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Corresponding Member of the Academy of Sciences of the USSR V. M. VDOVENKO, L. G. MASHIROV,

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Abstract

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Corresponding Member of the Academy of Sciences of the USSR V. M. VDOVENKO, L. G. MASHIROV,
D. N. SUGLOBOV

URANYL PERCHLORATE COMPLEXES WITH NEUTRAL LIGANDS

At present little is known about the complex chemistry of uranyl perchlorate ([1–3]). At the same time, this salt is of great interest from the standpoint of the coordination properties of the uranyl ion. The large singly charged perchlorate ion should be displaced more readily and more completely than most other anions from the coordination sphere of the central ion by other ligands. Therefore, here one may expect a stronger interaction of the uranyl ion with electron-donor molecules.

In the present work a series of uranyl perchlorate complexes with certain neutral ligands is described, and, on the basis of measurements of their vibrational spectra, the composition of the coordination sphere of uranium and the character of coordination of the perchlorate ion have been determined.

Being a polyatomic anion, the perchlorate ion in the general case can coordinate either monodentately or bidentately, attaching to the central atom through one or two oxygen atoms. Tridentate coordination with the uranyl ion, apparently, should be excluded from consideration. Coordination should distort the symmetric tetrahedral configuration of ClO_4^-, and in the infrared spectrum, instead of the two bands for the free perchlorate ion (symmetry group T_d), owing to the removal of prohibitions and degeneracies, 6 fundamental frequencies will be observed in the case of monodentate (C_{3v}) coordination and 8 frequencies in the case of bidentate (C_{2v}) coordination of ClO_4^-. The assignment of the frequencies of the ClO_4^- ion under conditions of its different coordination with the uranyl ion is given in ([1,4]).

Thus, establishing the denticity of the perchlorate ion from the number of bands in the infrared spectrum, in combination with determination of the stoichiometric composition of the complex, makes it possible to find the coordination number (c.n.) of UO_2^{2+}.

Strong organic bases—pyridine and antipyrine—a weak donor—nitromethane—and substances intermediate in base strength—camphor, tributyl phosphate, dibutyl ether, methanol, and acetonitrile—were used as ligands. The complex with antipyrine was isolated from aqueous solution, while the others were obtained by treating anhydrous uranyl perchlorate with the corresponding solvent.

The composition of the complexes was checked by analyses for uranium, water, and, in a number of cases, ClO_4^-. In the pyridinate the pyridine content was also determined. Spectra of suspensions of the complexes in Vaseline oil were measured on IKS-14 and IKS-12 spectrometers. Windows of fused silver chloride were used in the measurements.

Table 1 gives the compositions of the compounds obtained. In addition, it indicates for them the mode of attachment of ClO_4^- to the central ion (0—absence of coordination, 1—monodentate and 2—bidentate coordination), the c.n. of the uranyl ion, the frequency of the antisymmetric stretching vibration ν_3 of UO_2^{2+}, and the measure of ligand basicity according to Gordy ([5])—the shift of the OD frequency of deuteromethanol in the medium of the given liquid relative to benzene. Table 1 also gives data on uranyl perchlorate, its hydrates, and anionic complexes, taken from works ([1,4]).

As can be seen, the uranyl ion in coordination compounds of uranyl perchlorate, with the exception of anionic complexes and the complex with nitromethane, is characterized by c.n. 5. The list of compounds of $UO_2(ClO_4)_2$ with c.n. 5 apparently can be expanded to include complexes with sulfoxides and pyridine oxide described in ([2,3]). It is known that, at ordinary donor-acceptor bond lengths of 2.4-2.5 Å, no more than 5 oxygen atoms can be accommodated in the coordination sphere of UO_2^{2+} ([6]). However,

Table 1

Composition, frequency ν_3 of the uranyl ion, its coordination number, and denticity of ClO_4^- in uranyl perchlorate complexes

Ligand	Number of ligands in the complex with $UO_2(ClO_4)_2$	Denticity of ClO_4^-	C.n. UO_2^{2+}	$\nu_3 UO_2^{2+}$	$\Delta\nu_{OD}$ CH_3OD
Pyridine	5	0	5	886	187
Antipyrine	5	0	5	907	–
Methanol	–	0	–	942	–
Tributyl phosphate	2	1–2	5	952	117
Camphor	3	1	5	952	–
Water	5,7	0	5	958	–
Dibutyl ether	2	1–2	5	960	110
Acetonitrile	3	1	5	962	63
ClO_4^-	2	1	4	964	–
ClO_4^-	1	2	6	967	–

