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Calorimetric Study on Uranyl(VI) Complexes with Imidazole

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Imidazole, an important donor system in metal ion binding in bioinorganic molecules [1, 2], does not seem to be directly involved in UO_2^{+2} coordination in aqueous solutions [3, 4]. In methanol solutions, however, the imidazole nitrogens may coordinate directly to uranyl ions with formation of different molar ratio solutions [4].

The recent NMR study [4] has also shown that the kind of uranyl salt (acetate or nitrate) used may influence considerably the coordination equilibria in the studied solutions. Due to the potential importance of UO_2^{+2} imidazole interactions in bioinorganic systems we have undertaken the more quantitative study on this system.

The calorimetric results obtained for the UO_2^{+2}–imidazole complexes are presented in this communication. For the calorimetric measurements the modified method of a non-continuous calorimetric titration was used.

Experimental

Calorimetric Measurements

Calorimetric measurements were carried out in a semimicrocalorimeter at 298.15 ± 0.005 K. The temperature variations were measured by means of a thermistor with 5.10^{-4} °C precision. Two-stage water thermostate allowed to keep temperature within $\pm 5.10^{-3}$ °C range during the measuring time.

The calorimetric curve (temperature vs. time) was used to obtain the corrected temperature increment by applying the standard Dickinson method [5]. After each measurement the unit was recalibrated electrically. Each measurement of a reaction heat for a given molar ratio was carried out independently to avoid the error accumulation resulting from the non-continuous titration.

Materials

The 0.1 *M* solutions of uranyl were prepared with $UO_2(NO_3)_2\cdot 6H_2O$ (Merck) or $UO_2(CH_3COO)_2\cdot 2H_2O$ (Lachemia) in methanol. Imidazole (Loba Chemie) was also dissolved in methanol with 0.1 *M* concentration.

Results and Discussion

The results obtained from the calorimetric titrations are presented in Table I. Dilution effects of uranyl salts, as well as of imidazole, were found to be negligible. The results presented above clearly support the stoichiometry of the formed complexes found earlier with NMR experiment [4] *i.e.* $1{:}1/UO_2$: imidazole for acetate and 1:2 for nitrate solutions.

TABLE I. The Enthalpy of Formation of Imidazole Complexes with UO_2^{++} Ion in Methanole at 298.15 K.

$UO_2(NO_3)_2$–imidazole solutions		$UO_2(CH_3COO)_2$–imidazole solutions	
$\frac{n_{imid.}}{n_{UO_2^{++}}}$	Q (J)	$\frac{n_{imid.}}{n_{UO_2^{++}}}$	Q (J)
0.1667	0.67	0.1667	0.67
0.3333	1.26	0.3333	0.88
0.5000	2.38	0.5000	0.96
0.6667	2.97	0.6667	1.30
0.8333	4.27	0.8333	1.63
1.0000	5.15	1.0000	1.80
1.2000	5.90	1.5000	1.84
1.5000	7.03	2.0000	1.80
2.0000	8.79		
3.0000	9.08		
4.0000	9.08		
5.0000	9.25		

Assuming that during reactions the only source of the measured heat is a complex formation, the obtained calorimetric data were used to evaluate the complex formation enthalpies (ΔH_f) using the least squares method. The obtained values are:

$\Delta H_{f,1:1} = -6.23 \pm 0.12$ kJ/mol, for acetate

and

$\Delta H_{f,1:2} = -32.80 \pm 0.59$ kJ/mol, for nitrate solutions.

The different stoichiometry of uranyl imidazole complexes found for uranyl acetate and nitrate clearly shows the involvement of acetate anion in the direct binding of uranyl ion in methanol solution. Acetate, able to form a chelate with UO_2^{+2} ion [6], is much less disposed for the substitution by imidazole than is nitrate. Also the very high ratio of ΔH_f found for 1:2 molar ratio complex (nitrate solution)

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to that of 1:1 molar ratio complex (acetate solution) *i.e.* 5.26:1 derives most likely from the different complexation mechanisms occurring in both solutions. The strong involvement of acetate when compared to other systems in the uranyl binding is also seen in IR spectra of uranyl salts in methanol solutions (Table II).

TABLE II. Assymetric UO_2^{++} Vibration for the Different Uranyl Salts in Methanol Solution.

Compound (in methanol)	$\nu_{as}\ UO_2^{++}$ (cm^{-1})
$UO_2(NO_3)_2$	949
UO_2Cl_2	943
$UO_2(ClO_4)_2$	942
UO_2SO_4	939
$UO_2(CH_3COO)_2$	934

The lowest energy of an assymetric UO_2^{+2} situation observed for $UO_2(CH_3COO)_2$ suggests the strongest involvement of CH_3COO^- in the equatorial binding to UO_2^{+2} ion, *i.e.* distinct weakening of U–O bond. Thus in $UO_2(CH_3COO)_2$ and imidazole-containing solutions the major form seems to be a ternary complex in which the UO_2^{+2} ion binds acetate and imidazole molecules simultaneously.

Concluding, one can say that the calorimetric results have supported earlier NMR studies of uranyl (VI) imidazole solutions showing also that imidazole uranyl bond may play an important role in bioinorganic complexes.

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