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Magnetic and Spectral Properties of 3,5-Dichloropyridine Adducts of Dimeric Copper(II) Acetate, Chloroacetate, and Dichloroacetate

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Three complexes with the empirical formula of $Cu(RCOO)_2 \cdot L$, where $R=CH_3$, CH_2Cl, or $CHCl_2$ and L=3,5-dichloropyridine, were prepared and studied. These complexes display the antiferromagnetic behavior typical of dimeric copper(II) carboxylates. The singlet-triplet splitting energy ($-2J$) is 349 cm^{-1} for the acetate, 340 cm^{-1} for the monochloroacetate and 312 cm^{-1} for the dichloroacetate. Comparison of their magnetic and electronic spectral properties with those of the corresponding pyridine adducts indicates that both the $-2J$ and $\tilde{\nu}_{max}$(absorption maximum of Band I) values of the respective 3,5-dichloropyridine adducts are higher than those of the pyridine adducts. The influence of the pyridines on both the magnetic and spectral properties was discussed.

It has already been pointed out that the antiferromagnetic interaction in dimeric copper(II) carboxylate adducts, $[Cu(RCOO)_2 \cdot L]_2$ (*cf.* Fig. 1), tends to increase as either the addend ligand L or the carboxylate substituent R becomes a stronger electron donor.[1] Therefore, the singlet-triplet separation ($-2J$, a measure of the magnitude of the magnetic interaction) is expected to increase as the pK_a of L becomes higher.[2] In the previous study of dimeric copper(II) acetate adducts with thiazoles,[3] however, we have found that, while the pK_a of thiazole (2.44)[4] is lower than that of pyridine (5.32),[5] the $-2J$ value of the thiazole adduct (344 cm^{-1}) is higher than that of the pyridine adduct (325 cm^{-1}).[6]

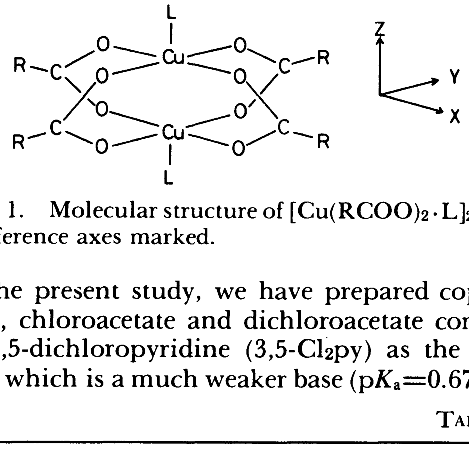

Fig. 1. Molecular structure of $[Cu(RCOO)_2 \cdot L]_2$ with reference axes marked.

In the present study, we have prepared copper(II) acetate, chloroacetate and dichloroacetate complexes with 3,5-dichloropyridine (3,5-Cl_2py) as the addend ligand which is a much weaker base (pK_a=0.67)[7] than pyridine (py). The magnetic and spectral properties of the copper(II) carboxylate complexes with 3,5-dichloropyridine and pyridine were compared with each other and the influence of the addend ligands on the magnetic interaction was discussed. The magnetic susceptibilities of dimeric copper(II) acetate complexes with 4-cyanopyridine (4-CNpy)[8] and caffeine (caf)[9] were also re-examined to contribute to the discussion.

Experimental

Syntheses. $Cu(CH_3COO)_2 \cdot L$ (L=3,5-Cl_2py and 4-CNpy): A solution of 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) with a few drops of glacial acetic acid. After the solution had been allowed to stand overnight at *ca.* 5 °C in a freezer, the separated green crystals were collected, washed with ethanol and dried at *ca.* 60 °C.

