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THERMAL ANALYSIS OF *CIS*- AND *TRANS*-POTASSIUM BIS-MALONATE AND BIS-MONOMETHYLMALONATE CHROMATE(III) COMPLEXES*

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ABSTRACT

The *cis*- and *trans*-potassium bis-malonate chromate(III) dihydrate and *cis*- and *trans*-potassium bis-monomethilmalonate chromate(III) dihydrate were prepared and analyzed by TG, DTG and DSC. Detailed results are reported and the thermal stability order is discussed in terms of steric hindrance in the two configurations. Data for the corresponding tris compounds are also reported as reference.

INTRODUCTION

Some aspects related to the thermal stability order of solid complexes have been investigated in previous papers[1–7]. Relations between the thermal stabilities and the stability of complexes in aqueous solution[1] or the basicity of ligands were also discussed.

However, the influence of the structure of solid complexes on the thermal stability, when the chemical formula is the same and only configurations are different, has not been greatly investigated. Particularly, it seems that no rules can be found to suggest the pathway followed by a thermal decomposition when the starting product is the same but obtained, for example, from *trans* or *cis* complexes. In some cases, the pathway seems to be the same; in others the thermal trend is different as, for example, for *cis*-/*trans*-di(*p*-methilbenzoate)bis(ethylendiammine)cobalt(III) nitrate[8], where only a reaction step is shifted in temperature, or for *cis*-/*trans*-potassium bis(oxalate)diaquochromate(III)[9], where the decomposition of the anhydrous oxalate takes place in a single step when formed from *cis*-diaquo and in multiple steps from *trans*-diaquo.

In the present paper, the thermal behaviour of bis complexes, $M'L_2 \cdot 2H_2O$, has been investigated either as *cis* or *trans* complexes. Ligands (L) are malonate (malo) or monomethylmalonate (m-malo) while M′ is the group KCr^{4+}. Corresponding $ML_3 \cdot nH_2O$ tris-complexes were also reported as reference, with $M = K_3Cr^{6+}$ (ref. 7).

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TABLE 1

ELEMENTAL ANALYSIS OF THE COMPOUNDS OBTAINED

Compound[a]	*M.wt.*	*C%*		*H%*		*Cr%*	
		Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*
$M'malo_2 \cdot 2H_2O$							
cis	331.21	21.76	20.8	2.43	2.8	15.70	15.5
trans	331.21	21.76	19.9	2.43	3.0	15.70	15.6
$M'm\text{-}malo_2 \cdot 2H_2O$							
cis	359.26	26.75	25.8	3.36	3.4	14.47	14.6
trans	359.26	26.75	25.9	3.36	3.7	14.47	14.4

[a] $M' = KCr^{4+}$.

EXPERIMENTAL

cis- and *trans*-potassium bis(methylmalonate) diaquochromate(III) (*cis*- and *trans*-$M'm\text{-}malo_2$) as well as *cis*- and *trans*-potassium bis(malonate) diaquochromate(III) (*cis*- and *trans*-$M'malo_2$) have been prepared according to the procedure of Chang[10, 11] by mixing the carboxylic acids with potassium dichromate with initial molar ratio 5:1.

Absolute ethanol and ether were used in order to induce the precipitation of *cis* complexes, and to wash all the compounds obtained. After precipitation, the solids were quickly dried and maintained in a dry atmosphere. The chromium yield ranged from 20 to 40%. All the solid compounds obtained were checked by elemental analysis and chromium titration. Results are shown in Table 1. TLC was used in order to check the purity of each isomer.

