interest are studies of spinels, perovskites, and silicates, which often dissolve with difficulty in more conventional calorimetric solvents. A first report dealing with the enthalpy changes associated with the transformation of the metastable modifications of Al_2O_3 to α-Al_2O_3 (corundum) has been published.[6]

Reactions in Molten Salt Solutions. I.
Uranate and Neptunate Formation in Molten Lithium Nitrate–Sodium Nitrate[1]

By W. T. CARNALL, S. J. NEUFELDT, AND A. WALKER

The reaction of U(VI), Np(V), and Np(VI) with BrO_3^- in molten $LiNO_3$–$NaNO_3$ resulted in the formation of solid compounds which could be separated from the melt and which were characterized as new mixed alkali metal–actinide oxide phases. The infrared spectra of these compounds, and their cell constants evaluated from X-ray diffraction patterns, were compared with those of pure $Na_2U_2O_7$, $Na_2Np_2O_7$, and $CaUO_4$. A close structural relationship with the latter compounds was shown to exist. Interpretations of some of the infrared absorption bands of the compounds studied were offered, and U–O_I and Np–O_I bond distances were calculated.

In an attempt to prepare and isolate higher oxides of the actinides, we have for some time been studying certin reactions of these elements in anhydrous molten nitrate salt media. The present communication summarizes our results with uranium and neptunium in the $LiNO_3$–$NaNO_3$ eutectic.

Spectrophotometric studies have shown that lower oxidation states of uranium are rapidly oxidized to the hexavalent state, while those of neptunium are oxidized to the pentavalent state in molten nitrate salts.[2] Under certain conditions the hexavalent state of neptunium can also be observed in the melt, but the pentavalent state is the stable species.

In the course of our work it was found that the addition of solid anhydrous $NaBrO_3$ to solutions of U(VI), Np(V), or Np(VI) in $LiNO_3$–$NaNO_3$ initiated a reaction that resulted in the formation of a solid actinide-containing compound which could be separated from the bulk of the solvent by filtration. Duke and Lawrence[3] have studied the kinetics of the reaction of BrO_3^- with a number of metal ions in molten alkali nitrate media. In the case of Zn^{2+}, their results were consistent with the reaction

$$2Zn^{2+} + 4BrO_3^- = 2ZnO + 2Br_2 + 5O_2$$
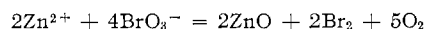
By analogy, the reaction of BrO_3^- with the actinide species in solution might have been expected to yield the corresponding trioxide. However, the product actually separated proved to be complex and could be identified as a mixed alkali metal–actinide oxide.

There are numerous references to the characterization of compounds of the form $A_2O \cdot xUO_3$, the alkali metal uranates, where A is an alkali metal element and x may be a fractional or a whole number,[4] but much less work has been published with respect to the corresponding compounds of the transuranium elements, the actinates.[5]

The present technique of preparation is new. It involves reaction at much lower temperatures than normally required and thus is of particular interest in synthesizing alkali metal actinates which may have a limited region of thermal stability. Information relative to the structure of the compounds isolated was obtained from X-ray diffraction patterns and infrared spectra.

Experimental

The preparation and handling of the $LiNO_3$–$NaNO_3$ eutectic (m.p. 206°, 44.8 mole % $NaNO_3$) was carried out in a manner described previously for the $LiNO_3$–KNO_3 eutectic.[6] Reagent grade chemicals were employed. Spectroscopically pure UO_3 and NpO_2 were used to prepare the corresponding actinyl nitrates, which were then dried at ~200°, prior to combination with the eutectic in quartz or borosilicate glass tubes. Insoluble material was dissolved with the aid of NH_4NO_3.[6] The reaction vessel was frequently a spectrophotometer cell, which made it possible to check for the absence of H_2O absorption bands near 2.0 μ, after treatment of the melt with a stream of dry N_2 gas, before initiating the reaction.

(1) Based on work performed under the auspices of the U. S. Atomic Energy Commission. Presented in part at the 149th National Meeting of the American Chemical Society, Detroit, Mich., April 1965.

(2) D. M. Gruen, R. L. McBeth, J. Kooi, and W. T. Carnall, *Ann. N. Y. Acad. Sci.*, **79**, 941 (1960).

(3) F. R. Duke and W. W. Lawrence, *J. Am. Chem. Soc.*, **83**, 1269 (1961).

