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The Energy Relations and the Nature of the Bond in Anhydrous Uranyl Compounds with Acido-ligands

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The energy relations governing the interaction of the uranyl ion with acido-ligands in a series of anhydrous crystalline uranyl complex salts are examined. Using the ideas concerning the electronegativity of the interacting species, the amount of ionic character of the bonds between UO_2^{2+} and anions has been estimated (approximately 60-70%), which makes it possible to calculate the contribution of the electrostatic interaction to the crystal lattice energies of the anhydrous salts. It is shown that the stretching vibration frequencies of the uranyl ion in its complexes with acido-ligands are in no way correlated with the basicity and the electronegativity of the ions. The vibrational characteristics of the uranyl ion depend on many parameters (the structure of the complex, the symmetry of the molecule, the nature of the acido-ligand, the outer-sphere cation, etc.). The bibliography includes 72 references.

CONTENTS

I. Introduction 1062
II. The lattice energies of complex uranyl salts 1063
III. Estimation of the contribution of the electrostatic interaction of UO_2^{2+} with acido-ligands 1065
IV. Analysis of the vibration frequencies of the UO_2^{2+} ion in its complexes with acido-ligands 1066

I. INTRODUCTION

The problem of the nature of the bonds in uranyl compounds still remains paramount in the chemistry of uranium. It is indissolubly linked with the understanding of the causes of the extremely high stability of the UO_2^{2+} group in solutions and in the solid phase and also with the characteristics of its interaction with acido-ligands and neutral ligands. In view of the complexity of the problem as a whole, in the present review we shall consider only the bonding between the uranyl ion and acido-ligands in anhydrous crystalline salts.

Before proceeding to the direct estimation of the character of the bond between the uranyl ion and the acido-ligands, we shall deal briefly with the principal stages in the development of studies undertaken to understand the nature of the bonds in the uranyl group itself and the influence on the latter by equatorial ligands.

On the basis of the principle that the sum of the orders of the bonds formed by an atom in a compound is equal to the valence of the latter, Zachariasen[1] found that the multiplicity of the bonds in the uranyl group is less than two. Subsequently, in order to account for the high stability of the UO_2^{2+} group, it was suggested[2,3] that the unshared electron pairs of the oxygen atoms are also involved in the reaction, which increases the multiplicity of the bonds in the OUO group. Later Vedovenko et al.,[4] who also used the valence principle, proposed a method for the estimation of bond orders somewhat different from that of Zachariasen,[1] based on the assumption that the sum of the bond orders is equal to the valence of only the central uranium atom. Here it was postulated that the bonds between uranium and the species surrounding it are covalent and that the charge on the uranium atom approaches zero ($^{+}O\equiv U\equiv O^{+}$). Equatorial ligands influence the bond strength in the OUO group in such a way that the enhancement of the electron-donating properties of the atoms entails the displacement of the unshared pairs and even of some of the valence electrons of the yl oxygen and a decrease of the uranium-oxygen bond order. Using the Pauling relation between the average bond strength S and the valence of the ion, i.e. $S=V/N$, where V is the valence and N the coordination number, the strength of the bonds in the OUO group has been estimated[4-7] from the equation

$$R=R_1-\lg n, \qquad (1)$$

where R is the length of a bond whose order is n and R_1 the length of a bond whose order is unity and which amounts to 2.07 Å for a single bond in the UO_3 group. On the basis of the covalent model of the structure of uranyl compounds, a number of investigators[4-6] were able to explain a series of features of the spectroscopic properties of certain uranium(VI) coordination compounds.

The theory of the structure of uranyl compounds was developed further in the studies of Glebov,[8] who analysed in detail the possibilities of the principle in relation to uranyl compounds and showed that, for uranium(VI) coordination numbers of 6, 7, and 8, the ratio of the bond length and the bond strength is constant for almost all real uranium compounds. The following relation exists between R_{UL} and R_{UO}:

$$R_{UL}^{N-2}=\langle R_N\rangle^N/R_0^2, \qquad (2)$$

where $\langle R_N\rangle$ is the geometrical mean of R_{UL} and R_{UO}, which hardly changes in the series of compounds with identical coordination numbers.

At the same time the author showed[8,9] that, as a result of the endeavour to maintain the valence principle, the calculated bond orders in the uranyl group are not more than 1.5. In particular, Eqn.(1), which is satisfactorily applicable to uranates and uranium hydroxides and oxides, yields bond orders for uranyl complexes of less than 1.5. In addition, it has been noted[8] that a high multiplicity of the bonds, which entails a high degree of delocalisation of the bonding electrons of the uranyl group with a charge on the uranium atom close to zero, conflicts with structural data, according to which the equatorial ligands, including highly charged negative ligands, are disposed around the uranium atom, while in the UO_2Cl_2,[10] UO_2SO_4, UO_2SeO_4, UO_2MoO_4, UO_2CrO_4, and UO_2WO_4[12] structures the oxygen atom of the OUO group serves simultaneously as a ligand for a neighbouring layer. This presupposes a fairly high positive charge on the uranium atom and a negative charge on the oxygen atoms. The following distribution of charge in the uranyl group has been proposed: $^{-0.6}O-U^{3.2}-O^{-0.6}$,

and it has been suggested that it is in reality more ionic than would appear within the framework of the covalent model.

An anomalous dependence of the stretching vibration frequencies of the OUO group on the interatomic distances in it has also been observed.[8,9] For compounds with oxygen-containing ligands where R_{UO} is in the range 1.65–1.80 Å, the stretching vibration frequencies of the bonds are smaller the shorter the bond. It has been noted that when a linear relation is maintained between the frequencies ν_{as} and ν_s of the UO_2^{2+} group, the ratios between K (the bond force constant, mdyn A^{-1}) for U–O and the distance R_{UO}, expressed by Badger's formula $R_{UO} = 1.08\,K^{-1/3} + 1.17$ and its various modifications ($K = 3.33 \times 10^{(2.07 - R_{UO})} - 0.73$; $R_{UO} = 1.993\,K^{-1/3} + 0.666$),[8] are inapplicable to the uranyl compounds indicated. This led the author[8] to divide all uranium(VI) compounds into two groups. Complexes with oxygen-containing ligands where the distances R_{UO} in the OUO group do not exceed 1.8 Å were assigned to the first group. Compounds of the type of uranates and uranium hydroxides and oxides were assigned to the second group. It has been shown[8] that, in order to account for the observed anomalous behaviour of $\nu(UO_2^{2+})$ for uranyl coordination compounds, it is essential to take into account the contribution of the inner 6*p* and 6*s* shells to the formation of chemical bonds in the OUO group, which had been disregarded in earlier studies.

