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SOLID STATE DECOMPOSITION STUDIES OF SOME METAL(II)SALICYLATO COMPLEXES

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ABSTRACT

Divalent copper, iron, zinc, manganese and nickel salicylato, 5-chloro, 5-bromo, 5-iodo and 5-nitrosalicylato complexes have been prepared and their mode of thermal decomposition studied by thermogravimetry and mass spectrometry. The decomposition of the complexes occurs in three stages and the final product is metal oxide in each case.

INTRODUCTION

Salicylic acid is a diprotic acid which forms in aqueous solutions hydrogensalicylate ($Hsal^-$) and salicylate (sal^{2-}) ions. Salicylic acid and its derivatives form metal complexes with a number of metal ions (ref. 1). Metal salicylates have been used as additives in technology (propellants) and in medicine. Aspirin and salicylate are known as drugs possessing many therapeutic properties, like analgetic, antipyretic and anti-inflammatory effects (ref. 2).

In the literature there are a few papers concerning thermal decomposition of unsubstituted copper(II), nickel(II) and cobalt(II) salicylato complexes (refs. 3-6).

The present paper reviews our studies about the thermal behaviour of 5-substituted metal(II)salicylato complexes.

EXPERIMENTAL

Preparation and analysis of the compounds

The preparation of the salicylato and 5-substituted salicylato complexes with copper(II), iron(II), manganese(II) and nickel(II) ions have been described earlier (refs. 7-9). In Table 1 the analytical data are given for the present complexes.

Methods

The methods of the analysis and thermoanalytical experiments have been described in detail earlier (refs. 7-9).

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TABLE 1

Analytical data for the present metal(II) - 5-substituted salicylato compounds.

Compound[a]	Analysis (%)[b]		IR bands (cm^{-1})		
	M	C	$\nu_{as}(COO^-)$	$\nu(OH)$	ν(other)
$Cu(5\text{-}Clsal)_2 \cdot 3H_2O$	13.7(13.8)	36.2(36.5)	1590 s	3310 s	652 (Cl) m
$Cu(5\text{-}Brsal)_2 \cdot 3H_2O$	11.6(11.6)	30.7(30.6)	1580 s	3320 s	625 (Br) m
$Cu(5\text{-}Isal)_2 \cdot 3H_2O$	10.4(9.9)	26.4(26.1)	1587 s	3380 s	432 (I) m
$Cu(5\text{-}NO_2sal)_2 \cdot 2H_2O$	13.1(13.7)	36.0(36.3)	1590 s	3270 s	1340(NO_2) s
$Fe(sal)_2 \cdot 2H_2O$	15.0(15.2)	48.1(45.9)	1600 s	3370 s	1230 (CO) s
$Fe(5\text{-}Clsal)_2 \cdot 2H_2O$	12.6(12.8)	40.3(38.7)	1595 m	3390 s	730 (Cl) m
$Fe(5\text{-}Brsal)_2 \cdot 2H_2O$	10.5(10.7)	33.4(32.1)	1590 m	3400 s	700 (Br) m
$Fe(5\text{-}Isal)_2 \cdot 2H_2O$	8.8(9.1)	27.5(27.3)	1580 m	3400 s	685 (I) m
$Fe(5\text{-}NO_2sal)_2 \cdot 3H_2O$	13.8(11.8)	32.9(35.5)	1590 s	3300 s	1330(NO_2) s
$Mn(sal)_2 \cdot 2H_2O$	15.1(15.0)	45.3(46.0)	1580 s	3400 s	1240 (CO) s
$Mn(5\text{-}Clsal)_2 \cdot 2H_2O$	12.9(12.9)	38.7(38.7)	1615 s	3430 s	655 (Cl) m
$Mn(5\text{-}Brsal)_2 \cdot 2H_2O$	10.7(10.5)	34.5(32.2)	1580 s	3380 s	630 (Br) m
$Mn(5\text{-}Isal)_2 \cdot 2H_2O$	8.9(8.9)	26.9(27.3)	1585 s	3430 s	615 (I) m
$Zn(sal)_2 \cdot 2H_2O$	17.6(17.4)	43.6(44.8)	1590 s	3260 s	1240 (CO) s
$Zn(5\text{-}Clsal)_2 \cdot 2H_2O$	14.9(14.7)	36.6(36.2)	1590 s	3450 s	675 (Cl) m
$Zn(5\text{-}Brsal)_2 \cdot 2H_2O$	12.5(12.3)	31.1(31.5)	1585 s	3100 s	630 (Br) m
$Zn(5\text{-}Isal)_2 \cdot 2H_2O$	10.5(10.3)	25.2(26.8)	1578 s	3060 s	615 (I) m
$Zn(5\text{-}NO_2sal)_2 \cdot 2H_2O$	13.8(14.0)	30.4(36.1)	1590 s	3400 s	1340(NO_2) s
$Ni(sal)_2 \cdot 4H_2O$	14.4(14.5)	44.2(41.5)	1600 s	3350 s	1230 (CO) s
$Ni(5\text{-}Clsal)_2 \cdot 4H_2O$	12.3(12.3)	35.3(35.5)	1585 s	3370 s	655 (Cl) m
$Ni(5\text{-}Brsal)_2 \cdot 4H_2O$	10.3(10.4)	30.3(29.9)	1570 s	3440 s	630 (Br) m
$Ni(5\text{-}Isal)_2 \cdot 4H_2O$	8.7(8.9)	24.3(25.6)	1550 s	3440 s	618 (I) m
$Ni(5\text{-}NO_2sal)_2 \cdot 4H_2O$	11.9(11.9)	30.6(34.0)	1590 s	3400 s	1340(NO_2) s

