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THE RELATION BETWEEN STRUCTURE AND DEHYDRATION OF $K_2MF_5H_2O$ COMPOUNDS

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ABSTRACT

The complexes $K_2MF_5H_2O$ can be devided into two structurally different groups. The dehydration of these compounds has been studied by thermogravimetry, differential thermal analysis and differential scanning calorimetry. It was shown that thermal analysis can not be used to distinguish between coordinated and structural water. In the series of compounds with coordinated water the DTA peak temperatures as well as dehydration enthalpies can be correlated to the crystal field stabilization energy.

INTRODUCTION

The hydrates are usually classified according to the bonding of water molecules in the structure (1,2). The proposals for classification, given in the literature are essentialy the same and are based on the type of coordination of the lone pair orbitals. In the first group each water is coordinated by only three neighbours of which one presents a positive charge and two present negative charges. The second group comprises the structures in which the cations are not directly coordinated by water molecules. Each molecule is tetrahedrally coordinated, with the lone pair orbitals usually involved in hydrogen bonding.

It was proposed that structural water can be eliminated below 150°C, while coordinated water needs at least 200°C to be removed (3). There is a disagreement to this opinion (4) saying that the dehydration temperature can not be "a priori" used for the differentiation of water molecules.

The compounds $K_2MF_5H_2O$ belong to two structural types. For M= Al,Mn (5,6) the tervalent metals are octahedrally coordinated by fluorine atoms. Octahedra share trans-vertices to form infinite chains. Water molecules are located in the lattice between the anionic chains. For M=V, Cr,Fe,Ga the central atoms are surrounded by five fluorine atoms, resulting in $[MF_5H_2O]^{2-}$ anions (7,8).

EXPERIMENTAL

The complexes $K_2MF_5H_2O$ (M=Al,Ga,V,Cr,Mn,Fe) have been prepa-

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red as described elsewhere (9-14) and analysed for potassium, fluorine and tervalent metals. Elemental analysis was in good agreement with the theoretical values.

TG, DTG and DTA curves have been recorded by means of a Mettler thermoanalyser TA1. Experimental conditions: Pt-crucibles, sample masses 100 mg, heating rate 6 $Kmin^{-1}$, flowing dry air with 5 lh^{-1}, α-Al_2O_3 as reference substance for DTA. All curves were run four times. DTA peaks were calibrated by $BaCl_2.2H_2O$, $CaSO_4.2H_2O$ and $NaNO_3$.

DSC measurements were obtained on a Mettler TA 2000C thermoanalyser. Experimental conditions: Pt-crucibles, sample masses 10 mg, heating rates 4,6,8,10,12 $Kmin^{-1}$, dry air atmosphere of 0.6 lh^{-1} flow rate, α-Al_2O_3 as reference. The instrument has been calibrated with the specific heat of alumina.

RESULTS AND DISCUSSION

DTA and DSC peak temperatures together with the reaction enthalpies are given in Table 1. DTA effects for 100 mg samples are also shown in Figure 1. There is considerable variation in the dehydration temperatures, the lowest values beeing those for Al and Fe, which possess structural and coordination water respectively. The second compound with structural water ($K_2MnF_5H_2O$) dehydrates at higher temperature than do some compounds with coordinated water. It is evident that the decomposition temperatures for hydrates with structural water are not necessarily lower than those with coordinated one, therefore they can not be used to distinguish between the two types of water molecules. The same is true for the reaction enthalpies.

There is a great variation of temperatures and of reaction enthalpies for the elimination of coordinated water. In Figure 2, these data are plotted as a function of d-configuration of M^{3+} ions. The diagram is similar to well known humped curves, representing the effect of crystal fields on the thermodynamic properties of solids. There is a good correlation, for example, (15) between the hydration enthalpies of trivalent cations and crystal field stabilization energies (CFSE) for their high-spin configurations in octahedral environment. The dehydration enthalpies for the group of isothermal compounds, $K_2MF_5H_2O$, M=V,Cr,Fe,Ga follow the same trend. The CFSE values for Fe^{3+} and Ga^{3+} are zero, therefore a straight line has been drawn through the corresponding values of the dehydration enthalpies (Figure 2). An increase in dehydration heat from Fe^{3+} to Ga^{3+} reflects the diminished size of the cation. For V^{3+} and Cr^{3+} the CFSE values are 6Dq and 12Dq respectively, therefore the dehydration heats lie above the straight line which connects the ions having zero CFSE. Since the decomposition of these complexes occurs by breaking the metal-water bond, it is logical that the thermal stability is in direct relation to the strength of this bond.

