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Synthesis and Physicochemical Study of Di(1,3,7-trimethylpurine-2,6-dione) 12-Tungstosilicate $(C_8N_4O_2H_{11})_2H_2SiW_{12}O_{40}$

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Abstract—The di(1,3,7-trimethylpurine-2,6-dione) dihydrogen 12-tungstosilicate $(C_8N_4O_2H_{11})_2H_2SiW_{12}O_{40}$ (**I**) was synthesized and studied using chemical methods, IR and ^{1}H NMR spectroscopy, X-ray phase analysis, and the thermogravimetry technique.

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Heteropoly compounds constitute an extensive part of coordination chemistry. The oxo-metal sphere of these compounds acts as a single ligand bonded to one or sometimes to few complexing elements. Numerous studies in this area performed for over 180 years have resulted in accumulation of a large experimental data [1–10]. However, many iproblems related to the chemistry of these compounds have not yet been sufficiently studied. The ideas about the structure of heteropoly compounds and, consequently, the interpretation of theoretical concepts concerning their physical and chemical properties have changed during this time repeatedly.

Insular structure of these compounds, high symmetry of isolated polyatomic heteropolyanions, and a large surface with a relatively small negative charge impart unique properties to the heteropoly compounds. The heteropoly compounds are widely used as homogeneous and heterogeneous catalysts. It is interesting to study the dependence of catalytic activity of heteropoly compounds on their composition and structure. Currently they are among the most popular materials for new catalysts possessing high selectivity and activity, low corrosivity and toxicity, relative ease of synthesis and regeneration. The number of reactions showing high activity of heteropolyacids and their salts is large and still growing. It is promising to use heteropoly compounds as catalysts for the fine organic synthesis [11–16].

Currently a promising trend is modeling, synthesis, and identification of structural characteristics of new hybrid materials formed through a combination of organic and inorganic building blocks. The creation of such inorganic–organic compounds opens new fields of research in materials chemistry, based on the interrelation of organic and inorganic chemistry. This way is useful for obtaining multifunctional materials combining magnetic, electrical and (or) optical properties of solids. Synthesis of inorganic–organic hybrid compounds using polyoxometalate groups as nanobuilding blocks is very attractive because it provides an opportunity to realize a huge number of potentially important functions of polyoxometalates in such diverse areas as catalysis, molecular magnetism, photochemistry, and medicine [17–27].

The organic block we chose for the synthesis was caffeine (1,3,7-trimethylpurine-2,6-dione), a purine alkaloid well known in biochemistry and medicine, a component of various drugs. The complex salt based on 12-tungstosilicic acid was prepared by the reaction of the tungstosilicic heteropolyacid with caffeine. The preliminary prepared heteropolyacid was dissolved in water and passed through a cation exchange resin to

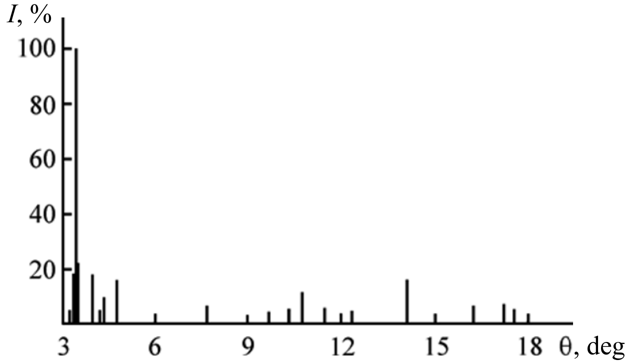
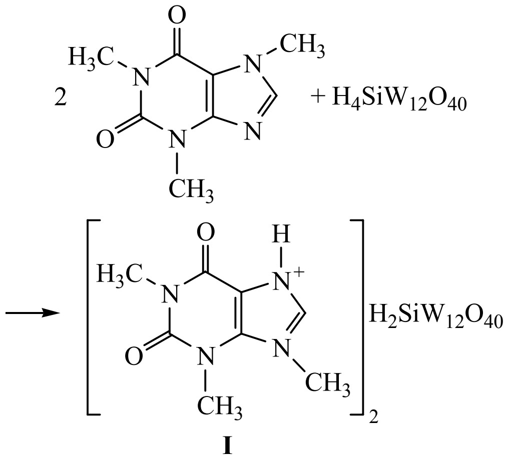


Fig. 1. X-ray diffraction bar chart of compound **I**.

remove sodium ions, and then recrystallized from ether. Caffeine is readily soluble in hot water, so the synthesis was carried out in aqueous solution with permanent stirring and heating the system up to 70°C. We failed to prepare a neutral caffeine salt with 12-tungstosilicic acid even using the caffeine excess due to low acidity of the 12-tungstosilicic acid in the third and fourth dissociation stages and the rather low basicity of caffeine. Under these conditions the hydrolysis apparently occurs of the neutral salt. A positive result was obtained in the synthesis of acid salt at a caffeine–heteropolyacid molar ratio 2:1 according to the scheme:



