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THERMAL ANALYSIS OF SOME CHROMIUM(III) COMPLEXES WITH DICARBOXYLIC LIGANDS

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ABSTRACT

The solid chromium(III) complexes with a series of dicarboxylic ligands were prepared as potassium salts and examined by TG, DTG and DSC. The results are discussed in terms of basicity by arranging the ligands in proper series.

INTRODUCTION

As a continuation of a systematic study of the factors affecting the thermal properties of solid compounds obtained by reaction between metal ions and organic ligands[1–6], a new series was examined by TG, DTG and DSC.

The series discussed in the present paper consists of chromium(III) complexes of dicarboxylic ligands. It is identified by the general formula, $ML_3 \cdot nH_2O$, where M represents K_3Cr^{6+}, since solid compounds were obtained by salification with potassium. The series of ligands is malonate, monomethylmalonate, dimethylmalonate, oxalate, maleate, succinate and ftalate. In the text, these anions are reported as malo, m-malo, d-malo, oxal, male, succ and ftal, respectively. In order to study their thermal stability as a function of the ligands[3, 6], the compounds may be arranged in three subseries:

A, M oxal_3, M malo_3, M succ_3
B, M male_3, M ftal_3, M succ_3
C, M malo_3, M m-malo_3, M d-malo_3

Here they show changes in A, the paraffinic chain; B, the C–C bond; and C, the number of methyl substituents.

EXPERIMENTAL

Instrumentation

The TG, DTG and DSC curves of the solid complexes were obtained using a Du Pont Model 990 DSC cell and console and a model 951 thermobalance. The heating rate used was 10°C min^{-1} on samples whose mass ranged from 1 to 10 mg. The furnace atmosphere consisted of dry air at a flow rate of 50–100 ml min^{-1}. All

TABLE 1

ANALYSIS OF THE COMPOUNDS

Compound[a]	*Mol. wt.*	*C (%)*		*H (%)*		*Cr (%)*	
		Calc.	*Found*	*Calc.*	*Found*	*Calc.*	*Found*
M $malo_3 \cdot 3H_2O$	529.48	20.42	20.6	2.28	2.4	9.82	10.0
M m-$malo_3 \cdot 3H_2O$	571.58	25.22	25.9	3.17	3.5	9.09	9.4
M d-$malo_3 \cdot 3H_2O$	613.66	29.36	30.3	3.94	4.2	8.47	8.7
M $oxal_3 \cdot 3H_2O$	487.40	14.78	14.6	1.24	0.8	10.67	9.8
M $succ_3 \cdot 3H_2O$	571.58	25.20	22.6	3.10	3.1	9.09	9.0
M $male_3 \cdot 2H_2O$	547.30	26.41	25.7	1.83	2.3	9.50	9.1
M $ftal_3 \cdot 2H_2O$	697.30	41.34	34.7	2.30	2.7	7.46	7.5

[a] M $= K_3Cr^{3+}$.

temperatures were corrected for thermocouple non-linearity and are, of course, procedural temperatures.

Preparation of compounds

All compounds were prepared by adapting the procedure suggested by Chang[7, 8] for potassium tris(malonate)chromate trihydrate. Chromium(III) hydroxide was obtained from the corresponding chloride and subsequently mixed with a stoichiometric amount of the organic acid. After heating, the solid compounds were precipitated by adding a slight excess of potassium carbonate and then ethanol or diethyl ether/ethanol mixture. The chromium yield ranged between 30 and 60%.

Using the above procedure, it was impossible to obtain the potassium tris(oxalate)chromate(III) trihydrate. This compound was prepared according to the method proposed in ref. 9. The chromium yield was about 90%. All the solid compounds obtained were controlled by elemental analysis and titration, with Mohr salt[10], of the chromium present in a solution obtained by dissolving a known amount of the solids by addition of small portions of hot perchloric acid. The results obtained are listed in Table 1.

