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AMES, IOWA

[CONTRIBUTION FROM THE DEPARTMENT OF CHEMISTRY OF THE UNIVERSITY OF KANSAS]

Some Observations on Lower Halides of Indium

BY RONALD J. CLARK, ERNEST GRISWOLD AND JACOB KLEINBERG

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Indium monohalides and dihalides have been prepared conveniently by reaction of the metal with appropriate quantities of mercury(I) or mercury(II) halides. A phase study of the system $InCl$–$InCl_3$ has demonstrated the unlikelihood of the existence of $InCl_2$; the most stable species found in the system has a composition In_2Cl_3 and is reasonably formulated as $In_3^{I}[In^{III}Cl_6]$. The compound $In[AlCl_4]$ has been prepared and characterized.

Recent work[1–3] has provided strong evidence that in gallium dichloride two oxidation states of gallium are exhibited and that the compound is best formulated as $Ga^{I}[Ga^{III}Cl_4]$. The present investigation was undertaken to obtain information which might shed light on the oxidation state(s) in the substance reported to have the composition $InCl_2$.

In the course of this work, it was found that the method developed in this Laboratory for the preparation of gallium dihalides,[4] namely, reaction of the metal with mercury(I) or mercury(II) halide, was applicable to the synthesis of both indium monohalides and dihalides. Moreover, a similar reaction carried out in the presence of elemental aluminum yielded the indium(I) compound $In[AlCl_4]$. In view of conflicting reports in the literature on the melting behavior of $InCl_2$, a phase study of the system $InCl$–$InCl_3$ was undertaken. The results of this study showed that it is highly doubtful that $InCl_2$ exists as a definite compound.

Preparation of Lower Halides of Indium.—Methods previously reported for the preparation of the dihalides include reduction of trihalides with indium metal,[5,6] reaction of metal with hydrogen halide,[7] direct union of the elements[8,9] and reduction of trihalide with hydrogen in the presence of hydrogen halide.[10] Monohalides have been obtained by reduction of trihalide[6] or dihalide[7,11] with the metal and by direct combination of the elements.[8,9] The lower halides can be prepared in a much more convenient fashion by reaction in appropriate stoichiometric quantities between mercury(I) or mercury(II) halide with indium metal as described below.

Experimental

The indium metal employed was obtained from the Fairmount Chemical Company and had a reported purity of 99.97%. Mercury(I) chloride, for the preparation of the lower indium chlorides, and mercury(II) bromide and iodide, for the synthesis of lower bromides and iodides, were of reagent grade, meeting ACS specifications. The reaction vessel used in all preparations consisted of a 20 × 0.8 cm. thick-walled Pyrex tube with a one cm. well located about 6 cm. from the closed end of the tube. Throughout the work described in this paper, transfers of moisture- or oxygen-sensitive materials were carried out in a dry box under nitrogen.

Essentially stoichiometric proportions of mercury halide and indium metal were employed in all preparations, except that of the monochloride. When the theoretical quantities of indium and mercury(I) chloride were taken, a product of the composition $InCl_{1.19}$ was obtained. A large excess of the metal was necessary in order that a product approximating $InCl$ in composition be formed.

The preparative procedure described below for indium monoiodide may be regarded as typical. To the reaction tube, 1.2214 g. (0.00269 mole) of mercury(II) iodide and 0.6266 g. (0.00546 mole) of indium metal were added. The tube was then evacuated to a pressure of 10–15 μ and sealed. Reaction was effected by heating to about 400° in a muffle furnace for about 30 min., after which the tube was tilted to allow the mercury formed in the reaction to collect in the well. To ensure complete removal of mercury, the end of the tube containing the indium product was heated at about 350° for 2 hr. in a tube furnace, while the portion to which the well was attached was maintained at room temperature.

Reaction temperatures for the preparation of the other halides were as follows: monochloride, 325°; monobromide, 350°; the dihalides, 350°.

