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Copper(II) Complexes with Phthalic Acid[*1]

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Three copper(II) complexes with phthalic acid, [Cuph(H_2O)] (I) (ph=$C_6H_4(COO)_2$), [Cu(Hph)$_2$(H_2O)$_2$] (II), and [Cuph]$_2$ (III), were prepared. Compound I was prepared from an aqueous solution of copper sulfate and phthalic acid within the temperature range of 60—79°C. It was a light blue crystal forming a hexagonal unit, the parameters being a=13.07 Å and c=13.98 Å and with the chemical unit Z equalling 8. II was prepared at a temperature below 60°C. It was a blue crystal having a hexagonal unit of a=11.42 Å, c=13.68 Å, and Z=4. The magnetic moments of I and II were 1.87 B. M. and 1.96 B. M. (both 21.5°C) respectively, showing I and II to have a monomer structure with respect to the two copper atoms. III could be prepared at temperatures above 79°C. It was a bluish-green crystal containing a hexagonal unit of a=12.77 Å, c=13.02 Å, and Z=4. The magnetic moment of III was found to be 1.54 B. M. (18.4°C), suggesting that complex III consisted of a dimer structure with respect to the copper atoms. The appearance of a shoulder near 370 mμ in the reflection spectra of the copper complex III in the powdered crystalline state confirmed the suggestion of a dimer structure.

A number of copper(II) complexes of organic acids have been observed to have subnormal magnetic moments,[1-7] which were much less than the approximate value of 1.9 B. M.[8] exhibited by copper(II) sulfate pentahydrate at room temperature. On the basis of this anomalous paramagnetic behavior, it has been established that a favorable metal-metal bond[5,7,9-14] is formed

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1) J. Lifschitz and E. Rosenbohm, *Z. Electrochem.*, **21**, 499 (1951).

2) M. Kato, H. B. Jonassen and J. C. Fanning, *Chem. Revs.*, **64**, 99 (1964).

3) E. Kokot and R. L. Martin, *Inorg. Chem.*, **3**, 1306, (1964).

4) B. J. Edmondson and A. B. P. Lever, *ibid.*, **4**, 1608 (1965).

5) D. Lawton and R. Mason, *J. Am. Chem. Soc.*, **87**, 921 (1965).

6) L. Dubicki, C. M. Harris, E. Kokot and R. L. Martin, *Inorg. Chem.*, **5**, 93 (1966).

7) B. N. Figgis and D. J. Martin, *ibid.*, **5**, 100 (1966).

8) J. Amiel, *Compt. rend.*, **213**, 240 (1941).

9) J. Ploquin, *Bull. Soc. Chim. France,* **18**, 757 (1951).

10) J. N. van Niekerk, F. R. L. Schoening and J. F. de Wet, *Acta Cryst.*, **6**, 501 (1953).

11) P. Taha and G. Wilkinson, *J. Chem. Soc.*, **1963**, 5406.

12) T. A. Stephenson, E. Bannister and G. Wilkinson, *ibid.*, **1964**, 2538.

13) M. R. Churchill and R. Mason, *Nature,* **204**, 777 (1964).

14) I. I. Chernyaev, E. W. Shenderetskaya, L. A. Nazarow and A. S. Antsyshkina, "Theory and Structure of Complex Compounds," B. Jezowska-Trzebiatowska, ed., Pergamon Press, New York (1964), p. 25.

between the two copper ions in complexes. It has been also known that this magnetic behavior depends upon the nature of the acids which are used as the donor ligands.[2,4,6,9,15-19]

Despite the considerable interest in the study of the complexes with such aromatic dicarboxylic acids as the phthalic acid due to some steric factors being involved with the stability of the complexes, no remarkable success in the preparation on these complexes in aqueous media, especially those with subnormal paramagnetic moments, has been reported, though a few complexes have been prepared in suitable organic media.[20-22]

For the preparation of copper(II) complexes, two kinds of copper(II) compounds have commonly been used as starting materials, (1) copper(II) sulfate pentahydrate, $CuSO_4 \cdot 5H_2O$,[23] and (2) copper(II) acetate monohydrate, $Cu(CH_3COO)_2 \cdot H_2O$.[24] From the structural viewpoint, the former has been known as an aquo complex-salt-keeping monomer[25] which exhibits a normal paramagnetic moment,[8] whereas the latter has been recognized to have a binuclear structure such as $Cu_2(CH_3COO)_4 \cdot 2H_2O$[26] in the crystalline state and to exhibit a subnormal magnetic moment[1,2,27,28] due to the Cu—Cu bond in the molecule. It may be reasonable, in view of the above structures, to say that the selection of the latter as a starting material would be advantageous for the successful preparation of copper complexes with a dimer structure in organic solvents. Therefore, it may be unprofitable to use the former for the preparation of dimer complexes. However, such a conception may not always be applicable to preparation in an aqueous solution, since copper acetate hydrate, which has a dimer structure in the crystalline state, also dissociates to a monomer structure in an aqueous solution in a manner similar to copper sulfate hydrate.

