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Intracomplex Compounds of Uranium (VI) with Azomethine Derivatives

It is known that, depending on the coordination capacity and structure of the ligands, as well as on certain other factors, uranium (VI) can exhibit different coordination numbers.

Alongside intracomplex uranyl compounds in which uranium has coordination number 6 ([1–3]), there are indications that certain derivatives of the formazyl and azomethine series, being tridentate ligands, form complexes with the uranyl ion in which uranium (VI) exhibits coordination number 5. On the other hand, in uranyl oxinate the coordination number of uranium may be 6 or 8, depending on the number of attached molecules of 8-oxyquinoline ([3–5]).

The present communication is devoted to the study of certain questions of the stereochemistry of intracomplex uranium compounds with Schiff bases. The intracomplex uranium compounds described can be divided into three groups depending on the nature of the ligand. We used three types of Schiff bases obtained from aromatic *o*-hydroxyaldehyde and ethylenediamine (A), an aromatic amine (B), and 2-aminopyridine (C):

[structural formulas of Schiff bases A, B, and C]

Schiff bases of the disalicylalethylenediimine type are tetradentate ligands. Analysis shows that uranium complexes of the first type always contain in their composition no more than one molecule of solvent (Table 1). Its removal occurs only after prolonged heating at 160—180°. The difficulty with which the complex loses this molecule of solvent, as well as its nature, speak in favor of the fact that here, apparently, the formation of a donor-acceptor bond takes place. Then the coordination number of uranium in such compounds is equal to 7, and with removal of the solvent molecule it becomes equal to 6.

An entirely different picture is observed in the case of uranyl complexes of the second type. These complexes contain two molecules of pyridine. They are not removed even if the preparation is kept for a long time at 160–180°. When the temperature is raised to 200–220°, the complexes decompose. Evidently, here too a donor-acceptor bond of pyridine with the central atom arises. The coordination number of uranium(VI) in such complexes is apparently 8.

Table 1

Name	Formula	Found, % U	Found, % C	Found, % H	Found, % N	Found, % R	Calculated, % U	Calculated, % C	Calculated, % H	Calculated, % N	Calculated, % R
I. Uranium disalicylalethylenediiminate	$[UO_2(C_{16}H_{14}O_2N_2)\cdot(C_2H_5OH)]$	7,82	40,89	—	—	—	7,91	—	—	—	—
Uranium di-(5-bromosalicylal)-ethylenediiminate	$[UO_2(C_{16}H_{12}N_2O_2Br_2)\cdot(C_5H_5N)]$	10,59	32,47	—	—	—	10,70	—	—	—	—
Uranium di-(5-bromosalicylal)-ethylenediiminate	$[UO_2(C_{16}H_{12}N_2O_2Br_2)]$	4,11	—	34,44	—	—	4,04	—	—	—	—
II. Uranium 2-hydroxy-1-naphthal-4-iodoanilinate	$[UO_2(C_{17}H_{11}NOJ)_2\cdot(C_5H_5N)_2]$	5,09	—	20,30	—	4,70	—	—	—	—	—
Uranium 4-methyl-salicylal-4-iodoanilinate	$[UO_2(C_{14}H_{11}NOJ)_2\cdot(C_5H_5N)_2]$	5,68	—	21,62	—	5,09	—	—	—	—	—

Name	Formula	Found, % U	Found, % C	Found, % H	Found, % N	Found, % R	Calculated, % U	Calculated, % C	Calculated, % H	Calculated, % N	Calculated, % R
III. Uranium 2-(6-bromo-2-hydroxy)-1-naphthalamino-pyridinate	$[UO_2(C_{16}H_{10}N_2OBr)_2]$	[illegible]	[illegible]	[illegible]	5,93	–	21,81	41,65	2,19	6,08	–

Earlier, one of us indicated (6) that inner-complex compounds of uranyl with Schiff bases of the 2-aminopyridine series are distinguished by very great stability, while Schiff bases of this type themselves have a strong tendency toward complex formation with the uranyl ion. It was also noted that these complexes, as a rule, are formed in the case when the heterocyclic nitrogen is in position 2 relative to the azomethine grouping.

If the uranyl complex with salicylalaniline is formed only with great difficulty, then 2-salicylalaminopyridine readily gives a complex already in a neutral medium. Since 2-salicylalaminopyridine differs from salicylalaniline only by the presence of heterocyclic nitrogen, it is natural to assume that such a sharp increase in the complex-forming ability of 2-salicylalaminopyridine may be attributed to the influence of this heterocyclic nitrogen. On the other hand, it was not possible to obtain a uranium complex with 3-salicylalaminopyridine. Consequently, the stability of the complex depends mainly on the position of the heterocyclic nitrogen relative to the azomethine grouping. Analysis of complexes of this type shows that they do not contain solvent molecules in their composition.

All that has been set forth above indicates that, in the complex compounds of uranyl with azomethine derivatives of the 2-aminopyridine series, coordination saturation of uranium(VI) takes place. This is possible only in the case when the heterocyclic nitrogen is coordinatively bonded to the central atom. The coordination number of uranium(VI) in these compounds is, in all probability, equal to 8. Thus, depending on the properties of the Schiff base, uranium exhibits a variable coordination number. Taking into account that the uranyl ion has a linear structure (7), of all possible models of the structure of uranium(VI) complexes with coordination numbers 6, 7, and 8, preference should be given to those in which the ligand atoms bonded to uranium lie in a plane perpendicular to the direction O–U–O.

According to the supposition of Connick and Hugus (8), the high stability of

structural formulas I and II

Figure 1: structural formulas I and II

structural formulas IIIa and IIIb

Figure 2: structural formulas IIIa and IIIb

UO_2^{2+} is explained by the participation of the uranium $5f$ orbitals in the formation of bonds with oxy-

Then, for coordination numbers 6, 7, and 8, the structures of the complex compounds will correspond to a tetragonal bipyramid ($5f^3 6d^2 7s$) I, a pentagonal bipyramid ($5f^3 6d^3 7s$) II, and a hexagonal bipyramid ($5f^3 6d^3 7s 7p$) III (a, b):

where $R = C_6H_4, C_6H_3Br$ (I); $R = C_6H_4, C_6H_3Br$; $R' = C_2H_5OH, C_5H_5N$ (II).

where $R = C_{10}H_6, CH_3C_6H_3$; $R' = C_6H_4J$; $R'' = C_5H_5N$ (III a); $R = C_{10}H_5Br$ (III b).

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Note: Figure translations are in progress. See original paper for figures.

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