AMMONIUM URANYL CARBONATES — COMPLEX COMPOUNDS WITH VARIABLE COORDINATION NUMBER?

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A series of ammonium uranyl carbonate (AUC) solid samples were prepared. Their chemical composition varied systematically and corresponded to the formula $(NH_4)_x[UO_2(CO_3)_y]$ with molar coefficients from $x = 4 \cdot 0$ and $y = 3 \cdot 0$ to $1 \cdot 1$ and $1 \cdot 3$, resp. The first samples of this series, with x in the range $4 \cdot 0 - 2 \cdot 7$ and y in the range $3 \cdot 0 - 2 \cdot 3$, revealed identical IR spectra as well as X-ray patterns, in contrast to the other ones. A reliable explanation of this fact is not at hand, one of the possibilities being the variable coordination number of the uranyl central ion.

IR spectra of AUC and its sodium analogue were confronted, too, with the conclusion that architecture of both complexes is the same but with distinct quantitative differences.

Conditions for the preparation of complex uranyl tricarbonates with various cations, first of all of 1st and 2nd groups of the periodic system, have been known for some time[1] and also their infrared (IR) spectra have been measured[2,3]. In the present paper IR spectra of tetraammonium uranyl tricarbonate, $(NH_4)_4[UO_2(CO_3)_3]$, one of the most common compounds of this type, will be discussed. The role of this compound is of arising importance in the nuclear fuel technology[4,5] where it is usually abbreviated in AUC. Besides the usual way of precipitation of uranium using concentrated ammonium carbonate solutions[1] we have also applied a new alternative of the preparation, the precipitative reextraction of uranium of an organic phase. Chemical aspects of this preparation will be described elsewhere.

The spectra obtained are compared with the spectrum of an AUC sample measured in the range $1\,600 - 30\ cm^{-1}$ and discussed only briefly[2] and also with the spectrum of the sodium analogue, $Na_4[UO_2(CO_3)_3]$, abbreviated in NaUC, thoroughly analysed quite recently[6].

EXPERIMENTAL

The samples AUC-A (Table I) and its sodium analogue NaUC were prepared according to the literature[1] using an excess of the appropriate carbonate, M_2CO_3. For preparation of the other AUC samples the precipitative reextraction of $0 \cdot 19$ mol l^{-1} uranyl nitrate solvate in 30% kerosene solution of tri-n-butylphosphate by means of an aqueous ammonium carbonate solution was applied. The aqueous solution contained comparable concentrations of both carbonate forms, *i.e.* HCO_3^- and CO_3^{2-}, because the molar ratio of its basic components, NH_3/CO_2, equaled $1 \cdot 56$ at total carbonate concentration $1 \cdot 20$ mol l^{-1}. The overall reaction, taking place during

contacting appropriate volumes of both non-mixing liquid phases, can be followed by means of the pH measurement of the composed system (a suspension of the uranium precipitate in an emulsion of two liquids). Regardless of the interpretation of these pH values, they are important preparatively because some properties of the precipitate formed, *e.g.*, the surface area of uranium dioxide prepared from it, depend distinctly upon these values.

IR spectra in the region $4\,000-200$ cm^{-1} in Nujol mull, as well as in KBr pellets in the $1\,500$ to $1\,300$ and $3\,000-2\,800$ cm^{-1} regions, were recorded using a Perkin–Elmer 225 spectrometer with CsCl windows. In addition, for additional measurements in the region $3\,800-1\,300$ cm^{-1} a UR-20 apparatus and UVASOL Merck (polychlorotrifluoroethylene oil) were used. For the X-ray analysis the classical Debye–Scherrer method, using a Mikrometa apparatus with chamber radius 114.6 mm and nickel filtered CuK$_\alpha$ radiation, was applied. Uranium content was determined in three independent series — twice gravimetrically as U_3O_8, once by vanadate titration after the reduction to U(IV) by means of zinc amalgam. Ammonia was determined in two independent series after its absorption in 5% boric acid solution by titration with 0.05 mol l^{-1} sulfuric acid using mixed indicator (bromcresol green and methyl red). The carbonate content was estimated after thermal decomposition of the sample and absorption of the evolved carbon dioxide in aqueous solution of barium perchlorate coulometrically, or after decomposition in boiling sulfuric acid (1 : 1), absorption of carbon dioxide in excess 0.2 mol l^{-1} sodium hydroxide and acidimetric titration.

