14. FT-IR Investigation of Rare-Earth and Metal-Ion Solvation

Part 14

Interaction between Uranyl Perchlorate and Dimethyl Sulfoxide in Anhydrous Acetonitrile[1]

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The interaction between the uranyl ion and perchlorate in anhydrous acetonitrile has been investigated by FT-IR and *Raman* spectroscopy. Vibrations assigned to uncoordinated (u), monodentate (m), and bidentate (b) perchlorate anions were identified in 0.075M solutions. Quantitative data indicate that perchlorate is distributed as follows: 37 ± 2% are uncoordinated, 36 ± 7% are monodentate, and 27 ± 7% are bidentate. This is in agreement with the conductivity of the solutions which is at the lower end of the range accepted for 1:1 electrolytes. The splittings $\nu_4-\nu_1$(m) and $\nu_8-\nu_1$(b) of 147 and 246 cm^{-1}, respectively, point to a large inner-sphere interaction. An equilibrium occurs between two differently coordinated species. Various amounts of DMSO were added to 0.05M perchlorate solutions ($R' = [DMSO]_t/[UO_2^{2+}]_t = 1-10$). The ν_7 (SO) and ν_{22} (CS) vibrations of DMSO were used to determine the average number of coordinated DMSO molecules per uranyl ion, which is close to 4. Some bidentate perchlorate ions are still present in these solutions, but all the MeCN molecules (2.6 on average) are expelled out of the inner coordination sphere. The data can again be interpreted in terms of an equilibrium between differently coordinated species. The average coordination number of the uranyl ion is 4.4, as the perchlorate salt in MeCN solution, and may be somewhat smaller in the presence of DMSO. The possible presence of dimeric species is also discussed.

Introduction. – The dioxouranium(VI), or uranyl, ion is one of the more stable form of uranium. The $O=U=O^{2+}$ entity is linear both in the solid state and in solution [2], the two axial oxide ligands are kinetically inert, and substitution only takes place in the equatorial plane. In the solid state, 4–6 monodentate ligands lie usually in this plane [3] while in solution a coordination number of 5 is common [4].

The perchlorate ion is often considered as a weakly interacting anion. However, recent studies have shown that perchlorato complexes may have strong metal–perchlorate bonds [5]. *Vdovenko et al.* [6] have investigated the bonding between ClO_4^- and uranyl ion in hydrated and anhydrous uranyl perchlorates by vibrational spectroscopy. In these salts, the ClO_4^- groups are bonded in the inner coordination sphere of the uranyl ion; they behave as monodentate ligands in the trihydrate and as bidentate anions in both the monohydrate and the anhydrous salt.

Until now, little attention has been devoted to the solvation of the uranyl ion in anhydrous solutions despite the fact that uranyl perchlorate is often used to synthesize complexes in nonaqueous solvents [7]. In previous papers, we have shown how FT-IR difference spectra can be used to unravel the coordination mode of ClO_4^-, NO_3^-, dimethyl

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[1] Part 13: [1].

sulfoxide (DMSO), and MeCN bonded to metal ions [8–11]. We have studied the lanthanide perchlorates [8] [9] and nitrates [10] [11] in anhydrous MeCN and have determined the coordination numbers of the Ln^{III} ions. In this paper, we aim at determining the average number and the coordination mode of ClO_4^- anions bonded to UO_2^{2+} in anhydrous solutions in MeCN, as well as the number of DMSO molecules that can be bonded in the equatorial plane. The study is completed by a vibrational analysis of anhydrous uranyl perchlorate and its DMSO adduct $UO_2(ClO_4)_2 \cdot 4DMSO$.

Experimental. – *Reagents.* Anh. uranyl perchlorate was obtained by heating the hydrated salt (*Strem Chemicals*) *in vacuo* (10^{-2} mm Hg, 2–3 days, 50°; 10^{-6} mm Hg, stepwise heating to 85–90° during 4–5 weeks). The absence of H_2O was checked by IR spectroscopy and *Karl Fischer* titration using a *Mettler DL-18* apparatus. Anh. MeCN and DMSO were prepared as described in [8] [9]. All the solns. were prepared in a dry box under N_2 atmosphere ($\leqslant$ 10 ppm H_2O). The uranyl concentration was determined by pulsed polarography using a *Metrohm E 505* apparatus after dilution by aq. 0.5M HCl [12].

The $UO_2(ClO_4)_2 \cdot n$DMSO adduct was prepared as follows [13]. *Ca.* 2 g of hydrated uranyl perchlorate were dissolved in 10 ml of MeOH, and 1.3 ml of DMSO were added dropwise under stirring. The precipitate was filtered, washed with dry benzene, recrystallized twice in MeCN, and dried 2 d over P_4O_{10} *in vacuo* (10^{-2} mm Hg). The number *n* of DMSO molecules was 3.9, as calculated from a polarographic determination of uranyl. The adduct is not stable, and part of the DMSO is readily lost upon storage in a desiccator, *n* decreasing progressively to 2.5.

Spectroscopic Measurements. FT-IR spectra were recorded with an *IFS-113v Bruker* vacuum spectrometer. Calibration was performed as described in [1] [9–11]. The mid-IR spectra were measured under the following conditions: 1-cm^{-1} resolution, 500 scans, *Blackman-Harris* 3-term apodisation, optical path between 23 and 100 µm, AgCl windows. The cell thickness was determined before each measurement by the method of interference fringes [14], and observed absorbances were corrected accordingly. The far-IR spectra were recorded under the same experimental conditions except that polyethylene windows were used. The reported data are averages of several measurements performed on at least two independently prepared solns. The solid samples were studied as nujol mulls in the mid-IR region and as polyethylene pellets in the far-IR region.

