1245 to 1238 cm^{-1} and upward shifts of the 1346-cm^{-1} CH_2 wagging peak to 1350 cm^{-1} and of the 1412- and 1432-cm^{-1} bands to 1418 and 1434 cm^{-1}, respectively, with a reversal of relative intensity and probably also assignment of the latter pair.[1] In addition, the CH_2 stretching band at 2955 cm^{-1} moved to lower frequency and appeared to weaken. Bands arising from CH_2 motions should be especially sensitive to the overall ODA conformation owing to variable vibrational coupling between the two CH_2 groups. Significantly, the above spectral alterations were in the same direction as those induced by Ca^{2+} as it converts ODA solely to the trans,trans form in aqueous solution.[1] These observations strongly suggest that the ODA ligand in $LiODA^-$ also adopts the trans,trans conformation; the same is very likely true for ODA complexes of other alkali metal ions. Consequently, the only contribution to the C–C stretching region made by ODA when complexed to an alkali metal ion should be a single band at *ca.* 950 cm^{-1}, just as with CaODA (Figure 1F). One of the assumptions on which the calculation of formation quotient was based, that the ~917-cm^{-1} band could be attributed entirely to *uncomplexed* ODA, thus appears quite reasonable.

The question of the role played by the ODA ether oxygen atom was approached through spectral comparison with the glutarate dianion, the five-carbon dicarboxylate analog of ODA. In contrast to the situation with ODA, the Raman spectrum of aqueous 1.0 *M* sodium glutarate was totally unaltered when the solution was also made 2.5 *M* in LiCl, most importantly in the conformation-sensitive C–C stretching region between 850 and 1000 cm^{-1}. The ether oxygen atom apparently is an essential structural factor in the detectable association between ODA and alkali metal ions, as it also is for the Ca^{2+}-ODA complex system.[1]

Several considerations, then, support the intuitive notion that the trans,trans ODA conformer functions as a tridentate chelate ligand in the systems under study: (1) participation of the ether oxygen atom, (2) absence of appreciable 2:1 alkali metal-ODA complexes, and (3) the observed conformational transition of ODA upon complexation. The resultant formation of two five-membered chelate rings involving both carboxylate groups and the ether oxygen atom no doubt imparts the measurable stability to the complexes.

Previous Raman studies of aqueous alkali metal complexation differ from the present work in the manner in which such binding was spectrally manifested. The earlier evidence was based on either (1) removal of the degeneracy of certain anion vibrational modes (*i.e.*, band splitting) upon ion-pair formation, as with concentrated $LiNO_3$ and $NaNO_3$ solutions,[9] or (2) competitive interference by an alkali metal ion in an existing equilibrium, leading to intensity perturbations such as those resulting from the competition between Na^+ and H^+ for SO_4^{2-}.[10] The spectra presented here for alkali metal-ODA solutions demonstrate how Raman conformational analysis can aid in the systematic study of metal complex formation in aqueous solution.

Acknowledgments. The author is grateful to K. W. Littlepage and A. J. Fehl for experimental assistance.

Registry No. Cs_2ODA (complex), 42230-49-9; K_2ODA (complex), 42230-50-2; Na_2ODA (complex), 42230-51-3; Li_2ODA (complex), 42230-52-4; Cs_2ODA (salt), 42249-34-3; K_2ODA (salt), 19900-81-3; Na_2ODA (salt), 35249-69-5; Li_2ODA (salt), 42246-29-7.

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Contribution from the Inorganic Chemistry Laboratory,
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A Sodium Uranium Bronze and Related Phases

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Received April 5, 1973

The possibility that the ions Na^+, Ca^{2+}, Mg^{2+}, and In^{3+} may be incorporated into the α-UO_3 structure has been investigated. Of these ions only Na^+ is readily introduced to form a nonmetallic uranium bronze Na_xUO_3 ($0 < x < 0.14$). Powder neutron diffraction and infrared spectroscopy indicate that the Na^+ ions occupy the vacant sites in the α-UO_3 structure up to the expected sodium limit of about 12% of the total cation sites. Under oxidizing conditions, all the uranium is oxidized to U(VI) to give a related nonstoichiometric phase of upper limit $Na_{0.165}U_{0.973}O_3$. At low oxygen pressures and low sodium contents, on the other hand, reduction occurs leading to the formation of new phases with compositions M_3O_8 and $M_{22}O_{58}$ (where M = Na + U).