It is well known as an empirical fact that many salts with lesser hydrated water[29] may, in general, be preferably crystallized out in an aqueous solution, as the temperature of the solution is rather higher. It can, therefore, be expected that complexes with a dimer structure in respect to the central metal ions will be easily produced in an aqueous solution at a higher temperature. Copper complexes with dimer structures were prepared on the basis of this principle.

Experimental

Preparation. *Phthalatoaquocopper(II).* $[CuphH_2O]$*2 (I). Copper(II) sulfate pentahydrate (8.3 g; 0.03 M) and potassium hydrogen phthalate (20 g; 0.1 M) were dissolved in about 200 m*l* of hot water. The pH of the blue solution was about 3.1. When this solution was concentrated on a water bath at 80°C, a light blue crystal was precipitated. The crystal was washed with a small amount of water, ethanol, and ether in turn, and then dried *in vacuo.*

The results of chemical and thermal analyses are: Found, Cu, 25.20; C, 38.76; H, 2.33%. Calcd for $[Cu(C_8H_4O_4)(H_2O)]$, Cu, 25.81; C, 39.02; H, 2.46%.

Bis-(hydrogen phthalato)diaquocopper(II), $[Cu(Hpn)_2 \cdot (H_2O)_2]$ (II). When the solution filtered off the above crystal I was allowed to stand for a while at room temperature without any heating, a blue crystal was precipitated. It was washed several times with a mixture of ethanol and water(1 : 2), ethanol, and ether, and then dried in air. The crude product was recrystallized from a small amount of water at room temperature.

Found: Cu, 14.67; C, 44.65; H, 3.26%. Calcd for $[Cu(C_8H_5O_4)_2(H_2O)_2]$, Cu, 14.80; C, 44.65; H, 3.26%.

Phtalatocopper(II), $[Cu\ ph]_2$ (III). When the solution provided to prepare the crystal I was heated a while at about 100°C, a bluish-green crystal was obtained. It was washed with water and ethanol in turn, and dried *in vacuo.*

Found: Cu, 27.48; C, 41.46; H, 1.92%. Calcd for $[Cu(C_8H_4O_4)]$: Cu, 27.90; C, 42. 16; H, 1.75%.

Thermal Decomposition Product (IV) from I. The complex I was thermally decomposed with a Shimadzu Thermano-Balance. The product obtained up to 210°C was analyzed as:

Found: Cu, 27.69; C, 41.53; H, 1.78%. Calcd for $[Cu(C_8H_4O_4)]$: Cu, 27.90; C, 42.16; H, 1.75%.

Thermal Decomposition Product (V) from II. The complex was thermally decomposed with the same thermobalance as above. The product obtained up to 210°C was analyzed as:

Found: Cu, 27.05; C, 42.86; H, 1.85%. Calcd for $[Cu(C_8H_5O_4)]$: the same as above.

The preparation of these complexes using copper(II) acetate as a staring material was attempted in a way similar to that described above in order to compare the temperature of preparation in this case with that in the case when copper sulfate was used.

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15) M. Kondo and M. Kubo, *J. Phys. Chem.*, **62**, 1558 (1958).

16) J. Lewis and R. C. Thomson, *Nature,* **200**, 468 (1963).

17) M. Inoue, M. Kishita and M. Kubo, *Inorg. Chem.*, **3**, 239 (1964).

18) R. P. Gillard, D. M. Harris and G. Wilkinson, *J. Chem. Soc.*, **1964**, 2838.

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

20) M. Bobtelsky and I. BarGadda, *Bull. Soc. Chim. France,* **1953**, 276, 687.

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

22) Y. Hasegawa, M. Kishita and M. Kubo, Read at the 14th Annual Meeting of the Chemical Society of Japan, Tokyo, April, 1961.

23) W. E. Henderson and W. C. Fernelius, "Inorganic Preparation," McGraw-Hill, N. Y. (1935), p. 9.

24) G. Brauer, "Handbuch der Präparativen Anorganischen Chemie," Ferdinand Enke, Stuttgart (1954), p. 762.