$Cu(CH_3COO)_2 \cdot$caf: This complex was prepared according to the method of Melník.[9]

$Cu(ClCH_2COO)_2 \cdot L$ and $Cu(Cl_2CHCOO)_2 \cdot L$ (L=3,5-Cl_2py and py): A solution of L (5 mmol) in chloroform (20 ml) was added to one of the carboxylates (5 mmol), $Cu(ClCH_2COO)_2$ and $Cu(Cl_2CHCOO)_2$, suspended in chloroform (30 ml). After the resulting solution had been concentrated to one-third of its volume, it was allowed to stand overnight at *ca.* 5 °C in a freezer. The green crystals were collected, washed with benzene and dried at *ca.* 60 °C.

The results of the elemental analyses are given in Table 1.

Table 1. Analytical data

Complex	Found (Calcd) (%)			
	C	H	N	Cu
$Cu(CH_3COO)_2$(3,5-Cl_2py)	32.70 (32.79)	2.75 (2.75)	4.05 (4.25)	19.17 (19.28)
$Cu(CH_3COO)_2$(4-CNpy)	41.87 (42.03)	3.62 (3.53)	9.94 (9.80)	22.32 (22.24)
$Cu(CH_3COO)_2$(caf)	38.38 (38.35)	4.31 (4.29)	14.96 (14.91)	16.83 (16.91)
$Cu(ClCH_2COO)_2$(3,5-Cl_2py)	27.06 (27.13)	1.76 (1.77)	3.48 (3.51)	15.90 (15.95)
$Cu(ClCH_2COO)_2$(py)	33.00 (32.79)	2.77 (2.75)	4.13 (4.25)	19.19 (19.28)
$Cu(Cl_2CHCOO)_2$(3,5-Cl_2py)	23.07 (23.13)	1.08 (1.08)	2.93 (3.00)	13.43 (13.60)
$Cu(Cl_2CHCOO)_2$(py)	27.61 (27.13)	1.80 (1.77)	3.43 (3.51)	15.78 (15.95)

Physical Measurement. Magnetic susceptibilities in the temperature range of 80—300 K were determined by the Faraday method. The correction for diamagnetic contribution (χ_{dia}) was made by use of Pascal's constants.[10] The cryomagnetic data were fitted to the Bleaney-Bowers equation (1) allowing for the presence of paramagnetic impurity,[11]

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

where P is the mole fraction of the noncoupled copper(II) impurity, g_i is the average g factor for the impurity which was fixed at 2.2 throughout the present study, and the other symbols have their usual meanings. The best-fit parameters, $-2J$, g, $N\alpha$, and P, were obtained by using a nonlinear least-squares program written by T. Nakagawa (The University of Tokyo) and Y. Oyanagi (The University of Tsukuba), SALS (model D), on a FACOM M-200 computer at the Nagoya University Computation Center. As a convenient statistical indicator of the quality of the least-squares fits, the discrepancy index, σ_{dis}, was employed:

$$\sigma_{dis} = \left[\frac{\sum(\chi_{obsd}-\chi_{calcd})^2}{\sum\chi_{obsd}^2}\right]^{1/2} \tag{2}$$

The thermal magnetic data are shown in Figs. 2 and 4 as plots of χ_A *vs.* T. The values of χ_{dia}, g, $N\alpha$, P, $-2J$, and σ_{dis} are summarized in Table 2.

