Thermal Dehydration and Decomposition of Dioxalato Complexes of Be(II), Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) in Solid State

Kenzo Nagase, Katsuya Sato,* and Nobuyuki Tanaka*

College of General Education, Tohoku University, Kawauchi, Sendai 980

**Department of Chemistry, Faculty of Science, Tohoku University, Aoba, Aramaki, Sendai 980*

(Received July 10, 1974)

The structures of anhydrous dioxalato complexes $K_2[M(C_2O_4)_2]$ (M: Mn(II), Co(II), Ni(II), Cu(II), and Zn(II)) prepared by heating their hydrates, were examined by means of infrared absorption and visible reflectance spectroscopy. It was found that the anhydrous complexes of Mn(II), Co(II), and Zn(II) exist in a polynuclear octahedral form with a bridging oxalate group, and those of Ni(II) and Cu(II), in a monomer form. On further heating, the complexes of Be(II), Mn(II), and Zn(II) decomposed into the corresponding metal oxides and potassium oxalate, and those of Co(II), Ni(II), and Cu(II) into the corresponding metals and potassium oxalate. Except for the beryllium(II) complex, the complexes decomposed at lower temperatures with an increase in $1/r$, where r is the radius of metal ion.

The thermal properties of bivalent metal oxalates(monooxalato-type complex) and trioxalato-type complexes of tervalent metals have been extensively studied. However, only fragmentary information is available on the thermal decomposition reactions of dioxalato-type complexes of bivalent metals. The TG, DTA, and EG curves for $K_2[Cu(C_2O_4)_2]\cdot 2H_2O$, $K_2[Zn(C_2O_4)_2]\cdot 2H_2O$, $K_2[Pd(C_2O_4)_2]\cdot 3H_2O$, and $K_2[Pt(C_2O_4)_2]\cdot 2H_2O$ were presented and the reaction stoichiometries discussed.[1,2]

Most bivalent metal oxalates(monoxalato-type complexes) exist in a polynuclear form with bridging oxalate groups, the water molecules contained being coordinated directly to the metal ions.[3] Thus, the dehydration temperatures are considerably high (>100 °C). The nature of the metal ions is well reflected not only on the dehydration reactions but also on the decomposition reactions of the anhydrous salts. Trioxalato-type complexes of tervalent metals exist in the mononuclear octahedral form. The coordination number of tervalent metals is usually six, and thus in these complexes, all coordination positions are occupied by the oxygen atoms of three bidentate oxalate groups. All the water molecules contained are crystalline water and dehydration takes place below 100 °C. Interest in the thermal reactions of these complexes has been limited to the decomposition reactions of the anhydrous salts. Dioxalato complexes seem to be of particular interest, since they exist in either a mononuclear or a polynuclear form. The metal ions with coordination number 4 will be mononuclear, whereas those with the number 6 can form both the mononuclear (two of the six positions are occupied by two water molecules) and polynuclear (the bridging oxalate groups act as quadridentate ligand) form complexes. In the case of anhydrous dioxalato complexes, the complexes of the metals with the number 6 should exist in the polynuclear form.

We have examined the structures of the anhydrous dioxalato complexes of Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) prepared by heating their hydrates in solid state by means of infrared absorption and visible reflectance spectroscopies. The thermal properties, as determined by the techniques of TG, DTA, DSC, and EG, are given for $K_2[Be(C_2O_4)_2]$, $K_2[Zn(C_2O_4)_2]\cdot 5H_2O$, $K_2[Mn(C_2O_4)_2]\cdot 2H_2O$, $K_2[Co(C_2O_4)_2]\cdot 6H_2O$, $K_2[Ni(C_2O_4)_2]\cdot 6H_2O$, and $K_2[Cu(C_2O_4)_2]\cdot 2H_2O$.

