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The Structures and Thermal Behaviors of Bivalent Metal Succinates in the Solid State

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The relations between the structures and thermal behaviors of the succinates of Mg(II), Co(II), Ni(II), Cu(II), Zn(II), Cd(II), and Pb(II) were studied. In the case of the copper salt, the dehydration of its dihydrate began easily at room temperature. However, the tetrahydrates of Mg, Co, and Ni held their waters more tightly, and changed from crystalline to amorphous state in the course of dehydration which began at 50—60 °C. The anhydrous salts of Mg and Co recrystallized at 306 and 272 °C, respectively, with a sharp exotherm on each DTA curve. The cobalt salt showed stepwise color changes, pink $\xrightarrow{\text{dehydration}}$ bluish violet $\xrightarrow{\text{recrystallization}}$ pink. $PbC_4H_4O_4$ exhibited a phase transition from tetragonal to cubic at 160 °C with $\Delta H = 2.5$ kJ/mol and $\Delta S = 5.9$ J/deg·mol. The phase transition was reversible and seems to be accompanied with a conformational change of the succinate ion.

The structures of the copper salts of α,ω-dicarboxylic acids, $HOOC(CH_2)_{n-2}COOH$ with $n=2-10$ have been investigated by means of magnetic[1] and infrared measurements,[2] and it was found that, when n is even, the carbon chain assumes the *trans* conformation.[2] The structures of α,ω-dicarboxylates of other metals, on the other hand, have been determined in the case of the oxalates of Mg(II), Mn(II), Fe(II), Co(II) and Ni(II) by X-ray analyses, and it was found that two water molecules contained in the salts coordinate to the metals and the oxalate ion acts as a quadridentate ligand.[3]

This work was undertaken to obtain detailed information on the compositions and structures of the various bivalent metal succinates by means of infrared and diffuse reflectance spectroscopies and thermal analysis.

In the course of the TG-DTA measurements, heat changes without any weight-loss were found for magnesium, cobalt and lead succinates. It was considered to be worthwhile to investigate the nature of the heat changes, since a conformational change of succinate ion or a change of coordination structure is expected to occur.

Experimental

Materials. The metal succinates were prepared by the reaction of the corresponding metal carbonates with succinic acid. The results of the elemental analyses for C and H agreed with those calculated within ±0.3% (Table 1).

Apparatus and Procedure. Infrared absorption spectra were measured from 4000 to 250 cm^{-1} by KBr disk method with a Hitachi 215 spectrophotometer. The spectra at elevated temperatures were recorded with the apparatus equipped with a standard heating cell. Diffuse reflectance spectra were measured with a Hitachi EPS-3T spectrophotometer using a standard integrating sphere attachment; in the case of heated samples, they were cooled to room temperature and brought to measurements.

Powder X-ray diffraction diagrams at room temperature and those at elevated temperatures were obtained with a Toshiba diffractometer ADG-101 equipped with a standard high temperature sample holder. Fe Kα radiation and a manganese filter were used for cobalt salts, and Cu Kα radiation and a nickel filter for all other salts.

Thermogravimetric (TG) and differential thermal analytical (DTA) curves were obtained with a Shinku Riko TGD-3000 apparatus at a heating rate of 10 °C/min in an atmosphere of nitrogen flowing at 50 ml/min. About twenty milligrams of powdered sample in a platinum crucible were used in each measurement. Calorimetric measurements were carried out with a Rigaku Denki 8002 CS differential scanning calorimeter at a heating rate of 5 °C/min in an atmosphere of nitrogen flowing at 40 ml/min. The apparatus was calibrated against the transition heat of KNO_3.

Results and Discussion

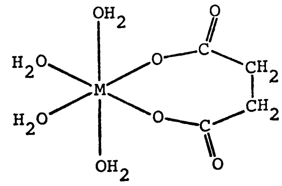
In general, water molecules in inorganic salts gives symmetric and antisymmetric O–H stretching bands at 3500—3000 cm,$^{-1}$ and it is well known that ν(O–H) of crystal water appears at a higher frequency than that of coordinated water. The values of ν(O–H) of the hydrated succinates of Mg, Co, Ni and Cu are given in Table 1. The value of the copper salt is considerably higher (by *ca.* 300 cm^{-1}) than those of the other salts which are similar with each other. This result seems to suggest that the water in the copper salt is crystal water (or very weakly coordinated water), while that in the other salts is commonly coordinated water.