It was believed for a long time that only the 5*f*, 6*d*, and 7*s* electrons participate in the formation of the molecular orbitals of uranyl. A quasi-relativistic calculation[13] of the molecular orbitals of uranyl on the basis of the non-empirical version of LCAO-MO showed that inner 6*p* atomic orbitals interact actively with the orbitals of the oxygen atom and that their participation strengthens the bonds in the uranyl group. The inner 6*s* and 6*p* molecular orbitals ensure the presence of approximately 30% of the overall electron density in the uranyl group, which is probably equivalent to the existence of additional valence possibilities for the ions of actinide elements. It was established that a change in the distance R_{UO} does not affect the populations of the outer 7*s*, 6*d*, and 5*f* orbitals of the uranium atom, altering only the electron population of the 6*p* orbitals. The latter are actively involved in the interaction with oxygen atoms for $R_{UO} \leq 1.8$ Å, whereas for longer interatomic distances ($R_{UO} \geq 1.8$ Å) the participation of the inner uranium shells in the formation of bonds is insignificant.

In the uranyl coordination compounds with $R_{UO} = 1.7$–1.8 Å the bonding in the OUO group is ensured by both the outer 6*d* orbitals of uranyls (the formation of $6d_\nu$–$2s$ and $6d_\pi$–$2p_\pi$ bonds with the oxygen atoms) and by the inner 6*p* orbitals of the uranium (the formation of bonds of the type $6p_\sigma$–$2s$). The outer and inner MO of uranyl are then linked in such a way that the activation of the inner orbitals destabilises the outer MO.[8]

A complex relation is observed in the distribution of electron density. The independence of the charge density on uranium of the interatomic distance (within the limits 1.73–2.79 Å) conflicts with the traditional ideas, according to which the population of the AO diminishes with increase of the atomic distances, lowering the degree of covalence of the bonds in the OUO group and diminishing the shift of the electron density from the oxygen atoms to uranium.

In order to explain the dependence of the stretching vibration frequencies of the UO_2 group on R_{UO}, ideas concerning the shape and depth of the potential well for the OUO bonds in uranyl compounds have been used.[8,14] An increase of the depth and steepness of the potential well with decrease of the distance R_{UO} corresponds to the normal relation between ν_{as} and R_{UO}, while the anomalous behaviour corresponds to an increase of the depth of the potential well accompanied by a decrease of its curvature.

Glebov[8,15] also attempted to take into account the influence of the ligand crystal field on the electronic structure of the uranyl group by carrying out calculations for clusters with six point charges in the equatorial plane of the uranyl group. The influence of the crystal field was characterised by a corresponding quantity, which represents the difference between the energies of the crystal field generated by the ligands on the uranium atom and on the uranyl oxygen atoms. These quantities were estimated from structural data, amounting to approximately 16–10 eV for uranates and to less than 8 eV for the coordination compounds. As a result, it was concluded that an increase of the crystal field of the equatorial ligands influences in the first place the electron populations of the outer AO of uranium, diminishing them. At the same time the populations of the inner AO of uranium change to a much lesser extent.

Thus Glebov[8,9,13–18] noted the principal contradictions arising in the interpretation of the characteristic features of the bonding in the OUO group within the framework of the covalent model and also outlined explanations of the anomalous properties of the compounds investigated. His conclusions refer predominantly to an isolated OUO group, which is virtually unperturbed by real ligands. The latter were taken into account only for oxygen-containing ligands, the class of halides as well as nitrogen-containing uranyl complexes being excluded from consideration. As before, questions associated with the constancy of the distances R_{UO}, which remain unaltered within the limits ~1.7–1.8 Å regardless of the coordination number of UO_2^{2+} while the distances R_{UL} change appreciably from one complex to another, remained unelucidated.

In discussing the bond strengths in uranyl complexes, it is necessary to take into account also the state of the substance to which they correspond. Indeed, analysis of the data for the interaction of the uranyl ion in aqueous solutions with acido-ligands such as Br^-, Cl^-, NO_3^-, and SO_4^{2-} has shown that weak complexes are formed in this case. The logarithms of their stability constants ($\lg K_1$) are −0.3, −0.1, −0.3, and 1.9 respectively.[16–18]

II. THE LATTICE ENERGIES OF COMPLEX URANYL SALTS

The concept of the lattice energy of the complex salts was introduced by Yatsimirskii[19] who regards it as the change in the internal energy of the substance of passing from the solid salt to the ionic gas consisting of the same ions as the crystal According to Yatsimirskii,[19] the lattice energy can be estimate from the equation

$$E_C = \Delta H_C^0 + \Delta H_A^0 - \Delta H_{CA}^0 \qquad (3)$$

where ΔH_C^0, ΔH_A^0, and ΔH_{CA}^0 are the enthalpies of formation of the gaseous cation and anion and of the crystalline salt respec tively. Since Eqn.(3) is not related to either the nature of the ions or the nature of the forces acting between them, the lattice energies determined from it and referred to as experimental are evaluated from experimental thermodynamic data.

The heats of formation of certain anhydrous complex salts known at the present time as well as the heat of formation of the gaseous UO_2^{2+} ion determined by Marcus[20] ($\Delta H_{f,298.15}^0 = 289.2 \pm 4.8$ kcal mol^{-1}) enabled us to calculate the crystal lattice energies for a series of anhydrous uranyl complexes. The heats of formation of the anions of certain uranyl salts are indicated in a handbook[21] and in a monograph.[19] The results of the calculation presented in Table 1 show that the lattice energies of the salts increase steadily on passing from uranyl perchlorate to the carbonate. Unfortunately, the list of complexes is limited to relatively simple uranyl salts, since there are no literature data for the heats of formation of complexes

of crystalline compounds and gaseous complexes of anions containing the uranyl group. In the absence of such data, the ionic lattice interaction energies can be calculated by means of the Kapustinskii equation,[22] which takes into account only the ionic charges and sizes:

$$E_C = 287.2 \cdot \frac{\Sigma_n Z_C Z_A}{r_C + r_A}\left(1 - \frac{0{,}345}{r_C + r_A}\right), \qquad (4)$$

where Σ_n is the total number of cations and anions forming the molecule of the given salt, Z_C and Z_A are the formal ionic charges, and r_C and r_A are the ionic radii.

Table 1. The crystal lattice energies of uranyl compounds.