Experimental

Materials. The dioxalato complexes were prepared as follows: Beryllium(II) complex was obtained by adding $K_2C_2O_4$ to an aqueous solution of $BeSO_4\cdot 4H_2O$. For the other complexes, the corresponding metal oxalates were dissolved in an aqueous solution containing a stoichiometric amount of $K_2C_2O_4$. After filtration, the desired samples were crystallized from the filtrates by addition of methanol. The results of elemental analyses for C and H agreed with the calculated values within ±0.3% for all the complexes.

Measurements. Thermogravimetric (TG) and differential thermal analytic (DTA) curves were obtained in the range from room temperature to 1000 °C with a Shinku Riko TGD-3000, at a heating rate of 5 °C/min in a nitrogen atmosphere with a 50 ml/min flow rate. 20 mg of powdered sample was placed in a platinum crucible and used in each measurement. Heats of dehydration and decomposition were determined with a Rigaku Denki 8002 CS differential scanning calorimeter (DSC) at a 5 °C/min heating rate in a nitrogen atmosphere with a 30 ml/min flow rate. 20 mg of powdered sample was placed in an aluminum crucible, a lid of the same material being then placed inside the crucible. The instrument was calibrated against the heat of transition of KNO_3 which appears at 128 °C with ΔH of 12.28 kcal/mol.

The infrared absorption spectra were measured in the frequency region 2500—400 cm^{-1} with a Hitachi EPI-2G spectrophotometer by the KBr disk method. The sample heated to a given temperature was cooled to room temperature and its spectrum was recorded. A Hitachi EPS-3T spectrophotometer equipped with a standard integrating sphere attachment was used for the measurements of the reflectance spectra in the frequency range 30000—15000 cm.$^{-1}$ MgO was used as a reference material.

The evolved gas (EG) curves were obtained by conductometric technique at a heating rate of 5 °C/min in a helium atmosphere with a 50 ml/min flow rate. Evolved gas analyses (EGA) were carried out for each EG peak with an active charcoal column (2 meters long) and a helium carrier gas (50 ml/min). Procedures for EG and EGA were described previously.[2]

Results and Discussion

TG and DTA Studies. The TG curves for the

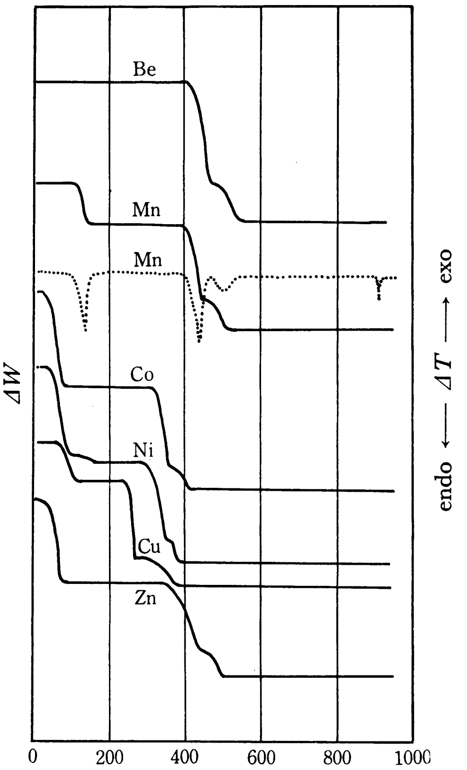


Fig. 1. TG(solid line) and DTA(dotted line) curves of dioxalato complexes in a flowing nitrogen atmosphere.

Be(II), Mn(II), Co(II), Ni(II), Cu(II), and Zn(II) complexes are given in Fig. 1. Curves for Be(II), Mn(II), Co(II), and Ni(II) complexes seem to have been given for the first time. For the sake of comparison, the curves of the remaining complexes[1] were reproduced under the conditions of the present work. The DTA curves were also obtained for all the complexes. As an example, the curve of $K_2[Mn(C_2O_4)_2]\cdot 2H_2O$ is given in Fig. 1. All the complexes decomposed through two or three steps. The initial weight-loss temperatures (t_i) and DTA peak temperatures (t_m) for each stage are summarized in Table 1 and the wieght-loss data (ΔW) in Table 2.