Introduction

The structure of α-UO_3 closely resembles a uranium-deficient α-U_3O_8.[1] Electron diffraction patterns can be indexed on an orthorhombic unit cell with dimensions $a = 6.84$, $b = 43.45$, and $c = 4.157$ Å, which may be considered to have a nominal composition $U_{22}O_{58}$ but with 12.1% cation vacancies to restore the O/U stoichiometry to 3:1. This abnormal structure raises the question whether the overall reaction

$$xM + UO_3 = M_xUO_3$$

can be effected to produce a series of uranium bronzes in which the vacant sites of the α-UO_3 structure are filled [with a consequential reduction of some U(VI)]. In this case, the composition limit would, of course, be $x = 0.14$. We have therefore investigated the reaction

$$xNaUO_3 + (1 - x)UO_3 = Na_xUO_3$$

and analogous reactions for Mg^{2+}, Ca^{2+}, and In^{3+}.

There are only two investigations which may be related to the present study. There is an indication[2] that between

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[1] C. Greaves and B. E. F. Fender, *Acta Crystallogr., Sect. B*, **28**, 3609 (1972).

[2] D. G. Kepert, M.Sc. Thesis, University of Melbourne, 1960.

$Na_{0.4}UO_3$ and $Na_{0.67}UO_3$ two phases exist which give X-ray diffraction patterns similar to $Na_2U_2O_7$ and α-U_3O_8, and at lower sodium contents, Carnall, *et al.*,[3] provide evidence for an orthorhombic phase of approximate composition $Na_2O \cdot 13UO_3$ with unit cell dimensions $a = 6.807$, $b = 15.934$, and $c = 8.254$ Å.

Experimental Section

$NaUO_3$ was prepared from "Specpure" Na_2CO_3 and UO_2 (previously heated at 1000° in hydrogen) using the solid-state reactions

$$Na_2CO_3 + UO_2 \xrightarrow{O_2,\ 800^\circ} \alpha\text{-}Na_2UO_4 + CO_2$$

$$\alpha\text{-}Na_2UO_4 + UO_2 \xrightarrow{700^\circ} 2NaUO_3$$

The second stage was carried out in an evacuated, platinum-lined silica capsule. Known weights of $NaUO_3$ and α-UO_3 (from $UO_4 \cdot 2H_2O$ heated at 500° in air for 4 hr) were ground together and then heated at 500° for 24 hr in an evacuated, sealed silica tube. Homogeneous products were obtained which were characterized by X-ray diffraction using copper Kα radiation (λ 1.5418 Å) and a Debye-Scherrer camera of diameter 11.46 cm. Similar preparations were carried out at 730° in (a) a silica capsule and (b) a gold container under an oxygen pressure at 160 atm. In contrast to the experiments at 500°, a buildup of pressure within the sealed capsules indicated that oxygen was lost by samples of low sodium content. Under high oxygen pressure, oxidation of U(V) to U(VI) was found to occur. Debye-Scherrer X-ray photographs of the reaction products could be indexed as a single phase. For the samples prepared in silica tubes, sodium analysis by atomic absorption spectroscopy indicated that sodium loss due to diffusion into the silica was negligible. Densities were estimated pycnometrically at 20° using AnalaR CCl_4 (density 1.594 g cm^{-3}).

Infrared spectra of all samples were recorded on a Perkin-Elmer Model 457 double grating spectrometer. About 5 mg of each reaction product was ground with approximately 150 mg of dry potassium chloride, and the mixture was pressed into a pellet in an evacuated die under a pressure of about 10 ton in.$^{-2}$. Neutron diffraction measurements at room temperature were carried out on one polycrystalline bronze sample which was contained in a thin-walled vanadium can. The PANDA diffractometer at A.E.R.E. Harwell was used with neutrons of wavelength 1.485 Å obtained by reflection from the 331 planes of a germanium monochromator using a takeoff angle of 70°. Electron diffraction patterns and transmission electron micrographs were obtained for this and other samples using two microscopes (a JEM 6A and a JEM 100U) operated at 100 kV.

