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PHASE TRANSITION OF LEAD(II) SUCCINATE

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Lead(II) succinate exhibited a phase transition from tetragonal to cubic at 160°C, with ΔH = 0.6 kcal/mol and ΔS = 1.4 cal/mol deg. The phase transition was reversible and characterized by accompanying a great change in infrared absorption spectrum.

In the course of the study on the thermal behavior of a number of metal succinates in solid state, heat changes without any weight-loss were observed on the DSC curves of magnesium(II), cobalt(II) and lead(II) succinates. Although the peaks of the magnesium and cobalt salts corresponded merely to the phase transition from amorphous state to crystalline state, the nature of the peak of the lead salt was complicated. The dicarboxylates such as oxalate and malonate form stable five- or six-membered chelate rings with metals, but succinate chelates of metals are not so stable owing to the seven-membered rings. In the case of metal succinates, therefore, a change in bonding structure can be expected to occur even at mild condition. In order to investigate the nature of the heat change of lead succinate, X-ray diffraction analyses and infrared absorption spectroscopies for the samples before and after the heat change will be demonstrated.

The samples were prepared by the reactions of the corresponding metal carbonates with a succinic acid. The results of the elemental analyses for C and H agreed with the calculated values within ± 0.3%. The TG-DSC curves were obtained with a Rigaku Denki 8002 CS at a heating rate of 3°C/min in a flowing nitrogen atmosphere. About twenty milligrams of powdered sample in an aluminum crucible with a lid of the same material were used in each measurement. The instrument was calibrated against the transition of KNO_3 which appears at 128°C with ΔH of 12.28 kcal/mol. X-ray diffractions and those at high temperature were measured with a Toshiba diffractometer ADG-101 and that equipped with a standard high temperature sample holder, respectively.

Infrared absorption spectra were measured in the region of 2500-250 cm^{-1} by the KBr disk method with a Hitachi 215 spectrophotometer. The spectra at high temperature were measured with the apparatus equipped with a standard high temperature sample holder.

The TG-DSC curves of lead(II) succinate are given in Fig. 1. The decomposition did not take place up to 300°C, but an endotherm was observed at 160°C. An exotherm was also reflected on the cooling curve and so the heat change is reversible. ΔH and ΔS for the endothermic passage were 0.6 kcal/mol and 1.4 cal/mol·deg, respectively.

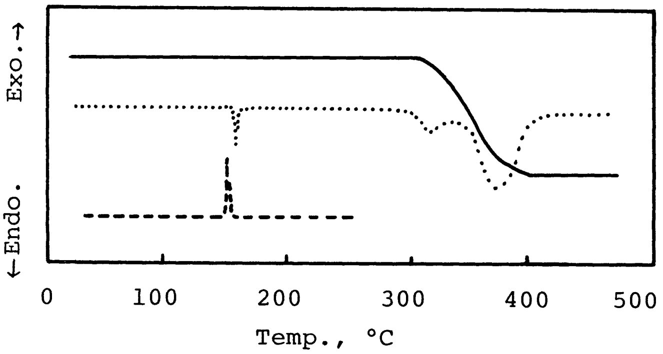


Fig. 1 TG-DSC curves of lead(II) succinate in a nitrogen atmosphere: ——; TG curve, ……; heating curve of DSC and ----; cooling curve of DSC.

The X-ray diffraction lines of lead(II) succinate whose assignments are given in Table 1, indicated the transition from tetragonal to cubic through the endothermic passage. It is characteristic of the structural change from cubic

Table 1 X-ray diffraction lines of $PbC_4H_4O_4$ and their assignments. CuKα radiation with a nickel filter was used.

	d/Å	I*	$\sin^2\theta$	hkl	$\sin^2\theta$(calcd.)
at room temp.	6.32	m	0.0149	211	0.0157
	5.98	m	0.0166	112	0.0164
	3.78	vs	0.0415	400	0.0413
	3.69	s	0.0436	410	0.0439
at 200°C	6.19	s	0.0155	211	0.0155
	3.78	vs	0.0415	400	0.0413
	3.69	s	0.0436	410	0.0439
	3.35	w	0.0529	420	0.0516

* Intensities are graded by vs(very strong), s(strong), m(medium) and w(weak).

to tetragonal that the lines of (40·0) and (41·0) are not shifted and the line of (211) splits into (211) and (112). The lattice constants calculated were a = b = c = 15.2 Å for cubic, and a = b = 15.2 and c = 14.6 Å for tetragonal.

In Fig. 2, the infrared absorption spectra of $PbC_4H_4O_4$ obtained at room temperature[A] and at 200°C[B] are given, with the spectrum of $CuC_4H_4O_4$ which was obtained by heating $CuC_4H_4O_4 \cdot 2H_2O$ at 120°C. The spectrum of $CuC_4H_4O_4$ was almost identical to that of $CuC_4H_4O_4 \cdot 2H_2O$. There is a great difference between [A] and [B], indicating that the phase transition from tetragonal to cubic is attended by a change in bonding structure. Upon cooling to room temperature, the spectrum returns to its original one. Therefore, the spectral change is reversible.

