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Influence of Ligand Substitution on Uranium–Ligand Bond Energies in the Equatorial Plane of Uranyl Compounds*

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Abstract—In this paper, a general treatment of the chemical mutual influence of ligands in the equatorial plane of the uranyl ion UO_2^{2+} is described. The description based on the use of empirical theoretical methods. In the frame of these methods, the uranium–ligand bond energies in the coordination sphere of the uranyl compounds $UO_2(NO_3)_2L_2$ and $UO_2(C_2O_4)_2L_2$ (L is mono- or bidentate ligand) are calculated. Two kinds of regularities are considered and classified: the proportional dependence between the bond energy of L and bond energy of other ligands ("Fid-effect" of the first type) and the reversibly proportional dependence between these bond energies ("Fid-effect" of the second type). The chemical nature of both effects is described. The ligands are classified in the frame of potential application for liquid–liquid extraction.

When two or more ligands (L) are involved in mixed complexes, the mutual perturbation of the electron structure of each ligand occurs through the interaction between all ligands and between the ligands and the metal ion (M) [1–3]. In 1926, I. Chernayev [1] put forward the fruitful idea that the ligands in the first coordination sphere of M have influence on each other, resulting in a weakening or strengthening of the metal–ligand bonds, i.e. a decreasing or increasing D_0(M–L) bond energy. These regularities, observed for complexes with a square (CN = 4) or octahedral (CN = 6) coordination of M, were called the "trans-effect". The first attempts at understanding the trans-effect were made in the theory of Chatt and Orgel [2, 3]. First, the mechanism of ligand substitution was investigated. Second, the chemical properties connected with the reaction ability were separated from those depending on the thermodynamic parameters of coordinated bonds.

Indeed, the study of the effects of the mutual influence of ligands in mixed complexes is relevant at present, especially for application in liquid–liquid extraction reactions in which one only deals with mixed complexes. Systematic investigations of the structure of mixed complexes were scarce up to this study. Moreover, the old theoretical concepts [1–3] concern mostly complexes of *d*-transition elements with CN = 6. The theoretical concepts of the mutual influence of ligands in *f*-element mixed complexes, especially actinide (An) complexes, have not yet been developed. Moreover, their interpretation in such complexes is not trivial since no direct measurements of An–L bond energies were made and the thermodynamic data are very poor in this field.

However, one must keep in mind that theoretical predictions remain qualitative, since the mixed actinide and lanthanide complexes are complicated and the calculation of M–L bond energies in the frame of molecular orbital methods is not always possible. In the problem of the mutual influence of ligands, one has to recognize several effects: (1) the importance of the M–L bond type, (2) the possibility of a direct $L^1 \longrightarrow M$ and back donation $L^2 \longleftarrow M$, $L^3 \longleftarrow M$, (3) the repulsion between ligands, (4) the geometry factors, and (5) the interaction of ligands with solvents [4].

In the general case, donor–acceptor and steric interactions are thought to be the most important. Thus, it appears necessary to classify the interactions as steric and electron-donor–acceptor ones.This work is aimed at considering the thermodynamic (or energetical) aspect of the mutual influence of ligands in the equatorial plane of the uranyl cation UO_2^{2+} with CN = 6. For this purpose, uranyl amide complexes $UO_2(NO_3)_2Am_2$ (Am is monoamide $R^1C(O)NR^2R^3$) formed during the extraction of uranyl ions from a nitric acid solution by monoamides were considered [5]. However, in order to draw general conclusions about the mutual ligand effects, it is important to have an experimental data base that is as large as possible. Thus, numerous data concerning uranyl oxalate complexes $UO_2(C_2O_4)_2L_2$ were also analyzed.

The equatorial plane of UO_2^{2+} has an important peculiarity. The plane is slightly deformed (i.e., it

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Table 1. R_e(U–L) distances for all U–O and U–N bonds in $[UO_2(NO_3)_2Am_2]$ complexes (Am = $R^1CONR^2R^3$)

