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Short Communication

Preparation and properties of potassium octafluorotrioxodivanadate(V) $K_4V_2O_3F_8$

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The polymerization of the vanadate ion has been studied extensively [1 - 3], and ions such as $V_2O_7{}^{4-}$, $V_3O_8{}^{-}$, $V_3O_9{}^{3-}$, $V_{10}O_{28}{}^{6-}$, *etc.* are reported in the literature. Recently, interesting heteropolyvanadates with transition-metal central atoms have been prepared and characterized by X-ray crystallographic examination [4, 5]. Potassium pentafluoromono-oxovanadate(V), K_2VOF_5, and similar other salts of fluoro-oxovanadates have been known for some time. However, the polymerization of these ions either in solution or in the solid state has not been accomplished previous to the present investigation. Indeed, salts of isopoly or heteropoly acids resulting from the condensation of oxofluoro anions have seldom been reported. In this paper, the preparation and properties of the salt of an isopoly oxyfluoro anion is reported for the first time.

Experimental

Preparation of K_2VOF_5

Approximately 10 g of V_2O_5 was weighed into a plastic beaker. To this, 40 g of KF was added followed by 300 cm^3 of 30% HF. The mixture was heated and stirred until the solid material dissolved. Upon cooling in an ice bath, K_2VOF_5 crystallized out. The compound was washed with 20% ethanol and dried. Approximately 8 g of the compound was isolated. Analysis: Found: F, 38.95%; V, 21.7%. K_2VOF_5 requires F, 39.6%; V, 21.25%.

Titration of K_2VOF_5 with KOH

The pH, as well as the free fluorine concentration, was determined experimentally with the use of a pH meter and fluoride ion electrode, respectively. The data obtained were plotted as total fluorine *versus* cm^3 of base added. The total fluorine was the summation of the experimentally measured fluoride plus undissociated [HF]. The amount of undissociated [HF] was calculated from known values of [H$^+$], [F$^-$] and K_a for hydrofluoric acid. The graph yielded one break corresponding to the equivalent ratio between K_2VOF_5 to KOH at 1:2. The tendency of the vanadate ion to polymerize over the pH range 3 - 5 with a vanadium concentration $-\log[V]_{total}$ up to 3.5 is well known [1]. Hence, during the present investigation $-\log[V]_{total}$ was varied from 0.2 to 1.0 and the pH from 3.3 to 5.3.

The possible reactions which occur are given below:

$$K_2VOF_5 + 2KOH \rightarrow K_3VO_2F_4 + KF + H_2O \tag{1}$$

At low pH,

$$K_3VO_2F_4 + H^+ \rightarrow K_2HVO_2F_4 + K^+ \tag{2}$$

In concentrated solution,

$$2K_2HVO_2F_4 \rightarrow K_4V_2O_3F_8 + H_2O \tag{3}$$

Since the compound isolated did not exhibit any OH frequency in its IR spectrum, the formation of hydroxy fluoro complexes was ruled out. In the above equations, vanadium is assumed to be 6-coordinated; however, 7-coordinated vanadium compounds have recently been reported [6, 7].

Preparation of $K_4V_2O_3F_8$

The compound K_2VOF_5 was used as the starting material for the preparation of $K_4V_2O_3F_8$. Approximately 1.5 g of K_2VOF_5 was dissolved in 150 cm^3 of water in a plastic beaker. The water was heated to hasten solution and 2 equiv of an aqueous solution of KOH was then added to the above. The resulting clear yellow solution was placed in a plastic vacuum desiccator. Upon evaporation, bright yellow crystals were formed. These were filtered, washed with cold water and the compound analyzed. Analysis: Found: K, 36.0%; V, 22.1%; F,32.8%. $K_4V_2O_3F_8$ requires K, 34.12%; V, 22.2%; F, 33.15%.

X-Ray study

The X-ray diffraction diagram of $K_4V_2O_3F_8$ was obtained using a Picker X-ray diffractometer. The *d* values with the tentative assignments are given in Table 1. All these observed *hkl* values are within ±0.01% of the calculated values obtained by means of a programmed IBM computer.

The *d* spacings agree reasonably well with a tetragonal lattice, the dimensions of each unit cell being $a = 9.77$ Å and $c = 10.56$ Å. The compound was characterized by comparing this spectrum with those obtained from K_2VOF_5, KF and KVO_3. The *d–I* match clearly revealed that $K_4V_2O_3F_8$ is not a mixture of other previously reported compounds. The crystal structures of K_2RuCl_6 and the hydrated dimer, $K_4Ru_2Cl_{10}O \cdot H_2O$, have been reported as cubic [8] and tetragonal [9], respectively. The unit cells, as expected, are larger in the ruthenium compounds.

DTA studies of K_2VOF_5 and $K_4V_2O_3F_8$ have been undertaken. Both compounds decomposed at higher temperatures but $K_4V_2O_3F_8$, unlike K_2VOF_5, gave an endothermic peak at 362 °C.

TABLE 1

hkl	*d*/Å	*I*
113	3.14	14
310	3.08	100
311	2.97	26
203	2.85	11
322	2.40	33
331	2.25	52
412	2.17	45
105	2.06	58
304	2.06	50
205	1.94	10
215	1.90	38
423	1.86	8
502	1.84	17
315	1.74	8
513	1.68	20
531	1.65	30
611	1.59	7
217	1.43	15
545	1.24	10

Raman and infrared studies

The solid-state infrared and Raman spectra of $K_4V_2O_3F_8$ have been measured. Raman:935, 900, 640, 490, 360, 325, 240, 210 cm^{-1}. Infrared: 910, 880, 730, 525, 510, 330, 310 cm^{-1}.

The idealized overall symmetry of the molecule is C_{2v} with two terminal V=O groups. In the Raman spectrum, absorptions at 935, 900 and 360 cm^{-1}, and in the infrared spectrum at 910, 880 and 330 cm^{-1}, have been assigned to the V=O group, whilst peaks at 490 and 240 cm^{-1} in Raman spectrum and at 525, 510 and 310 cm^{-1} in the infrared spectrum are attributed to the V–F link. These assignments are in good agreement with literature values [10, 11]. The peak at 730 cm^{-1} in the infrared spectrum as well as the 640 and 210 cm^{-1} peaks of the Raman spectrum are attributed to the asymmetric and symmetric stretching and deformation of V–O–V links, respectively [11]. As expected, the V–O bond order of the V–O–V link is higher than that of a single σ bond. This is due to the donation of the lonepair electrons of the oxygen atom to the empty π levels of vanadium.

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