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Preparation and characterization of triaqua-hydroxo-enneafluorodichromates(III)

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Abstract

Isolation and properties of the new triaqua-hydroxo-enneafluorodichromates(III), $M_4[Cr_2(OH)F_9(H_2O)_3]\cdot nH_2O$, where $M=Na^+$ ($n=1$); K^+ ($n=0$); NH_4^+ ($n=3$); $1/2\,enH_2^{2+}$ ($n=0$, en = ethylenediamine) and $1/3[Co(NH_3)_6]^{3+}$ ($n=6$) are described. The compounds have been characterized by elemental analyses, molar conductance, thermogravimetry, magnetic susceptibility, IR and X-ray powder diffraction data. © 1997 Elsevier Science S.A.

Keywords: Triaqua-hydroxo-enneafluorodichromates (III); Molar conductance; Thermogravimetry; Magnetic susceptibility; X-ray powder diffraction

1. Introduction

Hydroxo-bridged dinuclear Cr(III) complexes are well known [1,2], but hydroxo-fluorodichromates(III) have not yet been reported. In this communication we describe the isolation and characterization of some compounds of a new complex ion, $[Cr_2(OH)F_9(H_2O)_3]^{4-}$.

2. Experimental

2.1. Preparation of $(enH_2)+Cr_2O_7$

$(NH_4)_2Cr_2O_7$ (0.05 mol) dissolved in 25 ml water was mixed with ethylenediamine (0.05 mol), when a vigorous reaction took place with the evolution of ammonia. A yellow solid, which separated from the reaction mixture on cooling (~5°C), was filtered. The isolated crude product was dissolved in 20 ml water and then acidified with dil. HCl. The desired compound separated as orange crystals on cooling. These were filtered off, dried in air and analysed.

2.2. Preparation of $K_4[Cr_2(OH)F_9(H_2O)_3]$

$K_2Cr_2O_7$ (2.95 g, 0.01 mol) and KF (1.15 g, 0.02 mol) were dissolved in 30 ml of water in a polythene beaker and 40% HF (3.5 ml, 0.07 mol) added followed by 20 ml ethanol. The resulting solution mixture was then heated on a water bath. The solution turned gradually green and after about 45 min green crystals separated from the solution. These were filtered by suction, washed twice with water (5 ml) and dried over fused $CaCl_2$. Following the above procedure and starting from $M^I_2Cr_2O_7$, M^IF and HF ($M=NH_4^+$, Na^+ and $1/2\,enH_2^{2+}$), we obtained $(NH_4)_4[Cr_2(OH)F_9(H_2O)_3]\cdot 3H_2O$, $Na_4[Cr_2(OH)F_9(H_2O)_3]\cdot H_2O$ and $(enH_2)_2[Cr_2(OH)F_9(H_2O)_3]$ as green crystalline solids. $[Co(NH_3)_6]_4[Cr_2(OH)F_9(H_2O)_3]_3\cdot 6H_2O$ was isolated as a dirty green precipitate on adding aqueous $[Co(NH_3)_6]Cl_3$ solution (5%) to a concentrated aqueous solution of the ammonium compound. It separated slowly from solution. It was filtered, washed with water and dried as before. $K_4[Cr_2(OH)F_9(H_2O)_3]$ was also obtained on slow evaporation of an aqueous solution containing $CrF_3\cdot 3H_2O$ and KF (2:3) in a desiccator over fused $CaCl_2$.

2.3. Analysis

The compounds were analysed by standard procedures [3]. Magnetic susceptibility, IR and thermogravimetric (TGA) measurements were carried out as reported earlier [4]. X-ray powder diffraction curves were recorded using a X-ray diffractometer (Rigaku-Miniflex, Japan) with Cu Kα radiation and nickel filter. The data were given in Tables 1 and 2.

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3. Results and discussion

The isolated hydroxo-fluorodichromates(III) are crystalline and non-hygroscopic solids. They are sparingly soluble in water, the ammonium compound is, however, more soluble than the others (Table 1) and its recrystallisation is possible from water. The molar conductance values of 565 Ω^{-1} cm^2 mol^{-1} observed for $(NH_4)_4[Cr_2(OH)F_9(H_2O)_3]\cdot 3H_2O$ (10^{-3} M in water at 26°C) indicates a (4:1) electrolytic nature. The conductance values remain almost unchanged even after a week showing negligible dissociation of the complex anion, thereby indicating its high stability. On dehydration over P_2O_5 in vacuo, the sodium, ammonium and hexaminecobalt(III) salts lost one mole, three moles and six moles of water respectively, forming the corresponding trihydrates. On the other band, no loss of water molecules was observed from potassium and ethylenediaminium salts. The thermogram (recorded in air up to 500°C) of $M_4[Cr_2(OH)F_9(H_2O)_3]$ (M = Na^+ and K^+), showed the formation of a stable intermediate product between 300 and 370°C with observed losses of 11.66% for the potassium salt and 13.57% for the sodium salt. Thereafter the compound

Table 1
Analytical, solubility, magnetic moment and thermal decomposition data for triaqua-hydroxoenneafluoro dichromates (III)

