May, 1983] © *1983 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, ***56***, *1549—1550 (1983)* 1549

Dimeric Copper(II) Acetate Complexes of Thiazoles and Oxazoles

Tadashi Tokii and Yoneichiro Muto*

Department of Chemistry, Faculty of Science and Engineering, Saga University, Saga 840

(Received October 18, 1982)

Synopsis. Copper(II) acetate monoadducts, Cu($CH_3COO)_2\cdot L$ (L = thiazole, benzothiazole, benzoxazole, 2-methylbenzothiazole, 2-methylbenzoxazole, 2,4-dimethylthiazole, or 2,4,5-trimethylthiazole) were prepared, and they all show antiferromangnetism ($-2J = 318$—$344\ \mathrm{cm}^{-1}$) of copper(II) dimer type. The variation in magnetic interaction with the steric nature of the ligand, L, is discussed.

The recent X-ray studies on dimeric copper(II) carboxylate adducts with pyridine analogues have demonstrated that ortho-substituents in the pyridine ring of the ligands make copper atoms displace out of the plane of the four carboxylate-oxygen atoms toward the nitrogen atom by the mutual repulsion between the substituents and the oxygen atoms.[1,2] Under such conditions the steric effect is expected to enhance the metal–metal distance; in fact, the Cu–Cu distance in dimeric copper(II) acetate adducts with pyridine (py), quinoline (quin), and 2-picoline (2-pic) increases in the order, py (2.630 Å)[3] < quin (2.652 Å)[1] < 2-pic (2.671 Å),[4] as expected from the effectiveness of the steric effect. However, no significant correlation has been observed between the Cu–Cu distance and the magnitude of the singlet-triplet separation ($-2J$) in these adducts. In this work we prepared seven copper(II) acetate adducts, $Cu(CH_3COO)_2\cdot L$, where L = thiazole (tz), benzothiazole (btz), benzoxazole (boz), 2-methylbenzothiazole (2-mbtz), 2-methylbenzoxazole (2-mboz), 2,4-dimethylthiazole (2,4-dmtz) or 2,4,5-trimethyloxazole (2,4,5-tmoz), and measured their magnetic susceptibilities as a function of temperature in order to obtain information on the effect of the ortho-substituents in L upon the magnetic interaction.

Experimental

Synthesis. A typical synthetic method is as follows. A solution of the ligand L (5 mmol) in ethanol (5 ml) was added to a solution of $Cu(CH_3COO)_2\cdot H_2O$ (5 mmol) in ethanol (30 ml). After keeping the solution overnight at *ca.* 5 °C in a freezer, the separated green crystals were collected, washed with ethanol and dried at *ca.* 60 °C. **1.** $Cu(CH_3COO)_2\cdot$(tz). Found: C, 31.66; H, 3.57; N, 5.05; Cu, 23.69%. Calcd for $C_7H_9NO_4SCu$: C, 31.52; H, 3.40; N, 5.25; Cu, 23.82%. **2.** $Cu(CH_3COO)_2\cdot$(btz). Found: C, 41.66; H, 3.70; N, 4.34; Cu, 20.01%. Calcd for $C_{11}H_{11}NO_4SCu$: C, 41.70; H, 3.50; N, 4.42; Cu, 20.06%. **3.** $Cu(CH_3COO)_2\cdot$(boz). Found: C, 43.80; H, 3.84; N, 4.45; Cu, 21.03%. Calcd for $C_{11}H_{11}NO_5Cu$: C, 43.93; H, 3.69; N, 4.66; Cu, 21.13%. **4.** $Cu(CH_3COO)_2\cdot$(2-mbtz). Found: C, 43.43; H, 3.95; N, 4.16; Cu, 19.22%. Calcd for $C_{12}H_{13}NO_4SCu$: C, 43.57; H, 3.96; N, 4.23; Cu, 19.21%. **5.** $Cu(CH_3COO)_2\cdot$(2-mboz). Found: C, 45.65; H, 4.12; N, 4.46; Cu, 20.26%. Calcd for $C_{12}H_{13}NO_5Cu$: C, 45.79; H, 4.16; N, 4.45; Cu, 20.19%. **6.** $Cu(CH_3COO)_2\cdot$(2,4-dmtz). Found: C, 36.87; H, 4.50; N, 4.67; Cu, 21.71%. Calcd for $C_9H_{13}NO_4SCu$: C, 36.67; H, 4.44; N, 4.75; Cu, 21.55%. **7.** $Cu(CH_3COO)_2\cdot$(2,4,5-tmoz). Found: C, 40.90; H, 5.10; N, 4.73; Cu, 21.65%. Calcd for $C_{10}H_{15}NO_5Cu$: C, 41.02; H, 5.16; N, 4.78; Cu, 21.70%.

