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Abstract

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CHEMISTRY

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THALLIUM CHALCOGENOHALIDES

(Presented by Academician I. I. Chernyaev on 14 V 1964)

Mixed halides of trivalent thallium had already been known for a very long time ([1,2]); mixed chalcogenides and halogenochalcogenides of thallium of composition Tl_2YZ_2 and Tl_2YX_4, where Y and Z are chalcogens and X are halogens, were obtained only in the very recent years ([3,4]). These works demonstrate the fundamental possibility of adding chalcogens to halides of monovalent thallium, thereby completing the cycle of syntheses of mixed thallium halides and chalcogenides.

The addition of sulfur to TlCl, TlBr, and TlJ was carried out in sealed ampoules, in which finely ground mixtures of the reagents were heated at $t = 180^\circ$ for 30 h and then slowly cooled to room temperature. The addition of selenium was carried out by jointly heating finely ground mixtures of equimolecular amounts of thallium halides and selenium at $t = 280^\circ$ for 40 h. Therefore the starting substances were taken in equimolecular amounts, and the analysis was performed only for thallium. Precipitation of thallium in the form of chromate was carried out three times for each sample (the mean values of the analyses are given in Table 1), and monitoring of the course of the process was carried out by physicochemical study of its products.

Table 1

Thallium content in chalcogenohalides

Composition	Calculated, %	Found, %	Composition	Calculated, %	Found, %
TlClS	75.17	75.12	TlClSe	64.11	63.93
TlBrS	64.63	64.74	TlBrSe	67.86	57.43
TlJS	56.25	55.95	TlJSe	48.68	48.96

Microscopic examination of the products of chalcogenation of thallium halides showed that the solid phases are homogeneous, weakly anisotropic samples. In

the case of thallium sulfobromide, the immersion method made it possible to measure the mean refractive index n_D, 2.30.

Table 2

Composition	Mixture	Sinter	Composition	Mixture	Sinter
TlClS	5.449	5.379	TlClSe	6.198	6.445
TlBrS	5.924	5.852	TlBrSe	6.543	6.726
TlJS	5.805	5.308	TlJSe	6.379	6.632

Table 2 gives the density values of the starting mixtures and the products obtained, measured by the pycnometric method. In all cases of the sulfides, the density of the sinter is noticeably less than the specific gravity of the mixture, and the difference exceeds the measurement error by an order of magnitude. In the case of the selenides, the difference averages 0.2, and the density of the product of interaction of selenium and TlX is always greater than that of the starting mixture. The different sign of the mea-

Table 3

X-ray constants of thallium chalcogen halides

TlClS	TlBrS	TlJS	TlClSe	TlBrSe	TlJSe
3 3,6187	2 4,962	1 3,89510	2 3,8721	1 4,382	3 3,37510
3,21110	3,884	3,3957	3,03010	3,9924	3,2446
2,5364	3,6142	3,2742	2,7292	3,12310	2,6956
2,1176	3,10210	2,7239	2,2243	2,8212	2,6272
1,8368	2,6216	2,6825	1,9234	2,2961	2,3124
1,6733	2,2233	2,3253	1,7218	2,2036	2,1641
1,3202	2,0412	2,0621	1,5713	1,9903	2,0831
1,1161	1,9825	1,8862	1,3623	1,7973	2,0532
1,0031	1,7431	1,7303	1,2825	1,7779	1,9871
0,9815	1,5744	1,6291	1,2161	1,6241	1,8693
0,9671	1,4161	1,5232	1,1591	1,5576	1,7601
0,9423	1,3401	1,4371	1,1116	1,4062	1,7322
0,9181	1,2933	1,3443	1,0191	1,3287	1,7111
0,8782	1,0622	1,2652	0,9283	1,2568	1,6331
0,8322	0,9331	1,1032	0,9032	1,0636	1,518
0,8141	0,9032	0,9591	0,8571	0,9374	
0,778	0,8571	0,867	0,8362	0,8904	
	0,8311		0,8171	0,812	
	0,8081		0,783		
	0,7691				
	0,737				

changes in densities upon chalcogenation of thallium halides indicate that in this case we are dealing not with an interstitial solid solution, but with new compounds. To verify this assumption, an X-ray study of the samples was carried out.

Table 3 gives the X-ray constants of thallium chalcogen halides; comparison of these with the X-ray diffraction patterns of TlX, S, and Se shows the complete absence of the latter substances even in the form of impurities. Thus, thallium chalcogen halides are individual compounds. The X-ray photographs were taken with filtered copper radiation; intensities were estimated on a 10-point scale.

Thallium chalcogen halides do not dissolve in water or in organic liquids, but are decomposed by hot oxidizing acids and by alkali, with precipitation of the chalcogen. However, carbon disulfide does not wash sulfur out of thallium sulfohalides, which indicates sufficient strength of the Tl–S bond.

Thermographic investigation of the thallium chalcogen halides showed that all the compounds synthesized by us have three principal thermal effects—one exothermic and two endothermic; Fig. 1 reproduces thermograms obtained at a rate of 8 degrees per 1 min. As can be seen from the graph, the exothermic effects for all substances

Fig. 1

appear at a temperature of about 100°; the endothermic effects in the thallium sulfohalides occur at temperatures of $\sim 120^{\circ}$ and in the region 430-460°, and in the selenohalides at $\sim 220^{\circ}$ and also in the region 430-460°.

The exo-effect is associated with the transition $Tl^{III} \rightarrow Tl^{I}$, which always occurs in salts of trivalent thallium at elevated temperatures. The reduction of thallium is accompanied by the elimination of the chalcogen, which accordingly melts at 120 or 220° (1st endo-effect), after which melting of TlX occurs (2nd endo-effect). These processes are also clearly visible upon visual observation of thallium chalcogenohalides during their heating. The valence transition of thallium is accompanied by darkening (sulfosalts) or even blackening (selenosalts). Therefore, it can subsequently be studied quantitatively by a spectroscopic method.

In the case of thallium sulfo- and selenoiodides there is also a small endo-effect, the nature of which is not yet clear.

In conclusion, one apparent contradiction should be explained. Chalcogenohalides are obtained by prolonged heating at elevated temperatures (180 or 280°) and do not blacken or decompose, whereas subsequent heating to 100° leads to their decomposition. The fact is that the reaction TlX + Y proceeds at low temperatures (it begins already when the powders are ground at room temperature), while high temperatures lead only to melting of the chalcogen and its uniform distribution. Thus, chalcogenation actually occurs during the slow cooling of the TlX + Y mixture, which does not blacken at high tempera-

ture simply because there is not yet any trivalent thallium there. Therefore, the observed valence transition $Tl^{III} \rightarrow Tl^{I}$ is the best proof of the preparation of new compounds of trivalent thallium.

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REFERENCES

1. V. Thomas, C. R. **134**, 545 (1902).
2. I. Gewecke, Lieb. Ann., **366**, 230 (1909).
3. S. S. Batsanov, I. Kh. Petrova, Izv. SO AN SSSR, No. 7, 121 (1960).
4. S. S. Batsanov, I. Kh. Petrova, Izv. Vyssh. uchebn. zaved., khim., **4**, 349 (1961).

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