Table III. *P* and *K* values for Cobalt(II)-Dithio Systems (cm^{-1})

	$Co(sacsac)_2$	$Co(mnt)_2{}^{2-}$	$Co(C_5H_4CS_2)_2{}^{2-}$
P	0.016[a]	0.020[b]	0.017
K		0.47[b]	0.17

[a] Calculated using the data in ref 15. [b] Reference 16.

ferences between the d_{yz} and the d_{z^2}, $d_{x^2-y^2}$, and d_{xy} orbitals, respectivity. A weak band is observed at 33,500 cm^{-1} but no other peaks can be picked out of the complex ligand uv-vis peaks.

Using a spin-orbit coupling constant of 400 cm^{-1}, lowered from the free-ion value, 515 cm^{-1},[15] to the same extent as *P*, yields excitation energies to the d_{z^2}, $d_{x^2-y^2}$, and d_{xy} orbitals of 9200, 46,800, and 14,800 cm^{-1}. Similar calculations for $Co(mnt)_2{}^{2-}$ give values of 3500, 46,000, and 12,400 for the corresponding transitions. Thus again, even though the geometries are different for $Co(mnt)_2{}^{2-}$ and $Co(C_5H_4CS_2)_2{}^{2-}$, it would appear that the electronic effects at the cobalt are quite similar.

While this approach to determining the ground state should be applicable to any system of D_{2h} or D_{4h} symmetry, in order to test its validity, we applied the method to the previously studied $Cu(C_5H_4CS_2)_2{}^{2-}$ system where the ground state is d_{xy} (using the coordinate system in Figure 1).

The equations become

$$g_{xx} = g_{yy} = 2 - 2\alpha_2 \tag{7}$$

$$g_{zz} = 2 - 8\alpha_1 \tag{8}$$

$$A_{xx} = A_{yy} = P[-2\alpha_2 - K + {}^2/_7 + {}^3/_7\alpha_2] \tag{9}$$

$$A_{zz} = P[-8\alpha_1 - K - {}^4/_7 - {}^3/_7(2\alpha_2)] \tag{10}$$

Solving eq 7-10 for *K* and *P* yields 0.586 and 0.0167 cm^{-1}, respectively. *P* is 48% of the free-ion value. The coefficient for the *d portion of the molecular orbital* was previously determined to be 0.73.[1] Normally, this value squared (0.53) is taken as the effective unpaired spin density in the d orbital. The correspondence in the lowering of the *P* value, an indication of covalency, and the spin density in the d portion of the molecular orbital seems quite good. While a quantitative comparison cannot be and should not be made, it would appear that these approaches to covalency do confirm the predicted effects of the ligand, that of being a strong electron acceptor in the out-of-plane fashion.

Acknowledgment. This work was supported by a grant (2385-G3) from the donors of the Petroleum Research Fund, administered by the American Chemical Society. B. J. K. thanks the Allied Chemical Corp. for financial support during the period 1972-1973.

Registry No. $Na_2C_5H_4CS_2 \cdot C_4H_8O$, 36487-17-9; $[(C_2H_5)_4N]_2Co(C_5H_4CS_2)_2$, 42230-16-0; $[(C_2H_5)_4N]_2Cd(C_5H_4CS_2)_2$, 42230-17-1.

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Contribution from The Procter & Gamble Company,
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Raman Spectral Evidence for Oxydiacetate Chelation of Alkali Metal Ions in Aqueous Solution. Interconversion among Ligand Rotational Isomers

