of the h0l zone is $R = 0.17$. The coordinates will subsequently be determined more accurately from three-dimensional electron density distributions and by the method of least squares.

The $[RuNO(NH_3)_5]Cl_3 \cdot H_2O$ structure can be represented as follows: the octahedral complexes are arranged with the edge of the octahedron along y in such a way that Ru, $NH_{3(1)}$ and $NH_{3(2)}$ lie on the level $y \approx {}^1\!/_4$; $NH_{3(3)}$ and $NH_{3(5)}$ at $y \approx 0$; $NH_{3(4)}$ and N at $y \approx {}^1\!/_2$. An analogous complex is situated at the level ${}^3\!/_4$. The chlorine ions and water molecules are close-packed between the octahedra in the layers $y \approx {}^1\!/_4$ and ${}^3\!/_4$. The Cl_1 and Cl_2 from the layer ${}^3\!/_4$ lie above the $NH_{3(1)}$ and $NH_{3(2)}$ lying on ${}^1\!/_4$, and the Cl_3 (${}^3\!/_4$) lies above the H_2O (${}^1\!/_4$) and vice versa. This creates columns of atoms alternating along the y axis: $-Cl-NH_3-Cl$ and $-Cl-H_2O-Cl$. In projection along this direction the complexes are arranged in a distorted hexagonal motif in which the "triangles" are occupied by chlorine ions and water molecules. The Cl atoms and the three types of particle $-H_2O$, $NH_{3(1)}$ and $NH_{3(1)}-$have approximately identical surroundings—13 or 14 nearest neighbors at distances corresponding to (or greater than) the sums of the intermolecular radii.

The structural motif of $[RuNO(NH_3)_5]Cl_3 \cdot H_2O$ shows some similarity to the structure of Chugaev's salt $[Pt(NH_3)_5Cl]Cl_3 \cdot H_2O$ [6].

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A PRELIMINARY X-RAY STUDY OF SOME TRIPHENYLOXONIUM SALTS

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The question of the structure of triphenyloxonium compounds [1] has been discussed several times in the literature and is of considerable theoretical interest. Triphenyloxonium salts have been observed to have peculiarities of behavior in electrophilic substitution reactions, for example in nitration [2]. Almost pure tri-p-nitrophenyloxonium tetrafluoroborate is formed in this reaction, whereas triphenylsulfonium, phenyltrimethylammonium and diphenylbromonium tetrafluoroborates show the m-substitution characteristic of other onium compounds, and are nitrated only in the m-position.

These peculiar properties, and also the incomparably greater stability of triphenyloxonium salts compared with the trialkyloxonium compounds, led Syrkin to propose [3] an oxanoic structure of the type $[(C_6H_5)_3O]^+X^-$. In this case, apart from the two normal bonds using the unpaired 2p electrons, there are two donor bonds formed by using the unshared $2s^2 2p^2$ electrons, so that a D_{3h} configuration is achieved ($\sigma^3\pi$ — three σ-bonds in a plane and a fourth π-bond with a negative charge delocalized over the nine ortho- and para-positions of the phenyl rings).

Since the determination of the configuration of the triphenyloxonium cation should give a complete and exhaustive answer to the problem of the structure of the whole class of triphenyloxonium compounds, we have carried out a preliminary study of a series of oxonium salts* to choose the most suitable crystals for a complete x-ray structural analysis. The results of these measurements are given in the table.

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* Synthesized by Nesmeyanov and Tolstaya [1].

It is seen that most of the salts studied crystallize with two crystallographically independent molecules in the lattice. From the methodological point of view, the most useful compound for study is $[(C_6H_5)_3O]I$, and we expect to complete a total solution of its structure in the near future.

Compound	a, A	b, A	c, A	β°	*N*	Space group	*N*[*]
$[(C_6N_5)_3O]I$	9,33	18,67	9,56	~90°	4	$P2_1$[**]	2
$[C_6H_5)_3O]\,Br\cdot 2H_2O$	16,91	23,70	16,78	~90°	16	$I2/c$	2
$[(C_6H_5)_3O]\,Cl\cdot 2H_2O$	16,84	23,84	16,66	~90°	16	$I2/c$	2
$[(C_6H_5)_3O]BF_4$	9,49	18,38	9,52	~90°	4	$P2_1/m$ or $P2_1$	1 or 2
$[(C_6H_5)_3O][B(C_6H_5)_4]$	12,50	18,08	13,86		4	$P2_12_12_1$	1

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[*] Number of crystallographically independent molecules.

[**] The space group was determined unequivocally from the distribution of the maxima of the Paterson function P(0vw).

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ON THE MECHANISM OF THE ADDITION OF A PROTON TO METHANE

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In the previous paper [1] a calculation of the proton affinity of methane and its homologs was carried out with the assumption of a purely electrostatic interaction between H^+ and the CH_3-R molecule. The energy of interaction of $R-CH_3+H^+$ was shown to be 80-90 kcal/mole at the equilibrium distance $C-H^+=1.3$ A, which is less than the experimental estimate of ≈120 kcal/mole [2].

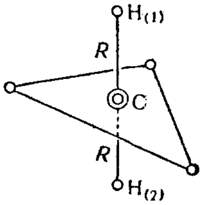

Fig. 1.

In the present paper an attempt is made to calculate the energy of formation of CH_5^+ using the one electron approximation of the molecular orbital method. The two most likely configurations of the CH_5^+ ion are discussed: 1) the trigonal bipyramidal configuration (Fig. 1), and 2) the configuration arising by the addition of H_2^+ to the CH_3 radical (Fig. 2).

In calculations on the configuration of the trigonal bipyramid the equatorial C—H bonds were considered to be localized two-electron bonds formed from the 1s orbitals of the H atoms and $2s2p^2$ hybrid orbitals of the C atom. The two axial bonds were considered to arise from bonding molecular orbitals formed from the 1s orbitals of the atoms $H_{(1)}$ and $H_{(2)}$ and the $2p_z$ orbital of the C. They have the form: