

# ESR STUDY OF COPPER(II) DIMERS

Ikuo SUZUKI

*Department of Electrical and Computer Engineering*

(Received August 17, 1989)

The ESR spectrum at room temperature of  $[\text{Cu}(\text{CCl}_3\text{COO})_2(\text{caf})]_2$  (pale green form) differed from the spectra of  $[\text{Cu}(\text{CCl}_3\text{COO})_2(\text{caf})]_2$  benzene and  $[\text{Cu}(\text{CCl}_3\text{COO})_2(\text{caf})]_2$  (light green form), possibly indicating trigonal bipyramidal coordination to Cu(II). The temperature dependence of the ESR spectrum was observed for the crystal  $[\text{Cu}(\text{ph}_3\text{CCOO})_2(\text{py})]_2$  benzene, which has a trigonal bipyramidal coordination.

## 1. INTRODUCTION

There are many investigations for copper(II) carboxylate dimers. The first measurement of ESR spectra were performed by Bleaney and Bowers.<sup>1)</sup> The variable-temperature magnetic susceptibility of copper(II) acetate monohydrate was measured by Figgis and Martin.<sup>2)</sup> The unusual cage-type dimeric structure of this crystal with a Cu-Cu distance of 2.64 Å had been determined by van Niekerk and Schening.<sup>3,4)</sup> Magnetic susceptibility data for copper(II) dimers, with a pair of interaction ions of spin 1/2, are widely known to fit the modified Bleaney-Bowers equation<sup>5)</sup>

$$\chi_A = \frac{Ng^2\beta^2}{3kT} \left[ 1 + \left( \frac{1}{3} \right) \exp(-2J/kT) \right]^{-1} (1-P) + \frac{Ng_i^2\beta^2}{4kT} P + N\alpha$$

where  $A$  is the paramagnetic susceptibility per metal atom after the coreaction for diamagnetism,  $P$  the mole fraction of the monomeric copper(II) impurities,  $g_i$  the average  $g$  factor of the impurity, and  $-2J$  the singlet-triplet separation.  $N\alpha$  is the temperature-independent paramagnetism.

The recent structural studies on dimeric copper(II) carboxylate adducts,  $[\text{Cu}(\text{RCOO})_2\text{L}]_2$ , have shown that the metal-metal distance becomes longer as either the acidity of the parent carboxylic acid,  $\text{RCOOH}$ , or the basicity of the axial ligand,  $\text{L}$ , becomes greater.<sup>6)</sup> A greater Cu-Cu distance is usually associated with a longer displacement of the copper(II) ions from the equatorial plane containing four oxygen atoms. So the variations of both the group  $\text{R}$  and the ligand  $\text{L}$  affect the strength of the Cu

-O bonds in the  $\text{CuO}_4$  plane with an accompanying deformation of the bridging framework. Dimeric copper(II) trichloroacetate adducts were used for the study of the structural factors influencing magnetic properties. Recently, we observed the temperature dependence of the ESR spectra for the crystal  $[\text{Cu}(\text{ph}_3\text{CCOO})_2]$  gamma-picoline, although the crystal structure were determined as the axial ligand. In this paper we discuss the ESR studies of the copper(II) dimers studied with N. Kato et al.<sup>7-10)</sup>

## 2. EXPERIMENTAL

Polycrystalline powder ESR spectra were recorded on a JEOL JESME-2 spectrometer in the X-band range. The temperature dependence spectra were taken from the room temperature to liquid nitrogen temperature by the liquid nitrogen gas flow method.

Six samples were prepared. (1)  $[\text{Cu}(\text{CCl}_3\text{COO})_2(\text{caf})]_2$  (2bz), which were synthesized by adding two solutions of caffeine in benzene and  $\text{Cu}(\text{CCl}_3\text{COO})_2 \cdot 3\text{H}_2\text{O}$  in benzene and 2,2-dimethoxypropane, (2)  $[\text{Cu}(\text{CCl}_3\text{COO})_2(\text{caf})]_2$  (light green form) and (3)  $[\text{Cu}(\text{CCl}_3\text{COO})_2(\text{caf})]_2$  (pale green form). These compounds were prepared in the same way as (1), using toluene instead of benzene. Other three crystals were  $[\text{Cu}(\text{ph}_3\text{CCOO})_2\text{gamma-pic}]_2$  (bz) and  $[\dots]$  toluene.