Introduction of Ca^{2+}, Mg^{2+}, and In^{3+} into the α-UO_3 lattice was attempted using similar procedures to that outlined above and the reaction routes below.

$$CaCO_3 + UO_2 \xrightarrow[800^\circ]{\textit{in vacuo}} CaUO_3 + CO_2$$

$$xCaUO_3 + (1 - x)UO_3 \xrightarrow[730^\circ]{\text{capsule}} Ca_xUO_3 \quad (1)$$

$$xCaUO_4 + xUO_2 + (1 - 2x)UO_3 \xrightarrow[730^\circ]{\text{capsule}} Ca_xUO_3 \quad (2)$$

$$xMg(NO_3)_2 \cdot 6H_2O + (1 - 3x)UO_3 + xU_3O_8 \xrightarrow{\text{air, } 730^\circ} Mg_xUO_3 \quad (3)$$

$${}^1/_2xIn_2O_3 + {}^3/_2xUO_2 + (1 - {}^3/_2x)UO_3 \xrightarrow[730^\circ]{\text{capsule}} In_xUO_3 \quad (4)$$

No successful preparations were obtained, however. For instance, X-ray diffraction showed that under the conditions employed, the products from routes 1 and 2 consisted of $CaUO_4$ and U_3O_8, the oxygen loss resulting in a buildup of pressure within the sealed capsule.

Results

Na_xUO_3, the Bronze Phase. X-Ray powder patterns of the reaction products Na_xUO_3 ($x \leqslant 0.15$) could be indexed in terms of a single hexagonal phase whose unit cell parameters were similar to those of α-UO_3 (see, for example, the compound $Na_{0.10}UO_3$ in Table I). Samples for which $0.25 > x > 0.15$ gave diffraction patterns consistent with the presence of an orthorhombic phase in addition to the hexagonal phase. The orthorhombic unit cell dimensions ($a = 6.89 \pm 0.01$, $b = 11.73 \pm 0.02$, and $c = 17.76 \pm 0.05$ Å) resemble those of $Na_2U_2O_7$ ($a = 6.812$, $b = 11.790$, and $c = 17.742$ Å).[4] The sodium composition limit of the bronze can therefore be estimated as $Na_{0.15}UO_3$, although the actual limit is probably lower because of the insensitivity of the X-ray powder technique to small amounts (2-5%) of a second phase.

Table I. Unit Cell Data (Å)

	Symmetry	a^a	b^a	c^a
α-UO_3	Hexagonal	3.951 (3)		4.157 (3)
α-U_3O_8	Orthorhombic	6.712 (3)	11.934 (6)	4.144 (2)
$Na_{0.025}UO_{3-x}$	Orthorhombic	6.718 (8)	11.90 (1)	4.142 (4)
$Na_{0.11}UO_{2.93}$	Hexagonal	3.947 (1)		4.154 (1)
$Na_{0.10}UO_3$	Hexagonal	3.955 (3)		4.163 (3)
$Na_{0.146}U_{0.976}O_3$	Hexagonal	3.962 (2)		4.170 (2)

^{a} Figures in parentheses give the standard deviation of the final digit.

Neutron Diffraction. A sample of nominal composition $Na_{0.10}UO_3$ was studied in detail by powder neutron diffraction. A uranium valence state determination showed the stoichiometry to be $Na_{0.1}UO_{2.98\pm0.02}$. The neutron diffraction profile strongly resembled that of α-UO_3, showing intense hexagonal subcell reflections with additional weak superlattice peaks. Neglecting the superlattice reflections, 17 intensities were measured for $2\theta \leqslant 93°$, and atom positions in several trial structures were refined using a least-squares program written by Wiseman; this minimizes the function $\Sigma_i w_i (I_{\text{obsd}} - I_{\text{calcd}})_i^2$ where $w_i = 1/\sigma_i^2$ and σ_i is the standard deviation of $(I_{\text{obsd}})_i$. [The standard deviation of $(I_{\text{obsd}})_i = \sqrt{P_i + B_i}$ where P_i and B_i are the counts summed over the peak and backgrounds, respectively.] The scattering lengths used were $b_O = 0.577 \times 10^{-12}$ cm,[5] $b_{Na} = 0.351 \times 10^{-12}$ cm,[5] and $b_U = 0.850 \times 10^{-12}$ cm.[6,7]

