Structural, Magnetic and Spectroscopic Characterization of Novel Di-μ-carboxylato-Bridged Binuclear Copper(II) Complexes with 1,10-Phenanthroline

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(Received September 25, 1989)

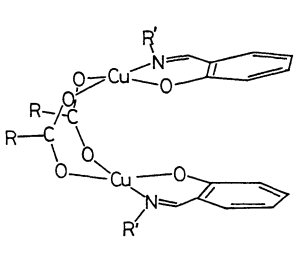
Bis(μ-carboxylato-*O*,*O*′)-diaquabis(1,10-phenanthroline)dicopper(II) dinitrate tetrahydrates, $[Cu(RCOO)(phen)(H_2O)]_2(NO_3)_2\cdot 4H_2O$, where R=H, CH_3, and $(CH_3)_3C$, were prepared and characterized by elemental analyses, electronic spectra, magnetic susceptibilities, and X-ray structure analysis. The magnetic susceptibility data conform to the usual dimer equation. The $-2J$ values are 125 cm^{-1} for formate, 86 cm^{-1} for acetate, and 99 cm^{-1} for 2,2-dimethylpropanoate. The crystal structures of $[Cu(HCOO)(phen)(H_2O)]_2(NO_3)_2\cdot 4H_2O$ (**1**) and $[Cu(CH_3COO)(phen)(H_2O)]_2(NO_3)_2\cdot 4H_2O$ (**2**) were determined by the single-crystal X-ray diffraction method. The crystallographic data are: Compound **1**, monoclinic, *I*2/*a*, *a*=18.850(2), *b*=9.775(2), *c*=17.752(2) Å, β=99.03(1)°, *V*=3230.4(8) Å^3, *Z*=4, *R*=0.055 for 2511 observed unique reflections; Compound **2**, monoclinic, *C*2/*c*, *a*=18.563(4), *b*=14.272(5), *c*=14.126(3) Å, β=106.72(2)°, *V*=3584(2) Å^3, *Z*=4, *R*=0.082 for 2092 reflections. The complexes consist of dimeric $[Cu(RCOO)(phen)(H_2O)]_2^{2+}$ cations with five-coordinated copper ions linked by two carboxylato ions in a syn-syn bridging arrangement. The Cu···Cu distances are 3.103(2) Å for **1** and 3.063(3) Å for **2**.

A large number of binuclear copper(II) carboxylate adducts, $[Cu(RCOO)_2\cdot L]_2$, have been isolated and their magneto-structural correlations have extensively been studied.[1-3] In most $[Cu(RCOO)_2\cdot L]_2$ complexes two copper(II) ions are bridged in pairs by four carboxylato groups (RCOO) with two additional unidentate ligands (L) occupying the terminal positions, resulting in a cage-type dimeric structure. Previously we found that bis(*N*-R′-salicylideneaminato)-copper(II) complexes, Cu(salN-R′)$_2$, react with copper(II) carboxylates, $Cu(RCOO)_2$, to yield a series of the complexes with the formula $[Cu(RCOO)(salN-R')]_2$, where R=ethyl, chloromethyl, and dichloromethyl; R′=phenyl and *p*-tolyl.[4-6] These complexes show antiferromagnetic behavior, in conformity with the Bleaney-Bowers equation (Eq. 1)[7]

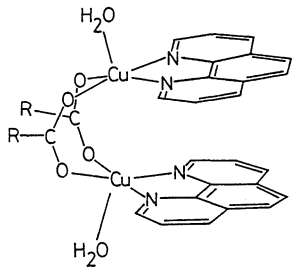
$$\chi_A=\frac{Ng^2\beta^2}{3kT}[1+1/3\exp(-2J/kT)]^{-1}+N\alpha \qquad (1)$$

where $-2J$ is equal to the energy separation between the lowest singlet and triplet levels, which gives the degree of the strength of the magnetic interaction.

