method of Bent and French[8] and the method of continuous variations used by Kleiner are based on Beer's law. From the work of Reeves and Jonassen there is reason to suspect polymerization in solutions with these titanium(IV) concentrations, which would also render the conclusions somewhat invalid. Second, not in all solutions is the peroxide concentration high enough to ensure complete complexing of the titanium(IV). Third, there is no reference to the change with time in the absorption spectra, which we have always observed. Finally, the effective wave length of his filter, 465 mμ, is quite far from the peak of the absorption band (410 mμ).

Using the same procedure employed by Gastinger, we have determined the effect of fluoride on the stability of the peroxy–titanium(IV) complex, with the result that, over the concentration range investigated, the stability of the peroxy–titanium (IV) complex is essentially unaffected by the presence of fluoride.

A possible interpretation of the results reported here can be found in current theories of the absorption spectra of ions in solution recently discussed by Bjerrum and co-workers.[9] The fluoride ion represents a change in the solvent in our case, which alters the crystal field bands slightly by changing the point dipole moment for the second coördination sphere. This brings about the change in the position of the absorption band. The extinction coefficient change is also correct in sign since a change from water to methanol should produce an opposite effect to that obtained in changing the solvent from water to aqueous fluoride. A more quantitative treatment along these lines must be deferred until further refinements are made in these theories.

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[8] H. E. Bent and C. L. French, THIS JOURNAL, **63**, 568 (1941).

[9] J. Bjerrum, A. W. Adamson and O. Bostrup, *Acta Chem. Scand.*, **10**, 329 (1956).

SAYREVILLE, N. J.

[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT OF CORNELL UNIVERSITY]

Fluoride Complexes of Indium(III)[1]

BY JOHN E. ROBERTS[2] AND A. W. LAUBENGAYER

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Aqueous systems of indium(III) fluoride with each of 15 cations have been studied. Only the ammonium ion and the cobalt(II) ion produced identifiable fluoroindate complexes. Thermal analysis of the system lithium fluoride–indium(III) fluoride showed that only the compound Li_3InF_6 is stable in this system.

Introduction

Ammonium hexafluoroindate, $(NH_4)_3InF_6$, has been prepared and characterized by Huysse[3] and by Hannebohn and Klemm.[4] The latter could not prepare sodium hexafluoroindate, Na_3InF_6, although Ensslin and Dreyer[5] reported this compound and Sunden[6] isolated a precipitate of this composition. Polarographic[6,7] and potentiometric[8] measurements have identified InF^{++}, InF_2^+ and InF_4^- ions in solution although no solids containing these ions have been isolated.

In view of the large number of fluoro-complexes known for related elements, particularly gallium,[9] it is reasonable to expect similar compounds for indium. The formation of indium fluoride complexes will be complicated, however, by the hydrolysis of indium fluoride.[10]

If the value 1.3 is assumed for the electronegativity of indium, the indium–fluorine bond may be expected to be about 90% ionic,[11] and the radius ratio gives a maximum coördination number of indium toward fluorine of eight. Such highly coördinated complexes should be stabilized by the triple charge on the indium ion but mutual repulsion between adjacent fluorine atoms could decrease the maximum coördination number.

Experimental

Preparation of Materials.—Anhydrous indium trichloride was prepared from spectrographically pure indium metal by the method of Baxter and Alter,[12] purified by triple sublimation in dry nitrogen and converted to the anhydrous trifluoride by heating in a stream of dry hydrogen fluoride at 700° for three hours. *Anal.* Calcd. for InF_3: In, 66.8; F, 33.2. Found: In, 66.5; F, 33.4. All attempts to prepare InF_3 by dehydrating $InF_3 \cdot 3H_2O$, even in an HF atmosphere led to hydrolyzed products of variable composition.[10]

Hydrated indium trifluoride was prepared by dissolving spectrographically pure indium metal in strong nitric acid and repeatedly evaporating the solution to dryness with 40% hydrofluoric acid. The residue was dissolved in hot dilute hydrofluoric acid, the solution evaporated to incipient crystallization and allowed to cool. The colorless crystals were separated by decantation, washed with 40% hydrofluoric acid and dried over soda lime. *Anal.* Calcd. for $InF_3 \cdot 3H_2O$: In, 50.8; F, 25.2. Found: In, 50.3; F, 25.9. Microscopic examination showed the crystals to be tetragonal, the common view being rectangular prisms showing negative elongation. An occasional square basal pinacoid showing a negative uniaxial optic axis figure was observed. Refractive indices for white light at room temperature: $\epsilon = 1.43 \pm 0.01$ and $\omega = 1.47 \pm 0.01$.

