August, 1987] © 1987 The Chemical Society of Japan Bull. Chem. Soc. Jpn., 60, 2849—2852 (1987) 2849

Magnetic Properties of Dimeric Copper(II) Trichloroacetate Adducts with 3-Substituted Pyridines

Yoneichiro Muto,* Michio Nakashima,† Tadashi Tokii, Michinobu Kato,†† and Ikuo Suzuki†††
Department of Chemistry, Faculty of Science and Engineering, Saga University, Saga 840
†Research Institute for Diseases of the Chest, Faculty of Medicine, Kyushu University,
3-1-1 Maidashi, Higashi-ku, Fukuoka 812
††Aichi Prefectural University, Mizuho-ku, Nagoya 467
†††Department of Electrical and Computer Engineering, Nagoya Institute of Technology, Showa-ku,Nagoya 466
(Received January 13, 1987)

Dimeric copper(II) trichloroacetate adducts with 3-substituted pyridines, $[Cu(Cl_3CCOO)_2(3\text{-}Xpy)]_2$ where X=Cl, Br, H, CN, and CH_3, have been prepared. Magnetic susceptibility and ESR data show that both the singlet-triplet separation ($-2J$) and the zero field splitting (D) decrease in the order: 3-Clpy adduct (193 and 0.397 cm^{-1})≈3-Brpy adduct (191 and 0.399 cm^{-1})>py adduct (188 and 0.385 cm^{-1})>3-CNpy adduct (138 and 0.216 cm^{-1})>3-CH_3py adduct (83 and 0.182 cm^{-1}). Electronic spectra indicate that the adducts with X=Cl, Br, and H have a distorted square-pyramidal copper(II) geometry and that those X=CN and CH_3 have a distorted trigonal-bipyramidal geometry. Form these results, it is concluded that the strength of antiferromagnetic interaction in $[Cu(Cl_3CCOO)_2(3\text{-}Xpy)]_2$ complexes decreases as the distortion of copper(II) geometry increases from square-pyramid toward trigonal-bipyramid.

Recent structural studies on dimeric copper(II) carboxylate adducts, $[Cu(RCOO)_2\cdot L]_2$, have demonstrated that the metal-metal distance becomes longer as either the acidity of the parent carboxylic acid RCOOH[1)] or the basicity of the axial ligand L[2)] becomes stronger. Then, a longer Cu-Cu distance is usually associated with a greater displacement of the metal ion from the equatorial plane composed of four oxygen atoms. Consequently, the variation of both the group R and the ligand L affects the strength of the Cu-O bonds in the CuO_4 basal plane accompanying a deformation of the bridging framework. For 13 dimeric copper(II) acetate adducts reported up to date, Cu-Cu distances span a narrow range of 2.581—2.671 Å with a variation of 0.09 Å.[2)] On the other hand, Cu-Cu distances found for dimeric copper(II) trichloroacetate adducts, $[Cu(Cl_3CCOO)_2\cdot L]_2$, span a considerably wide range: 2.731 Å for L=benzonitrile (PhCN),[3)] 2.776 Å for L=2-chloropyridine (2-Clpy),[1)] 2.852 Å for L=caffeine,[4)] 3.197 Å for L=2,2,5,5-tetramethyl-1-pyrrolidinyloxyl,[5)] and 3.256 Å for L=2,2,6,6-tetramethyl-1-piperidinyloxyl.[5)] The coordination environment around each copper(II) ion in the first three adducts is square-pyramidal, whereas that in the last two adducts is trigonal-bipyramidal. These structural data indicate that, for the variation of L, the bridging trichloroacetato ligand coordinates more flexibly than the bridging acetato ligand does. Dimeric copper(II) trichloroacetate adducts may therefore be a suitable choice for the study of structural factors which affect the magnetic properties of copper(II) carboxylate dimers.

Table 1. Analytical Data of $Cu(Cl_3CCOO)_2(3\text{-}Xpy)$

X	Found (Calcd)/%			
	C	H	N	Cu
Cl	21.85 (21.53)	0.87 (0.87)	2.68 (2.79)	12.58 (12.66)
Br	19.83 (19.78)	0.81 (0.73)	2.35 (2.56)	11.78 (11.63)
H	22.88 (23.13)	1.17 (1.08)	2.87 (3.00)	13.62 (13.60)
CN	24.33 (24.39)	0.82 (0.82)	5.81 (5.69)	12.98 (12.90)
CH_3	24.70 (24.95)	1.53 (1.46)	2.80 (2.91)	13.19 (13.19)

This paper reports results of synthetic, magnetic, and spectroscopic studies on five copper(II) trichloroacetate adducts with 3-substituted pyridines, $Cu(Cl_3CCOO)_2(3\text{-}Xpy)$, where X=Cl, Br, H, CN, and CH_3.

