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Synthesis of Copper(II) Complexes with Maleic Acid[1*]

Kazuo GORA, Eishin KYUNO and Ryokichi TSUCHIYA

Department of Chemistry, Faculty of Science, Kanazawa University, Kanazawa

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Three copper(II) complexes with maleic acid, [Cu mal(H_2O)] (I) (mal=$C_2H_2(COO)_2$), [Cu(Hmal)$_2$(H_2O)$_4$] (II) and [Cu$_2$(Hmal)$_4$]·H$_2$mal·4EtOH (III) (EtOH=C_2H_5OH), were synthesized. Compound I was prepared from an aqueous solution of copper(II) sulfate pentahydrate and sodium hydrogenmaleate at room temperature as fine blue crystals. Compound II was prepared by adding little by little copper(II) hydroxide or copper(II) hydroxycarbonate to an aqueous solution of maleic acid at a temperature below 0°C in an ice-salt bath, obtaining light-blue powdered crystals. Compound III was prepared by heating a mixed alcoholic solution of maleic acid anhydride, copper(II) sulfate pentahydrate and sodium carbonate anhydride (3 : 1 : 1) in a flask with a reflux condenser for two hours. Fine bluish-green crystals were obtained. By using copper(II) hydroxide instead of copper(II) sulfate in the above preparation, a better yield can be obtained. The effective magnetic moments of I and II were 2.00 B. M. (20°C) and 1.97 B. M. (20°C), respectively, which are relatively close to the spin-only value of the divalent copper ion. On the other hand, the magnetic moment of III was subnormal, being 1.12 B. M. (18°C). The reflection spectrum of III gave a shoulder near 370 mμ, which is specific to green copper complexes. The product (IV) obtained by the thermal decomposition of I at 220°C and the product (V) obtained from II at 160°C, which are presumed to have the chemical formula [Cu-mal(H_2O)$_{0.1}$] and [Cu(Hmal)(mal)$_{1/2}$], respectively, gave normal magnetic moments, 1.91 and 1.89 B. M. (20°C). However, product (VI), obtained by expelling the alcohol from III had a magnetic moment of 1.31 B. M. (17°C). Different from the corresponding copper(II) phthalate complexes, no green copper complexes having subnormal magnetic moments could be obtained through dehydration of the blue maleate complex I or the light-blue complex II having normal magnetic moments.

Maleate anions coordinate to metal ions as seven-membered chelate ligands in the same way as succinate and phthalate anions. The fact that the copper(II) succinate complex has a subnormal effective magnetic moment, 1.40 B. M., has already been reported by Kubo *et al.*1)

The copper(II) complexes with phthalic acid have been prepared and discussed for dimer or monomer structures with respect to two copper atoms in an earlier paper.2) It was found by the authors that, in an aqueous solution at low temperature below 79°C, monomer phthalate complexes were produced preferably, whereas the dimer began to crystallize at temperatures above 79°C. On the basis of these results, it is assumed that the tendency of hydration of copper(II) ion in an aqueous solution would decrease steadily as the temperature is elevated. Instead of the use of an aqueous medium, some suitable organic solvents have been known to be effective for the preparation of several complexes having subnormal magnetic moments.3,4)

Although the properties of the copper(II) complexes with maleic acid are partly known,5) further investigation has not progressed. The present study is an attempt to prepare new copper(II) complexes with maleic acid in different media and to discuss their properties.

In the case of copper(II) phthalate complexes, a green complex having a dimer structure with respect to two copper atoms was obtained by the thermal decomposition of the blue and light-blue complexes. This was ascertained through reflection spectra and X-ray diffraction measurements carried out in an earlier paper.2)

Despite great interest in the color and structural changes which take place in the thermal decomposition process of copper(II) phthalate complexes as above, such a study has rarely been made for other copper(II) complexes. A further purpose of this study is to find whether or not green copper maleate complex can be obtained through thermal

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1) O. Asai, M. Kishita and M. Kubo, *J. Phys. Chem.*, **63**, 96 (1959).

2) I. Shimizu, R. Tsuchiya and E. Kyuno, This Bulletin, **40**, 1162 (1967).

3) M. Bobtelsky and I. Bargadda, *Bull. Soc. Chim. France*, **1953**, 276, 687.

4) C. V. Souvray, *Compt. rend.*, **233**, 164 (1951).