TABLE 1. STRETCHING FREQUENCIES OF WATER (ν(O–H)), INITIAL DEHYDRATION TEMPERATURES (T_{H_2O}) AND WEIGHT-LOSSES (ΔW) FOR VARIOUS METAL SUCCINATES

Formulas	ν(O–H)/ cm^{-1}	T_{H_2O}/ °C	ΔW_{obsd}/ %	ΔW_{calcd}/ %
$MgC_4H_4O_4\cdot4H_2O$	3100	62	31.2	33.9
$CoC_4H_4O_4\cdot4H_2O$	3075	53	27.8	29.2
$NiC_4H_4O_4\cdot4H_2O$	3050	61	28.8	29.2
$CuC_4H_4O_4\cdot2H_2O$	3370	25	14.8	16.7
$ZnC_4H_4O_4$	—	—	—	—
$CdC_4H_4O_4$	—	—	—	—
$PdC_4H_4O_4$	—	—	—	—

Dehydration temperature gives information about the dissociation energy of the metal-coordinated water bonding. Assuming an electrostatic model, it is expected that the bond energy increases with the increase of $1/r$, where r means ionic radius of metal. The initial dehydration temperatures (T_{H_2O}) of the hydrated succinates are also given in Table 1, together with the corresponding weight-loss. For the salts of Mg, Co and Ni, the change of T_{H_2O} with $1/r$ is reasonable, but T_{H_2O} of the copper salt is too much lower than the value expected from the ionic radius of copper. Thus, the thermal data also support the view obtained from the IR study.

In the frequency region of 4000—250 cm^{-1}, the infrared absorption patterns of the salts of Mg, Co and Ni were very similar with each other, suggesting that the bonding structures of these salts are identical. The diffuse reflectance spectra of the cobalt and nickel salts indicated that the metals are surrounded octahedrally by six oxygen atoms. Since all of four water molecules contained were found to be the same kind of coordinated water, the structure represented by [**A**] seems to be most probable for these salts, although other possibilities can not be ruled out. According to Kuroda and Kubo,[2) the succinate ion in the copper salt assumes the zigzag chain form resulting from the *trans* conformation about the $-CH_2-CH_2-$ bond. It is expected that the succinate ion forming the chelate ring in [**A**] will give more complicated spectral pattern in the frequency region of methylene group than that of the *trans* conformation. The comparison of the spectral pattern of the cobalt salt (Curve 1 in Fig. 2) with that of the copper salt (Curve 3 in Fig. 6) seems to support this expectation. The spectral pattern of succinic anhydride in the frequency region of methylene group was also found to resemble that of the cobalt salt.



[**A**]

Except for the copper salt, the anhydrous salts obtained by heating the corresponding hydrates at 170 °C, gave no X-ray diffraction lines, and their infrared absorption bands were broad, compared with those of their hydrates. In the case of the copper salt, on the other hand, the X-ray diffraction and infrared absorption patterns remain almost unchanged by dehydration. This difference is probably due to the fact that, in the former case, the removal of coordinated water will alter not only the crystal lattice but also the coordination structure. In fact, striking color changes, pink→bluish violet for the cobalt salt and bluish green→yellow for the nickel salt, were observed in the course of the dehydration.

The anhydrous salts of Mg and Co gave a sharp exotherm at 306 and 272 °C, respectively, on the DTA curves which are shown in Fig. 1, together with the TG curves. The X-ray diffraction, infrared absorption and diffuse reflectance data of the cobalt salts before and after the exothermic process are shown in Figs. 2, 3 and 4, respectively, together with those of its hydrate. The X-ray results indicate that the anhydrous salt is

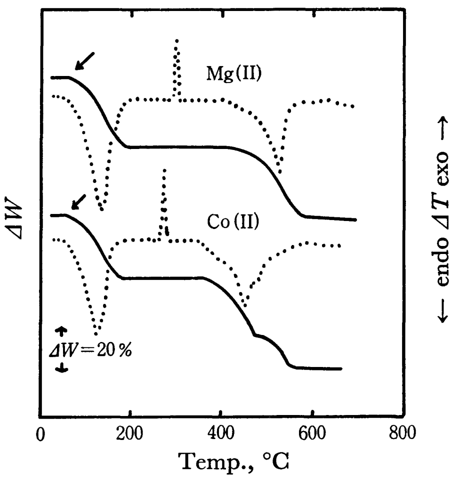


Fig. 1. TG-DTA curves of $MgC_4H_4O_4 \cdot 4H_2O$ and $CoC_4H_4O_4 \cdot 4H_2O$ in a flowing nitrogen atmosphere:
—— indicates TG; ······ DTA.
Points corresponding to T_{H_2O} are indicated with arrows.