For analysis of the chlorides, the products were dissolved in dilute nitric acid. Indium was determined on a portion of the solution by precipitation with 8-hydroxyquinoline.[12,13] Chloride was titrated with standard silver nitrate solution, using a Beckman Model K Automatic Titrator, the electrode system consisting of a silver indicator electrode and a calomel reference electrode equipped with saturated potassium nitrate bridge. Dissolution of the bromide samples required somewhat more concentrated nitric acid and it was necessary to provide for the collection and reduction of elementary bromine formed in the dissolving process. The method of Spitzer[14] was utilized for this purpose. Indium and halide were determined as described above for the chlorides. Analysis for indium and halogen in the iodides was performed on separate samples of the solid products. For the determination of indium, a sample was heated with dilute nitric acid until iodine was no longer evolved and then the indium was precipitated with 8-hydroxyquinoline as before. In the analysis for iodide, a sample was heated for 2 hr. on a steam-bath with an excess of standard silver nitrate solution in the presence of nitric acid. The precipitated silver iodide was collected, washed with dilute nitric acid, dried at 110° and weighed.

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(2) L. A. Woodward, G. Garton and H. I. Roberts, *J. Chem. Soc.*, 3723 (1956).

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(11) M. Wehrli and E. Miescher, *Helv. Phys. Acta*, **7**, 298 (1934).

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(13) C. Duval, "Inorganic Thermogravimetric Analysis," Elsevier Publishing Co., New York, N. Y., 1953.

(14) L. Spitzer, *Ind. Eng. Chem.*, *Anal. Ed.*, **8**, 465 (1936).

Typical compositions of the products expressed in atomic ratios are given in Table I.

TABLE I

ANALYTICAL COMPOSITIONS OF LOWER HALIDES

Monohalides	Atomic ratio halogen: indium	Dihalides	Atomic ratio halogen: indium
Chloride	1.19[a]	Chloride	2.01
	1.13[b]		1.96
	1.06[c]		1.98
	1.05[d]		1.94
Bromide	1.01	Bromide	2.01
	1.06		1.93
	1.07		1.97
	1.03		
	1.00		
Iodide	0.99	Iodide	1.95
	1.01		2.06

[a] Stoichiometric ratio of reactants. [b] 26.9% indium in excess. [c] 46.1% indium in excess. [d] 76.5% indium in excess.

Discussion

The physical appearance of each of the monohalides was identical with that described in the literature. Thus, they were red to black in the solid state and gave similarly colored melts. The identities of the monobromide and monoiodide were established definitely by the close agreement of their X-ray patterns with those previously reported.[15,16] No X-ray pattern of the monochloride appears to be available in the literature. However, the product obtained from reaction of mercury(I) chloride with indium gave a pattern identical with that of the monochloride formed by reduction of the trichloride with the metal.

The physical appearances of the dihalides agreed with those given for these substances in the literature. However, the X-ray diffraction pattern of the "dichloride" prepared by the present method differed markedly from that reported by Aiken, Haley and Terrey[10] but corresponded closely to the pattern obtained from the "dichloride" prepared by interaction of the appropriate stoichiometric quantities of indium trichloride and indium metal. Attempts to obtain the "dichloride" by the method of Aiken, *et al.*, *i.e.*, by reduction of indium trichloride with hydrogen in the presence of hydrogen chloride, gave materials of variable composition, *e.g.*, $InCl_{1.93}$, $InCl_{1.62}$. Moreover, it should be pointed out that, whereas Aiken and coworkers reported that the "dichloride" melted at 235°, Klemm[5] stated that the material melted over the range 235–270°. Klemm regarded this behavior as indicating that the "dichloride" melted incongruently. In view of these conflicts, it seemed desirable to investigate the melting behavior and phase relationships in the system $InCl–InCl_3$ in an attempt to characterize the "dichloride" more definitely.

Experimental

Phase Study of the $InCl–InCl_3$ System

Melting ranges and cooling curves were determined for materials of composition varying from InCl to $InCl_{2.10}$. The samples were prepared from indium trichloride and indium metal in the following manner. Indium trichloride, made in high purity by the direct chlorination of the metal, was placed in a dry, out-gassed Pyrex tube. The quantity of indium required to give the desired composition was added and the tube evacuated and sealed. The contents were then heated to temperatures sufficiently high to produce a homogeneous melt, about 325° in most cases. The melt was cooled rapidly and the solid was removed and ground.