Relative error calculated from the results of the all independent determinations cited is for uranium less than 1%, for ammonia less than 3%, for carbonate 5%. The calculated deviations of the molar ratios $(C/U)_{exp}$ and $(N/U)_{exp}$ (Table I) decrease with higher uranyl fractions because of the lowest determination error for uranium, and *vice versa* as for the other ions. In addition to tables where the molar ratios are for the sake of clarity cited to within hundredths, currently it may be sufficient to cite them to within tenths.

TABLE I

Chemical composition of the samples prepared

Sample	pH^a of prep.	% UO_2^{2+}	% CO_3^{2-}	% NH_4^+	Total	$(C/U)_{exp}^b$
AUC-A^c	—	50·80	35·10	13·81	99·71	3.11 ± 0.19
AUC-B	8·5	53·79	32·78	12·97	99·54	2.74 ± 0.17
AUC-C	7·5	57·40	31·18	12·01	100·59	2.45 ± 0.15
AUC-D	7·0	58·73	30·53	10·40	99·66	2.34 ± 0.14
AUC-E	6·5	63·55	26·18	7·82	97·55^d	1.85 ± 0.12
AUC-F	5·5	71·40	20·43	5·00	96·83^d	1.29 ± 0.08

^{a} pH of preparation denotes pH values of the suspension of the solid in emulsion of two immiscible liquids at the end of precipitative reextraction. The first precipitate was formed at pH = 4·5; above pH = 6·5 the formed precipitate mostly dissolved, from pH = 7·0 it was formed again abundantly. ^{b} Given is the maximum deviation calculated from the analytical limits, see the text. ^{c} Theoretical composition of $(NH_4)_4[UO_2(CO_3)_3]$ is as follows: 51·71% UO_2^{2+}, 34·47% CO_3^{2-},

RESULTS

In spite of distinct differences in chemical composition of the samples AUC-A to AUC-D (Table I), their IR spectra as well as their diffraction patterns were the same. On the other hand, the spectra and X-ray patterns of the samples AUC-E and AUC-F are very similar to each other but distinctly different from those cited above. It can be seen from Table I that merely the sample AUC-A, prepared by the use of about twentyfold molar excess of ammonium carbonate, corresponds to the required formula $(NH_4)_4[UO_2(CO_3)_3]$. The molar ratio of the components in the other samples, $(N/U)_{exp}$ and $(C/U)_{exp}$, is considerably lower than the theoretical values 4·0 and 3·0, resp. The sum of the three basic components indicates (Table I) that samples AUC-A to AUC-D did not contain any further component to a substantial extent. Really, the calculation confirmed that any other assumption (e.g., that with bidentate carbonate coordination to uranyl amounting the found ratio $(C/U)_{exp}$, the common[1] uranyl coordination number 6 was reached by coordination of water molecules) worsened the agreement between calculated and experimental values. The situation found may be expressed by the formula $(NH_4)_x[UO_2(CO_3)_y]$, where $x \leqq 4$ and $y \leqq 3$; the empirical lowest limit is $x = 2·65$, $y = 2·34$. The relations $x = 2(y - 1)$ or $y = (x + 2)/2$ follow from the electroneutrality condition. Hence, using $x = (N/U)_{exp}$ the values of $y = (C/U)_{calc}$ may be calculated, and *vice versa* (Table I).

TABLE I
(Continued)

$(C/U)_{calc}$	$(N/U)_{exp}{}^b$	$(N/U)_{calc}$	IR Spectrum	Structure
3·04	4·07 ± 0·16	4·22	peculiar	AUC
2·81	3·61 ± 0·15	3·58	that of AUC-A	AUC
2·57	3·13 ± 0·12	2·90	that of AUC-A	AUC
2·34	2·65 ± 0·10	2·68	that of AUC-A	AUC
—	1·83 ± 0·08	—	other than AUC-A, see the Fig.	hydroxocarbonate[e]
—	1·05 ± 0·04	—	very similar to AUC-E	hydroxocarbonate[e]

13·82% NH_4^+. [d] OH/U equals 0·16 for AUC-E and 0·70 for AUC-F, provided the difference up to 100% corresponds to hydroxyl groups. [e] For this hydroxo carbonate the formula $(NH_4)_3$. $.[(UO_2)_2(OH)(CO_3)_3(H_2O)_5]$ has been assigned[10] for which it holds true: $UO_2^{2+} = 61·28$, $CO_3^{2-} = 20·43$, $NH_4^+ = 6·14\%$, $OH^- = 1·93\%$, $H_2O = 10·22\%$.

