Journal of Thermal Analysis, Vol. 49 (1997) 1221-1226

THERMAL DEHYDRATIONS
Calcium copper acetate hexahydrate and calcium cadmium acetate hexahydrate

Y. Masuda[1], K. Minagawa*, W. Morita*, Z. Zhong[2]** and P. K. Gallagher***

*Niigata University, Faculty of Science, Department of Environmental Science,
8050 Ikarashi-2, Niigata 950-21, Japan
**The Ohio State University, Department of Chemistry and Material Science & Engineering,
Columbus, OH 43210-1173, USA

Abstract

The behaviour of thermal dehydrations of isomorphous complexes of calcium copper acetate hexahydrate, $CaCu(CH_3CO_2)_4 \cdot 6H_2O$ and calcium cadmium acetate hexahydrate, $CaCd(CH_3CO_2)_4 \cdot 6H_2O$ was studied by means of thermal analyses and X-ray structural analysis. The enthalpy changes for the dehydration of $CaCu(CH_3CO_2)_4 \cdot 6H_2O$ and $CaCd(CH_3CO_2)_4 \cdot 6H_2O$ were 315±9.7 and 295±8.0 kJ mol^{-1}, respectively. The DSC curves of the dehydrations indicated that the seemingly simple dehydrations are more complex than they appear at first sight. Apparent activation energies for the dehydrations of $CaCu(CH_3CO_2)_4 \cdot 6H_2O$ and $CaCd(CH_3CO_2)_4 \cdot 6H_2O$ were 85.7±7.4 and 87.9±12.5 kJ mol^{-1}, respectively.

Keywords: calcium cadmium acetate hexahydrate, calcium copper acetate hexahydrate, complexes, thermal analysis, thermal dehydration

Introduction

Calcium copper acetate hexahydrate, $CaCu(CH_3CO_2)_4 \cdot 6H_2O$ and calcium cadmium acetate hexahydrate, $CaCd(CH_3CO_2)_4 \cdot 6H_2O$ are known to adopt a similar tetragonal crystal structure with space group I4/m. These hydrates consist of polymeric chains of bidentate acetate ion bridged calcium and copper or cadmium atoms. The chains aligned along the c-axis are bound together by solvent cages of twelve water molecules. The water molecules coordinate only to the Ca^{2+} ions and their role in the structures are to fill the voids in the lattice and to bind the polymeric chains together. Each water molecule coordinated to Ca^{2+} ion is hydrogen-bonded to the remaining water molecules to form the cage cluster of twelve water molecules [1, 2].

---

[1] Author to whom all correspondence should be addressed.

[2] Present adress: Zincair Powercorporation, 4440 Warrensville Center Road Suite N, Cleveland, OH 44128-2837, USA.

0368–4466/97/ $ 5.00

John Wiley & Sons Limited
Chichester

It is interesting to study the behaviour of the water molecules held in the crystal structures during the thermal dehydration. In the present paper, the thermal dehydrations of these hydrates were studied by means of TG–DTA, DSC and X-ray diffraction analysis. In addition, the kinetics of the thermal dehydrations of these hydrates were studied on the basis of thermogravimetry.

Experimental

Crystals of calcium acetate hexahydrate, $CaCu(CH_3CO_2)_4{\cdot}6H_2O$ and calcium cadmium acetate hexahydrate, $CaCd(CH_3CO_2)_4{\cdot}6H_2O$ were prepared from the solutions of calcium acetate and copper acetate, and those of calcium acetate and cadmium acetate, respectively. These hydrates were identified by means of FT-IR, TG and their powder X-ray diffraction profiles.