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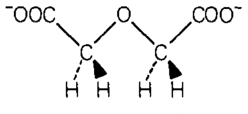
Raman spectra of aqueous solutions of alkali metal oxydiacetates [$O(CH_2COO)_2{}^{2-}$, ODA, with counterions Li^+, Na^+, K^+, and Cs^+] have yielded direct evidence for complexation between anion and cation. The apparent order of complex stabilities follows that of the inverse of the cation crystal radii, $Li^+ > Na^+ > K^+ > Cs^+$. This association is spectrally manifested principally in the C–C stretching region between 900 and 1000 cm^{-1}, where intensity changes result from interconversion among ODA rotational isomers. Whereas the natural (*i.e.*, unperturbed) ODA conformer distribution contains considerable nonplanar CCOCC skeletal structure, only the planar trans,trans form appears to complex alkali ions. In so doing, the trans,trans conformer functions as a tridentate chelate ligand, binding through both carboxylate groups and the ether oxygen atom. Quantitative treatment of Raman intensities suggests that the 1:1 chelate predominates in the Li^+–ODA system; presumably this also holds for the other alkali metal ions which bind ODA. The concentration formation quotient for aqueous $LiODA^-$ is calculated as 0.24 ± 0.01 M^{-1} at *ca.* 30°.

Introduction

Recently, we reported the combined use of X-ray crystallography and Raman spectroscopy to structurally characterize complexation between Ca^{2+} and the relatively simple ether-carboxylate ligand, oxydiacetate [$O(CH_2COO)_2{}^{2-}$, ODA].[1,2] By applying both techniques to examine the structure of crystalline $CaODA \cdot 6H_2O$ and then relating this structure spectroscopically to that of the 1:1 aqueous solution species, we were able to demonstrate the equivalence of the ligand's CCOCC skeletal conformation in these solid-state and solution environments (planar trans,trans,[3] shown below). A further conclusion was that in the absence of a strongly coordinating metal ion such as Ca^{2+}, ODA exists in solution as a mixture of rotational isomers having considerable nonplanar skeletal content (*i.e.*, presumably with the trans,gauche and gauche,gauche conformers predominating). Addition of Ca^{2+} to such a solution induces conformational conversion to the trans,trans form as a con-



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(2) Abbreviations: oxydiacetic acid, H_2ODA; oxydiacetate dianion, ODA.

(3) The term "trans" is used here in the conformational sense; elsewhere the synonymous term "anti" may be used. Other spectroscopically distinguishable ODA skeletal conformations are trans,gauche and gauche,gauche.

sequence of tridentate Ca^{2+} chelation involving one oxygen from each carboxylate group and the ether oxygen atom. The resulting planar ODA backbone, identical with that found in the solid $CaODA \cdot 6H_2O$ structure, apparently allows overall optimization of the three electrostatic calcium-oxygen interactions.

During the course of the previous work, some interesting features were noted in comparing Raman spectra of Ca^{2+}-free ODA solutions containing different alkali metal counterions (Li^+, Na^+, K^+, Cs^+). The description and interpretation of these spectral observations constitute the subject of the present paper. Raman spectroscopy affords direct evidence that alkali metal ions, too, can alter the population of ODA skeletal conformations in water through preferential binding to a single rotational isomer. Intensity measurements have yielded the relative stabilities of such alkali metal-ODA species.

Experimental Section

The preparation of oxydiacetate solutions for Raman analysis has been described previously.[1]

Raman spectra were recorded on a Cary 81 spectrophotometer using the 5145-Å line from a Coherent Radiation Laboratories Model 52 Ar^+ laser as excitation source. Operating conditions and procedures have been described earlier.[1]

For quantitative intensity measurements with the aqueous Li^+-ODA system, the 1048-cm^{-1} band of added NO_3^- (as 0.24 M $CsNO_3$) served as internal intensity standard. In order to correct the NO_3^- 1048-cm^{-1} intensity for the (minor) contribution at 1052 cm^{-1} arising from ODA, a height equal to that of the ~1240-cm^{-1} ODA band was subtracted. The 1052- and 1240-cm^{-1} peaks are roughly equally intense in spectra of aqueous ODA. Spectra were run in triplicate for these particular measurements.

Results and Discussion

Spectral Assignments. The Raman frequencies and relative intensities listed in Table I for 1.0 M Na_2ODA are *generally* representative of spectra recorded for the four aqueous alkali metal oxydiacetates included in this study (Li^+, Na^+, K^+, Cs^+). The corresponding assignments have been discussed in some detail in connection with our previous investigation of Ca^{2+}-ODA complexation.[1] Several conclusions from that earlier work bear directly on the present spectral analysis and are briefly summarized below.