25) C. A. Beevers and H. Lipson, *Proc. Roy. Soc.*, **A146**, 570 (1934).

26) J. N. van Niekerk and F. R. L. Schoening, *Acta Cryst.*, **6**, 227 (1953); *Nature*, **171**, 36 (1953).

27) J. Amiel, *Compt. Rend.*, **207**, 1097 (1938).

28) A. Mookerjee, *Indian J. Phys.*, **19**, 63 (1945).

29) T. I. Taylor and H. P. King, *J. Chem. Phys.*, **4**, 601 (1936).

*2 $ph = C_6H_4(COO)_2$.

Measurement. Thermal analysis was made with a Shimadzu Thermano-Balance. The magnetic susceptibility was measured by the Gouy method in a powdered sample. The ultraviolet and visible absorption spectra of the complexes in an aqueous solution were obtained with a Hitachi EPU-2A Spectrophotometer; the reflection spectra in a finely-powdered solid state were obtained with the same spectrophotometer equipped with the standard Hitachi reflection attachment. The infrared spectra of these complexes were obtained in the Nujol or HCB mull state and in a potassium bromide disk by the use of a Nippon-Bunko DS-301 IR-Spectrophotometer. The pH and electric conductivity were measured with a Toa-Denpa Model HM-8 pH meter and a Yokogawa BV-Z-12A Universal Bridge respectively. X-Ray powder patterns were obtained with a Rigaku-Denki Geiger-flex X-ray Analyzer.

Results and Discussion

Conditions for the Formation of Three Copper(II) Phthalato Complexes. The lower critical temperature at which the copper(II) complexes I, II and III could be crystallized were observed. They are listed in Table 1 for the cases where copper(II) sulfate and copper(II) acetate were used as the starting materials.

It may be found in Table 1 that the complex I can be easily obtained at room temperature, but the temperature required for the formation of the complexes becomes higher in the order of the complex I and III when copper sulfate is used as the starting material in an aqueous solution, and, when copper acetate is used a still higher temperature is required for the preparation of these complexes.

Table 1 suggests that copper(II) sulfate pentahydrate is preferable to copper(II) acetate monohydrate for the preparation of the copper(II) phthalato complexes in spite of the prediction that the use of copper acetate would be advantageous because of the dimer structure in the crystalline state. The reasons for this are very complicated, but they are partly discussed below.

It has been understood, in view of the reaction mechanism, that most substitution reactions, including the replacement of one ligand in the complex by another, in general proceed through the corresponding aquo complex as a temporary intermediate by means of rapid acid hydrolysis. In order to compare the extents of the formation of the copper(II) phthalato complexes with each other when copper(II) sulfate or copper(II) acetate is used as the starting material, the equilibrium constants in the following two equations were evaluated as below by using the formation constants of the related acido complexes:*3

$$[\mathrm{CuSO_4(H_2O)_4}] + \mathrm{C_8H_4O_4}^{2-} = [\mathrm{Cu\,ph(H_2O)_4}] + \mathrm{SO_4}^{2-}$$

$$\log k_1 = 1.71 \text{ (ionic strength } \mu = 0,\ 25^\circ\mathrm{C})$$

$$\log k_1 = 2.6 \text{ (ionic strength } \mu = 0.4\text{—}1.0,\ 18\text{—}25^\circ\mathrm{C}) \qquad (1)$$

$$[\mathrm{Cu(CH_3COO)(H_2O)_5}] + \mathrm{C_8H_4O_4}^{2-} = [\mathrm{Cu\,ph(H_2O)_4}] + \mathrm{CH_3COO}^-$$

$$\log k_1 = 1.81 \text{ (ionic strength } \mu = 0,\ 25^\circ\mathrm{C})$$

$$\log k_1 = 1.9 \text{ (ionic strength } \mu = 0.4\text{—}1.0,\ 18\text{—}25^\circ\mathrm{C}) \qquad (2)$$

The equilibrium constants of the substitution reaction (2) are seen to rise only slightly with an increase in the ionic strength, whereas that of (1) exhibits a remarkable increase. This shows that, in higher ionic strengths, phthalatocopper(II) complexes can, in general, be more easily prepared from copper(II) sulfate than from the copper(II) acetate. In addition, although the solubility of a complex may also affect the formation of crystals, there are no available evidence to explain it.

In short, the best conditions for the preparation of a phthalatocopper(II) complex with a subnormal magnetic moment are the use of copper(II) sulfate pentahydrate as the starting material at a high temperature and a high ionic strength.