Experimental

Syntheses. $Cu(Cl_3CCOO)_2(3\text{-}Xpy)$ (X=Cl, Br, H, CN, and CH_3): $Cu(Cl_3CCOO)_2\cdot 3H_2O$ (1 mmol) and 3-Xpy (1 mmol) were suspended in a mixture of a solvent (benzene for X=Cl, Br, and CH_3; chloroform for X=H and CN) (30 ml) and 2,2-dimethoxypropane (1 ml). The mixture was warmed gently with stirring and then filtered. After the solution had been concentrated to one-third of its original volume, it was allowed to stand overnight at ca. 5 °C in a refrigerator. The separated green crystals were collected, washed with petroleum ether, and dried in vacuo at room temperature.

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

Physical Measurements. The magnetic susceptibility in the temperature range of 80—300 K was determined by the Faraday method. The correction for diamagnetic contribution was made by use of Pascal's constants.[6)] The cryomagnetic data were applied to the modified Bleaney-Bowers equation

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

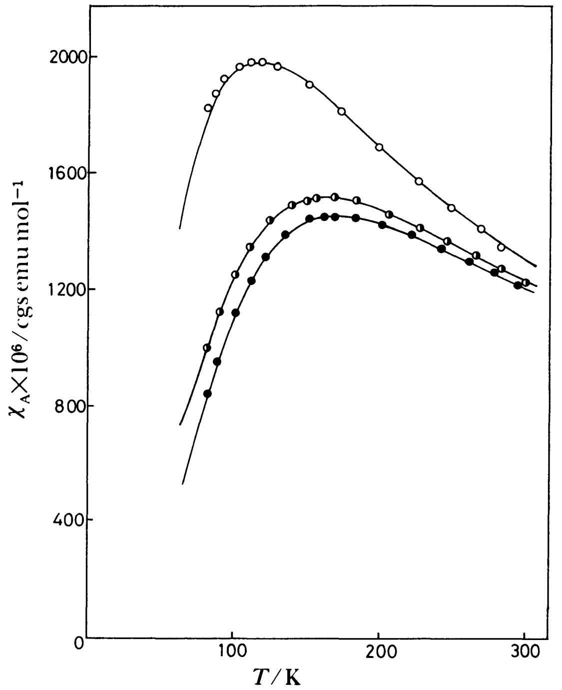

Fig. 1. Variation of magnetic susceptibilities with temperature. (●): $Cu(Cl_3CCOO)_2(3\text{-}Brpy)$, (○): $Cu(Cl_3CCOO)_2(py)$, (○): $Cu(Cl_3CCOO)_2(3\text{-}CNpy)$. The solid curves were obtained as described in the text.

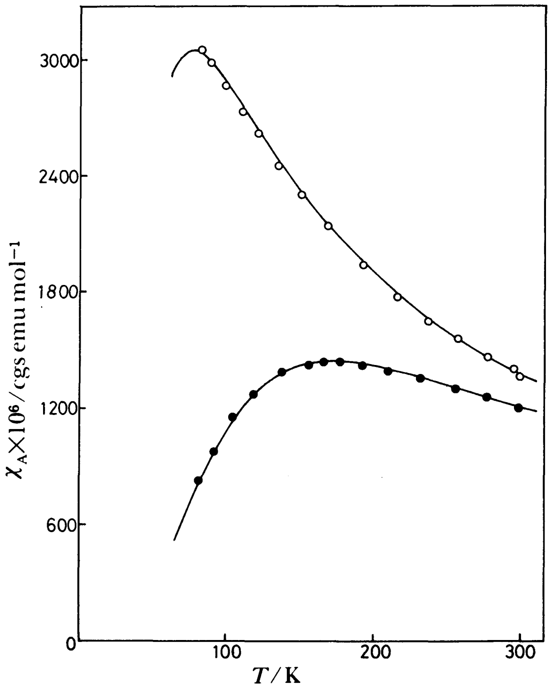

Fig. 2. Variation of magnetic susceptibilities with temperature. (●): $Cu(Cl_3CCOO)_2(3\text{-}Clpy)$, (○): $Cu(Cl_3CCOO)_2(3\text{-}CH_3py)$. The solid curves were obtained as described in the text.

where P is the mole fraction of the noncoupled copper(II) impurity and g_i is the average g factor for the impurity. The values of g_i of 2.2 and $N\alpha$ of 60×10^{-6} cgs emu (1 cgs emu$=4\pi\times10^{-6}$ m^3) were used throughout the present study.