With samples which gave light-colored melts, the melting ranges were determined. This was accomplished in a hot stage melting point apparatus, which was constructed from a cylindrical brass block of 9 cm. diameter and 2.5 cm. thickness, suitably drilled in the horizontal direction to accommodate a capillary melting point tube and a thermocouple. An axial hole which intersected the horizontal one permitted observation of the sample. A nichrome wire embedded in the brass block about 1 cm. from the outer edge and connected to an appropriate power source served as the heating unit, temperatures being taken by means of an iron–constantan thermocouple connected to a Wheelco Model 311 portable potentiometer. The capillary melting point tube was filled with sample (a few mg.) in a dry box, sealed and introduced into the block. The temperature of the block was raised to within a few degrees of the melting point of the sample, the block placed under a microscope of 56× magnification and the sample observed as the temperature was raised slowly through the melting range. The temperatures at which melting began and at which the crystals finally disappeared were recorded.

With samples which gave deep red melts (compositions below about $InCl_{1.4}$), it was necessary to employ the cooling curve technique in order to obtain melting point information; and this procedure was also used for some mixtures of higher chlorine content as a check on the direct melting range determinations. The sample tube consisted of a 12 × 60 mm. Pyrex tube surrounded by a vacuum jacket and sealed onto a tube 70 by 22 mm. which was fitted with a rubber stopper carrying a 360° thermometer. Five to six grams of sample was transferred to the tube in a dry box, the tube then flushed with purified dry nitrogen and immersed in a silicone oil-bath which was heated by a Glas-Col heating mantle. The sample was brought to about 30° above its melting point and then the oil-bath was allowed to cool at a rate of approximately 3° per min. Temperatures of both sample and bath were recorded every 25 sec. while the sample was stirred with the thermometer. Time–temperature plots for both sample and bath were made.

The results of the phase study of the $InCl–InCl_3$ system over the range investigated are shown in Fig. 1.

Discussion

It is significant that the phase diagram (Fig. 1) gives no indication of the existence of "indium dichloride" as a true compound. Certainly no congruently melting compound of the composition $InCl_2$ appears. Moreover, the persistence of the eutectic temperature (230°) as the initial softening point for mixtures of compositions well beyond $InCl_2$ argues strongly against the existence of this species even as an incongruently melting compound.

The most striking feature of the phase diagram is the pronounced maximum at 25 mole % $InCl_3$. The fact that the maximum occurs exactly at this point, taken together with the general appearance of the phase diagram in this region, constitutes strong evidence for the existence of the compound of the empirical composition In_2Cl_3. The diagram also indicates the occurrence of two other compounds: one of composition In_4Cl_5 and the other of undetermined composition, melting incongruently at about 252°.

The substance of composition In_2Cl_3 may be formulated as $In_3{}^{I}[In^{III}Cl_6]$. The postulation of an $[InCl_6]^{3-}$ ion is consistent with radius ratio consid-

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[15] N. C. Stephenson and D. P. Mellor, *Australian J. Sci. Research*, **A3**, 581 (1950).

[16] R. E. Jones and D. H. Templeton, *Acta Cryst.*, **8**, 847 (1955).