The crystals were pulverized with a mortar and pestle and sieved to a narrow fractions of 100–150 mesh sizes. The dehydrations were followed by means of a Rigaku Thermoflex TAS-200 at heating rates from 2 to 20 K min^{-1}. About 5 mg of sample was weighed in an aluminum crucible, and measured by use of α-Al_2O_3 as a reference material. Each measurement was carried out in a flowing atmosphere of nitrogen (flow rate 90 cm^3 min^{-1}). The enthalpy change for the dehydration, ΔH was measured by means of a Rigaku Thermoflex TAS-200 DSC. About 3 mg of sample was used for the measurements. The DSC instrument was calibrated with the heat of transition of potassium nitrate (400.9 K, ΔH=5.4 kJ mol^{-1}) and the heats of fusion of gallium, indium, tin, lead and zinc (Ga: 309.94 K, ΔH= 5.59 kJ mol^{-1}; In: 430 K, ΔH=3.3 kJ mol^{-1}; Sn: 505 K, ΔH=7.07 kJ mol^{-1}; Pb: 600.6 K, ΔH=4.77 kJ mol^{-1}; and Zn: 692.7 K, ΔH=6.57 kJ mol^{-1}) [3].

IR spectrum was measured from 400 to 4400 cm^{-1} by means of a diffuse reflectance method with a Horiba FT-300 spectrophotometer. The crystal structure of $CaCd(CH_3CO_2)_4{\cdot}6H_2O$ was analyzed by means of an automated single crystal diffractometer, Rigaku AFC-7S. The X-ray powder diffraction profiles were obtained with a Rigaku Geigerflex RAD 3R diffractometer equipped with a standard high temperature sample holder, and MoK_α a radiation and a graphite monochrometer were used for all measurements. The diffraction data were collected at 0.02° intervals.

Results and discussion

Figure 1 shows the TG-DTA curves of both the hydrates. The smooth TG-DTA curves and agreement between the calculated and observed mass loss values ($CaCu(CH_3CO_2)_4{\cdot}6H_2O$: calculated: 24.1%, observed: 24.0% and $CaCd(CH_3CO_2)_4{\cdot}6H_2O$: calcd.; 21.8%, obsd. ; 21.3%) suggest that the dehydrations proceed successively without any intermediate hydrate. The dehydration temperature ranges of $CaCd(CH_3CO_2)_4{\cdot}6H_2O$ were shifted to lower side than those of $CaCu(CH_3CO_2)_4{\cdot}6H_2O$, and the enthalpy changes, ΔH for the dehydrations of $CaCu(CH_3CO_2)_4{\cdot}6H_2O$ and $CaCd(CH_3CO_2)_4{\cdot}6H_2O$ were 315±9.7 and 295±8.0 kJ mol^{-1}, respectively. These facts indicated that the water molecules in the crystal of $CaCu(CH_3CO_2)_4{\cdot}6H_2O$ were slightly more stable than those of $CaCd(CH_3CO_2)_4{\cdot}6H_2O$.

The stability of the hydrates would be ascribable to the crystal structure. Although both the hydrates have a similar crystal structure (Fig. 2), from the consideration of the bond angle of the adjacent hydrogen atoms with oxygen, the strain of

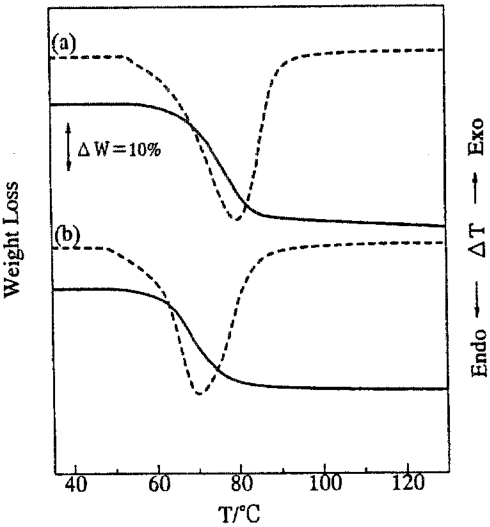

Fig. 1 The TG (solid line) and DTA (dotted line) curves of $CaCu(CH_3CO_2)_4 \cdot 6H_2O$ (a); and $CaCd(CH_3CO_2)_4 \cdot 6H_2O$ (b)

