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Studies on Double Malonates. II.[†] Potassium Rare Earth Malonates, $K_5Ln(C_3H_2O_4)_4$ (Ln=Gd–Ho or Y)

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Double malonates of some of the rare earths with potassium having formula $K_5Ln(C_3H_2O_4)_4$ were synthesized. The lattice parameters of the compounds were determined by X-ray powder diffractometry. Infrared absorption spectroscopy was employed to throw some light on the nature of Ln–O bonding, while the thermoanalytical techniques were made use of in proposing the thermal decomposition mechanism of some of the double malonates.

Davitashvili and his coworkers have carried out a systematic study of the double oxalates of rare earth elements with alkali metals.[1–5] However, practically no attention has been paid to the corresponding double compounds of malonic acid — the next higher homologue of oxalic acid; the only report available in the literature being on the cerium(III) double malonates.[6] Thus, it was thought worthwhile to carry out systematic work on such type of double malonates, taking rare earths and different alkali or pseudo alkali metals.[7] The present paper, which is a part of this investigation, deals with the potassium double malonates, $K_5Ln(C_3H_2O_4)_4$, where Ln=Gd–Ho or Y.

Experimental

Synthesis. The normal rare earth malonates were precipitated by adding slowly about 14 cm³ of aqueous potassium malonate solution (134 mg $(C_3H_2O_4)^{2-}$ cm⁻³), to the aqueous *ca.* 0.011 M rare earth nitrate solution, with constant stirring. The precipitate obtained was filtered, washed free of nitrate ions and excess of potassium malonate, and dried over silica gel under vacuum till constant weight.

The normal rare earth malonates were dissolved in the aqueous potassium malonate solution in Ln^{3+}: $(C_3H_2O_4)^{2-}$ molar proportion of 1 : 5 since it was observed that for the molar proportions equal to 1 : 2, 1 : 3, and 1 : 4, a syrupy product was obtained on evaporation. The turbid mixture was warmed to get a clear solution, which gave the desired product when allowed to crystallize slowly over silica gel. The crystals formed were picked up from the mother liquor and were washed with 50 cm³ of 90% methanol; dried over silica gel under vacuum and stored in a desiccator because of its hygroscopic nature. All the chemicals used were of reagent grade quality.

It is interesting to note here that although the normal rare earth malonates and potassium malonate were mixed in the Ln^{3+}: $(C_3H_2O_4)^{2-}$ mole ratio as 1 : 5, the synthesized compounds were in the mole ratio 1 : 4.

Chemical Analysis. The rare earth contents of the double malonates were determined complexometrically. The potassium percentage was determined flame photometrically.

The malonate contents were determined using ion-exchange technique. Since the compounds tend to hydrolyse on dissolving in water, known volume of dilute hydrochloric acid was used for dissolution. The sample solution was passed through a cation exchanger (Seralite SRC 120) in hydrogen form (washed free of excess acid used for regeneration) at a rate of 2—3 cm³min⁻¹. As the malonate ion gets adsorped on the strongly acidic sulphonated resin,[8] the column was eluted with 100—150 cm³ of hot deionised water (363—373 K), to facilitate the complete desorption of the anion. The rate of flow of the effluent was 6—7 cm³min⁻¹ while washing the column with hot water so as to keep the resin warm throughout. The eluate thus obtained contains the malonic acid (equivalent to the malonate ion in the compound) plus the hydrochloric acid used for dissolution. This eluate was titrated with standard sodium hydroxide solution. The hydrochloric acid used for the dissolution was determined by following the same procedure as used for the sample solution so as to compensate for procedural errors. The reading corresponding to malonic acid was obtained by subtracting the reading corresponding to hydrochloric acid from the total reading for the eluate. The analytical results are given in Table 1.

Table 1. Results of chemical analysis of $K_5Ln(C_3H_2O_4)_4$

Ln	K/%		Ln/%		$C_3H_2O_4$/%	
	Calcd	Found	Calcd	Found	Calcd	Found
Gd	25.70	25.93	20.67	20.78	53.63	53.40
Tb	25.65	25.73	20.84	20.90	53.51	53.71
Dy	25.61	25.45	21.13	21.23	53.26	53.45
Ho	25.45	25.71	21.46	21.35	53.09	53.00
Y	28.26	28.60	12.84	12.61	58.90	58.60

Instrumentation. Nickel filtered Cu *Kα* radiation (mean λ=154.18 pm), operated on Philips X-ray diffractometer model No. PW 1009/30-NRD 1023, was used for the X-ray powder diffraction study. The relative intensities of the reflexions were calculated by taking that of the highest peak as 100.