Amide	R^1	R^2	R^3	R_e(U=O), Å	R_e(U–O_{Am}), Å	R_e(U–O_{NO_3}), Å	R_e(U–N_{NO_3}), Å
DBBA	C_3H_7	C_4H_9	C_4H_9	1.765, 1.766	2.367, 2.389	2.495, 2.508, 2.491, 2.504	2.880, 2.874
DBBzA	Ph	C_4H_9	C_4H_9	1.766, 1.766	2.371, 2.365	2.486, 2.502, 2.483, 2.503	2.864, 2.847
DBcHA	cHexyl	C_4H_9	C_4H_9	1.763, 1.766	2.362, 2.381	2.495, 2.508, 2.487, 2.501	2.878, 2.869
DBDA	C_9H_{19}	C_4H_9	C_4H_9	1.766, 1.763	2.368, 2.368	2.491, 2.503, 2.491, 2.503	2.871, 2.871
DBDDA	$C_{11}H_{23}$	C_4H_9	C_4H_9	1.767, 1.765	2.360, 2.376	2.488, 2.507, 2.499, 2.511	2.869, 2.886
DBHA	C_5H_{11}	C_4H_9	C_4H_9	1.766, 1.764	2.364, 2.372	2.494, 2.504, 2.487, 2.500	2.875, 2.866
DBiBA	$CH(CH_3)_2$	C_4H_9	C_4H_9	1.764, 1.766	2.365, 2.357	2.489, 2.501, 2.491, 2.502	2.871, 2.869
DBOA	C_7H_{15}	C_4H_9	C_4H_9	1.766, 1.764	2.366, 2.372	2.490, 2.501, 2.492, 2.504	2.869, 2.875
DBtBA	$C(CH_3)_3$	C_4H_9	C_4H_9	1.766, 1.765	2.357, 2.362	2.484, 2.504, 2.486, 2.503	2.866, 2.853
DcHBA	C_3H_7	cHexyl	cHexyl	1.766, 1.766	2.361, 2.361	2.488, 2.505, 2.488, 2.505	2.871, 2.871
DEODA	$C_{17}H_{35}$	C_2H_5	C_2H_5	1.766, 1.765	2.367, 2.361	2.493, 2.506, 2.486, 2.500	2.875, 2.864
DHBA	C_3H_7	C_6H_{13}	C_6H_{13}	1.766, 1.763	2.398, 2.370	2.491, 2.504, 2.495, 2.508	2.883, 2.874
DHiBA	$CH(CH_3)_2$	C_6H_{13}	C_6H_{13}	1.764, 1.766	2.353, 2.362	2.491, 2.504, 2.486, 2.500	2.863, 2.872
DOBA	C_3H_7	C_8H_{17}	C_8H_{17}	1.766, 1.763	2.398, 2.375	2.490, 2.504, 2.494, 2.515	2.874, 2.875
DOiBA	$CH(CH_3)_2$	C_8H_{17}	C_8H_{17}	1.765, 1.766	2.352, 2.361	2.485, 2.501, 2.489, 2.501	2.861, 2.869
DPhBA	C_3H_7	C_4H_9	Ph	1.766, 1.762	2.409, 2.409	2.499, 2.497, 2.495, 2.503	2.881, 2.868
MBHA	C_5H_{11}	CH_3	C_4H_9	1.763, 1.766	2.377, 2.370	2.489, 2.508, 2.488, 2.502	2.870, 2.869
MBOA	C_7H_{15}	CH_3	C_4H_9	1.766, 1.763	2.369, 2.369	2.490, 2.502, 2.490, 2.502	2.870, 2.870
MBDA	C_9H_{19}	CH_3	C_4H_9	1.766, 1.763	2.370, 2.370	2.490, 2.503, 2.490, 2.503	2.870, 2.870

remains perpendicular to the UO_2^{2+} axial group) whatever the ligand volume. Only the perimeter of the coordination sphere changes accordingly with the U–L bond lengths R_e(U–L). Thus, steric effects have an impact on bond lengths but do not influence the O=U–L angles.

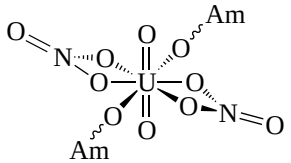
The theoretical methods chosen for this study allowed us to distinguish the various cases of steric weakening (strengthening) of bonds in the equatorial plane. This effect ("Fid-effect") was described in [4] for the lanthanide nitrate complexes with malonamide ligands having CN = 8. In this work, the investigation is extended in the frame of the structural-thermodynamic model (STM) considered in [4]. Existing quantum-chemical methods do not allow one to describe quantitatively the geometry of large-size uranyl amide complexes. That is why we used more empirical methods in our calculations. It turns out that satisfactory results may be obtained in the frame of molecular dynamics (MD) methods with accurately chosen empirical parameters for description of the U–L bonds [5].

The general procedure of the U–L bond energy calculation presented here employs a combination of MD simulations and STM. The approach allows one to calculate D_0(U–L) bond energies depending on the nature of the interaction between ligands in the first coordination sphere. To our knowledge, the calculations of U–L bond energies for a large set of uranyl complexes are presented for the first time.

The sum of bond energies for all bonds of the equatorial plane D_0(U–L) determines the formation enthalpy of isolated complexes and consequently, the formation enthalpy of complexes in the two-phase extraction process if the complex formation, in the organic phase, corresponds to the coordination mechanism [4]. The experimental values of extraction enthalpies may be used to discuss the ligand effects in the first coordination sphere of complexes.

MOLECULAR DYNAMICS (MD) SIMULATIONS

In the present work, the equilibrium geometry of uranyl nitrate complexes of the type $[UO_2(NO_3)_2Am_2]$ with bidentate nitrate groups and monodentate monoamides,



was calculated using MD simulations for 19 complexes with the monoamides listed in Table 1. Every complex is considered, in vacuum, to be an isolated species even if the parameterization of the MD methods was made on the basis of data for the solid state [5]. Calculations were performed using the Insight II program from Molecular Simulations Inc. [6] on a R10000 Silicon

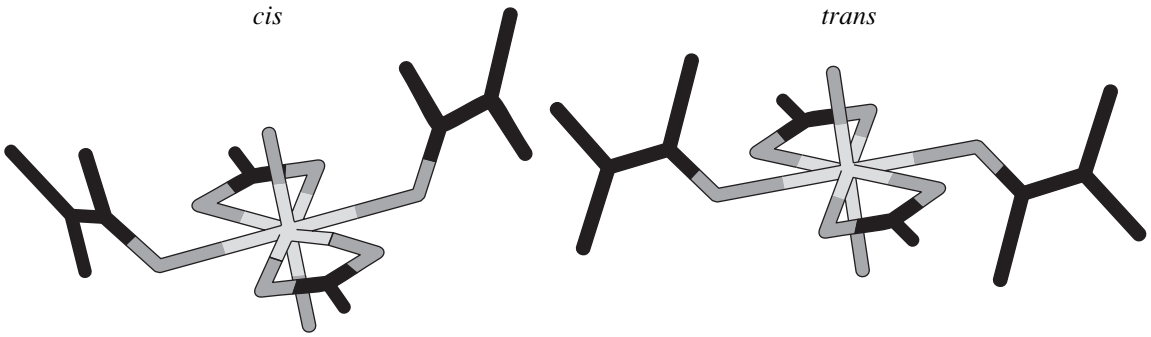


Fig. 1. *Cis*- and *trans*-conformations of $[UO_2(NO_3)_2Am_2]$ complexes considered as starting geometries for the MD simulations of the nineteen complexes.