(4) V. I. Spitsyn, Ed., "Investigations in the Field of Uranium Chemistry," Moscow University Press, 1961. Argonne National Laboratory Translation 33 (1964).

(5) C. Keller, Kernforschungszentrum Karlsruhe Report KFK-225, Feb. 1964.

(6) W. T. Carnall, *Anal. Chem.*, **34**, 786 (1962)

Following the reaction between $NaBrO_3$ and the actinide species, the bulk of the melt was removed by filtration and the remaining solid product was washed free from melt with either (1) H_2O at 25° or (2) liquid NH_3 at −38°. The two different methods were employed so as to determine whether the solvent had any effect on the product from the fused nitrate. No solubility of the reaction product in either solvent was indicated. Samples thus separated, and heated either at 100° under vacuum for several hours or at 600°, gave practically identical analyses.

In the course of the investigation, actinates were also prepared by heating mixtures of UO_3 and alkali metal carbonates to 600–800°. All products were dissolved in dilute acid with slight warming as a first step in the analysis. The course of the dissolution was closely observed in order to detect any slightly soluble components—particularly U_3O_8 in the case of the uranates ignited at 800°. Analyses for lithium and sodium were made using a flame photometer with suitable standards, while uranium was determined by a colorimetric method,[7] and neptunium was determined spectrophotometrically. Nitrate analyses were also performed.

Infrared spectra were measured from 4000 to 166 cm.$^{-1}$ employing two different grating spectrophotometers. Characteristic absorption bands for the compounds studied were all found at <1000 cm.$^{-1}$. The resolution from 1000 to 300 cm.$^{-1}$ was better than 3 cm.$^{-1}$, while that from 300 to 166 cm.$^{-1}$ was better than 2 cm.$^{-1}$. Calcium uranate, $Na_2U_2O_7$, and $K_2U_2O_7$ were also examined in the 166–70 cm.$^{-1}$ region. Both the Nujol mull and KBr disk techniques were employed from 1000 to 300 cm.$^{-1}$. Since there were no extraneous absorption peaks introduced using KBr, and since the disk technique gave sharper bands, spectra obtained in that medium are presented in Figure 1. Bands at <300 cm.$^{-1}$ were observed only in Nujol mulls using polyethylene windows. They are not shown in the figure.

Results

The reaction of $NaBrO_3$ with clear solutions of UO_2^{2+} in molten $LiNO_3$–$NaNO_3$ was studied at several different temperatures ranging from 210°, which was practically the lowest temperature attainable, to ~270°. At higher temperatures the uranium species showed evidence of thermal decomposition independent of the BrO_3^- reaction. In contrast to this behavior in the melt, pure anhydrous $UO_2(NO_3)_2$ begins to decompose at temperatures as low as 170°.[8] The product of the thermal decomposition of U(VI) in the melt was also an alkali metal uranate and not a pure oxide phase, although thermal decomposition of pure $UO_2(NO_3)_2$ or $UO_2(NO_3)_2·6H_2O$ can yield any one of several different crystal modifications of pure UO_3, depending upon the conditions employed.[9]

Analysis of the complex product of the reaction of UO_2^{2+} with BrO_3^- showed no variation with the temperature at which the reaction was carried out. Typical results are found in Table I. The analyses were consistent with a product approaching the composition of $Na_2U_2O_7$, but also containing a small amount of lithium. The analysis of a sample of $Na_2U_2O_7$ prepared by igniting the appropriate amounts of Na_2CO_3 and UO_3 at 800° is also included in the table. The X-ray diffraction pattern and the infrared spectrum of this sample will be referred to later.

(7) C. Crouthamel and C. Johnson, *Anal. Chem.*, **24**, 1780 (1952).

(8) C. C. Addison, H. A. J. Champ, N. Hodge, and A. H. Norbury, *J. Chem. Soc.*, 2534 (1964).

(9) V. J. Wheeler, R. M. Dell, and E. Wait, *J. Inorg. Nucl. Chem.*, **26**, 1829 (1964).

TABLE I
ANALYSES OF ALKALI METAL ACTINATES FORMED BY REACTION IN MOLTEN $LiNO_3$–$NaNO_3$

Reaction temp., °C.	% Na	% Li	% M	Molar ratio[b] $MO_3/(Na_2O + Li_2O)$
220	6.25	0.2	76.2 (U)	2.13
240	6.10	0.3	74.5 (U)	2.03
270	6.15	0.3	75.0 (U)	2.03
(800)[a]	7.32	0.0	75.4 (U)	1.99
225	5.74	0.3	74.9 (Np)	2.16
250	6.75	0.3	73.5 (Np)	1.92
(700)[a]	7.4	0.0	74.9 (Np)	1.96

[a] Pure sodium diactinates prepared from Na_2CO_3 and UO_3 or Np_3O_8. [b] M = U or Np.