Compound	$-\Delta H^0_{f,A(g)}$, kcal mol^{-1}	$-\Delta H^0_{CA(c)}$, kcal mol^{-1}	Refs.	E^1_C, kcal mol^{-1}	E^2_C, kcal mol^{-1}
$UO_2(ClO_4)_2$	91.5	302.5	[21]	408.7	416.3
UO_2Br_2	59.9	271.8	[24]	443.2	460.2
UO_2Cl_2	62.5	297.1	[25]	461.3	479.2
UO_2Cl_2	62.5	300.0	[26]	464.2	479.2
$UO_2(NO_3)_2$	80.0	330.8	[20]	460.0	468.9
$UO_2(SCN)_2$	11.6	210.1	[21]	476.1	478.3
UO_2SO_4	178	440.9	[27]	552.1	563.4
UO_2SO_4	178	451.2	[28]	562.4	563.4
UO_2F_2	66.9	397.9	[29]	553.3	551.4
UO_2F_2	66.9	395.5	[29]	550.9	551.4
UO_2F_2	66.9	394.7	[30]	550.1	551.4
$UO_2(HCOO)_2$	107.1	447.1	[31]	521.1	511.4
$UO_2(CH_3COO)_2$	122.0	467.9	[29]	513.1	509.9
$UO_2(CH_3COO)_2$	122.0	476.1	[32, 33]	521.3	509.9
$UO_2(OH)_2$	40.0	365.2	[21]	573.4	539.6
UO_2CO_3	47	405.6	[21]	647.8	631.9

Notation: $-\Delta H^0_{f,A(g)}$ is the enthalpy of formation of gaseous anions, $-\Delta H^0_{CA(c)}$ the enthalpy of formation of the crystalline salt, and E^1_C and E^2_C are the lattice energies of the complex uranyl salts calculated from the Yatsimirskii and Kapustinskii equations respectively.

According to Marcus,[20] the radius of the uranyl ion is 1.40 Å. Table 1 also presents the results of the calculation of the lattice energies of the uranyl salts from Eqn.(4). Evidently the lattice energies calculated from the Kapustinskii equation, which takes into account only the electrostatic interactions between the ions, agree fairly well with the values obtained from thermal-chemical data.[3,4]

Yatsimirskii[23] believes that the interaction energy in a complex is determined in a general form by the equation

$$E_C = E_i + C + E, \qquad (5)$$

where E_i is the energy of the interaction between the ions calculated from the Kapustinskii equation, E the energy of extra-stabilisation by the crystal field, and C the energy of formation of the covalent bond in the crystal.

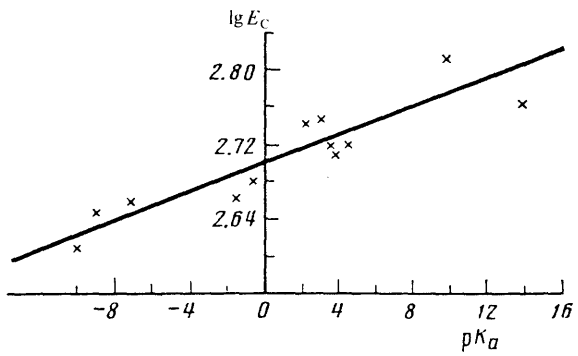
The covalent component of the bond between the cation and anion, arising as a result of partial charge transfer, is as a rule determined from the difference $\Delta E_{cov} = E_C - E_i$. For the salts considered, ΔE_{cov} does not exceed +20 kcal mol^{-1}. This value is probably determined not only by the nature of the bonds in the compounds investigated but also by the experimental errors in the determination of the heats of formation. Overall, it follows from Table 1 that the lattice energies found for the uranyl salts agree well with the values obtained from purely electrostatic considerations. At first sight it appears that, knowing the lattice energies, it is possible to estimate fairly readily the energies of the bonds between the uranyl ion and the acido-ligands in the anhydrous salts. However, in reality this is extremely difficult because the overall compositions of the salts say nothing about the way in which the ligands are bound and about the coordination number of the uranyl group. These compounds are formally coordination-saturated and they cannot be regarded as island structures. The coordination possibilities of the UO_2^{2+} group in them are utilised by the formation of polymers. This is achieved both by binding the uranyl ions via bridging ligands (Cl^-, SO_4^{2-}, $C_2O_4^{2-}$, etc.) and as a result of the involvement in the coordination of the oxygen atoms of the OUO groups in neighbouring layers.

As an illustration, one may refer to the structural data for UO_2Cl_2 [10] and compounds of the type UO_2EO_4 (where E = S, Se, Cr, Mo, or W).[11,12] The coordination polyhedron of the uranium in these complexes is a pentagonal bipyramid, whose equatorial plane is formed by four bridging chlorine or oxygen atoms of the EO_4^{2-} groups and the oxygen atom which plays a dual role. In the polymer structure the uranyl oxygen atom occupying the axial position in one polyhedron belongs to the plane of the pentagonal base of another polyhedron.

Table 2. Contributions of the electrostatic components of the U–L bonds to the crystal lattice energies of uranyl complexes.

Compound	R_{UL}, Å × m*	i_{UL}	E_e, kcal mol^{-1}	E_C, kcal mol^{-1}	ΔE_{cov}, kcal mol^{-1}
UO_2Cl_2	2.73×4	0.66	321.1	461.3	139.7
UO_2SO_4	2.30–2.49	0.74	409.5	552.1	142.6
UO_2F_2	2.43×6	0.74	606.6	553.3	–53.3
UO_2CO_3	2.50×4 (2.44×2)	0.71	570.3	631.9	61.6
$UO_2(OH)_2$	2.30×4	0.67	386.9	539.6	152.7

* Number of bonds.



Dependence of lg E_C for uranyl salts on the basicity of the acido-ligand.[34]

Returning now to the crystal lattice energies of the anhydrous uranyl complexes (Tables 1 and 2), we may note that the sequence in which the lattice energies increase for the principal inorganic anions is fairly satisfactorily correlated with the variation of the basicities of the acido-ligands. The relation between lg E_C and pK_a shown in Fig.1, which has been treated by the method of least squares, can be described

by the following equation:

$$\lg E_C = 0.01 pK_a + 2,70. \quad (6)$$

Analysis of the thermodynamic quantities permits a number of conclusions. Firstly, the logarithms of the crystal lattice energies of the uranyl complexes vary linearly with the basicities of the acido-ligands. Secondly the $\lg E_C - pK_a$ relation can be used for a qualitative estimation of the lattice energies of anhydrous uranyl salts whose heats of formation are unknown. Finally, the calculation of the crystal lattice energies of the uranyl complexes, taking into account the electrostatic interaction only, indicates an appreciable amount of the ionic character of the bonds between UO_2^{2+} and the acido-ligands in the crystalline uranyl complexes.

III. ESTIMATION OF THE CONTRIBUTION OF THE ELECTROSTATIC INTERACTION OF UO_2^{2+} WITH ACIDO-LIGANDS

The fact that the bonds between UO_2^{2+} and acido-ligands are to a large extent electrostatic agrees with the classification of the uranyl cation as a hard Lewis acid.[35-37] In this connection it therefore becomes necessary to estimate quantitatively the amounts of ionic character of the bonds and the charges of the interacting ions. In order to estimate the electrostatic contribution, we employed the concept of electronegativity (EO), in which any bond is regarded as a superposition of covalent and ionic components.[38,39] Pauling, who introduced the concept of EO,[38] characterises electronegativity as the ability of an atom in a molecule (or in general in a chemical bond) to attract valence electrons. The EO theory was developed further in other investigations.[39-41,42-44] Sanderson[39-41] demonstrated the possibility of determining not only the effective charges and the coefficients of the ionic character and covalence but also the energies of the electrostatic and covalent bonding of the atoms in the molecule. For this purpose, one finds the geometrical mean of the EO on formation of the molecule and the EO of each atom is calculated relative to it. The bonding energies calculated for hundreds of organic and simple inorganic compounds differ from the experimental values by not more than 5%.

