Infrared Spectroscopic Studies on the Actinide Complexes.
I. Assignment of Fundamental Vibrations, by Normal Coordinate Analysis, of Oxydiacetatodioxouranium(VI)

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The vibrational spectrum of oxydiacetatodioxo-uranium(VI) is reported. The fundamentals of UO_2-(oda) (oda = $^-OOCH_2COCH_2COO^-$) are assigned on the basis of a normal coordinate analysis, with the potential energy distribution (P.E.D.), by a twenty seven parameters Urey–Bradley force field. The calculated frequencies are in good agreement with those observed, with a mean deviation less of 0.5 %.

Introduction

The ability of the UO_2^{2+} ion to react with polyfunctional ligands containing carboxylic groups, to give complex species of various kinds, has been established by several authors [1]. However, reliable information from a spectroscopic point of view on the assignment of the frequencies and on the values of the force constants is not yet available.

We report here a normal coordinate analysis carried out on the $[UO_2(oda)]_n$ compound, in order to assign the normal frequencies with the potential energy distribution, using a simple Urey–Bradley force field [2, 3].

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The preparation of this compound, a first approximate assignment of more characteristic frequencies, [4] and the X-ray crystal structure, have been previously reported [5, 6].

Experimental

The infrared spectrum in the 4000–300 cm^{-1} region was recorded in KBr pellets on a Perkin–Elmer 621 spectrophotometer [4] and in the far infrared region using nujol mulls in polythene discs on a Beckman IR 11 spectrophotometer. The spectra are reported in Fig. 1.

The Raman spectrum of the powder was recorded on a Jarrell–Ash 25-300 spectrometer with a Spectra Physics Model 125 A He–Ne laser as exciting source.

Isotopic substitution carried out with D_2O (99.75%) on both complex and anhydrous ligand, monitored by ^1H N.M.R. (Varian T60), does not exceed 10% of yield.

Normal Coordinate Analysis

The X-ray crystal analysis of $[UO_2(oda)]_n$ has shown that the crystals belong to the tetragonal space group $P_{4_12_12}$, $Z = 4$, $a = 8.148$, $c = 11.051$ Å [6]. A unit cell contains four formula units and belongs to
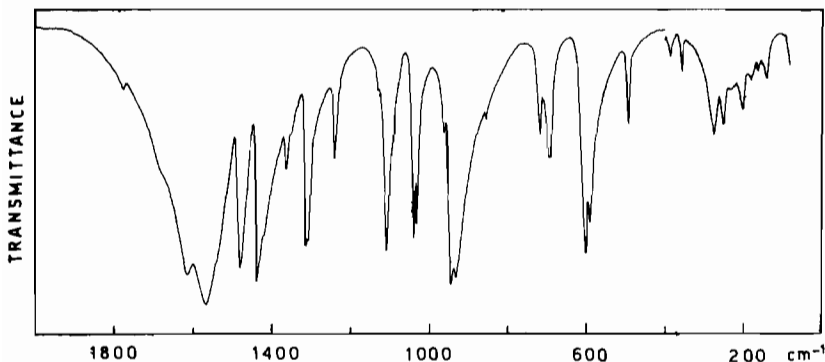

Figure 1. Infrared spectrum of $[UO_2(oda)]_n$ in the 2000–100 cm^{-1} region.

the factor group D_4. The positional symmetry of the structural group is nearly C_{2v}, all atoms being coplanar within the standard deviation.

The calculations were performed, using our computer program UBATOR, by considering only the molecular entities, neglecting intermolecular effects. Calculations of the coupling and of the force constants that describe the movement of the unit molecule in relation to one another, would necessitate a four units molecule or unit cell analysis, but this problem is beyond the scope of this paper. The analysis for the U(oda) entity was carried out for the in plane internal coordinates, but for methylene groups also for the out-of-plane ones. Forty-one modes of vibrations result, which can be described by the representation: $19A_1 + 3A_2 + 3B_1 + 16B_2$.

All the vibrations are Raman active and all but the vibrations of species A_2 infrared active (the Raman spectrum does not allow an assignment of the fundamentals, but only of the symmetric stretching of the UO_2 group).

The G and F matrices were constructed using 41 internal coordinates, chosen as the changes in bond length and bond angles. The G matrix elements of U(oda) were evaluated using the molecular dimensions reported in Ref. 6. The geometry of the molecular unit used is shown in Fig. 1. The F matrix was obtained using a Urey–Bradley potential function. Initial constants are estimated from similar systems. A preliminary assignment was made, then we solved Wilson's secular equation [7], diagonalising the G and F matrices by Jacobi's method [8, 9] and the UBFF was refined from initial set by carrying out a least squares fit of the calculated to the observed frequencies.