Graphics workstation. The molecular systems were considered in vacuum for these calculations. The "cvff" [7] molecular mechanics force field was used for the calculations. The "cvff" potential energy was the following:

$$E = \sum_{\text{bonds}} k_r(r - r_0)^2 + \sum_{\text{angles}} k_\theta(\theta - \theta_0)^2 + \sum_{\text{dihedrals}} k_\varphi\left[1 + \cos(n\varphi - \varphi_0)\right] + \sum_{sp^2} k_\chi \times [1 + \cos(2\chi - 180)] + \sum_{i,\, j(j>i)} \left(\frac{\sqrt{A_i A_j}}{r_{ij}^{12}} - \frac{\sqrt{B_i B_j}}{r_{ij}^{6}}\right) + \sum_{i,\, j(j>i)} \frac{q_i q_j}{\varepsilon r_{ij}},$$

where r_0 is the ideal bond length and k_r is the force constant for bond length deformations, θ_0 is the ideal angle and k_θ is the force constant for bond angle deformations, φ_0 is the ideal dihedral and k_φ is the force constant for rotations around bonds, χ is the ideal angle and k_χ is the force constant for out-of-plane deformations, A and B are the Lennard–Jones parameters and r_{ij} is the interatomic distance, q_i and q_j are the atomic charges, and ε is the dielectric constant.

The force field parameters used to describe U interactions with other atoms were added in the "cvff" force field [7] according to the "Valence Force Field" procedure, where the bonds between the metal ion and ligands are described in an explicit manner [8].

MD simulations of 100 ps were performed in the gas phase at 500 K, with a time step of 1 fs in order to explore conformational space. For each simulated complex, two different initial geometries (*cis* and *trans*) were considered (Fig. 1), and after each MD, ten conformations were selected in order to minimize their energies; i.e. for each considered uranyl nitrate complex, twenty conformations were minimized. The conformation with the lower energy was then selected and the U–O and U–N distances were analyzed. The results of quantitative evaluations of the equilibrium internuclear distances R_e(U=O) and R_e(U–O_L) are given in Table 1.

The monodentate amide group is connected with the uranium atom by the oxygen atom of the O=C< amide group, which has a planar structure. The interaction of monoamide with other ligands in the equatorial plane of the uranyl cation depends on the molecular volume of the R^1, R^2, and R^3 groups (i.e. on the steric factors) of the monoamides. One may thus expect a change in the equilibrium internuclear distances R_e(U–O_L) in uranyl amide complexes to depend on the structure of the monoamide without any aforenoted deformation of the equatorial plane. Of course, this is only valid if the R^1, R^2, and R^3 radicals of the amides do not greatly differ from each other. This means that with a change in R^i (i = 1, 2, 3) there is no redistribution of the electron density in the amide carbonyl groups. Thus, in this sense, the classification of similar monoamides should be of importance.

EQUATIONS OF THE STRUCTURAL-THERMODYNAMIC MODEL

Let us write the total electronic energy (E_{tot}) for the system with i atoms and j bonds through pair interactions:

$$E_{\text{tot}} = \sum_i E_{\text{at},\, i} + \sum_j D_{0,\, j}, \qquad (1)$$

where $E_{\text{at},\, i}$ is the total electron energy of an atom i and $D_{0,\, j}$ is the interaction energy of a j^{th} pair of atoms. In the simple case of a diatomic molecule A_2, the equations of STM [4] are written as

$$D_0(\text{AA}) = k\theta_{\text{A}}^2, \qquad (2)$$

$$\ln\theta_{\text{A}} = \chi_{\text{SI}}^{di}(\text{A}) + \gamma(\text{AA}), \qquad (3)$$

where k = 1 eV and D_0(AA) is the summation of the structural independent parameters χ_{SI}^{di}(A) and the struc-

tural dependent component γ(AA):

$$\gamma(\mathrm{AA}) = \frac{R_0^2 - R_e^2}{R_0 R_e}, \quad (4)$$

where R_0 is the radius of an atom in the ground state, which corresponds to the maximum of the radial function for the outer electronic shell. In the case of the hydrogen atom, R_0 is the Bohr radius a_0 = 0.529167 Å, which is calculated theoretically and evaluated from experimental spectral measurements. The values of R_0 may be evaluated from the solution of Dirac–Fock equations. The value $\chi_{\mathrm{SI}}^{di}(\mathrm{A})$ is an empirical parameter [4]. In the first approximation, this value may be considered as the relative chemical potential (RCP) of an atom in a molecular system: $\chi_S^{\mathrm{A}} = \frac{\mu_{\mathrm{A}}}{\mu_0}$ and $\mu_{\mathrm{A}} = -\left(\frac{\partial E}{\partial N}\right)_N$, where μ_{A} is the chemical potential normalized accordingly to the Li atom in molecule Li_2(gas) and N is the number of electrons.