RESULTS

The results obtained are shown in Figs. 1–7 and data are summarized in Table 2 where some thermal decomposition steps are reported. For each compound, the starting temperature of the thermal decomposition of the anhydrous compound is also reported. This is because the first reaction step in the anhydrous thermal decomposition is not reported in all cases owing to unassigned and/or unresolved reactions. Some tentative reaction assignment to the decomposition steps is also reported. The thermal stability of potassium oxalate, assumed to be intermediate in the M $ftal_3$ decomposition, was checked separately up to 520°C. At higher tempera-

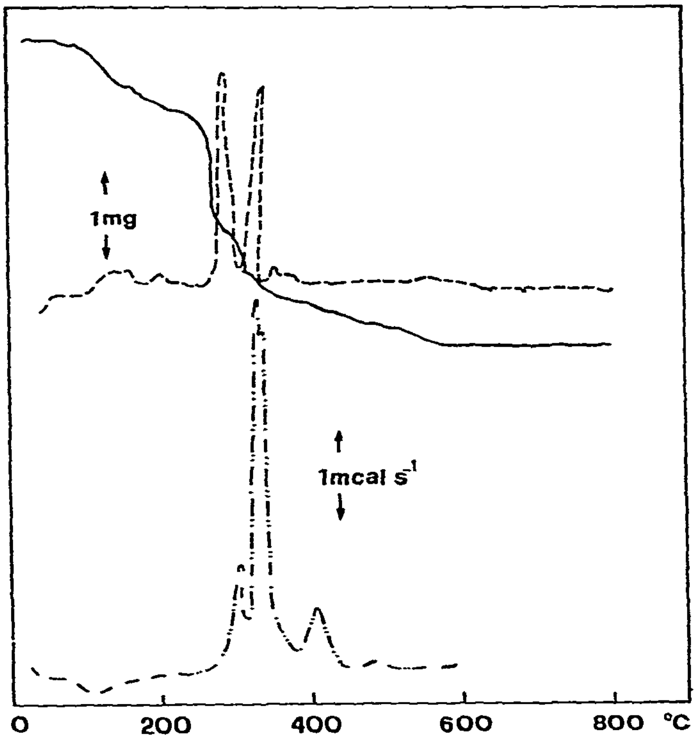

Fig. 1. Potassium tris(malonate)chromate(III) 3-hydrate. —, TG; ----, DTG; —..—, DSC.

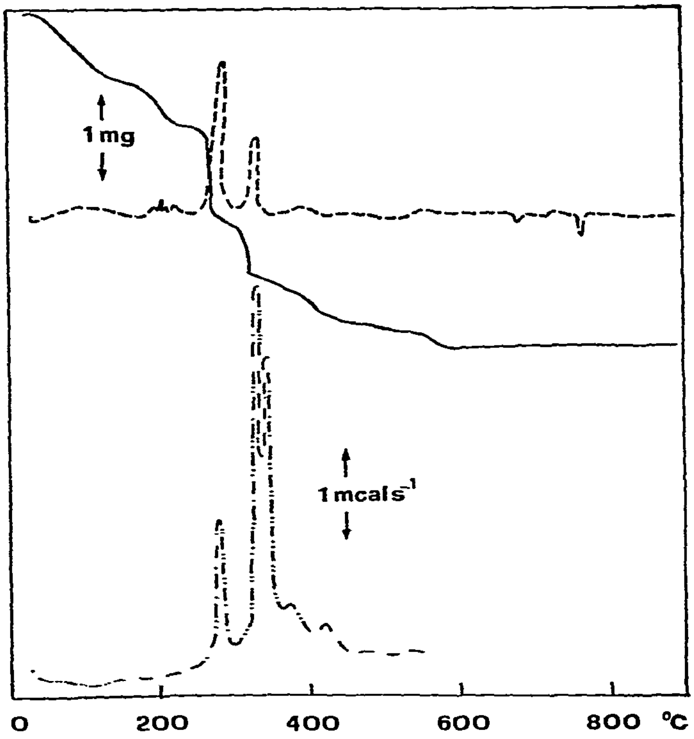

Fig. 2. Potassium tris(monomethilmalonate)chromate(III) 3-hydrate. —, TG; ----, DTG; —..—, DSC.