Except for the Be(II) complex, the complexes liberate the water molecules contained in the order of increasing temperature, Zn(II)<Co(II)<Ni(II)<Cu(II)<Mn(II), giving well-defined plateaus for the anhydrous complexes (dehydration—stage 1) on the TG curves. Dehydration of Ni(II) and Zn(II) complexes gave two peaks on each DTA curve, suggesting that all the waters are not held in the same way. The values of t_i of the dehydration varied over the range 18—112 °C with the central metals. The relation between t_i (t_{H_2O}) and $1/r$, where r is ionic radius, is given in Fig. 2. Except for $K_2[Mn(C_2O_4)_2]\cdot 2H_2O$, t_i increased almost linearly with the increase of $1/r$, suggesting that an electrostatic interaction exists to some extent between the water molecules and the central metal ions. Dehydration of the Mn(II) complex took place at the highest temperature, the point (Fig. 2) deviating a great deal from linearity. Thus, two water molecules of the Mn(II) complex might coordinate directly to the metal ion, and the complex should be formulated as $K_2[Mn(H_2O)_2(C_2O_4)_2]$.

TABLE 1. INITIAL WEIGHT-LOSS TEMPERATURES (t_i) AND DTA PEAK TEMPERATURES (t_m)

Complex	Dehydration (°C)		Decomp. of complex (°C)		Decomp. of $K_2C_2O_4$ (°C)	
	t_i	t_m	t_i	t_m	t_i	t_m
Be(II)	—	—	402	453	469	531
Me(II)	112	129	394	440	450	505
Co(II)	31	68	312	339	364	377
Ni(II)	38	72, 85	295	340	—	375
Cu(II)	63	100	242	270	300	370
Zn(II)	20	40, 70	350	420	—	488

TABLE 2. PERCENTAGE OF WEIGHT-LOSS

Complex	Dehydration		Decomp. of complex		Decomp. of $K_2C_2O_4$	
	obsd	calcd	obsd	calcd	obsd	calcd
Be(II)	—	—	27.1	27.4 $(CO+CO_2)$	10.2	10.6 (CO)
Mn(II)	10.8	10.4	20.0	20.9 $(CO+CO_2)$	7.9	8.1 (CO)
Co(II)	23.9	25.6	20.9	20.9 $(2CO_2)$	6.2	6.7 (CO)
Ni(II)	23.1	25.7	20.2	20.9 $(2CO_2)$	6.1	6.7 (CO)
Cu(II)	9.2	10.2	23.4	24.9 $(2CO_2)$	7.2	7.9 (CO)
Zn(II)	22.0	22.0	16.5	17.7 $(CO+CO_2)$	6.3	6.8 (CO)

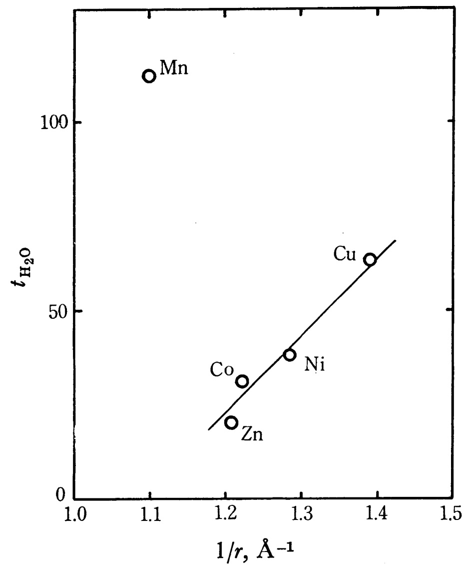


Fig. 2. Relation of initial weight-loss temperatures of the dehydration (t_{H_2O}) with $1/r$ for dioxalato complexes.