The densities of the double malonates were determined by floatation method, using bromoform–hexane mixture as the working medium.

The densities of the double malonates were determined by malonates, were made in the frequency range 4000—400 cm⁻¹ with a Perkin-Elmer model 377, by CsBr disc method; while the spectra of some of the intermediates obtained by isothermally heating the original compound, were scanned on Beckman IR-4250 spectrophotometer in the frequency range 4000—200 cm⁻¹ using KBr pellet technique.

The TG and DTG curves of the gadolinium and holmium double malonates were scanned on a sophisticated Mettler Recording Vacuum Thermoanalyser (No. 84), in dry air, with a flow rate of 100 cm³min⁻¹. A Pt/Pt-Rh thermocouple

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[†] For Part I, See M. A. Nabar and B. N. Jukar, *Can. J. Chem.*, **62**, 348 (1984).

[††] 1 M=1 mol dm⁻³.

Table 2. Crystal data for $K_5Ln(C_3H_2O_4)_4$

Ln	a/pm	b/pm	c/pm	β/deg	V/pm^3 × 10^6	D_{calcd}/Mg m^{-3}	D_{obsd}/Mg m^{-3}
Gd	743±1	1367±2	991±1	93.10±0.16	1005	2.51	2.48
Tb	746±1	1366±3	989±1	13.79±0.17	1006	2.52	2.50
Dy	746±1	1367±2	987±1	93.46±0.10	1005	2.53	2.52
Ho	742±1	1363±2	985±1	93.20±0.10	996	2.56	2.54
Y	746±1	1365±2	988±1	93.28±0.13	1004	2.29	2.30

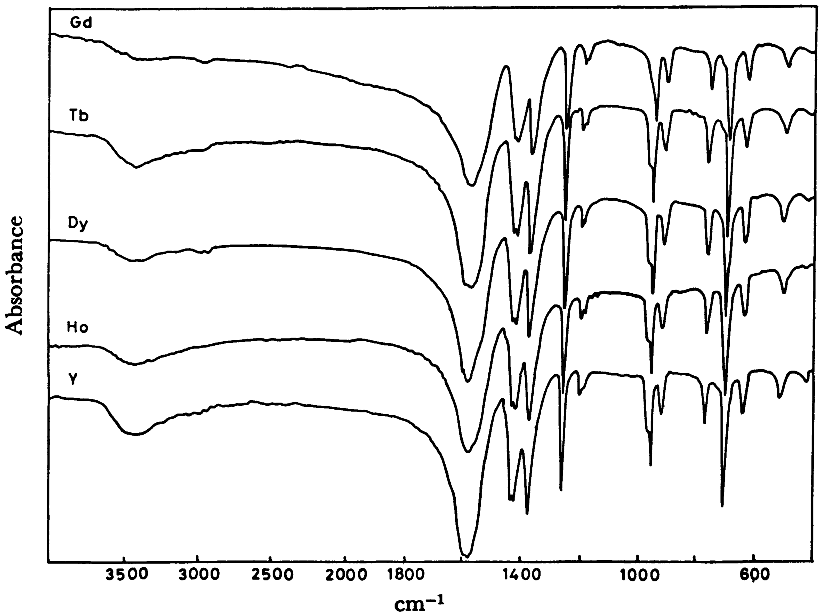

Fig. 1. Infrared absorption spectra of $K_5Ln(C_3H_2O_4)_4$.

Table 3. X-Ray powder diffraction data for $K_5Dy(C_3H_2O_4)_4$

$h\ k\ l$	d_{calcd}/pm	d_{obsd}/pm	I/I_0
0 1 1	799	798	31
1 0 0	745	745	31
0 2 0	683	684	31
1 0 $\bar{1}$	612	614	31
0 0 2	493	492	35
1 2 1	441	441	27
1 1 $\bar{2}$	404	404	15
2 0 0	372	370	77
0 0 3	328	328	100
2 2 1	306	306	12
2 0 $\bar{2}$	306		
2 0 2	289	290	19
1 4 2	260	259	92
0 0 4	246	247	19
1 5 1	247		
3 1 0	244	244	12
2 1 3	236	235	15
1 1 $\bar{4}$	235		
3 1 2	214	214	15
2 5 1	213		
2 3 3	212	212	23
1 6 1	212		
1 5 $\bar{3}$	204	204	42
3 2 3	185.3	185.4	27
2 3 4	183.1	183.3	19

was used for temperature detection. The samples were heated in an alumina crucible of volume 0.5 cm^3, at a rate of 10 K min^{-1}. The DTA curves were obtained with the help of an instrument fabricated in this laboratory.[7]