TABLE II
Numerical data on the IR spectra (band positions in wavenumbers)

AUC^a		AUC^b		NaUC^c		AUC-E^d	
lattice vibrations	88						
δ_{LUL}	105						
δ_{OUL}	135						
	165						
δ_{UL}	225			$\nu(U-lig)$	217 w-m		222 sh
	237	$\nu(U-O_{lig})$	235 m-s				228 s
						$\nu(U-O_{lig})$	225 s
$\nu_2(UO_2)$	276	$\nu_2(UO_2)$	273 s (1 × 272)	$\nu(U-O_{lig})$	270 m-s		270 sh
	300 sh				308 sh		308 m-s
				$\nu_2(UO_2)$	320 s		355 w, sh
			460 w, b (1 × 453)			$\nu_2(UO_2)$	460 w-m
						H₂O or OH libration	555 vw, vb
$\nu_3(CO_3)$	685	$\nu_5(CO_3)$	691 m-s, sp(1 × 690)	$\nu_5(CO_3)$	703 m, sp		690 m, sp
$\nu_5(CO_3)$	715	$\nu_3(CO_3)$	718 s, sp (2 × 720)	$\nu_3(CO_3)$	736 s, sp	$\nu_5(CO_3)$	701 m-s, sp
						$\nu_3(CO_3)$	732 s, sp
							787 w
							831 m, sp
$\nu_6(CO_3)$	839	$\nu_6(CO_3)$	829 vw, sp (2 × 830)	$\nu_6(CO_3)$	827 s, sp	$\nu_6(CO_3)$	838 w-m, sp
			843 m, sp (1 × 845)				850 w, sp
			853 vw, sp (2 × 855)			deformation of carbonates or hydroxyls	908 s
$\nu_3(UO_2)$	883	$\nu_3(UO_2)$	889 s (2 × 890)	$\nu_3(UO_2)$	843 s, sp	$\nu_3(UO_2)$	935 vw, sh
			935 vw, sh		862 sh		985 w
			f				1 030 vw
							1 043 vw

$\nu_1(CO_3)$	1 045	1 050 m-s, sp (1 × 1 051)	$\nu_2(CO_3)$	1 062 m, sp	$\nu_2(CO_3)$	1 052 m, sp	$\nu_2(CO_3)$
		(2 × 1 052)					
		1 060 w, sp				1 072 w-m, sp	$\nu_1(CO_3)$
		1 085 w				1 300 s	} NH$_4$ deformations
$\nu_2(CO_3)$	1 332	1 340 vs (1 × 1 338)	$\nu_1(CO_3)$, $\nu_4(NH_4)$	1 340 s, b	$\nu_1(CO_3)$	1 390 s	
		1 430 s				1 415 s	
						1 440 sh	
$\nu_4(CO_3)$	1 500	1 515 vs, b (1 × 1 520)	$\nu_4(CO_3)$, $\nu_2(NH_4)$	1 560 s, b	$\nu_3(CO_3)$	1 523 vs	$\nu_4(CO_3)$
		1 575 sh (1 × 1 585)				1 595 s	} NH$_4$ deformations
		1 678 m (1 × 1 674)				1 678 m	
		(2 × 1 680)					
		1 735 w (1 × 1 738)				1 778 w	} combination
		1 750 w (2 × 1 755)				1 810 w, b	} bands with NH$_4$
		1 780 w-m				2 060 w	} participation
		2 110 w (1 × 2 105)	$\nu_1(n)^g$			2 590 w	
		(1 × 2 100)				2 800 m	
		2 850 m, b	$\nu_1(n)^g$			2 920 m, sh	
		3 020 s, vw (1 × 3 040)	$\nu_1(n)^g$			3 080 s	$\nu(N{-}H)$ or $\nu(O{-}H)$
		(2 × 3 050)					
		3 190 vs, b (3 × 3 200)	$\nu_1(n)^g$			3 210 vs	$\nu(OH)$
		3 540 w, sh (2 × 3 550)				3 320 s	
						3 560 w, vb, sh	