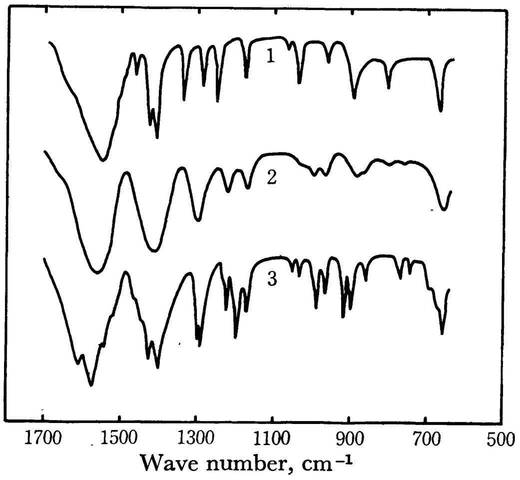


Fig. 2. Infrared absorption spectra of cobalt salts:
(1) $CoC_4H_4O_4 \cdot 4H_2O$, (2) and (3) $CoC_4H_4O_4$ heated up to 170 and 300 °C, respectively.

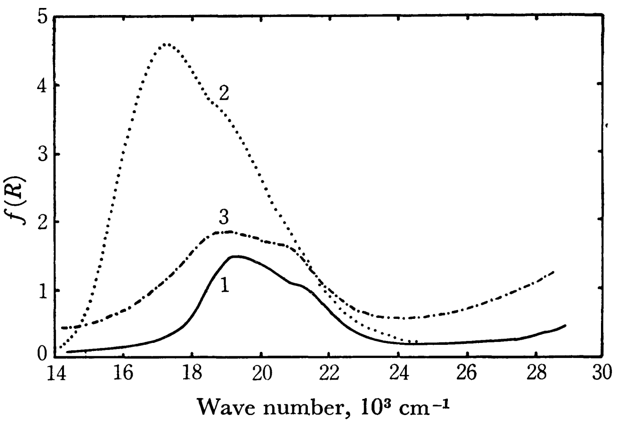


Fig. 3. Reflectance spectra of cobalt salts:
(1) $CoC_4H_4O_4 \cdot 4H_2O$, (2) and (3) $CoC_4H_4O_4$ heated up to 170 and 300 °C, respectively.

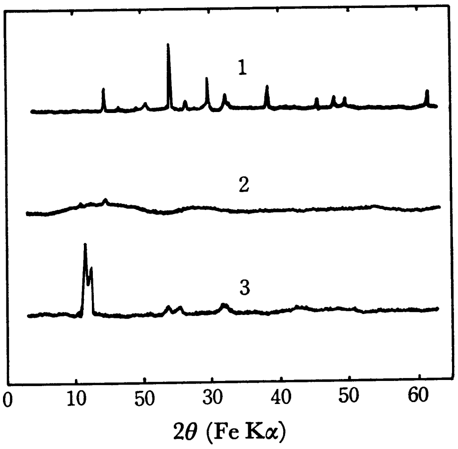


Fig. 4. X-ray diffraction patterns of cobalt salts: (1) $CoC_4H_4O_4 \cdot 4H_2O$, (2) and (3) $CoC_4H_4O_4$ heated up to 170 and 300 °C, respectively.

converted from amorphous to crystalline state through the exothermic process.[4] The infrared absorption bands become thereby remarkably sharper, showing that the crystallized salt has a rigid bonding structure. Along with these changes, the salt becomes pink again, and its reflectance spectrum shows that it has an essentially octahedral coordination structure, just as in the case of the hydrate, so that the formation of weak Co–O bonds between the coordinated oxygen atoms and adjacent Co ions must be postulated. Except for the absence of color change, the magnesium salt gave data which are similar to those of the cobalt salt. Therefore, the nature of the exotherm of the magnesium salt seems to be identical with that of the cobalt salt. By the DSC measurements, the enthalpy changes corresponding to the exothermic processes were obtained: $\Delta H = -10.0$ kJ/mol (cobalt) and -10.9 kJ/mol (magnesium). The entropy changes calculated were -18.3 J/deg·mol (cobalt) and -18.8 J/deg·mol (magnesium), respectively.

