other similar groups. Unfortunately, this frequency has not been observed by Raman methods and, as an infrared band arising from such a vibration lies beyond the limits of rocksalt spectrometry, no data could be obtained on this point during the present study. Further study of this region seems desirable.

Summary

Measurements of the infrared transmission of potassium cyanate solutions have been made in the region 2 to 14 μ. For freshly prepared solutions intense bands were observed at 4.6 and 11.5 μ and a less intense band near 7.4 μ. In the spectra of solutions which had been allowed to stand for several days, the absorption in the 7 μ regions was found to be more intense, while additional absorption bands made their appearance near 3.5 and 5.9 μ. It is suggested that the 4.6 and 11.5 μ bands arise from vibrations of the cyanate ion, while the additional absorption is produced by ammonium and carbonate groups formed by hydrolysis.

GAINESVILLE, FLORIDA RECEIVED JUNE 24, 1940

[CONTRIBUTION FROM THE NOYES CHEMICAL LABORATORY OF THE UNIVERSITY OF ILLINOIS]

Contributions to the Chemistry of Indium. I. Indium Oxalate and Oxalatoindates

BY THERALD MOELLER

The formation of an insoluble oxalate of indium as a result of mixing concentrated "neutral" indium salt solutions with oxalic acid or alkali oxalate solutions has been described by Winkler,[1] and a recalculation of his analytical data for the material gives the formula $In_2(C_2O_4)_3 \cdot 6H_2O$. This precipitation also has been suggested for the microchemical detection of indium.[2]

However, it will be shown that only when oxalic acid is the precipitant do the analytical data correspond to a ratio of 1.5 oxalates to 1 indium. With sodium, potassium and ammonium oxalates this ratio becomes 2 to 1, indicating the formation of dioxalatoindates.

By analogy to aluminum, trioxalatoindates also should form. However, only compounds of unusual compositions result under conditions favorable to the formation of the trioxalato salts.

Experimental

Materials Used.—A sample of 99.98% pure indium[3] was digested with hot dilute sulfuric acid until only a small amount of the metal remained undissolved. Hydrous indium hydroxide was then precipitated from the filtered solution with ammonium hydroxide, washed, and redissolved in dilute sulfuric acid, this process being repeated three times. Finally, anhydrous indium sulfate was prepared as described by Seward.[4] Analysis proved it to be pure.

Other chemicals were of analytical reagent quality.

Analytical Procedures.—Oxalate was determined by dissolving the samples in hot 0.3 *N* sulfuric acid and titrating with standard potassium permanganate.

To eliminate the slight inhibitory effect exerted by the oxalate ion upon the precipitation of indium hydroxide, oxalate was completely destroyed by heating the weighed samples with concd. sulfuric acid until frothing ceased and sulfur trioxide fumes were evolved. The residues were then taken up in cold water, and the indium precipitated as hydroxide with ammonium hydroxide and weighed as the oxide. Addition of ammonium hydroxide to cold solutions followed by boiling the suspensions for two minutes gave precipitates which settled rapidly, filtered easily, and showed little tendency to peptize on excessive washing.

Ammonium was determined in the usual fashion by liberation of ammonia and distillation into standard acid.

Indium Oxalate Decahydrate.—To a warm solution of 1 g. of anhydrous indium sulfate in 5 ml. of water was added a solution of 0.9739 g. of oxalic acid in 10 ml. of warm water. A voluminous white precipitate formed immediately. After cooling, this precipitate was washed until sulfate-free and dried on the filter paper in a current of air at room temperature. The dry product was compact and silvery white in appearance and made up of needle-like crystals. It was somewhat soluble in cold water, more so in hot water. On ignition, indium oxide remained as residue and carbon dioxide, carbon monoxide, and water vapor were evolved.

Anal. Calcd. for $In_2(C_2O_4)_3 \cdot 10H_2O$: In, 34.07; C_2O_4, 39.19. Found: In, 34.24; C_2O_4, 39.20; C_2O_4/In, 1.493.

Dioxalatoindates.—To warm solutions of 1 g. of anhydrous indium sulfate in 5 ml. of water were added warm solutions of sodium, potassium and ammonium oxalates containing the equivalent of two oxalate ions to one indium, the volume in each case being kept as small as possible. Precipitates of white finely-divided octahedral crystals formed and were purified and dried as above. Analytical results are summarized in Table I. The presence of sodium and potassium was established by flame tests.

These compounds are but slightly soluble in cold water, more soluble in hot water, and readily soluble in hot dilute sulfuric acid.

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[1] Winkler, *J. prakt. Chem.*, **102**, 292 (1867).

[2] Huysse, *Z. anal. Chem.*, **39**, 10 (1900).

[3] From the Indium Corporation of America, Utica, New York.

[4] Seward, THIS JOURNAL, **55**, 2740 (1933).