The equations of STM may be extended to the AB molecule and may be written as

$$D_0(\mathrm{AB}) = k\theta_{\mathrm{A}}\theta_{\mathrm{B}} = k\exp\left\{\sum_{\mathrm{A,B}}\chi_{SI}^{di} + \sum_{\mathrm{A,B}}\gamma(\mathrm{AB})\right\} \quad (5)$$

with

$$\sum_{\mathrm{A,B}}\chi_{SI}^{di} = \chi_{SI}^{di}(\mathrm{A}) + \chi_{SI}^{di}(\mathrm{B}) = \chi_{SI}^{di}(\mathrm{AB})\exp\left(\frac{R_e - R_e^{di}}{R_e + R_e^{di}}\right), \quad (6)$$

where R_e(A–B) and R_e^{di}(A–B) are the equilibrium distances of the A–B bond in the considered compound and in the AB diatomic molecule, respectively.

In the case of a given type of bond (for example, U–O), the value χ_{SI}^{di}(U–O) is constant. For the use of STM, the following scheme of calculations is applied.

1. Calculation of χ_{SI}^{di}(A–B) using the experimental data for diatomic molecule AB(g) in its ground state. It is necessary to know the values of R_e^{di}(A–B) and D_0^{di}(A–B).

2. Evaluation of $\sum_j D_{0,j}$ for the given compound of its fragments using χ_{SI}^{di}(A–B) calculated in the first step and the equilibrium distances of A–B bonds in the considered molecular systems.

The scheme of calculations may involve supplementary steps if data for diatomic molecules in the gas phase are unknown. In this case, the system of equations for di- or many-atomic molecules may be used. These molecules must be reliable reference molecules. From the system of equations, the values of χ_{SI}^{di}(A–B), D_0^{di}(A–B), and R_e^{di}(A–B) may be calculated and the unknown parameters of the molecular systems may be predicted. This approach will be used to calculate the $D_0(\mathrm{U–O_L})$ and $D_0(\mathrm{U–N_L})$ bond energies in the uranyl complexes.

THE APPLICATION OF STM FOR THE CALCULATION OF U–O AND U–N BOND ENERGIES [9]

The next step in the calculation procedure is the evaluation of D_0(U–O) in the frame of STM [4], which uses previously calculated equilibrium internuclear distances R_e(U–O). An investigation of the problem of the semiempirical quantitative relation R_e vs D_0 has already been made by Zachariasen [10], who used the idea of U–L bond strength in the framework of Pauling's valence principle [11]. Namely, the average bond strength (bond order (S)) is equal to the V formal valence of the metal ion divided by coordination number: S = V/CN. The sum of the strength of bonds for U^{6+} was accepted to be constant to within 10%.

Here, we use a completely new type of relation R_e vs D_0 for U–L bonds that had been used earlier to calculate bond energies for Ln–O bonds [4, 12]. This approach has the advantage of not being limited by the formal valence of the metal ion, i.e., by the outer orbitals of the uranium atom. Let us consider the choice of the parameter for the uranium compounds. The main equation of STM for the complexes involving U–O bonds may be written as

$$\chi_{SI}^{di}(\mathrm{UO}) = \ln D_0^{di}(\mathrm{UO}) - \frac{R_0(\mathrm{U})^2 - R_e^{di}(\mathrm{UO})^2}{R_0(\mathrm{U})R_e^{di}(\mathrm{UO})} - \frac{R_0(\mathrm{O})^2 - R_e^{di}(\mathrm{UO})^2}{R_0(\mathrm{O})R_e^{di}(\mathrm{UO})}, \quad (7)$$

where D_0(U–O) is the interaction energy in the U–O bond; R_0(U) and R_0(O) are the radii of maximal electron density of the outer orbital in the ground state of U and O free atoms, respectively; and R_e^{di} are the parameters of the diatomic gas-phase molecule UO(g) in the ground state. The values of R_0(U) and R_0(O) were calculated according to the Hartree–Fock–Dirac method, accurately taking into account the relativistic and other corrections [13]. They are equal to 1.9352 and 0.4628 Å, respectively.

Known experimental data do not allow one to calculate the parameter χ_{SI}^{di}(U–O) using only one equation, as noted in the end of the previous section. It is necessary to solve the system of equations with careful anal-

ysis of all accessible experimental data for the simple systems UO(g.), UO_2(g.), and UO_3(g.).

The uncertainty in the calculated thermodynamic functions UO(g.) at low temperatures is caused by the uncertainty of the ground state type. The evaluation of energy for hundreds of connected valence states belonging to the configuration of molecular shell and to the lowest configuration of the uranium atom is very complicated. The D_0(U–O(g.)) dissociation energy was determined experimentally and is equal to 750 ± 15 kJ/mol. However, the R_e(U–O(g.)) value is not known and was evaluated from a comparison with R_e(La–O(g.)), R_e(Th–O(g.)), and R_e(W–O(g.)) [14]. This indirect evaluation results in R_e(U–O(g.)) = 1.82 ± 0.05 Å.

Th UO_2 molecule has a linear structure corresponding to the point symmetry group D_h. Similar indirect evaluations result in an interatomic distance of R_e(U–O(g.)) = 1.80 ± 0.05 Å in UO_2(g.). On the other hand, the HF and MP2 quantum-chemical methods give values of R_e(U–O(g.)) = 1.817 and 1.797 Å, respectively [15]. The formation enthalpy of the molecule UO_2(g.) in the ground state is $\Delta_f H^0(UO_2(g.)) = -476.2 \pm 20$ [14] or –467.2 ± 2 kJ/mol with the accepted enthalpy of formation of an uranium atom in the ground state $\Delta_f H^0(U(g.)) = -536 \pm 8$ kJ/mol [14].