Ligand	Number of ligands in the complex with $UO_2(ClO_4)_2$	Denticity of ClO_4^-	C.n. UO_2^{2+}	$\nu_3 UO_2^{2+}$	$\Delta\nu_{OD}$ CH_3OD
Water	3	1	5	967	–
Water	1	2	5	974	–
Nitromethane	2	2	6	972	–
Uranyl perchlorate	0	2	–	996	–

in the case of coordination of polyatomic anions with closely spaced oxygen atoms, the c.n. can rise to 6. A typical example of such a situation is encountered in nitrate complexes of uranyl. The O–O distances, 2.41 Å in the ClO_4^- ion, are greater than in the NO_3^- ion (2.16 Å) and are probably close to the upper limit at which complexes with c.n. 6 are still sufficiently stable. These include the triperchlorate complex and the complex with nitromethane. The existence of the latter is undoubtedly due to the low basicity of CH_3NO_2 molecules, which at the same time are capable of being retained in the complex at a considerable distance from the uranium atom ($\sim$ 2.8 Å), mainly through ion–dipole interaction. All stronger donors, on approaching the uranium atom to shorter distances, already displace ClO_4^- ions partly or completely from the coordination sphere of uranium. In this case the c.n. of UO_2^{2+} decreases to 5.

The degree of substitution of ClO_4^- by ligands is determined by their basicity and by the polarity of the medium from which the compound crystallizes. When complexes are isolated from pyridine (dielectric constant $\varepsilon = 12$), methanol ($\varepsilon = 33$), and water ($\varepsilon = 79$), the anions are completely displaced into the outer sphere. The combination of basicity and polarity characteristic of acetonitrile is sufficient only for partial displacement of ClO_4^- (monodentate coordination). Of interest is the case of mixed mono- and bidentate coordination of ClO_4^- in complexes with butyl ether and tributyl phosphate, in which c.n. 5 is also realized. From solubility data ([7]) it follows that $UO_2(ClO_4)_2 \cdot 2C_8H_{18}O$ is an individual chemical compound. Thus, it may be assumed that in this complex and, apparently, in the complex with tributyl phosphate, one of the ClO_4^- groups is attached to the same uranium atom by two oxygen atoms, and the second by one oxygen atom.

The regular lowering of the frequencies of the valence vibrations of the uranyl group, noted for nitrate complexes of uranyl ([8]), as the

the increase in the basicity of the ligand is also clearly expressed in the case of perchlorate complexes (see Table 1). However, the latter, owing to the smaller

coordination number, or, in other words, the smaller shielding action of the anion, are characterized by larger frequency shifts.

Table 2

Shifts of $\Delta\nu_3 UO_2^{2+}$ upon coordination of ligands, per 1 ligand (in cm^{-1})

Ligand	Uranyl nitrate	Uranyl perchlorate
Acetonitrile	14	16
Ether	16	21
Tributyl phosphate	16	25
Pyridine	23	34

These shifts, which characterize the donor-acceptor interaction of uranium with the ligands, may be estimated per ligand in the following way. If one assumes that the nature of the interaction of the anions with the cation in anhydrous salts and anionic complexes (for example, in $UO_2(ClO_4)_2$ and $UO_2(ClO_4)_3^-$) is approximately the same, then from the corresponding values of the $\nu_3 UO_2^{2+}$ frequencies it is easy to find the contribution of the anions, and then of the other ligands, to the total shift. We obtain $\Delta\nu_3 ClO_4^-$ (bident.) = 29 cm^{-1}, $\Delta\nu_3 ClO_4^-$ (monodent.) = 22 cm^{-1}, and, according to (8), $\Delta\nu_3 NO_3^-$ (bident.) = 33 cm^{-1}. Hence, for the hypothetical "free" ion UO_2^{2+} with the triple bond U ≡ O, from the perchlorate data we have ν_3 = 1054 cm^{-1}, and from the nitrate data—a close figure, ν_3 = 1043 cm^{-1}. Table 2 illustrates the influence of the anion on the donor-acceptor interaction of the uranyl ion with ligands.

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