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THERMAL DECOMPOSITION OF SCANDIUM(III) 2-CHLORO-, 3-CHLORO, 4-CHLORO- AND 2,4-DICHLOROBENZOATES IN AN AIR ATMOSPHERE

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Abstract

The conditions of thermal decomposition of hydrated scandium(III) chlorobenzoates were studied. On heating, the carboxylates decompose in many steps. The hydrated complexes first lose water of crystallization in one or two steps and then anhydrous compounds are transformed to Sc_2O_3 with formation of $Sc_2O(CO_3)_2$ intermediate. The dehydration of the complexes is accompanied by an endothermic effect and the decomposition of anhydrous complexes by strong endothermic effects. The anhydrous complexes are melted at 255–300°C.

Keywords: chlorobenzoates, decomposition, dehydration, scandium(III) complexes

Introduction

Scandium(III) often forms an octahedral coordination sphere in aqueous solution. The compounds of scandium(III) undergo hydrolysis and polymerization. These processes depend on the concentration and *pH* of the solution [1, 2]. In solutions of concentrations less than 10^{-3} mol·dm^{-3} and *pH* between 1 and 4, scandium ions exist as hexahydrate $[Sc(H_2O)_6]^{3+}$. In solutions of $pH > 4$ scandium(III) ions are hydrolyzed forming hydroxosalts. At concentrations exceeding 10^{-3} mol·dm^{-3}, the hydrolysis becomes more complicated, involving multi-step polymerization. These properties of scandium(III) ions make preparation of scandium(III) complexes very difficult. Preparation of scandium(III) complexes with carboxylic acids is especially difficult because of the fact that these acids are very often sparingly soluble in water and the solution of their salts generally have a $pH > 4$. This is why preparation of neutral scandium(III) complexes from aqueous solution is almost impossible.

In previous papers we have described the complexes of scandium(III) with 2-chloro, 3-chloro-, 4-chloro and 2,4-dichlorobenzoic acid prepared in aqueous solutions with formulae $Sc(ClC_6H_4COO)_3{\cdot}0.5H_2O$ [3–5], $Sc_2O(ClC_6H_4COO)_2(OH)_2$ [6–8], $Sc_2O(ClC_6H_4COO)_4{\cdot}1.5H_2O$ [9, 10], and $Sc_5O_6(Cl_2C_6H_3COO)_3{\cdot}4H_2O$

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[11, 12]. All complexes except scandium 2-chlorobenzoate and 3-chlorobenzoate are amorphous solids. Their IR and X-ray spectra were recorded. The conditions and products of thermal decomposition were studied, too.

The aim of this work has been to prepare the neutral scandium(III) chlorobenzoates from ethanolic solution and examine their thermal decomposition in an air atmosphere.

Experimental

Scandium(III) complexes with 2-chloro, 3-chloro- and 2,4-dichlorobenzoic acids were prepared at room temperature by adding 0.2 mol/l solution of 2-chloro-, 3-chloro or 2,4-dichlorobenzoic acid in ethanol to a suspension of $Sc(OH)_3$ in 5:1 water–ethanol mixture using a small excess of precipitant. The precipitate formed was stirred in the mother liquid for 0.5 h, then it was filtered off, washed with ethanol and dried to a constant mass at 30°C.

Scandium 4-chlorobenzoate was prepared at room temperature by adding an equivalent amount of 0.2 mol/l solution of $Sc(NO)_3$ in ethanol to a solution of ammonium 4-chlorobenzoate in 1:10 (v/v) water-ethanol mixture, and crystallizing. The precipitate formed was filtered off, washed with ethanol and dried to a constant mass at 30°C.

The thermal stabilities of the complexes were studied: the TG, DTG and DTA curves were recorded. The measurements were carried out with a Q-1500 D derivatograph at a heating rate of 10 deg·min^{-1} at the following sensitivities: TG – 100 mg, DTA – 500 μV, DTG – 500 μV. 100 mg samples were heated in air atmosphere in platinum crucibles up to 1000°C. Al_2O_3 was used as reference material. The results obtained are presented in Tables 1, 2 and in Figs 1–4.