Analysis of the data was based on the structure of α-UO_3 deduced from earlier neutron diffraction measurements,[1] namely on an idealized orthorhombic unit cell for α-U_3O_8[8] (space group $C222$, Figure 1) with a reduced uranium occupation parameter to reestablish the correct stoichiometry. Several models for $Na_{0.10}UO_3$ involving either substitutional or interstitial sodium were refined in accordance with the following assumptions. (i) Cell parameters for the orthorhombic cell were assigned the values 6.850, 11.865, and 4.163 Å, *i.e.*, $\sqrt{3}a$, $3a$, and c, where a and c are the hexagonal subcell cell parameters quoted in Table I. (ii) The temperature factors for metal and oxygen atoms, respectively, were constrained to be equal. (iii) Uranium vacancies and substitutional sodium ions were present in a random arrangement, and for each of these defects two oxygen atoms were displaced in the z direction, the displacements caused by both vacancies and sodium ions being equal to that determined for α-UO_3, *i.e.*, 0.4 Å. (iv) Interstitial sodium ions situated between the pseudo-hexagonal layers of uranium atoms produced negligible oxygen displacements. (v) The ratio Na/U was fixed at 1:10. The variables to be refined are thus a scale factor, a uranium occupation parameter, three oxygen positional parameters, and two temperature factors.

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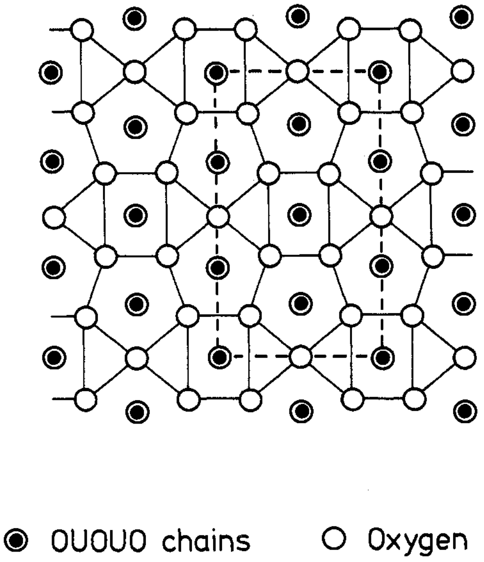

Figure 1. The structure of α-U_3O_8 proposed by Andresen.[8]

It was found that a trial structure in which sodium occupies uranium vacancies converged after three cycles to an R (intensity) index of 0.024 (Tables II and III). Models involving interstitial sodium gave consistently poorer R indexes, the best interstitial structure being for a random distribution of sodium, for which R was 0.044. It therefore appears as though the structure of $Na_{0.10}UO_3$ is analogous to that of α-UO_3, but with most of the vacancies on the cation sublattice now occupied by sodium. The refined uranium occupation parameter implies a stoichiometry $Na_{0.10}UO_{2.96 \pm 0.04}$.

Electron Microscopy. The electron diffraction patterns of $Na_{0.10}UO_3$ were identical with those obtained from α-UO_3 with characteristic clusters of three superstructure reflections on the 001 reciprocal lattice plane attributed to twinning effects (Figure 4a of ref 1). The superlattice reflections lying along $[110]_h$ directions corresponded to $9/22(110)_h$ and $13/22(110)_h$, where the subscript h refers to the hexagonal unit cell of Table I; all spots were therefore indexed on an orthorhombic unit cell with parameters $a_0 = \sqrt{3}a_h$, $b_0 = 11a_h$, and $c_0 = c_h$. Other crystals in the composition range $Na_{0.025}UO_3$ to $Na_{0.14}UO_3$ gave similar patterns.

Infrared Spectroscopy. The infrared spectra of the bronze samples are summarized in Table IV. When compared with the spectrum of α-UO_3, it can be seen that as sodium is introduced into the structure, a small peak develops at 912 cm^{-1} between the peaks comprising the α-UO_3 doublet (890 and 930 cm^{-1}). A further increase in the Na/U ratio causes the absorption at 930 cm^{-1} to decrease in intensity until at $Na_{0.11}UO_3$ it is barely perceptible. The 890-cm^{-1} peak, on the other hand, does not noticeably grow weaker but appears to shift to slightly higher frequency, and the additional peak is now seen as a shoulder on this band, at about 910 cm^{-1}. For $Na_{0.135}UO_3$ and samples of higher sodium content in which the uranium vacancies are completely filled with sodium atoms, a single fairly broad absorption band at about 900 cm^{-1} probably reflects the complete filling of uranium vacancies.

