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Hydroxylammonium fluorometalates: Synthesis and characterisation of a new fluorocuprate and fluorocobaltate

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ABSTRACT

The first layered hydroxylammonium fluorometalates, $(NH_3OH)_2CuF_4$ and $(NH_3OH)_2CoF_4$, were prepared by the reaction of solid NH_3OHF and the aqueous solution of copper or cobalt in HF. Both compounds crystallize in monoclinic, $P2_1/c$, unit cell with parameters: $a = 7.9617(2)$ Å, $b = 5.9527(2)$ Å, $c = 5.8060(2)$ Å, $\beta = 95.226(2)^\circ$ for $(NH_3OH)_2CuF_4$ and $a = 8.1764(3)$ Å, $b = 5.8571(2)$ Å, $c = 5.6662(2)$ Å, $\beta = 94.675(3)^\circ$ for $(NH_3OH)_2CoF_4$, respectively. Magnetic susceptibility was measured between 2 K and 300 K giving the effective Bohr magneton number of 2.1 for Cu and 5.2 BM for Co. At low temperatures both complexes undergo a transition to magnetically ordered phase. The thermal decomposition of both compounds was studied by TG, DSC and X-ray powder diffraction. The thermal decomposition of $(NH_3OH)_2CuF_4$ is a complex process, yielding NH_4CuF_3 as an intermediate product and impure Cu_2O as the final residue, while $(NH_3OH)_2CoF_4$ decomposes in two steps, obtaining CoF_2 after the first step and CoO as the final product.

1. Introduction

Hydroxylammonium fluorometalates with a general formula $(NH_3OH)_xMF_y$ are interesting for the study of hydrogen bonds, since they include all three elements that are capable to form strong hydrogen bonds (O, N and F). Although the first hydroxylammonium fluorometalates (M = Si, Ti) were reported in 1908 by Ebler and Schott [1], until 1990 only three new compounds (M = U, Th) were reported [2,3]. Since the early 90s, our laboratory has reported on the synthesis and properties of a number of new hydroxylammonium fluorometalates of main group elements (M = Al, Ga, In, Si, Ge) [4–9] and transition metals (M = Ti, Zr, Hf, Cr, V) [10–14]. The main advantage of our method is the use of solid NH_3OHF, prepared by adding an ethanol solution of NH_2OH to an aqueous solution of hydrofluoric acid [15], instead of aqueous or ethanolic hydroxylammonium solutions used by earlier researchers. To the best of our knowledge, no reports about hydroxylammonium fluorocuprates and -cobaltates have been published, so we decided to study reactions in the systems NH_3OHF–Cu–HF (aq) and NH_3OHF–Co–HF (aq). The main aim of the work was to fulfill the inorganic systematics in the field of interest.

Since the chemistry of hydroxylammonium is analogous to that of ammonium and hydrazinium, we also reviewed publications reporting fluorocuprates and -cobaltates of ammonium and hydrazinium. Ammonium fluoride complexes, NH_4CoF_3 and NH_4CuF_3, have been known long ago [16] while $(NH_4)_2MF_4$ type compounds (M = Co, Cu, Ni), isostructural with K_2NiF_4, have been reported by Crocket and Grossman [17]. Later, Troyanov et al. [18,19] also reported on the synthesis and crystal structure of three ammonium fluorocuprates, NH_4CuF_3, $(NH_4)_2CuF_4$ and $(NH_4)_2CuF_4{\cdot}2H_2O$. Siebert and Breitenstein [20] obtained $[Co(NH_3)_6]CoF_6$ by the thermal decomposition of $[Co(NH_3)_6]F_3$ and determined its crystal structure whereas the synthesis and structural assessment of hydrazinium fluorocobaltate, $(N_2H_4)_2CoF_2{\cdot}2H_2O$, has been reported by Bhattacharjee et al. [21].

