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Abstract

Full Text

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COMPLEX COMPOUNDS OF INDIUM OF LOWER VALENCE

SYNTHESIS AND STUDY OF THE PROPERTIES OF AMMONIATES OF INDIUM MONOHALIDES

(Presented by Academician I. I. Chernyaev, 16 VII 1962)

Recent years have been characterized by great success in the development of the chemistry of transition elements in unusually low oxidation states. At the same time, nontransition metals of lower valences have been studied comparatively little; for a number of them some simple compounds have been isolated and studied, while complex compounds have not been studied at all. Monovalent indium is known in the form of halides, and also compounds with elements of the sixth group—oxygen, sulfur, selenium, tellurium—the most complete information on which may be obtained from the monograph by Bleszynski and Abramova ([1]). Monovalent indium in compounds with halogens, under the action of water and, as our investigation has shown, of a number of other reagents, disproportionates to metallic indium and In III according to the equation:

$$3\mathrm{In}\Gamma \rightarrow 2\mathrm{In}_{\mathrm{met}} + \mathrm{In}\Gamma_3.$$

The iodide InJ, unlike other halides, under the action of water in the presence of atmospheric oxygen is slowly oxidized to In III according to the following equation

$$\mathrm{InJ} + \frac{1}{2}\mathrm{O}_2 + 2\mathrm{H}_2\mathrm{O} = \mathrm{In(OH)}_3 + \mathrm{HJ}.$$

Complex compounds of monovalent indium had not been studied up to the present time. The present investigation is the first attempt at the synthesis of amino compounds of indium monohalides and at the study of the reaction of interaction with ammonia as a function of conditions.

Table 1

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Figure 1 and Figure 2 thermograms

Figure 1: Figure 1 and Figure 2 thermograms

Compound	Indium found	Indium calcd.	Halogen found	Halogen calcd.	Ammonia found	Ammonia calcd.
InJ · NH_3	44.7	44.4	49.4	49.0	7.0	6.6
InJ · $2NH_3$	41.3	41.6	46.2	46.0	12.8	12.4
InBr · NH_3	53.6	54.2	37.7	37.8	8.6	8.0
InBr · $2NH_3$	50.4	50.2	35.2	34.9	14.1	14.9

Liquid ammonia, as shown by Klemm's investigations ([2]), causes decomposition of InCl into metallic indium and In III. A more detailed study of the action of dry, liquid, or gaseous ammonia on monoiodide and monobromide of indium showed that, depending on the conditions, ammonia forms addition products with the monohalides or causes a disproportionation reaction.

Under the action of dry gaseous ammonia at a pressure equal to 3–4 atm and $t \approx 0°C$, addition products of composition $InГ{\cdot}2NH_3$ are formed; when the initial ammonia pressure is lowered to 2–2.5 atm, one molecule of NH_3 is added to the monohalides. Analytical data for the synthesized compounds are presented in Table 1. Both the mono- and diammoniates of indium monohalides are black substances insoluble in water; in the solid phase, under the action of water, they readily disproportion–

react to form In_{met} and In^{III}. In air they also gradually undergo a disproportionation reaction; in this respect the iodide ammines are relatively more stable than the bromides. The compounds do not dissolve in dilute nitric and hydrochloric acids; in the solid phase, under the action of the latter, a dissociation reaction into the monohalide and ammonia occurs according to the equation

$$InГ \cdot 2NH_3 = InГ + 2NH_3.$$

When heated to 120–150° in the case of the iodide and to 145° in the case of the bromide (Fig. 1), the ammines decompose in two directions: they dissociate

Fig. 1. Thermograms of indium monohalide ammines:
a–$InBr \cdot 2NH_3$;
b–$InI \cdot 2NH_3$

Fig. 2. Thermograms of the disproportionation products of the ammines: *a*–monobromide, *b*–monoiodide

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to a greater extent into $In\Gamma$ and NH_3, and simultaneously disproportionate into In_{met} and the corresponding pentaammine of trivalent indium according to the equation:

$$2In\Gamma \cdot 2NH_3 = 2In_{met} + In\Gamma_3 \cdot 5NH_3 + NH_3.$$

These transformations of the substance on the thermograms of the ammines (Fig. 1) correspond to exothermic effects; moreover, the effect on the thermogram of $InBr \cdot 2NH_3$ is less clearly expressed because of the superposition on it of the endothermic effect of melting of metallic indium.