The application to uranyl compounds of the methods for the calculation of the effective atomic charges and of the amounts of ionic character of the bonds proposed by Sanderson[39-41] did not, however, yield reasonable results for the following reasons. In these calculations no account was taken of the coordination possibilities of uranium and they are hindered by the lack of data for the change in the electronegativity of uranium following the loss of an electron. In addition, and this is most significant, in the case of uranyl complexes with oxygen-containing ligands the oxygen atoms of the OUO group and of the anions are regarded as equivalent. The latter is probably valid only for a small number of compounds such as uranates in which the lengths of the bonds between the uranium atom and all the oxygen atoms surrounding it are comparable to the lengths of the uranium–oxygen bonds in the axial positions; the very concept of the uranyl group is abolished for such compounds.

It is preferable to use formulae for the calculation of the amounts of ionic character of bonds and effective charges proposed by Batsanov[42-44] for coordination crystals. The principal difference between the latter and molecules consists in the fact that the coordination number of an atom in such crystals is greater than its valence. The average "amount of ionic character of the bond" in the crystal is given by the following formula in the case of polyvalent atoms:

$$i_{cr} = \frac{Zi_{mol} + (K - Z)i_e}{K}, \quad (7)$$

where Z is the valence of the atom, K the coordination number, and i_{mol} the amount of ionic character of the bond determined from the difference between the EO of the anion and the metal (ΔX).[42,43] The covalent component is estimated from the polarity of the bonds between UO_2^{2+} and the anions. The latter is determined by the competition between two factors—the attraction of electrons by the metal atom, which is proportional to its electronegativity X_M, and the ability of the metal to give up electrons to the anions, which is proportional to its ionisation potential I_A in the valence state. The following relation has been proposed for the determination of the polarisation component of the bond, called the "electrostatic ionic character of the bond":[42-44]

$$i_e = \frac{I_A - X_M}{I_A + X_M}. \quad (8)$$

The degree of covalence of the bond is then calculated from the difference $1 - i_e$.

The EO have been published[42-44] for acido-ligands (NO_3^-, ClO_4^-, SO_4^{2-}, etc.) taking into account the interactions within the corresponding group. The knowledge of i_{cr} makes it possible to calculate the effective atomic charges Z^*, which characterise the distribution of electron density in the region of the chemical bond:

$$Z^* = Z - K(1 - i_{cr}). \quad (9)$$

The quantity in brackets corresponds to the degree of covalence of the bond, since the overall contribution of all the interactions is assumed to be unity.

The electronegativity of the uranyl ion UO_2^{2+} was assumed to be 1.38.[45] Its estimation from the formulae proposed by Zhang[46] and Allred[47] leads to approximately the same value. The ionisation potentials of anions were given in a handbook[48] and in another publication.[49] In the calculation the uranyl group was regarded as a bivalent point cation in which the interaction of the uranium and oxygen atoms is disregarded. The quantity i_{mol} was determined from tabulated data on the basis of the relation between the amount of ionic character of the bonds and ΔX.[42,43]

The calculations showed that the amounts of ionic character of the bonds between UO_2^{2+} and the anions are mainly in the range 60–70% for all the anhydrous solid complexes. The increase of the coordination number (C.N.) from four to six is not then unduly reflected in the change of the amount of ionic character of the bond, since the effective charge Z^*_{eff} is very significantly reduced. Naturally the concept of the effective charge on the uranyl ion is fairly arbitrary; it reflects in only a simplified form the distribution of charges in the case where the uranyl ion is regarded as a doubly charged cation.

Like the effective charges, the amounts of ionic character of the bonds do not exhibit an explicit dependence on the nucleophilicity of the anions, although, overall, a definite tendency towards a decrease of the amounts of ionic character of the bonds between the uranyl ion and the equatorial ligands can be traced as the basicity of the ligands increases. The closeness of the amounts of ionic character of the bonds between UO_2^{2+} and the acido-ligands in different uranyl compounds can serve as evidence that the mechanism of the interaction of these species is predominantly electrostatic and confirms the assignment of the uranyl[35-37] to hard Lewis acids.

Using the ideas developed by Batsanov[44] for mixed three-centre systems $A_1–M–A_2$ or $M_1–A–M_2$, it is possible to put forward certain considerations concerning the character of the bonding in the uranyl group in complexes having the general formula UO_2X_n. According to the Pauling principle, which requires a constant population of the metal orbitals and

the possibility of saturating the EO, an increase in the amount of ionic character of the A_1–M bond (or the M_1–A) bond should be accompanied by an increase of the degree of covalence of the M–A_2 (or A–M_2) bond. This is usually expressed by a change in the lengths of the corresponding bonds and their vibration frequencies in such a way that the greater ionic character of one of these bonds entails a greater covalent character of the other. Since the structure of uranyl compounds is such that the oxygen atoms of the OUO group are in the *trans*-positions with respect to the equatorial ligands, an increase of the amount of ionic character of the UO–L bond should probably tend to increase the degree of covalence of the U–O bonds. Indeed, analysis[50] of structural data for uranyl complexes having coordination numbers of 4, 5, and 6 shows unambiguously that the greater the R_{UL}, the smaller the R_{UO}.

In the series of isostructural anhydrous uranyl compounds UO_2MoO_4, UO_2SeO_4, UO_2SO_4,[11,12] and UO_2Cl_2,[10] in which the uranium polyhedron is a pentagonal pyramid, an increase of R_{UL} (2.30–2.35, 2.30–2.49, 2.30–2.54, and 2.52–2.73 respectively) is accompanied by a shortening of the R_{UO} distances (1.76 and 1.81, 1.78 and 1.79, 1.73 and 1.80, and 1.73 and 1.78 Å). This is equivalent to an increase of the degree of covalence of the uranium–oxygen bonds in the OUO with increase of the amount of ionic character of the bonds with the acido-ligands. The high degree of covalence of the bonds in the OUO group and the electrostatic character of the interaction with the acido-ligand are in good agreement with the autonomous chemical behaviour of UO_2^{2+} and the constancy of the bond length R_{UO} in the range 1.65–1.80 Å regardless of the nature of the ligand and the coordination number.