Curve analysis of the IR spectra into their individual components was performed on a *VAX-8850* computer using *Lorentzian* functions to simulate the absorption lines [15]. *Raman* spectra were measured with a *Spex Ramalog-4* instrument using either a Kr laser (solid samples) or an Ar laser (solns.).

Results and Discussion. – *FT-IR and* Raman *Spectra of Solid* $UO_2(ClO_4)_2$ *and* $UO_2(ClO_4)_2 \cdot 4DMSO$. According to data reported in [5], the local symmetry of the ClO_4^- anion is reduced from T_d to C_{3v}, if the anion behaves as a monodentate species or to C_{2v} or C_s, if it behaves as a bidentate moiety. In an earlier study, *Vdovenko et al.* [6] have concluded to the exclusive presence of bidentate ClO_4^- in anhydrous $UO_2(ClO_4)_2$. The

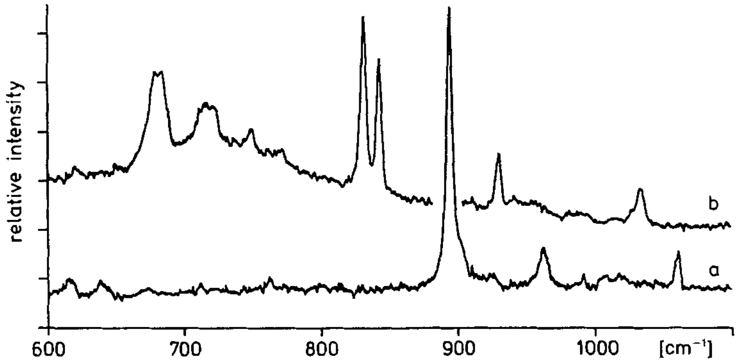

Fig. 1. Raman *spectra of* a) $UO_2(ClO_4)_2$ *and* b) $UO_2(ClO_4)_2 \cdot 4DMSO$

analysis of the vibrational spectra reported in *Fig. 1* and *Table 1* reveals a more complex situation. Nine bands or groups of bands are expected for a bidentate perchlorate [11] and all of them are observed. However, some modes are split into two components, pointing to the presence of inequivalent ClO_4^- groups, and additional bands may arise from differently coordinated anions, bridging or tridentate [5] [16]. Our assignment for bidentate ClO_4^- differs from the one proposed by *Vdovenko et al.* [6], but is consistent with previous work [5a] [8] [11].

Assuming a linear structure for UO_2^{2+} with $D_{\infty}h$ symmetry, four normal modes are expected for this cation [17]. The asymmetric stretching frequency ν_3 occurs in the range

Table 1. *IR and* Raman *Vibrations* [cm^{-1}] *Observed in Solid* $UO_2(ClO_4)_2$ *and* $UO_2(ClO_4)_2\cdot 4DMSO$

$UO_2(ClO_4)_2\cdot 4DMSO$		Assignment[a])	$UO_2(ClO_4)_2$		Assignment[a])
IR	*Raman*		IR	*Raman*	
1514*s*	1524*w*	ν(P bridging?)	1623*w*	–	
1422*m*	1414v*w*	ν_4(D)	–		
1342*w*	–	ν_{19}(D)	1262*m*	–	ν_8(P,b)
1321*w*	–		1232*s*	–	
1306*s*	–	ν_6(D)	1145*m*	–	ν_6(P,b)
1283*s*		ν(P bridging?)	1113*m*	–	
1096*s*	–	ν_3(P)			
1035(sh)	1032*m*	ν_{20}(D)	1046*m*	1060*m*	ν_1(P,b)
1030					
985*s*	–	ν_7(D) + ν_3(U)	990*s*	–	ν_3(U)
949*s*	–	ν_3(U)	974*s*		
942v*s*	–	ν_9(D)	964*s*	962*m*	ν_2(P,b)
–	930*m*	ν_1(P)			
923*s*	–	ν_3(U)	916*m*	–	
–	908v*w*	ν_1(U)	899*m*	894*s*	ν_1(U)
–	842*m*		–		
	830*m*		799*w*	–	
748*m*	750*w*		781*w*	–	
722*m*	718*m*	ν_{22}(D)	764*w*	762v*w*	
682*w*	682*m*	ν_{10}(D)	690*m*	–	
			652*w*	–	ν_3(P,b)
			643 (sh)	640v*w*	ν_7(P,b)
623*s*	621v*w*	ν_4(P)	615*w*	617v*w*	ν_9(P,b)
			545*w*	–	ν_5(P,b)
			470*w*	463*w*	ν_4(P,b)
429*s*	434*m*	ν(U··O)	427*w*	–	ν(U··O)
–	413*w*				
356*m*	355*m*	ν_{23}(D)			
317*w*	317*w*	ν_{12}(D)			
263*s*	–	δ(O··U=O)			
251*s*	–	δ(O··U=O)	254*s*	–	δ(O··U=O)
			242 (sh)	236*m*	
211*w*	205*w*	ν_2(U)	211*w*	–	ν_2(U)
188*w*	–		190*w*	193*w*	
160v*w*	156 (sh)	δ(O··U··O)	159v*w*	170v*w*	δ(O··U··O)