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[1] Taken from the Ph.D. thesis of John E. Roberts, Cornell Univ., June, 1947. Presented at the 111th meeting of the American Chemical Society, Atlantic City, N. J., April 15, 1947.

[2] Department of Chemistry, Univ. of Mass., Amherst, Mass.

[3] A. C. Huysse, *Z. anal. Chem.*, **39**, 9 (1900).

[4] O. Hannebohn and W. Klemm, *Z. anorg. allgem. Chem.*, **229**, 337 (1936).

[5] F. Ensslin and H. Dreyer, *ibid.*, **249**, 119 (1942).

[6] L. G. Hepler, J. W. Kury and Z. Z. Hugus, *J. Phys. Chem.*, **58**, 26 (1954).

[7] J. A. Schufle and H. M. Eiland, THIS JOURNAL, **76**, 960 (1954).

[8] N. Sunden, *Svensk. Kem. Tidskr.*, **66**, 50 (1954).

[9] W. Pugh, *J. Chem. Soc.*, 1046, 1959 (1937).

[10] J. E. Roberts and A. W. Laubengayer, unpublished research.

[11] L. Pauling, "The Nature of the Chemical Bond," Cornell University Press, Ithaca, N. Y., 1940, pp. 69–75.

[12] G. P. Baxter and C. M. Alter, THIS JOURNAL, **55**, 1944 (1933).

Pure lithium fluoride was prepared by treating pure lithium carbonate with excess hydrofluoric acid and repeatedly evaporating the solution with portions of hydrofluoric acid. The product was dried at 110° and melted sharply at 842°.

All other reagents were of analytical reagent quality.

Analytical Methods.—Indium was determined by double precipitation with ammonia and ignition to In_2O_3. Fluoride was determined in the filtrate either as lead chlorofluoride[13] or triphenyltin fluoride[14] depending on the amount of fluoride present. Cobalt was determined as the 8-quinolinate after separation by the cobaltinitrite method. Alkali metals were determined by evaporating solutions to dryness with concentrated sulfuric acid and weighing the anhydrous sulfate. Interfering elements were removed by standard methods.

Microscopic methods were used for qualitative identification. The cesium indium alum test identified indium. The triphenyltin test was adapted to a micro scale for the detection of fluoride; the hexagonal prisms and basal sections were characteristic and provided a very sensitive test for fluoride.

Aqueous Ammonium System.—Ammonium hexafluoroindate was prepared by the method of Hannebohn and Klemm.[4] The first crop of crystals was recrystallized from very dilute hydrofluoric acid and the large colorless well-formed octahedra analyzed. *Anal.* Calcd. for $(NH_4)_3InF_6$; F, 40.1; In, 40.6. Found: F, 41.16; In, 40.3. The high fluorine content was attributed to occluded hydrofluoric acid. The refractive index for white light at room temperature was 1.412 ± 0.002 and the power X-ray diffraction pattern is shown in Table I.

Aqueous Systems with Other Nitrogen Cations.—Systems containing hydroxylamine, aniline, hydrazine, pyridine, dimethylaniline and tetramethylammonium in hydrofluoric acid were studied by evaporating solutions of these substances with solutions of indium fluoride in various proportions. In no case could evidence be found for the production of complex or double salts.

Aqueous Cobalt System.—Equimolar quantities of cobaltous fluoride and indium fluoride were dissolved in very dilute hydrofluoric acid and evaporated to incipient crystallization. The resulting red crystals were recrystallized from water which was slightly acidified with hydrofluoric acid. The air-dried product was characterized by analysis and optical properties. *Anal.* Calcd. for $CoInF_5 \cdot 7H_2O$: Co, 14.8; F, 24.1; In, 29.0. Found: Co, 15.0; F, 23.5; In, 30.0. Drying for six hours at 125° caused a weight loss of 26.9% and a reversible color change from red to blue. The loss of six moles of water per formula weight would amount to 27.4%.

The optical properties are summarized in Fig. 1. The crystals are monoclinic, optically negative. $2V$ was determined by calculation from the refractive indices and agreed well with the value estimated from a Bxa figure. $\alpha = 1.440$, $\beta = 1.4425$, $\gamma = 1.444$ all to ±0.002. $2V$ is greater for blue than for red light. The crystals are dichroic; β is pink, γ is yellow. Inclined dispersion was not detected.