Dissolution of $NpO_2(NO_3)_2·xH_2O$ in the $LiNO_3$–$NaNO_3$ melt at ~215° gave a clear solution whose absorption spectrum was very similar to that of NpO_2^{2+} in aqueous solution at 25°. However on standing, even within 5–10 min., the gradual decomposition of NpO_2^{2+} to NpO_2^+ was obvious. At higher temperatures, only the spectrum of NpO_2^+ was observed. We were able to establish that regardless of whether the bromate reaction was carried out at ~215° with essentially pure NpO_2^{2+} or at 250° with NpO_2^+, the reaction product gave the same analysis and contained only Np(VI). The results shown in Table I were typical and proved to be essentially identical with those obtained in the uranium reaction. Pure $Na_2Np_2O_7$ was prepared for purposes of comparison with the melt product by fusion of Na_2CO_3 and Np_3O_8 at 700°.

Since the uranate isolated from the nitrate melt proved to be thermally stable at 800°, several additional samples were prepared for purposes of comparison by igniting mixtures of alkali metal carbonates with UO_3. A sample corresponding to the analysis of the complex uranate as shown in Table I was prepared from Li_2CO_3, Na_2CO_3, and UO_3. The X-ray diffraction pattern and infrared spectrum of this product after ignition at 750° were very similar to those of the complex uranate. These results added support to the argument that lithium detected in the analysis of the product from the melt was indeed an integral component of the complex uranate.

The X-ray diffraction patterns of the lithium–sodium uranate and neptunate obtained from the fused nitrate proved to be very similar to those of $Na_2U_2O_7$ and $Na_2Np_2O_7$. All are defect structures of the $CaUO_4$ type.[10] While the higher angle reflections of the complex uranate heated at temperatures < ~300° were quite indistinct, there appeared to be very little change in the diffraction pattern upon stepwise heating of the sample to 800°. We were able to index all of the observed lines in an orthohexagonal cell. The results given in Table II are those for the water washed product heated to 800°. Essentially the same cell dimensions were obtained for samples of the NH_3-washed uranate. The calculated density for three molecules per unit cell is 6.68 g./cm.^{3}. The measured density was 6.28 g./cm.^{3}.

(10) W. H. Zachariasen, *Acta Cryst.* **1**, 281 (1948).

TABLE II
RESULTS OF X-RAY DIFFRACTION STUDIES

Compounds	a, Å.	b, Å.	c, Å.	Type[a]
$CaUO_4$[b]	3.86		17.50	r-h
$Na_2U_2O_7$[b]	3.93	6.81	17.76	o-h
$(Li,Na)_2U_2O_7$[c]	3.92	6.79	17.64	o-h
$Na_2Np_2O_7$	3.91	7.27	17.11	o
$(Li,Na)_2Np_2O_7$	3.92	6.77	17.65	o

[a] r-h = hexagonal indexing of actual rhombohedral cell,[10] o-h = orthohexagonal indexing, o = orthorhombic indexing. [b] ρ_{calcd} = 6.65; ρ_{measd} = 6.44. [c] ρ_{calcd} = 6.8; ρ_{measd} = 6.28.

Discrepancies of this magnitude have been observed for a number of other alkali metal uranates.[11]

The sample of $Na_2U_2O_7$ whose analysis was referred to earlier could also be indexed in an orthohexagonal cell using the same constants obtained by Kovba and co-workers,[11] Table II. The calculated density for three molecules per unit cell is 6.65 g./cm.³. The measured value was 6.44 g./cm.³. While the parameters for the complex uranate were very similar to those of $Na_2U_2O_7$, the structures were distinct. This was further indicated by the infrared spectra of the compounds.

The crystal lattice of $Na_2Np_2O_7$ was found to have orthorhombic symmetry, as was also the case for the complex neptunate. In both instances the samples had been heated to 700°. The cell parameters are given in Table II. The results were again consistent with three molecules per unit cell. The constants determined in the present investigation for $Na_2Np_2O_7$ differ only slightly from those reported by Keller.[5]

Infrared spectra also revealed a close structural relationship between the complex uranate, complex neptunate, $Na_2U_2O_7$, and $Na_2Np_2O_7$. Results shown in Figure 1 demonstrate that bands in all four compounds occur at nearly the same energies. The differences in the spectra are due primarily to differences in band intensities, with the exception of a prominent extra band in $Na_2U_2O_7$ observed at ~780 cm.⁻¹.