[a]) *s*: strong; *m*: medium; *w*: weak; v*w*: very weak; sh: shoulder; P: unassociated perchlorate; P,b: bidendate perchlorate; U: uranyl, D: DMSO.

of 974–990 cm^{-1}; it is *Raman*-forbidden and indeed does not appear in *Fig. 1*. This vibration is split into two bands, pointing either to different chemical environments for the uranyl ion or to unit-cell coupling [17d]. The symmetric stretching ν_1 is IR-forbidden, but has been reported as a weak absorption [17c, d] [18] and appears at 899 cm^{-1} and 894 cm^{-1} in the IR and *Raman* spectra, respectively. We assign the IR-allowed bending frequency ν_2 to the weak band at 211 cm^{-1}. The O···U=O bending modes, where O···U denotes an O-atom of an equatorially bonded ClO_4^- anion, are assigned in the range 236–254 cm^{-1}: these vibrations have been reported at 263 cm^{-1} for $UO_2Cl_2 \cdot n$DMSO [19]. The other weak bands between 118 and 170 cm^{-1} are assigned to the deformation modes of two O···U···O bonds outside the plane perpendicular to UO_2^{2+}, as previously shown for hydrated uranyl chloride [19].

In the vibrational spectra of the sulfoxide solvate $UO_2(ClO_4)_2 \cdot 4$DMSO (*Fig. 1* and *Table 1*), three bands can be assigned to uncoordinated ClO_4^- ions: the ν_3 and ν_4 (IR) and ν_1 (*Raman*) modes. It appears that a portion of the ClO_4^- ions are expelled out of the inner coordination sphere by DMSO molecules. The presence of coordinated (bridging?) ClO_4^- ions cannot be ruled out (*cf.* bands at 1514 and 1283 cm^{-1}), but the bands attributable to mono- or bidentate ClO_4^- ions are not found. The S=O stretch is shifted 70 cm^{-1} to lower frequency, indicating that DMSO is coordinated through the O-atom. This shift is larger than the one observed for lanthanide adducts, *ca.* −50 to −60 cm^{-1} [10] [13], pointing to a stronger interaction with UO_2^{2+}. The C–S stretching band is displaced 25 cm^{-1} to 722 cm^{-1}. Four vibrational modes are expected to lie in the range of 920 to 990 cm^{-1}: $\nu_3(UO_2^{2+})$ (IR), ν_7(DMSO), ν_9(DMSO), $\nu_1(ClO_4^-)$, (IR and *Raman*), the first two overlapping. Therefore, the anti-symmetric stretching mode of UO_2^{2+} is split into two, possibly three, components, as observed for the anhydrous perchlorate. In the low-frequency region, we assign the bands at 429 cm^{-1} (IR) and at 434 or 413 cm^{-1} (*Raman*) to an uranium–O(DMSO) stretching vibration. The ν_2 vibration of $O{=}U{=}O^{2+}$ is observed as weak bands at 211 cm^{-1} (IR) and at 205 cm^{-1} (*Raman*).

Solution Study of $UO_2(ClO_4)_2$ in Anhydrous MeCN. The molar conductivity of a 0.002M solution of uranyl perchlorate in anhydrous MeCN is equal to 111 $\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$. This value is at the lower end of the range accepted for 1:1 electrolytes (120–160 $\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$ [20]) and points to a portion of the ClO_4^- ions being replaced by solvent molecules in the inner coordination sphere.

The FT-IR difference spectra of 0.075M solutions in anhydrous MeCN confirm this finding (*Fig. 2* and *Table 2*): the two absorption bands at 626 and 1102 cm^{-1} arising from unassociated perchlorate (u, T_d) are clearly seen. Several other small absorption bands can be assigned to monodentate (m, C_{3v}) and to bidentate (b, C_{2v} or C_s) ClO_4^- ions. Indeed, most of the corresponding IR-active modes of these moieties [11] are found, except ν_6(m) and ν_4(b). Moreover, ν_3(m) interferes with ν_3(b) and ν_7(b). For bidentate ClO_4^-, some of the vibration bands are shifted with respect to those observed for the anhydrous solid salt: ν_8(b) appears at 1259 cm^{-1} (+27 cm^{-1}), ν_6(b) at 1168 cm^{-1} (+23 cm^{-1}), and ν_2(b) at 967 cm^{-1} (+5 cm^{-1}). Upon complexation, the $\nu_3(T_2)$ vibrational mode of unassociated ClO_4^- is split into $\nu_1(A_1)$ at 1033 and $\nu_4(E)$ at 1180 cm^{-1} for monodentate ClO_4^- and into $\nu_1(A_1)$, $\nu_6(B_1)$, and $\nu_8(B_2)$ at 1013, 1168, and 1259 cm^{-1}, respectively, for bidentate ClO_4^-. The magnitude of this splitting is indicative of the strength of the $UO_2^{2+} \cdots ClO_4^-$ interaction. We find a value of 147 cm^{-1} for $\nu_4 - \nu_1$(m), close to the values reported for inner-sphere complexes, *e.g.* 117 to 140 cm^{-1} for anhydrous solutions of lanthanide perchlorates [8], 128 and 135

