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# OXO-FLUORO-ALUMINATES AND -GALLATES

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## SUMMARY

The preparations of $(NH_4)_2HAl_2OF_7$, $(NH_4)H_2AlOF_4$, $(NH_4)_2HGa_2OF_7.3.5H_2O$ and $(NH_4)_2HGaOF_4$ are described. IR spectra suggest the presence of -M-O-M-O- chains in these compounds. On isothermal heating at 180°C $(NH_4)H_2AlOF_4$ decomposes to give $(NH_4)HAlOF_3$, and at 150°C $(NH_4)_2HGaOF_4$ yields $(NH_4)H_2GaOF_4$. At 180°C $(NH_4)_2HGa_2OF_7.3.5H_2O$ yields the anhydrous compound.

## INTRODUCTION

Some results [1-5] have been published on the oxofluorides of aluminium and gallium, but no oxofluoroaluminate has been reported. Baffier[6] obtained a non-stoichiometric oxofluorogallate, $Mg_vGa_w\Delta_xO_yF_z$ (where $\Delta$ = vacant cation sites). In the present paper the isolation and properties of some oxofluoro-aluminates and -gallates are described.

## EXPERIMENTAL AND DISCUSSION

### Oxofluoroaluminates

1. Ammonium dihydrogen oxotetrafluoroaluminate, $(NH_4)H_2AlOF_4$ : pyridinium tetrafluoroaluminate, $C_5H_6NAlF_4$ [7] (1 g) was dissolved in the minimum of water and a concentrated solution of ammonium acetate (0.5 g) was added with constant stirring. Pyridine was evolved during the reaction and the pH of the solution remained at about 6 during crystallisation. The white crystals formed were filtered, washed with alcohol and dried in air.

2. Diammonium hydrogen oxoheptafluorodialuminate, $(NH_4)_2HAl_2OF_7$ : $(AlF_3)_3.HF.6H_2O$ (1 g), prepared by treating a solution of freshly precipitated $Al(OH)_3$ in HF (40%) with acetone, was dissolved in the minimum of water and glacial acetic acid (2 ml) was added. Ammonium acetate (2.3 g) in water (11 ml) with a pH adjusted to 3.5 with glacial acetic acid (19.6 ml) was mixed with the aluminium fluoride solution with constant stirring. The mixture was kept on a water bath for a few minutes when crystallisation occurred to give white crystals which were filtered, washed with water, then with alcohol and dried in air.

## Oxofluorogallates

1. Ammonium hydrogen oxotetrafluorogallate, $(NH_4)_2HGaOF_4$ : $GaF_3.3H_2O$ (1 g) was dissolved in the minimum of dilute acetic acid (pH 2.4) on a hot water bath. Ammonium acetate (1.3 g) in water (6 ml) with a pH adjusted to 2.85 - 3.02 with glacial acetic acid (22 ml) was mixed with the gallium fluoride solution. On addition of alcohol white crystals were obtained, which were filtered, washed with alcohol and dried in air.

2. Ammonium hydrogen oxoheptafluorodigallate hydrate, $(NH_4)_2HGa_2OF_7.$-$3.5H_2O$ : the compound was prepared as above but at pH 4.01.

The compounds obtained at intermediate pH values seemed to be mixtures of the above two compounds. Both oxofluorogallates can be recovered unchanged and thus recrystallised by adding alcohol to aqueous solutions which had been faintly acidified with dilute acetic acid.

Fluorine was determined as PbClF [7], metals as their oxides and nitrogen by Dumas' method. Analytical results are reported in Table 1.

Oxofluoro-aluminates and -gallates were obtained as micro-crystalline materials. They are readily soluble in water and insoluble in common organic solvents.

TABLE 1

Analytical and IR data of oxofluoro-aluminates and -gallates

| Compounds | Found (%) | | | Calcd. (%) | | | $\nu_{M-F}$ ($cm^{-1}$) | $\nu_{M-O}$ ($cm^{-1}$) |
|---|---|---|---|---|---|---|---|---|
| | N | Al/Ga | F | N | Al/Ga | F | | |
| $(NH_4)H_2AlOF_4$ | 10.10 | 19.50 | 54.60 | 10.07 | 19.42 | 54.67 | 580(s) | 770(sb) |
| $(NH_4)HAlOF_3$ | 11.62 | 22.40 | 47.81 | 11.77 | 22.70 | 47.90 | - | - |
| $(NH_4)_2HAl_2OF_7$ | 11.83 | 22.14 | 55.00 | 11.67 | 22.50 | 55.33 | 600(s) | 700(sb) |
| $(NH_4)_2HGaOF_4$ | 14.00 | 35.20 | 38.54 | 14.09 | 35.08 | 38.24 | 480(s) | 730(sb) |
| $(NH_4)H_2GaOF_4$ | 7.60 | 38.30 | 41.90 | 7.70 | 38.36 | 41.82 | 480(s) | 730(sb) |
| $(NH_4)_2HGa_2OF_7.3.5H_2O$ | 7.23 | 35.77 | 34.69 | 7.21 | 35.89 | 34.24 | 470(s) | 720(sb) |
| $(NH_4)_2HGa_2OF_7$ | 8.50 | 42.90 | 40.98 | 8.60 | 42.84 | 40.87 | - | - |