Since we were not able to prepare single crystals of the compounds under investigation, it seemed worthwhile to glean as much information from the infrared spectra as possible including the calculation of bond lengths. As an aid in interpreting our data, we also obtained the infrared spectrum of $CaUO_4$ (Figure 1).

In $CaUO_4$, each uranium is surrounded by eight oxygen atoms. Of the six secondary oxygens (O_{II}), three lie slightly above and three slightly below a plane containing the uranium atoms. The uranyl bonds (O_I-U-O_I) are normal to this surface. The structure of $CaUO_4$ is thus made up of stacked hexagonal (UO_2)O_2 layers with calcium atoms lying in between and holding the planes together.[10] Each calcium atom is bonded to six O_I and two O_{II}.

If we consider only the symmetry properties of the uranium atom and its eight nearest neighbor oxygens, the point group is D_{3d}. Group theoretical analysis predicts seven infrared-active frequencies, four of which
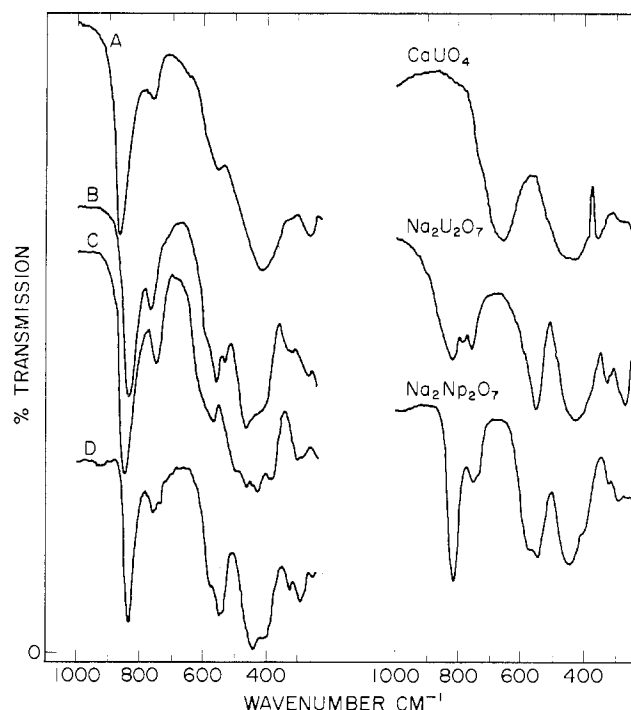

Figure 1.—The infrared absorption spectra (300–1000 cm.⁻¹) of (A) complex uranate separated from the nitrate melt, washed and dried at 25°; (B) complex uranate heated to 800°; (C) complex neptunate (25°); (D) complex neptunate (800°), $CaUO_4$, $Na_2U_2O_7$, and $Na_2Np_2O_7$.

will be doubly degenerate. In addition, there are six Raman-active modes. The symmetry species and the corresponding number of vibrations are

A_{1g}	Three Raman-active modes only
A_{2u}	Three infrared-active modes only
E_g	Three Raman-active modes only
E_u	Four infrared-active modes only
A_{1u}	One inactive

Of the three nondegenerate modes belonging to the A_{2u} representation, one must be the asymmetric stretch of the O_I-U-O_I bonds. This should give rise to the highest frequency vibration characteristic of the system since the U-O_I bond distance is much shorter than that of U-O_{II}. Similarly, we can picture a second A_{2u} species as essentially a bending mode of the six U-O_{II} bonds. This might be expected to constitute the lowest energy vibration of the set, since these bonds are relatively weak.

Jones[12] and more recently Hoekstra[13,14] have summarized infrared and U-O_I bond length data for a large number of uranyl salts. The bond lengths were calculated using Badger's relationship[15] in the form derived by Jones,[12] and good agreement was found with crystallographic bond lengths in those few compounds where the latter have been determined. Application of the expression to the compounds of interest in the present investigation required some modification, since we were not able to observe a combination frequency (U-O_I asymmetric plus symmetric stretch), even in thick samples. Jones used such a frequency to obtain a

(11) L. M. Kovba, E. A. Ippolitova, Yu. P. Simanov, and V. I. Spitsyn, *Dokl. Akad. Nauk SSSR*, **120**, 1042 (1958).

