STRUCTURE AND VIBRATIONAL IR SPECTRA
OF A UCl₄·2DMSO COMPLEX

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Structural models are designed and spectral characteristics are computed based on DFT calculations for a complex of uranium tetrachloride with two molecules of dimethylsulfoxide (UCl₄·2DMSO). The calculations were carried out using a B3LYP hybrid functional in the LANL2DZ effective core potential approximation for the uranium atom and a cc-pVDZ all-electron basis set for all other atoms. Two structural variants were found for the complex. In the first of them, which is more stable, DMSO molecules are coordinated to the central uranium atom through oxygen atoms whereas in the second one, whose energy is 225 kJ/mol higher, the coordination proceeds through sulfur atoms. The obtained spectral characteristics are analyzed and compared with experimental data. Spectral features that are characteristic of the complexation process are identified. The adequacy of the proposed models and the agreement between calculation and experiment are demonstrated.

Keywords: *ab initio calculation, density functional theory, effective core potential, IR spectrum, uranium tetrachloride (UCl₄), dimethylsulfoxide (DMSO), coordination complexes.*

Introduction. Dimethylsulfoxide (DMSO) occupies a special place among polar organic solvents containing C=O, S=O, or P=O electron-donating groups and; consequently, tending to form coordination complexes. In contrast with dimethylformamide (DMF), hexamethylphosphoramide (HMPA), and other compounds, DMSO can coordinate to the central metal atom in certain instances not only through the O atom but also through the S atom [1–5]. The latter type of coordination is accompanied by a short-wavelength shift of the S=O stretching vibrational frequency whereas coordination of the former type shifts the frequency to longer wavelength. Thus, the spectral position of this vibrational frequency can act as a highly reliable signature of the complex structure.

Herein structural variants of the complex of UCl₄ with two DMSO molecules are discussed based on quantum-chemical calculations of the electronic structure and an analysis of previously obtained IR spectra [6, 7]. Such complexes provide an example of polymerization involving organic and inorganic ligands and, in particular, can serve as a model for uranium complexation. Their spectral and structural characteristics can be used for the preparation of uranium oxides that are used in nuclear energy.

Experimental and Calculations. IR absorption spectra of pure DMSO and UCl₄·2DMSO pressed into KBr pellets [6], suspended in a mineral-oil mull [7] for the middle IR region, or pressed into a polymeric matrix [6] for the long-wavelength region were recorded on a Vertex 70 spectrophotometer (Bruker) in the ranges 400–4000 cm⁻¹ [6, 7] and 50–400 cm⁻¹ [6]. The equilibrium structure was optimized and the force field, fundamental vibrational frequencies, and intensities in IR spectra were calculated in a harmonic approximation using the applied quantum-chemical program GAMESS-US [8, 9]. The results were visualized using the MacMolPlt program [10]. The LANL2DZ effective core potential (ECP) that replaces 78 inner electrons was used for the U atom [11]. The DZ-basis sets that were specially developed for this ECP were used for the remaining electrons of the U atom. The other atoms were described by the cc-pVDZ standard all-electron basis set [12]. The ECP and corresponding basis sets were generated

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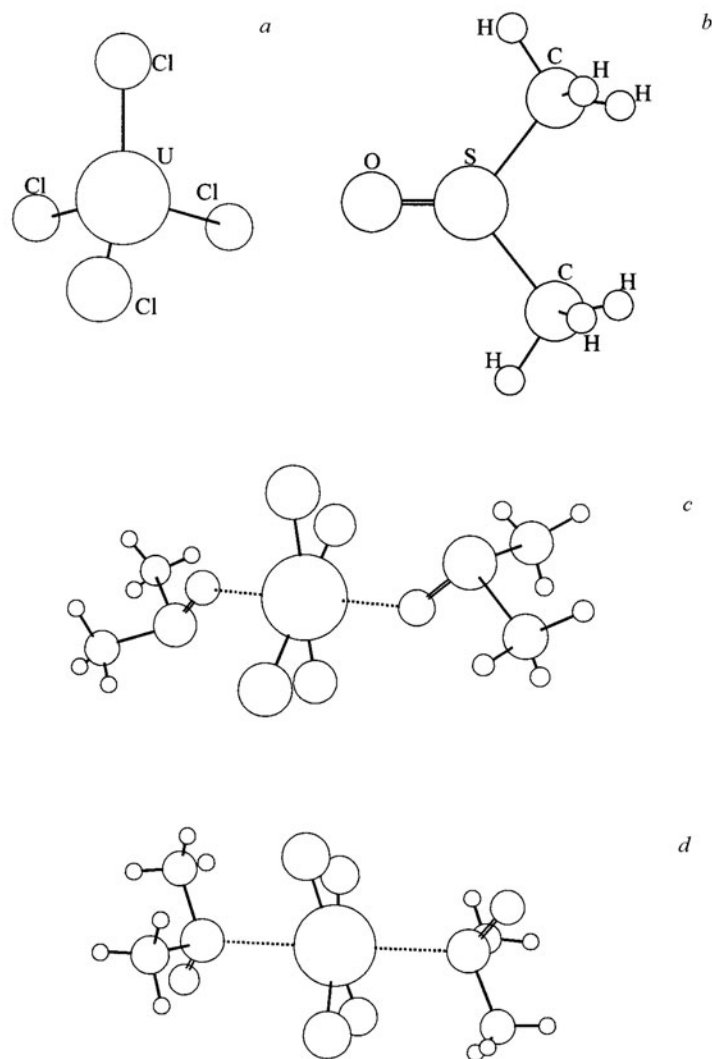
Fig. 1. Equilibrium configurations of UCl$_4$ (a), DMSO (b), and UCl$_4$·2DMSO complexes (*A* and *B*) with coordination through O (c) and S atoms (d), respectively.

using the Extensible Computational Chemistry Environment Basis Set Database [13–15]. The hybrid exchange-correlation functional B3LYP was also used in all calculations [16–18].

Results and Discussion. *Uranium tetrachloride (UCl$_4$).* Equilibrium configurations of D_{2d} symmetry were obtained from our calculations [19] of isolated UCl$_4$ and UF$_4$ molecules (Fig. 1a). It was shown [19] that the structural and spectral-energetic characteristics of the uranium tetrahalides calculated by us for the D_{2d} model were in principle consistent with experimental results (Tables 1 and 2) that suggested a regular tetrahedral structure of T_d symmetry [20]. The bond lengths for UCl$_4$ were 2.543 Å. The ClUCl angles were less than the tetrahedral value (109.47°) by 0.26°. The triply degenerate (for the T_d model) stretching vibration ν_3 was split into two components, i.e., doubly degenerate *E* with frequency 332.4 cm^{-1} and non-degenerate B_2 with frequency 332.0 cm^{-1} (both vibrations had practically the same intensity in the IR spectrum). The frequency of the fully symmetric stretching vibration ν_1 was 324.2 cm^{-1} (IR inactive). Triply degenerate bending vibration ν_4 was also split into two components with frequencies 50.2 cm^{-1} (B_2) and 49.7 cm^{-1} (*E*). The frequency of bending vibration ν_2 was 46.2 cm^{-1}. (All bending vibrations were split in the IR spectrum. However, the intensities of the corresponding absorption bands were 1–2 orders of magnitude

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TABLE 1. Structural Parameters of UCl$_4$, DMSO, and Two Variants of the UCl$_4$·2DMSO Complex

Parameter	UCl$_4$		DMSO		Complex, calc.	
	calc.	expt.[22]	calc.	expt. [21]	A	B
R(UCl)	2.543	2.503 ± 0.003	–	–	2.655 2.612	2.565 2.611
R(S=O)	–	–	1.5026	1.4837 ± 0.0011	1.5808	1.5225
R(CS)	–	–	1.8284	1.8071 ± 0.0008	1.8196	1.8268
R(CH) (average)	–	–	1.1008	1.0934 ± 0.0023	1.0994	1.0990
R(U...O) or R(U...S)	–	–	–	–	2.3587	3.0520
CSC	–	–	96.73	96.56 ± 0.06	100.47	100.53
O=SCC	–	–	109.12	115.43 ± 0.05	104.79	113.99

weaker than that of stretching vibration ν$_3$.) Table 2 compares characteristics of the UCl$_4$ vibrational spectrum that were calculated in a harmonic approximation with experimental data for the gas phase at ~900 K [21]. The frequencies (in cm^{-1}) and band intensities in the experimental spectra (in percent absorption) are also given. The intensities in the calculated spectra were normalized to the intensity of the strongest band in the corresponding spectrum. Figure 2a shows the calculated UCl$_4$ spectrum.

