ISSN 1070-3632, Russian Journal of General Chemistry, 2009, Vol. 79, No. 6, pp. 1063–1066. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © O.A. Kutanova, G.Z. Kaziev, Holguin Quinones, N.N. Lobanov, L.A. Morales Sánchez, 2009, published in Zhurnal Obshchei Khimii, 2009, Vol. 79, No. 6, pp. 891–894.

Synthesis and Study of 1,3,7-Trimethylpurine-2,6-dione Hydrogen Dodecatungstenphosphate of Composition $(C_8N_4O_2H_{11})_2HPW_{12}O_{40}$

O. A. Kutanova[a], G. Z. Kaziev[a], Holguin Quinones[b], N. N. Lobanov[c], and L. A. Morales Sánchez[d]

[a] *Moscow State Pedagogical State University, Nesvizhskii per. 3, Moscow, 119021 Russia*

[b] *Universidad Autonoma Metropolitana, Mexico City, Mexico*

[c] *Peoples' Friendship University of Russia, Moscow, Russia*

[d] *Instituto Politecnico Nacional, Mexico City, Mexico*

Received October 13, 2008

Abstract—1,3,7-Trimethylpurine-2,6-dione hydrogen dodecatungstenphosphate $(C_8N_4O_2H_{11})_2HPW_{12}O_{40}$ (**I**) was synthesized. The compound was examined by chemical analysis, IR spectroscopy, X-ray phase analysis and thermogravimetry. The compound **I** was established to crystallize into monoclinic systems having parameters of elementary cell: a = 10.9129(75), b = 9.1346(70), c = 26.185(23) Å, β = 81.05(27), Z = 2, d_{calc} = 4.35 g cm^{-3}, V = 2578(4) Å^3.

DOI: 10.1134/S1070363209060036

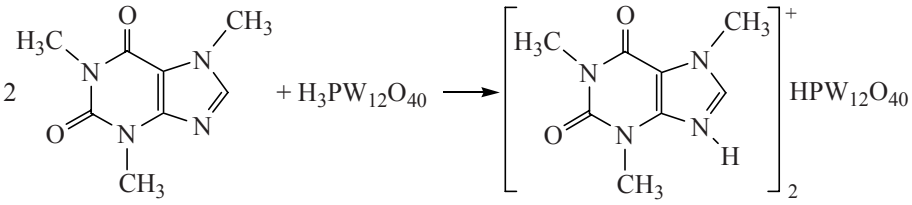
Heteropolycompounds are complex coordination compounds having unique structure and various properties [1–4]. Heteropolycompounds differ from ordinary coordination compounds: they have no discrete ligands coordinated around central atom. Heteropolycompounds are of scientific interest to the many researchers in chemistry, physics and biochemistry. They have extensive applications in the various fields of science and technology: medicine, analytical chemistry, heterogeneous and homogeneous catalysis, fine organic synthesis, photochemistry and others [5–8].

The promising directions in the materials science comprise design, synthesis and structural constants determination of the new hybrid materials obtained by assembling organic and inorganic multicomponent blocks [9–12]. Creation of these organo-inorganic compounds opens new fields of research in the materials chemistry, the basis for which is connection between organic and inorganic chemistry. Such compounds can be used for obtaining multifunctional materials [13–14]. Study of synthesis conditions, structure and properties of these new complexes is of scientific value and forms theoretical basis for producing the materials having predetermined properties. Therefore the problems of synthesis and studying physicochemical properties of the new unexplored previously heteropolycompounds of various structural type remain actual.

This work is devoted to the synthesis and study of physicochemical properties of hybrid organo-inorganic heteropolycompounds 1,3,7-trimethylpurine-2,6-dione hydrogen dodecatungstenphosphate **I** of composition $(C_8N_4O_2H_{11})_2HPW_{12}O_{40}$.