Oxidized Bronze, $Na_xU_{(1-1/6x)}O_3$. Heating the sodium uranium bronze samples at 730° under an oxygen pressure of 160 atm caused a color change from green to a pale brown very similar to that of α-UO_3 heated under these conditions. The color change suggested that oxidation of U(V) to U(VI) had occurred and this was confirmed by the determination

Table II. Atom Positions in $Na_{0.10}UO_3$ (Space Group $C222$)

		x	y	z	B, Å^2	P
U(1)	2(a)	0.0	0.0	0.0	0.6 ± 0.2	0.892 ± 0.011
U(2)	4(g)	0.0	0.309 ± 0.001	0.0	0.6 ± 0.2	1.784[a]
O(1)	2(d)	0.0	0.0	0.5	1.0 ± 0.2	0.784[a]
O(2)	4(h)	0.0	0.309 ± 0.001	0.5	1.0 ± 0.2	1.567[a]
O(3)	4(i)	0.0	0.0	0.4	1.0 ± 0.2	0.216[a]
O(4)	8(l)	0.0	0.309 ± 0.001	0.4	1.0 ± 0.2	0.433[a]
O(5)	2(b)	0.0	0.5	0.0	1.0 ± 0.2	0.982[b]
O(6)	8(l)	0.163 ± 0.002	0.137 ± 0.001	0.0	1.0 ± 0.2	3.928[b]
Na(1)	2(a)	0.0	0.0	0.0	0.6 ± 0.2	0.089[a]
Na(2)	4(g)	0.0	0.309 ± 0.001	0.0	0.6 ± 0.2	0.178[a]

[a] These occupation parameters are dependent on the value for atom U(1): $P_{U(2)} = 2P_{U(1)}$; $P_{O(1)} = 1.0 - 2P_{U(1)}$; $P_{O(2)} = 2.0 - 4P_{U(1)}$; $P_{O(3)} = 2(1.0 - P_{U(1)})$; $P_{O(4)} = 4(1.0 - P_{U(1)})$; $P_{Na(1)} = 0.1P_{U(1)}$; $P_{Na(2)} = 0.2P_{U(1)}$. [b] These occupation parameters are fixed at their value for α-UO_3 containing 12.1% of cation vacancies; any oxygen loss incurred during preparation is thus reflected in an increase in the uranium occupation parameters.

Table III. Calculated and Observed Intensities[a]

hkl	I_{calcd}	I_{obsd}	σ-(I_{obsd})
001	11.43	11.43	0.17
200 130	14.46	14.43	0.18
201 131	1.10	0.92	0.12
002	9.95	10.30	0.33
330 060	15.14	15.43	0.30
331 061 132 202	10.90	10.85	0.19
400 260	4.75	4.54	0.17
261 401	0.20	0.36	0.10
062 332	14.47	14.35	0.40
003	1.52	1.67	0.17
402 262	5.02	4.84	0.20
460 203 133 190 530	3.23	3.80	0.30
461 191 531	0.20	0.23	0.10
063 333 600 390	5.73	5.65	0.40
192 532 462 391 601	5.60	5.73	0.40
403 263	0.28	0.20	0.10
004	2.22	2.24	0.20

[a] $R(I) = 0.024$ (17 intensities).

Table IV. Infrared Absorption Bands in the Uranyl Region (850–950 cm^{-1})[a]

	890 cm^{-1}	900 cm^{-1}	912 cm^{-1}	930 cm^{-1}
α-UO_3	s			s
α-U_3O_8				
Bronze samples				
$Na_{0.05}UO_3$	s		m	s
$Na_{0.08}UO_3$	s		s	w
$Na_{0.11}UO_3$	s		s, sh	vw, sh
$Na_{0.135}UO_3$		s, br		
Oxidized bronzes				
$Na_{0.050}U_{0.990}O_3$	s		w	s
$Na_{0.079}U_{0.987}O_3$	s		m	s
$Na_{0.127}U_{0.979}O_3$	s		s	m, sh
$Na_{0.146}U_{0.976}O_3$	s		s, sh	vw, sh
$Na_{0.165}U_{0.973}O_3$		s, br		
Reduced bronzes				
$Na_{0.025}UO_{3-x}$		m, br		
$Na_{0.050}UO_{3-x}$		s, br		
$Na_{0.110}UO_{3-x}$		s, br		

[a] s = strong, m = medium, w = weak, vw = very weak, sh = shoulder, br = broad.

of the uranium valence state. The following evidence indicates that oxidation is accompanied by an increase in the number of uranium vacancies which in turn may be filled by Na^+ ions. (i) The variation of infrared spectra with increasing sodium content (Table IV) resembles that observed in the bronze. However, at a given Na/U ratio, the peak at 930 cm^{-1} is more intense in the oxidized sample and the single broad band at about 900 cm^{-1} is now obtained at a Na/U ratio of 0.17 compared with 0.135 in the bronze. (ii) Debye-Scherrer X-ray photographs indicated a hexagonal unit cell or subcell similar to α-UO_3 and the bronzes (see Table I) but the upper composition limit of this phase now appears to be at a Na/U ratio of 0.18. (iii) Electron diffraction patterns indicate that the α-UO_3 structure is retained so that the unit cell has nominal composition $M_{22}O_{58}$ ($MO_{2.636}$). Assuming oxidation of U(V) to U(VI) occurs, elimination of all vacancies would be expected at a Na/U ratio of 0.17, in excellent agreement with X-ray and infrared evidence. The correct formulation of this phase should therefore be $Na_xU_{(1-1/6x)}O_3$.