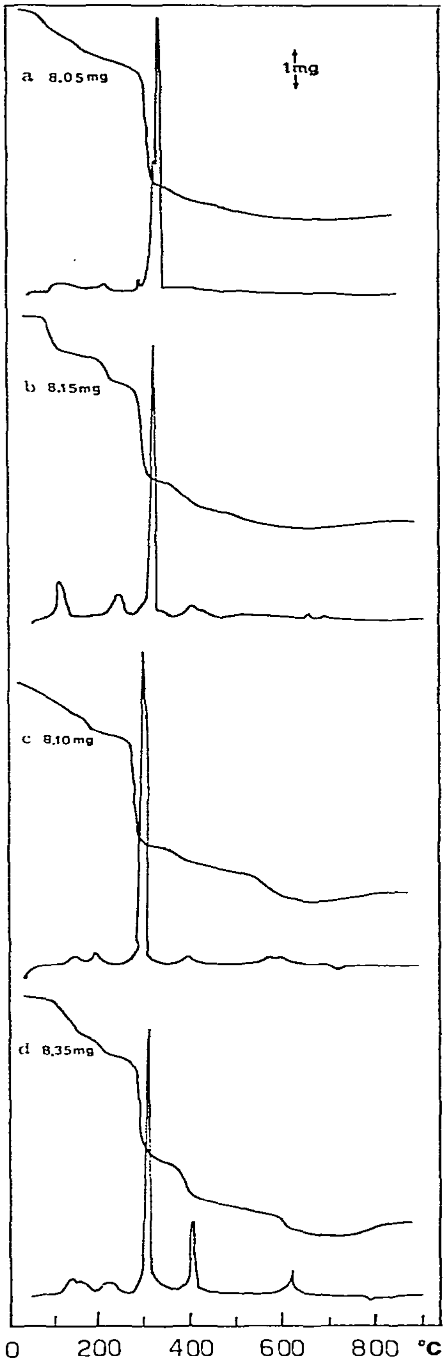
RESULTS

The thermal behaviour of the examined compounds is shown in Figs. 1 and 2 where TG, DTG and DSC are reported for malo and m-malo compounds, respectively. Data are also summarized in Table 2, where pdt's derived from DSC are reported. The procedural decomposition temperatures (pdt) of the last column are obtained from TG data owing to the fact that the maximum DSC temperature attainable is 500°C.

In Table 2, arrows represent each peak shown in DSC. TG data are given as mass loss corresponding to each peak due to water loss, or as residual percent after the completion of the last peak represented. Possible assignments are shown as chemical formulae corresponding to the mass loss or to the residual.

DISCUSSION

Looking at the results shown in Table 2, where data of the corresponding tris compounds $K_3Cr\ malo_3 \cdot 3H_2O$ and $K_3Cr\ m\text{-}malo_3 \cdot 3H_2O$ published in a previous paper[7] are also reported, some observations may be made.



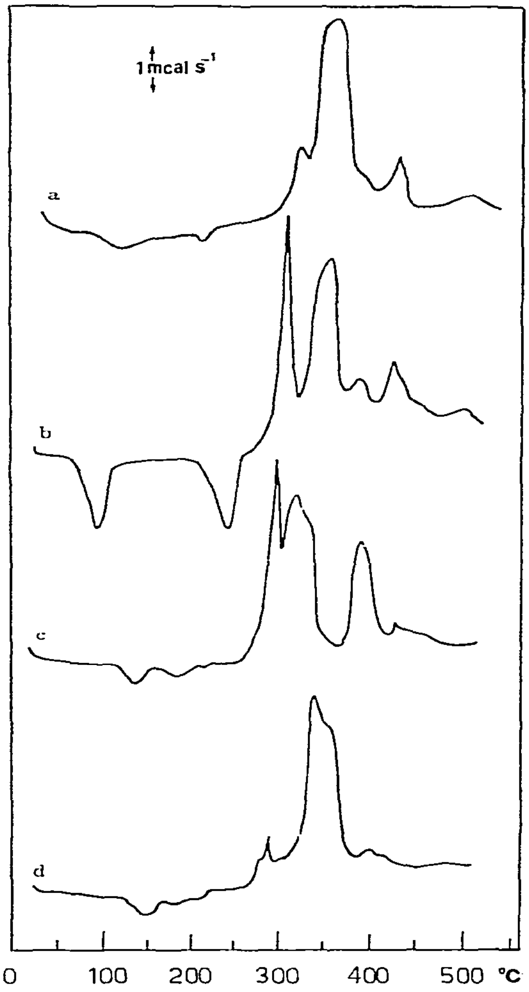


Fig. 1. TG and DTG in air atmosphere. Heating rate 10°C min^{-1}. a, *cis*-M'malo$_2 \cdot 2H_2O$; b, *trans*-M'malo$_2 \cdot 2H_2O$; c, *cis*-M'm-malo$_2 \cdot 2H_2O$; d, *trans*-M'm-malo$_2 \cdot 2H_2O$. Initial weights are shown.

Fig. 2. DSC in air atmosphere. Heating rate 10°C min^{-1}. a, *cis*-M'malo$_2 \cdot 2H_2O$; b, *trans*-M'malo$_2 \cdot 2H_2O$; c, *cis*-M'm-malo$_2 \cdot 2H_2O$; d, *trans*-M'm-malo$_2 \cdot 2H_2O$.

