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Absorption Spectra of Tetrahalodioxouranium(VI) Complexes at 4.2 °K. I. Di(tetramethylammonium)uranyltetrachloride

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Single crystal spectra of $(Me_4N)_2UO_2Cl_4$ have been recorded at 4.2 °K, using polarized radiation. The analysis of the electronic absorption bands shows several progressions in the region 20,000–28,000 cm^{-1}, some of them strongly polarized. The most intense bands clearly show progressions $(R + n\nu_1)$, where ν_1 assumes the mean value of 700 cm^{-1} and therefore it has been taken as the symmetric stretching wavenumber of the uranyl group in the excited states.

Introduction

The coordination chemistry of the uranyl group has been investigated in details from the point of view of both chemical and physical properties [1, 2].

As far as electronic spectra are concerned, it has been recognized that all these spectra are quite similar, showing a band envelope centered around 24,000 cm^{-1}. This allows one to consider the spectral behaviour of the uranyl complexes as being mainly due to electronic transitions located in the uranyl moiety, whose intensity and energy are influenced to a small extent by the coordinated ligands.

Recently, the analyses of electronic spectra of uranyl compounds have received a great deal of attention, from both theoretical and experimental points of view [3–16]. In spite of this the analyses are for the most part different in their conclusions.

All these attempts reveal that the spectroscopy uranyl complexes is still actual, being far from a complete solution. Particularly, the very low temperature spectra with polarized light of single crystals, whose structures have been previously determined, are needed.

In an effort to shed light upon this question, we have undertaken an investigation at 4.2 °K of compounds having the general formula $(R_4N)_2UO_2X_4$, where R = alkyl group and X = Cl or Br.

The crystal structures of these compounds have been already published by us [17]. In the present paper the spectra of single crystals of $(Me_4N)_2UO_2Cl_4$ are reported.

Experimental

Uranium trioxide was treated with aqueous HCl in slight excess over the stoichiometric amount. A Me_4NCl solution was then added until the mole ratio Me_4NCl/UO_2Cl_2 reached the value of 2. The resulting solution was concentrated by slow evaporation at room temperature and separated yellow–green crystals which were allowed to grow up to several millimeters in dimensions in the most favourable case.