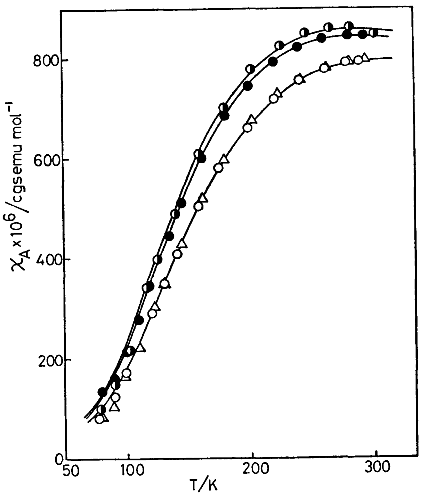

Fig. 1. Variation of magnetic susceptibilities with temperature.
△: $Cu(CH_3COO)_2\cdot$(tz), ○: $Cu(CH_3COO)_2\cdot$(btz), ◑: $Cu(CH_3COO)_2\cdot$(2-mbtz), ●: $Cu(CH_3COO)_2\cdot$(2,4-dmtz).
The solid curves were obtained as described in the text.

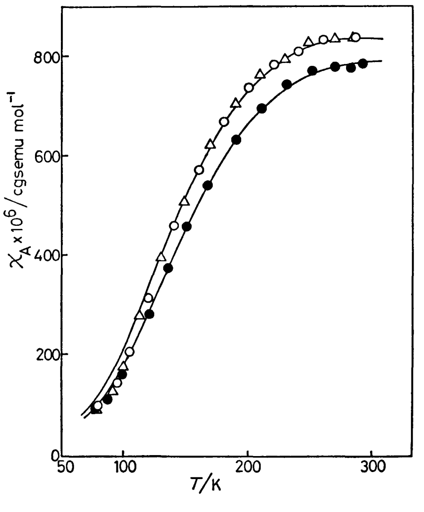

Fig. 2. Variation of magnetic susceptibilities with temperature.
●: $Cu(CH_3COO)_2\cdot$(boz), ○: $Cu(CH_3COO)_2\cdot$(2-mboz), △: $Cu(CH_3COO)_2\cdot$(2,4,5-tmoz).
The solid curves were obtained as described in the text.

Physical Measurement. Magnetic susceptibilities in the temperature range of 80—300 K were determined by the Gouy method. The correction for diamagnetic contributions was made by the use of Pascal's constant.[5] The cryomagnetic data are shown in Figs. 1 and 2 as plots of

Table 1. Magnetic data

	Complex	g	$-2J/\mathrm{cm}^{-1}$
1	$Cu(CH_3COO)_2\cdot$(tz)	2.20	344
2	$Cu(CH_3COO)_2\cdot$(btz)	2.20	344
3	$Cu(CH_3COO)_2\cdot$(boz)	2.19	344
4	$Cu(CH_3COO)_2\cdot$(2-mbtz)	2.20	318
5	$Cu(CH_3COO)_2\cdot$(2-mboz)	2.20	327
6	$Cu(CH_3COO)_2\cdot$(2,4-dmtz)	2.20	322
7	$Cu(CH_3COO)_2\cdot$(2,4,5-tmoz)	2.20	327

the corrected molar magnetic susceptibility (χ_A) *vs.* the temperature (T).

Results and Discussion

Complexes **1**—**7** were readily isolated by the reaction of $Cu(CH_3COO)_2\cdot H_2O$ with the ligand in ethanol. However, under the similar conditions no adduct formation was observed between copper(II) acetate and benzo[*b*]thiophene or benzofuran. This finding indicates that the nitrogen atom in the ligand L is most probably the donor atom.

The variable-temperature magnetic susceptibility data were analyzed by the Bleaney-Bowers equation,

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

where each symbol has the usual meaning. As can be seen in Figs. 1 and 2, the thermal magnetic data are well represented by Eq. 1. The g and $-2J$ values listed in Table 1 were evaluated from the best-fit of the experimental data to Eq. 1, assuming $N\alpha = 60 \times 10^{-6}$ cgs emu mol^{-1} (1 cgs emu mol^{-1}=$4\pi\times10^{-6}$ m^3 mol^{-1}). On the basis of the magnetic behavior, a dimeric structure similar to that found in copper(II) acetate monohydrate can be assigned for the present acetate complexes.