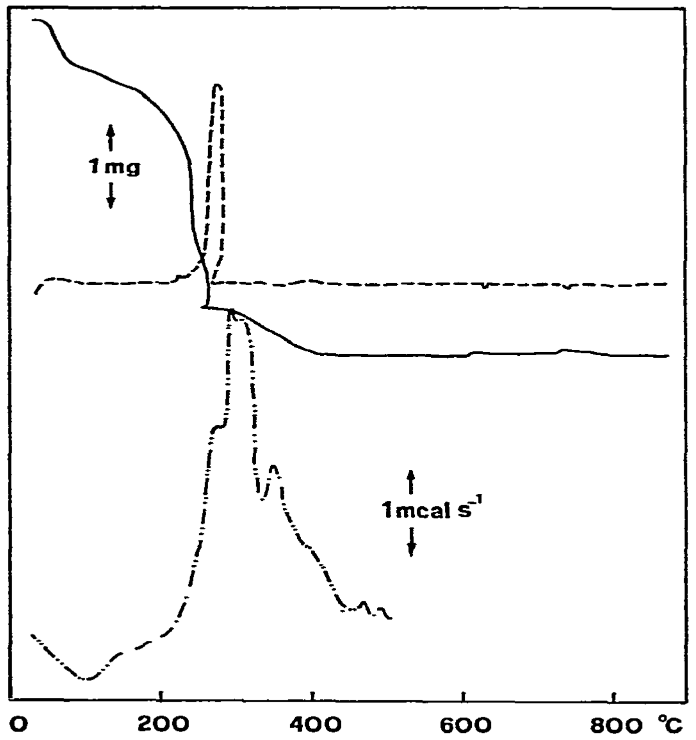

Fig. 3. Potassium tris(dimethilmalonate)chromate(III) 3-hydrate. —, TG; ––––, DTG; —..—, DSC.

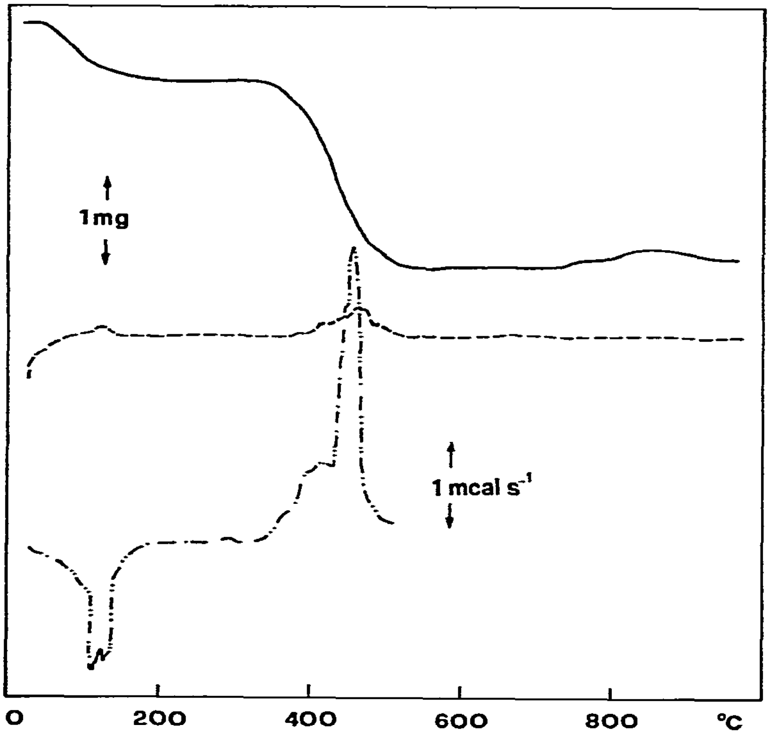

Fig. 4. Potassium tris(oxalate)chromate(III) 3-hydrate. —, TG; ––––, DTG; —..—, DSC.