Compound	Analysis: found (calc.) (%)				S (g l^{-1})	T_d (°C)	μ_{obs} (B.M)
	Na/K	N	Cr	F			
$K_4[Cr_2(OH)F_9(H_2O)_3]$	31.14 (31.07)	–	20.69 (20.71)	34.33 (34.06)	3.55	120	3.65
$Na_4[Cr_2(OH)F_9(H_2O)_3]\cdot H_2O$	20.22 (20.17)	–	22.07 (22.80)	37.56 (37.50)	1.2	130	3.65
$(NH_4)_4[Cr_2(OH)F_9(H_2O)_3]\cdot 3H_2O$	–	12.60 (11.86)	21.84 (22.03)	36.07 (36.23)	11.50	90	3.72
$(enH_2)_2[Cr_2(OH)F_9(H_2O)_3]$	–	12.39 (11.91)	22.27 (22.12)	36.82 (36.38)	2.07	90	3.69
$[Co(NH_3)_6]_4[Cr_2(OH)F_9(H_2O)_3]_3\cdot 6H_2O$	–	18.54 (18.77)	16.75 (17.43)	28.65 (28.66)	1.05	80	–
$K_4[Cr_2(OH)_4F_6]$	34.50 (35.29)	–	23.09 (22.53)	26.34 (25.79)	–	–	3.65
$Na_4[Cr_2(OH)F_6]\cdot 6H_2O$	18.39 (18.93)	–	21.26 (21.40)	23.99 (23.45)	–	–	3.68

T_d, initial decomposition temperature.
μ_{obs}, observed magnetic moment at room temperature.
S, solubility at 26°C.

Table 2
Infrared spectra (in cm^{-1}) and X-ray diffraction data (d, A°) for: I, $K_4[Cr_2(OH)F_9(H_2O)_3]$; II, $Na_4[Cr_2(OH)F_9(H_2O)_3]$; III, $(NH_4)_4[Cr_2(OH)F_9(H_2O)_3]$

I	II	III	Probable band assignments	X-ray diffraction data		
				I	II	III
280(w)				5.61(W)	5.09(W	5.65(W)
300(m,sp)	300(m,sp)	280(w)	νCr–F$^{(bridging)}$			
330(m,sp)		300(m,sp)			4.57(m)	5.46(m)
510–530(vs,b)	540(vs)	525(vs)	νCr–F$^{(terminal)}$	5.06(s)	4.50(m)	5.15(s)
				4.92(s)	3.93(m)	4.92(s)
740–760(m,b)	–	740–750(m,b)	νCr–OH_2	4.67(m)	2.79(m)	4.70(m)
				3.30(w)	2.36(w)	3.30(m)
–	1040,1070, 1080(vs,T)	–	δOH	2.88(m)	1.97(w)	2.71(w)
1550–1650(m,b)	1640(s)			2.71(m)		2.65(m)
		1410 and 1440(vs,D)	νNH, δHOH	2.50(m)		2.52(m)
		1600–1660(w,b)		2.31(w)		1.98(m)
2340–2430 (m,b)	2320–2490 (m,b)	2380–2480 (m,b)	νOH	1.97(m)		1.82(w)
				1.93(w)		
3040–3170 (s,b)	3100–3400 (s,b)	3100–3250 (s,b)	νOH, νNH	1.89(w)		

s, strong; m, medium; b, broad; w, weak; vs, very strong; D, doublet; T, triplet; Sp, sharp.

decomposed gradually. Isothermal heat treatment of $M_4[Cr_2(OH)F_9(H_2O)_3]$ ($M=Na^+$ and K^+) at 300°C yielded (Table 1) a hygroscopic residue, $M_4[Cr_2(OH)_4F_6]$ (calculated loss of 11.95% for the K compound and 13.6% for the Na compound). Formation of this residue can be rationalized as follows.

$$M_4[Cr_2(OH)F_9(H_2O)_3] \xrightarrow[-3HF]{300°C} M_4[Cr_2(OH)_4F_6]$$

($M=Na^+$ and K^+)

This loss of HF from the compounds indicated the simultaneous removal of some part of the fluoride ions and water molecules. It seemed, therefore, that the three water molecules in the starting trihydrates might be complexed forming a triaqua species, $[Cr_2(OH)F_9(H_2O)_3]^{4-}$. Ammonium and ethylenediaminium salts decomposed directly to green Cr_2O_3 at around 450°C without forming any intermediate products.

Important IR spectral bands along with their tentative assignments are shown in Table 2 for M_4^I $[Cr_2(OH)F_9(H_2O)_3]$, $M=K^+$(I), Na^+(II) and NH_4^+ (III). The strong band at $\sim 1080\ cm^{-1}$ assigned for the Cr–OH bending mode [5] in compound II, was not observed in the IR spectra of compounds I and III; instead a medium but broad band showed at $\sim 740\ cm^{-1}$ for the latter two compounds. In sodium compound II, no band was found at $\sim 740\ cm^{-1}$. Gamo [6] assigned the bands at 650–880 cm^{-1} of inorganic salts to be rocking modes of coordinated water. The TGA data supported the presence of aqua-water in hydroxo-fluoro compounds (see Section 2.3). The band at $\sim 740\ cm^{-1}$ might therefore be due to $\nu Cr–OH_2$. The characteristic ν Cr–F (terminal) frequency appeared in the 510–540 cm^{-1} region [5,7] and the bridging Cr–F frequency at around 300 cm^{-1} [5]. The magnetic moment data for the compounds corresponded to the spin-only value for $3d^3$ Cr(III) ion. The anionic complexes probably contain six-coordinate chromium (III) but the detailed structure is not known. In the X-ray powder diffraction patterns, the *d* values (Table 2) were found to be almost identical for $K_4[Cr_2(OH)F_9(H_2O)_3]$ and $(NH_4)_4[Cr_2(OH)F_9(H_2O)_3]$, suggesting similar structures. The *d* values of $Na_4[Cr_2(OH)F_9(H_2O)_3]$ on the other hand, were different from those of the above two compounds.

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