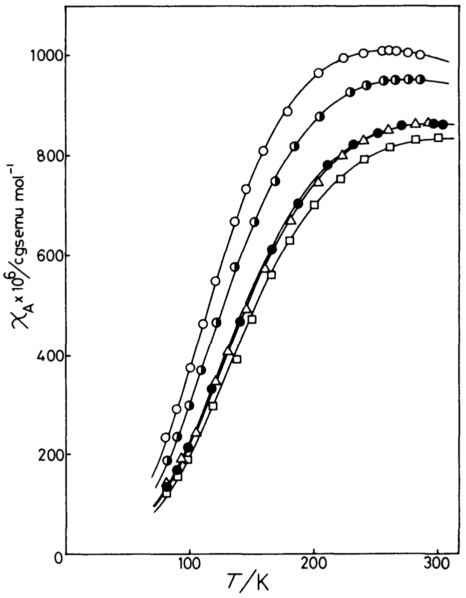

Fig. 2. Variation of magnetic susceptibilities with temperature.
(□) $Cu(CH_3COO)_2(3,5\text{-}Cl_2py)$, (△) $Cu(ClCH_2COO)_2(3,5\text{-}Cl_2py)$, (●) $Cu(ClCH_2COO)_2(py)$, (◑) $Cu(Cl_2CHCOO)_2(3,5\text{-}Cl_2py)$, (○) $Cu(Cl_2CHCOO)_2(py)$. The solid curves were obtained as described in text.

Reflectance spectra were recorded on a Hitachi Recording Spectrophotometer 323.

Results and Discussion

The variable-temperature magnetic susceptibility data of the complexes prepared in the present study are well represented by Eq 1, indicating that the complexes all have a dimeric structure similar to that found for copper(II) acetate monohydrate, $[Cu(CH_3COO)_2\cdot H_2O]_2$.[12] From Table 2, we can see the following trends in the magnetic properties. First, the antiferromagnetic interactions in the respective 3,5-dichloropyridine adducts are stronger than those in the corresponding pyridine adducts. Secondly, the $-2J$ values in both the series of 3,5-dichloropyridine and pyridine adducts decrease as the parent carboxylic acids become stronger.

The reflectance spectra of the complexes resemble with each other in shape and are quite similar to those of $[Cu(CH_3COO)_2(py)]_2$ (*cf.* Fig. 3).[13] The spectra show two bands having maxima at *ca.* 26000 cm^{-1} (Band II)[14] and *ca.* 14000 cm^{-1} (Band I)[14] with a shoulder at *ca.* 8000 cm^{-1}. The wave numbers of the

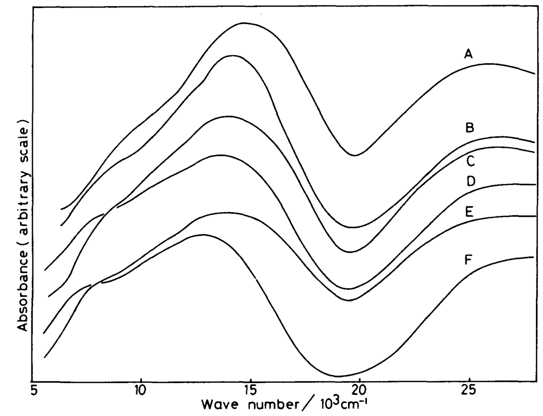

Fig. 3. Reflectance spectra of $Cu(CH_3COO)_2(3,5\text{-}Cl_2py)$ (A), $Cu(CH_3COO)_2(py)$ (B), $Cu(ClCH_2COO)_2(3,5\text{-}Cl_2py)$ (C), $Cu(ClCH_2COO)_2(py)$ (D), $Cu(Cl_2CHCOO)_2(3,5\text{-}Cl_2py)$ (E), and $Cu(Cl_2CHCOO)_2(py)$ (F).

TABLE 2. MAGNETIC DATA

Complex	$\chi_{dia}\times10^6$ / cgs emu[a)]	g	$N\alpha\times10^6$ / cgs emu[a)]	$P\times10^2$	$-2J$ / cm^{-1}	$\sigma_{dis}\times10^3$
$Cu(CH_3COO)_2(3,5\text{-}Cl_2py)$	−153	2.27_3	60	0.28	349	8.08
$Cu(CH_3COO)_2(py)$[b)]	−121	2.18_1	60	1.10	333	2.22
$Cu(CH_3COO)_2(4\text{-}CH_3py)$[b)]	−132	2.18_2	60	0	333	1.73
$Cu(CH_3COO)_2(4\text{-}CNpy)$	−127	2.24_3	60	0	345	7.45
$Cu(CH_3COO)_2(caf)$	−163	2.24_6	60	0.04	353	6.39
$Cu(ClCH_2COO)_2(3,5\text{-}Cl_2py)$	−181	2.28_7	60	0.43	340	4.41
$Cu(ClCH_2COO)_2(py)$	−147	2.26_2	60	0.18	333	4.56
$Cu(Cl_2CHCOO)_2(3,5\text{-}Cl_2py)$	−209	2.28_8	80	0.17	312	3.15
$Cu(Cl_2CHCOO)_2(py)$	−175	2.25_5	68	0.49	288	2.93