I

^{1}H NMR chemical shifts (ppm), solvent acetone-d_6

Group	Compound	
	caffeine	**I**
$^1CH_3$	3.25	3.28
$^3CH_3$	3.44	3.51
$^5CH_3$	3.95	4.07
CH	7.78	7.32
$^+N^9H$	–	8.15

At cooling crystals of octahedral shape of a bright yellow color precipitated from the solution. Compound **I** is poorly soluble in water, and cooling of the solution led to practically instant precipitation of crystals and formation of conglomerates, therefore it was difficult to obtain a single crystal of a large size from the aqueous solution. The hetropoly compound **I** is weakly soluble in alcohol, carbon tetrachloride, soluble in acetone and dimethylsulfoxide (DMSO).

The resulting complex **I** was washed with the double distilled water and dried in a desiccator over concentrated sulfuric acid. Its composition was determined by chemical and mass spectrometric methods.

Found, %: C 6.16, N 3.13, O 22.83, Si 0.86, W 68.27. $(C_8N_4O_2H_{11})_2H_2SiW_{12}O_{40}$. Calculated, %: C 5.84, N 3.43, O 21.86, Si 0.86, W 67.56. By the XRD, the crystals are monoclinic: a = 8.9460, b = 9.5018, c = 7.9860 Å, $\alpha = 90.00$, $\beta = 104.69$, $\gamma = 90.00$, $V = 656.63$ Å^3. Figure 1 shows X-ray diffraction bar chart of the complex $(C_8N_4O_2H_{11})_2H_2SiW_{12}O_{40}$.

Assignment of the signals in the ^{1}H NMR spectra is based on the data of [28–31]. In the ^{1}H NMR spectrum of **I** (see the table) there are all the signals corresponding to the organic fragment, but in contrast to the spectrum of the free caffeine there is a signal at δ 8.15 ppm, which broadens at heating the solution to 45°C. This fact indicates the protonation of nitrogen atom N^9 in the five-membered ring at the formation of compound **I**. Judging from this we conclude that the organic fragment is bound to the heteropoly anion through the nitrogen atom N^9. Compared to caffeine spectrum, the signals of protons of the methylene groups at the nitrogen atoms of compound **I** are shifted downfield, and the proton signal of the CH group in the five-membered ring is shifted upfield (δ = 7.32 ppm), also due to the influence of the protonated nitrogen N^9. Similar ^{1}H NMR spectrum was obtained for the compound $(C_8N_4O_2H_{11})_2H_2SiW_{12}O_{40}$ we synthesized earlier [31].

The structure of compound **I** presumably includes the isolated complex heteropoly anoin $[SiW_{12}O_{40}]^{4-}$ and organic cation $(C_8N_4O_2H_{11})^+$. The contact of the heteropoly anion with the 1,3,7-trimethylpurine-2,6-dione organic cation occurs through the electrostatic interaction.

The assignment of signals in the IR spectra was performed using published data [32]. The IR spectroscopic studies (Fig. 2) showed that the outer-sphere organic cation has no significant effect on the

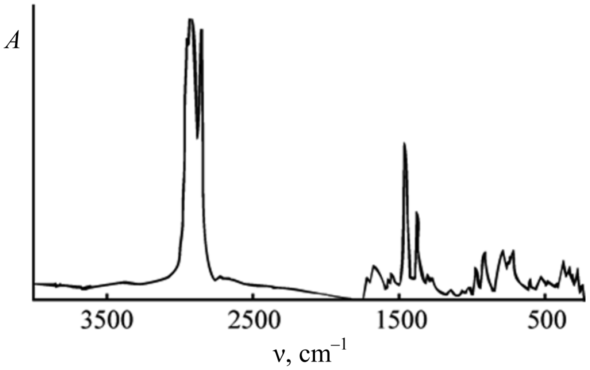


Fig. 2. IR spectrum of compound **I**.

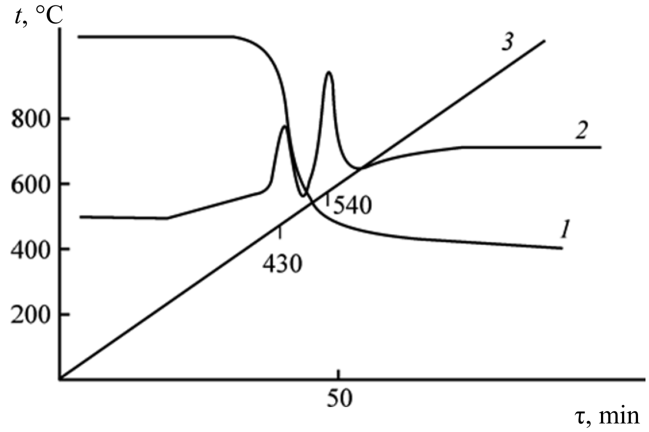


Fig. 3. Thermogram of compound I. (*1*) DTG, (*2*) DTA, and (*3*) TG.

character of the metal–oxygen bonds of the heteropoly anion of 12th row.