Dimethylsulfoxide (DMSO). The molecular structure of DMSO has been studied several times by experimental and theoretical methods [21, 24–27]. The geometric parameters of DMSO were determined highly accurately. The geometry of DMSO was optimized initially assuming that the equilibrium configuration possessed C_s symmetry. However, it was discovered during calculation of the Hessian that the CH$_3$ antisymmetric torsion mode for such a structure had an imaginary frequency. Therefore, the final optimization was performed without symmetry constraints. The next calculation of the Hessian confirmed the stability of such a configuration (Fig. 1b). Table 1 compares calculated DMSO structural parameters and experimental data for the gas phase [21] (bond lengths are given in Å; angles, in degrees). These data showed that the calculation in the B3LYP/cc-pVDZ approximation reproduced adequately the experimental structural parameters for the isolated DMSO molecule. Deviations of the calculated S=O and CS bond lengths from the experimental values were 1.3%; of the CH bond lengths, 0.7%. The CSC angle was reproduced with an error 0.2%. The greatest error (–5.5%) was observed for the dihedral angle between a plane containing the S=O bond and the plane containing the two CS bonds. It is noteworthy that a similar error was also observed for DMF [28]. This is apparently typical of the approximation that was used.

An analysis of calculated vibrational spectra of DMF monomer and dimer [28] in addition to the complex UCl$_4$·2DMF [19] showed that the frequencies of CH stretching vibrations were elevated by ≈3%; of the carbonyl, by 4%, if the B3LYP/cc-pVDZ approximation was used. The frequencies of other stretching and bending vibrations of DMF were elevated less significantly. The frequencies of the stretching vibrations of the "core" molecule turned out to be relatively insensitive to scaling of the force constants. Therefore, the force constant matrices were partially scaled [19, 28]. Calculation of the vibrational spectrum of the isolated DMSO molecule (Table 2) indicated that the frequencies of CH stretching vibrations were also elevated by an average of 4%. The frequency of the S=O stretching vibration (1086 cm^{-1}) was lowered by 1.5% relative to its value for the gas phase (1102 cm^{-1} [1]) and elevated by 1.5, 3.0, and 4.5% relative to values for the pure liquid (1070 cm^{-1} [2]), solution (1055 cm^{-1} [1]), and KBr pellets (1039 cm^{-1} [6]), respectively. Calculated frequencies of other stretching and bending vibrations of DMSO also differed insignificantly from the experimental values. Thus, it was not necessary to scale the force fields of the isolated DMSO molecule and the UCl$_4$·2DMSO complexes. Absorption bands in the IR spectrum of DMSO [6] (Table 2) were assigned based on our calculation and were consistent with published data [1, 2]. Figure 2b shows a portion of the calculated spectrum.

UCl$_4$·2DMSO complex. Two variants of DMSO coordination to the central U atom were examined for the UCl$_4$·2DMSO complex. In the first (variant *A*), coordination occurs through the O atoms; in the second (variant *B*),

TABLE 2. Frequencies and Intensities in Experimental and Calculated IR Vibrational Spectra of UCl_4, DMSO, and the $UCl_4 \cdot 2$DMSO Complexes