a) 1 cgs emu mol^{-1}=$4\pi\times10^{-6}$ m^3 mol^{-1}. b) Ref. 13.

TABLE 3. REFLECTANCE SPECTRAL DATA

Complex	Band I $\tilde{\nu}_{\max}/10^3$ cm^{-1}		Band II $\tilde{\nu}_{\max}/10^3$ cm^{-1}
$Cu(CH_3COO)_2(3,5\text{-}Cl_2py)$	14.7	9.5[a)]	25.7
$Cu(CH_3COO)_2(py)$[b)]	14.1	9.1[a)]	26.4
$Cu(ClCH_2COO)_2(3,5\text{-}Cl_2py)$	14.0	8.0[a)]	26.2
$Cu(ClCH_2COO)_2(py)$	13.6	7.5[a)]	26.5
$Cu(Cl_2CHCOO)_2(3,5\text{-}Cl_2py)$	13.6	7.7[a)]	broad
$Cu(Cl_2CHCOO)_2(py)$	12.8	7.4[a)]	broad

a) Shoulder. b) Ref. 13.

band maxima ($\tilde{\nu}_{\max}$) are listed in Table 3 and their spectral curves are shown in Fig. 3. For comparison, the reflectance spectral curve of $[Cu(CH_3COO)_2(py)]_2$[13)] is given in Fig. 3. It is now generally recognized that Bands I and II can be assigned respectively to a ligand field transition involving the positive hole promotion $d_{x^2-y^2}\rightarrow d_{xz}$, d_{yz}[15,16)] (*cf.* the coordinate system given in Fig. 1) and to a charge transfer from the carboxylato-oxygen atoms to the metal ion.[17,18)] Accordingly, Band I is expected to be sensitive to the nature of both the ligands $RCOO^-$ and L. As can be seen in Table 3 and Fig. 3, the $\tilde{\nu}_{\max}$ values of Band I for the 3,5-dichloropyridine adducts are higher than those for the corresponding pyridine adducts. The order of the increase in the $\tilde{\nu}_{\max}$ values is the same as that in the $-2J$ values, giving a linear relation between the $\tilde{\nu}_{\max}$ and $-2J$ values ; *i.e.*, "higher $\tilde{\nu}_{\max}$—higher $-2J$". This linear relation may be explained in terms of the electroneutrality principle[19)] as follows. In dimeric copper(II) carboxylate adducts, $[Cu(RCOO)_2\cdot L]_2$, when the L→Cu donation becomes weaker, the covalent Cu—O bonds in the CuO_4 basal plane will become stronger to maintain the electroneutrality over the whole molecule; *i.e.*, a weaker L→Cu donation will cause a stronger ligand field of the four carboxylato-oxygen atoms around the metal ion. This leads to a larger splitting of the d-d energy levels, resulting in a blue shift of Band I. This assumption is consistent with the observation by Dubicki and Martin[8)] that, in a series of dimeric copper(II) acetate adducts with pyridine analogues, Band I shifts to a higher energy as the pK_a of the addend ligand decreases. For the mechanism of the magnetic interaction in dimeric copper(II) carboxylates, experimental evidence[20–23)] shows that the spin-coupling between the unpaired electrons of copper(II) ions operates predominantly by superexchange interaction through the bridging carboxylato ligands rather than by direct Cu—Cu interaction. Accordingly, the magnetic interaction will become stronger as the Cu—O bonds become stronger. In the present complexes, the increase in both $-2J$ and $\tilde{\nu}_{\max}$ accompanied with the replacement of pyridine with 3,5-dichloropyridine takes place in accord with the expectation based on their pK_a values (py=5.32[6)] and $3,5\text{-}Cl_2py=0.67$[7)]) as stated above. The effect of Cu→L π-back-donation on the magnetic interaction in the present adducts may not be entirely negligible. However, the π-back-donation will make the metal more positive and thus will enhance the antiferromagnetic interaction: an effect of the same trend as caused by weak L→Cu σ donation.