TABLE I

DIOXALATOINDATES

For	Calcd. In	Calcd. C_2O_4	Calcd. Other	Found In	Found C_2O_4	Found Other	Found C_2O_4/In
$NaIn(C_2O_4)_2 \cdot 3H_2O$	31.20	47.85	6.25 (Na)	31.35	47.00	....	1.955
$KIn(C_2O_4)_2 \cdot 4H_2O$	28.55	43.79	9.73 (K)	28.49	43.89	....	2.006
$NH_4In(C_2O_4)_2 \cdot 2H_2O$	33.28	51.04	5.23 (NH_4)	33.25	50.77	5.07 (NH_4)	1.990

Further evidence for the formation of these insoluble dioxalatoindates is given in Fig. 1. Ten-ml. portions of 0.0500 *M* indium sulfate solution were titrated with 0.2000 *M* solutions of sodium, potassium, and ammonium oxalates, the changes in *p*H being followed with a Beckmann Laboratory Model *p*H Meter. While the *p*H values as such are probably without significance, the fact that the *p*H of the indium sulfate solution (2.03) differs markedly from those of the oxalate solutions (all above 6) indicates that at the completion of precipitation a sudden change in *p*H should occur. With all three salts, the breaks correspond to an oxalate to indium ratio of practically 2. A similar titration using 0.2000 *M* oxalic acid solution was inconclusive, due probably to the fact that the *p*H of the oxalic acid (1.09) differed so slightly from that of the indium sulfate solution.

Trioxalatoindates.—In accordance with the method suggested for the preparation of potassium trioxalatoaluminate,[5] suspensions of freshly precipitated and thoroughly washed hydrous indium hydroxide were boiled with solutions of slightly more than enough potassium acid oxalate to satisfy the ratio $3C_2O_4^=$ to $1In^{+++}$. The indium hydroxide dissolved readily, going through the colloidal stage, and upon evaporation white crystals of indefinite appearance were deposited. Flame tests showed the presence of potassium. Analytical data for these materials are given in Table II.

TABLE II

POTASSIUM TRIOXALATOINDATE

Sample	In, %	C_2O_4, %	C_2O_4/In
1	18.04	47.83	3.46
70	17.85	47.11	3.44
84	17.86	47.62	3.48

Calcd. for $K_2C_2O_4 \cdot 2K_3[In(C_2O_4)_3] \cdot 7H_2O$: In, 17.87; C_2O_4, 47.95.

Although the oxalate to indium ratio approaches 3.5 to 1 and the analytical data agree fairly well with the above formula, it is doubtful that a definite potassium trioxalatoindate results. From a more concentrated solution without evaporation, crystals were obtained which analyzed for In, 30.32%; C_2O_4, 46.27%; C_2O_4/In, 1.99. Evaporation of the mother liquor gave another crop analyzing for In, 6.24%; C_2O_4, 55.24%, and consisting largely of potassium oxalate. Thus the products obtained may well have contained the dioxalato salt mixed with potassium oxalate or acid oxalate.

Discussion

It has been found impossible to prepare indium oxalate hexahydrate by a repetition of Winkler's procedure. Furthermore, Winkler's (and other authors') application of the term "neutral" to indium salt solutions is misleading. As will be shown in a later paper, any attempt to bring a simple indium salt solution to the neutral point results in the precipitation of hydrous indium hydroxide in the *p*H range 3 to 4.

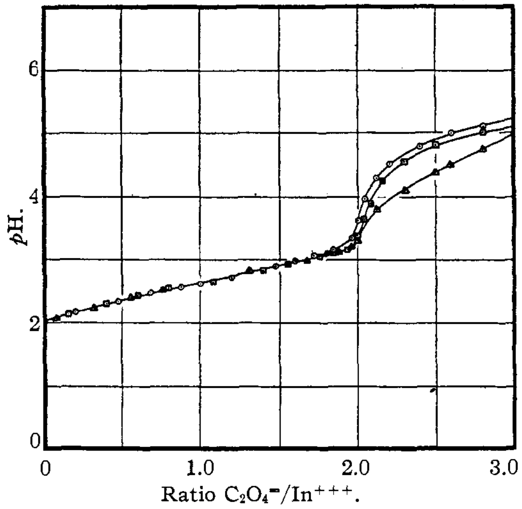

Fig. 1.—Titration of indium sulfate solution with soluble oxalates: ⊙, potassium oxalate; ⊡, ammonium oxalate; △, sodium oxalate.

Inasmuch as the coördination number of indium is generally six,[6] the dioxalatoindate ion may be assumed to be $[In(C_2O_4)_2(H_2O)_2]^-$, the two water molecules being necessary to fill the coördination sphere. *cis* and *trans* isomers should exist, and the *cis* form should consist of two enantiomorphs and theoretically be resolvable. No work has been done in this connection.

That dioxalato derivatives result upon the addition of soluble oxalates to indium sulfate solutions, whereas a normal indium oxalate is produced by the action of oxalic acid, may possibly be explained as follows. The addition of oxalate ion forms the dioxalatoindate ion, $[In(C_2O_4)_2(H_2O)_2]^-$, which gives an insoluble compound with sodium, potassium or ammonium ion. With oxalic acid,

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(5) "Inorganic Syntheses," Vol. I, McGraw-Hill Book Company, Inc., New York, N. Y., 1939, p. 36.