In contrast to *d*-block elements, the geometry of the coordination sphere of uranyl is apparently determined mainly by electrostatic and steric factors and not by the degree of overlap of the uranyl and ligand orbitals. This agrees with the absence of a correlation between R_{UO} and R_{UL}, on the one hand, and the ligand crystal field energies, estimated by Glebov,[15] on the other. The high strengths of the bonds in the crystalline complexes of uranyl with ligands which give rise to the weakest complexes in solution (ClO_4^-, Cl^-, NO_3^-, and SO_4^{2-}) can be readily accounted for on the basis of the concept of the electrostatic character of the interaction of UO_2^{2+} with acido-ligands. This is indicated by the high crystal lattice energies of uranyl sulphate, fluoride, carbonate, and nitrate (Table 1) calculated from thermodynamic data. The increase in the stability of the compounds of the above most electronegative anions in the crystalline state is probably achieved as a result of the formation of extremely strong electrostatic bonds with the acido-ligands.

On the other hand, the idea of a large amount of ionic character of the bonds between UO_2^{2+} and equatorial ligands, especially the most electronegative of these, makes it possible to understand the tendency of these bonds to ionise in solution and hence their weak capacity for complex formation.

The electrostatic nature of the bonding between UO_2^{2+} and the ligands agrees well with the known facts indicating the preferential interaction of the above cation with hard bases containing oxygen or halogen atoms. Under the usual conditions, the uranyl ion does not form bonds with soft bases containing nitrogen, sulphur, and phosphorus electron-donating atoms. Such reactions become possible only in a series of organic solvents exhibiting a much smaller solvating effect and polarising capacity than water.

The estimated amounts of ionic character of the bonds in the uranyl compounds can be used to calculate the electrostatic contributions to the crystal lattice energies E_{lat} with the aid of the equation proposed by Sanderson,[39–41] in which E_{lat} is regarded as the sum of the electrostatic (E_e) and covalent (E_{cov}) contributions:

$$E_{lat} = t_e E_e + t_c E_{cov},$$

where t_e and t_c are respectively the coefficients of the ionic character and covalence of the bonds, whose sum is unity.

The electrostatic interaction energy is

$$E_e = t_e \times 332 e^2/R_0,$$

where R_0 is the bond length and 332 is a coefficient which makes it possible to express the bond energy in kcal mol^{-1}.

The covalent contribution is calculated as the geometrical mean of the energies of two homeopolar bonds.[39–41] We calculated[53] the electrostatic contributions E_e to the crystal lattice energies for a series of uranyl salts with known structures (Table 2). In the calculation of E_e, the amounts of ionic character of the bonds i_{UL} calculated by ourselves were adopted as the t_e. For UO_2SO_4 with different U–ligand bond lengths, their values were either averaged or the length of each bond was taken into account. Comparison of the E_e with the crystal lattice energies of the uranyl salts showed that the electrostatic interactions make the main contribution to the crystal lattice energy.

The overall contribution of the covalent interaction energy and the energy of the extra-stabilisation by the crystal field can be estimated from the difference $\Delta E_{cov} = E_c - E_e$, because, according to Yatsimirskii,[23] the energy of the interaction in the complex is determined in the general form by Eqn.(5). It follows from Table 2 that ΔE_{cov} is much smaller than E_e; it is negative only for uranyl fluoride, which is probably associated with errors in the determination of the UO_2F_2 structure;[51] the structure has been discussed by Ohwada.[52] It is known[53] that this structure is atypical for uranyl halides, which have a characteristic coordination number of five.

IV. ANALYSIS OF THE VIBRATION FREQUENCIES OF THE UO_2^{2+} ION IN ITS COMPLEXES WITH ACIDO-LIGANDS

In connection with the problem of the interrelation between the structure and properties of a substance (in particular spectroscopic properties), the determination of various correlations between the above characteristics is always regarded as important. Different views on this problem are held as regards uranyl compounds. It has been noted[35] that several spectrochemical series, differing in the sequence of the ligands, have been proposed for uranyl coordination compounds. Having applied the *d*-element spectrochemical series to uranyl compounds, McGlynn et al.[54] assumed that the stretching vibration frequencies ν_s and ν_{as} of the UO_2^{2+} ion decrease as a function of the nature of the ligands in the following sequence: $NO_3^- > F^- > H_2O >$ Phen ≅ Py $> NO_2^- > NCS^- > NH_3 >$ ethylenediamine $> CN^-$. The dependence of the state of the bonds in the UO_2^{2+} group on the nature of the ligands in uranyl complexes has been postulated by Dyatkina and Mikhailov.[3] These ideas were developed further in a study[4] whose authors concluded that the orders of the uranyl and equatorial bonds are inter-related and that the uranyl vibration frequencies are extremely sensitive to changes in bond orders and the corresponding force constants. The bond orders have been estimated for a series of compounds, including uranates and uranium oxides, and the frequencies ν_s and ν_{as} for UO_2^{2+} and the force constants have been compared. A dependence of the bond orders in the uranyl complexes on the nature of not only the ligands but also the outer-sphere cation has been noted.[56]

At the same time, there have been studies in which the absence of correlations between the vibration frequencies of uranyl and the nature of the ligands has been pointed out.

Having analysed complexes analogous to those investigated by McGlynn et al.,[54] Bullock[57] concluded that the series of frequencies estimated by McGlynn et al.[54] are erroneous. Volod'ko et al.[55] claim that the variation of the vibration frequencies of UO_2^{2+} in different compounds is not correlated with the position of the ligands in the spectrochemical series.

The absence of such correlations has also been noted by Day and Venanzi,[58] who regard the variation of the uranyl vibration frequencies as a result of the superposition of vibrational and electronic interactions. The former are determined by the vibration of the bonds between the uranium atom and the equatorial ligands, the intensity of these vibrations depending on the force constants of the system (including the metal–ligand bonds) and on the mass of the ligands. The electronic interaction arises as a consequence of electron transfer to the uranyl ion and is determined by the electron-donating capacity of the ligand. It is to be expected that the UO_2^{2+} vibration frequencies should decrease with increase of the electron-donating capacity. However, the superposition of the above two factors makes the changes in the vibration frequencies of the uranyl ion unpredictable. Bagnall and Wakerley,[59] who analysed 18 uranyl complexes, hold the same view.

Examination of the electronic spectra and the EO of uranyl compounds with various ligands led to the conclusion[60] that both the positions and intensities of the electronic transition bands are independent of the chemical nature of the ligands and are determined solely by the geometrical structures of the first coordination sphere of the uranium atom. The influence of the ligands can be taken into account only when the symmetries of the inner coordination sphere of uranium are identical.