5) S. U. Pickering, *J. Chem. Soc.*, **101**, 174 (1911).

decomposition of the blue or light-blue complex in the similar way as in the thermal preparation of the corresponding green copper(II) phthalate complexes described in an earlier paper.²⁾

Experimental

Syntheses. *Maleatoaquocopper(II)*, [Cu mal(H_2O)] (I). A solution of copper(II) sulfate pentahydrate (25 g; 0.1mol) in 100m*l* of water was mixed with a solution containing maleic acid (20g; 0.2mol) and sodium carbonate (11g; 0.1mol) in 2000m*l* of water. On allowing the mixed solution to stand for a while at room temperature, fine blue crystals precipitated out. After filtration, the precipitate was washed with a small amount of water, ethanol and ether in that order and then dried in a silicagel desiccator. The results of chemical and thermal analyses were: Found: Cu, 32.54; C, 24.58; H, 1.96%. Calcd for $[Cu(C_4H_2O_4)(H_2O)]$: Cu, 32.48; C, 24.56; H, 2.06%.

Bis(hydrogenmaleato)tetraaquocopper(II), $[Cu(Hmal)_2 \cdot (H_2O)_4]$ (II). When copper(II) hydroxycarbonate (12 g; 0.05mol) or copper(II) hydroxide (9.8g; 0.1mol) was added little by little to 300m*l* of an ice-cold aqueous solution containing maleic acid (20g; 0.2mol), a light-blue powder was obtained. It was washed several times with a mixture of ethanol and water (1 : 2), ethanol and ether and then air-dried. Found: Cu, 17.63; C, 26.96; H, 3.93%. Calcd for $[Cu(C_4H_3O_4)_2(H_2O)_4]$: Cu, 17.37; C, 26.28; H, 3.86%.

Tetra(hydrogenmaleato)dicopper(II) Maleate Tetraalcoholate $[Cu_2(Hmal)_4] \cdot H_2mal \cdot 4EtOH$ (III). By refluxing a mixed solution of maleic acid anhydride (30g; 0.3mol), copper(II) sulfate pentahydrate (25g; 0.1mol) and sodium carbonate (11g; 0.1mol) in alcohol (300m*l*) for two hours, a green solutuon was obtained. On allowing the solution to stand for a while at room temperature, green powdered crystals precipitated out. Through recystallization with a saturated ethanol solution, fine green crystals were obtained with a good yield. They were washed with a mixture of ethanol and water (1 : 2), ethanol and ether in a similar way as described above and air-dried. Found: Cu, 14.46; C, 38.28; H, 4.77%. Calcd for $[Cu_2(C_4H_3O_4)_4] \cdot (C_4H_4O_4) \cdot 4C_2H_5OH$: Cu, 14.31; C, 37.88; H, 4.54%.

Thermal Decomposition Product (IV) from I. When complex I was heated to 220°C, a violet compound was obtained. It was thought to have the formula $[Cu\,mal(H_2O)_{0.1}]$ after thermogravimetric (TG) analysis.

Thermal Decomposition Product (V) from II. Complex II was also heated at 160°C in the similar way as described above. The resulting blue powder was assigned to $[Cu(Hmal)(mal)_{1/2}]$ on the basis of its TG analysis.

This formula was also confirmed through elementary analysis: Found: Cu, 27.17; C, 31.16; H, 1.69%. Calcd for $[Cu(C_4H_3O_4)(C_4H_2O_4)_{1/2}]$: Cu, 26.96; C, 30.58; H, 1.71%.

Thermal Decomposition Product (VI) from III. Complex III was heated at 100°C in the same way. After TG analysis, the resulting compound was thought to corresponding to $[Cu_2(Hmal)_4] \cdot H_2mal$. It was also confirmed by an analysis of the copper content. Found: Cu, 17.95%. Calcd for $[Cu_2(C_4H_3O_4)_4] \cdot (C_4H_4O_4)$: Cu, 18.07%.

Measurements. Thermal analysis was carried out with a Shimadzu Thermano Balance. Magnetic susceptibilities were measured by the Gouy method using powdered sample at room temperature. The measurements of visible and UV absorption spctra were carried out in an ethanol solution with a Hitachi EPU-2A Spectrophotometer; reflection spectra of finely powdered solid samples were obtained with the same spectrophotometer equipped with a standard Hitachi reflection attachment. With a Nippon-Bunko DS-301 IR Spectrometer, the IR spectra of these complexes were measured in a Nujol or HCB mull state and in a KBr disk. The X-ray diffraction patterns were obtained with a Rigaku-Denki Geiger-flex X-ray Analyzer.