[a] sal = $C_6H_3(OH)COO^-$

[b] calculated values are given in parentheses

RESULTS AND DISCUSSION

The iron(II), manganese(II) and zinc(II) salicylato complexes crystallize from water with two, nickel(II) complexes with four, and copper(II) complexes with three water molecules except $Cu(5\text{-}NO_2sal)_2$ which has two crystal water molecules (see Table 1).

The main differences between the IR absorption spectra of each ligand acid and their metal complexes are: (a) there is a strong OH stretching band at 3060-3450 cm^{-1} in the complexes which can be attributed to water molecules, while the ligand acids have broad OH stretching bands between 3300 and 2500 cm^{-1} which are due to the bounded OH groups, and (b) the IR spectra of the pure ligand acids have strong COOH stretchings at 1650-1655 cm^{-1}, while the complexes have only antisymmetric COO^- stretchings at 1580-1615 cm^{-1} and symmetric stretchings at 1460-1430 and 1380-1330 cm^{-1}.

Fig. 1 shows the TG and DTG curves of $Zn(Clsal)_2 \cdot 2H_2O$. The complex is stable up to 368 K, after which it starts to decompose. According to the thermal analysis and mass spectrometry, the decomposition of the compound takes place in three stages. The first stage at 368-428 K (maximum at 405 K) corresponds the dehydration of two water molecules (weight loss of 7.9 %). The loss of H_2O above 373 K indicate that the water is probably bound in the coordination sphere of the zinc(II). In the second step at 428-588 K the loss of 5-chlorosalicylic acid occur. At a very narrow temperature range, 513-533 K, a vigorous reaction takes place with a maximum at 523 K. The weight loss of step II is 38.4 wt.% corresponding to liberation of one ligand acid molecule. The sharp peaks in the DTG curve between 573 and 650 K are probably due to the starting of step III and ending of step II. The third stage at 588-808 K and a weight loss of 38.4 wt.% corresponds to the loss of one 5-chlorosalicylic acid molecule.

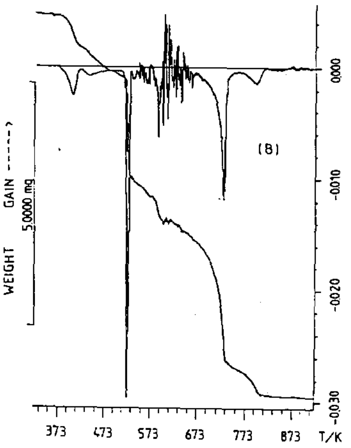

Fig. 1. TG and DTG plot of bis(2-hydroxy-5-chlorobenzoato)zinc(II) dihydrate.

The thermal decomposition of the other present metal(II) salicylato complexes is similar to that presented above for the bis(2-hydroxy-5-chlorobenzoato)-zinc(II) dihydrate. According to TG and DTG curves, mass spectra of the decomposition products, and X-ray diffraction analysis of the intermediate and final decomposition products, we propose that the decomposition scheme for the studied complexes is as follows:

$$M(5\text{-}Xsal)_2 \cdot nH_2O \xrightarrow[-\ nH_2O]{\text{step I}} M(5\text{-}Xsal)_2 \xrightarrow[-\ H\text{-}5\text{-}Xsal]{\text{step II}} M(5\text{-}Xsal) \xrightarrow[-\ H\text{-}5\text{-}Xsal]{\overset{O_2\ (\text{air})}{\text{step III}}} MO \text{ or } M'_2O_3$$

X = H, Cl, Br, I, NO_2; M = Cu, Ni, Mn, Zn; M' = Fe; n = 2, 3, 4

During the step III the liberated ligand molecules undergo further reactions, in which phenol, different halo and nitrophenols, and CO_2 are formed.

The DSC experiments were performed only for the various copper(II) complexes and iron(II) - 5-chlorosalicylato compound. The DSC curves recorded show to be very similar in shape. The enthalpy changes of the first two steps are both endothermic while the reactions in the step III seem to be very exothermic.

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