A similar conclusion follows also from the theoretical analysis of the absorption spectra of uranyl complexes.[61–64] The change in the mass of the ligand from 10 to 200 a.u. in the complexes UO_2X_n (where n = 4, 5, 6), for an unchanged internal force field of the uranyl group and when the remaining parameters such as the mass of the atom X, the lengths of the UX bonds, and their force constants are varied within specified limits, alters the frequencies ν_S of the UO_2^{2+} group by only 5 cm^{-1}, while the frequencies ν_{as} remain virtually constant. The frequencies ν_S and ν_{as} are also independent of the uranium–ligand bond length in the range 1.8–2.8 Å. The variation of the force field of the ligands within wide limits can alter the UO_2^{2+} vibration frequencies by not more than ~10 cm^{-1} in complexes with D_{4h} symmetry, by ~13 cm^{-1} for the D_{5h} symmetry, and by ~15 cm^{-1} for the D_{6h} symmetry. It has also been shown for halide complexes having the general formula $M_2[UO_2X_4]$ that the frequencies ν_{as} hardly change on replacement of any number of chlorine atoms by bromine atoms regardless of the symmetry of the complex anion associated with the same cation.[63,64] The force constants of the U–O bonds in these compounds are similar and amount to 6.6 to 6.8 mdyn A^{-1}.

The list of investigations in which the influence of ligands on the force constants and vibration frequencies of the bonds in uranyl compounds has been discussed may be greatly expanded, since we have mentioned only some of them. We may note that in the studies quoted, with the exception of Refs. 61–64, both complexes containing only acido-ligands (which consist of anions) and compounds with a mixed type of coordination sphere, containing acido-ligands and neutral ligands, were considered simultaneously. Such complexes should probably be discussed separately in order to eliminate the superposition of the two factors indicated when general relations are deduced.

In the present review we shall consider the behaviour of ν_{as} for the UO_2^{2+} group in uranyl complexes containing only acido-ligands, starting with anhydrous salts (Table 3). The study of the vibrational spectra of the latter is a fairly complex task not only because of the difficulty of synthesising these compounds but also because they are extremely hygroscopic. This factor has been frequently noted by various authors; in particular, we have demonstrated this for the anhydrous compounds UO_2Cl_2 [65] and $UO_2(NO_3)_2$,[66] whose infrared spectra changed very markedly after an extremely brief contact of the specimen with air. Thus, apart from the three intense absorption bands at 950, 835, and 775 cm^{-1}, a series of additional intense bands appeared in the UO_2Cl_2 spectrum in the range 950–900 cm^{-1}. The same situation probably obtains also for $UO_2(ClO_4)_2$, UO_2F_2, and UO_2Br_2, whose spectra are not only characterised, according to the data of different workers, by different frequencies ν_{as} (UO_2^{2+}) but also differ as regards the number of absorption bands[64] (Table 3).

Table 3. The vibration frequencies ν_{as} of the UO_2^{2+} group in the spectra of uranyl complexes.

Compound	ν_{as}, cm^{-1}	Refs.	Compound	ν_{as}, cm^{-1}	Refs.
$UO_2(ClO_4)_2$	996, 965, 961	[64]	$Cs_2[UO_2Br_4]$	925, 920	[64]
$UO_2(ClO_4)_2$	965	[5]	$(PyH)_2[UO_2Br_4]$	935	[64]
UO_2Br_2	945, 905	[64]	$Li_2[UO_2Cl_4]$	940	[64]
UO_2Cl_2	950	[65]	$Na_2[UO_2Cl_4]$	935	[64]
UO_2Cl_2	990, 980, 965	[66]	$K_2[UO_2Cl_4]$	925	[64]
UO_2Cl_2	977	[67]	$Rb_2[UO_2Cl_4]$	920	[64]
UO_2SO_4	930	[68]	$Cs_2[UO_2Cl_4]$	920	[64]
UO_2CrO_4	930	[68]	$(PyH)_2[UO_2Cl_4]$	924, 914	[64]
UO_2MoO_4	932	[68]	$NO[UO_2(NO_3)_3]$	940	[66]
UO_2WO_4	936	[68]	$NH_4[UO_2(NO_3)_3]$	952	[57]
UO_2F_2	1000	[52]	$K[UO_2(NO_3)_3]$	960	[57]
UO_2F_2	1010, 927, 923	[64]	$Rb[UO_2(NO_3)_3]$	955	[57]
$UO_2(CH_3COO)_2$	950	[64]	$Cs[UO_2(NO_3)_3]$	956	[57]
$UO_2(CH_3COO)_2$	942	[69]	$(NH_4)_2[UO_2(NO_3)_4]$	960	[55]
UO_2CO_3	930	[64]	$Rb_2[UO_2(NO_3)_4]$	945	[55]
UO_2CO_3	965	[4]	$(NH_4)_3[UO_2F_5]$	885, 877	[70]
β-$UO_2(OH)_2$	892	[9]	$K_3[UO_2F_5]$	870	[70]
γ-$UO_2(OH)_2$	890	[9]	$Rb_3[UO_2F_5]$	860	[70]
			$Cs_3[UO_2F_5]$	850	[70]
			$K_3[(UO_2)_2F_9]$	870, 858	[55]
			$Na[UO_2(CH_3COO)_3]$	931	[55]
			$Rb[UO_2(CH_3COO)_3]$	924	[55]
			$Cs[UO_2(CH_3COO)_3]$	920	[55]
			$(NH_4)_4[UO_2(CO_3)_3]$	888	[55]
			$Na_4[UO_2(CO_3)_3]$	876	[64]
			$K_4[UO_2(CO_3)_3]$	881	[55]
			$Rb_4[UO_2(CO_3)_3]$	877	[55]
			$Cs_4[UO_2(CO_3)_3]$	877	[55]
			$K_2[UO_2(CO_3)_2]$	856	[55]

Analysis of the vibration frequencies in the infrared spectra of anhydrous uranyl salts has shown that they exhibit no correlations with the basicities of the ligands; this is indicated by the data in Table 3, where the compounds are arranged in order of increasing pK_a of the ligands. Nor are there any correlations with the electronegativities of the anions. It is striking that the highest frequencies ν_{as} (UO_2^{2+}) correspond to anions with the highest EO (F^-, ClO_4^-, and NO_3^-). On the other hand, complexes with other anions, which also have high EO (SO_4^{2-} and CO_3^{2-}), have frequencies ν_{as} close to the vibration frequencies of compounds with less electronegative anions (Br^- and CH_3COO^-). Without ruling out the possibility of an inadequate reliability of the experimental vibration frequencies of certain anhydrous salts, the difficulties in determination of which were noted above, one can postulate that the above inconsistencies are determined also by the difference between the structures of the anhydrous uranyl salts. Table 3 also lists the frequencies ν_{as} (UO_2^{2+}) in the spectra of compounds with more complex compositions, incorporating a complex anion and outer-sphere cations. Analysis of the changes in the ν_{as}(UO_2^{2+}) listed in Table 4 following the replacement of the

ligand indicates the absence of a correlation between ν_{as} and the basicity of the acido-ligand. On the other hand, in the series of isostructural hexacoordinate uranyl complexes, containing bidentate acido-ligands, the transition from trinitrato- to triacetato- and tricarbonato-uranylates reveals a tendency towards a decrease of ν_{as} with increase of the basicities of the anions. However, the data for these three compounds are clearly insufficient to infer the existence of this type of general relation.