The secular equation involves $12(7A_1 + 5B_2)$ redundant coordinates each of which gives zero frequency in the solution. The initial thirty-one parameters were reduced to twenty-seven putting (see Table I): $H_1 = H_2$, $H_3 = H_4$, $F_1 = F_2$ and $F_3 = F_4$, all

these values being very close to zero and always very similar throughout the calculations.

The best set of force constants obtained after several trials of computation is given in Table I. The observed and calculated frequencies with the potential energy distribution [10] are given in Table II. The agreement is quite satisfactory in view of the complexity of the molecule, the mean deviation being less of 0.5%.

Results and Discussion

Five of the observed frequencies for our system can be attributed to superimposed or overlapping components of both A_1 and B_2 vibrational species. In fact, as one can see from Table II, there is a negligible splitting between all but a few of the corresponding A_1 and B_2 modes. The likely explanation for this is that the observed frequencies arise, to a first approximation, from internal motions of the isolated groups with negligible contribution from inter-group coupling. Alternatively, splitting may be more pronounced when the amplitude of vibration and hence the component of the potential energy for the linkage atoms is significant compared to the motions of the ring atoms. As a result, for U(oda) we expect similar molecular vibrations for corresponding A_1 and B_2 modes which occur above the 1300 cm^{-1} region of the spectrum, since in this region the predominant modes are those due to CH_2 and COO stretchings.

The vibrational modes of these groups should involve little or no interaction between neighboring groups. Thus, it is reasonable to consider the observed spectral bands in this region as arising from single group. However, at lower frequencies, modes involving U–O, C–C, C–O–C stretching and COO, COC and CH_2 angle bendings become more predominant, and some of these vibrations contain appreciable inter-group coupling and pronounced splitting effect.

TABLE I. Final Urey–Bradley Force Constants in 10^2 Nm^{-1}.

Stretching	Bending		Repulsive	
$K_1(U–O_1)$ = 1.50	$H_1(U–O_1–C_1)$	= 0.05	$F_1(U\cdots C_1)$	= 0.04
$K_2(U–O_3)$ = 1.10	$H_2(U–O_3–C_2)$		$F_2(U\cdots C_2)$	
$K_3(C_1–O_1)$ = 8.80	$H_3(O_1–U–O_1)$	= 0.05	$F_3(O_1\cdots O_1)$	= 0.06
$K_4(C_1–O_2)$ = 9.30	$H_4(O_1–U–O_3)$		$F_4(O_1\cdots O_3)$	
$K_5(C_1–C_2)$ = 2.50	$H_5(O_1–C_1–C_2)$ = 0.28		$F_5(O_1\cdots C_2)$ = 0.43	
$K_6(C_2–O_3)$ = 4.40	$H_6(O_1–C_1–O_2)$ = 0.27		$F_6(O_1\cdots O_2)$ = 2.32	
$K_7(C_2–H)$ = 4.00	$H_7(O_2–C_1–C_2)$ = 0.40		$F_7(O_2\cdots C_2)$ = 0.65	
	$H_8(C_1–C_2–O_3)$ = 0.63		$F_8(C_1\cdots O_3)$ = 0.19	
	$H_9(C_1–C_2–H)$ = 0.26		$F_9(C_1\cdots H)$ = 0.38	
	$H_{10}(H–C_2–H)$ = 0.43		$F_{10}(H\cdots H)$ = 0.12	
	$H_{11}(H–C_2–O_3)$ = 0.19		$F_{11}(H\cdots O_3)$ = 0.79	
	$H_{12}(C_2–O_3–C_2)$ = 0.27		$F_{12}(C_2\cdots C_2)$ = 0.65	

TABLE II. Calculated (ν_{cal}, cm^{-1}) and Observed (ν_{obs}, cm^{-1}) Frequencies and Potential Energy Distribution (PED) in Percentage.[a]

