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Structural, Magnetic and IR Spectroscopic Characterization of Dimeric Copper(II) Trichloroacetate Adduct with Benzonitrile. Nature of the Copper(II)-Bezonitrile Bond

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The benzonitrile adduct of copper(II) trichloroacetate, $[Cu(Cl_3CCOO)_2(PhCN)]_2$, was prepared and characterized. The dimeric structure was confirmed by an X-ray structural determination. This compound crystallizes in the triclinic space group $P\bar{1}$ with a=12.780(1), b=16.064(1), c=10.130(1) Å; α=108.39(1), β=113.34(1), γ=81.07(1)°. The crystal consists of two crystallographically independent dimeric units. Both units have the familiar dimeric copper(II) acetate monohydrate structure with Cu–Cu distances of 2.731(1) and 2.732(1) Å. Magnetic susceptibility data in the range of 80—300 K are well represented by the usual dimer equation with a singlet-triplet energy separation of $-2J$=224 cm^{-1}. The C≡N stretching frequency of benzonitrile in the compound shows an increase by 31 cm^{-1} from the free ligand value. On the basis of the X-ray crystallographic and IR spectroscopic results, the nature of the copper(II)-benzonitrile bond is discussed. For discussion magnetic and spectroscopic properties of some analogous nitrile adducts of copper(II) chloroacetates were also studied.

Studies on a number of dimeric copper(II) carboxylate adducts, $[Cu(RCOO)_2\cdot L]_2$, have revealed some of the factors which determine the extent of antiferromagnetic interaction in these complexes. On the effect of addend ligand L, Jotham *et al.*[1] have stated that the singlet-triplet separation ($-2J$, a measure of the magnitude of the magnetic interaction) in $[Cu(RCOO)_2\cdot L]_2$ complexes tends to increase as L becomes a stronger electron donor. On the other hand, Hibdon *et al.*[2] have reported that the magnetic interaction in a series of dimeric copper(II) acetate adducts with 4-substituted pyridine N-oxides becomes stronger as the π-back-donation from the metal ion to the addend ligand increases. However, Muto *et al.*[3] have recently found that, in a series of $[Cu(RCOO)_2\cdot L]_2$ complexes, where R=CH_3, $ClCH_2$, and Cl_2CH, and L=pyridine analogues, the value of $-2J$ increases as the basicity of the addend ligands becomes weaker. Then a larger $-2J$ has been attributed to a weaker σ-donation of the addend ligand. These apparent discrepancies prompted us to investigate the bonding nature between Cu–L in $[Cu(RCOO)_2\cdot L]_2$ complexes.

In the present study five complexes, $Cu(ClCH_2COO)_2(PhCN)$, $Cu(ClCH_2COO)_2(4\text{-}CH_3C_6H_4CN)$, $Cu(Cl_2CHCOO)_2(4\text{-}CH_3C_6H_4CN)$, $Cu(Cl_3CCOO)_2(PhCN)$, and $Cu(Cl_3CCOO)_2(4\text{-}CH_3C_6H_4CN)\cdot 1/2bz$, where PhCN=benzonitrile, $4\text{-}CH_3C_6H_4CN$=4-methylbenzonitrile and bz=benzene, have been prepared and characterized by means of magnetic susceptibility and IR spectroscopy measurements. The structure of the benzonitrile adduct of copper(II) trichloroacetate has been determined by a single-crystal X-ray structural analysis to obtain accurate information about the coordinating mode of the addend ligand. In particular relations of the stretching frequency of the C≡N group with its bond length have been studied.

Experimental

Syntheses. $Cu(ClCH_2COO)_2\cdot L$(L=PhCN and $4\text{-}CH_3C_6H_4CN$): A solution of L (10 mmol) in benzene (10 ml) was added to a solution of $Cu(ClCH_2COO)_2$ (2 mmol) in acetone (20 ml). The resulting solution was filtered and then concentrated to one-third of its volume. When petroleum ether was added to the solution, green crystals precipitated. The crystals were collected, washed with a 1:2 benzene–petroleum ether mixture and dried *in vacuo* at room temperature.

$Cu(Cl_2CHCOO)_2(4\text{-}CH_3C_6H_4CN)$: This compound was prepared from $Cu(Cl_2CHCOO)_2$ and $4\text{-}CH_3C_6H_4CN$ in the same manner as with $Cu(ClCH_2COO)_2\cdot L$.