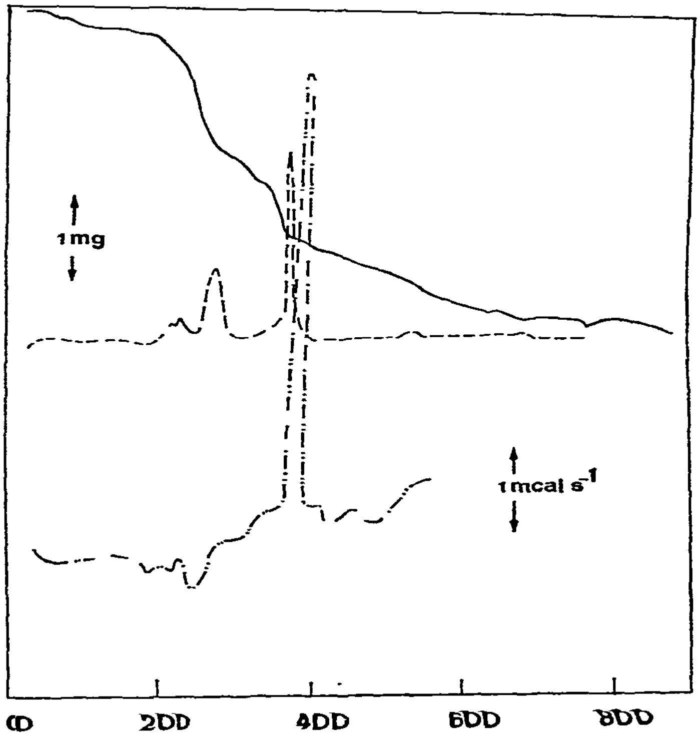

Fig. 5. Potassium tris(maleate)chromate(III) 2-hydrate. —, TG; ----, DTG; —..—, DSC.

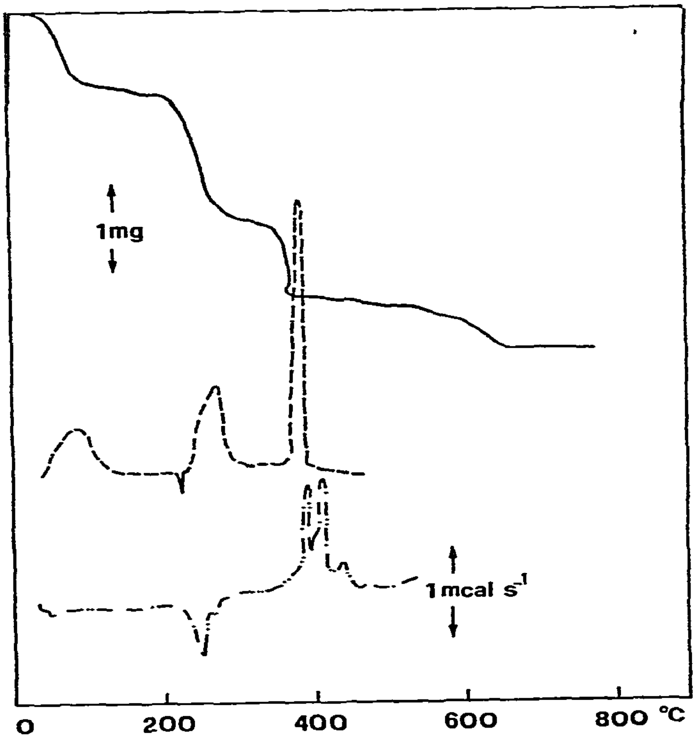

Fig. 6. Potassium tris(succinate)chromate(III) 3-hydrate. —, TG; ----, DTG; —..—, DSC.