Coordination of thiazole, benzothiazole or benzoxazole to the dimeric copper(II) acetate units will cause an increase in antiferromagnetic interaction as is seen in the $-2J$ value of the adducts, 344 cm^{-1}, a value somewhat larger than those reported for the well-characterized dimeric copper(II) acetate adducts (284—325 cm^{-1}).(6) It is also noted that the $-2J$ value of complex **2** is just the same as that of complex **1**; this suggests that the steric nature of the adjacent benzo group in benzothiazole does not exert any appreciable effect upon the magnitude of $-2J$. This observation is in accord with the fact that the $-2J$ of 320 cm^{-1} determined for $[Cu(CH_3COO)_2\cdot \mathrm{quin}]_2$ is practically identical with that of 325 cm^{-1} found for $[Cu(CH_3COO)_2\cdot \mathrm{py}]_2$.(6) On the other hand, the $-2J$ values for complexes **4**—**7** were found to fall in a rather low range of 318—327 cm^{-1}. For the mechanism of the magnetic interaction in dimeric copper(II) carboxylates, two models have been proposed: Cu–Cu direct exchange interaction, and superexchange interaction through the bridging carboxylato groups. The predominance of the latter mechanism has been recognized by some experimental evidence,(6–9) but it has also been suggested that the effect of the former interaction is not entirely negligible.(10) The direct interaction would be expected to decrease with increasing Cu–Cu separation, whereas the superexchange interaction may be affected by such structural features as the distances and angles within the Cu–O–C–O–Cu bridge and the geometry around the metal atom. In the present adducts, $Cu(CH_3COO)_2\cdot L$, the presence of methyl group at the 2-position of thiazole- or oxazole-ring will make the Cu–Cu distance increase with the displacement of the copper atom from its basal coordination plane toward the nitrogen atom in L, and will reduce both the direct and superexchange interactions. Thus, this steric effect seems to be the main factor for the decrease in the $-2J$ values of complexes **4**—**7** by 17—26 cm^{-1} as compared with those of complexes **1**—**3**.

Finally, it should be noted that the $-2J$ of complex **1** (344 cm^{-1}) is higher than that of $[Cu(CH_3COO)_2\cdot \mathrm{py}]_2$ (325 cm^{-1}).(6) The pK_a of the terminal ligand of the former complex (2.44)(11) is lower than that of the latter (5.32).(12) We have also evaluated the $-2J$ of 341 cm^{-1} for dimeric copper(II) acetate adduct with 3,5-dichloropyridine (pK_a=0.67).(13) These facts are not in accord with the observation that, in the pyridine and picoline adducts of copper(II) propionate, the value of $-2J$ decreases as the pK_a of the terminal ligand decreases.(14) Thus, these magnetic data suggest that the $-2J$ in dimeric copper(II) carboxylate adducts is not a simple function of the base strength of the terminal ligand.

References

1) Yu. A. Simonov, V. I. Ivanov, A. V. Ablov, L. N. Mikova, and T. I. Malinovskii, *J. Struct. Chem.* (Engl. Transl.), **17**, 444 (1977).

2) J. A. Moreland and R. J. Doedens, *Inorg. Chem.*, **17**, 674 (1978).

3) G. A. Barclay and C. H. L. Kennard, *J. Chem. Soc.*, **1961**, 5244.

4) F. Pavelcik and F. Hanic, *J. Cryst. Mol. Struct.*, **8**, 59 (1978).

5) P. W. Selwood, "Magnetochemistry," Interscience Publishers, New York (1956), pp. 78 and 91.

6) R. J. Doedens, *Prog. Inorg. Chem.*, **21**, 209 (1976).

7) D. M. L. Goodgame, N. J. Hill, D. F. Marsham, A. C. Skapski, M. L. Smart, and P. G. H. Troughton, *J. Chem. Soc., Chem. Commun.*, **1969**, 629.

8) R. A. Zelonka and M. C. Baird, *Inorg. Chem.*, **11**, 134 (1972).

9) R. L. Beddoes, J. A. Connor, D. Dubowski, A. C. Jones, O. S. Mills, and R. Price, *J. Chem. Soc., Dalton Trans.*, **1979**, 781.

10) T. Asakawa, M. Inoue, K. Hara, and M. Kubo, *Bull. Chem. Soc. Jpn.*, **45**, 1054 (1972).

11) A. Albert, R. Goldacre, and J. Phillips, *J. Chem. Soc.*, **1948**, 2240.

12) G. J. Hawkins and D. D. Perrin, *J. Chem. Soc.*, **1962**, 1351.

13) T. Tokii and Y. Muto, unpublished data.

14) W. E. Marsh, G. O. Carlisle, and M. V. Hanson, *J. Inorg. Nucl. Chem.*, **39**, 1839 (1977).