^{a} Data of ref.^{2} inclusive of the symbols. ^{b} The measured values of the AUC–A spectrum are given. If the band positions in spectra of the AUC–B to AUC–D differ, then these differing values and their number is cited in parenthesis. Characterization of the band shape and intensity is that for the AUC–A samples, deviations in spectra of the other three samples were quite minor. More detailed variations of intensity of the selected bands see Table III, their explanation is in the text. The symbols used for denotion of the carbonate frequencies are those of ref.^{8}. ^{c} The differences from the data in ref^6 are only minor. ^{d} The AUC–F spectrum differs from this one merely very little in positions and intensities of some bands. ^{e} Ref.^{6} cites, in addition, the values 130, 172, and 252 sh, assigned to U—O$_{lig}$ vibrations. ^{f} Two spectra contained the band 990 w, sh. ^{g} The nonaxial valence vibrations of ammonium groups with very strong hydrogen bridges^{14}, see the text.

Regardless of the considerable variations in chemical composition, the samples AUC-A to AUC-D reveal the same structure — their X-ray patterns agree one with another as well as with the literature data[1,7] for tetraammonium uranyl tricarbonate. As the intensity of the X-ray diffraction lines grows with atomic number, the invariation of the structural patterns means, first of all, the invariation of the positions of uranium atoms, the atomic number of which is by far the highest one within the discussed samples. These facts, together with the results of chemical analyses, may lead to the assumption that the general arrangement remains untouched also in the case of certain lowering of the number of the carbonate ligands, coordinated to uranyl, below the value 3·0 accompanied by lowering of NH_4/U ratio below 4·0 as required by the electroneutrality condition.

IR spectra of the samples from Table I are presented in Fig. 1, wave numbers of absorption bands together with some supplementary data are given in Table II. It turns out that IR spectra of the coordination compounds denoted AUC-A to AUC-D are quite similar.

The assignment of absorption bands in the overlapping region of the wave numbers is in accord with the assignment in ref.[2]. Analysis of the vibrational behaviour of the coordinated anion[6,8] together with the results of structural measurements[9] point to the conclusion that the carbonate ions are coordinated to the uranyl as bidentate ligands. The same type of ligand coordination is valid also for NaUC (ref.[6]), even though the positions of the carbonate absorption bands for AUC and NaUC differ considerably (Table II), documenting thus different bond strengths of ligands in these analogues.

Intensities of the selected bands, sufficiently narrow and intense to be treated, were measured, too. The height of these bands was expressed relatively to the height of the antisymmetric uranyl band $\nu_3(UO_2)$ for each individual sample AUC-A to AUC-D so that the uranyl ion served as an inner standard within each sample. For this relative band intensity it holds true: $E_x(\text{rel}) = E_x/E_{\nu_3(UO_2)} = (\ln I_0/\ln I)_x/ /(\ln I_0/I)_{\nu_3(UO_2)} = (\varepsilon \cdot k \cdot d)_x/(\varepsilon \cdot k \cdot d)_{\nu_3(UO_2)} = (\varepsilon \cdot k)_x/\varepsilon_{\nu_3(UO_2)}$, where d cancels out because it is identical for both the measured and the reference band; k_x stands for the set of bonds (harmonic oscillators) participating in the formation of the given absorption band related to one uranyl, i.e., to one complex unit. Accordingly, the values of k_x can be numerically expressed by means of the $(C/U)_{\exp}$ values — the proportionality constant we take for unity — provided the appropriate absorption band x is connected with vibrations of the coordinated carbonate ligand. The molar values

$$\varepsilon_x(\text{rel}) = \frac{E_x/E_{\nu_3(UO_2)}}{k_x} = \frac{E_x/E_{\nu_3(UO_2)}}{(C/U)_{\exp}} = \frac{\varepsilon_x}{\varepsilon_{\nu_3(UO_2)}}$$

were also calculated. From the numerical data collected in Table III it follows that the values of the relative intensity $E_x(\text{rel})$ for the band at 273 cm^{-1} are constant

for the individual AUC samples in contrast to the other bands, the intensity of which decreases from AUC-A to AUC-D. On the other hand, ε_x(rel) values for the 273 cm^{-1} band increase in the same direction, the values for the other bands being more or less constant. From that it can be concluded that the band at 273 cm^{-1} cannot be assigned to vibrations of the coordinated carbonates or to an interaction among them and the uranyl ion, whereas the other bands ought to be connected just with the carbonate ligand vibrations. This was the basis for the assignment of these bands in Table II.