On the basis of magnetic susceptibilities, IR spectra and X-ray structural analysis, it was concluded that those complexes possess a novel binuclear structure with two carboxylato-bridges represented by **I**.[4-6] Although a few copper(II) complexes with such di-μ-carboxylato-bridges have been reported,[8,9] no binuclear copper(II) complexes with di-μ-formato-, di-μ-acetato-, and di-μ-2,2-dimethylpropionato-bridges have been isolated so far. This paper reports the preparation and characterization of three copper(II) complexes as the first examples of di-μ-formato-, di-μ-acetato-, and di-μ-2,2-dimethylpropionato-bridged binuclear copper(II) complexes with 1,10-phenanthroline at remaining coordination sites represented by **II**. A preliminary report on the molecular structure and magnetic properties of **1** has appeared.[10]



I



II

Experimental

Syntheses. Compound **1**, $[Cu(HCOO)(phen)(H_2O)]_2(NO_3)\cdot 4H_2O$: Formic acid (10 mmol) and 1,10-phenanthroline (10 mmol) were dissolved in 50 cm^3 of water, and the resulting solution was adjusted to pH 5.0 with 1 mol dm^{-3} aqueous NaOH. To this solution 10 cm^3 of 1 mol dm^{-3} aqueous $Cu(NO_3)_2$ was added under stirring, and then the pH was adjusted to 4.0. Earlier precipitates were filtered off, and the filtrate was concentrated to one third of its volume. The deep blue crystals precipitated were collected, washed with water, and air-dried at room temperature. Found: C, 38.50; H, 3.69; N, 10.44; Cu, 15.42%. Calcd for $C_{13}H_{15}N_3O_8Cu$: C, 38.57; H, 3.73; N, 10.38; Cu, 15.70%.

Compound **2**, $[Cu(CH_3COO)(phen)(H_2O)]_2(NO_3)_2\cdot 4H_2O$: The synthetic procedure is similar to that for **1** except for the use of acetic acid instead of formic acid. Found: C, 39.97; H, 3.96; N, 10.00; Cu, 14.95%. Calcd for $C_{14}H_{17}N_3O_8Cu$: C, 40.14; H, 4.09; N, 10.03; Cu, 15.17%.

Compound **3**, $[Cu((CH_3)_3CCOO)(phen)(H_2O)]_2(NO_3)_2\cdot 4H_2O$: To a mixture of 2,2-dimethylpropionic acid (10 mmol) and

1,10-phenanthroline (10 mmol) in water (50 cm^3) was added 10 cm^3 of 1 mol dm^{-3} aqueous $Cu(NO_3)_2$ under stirring, and then the pH was adjusted to 2.8 with 1 mol dm^{-3} aqueous NaOH. After the resulting solution had been concentrated to one third of its volume, it was allowed to stand overnight in a refrigerator. The greenish blue crystals precipitated were collected, washed with water, and air-dried at room temperature. Found: C, 44.43; H, 4.85; N, 9.12; Cu, 13.56%. Calcd for $C_{17}H_{23}N_3O_8Cu$: C, 44.30; H, 5.03; N, 9.12; Cu, 13.79%.

Physical Measurements. The magnetic susceptibilities were determined by the Faraday method in the temperature range of 80—300 K. The effective magnetic moments per copper ion at room temperature were calculated with the equation

$$\mu_{eff} = 2.83\sqrt{(\chi_A - N\alpha)T} \quad (2)$$

where χ_A is the molar magnetic susceptibility corrected for the diamagnetism of the constituent atoms using Pascal's constant[11] and $N\alpha$ is the temperature-independent paramagnetism per mole of copper(II). The value of $N\alpha$ was assumed to be 60×10^{-6} emu (1 emu=$4\pi\times10^{-6}$ m^3). The observed magnetic susceptibility data were fitted to the Eq. 1. The best-fit parameters of $-2J$ and g were obtained by a nonlinear least-squares fitting procedure. The quantity of fit was estimated by means of a discrepancy index,

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

The magnetic data are given in Table 4 and are represented graphically in Fig. 4.