2. Results and discussion

2.1. Thermogravimetrical results

(a) The thermal decomposition of the new blue compound with a formula $(NH_3OH)_2CuF_4$ is shown in Fig. 1. The new compound is stable up to 353 K and decomposes in five partially overlapping steps. In the first step up to 453 K the sample loses 19.3% of its mass. The DSC curve shows a significant exothermic peak at this temperature. From 453 K to 523 K the mass is falling quite fast. Up to 523 K the sample loses 36.9% of its starting mass. At the end of the third temperature interval at 553 K the mass loss amounts to 41.0% and at 673 K 45.7%. Finally, at 1273 K 58.2% of the initial weight is lost.

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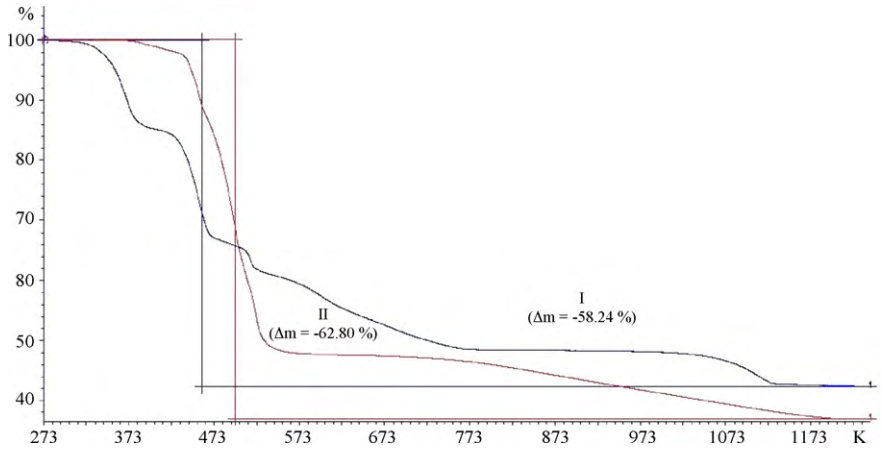

Fig. 1. Thermogravimetric analysis of $(NH_3OH)_2CuF_4$ (I) and $(NH_3OH)_2CoF_4$ (II).

The room temperature X-ray powder diffraction patterns are shown in Fig. 2. At 453 K, after the first significant decomposition step, the diffraction pattern shows that the prevalent product is NH_4CuF_3 with some traces of $CuF_2{\cdot}2H_2O$. At 523 K, traces of four compounds are present: NH_4CuF_3, Cu_2OHF_3, $CuF_2{\cdot}2H_2O$ and CuO. Besides CuO, there are also some traces of Cu_2OHF_3, CuF_2 and CuOHF present at 673 K. At 873 K the prevalent products are CuF_2, CuOHF and CuO. The final residue of the compound at 1273 K is Cu_2O with some traces of CuO.

The proposed parallel chemical reactions taking place during the thermal decomposition of $(NH_3OH)_2CuF_4$ could be described by following equations (first step):

$$3(NH_3OH)_2CuF_4 \rightarrow 3CuF_2{\cdot}2H_2O + 6HF + 2NH_3 + 2N_2$$

$$3(NH_3OH)_2CuF_4 \rightarrow NH_4CuF_3 + Cu_2OHF_3 + 2N_2 + NH_3 + 5H_2O + 6HF$$

Second step:

$$Cu_2OHF_3 \rightarrow CuOHF + CuF_2$$

$$Cu_2OHF_3 \rightarrow CuO + CuF_2 + HF$$

$$CuOHF \rightarrow CuO + HF$$

Final step:

$$CuF_2 + H_2O \rightarrow CuO + 2HF$$

$$2CuO \rightarrow Cu_2O + 1/2O_2$$

(b) The thermal decomposition of the new violet crystal compound with a formula $(NH_3OH)_2CoF_4$ in a nitrogen atmosphere is shown in Fig. 1. The TG curve shows two general decomposition steps. The first initial drift on the curve can be attributed to the loss of adsorbed water and HF. Up to 573 K the sample loses 51.4% of its starting mass while at 1173 K, 62.8% of the initial mass is lost and the mass of the residue does not change anymore. The products of the thermal decomposition at different temperatures and the final residue were identified by X-ray powder diffraction. The diffraction patterns are shown in Fig. 3. At 573 K, after the first significant decomposition step, the diffraction pattern shows that the prevalent product is CoF_2 and the same product is also present at 773 K. At 973 K the prevalent product of the decomposition is still CoF_2 with some traces of CoO. The final residue at 1273 K is CoO. The measured mass loss in the first step ($\Delta m_{meas}/m$ = 51.4%) is in good agreement with the value, calculated for the decomposition to CoF_2 ($\Delta m_{calc}/m$ = 52.2%):

$$3(NH_3OH)_2CoF_4 \rightarrow 3CoF_2 + 6HF + 2NH_3 + 2N_2 + 6H_2O$$

The second decomposition step can be described by the reaction:

$$CoF_2 + H_2O \rightarrow CoO + 2HF$$

The measured mass loss for both decomposition steps ($\Delta m_{meas}/m$ = 62.8%) is also in good agreement with the calculated value ($\Delta m_{calc}/m$ = 63.0%).

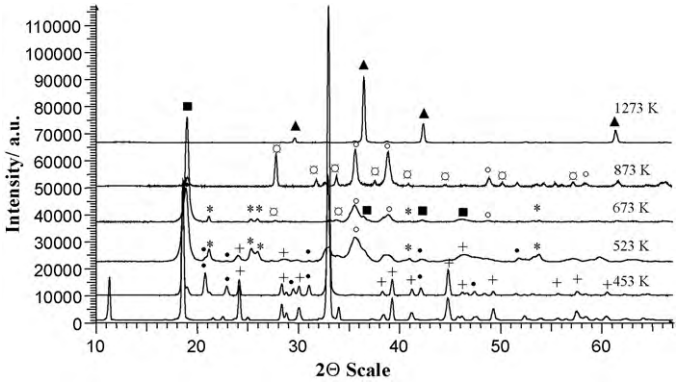

Fig. 2. X-ray diffraction patterns of $(NH_3OH)_2CuF_4$ (lowest) and the products of thermal decomposition at different temperatures: (+)$CuF_2{\cdot}2H_2O$ (PDF 000-25-0276), (●)NH_4CuF_3 (PDF 000-24-1105), (*)Cu_2OHF_3 (PDF 000-06-0170), (○)CuF_2 (PDF 010-70-1936), (°) CuO (PDF 010-70-6827), (■) CuOHF (PDF 000-07-0306), (▲) Cu_2O (PDF 000-05-0667).

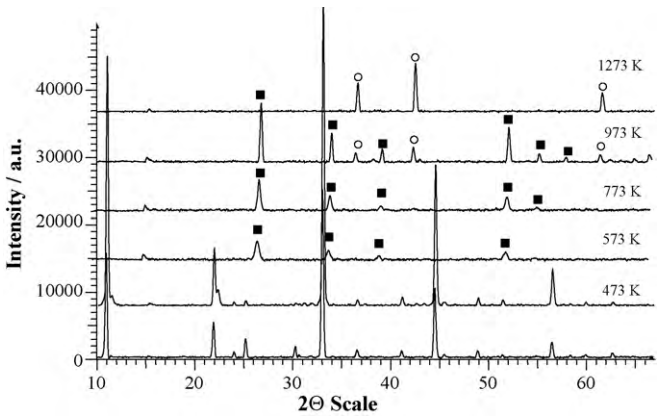

Fig. 3. X-ray diffraction patterns of $(NH_3OH)_2CoF_4$ (lowest) and the products of thermal decomposition at different temperatures: (■) CoF_2 (PDF 000–33-0417), (○) CoO (PDF 000-48-1719).