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THERMAL SOLID-SOLID PHASE TRANSITION OF SOME METAL OXALATO COMPLEXES

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Data were presented to show that anhydrous potassium trioxalatoaluminate(III),potassium trioxalatovanadate(III) and potassium trioxalatochromate(III) exhibit thermally solid-state transition to hexagonal without any decomposition. The values of enthalpy change were 0.9 and 1.3 kcal/mol for $K_3[Al(ox)_3]$ and $K_3[Cr(ox)_3]$, respectively.

Three complexes which cause the solid-state transition of their anhydrous phases, were found. The data of the transition obtained(temperature, enthalpy change, crystal structure) may give a valuable information on the study of thermal decomposition of metal complexes, since their decomposition accompanied a transition of a solid-phase.

The DTA curves which are shown in Fig. 1, were obtained at a heating rate of 5°C/min in vacuum. About 100-milligram sample in a quartz crucible was used for each measurement. For three complexes investigated, the first endothermic peak is due to dehydration. The second exothermic peaks which appear with a peak maximum at 252 and 270°C for $K_3[Al(ox)_3]3H_2O$ and $K_3[Cr(ox)_3]3H_2O$ respectively, have not been described in a literature. The corresponding peak is not seen on the curve of

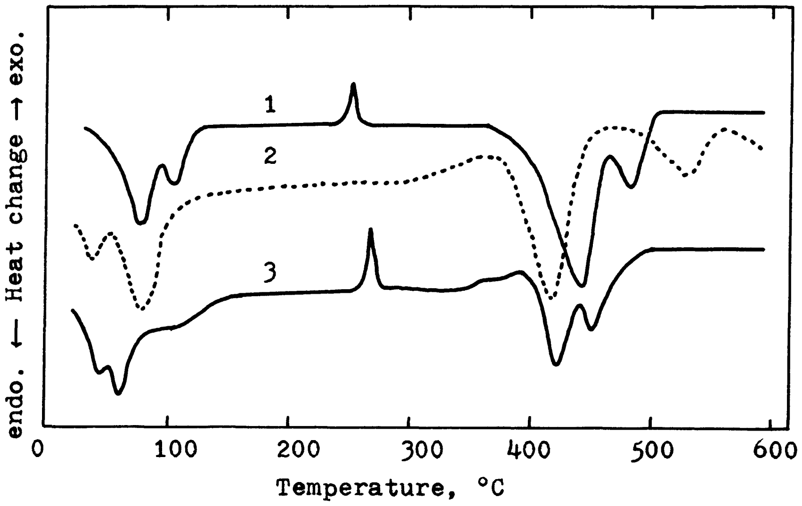

Fig. 1 DTA curves of (1) $K_3[Al(ox)_3]3H_2O$, (2) $K_3[V(ox)_3]3H_2O$ and (3) $K_3[Cr(ox)_3]3H_2O$.

$K_3[V(ox)_3]3H_2O$.

In order to investigate the nature of the exothermic peak, infrared and reflectance spectra and X-ray diffraction patterns were recorded. The infrared and reflectance spectra of the products obtained by heating $K_3[Al(ox)_3]3H_2O$ and $K_3[Cr(ox)_3]3H_2O$ up to 280°C in vacuum are almost near to those of the complexes before heating. This indicates that the decomposition of the anhydrous complexes did not occur in the exothermal passage. On the other hand, the X-ray diffraction patterns obtained at various temperatures are different as shown in Fig. 2. A comparison of the products from the thermal treatment of the anhydrous complex before and after the exothermal passage, shows that two types of the solid-state transition exist, i.e., one is the transition of crystalline state to other crystalline state, and the other is that of amorphous state to crystalline state. The structures of