As for the samples AUC-E and AUC-F, their IR spectra resemble each other considerably, simultaneously differing distinctly from those cited above (Fig. 1). Their X-ray patterns are practically identical and the same as that of the hydroxo carbonate[10] with formula $(NH_4)_3[(UO_2)_2(OH)(CO_3)_3(H_2O)_5]$, chemical composition of which does not correspond to our samples. It is worth noting that the relative content of the hydroxyl groups may be rather low (*e.g.*, below 2%, Table I) so that a misinterpretation of the chemical composition may easily take place.

TABLE III
Variations of the intensity characteristics of the selected bands[a]

Band x, cm^{-1}	AUC-A[b] $p = 3{\cdot}11^c$	AUC-B $p = 2{\cdot}74$	AUC-C $p = 2{\cdot}45$	AUC-D $p = 2{\cdot}34$	Assignment
273	1·172 0·38	1·103 0·40	1·072 0·44	1·121[d] 0·48	$\nu_2(UO_2)$
691	0·605 0·20	0·527 0·19	0·474 0·19	0·365 0·16	$\nu_5(CO_3)$
718	1·041 0·34	0·962 0·35	0·906 0·37	0·700 0·30	$\nu_3(CO_3)$
843	0·194 0·06	0·195 0·07	0·141 0·06	0·126 0·05	$\nu_6(CO_3)$
1 050	0·528 0·17	0·508 0·19	0·439 0·18	0·313 0·13	$\nu_2(CO_3)$

[a] In the upper line of the numerical columns, the relative intensities E_x(rel) $= E_x/E_{\nu_3(UO_2)}$ are given; in the lower line, the values of ε_x(rel) $= E_x$(rel)$/(C/U)_{exp}$, rounded to within hundredths. The subscript x relates to the given band of an AUC sample for which also the reference $\nu_3(UO_2)$ intensity values are read off in arbitrary units from the spectrum of each sample. [b] When the theoretical value C/U = 3·00 is used, then the ε_x(rel) values from above down are as follows: 0·39, 0·20, 0·35, 0·06, 0·18. [c] $p = (C/U)_{exp}$. [d] The average E_x(rel) value for the band 273 cm^{-1} equals 1·11 ± 0·027, *i.e.*, ±2·4%. The error represented as an average arithmetic deviation.

DISCUSSION

Vibrations of carbonate ions: Assignment of the carbonate ligand fundamentals poses no problem. Theoretical studies[6,8,11,12] require six absorption bands for the coordinated carbonate of C_{2v} symmetry (two of four fundamentals are split). In the measured spectra the bands are really found (Table II). In accord with this statement, our measurement of the relative intensities of the selected bands (Table III) makes possible to assign four of the observed bands to the carbonate vibrations. The fifth one does not vary in respect to the intensity of $v_3(UO_2)$ band what implies its assignment to the deformation vibration $v_2(UO_2)$. Similar quantitative comparison could not be applied to the weak intensity of the 235 cm^{-1} shoulder (Table II, Fig. 1). However, the shape of this band — demonstrated for each sample in Fig. 1 — indicates a systematic change of its intensity. Because of its low energy it may be assigned to interaction between uranyl and oxygens of the carbonate ligands, $v(U—O_{lig})$.

As for the type of coordination of the carbonate ligands to the uranyl in samples AUC-A to AUC-D, based upon the extent of splitting of the bands $v_1(CO_3)$ and $v_4(CO_3)$ it can be concluded that the coordination is bidentate. It is in accord with both spectroscopic[2] and structural[9] measurements.

The systematic changes in the relative intensities $E_x(rel)$ of carbonate bands indicate the fact (regardless of the analytical results) that a progressive variation of the C/U ratios in individual complexes might take place. This phenomenon could be explained by a lowering of the number of appropriate bonds in each complex, k_x. The more it could occur with a lowering of $\varepsilon_x(rel)$ values in the direction from AUC-A to AUC-D. This question cannot be unequivocally decided from the data in Table III because of their insufficient preciseness, nevertheless it seems likely that the $\varepsilon_x(rel)$ coefficients progressively decrease — for sample AUC-D perhaps more distinctly. This assumption is supported by the experimentally proven lowering of the hydrolytic stability of the AUC-C sample during an extensive washing (up to dissolving of about a half of the sample). After such a procedure IR spectrum was thoroughly changed — instead of sharp and intense bands merely broad and weak ones were found. Similar spectra of the AUC samples were obtained after thermal exposition to about 200°C in addition to colour changes from yellow to yellowish brown. Also X-ray patterns of the washed sample indicated almost amorphous material. The sample AUC-A went through analogous washing procedure without any change.