Assignment	Complex								DMSO or UCl_4			
	expt.				calc.				expt. [6]		calc.	
	[6]		[7]		A		B					
	ν	I	ν	I	ν	I	ν	I	ν	I	ν	I
ν_{as} CH₃	–	–	–	–	3190	0.01	3181	0	–	–	3154	0.03
					3190	0	3180	0.01				
ν_{as} CH₃	–	–	–	–	3183	<0.01	3162	0	–	–	3143	0.07
					3183	0	3162	<0.01				
ν_{as} CH₃	3013	0.9	–	–	3163	0	3152	0	–	–	3137	0.03
					3163	<0.01	3152	<0.01				
ν_{as} CH₃	–	–	–	–	3154	0	3148	<0.01	2999	0.7	3131	0.02
					3154	<0.01	3148	0				
ν_s CH₃	2927	0.5	–	–	3053	0	3037	0	–	–	3030	0.07
					3052	0.01	3037	0.02				
ν_s CH₃	–	–	–	–	3046	0.01	3029	0	2915	0.6	3024	0.06
					3046	0	3029	0.01				
δ_{as} CH₃	1437	0.5	–	–	1457	0.12	1452	0	1438	0.9	1449	0.14
					1456	0	1451	0.20				
δ_{as} CH₃	–	–	–	–	1439	0.02	1439	0.10	–	–	1429	0.01
					1438	0	1429	0				
δ_{as} CH₃	1423	0.6	1420	0.5	1437	0	1429	0	1414 [2]	–	1428	0.03
					1437	0.02	1429	0.04				
δ_{as} CH₃	–	–	–	–	1421	0.04	1414	0.09	1407	0.9	1413	0.06
					1421	0	1414	0				
Overtone ν_s CS	1320	0.3	1320	0.3	–	–	–	–	1320	shoulder	–	–
δ_s CH₃	1310	shoulder	1310	shoulder	1366	0.02	1327	0.09	1313	0.8	1325	0.07
					1366	0	1327	0				
δ_s CH₃	–	–	–	–	1339	<0.01	1298	0.03	1290 [2]	–	1299	0.01
					1339	0	1298	0				
ρ CH₃	1051	0.9	1021	0.6	1049	0	1042	0	954	0.9	1007	0.16
					1049	0.12	1041	0.44				
ρ CH₃	–	–	991	0.9	999	0	955	0	920	0.8	926	0.05
					999	0.10	955	0.08				
ρ CH₃	–	–	–	–	958	0.01	924	0	900	0.5	892	0.04
					958	0	924	0.02				
ν S=O	–	–	–	–	933	0	1078	0	1039	1.0	1086	1.00
					–	–	1078	1.00				
ν S=O + ρ CH₃	940	0.7	951	1.0	922	0.62	–	–	–	–	–	–
	918	1.0	941	1.0	920	1.00						

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TABLE 2. (Continued)

Assignment	Complex								DMSO or UCl$_4$			
	expt.				calc.				expt. [6]		calc.	
	[6]		[7]		A		B					
	ν	I	ν	I	ν	I	ν	I	ν	I	ν	I
ρ CH$_3$	–	–	906	0.9	– / 921	– / 0	913 / 912	0.07 / 0	–	–	868	0.05
ν$_{as}$ CS	786	0.4	–	–	696 / 696	0.02 / 0	674 / 674	0.09 / 0	698	0.8	649	0.20
ν$_s$ CS	668	0.5	–	–	656 / 656	0.01 / 0	636 / 636	0 / 0.03	665	0.7	626	0.09
Electron-transfer band	630	0.6	–	–	–	–	–	–	710±40 [23]	–	–	–
γ S=O	–	–	424	0.6	438 / 434	0 / 0.35	369 / 369	0.03 / 0	378 [2]	–	368	0.06
ρ S=O	315	0.2	–	–	329 / 328	0.07 / 0	301 / 300	0.14 / 0	329 [2]	–	310	0.08
δ CSC	303	0.2	–	–	310 / 308	0.04 / 0	271 / 269	0 / <0.01	305 [2]	–	284	<0.01
ν$_{as}$ UCl	270 / 256 / 235	0.8 / 0.9 / 0.7	–	–	292 / 278 / 250	0.27 / 0.27 / <0.01	313 / 300 / 266	0.65 / 0.53 / <0.01	337 [21]	–	332	1.00
ν$_s$ UCl	–	–	–	–	288	<0.01	304	<0.01	–	–	324	0
τ CH$_3$	–	–	–	–	277 / 275	0.01 / 0	245 / 244	0.01 / 0	–	–	188	0.01
τ CH$_3$	–	–	–	–	243 / 243	0 / <0.01	178 / 177	<0.01 / 0	–	–	115	<0.01
ν$_{as}$ U...O (U...S)	177	0.7	–	–	198	0.08	133	0.03	–	–	–	–
ν$_s$ U...O (U...S)	168	0.7	–	–	188	0	121	0.07	–	–	–	–

Note. ν$_{as}$, ν$_s$ and δ$_{as}$, δ$_s$ are antisymmetric and symmetric stretching and bending vibrations; ρ, rocking; γ, out-of-plane; σ, scissors; and τ, twisting vibrations.

