Russian Journal of General Chemistry, Vol. 75, No. 1, 2005, pp. 18–20. Translated from Zhurnal Obshchei Khimii, Vol. 75, No. 1, 2005, pp. 21–23.

Synthesis and Investigation of Indium Dodecatungstosilicate

G. Z. Kaziev, A. A. Dutov, S. I. Quinones, A. de Ita, and S. N. Sychkin

Moscow State Pedagogical University, Moscow, Russia
Universidad Autonoma Metropolitana Azcapotsalco, Mexico

Received January 28, 2003

Abstract — Indium dodecatungstosilicate of the composition $[In(OH)\cdot 5H_2O]_2[SiW_{12}O_{40}]\cdot H_2O$ is synthesized and studied by means of IR spectroscopy, thermogravimetry, and X-ray phase analysis. The crystals of this compound are triclinic, space group *P*1, *a* 13.079(3), *b* 13.795(3), *c* 13.967(3) Å, α 90.08(3)°, β 103.76(3)°, γ107.76(3)°, *Z* 2, and π_{calc} 4.900 g cm^{-3}.

Heteropoly compounds are representatives of coordination compounds rather complex and interesting from the theoretical viewpoint. They have found wide and versatile practical use in various fields of science and engineering.

Nowadays an important role in the chemistry of heteropoly compounds belongs to the synthesis of new compounds and investigation of their properties, aimed at extending the range of their practical use. Due to the unique combination of redox and acid–base properties, heteropoly compounds are widely used in catalysis, analytical chemistry, and other areas [1–3]. The structural anions of heteropoly acids have been described in detail in the review [4] and in [5–7].

The present work have been devoted to the synthesis and properties of indium dodecatungstosilicate.

In general, the synthesis of the salt can be presented by the following equation:

$$2In(NO_3)_3 + H_4[SiW_{12}O_{40}] + 18H_2O \longrightarrow \underset{\mathbf{I}}{[In(OH)\cdot 5H_2O]_2\cdot[SiW_{12}O_{40}]\cdot 6H_2O} + 6HNO_3.$$

By X-ray phase analysis we showed that the synthesized compound is isomorphous to Keggin structures $M_nW_{12}O_{40}^{(8-n)-}$ (M = B, P, Si, etc.). Comparison of the X-ray patterns with those retrieved from the database led us to conclude that the sample in hand contains no admixtures (indium oxide, indium nitrate, tungstic acid, and indium tungstates and silicates) and relates to triclinic syngony (see table and Fig. 1).

The IR spectra provide evidence for our assumption that the synthesized compound relates to the Keggin structural type [8]. The IR spectrum of compound **I** (Fig. 2) contains many bands, which reveals a complex nature of the $[SiO_4W_{12}O_{36}]^{4-}$ heteropoly anion. In the $[SiO_4W_{12}O_{36}]^{4-}$ anion we recognized bond groups whose vibrations are only slightly dependent on vibrations of other groups: 12 terminal (multiple) W=O_t bonds, 12 almost linear and 12 curved (angular) W–O^*–W and W–$^*O^*$–W bonds, respectively, and 12 ordinary W–O bonds with the oxygen atom common for three tungsten atoms and the central silicon atom.

It is commonly accepted that the absorption band near 995 cm^{-1} belongs to terminal (multiple) W=O bonds. The bands at 890 and 790 cm^{-1} relate to stretching vibrations of linear and angular W–O–W bonds, respectively. It is interesting to note that the absorption bands in the region of 790 cm^{-1} are stronger than

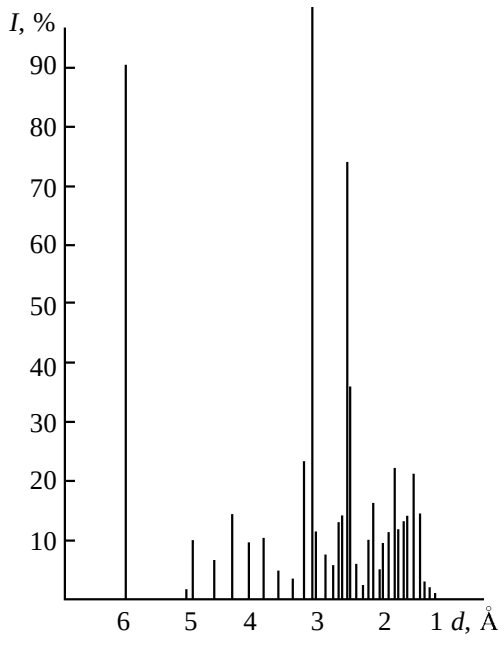

Fig. 1. X-ray diffraction pattern of $[In(OH)\cdot 5H_2O]_2\cdot[SiW_{12}O_{40}]\cdot 6H_2O$.

