

Trivalent Metal Fluoberyllates and Alums -Chromic Alums

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A. K. Ghosh and N. Ray¹ isolated an adduct of chromic fluoberyllate and fluoberyllic acid by the reaction between silver fluoberyllate and violet chromic chloride. From analytical data they mentioned the composition as $\text{Cr}_2(\text{BeF}_4)_3 \cdot \text{H}_2\text{BeF}_4 \cdot 24\text{H}_2\text{O}$. But they could not isolate the chromic fluoberyllate. In this communication preparation and properties of different chromic fluoberyllate alums, e. g. those of NH_4^+ , K^+ , Rb^+ , Cs^+ directly from chromic fluoberyllate² have been described. Their densities are also determined.

EXPERIMENTAL

All reagents used were of A. R. quality.

Fluoberyllic acid—Fluoberyllic acid³ was prepared according to the method of Ray et al.

Chromic fluoberyllate—Chromic fluoberyllate² was prepared by dissolving precipitated chromic hydroxide in fluoberyllic acid, concentrating the solution in a vacuum desiccator over concentrated sulfuric acid and precipitating with absolute alcohol, which was finally dried and collected.

Density—Densities were determined by the method of floatation using suitable mixtures of benzene and methylene iodide.

Methods of analysis—Fluoberyllate ion (BeF_4^{2-}) was determined as barium fluoberyllate at pH 4. Chromium was converted into chromate by digestion with sodium peroxide, treated with standard Mohr's salt solution, excess of which was back titrated with standard dichromate using barium diphenylamine sulfonate as indicator.

Ammonia was determined by Kjeldahl's method.

Fluoberyllate chromic-ammonium alum : $(\text{NH}_4)_2 \cdot \text{BeF}_4 \cdot \text{Cr}_2(\text{BeF}_4)_3 \cdot 24\text{H}_2\text{O}$ —An aqueous solution of 0.12 gm. of ammonium fluoberyllate was mixed with 0.65 gm. of chromic fluoberyllate. The solution was concentrated and crystallised by keeping in a vacuum desiccator over concentrated sulfuric acid at 0°. The crystals on examination under microscope were found to be octahedral in shape which effluoresce

1. A. K. Ghosh and N. Ray, *Z. anorg. allge. Chem.*, 1959, 300. No. 1-2, 102.
2. Trivalent metal fluoberyllates—Aluminium and Chromic fluoberyllates and alums, A. K. Baral, H. Saha, N. Ray, Communicated to this Journal.
3. T. K. Ghosh, T. N. Chakravarty and N. Ray, *Jour. Indian Chem. Soc.*, 1965, 42, No. 12, 847.

slowly. The loss in weight corresponds to the loss of twelve molecules of water on keeping in a desiccator over silica gel. The violet crystals are readily soluble in water. If dry acetone or alcohol is added to a concentrated violet aqueous solution in the cold, the violet compound is obtained, which on examination under microscope was found to be octahedral in shape. On keeping a crystal of the fluoberyllate alum in a saturated solution of sulfate alum parallel overgrowth was found to occur. With the loss of water molecules the crystal assumes a green colour and ultimately a green powder is left which was found to be slightly soluble in water.

0.0578 gm. of the substance consumed 8.085 ml of 0.9292 $\left(\frac{N}{20}\right)$ Mohr's solution.

0.1204 gm. of the substance gave 0.1162 gm. of BaBeF_4 .

Found, Cr=11.39%, BeF_4^{2-} =36.91%, NH_3 =3.69% (Determined by Kjeldahl's method). Calculated for $(\text{NH}_4)_2\text{BeF}_4\cdot\text{Cr}_2(\text{BeF}_4)_3\cdot 24\text{H}_2\text{O}$, Cr=11.40%, BeF_4^{2-} =37.28%, NH_3 =3.73%.

Density at 30° =1.84 gm/ml.

Fluoberyllate chromic-potassium alum : $\text{K}_2\text{BeF}_4\cdot\text{Cr}_2(\text{BeF}_4)_3\cdot 24\text{H}_2\text{O}$ —A sample of 0.17 gm. of K_2BeF_4 in aqueous solution was mixed with 0.65 gm. of chromic fluoberyllate and was crystallised as above at 0° . The first crop of crystals were of K_2BeF_4 . The second crop of crystals were violet in colour. The crystals on examination under microscope were found to be octahedral in shape which slowly effloresce losing its crystalline structure leaving a green powder. The conversion of colour is more rapid with rise in temperature. If to the violet solution of the alum dry acetone or alcohol is added, crystals of the alum were obtained but it was not possible to obtain any crystal from the green solution.

0.2078 gm. of the material consumed 28.23 ml. of 0.9292 $\left(\frac{N}{20}\right)$ Mohr's solution and 0.1724 gm. gave 0.1590 gm. of BaBeF_4 .

Found, Cr=11.06%, BeF_4^{2-} =35.27%. Calculated for, $\text{K}_2\text{BeF}_4\cdot\text{Cr}_2(\text{BeF}_4)_3\cdot 24\text{H}_2\text{O}$, Cr=10.9%, BeF_4^{2-} =35.63%.

Density at 30° =2.05 gm/ml.

Fluoberyllate chromic-rubidium alum : $\text{Rb}_2\text{BeF}_4\cdot\text{Cr}_2(\text{BeF}_4)_3\cdot 24\text{H}_2\text{O}$ —An aqueous solution of 0.26 gm. of Rb_2BeF_4 was mixed with 0.65 gm. of chromic fluoberyllate and was crystallised as in the above case at 0° . The crystals were deep violet in colour which was found to be octahedral in shape on examination under microscope. The crystals slowly effluoresce. With the loss of water molecules the crystal shape is also lost and a green powdery mass is left behind. The alum may also be precipitated from concentrated solution by dry acetone or alcohol.

0.1492 gm. of the substance consumed 18.1 ml. of 0.9292 $\left(\frac{N}{20}\right)$ Mhor's solution and 0.1562 gm. gave 0.1308 gm. of BaBeF_4 .

Found, Cr=9.78%, BeF_4^{2-} =32.00%. Calculated for, $\text{Rb}_2\text{BeF}_4\cdot\text{Cr}_2(\text{BeF}_4)_3\cdot 24\text{H}_2\text{O}$, Cr=9.93%, BeF_4^{2-} =32.48%.

Density at 30° =2.32 gm/ml.

Fluoberyllate chromic-caesium alum : $Cs_2BeF_4 \cdot Cr_2(BeF_4)_3 \cdot 24H_2O$ —A sample of 0.35 gm. of Cs_2BeF_4 in aqueous solution was mixed with 0.65 gm. of chromic fluoberyllate and was crystallised as usual at 0°. The crystals were deep violet in colour, which on examination under microscope was found to be octahedral in shape. The crystals slowly effluoresce. With the loss of water molecules the crystal shape is also lost leaving a green powdery substance. The alum may also be precipitated from concentrated solution by dry acetone or alcohol.

0.1824 gm. of the violet substance consumed 20.5 ml. of 0.9292 $\left(\frac{N}{20}\right)$ Mohr's solution and 0.3698 gm. gave 0.2868 gm. of $BaBeF_4$.

Found, Cr=9.15%, BeF_4^{2-} =29.58%. Calculated for, $Cs_2BeF_4 \cdot Cr_2(BeF_4)_3 \cdot 24H_2O$, Cr=9.53%, BeF_4^{2-} =29.77%.

Density at 30°=2.61 gm/ml.

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