Reduction of the Bronze. Bronze samples of low sodium content lost oxygen when heated at 730° to give a product which was shown by X-ray diffraction to consist of a single orthorhombic phase analogous to α-U_3O_8 (see, for example, $Na_{0.025}UO_{3-x}$ in Table I). The electron diffraction patterns of these reduced bronzes differed quite markedly from those of α-UO_3, but at higher sodium content (*e.g.*, at a Na/U ratio of 0.11) most diffraction patterns obtained were identical with those of α-UO_3, and X-ray diffraction patterns could also be indexed on a simple hexagonal cell (see, for instance, $Na_{0.11}UO_{2.93}$ in Table I).

The experimental densities (Table V) are all slightly lower than the calculated values, but they support the proposition that the structure has collapsed on reduction to eliminate most of the vacancies on the uranium sublattice. In order to obtain a quantitative estimate of the oxygen lost under these circumstances, two samples (Na/U = 0.05 and Na/U = 0.11) were prepared at 730° in an evacuated system of known volume connected to a manometer. From measurement of the pressure change, the stoichiometries of $Na_{0.05}UO_{2.81\pm0.01}$ ($M_3O_{8.03\pm0.03}$) and $Na_{0.11}UO_{2.93\pm0.01}$ ($M_3O_{7.92\pm0.03}$) were calculated. The stoichiometries suggest a collapse to a structure related to α-U_3O_8 at low sodium contents whereas for a Na/U ratio of 0.11, additional oxygen loss seems to occur to give a composition $MO_{2.64}$. It appears likely, therefore, that the structure of $Na_{0.11}UO_{2.93}$ also involves a unit cell of composition $M_{22}O_{58}$ (*i.e.*, $MO_{2.636}$) and although the crystallites of this compound were too small for satisfactory electron microscope study (typically <0.5 μ), it was possible to ascertain that their electron diffraction patterns were similar to those from α-UO_3.

The infrared spectra of both samples prepared at 730°, together with the spectrum of a sample with a Na/U ratio of 0.025 prepared similarly (Table IV), consist of a single absorption band in the uranyl region at about 900 cm^{-1}. Apart from the uranyl region, the spectra resemble α-U_3O_8 at low sodium contents and α-UO_3 at higher sodium compositions.

Discussion

Na_xUO_3. The structural behavior of the bronze, Na_xUO_3, is entirely consistent with the incorporation of sodium ions into the vacancies of the α-UO_3 structure. In particular, we note that (i) the experimentally estimated phase limit is close to the expected composition of $Na_{0.138}UO_3$ (ii) the neutron diffraction refinement indicates filling of the uranium vacancies (iii) with the introduction of sodium, no change in the electron diffraction patterns can be observed (iv) the changes observed in the infrared spectra with gradual uptake of sodium strongly support the filling of uranium vacancies by sodium and (v) density measurements are also consistent with this scheme.

Table V. Observed and Calculated Densities (g cm^{-3})

	Obsd density	Density calcd on a U occupation parameter of 0.879	Density calcd for complete occupancy of the cation sites
α-UO_3	7.2	7.43	
α-U_3O_8	8.2		8.42
$Na_{0.1}UO_3$	7.2	7.47	7.69
$Na_{0.025}UO_{3-x}$	8.0	7.57	8.29
$Na_{0.025}UO_3$	7.3	7.44	8.22

A detailed analysis of the infrared spectra is more complex, however, and an unambiguous interpretation is not possible. We have assumed in the following discussion that all infrared active vibrations in the uranyl region are attributable to $U(VI)\leftarrow O$ where $\leftarrow$ indicates a shortened U-O distance. This is justifiable on the grounds that no new features can be detected in the spectrum of samples known to contain both U(V) and U(VI) when compared with those containing U(VI) alone.