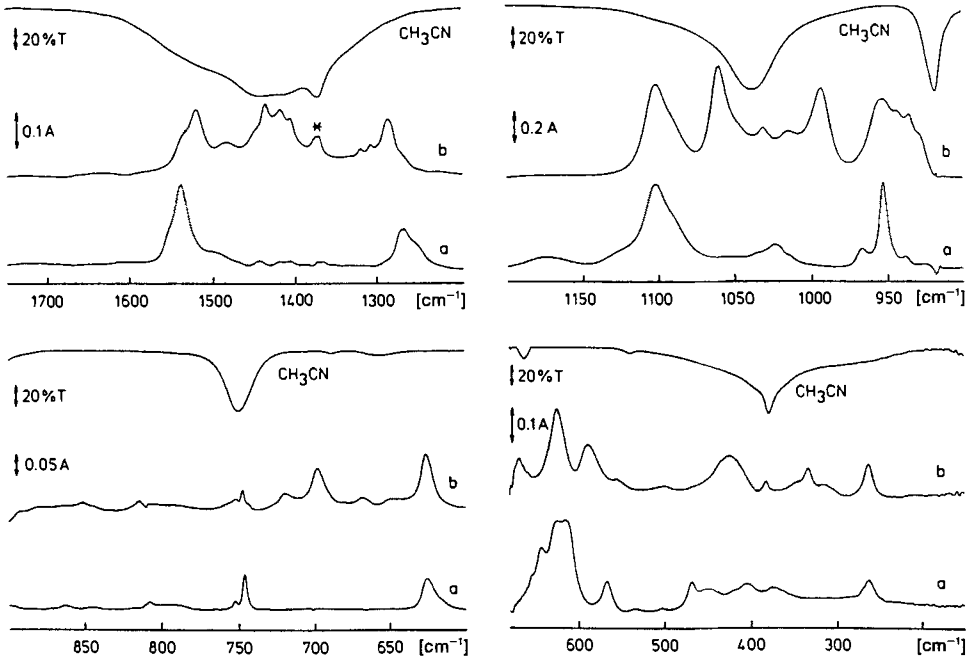

Fig. 2. *FT-IR Difference spectra of* a) *UO$_2$(ClO$_4$)$_2$ 0.075* M *in anhydrous MeCN and* b) *UO$_2$(ClO$_4$)$_2$ 0.05* M *in anhydrous MeCN containing 0.05* M *DMSO.* The upper trace displays the spectrum of bulk MeCN in transmission units. Stars denote incomplete compensation of the solvent.

Table 2. *Selected Vibrations* [cm^{-1}] *of UO$_2$(ClO$_4$)$_2$ Solutions 0.075* M *in MeCN and UO$_2$(ClO$_4$)$_2$ 0.1* M *in MeCN Containing 1* M *DMSO, with Proposed Assignments*

UO$_2$(ClO$_4$)$_2$ (0.75M)	Assignment[a])	UO$_2$(ClO$_4$)$_2$ (0.1M) [DMSO]$_t$/[UO$_2$]$_t$ = 10	Assignment[b])
2311	$\nu_3 + \nu_4$(A,c)	2291	$\nu_3 + \nu_4$(A)
2283	ν_2(A,c)	2253	ν_2(A)
1259	ν_8(P,b)	1450	ν_6(A)
1180	ν_4(P,m)	1374	ν_3(A)
1168	ν_6(P,b)	1324	ν_6(D,b)
1102, 1090 (sh)	ν_3(P,u)	1102	ν_3(P,u)
1033, 1022 (sh)	ν_1(P,m)	1062	ν_7(D)
1013	ν_1(P,b)	1032	ν_{20}(D,c)
967	ν_2(P,b)	1016	ν_{20}(D)
953	ν_3(U)	994	ν_7(D,c)
939	ν_4(A,c)	956	ν_3(U), ν_{20}(D)
928	ν_2(P,m)	947	ν_3(U)
644 (sh)	ν_3,ν_7(P,b), ν_3(P,m)	936, 931	ν_{21}(D,c), ν_{21}(D), ν_3(U)?
626	ν_4(P,u)	918	ν_4(A)
622 (sh)	ν_5(P,m)	719, 697	ν_{22}(D,c), ν_{22}(D)
615	ν_9(P,b)	680, 666	ν_{10}(D,c), ν_{10}(D)
398	ν_8(A,c)	625	ν_4(P,u)

[a]) P = ClO$_4^-$: u = uncoordinated, m = monodentate, b = bidentate; A,c = coordinated MeCN; sh = shoulder.
[b]) A = Free MeCN, D = free DMSO; D,c = coordinated DMSO.

cm^{-1} for solid Cu(ClO$_4$)$_2$·2H$_2$O, and Fe(ClO$_4$)$_3$·4H$_2$O [21], respectively. The ν_8–ν_1(b) splitting, 246 cm^{-1}, is also somewhat larger than those observed for the solutions of lanthanide perchlorate (194–206 cm^{-1} [8]). A splitting of 240 cm^{-1} [21] is reported for anhydrous Cu(ClO$_4$)$_2$, while the estimated value for outer-sphere interaction is 50 cm^{-1} [8]. These data are consistent with both ClO$_4^-$(m) and ClO$_4^-$(b) being bonded into the first coordination sphere of the uranyl ion. Additionally, the IR spectrum displays bands at 1276, 1540, and 1556 cm^{-1}, and a shoulder is observed in the *Raman* spectrum at 1501 cm^{-1}. These could point to the presence of other types of ClO$_4^-$ ions: vibrations from tridentate or bridging ClO$_4^-$ ions have been assigned above 1300 cm^{-1} [5].