$Cu(Cl_3CCOO)_2(PhCN)$: $Cu(Cl_3CCOO)_2\cdot 3H_2O$ (2 mmol) and PhCN (10 mmol) were suspended in a mixture of benzene (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 volume, it was allowed to stand overnight at *ca.* 5 °C in a refrigerator. The separated green crystals were collected, washed with a 1:2 benzene–petroleum ether mixture and dried *in vacuo* at room temperature.

$Cu(Cl_3CCOO)_2(4\text{-}CH_3C_6H_4CN)\cdot 1/2bz$: This compound was prepared from $Cu(Cl_3CCOO)_2\cdot 3H_2O$ and $4\text{-}CH_3C_6H_4CN$ as described above.

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

X-Ray Crystal Structure Determination of $Cu(Cl_3CCOO)_2(PhCN)$. A Rigaku AFC-5 automated four-circle diffractometer was used for all measurements. Crystal data and details of the data collection are summarized in Table 2. Lattice constants were determined by the least-squares refinement based on 35 reflections with 20°<2θ<30°. The intensity data were corrected for the Lorentz-polarization effects, but not for absorption.

Table 1. Analytical data

Complex	Found (Calcd) (%)			
	C	H	N	Cu
$Cu(ClCH_2COO)_2$-	37.63	2.61	4.14	17.76
(PhCN)	(37.36)	(2.57)	(3.96)	(17.97)
$Cu(ClCH_2COO)_2$-	39.03	3.01	3.72	17.34
$(4\text{-}CH_3C_6H_4CN)$	(39.20)	(3.01)	(3.81)	(17.28)
$Cu(Cl_2CHCOO)_2$-	33.15	2.09	3.06	14.60
$(4\text{-}CH_3C_6H_4CN)$	(33.01)	(2.08)	(3.21)	(14.56)
$Cu(Cl_3CCOO)_2(PhCN)$	26.88	0.94	2.94	12.88
	(26.51)	(1.03)	(2.85)	(12.93)
$Cu(Cl_3CCOO)_2$-	32.86	1.66	2.61	11.61
$(4\text{-}CH_3C_6H_4CN)\cdot 1/2bz$	(33.09)	(1.85)	(2.57)	(11.67)

Table 2. Crystal data and data collection details

Formula	$C_{22}H_{10}Cl_{12}Cu_2N_2O_8$
fw	982.86
Temp/K	292 ± 1
Cryst syst	triclinic
Space group	$P\bar{1}$
a/Å	12.780(1)
b/Å	16.064(1)
c/Å	10.130(1)
α/°	108.39(1)
β/°	113.34(1)
γ/°	81.07(1)
V/Å^3	1810.9(2)
Z	2
D_m/g cm^{-3}	1.78
D_c/g cm^{-3}	1.80
Radiation	graphite-monochromated Mo $K\alpha$ ($\lambda=0.71073$ Å)
μ(Mo $K\alpha$)/cm^{-1}	21.1
Cryst dimens/mm	$0.23\times0.23\times0.40$
Scan type	$\theta-2\theta$
Scan speed/° min^{-1}	3
Scan width/°	$1.4+0.5\tan\theta$
Standard reflcns	$(\bar{1}, \bar{3}, 0)$ $(\bar{2}, 0, 1)$ $(0, \bar{1}, 2)$
Decay of standard	±4%
2θ range/°	2.5—45.0
Total no. of obsd Reflcns	4989
no. of unique reflcns with $\lvert F_o\rvert>3\sigma(\lvert F_o\rvert)$	3694
Final no. of variables	456
Final residuals	
R	0.058
R_w	0.086

Table 3. Fractional positional parameters ($\times10^4$) and thermal parameters of non-hydrogen atoms with their estimated standard deviations in parentheses