through the S atoms. In contrast with the UCl$_4$·2DMF complex [19], only one equilibrium structure (with *trans* ligands) of point symmetry C_i was found for variant *A*. The spectrum of the model complex with coordination through the O atoms and *cis* ligands contained two imaginary frequencies for rocking vibrations of CSC groups in the DMSO molecules. This could be explained by steric hindrance arising upon close contact of the ligands. Hence, the formation of such a model complex seemed improbable. Therefore, it was not considered in analyzing and interpreting the experimental spectra [6, 7]. The structure of variant *B* also had point symmetry C_i although its energy according to the calculation was 225.4 kJ/mol greater.

The shape of UCl$_4$ changed significantly upon forming the UCl$_4$·2DMSO complex (like for UCl$_4$·2DMF [19]). This was accompanied by a reduction of the local symmetry of the UCl$_4$ group to C_{2h} and the adoption of a flattened shape. The U bonds (four UCl and two U...O or two U...S) formed a regular octahedral structure for complex *A* and close to it for complex *B*. The UCl bonds in both variants were lengthened and became nonequivalent (Table 1). In
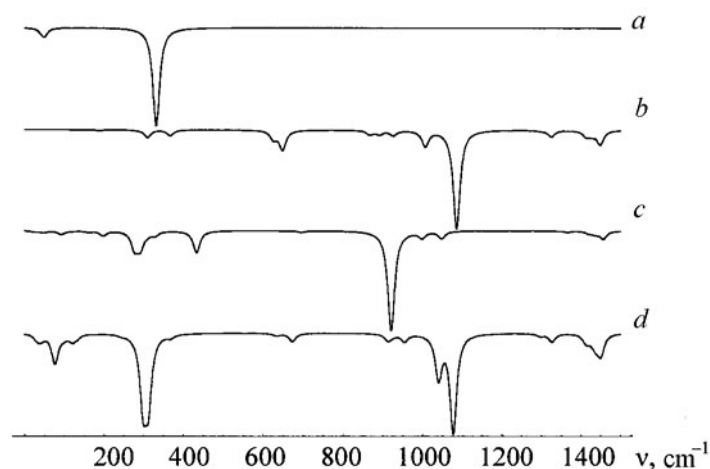
Fig. 2. Calculated IR spectra of UCl_4 (a), DMSO (b), and $UCl_4 \cdot 2DMSO$ complexes with coordination through O (c) and S atoms (d).

contrast to the UCl_4 group, the DMSO ligands in the complex retained in general their structure (Fig. 1b–d). The greatest changes were typical of the S=O bonds. They lengthened by 0.078 and 0.020 Å in complexes A and B. The CS bond lengths underwent smaller changes. They contracted by 0.009 and 0.002 Å. The bond lengths of the methyl H atoms also changed insignificantly.

Figure 2 shows portions of the two calculated (for variants A and B) IR spectra of the $UCl_4 \cdot 2DMSO$ complex. Table 2 compares the calculated frequencies and their corresponding band intensities with the experimental values. The strongest band in IR spectra of DMSO and the complex corresponded obviously to the S=O stretching vibration. The symmetric S=O stretching vibration was forbidden in IR spectra of both complex variants as a result of an alternate selection rule. The band for the S=O antisymmetric mode experienced a slight (8 cm^{-1}) long-wavelength shift and had a simple structure in variant B because DMSO was coordinated through the S atom. The complexation in variant A caused a substantial (>160 cm^{-1}) long-wavelength shift of the band for the S=O antisymmetric mode. Furthermore, this vibration was mixed (probably due to Fermi resonance) with one of the CH_3 rocking vibrations. This led to actual splitting of the band into two components (922 and 920 cm^{-1}) of similar strengths (0.62:1.00). These results were confirmed by experimental spectra of the complex (940 and 918 cm^{-1} [6] and 951 and 941 cm^{-1} [7]).