Results and Discussion

X-Ray Diffraction Study. The X-ray powder patterns for the present compounds show that the compounds are isomorphous. On analyzing with Ito's method,[9] the double malonates were found to possess a monoclinic symmetry, with two molecules per unit cell. The systematic absence of reflexes ($0k0 : k=2n+1$), suggests that the probable space group is $P2_1/m$ or $P2_1$. The lattice parameters were refined by least squares method. The unit cell dimensions and the other relevant data are given in Table 2. The decrease in unit cell volumes is not regular as is normally expected. The cell dimension "c" decreases from gadolinium to holmium linearly with decrease in ionic radii, but such regular decrease in "a" and "b" is not observed. The complete indexed data of dysprosium double malonate are given in Table 3, as a representative.

Infrared Spectroscopic Studies. The double malonates are isomorphous and hence expectedly their infrared spectra exhibit similar patterns (Fig. 1). The assignments for the various bands are based on the earlier reports.[6,10,11)]

A very strong band at ≈1585 cm^{-1} and a strong one at ≈1380 cm^{-1} have quite easily been assigned to the asymmetric and symmetric stretching vibrations of OCO group, respectively. It can be seen that these frequencies in case of the double malonates have shifted to higher and lower values, respectively, as against the corresponding frequencies in potassium malonate[10] (1563 and 1405 cm^{-1}), suggesting an increase in the covalent nature of Ln–O bond. A band with medium intensity at $\approx 780\ \mathrm{cm}^{-1}$ and the one with a strong intensity at $\approx 710\ \mathrm{cm}^{-1}$, are probably due to OCO deformation vibrations.

The C–H stretching vibrations are observed as two very weak bands in the region 3000—2900 cm^{-1}. Strong bands at ≈ 1440 and $\approx 1260\ \mathrm{cm}^{-1}$ are attributed to CH_2 bending and wagging modes, respectively.

A weak broad absorption is observed in the OH stretching region, probably due to the moisture absorbed by these hygroscopic compounds.

Thermoanalytical Investigation. In order to get the insight of the thermal decomposition mechanism, the double malonates of gadolinium and holmium were subjected to the thermoanalytical investigation as representatives of the series. The corresponding thermal curves are reproduced in Figs. 2 and 3. The thermoanalytical data are given in Table 4.

The anhydrous nature of the double malonates is reflected in non observance of the dehydration stage on the thermal curves; and the decomposition of both the compounds commences at 543 K. The breaks corresponding to the formation of an intermediate of probable composition $K_{10}Ln_2O(CO_3)_3(OCOCHOCO)_4$ are observed on the TG curves at 613 and 623 K for gadolinium and holmium compounds, respectively. Formation of such a type of intermediate has also been reported in the thermal decomposition of lanthanum malonate pentahydrate.[12] It is apparent from the TG and DTG curves of both the double malonates that the decomposition of holmium compound to $K_{10}Ho_2O(CO_3)_3(OCOCHOCO)_4$ is a two stage process, the first one involving formation of $K_{10}Ho_2O(CO_3)_{1.5}(OCOCHOCO)_{5.5}$, whereas the corresponding two stages in case of gadolinium double malonate are probably overlapped. The non observance of the first stage on the TG and DTG curves of gadolinium compound can probably be due to the comparatively larger amount of the sample taken in this case (57.77 mg as against 25.9 mg of holmium double malonate). A very sharp exotherm observed at 578 K on the DTA curve of holmium double malonate can be attributed to the formation of the first stage intermediate, $K_{10}Ho_2O(CO_3)_{1.5}(OCOCHOCO)_{5.5}$. From the analogy with