MeCN molecules bonded in the inner-sphere of the uranyl ion give rise to distinct IR absorptions that are shifted towards higher wave numbers: ν_8(CCN), ν_4(C–C), ν_2(CN) and the combination ν_3(HCN) + ν_4 appear at 398 (+20), 939 (+20), 2283 (+22), and 2311 (+21) cm^{-1}. They are also observed in the *Raman* spectrum, except ν_4 which interferes with ν_3(UO$_2^{2+}$). The observed shifts are comparable to those reported for solutions of lanthanide perchlorates [8].

We have determined the concentration of ClO$_4^-$(u) in the UO$_2$(ClO$_4$)$_2$ solutions with the help of calibration curves based on silver perchlorate solutions which are known to contain unassociated ClO$_4^-$ only [11]. Since the ν_3 vibration of ionic perchlorate is an asymmetric band comprised of two components, ν_3^a and ν_3^b [22] [23], a curve-fitting procedure was used (*Fig. 3*). Both the ν_3(u) and ν_4(u) modes of unassociated perchlorate

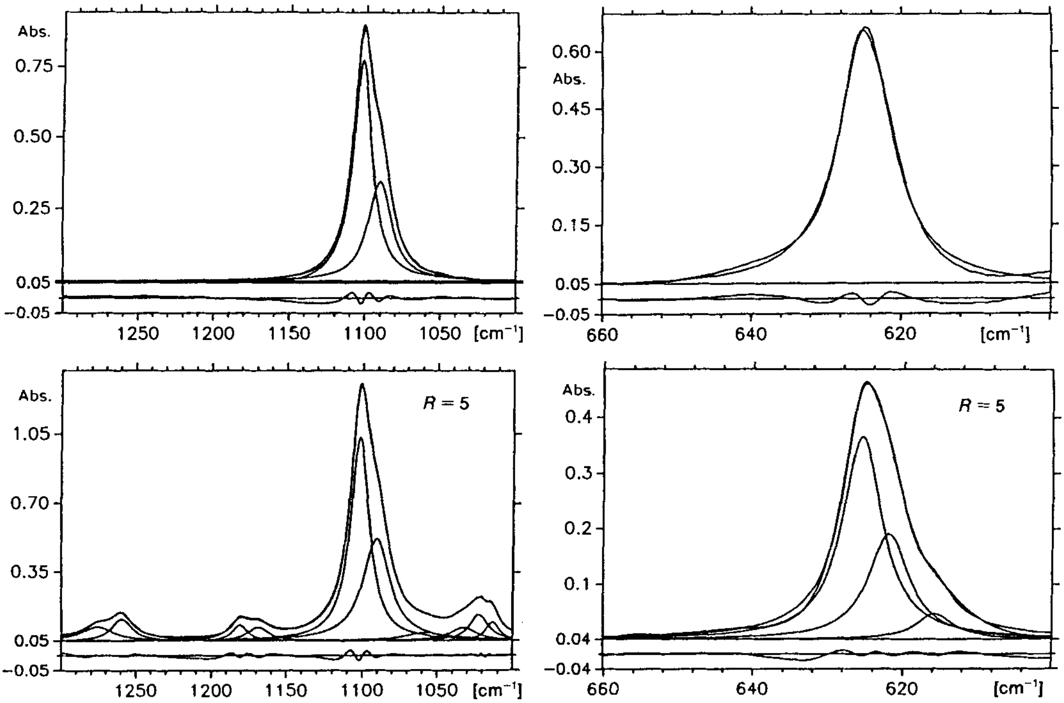

Fig. 3. *Typical curve analysis of the FT-IR difference spectra of AgClO$_4$ 0.2* M *in anhydrous MeCN* (top) *and UO$_2$(ClO$_4$)$_2$ 0.075* M *in anhydrous MeCN containing DMSO* (bottom)

follow the *Lambert-Beer* law up to an absorbance of *ca.* 1: $\varepsilon_{\nu 3a}^{max} = 1720 \pm 40$ l·mol^{-1}·cm^{-1} and $\varepsilon_{\nu 4}^{max} = 250 \pm 8$ l·mol^{-1}·cm^{-1}. The average number of uncoordinated ClO_4^- ions per UO_2^{2+} ion $\bar{n}_u$ was found to be 0.74 ± 0.04, meaning that 63% of the ClO_4^- ions are coordinated, on average, to the uranyl ion. This proportion is smaller in solutions of lanthanide perchlorates (39 to 52%, depending on the lanthanide ion [8]). To calculate the concentrations of differently bonded anions, addition of an excess ClO_4^- was made up to a ratio $R = [ClO_4^-]_t/[UO_2^{2+}]_t = 5$. No additional absorption band appears but the bands assigned to ClO_4^-(m) and ClO_4^-(b) become more intense. The average number of coordinated ClO_4^- anions per uranyl ion $\bar{n}_p$ amounts to 1.26, 1.51, 1.54, 1.66 for $R = 2, 3, 4$, and 5, respectively. This reflects the presence of an equilibrium between differently coordinated species. An estimate of the concentration of mono- and bidentate perchlorates may be done using *Koenig*'s method of internal standard [24] which was applied to two solutions having $R = 2$ and $R = 3$. The IR absorptions at 1276 (ν_8, b) and 1033 cm^{-1} (ν_1, m) were used: $[ClO_4^-(m)]/[ClO_4^-(b)] = 1.3 \pm 0.4$ for both $R = 2$ and 3. The result is not very accurate because of the large absorbance of ν_3(u) (~ 0.5 A, as compared to 0.02–0.06 A), but the molar absorption coefficients, 690 ± 50 and 170 ± 10 l·mol^{-1}·cm^{-1} for ν_8(b) and ν_1(m), respectively, are comparable to those reported for the same species in solutions of europium perchlorate [11].