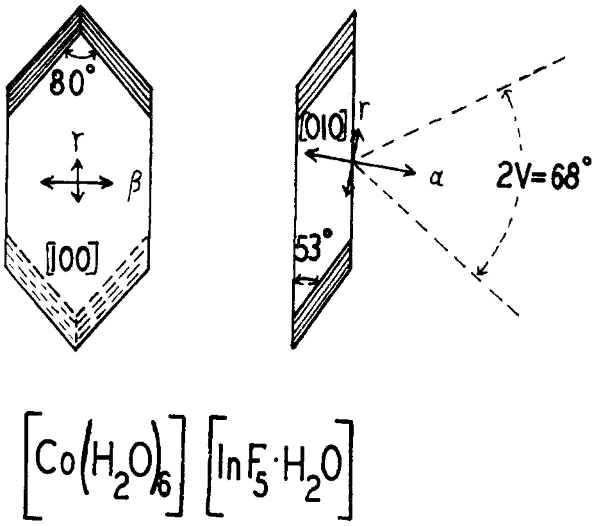

Fig. 1.

TABLE I

POWDER X-RAY DIFFRACTION · PATTERNS,[a] COPPER K_α RADIATION

$(NH_4)_3InF_6$		Li_3InF_6	
5.88vw	1.87m	4.53w	1.94m
5.37vs	1.85s	4.40s	1.775w
5.07vw	1.78m	4.30s	1.750s
4.64vs	1.765s	3.86s	1.737s
4.35vw	1.620w	3.06s	1.710vw
3.28vs	1.600vw	2.68m	1.700vw
3.06vw	1.560m	2.64m	1.662w
2.84s	1.528s	2.58vw	1.640w
2.76s	1.510vw	2.52w	1.610m
2.68vw	1.460w	2.40w	1.485s
2.59vw	1.435m	2.22m	
2.47vw	1.390w	2.16w	
2.36m	1.370w	2.12w	
2.29s	1.322w	2.08m	
2.08m	1.288w	2.00w	
2.05s	1.270w		
2.01s			

[a] Intensities estimated visually: s, strong; m, medium; w, weak; v, very.

Aqueous Systems with Other Metals.—By the same techniques attempts were made to prepare fluoroindates of lithium, sodium, potassium, silver, nickel, thallium(I) and zinc. In all cases the only products isolated were the original simple fluorides.

Systems in Anhydrous Liquid Hydrogen Fluoride.—Attempts to use anhydrous hydrogen fluoride as solvent for the preparation of fluoroindates were unsuccessful due to the insolubility of indium fluoride in the medium.

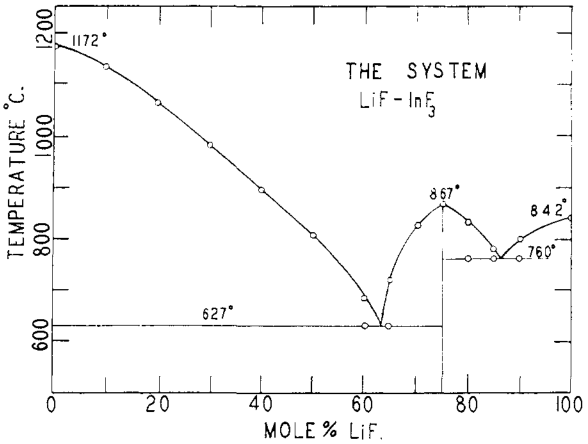

Fig. 2.

Thermal Analysis in the System LiF–InF_3.—Thermal analysis was carried out in a vertical electric furnace with an Alundum core wound with platinum ribbon as a heating unit. Samples were held in a 0.5-ml. platinum crucible which was supported on granular quartz in a tall platinum crucible. A platinum *vs.* platinum–rhodium thermocouple immersed in the sample permitted temperature measurement within 5°. An atmosphere of dry nitrogen was maintained throughout the experiments. The thermocouple was calibrated at the melting points of sodium chloride and potassium sulfate and the inversion point of potassium sulfate. Weighed samples of anhydrous lithium and potassium fluorides were intimately mixed in the small crucible and the temperature arrests in the heating and cooling curves found. The results are shown in Fig. 2.

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(13) N. H. Furman, "Scott's Standard Methods of Chemical Analysis," 5th ed., D. Van Nostrand Co., New York, N. Y., 1938, pp. 405–406.

(14) N. H. Furman and N. Allen, THIS JOURNAL, **54**, 4625 (1932).