Table 4. The vibration frequencies ν_{as} of the UO_2^{2+} group in the spectra of anionic uranyl complexes with Rb^+ as the outer-sphere cation.

Compound	pK_a	X (Ref. 24)	ν_{as}, cm^{-1}	Refs.
$Rb_3[UO_2Cl_5]$	~7	3.2	920	[64]
$Rb[UO_2(NO_3)_3]$	~1.4	3.8	955	[57]
$Rb_2[UO_2(NO_3)_4]$	~1.4	3.8	945	[55]
$Rb_3[UO_2F_5]$	3	4.0	860	[70]
$Rb[UO_2(Cl_3COO)_3]$	4.7	3.0	924	[55]
$Rb_4[UO_2(CO_3)_3]$	10.2	3.6	877	[55]

Note. The pK_a and the electronegativities X for the anion are quoted.

The analysis of the variation of the frequency $\nu_{as}(UO_2^{2+})$ under the influence of the outer-sphere cation is also of interest. It is known that there is competition in uranyl complexes between the uranyl ion and the outer-sphere cation: both withdraw electron density from the anion in the three-centre system U–A–M. The results of studies on chloride complexes were previously discussed by Vdovenko.[71] The data in Table 3 show that, in the series of isostructural tetrachloro- and pentafluoro-uranylates, the transition from Li^+ and Cs^+ entails a monotonic increase of the frequency $\nu_{as}(UO_2^{2+})$. From the standpoint of the theory of electronegativity, the EO of the outer-sphere cations diminishes on passing from Li^+ to Cs^+ (EO is 1.1 for Li^+, 0.9 for Na^+, 0.8 for Rb^+, and 0.7 for Cs^+).[42] Since the EO of the UO_2^{2+} group is 1.38,[45] i.e. is greater in absolute magnitude than the EO of metal ions, the electron density shifts from the anion to the uranyl ion, which means that the M–A bond is more electrostatic than the U–A bond and the amount of ionic character of the M–A bonds is greater the lower the EO of the outer-sphere cation. With increase of the amount of ionic character of the M–A bonds, there is a corresponding increase of the degree of covalence of the U–A bonds. The increase of the degree of covalence of the uranium–ligand bonds should induce a decrease of the frequency ν_{as} of the uranyl ion, which has in fact been observed for the halide complexes.

In the case of complex polyatomic polyfunctional anions, this type of relation breaks down. Table 4 shows that the frequencies ν_{as} in the spectra of uranyl nitrates and carbonates are almost insensitive to the effects of the outer-sphere cation.[72] However, this not only does not conflict with the effects discussed above but actually confirms them. Indeed, the electron density shifts from the oxygen atoms of the anions in such complexes and is distributed between the uranium atom and the central atom of the acido-ligand (such as the carbon atom in CO_3^{2-} or the nitrogen atom in NO_3^-) and not between the uranyl ion and the outer-sphere cation. As a consequence of this, the influence of the outer-sphere cation is hardly reflected in the vibration frequencies of the UO_2^{2+} ion.

The above analysis of the vibration frequencies of the UO_2^{2+} ion in its complexes with acido-ligands shows that, for the series of compounds indicated, the dependence of ν on the nature of the anions and in particular on their basicity is limited and cannot be regarded in isolation from the characteristics of specific structures. When the complexes contain neutral ligands, the situation probably becomes still more complex. A multiplicity of various structures of uranyl complexes having coordination numbers of 4, 5, and 6 are known; on passing from one compound to another, there is as a rule a change in not just one but immediately in a whole series of parameters characterising these structures. It is therefore almost impossible to relate the changes in the vibration frequencies of the UO_2^{2+} group solely to any one of them.

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Thus one may conclude that the energy relations governing the interaction of the uranyl group with acido-ligands in anhydrous complexes are described fairly accurately in terms of electrostatic ideas. This justifies the hypothesis that the above approach to the description of the interaction between the components of the complex is legitimate also in uranyl compounds having a more complex composition.

REFERENCES

1. W.H.Zachariasen, Acta Cryst., 1954, **7**, 795.
2. S.P.McGlynn and J.R.Smith, J.Mol.Spectrosc., 1961, **6**, 169.
3. M.E.Dyatkina and Yu.N.Mikhailov, Zhur.Strukt.Khim., 1962, **3**, 724.
4. V.M.Vdovenko, L.G.Mashirov, and D.N.Suglobov, Dokl.Akad.Nauk SSSR, 1966, **167**, 1299.
5. V.M.Vdovenko, L.G.Mashirov, and D.N.Suglobov,, Radiokhimiya, 1968, **10**, 587.
6. V.M.Vdovenko, V.A.Vodovatov, L.G.Mashirov, and D.N.Suglobov, Dokl.Akad.Nauk SSSR, 1973, **209**, 352.
7. V.M.Vdovenko, I.N.Ladygin, and D.N.Suglobov, Zhur. Prikl.Spektrosk., 1971, **15**, 1105.
8. V.A.Glebov, "Elektronnoe Stroenie i Svoistva Uranil'nykh Soedinenii" (The Electronic Structures and Properties of Uranyl Compounds), Energoatomizdat, Moscow, 1983.
9. V.A.Glebov, Koord.Khim., 1980, **6**, 1860.
10. J.C.Taylor and P.W.Wilson, Acta Cryst., 1973, **29B**, 1073.
11. N.P.Brandenburg and B.O.Loopstra, Acta Cryst., 1978, **34B**, 3734.
12. V.N.serezhkin, V.K.Trunov, and L.T.Makarevich, Kristallografiya, 1980, **25**, 858.
13. V.A.Glebov and V.S.Nefedov, Koord.Khim., 1981, **7**, 1664.
14. V.A.Glebov, Koord.Khim., 1981, **7**, 388.
15. V.A.Glebov, Koord.Khim., 1981, **7**, 1053.
16. S.Ahrland, Acta Chem.Scand., 1951, **5**, 1271.
17. D.Banerjea and K.K.Tripathi, J.Inorg.Nucl.Chem., 1961, **18**, 199.
18. R.A.Day and R.M.Powers, J.Amer.Chem.Soc., 1954, **76**, 3895.
19. K.B.Yatsimirskii, "Termokhimiya Kompleksnykh Soedinenii" (Thermochemistry of Complex Compounds), Izd. Akad.Nauk SSSR, Moscow, 1957.
20. J.Marcus, J.Inorg.Nucl.Chem., 1975, **37**, 493.
21. V.P.Glushko (Editor), "Termicheskie Konstanty Veshchestv" (Thermal Constants of Substances), Izd. VINITI, Moscow, 1965–1978.