The present data indicate that ClO_4^- is distributed as follows: 37 ± 2% are uncoordinated, 36 ± 7% are monodentate, and 27 ± 7% are bidentate. This information is not sufficient to get a precise representation of the species in equilibrium. However, if we assume the presence of mononuclear species only, and disregarding the coordination mode of the anion, the equilibrium could occur between $[UO_2(ClO_4)(MeCN)_x]^-$ (74%, I) and $[UO_2(ClO_4)_2(MeCN)_y]$ (26%, II). If dinuclear species were present, bidentate perchlorates could act as bridging ligands and the equilibrium could take place between (I), (II), and $[(ClO_4^m)UO_2(ClO_4^b)_nUO_2(ClO_4^m)_{n'}(MeCN)_z]$ with $n, n' = 0$ or 1.

Solution Study of $UO_2(ClO_4)_2$ in Anhydrous MeCN Containing DMSO. When increasing amounts of DMSO are added to a solution of uranyl perchlorate, this donor displaces all the MeCN molecules out of the inner coordination sphere, as well as part of the ClO_4^- ions (*Fig. 2*). Several vibrational modes of DMSO [10] are shifted by the complexation with the uranyl ion, and these shifts show little variation with the DMSO concentration: ν_{22} (697 cm^{-1} in free DMSO) +23 to +22 cm^{-1}, ν_9 (927 cm^{-1}) +9 cm^{-1}, ν_{20} (1016 cm^{-1}) +15 to +16 cm^{-1}, ν_7 (1060 cm^{-1}) −68 to −66 cm^{-1}, and ν_6 (1310 cm^{-1}) +13 to +14 cm^{-1} for $R' = [DMSO]_t/UO_2^{2+}]_t$ ranging between 1 and 10.

We have monitored the change in concentration of the species entering and leaving the inner coordination sphere of the uranyl ion. *Fig. 4* displays the change of absorbances of the ν_2 vibration and the $\nu_3 + \nu_4$ combination of bonded MeCN molecules *vs.* R'. Straight lines are obtained for both absorptions, pointing to a quantitative 1:1 replacement of MeCN by DMSO. Molar absorption coefficients can be calculated from the slopes of the plots: they amount to 230 ± 10 and 140 ± 10 l·mol^{-1}·cm^{-1} for ν_2 and $\nu_3 + \nu_4$, respectively, as compared to 38 and 8.4 l·mol^{-1}·cm^{-1} in bulk MeCN [11]. These absorption coefficients are 50% larger than those observed in lanthanide-nitrate solutions [9]. The intercepts of the straight lines reflect that, on average, 2.6 MeCN molecules are expelled per uranyl ion.

Due to the presence of the strong DMSO bands, a quantitative study of the perchlorate absorptions could not be performed, except for ν_3(u). The average number of

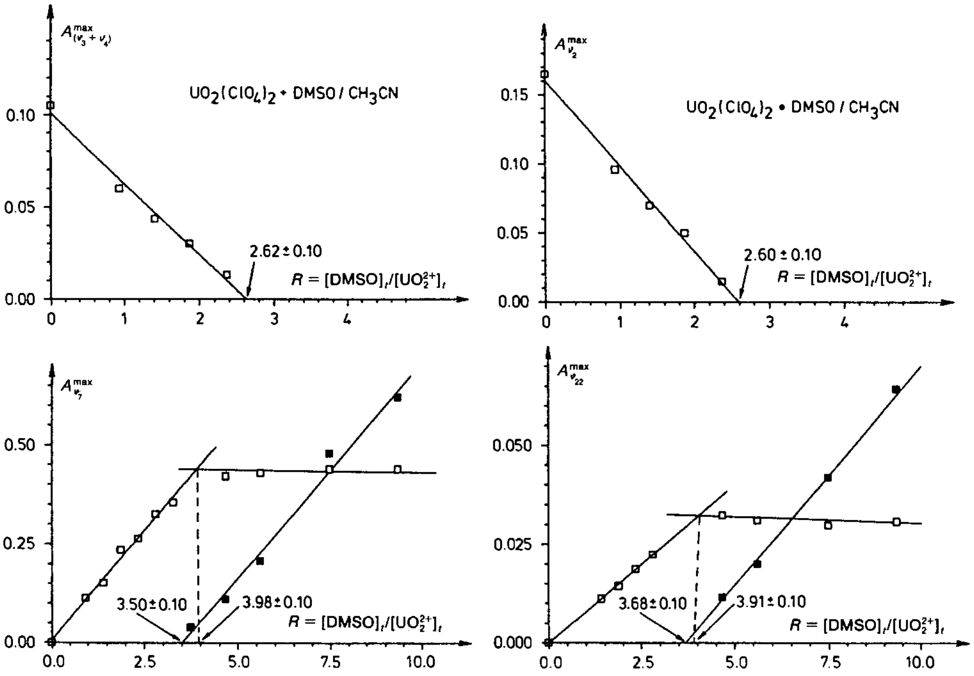

Fig. 4. *Absorbances of the* ν_2 *and* $\nu_3 + \nu_4$ *vibrations of bound MeCN* (top) *and of* ν_7*(SO) and* ν_{22}*(CS) modes of bonded and free DMSO* (bottom) *in* $UO_2(ClO_4)_2$ *0.05* M *in anhydrous MeCN containing DMSO.* R = [DMSO]$_t$/[UO$_2^{2+}$]$_t$.