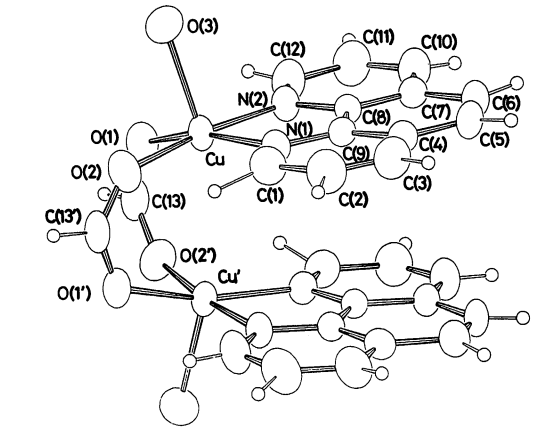
The electronic spectra of all the complexes investigated were recorded by the diffuse reflectance technique with a Hitachi 323 recording spectrophotometer.

X-Ray Crystal Structure Determination. Compound 1: A blue crystal of 0.4×0.4×0.5 mm in dimensions was sealed in a capillary tube together with mother liquor and mounted on a Rigaku four-circle diffractometer AFC-5. The diffraction intensities were measured using graphite monochromatized Mo$K\alpha$ radiation (λ=0.71073 Å). The cell dimensions were determined from 25 2θ values ($20<2\theta<27°$). The crystallographic data are: $[Cu_2(CHO_2)_2(C_{12}H_8N_2)_2(H_2O)_2]^{2+}(NO_3^-)_2\cdot4H_2O$, F.W.=809.6, monoclinic, space group $I2/a$, a=18.850(2), b=9.775(2), c=17.752(2) Å, β=99.03(1)°, V=3230.4(8) Å^3, Z=4, D_m (1,1,2,2-tetrabromoethane/dichloromethane)=1.68(2), D_x=1.66 Mg m^{-3}, μ=1.40 mm^{-1}. The θ-2θ scan technique was employed at a scan rate of 6° min^{-1} in θ. $2\theta_{max}$=55° ($0\leqq h\leqq24$, $0\leqq k\leqq12$, $-23\leqq l\leqq23$). The ratio of structure factors of five standard reflections, $|F_o|/|F_o|_{initial}$ was 1.00—1.10, by reference to which scaling of the intensity data was made. Absorption correction was applied ($0.59<A<0.67$). A total of 3842 reflections were measured and 2592 reflections with $|F_o|>3\sigma(|F_o|)$ were regarded as observed, among which 2511 were unique (R_{int}=0.024). Systematic absences (hkl, $h+k+l$ odd; $h0l$, l odd) indicated that the space group is Ia or $I2/a$. Assuming the centrosymmetric space group $I2/a$, the structure was successfully solved by the Patterson-Fourier method. The atomic parameters were refined by block-diagonal least squares. The function minimized was $\sum w||F_o|-|F_c||^2$, where $w^{-1}=\sigma^2(|F_o|)+(0.015|F_o|)^2$. Eight hydrogen atoms were located on the difference synthesis, and one of H atoms in phen was calculated. No hydrogen atoms of the water molecules could be located. Non-hydrogen atoms were refined anisotropically and H atoms isotropically. Final R=0.055, wR=0.071, and S=2.7 for 2511 unique reflections. Reflection/parameter ratio=9.5, $\Delta/\sigma<0.27$ for non-hydrogen atoms, and $-1.0<\Delta\rho<0.6$ e Å^{-3}. The calculations were carried out on a FACOM M-380R computer at Keio University with UNICS III program system.[12] Complex neutral-atom scattering factors were taken from International Tables for X-ray Crystallography.[13]