If we assume that the uranium vacancies are randomly distributed, then the proportion of $-OUOU\leftarrow O\square$ ($U\leftarrow O$) groups (looking along the *c* axis) should be about 9 times greater than the number of $\square O\rightarrow U\leftarrow O\square$ ($O\rightarrow U\leftarrow O$) units so that the two bands observed for α-UO_3 in the uranyl region are either (i) a split $U\leftarrow O$ localized frequency, (ii) a split $O\rightarrow U\leftarrow O$ band, or (iii) absorptions from a mixture of $O\rightarrow U\leftarrow O$ and $U\leftarrow O$. Interpretation in terms of either ii or iii would require an increase in the statistical proportion of $O\rightarrow U\leftarrow O$ units as a result of short-range order. We prefer, though it is not possible to be certain about this, to assume the vibrations are associated with $O\rightarrow U\leftarrow O$ units. Our reasoning stems from the fact that if the absorption bands were associated with two separate species, then introduction of sodium would be expected to lead to a decrease in frequency for both bands. This is not observed. We have also to consider that the spectra arise from splitting of the $U\leftarrow O$ vibration, but this has not previously been observed and, moreover, the peak at 912 cm^{-1} which appears at low sodium content but disappears when all vacancies are filled cannot be accounted for on this basis. On the other hand, splitting of the ν_3 frequency of the UO_2^{2+} cation has been reported for some uranyl compounds, *e.g.*, UO_2Cl_2[9] and uranyl nitrate complexes.[10] If $O\rightarrow U\leftarrow O$ groups are indeed responsible for the observed spectra, then either these units exist in chains, eliminating all $U\leftarrow O$ groups, or else the $U\leftarrow O$ species does not give rise to a detectable localized vibration mode in this region of the spectrum. In the absence of further information we prefer to base our arguments on the latter possibility.

Assignments made on this basis are collected in Table VI. The peak at 912 cm^{-1} which appears on the introduction of small amounts of sodium probably represents a configuration $\square O\rightarrow U\leftarrow ONa^+$ which, as the sodium concentration increases, is eventually replaced by $Na^+O\rightarrow U\leftarrow ONa^+$ and this unit, we believe, gives rise to the broad band at 900 cm^{-1}. The band width suggests an unresolved doublet as indicated in Table VI. Since a reduction in frequency is expected when the

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Table VI. Possible Infrared Peak Assignments

Unit	ν_3, cm^{-1}	Mean ν_3
$\square O \rightarrow U \leftarrow O \square$	930, 890	910
$Na^+ O \rightarrow U \leftarrow O \square$	912 (+895?)	904
$Na^+ O \rightarrow U \leftarrow ONa^+$	900 (905 + 895)	900

$O \rightarrow U \leftarrow O$ unit becomes coordinated to one sodium ion, it seems likely that the $\square O \rightarrow U \leftarrow ONa^+$ grouping gives rise to the ν_3 doublet indicated, one component of which is at approximately 895 cm^{-1}. The assignment implies that both the splitting of the uranyl band and the mean frequency decrease as the sodium content increases. It accounts for the fact that the absorption at 890 cm^{-1} does not decrease in intensity (unlike the 930-cm^{-1} band), as the vacancies are filled, but merely appears to shift to slightly higher frequency as the peak at 895 cm^{-1} becomes more intense.

Oxidized and Reduced Bronzes. The behavior of the bronze on oxidation and reduction gives rise to related phases which can be easily understood. We wish to make, however, two additional comments. For the oxidized samples, the composition range observed extends beyond the composition $Na_2O \cdot 13UO_3$ reported by Carnall, *et al.*[3] We did not, however, find the extra X-ray reflections they describe, although the infrared spectrum of their phase is very similar to ours at the same composition. In the reduced bronzes, it is interesting to note that when the vacancy (or sodium ion) concentration exceeds about 5%, the system appears to adopt the $M_{22}O_{58}$ unit cell (*cf.* α-UO_3, the bronze and the oxidized bronze) in preference to the M_6O_{16} cell of α-U_3O_8. The stability of the $M_{22}O_{58}$ cell is substantiated by the fact that once all the vacant uranium sites are filled with sodium, additional sodium is not incorporated by substitution for uranium, giving a reduced O/M ratio (*cf.* L-Ta_2O_5). Instead, a new phase forms which appears to be related to $Na_2U_2O_7$. In the latter compound, sodium ions are situated *interstitially* between the pseudo-hexagonal layers of uranium atoms.