22. A.F.Kapustinskii, Zhur.Obshch.Khim., 1943, **13**, 497.
23. K.B.Yatsimirskii, Zhur.Neorg.Khim., 1961, **6**, 518 (Russ.J.Inorg.Chem., 1961(3)].
24. G.Prins, E.H.P.Cordfunke, and W.Quweltjes, J.Chem. Thermodyn., 1978, **10**, 1003.
25. E.H.P.Cordfunke, W.Quwelties, and G.Prins, J.Chem. Thermodyn., 1976, **8**, 241.
26. E.Greenberg and E.F.Westrum, J.Amer.Chem.Soc., 1956, **78**, 4526.
27. E.H.P.Cordfunke and W.Quweltjes, J.Thermodyn., 1977, **9**, 1057.
28. B.B.Owens and S.W.Mayer, J.Inorg.Nucl.Chem., 1964, **26**, 501.
29. P.A.G.O'Hare and J.G.Malm, J.Chem.Thermodyn., 1982, **14**, 331.
30. E.H.Cordfunke and W.Quweltjes, J.Chem.Thermodyn., 1977, **9**, 71.
31. J.Bousquest, B.Bonneton, P.Claudy, D.Nathurin, and G.Turok, IV Conf.Int.Thermodyn.chim., Montpellier, 1975, Vol.1, p.169.
32. L.Thakur, M.F.Ahamd, and R.Prasad, Indian J.Chem., 1977, **15A**, 821.
33. L.Thakur, R.Prasad, A.K.Thakur, and M.F.Ahmad, Indian J.Chem., 1979, **18**. 258.
34. L.V.Kobets and D.S.Umreiko, Zhur.Neorg.Khim., 1985, **30**, 3158 [Russ.J.Inorg.Chem., 1985(12)].
35. R.G.Pearson, Uspekhi Khim., 1971, **40**, 1269 [Russ. Chem.Rev., 1971(7)].
36. Y.Shinkichi and T.Motaharu, J.Inorg.Nucl.Chem., 1975, **37**, 587.
37. R.D.Hancock and F.Marsicano, South African J.Chem., 1980, **33**, 77.
38. L.Pauling, "The Nature of the Chemical Bond" (Translated into Russian), Goskhimizdat, Moscow, 1977.
39. R.T.Sanderson, J.Amer.Chem.Soc., 1952, **74**, 272.
40. R.T.Sanderson, J.Amer.Chem.Soc., 1983, **105**, 2259.
41. R.T.Sanderson, J.Org.Chem., 1982, **47**, 3835.
42. S.S.Batsanov, "Elektrootritsatel'nost' i Effektivnye Zaryady Atomov" (The Electronegativity and Effective Atomic Charges), Izd.Znanie, Moscow, 1971.
43. S.S.Batsanov, Uspekhi Khim., 1968, **37**, 778 [Russ. Chem.Rev., 1968(5)].
44. S.S.Batsanov, Koord.Khim., 1977, **3**, 291.
45. A.Mudaliar, G.K.Agrawal, and A.S.Kapur, Thermochim.Acta, 1977, **19**, 136.
46. Y.Zhang, Inorg.Chem., 1982, **21**, 3886.
47. A.L.Allred, J.Inorg.Nucl.Chem., 1961, **17**(3/4), 215.
48. V.I.Vdeneev, L.V.Gurvich, V.N.Kondrat'ev, V.A.Medvedev, and E.A.Frankevich, Handbook, "Energiya Razryva Khimicheskikh Svyazei. Potentsialy Ionizatsii i Srodstvo k Elektronu" (Chemical Bond Dissociation Energies, Ionisation Potentials, and Electron Affinities), Izd.Akad.Nauk SSSR, Moscow, 1962.
49. E.A.Nechaev, Elektrokhimiya, 1983, **19**, 969.
50. V.A.Glebov, Koord.Khim., 1982, **8**, 970.
51. M.Atoji and M.J.McDermott, Acta Cryst., 1970, **28B**, 1540.
52. K.Ohwada, J.Inorg.Nucl.Chem., 1971, **31**(6), 1615.
53. Yu.N.Mikhailov, in "Khimiya Platinovykh i Tyazhelykh Metallov" (The Chemistry of Platinum and Heavy Metals), Izd.Nauka, Moscow, 1975, p. 127.
54. S.P.McGlynn, J.K.Smith, and W.C.Neely, J.Chem. Phys., 1961, **35**, 105.
55. L.V.Volod'ko, A.I.Komyak, and D.S.Umreiko, "Uranilovye Soedineniya" (Uranyl Compounds), Izd.Beloruss. Gos.Univ., Minsk, 1981, Vol.1.
56. K.Ohwada, J.Coord.Chem., 1976, **6**, 75.
57. J.I.Bullock, J.Inorg.Nucl.Chem., 1967, **29**, 2257.
58. J.P.Day and L.M.Venanzi, J.Chem.Soc., 1966, **A**(10), 1363.
59. K.W.Bagnall and M.W.Wakerley, Inorg.Nucl.Chem., 1975, **37**, 329.
60. C.Gorlier-Walrand and S.Ge Jaegere, Spectrochim Acta, 1972, **28A**, 257.
61. Yu.Ya.Kharitonov and N.A.Knyazeva, Zhur.Neorg. Khim., 1966, **11**, 2700 [Russ.J.Inorg.Chem., 1966(12)].
62. Yu.Ya.Kharitonov and N.A.Knyazeva, Zhur.Neorg. Khim., 1966, **11**, 2713 [Russ.J.Inorg.Chem., 1966(12)].
63. Yu.Ya.Kharitonov and N.A.Knyazeva, Radiokhimiya, 1967, **9**, 322.
64. Yu.Ya.Kharitonov and N.A.Knyazeva, Symposium, "Kolevatel'nye Spektry v Neorganicheskoi Khimii" (Vibrational Spectra in Inorganic Chemistry), Izd. Nauka, Moscow, 1971, p.219.
65. L.V.Kobets, V.S.Popov, L.P.Savchenko, I.K.Skutov and D.S.Umreiko, Koord.Khim., 1978, **4**, 406.
66. L.V.Kobets, G.N.Klavsut', and D.S.Umreiko, Zhur. Neorg.Khim., 1981, **26**, 173 [Russ.J.Inorg.Chem., 1981(1)].
67. V.M.Vdovenko, D.N.Suglobov, and V.A.Krasil'nikov, Radiokhimiya, 1963, **5**, 311.
68. L.M.Kovba, V.K.Trunov, and A.I.Grigor'ev, Zhur. Strukt.Khim., 1968, **6**, 919.
69. G.L.Galow, A.B.Van Cleaven, and R.Z.Foger, Canad J.Chem., 1960, **38**, 772.
70. N.Dao, Quy Nguyen, and M.Knidiri, Compt.rend., 1974, **C279**, 1145.
71. V.N.Vdovenko, L.G.Mashirov, A.I.Skoblo, and D.N.Suglobov, Zhur.Neorg.Khim., 1967, **12**(11), 2914 [Russ.J.Inorg.Chem., 1967(11)].
72. L.V.Kobets and D.S.Umreiko, Zhur.Prikl.Spektrosk., 1985, **43**(2), 240.

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