Atom	x	y	z	B_{eq}/Å^2
Cu(A)	−912(1)	180(1)	439(1)	4.2
Cu(B)	4088(1)	5181(1)	−1170(1)	4.2
Cl(A1)	1352(2)	2933(2)	3033(3)	7.9
Cl(A2)	−847(3)	3186(2)	846(4)	9.9
Cl(A3)	1142(5)	2796(2)	53(5)	14.1
Cl(A4)	1560(3)	221(2)	5485(3)	8.7
Cl(A5)	3452(2)	−153(3)	4564(3)	9.1
Cl(A6)	1894(4)	−1473(2)	3676(4)	11.2
Cl(B1)	3645(2)	2066(2)	−1260(3)	7.8
Cl(B2)	5838(3)	1811(2)	−1501(5)	9.9
Cl(B3)	3860(5)	2204(2)	−3886(3)	13.8
Cl(B4)	3441(3)	4776(2)	3702(3)	8.8
Cl(B5)	1552(2)	5154(3)	1264(3)	9.3
Cl(B6)	3115(4)	6475(2)	3260(5)	11.2
O(A1)	−485(5)	1397(4)	944(7)	5.7
O(A2)	1004(5)	1098(4)	243(7)	6.1
O(A3)	256(5)	65(4)	2358(6)	5.8
O(A4)	1751(4)	−231(4)	1638(6)	5.3
O(B1)	3989(5)	3893(4)	−1874(6)	6.1
O(B2)	5488(5)	3604(4)	40(6)	5.6
O(B3)	3258(4)	5238(4)	131(6)	5.4
O(B4)	4753(4)	4936(4)	2046(6)	5.6
N(A)	−2317(6)	538(5)	1175(8)	5.9
N(B)	2686(5)	5541(5)	−2950(7)	5.7
C(A1)	306(7)	1593(5)	714(9)	5.0
C(A2)	465(9)	2573(6)	1113(11)	6.4
C(A3)	1279(6)	−139(5)	2543(8)	4.5
C(A4)	2009(7)	−359(5)	4023(8)	4.7
C(A5)	−3048(6)	817(5)	1532(8)	4.5
C(A6)	−4010(6)	1180(6)	1966(8)	5.1
C(A7)	−4743(8)	613(9)	1909(11)	7.5
C(A8)	−5695(10)	963(14)	2244(13)	13.3
C(A9)	−5846(12)	1813(17)	2651(14)	17.6
C(A10)	−5147(14)	2395(11)	2798(14)	13.8
C(A11)	−4177(10)	2077(8)	2371(12)	8.6
C(B1)	4701(7)	3403(5)	−1174(8)	4.8
C(B2)	4544(9)	2421(6)	−1930(10)	6.6
C(B3)	3743(6)	5150(5)	1414(8)	4.2
C(B4)	2986(7)	5362(5)	2362(9)	4.9
C(B5)	1943(6)	5816(5)	−3767(8)	4.4
C(B6)	986(6)	6178(6)	−4797(9)	4.8
C(B7)	265(8)	5608(8)	−6032(10)	7.4
C(B8)	−701(10)	5986(13)	−6974(14)	12.6
C(B9)	−858(12)	6822(14)	−6688(21)	14.8
C(B10)	−137(14)	7420(11)	−5500(25)	14.6
C(B11)	855(10)	7086(8)	−4437(15)	8.5

The structure was solved by the heavy-atom method. Refinements were carried out by the block-diagonal least-squares method. Hydrogen atoms were inserted in their calculated positions and included in the refinement. The final R values were $R=\sum\lvert\lvert F_o\rvert-\lvert F_c\rvert\rvert/\sum\lvert F_o\rvert=0.058$, $R_w=[\sum w(\lvert F_o\rvert-\lvert F_c\rvert)^2/\sum w\lvert F_o\rvert^2]^{1/2}=0.086$. The weighting scheme was $w=(6.5+\lvert F_o\rvert+0.007\lvert F_o\rvert^2)^{-1}$. The final difference Fourier synthesis showed no peaks higher than 0.84 e Å^3.

The atomic scattering factors for Cu, Cl, O, N, C, and H and the anomalous dispersion corrections, $\Delta f'$ and $\Delta f''$