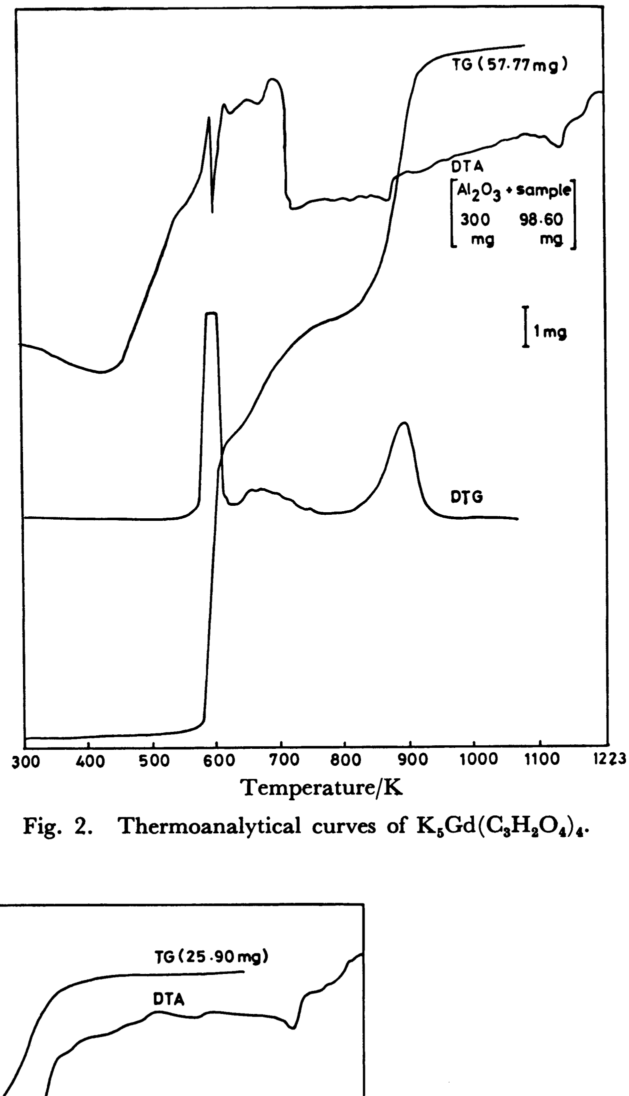

Fig. 2. Thermoanalytical curves of $K_5Gd(C_3H_2O_4)_4$.

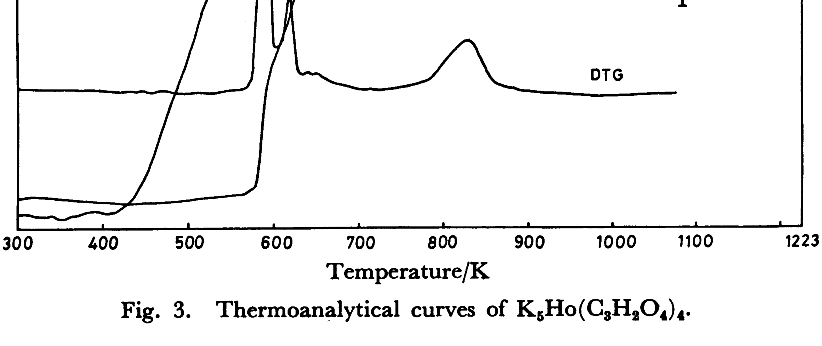

Fig. 3. Thermoanalytical curves of $K_5Ho(C_3H_2O_4)_4$.

Table 4. Thermoanalytical results for $K_5Ln(C_3H_2O_4)_4$

DTA temp/K	TG temp range/K	DTG temp/K	% Loss Calcd	% Loss Obsd	Interpretation
Ln=Gd					
					$2K_5Gd(C_3H_2O_4)_4$
588 (exo) 608 (exo) 648 (exo)	543— 613	588	14.20	13.31	↓ $K_{10}Gd_2O(CO_3)_3(OCOCHOCO)_4$
693	613— 743	663	4.28	5.02	↓ $K_{10}Gd_2O_2(CO_3)_{2.5}(OCOCHOCO)_{3.5}$
873 (endo)	743—1023	883	12.30	12.05	↓ $5K_2CO_3+Gd_2O_3$
1153 (endo)	—	—	—	—	Melting of K_2CO_3
Ln=Ho					
					$2K_5Ho(C_3H_2O_4)_4$
578 (exo)	543— 593	593	10.05	9.92	↓ $K_{10}Ho_2O(CO_3)_{1.5}(OCOCHOCO)_{5.5}$
598—683 (broad, exo)	593— 623	613	4.00	5.10	↓ $K_{10}Ho_2O(CO_3)_3(OCOCHOCO)_4$
	623— 723	643	4.20	4.05	↓ $K_{10}Ho_2O_2(CO_3)_{2.5}(OCOCHOCO)_{3.5}$
	723— 983	823	12.20	12.04	↓ $5K_2CO_3+Ho_2O_3$
1158 (endo)	—	—	—	—	Melting of K_2CO_3