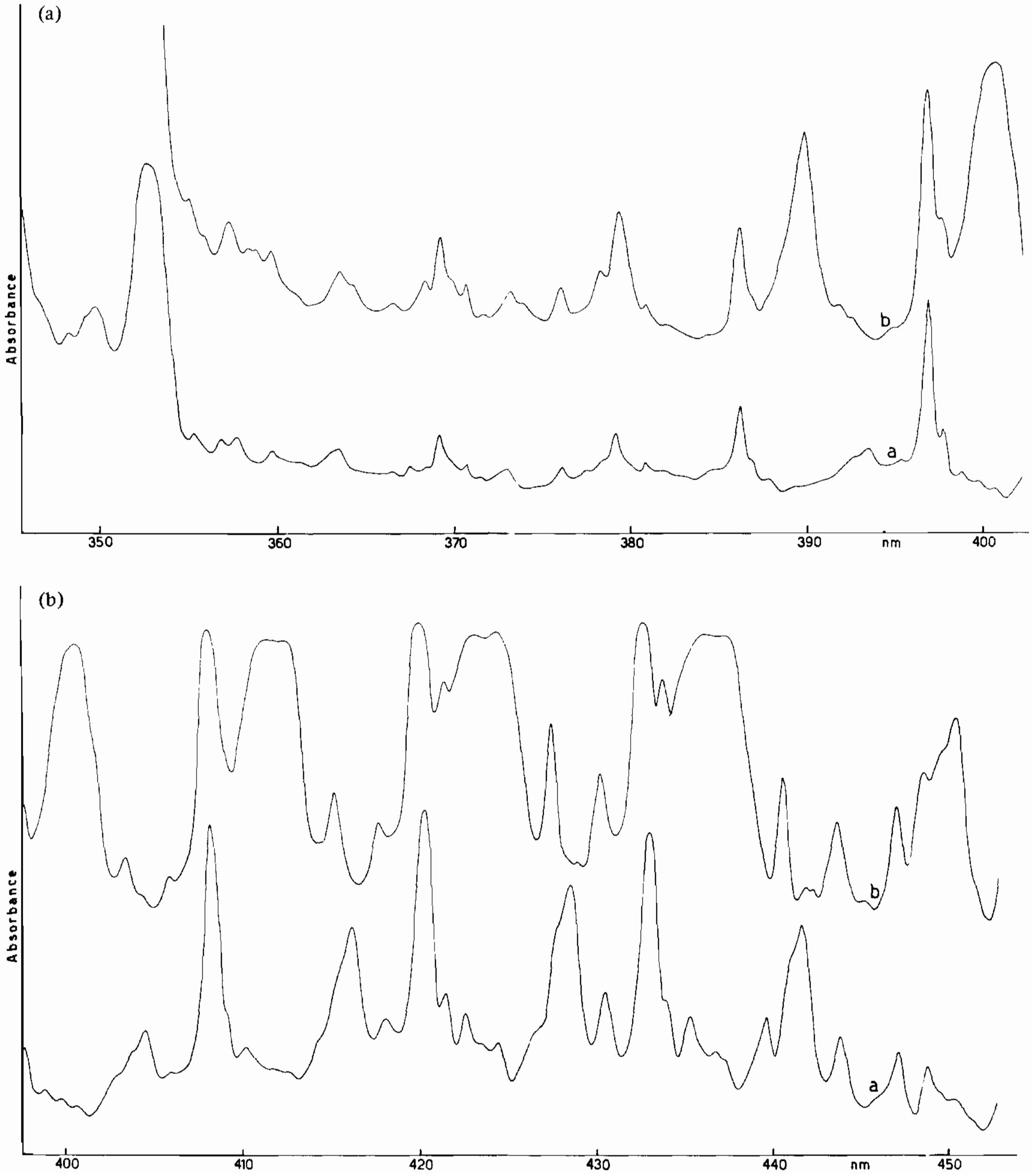
The crystal and molecular structure of the prepared compound, $(Me_4N)_2UO_2Cl_4$, was determined by X-ray diffraction techniques. There are two molecules in the unit cell of $P4_2/mnm$ space group with flattened $[UO_2Cl_4]^{2-}$ bipyramids having a local D_{4h} symmetry. The fourfold axes of the anions run along the uranyl group and perpendicularly to (001) so that they do not correspond to the fourfold crystallographic axes [17].

Single crystal spectra were measured using a Cary 14 spectrophotometer equipped with a conventional Oxford Instrument CF 100 continous flow helium cryostat. The incident radiation was polarized by a calcite Glan prism and the spectra were recorded with the electric vector polarized along or perpendicularly to the *c* axes. The orientation of the crystal axes was previously checked by taking Weissemberg photographs.

Results and Discussion

The polarized electronic spectra of single crystals at 4.2 °K are reported in the Figure while the corresponding band maxima are reported in the Table.

The low energy region of the spectra is characterized by low intense bands whose intervals have been attributed to the uranyl bending (ν_2) wavenumber and to crystal lattice vibrations (1). On assuming the band at 19,995 and 19,979 cm^{-1} in the two polarization directions as I_1 origin, the separations of 259 and 53–55 cm^{-1} can be related to these vibrations respectively. With such numbers many bands in this region can be easily fitted. Noteworthy, a very sharp and intense band appears at 20,654 and 20,661 cm^{-1} in the two polarizations respectively. Such band has been taken as I_2 origin and gives a very long progression of 9 sharp peaks whose separations is *ca.* 700 cm^{-1}. The first differences with the bands at 21,358 and 21,361 cm^{-1} respectively, namely 704 and 700 cm^{-1}, have been taken as the stretching of the uranyl group in the excited state (ν_1). A very intense band at 20,805 cm^{-1} is present only in the $\perp c$ polarization, and gives a long progression of the ν_1 vibrational frequency. Therefore, it has been assigned as I_3 origin.