The anhydrous complexes then decomposed on further heating to give metal oxides or metals and potassium oxalate (decomposition of anhydrous complex—stage II). The weight-loss data (Table 2) indicate that Be(II), Mn(II), and Zn(II) complexes gave BeO, MnO, and ZnO, respectively, and $K_2C_2O_4$, while Co(II), Ni(II), and Cu(II) complexes gave Co, Ni,

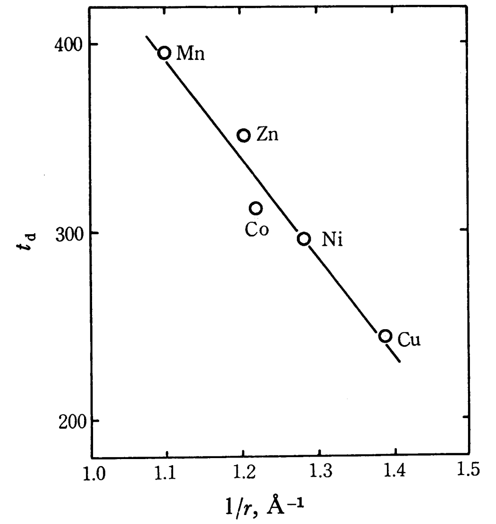


Fig. 3. Relation of initial weight-loss temperatures of the decomposition of the anhydrous dioxalato complexes (t_d) with $1/r$.

and Cu, respectively, and $K_2C_2O_4$. The values of t_i of the anhydrous complexes varied a great deal with the central metals. The plots of $t_i(t_d)$ *versus* $1/r$ are given in Fig. 3. Except for the Be(II) complex, t_i decreased with an increase in $1/r$, irrespective of the metals or the metal oxides formed as a solid decomposition product. This differs from the result obtained for the metal oxalate,[4] where the compounds giving metals decomposed at lower temperatures with an increase in $1/r$, while those giving the metal oxides decomposed in the reverse order.

Stage II which showed no well-defined plateau was followed by the decomposition of $K_2C_2O_4$ formed. The weight-loss data (Table 2) indicate that $K_2C_2O_4$ decomposed to K_2CO_3 to evolve one molecule of carbon monoxide (decomposition of $K_2C_2O_4$—stage III). It should be pointed out that the thermal stability of the potassium oxalate formed was influenced strongly by the metals or the metal oxides included in the decomposition products.

A small endotherm at 916—920 °C without any weight-loss was observed for all the complexes investigated. This corresponded to the melting point of K_2CO_3 formed. Pure K_2CO_3 also gave the same peak at 918 °C.

DSC Study. The enthalpy changes corresponding to the dehydration (ΔH_w), the decomposition of the anhydrous complexes (ΔH_{comp}) and the decomposition of $K_2C_2O_4$ (ΔH_{ox}) are given in Table 3. Since the number of water molecules contained in the complexes varied from 2 to 6, the values given for ΔH_w are the mean value per one mole of water. ΔH_w of the Mn(II) complex, dehydrated at the highest temperature, was the largest. ΔH_w decreased in the order Mn(II)$>$Cu(II)$>$Zn(II)$>$Co(II)$>$Ni(II), in line with that of ΔH_w of the metal oxalates.[4]

Table 3. Enthalpy changes

Complex	Dehydration ΔH_w, kcal/H_2O	Decomp. of complex $\Delta H_{comp.}$ kcal/comp.	Decomp. of $K_2C_2O_4$ ΔH_{ox}, kcal/$K_2C_2O_4$
Mn(II)	19.9	—	—
Co(II)	14.3	13	7
Ni(II)	13.7	16	6
Cu(II)	16.3	—	—
Zn(II)	14.6	—	—

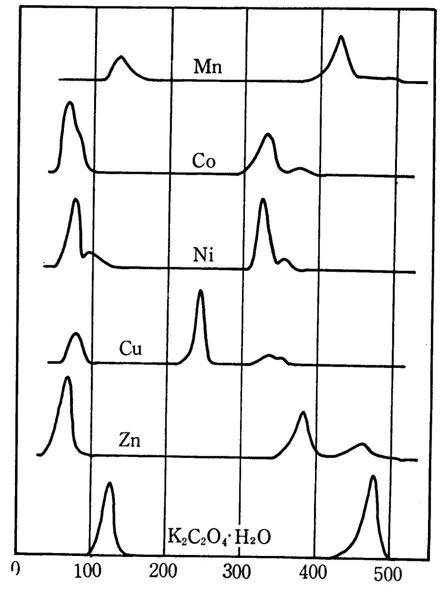


Fig. 4. Evolved gas curves of dioxalato complexes in a flowing helium atmosphere.