Table 2. Magnetic Parameters for $Cu(Cl_3CCOO)_2(3\text{-}Xpy)$

X	$-2J$/cm^{-1}	g	$P\times10^2$	$\sigma_{\text{dis}}\times10^3$
Cl	193	2.25	1.45	3.28
Br	191	2.24	1.25	3.99
H	188	2.25	4.06	3.72
CN	138	2.20	4.74	5.19
CH_3	83	2.17	0.87	5.45

The best-fit parameters of $-2J$, g, and P were obtained by the non-linear least-squares fitting procedure. The quantity of fit was estimated by means of a discrepancy index

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

The thermal magnetic data are shown in Figs. 1 and 2 as plots of χ_A vs. T. The values of $-2J$, g, p, and σ_{dis} are summarized in Table 2.

The IR spectrum of $Cu(Cl_3CCOO)_2(3\text{-}CNpy)$ was recorded on a Hitachi 260-10 IR Spectrophotometer with Nujol mulls.

Reflectance spectra were recorded on a Hitachi Recording Spectrophotometer 323. The wave numbers of the ligand-field band maxima in the range 5000—20000 cm^{-1} (so-called Band I) are collected in Table 3 and the spectral curves are shown in Fig. 3. For comparison, the reflectance spectral curve of $[Cu(Cl_3CCOO)_2(2\text{-}Clpy)]_2$ is also given in Fig. 3.

Polycrystalline powder ESR X-band spectra were recorded with a Jeolco JES-ME 2 Spectrometer at room temperature. The spectra are shown in Fig. 4 and the ESR parameters are given in Table 4.

Results and Discussion

The magnetic susceptibility data of the complexes, $Cu(Cl_3CCOO)_2(3\text{-}Xpy)$, are well represented by Eq. 1, which indicates that these complexes have a carboxylato bridged dimeric structure.[1-3] As shown in Table 2, the $-2J$ values of the 3-substituted pyridine adducts with X=Cl, Br, and H are comparable to those of $[Cu(Cl_3CCOO)_2(2\text{-}Clpy)]_2$ (217 cm^{-1})[1] and $[Cu(Cl_3CCOO)_2(PhCN)]_2$ (224 cm^{-1}),[3] whereas those of the adducts with X=CN and CH_3 are considerably small. Such a substituent effect of 3-CN and 3-CH_3 groups will be discussed later. For the 3-cyanopyridine adduct, the CN stretching vibration (2240 cm^{-1}) appears in almost the same region as the free 3-cyanopyridine ligand (2232 cm^{-1}),[7] which suggests that in this adduct the CN group does not coordinate to the metal ion.