(12) L. H. Jones, *Spectrochim. Acta*, **10**, 395 (1958); *ibid.*, **11**, 409 (1959).
(13) H. R. Hoekstra, *Inorg. Chem.*, **2**, 492 (1963).
(14) H. R. Hoekstra, *J. Inorg. Nucl. Chem.*, **27**, 801 (1965).
(15) R. M. Badger, *J. Chem. Phys.*, **2**, 128 (1934).

small correction to the force constant for the U–O$_I$ bond. Of the cases cited, this correction amounted to not more than 3% of the force constant based on the asymmetric stretching frequency alone. Thus the error is assumed to be quite small in neglecting the correction altogether, and the resulting relationship between ν_A, the asymmetric stretching frequency in cm.$^{-1}$, and the U–O$_I$ bond distance, $R_{U–O_I}$, is

$$R_{U–O_I} \text{ (Å.)} = 53.3\nu_A^{-2/3} + 1.17 \qquad (1)$$

The calculated values of $R_{U–O_I}$ using (1) are essentially identical with those given by Jones and Hoekstra.

Application of (1) to the 665 cm.$^{-1}$ band of CaUO$_4$, which according to our analysis should be the asymmetric stretching frequency, gives $R_{U–O_I}$ = 1.87 Å., in good agreement with the 1.91 ± 0.1 Å. obtained crystallographically.[10]

Kovba and co-workers proposed a structure for Na$_2$U$_2$O$_7$ in which the symmetry and uranium–oxygen bond distances are practically identical with those in CaUO$_4$.[11] On the basis of this structure we would assign the highest frequency absorption band in the spectra of the complex actinates, Na$_2$U$_2$O$_7$, and Na$_2$Np$_2$O$_7$ to the asymmetric stretching mode O$_I$–U–O$_I$ or O$_I$–Np–O$_I$.

Trace A (Figure 1) was obtained from a sample of the complex uranate which had been formed by reaction at 230°, cooled to −38°, and washed free of LiNO$_3$–NaNO$_3$ using liquid NH$_3$. It was then placed under vacuum for several hours at 25° and subsequently pressed into a KBr disk. Similar samples were heated in open vessels in increasing increments of 50° for 10 hr. before pressing into KBr. There was no change in the infrared spectra of these samples until ∼450°. At >450° the 860 cm.$^{-1}$ band shifted progressively to lower frequencies until at 800° it was observed at ∼820 cm.$^{-1}$, trace B. At this temperature it practically coincides with the highest frequency band of Na$_2$U$_2$O$_7$ prepared by igniting Na$_2$CO$_3$ and UO$_3$ at 800°.

The behavior of similar complex neptunate samples under the same conditions (Figure 1, traces C and D) followed that of the uranates except that the energy range over which the highest frequency band migrated was smaller (∼850 to 830 cm.$^{-1}$).

We found, therefore, experimental support for the assignment of the band observed near 820 cm.$^{-1}$ in Na$_2$U$_2$O$_7$, Na$_2$Np$_2$O$_7$, and the complex actinates to an asymmetric stretching mode. The observed intensity would be difficult to explain on any basis except that of an allowed fundamental frequency. In addition, the behavior in the complex actinates upon heating was consistent with the assignment, since the movement to lower frequencies suggests a decrease in the U–O$_I$ or Np–O$_I$ bond order resulting from a strengthening either of the heavy metal–secondary oxygen bonds, or of the Na–O$_I$ bonds which we assume bind the infinite actinide–O$_{II}$ layers together.

However, an inconsistency in the proposal of Kovba, *et al.*, is immediately obvious by virtue of the energy at which the high-frequency band is found in the Na$_2$U$_2$O$_7$-type compounds as compared to that in

CaUO$_4$. If in both cases the actinide–O$_I$ bond distance were the same, the asymmetric stretching modes should occur at essentially the same energy. Indeed from eq. 1, $R_{M–O_I}$ = 1.78 Å. based on an asymmetric stretching frequency at ∼820 cm.$^{-1}$. This is considerably shorter than the 1.92 Å. value arrived at by Kovba and co-workers[11] and necessitates a considerable modification of the U–O distances they suggested.