uncoordinated perchlorate $\bar{n}_u$ increases from 0.74 to 0.9 when R' increases from 0 to 10. All the bands assigned to monodentate ClO_4^- disappear while vibrations assigned to ClO_4^-(b) are still present when $R' = 10$: ν_8, ν_1, ν_7, ν_9, ν_5, and ν_4 are observed at 1274, 1014, 643, 615, 555, and 462 cm^{-1}, respectively. Finally, the molar conductivity of a 0.002M solution of $UO_2(ClO_4)_2$ with $R' = 10$ is larger than the conductivity in absence of DMSO, 134 $\Omega^{-1} \cdot cm^2 \cdot mol^{-1}$, indicating that anion dissociation has occured: in DMSO, 1:1 electrolytes have a lower conductivity than in MeCN [20].

The average number of coordinated DMSO molecules per UO_2^{2+} ion, $\bar{n}_d$ has been determined by monitoring the ν_7(S–O) and ν_{22}(C–S) stretching modes. The latter vibration is free from interferences, but its molar absorption coefficient is small and appears in a spectral range in which the IR detector used produces a more noisy signal. The results obtained with these two absorption bands are in excellent agreement. Molar-ratio plots (*Fig. 4*) indicate that $\bar{n}_d$ is equal to 3.95 ± 0.1, a value which corresponds to the stoichiometry of the solid adduct. Extrapolation of the curves representing the absorbances of the bands assigned to free DMSO reveals that free DMSO is present when R' reaches 3.6 ± 0.1. Since no MeCN remains in the inner coordination sphere for $R' > 2.6$, a straightforward interpretation of this figure is that either the average coordination number of the uranyl ion increases upon further addition of DMSO, as has been observed in the case of lanthanide ions [9] [10], or a ClO_4^- anion is replaced by a DMSO molecule. Since vibrations assigned to ClO_4^-(m) disappear upon addition of DMSO, the latter explanation is favored. To confirm the value obtained for $\bar{n}_d$, the average number of bonded DMSO molecules has also been calculated from the total DMSO concentration and the free DMSO concentration estimated from calibration curves ($\varepsilon(\nu_7) = 420 \pm 8$ and $\varepsilon(\nu_{22}) = 42 \pm 4\ \mathrm{l \cdot mol^{-1} \cdot cm^{-1}}$). Again, data obtained using the two absorption bands are identical, and we get the following values for $\bar{n}_d$: 3.6, 3.8, and 3.9 for $R' = 4$, 6, and 10, respectively.

If we refer to a simple model taking mononuclear species only into account, the above data can be interpreted as reflecting the following equilibrium:

$$[\mathrm{UO_2(ClO_4)}_x\mathrm{(DMSO)_3}]^{(2-x)+} + \mathrm{DMSO} \overset{K_4}{\leftrightarrows} [\mathrm{UO_2(ClO_4)}_x\mathrm{(DMSO)_4}]^{(2-x)+}$$

The apparent equilibrium constant K_4 was evaluated according to both the mole fraction and *Bjerrum*'s methods [25]. We find $\log K_4 = 1.4 \pm 0.2\ \mathrm{M^{-1}}$, which is of the same order of magnitude than similar constants reported for lanthanide nitrates [9] and lanthanide perchlorates [10]. The presence of at least two uranyl-containing species in the solutions with $R' = 4$ is confirmed by the splitting of the $\nu_3(\mathrm{UO_2^{2+}})$ vibration, which is R-dependent.

Conclusion. – This work shows that uranyl form strong inner-sphere complexes with both monodentate and bidentate $\mathrm{ClO_4^-}$ in anhydrous MeCN, contrary to what was observed in H_2O [26]. There is some uncertainty to whether dinuclear species, bridged by $\mathrm{ClO_4^-}$ anions, are present or not in these solutions. A similar situation prevails for solutions in which DMSO has been added, since some bonded bidentate $\mathrm{ClO_4^-}$ ions remain even after addition of 10 molecules of DMSO per uranyl ion. An average coordination number of 4.4 can be estimated for perchlorate solutions, MeCN contributing 2.6 and $\mathrm{ClO_4^-}$ 1.8 (0.7 monodentate, 1.1 bidentate). This number appears to be approximately the same in solutions containing DMSO: 4 of these molecules bind in the inner-coordination sphere and some bidentate $\mathrm{ClO_4^-}$ is still present. The observation of a solvate with 4 DMSO molecules is consistent with the stoichiometry of both the solid adduct isolated in this work and with the recently reported dimeric complex $[\mathrm{UO_2(DMSO)_4}]_3[\mathrm{Cr(SCN)_6}]_2$ [27].