## 3. CRYSTAL STRUCTURE

Dimeric copper(II) carboxylate adducts have the structure shown in Fig. 1. It has been pointed out that the antiferromagnetic interaction in  $[\text{Cu}(\text{RCOO})_2\text{L}]_2$  tends to increase as either the axial ligand  $\text{L}$  or the carboxylate substituent  $\text{R}$  becomes a

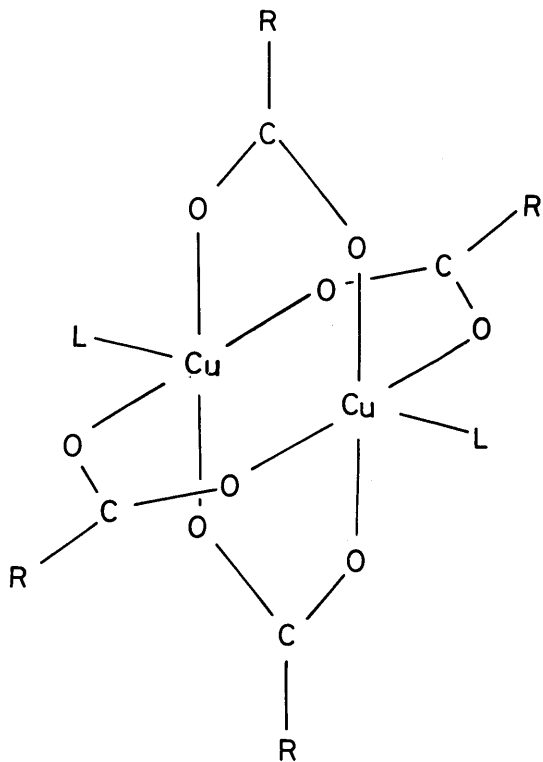


Fig. 1 Molecular structure of  $[\text{Cu}(\text{RCOO})_2\text{L}]_2$ .

stronger electron donor. The singlet-triplet separation ( $-2J$ ) is expected to increase as the  $pK_a$  of L becomes higher. In dimeric copper(II) carboxylate adducts,  $[\text{Cu}(\text{RCOO})_2\text{L}]_2$ , when the L-Cu donation becomes weaker, the covalent Cu-O bonds in the  $\text{CuO}_4$  basal plane becomes stronger to maintain the electroneutrality. For the mechanism of the magnetic interaction in dimeric copper(II) carboxylates, experimental evidence shows that the spin coupling between the unpaired electrons of copper(II) ions operates predominantly by a superexchange interaction through the bridging carboxylate ligand rather than by direct Cu-Cu interaction. Accordingly the magnetic interaction will become stronger as the Cu-O bonds become stronger. From these experimental results, Kato et al. concluded that the antiferromagnetic interaction in dimeric copper(II) carboxylate adducts should become stronger.<sup>7)</sup> However Hibdon and Nelson have reported that the antiferromagnetic interaction in a series of dimeric copper(II) acetate adducts with 4-substituted pyridine N-oxides becomes stronger as the  $\pi$ -band-donation

from the metal ion to the axial ligand increases.<sup>11)</sup>

The recent structural studies on dimeric copper(II) carboxylate adducts,  $[\text{Cu}(\text{RCOO})_2\text{L}]_2$ , have demonstrated that the metal-metal distance becomes longer as either the acidity of the axial ligand L becomes stronger. Therefore a larger Cu-Cu distance is usually associated with a greater displacement of the metal ion from the equatorial plane composed of four oxygen atoms. Therefore, by the coordination environment around each copper(II) ion the square pyramidal form changes to the trigonal bipyramidal. (Fig. 2) These structural data show that, for a variation in L, the binding acetate ligand does.