Species	No.	ν_{cal}	ν_{obs}	Description (PED) %
A_1	ν_1	2925	2926	$\nu_s CH_2(100)$
	ν_2	1565	1565	$\nu_{as}COO(87)$
	ν_3	1481	1481	$\delta CH_2(85)$, $\nu_s COO(11)$
	ν_4	1440	1440	$\nu_s COO(66)$, $\delta CH_2(23)$
	ν_5	1315	1306	$\omega CH_2(59)$, $\nu_s COO(11)$
	ν_6	1103	1109	$\nu_s COC(50)$, $\omega CH_2(29)$
	ν_7	983	–	$\nu CC(62)$
	ν_8	716	718	$\delta COO(58)$, $\delta ring(22)$
	ν_9	487	494	$\delta ring(39)$, $\delta COO(25)$, $\nu U-O_3(16)$
	ν_{10}	371	385	$\nu U-O_1(26)$, $\delta ring(24)$, $\nu CC(18)$, $\nu COC(17)$
	ν_{11}	284	274	$\nu U-O_1(32)$, $\nu U-O_3(31)$, $\delta ring(21)$
	ν_{12}	174	180	$\delta ring(48)$, $\nu U-O_3(27)$, $\nu U-O_1(17)$
A_2	ν_{13}	2871	–	$\nu_{as}CH_2(100)$
	ν_{14}	1229	–	$t CH_2(97)$
	ν_{15}	830	–	$\rho CH_2(86)$
B_1	ν_{16}	2874	2871	$\nu_{as}CH_2(100)$
	ν_{17}	1252	1240	$t CH_2(96)$
	ν_{18}	857	850	$\rho CH_2(86)$
B_2	ν_{19}	2927	2926	$\nu_s CH_2(100)$
	ν_{20}	1563	1565	$\nu_{as}COO(89)$
	ν_{21}	1482	1481	$\delta CH_2(87)$, $\nu_s COO(9)$
	ν_{22}	1436	1440	$\nu_s COO(71)$, $\delta CH_2(17)$
	ν_{23}	1288	1306	$\omega CH_2(62)$, $\nu_{as}COC(16)$, $\nu_s COO(11)$
	ν_{24}	1035	1034	$\nu_{as}COC(64)$, $\omega CH_2(27)$
	ν_{25}	907	–	$\nu CC(57)$
	ν_{26}	695	691	$\delta COO(45)$, $\delta ring(37)$
	ν_{27}	587	588	$\delta COO(37)$, $\delta ring(28)$
	ν_{28}	348	354	$\nu U-O_1(35)$, $\delta ring(34)$, $\delta COO(24)$
	ν_{29}	234	233	$\nu U-O_1(48)$, $\delta ring(40)$

[a] The rounded percentage potential energy distribution values are shown in parentheses; small values have been neglected. Abbreviations: ν = stretching, δ = deformation, ω = wagging, ρ = rocking, t = twisting; and, as subscripts, s = symmetric, as = antisymmetric.
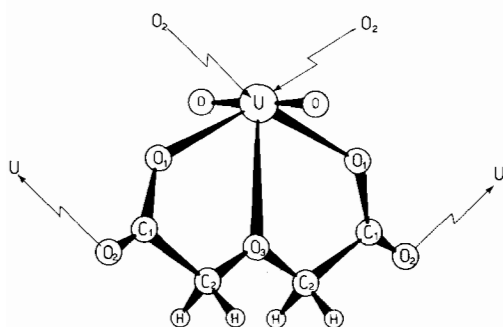
Figure 2. Molecular model of the repeating unit UO₂(oda).

We can now give a rather quantitative account of the changes observed in the infrared spectrum of $[UO_2(oda)]_n$ in respect to that of the free ligand reported in Fig. 1 of Ref. 4.

Seven fundamentals: ν_1, ν_5, ν_{16}, ν_{17}, ν_{18}, ν_{19}, ν_{23}, have been assigned to bands characterized by being found at almost identical position in the two compounds. According to the potential energy distribution, these bands are due to *internal* vibrations of methylene groups. The fundamentals $\nu_3(A_1)$ and ν_{21}-(B_2) are assigned to the in-phase and out-of-phase scissoring deformations of CH_2 respectively. This band falls at 1481 cm^{-1} and is not present in the spectrum of the disodium salt of the ligand. Its assignment was rather uncertain in the previous approximate assignment, because the frequency appeared to be higher than expected for a CH_2 group (*ca.* 1440 cm^{-1}), even if adjacent to a carbonyl group (*ca.* 1470 cm^{-1}); therefore one supposed that "it could be caused by coupling between the two C–O bonds involved in formation of the two five-membered rings" [4]. Our calculations show that this band must be assigned to the CH_2 deformation with small contribution from the symmetric COO stretching mode. The shift towards higher frequencies than expected can be explained with an increase of the electron

withdrawing ability for the carboxylic groups, adjacent to a CH$_2$ one, owing to the strong bonds formed between the carboxylic groups and the uranium atom.