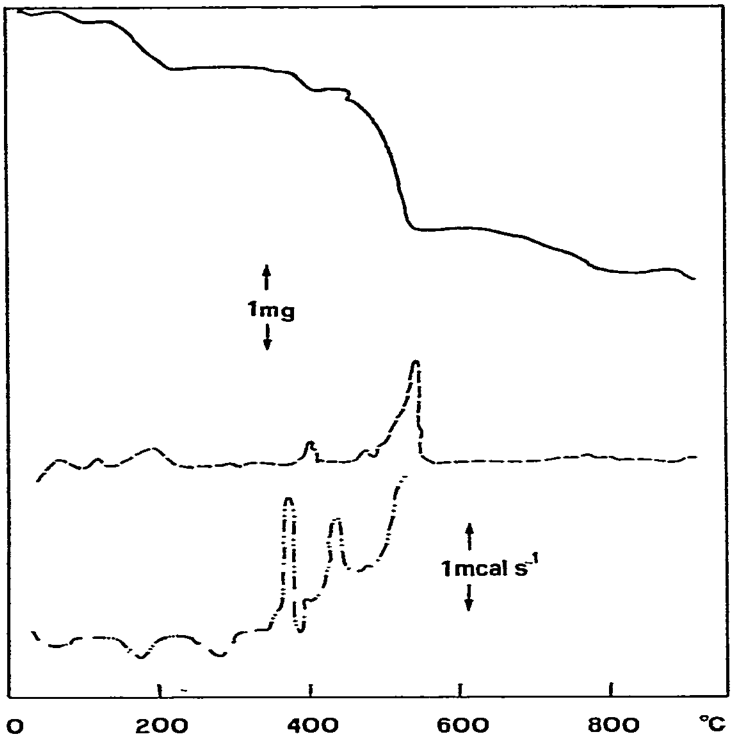

Fig. 7. Potassium tris(ftalate)chromate(III) 2-hydrate. —, TG; -----, DTG; —..—, DSC.

ture, the potassium carbonate was formed, being stable up to 850°C (the maximum experimentally raised temperature).

DISCUSSION

All the reported solid compounds resulted in the trihydrate, with two exceptions, M male$_3$ and M ftal$_3$ obtained as the dihydrate. Only for the latter compound was it possible to resolve the water loss in two steps, while for the other a single sharp step occurs in TG. A possible interpretation for multiple-step water loss has been discussed previously[2, 3].

The thermal stability scale of the anhydrous compounds inside the three series considered, according to the data reported in Table 2, is

A0, M oxal$_3$ > M malo$_3$ > M succ$_3$
B0, M male$_3$ > M ftal$_3$ > M succ$_3$
C0, M malo$_3$ > M m-malo$_3$ > M d-malo$_3$

The thermal stability order is reversed with respect to the basicity of the ligands (see Table 3) as previously observed[1, 3]. The pK_1 value scales are

A1, oxal < malo < succ
B1, male < ftal < succ
C1, malo < m-malo < d-malo

TABLE 2

THERMAL ANALYSIS OF THE COMPOUNDS

$M = K_3Cr^{6+}$; ↓ = endothermic; ↑ = exothermic. % Values are reported with respect to the anhydrous compounds. Values reported for water loss are preceded by a minus sign, indicating a "mass loss" during the step, while the remainder are expressed as "residue" at the completion of the step. Mixture A: mixture of chromium and potassium carbonate-oxide stoichiometrically corresponding to $CrK_3(CO_3)_{3/2}O_{3/2}$. Mixture B: mixture of chromium and potassium oxides stoichiometrically corresponding to CrK_3O_3.

Compound	*Mol. wt. anhyd.*	*Step 1*			*Step 2*			*Step 3*			*Start. dec. temp. of anhyd.*
		Calc. %	*Found %*	*pdt*	*Calc. %*	*Found %*	*pdt*	*Calc. %*	*Found %*	*pdt*	
M $malo_3 \cdot 3H_2O$	475.5	−11.7 $-3H_2O$	−11.4	90 120 ↓150	59.6 Mixture A	59.6	300 320 325	45.7 Mixture B	45.6	450 530 600	150
M m-$malo_3 \cdot 3H_2O$	517.6	−10.4 $-3H_2O$	−11.1	30 80 ↓140	54.7 Mixture A	55.9	↑270 310 320	41.9 Mixture B	42.0	450 540 600	110
M d-$malo_3 \cdot 3H_2O$	559.6	− 8.8 $-3H_2O$	− 9.0	30 60 ↓ 90	50.7 Mixture A	50.7	↑250 270 280	38.8 Mixture B	40.8	↑280 350 400	90
M $oxal_3 \cdot 3H_2O$	433.4	−12.5 $-3H_2O$	−12.3	50 110 ↓200				60.7 $K_2CrO_4 + \frac{1}{2} K_2CO_3$[a]	60.9	↑320 440 530	320