EXPERIMENTAL

Synthesis. Caffeine (1,3,7-trimethylpurine-2,6-dione), the purine alkaloid well known in biochemistry and medicine and used as a component of the various drugs, was used as an organic block for the synthesis. Complex salt on the basis of dodecatungsten hydrogen phosphate was obtained by reaction of this hetero-polyacid with caffeine. The synthesis was carried out in a box under nitrogen flow. Caffeine is very soluble in hot water, therefore the synthesis was carried out in water solution, at continuous stirring and heating to 70°C using the reagents molar ratio 2:1.



Bright yellow octahedral crystals precipitated on cooling. The obtained compound was washed with bidistilled water and dried over sulfuric acid. Compound **I** is slightly soluble in water. Crystals are precipitated instantaneously on cooling to form conglomerates, therefore it is difficult to obtain separate big-size crystals from water solution.

The compound composition was determined by chemical and mass-spectrometry method. The X-ray phase analysis was taken to confirm purity and individuality of compound prepared and also to obtain crystallographic data. Analysis was performed on a STOE IP automatic diffractometer by powder method using CuK_α radiation. Measurements were carried out by pointwise scanning in the 2θ angles range from 5° to 70° with scanning pitch 0.02º at room temperature (λ = 1.54051, exposure time in point 5 s). Calculations for determination of lattice parameters of compound **I** were taken on the effective Delone lattice (Delone transform maximum error 0.50). X-ray pattern indexing data are given in Table 1. Crystals are monoclinic: a = 10.9129(75), b = 9.1346(70), c = 26.185(23) Å, β = 81.05(27) Z = 2; d_{calc} = 4.35 g cm^{-3}, V = 2578(4) Å^3; average divergence 0.00758; M = 3270.29. In Fig. 1 is shown the X-ray line pattern for $(C_8N_4O_2H_{11})_2HPW_{12}O_{40}$.

The IR spectra were registered in the range of 500–4000 cm^{-1} on a Nicolet-380 Fourier spectrometer by reflection method on a ZnSe crystal. The spectra obtained were compared with the IR spectra of pure caffeine and heteropolyacid. The IR spectra were worked up by means of OMNIC package.

X-ray pattern indexing for $(C_8N_4O_2H_{11})_2HPW_{12}O_{40}$

Run no.	$2\theta_{exp}$	d_{exp}	d_{calc}	I	h	k	l	Run no.	$2\theta_{exp}$	d_{exp}	d_{calc}	I	h	k	l
1	6.8433	12.90570	12.93289	92.4	0	0	2	17	25.4229	3.50050	3.50023	14.4	–2	2	1
2	8.1936	10.78160	10.77993	100.0	1	0	0	18	26.7941	3.32440	3.33103	33.3	3	0	2
3	9.3780	9.42240	9.44225	59.4	1	0	1	19	27.1755	3.27860	3.28198	41.2	–3	1	3
4	9.6782	9.13080	9.13457	22.1	0	1	0	20	28.2600	3.15520	3.14742	11.3	3	0	3
5	15.4145	5.74340	5.70793	11.8	–1	1	3	21	28.4561	3.13390	3.13501	22.9	0	2	6
6	16.2147	5.46170	5.44868	7.4	–2	0	1	22	29.6114	3.01420	3.01435	20.1	–3	1	5
7	16.3643	5.41210	5.38997	10.7	2	0	0	23	29.8986	2.98590	2.98513	11.4	–2	0	8
8	17.2107	5.14780	5.17151	16.0	1	1	3	24	32.4345	2.75800	2.75702	10.6	3	0	5
9	18.8011	4.71580	4.72113	16.6	2	0	2	25	33.3073	2.68770	2.69130	12.0	3	2	2
10	18.9724	4.67360	4.67944	21.7	–2	1	1	26	33.7546	2.65310	2.65109	18.6	2	3	0
11	19.3233	4.58950	4.56818	8.9	0	2	0	27	33.9311	2.63970	2.63942	10.9	3	1	5
12	20.4577	4.33750	4.33716	25.4	–2	1	3	28	34.1390	2.62410	2.62406	29.5	0	3	5
13	21.6209	4.10670	4.11155	26.6	1	2	1	29	34.8077	2.57520	2.57045	8.5	3	0	6
14	21.9537	4.04520	4.03598	11.2	0	2	3	30	35.7037	2.51260	2.51337	10.3	–3	1	8
15	22.7392	3.90720	3.89861	8.7	0	1	6	31	35.8957	2.49960	2.49876	7.4	–2	2	8
16	24.7677	3.59160	3.59331	9.8	3	0	0								