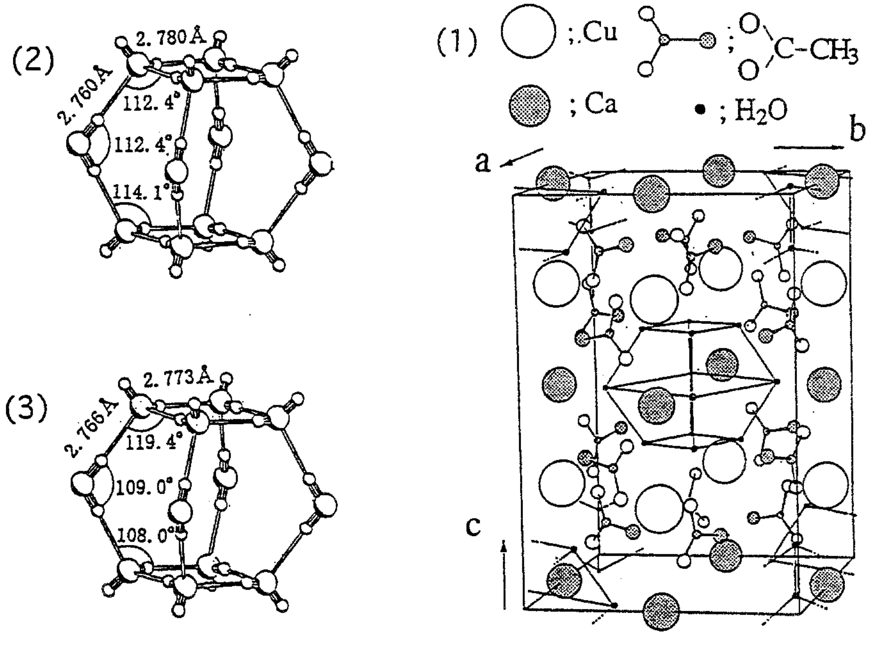

Fig. 2 Crystal structure. 1) The Crystal structure of $CaM(CH_3CO_2)_4 \cdot 6H_2O$, *M* is Cu or Cd, 2) Cage cluster of $CaCu(CH_3CO_2)_4 \cdot 6H_2O$, 3) Cage cluster of $CaCd(CH_3CO_2)_4 \cdot 6H_2O$

the cage cluster formed by the twelve water molecules of $CaCd(CH_3CO_2)_4{\cdot}6H_2O$ seems to be larger than that of $CaCu(CH_3CO_2)_4{\cdot}6H_2O$.

The smoothness of the TG-DTA curves (Fig. 1) for both the hydrates indicated that the dehydration seemed to take place as a one step reaction. Derivative thermogravimetric (DTG) curves for the dehydrations of $CaCu(CH_3CO_2)_4{\cdot}6H_2O$ were smooth, but two overlapping peaks appeared on the curves for $CaCd(CH_3CO_2)_4{\cdot}6H_2O$ with increase of the heating rate (Fig. 3). These facts indicated that the seemingly simple dehydrations are more complex than they appeared at first sight.

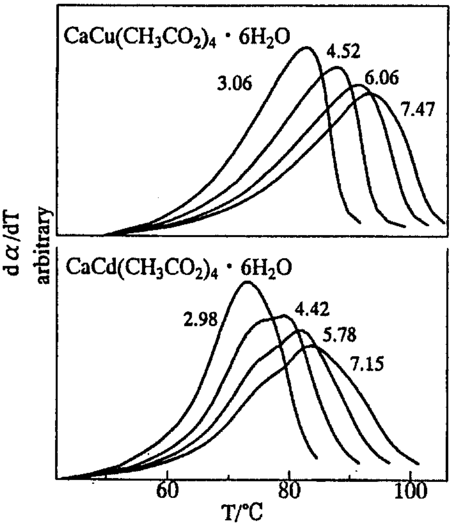

Fig. 3 The DTG curves for the dehydrations of $CaCu(CH_3CO_2)_4{\cdot}6H_2O$ and $CaCd(CH_3CO_2)_4{\cdot}6H_2O$; Figures mean heating rates (K min^{-1})