Fragments of the solidified melt containing 3LiF:1InF$_3$ were studied microscopically and by powder X-ray diffraction. Some grains showed a negative Bxa figure from which the optic axial angle was estimated to be about 60°. Approximate values of the refractive indices for white light at room temperature are $\gamma = 1.43$, $\alpha = 1.41$ and $\beta = 1.422$. No lines in the X-ray diffraction pattern could be attributed to the starting materials (Table I). The compound decomposed in water to form lithium fluoride and a product resembling that obtained from the hydrolysis of aqueous indium fluoride solutions.[10]

Discussion

The failure to obtain fluoro-indium complexes of the majority of cations studied is in marked contrast to the behavior of most elements closely related to indium, particularly gallium. The larger size of the indium ion may be largely responsible for this behavior. Although the reversible color change from pink to blue, which is observed when the cobalt salt is heated, is strongly indicative of the presence of hexahydrated cobalt(II) ions and hence of the formulation [Co(H$_2$O)$_6$] [InF$_5$(H$_2$O)], the possibility of formulating the compound as a fluoro-complex of cobalt(III) is not conclusively eliminated. Such a structure would require oxidation of the cobalt and the experimental conditions were not favorable for this. The stability of the ammonium salt can be attributed to hydrogen bonding and the absence of steric interference which could become important with the larger ions.

Thermal analysis of the lithium fluoride–indium fluoride system shows conclusively that only one compound exists in this system. The empirical composition is Li$_3$InF$_6$ and the compound melts congruently at 867°. The decomposition of the compound when it is placed in water is further confirmation that the fluoroindate ion is less stable than the hydrated indium ion or hydroxy-fluoro-indium complexes, a conclusion which is also deduced from the studies in aqueous solution.

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[CONTRIBUTION FROM THE CHEMISTRY DEPARTMENT, HORIZONS INCORPORATED]

Rare Earth Graphite Intercalates

BY R. C. VICKERY AND N. LUCILE CAMPBELL

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Intercalation in graphite of the whole series of rare earth chlorides has been investigated and some disagreements found with pre-existing incomplete studies. Only yttrium and gadolinium chlorides are found to intercalate consistently and in appreciable quantities. The light lanthanons do not intercalate, and inconsistent intercalation of heavy lanthanons appears attributable to variable degrees of hydration of the parent chlorides. Hall coefficient and magnetic susceptibility measurements confirm that the intercalates are ionic, while X-ray studies appear to confirm beliefs that the ions are located at imperfections in the graphite lattice. There appears some foundation for believing that ionic size and electronic structure are the major factors influencing intercalation.

Introduction

Croft[1] recently listed the varying reactions to intercalation in graphite of many elements in various ionic states and attempted to explain variations in degree of intercalation on the basis of interaction of vacant valence orbitals which could accept paired, but not single, electrons from 2-p-π orbitals of graphite atoms. Several criticisms of Croft's work[2] have developed but, theoretical aspects notwithstanding, his qualitative findings suggested immediately a new technique of rare earth separation potentially capable of applications to both gross and refined systems. Thus, yttrium and dysprosium appeared to be readily separable from erbium; similarly, ytterbium and scandium demonstrated differences in behavior which might well be the basis for a separational technique effective enough to supplement or supplant conventional amalgam-reduction techniques. Samarium apparently reacted differently from neodymium, while europium appeared separable from both gadolinium and samarium by graphite intercalation.

These pre-existing studies, however, were incomplete, the intercalation of terbium, holmium and lutetium not having been examined. In a generalized examination of these rare earth graphite intercalates we have now filled this deficiency while simultaneously checking the intercalation effects of the whole rare earth series. Results obtained, in comparison with those of Croft, are concisely shown in Table I. Table II records the results of some separations attempted.

TABLE I

INTERCALATION OF RARE EARTH CHLORIDES, %

Ion^{3+}	Croft[1]	Present work
Sc	. .	. .
Y	43	25.5
La	. .	. .
Ce	. .	. .
Pr	. .	. .
Nd	. .	. .
Sm	38	4.9
Eu	3	. .
Gd	16	19
Tb	n.i.[b]	2.5
Dy	22	2.0
Ho	n.i.[b]	. .[a]
Er	. .	. .
Tm	n.i.[b]	0.9
Yb	9	4.0
Lu	n.i.[b]	3.4

[a] See text. [b] n.i., not investigated.

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(1) R. C. Croft, *Nature*, **168**, 32 (1951); **172**, 725 (1953); *J. Appl. Chem.*, **2**, 557 (1952); *Australian J. Chem.*, **9**, 184 (1956).

(2) G. R. Hennig, Proc. Second. Conf. on Carbon, June, 1955, pp. 108, 111, Pub. 1956, University of Buffalo: W. Rudorf, V. Sils and R. Zeller, *Z. anorg. allgem. Chem.*, **283**, 229 (1956).