The electronic spectra of the adducts with X=Cl, Br, and H are similar to one another and closely resemble that of $[Cu(Cl_3CCOO)_2(2\text{-}Clpy)]_2$ (Fig. 3), giving a band maximum at ca. 12500 cm^{-1} and a low-energy shoulder at ca. 8000 cm^{-1}. The separation between these two peaks, $\Delta\tilde{\nu}_{\text{max}}=3890$—4930 cm^{-1}, is comparable to those observed for $[Cu(CH_3COO)_2(py)]_2$ (5000 cm^{-1})[8] and $[Cu(Cl_3CCOO)_2(2\text{-}Clpy)]_2$ (4900 cm^{-1}). These facts indicate that these three adducts have a distorted square-pyramidal copper(II) geometry similarly to $[Cu(Cl_3CCOO)_2(2\text{-}Clpy)]_2$.[1] On the other hand, the spectral feature of the adducts with X=CN and CH_3 is quite similar to those of distorted trigonal-bipyramidal copper(II) complexes such as $Cu_4OCl_6(Ph_3PO)_4$ ($\Delta\tilde{\nu}_{max}$=1300 cm^{-1}),[9] $[Cu(bpy)_2Cl]NO_3\cdot 3H_2O$ ($\Delta\tilde{\nu}_{max}$=2000 cm^{-1}),[10] $[Cu(bpy)_2CN]NO_3\cdot 2H_2O$ ($\Delta\tilde{\nu}_{max}$=2100 cm^{-1}),[11] and $[Cu(Ph_3CCOO)_2(py)]_2\cdot$benzene ($\Delta\tilde{\nu}_{max}$=2510 cm^{-1}).[12] The spectra of the latter two adducts show two peaks of about equal intensity with a separation of ca. 1800—1900 cm^{-1} in the range 10000—15000 cm^{-1} (Fig. 3 and Table 3). These $\Delta\tilde{\nu}_{max}$ values are comparable to those of the distorted trigonal-bipyramidal copper(II) complexes described above. The spectral similarity suggests that these two adducts have a distorted trigonal-bipyramidal copper(II) geometry, which may be produced rather by steric effects of the large CN and CH_3 substituents than by their electronic effects. Such a large size of substituents probably hinders smooth packing of molecules in crystal lattices, resulting in a steric strain in the coordination environment around the metal ion. Harrison et al.[10] demonstrated, in their study of $[Cu(bpy)_2Cl]X$ where X=ClO_4, $NO_3\cdot 3H_2O$, $1/2[(S_5O_6)\cdot 6H_2O]$, Cu^ICl_2, and $Cl\cdot 6H_2O$, that copper(II) complexes with a metal geometry close to the regular trigonal-bipyramid show a single broad peak in their electronic spectra at 12500 cm^{-1} (the $^2E'\leftarrow{}^2A_1'$ transition in the D_{3h} symmetry), whereas those with the square-pyramidally distorted trigonal-bipyramidal CuN_4Cl chromophore show a twin-peaked band in the region of 10000—14500 cm^{-1} with a maximum splitting of 4060 cm^{-1} for the complex whose metal geometry is closest to the regular square-pyramid. This fact suggests that, for five-coordinated copper(II) complexes, the $\Delta\tilde{\nu}_{max}$ value can be taken as a measure of the degree of distortion in metal geometry from square-pyramid to trigonal-bipyramid. As can be seen from Table 3, the $\Delta\tilde{\nu}_{max}$ value observed for the present complexes decreases in the order: 3-Clpy and 3-Brpy adducts>py adduct>3-CNpy adduct>3-CH_3py adduct. This order is just the same as that of the decrease in the $-2J$ values of these complexes (Table 2); there exists a parallel relation between $-2J$ and $\Delta\tilde{\nu}_{max}$ values (smaller $-2J$ with smaller $\Delta\tilde{\nu}_{max}$). This parallelism indicates that the strength of antiferromagnetic interaction in the present complexes decreases as the distortion of copper(II) geometry increases from square-pyramid toward trigonal-bipyramid.

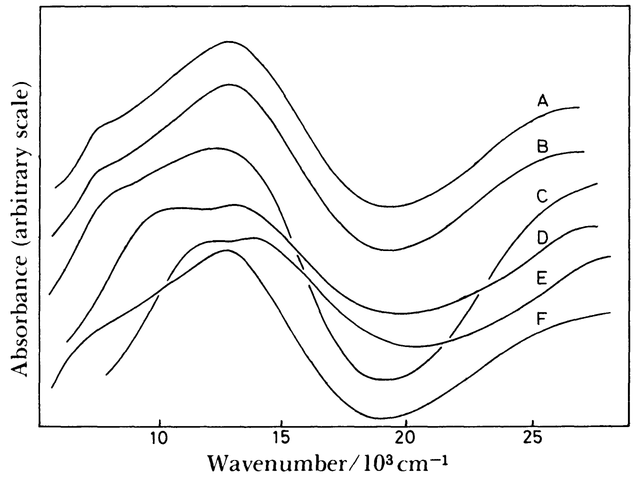

Fig. 3. Reflectance spectra of $Cu(Cl_3CCOO)_2\cdot L$. (A): L=3-Clpy, (B): L=3-Brpy, (C): L=py, (D): L=3-CNpy, (E): L=3-CH_3py, (F): L=2-Clpy.

Table 3. Reflectance Spectral Data of $Cu(Cl_3CCOO)_2(3\text{-}Xpy)$

X	$\tilde{\nu}_{max}\times 10^{-3}/cm^{-1}$		$\Delta\tilde{\nu}\times 10^{-3}/cm^{-1}$
Cl	12.50	7.57	4.93
Br	12.50	7.57	4.93
H	12.27	8.40	3.89
CN	12.82	10.86	1.96
CH_3	14.28	12.50	1.78

The ESR spectra of the present complexes show absorption bands arising from the triplet state. The parameters listed in Table 4 were evaluated by a general method for the analysis of powder ESR spectra of dimeric copper(II) complexes.[13] The ESR spectral feature of the adducts with X=Cl, Br, and H is the same as that usually observed for dimeric copper(II) carboxylate adducts, which have a square-pyramidal metal geometry.[13] For these three adducts, the common relation between zero field splitting (D) and resonance magnetic field (H_o), $D>H_o$,[13,14] was observed. On the other hand, the ESR spectra of the adducts with X=CN and CH_3 are quite different from those of the above three adducts (Fig. 4) and fundamentally the same as that of $[Cu(Ph_3CCOO)_2(py)]_2\cdot$benzene ($D$=0.204 cm^{-1}).[12] For the latter two adducts, an uncommon relation, $D<H_o$, was observed; this relation has recently been detected for $[Cu(Ph_3CCOO)_2(py)]_2\cdot$benzene, whose $-2J$ (184 cm^{-1}) is quite small as compared with those of common dimeric copper(II) carboxylates.[12] The order of decrease in the D values of the present complexes is the same as that in the $-2J$ values. Thus, it is concluded that the zero field splitting of $[Cu(Cl_3CCOO)_2(3\text{-}Xpy)]_2$ decreases as the distortion of the metal geometry increases from square-pyramid toward trigonal-bipyramid, just in the same way as the singlet-triplet separation does.