[s = strong, b = broad]

All compounds were studied by thermogravimetry on a manually operated thermobalance at a heating rate of 4°C/min. On the basis of TGA results isothermal heating of the compounds was made. The results are summarised below :

$$(NH_4)H_2AlOF_4 \quad (100°d) \xrightarrow[-HF]{180°} (NH_4)HAlOF_3$$

$$(NH_4)_2HGaOF_4 \quad (100°d) \xrightarrow[-NH_3]{150°} (NH_4)H_2GaOF_4$$

$$(NH_4)_2HAl_2OF_7 \quad (220°d) \xrightarrow{\qquad} \text{no definite compound}$$

$$(NH_4)_2HGa_2OF_7 \cdot 3.5H_2O \quad (60°d) \xrightarrow[-3.5H_2O]{180°} (NH_4)_2HGa_2OF_7$$

d = initial decomposition temperature.

IR spectra of KBr pellets were recorded (Table 1) on a Perkin-Elmer spectrophotometer over the range 4000 - 400 $cm^{-1}$. IR spectra of $(NH_4)H_2AlOF_4$, $(NH_4)_2HAl_2OF_7$, $(NH_4)_2HGaOF_4$ and $(NH_4)_2HGa_2OF_7 \cdot 3.5H_2O$ show broad bands between 700 - 800 $cm^{-1}$ which we take to indicate the presence of -M-O-M-O- (where M = Al and Ga) chains [8,9]. M-F vibrations are observed between 400 and 700 $cm^{-1}$ [10-15]. All compounds show bands at 1432, 3195 and 3230 $cm^{-1}$, which confirm the presence of $NH_4^+$ ions [16-18]. $(NH_4)_2HGa_2OF_7 \cdot 3.5H_2O$ shows additional bands at 3400, 1620 and 1230 $cm^{-1}$ confirming the presence of $H_2O$.

The IR spectrum of $(NH_4)H_2AlOF_4$ shows a strong broad band at 720 - 770 $cm^{-1}$ assigned to Al-O stretching vibrations but no bands at 1600 - 1640 and 3400 $cm^{-1}$ which would be observed if $H_2O$ were present [19]. Therefore we formulate this compound as an oxofluoroaluminate and not the simple hydrated tetrafluoroaluminate. None of the other three compounds show bands between 890 - 1000 $cm^{-1}$ indicating the absence of M-O-H bands [20] again favouring formulation as oxofluorometallates. The IR spectrum of $(NH_4)H_2GaOF_4$ again shows a strong band from Ga-O at 720 - 770 $cm^{-1}$.

X-ray diffraction photographs were taken in a Guinier camera using $CuK_\alpha$ radiation and the data are presented in Table 2. Comparison of the X-ray diffraction data of the oxofluoroaluminates and -gallates with that of $NH_4.HF_2$ reveals that our products are substantially free from this probable contaminant.

TABLE 2

X-ray diffraction data of oxofluoro-aluminates and -gallates

| I | | II | | III | | IV | |
|---|---|---|---|---|---|---|---|
| dA | Relative Intensity | dA | Relative Intensity | dA | Relative Intensity | dA | Relative Intensity |
| 13.9 | vw | 6.4 | vs(br) | 6.4 | ms | 5.22 | vs(br) |
| 6.35 | vs(br) | 3.6 | vs | 5.22 | vs(br) | 4.52 | s(br) |
| 5.1 | m(br) | 3.18 | ms | 5.15 | m | 3.20 | s |
| 4.9 | vs(br) | 3.11 | s | 5.00 | vs(br) | 2.26 | ms |
| 3.59 | s | 2.54 | m | 4.87 | m | 2.02 | m |
| 3.17 | m | | | | | 1.842 | m |
| 3.11 | s | 2.355 | m | 4.35 | m | 1.74 | m |
| 2.53 | m | 2.11 | m | 3.98 | m | 1.525 | m |
| 2.45 | m | 1.82 | m | 3.80 | m | 1.363 | mw |
| 1.818 | m | 1.795 | s | 3.20 | ms | 1.307 | mw |
| 1.79 | m | 1.602 | m | 3.16 | ms | | |
| | | 1.555 | m | 2.97 | m | | |
| | | 1.28 | m | 2.60 | s | | |
| | | 1.185 | m | 1.95 | ms | | |
| | | | | 1.83 | m | | |

I. $(NH_4)H_2AlOF_4$;   II. $(NH_4)_2HAl_2OF_7$;   III. $(NH_4)_2HGaOF_4$;   IV. $(NH_4)_2HGa_2OF_7.3.5H_2O$

vs = very sharp,  s = sharp,  m = medium,  w = weak,  br = broad.

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