There are no experimental data concerning the electronic states of the UO_3(g.) molecule. In [14], the enthalpies of formation were given to be $\Delta_f H^0(UO_3(g.))$ = –795.2 ± 15…–816 ± 2 kJ/mol for the ground-state molecule. IR investigations of UO_3(g.) in an argon matrix have shown that the point symmetry group of the gas-phase molecule in C_{2v} with two different equilibrium internuclear distances R_e(U–O) = 1.79 ± 0.05 Å for the first U–O bond and R_e(U–O) = 1.76 ± 0.05 Å for the two other bonds. However, a convenient reference compound for use in STM may be UO_2(cr.) in the cubic modification (structural fluorite type with CN = 8). The lattice parameter of UO_2(cr.) is a_0 = 5.471 Å and R_e(U–O) = 2.3689 ± 0.001 Å [14]. The bond energy D_0(U–O) is easily calculated (264.3 kcal/mol) from the equation

$$\Delta_f H^0(UO_2(cr.)) = \Delta_f H^0(U) + 2\Delta_f H^0(O) - 8D_0(U\text{–}O) \quad (8)$$

with $\Delta_f H^0(UO_2(cr.))$ = –1085, $\Delta_f H^0(U)$ = 536, and $\Delta_f H^0(O)$ = 246.8 kJ/mol.

The next step in using STM is the joint solution of the STM equations for UO(g.) and UO_2(cr.) in order to obtain R_e^{di}(U–O) and χ_{SI}^{di}(U–O). From the solution to the system of equations, one gets χ_{SI}^{di}(U–O) = 5.5071 and R_e^{di}(U–O) = 1.7 Å with D_0^{di}(U–O) = 765.5 ± 10 kJ/mol.

These parameters may be used for the UO_2(g.) molecule. With $\Delta_f H^0(UO_2(g.)) = -467.2$ and D_0(UO) = 748.4 kJ/mol, one gets R_e(U–O) = 1.797 ± 0.003 Å from the equations of STM. This value is in line with the results of quantum-chemical calculations at the MP2 level of theory [15].

Table 2. D_0(U–L) (kJ/mol) bond energies in the $[UO_2(NO_3)_2Am_2]$ complexes calculated using STM (Am = $R^1CONR^2R^3$)

Amide	$\Sigma D_0(U\text{–}O_{NO_3})$	$\Sigma D_0(U\text{–}N_{NO_3})$	$\Sigma D_0(U\text{–}O_{Am})$
DBBA	831.35	217.03	517.07
DBBzA	840.40	224.91	526.34
DBcHA	833.97	218.30	523.11
DBDA	835.07	219.18	526.34
DBDDA	830.98	216.87	526.39
DBHA	836.20	219.39	526.34
DBiBA	836.94	219.55	532.99
DBOA	835.44	218.84	525.39
DBtBA	839.27	223.42	534.42
DcHBA	835.86	219.18	532.97
DHBA	831.35	216.49	511.59
DHiBA	837.73	220.48	536.36
DOBA	829.54	217.93	509.25
DEODA	836.22	219.75	530.13
DOiBA	839.60	221.38	537.32
DPhBA	832.78	217.94	488.98
MBHA	835.50	219.73	521.17
MBOA	836.58	219.55	525.39
MBDA	835.83	219.55	524.45

Using the same calculation procedure and R_0(N) = 0.5389 Å [13], it is also possible to calculate the quantities χ_{SI}^{di}(U–N) = 4.8978 and R_e^{di}(U–N) = 1.898 Å. Note that, in the $[UO_2(NO_3)_2Am_2]$ compounds (Am is monoamide), there is no chemical bond with the N atom of the nitrate anion. However, in such complexes, the N atom is at a distance of less than 3 Å from the U atom, such that the interaction energies between the U and N atoms are not negligible. This is why we considered this interaction here.

DISCUSSION OF RESULTS

The case of proportional dependence between the sum of U–O(nitrate) and the sum of U–O(amide) bond energies (Fid-effect of the first type)

In Table 2, the results of calculations of D_0(U–O) and D_0(U–N) in $[UO_2(NO_3)_2Am_2]$ complexes on the basis of R_e(U–O) and R_e(U–N) are given. Figure 2 shows a proportional dependence between ΣD_0(U–

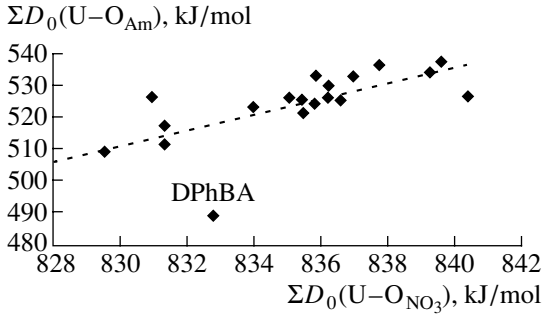


Fig. 2. Correlation between $\Sigma D_0(U-O_{NO_3})$ and $\Sigma D_0(U-O_{Am})$ for the $[UO_2(NO_3)_2Am_2]$ complexes.

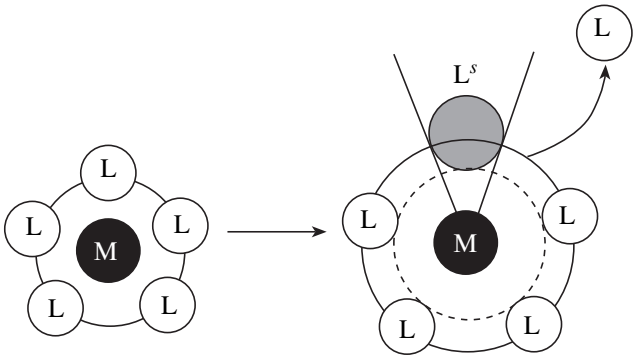


Fig. 3. Schematical illustration of the Fid-effect of the first order.