Thermal Decomposition. Complex I loses one mole of water by gradual heating up to 210°C (Weight loss found, 7.25%; calculated, 7.33%). The product is complex IV, as has been described

TABLE 1. THE LOWER CRITICAL TEMPERATURES FOR THE CRYSTALLIZATION OF THE COMPLEXES I, II AND III (°C)

Starting material	$[\mathrm{Cu\,ph(H_2O)}]$ (I)	$[\mathrm{Cu(Hph)_2(H_2O)_2}]$ (II)	$[\mathrm{Cu\,ph}]$ (III)
$\mathrm{CuSO_4 \cdot 5H_2O}$	60—79	<60	>79
$\mathrm{Cu(CH_3COO)_2 \cdot H_2O}$	<98	—	>98

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*3 The formation constants desired, log k_1, are:
$[\mathrm{CuSO_4(H_2O)_4}]$,
2.35 (μ=0, 25°C),30) 0.95 (μ=1.0, 20°C)31)
$[\mathrm{Cu(CH_3COO)(H_2O)_5}^+]$,
2.24 (μ=0, 25°C),32) 1.67 (μ=1.0, 20°C)33)
$[\mathrm{Cu\ ph(H_2O)_4}]$,
4.06 (μ=0, 25°C),34) 3.55 (μ=0.4, 18—25°C)20)

30) B. B. Owen and R. W. Gurry, *J. Am. Chem. Soc.*, **60**, 3074 (1938).

31) S. Fronaeous, *Acta Chem. Scand.*, **4**, 72 (1950).

32) M. Lloyd, V. Wycherley and C. B. Monk, *J. Chem. Soc.*, **1951**, 1786.

33) S. Fronaeous, Doctoral Diss., Lund, 1948.

34) J. M. Peacock and J. C. James, *J. Chem. Soc.*, **1951**, 2233.

Table 2. Infrared absorption spectra (cm^{-1})

I	II	III	IV	V
3400 (m)	3400 (m)	—	—	—
1670 (m)	1668 (m)	1614 (m)	1614 (m)	1614 (m)
1550 (m)	1562 (m)	1559 (m)	1559 (m)	1559 (m)

Table 3. Magnetic susceptibility and magnetic moment

	I	II	III	IV	V
$\chi_g \times 10^{-6}$	5.48	3.25	3.96	3.91	3.82
μ_{eff} (B. M.)	1.87	1.96	1.54	1.54	1.51
	(21.5°C)	(21.5°C)	(18.4°C)	(21.5°C)	(18.8°C)

above. Complex II loses one mole of water and one mole of phthalate ions at the same time up to 210°C (Weight loss found, 46.58%; calculated, 47.05%). The product is complex V.

Infrared Spectra. The wave numbers of the infrared absoption spectra found in the range of C=O and O–H stretching vibrations are listed in Table 2. It is found that the band of the C=O stretching vibration in the dehydration products IV (from I) and V (from II) are observed at wave numbers closely analogous to those of the complex III. It may also be noted that the band near 3400cm^{-1} observed in I and II is not detected in complexes III and their thermal decomposition products, IV and V. Hence, the polymerization accompanying dehydration presumably occurs by means of thermal decomposition.

Electrical Conductivity. The molar conductivity of the complex II is 129 ohm^{-1} mol^{-1} at 1.0×10^{-3} mol/*l*, and the pH of this solution is 3.4. These facts support the idea that the complex II contains hydrogen phthalate ions, which are capable of releasing hydrogen ions in an aqueous solution. Since the solubility of the other complexes are very small, the electrical conductivity could not be measured.

Magnetic Susceptibility. The magnetic susceptibility and the magnetic moment are shown in Table 3. It may be found in the table that the complexes I and II have normal magnetic moments of the spin-only value, whereas the complexes III, IV and V have subnormal magnetic moments, as expected. This suggests that the complexes I and II have a monomer structure, while III, IV and V have a dimer structure.

Reflection Spectra. The reflection spectra of the complexes I—V are shown in Fig. 1. As may be seen in this figure, the absorption bands are found at 638 mμ (d—d transition band) and 290 mμ (presumably the charge-transfer band). On the other hand, the bands of III appear near 670 and 290 mμ, and the shoulder is recognized near 370 mμ, as has, in general, been observed in copper(II) complexes including the Cu—Cu interaction.(35) It is also interesting that the thermal decomposition products IV (from I) and V (from II) have shoulders near 370 mμ similar to III.