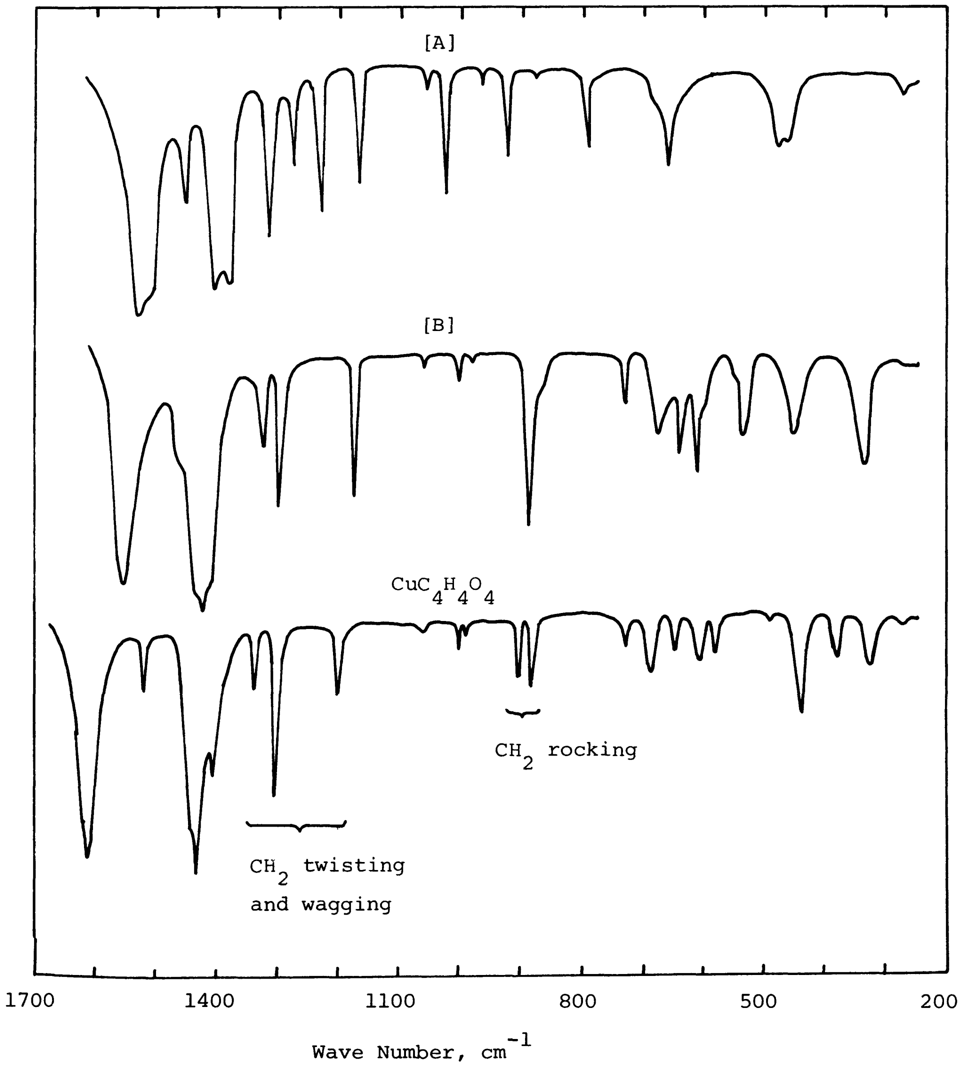
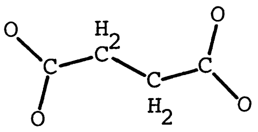


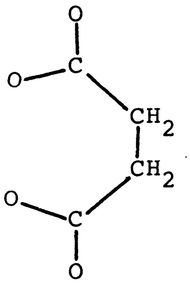
Fig. 2 Infrared absorption spectra of $PbC_4H_4O_4$ at room temperature[A], $PbC_4H_4O_4$ heated up to 200°C[B] and $CuC_4H_4O_4$. All measurements were carried out by the KBr disk method.

In order to obtain information on bonding structure, infrared spectra of other metal succinates were measured. The spectra of $CoC_4H_4O_4 \cdot 4H_2O$ and $NiC_4H_4O_4 \cdot 4H_2O$ were very similar to [A], while that of $CuC_4H_4O_4$ was very similar to [B] as shown in Fig. 2. No investigation is available on the bonding structures of the former complexes, but the structure of the copper salt has been investigated by the measurements of magnetic moment and infrared spectrum.1,2) The spectrum reported2) is identical with that in Fig. 2 over the frequency region of 2000-700 cm^{-1}. According to the previous paper1), the structure of succinate ion in the copper salt is shown by [I], but the methylene chain is, to some extent, distorted owing to the formation of σ bonds, compared with the methylene chain in the sodium salt. Since [B] is very similar to the spectrum of the copper salt, the structure of succinate ion in the lead salt above 160°C may be similar to [I].

[A] is more complicated than [B] in the frequency region of methylene group, indicating that some of the vibrational modes forbidden in [B] are allowed. A possible structure for the lead salt below 160°C is shown by [II], which can be converted to [I] by turning the chain at the CH_2-CH_2 bond.



[I]



[II]

References

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2) Y. Kuroda and M. Kubo, J. Phys. Chem., 64, 759 (1960).

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