A different degree of hydrolytic stability of the investigated samples was also found on their prolonged exposition to deuterium oxide vapours at room temperature. Besides certain changes in appearance, IR spectrum of the exposed AUC-A sample was quite similar to that of sample AUC-E (Fig. 1). It should be interpreted in terms of its transformation to a hydroxo carbonate; the AUC-C sample was transformed even more deeply, its IR spectrum did not conform to any other IR spectrum known. Nevertheless, its basic features corresponded to hydroxo carbonates. Just this

lowered chemical stability of the sample AUC-C in comparison to that of the sample AUC-A is in logic accord — even though it is not a proof — with potential quantitative changes in its spectral properties.

Vibrations of ammonium ions: Stretching vibrations of the ammonium ion, $\nu_3(NH_4)$, have been found in the range $3\,335 - 3\,100\,cm^{-1}$ as a consequence of different interaction of this ion with crystall lattice, higher interactions leading to lower frequencies[11]. Deformation vibrations, $\nu_4(NH_4)$, occuring slightly above $1\,400\,cm^{-1}$, are influenced by the interaction with lattice to a lesser extent. Since 1975 vibrational behaviour of the ammonium ion has been systematically studied in Canada[13] by an investigation of the influence of temperature on behaviour of a sample labelled with NH_3D^+ ion.

The valence vibrations $\nu_1(N-H)$ are differentiated there into axial ones $\nu_1(a)$ at about $3\,300\,cm^{-1}$ (may be hidden in the other bands), and nonaxial ones $\nu_1(n)$ within about $3\,200 - 2\,800\,cm^{-1}$; low energy of the latter documents high strength of hydrogen bonds, in which the nonaxial frequencies participate (see the above cited lower limit at $3\,100\,cm^{-1}$ for current case). Applying this scheme to our samples containing undoubtedly ammonium ions with strong hydrogen bonds[9], the axial frequency seems to be inactive or hidden in bands of the nonaxial frequencies at $3\,190$, $3\,020$ and $2\,850\,cm^{-1}$. The band at $1\,430\,cm^{-1}$ should be assigned to the deformation vibration $\nu_4(NH_4)$, that at $1\,678\,cm^{-1}$ is most likely deformation vibration $\nu_2(NH_4)$, in IR spectrum activated by strong hydrogen bonds[14]. Group
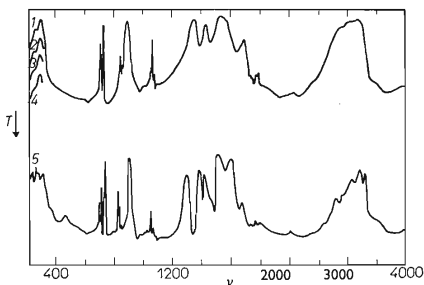

FIG. 1

IR spectra of the samples prepared. The numbers *1, 2, 3, 4, 5* denote spectra of the samples AUC-A, AUC-B, AUC-C, AUC-D and AUC-E, resp. Transmitance *T* is in arbitrary units, wavenumber ν in cm^{-1}

of mostly weak but distinct bands in the region $2\,110-1\,735\ \mathrm{cm}^{-1}$ may be connected with combination bands of deformation vibrations ν_2 or ν_4 with libration modes ν_6 (ref.[16]). It cannot be excluded that shoulder at $1\,575\ \mathrm{cm}^{-1}$ (perhaps it corresponds to the frequency at $1\,595\ \mathrm{cm}^{-1}$ in spectrum of AUC-E sample in which it is much more easily visible) belongs to the components of ammonium deformation vibrations. This shoulder can be also interpreted as another, doubled, carbonate frequency $\nu_4(CO_3)$ analogously to that for the potassium analogue KUC, $K_4[UO_2.(CO_3)_3]$, with values[2] $\nu_4(CO_3)$ at $1\,540$ and $1\,610\ \mathrm{cm}^{-1}$. Certain minor differences in coordination of individual carbonate ligands to uranyl, clearly indicated by the structural AUC investigation[9], seem to be supported by the above discussion.

