Crystal structures of $NaNiIO_6$, $NaMnIO_6$, and $KMnIO_6$

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$NaNiIO_6$ ($a = 4.962$, $c = 5.148$ Å, space group $P312$) is shown from X-ray powder patterns to be isostructural with trigonal $KNiIO_6$. Approximate coordinates for the oxygen atoms are given. $NaMnIO_6$ ($a = 4.972$, $c = 5.136$ Å) and $KMnIO_6$ ($a = 5.009$, $c = 6.000$ Å) are probably also isostructural but the broadening of the X-ray powder lines in these compounds makes a complete analysis impossible. Powder patterns for all three compounds are given.

$KNiIO_6$ and $NaNiIO_6$ were first prepared by Rây and Sarma (1). More recently Reimer and Lister (2) have characterized the manganese analogues and have shown by means of X-ray powder diffraction patterns that they are isomorphous with the corresponding nickel complexes. Also using X-ray powder diffraction, Vannerberg and Blockhammar (3) and Eddy and Vannerberg (4) have shown that $KNiIO_6$ consists of hexagonal sheets of linked NiO_6 and IO_6 octahedra with the potassium atoms lying in the octahedral holes between the sheets.

The samples used in this work were those prepared by Reimer and Lister (2). All four complexes are highly insoluble in water and it was not possible to obtain crystals large enough for a single crystal X-ray diffraction study. Consequently, X-ray powder patterns of each compound were recorded using a Philips horizontal diffractometer equipped with a focusing LiF monochromator. Filtered copper radiation was used throughout. The powder pattern of $KNiIO_6$ agreed with that observed by Vannerberg and Blockhammar (3). The powder patterns of the other three compounds could be indexed by assuming that they were isostructural. The crystal data, which were refined by least squares analysis, are summarized in Table I and the diffraction patterns are given in Tables II and III. Both the nickel complexes gave diffraction patterns which could be indexed out to high angles, but the lines in the manganese complexes were very broad and weak and could not be recorded much beyond a Bragg angle of 30 or 40 degrees. However, enough was visible to confirm that their unit cells were almost identical to the corresponding nickel complexes. The cause of the broadening of the lines was not examined but the fact that the degree of broadening was roughly proportional to the *l* index suggests that the crystals in the sample were 00.1 plates about 150 Å in thickness.

The diffractometer was used to record integrated intensities from the $NaNiIO_6$ sample in

TABLE I

Crystal data

Molecule	a(Å)	c(Å)	Space group	Remarks
$KNiIO_6$	4.964 ± 0.003* 4.969 ± 0.005†	6.004 ± 0.003* 6.000 ± 0.005†	$P312(D_3{}^1)$	1 K in 1(a) 1 Ni in 1(d) 1 I in 1(f) 6 O in 6(l)
$KMnIO_4$	5.009 ± 0.004	6.000 ± 0.021	$P312(D_3{}^1)(?)$	—
$NaNiIO_6$	4.962 ± 0.001	5.148 ± 0.001	$P312(D_3{}^1)$	1 Na in 1(a) 1 Ni in 1(d) 1 I in 1(f) 6 O in 6(l)
$NaMnIO_6$	4.972 ± 0.002	5.136 ± 0.007	$P312(D_3{}^1)(?)$	—

*Present work.
†Reference 3.

TABLE II

Crystal spacings, d, and intensities, I, for $NaNiIO_6$ and $NaMnIO_6$; observed and calculated structure factors for $NaNiIO_6$