Table 4. Evolved gas analyses (mol %)

Complex	Decomp. of complex		Decomp. of $K_2C_2O_4$	
	CO	CO_2	CO	CO_2
Be(II)	40	60	90	10
Mn(II)	55	45	80	20
Co(II)	0	100	50	50
Ni(II)	0	100	40	60
Cu(II)	0	100	84	16
Zn(II)	44	56	82	18

EG and EGA Studies. The EG curves of the complexes in a flowing helium atmosphere are given in Fig. 4, together with the EG curve of pure $K_2C_2O_4$. The evolved gas analyses for each EG peak are given in Table 4. The decomposition of anhydrous complexes can be divided into two types: the complexes of Be(II), Mn(II), and Zn(II) evolved one mole of carbon monoxide and one mol of carbon dioxide, while those of Co(II), Ni(II), and Cu(II) evolved two moles of carbon dioxide. This is consistent with the results from the TG in Table 2.

Although the TG curves indicate that stage III corresponds to the reaction

$$K_2C_2O_4 \longrightarrow K_2CO_3 + CO, \tag{1}$$

the EGA (Table 4) indicate the presence of CO_2 in addition to CO. The compositions of the gaseous mixtures varied with the complexes. For the complexes of Mn(II), Cu(II), Zn(II), and Be(II), the major gaseous product was CO, CO_2 being less than 20% (mol %) of the total products. On the other hand, the percentage of CO_2 for the complexes of Co(II) and Ni(II) reached 50—60%. Thus, the following reaction might be considered in addition to Reaction (1).

$$K_2C_2O_4 \longrightarrow K_2CO_3 + 1/2C + 1/2CO_2 \qquad (2)$$

The presence of carbon in the solid products was confirmed by chemical analyses after removal of K_2CO_3.

Infrared Absorption and Diffuse Reflectance Spectroscopic Studies. The infrared absorption spectra of the hydrated complexes with those of the anhydrous ones are compared in Figs. 5 and 6. For the complexes of Mn(II) and Co(II), the spectra of the hydrated complex differ a great deal from those of the anhydrous complex, suggesting that structural changes occurred in the course of dehydration. In the region 1500—1200 cm^{-1}, $K_2[Mn(C_2O_4)_2]\cdot 2H_2O$ exhibited two C–O stretching vibrations[5] at 1447 and 1303 cm^{-1}, while $K_2[Mn(C_2O_4)_2]$ showed absorptions at 1418, 1387(w), 1332, and 1282 cm^{-1}. The bands of the hydrated complex, and those at 1418 and 1282 cm^{-1} of the anhydrous complex could be assigned to the C–O stretching vibrations of the bidentate oxalate group (I); those at 1387(w) and 1332 cm^{-1} of the anhydrous complex would be due to the quadridentate oxalate group (II).