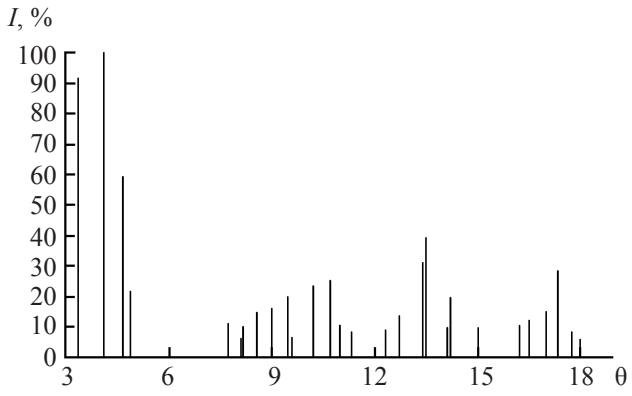


Fig. 1. X-Ray line pattern for $(C_8N_4O_2H_{11})_2HPW_{12}O_{40}$.

Thermogravimetric study was carried out on a Paulik–Paulik–Erday installation in the temperature range 20–1000°C, heating rate 10 deg min^{-1}. Aluminum oxide calcinated was used as a standard.

RESULTS AND DISCUSSION

Structure **I** contains presumably the isolated complex heteropolyanion $[PW_{12}O_{40}]^{3-}$ and organic cation $(C_8N_4O_2H_{11})^+$. Inclusion of crystallization water was not found. Contacts between heteropolyanion and 1,3,7-trimethylpurine-2,6-dione cation occur evidently through the electrostatic interaction and hydrogen bonding.

Assignment of the IR spectra absorption bands is difficult due to complexity of the heteropolycompound structure that contains metal-oxygen bonds of various types. Complete analysis of normal vibrations is often a problem for complex molecules. Therefore the bands assignment is carried out with the assumption of group vibrations as is done in the most of works on the vibration spectra of complex compounds. In the heteropolyanion $[PW_{12}O_{40}]^{3-}$ can be singled out 12 terminal double bonds $W{=}O_t$, 12 nearly linear and 12 bent bonds W–O–W respectively, 12 ordinary bonds W–O, in which the oxygen atoms are shared by three W atoms and the central phosphorus heteroatom [15]. However, through the anion complexity many vibrations can not appear owing to the both low intensity and casual degeneration, or they can fall outside of the measured range.

For compound **I** the bond vibrations in organic cation are characterized by the following absorption bands: the bands of ring backbone vibrations at 1582, 1556, 1508 and 1457 cm^{-1} belonging to the aromatic structure of the molecule and the bands of symmetric