#### 4. RESULTS AND DISCUSSION

Each copper atom has a distorted, square pyramidal coordination sphere with four coplanar oxygen atoms. The ESR spectral features of (3) are quite different from the room temperature spectra of (1) and (2) (Fig. 3). They are fundamentally the same as those observed for  $[\text{Cu}(\text{CPh}_3\text{COO})_2(\text{py})]_2$  (bz); ( $-2J = 184 \text{ cm}^{-1}$ , Cu-Cu =  $3.086 \text{ \AA}$ ), whose structure has recently been determined by Steward et al. and found to have a trigonal-bipyramidal metal geometry.<sup>12)</sup> For these complexes, an unfamiliar relation  $D < H_0$ , was observed, and this relation has been revealed for a number of copper(II) trichloroacetate adducts

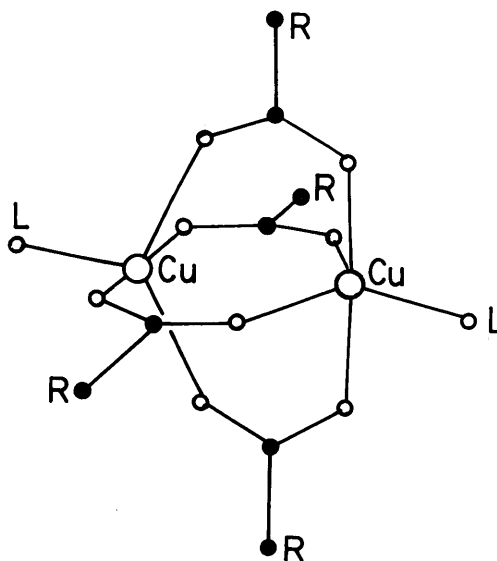


Fig. 2 Trigonal bipyramidal structure.

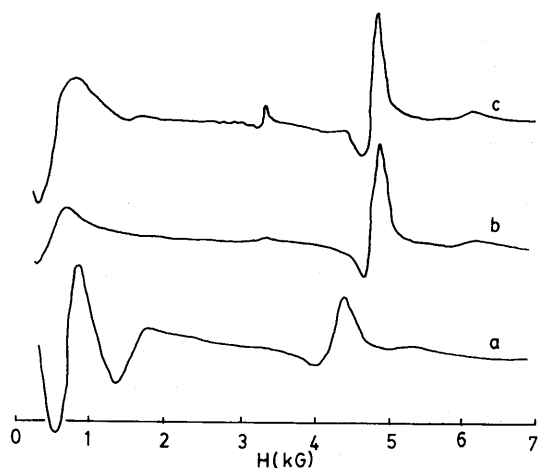


Fig. 3 Room temperature polycrystalline powder ESR spectra at X-band frequency. (a)Pale green form of  $[\text{Cu}(\text{CCl}_3\text{COO})_2(\text{caf})]_2$ , (3). (b) Light green form of  $[\text{Cu}(\text{CCl}_3\text{COO})_2(\text{caf})]_2$ , (2). (c) $[\text{Cu}(\text{CCl}_3\text{COO})_2(\text{caf})]_2$ (2bz), (1).



Fig. 4 X-band polycrystalline powder ESR spectra of  $[\text{Cu}(\text{CCl}_3\text{COO})_2(\text{caf})]_2$  (2bz), (1), at room temperature(RT) and liquid nitrogen temperature(77K).

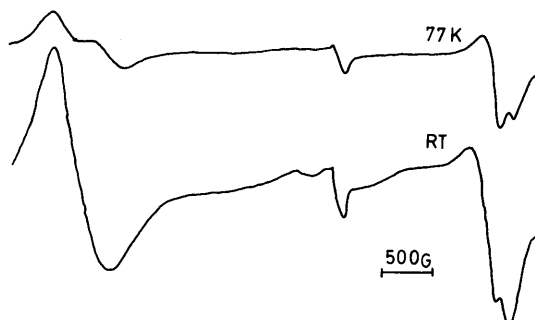


Fig. 5 X-band powder ESR spectra of  $[\text{Cu}(\text{Ph}_3\text{CCOO})_2(\text{py})]_2$ .

whereas  $-2J$  values are quite small compared with those of the common copper(II) carboxylates which have square-pyramidal metal geometry and obey the common relation  $D > H_0$ .

