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Abstract

Full Text

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STUDY OF THE IR SPECTRA OF INNER-COMPLEX COMPOUNDS OF URANYL WITH SCHIFF BASES AND DETERMINATION OF THE U=O BOND LENGTH

(Presented by Academician V. I. Spitsyn on 7 IV 1962)

The bands of the symmetric ν_1 and asymmetric valence vibrations ν_3 of the U=O bond in uranyl compounds lie in the ranges 830–880 cm^{-1} and 900–940 cm^{-1} , respectively. If the ν_1 band depends only slightly on the strength of the bond of the uranyl grouping with the ligands, then ν_3 is rather sensitive to changes of this kind. The force constant of the U–O bond is related in a definite way to the shift of the band of asymmetric valence vibrations, which in turn is determined by the strength of the uranium–ligand bond. Thus, for example, in the region of 1000 cm^{-1} , a shift of the ν_3 band of about 20 cm^{-1} corresponds to a change in the force constant by approximately 0.2 $\text{mdyn}/\text{\AA}$ and in the U=O bond length by 0.01 \AA . The IR spectra of inner-complex uranyl compounds with β -diketones (acetylacetone, benzoylacetone, and dibenzoylmethane) have been studied in works ^(1,2,10,11). The influence on the position of the ν_3 band of UO_2^{2+} in these inner-complex compounds by secondary ligands (water, pyridine, ammonia) was also studied.

In the present work we investigated the IR spectra (paste in Vaseline oil) in the region 700–1000 cm^{-1} of solid inner-complex uranyl compounds with various azomethine derivatives. The influence on the shift of the ν_3 band of such secondary ligands as water, methyl, ethyl, and butyl alcohols was investigated.

In all the complexes studied by us, an intense absorption band was found in the region 900–930 cm^{-1} , assigned to the asymmetric valence vibrations ν_3 of the uranyl grouping, and a less intense ν_1 band in the region 872–886 cm^{-1} .

The force constant $K_{\text{U-O}}$ of the uranium–uranyl oxygen bond was calculated by the formula

$$K_{\text{U-O}} = 0.029447 m_0 \left(\nu_1^2 + \frac{m_{\text{U}}}{m_{\text{O}} + m_{\text{U}}} \nu_3^2 \right),$$

where ν_1 and ν_3 are the wave numbers (cm^{-1}), and m_{O} and m_{U} are the masses of oxygen and uranium in atomic units.

To calculate the U–O bond length, the well-known Badger equation was used⁽⁵⁾

$$R_{ij} = \beta K_{ij}^{-1/3} + d,$$

which, in the case of uranyl compounds, takes the following form⁽⁴⁾:

$$R_{\text{U-O}} = 1.08 K_{\text{U-O}}^{-1/3} + 1.17,$$

where $R_{\text{U-O}}$ is the U–O bond length (Å), and $K_{\text{U-O}}$ is the force constant in mdyn/Å.

Table 1 gives the vibrational frequencies of the uranyl grouping, the force constants, and the U–O bond lengths.

The ν_3 band lies in the interval 901–930 cm^{-1} , which indicates approximately identical values of the force constants and U–O bond lengths.

The position of the ν_3 band for uranyl inner-complex compounds with one and the same Schiff base depends to some extent on the number and nature of the secondary ligands. Thus, for example, ν_3 and ν_1 of the uranyl complex with salicylal-*o*-oxyaniline, containing an alcohol molecule (ethanol and *n*-butanol), lie at 930 cm^{-1} and 872 cm^{-1} , respectively, whereas when they are replaced by four molecules of water (I), the frequency ν_3 is 905 cm^{-1} at an unchanged value of ν_1 . The water molecules are apparently bound to the uranyl ion or, in any case, change the character of the crystal field, which leads to a decrease in the force constant, i.e., to a certain increase in the length of the U–O bond.

In compound II, ν_1 and ν_3 are equal to 884 and 924 cm^{-1} . This may also be explained by a change in the ligand field as a result of the transformation of crystalline I into X-ray-amorphous II upon drying. In V, obtained by drying crystalline VI, which contains a methanol molecule, an increase in the frequency ν_1 is also observed. If ν_1 for the latter is 872 cm^{-1} , then for the inner-complex compound dried at 160°, it increases to 886 cm^{-1} . At the same time ν_3 remains practically unchanged. The force constant of the U–O bond in VIII is 7.15 mdyn/Å, which indicates approximately the same strength as in V and VI.

The strongest bond of the Schiff base with uranyl is formed in the case of VII. This is confirmed by the position of the $\nu_3 = 901 \text{ cm}^{-1}$ band and is explained by the fact that 2-(6-bromo-2-oxy-1-naphthalamino)-pyridine, like salicylal-*o*-oxyanilate, is a tridentate ligand. It is quite understandable that in VIII the length of the U–O bond ($R_{\text{U-O}} = 1.73 \text{ Å}$) proves to be the greatest among all the uranyl inner-complex compounds we investigated, and the bond order of U–O the smallest. According to Zachariassen⁽⁶⁾, the length of a single U–O bond is 2.12 Å, of a double bond 1.92 Å, and of a triple bond 1.84 Å.

The U–O bond lengths calculated by us compel the assumption that the order of this bond must be greater than two.

Using Gordy' s formula (⁷),

$$K_{ij} = aN [(x_i x_j)/R_{ij}]^{3/4} + b,$$

which relates the force constant, length, and bond order to the electronegativities (x_i and x_j) of the bonded atoms, we calculated the bond order of U–O in these compounds (see Table 1). It turns out that the bond order

Table 1

Force constants, bond order, and lengths of the U–O bond

No. of compound	Compound	ν_1, cm^{-1}	ν_3, cm^{-1}	Force constant K , mdyn/Å	U–O bond length, Å	U–O bond order
I	Tetrahydrate of uranyl salicylal- <i>o</i> -oxyanilate	872	905	6.98	1.73 ₅	2.2 ₀
II	Hemihydrate of uranyl salicylal- <i>o</i> -oxyanilate	884	924	7.22	1.72 ₉	2.2 ₅
III	Ethanolate of uranyl salicylal- <i>o</i> -oxyanilate	872	930	7.16	1.73 ₀	2.2 ₅
IV	Butanolate of uranyl salicylal- <i>o</i> -oxyanilate	872	930	7.16	1.73 ₀	2.2 ₅
V	Methanolate of uranyl di-5-bromosalicylal-ethylenediiminate	872	907	7.00	1.73 ₄	2.2 ₂

No. of com- pound	Compound	ν_1, cm^{-1}	ν_3, cm^{-1}	Force constant $K,$ $\text{mdyn}/\text{\AA}$	U—O bond length, \AA	U—O bond order
VI	Uranyl di-5- bromosalicylal- ethylenediiminate	886	908	7.10	1.73 ₂	2.2 ₅
VII	Uranyl 2-(6- bromo- 2-oxy- 1- naphthalamino)- pyridinate	876	901	6.97	1.73 ₅	2.2 ₀

of the U—O bond is 2.2-2.3. This confirms the recently expressed assumption⁽⁸⁾ that the presence of lone electron pairs (*sp*) of oxygen, on the one hand, and free electron orbitals (*fd*) of uranium—

on the other, allows for the possibility of the formation of additional bonds. In the limiting case, the bond order of the U—O bond may be equal to 4. There are indications [9] that uranium and oxygen in the uranyl ion are connected by one σ bond and two π bonds, which accounts for the high stability of the uranyl ion.

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