These bonds are stronger than in the analogous Th(oda)$_2$ complex [11], for which the same band falls at 1465 cm^{-1} with a weaker intensity. It is more difficult to explain the absence of this band in the spectrum of the free ligand. In a empirical context, we think that this absorption band is superposed in the free ligand by the COO symmetric stretching band with a strong coupling between them, which decrease for Th(oda)$_2$ (16% from our preliminary calculations [12]) and even more for UO$_2$(oda) (11%). The increase of intensity of this band on going from a strong coupling to a weak one, can be explained by taking into account the relative dipole moment gradients of the COO symmetric stretching and of the CH$_2$ scissoring modes which have an opposite sign, thereby suggesting, on the basis of our calculations, that higher intensity corresponds to weaker coupling.

In the disodium salt of the ligand the asymmetric and symmetric stretching frequencies of the carboxylic groups occur at 1600 and 1418 cm^{-1} respectively, while in the uranyl complex these bands fall at 1565 and 1440 cm^{-1} with variation on the relative intensities.

These bands present a very small coupling contribution from the other vibrations, therefore the separation between the two stretching frequencies, 125 cm^{-1} *versus* 182 cm^{-1} in the free ligand, is consistent with bidentate behaviour of the carboxylate groups [4, 11].

The symmetric and asymmetric stretching frequencies of the etheric group, ν_6 and ν_{24} are shifted towards lower wavenumbers, 30 and 20 cm^{-1} respectively, in comparison with the anionic ligand, confirming the coordination of the etheric oxygen to the uranium atom. The relatively small shift of these bands is justified by the rather strong contribution of wagging mode of CH$_2$ groups.

The assignment of the frequencies in the low spectrum region is less valuable and it is not possible to disregard lattice vibrations coupling. The doublet at 718 and 691 cm^{-1} can be due to the in plane COO bending and ring deformation modes. The sharp medium bands in the 500–350 cm^{-1} region are assigned to a strong coupling of the rings with the U–O$_3$ (494 cm^{-1}) and U–O$_1$ (385 and 354 cm^{-1}) stretching vibrations. Also the bands at 274, 233 and 180 cm^{-1}, found in the far infrared region, have the same kind of contribution; the dominant contribution of U–O$_1$ stretching in the two higher frequencies well agrees with the small but significant difference in the stretching force constants K_1 = 1.5 and K_2 = 1.1 × 10^2 Nm^{-1}, and it is consistent also with the bond lengths of U–O$_1$ (2.37 Å) and U–O$_3$ (2.55 Å). These force constants are greater than for the corre-

sponding Co(glycolato)$_2$ [13], since the ring stabilization is thermodynamically increased and more tightly bonded chelate rings are formed, the uranyl ion being harder than the cobalt ion.

The other force constant values are consistent with those expected from simple structural and chemical considerations.

The K_5 and K_7 values are similar to those found for the glycolate system, while the other constants are increased as expected.

The higher value for K_4 in respect to K_3, the C$_1$–O$_2$ bond having more double bond character, agrees with the polymeric structure of this complex.

The analysis of the UO$_2$ entity was carried out separately. It was shown that the error, arising in neglecting the interactions with the internal coordinates involving the ligand group, is expected to be quite small [14, 15]. The uranyl ion has three vibrational frequencies in $D_{\infty h}$ point group symmetry. The asymmetric stretching (IR active) is observed in the infrared spectrum as a strong band at 944 cm^{-1} with the characteristic feature; the symmetric stretching (Raman active) is observed in the Raman spectrum as a strong band at 860 cm^{-1} and in the infrared spectrum at 856 cm^{-1} with very little intensity, the combination band for these absorptions is also observed at 1785 cm^{-1}. The bending frequency (IR active), is more difficult to determine, owing to the presence of other bands in this region. We assign this mode to the frequency at 248 cm^{-1} which appears in the far IR region as a medium band [16].

The VFF force constants resulting on the assumption of a single triatomic model of the uranyl group are: K_{U-O} = 7.18, $F_{UO,UO'}$ = –0.22 and H_δ = 0.82 × 10^2 Nm^{-1}, where K_{U-O} is the force constant of the U–O bond, $K_{UO,UO'}$ gives the interaction of the two UO bonds and H_δ corresponds to the change of angle between the UO bonds.

We have found a quite satisfactory correlation, from Badger's relationship [14, 17, 18], between the U–O bond distance and force constants.

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