| | NaNiIO$_6$ | | | | | | | NaMnIO$_6$ | | |
| | | | | Structure factor | | | | | | |
hkl	d_{obsd} (Å)	d_{calcd} (Å)	I	$(\Sigma F_o{}^2)^{\frac{1}{2}}$	σ	$(\Sigma F_c{}^2)^{\frac{1}{2}}$	F_c	d_{obsd} (Å)	d_{calcd} (Å)	I
001	5.143	5.148	100	85.1	8.2	81.2		5.155	5.146	86
100	4.291	4.297	39	36.5	3.4	38.2		4.303	4.317	57
101	3.297	3.299	78	48.1	4.3	48.9		3.307	3.307	100
002	2.571	2.574	8	49.0	4.3	45.6		—	2.573	—
110	2.475	2.481	27	54.3	5.8	54.2		2.492	2.492	37
111 / 11Ī	2.227	2.235	51	83.6	8.2	71.8	{ 22.4 / 68.2 }	2.243	2.243	43
102	2.206	2.208	4	17.8	4.8	25.6		—	2.210	—
200	2.141	2.149	1	13.9	7.7	20.6		—	2.159	—
201	1.981	1.983	13	34.1	1.9	35.8		2.006	1.991	18
112 / 11Ī2	1.787	1.786	48	103.3	11.1	99.6	{ 54.5 / 83.3 }	1.791	1.790	53
003	1.716	1.716	—	17.3	29.8	20.7		—	1.715	—
202	1.649	1.649	4	24.5	3.8	30.2		—	1.654	—
210	1.623	1.624	4	33.2	5.8	26.1		—	1.632	10
103	1.593	1.594	8	33.7	2.9	33.1		—	1.594	—
211 / 21Ī	1.549	1.549	15	66.2	6.7	51.9	{ 30.0 / 42.4 }	1.561	1.555	16
300	1.4332	1.4324	14	69.2	7.7	66.8		1.4427	1.4390	24
113 / 11Ī3	1.4101	1.4113	14	71.6	7.7	68.1	{ 54.0 / 41.4 }	—	1.4130	—
301	1.3804	1.3800	—	39.4	7.2	43.6				
212 / 21Ī2	1.3711	1.3736	13	43.7	22.6	32.2	{ 19.8 / 25.5 }	1.3894	{ 1.3859 / 1.3780 }	17
203	1.3404	1.3408	5	32.7	4.3	39.0				
004	1.2851	1.2870	2	51.4	18.3	48.3				
302	1.2521	1.2516	5	35.6	4.8	37.8				
220	1.2403	1.2405	4	37.0	18.3	42.3				
104	1.2343	1.2329		18.8	18.8	21.9				
221 / 22Ī	1.2066	1.2060	5	50.4	7.2	47.9	{ 41.9 / 23.4 }			
310	1.1926	1.1918	2	35.1	10.6	25.8				
213 / 21Ī3	1.1793	1.1796	5	49.9	7.2	41.1	{ 31.0 / 27.1 }			
311 / 31Ī	1.1616	1.1611	6	55.7	6.7	46.4	{ 39.9 / 23.7 }			
114 / 11Ī4	1.1413	1.1424	6	58.1	6.7	64.0	{ 56.6 / 29.7 }			
222 / 22Ī2	1.1174	1.1175	6	62.9	3.4	64.6	{ 51.9 / 38.5 }			
204	1.1060	1.1041	—	12.5	15.9	20.7				
303	1.0995	1.0996	1	19.2	10.6	20.7				
312 / 31Ī2	1.0827	1.0815	—	13.0	32.2	28.5	{ 22.7 / 17.0 }			
400	1.0753	1.0743	—	13.0	32.2	22.0				
401	1.0525	1.0516	1	19.2	10.6	28.4				

TABLE II *(concluded)*

	NaNiO₆							NaMnIO₆		
				Structure factor						
hkl	d_{obsd} (Å)	d_{calcd} (Å)	I	$(\Sigma F_o{}^2)^{\frac{1}{2}}$	σ	$(\Sigma F_c{}^2)^{\frac{1}{2}}$	F_c	d_{obsd} (Å)	d_{calcd} (Å)	I
005	1.0325	1.0296	2	53.4	24.0	43.9				
214 } 21$\bar{4}$		1.0087		—	—	29.4	{ 22.9 } 18.4			
233 } 23$\bar{3}$	1.0065	1.0053	8	—	—	45.5	{ 28.8 } 35.2			
105		1.0013		—	—	28.0				
402	—	0.9914	—	—	—	19.8				
320	—	0.9858	—	—	—	17.0				
313 } 31$\bar{3}$	0.9783	0.9789	1	29.4	14.4	33.0	{ 21.0 } 25.4			
321 } 32$\bar{1}$	0.9667	0.9683	2	37.0	11.5	35.6	{ 23.5 } 24.9			
304	0.9581	0.9573	6	39.9	5.3	36.8				

TABLE III

Crystal spacings, *d*, and intensities, *I*, for KNiIO₆ and KMnIO₆

	KNiIO₆			KMnIO₆		
hkl	d_{obs} (Å)	d_{calcd} (Å)	I	d_{obs} (Å)	d_{calcd} (Å)	I
001	6.002	6.004	100	5.985	6.000	73
100	4.291	4.299	17	4.311	4.338	27
101	3.480	3.495	75	3.507	3.515	100
002	2.998	3.002	13	—	3.000	2
110	2.479	2.482 }	23	2.501	2.504 }	—
102	2.455	2.461 }			2.467 }	
111	2.292	2.294	15	2.309	2.311	29
200	2.151	2.149	—	—	2.169	19
201	2.023	2.024 }	13	2.032	2.040 }	18
003	1.973	2.001 }			2.000 }	
112	1.914	1.913	39	1.918	1.922	56
103	1.815	1.814	9	—	1.816	—
202	1.743	1.748	5	—	1.758	—
210	1.623	1.624	2	1.642	1.640	—
211	1.570	1.568 }	19	1.580	1.582 }	26
113	1.561	1.558 }			1.563 }	
004	1.501	1.501	2	—	1.500	—
203	1.4658	1.4647	6	—	1.4703	—
300	1.4328	1.4330 }	10		1.4460 }	12
212	1.4308	1.4290 }		1.4467	1.4387 }	
104	—	1.4171 }			1.4176 }	
301	1.3949	1.3938	4	1.4079	1.4057	7
302	1.2960	1.2932	7	—	—	—
114	1.2869	1.2844	7	—	—	—
213	1.2635	1.2614	6	—	—	—
220	1.2425	1.2410	2	—	—	—
204	1.2316	1.2306	1	—	—	—
221	—	1.2153	2	—	—	—
005	—	1.2008	—	—	—	—
310	1.1931	1.1923	1	—	—	—

