For ethylenediamine[2,10] and cobaltous ion log $k_1 = 5.89$; for manganous ion log $k_1 = 2.73$.

It is of interest to compare the values available for log k_1 of the various metal ions with ammonia and imidazole in Table III.

Table III

First Association Constants (Log k_1) for Ammonia and Imidazole with Various Metallic Ions

	Cu^{++}	Ni^{++}	Cd^{++}	Zn^{++}	Co^{++}	Mn^{++}	Ca^{++}
Ammonia[a]	4.15	2.80	2.65	2.37	2.11	..	−0.2
Imidazole	4.33[b]	3.27[c]	2.80[d]	2.57[e]	2.42	1.65	0.08[f]

[a] Ref. 4. [b] Ref. 3. [c] Ref. 11. [d] C. Tanford and M. L. Wagner, This Journal, **75**, 434 (1953). [e] Ref. 3. [f] J. Schubert, This Journal **76**, 3442 (1954).

The values for ammonia are at 30° and ionic strength 2 except for calcium ion which is at 23°. However, the temperature coefficient of log k_1 for the calcium complex is probably small.[11] The values for imidazole are all at 25° and ionic strength 0.16. Comparison of the values of log k_1 at different temperatures and ionic strengths is valid because the same correction term probably would be applied in all cases.

The average difference in log k_1 between imidazole and ammonia for all the metals is 0.3 ± 0.1 and is amazingly constant over a 10^4 range in binding capacity. Thus a value of log k_1 of 1.4 may be predicted with some assurance for the combination of manganous ion with ammonia. This would be difficult to determine directly due to the weak binding and the tendency of manganous ion to combine with hydroxide ion. An analysis similar to that previously given[3] indicates that no significant hydroxide formation occurs under the conditions of this study with imidazole and either cobaltous or manganous ion. The only "metal" ion investigated that does not fit the above table is hydrogen ion where log k_1 is 9.28 for ammonia and 7.11 for imidazole under the conditions used in each case. Imidazole forms metal complexes more avidly than one would predict from comparison of its acid ionization constant with that of ammonia. A relatively constant difference between other association or intrinsic constants may also be formulated with similar or slightly less success than described above with log k_1.

Just as the correspondence of the log k_1 values for imidazole and ammonia with various metal ions allows a prediction of the value for manganous ion and ammonia, so the known values of log k_1 for other metal ions with ammonia may be used to estimate a value of log k_1 for the same metal ion with imidazole by adding 0.3 to the log k_1 value for ammonia. This is particularly valuable in the study of proteins because many metals have been studied with ammonia[4] and the value of log k_1 is all that is needed as higher complexes are unlikely with proteins.

If the histidyl group is part of the active site of enzymes such as α-chymotrypsin a correspondence might be expected between the log k_1 values of the metal ions with imidazole and the inhibitory effects of the same metal ions on the enzyme catalyzed reactions.

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[10] H. Irving and R. J. P. Williams, *J. Chem. Soc.*, 3192 (1953).

[11] N. C. Li, T. L. Chu, C. T. Fujii and J. M. White, This Journal, **77**, 859 (1955).

[Contribution from the Department of Chemistry, The George Washington University]

The Fluoroplatinates. IV. Preparation, Density and Solubility of the Fluoroplatinates of Magnesium and the Alkaline Earth Metals

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Received May 1, 1958

The fluoroplatinates of magnesium, calcium and strontium were prepared by the reaction of fluoroplatinic acid with the oxide, hydroxide and carbonate of the respective metals. The barium fluoroplatinate was prepared by the reaction of lanthanum fluoroplatinate with barium chloride. The densities varied from 2.65 g./cm.³ for the magnesium fluoroplatinate to 6.04 g./cm.³ for the barium salt. The solubilities varied from 104.9 g./100 ml. of solution for calcium fluoroplatinate to 0.171 g./100 ml. of solution for the barium salt.