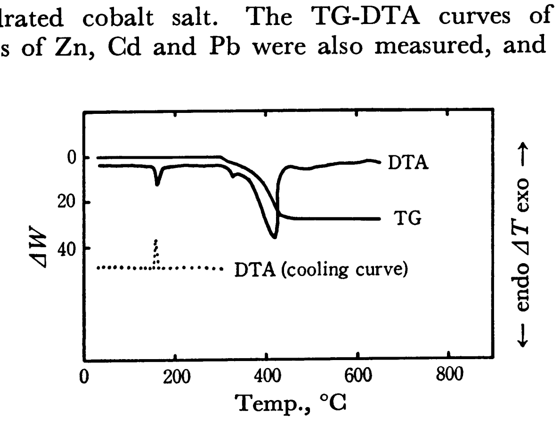


Fig. 5. TG-DTA curves of $PbC_4H_4O_4$: ······indicates cooling curve.

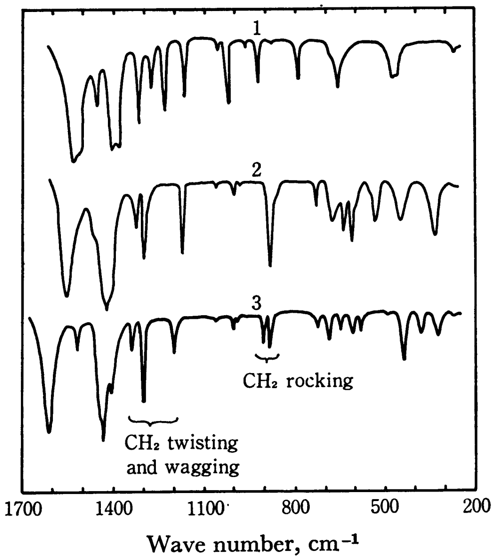
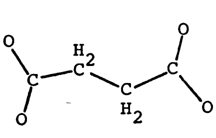


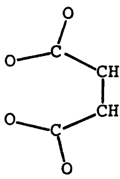
Fig. 6. Infrared absorption spectra of (1) $PbC_4H_4O_4$ at room temperature, (2) $PbC_4H_4O_4$ at 200 °C, and (3) $CuC_4H_4O_4$.

The succinates of Zn, Cd and Pb which were crystallized from the corresponding aqueous solution, were anhydrous. The infrared absorption patterns of the salts of Zn and Cd were similar to that of the copper salt in the frequency region of the methylene group, while that of the lead salt was similar to that of the hydrated cobalt salt. The TG-DTA curves of the salts of Zn, Cd and Pb were also measured, and only the lead salt gave an endotherm at 160 °C on the DTA curve without any weight-loss. The curves of the lead salt are given in Fig. 5, together with the cooling curve. An exotherm is observed at 153 °C on the cooling curve, and so the heat change is reversible. ΔH and ΔS of the endothermic process were 2.5kJ/mol and 5.9J/deg·mol, respectively. The analyses of the X-ray diffraction lines before and after the heat change indicated that the crystals of the lead salt changed from tetragonal to cubic at about 160 °C. The lattice constants calculated were $a=b=15.2$ and $c=14.6$ Å for the tetragonal (low temperature) form, and $a=b=c=$ 15.2 Å for the cubic (high temperature) form.

The phase transition of the lead salt was accompanied with a considerable change of the infrared spectrum. In Fig. 6, the infrared spectra at room temperature and at 200 °C are given. The spectral change is also reversible, *i.e.* the spectrum at 200 °C reverts to its original shape when the sample is cooled to room temperature. The spectrum at 200 °C is simpler than that at room temperature in the frequency region of the methylene group; while the latter is similar to that of the cobalt salt hydrate, the former is similar to that of the copper salt. Thus the phase transition seems to be accompanied with a conformational change of the succinate ion, and its possible structures below and above 160 °C can be represented by **[C]** and **[B]**, which can be changed into each other by rotating the chain around the $-CH_2-CH_2-$ bond.



[B]



[C]

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4) This peculiar change of the cobalt salt was already observed by Le V. My, G. Perinet, and R. Lafont, *C. R. Acad. Sci., Paris, Ser. C*, **268**, 406 (1969).