The multiplicity of bands attributed to each of certain ODA motions, *viz.*, the CH_2 deformation, wag, and twist modes, result in part from an in-phase-out-of-phase combination of interacting vibrations of the two CH_2COO^- groups. In contrast, Raman evidence suggests that the two C-C bonds vibrate virtually independently of one another;[1] the three peaks assigned to C-C stretching (Table I) accordingly are best viewed as arising not from coupled C-C vibrations but from vibrations of independent C-C oscillators in the various likely ODA rotational isomers in solution. Based primarily on comparison with the Ca^{2+}-ODA system, the ~950-cm^{-1} band is associated with trans moieties in the trans,trans and perhaps trans,gauche isomers, while the peaks at ~933 and ~917 cm^{-1} are related to gauche moieties in the trans,-gauche and gauche,gauche isomers. By exhibiting variable relative intensities, these prominent C-C stretching bands are a good monitor of solution alterations which cause interconversion among the ODA conformers. Accompanying effects are manifested in certain other spectral regions as well, though not as dramatically (*vide infra*).

Complex Formation and Structure. Figure 1 focuses on the C-C stretching region (850-1000 cm^{-1}) for each of the four alkali metal oxydiacetates studied. Included for comparison is the simpler spectrum of CaODA(aq) (Figure 1F), comprising a single peak characteristic of the trans,trans ligand conformer alone.[1] Inspection of Figure 1A-D reveals *differences in detail* among the spectra of formally equimolar (0.40 M) aqueous solutions of Cs_2ODA, K_2ODA, Na_2ODA, and Li_2ODA, differences which, as mentioned above, are diagnostic of changes in the distribution of ODA conformational isomers. In particular, the relative intensity of the highest frequency peak (~950 cm^{-1}, assigned to trans) increases in the order $Cs^+ < K^+ < Na^+ < Li^+$; this trend prevails regardless of whether heights of resolved or unresolved bands or areas of resolved bands are measured. Moreover, concurrent reduction in the height of the prominent ~917-cm^{-1} peak, relative to heights of CH_2 wag and twist bands used as internal standards, confirms that the population of trans moieties is in fact growing *at the expense of* nonplanar gauche moieties through the above cation sequence. It is difficult to treat the ~933-cm^{-1} band quantitatively, owing to its location between two other peaks; however, its intensity

Table I. Raman Frequencies and Assignments for Aqueous 1.0 M Sodium Oxydiacetate[a]

Freq, cm^{-1}	Assignment	Freq, cm^{-1}	Assignment
2955 m, dp	Asym CH_2 str	~1272 vw, dp	CH_2 twist
2927 s, p	Sym CH_2 str	1245 mw, dp	
2890 m, p	Overtone or combination	1129 w, dp	COC asym str
~2863 sh, w, p		1052 mw, p	COC sym str
~1597 sh, w, dp	COO^- asym str	987 vw, dp	CH_2 rock
1465 sh, w, p?	CH_2 def	952 m, p	C-C str
1449 mw, p		933 m, p	
1432 s, p		916 vs, p	
1412 vs, p	COO^- sym str	~713 b, w	Skel def
1346 m, p	CH_2 wag	593 mw, dp	
~1323 b, w, dp		~550 b, w, dp	
~1310 b, vw		467 m, dp	
		~352 b, mw, p	

[a] Abbreviations: s, strong; m, medium; w, weak; v, very; sh, shoulder; b, broad; p, polarized; dp, depolarized. For the complex contours near 950 and 1450 cm^{-1}, the data refer to resolved components.