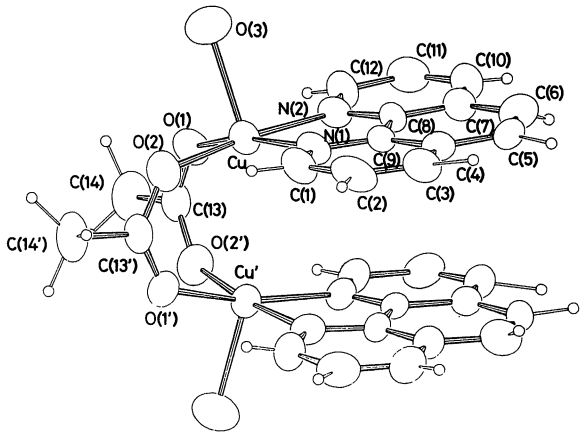
Compound 2: A blue crystal (0.4×0.4×0.4 mm) was sealed in a capillary tube. The crystallographic data are: $[Cu_2(C_2H_3O_2)_2(C_{12}H_8N_2)_2(H_2O)_2]^{2+}(NO_3^-)_2\cdot4H_2O$, F.W.=837.7, monoclinic, space group $C2/c$, a=18.563(4), b=14.272(5), c=14.126(3) Å, β=106.72(2)°, V=3584(2) Å^3, Z=4, D_m=1.61(2), D_x=1.55 Mg m^{-3}, μ=1.27 mm^{-1}. $2\theta_{max}$=55°($0\leqq h\leqq24$, $0\leqq k\leqq18$, $-18\leqq l\leqq18$). The ratio of structure factors of five standard reflections was 0.89—1.02. A total of 4242 reflections were measured and 2152 were observed, of which 2092 were unique (R_{int}=0.023; $0.58<A<0.69$). Systematic absences (hkl, $h+k$ odd; $h0l$, l odd) suggested that the possible space group is Cc or $C2/c$. Assuming the space group $C2/c$, the structure could be solved. The water molecules of crystallization were disordered. They are statistically located at five possible positions with the occupancy factors from 0.20 to 0.70. The sum of the occupancy factors of water of crystallization was assumed to be four based on an elemental analysis. Positions of four H atoms in phen were calculated. Hydrogen atoms and disordered water O atoms were refined isotropically. Final R=0.082, wR=0.078 and S=2.4 for 2092 reflections. Reflection/parameter ratio =7.4, $\Delta/\sigma<0.42$ for non-hydrogen atoms. $-0.4<\Delta\rho<0.6$ e Å^{-3}. The crystals of **2** effloresce more quickly in the air than those of **1**. The temperature factors B_{eq} of **2** are by ca. 50% larger than those of **1** reflecting poor crystallinity. Relatively large R value, 0.082 for **2** may be due to the disorder.

Results and Discussion

The Structures of Compounds 1 and 2. The final atomic parameters are listed in Table 1, and the bond lengths and angles within the complex cations in Table 2.[14] Structures of the complex cations are shown in Fig. 1. Two formate or acetate groups bridge the two copper atoms in a syn-syn form. Both the complex cations have a twofold axis of rotation through the center of the two carboxylate carbon atoms. The coordination around each copper atom is approximately square pyramidal with two nitrogen donors of a phenanthroline, two oxygen donors of two carboxylates occupying basal sites and an axial coordination of a water molecule. This bond distance Cu-O (H_2O) is significantly longer than those of Cu-O (formate) bond in the basal plane. The Cu···Cu distances are 3.103(2) Å in Compound **1** and 3.063(3) Å in Compound **2**, longer by 0.3—0.5 Å than the corresponding ones in the usual copper(II) carboxylate dimers of $[Cu(RCOO)_2\cdot L]_2$.[2,3] The structure of the $Cu_2(OCO)_2$ moiety deforms from that in the typical central cage of the dimeric copper acetate because of imbalance in binding. The structures are essentially



(1)



(2)

Fig. 1. An ORTEP drawing of the complex cations with thermal ellipsoids scaled at the (1) 50% and (2) 35% probability level.[15] Hydrogen atoms are represented by circles of radius 0.08 Å. The water H atoms could not be located on difference synthesis.