From the experimental results and discussion stated above, we can conclude that, contrary to the result by Jotham, Kettle and Marks,[1)] the antiferromagnetic interaction in dimeric copper(II) carboxylate adducts should become stronger as the basicity of the addend ligands becomes weaker. The values of $-2J$ for dimeric copper(II) acetate adducts with some pyridine analogues were previously reported to decrease as the pK_a values of the addend ligands decrease: $4\text{-}CH_3py$ (325 cm^{-1})>$4\text{-}CH_3COpy$ (311 cm^{-1})>4-CNpy (300 cm^{-1}).[8)] However, we have found the reverse order: $4\text{-}CH_3py$ (333 cm^{-1})<4-CNpy (345 cm^{-1}) (*cf.* Table 2 and Fig. 4). We have further found that the $-2J$ of the 4-cyanopyridine adduct of dimeric copper(II) trichloroacetate (229 cm^{-1}) is higher than that of the corresponding pyridine adduct (189 cm^{-1}).[24)] The present result can explain the apparent anomalous magnetism of dioxane adducts. Dioxane has no appreciable π-acceptor ability, and it usually appears to be the weakest base (pK_a=−2.92)[25)] in a series of adducts for a given copper(II) carboxylate dimer. Thus, dioxane adducts usually give the highest values in both $-2J$ and $\tilde{\nu}_{\max}$ (Band I) for dimeric copper(II) carboxylate adducts.[26)] For the 3,5-dichloropyridine and pyridine adducts, both $-2J$ and $\tilde{\nu}_{\max}$ values decrease as the parent carboxylic acid becomes stronger (*cf.* Tables 2 and 3). This trend can be explained in terms of weakening of the ligand field strength of the four carboxylato-oxgen atoms.[8,27)]

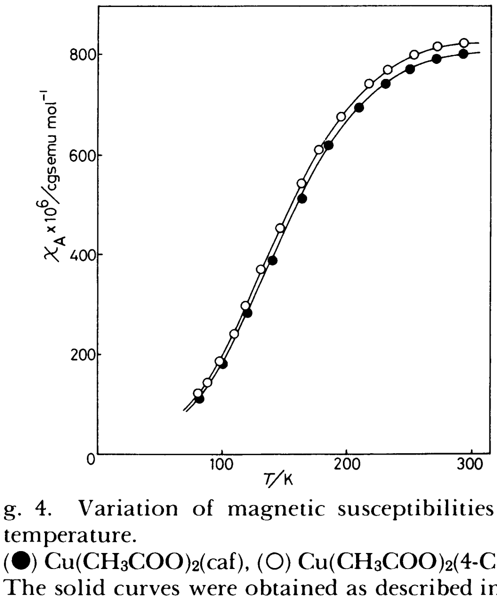

Fig. 4. Variation of magnetic susceptibilities with temperature.
(●) $Cu(CH_3COO)_2(caf)$, (○) $Cu(CH_3COO)_2(4\text{-}CNpy)$.
The solid curves were obtained as described in text.