O_{NO_3}) and $\Sigma D_0(U-O_{Am})$. This is a general trend indicating that the weakening of U–O bonds with monoamide ligands is accompanied by the weakening of the four bonds with bidentate nitrate groups: $D_0(U-O_{NO_3})$ increases when $D_0(U-O_{Am})$ increases. This trend is not valid for complexes with DPhBA; this can be explained by the higher steric hindrance of the two phenyl R^1 and R^2 substituents on the monoamide ligand. For this complex, $D_0(U-O_{Am})$ is very low compared to other complexes, meaning that the U–O bond distance is large.

The weakening of nitrate bonds with the introduction of monoamide ligands, which are more sterically hindered than nitrate ions, is called the Fid-effect of the first order and is illustrated in Fig. 3.

The Case of Reversibly Proportional Dependence between the Sum of the U–O_{NO_3} and the Sum of the U–O_{Am} Bond Energies is the Fid-effect of the Second Order

Let us now consider the opposite case, namely, a reversibly proportional dependence between the considered values D_0. Let us propose that the interaction energy of a ligand coming into the coordination sphere of the uranium atom results in an energy of sterical repulsion of this ligand by other ligands in the equatorial plane. In this case, with decreasing $R_e(U-O_{Am})$, the values $D_0(U-O_{Am})$ increase but the values $D_0(U-O)$ with other ligands (anions) decrease. The introduction of ligand A into the coordination sphere increases the coordination sphere perimeter. This effect is called the Fid-effect of the second order.

This type of interaction can be discussed for uranyl compounds with total CN = 6 (in the equatorial plane). From a structural point of view, complexes with bidentate substituents $L = R^1R^2NO^-$ were studied in detail in [16–22]. That is why this class of complexes was selected in order to demonstrate the Fid-effect of the second order. For this purpose, various oxalato complexes of known X-ray solid-state structure have been considered [22]. The results of the structural analysis of these data are presented in Table 3 together with the results of the application of STM for these complexes.

In the structural analysis of complexes 1 to 5, the average U–O distances with the oxalate anions were considered and the bond energies were summed over the four U–O distances of the two bidentate anions. Note that, for the complex 2, oxalate anions are bridged between several metallic centers; that is why only four U–O distances were considered even when the complex formula exhibited three oxalato groups. Finally, in complex 6, the oxalate groups are coordinated by different oxygen atoms relative to the C–C bond in the equatorial plane [23]. One oxalate group differs from the two others and exhibits a longer U–O bond distance.

The difference in the bond energies of different oxalate groups (two oxalate groups at short distances and one at long distannces) for complex 6 is $\Delta = 107.1 \pm 20$ kJ/mol. For comparison, we can note that the difference in the bond energy of oxalate group and, for example, *N*-methylhydroxylamine in complex 1 is $\Delta = -78.72$ kJ/mol.

In Fig. 4, the dependence between Δ and $\sum_{i=1}^{4} D_0(U-O_L)_{av}$ is given for complexes 1–6 considered above. The deviation of points form $\Delta = 0$ in Fig. 4 characterizes the donor–acceptor properties of the substituting ligand (L^s) relative to the "main" oxalate ligands. Accordingly to the donor–acceptor properties, electron density redistribution in the complexes takes place with the participation of the uranyl group. Thus, one sees that the effect of electron density redistribution for various L is reflected in the experimental values $R_e(U-O)$. In MD methods, these electronic factors are impossible to take into account.

The General Case of Manifestation of Both Effects

In the correlation $D_0(U-O_{L^s})$ with $D_0(U-O_L)$, the number of complexes can be extended in order to make

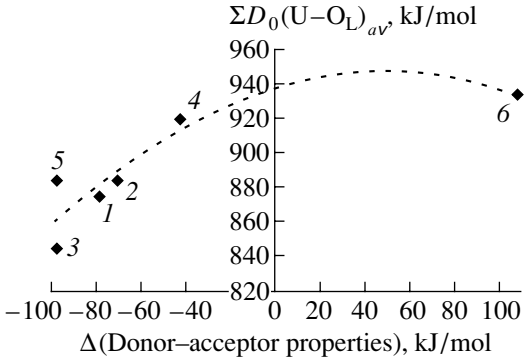


Fig. 4. Dependence of the donor–acceptor properties (Δ value) of the substituting ligand on the total bond energy of bonds U–O_L for complexes *1–6*.

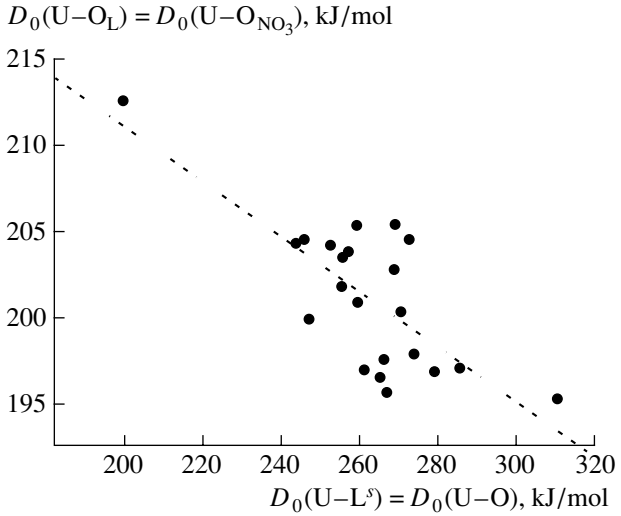


Fig. 5. The energetics of the Fid-effect for the interaction of P=O and C=O groups with the uranyl cation.