Results and Discussion

Conditions for the Formation of These Copper(II) Maleate Complexes. Complex I was obtained at room temperature, but complex II was prepared at a lower temperature in an ice-salt bath. However, II was sometimes contaminated with a small amount of I even at the low temperature when copper(II) salt was added in relatively larger amounts at a time. The use of copper(II) hydroxide instead of copper(II) hydroxycarbonate, in general, led to rather good yields.

Complex III could not be obtained in a medium consisting of ethanol and water (1 : 1), but was obtained only refluxing an alcoholic solution of the materials required for preparation. On the other hand, I was formed preferably in aqueous media at approximately 100°C and III was transformed to I in the presence of water. These results suggest that the existence of water obstructs the formation of III.

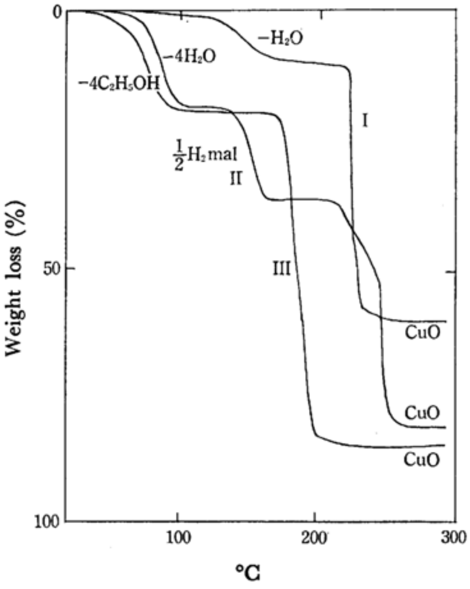

Fig. 1. TG curves for copper(II) maleate complexes.

I $[Cu\,mal(H_2O)]$

II $[Cu(Hmal)_2(H_2O)_4]$

III $[Cu_2(Hmal)_4] \cdot (H_2mal) \cdot 4EtOH$

Thermal Decomposition. Figure 1 shows the TG curves for complexes I, II and III. The thermal decomposition processes in these complexes are expressed as follows:

$$\mathrm{I} \xrightarrow{220^\circ\mathrm{C}} [\mathrm{Cu\,mal(H_2O)_{0.1}}] \xrightarrow{235^\circ\mathrm{C}} \text{decompose}$$

$$\mathrm{II} \xrightarrow{100^\circ\mathrm{C}} [\mathrm{Cu(Hmal)_2}] \xrightarrow{160^\circ\mathrm{C}} [\mathrm{Cu(Hmal)(ma)_{1/2}}] \xrightarrow{260^\circ\mathrm{C}} \text{decompose}$$

$$\mathrm{III} \xrightarrow{100^\circ\mathrm{C}} [\mathrm{Cu_2(Hmal)_4}]\cdot\mathrm{H_2mal} \xrightarrow{200^\circ\mathrm{C}} \text{decompose}$$

The complexes I and II have already been prepared by Pickering,5) who, however, found the composition of the complex to be $[\mathrm{Cu(Hmal)_2}]\cdot 8\mathrm{H_2O}$, which loses four hydrated water molecules upon heating at 100°C and then loses the remaining four water molecules at 170°C, differing from complex II obtained by the present authors.

Although transformation from complex III to I in the presence of water easily took place as described above, the reverse reaction *via* thermal decomposition was not achieved, apart from the case of the corresponding phthalate complexes.2)

Magnetic Susceptibility. The effective magnetic moments of these complexes evaluated from magnetic susceptibility measurements are given in Table 1. It is seen in the table that complexes I and II and their thermal decomposition products have normal magnetic moments of a spin-only value for divalent copper ion, exhibiting no specific interactions between two copper atoms, whereas both complex III and its thermal decomposition product possess a subnormal magnetic moment, probably due to a strong interaction between Cu(II)-Cu(II) atoms in a molecule.