TABLE 2 *(continued)*

Compound	*Mol. wt. anhyd.*	*Step 1*			*Step 2*			*Step 3*			*Start. dec. temp. of anhyd.*
		Calc. %	*Found %*	*pdt*	*Calc. %*	*Found %*	*pdt*	*Calc. %*	*Found %*	*pdt*	
M $male_3 \cdot 2H_2O$	511.3	− 7.0 $-2H_2O$	− 6.6	↓ 30 70 150				42.5 Mixture B	43.4	↑ 500 600 700	180
M $succ_3 \cdot 3H_2O$	517.3	−10.4 $-3H_2O$	−12.7	↓ 30 65 80	51.9 Mixture A	52.1	↑ 300 370 400	42.0 Mixture B	41.5	500 600 700	90
M $ftal_3 \cdot 2H_2O$	661.3	− 5.4 $-2H_2O$	− 5.2	↓ 30 60 ↓ 60 110	59.1 Mixture A	59.6	↑ 300 500 530	52.8 Mixture B	52.6	600 740 800	110

[a] W. W. Wendland and T. D. George, *J. Inorg. Nucl. Chem.*, 17 (1961) 69.

TABLE 3

STABILITY CONSTANTS AT 25 °C AND 0.1 M IN NaClO$_4$

From L. G. Sillen and A. E. Martell, *Stability Constants*, Chemical Society, London, 1971.

Acid	*log*K_1 (pK_2)	*log*K_2 (pK_1)	*log*K_1 + *log*K_2	*log*K_{Cr}			*log* β_3
				1	*2*	*3*	
malo	5.32	2.66	7.98	7.06	5.79	3.30	16.15
m-malo	5.46	2.97	8.43				
d-malo	5.81	3.08	8.89				
oxal	3.81	1.37	5.18	5.34	5.17	4.93	15.44
succ	5.21	4.00	9.21	6.42	4.57	2.86	13.85
ftal	5.13	2.91	8.04	5.52	4.48	2.48	12.48
male	5.79	1.92	7.71	5.4	3.0	1.9	10.3

The pK_2 value scales are

A2, oxal $<$ malo $\simeq$ succ
B2, male $\gtrsim$ ftal $\gtrsim$ succ
C2, malo $<$ m-malo $<$ d-malo

Considering the sum pK_1 + pK_2 as the expression of the total basicity of the ligands, the following scales are obtained.

A12, oxal $<$ malo $<$ succ
B12, male $<$ ftal $<$ succ
C12, malo $<$ m-malo $<$ d-malo

In the above sequences, only the B2 shows an inversion with respect to the described order, even if, numerically, of limited amount. However, all discrepancies with respect to the proposed order disappear when considering the total basicity of the ligands (see A12, B12 and C12 series).

The inversion of the order of thermal stability with respect to the order of the stability constants in solution has been previously discussed[1] in terms of contribution of inter- and intramolecular bonds to the solid state stability. This interpretation agrees also with the coupled donor/acceptor reactions described from a phenomenological point of view by Mayer and Gutmann[11]. In this picture, the ligand basicity seems to be more appropriate than the complex stability in solution to describe the relative contribution of the intramolecular bonds to the solid lattice when the same metal acceptor is considered in a series. In fact, at least for the formation of the hard–hard complexes, the basicity of the ligands is a measure of a metal–ligand interaction that is not affected by other factors (i.e. steric hindrance) playing in solution a role which is not necessarily related to the solid structure. This suggestion, which would be confirmed by a larger number of experimental data, is in accordance with data obtained in previously studied compounds[3, 6]. Particularly for the complexes studied in the present work (from the disposable data reported in Table 3 with respect to the log β_3 of chromium(III) complexes) it is possible to obtain the series

A3, oxal $<$ malo $>$ succ
B3, male $<$ ftal $<$ succ

In the A3 sequence, the order is reversed with respect to that described and it is interesting to note that the inversion occurs when succ is considered, for which a larger steric hindrance in solution is expected when the ligand acts as bidentate.

Looking at the number of reaction steps resolved in TG for the anhydrous decomposition, it appears to be smaller at higher decomposition temperature. In fact, only M oxal$_3$ and M male$_3$ show a single-step rapid decomposition corresponding to the highest temperatures in the series examined. This is not surprising when considering that higher decomposition temperature corresponds to a lower ability of the species to arrange themselves in intermediate compounds.

Finally, with respect to the influence of the substituents on the thermal stability, it is possible to observe in the C series that, after a demethylation and/or decarboxylation, the thermal decompositions of M malo$_3$, M m-malo$_3$ and M d-malo$_3$ follow a common procedure to give a mixture of oxides and carbonates and, subsequently, of oxides.

ACKNOWLEDGEMENT

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