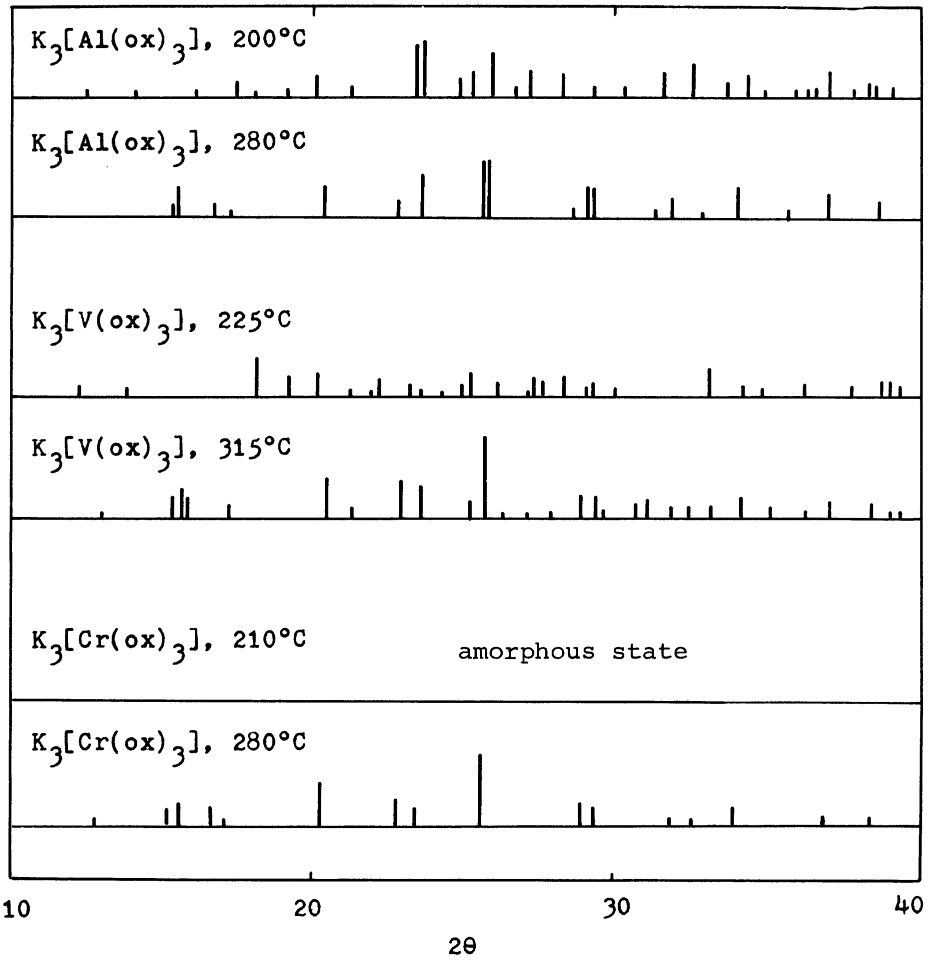

Fig. 2 X-ray diffraction patterns of the anhydrous complexes. (CuKα)

anhydrous aluminium and vanadium complexes before the transition are not yet clear, since their patterns are complicated. Although the exothermic peak is not seen on the curve of $K_3[V(ox)_3]3H_2O$, the phase transition is observed by heating the complex up to 315°C as shown in Fig. 2.

The analyses of the X-ray diffraction patterns indicates that the crystal structure after the transition is hexagonal for all of the complexes investigated. The result for $K_3[Cr(ox)_3]$ is shown in Table 1 as an example. The lattice constants of $K_3[Cr(ox)_3]$ were a=18.2 and c=11.8 Å which are almost the same for the other two complexes.

Table 1 Assingnment of X-ray diffraction lines of $K_3[Cr(ox)_3]$ heated at 280°C (after the exothermal passage). CuKα

2θ	I	$\sin^2\theta$	hk·l	$\sin^2\theta$ (calcd.)
9.1	w	0.0063	11·0, 01·1	0.0069, 0.0066
12.8	w	0.0124	20·1	0.0135
15.2	m	0.0175	10·2	0.0195
15.6	m	0.0184	12·1	0.0204
16.5	m	0.0206	30·0	0.0207
17.1	w	0.0221	02·2	0.0264
20.3	s	0.0311	22·0	0.0276
22.6	m	0.0391	00·3	0.0387
23.4	m	0.0411	04·1	0.0411
25.6	vs	0.0491	23·1, 14·0	0.0480, 0.0483
28.9	m	0.0623	33·0	0.0621
29.3	m	0.0640	22·3	0.0653
31.8	w	0.0751	05·2	0.0747
32.5	w	0.0783	15·1	0.0756
33.9	m	0.0850	12·4	0.0849
36.8	w	0.0996	61·1	0.1032
38.3	w	0.1076	04·4	0.1056

The enthalpy change of the transition was estimated from a comparison between the peak area of the transition and that of the dehydration of which value has been measured by a differential scanning calorimetry.(1) The values obtained were 0.9 and

1.3 kcal/mol for $K_3[Al(ox)_3]$ and $K_3[Cr(ox)_3]$, respectively.

Reference:

1) K. Nagase, Bull. Chem. Soc. Japan, in press.

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