Other noticeable differences between IR spectra of variant A and pure DMSO were due to complexation and were predicted by our calculation. The short-wavelength shift of bands for ρ CH_3 rocking vibrations (average ~60 cm^{-1} according to the calculation and ~40 cm^{-1} in the spectrum), the ν_{as} CS antisymmetric stretching vibration (47 cm^{-1} according to the calculation and 88 cm^{-1} in the spectrum), and the γ S=O out-of-plane bending vibration (70 cm^{-1} according to the calculation and 46 cm^{-1} in the spectrum) should be pointed out. All these bands were strong in the IR spectrum and could act as a reliable signature of complexation. Short-wavelength shifts of the ρ CH_3 rocking modes and (to a lesser extent) the ν_{as} CS stretching mode were also observed in the spectrum of variant B. It could be concluded from this that such spectral changes were typical of complexation in general regardless of the type of coordination (through the O or S atom). The band for the γ S=O vibration in the spectrum of variant B did not experience a short-wavelength shift. A broad weak band with a poorly resolved maximum near 630 cm^{-1} in the spectrum of the sample pressed in KBr [6] was most likely correlated with an electronic transition between the ground state and one of the excited sublevels of the U^{4+} $^3H_4$ ground state [23].

Splitting of the UCl antisymmetric stretching vibration into three components as a result of symmetry lowering of the UCl_4 group in the complex was accompanied by a long-wavelength frequency shift (292, 278, and 250 cm^{-1} in variant A; 313, 300, and 266 cm^{-1} in variant B). These data were confirmed by the long-wavelength spectrum of $UCl_4 \cdot 2DMSO$ (Fig. 3) that contained a strong band that could be represented as the sum of three envelopes with centers at 270, 256, and 235 cm^{-1}. According to the calculation, another 15 mixed bending vibrations with complicated
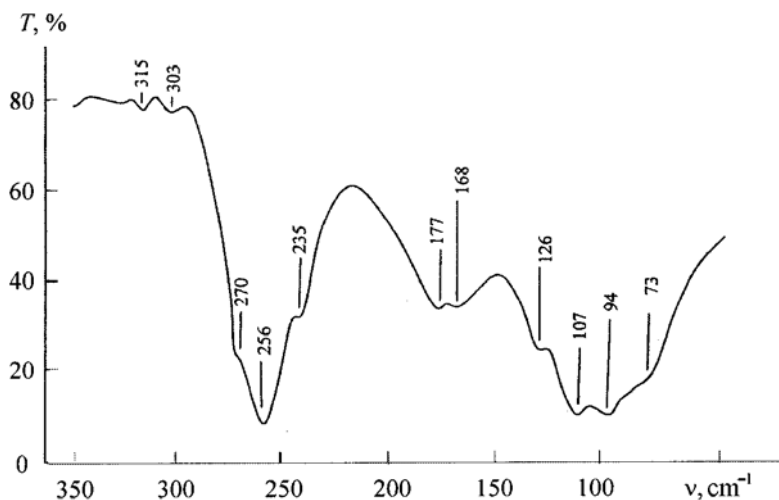
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Fig. 3. Long-wavelength IR absorption spectrum of UCl_4 + DMSO in a polymeric matrix [6].

shapes that were due to the ligands and UCl_4 were located at lower frequencies. The frequencies and intensities of these bands were of little information value and were not included in Table 2.

Conclusion. Quantum-chemical modeling of the structure of the $UCl_4 \cdot 2$DMSO complex predicted the existence of two stable configurations of C_i symmetry in which the electron-donating organic ligands were coordinated through O and S atoms. The first variant turned out to be more stable. The structure of the DMSO molecule remained practically unchanged upon coordination whereas the shape of the UCl_4 group was noticeably distorted. Formation of the first structural variant was accompanied by significant long-wavelength shifts and splitting of bands for the S=O and UCl stretching vibrations in addition to short-wavelength shifts of bands for methyl rocking vibrations, the antisymmetric CS stretching vibration, and the out-of-plane S=O bending vibration. The spectrum of the second variant underwent less noticeable changes in comparison with spectra of the isolated DMSO molecule and UCl_4. The short-wavelength shift of the S=O stretching vibration was not predicted by the calculation. Formation of the $UCl_4 \cdot 2$DMSO complex with coordination through the S atoms seemed improbable. Thus, the structure of the first variant could serve as a successful model structure for the coordination sphere of U^{4+}. The characteristics of the IR vibrational spectrum that were calculated on the basis of this variant reproduced adequately in general the experimental data.

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