In contrast to the IR spectrum of caffeine, in the IR spectrum of its complex salt with the heteropoly cation strong bands are observed at 500–1000 and 400–200 cm^{-1}. The bands in the region of 1000–900 cm^{-1} are due to the vibrations of the groups with the multiple M=O (complex) bond, in the region of 900–400 cm^{-1}, due to the stretching vibrations of the M–O–M bridge bonds. The asymmetric stretching M–O–M vibrations are recorded at 889 cm^{-1}, and to the symmetric stretching vibrations of this group may be assigned the bands at ~200 cm^{-1}. At 540 and 977 cm^{-1} the symmetric and asymmetric stretching vibrations of the M=O (complex) groups are registered. Vibrations of internal SiO_4 tetrahedron lead to the absorption at 917 and 534 cm^{-1}. The bands in the region 400–200 cm^{-1} are due to both bending vibrations of terminal M=O groups and vibrations of the core of heteropoly anion.

The bond vibrations of the organic cation in the synthesized compounds are characterized by the following absorption bands: the aromatic structure of the molecule is represented by the bands of skeletal vibrations of the rings (1582, 1556–1543, 1508, 1457 cm^{-1}); the symmetrical bending vibrations of the bonds of nitrogen atoms in the ring occur at 1575 and 1361 cm^{-1}. Vibrations of the carbonyl group ν(C=O) appear as strong bands at 1285, 1653, and 1716 cm^{-1}. The stretching and bending vibrations of C–H groups of the organic cation are recorded at 973–971 and 722 cm^{-1}. In the region 1461.7, 1377.1, 2924, and 2854 cm^{-1} there are the bands of vaseline.

Thermogravimetric study of **I** showed that this compound is quite thermally stable. At heating on the DTA curve (Fig. 3) exothermic effects are observed at 430ºC and 540ºC. The analysis of the infrared spectrum of products of the thermal decomposition indicated burning of the organic cation. After heating to 540ºC the spectrum contained no peaks of the organic part, which confirms the complete decomposition of the compound. The endothermic peak at 90–140ºC, commonly indicating the presence of crystallization water, was not registered for compound **I**. The thermal stability of compound **I** is lower than that of similar compounds based on the dodecatungstophosphate $(C_8N_4O_2H_{11})_2HPW_{12}O_{40}$, for which the exothermic effects on DTA curve occur at 480ºC and 550ºC [31].

From the thermogravimetric data we calculated the effective activation energy of some thermal processes taking into account the reaction order, and the kinetic rate equations were proposed. The technique of the thermal analysis can reveal the nature of the limiting stage, as well as allows the estimation of the variation of the surface of the reaction zone during the high-temperature heterogeneous process of a substance transformation. The presentation of the experimental derivatography data in the α–T and $[d\alpha/d\tau]$–T coordinates (where α is a degree of transformation, T is temperature, K, and τ is time, s) allows the application of the equation of the heterogeneous kinetics [33–35]. Analyzing the calculations, we were able to conclude that the considered thermal processes were described by the first order kinetic rate equation $W(T, \alpha) = 1.2\times10^6\exp[-(9.23\times10^4)/(RT)](1 - \alpha)$, as evidenced by the straightening of the experimental curves in the coordinates ln $[(d\alpha/d\tau)/f(a)] - 1/T$. It is seen from the values of activation energy that the destruction of the heteropoly compound occurs in the kinetic region of a heterogeneous process.

EXPERIMENTAL

The crystallographic data were obtained on an automatic diffractometer D8 by the powder method with the use of CuK_α radiation. The registration was carried out by scanning by points in the range of 2θ angles from 10 to 100 with a 0.02° scan step at room temperature.

The ^{1}H NMR spectra were taken from solutions in acetone-d_6 on a JEOL JNM-ECX400 spectrometer with operating frequency 400 MHz. Chemical shifts are given relative to TMS as external reference.

The IR spectra of compound **I** and its degradation products formed during the thermogravimetric analysis were recorded in the wavenumber range 200–4000 cm^{-1} on a Nicolet 380 Fourier spectrometer by transmitting method from the powder triturated with vaseline, using CsI windows. The resulting spectra were compared with the IR spectra of pure caffeine and the heteropolyanion. The IR spectra were processed using OMNIC software.

The thermogravimetric analysis was carried out on a Paulik–Paulik–Erdey Q-1500 instrument in the range of 20–1000°C, heating rate 10 deg min^{-1}, with calcined alumina as a reference.

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