Results and discussion

It has been found on the basis of elemental and thermogravimetric analysis [13] that scandium(III) chlorobenzoates are hydrates with a molar ratio of the metal to ligand of 1:3 and different degrees of hydration. Scandium(III) 2-chlorobenzoate and 2,4-dichlorobenzoate are hemihydrates, the 3-chlorobenzoate is a monohydrate, and the 4-chlorobenzoate a sesquihydrate. Analysis of IR spectra [13] confirms the results of elemental analysis. All the prepared complexes are white crystalline solids sparingly soluble in water [13].

When heated in air the prepared complexes decompose in many steps in different ways. Scandium(III) 2- and 3-monochlorobenzoates are dehydrated endothermally over the temperature range from 30 to 300°C in one step and the 4-chlorobenzoate in two steps, transforming into anhydrous compounds stable up to 335–390°C. Only the scandium 2,4-dichlorobenzoate decomposes immediately on heating after losing 0.5 water molecule.

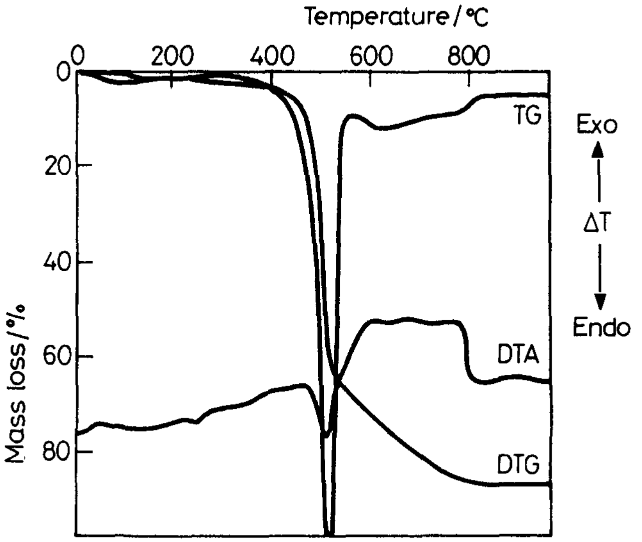

Fig. 1 TG, DTG and DTA curves of Sc(III) 2-chlorobenzoate

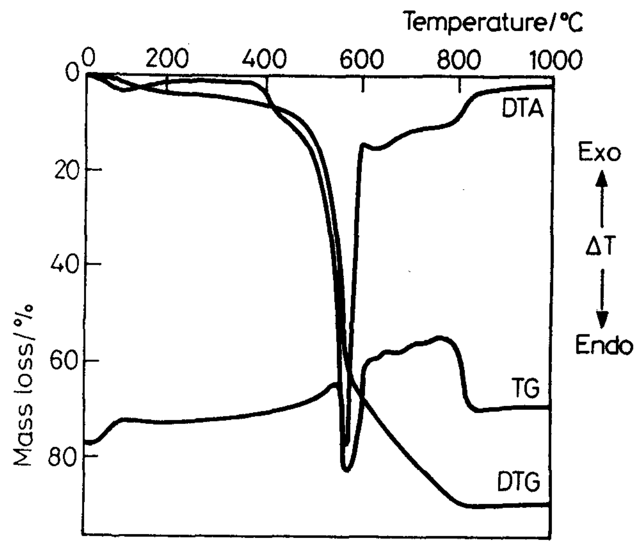

Fig. 2 TG, DTG and DTA curves of Sc(III) 3-chlorobenzoate

The low temperature of dehydration of the scandium(III) complexes suggests that the water of crystallization is probably a lattice water and the molecules of scandium 2-chloro-, 4-chloro- and 2,4-dichlorobenzoates are probably dimers with formulae $[Sc(ClC_6H_4COO)_3]_2 \cdot H_2O$, $[Sc(ClC_6H_4COO)_3]_2 \cdot 3H_2O$ and $[Sc(Cl_2C_6H_3COO)_3]_2 \cdot H_2O$. Scandium(III) 2-chlorobenzoate prepared from

Table 1 Temperature of dehydration of scandium(III) chlorobenzoates in an air atmosphere