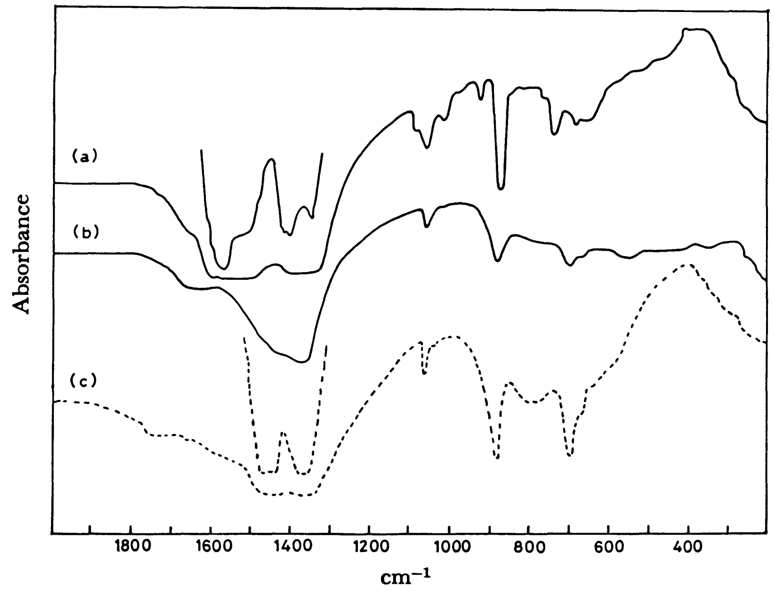

Fig. 4. Infrared absorption spectra of $K_5Ho(C_3H_2O_4)_4$ heated at a) 648 K, b) 723 K, and c) K_2CO_3.

the holmium compound, a similar sharp exotherm at 588 K in case of gadolinium compound can be accounted for the formation of a similar intermediate.

The intermediate $K_{10}Ln_2O(CO_3)_3(OCOCHOCO)_4$, decompose exothermically to give $K_{10}Ln_2O_2(CO_3)_{2.5}(OCOCHOCO)_{3.5}$ in the temperature range 613—743 and 623—723 K, in case of gadolinium and holmium compounds, which in turn decompose to give mixture of respective rare earth oxide and potassium carbonate, at temperatures 1023 and 983 K, respectively. The endothermic effect observed at 873 K on the DTA curve of gadolinium compound is probably due to the final decomposition; however, the corresponding effect in case of holmium double malonate is not easily discernible. The endothermic activities observed at about 1153 K in case of both the compounds are probably due to the melting of potassium carbonate formed (mp of K_2CO_3 is 1174 K[13]).

The following mechanism can thus be proposed for the decomposition of the double malonates:

$$2K_5Ln(C_3H_2O_4)_4 \longrightarrow$$
$$K_{10}Ln_2O(CO_3)_{1.5}(OCOCHOCO)_{5.5} \longrightarrow$$
$$K_{10}Ln_2O(CO_3)_3(OCOCHOCO)_4 \longrightarrow$$
$$K_{10}Ln_2O_2(CO_3)_{2.5}(OCOCHOCO)_{3.5} \longrightarrow$$
$$5K_2CO_3 + Ln_2O_3$$

The holmium double malonate heated isothermally at 550 K (21 % loss), on qualitative analysis indicated the presence of carbonate. The infrared spectra of the intermediate (Fig. 4a) exhibits no bands ascribable to CH_2 wagging mode, indicating the absence of malonate group. A very weak band, however, is detected at $\approx 3000\,\mathrm{cm}^{-1}$, suggesting the presence of CH group. These observations support the assumption that the (OCOCHOCO) group is present in the intermediate. The intermediate obtained was contaminated with free carbon which might have formed due to the disproportionation of liberated CO, as has been suggested earlier in the study of lanthanum oxalate.[14]

The spectrum of the final decomposition product exhibits the bands characteristic of potassium carbonate and holmium sesquioxide (Fig. 4b).

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