Temperature variation ESR measurements showed that the ESR spectral features of (1) at liquid nitrogen temperature were quite different from those at room temperature.(Fig. 4) The low temperature ESR spectrum shows essentially the same as the room temperature ESR spectrum of (3) accompanying the uncommon relation,  $D < H_0$ . The spectral interconversion accompanied by  $D > H_0$  thus takes place reversibly. This interesting finding prompted us to attempt a low temperature structural study of (1). However, the crystals cracked upon cooling and were unstable for an X-ray crystallographic investigation. From the magnetic data above it may be speculated that the structural of (3) perhaps has the copper atoms in a trigonal-bipyramidal environment, and from the ESR data one may guess at the possibility of such an environment also for the low-temperature form of (1). The  $g$  values obtained by ESR are shown in Table 1.

Recently, the unusual magnetic properties ; the unusually low value for  $-2J$ , the uncommon ESR spectra pattern, the uncommon relationship  $D < H_0$  ; of  $[\text{Cu}(\text{Ph}_3\text{CCOO})_2(\text{py})]_2$  (benzene) were observed by Steward. (Fig. 5)

The elucidation of the magneto structural correlations for copper(II) carboxylate dimers should be an important goal of modern magneto chemistry. The superexchange mechanism in those dimeric copper(II) systems is an interesting puzzle. Structural, magnetic and theoretical studies are carried out focusing the attention onto this final goal by Kato et al. and present author.

Table 1 ESR parameter.

Compound	$g_{\parallel}$	$g_{\perp}$	$g_{av}$	$D(\text{cm}^{-1})$
(1) RT	2.488	2.142	2.263	0.372
77K	2.389	2.139	2.225	0.220
(2) RT	2.468	2.109	2.235	0.366
77K	2.454	2.102	2.225	0.367
(3) RT	2.317	2.143	2.203	0.237
77K	2.305	2.152	2.204	0.223

## REFERENCES

- 1) B. Bleaney and K. D. Bowers, Proc. Roy. Soc. London **A214**(1952) 451.
- 2) B. N. Figgis and R. L. Martin, J. Chem. Soc. (1956) 3837.
- 3) J. N. van Niekerk and F. R. L. Schoening, Nature (London) **171** (1953) 36.
- 4) J. N. van Niekerk and F. R. L. Schening, Acta Cryst. **6** (1953) 227.
- 5) K. E. Hyde, G. Gordon and G. F. Kckoszka, J. Inorg. Nucl. Chem. **30** (1968) 2155.
- 6) V. M. Rao, D. N. Sathyanarayana and H. Mar-nobar, J. Chem. Soc. A (1969) 6464.
- 7) M. Kato and Y. Muto, Coord. Chem. Rev. **92**(1988) 45.
- 8) H. Horie, S. Hasebye, M. Kato, E. A. Meyers, Y. Muto, I. Suzuki, T. Tokii and R. A. Zingaro, Acta Chem. Scand. **A40** (1986) 579.
- 9) Y. Muto, N. Hirashima, T. Tokii, M. Kato and I. Suzuki, Bull. Chem. Soc. Jpn. **59** (1986) 3672.
- 10) Y. Muto, M. Nakashima, T. Tokii, M. Kato and I. Suzuki, Bull. Chem. Soc. Jpn. **60** (1987)2849.
- 11) D. Hibdon and J. H. Nelson, Inorg. Chim. Acta **7** (1973) 629.
- 12) O. W. Steward, M. Kato, S. C. Chang, M. Sax, C. H. Chang, T. Tawura, C. F. Jary, Y. Muto, T. Tokii, J. Pletcher and C. S. Yoo, Proc. 23rd *Int. Conf. Coord. Chem.* Boulder, CO. USA, July 29 -August 3, 1984, p. 247.