TABLE 4. INTERATOMIC DISTANCES (l/Å) AND BOND ANGLES (ϕ/°) WITH THEIR ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(1) Binuclear molecule A			
(a) Copper coordination spheres			
Cu(A)-Cu(A)$^{\mathrm{i}}$ a)	2.731(1)	Cu(A)-O(3A)	1.967(5)
Cu(A)-O(A1)	1.965(6)	Cu(A)-O(A4)$^{\mathrm{i}}$	1.969(5)
Cu(A)-O(A2)$^{\mathrm{i}}$	1.955(6)	Cu(A)-N(A)	2.141(9)
O(A1)-Cu(A)-O(A3)	90.1(3)	O(A3)-Cu(A)-O(A4)$^{\mathrm{i}}$	165.6(3)
O(A1)-Cu(A)-O(A4)$^{\mathrm{i}}$	88.0(3)	O(A1)-Cu(A)-N(A)	94.4(3)
O(A1)-Cu(A)-O(A2)$^{\mathrm{i}}$	165.0(3)	O(A2)$^{\mathrm{i}}$-Cu(A)-N(A)	100.6(3)
O(A2)$^{\mathrm{i}}$-Cu(A)-O(A3)	88.4(3)	O(A3)-Cu(A)-N(A)	97.2(3)
O(A2)$^{\mathrm{i}}$-Cu(A)-O(A4)$^{\mathrm{i}}$	89.8(3)	O(A4)$^{\mathrm{i}}$-Cu(A)-N(A)	97.3(3)
(b) Trichloroacetate ion			
C(A1)-O(A1)	1.228(13)	C(A3)-O(A3)	1.250(10)
C(A1)-O(A2)	1.238(11)	C(A3)-O(A4)	1.245(12)
C(A1)-C(A2)	1.522(13)	C(A3)-C(A4)	1.538(11)
C(A2)-Cl(A1)	1.775(9)	C(A4)-Cl(A4)	1.741(9)
C(A2)-Cl(A2)	1.775(11)	C(A4)-Cl(A5)	1.756(9)
C(A2)-Cl(A3)	1.761(15)	C(A4)-Cl(A6)	1.729(9)
Cu(A)-O(A1)-C(A1)	123.1(5)	Cl(A1)-C(A2)-Cl(A3)	108.0(6)
Cu(A)-O(A2)$^{\mathrm{i}}$-C(A1)$^{\mathrm{i}}$	123.2(7)	Cl(A2)-C(A2)-Cl(A3)	109.2(6)
Cu(A)-O(A3)-C(A3)	123.8(6)	O(A3)-C(A3)-O(A4)	127.3(7)
Cu(A)-O(A4)$^{\mathrm{i}}$-C(A3)$^{\mathrm{i}}$	123.2(4)	O(A3)-C(A3)-C(A4)	115.7(8)
O(A1)-C(A1)-O(A2)	128.4(8)	O(A4)-C(A3)-C(A4)	116.8(7)
O(A1)-C(A1)-C(A2)	115.2(8)	C(A3)-C(A4)-Cl(A4)	112.8(6)
O(A2)-C(A1)-C(A2)	116.3(10)	C(A3)-C(A4)-Cl(A5)	111.2(7)
C(A1)-C(A2)-Cl(A1)	108.2(7)	C(A3)-C(A4)-Cl(A6)	106.2(5)
C(A1)-C(A2)-Cl(A2)	112.2(7)	Cl(A4)-C(A4)-Cl(A5)	108.5(4)
C(A1)-C(A2)-Cl(A3)	111.1(7)	Cl(A4)-C(A4)-Cl(A6)	109.8(6)
Cl(A1)-C(A2)-Cl(A2)	108.0(5)	Cl(A5)-C(A4)-Cl(A6)	108.1(5)
(c) Benzonitrile			
N(A)-C(A5)	1.113(12)	C(A8)-C(A9)	1.303(33)
C(A5)-C(A6)	1.445(12)	C(A9)-C(A10)	1.326(32)
C(A6)-C(A7)	1.378(17)	C(A10)-C(A11)	1.440(26)
C(A7)-C(A8)	1.381(17)	C(A11)-C(A6)	1.375(15)
Cu(A)-N(A)-C(A5)	171.9(9)	C(A8)-C(A9)-C(A10)	125.6(16)
N(A)-C(A5)-C(A6)	178.9(9)	C(A9)-C(A10)-C(A11)	118.4(15)
C(A5)-C(A6)-C(A7)	118.6(8)	C(A10)-C(A11)-C(A6)	115.7(13)
C(A6)-C(A7)-C(A8)	118.3(13)	C(A11)-C(A6)-C(A7)	122.8(10)
C(A7)-C(A8)-C(A9)	119.0(18)	C(A11)-C(A6)-C(A5)	118.6(10)
(2) Binuclear molecule B			
(a) Copper coordination spheres			
Cu(B)-Cu(B)$^{\mathrm{ii}}$	2.732(1)	Cu(B)-O(B3)	1.968(7)
Cu(B)-O(B1)	1.972(6)	Cu(B)-O(B4)$^{\mathrm{ii}}$	1.965(7)
Cu(B)-O(B2)$^{\mathrm{ii}}$	1.959(5)	Cu(B)-N(B)	2.138(6)
O(B1)-Cu(B)-O(B3)	90.1(3)	O(B3)-Cu(B)-O(B4)$^{\mathrm{ii}}$	165.6(2)
O(B1)-Cu(B)-O(B4)$^{\mathrm{ii}}$	88.3(3)	O(B1)-Cu(B)-N(B)	100.4(2)
O(B1)-Cu(B)-O(B2)$^{\mathrm{ii}}$	165.5(2)	O(B2)$^{\mathrm{ii}}$-Cu(B)-N(B)	94.1(3)
O(B2)$^{\mathrm{ii}}$-Cu(B)-O(B3)	87.7(3)	O(B3)-Cu(B)-N(B)	97.6(3)
O(B2)$^{\mathrm{ii}}$-Cu(B)-O(B4)$^{\mathrm{ii}}$	90.3(3)	O(B4)$^{\mathrm{ii}}$-Cu(B)-N(B)	96.8(3)
(b) Trichloroacetate ion			
C(B1)-O(B1)	1.252(10)	C(B3)-O(B3)	1.242(10)
C(B1)-O(B2)	1.224(8)	C(B3)-O(B4)	1.241(8)
C(B1)-C(B2)	1.526(12)	C(B3)-C(B4)	1.551(14)
C(B2)-Cl(B1)	1.782(14)	C(B4)-Cl(B4)	1.753(10)
C(B2)-Cl(B2)	1.755(11)	C(B4)-Cl(B5)	1.745(8)
C(B2)-Cl(B3)	1.760(9)	C(B4)-Cl(B6)	1.732(8)
Cu(B)-O(B1)-O(B1)	122.0(4)	Cl(B)-C(B2)-Cl(B3)	107.7(6)
Cu(B)-O(B2)$^{\mathrm{ii}}$-C(B1)$^{\mathrm{ii}}$	123.4(6)	Cl(B)-C(B2)-Cl(B3)	109.7(6)