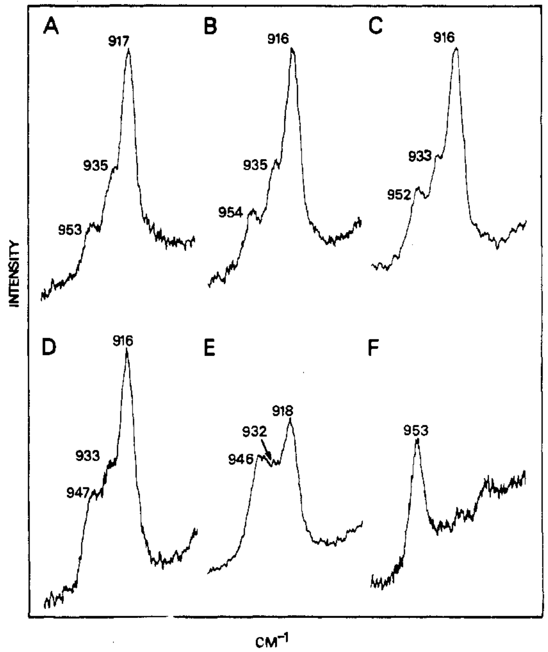

Figure 1. The 850-1000-cm^{-1} Raman spectral region for aqueous (A) 0.40 M Cs_2ODA, (B) 0.40 M K_2ODA, (C) 0.40 M Na_2ODA, (D) 0.40 M Li_2ODA, (E) 0.40 M Li_2ODA + 1.5 M LiCl, and (F) 0.18 M Ca^{2+}-ODA, three-fourths neutralized (weak bands at 890 and 915 cm^{-1} arise from H_2ODA). The ordinate scale is not necessarily the same for all spectra.

behavior appears generally to parallel that of the ~917-cm^{-1} band.

These systematic, cation-dependent changes in the ODA conformer population are most satisfactorily attributed to different degrees of complex formation between the various alkali metal ions and ODA. From these spectra alone, however, the stability order of the complexes cannot be unambiguously established. Despite the similarity in frequency between the peak from the CaODA(aq) complex (Figure 1F) and the higher frequency C-C stretching band in the alkali metal-ODA spectra, it is not yet known *with certainty* which of the C-C stretching bands is associated with complexed ODA in the alkali metal systems. Two additional types of experiment help to define the correct stability order. (1) As shown in Figure 1E for Li^+, addition of excess metal ion strengthens the highest frequency C-C stretching band at the expense of the others. (2) Lowering the solvent dielectric constant should enhance association between oppositely charged ODA and alkali metal cations. This prediction was tested for 0.67 *M* Li_2ODA and Na_2ODA using a 1:2 volume ratio of CH_3OH-H_2O as solvent. Raman spectra of these solutions exhibited a measurable increase in relative intensity of the ~950-cm^{-1} peak, compared with spectra of similar solute concentrations in water alone. These results plainly associate the ~950-cm^{-1} line with complexed ODA, as we might have suspected; the apparent stability order, indeed, is $Li^+ > Na^+ > K^+ > Cs^+$.

Other workers have found the identical stability order for alkali metal complexes of aminopolycarboxylates,[4,5] polyphosphates,[6] polyphosphonates,[7] and malate (a hydroxycarboxylate).[8] In such cases where electrostatic metal-ligand interaction dominates, this stability order can be understood if the anionic ligand at least partially displaces the solvent sheath directly surrounding the cation.[6] The charge density of the exposed metal ion, which decreases as the anhydrous ionic radius increases, can then be directly sensed by the ligand. This condition suggests a possible explanation for the singular C-C stretching frequency noted for $LiODA^-$ (946 cm^{-1} in Figure 1), compared with the average for the other complex species examined (953 cm^{-1}): since Li^+ is the most strongly solvated of the cations considered, perhaps a larger portion of the inner hydration sphere of complexed Li^+ remains intact than for the other alkali cations, thereby introducing some slight perturbation in the trans,trans ODA structure in $LiODA^-$, whether for steric reasons or otherwise, not found in the other complexes.