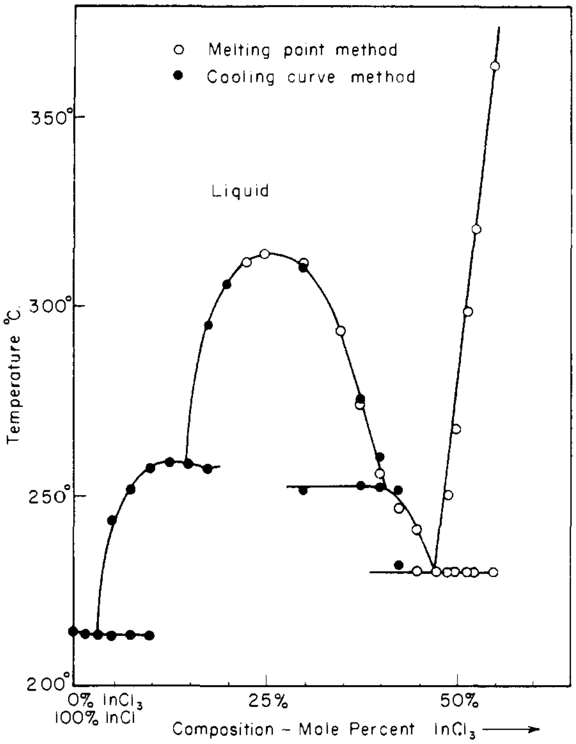

Fig. 1.—Phase diagram of the InCl–$InCl_3$ system.

erations.[17] The radii of the In^{3+} and Cl^- ions have been calculated to be 0.81 and 1.81 Å., respectively, giving a ratio of cation:anion of 0.447. This value exceeds the minimum (0.414) expected for octahedral coördination. In this connection, it is noteworthy that the phase diagram of the indium–iodine system[18] gives evidence for the existence of InI_2 as a congruently melting compound but shows no indication that In_2I_3 exists. The non-existence of In_2I_3 is not unexpected, if the assumption is made that such a substance would have the $In_3^I[In^{III}I_6]$ formulation. The radius ratio, $In^{3+}:I^-$, is 0.375, distinctly below the minimum ratio for six-coördination. On the other hand, a radius ratio of 0.375 exceeds the minimum value (0.225) for tetrahedral coördination. Therefore, if it is assumed that the diiodide contains both monopositive and tripositive indium, a formulation $In^I[In^{III}I_4]$, analogous to that demonstrated for gallium dichloride,[1,2] would be reasonable. It should be pointed out that the radius ratio $In^{3+}:Br^-$ is 0.415, just above the lower limit for six-coördination. A phase study of the indium–bromine system would be of interest in determining whether the radius ratio can be further correlated with the types of compounds formed.

Additional information regarding the species In_2Cl_3 was obtained from a study of the extraction with ether of materials having a composition of $InCl_2$. For example, when 0.33 g. of "$InCl_2$" was shaken with 3 ml. of dry ether at 30° for 12 days, the solid residue had a composition of $In_2Cl_{2.96}$ and the liquid phase contained pure indium trichloride. Single extractions of this type varying in duration from a few minutes to about two weeks yielded essentially the same result. Moreover, with increases in the proportion of ether, the chloride content of the residue dropped but slightly. These experiments are entirely consistent with the evidence from the phase diagram that "$InCl_2$" should be regarded as a mixture of $InCl_3$ and lower chlorides, the most stable of which is In_2Cl_3.

In contrast to the results of the single extractions, *continuous* ether extraction (for 60–70 hr.) of "$InCl_2$" yielded residues approaching InCl in composition; again, the liquid phase contained only $InCl_3$. These results offer substantial evidence that In_2Cl_3 contains both indium(I) and indium(III). The formation of indium monochloride may be regarded as resulting from replacement of chloride ion in $[InCl_6]^{3-}$ by the stronger Lewis base, ether

$$In_3^I[In^{III}Cl_6] + Et_2O \longrightarrow 3InCl + InCl_3 \cdot Et_2O$$

The compound In_2Cl_3 is white to orange in the solid state, the color apparently depending on the rate of cooling and being definitely affected by the presence of very small amounts of InCl or $InCl_3$. In the presence of traces of the latter, the color is white, whereas a slight excess of InCl results in a red product. The pure compound melts sharply at 314° to give a light red liquid.