The trend toward band splitting near 638—670 mμ is also observed in I and II. It may be explained by the fact that the complexes I and II have a rather square planar symmetry, while III—V have a rather octahedral symmetry from the viewpoints of the crystal field and the molecular orbital scheme.(36,37)

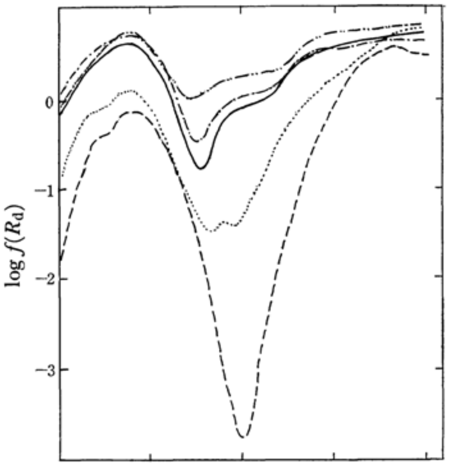

Fig. 1. Reflection spectra of copper(II) phthalato complexes.
······ complex I, ---- complex II
—— complex III
-·-·- thermal decomposition product IV
-··-·· thermal decomposition product V

$$f(R_d) = \frac{(1-R_d)^2}{2R_d}, \quad R_d\text{: relative reflection index}$$

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(35) S. Yamada, H. Nakamura and R. Tsuchida, This Bulletin, **30**, 953 (1957).
(36) O. G. Holmes and D. S. McClure, *J. Chem. Phys.*, **26**, 1686 (1957).
(37) L. S. Forster and C. J. Ballhausen, *Acta Chem. Scand.*, **16**, 1385 (1962).

TABLE 4. RESULTS OF X-RAY DIFFRACTION ANALYSIS

Complexes	I	II	III
Crystal system	Hexagonal	Hexagonal	Hexagonal
Axial parameter *a* (Å)	13.07	11.42	12.77
c (Å)	13.98	13.68	13.02
Chemical unit *Z*	8	4	4

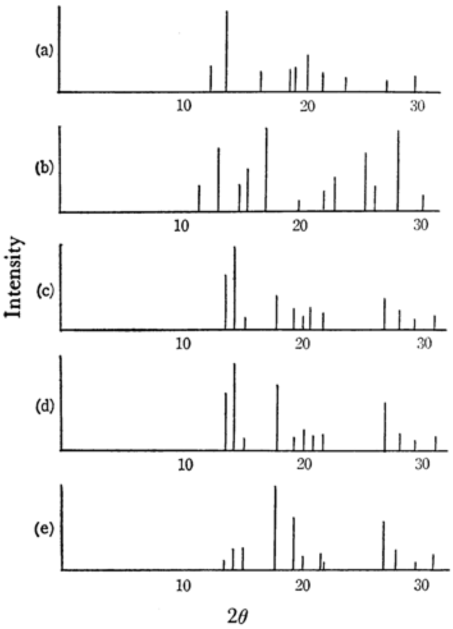

Fig. 2. X-Ray diffraction patterns.
(a) complex I, (b) complex II,
(c) complex III
(d) thermal decomposition product IV
(e) thermal decomposition product IV

X-Ray Powder Method. In order to study whether the thermal decomposition products IV (from I) and V (from II) are completely identical with III, the X-ray powder diffraction method was applied to the related complexes, I—V. The patterns are shown in Fig. 2. The results of the X-ray analysis of I, II and III are summarized in Table 4.

The complexes I, II and III are light blue, blue, and bluish-green respectively, and their X-ray patterns are different from each other. On the other hand, the patterns of IV and V are in good agreement with that of III, though the intensities of a few diffraction lines are somewhat abnormal, as is shown in Fig. 2 and Table 4.

Summary

1) The preparation of the copper(II) complex with phthalic acid which has a subnormal magnetic moment was accomplished at a high temperature and a high concentration in an aqueous solution. It is presumed to have a dimer structure with respect to the two adjacent copper atoms. Its chemical formula is [Cu ph] (I). The related complexes, [Cu ph(H_2O)] (II) and [Cu(Hph)$_2$(H_2O)$_2$] (III), were also prepared.

2) The chemical composition of these complexes were discussed on the basis of the information gathered from spectroscopic measurements, and a study of the thermal decomposition and the electrical conductivity.

3) It was also found that the thermal decomposition of I and II gave the complex III. This was validated by the magentic susceptibility, the reflection spectra, and the results of the X-ray powder diffraction analysis.

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