1070-3632/05/7501-0018

X-ray diffraction data for $[In(OH)\cdot 5H_2O]_2\cdot[SiW_{12}O_{30}]\cdot 6H_2O$

Peak no.	1/2*Q*	*I*, %	*d*, Å	Peak no.	1/2*Q*	*I*, %	*d*, Å
1	7.35	90	6.0259	31	24.5	3.46	1.85894
2	8.75	2	5.0675	32	24.85	8.39	1.83439
3	9.0	8.79	4.9279	33	25.875	11.19	1.76676
4	9.7	6.4	4.5753	34	26.5	7.46	1.72769
5	10.25	14	4.3322	35	27.42	21.93	1.67399
6	11.0	9.6	4.0401	36	28.1	7.33	1.63667
7	11.075	6.6	4.0149	37	28.2	5.59	1.63134
8	11.65	9.9	3.8176	38	28.7	9.59	1.60527
9	12.1	1.8	3.6776	39	29.4	11.66	1.57035
10	12.5	4.5	3.5617	40	29.75	7.73	1.55354
11	13.3	3.5	3.3510	41	30.8	12.79	1.50552
12	14.1	23	3.1644	42	31.175	11.59	1.48941
13	14.7	100	3.0379	43	31.75	3.19	1.46497
14	15.15	11.5	2.9497	44	32.35	13.59	1.44067
15	16.0	7.7	2.7968	45	32.7	7.99	1.42694
16	16.7	5.3	2.6827	46	33.3	4.66	1.40411
17	17.2	12.5	2.6069	47	33.925	8.59	1.38144
18	17.4	12.3	2.5779	48	35.0	20.79	1.34401
19	17.7	14	2.5355	49	36.25	3.33	1.30370
20	18.195	14.39	2.4695	50	37.5	4.66	1.26633
21	18.5	74.13	2.4295	51	38.31	14.39	1.24354
22	18.85	35.99	2.3860	52	39.6	9.06	1.20938
23	19.6	5.59	2.2981	53	40.4	3.19	1.18942
24	20.525	2.66	2.1992	54	40.8	5.19	1.17978
25	20.9	3.73	2.1609	55	43.25	2.93	1.12509
26	21.25	4.0	2.1270	56	43.5	1.19	1.11990
27	21.525	10.13	2.1015	57	43.65	0.66	1.11683
28	21.9	10.66	2.0668	58	46.3	1.86	1.06629
29	22.35	15.59	2.02725	59	46.5	1.33	1.06275
30	24.0	4.66	1.89531				

those in the region of 890 cm^{-1}, even though the number of bonds associated with these two band groups is the same. This observation suggests that the angular bond is more ionic in nature [8]. The absorption band at 460 cm^{-1} evidently relates to vibrations of the W–O bonds formed by the oxygen atom common for the tungsten and the central tetrahedral silicon atom. The absorption bands of the Si–O bonds of the tetrahedron are observed at 610 and 935 cm^{-1}. The band of the In–O bond at 735 cm^{-1} is characteristic. The water molecules give deformation vibration bands at 1620 cm^{-1} and stretching vobration bands at 3100–3650 cm^{-1}. The spectrum lacks bands at 1400 cm^{-1} due to CO_2 or CO_3^{2-} vibrations, which provides evidence for the purity of the synthesized compound.

The thermoanalytical curves of compound **I** are shown in Fig. 3. Dehydratation of indium dodecatungstosilicate **I** begins at 100°C and proceeds stepwise. The DTA and TG curves reveal two endo effects accompanied by weight loss and ending at 160 and 250°C, respectively. The first weight-loss step

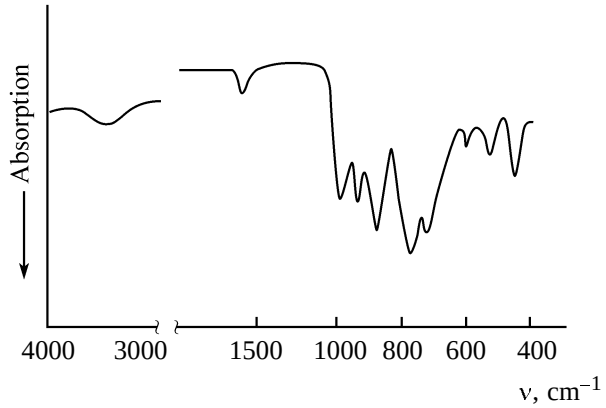

Fig. 2. IR spectrum of $[In(OH)\cdot 5H_2O]_2\cdot[SiW_{12}O_{40}]\cdot 6H_2O$.