The Li^+-ODA system was selected for further investigation to gain some idea of both complex stoichiometry and the magnitude of the formation quotient(s) involved. Quantitative measurement of the intensity (height) of the unresolved ~917-cm^{-1} band, with the 1048-cm^{-1} line of added NO_3^- (0.24 *M*) serving as an internal standard (see Experimental Section), provided an estimate of the concentration formation quotient for a 1:1 $LiODA^-$ species. For these determinations solutions were prepared in which the formal concentration of ODA was set at 0.40 *M* (as the Cs^+ salt) and that of Li^+ was 0.0, 1.0, or 2.5 *M* (as the chloride). Since Cs^+ shows least indication of complex formation with ODA, the spectrum of 0.40 *M* Cs_2ODA with no added Li^+ was considered approximately to represent the natural conformer distribution of free (uncomplexed) ODA. For this solution the normalized band height at 917 cm^{-1}, 0.28_5, was taken to represent 0.40 *M* free ODA. In the presence of 1.0 *M* Li^+, the normalized 917-cm^{-1} band height was 0.234 (0.33 *M* free ODA), whereas with 2.5 *M* added Li^+ it was measured as 0.18_1 (0.25 *M* free ODA). Both sets of values were inserted into the expression for *K*

$$K = \frac{[\mathrm{LiODA}^-]}{[\mathrm{Li}^+][\mathrm{ODA}]} = \frac{0.40 - [\mathrm{ODA}]_{\mathrm{free}}}{([\mathrm{Li}]_{\mathrm{total}} - (0.40 - [\mathrm{ODA}]_{\mathrm{free}}))[\mathrm{ODA}]_{\mathrm{free}}}$$

The average K_{LiODA^-} so calculated is $0.24 \pm 0.01\ M^{-1}$ at *ca.* 30°.

The above solution conditions initially were assumed to favor formation of a 1:1 metal-ligand complex. Indeed, the relatively small variation of the calculated quotient as the stoichiometric ratio $[Li^+]:[ODA]$ was varied indicates that multinuclear Li^+ species are in fact insignificant in these solutions. Owing to experimental limitations, possible complexes having ODA:Li^+ ratios greater than unity could not be easily or reliably studied. Although such species are considered relatively unimportant in the present system, since their formation would require the close approach of two negatively charged ions (*e.g.*, ODA and $LiODA^-$), the results of this study do not rule out their existence.

Underlying the above calculations were two further assumptions. First, the *height* of the *unresolved* ~917-cm^{-1} peak was used as a convenient concentration measure of uncomplexed ODA since its magnitude was found not to be noticeably influenced by the weaker neighboring band at ~933 cm^{-1} (using a Du Pont 310 curve resolver). Its assumed linear dependence on the concentration of free ODA probably holds for the relatively dilute solutions examined. The second assumption, that the dilute NO_3^- standard (0.24 *M*) does not compete favorably with ODA for Li^+ association, appears valid in view of a recent estimate that the formation constant for $LiNO_3$(aq) is perhaps a factor of 10 smaller than that measured here for $LiODA^-$.[9]

Apparently this is the first study of aqueous complex equilibria involving alkali metal ions and an ether-carboxylate ligand, judging from the absence in the literature of stability constants for such systems. Nonetheless, the measured stability quotient for $LiODA^-$ may profitably be compared, though only roughly, with that for the 1:1 Li^+ complex with the related hydroxydicarboxylate ligand malate ($OOCCH_2$-$CHOHCOO^{2-}$). Like most aqueous alkali metal complexes, the malate complex is quite weak, having a stability constant of 2.4 M^{-1} at 25°.[8] It is seen that $LiODA^-$, with $K = 0.24\ M^{-1}$, is somewhat weaker still, very likely reflecting, at least in part, the energy price necessary to bring about the ODA conformational transition which is detected spectroscopically. Inspection of molecular models suggests that extensive bond reorientation might not be required for efficient metal binding by malate ion.

Information concerning the overall conformation of complexed ODA was found in the Raman spectrum of an ODA solution containing excess Li^+ (1.0 *M* Li_2ODA + 2.5 *M* LiCl). Compared with the data presented in Table I, definite changes in frequency and intensity were noted in this spectrum in those regions related to CH_2 motions. Specifically, there was a downward shift of the stronger CH_2 twisting band from

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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,
University of Oxford, Oxford, England

A Sodium Uranium Bronze and Related Phases

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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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