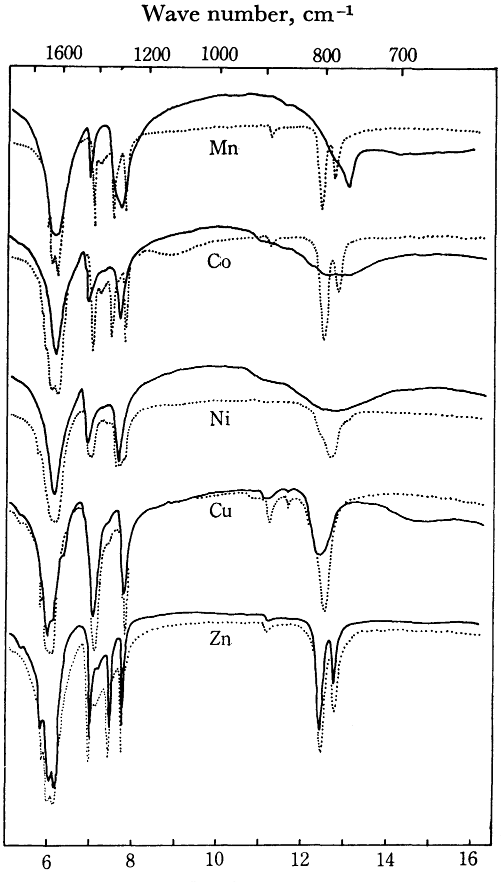


Fig. 5. Infrared absorption spectra of dioxalato complexes before and after the dehydration: —— indicates $K_2[M(C_2O_4)_2]\cdot nH_2O$ and ……, $K_2[M(C_2O_4)_2]$.

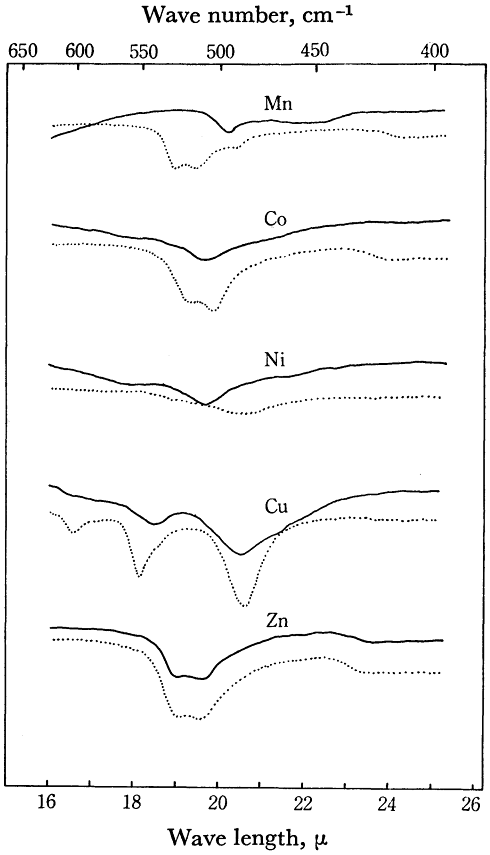
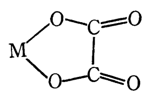
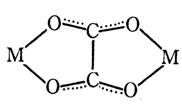


Fig. 6. Infrared absorption spectra of dioxalato complexes before and after the dehydration: —— indicates $K_2[M(C_2O_4)_2]\cdot nH_2O$ and ……, $K_2[M(C_2O_4)_2]$.



I



II

The assignments are supported by comparison of the spectra of the anhydrous complex with those of MnC_2O_4 and $K_6(C_2O_4)_2Mn(OX)Mn(C_2O_4)_2$, where OX denotes a quadridentate oxalate group.[6] The oxalate groups in MnC_2O_4 are also confirmed to act as quadridentate groups by X-ray analysis.[3] Manganese oxalate shows only two bands at 1337(w) and 1319 cm^{-1}, while $K_6(C_2O_4)_2Mn(OX)Mn(C_2O_4)_2$ shows absorptions at 1415, 1385(w), 1310, and 1285 cm^{-1}.[6] In the region 900—650 cm^{-1}, considerable differences were observed in the spectra of $K_2[Mn(C_2O_4)_2]\cdot 2H_2O$ and its anhydrous complex: the hydrated complex gave two broad bands at 766 and 696 cm^{-1}, and the anhydrous complex three narrow bands at 885, 798, and 780 cm^{-1}. The bands at 696 cm^{-1} in the hydrated complex might correspond to coordinated waters; $MnC_2O_4\cdot 2H_2O$ also shows a characteristic band of the coordinated waters at 724 cm^{-1}. This is consistent with results from TG (the hydrated complex should be formulated as $K_2[Mn(H_2O)_2(C_2O_4)_2]$). The bands appearing in the region 600—400 cm^{-1} give direct information on the coordination bond. Oxalato complexes, in general, exhibit M–O stretching modes in this region.[5] The spectrum of the anhydrous complex in this region differes from that of the hydrated one, suggesting a change of the bonding structure by dehydration.