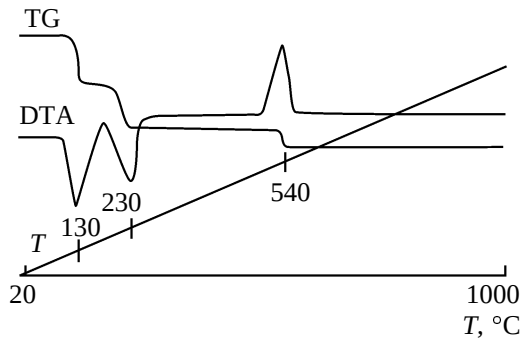

Fig. 3. Thermoanalytical curves of $[In(OH)\cdot 5H_2O]_2\cdot[SiW_{12}O_{40}]\cdot 6H_2O$.

at 100–160°C involves loss of 6 molecules of crystallization water. The second step at 200–250°C involves loss of 5 water molecules and formation of a thermodynamically stable salt $(InOH)_2[SiW_{12}O_{40}]$. The exothermic effect at 540°C is caused by decomposition of the salt with simultaneous loss of one water molecule, which was confirmed by the IR spectrum of the decomposition products.

The thermal decomposition can be represented by the following scheme:

$$[In(OH)\cdot 5H_2O]_2\cdot[SiW_{12}O_{40}]\cdot 6H_2O$$
$$\xrightarrow[-6H_2O]{130^\circ C} [In(OH)\cdot 5H_2O]_2\cdot[SiW_{12}O_{40}]$$
$$\xrightarrow[-5H_2O]{230^\circ C} [In(OH)]_2\cdot[SiW_{12}O_{40}]$$
$$\xrightarrow[-H_2O]{540^\circ C} In_2O_3 + 12WO_3 + SiO_2.$$

EXPERIMENTAL

X-ray phase analysis was carried out on a DRON-2 diffractometer by the powder technique, CuK_α radiation. Thermal analysis was carried out on a Paulik–Erdey–Paulik instrument in the temperature range 20–1000°C, heating rate 190 deg min^{-1}, sample 400 g. The reference was calcined aluminum oxide. The IR spectra were measured on a Perkin–Elmer spectrometer in the range 400–4000 cm^{-1} for suspension in Vaseline oil placed between KBr plates.

The starting reagents were a 0.1 M solution of silicotungstic acid prepared from the analytical grade reagent and a 0.01 M solution of indium nitrate. Indium dodecatungstosilicate was prepared by the exchange reaction of stoichiometric amounts of silicotungstic acid and indium nitrate at pH 4.5 under 30-min heating on a water bath. The reaction mixture was then left to stand at room temperature for a day. Colorless crystals formed and were filtered off and crystallized from a hot solution. Two days later, colorless crystals of regular form dropped and were filtered off, washed with ethanol and dried.

Chemical analysis of the product was carried out according to the procedure in [10]. Found, %: In_2O_3 8.01; SiO_2 1.66; WO_3 80.82; H_2O 9.51. $[In(OH)\cdot 5H_2O]_2\cdot[SiW_{12}O_{40}]\cdot 6H_2O$. Calculated, %: In_2O_3 8.11; SiO_2 1.75; WO_3 81.21; H_2O 8.93.

ACKNOWLEDGMENTS

The work was financial supported in part by the Russian Foundation for Basic Research (project no. 02-03-32136).

REFERENCES

1. Nikitina, E.A., *Geteropolisoedineniya* (Heteropoly Compounds), Moscow: Goskhimizdat, 1962.
2. Kozhevnikov, I.V., *Usp. Khim.*, 1993, vol. 62, p. 510.
3. Maksimov, G.M., *Usp. Khim.*, 1995, vol 64, p. 480.
4. Kazanskii, L.P., Torchenkova, E.A., and Spitsyn, V.I., *Usp. Khim.*, 1974, vol. 43, p. 1173.
5. Porai-Koshits, M.A. and Atovmyan, L.O., *Itogi Nauki Tekh., Ser. Kristallokhim.*, 1985, vol. 19, p. 3.
6. Spitsyn, V.I., Torchenkova, E.A., and Kazanskii, L.P., *Itogi Nauki Tekh., Ser. Neorg. Khim.*, 1984, vol. 10, p. 65.
7. Sergienko, V.S. and Poray-Koshits, M.A., *Itogi Nauki Tekh., Ser. Kristallokhim.*, 1985, vol. 19, p. 79.
8. Kazanskii, L.P., *Izv. Akad. Nauk SSSR, Ser. Khim.*, 1975, no. 3, p. 502.
9. Kazanskii, L.P. and Golubev, A.M., in *Khimiya soedinenii Mo(VI) i W(VI)* (Chemistry of Mo(VI) and W(VI) Compounds], Novosibirsk: Nauka, 1979, p. 66.
10. Hillebrand, W.F., Lundell, G.E.F., Bright, H.A., and Hoffman, J.I., *Applied Inorganic Analysis*, New York: Wiley, 1953, 2nd ed.