the same as that in $[Cu(PhC_2H_4COO)(phen)(H_2O)]_2$-$(NO_3)_2 \cdot 2H_2O$ (Cu··· Cu=3.054(1) Å).[9] Although the dihedral angles between the basal coordination planes around the copper atoms are 22.4° in **1** and 22.6° in **2**, the angles between the phen planes are only 5.7° in **1** and 4.7° in **2**. The tilting of the basal planes around copper atoms is reflected on the Cu-O-C angles of the carboxylates. The angles have average values of 128.6° for **1** and 129.2° for **2**, about 5° greater than those found in the structures of $[Cu(RCOO)_2 \cdot L]_2$ complexes.[2,3] In the CuO_2N_2 basal plane of both Compounds **1** and **2** the O(1)-Cu-N(1) and O(2)-Cu-N(2) angles are different from each other: 164.0(2)° and 173.5(2)° for **1**: 165.8(3)° and 172.8(3)° for **2**, respectively. On the other hand, the corresponding two O-Cu-O angles(trans) in the CuO_4 basal plane of distorted square-pyramidal copper(II) carboxylates, $[Cu(RCOO)_2 \cdot L]_2$, are almost the same as each other in the range of 164—169°.[3,16-19] This fact suggests that in both **1** and **2** the distortion of metal geometry from square pyramidal to trigonal bipyramidal is slightly larger than that in the $[Cu(RCOO)_2 \cdot L]_2$ complexes. There is no significant difference in the carboxylate bridges between **1** and **2**: the mean Cu-O distance and O-C-O bond angle are 1.961(4) Å and 127.7(5)°, and 1.962(6) Å and 126.1(8)°, respectively.

Table 1. Fractional Coordinates ($\times 10^4$, $\times 10^5$ for Cu) and Equivalent Isotropic Thermal Parameters ($\times 10$)

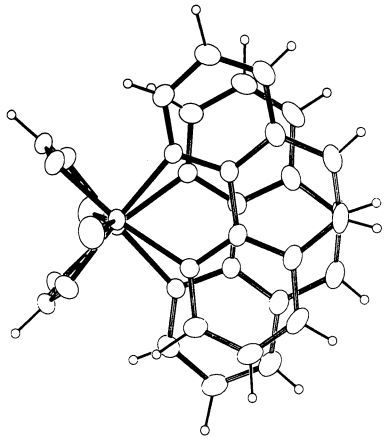
	Atom	x	y	z	B_{eq}/Å^2
1	Cu	18793(4)	3157(7)	4799(4)	27
	O(1)	1552 (2)	−1118 (4)	−268 (2)	37
	O(2)	2619 (2)	−888 (4)	1024 (2)	39
	O(3)	1187 (2)	−285 (5)	1284 (3)	49
	N(1)	2315 (2)	2017 (4)	995 (2)	26
	N(2)	1213 (2)	1685 (4)	−102 (3)	27
	C(1)	2860 (3)	2131 (6)	1574 (3)	35
	C(2)	3092 (4)	3407 (7)	1870 (4)	42
	C(3)	2770 (4)	4559 (6)	1583 (3)	41
	C(4)	2183 (3)	4480 (5)	968 (3)	30
	C(5)	1793 (4)	5627 (5)	624 (4)	37
	C(6)	1233 (3)	5469 (6)	50 (4)	37
	C(7)	1011 (3)	4124 (6)	−220 (3)	31
	C(8)	1380 (3)	3002 (5)	99 (3)	24
	C(9)	1986 (3)	3174 (5)	712 (3)	25
	C(10)	422 (3)	3879 (7)	−795 (4)	42
	C(11)	249 (3)	2555 (7)	−1001 (4)	46
	C(12)	655 (3)	1480 (6)	−644 (4)	39
	C(13)	1829 (3)	−1383 (6)	−843 (3)	33
	N(3)	4897 (3)	2591 (6)	3269 (3)	43
	O(4)	4346 (3)	2137 (6)	3488 (4)	73
	O(5)	5370 (3)	1818 (5)	3121 (3)	62
	O(6)	4944 (3)	3859 (5)	3185 (3)	62
	O(7)	6036 (3)	4754 (5)	2400 (3)	56
	O(8)	6699 (4)	2308 (5)	2298 (3)	79
2	Cu	2594(6)	27993(8)	36320(8)	42
	O(1)	946 (3)	3714 (4)	3360 (4)	52
	O(2)	−601 (3)	3685 (4)	3281 (4)	55
	O(3)	512 (4)	3245 (5)	5185 (5)	75
	N(1)	−414 (3)	1693 (5)	3620 (5)	44
	N(2)	1050 (3)	1776 (5)	3877 (4)	40
	C(1)	−1147 (4)	1704 (6)	3495 (6)	50
	C(2)	−1535 (5)	862 (7)	3463 (7)	63
	C(3)	−1195 (5)	29 (6)	3544 (6)	57
	C(4)	−406 (5)	10 (6)	3685 (6)	49
	C(5)	49 (6)	−821 (6)	3802 (6)	61
	C(6)	813 (5)	−757 (7)	3983 (7)	63
	C(7)	1168 (5)	120 (6)	4009 (6)	46
	C(8)	753 (4)	914 (5)	3880 (5)	37
	C(9)	−35 (4)	873 (6)	3706 (5)	38
	C(10)	1928 (6)	214 (7)	4201 (7)	60
	C(11)	2233 (5)	1073 (7)	4229 (6)	59
	C(12)	1769 (5)	1847 (6)	4072 (7)	51
	C(13)	987 (4)	3987 (6)	2560 (7)	45
	C(14)	1530 (5)	4743 (7)	2526 (8)	72
	N(3)	1824 (4)	2354 (6)	7186 (6)	77
	O(4)	1728 (4)	2146 (6)	6309 (5)	98
	O(5)	2286 (5)	1984 (6)	7846 (7)	127
	O(6)	1424 (6)	2880 (7)	7404 (8)	165
	O(7)[a]	−1909 (7)	3141 (10)	5481 (10)	130
	O(8)[a]	−987 (10)	4763 (13)	4949 (13)	112
	O(9)[a]	−730 (19)	3486 (27)	6024 (25)	82
	O(10)[a]	145 (18)	3732 (21)	8049 (20)	126
	O(11)[a]	−597 (16)	4339 (22)	5641 (21)	116