Let us mention the weak and broad band at $3\,540\ \mathrm{cm}^{-1}$, probably a combination one, occurring also in the spectrum of AUC-E sample. The position indicates a $\nu(O-H)$ band, nevertheless the formula of tetraammonium uranyl tricarbonate contains no hydroxyl groups. Neither is it a residual water because this band occurs also in spectra of NaUC and KUC samples, without any change after 4 hours drying at $150°C$ (AUC samples do not withstand such treatment because their decomposition, visualized by colour changes, starts as low as at $100°C$). This band is only very slightly shifted, $i.e.$ in fact uninfluenced, in the spectrum of the AUC-E sample, containing undoubtedly some kind of hydroxyl group. It is in line with the assumption that this band is a combination one.

AUC-E spectrum: In this spectrum we are interested, first of all, as in a completing source of information to the preceding spectra, to which it is rather resembling. Except the uranyl frequencies $\nu_3(UO_2)$ and $\nu_2(UO_2)$ which are shifted only a little, frequencies of the other parts of the complex molecule are more numerous (Fig. 1). It refers to a more complicated force field in which the particles vibrate, for instance because of the presence of new atomic groups within the molecule. In accord with the results of chemical analysis, some new bands (*e.g.*, that at $3\,320\ \mathrm{cm}^{-1}$) belonging evidently to $\nu(O-H)$ vibrations, can be found. The quite new, medium band at $460\ \mathrm{cm}^{-1}$ might be assigned to water or hydroxyl librations. Our assumption that AUC-E samples contain more likely OH^- that H_2O is based on the shape of spectral envelope in vicinity of $1\,600\ \mathrm{cm}^{-1}$. Only a shift of spectral bands ($1\,515$, $1\,575$, and $1\,678\ \mathrm{cm}^{-1}$ for AUC-A in comparison with $1\,523$, $1\,595$, and $1\,678\ \mathrm{cm}^{-1}$ for AUC-E) together with certain variations of their intensity can be observed, without any new band assignable to $(H-O-H)$ deformation.

In principal, we consider the samples AUC-E and AUC-F to be hydroxo carbonates within which the remaining carbonate ligands persist in bidentate coordination.

Comparison of AUC-A *and* NaUC *spectra:* Frequency $\nu_3(UO_2)_{AUC}$ is distinctly higher than the analogous one $\nu_3(UO_2)_{NaUC}$. Starting from the existing theories[6,15-18] it indicates a stronger ligand coordination on the equator of the uranyl ion in the case of NaUC. It should result in higher $\nu(U-O_{lig})_{NaUC}$ frequencies, too. Even though

the found band energies are not in contrast to it, simultaneously they do not confirm it clearly, mainly because the different band systems exist in both spectra in the region below 400 cm^{-1} (Table II).

As for the bond strength inside the carbonate ligands, it is stronger in NaUC in comparison with AUC because both valence and in-plane deformation vibration of the carbonate (i.e. symmetric and antisymmetric valence vibrations v_2 and v_4 together with in-plane deformations v_3 and v_5) are higher for NaUC samples. Merely out-of-plane deformation vibration v_6 is lower for NaUC, the valence vibration v_1 being the same. This behaviour together with the opposite one of the uranyl central ion can be schematically reproduced as follows:

$$(v \quad \text{and} \quad \delta_{\text{in-plane}})(CO_3)_{AUC} < (v \quad \text{and} \quad \delta_{\text{in-plane}})(CO_3)_{NaUC}$$

$$\delta_{\text{out-of-plane}}(CO_3)_{AUC} > \delta_{\text{out-of-plane}}(CO_3)_{NaUC}$$

$$v_3(UO_2)_{AUC} > v_3(UO_2)_{NaUC}$$

$$v_2(UO_2)_{AUC} < v_2(UO_2)_{NaUC}$$

Briefly spoken, in a particle (UO_2^{2+} or CO_3^{2-}) with stronger bonds, i.e., with higher values of valence vibrations, out-of-plane deformations within this particle reveal lower energies.

The comparison of AUC and NaUC spectra indicates a qualitative conformity in the architecture of the anionic part of the complexes (the same symmetry, the same number of ligands and their bidentate coordination), however with distinct quantitative deviations. Differing properties of the appropriate outer sphere cations may be one of the possible reasons.

Coordination number of the uranyl ion: If carbonates are the only ligands of the inner coordination sphere, and their coordination is bidentate, then the uranyl ion coordination number should amount double the $(C/U)_{\text{exp}}$ values. That is indisputable for the sample AUC-A for which the uranyl coordination number equals obviously 6. Not so clear is the situation for the samples AUC-B to AUC-D having the same, or at least very similar, crystal and molecular structure. The uranyl coordination number, defined according to the above instruction, equals then 5·4, 5·0 and 4·7, resp., accordingly, it can differ from 6 significantly both in absolute (up to more than one unit) and relative terms (up to about 20%). The problem lies just in an interpretation of the invariation of the IR spectra when we start from the existing theories[6,15−18] on bonds in uranyl which require a relationship between the $v_3(UO_2)$ frequency and the uranyl coordination number.

