visible spectrum contains features at 14 165 cm<sup>-1</sup> (<sup>4</sup>A<sub>2g</sub> → <sup>2</sup>E<sub>g</sub>), 20 240 cm<sup>-1</sup> (<sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>2g</sub>), and 28 900 and 33 570 cm<sup>-1</sup> O(π) → Mn(t<sub>2g</sub>) CT, very similar to those of the MMnIO<sub>6</sub>, as would be expected. The spectra were also recorded for solutions of the complex in 2 mol dm<sup>-3</sup> HClO<sub>4</sub>, 2 mol dm<sup>-3</sup> NaOH, and distilled water. In the water and the acid solution slow decomposition to permanganate occurs, but this is not evident in the alkaline solution after several hours at room temperature. In the alkaline solution the <sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>2g</sub> transition occurs at 20 576 cm<sup>-1</sup> (ε<sub>mol</sub> = 270 mol<sup>-1</sup> dm<sup>3</sup> cm<sup>-1</sup>). When the pH is lowered, the band maximum becomes less well-defined, and appears to shift slightly to higher energy, but a more detailed study of the spectrum as a function of pH is precluded by the quite rapid appearance of the characteristic<sup>23</sup> highly structured spectrum of MnO<sub>4</sub><sup>-</sup>.

**K<sub>2</sub>[Mn(IO<sub>3</sub>)<sub>6</sub>].** The hexakis(iodato)manganate(IV) complex is produced by reaction of MnO<sub>2</sub>, HIO<sub>3</sub>, and KIO<sub>3</sub> in water,<sup>14</sup> as a brownish powder, which dissolves in water to give a yellow-brown solution and which slowly deposits MnO<sub>2</sub> on standing. X-ray powder diffraction shows it to be isomorphous with the corresponding Pb and Zr complexes,<sup>32,33</sup> and the IR spectrum is consistent with monodentate iodate ligands.<sup>34</sup> The magnetic

moment (3.87 μ<sub>B</sub>) and its diffuse reflectance spectrum with bands at 14 200 (w) (<sup>4</sup>A<sub>2g</sub> → <sup>2</sup>E<sub>g</sub>), 18 116 (sh) (<sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>2g</sub>), 23 000 (<sup>4</sup>A<sub>2g</sub> → <sup>4</sup>T<sub>1g</sub>), and ca. 28 000 and 35 200 cm<sup>-1</sup> O(π) → Mn(t<sub>2g</sub>) are again consistent with the manganese(IV) formulation and suggest that the iodate ligands exert a weaker ligand field than the periodates. The manganese K-edge EXAFS shows the manganese to be coordinated by six oxygen atoms at a distance of 1.90 Å with a second shell of six iodine atoms at 3.44 Å in good agreement with the structure of the isomorphous K<sub>2</sub>Ge(IO<sub>3</sub>)<sub>6</sub>.<sup>32</sup> The data from this complex again suffer severely from absorption by the six iodine atoms surrounding the manganese center. The refined parameters for this complex are given in Table III.

**Other Complexes.** Spectrophotometric examination of mixtures of periodate ions and MnO<sub>4</sub><sup>-</sup> in neutral or acid solution, or with MnO<sub>4</sub><sup>2-</sup> or MnO<sub>4</sub><sup>3-</sup> in alkali, gave no evidence of complex formation. Attempts to reduce the Mn(IV) complexes to Mn(III) were also unsuccessful, and cyclic voltammetry of the [Mn(HIO<sub>6</sub>)<sub>2</sub>(H<sub>2</sub>IO<sub>6</sub>)]<sup>7-</sup> ion showed only complex and irreversible oxidation and reduction phenomena. We conclude that Mn(IV) is the preferred oxidation state of the element in the presence of periodate ligands, although the tendency of the complexes to decompose in solution to MnO<sub>4</sub><sup>-</sup> with reduction of the periodate is notable. Insolubility presumably prevents this in the case of the MMnIO<sub>6</sub> type.

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**Registry No.** Na<sub>7</sub>[Mn(HIO<sub>6</sub>)<sub>2</sub>(H<sub>2</sub>IO<sub>6</sub>)]·18H<sub>2</sub>O (coordinate entry), 141221-58-1; NaMnIO<sub>6</sub>·H<sub>2</sub>O, 141221-59-2; KMnIO<sub>6</sub>·1.5H<sub>2</sub>O, 141221-60-5; RbMnIO<sub>6</sub>·H<sub>2</sub>O, 141221-61-6; CsMnIO<sub>6</sub>·2H<sub>2</sub>O, 141221-62-7; K<sub>2</sub>[Mn(IO<sub>3</sub>)<sub>6</sub>], 55866-55-2; MnSO<sub>4</sub>, 7785-87-7; Na<sub>7</sub>[Mn(HIO<sub>6</sub>)<sub>2</sub>(H<sub>2</sub>IO<sub>6</sub>)]·18H<sub>2</sub>O (salt entry), 141221-63-8.

**Supplementary Material Available:** Tables of X-ray data collection parameters, hydrogen atomic coordinates, anisotropic thermal parameters, full bond distance and angle data, and EXAFS data (30 pages); a listing of structure factors (15 pages). Ordering information is given on any current masthead page.

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