TABLE 4. Continued

Cu(B)-O(B3)-C(B3)	122.6(5)	O(B3)-C(B3)-O(B4)	128.9(9)
Cu(B)-O(B4)^{ii}-C(B3)^{ii}	122.5(6)	O(B3)-C(B3)-C(B4)	115.2(6)
O(B1)-C(B1)-O(B2)	128.9(7)	O(B4)-C(B3)-C(B4)	115.9(7)
O(B1)-C(B1)-C(B2)	115.1(6)	C(B3)-C(B4)-Cl(B4)	112.3(6)
O(B2)-C(B1)-C(B2)	115.9(7)	C(B3)-C(B4)-Cl(B5)	112.5(5)
C(B1)-C(B2)-Cl(B1)	107.4(8)	C(B3)-C(B4)-Cl(B6)	105.3(7)
C(B1)-C(B2)-Cl(B2)	112.4(7)	Cl(B4)-C(B4)-Cl(B5)	108.5(6)
C(B1)-C(B2)-Cl(B3)	111.3(7)	Cl(B4)-C(B4)-Cl(B6)	109.4(4)
Cl(B1)-C(B2)-Cl(B2)	108.2(6)	Cl(B5)-C(B4)-Cl(B6)	108.7(5)
(c) Benzonitrile			
N(B)-C(B5)	1.122(9)	C(B8)-C(B9)	1.283(30)
C(B5)-C(B6)	1.440(10)	C(B9)-C(B10)	1.374(23)
C(B6)-C(B7)	1.371(11)	C(B10)-C(B11)	1.457(22)
C(B7)-C(B8)	1.415(18)	C(B11)-C(B16)	1.388(15)
Cu(B)-N(B)-C(B5)	172.2(6)	C(B8)-C(B9)-C(B10)	124.9(16)
N(B)-C(B5)-C(B6)	179.1(8)	C(B9)-C(B10)-C(B11)	118.1(16)
C(B5)-C(B6)-C(B7)	118.1(8)	C(B10)-C(B11)-C(B6)	114.7(10)
C(B6)-C(B7)-C(B8)	116.6(12)	C(B11)-C(B6)-C(B7)	125.0(9)
C(B7)-C(B8)-C(B9)	120.7(12)	C(B11)-C(B6)-C(B5)	116.8(7)

a) Superscripts (i) and (ii) refer to the equivalent positions ($-x$, $-y$, $-z$) and ($1-x$, $1-y$, $-z$), respectively.