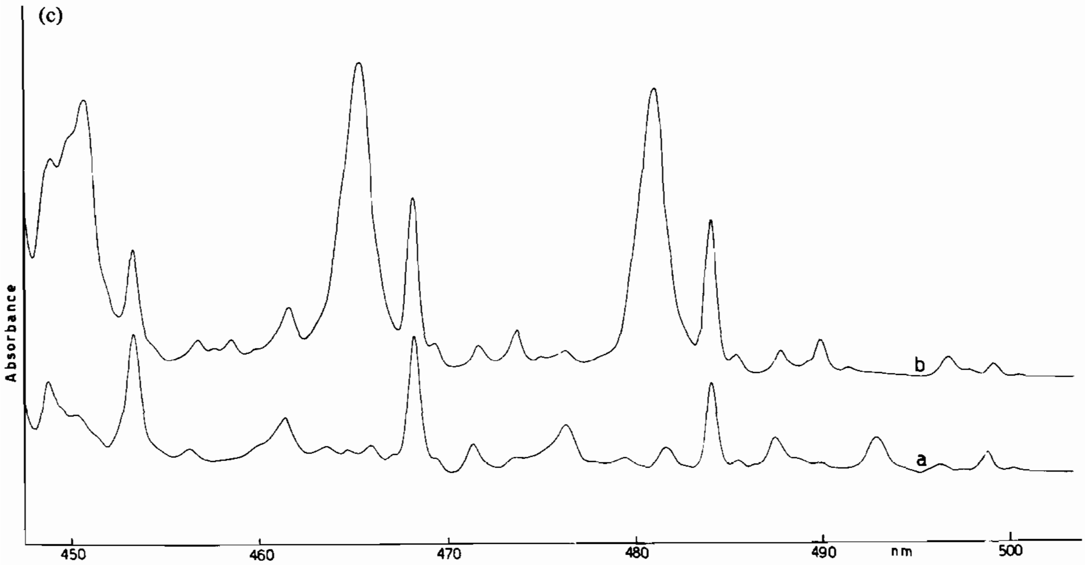


Figure 1. Absorption spectra of $(Me_4N)_2UO_2Cl_4$ with radiation polarized parallel (a) (//) or perpendicularly (b) (⊥) to the *c* crystallographic axes.

TABLE. Absorption Bands of $(Me_4N)_2UO_2Cl_4$ at 4.2 °K.

Wavenumber, cm^{-1}		
//*c*	⊥*c*	
19,995	*19,979*	I_1
20,048	20,034	$I_1 + l$
20,100	20,091	$I_1 + 2l$
20,158	20,133	$I_1 + 3l$
20,254		$I_1 + \nu_2$
20,293		$I_1 + l + \nu_2$
	20,355	$I_1 + 2l + \nu_2$
20,410	20,413	$I_1 + 3l + \nu_2$
20,465	20,454	$I_1 + 4l + \nu_2$
20,515	20,503	$I_1 + 2\nu_2$
20,565		$I_1 + l + 2\nu_2$
20,598	20,603	$I_1 + 2l + 2\nu_2$
20,654	*20,661*	I_2
20,715	20,735	$I_1 + 4l + 2\nu_2$
20,761		$I_1 + 3\nu_2$
	20,805	I_3
20,853		$I_1 + 2l + 3\nu_2$
20,928	20,921	$I_1 + \nu_2 + \nu_1$
20,996	20,998	$I_1 + l + \nu_1 + \nu_2$
	21,055	$I_1 + 2l + \nu_1 + \nu_2$
21,114	21,113	$I_1 + 3l + \nu_1 + \nu_2$
21,216	21,202	$I_1 + 2\nu_2 + \nu_1$
21,307	21,308	$I_1 + 2l + 2\nu_2 + \nu_1$
21,358	21,361	$I_2 + \nu_1$
21,405		$I_1 + 4l + 2\nu_2 + \nu_1$
21,459	21,450	$I_1 + 3\nu_2 + \nu_1$
	21,490	$I_3 + \nu_1$
21,520		$I_1 + l + 3\nu_2 + \nu_1$
21,568	21,570	$I_1 + 2l + 3\nu_2 + \nu_1$
21,673	*21,665*	I_4
21,730	21,754	$I_1 + 2l + \nu_2 + 2\nu_1$

