



Soviet-era science, translated into English

Chemistry

{: style="text-align: right;"}
1962

SovietRxiv

View the original and related papers at <https://sovietrxiv.org/items/ru-196201.32609>

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.

Abstract

Full Text

Chemistry { : style= "text-align: right;" }

A. P. KOCHETKOVA, V. G. TRONEV, O. N. GILYAROV

COMPLEX COMPOUNDS OF INDIUM OF LOWER VALENCE

SYNTHESIS AND STUDY OF THE PROPERTIES OF AMMINES OF INDIUM DIHALIDES

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

The study of amino compounds of indium dihalides is of interest for a number of reasons. Since dihalides disproportionate into compounds of mono- and trivalent indium according to the equation $2\text{In}\Gamma_2 = \text{In}\Gamma + \text{In}\Gamma_3$, this property can be used for the synthesis and study of the corresponding compounds of monovalent indium. On the other hand, up to the present time the question of the oxidation state of indium in compounds with formal valence 2 has been controversial. Diamagnetic compounds of "divalent" indium are regarded either as complex compounds of mono- and trivalent indium, of structure $\text{In}^+[\text{In}\Gamma_4]^-$ ⁽¹⁾, or as symmetrically constructed molecules with a metal–metal bond ⁽²⁾. The ionic structure has been proved for gallium dichloride both by the X-ray structural method ⁽³⁾ and by a number of other methods ^(4,5). Apparently other gallium dihalides also have an analogous structure ^(4,5). Coordination compounds of gallium of the general composition $\text{GaA}_2\Gamma_2$ (A is a monodentate addend) are accordingly assigned the structure $[\text{GaA}_4]^+[\text{Ga}\Gamma_4]$ ^(6,7).

Interpretation of the results obtained in the study of compounds of indium dihalides with ammonia is difficult if one assumes an ionic structure for them, whereas explanation of the composition and properties of the compounds on the basis of dimeric molecules with a metal–metal bond appears simpler and more natural.

Indium diiodide and dibromide, under the action of dry gaseous ammonia at a pressure of 3–4 atm and room temperature, form compounds of composition $\text{In}_2\Gamma_4 \cdot 6\text{NH}_3$; at lowered temperature (several degrees below zero) the reaction between NH_3 and the dihalides leads to compounds of composition $\text{In}_2\Gamma_4 \cdot 8\text{NH}_3$. It is not possible to obtain compounds with 6 molecules of NH_3 at lowered temperature even with a considerable decrease in the ammonia pressure.

Table 1

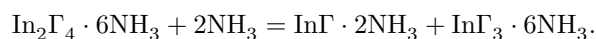
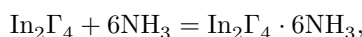
Compound	Indium, % found	Indium, % calc.	Halogen, % found	Halogen, % calc.	Ammonia, % found	Ammonia, % calc.
$\text{In}_2\text{J}_4 \cdot 6\text{NH}_3$	27.5	27.4	60.7	60.5	12.8	12.2
$\text{In}_2\text{J}_4 \cdot 8\text{NH}_3$	26.3	26.3	57.8	58.1	16.0	15.6
$\text{In}_2\text{Br}_4 \cdot 6\text{NH}_3$	35.0	35.2	48.8	48.1	16.5	15.7
$\text{In}_2\text{Br}_4 \cdot 8\text{NH}_3$	34.1	33.5	46.2	46.7	19.5	19.8

The synthesis of the ammines of indium dihalides was carried out by the method already described in a communication (8). The analytical data for the isolated ammines are given in Table 1.

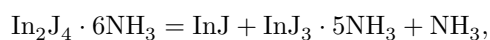
The compounds of the diiodide and dibromide with ammonia have, respectively, a bright red and an orange-red color.

For the ammines of indium dihalides the disproportionation reaction is mainly characteristic. Already under the conditions of synthesis, i.e., at an NH_3 pressure of 3–4 atm and room temperature, prolonged action of ammonia

causes blackening of the amminates as a result of the disproportionation reaction. The disproportionation products are initially amminates of mono- and trivalent indium, and the reaction of the dihalides with ammonia can thus be represented in the form of the following equations,



The composition of the amminates formed, In I and In III, as well as the character of further decomposition as a result of prolonged action of ammonia—namely, the disproportionation of In I into metallic In and In III—are evident from the preceding communication (8). The disproportionation reaction of the indium dihalide compounds with ammonia also occurs when they are heated in an inert atmosphere. The compounds $\text{In}_2\Gamma_4 \cdot 8\text{NH}_3$, at 85° in the case of the iodide and 60° in the case of the bromide (Fig. 1), pass, with the elimination of 2 molecules of ammonia, into compounds of composition $\text{In}_2\Gamma_4 \cdot 6\text{NH}_3$. The further transformations of the hexaamminates on heating proceed somewhat differently, namely:



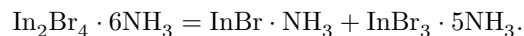


Fig. 1. Thermograms of amminates of indium dihalides:

a) $\text{In}_2\text{Br}_4 \cdot 8\text{NH}_3$;

b) $\text{In}_2\text{J}_4 \cdot 8\text{NH}_3$

The first of the reactions given corresponds to an exothermic effect at 120° , and the second at 85° . The formation of InJ in the first case and of the amminate InBr in the second is explained by the fact that $\text{In}_2\text{J}_4 \cdot 6\text{NH}_3$ disproportionates at a temperature at which the mono-iodide amminate is already unstable, whereas the disproportionation temperature of $\text{In}_2\text{Br}_4 \cdot 6\text{NH}_3$ is lower in comparison with the decomposition temperature of the InBr amminate, as follows from data on the thermal stability of amminates of monovalent indium (8).