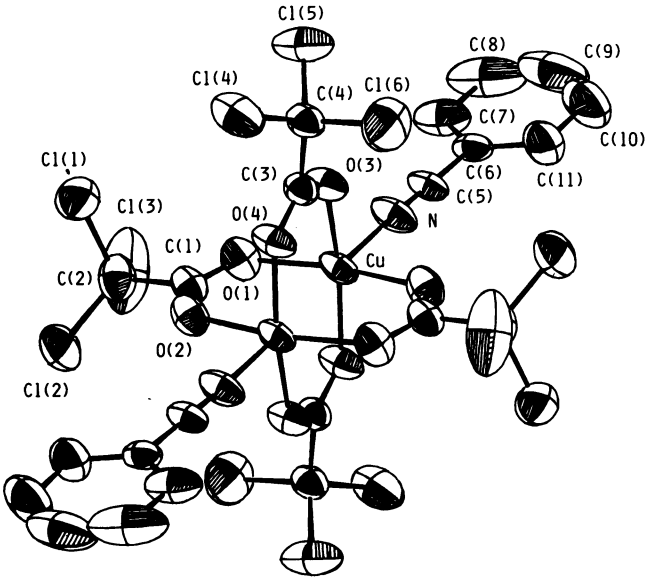

Fig. 1. Molecular structure of $[Cu(Cl_3CCOO)_2(PhCN)]_2$ with thermal ellipsoids (50% probability level).

for Cu, Cl, O, N, and C, were taken from the International Tables for X-Ray Crystallography.[4] All the calculations were carried out on the FACOM-200 computer in the Computer Center of Kyushu University by use of a local version[5] of the UNICS-II and the ORTEP programs. The final positional and thermal parameters with their estimated standard deviations are given in Table 3. The coordinates and isotropic temperature factors of the hydrogen atoms, the anisotropic thermal parameters of the non-hydrogen atoms, and the F_o-F_c tables have been deposited as Document No. 8514 at the Office of the Editor. A perspective drawing of the dimeric molecule and numbering system are illustrated in Fig. 1. The bond distances and angles are tabulated in Table 4.

Magnetic 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.[6] The cryomagnetic data were fitted to the Bleaney-Bowers equation (1) allowing for the presence of paramagnetic impurity,[7]

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

where P is the mole fraction of the noncoupled copper(II) impurity, g_i is the average g factor for the impurity, and the other symbols have their usual meanings. The values of $g_i=2.2$ and $N\alpha=60\times10^{-6}$ cgs emu (1 cgs emu$=4\pi\times10^{-6}$ m^3) were used throughout the present study. The best-fit parameters, $-2J$, g, and P, were obtained by using a nonlinear least-squares program, SALS (model D).[3] As a convenient statistical indicator of the quality of the least-squares fits, the discrepancy index σ_{dis} ($\sigma_{dis}=[\sum(\chi_{obsd}-\chi_{calcd})^2/\sum\chi_{obsd}^2]^{1/2}$) was employed. The thermal magnetic data are shown in Figs. 2 and 3 as plots of χ_A *vs.* T. The values of χ_{dia}, g, P, $-2J$, and σ_{dis} are summarized in Table 5.

IR Measurement. IR spectra were recorded on a Hitachi 260-10 IR Spectrophotometer as Nujol mulls. The C≡N stretching frequencies observed for the complexes and those for the free nitriles are given in Table 6.