It must be noted here that the extremely high $-2J$ values have been reported for dimeric copper(II) acetate adducts of quinuclidine ($495\pm49\,\mathrm{cm}^{-1}$)[28] and caffeine ($700\,\mathrm{cm}^{-1}$).[9] These high $-2J$ values are unacceptable on referring to our present conclusion. The pK_a value of quinuclidine (11.49)[29] is very large. Actually, Jotham, Kettle, and Marks have re-evaluated the $-2J$ value of the quinuclidine adduct to be $318\,\mathrm{cm}^{-1}$ by applying a least-squares fitting procedure to the reported magnetic data.[1] For the caffeine adduct, the reported magnetic susceptibilities do not agree completely with the values calculated by Eq. 1 using the reported parameter values of $-2J=700\,\mathrm{cm}^{-1}$, $g=2.20$, $N\alpha=0$, and $P=0$. Accordingly, we repeated the magnetic measurement on the newly prepared caffeine adduct. The least-squares fitting of the cryomagnetic data gave a $-2J$ value of $353\,\mathrm{cm}^{-1}$ (*cf.* Table 2 and Fig. 4). These renewed $-2J$ values are not abnormally high and are just comparable to those reported for well-characterized dimeric copper(II) acetate adducts.[20]

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References

1) R. W. Jotham, S. F. A. Kettle, and J. A. Marks, *J. Chem. Soc., Dalton Trans.*, **1972**, 428.

2) W. E. Marsh, G. O. Carlisle, and M. V. Hanson, *J. Mol. Struct.*, **40**, 153 (1977); *J. Inorg. Nucl. Chem.*, **39**, 1839 (1977).

3) T. Tokii and Y. Muto, *Bull. Chem. Soc. Jpn.*, **56**, 2363 (1983).

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

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

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

7) A. Fischer, W. J. Galloway, and J. Vaughan, *J. Chem. Soc.*, **1964**, 3591.

8) L. Dubicki and R. L. Martin, *Inorg. Chem.*, **5**, 2203 (1966).

9) M. Melník, *J. Inorg. Nucl. Chem.*, **43**, 3035 (1981).

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

11) A. P. Ginsberg, *Inorg. Chim. Acta Rev.*, **5**, 45 (1971).

12) J. N. van Niekerk and F. R. L. Schoening, *Acta Crystallogr.*, **6**, 227 (1953).

13) M. Kato, Y. Muto, and T. Tokii, 37th Annual Meeting of the Chemical Society of Japan, Tokyo, April 1978, Proceedings I, p. 255; ACS/CSJ Chemical Congress, April 1979, Honolulu, Hawaii, Abstracts I, Inorg. 465.

14) S. Yamada, H. Nakamura, and R. Tsuchida, *Bull. Chem. Soc. Jpn.*, **30**, 953 (1957)

15) G. F. Kokoszka, H. C. Allen Jr., and G. Gordon, *J. Chem. Phys.*, **42**, 3693 (1965).

16) C. W. Reimann, G. F. Kokoszka, and G. Gordon, *Inorg. Chem.*, **4**, 1082 (1965).

17) L. Dubicki, *Aust. J. Chem.*, **25**, 1141 (1972).

18) S. Kida, Y. Nishida, and M. Sakamoto, *Bull. Chem. Soc. Jpn.*, **46**, 2428 (1973).

19) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell Univ. Press, New York (1960), p. 172.

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

21) 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.

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

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

24) H. Horie, K. Matsuyama, F. Utsunomiya, T. Tokii, Y. Muto, M. Kato, and I. Suzuki, 33rd Conference on Coordination Chemistry of the Chemical Society of Japan, Toyonaka, October 1983, Proceedings, p. 498.

25) E. M. Arnett and C. Y. Wu, *J. Am. Chem. Soc.*, **82**, 4999 (1960)

26) M. Melník, *Finn. Chem. Lett.*, **1978**, 255; *Coord. Chem. Rev.*, **36**, 1 (1981).

27) T. Tokii and Y. Muto, *Bull. Chem. Soc. Jpn.*, **49**, 1849 (1976).

28) E. D. Stevens and J. T. Yoke, *Inorg. Chim. Acta.*, **4**, 244 (1970).

29) R. G. Pearson and F. W. Williams, *J. Am. Chem. Soc.*, **76**, 258 (1954).