The chemical literature contains no data on the preparation, composition, density or solubility of the fluoroplatinates of magnesium, calcium, strontium or barium. The barium fluoroplatinate was prepared by Klemm[2] presumably by heating a mixture of a barium salt and platinum in a stream of fluorine, although no details of the method were published. Cox[3] reported that Sharpe has prepared the strontium fluoroplatinate, but the procedure was not described. The present work was undertaken to prepare the fluoroplatinates of magnesium and the alkaline earths and to study some of their properties.

Experimental

Preparation of Reagents. Lanthanum Fluoride.—A slight excess of 48% hydrofluoric acid was added to a hot solution of lanthanum ammonium nitrate in a polyethylene beaker. After the precipitate of lanthanum fluoride had settled, it was filtered and washed, first with water and then with acetone. It was dried overnight at 110° and for 0.5 hr. at 400°.

Platinum Powder.—Platinum foil (>99.9% pure) (purchased from The American Platinum Works) was dissolved in boiling aqua regia and the resulting solution was diluted to ten times its volume and filtered. Hydrazine was added in small amounts until all of the platinum had precipitated. It then was filtered off, washed with water followed by acetone and dried in a furnace at 500–600°.

[1] Abstracted from a portion of the dissertation submitted by Marriner K. Norr in partial fulfillment of the requirements for the degree of Doctor of Philosophy.

[2] W. Klemm, *Angew. Chem.*, **66**, 468 (1954).

[3] B. Cox, *J. Chem. Soc.*, 876 (1956).

Fluorine.—Fluorine was generated by a Harshaw Fluorine Cell, Model L, manufactured by The Harshaw Chemical Company. The electrolyte, approximately $KF \cdot 2HF$, melted a little below 100° and was kept molten by a boiling water jacket. The cell was operated at 6–7 volts and 20–30 amperes.

Lanthanum Fluoroplatinate.—Solutions of lanthanum fluoroplatinate were prepared by the method of Perros and Naeser,[4] except that platinum powder rather than the foil was used.

Hydrogen-charged Cation-exchange Resin.—Sodium-charged Amberlite IR-120 synthetic cation-exchange resin was treated with portions of 1:3 hydrochloric acid until a colorless supernatant liquid was obtained. The resin was filtered through a büchner funnel and washed with distilled water until the washings showed no turbidity upon the addition of a few drops of silver nitrate solution.

Fluoroplatinic Acid.—A solution of lanthanum fluoroplatinate was stirred with an excess of the hydrogen-charged resin for 15 minutes. The addition of a few drops of 48% hydrofluoric acid to several milliliters of the supernatant liquid showed no turbidity, thus indicating the absence of lanthanum. The solution of fluoroplatinic acid was separated from the resin by filtration and then evaporated to a small volume in a vacuum desiccator containing sodium hydroxide.

Preparation of the Fluoroplatinates. Magnesium Fluoroplatinate.—Just enough magnesium oxide was added to a solution of fluoroplatinic acid to raise the *p*H of the latter to 7.0 (measured with a Beckman *p*H Meter, Model G). The solution was filtered, concentrated over sodium hydroxide in a vacuum desiccator, filtered again to remove a small amount of decomposition products and added to about five times its volume of acetone. The resulting small yellow crystals of magnesium fluoroplatinate were filtered off, dissolved in a minimum volume of water and precipitated as before. They were filtered off, washed with acetone and dried overnight in the atmosphere.

Calcium Fluoroplatinate.—The calcium salt was prepared similarly, using calcium hydroxide. However, upon pouring the concentrated solution of the salt into the acetone, a heavy yellow "oil," rather than a precipitate, was obtained. The upper phase was decanted and replaced with an equal volume of fresh acetone. The resulting yellow crystals were dissolved in a minimum volume of water and precipitated as before. The salt was then filtered off, washed with acetone and dried in air.