TABLE. (Cont.)

//*c*	⊥*c*	
	21,810	$I_1 + 3l + \nu_2 + 2\nu_1$
	21,855	$I_1 + 4l + \nu_2 + 2\nu_1$
21,887	21,895	$I_1 + 2\nu_2 + 2\nu_1$
	21,997	$I_1 + 2l + 2\nu_2 + 2\nu_1$
22,053	22,059	$I_2 + 2\nu_1$
22,157	22,140	$I_1 + 3\nu_2 + 2\nu_1$
	22,189	$I_3 + 2\nu_1$
22,205		$I_1 + l + 3\nu_2 + 2\nu_1$
22,236	*22,230*	I_5
22,280	22,279	$I_5 + l$
22,361	22,356	$I_4 + \nu_1$
	22,446	$I_3 + \nu_2 + 2\nu_1$
22,530	22,527	$I_5 + l + \nu_2$
22,644	*22,632*	I_6
22,668	22,683	$I_6 + l$
22,748		$I_2 + 3\nu_1$
22,874	22,871	$I_3 + 3\nu_1$
22,893	22,939	$I_5 + \nu_1$
22,971	22,980	$I_5 + l + \nu_1$
23,044	23,052	$I_4 + 2\nu_1$
23,093	*23,111*	I_7
23,222	23,239	$I_5 + l + \nu_2 + \nu_1$
23,337		$I_6 + \nu_1$
23,372	23,388	$I_6 + l + \nu_1$
23,438		$I_2 + 4\nu_1$
23,554	23,560	$I_3 + 4\nu_1$
23,609	23,642	$I_5 + 2\nu_1$
23,661		$I_5 + l + 2\nu_1$
23,722	23,724	$I_4 + 3\nu_1$
23,803	23,805	$I_7 + \nu_1$
23,916	23,933	$I_5 + l + \nu_2 + 2\nu_1$
24,026		$I_6 + 2\nu_1$

TABLE. (Cont.)