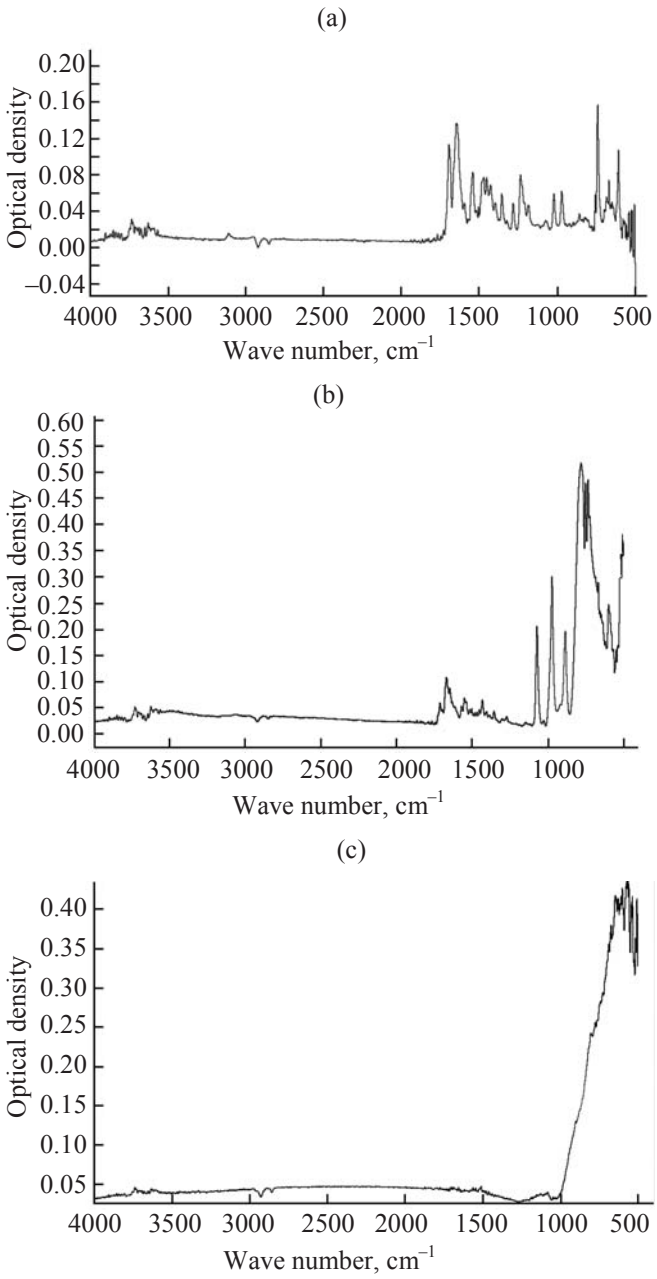


Fig. 2. IR spectra of (a) caffeine, (b) compound **I,** and (c) compound **I** after the heating to 550°C.

bending vibrations at 1575 and 1361 cm^{-1} assigned to the ring nitrogen atoms. Strong bands at 1653 and 1716 cm^{-1} originate from the carbonyl group vibration.

Contrary to the IR spectrum of caffeine (Fig. 2a), in the spectrum of its complex salt with the heteropolyanion (Fig. 2b) there are strong bands at 500–1000 cm^{-1}. The absorption bands at 1000–900 cm^{-1} belong to vibrations of $W{=}O_t$ double bond. Stretching

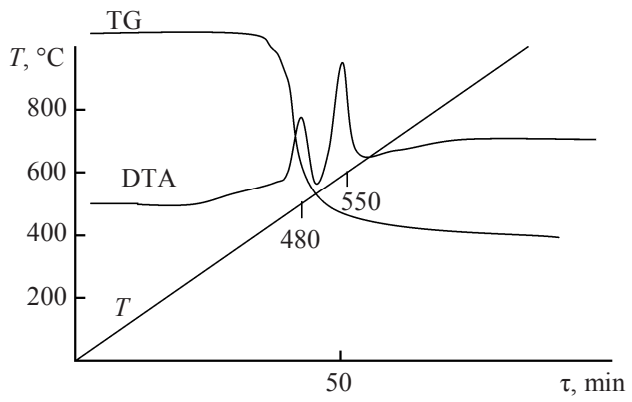


Fig. 3. The thermogram of $(C_8N_4O_2H_{11})_2HPW_{12}O_{40}$.

vibrations of W–O–W bridge bonds are observed in the region of 900–400 cm^{-1}. Absorption bands from PO_4 tetrahedral anion appear at 603, 552 and 1077 cm^{-1}; symmetrical and asymmetrical stretching vibrations of W–O–W bonds give rise to the absorption bands at 510, 522 and 889 cm^{-1} respectively. Absorption bands in the region 540 and 977 cm^{-1} correspond to symmetric and asymmetric stretching vibrations of $W{=}O_t$ bond.