It should be emphasized at this point that the X-ray diffraction results only establish the similarity in the uranium positions in the compounds under investigation to those in CaUO$_4$. There is no crystallographic evidence which has established the existence of uranyl groups in the sodium diactinates studied here. However, the infrared spectra are quite consistent with the assumption that these groups are present. The energy of the bands observed merely suggests a modification of the oxygen position compared to those in CaUO$_4$.

If we assume that there are two U–O$_I$ bonds, using Na$_2$U$_2$O$_7$ as an example of the type of compounds we are considering, then there are 1.5 O$_{II}$ instead of 2 O$_{II}$ as in CaUO$_4$. Thus a U–6O$_{II}$ coordination for each U atom is clearly not possible under the conditions assumed. Since fully one-quarter of the oxygen atoms per uranium would be missing, a CaUO$_4$-type structure with randomly placed oxygen vacancies seems unlikely. It may be mentioned that one solution to the problem would be to allow for mixed U–O$_{II}$ coordination. On this basis a possible structure would be one in which 75% of the uranium atoms were coordinated to 4 O$_{II}$ and 25% to 6 O$_{II}$. The question of whether the two different uranium atom sites would give rise to two different O$_I$–U–O$_I$ frequencies, *i.e.*, two quite different U–O$_I$ bond lengths, cannot be unequivocally answered. Certainly we would predict the U–O$_{II}$ bond distances to be different from those in CaUO$_4$. The broader bands found in all of the compounds shown in Figure 1 in the 300–600 cm.$^{-1}$ region are not necessarily pure modes, but in part can be attributed to vibrations of these M–O$_{II}$ bonds. We assume that the four doubly degenerate E$_u$ modes and one nondegenerate A$_{2u}$ mode summarized earlier are to be assigned to CaUO$_4$ bands in this region.

Although the site symmetry in the diactinate type compounds is not known, frequencies arising from M–O$_{II}$ vibrations would still be expected in this same general energy range. One merely expects bands at somewhat different energies than those observed in CaUO$_4$. The latter is clearly consistent with the experimental results. The bands observed in the far-infrared for the compounds studied are summarized in Table III. In all cases the region examined extended down to 166 cm.$^{-1}$. For CaUO$_4$, Na$_2$U$_2$O$_7$, and K$_2$U$_2$O$_7$ the lower limit was 70 cm.$^{-1}$. Hoekstra[14] has also reported the infrared spectra of Na$_2$U$_2$O$_7$ and K$_2$U$_2$O$_7$ at frequencies >200 cm.$^{-1}$.

Jones[12] has pointed out that for a number of different uranyl compounds one can identify an asymmetric stretching frequency of the O$_I$–U–O$_I$ group in the 850 to 1000 cm.$^{-1}$ range, and a frequency near 200 cm.$^{-1}$

TABLE III
ABSORPTION BANDS OBSERVED IN THE FAR-INFRARED REGION
(CM.$^{-1}$)^a

$CaUO_4$	286 m,	165 w,	~75 w		
$Na_2U_2O_7$	291 sh,	272 m,	207 m,	148 w,	99 m
$K_2U_2O_7$	292 sh,	280 m,	160 m,	128 w,	~80 w
$Na_2Np_2O_7$	308 m,	196 sh,	206 m		
$(Li,Na)_2U_2O_7$	282 m,	206 m			
$(Li,Na)_2Np_2O_7$	302 m,	196 sh,	208 m		

^{a} sh, shoulder on adjacent band; intensity: m, medium; w, weak.

which results primarily from a bending mode of the U–L bonds where L refers to the ligands in or near the plane normal to the uranyl group.

In the uranates, the U–O_I bond strength is appreciably reduced, due at least in part to stronger bonding in the secondary plane compared to those uranyl compounds with bands in the 900–1000 cm.$^{-1}$ range. We would also expect the frequency of the U–L (U–O_{II}) bending mode in the uranates to differ from that in the indicated uranyl compounds. One would predict that it would be found at energies >200 cm.$^{-1}$. From Table III it is seen that the only band observed in $CaUO_4$ in the 300–200 cm.$^{-1}$ range was at 286 cm.$^{-1}$; moreover, a band at essentially the same energy was found in all of the actinates investigated. This latter fact suggested that a U–O (Np–O) mode was involved.