Results and Discussion

The crystal structure of the copper(II) trichloroacetate adduct with benzonitrile contains two independent centrosymmetric $[Cu(Cl_3CCOO)_2(PhCN)]_2$ molecules; they are abbreviated as A and B. The two independent molecules are quite similar to each other in shape, although there are small differences in their interatomic distances and bond angles. As shown in Fig. 1, each molecule has the well-known dimeric copper(II) acetate monohydrate structure. The benzonitrile is bound to the copper atom in a linear fashion through the terminal nitrogen atom. The coordination geometry around each copper atom is best described as a distorted square pyramid with four carboxylato oxygen atoms in the basal plane (Cu-O 1.955—1.969 Å for A and 1.959—1.972 Å for B) and a nitrile nitrogen atom in the apical position (Cu-N 2.141(9) Å for A and 2.138(6) Å for B), in a similar way to that observed in [Cu(Cl$_3$CCOO)$_2$(2-chloropyridine)]$_2$.[8] The basal

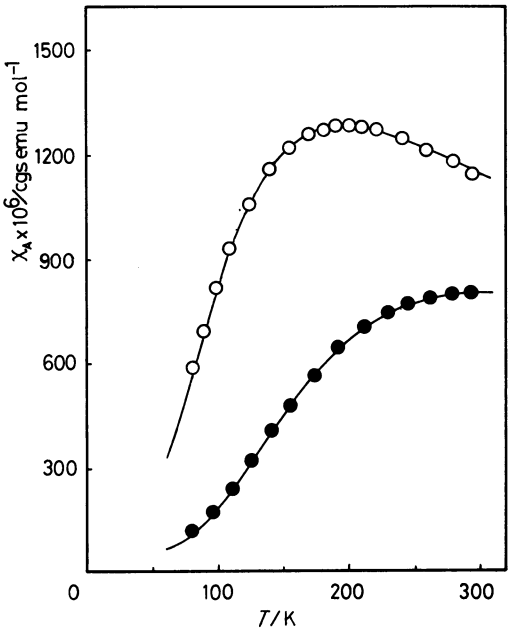

Fig. 2. Variation of magnetic susceptibilities with temperature.
(●): Cu(ClCH$_2$COO)$_2$(PhCN), (○): Cu(Cl$_3$CCOO)$_2$(PhCN).
The solid curves were obtained as described in the text.

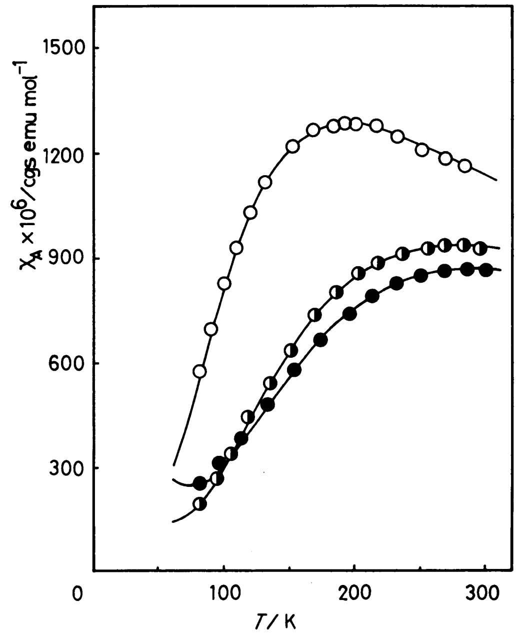

Fig. 3. Variation of magnetic susceptibilities with temperature.
(●): Cu(ClCH$_2$COO)$_2$(4-CH$_3$C$_6$H$_4$CN), (◑): Cu(Cl$_2$CHCOO)$_2$(4-CH$_3$C$_6$H$_4$CN), (○): Cu(Cl$_3$CCOO)$_2$(4-CH$_3$C$_6$H$_4$CN)$_2$·1/2 bz.
The solid curves were obtained as described in the text.

TABLE 5. MAGNETIC DATA

Complex	$\chi_{\mathrm{dia}}\times10^6$ / cgs emu	g	$P\times10^2$	$-2J$ / cm^{-1}	$\sigma_{\mathrm{dis}}\times10^3$
Cu(ClCH$_2$COO)$_2$(PhCN)	−165	2.23_5	0.33	352	4.96
Cu(ClCH$_2$COO)$_2$(4-CH$_3$C$_6$H$_4$CN)	−177	2.25_8	2.60	339	7.43
Cu(Cl$_2$CHCOO)$_2$(4-CH$_3$C$_6$H$_4$CN)	−211	2.28_2	0.90	314	3.56
Cu(Cl$_3$CCOO)$_2$(PhCN)	−234	2.26_1	2.11	224	3.23
Cu(Cl$_3$CCOO)$_2$(4-CH$_3$C$_6$H$_4$CN)·1/2bz	−273	2.23_6	0.90	216	6.18