reflection. An estimated standard error (σ) was assigned to each measurement and the data were corrected for the Lorentz effect and the polarization occurring in both the sample and monochromator. The structure of $NaNiIO_6$ was assumed to be the same as that of $KNiIO_6$. Models in which the Ni and I atoms were in turn placed in 1(a) gave considerably worse agreement. Unfortunately, in the space group $P312$, which Vannerberg and Blockhammar (3) found for $KNiIO_6$, only those reflections with either h, k, or l equal to zero can be measured unambiguously. The intensities measured for the remainder were the sum of the intensities of the hkl and $hk\bar{l}$ reflections which are not equivalent. Consequently, the initial refinement involved only the use of the $h0l$ and $hk0$ reflections. The position of the oxygen atom was chosen to give reasonable bond distances (Na—$O = 2.4$ Å, Ni—$O = 2.1$ Å, I—$O = 1.9$ Å), and the scale and individual isotropic temperature factors were varied in a least squares refinement which minimized the sum of the squares of the differences between the observed and calculated structure factors, F_o and F_c, respectively, weighted according to the estimated standard errors. The resulting weighted agreement index (R) was 0.14 and an application of the χ^2 test, using the estimated standard errors as a measure of the expected deviation in individual measurements, led to a probability[1] $P(\chi^2)$ of 5%. The scale, isotropic temperature factors, and the coordinates of the oxygen atom were then refined, at each stage the values of $F_o(hkl)$ and $F_o(hk\bar{l})$ being chosen so that $F_o^2(hkl) + F_o^2(hk\bar{l})$ agreed with the observed intensity and $F_o(hkl)/F_o(hk\bar{l})$ was the same as $F_c(hkl)/F_c(hk\bar{l})$ for the previous round. After several rounds, no further significant changes occurred, R was equal to 0.105 and $P(\chi^2)$ was equal to 76%. The final set of parameters is given in Table IV.

The results of this study are not, unfortunately, as accurate as could be wished. All four compounds appear to be isostructural but the broad lines in the powder patterns of $KMnIO_6$ and $NaMnIO_6$ do not permit refinement of their structures. The refinement of the structure of

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[1]$P(\chi^2)$ measures the probability of finding worse agreement between the observed and calculated structure factors, assuming that the latter are calculated from the correct model.

TABLE IV

Positional and temperature parameters and interatomic distances in $NaNiIO_6$

| Parameter* | NaNiIO₆ | | KNiIO₆‡ |
	Initial model	Final model†	
$x(O)$	0.630	0.608(0.014)	0.671
$y(O)$	0.040	−0.013(0.019)	0.039
$z(O)$	0.280	0.312(0.006)	0.312
$B(Na, K)$ (Å²)	−2.3	−0.3(1.2)	4.4
$B(Ni)$ (Å²)	−0.2	2.1(0.9)	3.2
$B(I)$ (Å²)	0.4	0.3(0.4)	1.2
$B(O)$ (Å²)	−0.4	−0.2(0.8)	1.7
R	0.145	0.105	0.120
$P(\chi^2)$	0.05	0.76	
Ni—O (Å)	2.06	1.78(0.13)	2.10(0.06)
I—O (Å)	1.95	1.87(0.13)	1.85(0.06)
Na, K—O(Å)	2.42	2.35(0.13)	2.56(0.06)

*$x(O)$, $y(O)$, $z(O)$ are the coordinates of the oxygen atom, B is the isotropic temperature factor.
†Standard errors are given in parentheses.
‡From ref. 4.

$NaNiIO_6$ leads to temperature factors which are rather small, two being negative, although not significantly so. The Ni—O and I—O distances, whose errors are estimated to be at least 0.13 Å, do not differ significantly from the values found in $KNiIO_6$ (Table IV) nor does the Na—O distance differ significantly from the value of 2.35 Å expected from the sum of the crystal radii (5). As was observed by Vannerberg and Blockhammar (3), the X-ray diffraction analysis shows no sign of the water which has been found in the chemical analyses of all these complexes. It can be assumed that since the crystallites composing the sample are very small, the water is adsorbed onto the crystal surfaces and is not true water of crystallization.

Acknowledgments

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