Preparation of Indium(I) Tetrachloroaluminate

A substance of the composition $InAlCl_4$ was prepared from mercury(II) chloride and indium and aluminum metals in the stoichiometric proportions required by the equation

$$2HgCl_2 + In + Al \longrightarrow InAlCl_4 + 2Hg$$

The preparative technique employed was essentially that described for the monohalides and dihalides. In a typical preparation 3.6061 g. (0.01328 mole) of mercury(II) chlo-

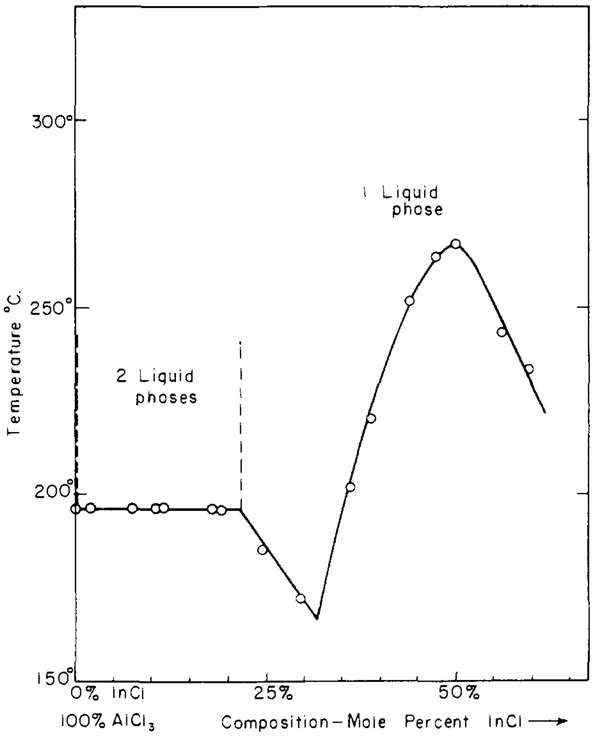

Fig. 2.—Phase diagram of the InCl–$AlCl_3$ system.

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[17] L. Pauling, "The Nature of the Chemical Bond," 2nd Ed. Cornell University Press, Ithaca, N. Y., 1940, p. 346, 382.

[18] E. A. Peretti, THIS JOURNAL, **78**, 5745 (1956).

ride, 0.7610 g. (0.00663 mole) of indium and 0.1792 g. (0.00664 mole) of aluminum were employed, the reaction temperature being 325°.

For analysis, the product was dissolved in nitric acid, hydrogen chloride evolved being trapped and combined with the solution. The separation of indium was effected by the method of Moser and Siegmann,[19] in which indium was precipitated as the sulfide while the aluminum was kept in solution by means of sulfosalicylic acid in an ammonium acetate–acetic acid buffer. The sulfide was dissolved with dilute hydrochloric acid and the indium found as described previously. The aluminum was determined on an aliquot of the indium-free solution by precipitation with 8-hydroxyquinoline.[20] Another aliquot was analyzed for chloride as described for the indium chlorides. *Anal.* Calcd. for $InAlCl_4$: In, 40.47; Al, 9.51; Cl, 50.02. Found: In, 40.51; Al, 9.69; Cl, 49.74.

Discussion

The color of $InAlCl_4$ generally was white in the solid state but occasionally showed a yellow appearance. It melted sharply at 267–268° to give a colorless or pale yellow melt and was extremely sensitive to moisture. Its identity as a true compound was demonstrated by a study of melting behavior in the system $InCl–AlCl_3$ (Fig. 2). The technique employed in this study was that described for the $InCl–InCl_3$ system. It is apparent from Fig. 2 that a sharp maximum occurs at 50 mole % InCl. Moreover, the melting point and appearance of the material at this composition were identical with those of $InAlCl_4$ prepared by the procedure noted above. In view of the ability of aluminum chloride to function as a Lewis acid, there is little doubt that the compound should be formulated as indium(I) tetrachloroaluminate, $In[AlCl_4]$.

Indium(I) tetrachloroaluminate exhibits interesting behavior toward ether. Even when exposed to ether vapor, the compound immediately turned brilliant yellow. Treatment with an excess of liquid ether left a yellow residue which upon analysis proved to be indium monochloride.[21] The ether solution was found to contain no indium but contained aluminum chloride. Here again, as in the ether extractions of In_2Cl_3, it seems reasonable to suppose that the ether, functioning as a stronger Lewis base than chloride ion, replaces the latter from combination with aluminum chloride.

$$In[AlCl_4] + Et_2O \longrightarrow InCl + AlCl_3{\cdot}Et_2O$$

Acknowledgments.—The authors are indebted to the Atomic Energy Commission for a grant in support of this investigation. R. J. C. wishes to express his appreciation to the Eastman Kodak Company for a fellowship held during part of the investigation.