CONCLUSIONS

Dehydration temperatures for the hydrates as well as the corresponding enthalpies depend on several factors, one of them being the strength of bonds formed by water molecules in the crystal. The strength of these bonds can vary considerably even for isostructural hydrates. The results of thermal analysis only, should not be used as a criterion for distinguishing between structural and coordinated water.

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Table 1. Dehydration of $K_2MF_5H_2O$

$K_2MF_5H_2O$ M	DTA (°C)	DSC (°C)	ΔH(DTA) (kJ/mol)	ΔH(DSC) (kJ/mol)
Al	160	123	71.2(2.7)	61.6(1.3)
Mn	198	160	67.5(2.0)	53.5(1.5)
V	215	215	65.2(2.3)	65.1(2.1)
Cr	320	318	73.5(3.1)	67.7(2.2)
Fe	135	130	50.0(2.3)	58.4(0.6)
Ga	190	188	62.2(1.7)	62.7(1.2)

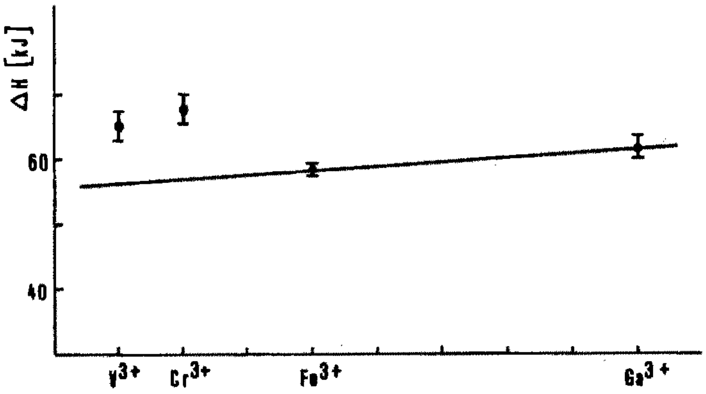

Fig.2. Dehydration enthalpies from DSC

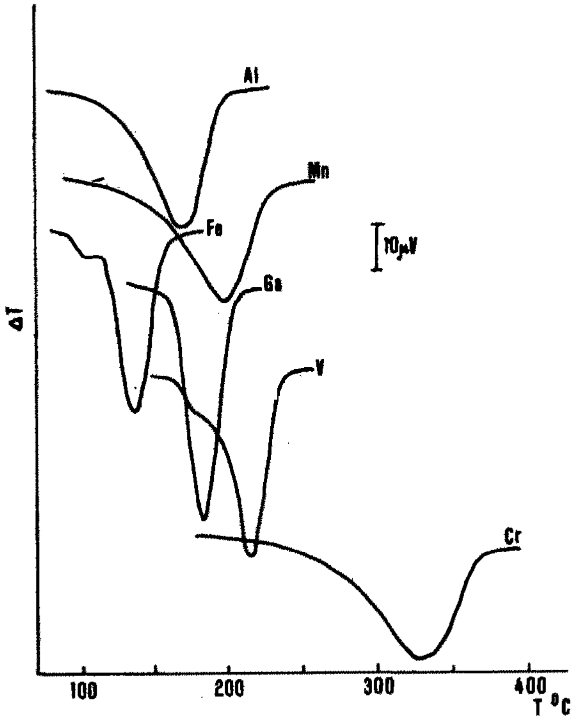

Fig.1. DTA curves of $K_2MF_5H_2O$