Scandium(III) complexes		*T* range of dehyd./	DTG peak temp./	Effects		M.p./	Loss of mass/%		Loss of H_2O
				exo/	endo/				
name	formula	°C					calcd.	found	*n*
2-chlorobenzoate	$Sc(ClC_6H_4COO)_3 \cdot 0.5H_2O$	30–235	100	65	140	255	1.73	1.50	0.5
3-chlorobenzoate	$Sc(ClC_6H_4COO)_3 \cdot H_2O$	40–220	110	120	190	–	3.40	3.50	1.0
4-chlorobenzoate	$Sc(ClC_6H_4COO)_3 \cdot 1.5H_2O$	50–180	100	80	190	290	1.67	1.50	0.5
		180–210	200				5.02	5.00	1.0
2,4-dichlorobenzoate	$Sc(Cl_2C_6H_3COO)_3 \cdot 0.5H_2O$	30–300	115	100	160	300	1.40	1.50	0.5

Table 2 Temperature data of decomposition of scandium chlorobenzoates in an air atmosphere

Complexes	Temperature range		Loss of mass/ %		DTG peak T/	T range decomp./ to Sc_2O_3	Loss of mass/ %		Endo-effect/	T of oxide formation T_k/
	dehyd./	decomp./ to $Sc_2O(CO_3)_2$								
	°C		calcd.	found	°C		calcd.	found	°C	
(2) $Sc(ClC_6H_4COO)_3$ $\cdot 0.5H_2O$	30–235	335–610	72.54	72.00	515 610	610–795	86.76	87.00	505	795
(3) $Sc(ClC_6H_4COO)_3$ $\cdot H_2O$	40–220	390–640	73.01	73.00	570 640	640–810	87.00	86.50	580	810
(4) $Sc(ClC_6H_4COO)_3$ $\cdot 1.5H_2O$	50–210	365–655	73.46	74.00	555 655	655–835	87.41	88.00	560	835
(2, 4) $Sc(Cl_2C_6H_3COO)_3$ $\cdot 0.5H_2O$	30–300	300–600	77.09	77.00	500 600	600–720	88.95	89.00	510	720

(2), (3), (4), (2, 4) – position of the Cl atom in the benzene ring relative to the COO^- group