the correlation more reliable. Using the X-ray data from [24] for the $[UO_2(NO_3)_2L^s_2]$ complexes, where L^s is a monodentate ligand involving C=O and P=O groups, the values $D_0(U–O_{L^s})$ were correlated with $D_0(U–O_L)$ for 22 complexes in which there are U–O_L bonds (Fig. 5). In these complexes, the $D_0(U–O_{L^s})$ bond energy changes are approximately 100 kJ/mol. The correlation in Fig. 5 demonstrates that the Fid-effect of the second order predominates, although a partial superposition of the Fid-effect of the first order exists. The superposition of Fid-effects of the first and second order results in scattering of points. The scattering of points is also due to the uncertainty in the experimental values of R_e(U–O), which is 0.01–0.04 Å. It is impossible to subdivide completely both Fid-effects. However, in series of similar compounds, it is useful to distinguish trends in the studied dependences. This approach makes it possible to analyze the manifestation of different steric effects.

Table 3. D_0(A–B) bond energies in uranyl oxalato complexes calculated in using STM

No.	Complex	Bond distances, Å			Bond energy, kJ/mol	
1	$[UO_2(C_2O_4)(CH_3NHO)]^{3-}$ [22]	Oxygen (oxalato)	R_e(U–O)	2.475*	ΣD_0(U–O)	874.0
		Oxygen (ligand)	R_e(U–O)	2.321	D_0(U–O)	288.0
		Nitrogen	R_e(U–N)	2.390	D_0(U–N)	227.7
2	$[(UO_2)_2(C_2O_4)_3(i\text{-}C_3H_7NHO)]^{4-}$ [22]	Oxygen (oxalato)	R_e(U–O)	2.469*	ΣD_0(U–O)	883.5
		Oxygen (ligand)	R_e(U–O)	2.287	D_0(U–O)	306.2
		Nitrogen	R_e(U–N)	2.449	D_0(U–N)	206.3
3	$[UO_2(C_2O_4)\{(CH_3)_2NO\}]^-$ [22]	Oxygen (oxalato)	R_e(U–O)	2.495*	ΣD_0(U–O)	843.2
		Oxygen (ligand)	R_e(U–O)	2.30	D_0(U–O)	299.1
		Nitrogen	R_e(U–N)	2.41	D_0(U–N)	220.2
4	$[UO_2(C_2O_4)_2(ONC(CH_3)CHNOH)]^{3-}$ [22]	Oxygen (oxalato)	R_e(U–O)	2.447*	ΣD_0(U–O)	919.1
		Oxygen (ligand)	R_e(U–O)	2.305	D_0(U–O)	296.4
		Nitrogen	R_e(U–N)	2.451	D_0(U–N)	205.6
5	$[UO_2(C_2O_4)_2(CH_3)_2CNO]^{3-}$ [22]	Oxygen (oxalato)	R_e(U–O)	2.469*	ΣD_0(U–O)	883.5
		Oxygen (ligand)	R_e(U–O)	2.27	D_0(U–O)	315.6
		Nitrogen	R_e(U–N)	2.40	D_0(U–N)	223.9
6	$[UO_2(C_2O_4)_3]^{4-}$ [23]	Oxalato (short)	R_e(U–O)	2.438*	ΣD_0(U–O)	934.0
		Oxalato (long)	R_e(U–O)	2.583	ΣD_0(U–O)	360.0

* Average values of the U–O bond lengths between the U and oxalate groups.

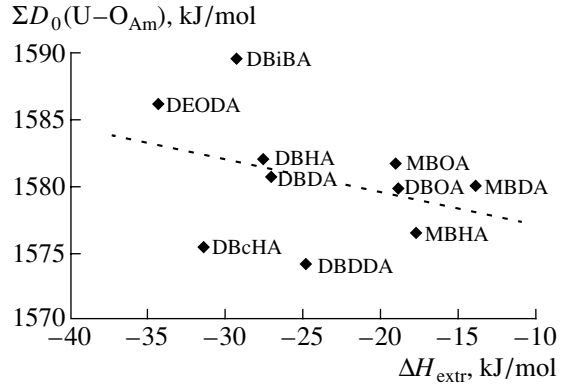


Fig. 6. The qualitative trend in the correlation between the sum of bond energies D(U–O_{Am}) and experimental values of ΔH_{extr} (see text).

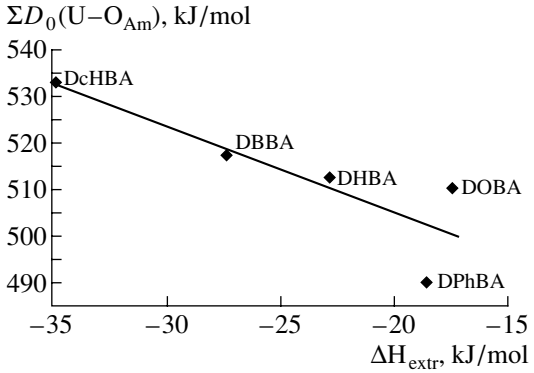


Fig. 7. Correlation between the sum of bond energies D(U–O_{Am}) and experimental values of ΔH_{extr}.