Further transformation on heating includes the decomposition of the amminates of trivalent indium and their reaction with InI, as a result of which the final decomposition products of the indium dihalide amminates on heating are dihalides.

Water very readily decomposes the ammine halides to metallic indium, with intermediate formation of In I. Atmospheric moisture acts in an analogous manner—in air the compounds rapidly turn black because of the formation of metal.

In an inert atmosphere and in dry air, amminates of both composition $\text{In}_2\Gamma_4 \times 6\text{NH}_3$ and $\text{In}_2\Gamma_4 \cdot 8\text{NH}_3$ are stable and over a long period do not change their composition or color.

If, for the amminates of indium dihalides, by analogy with gallium, an ionic structure were assumed, then it would be necessary to admit the formation of a relatively stable monovalent hexacation $[\text{In}(\text{NH}_3)_6]^+$, which is in contradiction with the experimental facts. From our investigations of the amminates of trivalent indium (8) it is known that InJ_3 and InBr_3 form hexaamminates at room temperature. And although the latter, on heating, pass into pentaamminates at comparatively high temperatures (110 and 50° , respectively), they already at room temperature

are characterized by a high elasticity of ammonia vapor and, on storage, lose ammonia, as a result of which the hexaammine tribromide readily passes into the pentammine (8); InCl_3 at room temperature does not form a hexaammine at all (9).

In light of these facts, the coordination of 6 ammonia molecules by monovalent indium, and the relatively high stability of the hexaammine cation with a significantly lower electrostatic characteristic of In I as compared with In III, do not appear possible.

Indium monohalides add at most 2 molecules of ammonia (8), and an increase in the ability of monovalent indium in the dihalides to coordinate a larger number of NH_3 molecules could hardly be explained by the influence of the anion.

Moreover, our investigations of the action of ammonia on complex indium halides of composition Me_3InF_6 and $\text{Me}_2\text{InF}_5 \cdot \text{H}_2\text{O}$ showed that the latter decompose very readily into the alkali halide and the ammoniate of trivalent indium according to the scheme: $\text{Me}_3\text{InF}_6 + x\text{NH}_3 = 3\text{MeF} + \text{InF}_3 \cdot x\text{NH}_3$, and there is hardly any reason for strengthening the anion $[\text{InI}_4]^-$, which is assumed in the ionic structure of the dihalides.

The explanation of the fact of formation, as well as of the relative stability, of compounds of composition $\text{In}_2\text{I}_4 \cdot 6\text{NH}_3$ and $\text{In}_2\text{I}_4 \cdot 8\text{NH}_3$, and of other properties, is simple if they are represented as dimeric molecules with an In—In bond. In this case the aminodihalides of indium are, in essence, compounds of trivalent indium which, owing to the presence of the In—In bond, exhibit properties not characteristic of the ammoniates of indium trihalides, in particular the ability to undergo disproportionation. The latter may be regarded as the result of displacement of the electron pair binding the two indium atoms toward one of the indium atoms under the action of one reagent or another, i.e., as a process of replacement of one ligand by another. The differing ability of the dihalides to undergo disproportionation upon the action of a series of amines is apparently a manifestation of the differing strength of the bonds formed by indium with these amines.

It is evident that the synthesis of complex compounds of indium dihalides and a more thorough study of their properties by various methods will make it possible to penetrate more deeply into their nature and to establish the oxidation state of indium in compounds with formal valence 2.

Institute of General and Inorganic Chemistry
named after N. S. Kurnakov

Received
4 VII 1962

LITERATURE CITED

1. R. J. Clark, E. Griswold, J. Kleinberg, *J. Am. Chem. Soc.*, **80**, No. 18 (1958).
2. V. D. Puzako, Abstract of dissertation, Sverdlovsk, 1956.
3. G. Garton, H. M. Powell, *J. Inorg. and Nucl. Chem.*, **4**, 84 (1957).
4. L. A. Woodward, G. Garton, H. Roberts, *J. Chem. Soc.*, **1956**, 3723.
5. L. A. Woodward, N. N. Greenwood et al., *J. Chem. Soc.*, **1958**, 1505.
6. S. M. Ali, F. M. Brewer et al., *J. Inorg. and Nucl. Chem.*, **9**, No. 2, 124 (1959).

7. F. M. Brewer, J. R. Chadwick, G. Garton, *J. Inorg. and Nucl. Chem.*, **23**, No. 1–2, 45 (1961).
8. A. P. Kochetkova, V. G. Tronev, O. N. Gilyarov, *DAN*, **147**, No. 5 (1962).
9. A. P. Kochetkova, V. G. Tronev, *ZhNKh*, **2**, issue 9 (1957).

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

Source: Math-Net.Ru and CyberLeninka. Machine translation. Verify with the original.