

단 신

Copper(II) Acetate Amide 착물의 합성 및 분석

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Preparation and Analysis of Copper(II) Acetate Amide Complexes

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This work relates to binuclear carboxylate-bridged complexes $M_2(RCOO)_4 \cdot L_2$ ($M=Mo^{II}$, Cr^{II} , W^{II} , Rh^{II} , or Cu^{II}). The work by Larworthy and Tabatabai¹ on the chromium acetate binuclear structure showed that the carboxylate dimer structure is destroyed by the addition of ammonia. The physicochemical behaviour of chromium(II) and copper(II) compounds are well established and structural and magnetic similarities exist between them.² The peculiar differences between these two compounds as follows: i) Chromium(II) complexes, especially in solution, are very rapidly oxidized by air, and this property restricts synthesis.^{3a} ii) The copper(II) oxidation state is not only the most stable of all the states (0 to IV), but is also the most prolific in the formation of complexes.^{3b}

Therefore, this work has two aims. Firstly, it is to examine whether the dimeric structure of copper(II) acetate would be destroyed by the reaction with amides. Secondly, if the dimeric structures would retain, then it is to find out whether the copper(II) acetate amide complexes are the nitrogen-bonded or the oxygen-bonded. For the interaction with a metal ion, the amide can coordinate either through the nitrogen atom of the NH_2 group or through the oxygen atom of the $C=O$ group.^{4,5} Formamide complex with nitrogen bonded to pentaaminocobalt(III) has been reported by Balahura and Jodan.⁶ An oxygen-bonded amide complex was reported by Lees *et al.*^{7,8}

EXPERIMENTAL

Copper(II) acetate monohydrate was obtained from Aldrich Chemical Co. and used without further purification. Formamide (FA), N-methylformamide (NMF), and N,N-dimethylformamide (DMF) were also supplied by Aldrich Chemical Co. Amides were stored over 3Å molecular sieves and purified by the method described in reference 9. Melting points were determined on a Gallenkamp melting point apparatus and were uncorrected. Elemental analysis were carried out using a Carlo-Erba 1106 Elemental Analyser.

Preparation of copper(II) acetate FA dimer complex. A solution of copper acetate monohydrate dimer (2.0 g, 20 mmol) in FA (20.0 mL) was stirred vigorously for 6 h at room temperature under a nitrogen atmosphere. The precipitates were collected by filtration and washed with ether (20 mL). $Cu_2(CH_3COO)_4 \cdot 2FA$ was obtained in 88.7% yield (2.10 g) as a greenish blue powder. mp: 214~215 °C. Anal. Calcd. for $C_{10}H_{18}N_2O_{10}Cu_2$: C, 26.55; H, 3.98; N, 6.19. Found: C, 26.35; H, 3.77; N, 6.11.

Preparation of copper(II) acetate NMF dimer complex. The complex was prepared by the same method as for the FA dimer. $Cu_2(CH_3COO)_4 \cdot 2NMF$ was obtained in 79.4% yield (1.91 g) as a greenish blue powder (a little darker than the FA dimer). mp: 249~250 °C. Anal. Calcd. for $C_{12}H_{22}N_2O_{10}Cu_2$: C, 29.93; H, 4.57; N, 5.82. Found: C, 29.64;

H, 4.38; N, 5.98.

Instrumentals. Solid state diffuse reflectance visible spectra were recorded in the range 200-800 nm using an integrating sphere diffuse reflectance attachment on the P-E 550 spectrophotometer (barium sulphate reference) fitted with a Pye-Unican SP 890 diffuse reflectance accessory. Magnetic measurements were carried out by the Gouy method on an apparatus obtained from JMC Equipment Division. Infrared spectra were recorded on a Perkin-Elmer 598 spectrophotometer.

RESULTS AND DISCUSSION

Solid Diffuse Reflectance Spectra. The solid diffuse reflectance spectra consist of three characteristic peaks which correspond to those of copper(II) acetate: the bands at 700, 375 and 300 nm. Table 1 shows the data obtained from the diffuse reflectance spectra. Yamada *et al.*¹⁰ stated that the band at 700 nm is due to the normal metal-ligand interaction, and the band at 300 nm is due to the coordinated acetate groups. Tsuchida and Yamada¹¹ has assumed that the copper-to-copper linkage in the copper(II) dimer appears at 375 nm. These assignments have been confirmed further in their later work¹⁰ for the copper(II) propionate monohydrate. Bukowska-Strazyszewska *et al.*¹² reported that the band at 380 nm in tetrakis(μ -crotonate) bis(quinoline)dycopper(II) is due to the $d-d$ transition, $(d_{xz}, d_{yz}) \rightarrow (d_{x^2-y^2})$. Therefore, the bands at 370 nm and 371 nm shown in Table 1 should be based on the copper-to-copper bond. This is different from that of a typical copper(II) compound which shows only two peaks: one in the visible region and the other in the UV region.²