Table 1 Apparent activation energies for the dehydration of $CaCu(CH_3CO_2)_4{\cdot}6H_2O$ and $CaCd(CH_3CO_2)_4{\cdot}6H_2O$

α	E/kJ mol^{-1}	
	$CaCu(CH_3CO_2)_4{\cdot}6H_2O$	$CaCd(CH_3CO_2)_4{\cdot}6H_2O$
0.2	102.5	113.5
0.3	93.8	103.3
0.4	88.4	92.7
0.5	83.9	84.9
0.6	80.8	79.8
0.7	78.3	75.2
0.8	75.3	69.9

Apparent activation energies, E for both the dehydrations were obtained by use of the Ozawa method [4, 5]. The complicating future of the dehydration mechanism

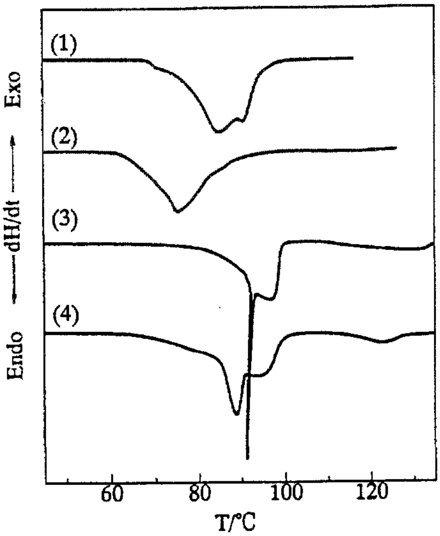

Fig. 4 The DSC curves for the dehydrations of, 1) $CaCu(CH_3CO_2)_4 \cdot 6H_2O$ – using an open cell; 2) $CaCd(CH_3CO_2)_4 \cdot 6H_2O$ – using an open cell; 3) $CaCu(CH_3CO_2)_4 \cdot 6H_2O$ – using a pin hole cell; 4) $CaCd(CH_3CO_2)_4 \cdot 6H_2O$ – using a pin hole cell

seemed to be reflected in the fact that the activation energies, E, obtained for both the dehydrations tended to decrease with increase in the dehydration fraction (Table 1). The average values of E for the dehydrations of $CaCu(CH_3CO_2)_4 \cdot 6H_2O$ and $CaCd(CH_3CO_2)_4 \cdot 6H_2O$, were 85.7±7.4 and 87.9±12.5 kJ mol^{-1}, respectively. The former was comparable to that, 81.3 kJ mol^{-1}, obtained for the dehydration of $CaCu(CH_3CO_2)_4 \cdot 6H_2O$ by means of the isothermal method [6].

The DSC curves obtained on heating rate of 2 K min^{-1} (Fig. 4), which are not as simple as those of the DTA curves (Fig. 1), indicate the complicating feature of the dehydration. The DSC curves obtained by use of a shield pan with an aluminum plate bored a hole of about 100 μm diameter are also shown in Fig. 4. Although the overlapping peaks were not resolved to the respective peak, the dehydration processes of both the hydrates seemed to be made up at least by three stages. These stages must correspond to the respective dissociation events of the water molecules under different bonding conditions in the crystal. But further details of these events have not been clarified at present.

* * *

The authors wish to express their thanks to Associate Professor Yasuhiko Yukawa of the Niigata University for the analysis of the X-ray-intensity data.

References

1 D. W. Lango and C. Hare, Chem. Commun., (1967) 890.
2 E. A. Klop, A. J. M. Duisenberg and A. L. Spek, Acta Crystallogr. Sect.C, (1983) 1342.

3 The Chemical Society of Japan (Ed.), Kagaku Binran Kisohen II (Handbook of Chemistry), 4rd, Maruzen, Tokyo 1993, pp. 243–248.
4 T. Ozawa, Bull. Chem. Soc. Jpn., 38 (1965) 1881.
5 T. Ozawa, J. Thermal Anal., 2 (1970) 301.
6 Y. Masuda, S. Shirotori, K. Minagawa, P. K. Gallager and Z. Zhong, Thermochim. Acta, 282/283 (1996) 43.