It is noted here that the values of g_{av} obtained from

Table 4. ESR Parameters for $Cu(Cl_3CCOO)_2(3\text{-}Xpy)$

X	D/cm^{-1}	$g_{/\!/}$	$g_{\perp}$	g_{av}[a)]
Cl	0.397	2.536	2.143	2.282
Br	0.399	2.575	2.154	2.304
H	0.385	2.562	2.159	2.301
CN	0.216	2.425	2.155	2.248
CH_3	0.182	2.396	2.183	2.256

a) $g_{av}=[1/3(g_{/\!/}^2+2g_{\perp}^2)]^{1/2}$.

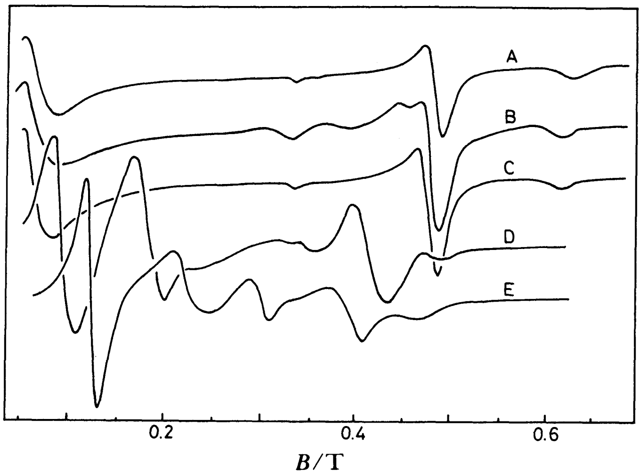

Fig. 4. Room-temperature polycrystalline powder ESR spectra of $Cu(Cl_3CCOO)_2(3\text{-}Xpy)$ at X-band frequency. (A): X=Cl, (B): X=Br, (C): X=H, (D): X=CN, (E): $X=CH_3$.

the present ESR study are smaller than those estimated from the magnetic susceptibility measurements (Tables 2 and 4); this is often observed for dimeric copper(II) carboxylates. The reason for this fact, however, is not clear at present.

References

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

2) V. M. Rao, D. N. Sathyanarayana, and H. Manobar, *J. Chem. Soc., Dalton Trans.*, **1983**, 2168.

3) M. Nakashima, M. Mikuriya, and Y. Muto, *Bull. Chem. Soc. Jpn.*, **58**, 968 (1985).

4) H. Horie, S. Husebye, M. Kato, E. A. Meyers, Y. Muto, I. Suzuki, T. Tokii, and R. A. Zingaro, *Acta Chem. Scand., Ser, A*, **40**, 579 (1986).

5) L. C. Porter, M. H. Dickman, and R. J. Doedens, *Inorg. Chem.*, **25**, 678 (1986).

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

7) R. E. Clarke and P. C. Ford, *Inorg. Chem.*, **9**, 495 (1970).

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

9) J. A. Bertrand, *Inorg. Chem.*, **6**, 495 (1967).

10) W. D. Harrison, D. M. Kennedy, M. Power, R. Sheahan, and B. J. Hathaway, *J. Chem. Soc., Dalton Trans.*, **1981**, 1556.

11) S. Tyagi and B. J. Hathaway, *J. Chem. Soc., Dalton Trans*, 1983, 199.

12) O. W. Steward, M. Kato, S. C. Chang, M. Sax, C. H. Chang, T. Taura, C. F. Jury, Y. Muto, T. Tokii, J. Pletcher, and C. S. Yoo, Proc, 23rd. Int. Conf. on Coord. Chem., Boulder, CO, USA, July 29, August 3, 1984., Proceedings, p. 247.

13) J. R. Wasson, C. I. Shyr, and C. Trapp, *Inorg. Chem.*, **7**, 469 (1968).

14) J. H. Price, J. R. Pilbrow, K. S. Murray, and T. D. Smith, *J. Chem. Soc., A*, **1970**, 968.