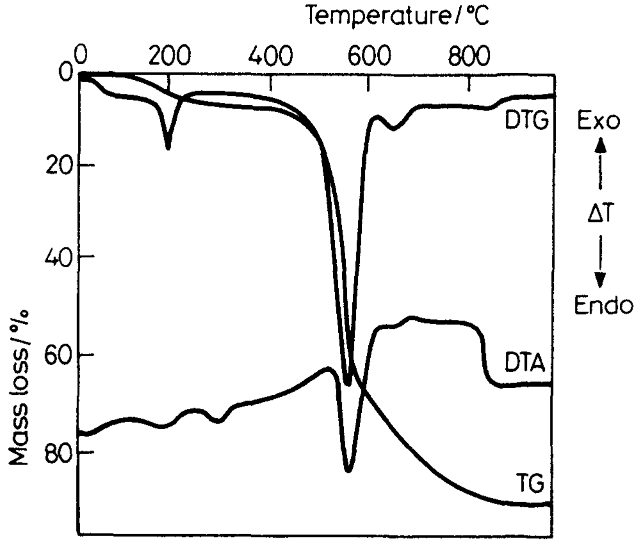

Fig. 3 TG, DTG and DTA curves of Sc(III) 4-chlorobenzoate

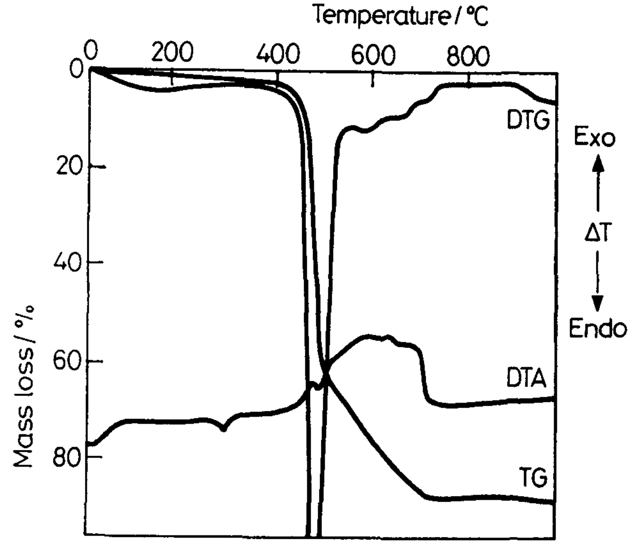

Fig. 4 TG, DTG and DTA curves of Sc(III) 2,4-dichlorobenzoate

aqueous ethanol solution differs from that prepared from aqueous solution [4] by the manner of bonding of crystallization water. In the first complex the water of crystallization is a lattice water, whereas in the second complex the water of crystallization is in the inner sphere. This fact explains the difference in structure of the two complexes. Scandium(III) 2-chlorobenzoate, having inner-sphere crystallization water, is a complex with a higher degree of order and higher degree of crystallinity [4, 13] than the second one.

In the temperature range 30–140°C an exothermic peak is observed in the DTA curve of the studied complexes. It follows from thermal data for scandium(III) benzoate [10] that in this range a polymorphic change takes place. For scandium(III) 2-chloro-, 3-chloro-, 2,4-dichloro- and 4-chlorobenzoate (the first step of dehydration) the exothermic effect connected with the polymorphic change is so strong that it partially masks the endothermic effect of dehydration.

The dehydration temperature of hydrated scandium(III) chlorobenzoates changes with the change in Cl atom position in the order:

4-chloro- < 3-chloro- < 2-chloro- < 2,4-dichlorobenzoate

It is probably connected with the number of waters of crystallization and the way of bonding. Scandium(III) 2,4-dichlorobenzoate hemihydrate has the highest temperature of dehydration, which may be due to formation of an additional hydrogen bond.

Anhydrous scandium(III) chlorobenzoates (except the 3-chlorobenzoate) melt at a temperature of 255–300°C involving a strong endothermic effect, and then decompose endothermally to yield scandium(III) oxocarbonates $Sc_2O(CO_3)_2$ in the temperature range 300–655°C, which, on further heating decompose to give Sc_2O_3 at 720–835°C.

The temperatures of formation of scandium(III) oxocarbonates and Sc_2O_3 increase in the order:

2,4-dichloro- < 2-chloro- < 3-chloro- <4-chlorobenzoate

On the basis of these data it is possible to confirm the influence of the position of the chlorine atom in the benzene ring on the thermal stability. Transfer of the chlorine atom from ortho- to para position produces a higher thermal stability of scandium(III) monochlorobenzoate. The presence of two chlorine atoms in the benzene ring in scandium(III) 2,4-dichlorobenzoate decreases the thermal stability compared to the other complexes. It is connected with the change in polarity of the molecule and in density of the electron cloud on the carbon in the COO^- group.

Y, La and lanthanide 3-chlorobenzoates decompose to yield oxides via oxochlorides [14] and their temperatures of formation (especially for light lanthanides) are higher than that of formation of Sc_2O_3, which is due to the high value of heat of formation [15] and high stability of the oxide. Scandium(III) chlorobenzoate forms less stable complexes than other rare earths. It is connected probably with the small ionic radius of Sc^{3+}, the different properties and different action of Sc^{3+} ion on the 3-chlorobenzoate ligand compared to other rare earth elements.

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Zusammenfassung — Es wurden die Umstände bei der thermischen Zersetzung von hydratierten Skandium(III)chlorobenzoaten untersucht. Beim Erhitzen zersetzen sich die Carbo- xylate in vielen Schritten. Die hydratierten Komplexe verlieren zuerst Kristallwasser in ein oder zwei Schritten, die wasserfreien Verbindungen werden dann über die Zwischenstufe $Sc_2O(CO_3)_2$ zu Sc_2O_3 umgewandelt. Die Dehydratation der Komplexe wird von einem endothermen Effekt begleitet und die Zersetzung der wasserfreien Komplexe durch starke endotherme Effekte. Die wasserfreien Komplexe schmelzen bei 255–300°C.