//c	⊥*c*	
24,075	24,085	$I_6 + 1 + 2\nu_1$
24,130		$I_2 + 5\nu_1$
24,236	24,250	$I_3 + 5\nu_1$
24,290	24,321	$I_5 + 3\nu_1$
24,374	24,371	$I_5 + 1 + 3\nu_1$
24,499	24,504	$I_7 + 2\nu_1$
24,632	24,631	$I_5 + 1 + \nu_2 + 2\nu_1$
24,716	24,728	$I_6 + 3\nu_1$
24,762	24,780	$I_6 + 1 + 3\nu_1$
24,814		$I_2 + 6\nu_1$
24,954	24,968	$I_3 + 6\nu_1$
25,012	25,030	$I_5 + 4\nu_1$
25,070		$I_5 + 1 + 4\nu_1$
25,143	25,157	$I_7 + 1 + 3\nu_1$
25,198	25,205	$I_7 + 3\nu_1$
25,298	25,329	$I_5 + 1 + \nu_2 + 4\nu_1$
25,408		$I_6 + 4\nu_2$
25,464	25,482	$I_6 + 1 + 4\nu_1$
	25,524	$I_2 + 7\nu_1$
25,689	25,656	$I_3 + 7\nu_1$
25,774	25,779	$I_5 + 1 + 5\nu_1$
25,861	25,858	$I_7 - 1 + 4\nu_1$
25,891	25,901	$I_7 + 4\nu_1$
25,995	26,010	$I_5 + 1 + \nu_2 + 5\nu_1$
26,189	26,177	$I_6 + 1 + 5\nu_1$
26,257	26,254	$I_2 + 8\nu_1$
26,330		I_8
26,372	26,365	$I_3 + 8\nu_1$; $I_8 + 1$
26,427	26,437	$I_3 + 1 + 8\nu_1$
26,493		
26,582	26,594	$I_7 + 5\nu_1$
	26,747	
26,803	26,796	
26,909	26,908	
26,982	26,976	
27,048	27.040	$I_8 + \nu_1$
27,086	27,091	$I_3 + 9\nu_1$; $I_8 + 1 + \nu_1$
27,142	27,148	$I_3 + 1 + 9\nu_1$
27,212		
27,284	27,278	$I_7 + 6\nu_1$
	27,458	
27,508	27,508	
27,544		
27,676		
	27,722	$I_8 + 2\nu_1$
27,800	27,800	$I_3 + 10\nu_1$; $I_8 + 1 + 2\nu_1$
	27,864	$I_3 + 1 + 10\nu_1$
	27,898	
27,954		
	27,989	
28,023		
	28,109	
28,149	28,168	
28,349		I_9
28,587		
28,626		
28,714		
28,873		

The middle region of the spectra shows a more complicated pattern due to the overlapping of the previous progressions with some new origins. These origins have been assigned to the 21,673 (‖) and 21,665 (⊥) cm^{-1} bands as I_4, to the 22,236 (‖) and 22,230 (⊥) as I_5, to the 22,644 (‖) and 22,632 (⊥) cm^{-1} as I_6 and to the 23,093 (‖) and 23,111 (⊥) cm^{-1} as I_7. In this region some progressions are also strongly polarized. The low intensity and high energy region is indeed very difficult to assign. Nevertheless, a progression with the 26,330 cm^{-1} band as I_8 origin has been observed only in the parallel spectrum. A high intensity band has been also detected at 28,349 cm^{-1} in the ‖ *c* spectrum and must be considered as a new I_9 origin.

Such an analysis of the spectra, mainly based on the intensity distribution all along the progressions, shows eight band origins in the 19,500–28,000 cm^{-1} range. If all these origins have to be correlated to different electronic excited states, all the available models of uranyl group energy levels seem inadequate.

It is interesting to note that some of the present origins, *i.e.* those in the 20,600, 22,600 and 26,300 cm^{-1} regions, bear a close resemblance with a UO_2^{2+} spectrum calculated by De Jaegere and Gorller-Walrand [8] and with De Jaegere and Vanquickenborne [9] assignment for $D_{4h}(4)$ complexes. On the other hand, as far as Brint and McCaffery [12] model is concerned, no origin has been found in the 24,000 cm^{-1} zone while other origins are in good agreement.

In conclusion, this first paper, dealing with the electronic spectrum of $(Me_4N)_2UO_2Cl_4$, presents many band maxima grouped into several progressions arising from the lattice or from the ν_1 and ν_2 vibrational modes of uranyl group. No evidence has been found for the excitation of the asymmetric stretching mode (ν_3) of UO_2^{2+}, which is expected at a frequency greater than 700 cm^{-1}.

The assignment of the 259 cm^{-1} wavenumber to the uranyl bending mode in the excited states may be questioned, being at the same wavenumber as in the ground state [18, 19]; perhaps, it may be connected with U–Cl vibrations. A comparison with the spectra of the isomorphous complex $(Me_4N)_2UO_2Br_4$ [17], which are being scanned, will resolve this problem.

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