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[19] L. Moser and F. Siegemann, *Monatsh. Chem.*, **55**, 14 (1930).

[20] W. F. Hillebrand, G. E. F. Lundell, H. A. Bright and J. I. Hoffman, "Applied Inorganic Analysis," 2nd Ed., John Wiley and Sons, Inc., New York, N. Y., 1953, p. 507.

[21] Since the monochloride as made by high temperature procedures is deep red in color, it is conceivable that the yellow form is a different crystalline modification.

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[CONTRIBUTION NO. 619 FROM THE INSTITUTE FOR ATOMIC RESEARCH AND DEPARTMENT OF CHEMISTRY, IOWA STATE COLLEGE. WORK WAS PERFORMED IN THE AMES LABORATORY OF THE U. S. ATOMIC ENERGY COMMISSION]

Intermolecular Metal–Metal Bonds and Absorption Spectra of Some Nickel(II) and Palladium(II) Complexes of *vic*-Dioximes[1]

BY CHARLES V. BANKS AND DENNIS W. BARNUM

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Intermolecular metal–metal bonds in certain square planar complexes of Ni(II), Pd(II), Pt(II) and Au(III) give rise to an absorption band in the visible region of the spectrum. This band gives rise to unusual dichroism in crystals of these complexes. The absorption spectra of single crystals of some nickel complexes were measured using plane polarized light and it was shown that complexes containing strong metal–metal bonds show "abnormal" dichroism while complexes with very weak metal–metal bonds show practically "normal" dichroism. The absorption spectra of colloidal suspensions of several of the complexes were measured. The position of the band due to metal–metal bonding depends primarily on the length of the metal–metal bonds, the central metal ion and the crystal structure. The position of this band also depends, but to a much lesser extent, on the particle size, since this affects the selective scattering of light on the long wave length side of an absorption band.

Introduction

Certain square planar complexes of nickel(II), palladium(II), platinum(II) and gold(III) have been shown to contain intermolecular metal–metal bonds.[2–4] These bonds form a chain of metal atoms that extends throughout the length of the crystal. The lengths of these relatively weak metal–metal bonds range from about 3.2 to 3.6 Å. Nevertheless, they contribute enough to the stability of the crystal that they affect the properties appreciably. The most striking example of this is the outstanding selectivity of nickel dimethylglyoxime as a gravimetric reagent for nickel.[2] The solubility of several complexes containing metal–metal bonds is discussed in the preceding paper.[5]

Complexes containing metal chains have an absorption band in the visible region of the spectrum. This band is most easily detected in the absorption spectrum of the complex in colloidal suspension and it gives rise to unusual dichroism in the single crystal.

Yamada and Tsuchida,[6] using plane polarized light, measured the absorption spectra of microscopic crystals of the copper(II), nickel(II) and

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[1] No. XXII in a series on "Chemistry of the *vic*-Dioximes." Previous paper in this series is No. XXI, THIS JOURNAL, **80**, 3579 (1958). Abstracted from dissertation submitted by Dennis W. Barnum to graduate faculty of Iowa State College in partial fulfillment of requirements for degree of doctor of philosophy, 1957.

[2] L. E. Godycki and R. E. Rundle, *Acta Cryst.*, **6**, 487 (1953).

[3] R. E. Rundle, THIS JOURNAL, **76**, 3101 (1954).

[4] M. Atoji, J. W. Richardson and R. E. Rundle, *ibid.*, **79**, 3017 (1957).

[5] C. V. Banks and D. W. Barnum, *ibid.*, **80**, 3579 (1958).

[6] S. Yamada and R. Tsuchida, *ibid.*, **75**, 6351 (1953).