TABLE 6. C≡N STRECHING VIBRATIONS (cm^{-1}) FOR NITRILE ADDUCTS OF COPPER(II) CHLOROACETATES

Complex	Coordinated	Free[a]	$\Delta\tilde{\nu}$C≡N[b]
Cu(ClCH$_2$COO)$_2$(PhCN)	2257	2231	26
Cu(ClCH$_2$COO)$_2$(4-CH$_3$C$_6$H$_4$CN)	2264	2230	34
Cu(Cl$_2$CHCOO)$_2$(4-CH$_3$C$_6$H$_4$CN)	2262	2230	32
Cu(Cl$_3$CCOO)$_2$(PhCN)	2262	2231	31
Cu(Cl$_3$CCOO)$_2$(4-CH$_3$C$_6$H$_4$CN)·1/2 bz	2264	2230	34

a) Ref. 17. b) Change in $\tilde{\nu}$C≡N on coordination.

atoms in both A and B are almost coplanar with the largest deviation of 0.004 Å. The copper atoms in A and B are shifted from the basal planes toward the apical nitrogen atoms by 0.251 and 0.247 Å, respectively. The Cu–Cu separation (2.731(1) Å for A and 2.732(1) Å for B) is slightly shorter than that in the 2-chloropyridine adduct (2.766(3) Å).[8] The other bond distances and angles about the coordination sphere (*cf.* Table 4) are comparable to those found for the 2-chloropyridine adduct. A noteworthy feature of the coordinated benzonitrile is the C–N distances of 1.113(12) Å (A) and 1.122(9) Å (B), which are significantly shorter than that in the free molecule (1.159(2) Å).[9] This apparent shortening indicates that the C≡N bond strength increased upon formation of the CN→metal coordination bond.[10,11]

The magnetic susceptibility data of the complexes prepared in the present study are well represented by Eq. 1 (*cf.* Figs. 2 and 3), indicating that all the complexes have a dimeric structure similar to that found for $[Cu(Cl_3CCOO)_2(PhCN)]_2$. The $-2J$ values found for the respective benzonitrile adducts are larger than those found for the corresponding 4-methylbenzonitrile adducts. This fact is in accord with the previous conclusion that the antiferromagnetic interaction in dimeric copper(II) carboxylate adducts becomes stronger as the basicity of the addend ligands becomes weaker,[3] because benzonitrile must be less basic than 4-methylbenzonitrile. From Table 5, we can also see that the $-2J$ values in both the benzonitrile and 4-methylbenzonitrile adducts decrease as the pK_a values of the parent carboxylic acids become smaller. This trend can be explained in terms of weakening of the ligand field strength of the four carboxylato oxygen atoms.[3,12,13]

A remarkable feature of the IR spectra of the present complexes is that, in each case, the C≡N stretching absorption appears at a higher wavenumber by 30—40 cm^{-1} than that of the free nitrile (*cf.* Table 6). Such an increase in $\tilde{\nu}$C≡N has been attributed to an increase in the C≡N bond strength resulting from a hybridization change in the coordinated CN group or a greater contribution of the donor atom N_{2s} orbital to the CN σ-bonding system upon σ-donation of the lone pair of electrons on the nitrile nitrogen atom.[14,15] Thus, both of the shortening of the CN bond and the increase of the $\tilde{\nu}$ C≡N observed for $[Cu(Cl_3CCOO)_2(PhCN)]_2$ can be ascribed to the formation of a CN→metal σ-donating bond. On the other hand, if the metal—addend ligand bond is, on the whole, the type of C≡N← metal π-back bonding, the CN bond order should decrease; consequently, the $\tilde{\nu}$C≡N is expected to decrease.[11,16,17]

Thus, the X-ray crystallographic, magnetic and IR spectroscopic results indicate that the nitriles in the present complexes act as the σ-donor ligands. This conclusion is in accord with the recent claim by Rao *et al.* that the pyridine molecule in $[Cu(CH_3COO)_2(py)]_2$ complex functions as a σ-donor base.[18]

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