Strontium Fluoroplatinate.—Just enough strontium carbonate was added to a solution of fluoroplatinic acid to bring the *p*H of the latter to 4.0. From this point on the preparation of the strontium salt was identical with that of the magnesium compound.

Barium Fluoroplatinate.—To a clear solution of lanthanum fluoroplatinate was added an excess of concentrated barium chloride solution. The yellow barium fluoroplatinate precipitate was filtered off, washed with water, then acetone and dried overnight in the air.

Analyses.—The presence of the fluoroplatinate ion in each salt was confirmed by the absorption spectrum (measured by a Beckman Spectrophotometer, Model DU) of its solution. The cation content of each compound was determined by a standard procedure: magnesium as the pyrophosphate, calcium as the carbonate and strontium and barium as the sulfates. The values obtained were consistent with the formulas given in Table I.

TABLE I

ANALYSES OF THE FLUOROPLATINATES

Compound	Cation, % Obsd.	Theor.
$MgPtF_6 \cdot 6H_2O$	5.48	5.51
$CaPtF_6 \cdot 2H_2O$	10.32	10.40
$SrPtF_6 \cdot 2H_2O$	20.35	20.24
$BaPtF_6$	30.89	30.77

Physical Properties. Solubility.—All four salts were insoluble in acetone, ethyl ether, benzene and acetic acid. The magnesium compound was somewhat soluble in absolute ethanol, but the other three were insoluble.

During the course of this study it was noted that concentrated aqueous solutions of these salts (except the barium) showed some decomposition. Accordingly, accurate solubility determinations could not be obtained by the conventional procedure of evaporating a known volume of the saturated solution to dryness and then weighing the salt so obtained.

Saturated aqueous solutions of the four fluoroplatinates (each in contact with the corresponding solid salt) were agitated in a 25.0 ± 0.2° water-bath. One-milliliter portions (10 ml. in the case of the barium because of its low solubility) were pipetted into weighed, covered platinum crucibles, evaporated to dryness and ignited to constant weight at 600°.

The weight of salt represented by one gram of its ignited residue was determined by igniting a known weight of the salt. The results are shown in Table II.

TABLE II

IGNITION OF THE FLUOROPLATINATES

Compounds	Assumed comp. of residue	Ratio: $\frac{\text{Wt. of compd.}}{\text{Wt. of residue}}$ Obsd.	Theor.
$MgPtF_6 \cdot 6H_2O$	$MgF_2 + Pt$	1.710	1.714
$CaPtF_6 \cdot 2H_2O$	$CaF_2 + Pt$	1.413	1.410
$SrPtF_6 \cdot 2H_2O$	$SrF_2 + Pt$	1.353	1.349
$BaPtF_6$	$BaF_2 + Pt$	1.210	1.205

The weight of salt in one milliliter of its saturated solution was calculated by multiplying the weight of the ignited residue obtained therefrom by the appropriate ratio in Table II. From this, the solubility in grams per 100 ml. of saturated solution was obtained. The results are listed in Table III.

TABLE III

PROPERTIES OF FLUOROPLATINATES

Compound	Density, g./cm.^{3} at 25°	Solubility in water, g./100 ml. soln. at 25°
$MgPtF_6 \cdot 6H_2O$	2.65	67.9
$CaPtF_6 \cdot 2H_2O$	4.13	104.9
$SrPtF_6 \cdot 2H_2O$	4.42	98.6
$BaPtF_6$	6.04	0.171

Density.—The densities were determined at 25.0 ± 0.2° using a 5-ml. pycnometer. The displacement liquid was reagent grade toluene. The pycnometer was brought to the proper temperature by placing it in an air-bath within a temperature-controlled water-bath. The results are included in Table III.

Acknowledgment.—Part of this investigation was performed under the terms of contract AT(30-1)-821 with the Atomic Energy Commission, Washington, D. C.

WASHINGTON, D. C.

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[4] T. P. Perros and C. R. Naeser, THIS JOURNAL, **75**, 2516 (1953).