Comparison of the infrared absorption spectra of the complexes of other metals in a similar way give valuable information on the prediction of the bonding structures of the complexes. The spectra of the anhydrous complexes of Co(II) and Zn(II) and also the hydrated complex of Zn(II) are very similar to that of the anhydrous manganese(II) complex in the range 2000—400 cm^{-1}, indicating that these complexes have essentially the same structure.

The anhydrous complexes of Ni(II) and Cu(II) show no characteristic bands of the bridging oxalate group. Each oxalate ligand might essentially act as a bidentate group.

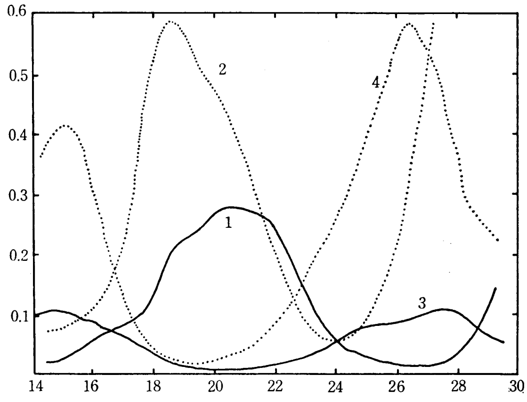


Fig. 7. Reflectance spectra of (1) $K_2[Co(C_2O_4)_2]\cdot 6H_2O$, (2) $K_2[Co(C_2O_4)_2]$, (3) $K_2[Ni(C_2O_4)_2]\cdot 6H_2O$ and (4) $K_2[Ni(C_2O_4)_2]$.

The diffuse reflectance spectra in the visible region (Fig. 7) were obtained in order to study the structures of the colored complexes. The spectrum of the hydrated complex of Ni(II) was similar to that of $NiC_2O_4\cdot 2H_2O$, the nickel ion of which is surrounded octahedrally with six oxygen atoms. $[Ni(H_2O)_6]^{2+}$ in aqueous solution also gives a similar absorption pattern. Thus, the hydrated nickel(II) complex has an octahedral coordination structure. It is blue while the anhydrous nickel(II) complex is bluish green. The spectrum of the latter is similar to that of the hydrated complex, except for the change in apparent intensities and the relatively small shifts of the absorption bands. Thus the Ni(II) ion in the anhydrous complex is also in an approximately octahedral structure, probably due to the formation of weak Ni–O bonds between the non-coordinated oxygen atoms of one $[Ni(C_2O_4)_2]^{2-}$ unit and Ni ions in adjacent units; Appearance of somewhat broad bands of the anhydrous complex might be due to this effect. As to the Co(II) complexes, the spectrum of the hydrated complex is similar to that of $CoC_2O_4\cdot 2H_2O$ and of $[Co(H_2O)_6]^{2+}$, the spectrum of the anhydrous complex not differing very much either. This indicates the essentially octahedral structures of both hydrated and anhydrous complexes. In the case of the copper complex, it seems that there is no remarkable structural change in the course of dehydration. The copper(II) ion seems to be surrounded square-planarly with four oxygen atoms of two bidentate oxalate groups, since a copper(II) ion usually tends to form such square planar (or tetragonal distorted) complexes. Thus, the infrared spectrum of the copper(II) complex in the region 600—400 cm^{-1} differs a great deal from that of the anhydrous Ni(II) complex.

