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ON THE THERMAL DECOMPOSITIONS OF THE TRIVALENT TRIOXALATO COMPLEXES OF Al, Cr, Mn, Fe AND Co

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Abstract

The thermal decompositions of the complexes $K_3[M(ox)_3]\cdot 3H_2O$ (M=Al, Cr, Mn, Fe, Co; $ox=C_2O_4^{2-}$) were studied. Dehydration of the complexes occurs up to 200°C, this being a three-step process for M=Al, Cr, Mn and Co, and a two-step process for M=Fe. Decomposition of the dehydrated complexes proceeds in several steps. For M=Al, Cr and Fe, the decomposition takes place with the evolution of CO, whereas for M=Mn and Co the decomposition of the oxalate ligand yields solid C besides CO. The temperature of CO liberation decreases in the series Cr<Al<Co<Mn<Fe. For M=transition metal, this trend can be explained by the fact that the strength of the C–C bond in the oxalate ligand decreases in the series Cr<Co<Mn<Fe.

Keywords: metal oxalate complexes, PM3(tm) calculations, thermogravimetry

Introduction

The thermal properties of metal oxalates and of metal oxalato complexes have been extensively studied [1]. It has been found that the nature of the metal ions in the complexes influences not only the dehydration, but also the decomposition of the anhydrous complexes [2]. Furthermore, the thermal stability of the anhydrous complex additionally depends on the central cation: the thermal stability decreases as the electron affinity of the central metal ion increases [3].

Transition metal oxalato complexes have recently again attracted attention: various types of molecular assemblies exhibiting spontaneous magnetization are based on transition metal oxalato complexes [4, 5]. These ferromagnetic substances are two- or three-dimensional networks that are assembled with transition metal ions linked through bis-chelating oxalate ligands.

In the present paper, we examine thermogravimetric data obtained on the trioxalato complexes of trivalent Al, Cr, Mn, Fe and Co, with the aim of establishing a possible correlation between these data and the relevant bond lengths in the complexes.

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Experimental

The oxalato complexes $K_3[M(ox)_3]\cdot 3H_2O$ were prepared by following procedures described in the literature [6–9].

Instrumentation

Thermal analysis measurements were performed by using the TG 951 module of a TA2000 thermal analyser (TA Instruments, Inc.). The samples were heated from 20 to 600°C at a heating rate of 10°C min^{-1} under a helium flow of 50 ml min^{-1}.

Calculations

The geometries of $[M(ox)_3]^{3-}$ were obtained by means of semi-empirical quantum-mechanical PM3(tm) calculations [10].

Results

The thermogravimetric (TG) and corresponding derivative (DTG) curves of the complexes $K_3[M(ox)_3]\cdot 3H_2O$ are shown in Figs 1 and 2. The temperature ranges and the percentage mass losses are given in Table 1.

Table 1 Temperature ranges and mass losses for the oxalato complexes

Complex	Dehydration			Decomp. of anhydrous complex		
	Temp. range/°C	Mass loss/%		Temp. range/°C	Mass loss/%	
		obsd.	calcd.		obsd.	calcd.
$K_3[Al(ox)_3]\cdot 3H_2O$	26–200	10.7	11.7	245–700	37.4	36.3 (6CO)
$K_3[Cr(ox)_3]\cdot 3H_2O$	28–210	11.5	11.1	250–720	33.5	34.4 (6CO)
$K_3[Mn(ox)_3]\cdot 3H_2O$	28–200	12.1	11.0	200–660	26.5	27.7 (4CO+2C)
$K_3[Fe(ox)_3]\cdot 3H_2O$	26–150	11.6	11.0	210–670	34.5	34.2 (6CO)
$K_3[Co(ox)_3]\cdot 3H_2O$	22–190	10.3	10.9	190–400	30.0	30.7 (5CO+C)

All TG-DTG curves exhibit several steps. Dehydration of the complexes occurs up to 200°C. Three-step dehydration can be seen for the Al, Cr, Mn and Co oxalato hydrates, whereas for the Fe oxalato hydrate the dehydration proceeds in two steps. The Cr and Al oxalato hydrates display the lowest dehydration temperatures. The most intensive DTG maximum for these complexes is at around 85°C. For the Mn and Fe complexes, the most intensive DTG maxima are at about 105°C, while for the Co oxalato hydrate the DTG maximum is at the highest temperature in the series, 126°C. It should be added at this point that an explanation of the variation in the dehydration temperatures of the complexes could not be explicity given. It was earlier found [11–13] that the water molecules in these complexes are engaged in at least two types of bonding interactions: besides being extensively H-bonded to the trioxalate ions and to other water molecules, water is also coordinated to the K^+.

