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THERMAL DECOMPOSITION STUDIES OF SOME SUBSTITUTED CADMIUM /II/ SALICYLATO COMPLEXES

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ABSTRACT

Hydrous cadmium /II/ salicylate as well as 5-chloro, 5-bromo, 5-iodo, and 5-nitrosalicylato complexes have been prepared and characterized on the basis of elemental analysis and IR studies. The thermal behaviour of these complexes have been determined by employing TG and DTG techniques. The results of thermal analysis, mass spectrometric and scanning electron microscopy studies reveal that the decomposition of these complexes contains three or four stages depending on the complex.

INTRODUCTION

The salicylate complexes of cadmium have been studied by various investigators in solutions.[1-3] Venkatasubramanian[4] has reported that the crystals of cadmium salicylate dihydrate belong to the monoclinic system where the space group is $P2_1/a$. Recently Kharitonov et al.[5] proposed the thermal transformations of the cadmium salicylato complex.

In earlier papers we have reported the thermal behaviour of copper /II/, iron /II/, zinc /II/, manganese /II/ and nickel /II/ salicylato complexes.[6-9]

EXPERIMENTAL

The ligand acids, as well as 3 $CdSO_4 \cdot 8 H_2O$, were supplied commercially /Fluka AG/ as the purest available grade and were used without further purification. Bis /2-hydroxybenzoato/ cadmium /II/ dihydrate, bis /2-hydroxy-5-chlorbenzoato/cadmium/II/ dihydrate, bis /2-hydroxy-5-bromobenzoato/cadmium/II/ dihydrate, bis /2-hydroxy-5-iodobenzoato/cadmium/II/ dihydrate and bis/2-hydoxy-5-nitrobenzoato/cadmium/II/ dihydrate reported in Table 1 were prepared following a procedure described elsewhere.[6,8] The methods of the analysis and thermoanalytical experiments were the same as described previously.[10]

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RESULTS AND DISCUSSION

The IR spectra of pure ligand acids have strong COOH stretchings at 1650-1655 cm^{-1}, while the complexes have only antisymmetric COO^- stretchings at

Table 1. Analytical data for the cadmium/II/ salicylato complexes.

Compound[a]	Analysis (%)[b]		IR bands (cm^{-1})		
	Cd	C	$\nu_{as}(COO^-)$	ν(OH)	ν(other)
$Cd(sal)_2 \cdot 2H_2O$	26.7(26.6)	38.5(39.8)	1580 S	3430 S	1245(CO) s
$Cd(5\text{-Clsal})_2 \cdot 2H_2O$	24.3(22.9)	33.2(34.2)	1580 S	3360 S	650(Cl) m
$Cd(5\text{-Brsal})_2 \cdot 2H_2O$	20.4(19.4)	27.6(29.0)	1580 S	3350 S	630(Br) m
$Cd(5\text{-Isal})_2 \cdot 2H_2O$	16.4(16.7)	24.5(24.9)	1545 S	3450 S	610(I) m
$Cd(5\text{-}NO_2sal)_2 \cdot 2H_2O$	22.0(21.9)	31.4(32.8)	1595 S	3400 S	1335(NO_2) s

[a] sal = $C_6H_3/OH/COO^-$, [b] calculated values are given in parentheses

1580 - 1615 cm^{-1} and symmetric stretchings at 1430 - 1460 and 1330 - 1380 cm^{-1}.

The TG and DTG curves are presented in Fig. 1. excluding the 5-nitrosalicylato complex. The experimental results of TG, DTG and mass spectrometry show that the first stage in the decomposition process of the compounds takes place at 323 - 418 K and corresponds to the dehydration of two water molecules. In the second step, at 418 - 598 K, the loss of ligand acid occurs in the same manner as discribed earlier for the corresponding copper, iron, zinc and nickel complexes.[6,8,9] In the third step the loss of one ligand acid molecule takes place in the case of the cadmium salicylato complex. For the 5-substituted cadmium salicylato complexes the third and fourth stage partly overlap. Mass spectrometric and scanning electron microscopic results show that during these stages the decomposition products contain partly ligand acid but also there are cadmium halides /$CdCl_2$, $CdBr_2$ and CdI_2/. In the case of the 5-iodosalicylato complex the third and fourth stage overlap completely while for the 5-chloro- and 5-bromosalicylato complexes loss of CdBr or $CdCl_2$, respectively, begins a little later.

Figure 2 shows scanning electron microscopy picture from the solid decomposition residue of the 5-bromosalicylato complex after heating twentyfive minutes at 723 K in air. In the picture there are crystals /$CdBr_2$/ and an amorphous substance /CdO/.

The final decomposition product of these studied complexes is CdO, excluding the 5-iodosalicylato complex where all the cadmium disappears as CdI_2. Respectively in the case of the 5- bromo-salicylato complex it looses more $CdBr_2$ that from the 5-chloro-salicylato complex.

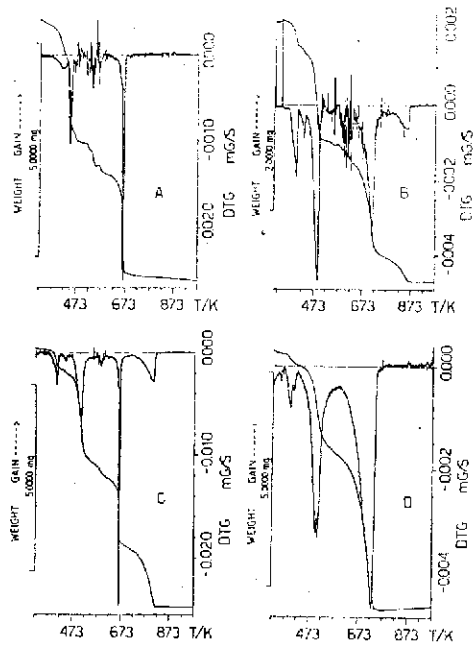

Fig. 1. TG and DTG plots of bis/2-hydroxybenzoato/cadmium/II/ dihydrate /A/ ; bis/2-hydroxy-5-chlorobenzoato/cadmium/II/ dihydrate /B/ ; bis/2-hydroxy-5-brombenzoato/cadmium/II/ dihydrate /C/ ; and bis/2-hydroxy-5-iodobenzoato/cadmium/II/ dihydrate /D/.

The following decomposition scheme for the 5-bromosalicylato complex is proposed :

$$Cd/5\text{-}Brsal/_2 . 2H_2O \xrightarrow[-\,2H_2O]{\text{step I}} Cd/5\text{-}Brsal/_2$$

$$\xrightarrow[-5\text{-}Brsal]{\text{step II}} Cd/5\text{-}Brsal/^+ \xrightarrow[-5\text{-}Brsal\,+\,CdBr_2]{\text{steps III-IV/}O_2\ /air/} CdO$$

For the 5-nitrocomlex, which was found to decompose explosively, only the loss of water molecules, having a maximum at 355 K, was determined.

Fig. 2. The scanning electron microscopy picture taken of the 1050 fold enlargement from the decomposition residue of the 5-bromosalicylato complex after heating to 723 K.

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