The strong absorption bands at 784 and 889 cm^{-1} originate from the stretching asymmetric bending and pseudolinear vibrations of W–O–W bonds. We emphasize that in all cases the intensity of band at 784 cm^{-1} is somewhat higher than that of band at 889 cm^{-1}, although the number of bonds caus these vibrations is equal. This can be explained by the fact that the bent bond is more ionic. Absorption bands from PO_4 internal tetrahedron appear at 1076 and 638 cm^{-1}. Analogous conclusions were drawn in some works [16–19], where vibration spectra of compounds containing heteropolyanion of this type were studied.

The two exothermal effects at 480 and 550ºC are observed on the DTA curve at the heating of the synthesized compound **I** (Fig. 3).

The IR spectrum of pyrolysis products was recorded. By the data of analysis organic cation burn out. Organic part peaks are absent over 550ºC that confirms total decomposition of compound (Fig. 2c). Endothermal peak in the region 90–140ºC testifying presence of crystallization water was not registered for compound **I**.

REFERENCES

1. Porai-Koshits, M.A. and Atovmyan, L.O., *Itogi Nauki i Tekhniki, Ser. Kristallokhimiya*, vol. 19, Moscow: VINITI, 1985, p. 3.
2. Spitsin, V.I., Torchenkova, E.A., and Kazanskii, L.P., *Itogi Nauki i Tekhniki, Ser. Neorg. Khim*., vol. 10, Moscow: VINITI, 1984, p. 65.
3. Sergienko, V.S. and Porai-Koshits, M.A., *Itogi Nauki i Tekhniki, Ser. Kristallokhimiya*, vol. 19, Moscow: VINITI, 1985, p. 79.
4. Kaziev, G.Z., Karamnov, M.A., Ol'gin Kin'yones, S., et.al., *Zh. Neorg. Khim*., 2003, vol. 48, no. 5, p. 782.
5. Hargmann, J.P., Hargmann, D., and Zubieta, J., *Angew. Chem. Int*., 1999, vol. 38, p. 2638.
6. Awaga, K., Coronado, E., and Drillon, M., *MRS Bull*., 2000, p. 52.
7. Baker, L.C.W. and Glick, D.G., *Chem. Rev*., 1998, vol. 98, no. 1, p. 4.
8. Hill, C.L., *Chem. Rev*., 1998, vol. 98, p. 1.
9. Kaziev, G.Z., Dutov, A.A., Ol'gin Kin'yones, S., et.al., *Koord. Khim*., 2005, vol. 31, no. 4, p. 1.
10. Vasilyev, M., Porovitz-Biro, R., Shimon, L.J.W., and Neumann, R., *J. Mol. Struct*., 2003, vol. 656, p. 27.
11. Ol'gin Kin'yones, S., Kaziev, G.Z., De Ita, A., Koroteev, A.M., et.al., *Koord. Khim*., 2007, vol. 33, no. 9, p. 660.
12. Kaziev, G.Z., Dutov, A.A., Ol'gin Kin'yones, S., Koroteev, A.M., Bel'skii, V.K., et. al., *Koord. Khim*., 2005, vol. 31, no. 4, p. 273.
13. Coronado, A.E., Galan-Mascaros, J.R., Gomez-Garcia, C.J., and Lauhkin, V.L., *Nature*, 2000, vol. 408, p. 447.
14. Vasilyev, M., Popovitz-Biro, R., Shimon, L.W.J., and Neumann, R., *J. Mol. Struct*., 2003, vol. 656, p. 27.
15. Rocchiccioli-Deltcheff, C., Fournier, M., Thouvenot, R.T., and Frank, R., *Inorg. Chem*., 1983, vol. 22, p. 207.
16. Beattie, L.R. and Gall, M.J., *J. Chem. Soc*., 1981, no. 22, p. 3569.
17. Nakamoto, K., *IK-spektry neorganicheskikh soedinenii* (IR Spectra of Inorganic Compounds), Moscow: Mir, 1965.
18. Kazanskii, L.P. and Golubev, A.M., *Khimiya soyedinenii Mo(VI) i W(VI)* (Chemistry of Mo(VI) and W(VI) Compounds), Novosibirsk: Nauka, 1979.
19. Kazanskii, L.P., *Izv. Akad. Nauk SSSR, Ser. Khim*., 1975, no. 3, p. 502.