The mentioned theories are in accord that during coordination of ligands to uranyl as a central ion an occupation of pure uranium orbitals (not participating in bonds with uranyl oxygens O_I) by ligand electrons takes place. An electrostatic repulsion

of the uranyl oxygens by the ligand electrons results then in a weakening of the U—O_l bond and in decreasing $v_3(UO_2)$ frequency. Really, the values of this frequency substantially differ in individual cases — the range $1\,000-800\ cm^{-1}$ is quoted[19], some concrete examples see below — indicating thus distinct differences in strength of U—O_l uranyl bond. This limit case of the uncoordinated uranyl has been expressed[17,19] using the scheme $[O\!\equiv\!U\!\equiv\!O]^{2+}$ with triple bonds which are loosened to a varying extent as a consequence of the ligand coordination on the equator of the uranium atom. Loosening of the U—O_l uranyl bond (*i.e.*, higher degree of the electrostatic repulsion between uranium and oxygen as the consequence of the greater negative charge in the uranium orbitals) depends according to this approach on both the ligand donor ability and the number of ligands (in other words, on the uranyl coordination number).

As a rule it is difficult to follow each of these parameters independently, nevertheless in some cases it is possible. For instance, the role of donor–acceptor properties of the ligand bonds can be studied with sodium[20] or ammonium[21] uranates, utilizing the relationship between $v_3(UO_2)$ frequency and molar ratios Na/U or NH_4/U. Uranates prepared by means of alkalization of aqueous uranyl solutions contain units of the type $\left[UO_2\!\!\begin{array}{c}OH\\\diagdown\!\!\diagup\\OH\end{array}\!\!UO_2\right]^{2+}$. The weakly acidic hydrogen of the hydroxyl bridges can be substituted for a cation, forming thus substituted bridges $\diagdown$ONa or $\diagdown$ONH_4. It causes an electron shift from the oxonium oxygen towards uranium atoms, *i.e.*, an enhancement of the donor properties of the bridge, leading to the decrease of $v_3(UO_2)$ frequency in relation to Na/U or NH_4/U values in the range $960-860\ cm^{-1}$ or $960-900\ cm^{-1}$, resp. It is worth noting that the shift of $v_3(UO_2)$ band occurs without any variation of its intensity; it implies that the substitution of bridges is in no way an isolated phenomenon in the individual complex units. In such a case the band for an unsubstituted bridge would be disappearing and simultaneously, that for the substituted one would be arising at lower energies. Instead, an averaging of the strength of donor-acceptor bonds between uranyl and ligands takes place within the solid.

AUC-A to AUC-D samples make possible to follow another isolated relationship *viz.*, an influence of the variation of uranyl coordination number on the values of $v_3(UO_2)$ frequency. In contradistincton to the theoretical requirements, experimental values of this frequency do not vary in the given series. For the explanation of this effect several hypotheses can be formulated, however, none of them can still be proved. Either our AUC samples are chemically identical and have the same uranyl coordination number; then, the results of chemical analyses would have to be in error and the calculated sum of the individual components would have to be, by chance, just 100% (Table I). But why the relative intensities of the carbonate vibration bands decrease and why the hydrolytic stability of individual samples is different?

Another possibility is that the analysis is correct and yet the uranyl coordination number equals 6, because a part of coordination places equaling $[6-2.(C/U)_{exp}]$ is occupied by other ligands, most likely OH^- or H_2O (these particles were not directly analyzed; their presence would have to be hidden in random deviations of the analytical results). However, these particles have other donor properties in comparison with the carbonates which ought to lead (according to the above explained theory) to certain observable changes of the spectral envelope, not to speak of the frequencies of their own O—H bonds.

Yet another interpretation is based on the assumption that the uranyl coordination number in the given complexes is really variable. In this case the theoretical ideas about the bonds in uranyl should be modified, or we have met here a peculiar case caused by a circumstance (*e.g.*, by an influence of outer-sphere cations, or by a special way of hybridization within the complex anion) which was not embedded into the theory.

Our future investigation will be aimed at a solution of this problem.

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