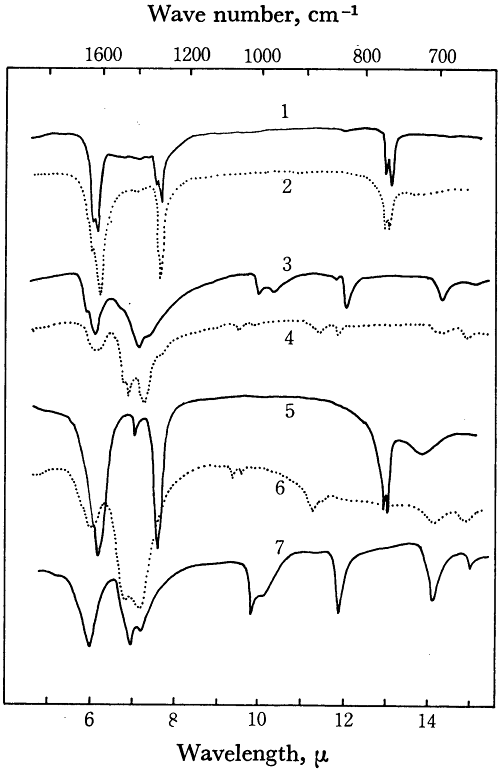


Fig. 8. Infrared absorption spectra of (1) products of the cobalt complex at the stage II, (2) products of the copper complex at the stage II, (3) products of the cobalt complex at the stage III, (4) products of the copper complex at the stage III, (5) $K_2C_2O_4$, (6) K_2CO_3, and (7) $KHCO_3$.

The solid products formed at stages II and III were confirmed by means of infrared absorption spectra. The infrared spectra of Co(II) and Cu(II) complexes at each stage are given in Fig. 8, together with those of pure $K_2C_2O_4$, K_2CO_3, and $KHCO_3$. The spectra of the decomposition products at stage II (curves 1 and 2, Fig. 8) were similar to the spectrum of pure $K_2C_2O_4$ (curve 5). The spectra at stage III (curves 3 and 4) showed the presence of $KHCO_3$ in addition to K_2CO_3. Formation of $KHCO_3$ might be due to the reaction between K_2CO_3 formed and H_2O in air, since the spectra were recorded after cooling the heated samples to room temperature in air. The infrared absorption data thus support the results obtained from TG and EGA.

In conclusion, all the spectral data indicate the following structures.

Mn(II) Complexes. The hydrated complex is formulated as $K_2[Mn(H_2O)_2(C_2O_4)_2]$, while the anhydrous one has a polymeric structure with both quadridentate and bidentate oxalate ligands.

Co(II) Complexes. The infrared spectra show a similar situation to that for the Mn(II) complexes, although the water molecules in the hydrated complex are held only loosely (Fig. 2). Both the complexes containing Co(II) in approximately octahedral environments.

Cu(II) Complexes. Both the hydrated and anhydrous complexes seem to be monomeric. Dehydration causes no remarkable change in the states of the central Cu(II), probably because of the tetragonal distortion of the complexes.

Zn(II) Complexes. Both the hydrated and anhydrous complexes have polymeric structures like $K_2Mn(C_2O_4)_2$; the water molecules are held extremely loosely, so that the dehydration occurs most easily.

Ni(II) Complexes. A similar situation to that for the Cu(II) complexes is seen, but here both complexes have essentially octahedral structures. A certain interaction between the $[Ni(C_2O_4)_2]^{2-}$ units in the anhydride should be postulated.

The authors wish to thank Prof. Kozo Sone for valuable discussions and Mr. Mitsuo Sato for the measurement of infrared absorption spectra. Expenses for the research were defrayed by a grant from the Ministry of Education.

References

1) K. Nagase, This Bulletin, **41**, 2166 (1972).

2) K. Nagase, *ibid.*, **46**, 144 (1973).

3) J. P. Largier, H. Pezernat, and J. Dubernat, *Rev. Chim. Miner.*, **6**, 1081 (1969).

4) K. Nagase, K. Sato, and N. Tanaka, to be published in this Bulletin.

5) K. Nakamoto, "Infrared Spectra of Inorganic and Coordination Compounds," John Wiley and Sons, Inc., New York (1963), pp. 211.

6) G. M. Bancroft, K. G. Dharmavardena, and A. G. Maddoch, *Inorg. Nucl. Chem. Lett.*, **6**, 403 (1970).