Below 270 cm.$^{-1}$, all of the sodium-containing compounds had a band near 208 cm.$^{-1}$, while $CaUO_4$ and $K_2U_2O_7$ exhibited bands at 165 and 160 cm.$^{-1}$, respectively. This variation in frequency would not be expected for the same U–O mode in compounds which show such similarities in X-ray structure and infrared spectra as do $Na_2U_2O_7$ and $K_2U_2O_7$.[14] This is, however, the same pattern of frequencies observed by Ferraro and Walker in their study of anhydrous metallic nitrates.[16] They found the frequency of bands near 200 cm.$^{-1}$ to vary considerably and to be strongly dependent on the atomic number of the cation. For example, comparable bands in $NaNO_3$ and KNO_3 were found at 217 and 152 cm.$^{-1}$, respectively, and were interpreted in terms of alkali metal lattice frequencies. Thus for $CaUO_4$ it appears much more reasonable to assign the remaining A_{2u} bending mode of the U–$6O_{II}$ group to the band at 286 cm.$^{-1}$ than to attempt to correlate it with the 165 cm.$^{-1}$ frequency. Similarly, even though a band was observed in the sodium actinates near 208 cm.$^{-1}$, a frequency which could be interpreted in terms of a U–O mode, the arguments just cited are relevant.

Consequently we would also assign a bending mode of the U–O_{II} (Np–O_{II}) bonds, the symmetry species of which cannot at present be identified, to the frequency near 285 cm.$^{-1}$ in alkali metal actinates. Bands exhibited by all of the compounds in Table III in the 210–160 cm.$^{-1}$ range are then characterized as alkali metal or alkali earth lattice frequencies.

It remains to offer some explanation for the bands in $Na_2Np_2O_7$, the complex actinates, and particularly in

$Na_2U_2O_7$ near 750 cm.$^{-1}$, which are still in the energy region consistent with asymmetric M–O_I stretching frequencies. The intensity of these bands argues against their being due to the symmetric O_I–M–O_I stretching mode which is infrared forbidden. In the case of $Na_2U_2O_7$, the intensity of the 750 cm.$^{-1}$ band also argues against combination frequencies. Jones reported the observation of a very weak combination band (U–O_I asymmetric plus symmetric stretching frequencies), in several uranyl compounds, from which he could establish the frequency of the symmetric stretch, but the symmetric mode itself was either not observed or seen only in thick samples.[12] Subsequent work by Hoekstra[13] has confirmed the absence of bands corresponding to the symmetric mode in many additional uranyl compounds. We were unable to detect combination bands for the compounds shown in Figure 1 in the 1500 cm.$^{-1}$ range even with very thick samples.

We think it probable that the extra bands found near 750 cm.$^{-1}$ in the sodium actinates occur as the result of the presence of two or more different types of M–O_I asymmetric stretch modes in the crystal lattice. A solution to the structural problem of O_{II} coordination about the actinide atoms in the diactinates, as discussed earlier, may well require more than one type of actinide atom site, in agreement with the assignment.

Mechanism of the Reaction

Duke and Shute[17] found that solutions of BrO_3^- in fused alkali metal nitrates at <300° were stable for several days; however, certain transition metal cations induced the rapid decomposition of BrO_3^-, with the formation of the corresponding metal oxide. Analysis of the gases liberated in such a study in molten $LiNO_3$–KNO_3 showed that only BrO_3^- was decomposed. No oxides of nitrogen were detected. In view of these facts, and considering the results of Duke and Lawrence,[3] it might have been anticipated that in the present investigation the mechanism would involve a rapid equilibrium followed by the slower decomposition of a complex

$$MO_2^{2+} + BrO_3^- \underset{}{\overset{fast}{\rightleftharpoons}} MO_2(BrO_3)^+ \xrightarrow{slow} MO_3 + xBr_2 + yO_2$$
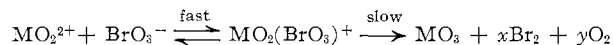
where M = U or Np. However, it is clear from the analyses that the actual reaction was much more complex, since the product contained both lithium and sodium. In effect, then, for each mole of MO_3 formed, nearly an equimolar amount of sodium and a small fraction of a mole of lithium was also converted to the corresponding oxide. One might have predicted that the entire reaction mechanism would involve BrO_3^- only as the oxygen donor, since Na^+ and Li^+ could also have initially formed a complex of the type $M_2BrO_3^+$ in association with a M(VI)–BrO_3^- species. An alkali metal–BrO_3^- complex was suggested by the results of Duke and Shute[17] when it was found that the presence of $LiNO_3$ during the catalytic decomposition of BrO_3^- by Br^- resulted in the production of Br^- and Li_2O.

(16) J. R. Ferraro and A. Walker, *J. Chem. Phys.*, **42**, 1273 (1965).

