

Short Communication

Ammonium zinc hexafluorotitanate(III) hexahydrate : $\text{NH}_4\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$

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Compounds of trivalent titanium and tetravalent vanadium, both having d^1 configuration, are of great interest to chemists^{1,2}. Assuming octahedral or tetragonal symmetry, one-electron molecular orbital energy levels have been calculated with fluorine and oxygen as ligands^{3,4}. The calculated values of the splitting of d levels were compared with the values obtained from the study of electronic spectra.

The known compounds of trivalent titanium have already been studied and the Dq values of the splittings are known. A new compound of Ti^{3+} was prepared in this laboratory and the splitting of the e_g-t_{2g} levels was found to be appreciably greater than reported in the literature. In this communication, the method of preparation and properties of ammonium zinc hexafluorotitanate(III) hexahydrate will be discussed. A typical preparation procedure is described below.

Ammonium pentafluorotitanate(III), $(\text{NH}_4)_2\text{TiF}_5$, was prepared by adding excess of NH_4HF_2 to 50 ml of a 20% TiCl_3 solution in hydrochloric acid. The violet compound formed was filtered, washed with cold dilute HF solution and added immediately to a warm HF solution containing 6 g of mossy zinc metal. Six g of NH_4HF_2 was then added and the solution was heated gently for 5 min. In the event that the initial 6 g of zinc dissolved, additional metal was added to insure a reducing atmosphere in the solution during the time of crystallization of the compound. The solution was filtered and transferred to a polyethylene basin for crystallization at 5°. Approximately 2 g of mossy zinc was kept immersed in solution. Well-defined violet crystals were formed overnight. Approximately 10 g of $\text{NH}_4\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$ was obtained by the method described above.

It was found that in the presence of platinum Ti^{III} is more easily oxidized. Hence, during the process of crystallization platinum dishes should not be used.

The crystals of $\text{NH}_4\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$ were stored under CCl_4 or kerosene. Calculated for $\text{NH}_4\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$: Ti, 13.56; NH_3 , 4.81; Zn, 18.50; F, 32.27%. Found: Ti, 13.11; NH_3 , 4.90; Zn, 18.31; F, 32.23%.

The relatively big crystals could be preserved under kerosene for weeks

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without fear of oxidation. When exposed to air, the compound was found to be efflorescent and was oxidized to tetravalent titanium.

Two absorption maxima were shown by this compound. The position of the peaks were at $22\,124\text{ cm}^{-1}$ and $14\,535\text{ cm}^{-1}$ respectively. In aqueous solution, the peak at $22\,124\text{ cm}^{-1}$ slowly shifted to $19\,608\text{ cm}^{-1}$. In the compound the bands are separated by 7500 cm^{-1} . Jahn-Teller effect alone cannot account for this much splitting. A distorted octahedron causing lowering of symmetry is possibly responsible for this splitting. From a crystallographic viewpoint⁵ it is difficult to have an ideal cubic structure for $(\text{NH}_4)_3\text{TiF}_6$. In addition, the cationic effect may be more pronounced in this compound than in simple alkali metal fluorotitanates. The 10 Dq values for four compounds are tabulated in Table 1.

TABLE 1

| Compound | Position of absorption bands (cm^{-1}) | 10 Dq | Reference | |
|---|---|--------|-----------|-------------------------|
| Na_2KTiF_6 | 18 900 | 16 000 | 17 450 | Bedon, Horner and Tyree |
| $(\text{NH}_4)_3\text{TiF}_6$ | 19 010 | 15 110 | 17 060 | |
| $\text{NH}_4\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$ | 22 124 | 14 535 | 18 328 | Present communication |
| $(\text{NH}_4)_2\text{TiF}_5$ | 19 000 | 15 115 | 17 058 | |

The nephelauxetic series consider fluoride as a stronger splitting agent than water, while according to the spectrochemical series, fluoride ion as a ligand is weaker than H_2O . The 10 Dq value for fluoride reported in the present communication is comparable to $18\,850\text{ cm}^{-1}$, the usually accepted 10 Dq value for $\text{Ti}(\text{H}_2\text{O})_6^{3+}$.

The powder diffraction pattern of this compound was taken and the d values as well as the intensities were tabulated. The d - I match clearly revealed that $\text{NH}_4\text{ZnTiF}_6 \cdot 6\text{H}_2\text{O}$ was not a mixture of ZnF_2 , $(\text{NH}_4)_2\text{TiF}_5$, etc. However, as stated earlier, the compound in the powdered form is not very stable. A similar compound of trivalent aluminum is reported in the literature⁶.

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