DETERMINATION OF EXTRACTION ENTHALPY USING DATA CALCULATED WITH STM

Our results in the field of monoamides and the Fid-effect of the first order may by reinforced by the experimental energy parameters. Here, thermochemical data for complexation in the extraction processes are used. With the coordination type of extraction corresponding to small concentrations of nitric acid in the two-phase system "aqueous solution–$\overline{\text{organic phase}}$", the extraction reaction is written as

$$UO_2^{2+} + 2NO_3^- + 2\overline{Am} \rightleftharpoons \overline{UO_2(NO_3)_2Am_2}\ (\Delta H_{extr}). \quad (9)$$

In the literature [25–32], the ΔH_{extr} values have been determined for extraction reactions with different monoamides (Am) (Table 4). In accordance with [4], ΔH_{extr} is expected to correlate linearly with D_0(U–Am)

Table 4. Available experimental data concerning uranyl nitrate extraction by monoamides $R^1CONR^2R^3$ (enthalpies of extraction and experimental conditions)

Amide	ΔH_{extr}, kJ/mol	[HNO_3], mol/l	[UO_2^{2+}], mol/l	[Am], mol/l	Diluent	T, K	Reference
DBBA	−27.20	3	Traces	0.5	Toluene	298	[25]
DBBzA	−21.76	3	Traces	0.5	Toluene	298	[25]
DBcHA	−31.38	3	Traces	0.5	Toluene	298	[25]
DBDA	−27.07	3.5	Traces		Dodecane	303	[26]
DBDDA	−24.89	3	10^{-3}	0.2	Toluene	298	[27]
DBHA	−27.61	3.5	Traces		Dodecane	303	[26]
DBiBA	−29.3	3.0	10^{-3}	0.2	Toluene	298	[25]
DBOA	−18.87	3.5	Traces		Dodecane	303	[26]
DBtBA	−25.10	3	Traces	0.5	Toluene	298	[25]
DcHBA	−34.85	2	10^{-5}	0.5	Dodecane	298	[28]
DHBA	−22.72	2	Traces	0.5		293	[29]
DHiBA	−19.80	3.0	10^{-5}	0.5		293	[29]
DOBA	−17.20	2	Traces	0.5	Dodecane	293	[30]
DEODA	−34.25	3	0.001	0.2			[31]
DOiBA	−21.40	2	Traces	0.5	Dodecane	293	[30]
BPhBA	−18.41	3	Traces	0.5	Toluene	298	[25]
MBHA	−17.71	2	?	0.5	Dodecane	298	[32]
MBOA	−19.03	2	?	0.5	Dodecane	298	[32]
MBDA	−14.10	2	?	0.5	Dodecane	298	[32]

for monoamides of the same type. In Figs. 6 and 7, the illustration of the correlation is given for two sets of monoamides: Am = $R^1CONR^3R^2$, where $R^1 = C_nH_m$; R^2 = H, C_2H_5, C_4H_9; and $R^3 = C_2H_5$, C_4H_9 (Fig. 6) and Am = $C_3H_7CONR^3R^2$, where $R^2 = C_4H_9$, C_5H_{11}, C_6H_5, C_6H_{13} and $R^3 = C_4H_9$, C_6H_{13} (Fig. 7).

There is acceptable qualitative agreement between the calculation in the frame of molecular dynamics and the STM model and extraction enthalpy. We understand that our comparison has an indirect character and that the extraction enthalpies compared arise from different experimental conditions. Further accumulation of experimental data would allow one to classify, more carefully, the ligand substituents relative to their extent of steric interaction.

Thus, it is necessary to emphasize the following. The effect of an L^s ligand substituting for other ligands in the equatorial plane of the UO_2^{2+} ion in mixed complexes, with mono- and bidentate L^s, was considered. Although the interaction of ligands in the equatorial coordination plane of the uranyl ion exhibits a complex character, it is possible to distinguish approximately two kinds of dependences between $D_0(U–O_{L^s})$ and $D_0(U–O_L)$.

The first one is a proportional correlation between $D_0(U–O_{L^s})$ and $D_0(U–O_L)$, i.e., a Fid-effect of the first type. One can present the following physical interpretation of the phenomena. Let us propose that the bond energies of ligands U–L and U–L^s in the equatorial plane insignificantly differ from one another, i.e., $D_0(U–L^s)$–$D_0(U–L)$, where D_0 is value of the order of steric interactions. In this case, the increasing volume of ligand L^s in the series of similar substituting ligands results in a more or less regular repulsion of other ligands and in a weakening of their bonds with the metal atom. Itself, substituting ligand L^s can manage (or cannot manage) the repulsion of its own molecular volume. If the volume of substituting ligand L^s is large enough, its bond with a metal atom will be weakened. This effect was shown in the case of complexes $[UO_2(NO_3)_2Am_2]$, where Am is monoamide.

The second kind of dependence between $D_0(U–O_{L^s})$ and $D_0(U–O_L)$ shows a reversibly proportional correlation which can be mainly considered in the frame of donor–acceptor interaction (Fid-effect of the second type). Although the scenario here is similar to the steric one, nevertheless, according to our calculations, the values of D_0 can be considered to be 100 kJ/mol for a series of similar substituents. In this case, the substituting ligand approaches the metal atom and moves the ligands which are weakly bonded with the metal ion away. The increase in bond energy $D_0(U–L^s)$ results in a decreasing bond energy of the metal atom with other ligands. In the general case, the Fid-effect can be represented by steric and electronic components as follows:

$$D(\text{Fid}) = D_{st}(U–L) + D_{el}(U–L).$$

These components may compensate each other, resulting in a scattering of points in the correlation plots. That is why, in mixed complexes, it is important to pick out similar sets of complexes in a determined energy interval.

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