The dehydration of the Mn and Co oxalato complexes is immediately followed by decomposition of the resulting anhydrous complexes. The TG curves of the other

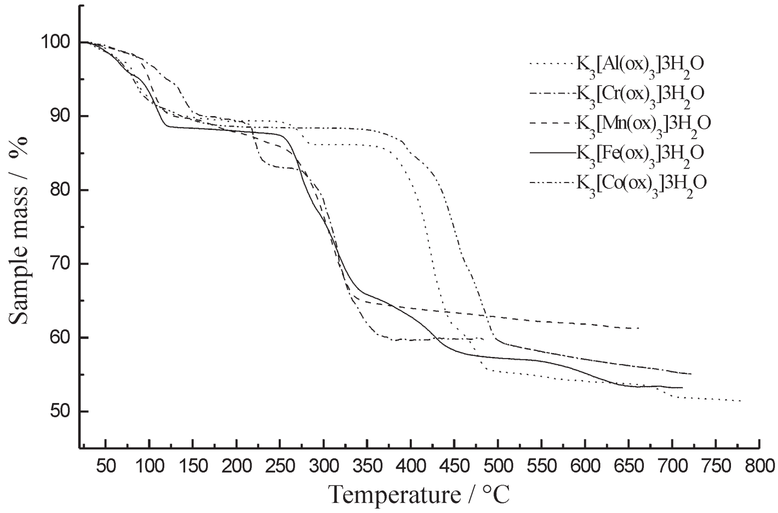

Fig. 1 TG curves of the metal oxalato complexes

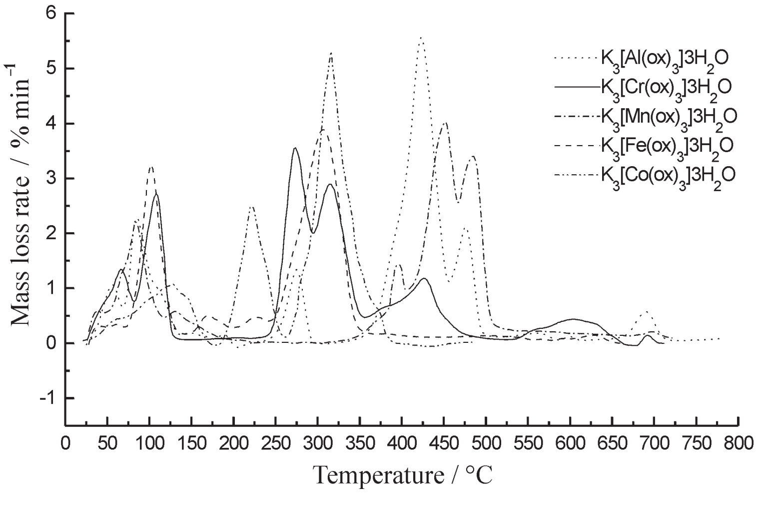

Fig. 2 DTG curves of the metal oxalato complexes

three complexes reveal a plateau over which the anhydrous oxalates are stable. Moreover, the mass loss data on the Mn and Co dehydrated complexes also differ from the data on the others, indicating a different decomposition mechanism for these two complexes (Table 1). The mass loss data for the dehydrated Al, Cr and Fe complexes demonstrate only the liberation of CO during the decomposition, whereas the dehydrated Mn and Co oxalato complexes yield solid C besides CO. It may be added that the dehydration temperatures and decomposition products differ from the data previously reported for the metal oxalato complexes [2]. Lower dehydration temperatures and lower mass losses during the decompositions of the dehydration complexes (CO_2 was assumed as a main decomposition product) were generally described earlier [2].

The decompositions of the dehydrated complexes proceed in several steps, as may be seen from the DTG curves, which contain several distinct maxima. The position of the most intensive DTG maximum varies with the central metal ion as follows (values in parentheses are temperatures in °C): Cr (454)<Al (423)<Co (315)<Mn (308)<Fe (274). This maximum can be attributed to the deoxalation process, which is accompanied by the loss of CO (Table 1).

The above trend can in part be rationalized if it is compared with the trend in the C–C bond lengths of the oxalato ligands in these complex anions. To do this, it does not seem appropriate to use the structural data obtained by means of X-ray crystallography. The available crystallographic data [11–13] refer to the hydrated species, i.e. to $K_3[M(ox)_3]\cdot 3H_2O$, in which extensive H-bonding is present between the lattice water molecules and the oxalate ligands. Such H-bonding can be expected to have a certain influence on the oxalate bond lengths, so that they will differ to some extent from the bond lengths in the dehydrated species (which actually exist at this stage of the thermal decomposition). Therefore, in the present discussion we use the bond lengths obtained via semi-empirical quantum-mechanical calculations, because these calculations can be performed on free $[M(ox)_3]^{3-}$. The C–C bond lengths (in pm) obtained by geometry optimisation of $[M(ox)_3]^{3-}$ by means of PM3(tm) calculations vary with the central metal ion in the following series: Cr (154.4)<Co (154.9)<Al (155.0)<Mn (155.4)<Fe (155.9). It is seen that for the transition metal ions (i.e. excluding Al) a correlation exists between the temperature of the strongest DTG maximum and the C–C bond length: the shorter (i.e. the stronger) the C–C bond, the higher the deoxalation temperature. This fact is not surprising, since the deoxalation process in which CO molecules are evolved must inevitably include the breaking of the C–C bond as an important step. It is not surprising that the Al complex does not fit into this correlation; because the absence of *d* electrons in the Al atom, as compared to transition metal atoms, can be expected to have at least some influence on the decomposition energetics of the Al complex.

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