(17) F. R. Duke and E. A. Shute, *J. Phys. Chem.*, **66**, 2114 (1962).

However, it will be recalled from the earlier discussion that a mixed alkali metal uranate was also obtained in the absence of BrO_3^- simply by raising the temperature of the nitrate melt above 300°. In this case, one can envision a direct (Lewis) acid reaction of a U(VI) complex with an O^{2-} species formed by the dissociation of NO_3^-

$$NO_3^- = NO_2^+ + O^{2-}$$

In order to determine whether the actinate formation resulted from a mixed $BrO_3^--NO_3^-$ mechanism in the 220–270° range, or was due entirely to BrO_3^- decomposition, we examined the infrared spectrum of the liberated gases. No oxides of nitrogen were detected. Thus the evidence indicated that the nitrate melt served only as an inert solvent for the reaction.

Summarizing our results, we see that the reaction of BrO_3^- and U(VI) in the nitrate melt gave rise to a new complex alkali metal uranate containing both lithium and sodium. A product of the same structure was then synthesized from a mixture of alkali metal carbonates and UO_3. The X-ray diffraction pattern and infrared spectrum of the complex uranate were similar to, but distinct from, those of $Na_2U_2O_7$. Reaction of Np(VI)

or of Np(V) with BrO_3^- gave one product only. It contained Np(VI) and was analytically essentially the counterpart of the complex uranate. There was, however, a much closer relationship between the cell constants (determined from X-ray powder patterns) and the infrared spectra of the complex neptunate and $Na_2Np_2O_7$ than was found with the corresponding uranium compounds. We were able to offer an interpretation of some of the infrared absorption bands both in the complex actinates and the pure sodium diactinates. The U–O_I and Np–O_I bond distances in all four of the sodium compounds studied was calculated to be approximately 1.78 Å.

This result is of particular interest since some authors have been tempted to assume that the similarity, for example, in the uranium positions in $Na_2U_2O_7$ with those in $CaUO_4$, as established by X-ray diffraction data, implies a similarity in U–O_I bond distances in the two compounds. The present findings argue strongly against this being the case.

Notes

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Configurational and Vicinal Contributions to the Optical Activity of Tris(l-propylenediamine)cobalt(III) Ion[1]

BY BODIE E. DOUGLAS

Corey and Bailar[2] have provided an explanation of stereospecific effects in terms of the conformations of chelate rings and the resulting interactions of substituents. It has been suggested[3,4] that $[Co(en)_3]^{3+}$ exists in solution as an equilibrium mixture of the lel and less stable ob forms. Mason favors this explanation for the relative intensities of the A_2 and E_a circular dichroism (CD) bands.

Vicinal and configurational effects have been shown to be separable and additive in $[Co(en)_2am]^{2+}$ (am = optically active amino acid anion)[5] and in $[Co(am)_3]$.[6]

(1) This work was supported by a research grant (GM 10829-07) from the Division of General Medical Studies, Public Health Service.
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(6) B. E. Douglas and S. Yamada, *ibid.*, **4**, 1561 (1965).

The stereospecific effects are expected to be smaller for α-amino acids than for substituted ethylenediamines because the chelate ring formed by the amino acid can assume a planar configuration with little or no strain.

In order to test the additivity of these effects for 1,2-propanediamine (pn), the CD was measured for a series of Co(III) complexes containing en and pn. Measurements were made for 0.005–0.01 M solutions in 1-cm. cells on a Roussel-Jouan Dichrograph.

The CD curves for (+)- and (−)-$[Co(l\text{-}pn)_3en]^{3+}$ are shown in Figure 1 for the first absorption band region. The complexes show one and two CD peaks, respectively, as reported for the tris(propylenediamine) complexes.[4] These curves were added to give the summation curve shown. If one assumes that the optical activity is the result of additive configurational and vicinal effects, then the configurational effects (for right and left spirals) should cancel to leave four times the vicinal effect of l-pn. The vicinal effect for two l-pn (taken as one-half the summation curve at each wave length) was subtracted from the experimental curves to give the curves shown in Figure 2. These curves are mirror images and are very similar to the curve for (+)-$[Co(en)_3]^{3+}$ where there is no vicinal effect. The peaks (E_a, lower frequency, and A_2) have the same relative height as for $[Co(en)_3]^{3+}$.

In order to press the test for additivity further, the vicinal effect for one l-pn (taken as one-fourth the value at each λ from the summation curve in Figure 1)