The exothermic effects on the differential curve of the monoiodide and monobromide ammines at 60–70° and 40–50°, respectively, probably correspond to their transition into a more stable crystalline form, since the composition and properties of the compounds (behavior toward water and air, toward dilute acids) heated to the corresponding temperatures remain unchanged. Ammines of indium(I) halides can also be obtained at room temperature, but in this case the ammonia should be introduced very carefully, in small portions.

If the ammonia pressure is raised to 6–8 atm or the monohalides are treated with liquid ammonia, gray-black disproportionation products are formed, the overall composition of which is expressed by the formula $In\Gamma \cdot 2NH_3$. To determine the composition of the products formed, the synthesis of amm-

ammiacates of indium trihalides under the same conditions, and their thermographic study was carried out. The trihalides (bromide and iodide) form hexaammiacates under the indicated conditions. The latter decompose on heating to monoammiacates according to the schemes:

$$InJ_3 \cdot 6NH_3 \xrightarrow{110^\circ} InJ_3 \cdot 5NH_3 \xrightarrow{230^\circ} InJ_3 \cdot NH_3;$$

$$InBr_3 \cdot 6NH_3 \xrightarrow{50^\circ} InBr_3 \cdot 5NH_3 \xrightarrow{205^\circ} InBr_3 \cdot 3NH_3 \xrightarrow{305^\circ} InBr_3 \cdot NH_3.$$

In the thermograms of the disproportionation products (Fig. 2) there are effects corresponding to the decomposition of the higher ammiacates of trivalent indium to lower ones, as well as effects of the melting of metallic indium; the melting temperature of metallic indium in the thermogram of Fig. 2a is shifted toward a higher temperature (175°), since other transformations of the substance occur simultaneously, in particular the reaction of metallic indium with an ammiacate of trivalent indium. The presence of metallic indium in the disproportionation products was also confirmed by X-ray diffraction.

On the basis of these data, the reaction of liquid or gaseous ammonia under a pressure of 6–8 atm with indium monohalides can be represented by the following equation

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$$3\text{In} + 6\text{NH}_3 = 2\text{In}_{\text{met}} + \text{In}_3 \cdot 6\text{NH}_3.$$

Because of the instability of the hexaammiacate of indium tribromide, which already at room temperature readily changes into the pentaammiacate, the mixture obtained upon disproportionation of the monobromide after brief storage has the composition

$$\text{InBr}_3 \cdot 5\text{NH}_3 + 2\text{In}_{\text{met}}.$$

The reverse reaction of metallic indium with ammiacates on heating, namely:

$$2\text{In}_{\text{met}} + \text{In}_3 \cdot x\text{NH}_3 \rightarrow 3\text{In} + x\text{NH}_3,$$

which already occurs at the melting temperature of indium, is shifted considerably to the right at higher temperatures, and the last effects in the thermograms (Fig. 2), at 345 and 270°, correspond to the melting of the monohalides with a small admixture of unreacted indium and In III ammiacates.

Thus, indium monohalides form mono- or diammiacates with ammonia. All attempts to obtain compounds with a higher content of ammonia molecules were unsuccessful, since, when the ammonia pressure is increased, disproportionation of In I occurs into In_{met} and In III.

Experimental Part

Synthesis of the starting indium monohalides was carried out by the reaction of metallic indium with an excess of halogen in a sealed evacuated tube. Heating the tube in an autoclave, in which nitrogen counterpressure was applied, made it possible to load up to 20 g of mixture into the tube. The temperature of the autoclave was raised very slowly to 350–400°, and the mixture was kept at this temperature for a long time. The monohalides were freed from admixture of trihalides by heating in a stream of hydrogen and were then distilled off from the excess metallic indium. The trihalides were also synthesized analogously by the reaction of metallic indium with the corresponding halogen.

Synthesis of ammiacates. To carry out the reaction between NH_3 and In , a weighed portion of the latter was placed in a transparent high-pressure autoclave, into which, after cooling, ammonia pressure was introduced, pred-

preliminarily dried over metallic sodium. The autoclave was kept for several hours at $t \approx 0^\circ$ for the reaction to proceed, after which the unreacted ammonia was released from the autoclave and the sorbed ammonia was evacuated under vacuum. The analytical data for the synthesized compounds are presented in Table 1.

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Recording and interpretation of thermograms. Thermograms were taken with differential recording on a Kurnakov pyrometer in a stream of dry, oxygen-free argon. To interpret the effects, the substance was heated under analogous conditions to the corresponding temperature and subjected to analysis and investigation of other properties.

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

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