TABLE 1. MAGNETIC MOMENTS, μ_{eff}, OF COPPER(II) MALEATE COMPLEXES

Complex	μ_{eff} B.M. (°C)
I	2.00 (20)
II	1.97 (20)
III	1.12 (18)
IV	1.91 (20)
V	1.89 (20)
VI	1.31 (17)

IR Spectra. The wave numbers of the band assigned to C=O stretching and of the specific absorption band concerning the maleate ion in IR spectra are listed in Table 2. In complexes II and III and their thermal decomposition products both free and coordinated carboxyl groups are found to coexist from the appearance of two strong bands in the regions 1720—1700 and 1660—1620 cm^{-1} assigned to both groups, respectively, whereas in complex I and its thermal decomposition product only one broad band is found in the range of 1660—1620 cm^{-1}, showing that all carboxyl groups are coordinated to the central metal ion in the molecule.

TABLE 2. IR SPECTRA OF COPPER(II) MALEATE COMPLEXES (cm^{-1})

$\nu_{\mathrm{(COOH)}}$ and $\nu_{\mathrm{(COOM)}}$ are stretching vibration of free and coordinated COO group; δ, specific absorption band of maleate

Complex	$\nu_{\mathrm{(COOH)}}$	$\nu_{\mathrm{(COOM)}}$	$\delta_{\mathrm{(mal)}}$
I	—	1665, 1620	854, 838
II	1700	1660	835
III	1715	1660—1620	863, 838, 822
IV	—	1660—1620	851, 832
V	1720	1650—1615	835, 825, 810
VI	1720	1650—1615	835, 825, 810

The fact that all the complexes show a specific band assigned to the maleate anion in the region 860—810 cm^{-1} confirms that the complex molecules hold maleate coordinated, not fumarate, in themselves.

Reflection Spectra. The reflection spectra of the complexes, I, II, III and IV are shown in Fig. 2. The absorption bands of I and II are found near 14.5×10^3 cm^{-1}, whereas IV gives a new, relatively strong band near 17.0×10^3 cm^{-1} instead of the depression of the former band at 14.5×10^3 cm^{-1}. This suggests that the new band can be assigned to the ligand field produced by maleate anion only coordinated to copper as a result of the liberation of coordinated water.

On the other hand, in complex III, there are two bands near 14.7 (d–d transition band) and at 27.0×10^3 cm^{-1}, the latter band appearing at almost the same position as that observed in the

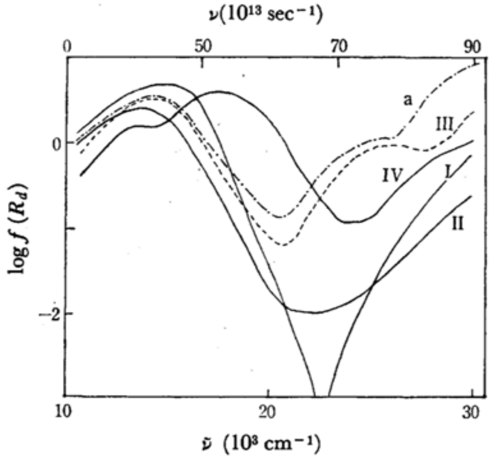

Fig. 2. Reflection spectra of copper(II) maleate complexes.

I $[\mathrm{Cu\,mal(H_2O)}]$
II $[\mathrm{Cu(Hmal)_2(H_2O)_4}]$
III $[\mathrm{Cu_2(Hmal)_4}]\cdot\mathrm{H_2mal}\cdot4\mathrm{EtOH}$
IV $[\mathrm{Cu\,mal(H_2O)_{0.1}}]$
a, $[\mathrm{Cu_2ph_2}]$ (for reference)

green copper(II) phthalate complex as already described in an earlier paper,(2) which is also shown by (a) in Fig. 2 for reference.

X-Ray Powder Pattern Measurement. Complexes I, II and III give essentially different X-ray powder patterns showing that their structures are different. In the copper(II) phthalate complexes, the interesting fact that the green complex, which has a subnormal magnetic moment, is also produced by the thermal decomposition of the blue or lightblue complex was verified from X-ray powder diffraction patterns in an earlier paper.(2) However, in the copper(II) maleate complexes, such a phenomenon has never been observed. Information on crystal structure was found only for I, which is a hexagonal system with the axial parameters a= 8.10 Å and c=10.59 Å, and of chemical units Z=4 with a density ρ=2.16.