Acknowledgment. We thank the Science Research Council and A.E.R.E. Harwell for the provision of neutron diffraction facilities and the University Support Group for some experimental assistance.

Registry No. UO_3, 1344-58-7; Na_xUO_3, 39390-02-8.

Notes

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Reactions of Octacyanomolybdate(IV). III. Infrared and Magnetic Studies of Compounds with Divalent First-Row Transition Metals

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Received April 16, 1973

Previously there have been systematic studies of six-coordinate transition metal complexes of cyanide[1-4] but little work in the area of eight-coordinate cyanide complexes appears to have been done. Except for $K_4Mo(CN)_8 \cdot 2H_2O$ little attention has been given to the spectral, magnetic, and structural properties of the salts of the octacyanomolybdate(IV) ion, specificially those of the divalent first-row transition metals.[5,6] In this note we report the results of infrared and magnetic studies of the series of compounds $M_2Mo(CN)_8 \cdot nH_2O$, where M = Mn^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, and Zn^{2+} and n varies from 2 to 9 depending on the cation in question. The results are disappointing in their lack of definition but emphasize the weakness of interactions with $Mo(CN)_8{}^{4-}$.

Experimental Section

Reagents and Physical Measurements. Potassium octacyanomolybdate(IV) was prepared by the method of Furman and Miller[7] from reagent grade materials. The divalent cation salts were of reagent grade and were used without further purification. Chemical microanalyses were performed by the Microanalytical Laboratory of the University of Illinois. Infrared spectra of the solid samples as Nujol mulls were recorded in the cyanide stretching region on a Beckman IR-7 spectrophotometer. Magnetic moments were determined by the Gouy method utilizing an electromagnet and a Sartorius 2403 balance with $Hg[Co(CNS)_4]$ as a standard.[8]

Hydrated Divalent Salts of Octacyanomolybdate(IV). All the divalent salts were prepared essentially in the same manner. Approximately 0.02 mol of the chloride salt (except for Cu^{2+}, where $CuSO_4$ was used) was dissolved in *ca.* 50 ml of distilled water. To each of the solutions was added 25 ml of freshly prepared 0.25 *M* $K_4Mo(CN)_8 \cdot 2H_2O$. In all cases except Mn^{2+} an immediate precipitate formed [$Mn_2Mo(CN)_8 \cdot 8H_2O$ required *ca.* 10 min standing time before precipitation occurred]. The solids were collected by filtration, washed with acetone, and vacuum dried.

Zinc Octacyanomolybdate(IV)-2-Water. *Anal.* Calcd for $Zn_2Mo(CN)_8 \cdot 2H_2O$: C, 20.40; H, 0.85; Zn, 27.76. Found: C, 20.88; H, 0.76; Zn, 27.76.

Copper Octacyanomolybdate(IV)-6.5-Water.[9] *Anal.* Calcd for $Cu_2Mo(CN)_8 \cdot 6.5H_2O$: C, 17.52; H, 2.39; Cu, 23.17. Found: C, 17.11; H, 2.39; Cu, 23.25.

Nickel Octacyanomolybdate(IV)-9-Water.[9] *Anal.* Calcd for $Ni_2Mo(CN)_8 \cdot 9H_2O$: C, 16.46; H, 3.10; Ni, 20.11. Found: C, 16.57; H, 2.90; Ni, 19.95.

Cobalt Octacyanomolybdate(IV)-9-Water.[9] *Anal.* Calcd for $Co_2Mo(CN)_8 \cdot 9H_2O$: C, 16.45; H, 3.11; Co, 20.17. Found: C, 16.81; H, 3.12; Co, 19.75.

Iron(II) Octacyanomolybdate(IV)-7.5-Water.[9] *Anal.* Calcd for $Fe_2Mo(CN)_8 \cdot 7.5H_2O$: C, 17.44; H, 2.74; Fe, 20.27. Found: C, 17.70; H, 2.64; Fe, 19.99.

Manganese Octacyanomolybdate(IV)-8-Water. *Anal.* Calcd for $Mn_2Mo(CN)_8 \cdot 8H_2O$: C, 17.22; H, 2.89; Mn, 19.69. Found: C, 16.99; H, 2.83; Mn, 19.99.

Results and Discussion

Infrared Spectra. Figure 1 shows the infrared spectra of $K_4Mo(CN)_8 \cdot 2H_2O$ and $Ni_2Mo(CN)_8 \cdot 9H_2O$ in the cyanide stretching region. The infrared absorbances of these com-

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