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REFERENCES

[1] J.-C. G. Bünzli, A. Milicic-Tang, *Helv. Chim. Acta* **1993,** *76,* 1292.

[2] L. Cattalini, U. Croato, S. Degetto, E. Tondello, *Inorg. Chim. Acta Rev.* **1971,** *5,* 19; S. Ahrland, J. O. Liljenzin, J. Rydberg, in 'Comprehensive Inorganic Chemistry, Actinides', Pergamon Press, New York, 1973, Vol. 5.

[3] N.W. Alcock, *J. Chem. Soc., Dalton Trans.* **1973,** 1616; N.W. Alcock, S. Esperas, *ibid.* **1977,** 893; L. R. Nassimbeni, A. L. Rodgers, *Cryst. Struct. Commun.* **1976,** *5,* 301.

[4] J. Crea, R. Diguisto, S.F. Lincoln, E.H. Williams, *Inorg. Chem.* **1977,** *16,* 2825; G.J. Honan, S.F. Lincoln, E.H. Williams, *J. Solution Chem.* **1978,** *7,* 443; H. Doine, Y. Ikeda, H. Tomiyasu, H. Fukutomi, *Bull. Chem. Soc. Jpn.* **1983,** *56,* 1989.

[5] M. Fourati, M. Chaabouni, C.H. Belin, M. Charbonnel, J.-L. Pascal, J. Potier, *Inorg. Chem.* **1986,** *25,* 1386; M. Fourati, M. Chaabouni, C. Belin, J.-L. Pascal, J. Potier, *New J. Chem.* **1990,** *14,* 695.

[6] V.M. Vdovenko, L.G. Mashirov, D.N. Suglobov, *Radiokhimiya (Engl. Transl.)* **1964,** *6,* 289.

[7] J. Lagrange, J.-P. Metabanzoulou, P. Fux, P. Lagrange, *Polyhedron* **1989,** *8,* 2251; J. Lagrange, J.-P. Metabanzoulou, P. Lagrange, *J. Chim. Phys.* **1989,** *86,* 1369.

[8] J.-C. G. Bünzli, V. Kasparek, *Inorg. Chim. Acta* **1991,** *182,* 101, and ref. cit. therein.

[9] J.-C. G. Bünzli, J.-P. Metabanzoulou, P. Froidevaux, L. Jin, *Inorg. Chem.* **1990,** *29,* 3875.

[10] A. Milicic-Tang, J.-C. G. Bünzli, *Inorg. Chim. Acta* **1992,** *192,* 201.

[11] J.-C. G. Bünzli, J.-R. Yersin, C. Mabillard, *Inorg. Chem.* **1982,** *21,* 1471; C, Mabillard, Ph. D. Thesis No. 515, Ecole Polytechnique Fédérale, Lausanne, 1983.

[12] I. M. Kolthoff, W. E. Harris, *J. Am. Chem. Soc.* **1945,** *67,* 1484.

[13] V. N. Krishnamurphy, S. Soundararajan, *J. Inorg. Nucl. Chem.* **1967,** *29,* 517.

[14] A. L. Smith, 'Applied Infrared Spectroscopy', in 'Chemical Analysis', Eds. P. J. Elving and J. D. Winefordner, John Wiley & Sons, New York, 1979, Vol. 54, pp. 117–118.

[15] L. Zekany, UVIR curve fitting program (ICMA, 1990).

[16] F. Favier, J.-L. Pascal, *J. Chem. Soc., Dalton Trans.* **1992,** 1997.

[17] a) B. W. Veal, D. J. Lam, W. T. Carnall, R. E. Hoeskt, *Phys. Rev. B* **1975,** *12,* 5651; b) S. Siegel, *J. Inorg. Nucl. Chem.* **1978,** *40,* 275; c) J. I. Bullock, *ibid.* **1967,** *29,* 2257; d) J. I. Bullock, *J. Chem. Soc.* **1969,** 781.

[18] S. P. McGlynn, J. K. Smith, W. C. Neely, *J. Chem. Phys.* **1961,** *35,* 105.

[19] G. Kaufmann, M. Leroy, *Bull. Soc. Chim. Fr.* **1966,** *12,* 3770.

[20] W. J. Geary, *Coord. Chem. Rev.* **1971,** *7,* 81.

[21] B. J. Hathaway, A. E. Underhill, *J. Chem. Soc.* **1961,** 3091.

[22] J.-C. G. Bünzli, C. Mabillard, J.-R. Yersin, *Inorg. Chem.* **1982,** *21,* 4214.

[23] J.-C. G. Bünzli, C. Mabillard, *Inorg. Chem.* **1986,** *26,* 2750.

[24] J. L. Koenig, D. Kormos, *Appl. Spectrosc.* **1979,** *33,* 349.

[25] M. T. Beck, I. Nagypal, in 'Chemistry of Complex Equilibria', John Wiley & Sons, New York, 1990, pp. 45.

[26] M. H. Brooker, C.-H. Huang, J. Sylwestrowicz, *J. Inorg. Nucl. Chem.* **1980,** *42, 1431.*

[27] T. G. Cherkasova, E. S. Tatarinova, O. A. Kuznetsova, B. G. Tryasunov, *Russ. J. Inorg. Chem. (Engl. Transl.)* **1990,** *35,* 451.