TABLE 2

Compound	M.wt. anhydr.	(1) Calc. %	Found %	pdt	(2) Calc. %	Found %	pdt	(3) Calc. %	Found %	pdt	(4) Calc. %	Found %	pdt	(5) Calc. %	Found %	pdt	(6) Calc. %	Found %	pdt
M′malo$_3$ · 3H$_2$O[a]	475.5	−11.7	−11.4	90 120 ↓ 150 $-3H_2O$		94.2	150 180 210		68.1	↑ 250 290 300	59.6	59.6	↑ 300 320 325 $K_3Cr(CO_3)_{3/2}O_{3/2}$		51.5	↑ ↑ ↑ 325 340 450	45.7	45.6	450 530 600 $3/2K_2O$ $1/2Cr_2O_3$
M′malo$_2$ · 2H$_2$O *cis*	295.2	−12.2	−12.4	40 90 ↓ 150 $-3H_2O$		94.4	150 205 ↓ 220		54.2	↑ 220 310 320		51.3	↑ ↑ 320 340 385	49.2	47.2	↑ ↑ 385 420 430 $KCr(CO_3)_{1/2}O_{3/2}$	41.7	41.7	430 485 600 $1/2K_2O$ $1/2Cr_2O_3$
M′malo$_2$ · 2H$_2$O *trans*	295.2	−12.2	−12.5	50 90 ↓ 160 $-2H_2O$		88.9	160 240 ↓ 250		57.6	↑ 250 300 320		54.2	↑ ↑ 320 345 370	49.2	49.0	↑ ↑ 370 420 440 $KCr(CO_3)_{1/2}O_{3/2}$	41.7	41.6	440 485 600 $1/2K_2O$ $1/2Cr_2O_3$

ıalo$_3$ · $3H_2O^a$	517.6	−10.4 −11.1	30 80 ↓ 140	88.8	140 190 220	83.9	↑ 220 260 270	54.7 55.9	↑ 270 310 320	47.6	↑ ↑ ↑ 320 340 450	41.9 42.0	450 540 600
		$-3H_2O$						$K_3Cr(CO_3)_{3/2}O_{3/2}$				$3/2K_2O$ $1/2Cr_2O_3$	
ıalo$_2$ · $2H_2O$	323.2	−11.1 −11.0	50 130 ↓ 150	94.5	150 180 ↓ 220	58.5 59.1	↑ 250 280 290	54.8	↑ ↑ 290 320 360	50.0	↑ ↑ 360 380 470	38.1 38.1	470 565 650
		$-2H_2O$				$KCr(CO_3)_{3/2}O_{1/2}$						$1/2K_2O$ $1/2Cr_2O_3$	
ıalo$_2$ · $2H_2O$	323.2	−11.1 −11.3	50 145 ↓ 160	92.7	160 190 ↓ 230	58.5 61.3	↑ 230 290 320	56.3	↑ ↑ 320 340 380	45.3	↑ ↑ 380 410 450	38.1 37.6	450 590 660
		$-2H_2O$				$KCr(CO_3)_{3/2}O_{1/2}$						$1/2K_2O$ $1/2Cr_2O_3$	

$_3Cr^{6+}$; M′ = KCr^{4+}; ↓ = endothermic; ↑ = exothermic.

ıes are reported with respect to the anhydrous compounds; values reported for water loss are preceded by a minus sign meaning "mass loss" during the step while the are expressed as "residual" at the end of the step.

7 with the characterization of other steps added.

With respect to the dehydration process described in column 1, it can be observed that water loss of the bis compounds (*cis*- and *trans*-) takes place at a lower temperature in the malo series with respect to the tris compound, while the reverse can be seen in the m-malo series.

The first decomposition step of the anhydrous compounds, column 2, is always characterized by a poorly-defined mass loss. However, for bis compounds, an endothermic peak, not corresponding to the melting, was observed while no thermal effect appeared in the tris DSC curves. Thermal stabilities account for the order

K_3Cr malo$_3$ $\lesssim$ *cis*-KCr malo$_2$ $<$ *trans*-KCr malo$_2$
K_3Cr m-malo$_3$ $<$ *cis*-KCr m-malo$_2$ $\lesssim$ *trans*-KCr m-malo$_2$

This behaviour can be interpreted in terms of steric hindrance in the solid lattice which decreases on moving from the tris compound to the bis in the *cis* to the *trans* configuration. The lack of an endothermic peak when the first mass loss of the anhydrous occurs, observed in the tris with respect to the bis compounds, may suggest that the latter are involved in some structural changes when thermal decomposition starts.

After the first decomposition step, described in column 2, the following thermal pathway is substantially the same for all the examined compounds. However, intermediates are mixtures of potassium and chromium oxides and/or carbonates which are different to one another, as shown by hypothetical residuals reported in columns 3–5. It can be suggested that analogous decomposition intermediates are obtained for all the compounds even if small differences in the thermal decomposition may be attributed to different initial compounds, as already observed[9].

For all the examined compounds, a mixture of potassium and chromium oxides is formed as the result of the last decomposition, as shown in column 6. This oxide mixture is stoichiometrically identical to $KCrO_2$ for the bis compounds and to K_3CrO_3 for the tris compounds. Owing to the fact that, in both cases, the thermal trend is the same, it seems more appropriate to report these residuals as oxide mixtures.

Concerning the thermal stability of the bis-malo compounds with respect to the bis-m-malo, the same relations as for the tris compounds have been found, which can be discussed as previously reported[7].

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