Infrared Spectra. The frequencies of the acetate groups are almost identical to the corre-

sponding groups in the copper acetate hydrate. The notable shifted frequencies are: ν_{NH} (3375, 3235 cm^{-1}); ν_{CH} (2924 cm^{-1}); ρ_{NH_2} (1053 cm^{-1}); $\nu_{\text{Cu-O}}$ (355 cm^{-1}) for $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{FA}$ and ν_{NH} (3353 cm^{-1}); ν_{CH} (2911 cm^{-1}); ρ_{NH} (670 cm^{-1}); ρ_{CN} (366 cm^{-1}) for $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{NMF}$. The above assignments have been made on the basis of the published ones.^{2,13-15} If we assume that the Cu (II) interacts with the oxygen of the amide, the C-N distance of amide will shorten and consequently the amide frequencies will increase. On the other hand, if the Cu(II) interacts with the nitrogen of the amide, the free rotation of the pyramid would exist about the C-N single bond,¹⁵ and then the C-N distance will be lengthened and the frequency will shift towards lower frequencies. The IR data show that the N-H and C-H stretching modes with the C-N twist mode are shifted to higher frequencies while the N-H and NH_2 rocking modes are shifted towards lower frequencies.

Magnetic Moment. Copper(II) acetate monohydrate with its subnormal magnetic moment is a dimeric molecule containing two copper ions. The effective magnetic moment, μ_{eff} , can be calculated by use of the formula.²

$$\mu_{\text{eff}} = 2.829(\chi_a T)^{\frac{1}{2}} \quad (1)$$

where, χ_a is the magnetic susceptibility per copper (II) ion corrected for the diamagnetic nonmetal part of the molecule. The values of diamagnetic susceptibility for corrections were obtained from Emsley *et al.*¹⁶ Unfortunately, the magnetic susceptibility of NMF could not be found in the literature. Therefore, the magnetic susceptibility of N-methylformamide was measured at room temperature and the value (22.553×10^{-6} cgs, emu) was obtained.

The values of μ_{eff} obtained from the above

Table 1. The data obtained from the reflectance spectra

	$\text{Cu}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$			$\text{Cu}_2(\text{OAc})_4 \cdot 2\text{FA}$			$\text{Cu}_2(\text{OAc})_4 \cdot 2\text{NMF}$		
λ (nm)	694	369	292	694	370	292	690	371	292
ν (cm^{-1})	14409	27100	34247	14409	27027	34247	14451	26954	34247
E (kJ.Mol)	171.5	322.5	480.5	171.5	321.6	407.5	172.0	320.8	407.5

Table 2. Magnetic properties of copper(II) compounds

Compound	$\chi_g \times 10^{-6}$	$\chi_a \times 10^{-6}$	μ_{eff}
	cgs, emu	cgs, emu	B.M
$\text{Cu}_2(\text{OAc})_4 \cdot 2\text{H}_2\text{O}$	4.066	1790.3	2.065, 2.04*
$\text{Cu}_2(\text{OAc})_4 \cdot 2\text{FA}$	2.790	1448.5	1.858
$\text{Cu}_2(\text{OAc})_4 \cdot 2\text{NMF}$	2.942	1602.3	1.954

*Data from Ref.7

formula (Eq. 1) are given in Table 2. As shown in Table 2, they are not significantly different from the corresponding values, μ_{eff} of Cu(II) 1.8-2.1 B.M², in the copper(II) acetate dimer. However, the values of the two products are lower than that of the copper acetate dihydrate. The magnetic interaction is affected by the nature of the attached ligand. The bulky ligands of the amides can supply less electron density to the central copper ions.² Therefore, the values shown in Table 2 are fairly reasonable on this assumption. The value for $\text{Cu}_2(\text{CH}_3\text{COO})_4 \cdot 2\text{H}_2\text{O}$ is in excellent agreement with that of Jotham and Kettle.¹⁷

The results suggest that the copper(II) acetate amides have been obtained and their structures seem to be dimeric. The solid diffuse reflectance spectra give strong evidence for the dimeric structures. In the copper(II) acetate amides, three bands based on copper-to-copper bond have been observed whereas typical Cu(II) compounds show only two peaks. The results of vibrational studies also give the evidence that the copper(II) acetate amide complexes are oxygen-bonded. In other words, both amides are coordinated *via* their oxygen atom to the copper(II) ion. The magnetic susceptibility of N-methylformamide at room temperature is 22.553×10^{-6} cgs, emu.

However, we were unable to synthesize the copper acetate DMF dimer by using the same method as for FA and NMF complexes.

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