(6) Morgan and Burstall, "Inorganic Chemistry. A Survey of Modern Developments," W. Heffer & Sons, Ltd., Cambridge, 1936, p. 96.

this anion might then combine with more indium ion to form $In[In(C_2O_4)_2(H_2O)_2]_3 \cdot 14H_2O$, or $2In_2(C_2O_4)_3 \cdot 10H_2O$. This would suggest that the compound referred to as the normal oxalate is dimeric with three-fourths of the indium in the complex and thus really a dioxalatoindate. Desiccation of this compound over anhydrous calcium chloride at 25° yields a product corresponding to $In_2(C_2O_4)_3 \cdot 4H_2O$, or $In[In(C_2O_4)_2(H_2O)_2]_3 \cdot 2H_2O$.

The dioxalatoindate complex is not extremely stable, for solutions of the compounds prepared give *nearly* complete precipitation of indium hydroxide when treated with ammonium hydroxide. Furthermore, on digestion with boiling water in quantity insufficient to dissolve it completely, the potassium compound gave a product analyzing for In, 50.17; C_2O_4, 27.72; C_2O_4/In, 0.72, and probably consisting of a mixture of basic salts resulting from hydrolysis.

A true potassium trioxalatoindate apparently does not result under the conditions employed. The formation of a material of indefinite crystalline structure corresponding to $K_2C_2O_4 \cdot 2K_3In(C_2O_4)_3 \cdot 7H_2O$ seems to be a function of the experimental conditions as already pointed out. This substance readily yields the dioxalato salt, for recrystallization of Sample 70 (Table II) gave a product analyzing for In, 29.10; C_2O_4, 44.01; C_2O_4/In, 1.975, values closely approaching those calculated for potassium dioxalatoindate. If any trioxalatoindate were present, the reaction could be formulated

$$[In(C_2O_4)_3]^{\equiv} + 2H_2O \longrightarrow [In(C_2O_4)_2(H_2O)_2]^{-} + C_2O_4^{=}$$

Furthermore, when a solution of Sample 84 (Table II) was treated with a solution of indium sulfate, a precipitate formed which analyzed for In, 28.49; C_2O_4, 43.80; C_2O_4/In, 2.001, values which agree almost exactly with those calculated for potassium dioxalatoindate.

Summary

1. Indium sulfate solution reacts with solutions of sodium, potassium and ammonium oxalates precipitating octahedral crystals of $Na[In(C_2O_4)_2(H_2O)_2] \cdot H_2O$, $K[In(C_2O_4)_2(H_2O)_2] \cdot 2H_2O$ and $NH_4[In(C_2O_4)_2(H_2O)_2]$.

2. With oxalic acid, the precipitate corresponds to $In_2(C_2O_4)_3 \cdot 10H_2O$, or *perhaps* $In[In(C_2O_4)_2(H_2O)_2]_3 \cdot 14H_2O$. On drying over anhydrous calcium chloride, this becomes $In_2(C_2O_4)_3 \cdot 4H_2O$, or $In[In(C_2O_4)_2(H_2O)_2]_3 \cdot 2H_2O$. Dimeric formulas are given as *possible* explanations for the compositions of the materials.

3. Attempts to prepare potassium trioxalatoindate have led to an indefinite material approximating $K_2C_2O_4 \cdot 2K_3[In(C_2O_4)_3] \cdot 7H_2O$.

4. Use of the term "neutral" as applied to simple indium salt solutions is seriously questioned.

URBANA, ILLINOIS RECEIVED JULY 8, 1940

[CONTRIBUTION FROM THE RESEARCH LABORATORIES OF THE UNIVERSAL OIL PRODUCTS COMPANY]

Notes on the Preparation and Properties of Some Aliphatic Hydrocarbons

BY LOUIS SCHMERLING, B. S. FRIEDMAN AND V. N. IPATIEFF

Several paraffinic hydrocarbons have been prepared for use in connection with studies in this Laboratory. Their physical constants are presented along with some improved simple methods of preparation. Anti-knock values are also given.

2-Methylpentane was prepared *via* 2-methylpentanol-4 which was obtained by hydrogenating mesityl oxide, a compound which is more readily available than 2-methylpentanol-2 which has been used for the same purpose.[1]

An attempt to use diacetone alcohol as the starting material for the synthesis of the hydrocarbon was unsuccessful. Hydrogenation of the keto-alcohol to the diol was accompanied by hydrogenolysis to isopropyl alcohol. The hydrogenolysis was decreased substantially by use of a lower temperature and of isopropyl alcohol as solvent. However, dehydration of the 2-methylpentanediol-2,4 over activated alumina did not yield methylpentadiene as expected; instead, the product consisted chiefly of acetaldehyde and isobutene. This result may be explained readily as follows:

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[1] P. L. Cramer and Mulligan, THIS JOURNAL, **58**, 373 (1936).