a) Population parameters of disordered H_2O: O(7), 0.7; O(8), 0.5; O(9), 0.2; and O(10) and O(11), 0.3.

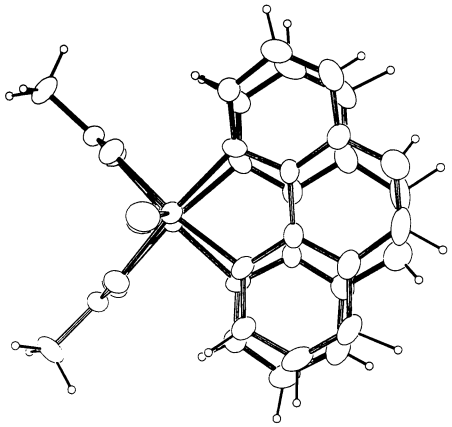
Table 2. Bond Lengths (Å) and Bond Angles (°)

	1	2		1	2
Bond length (Å)			Bond angle(°)		
Cu-O(1)	1.962(4)	1.939(6)	O(1)-Cu-O(2)	91.6(2)	92.8(2)
Cu-O(2)	1.959(4)	1.984(6)	O(1)-Cu-O(3)	95.4(2)	92.2(3)
Cu-O(3)	2.161(5)	2.201(7)	O(1)-Cu-N(1)	164.0(2)	165.8(3)
Cu-N(1)	2.010(4)	2.010(7)	O(1)-Cu-N(2)	91.3(2)	91.9(3)
Cu-N(2)	2.007(4)	2.029(7)	O(2)-Cu-O(3)	88.2(2)	89.4(2)
O(1)-C(13)	1.245(7)	1.218(12)	O(2)-Cu-N(1)	93.7(2)	92.6(3)
N(1)-C(1)	1.339(6)	1.321(9)	O(2)-Cu-N(2)	173.5(2)	172.8(3)
N(1)-C(9)	1.348(6)	1.353(11)	O(3)-Cu-N(1)	99.8(2)	100.9(3)
N(2)-C(8)	1.360(6)	1.349(10)	O(3)-Cu-N(2)	97.3(2)	95.8(3)
N(2)-C(12)	1.325(7)	1.287(11)	N(1)-Cu-N(2)	82.0(2)	81.6(3)
C(1)-C(2)	1.397(9)	1.395(13)	Cu-O(1)-C(13)	125.2(4)	128.3(6)
C(2)-C(3)	1.341(9)	1.335(13)	Cu-N(1)-C(1)	128.9(3)	127.3(6)
C(3)-C(4)	1.429(8)	1.420(13)	Cu-N(1)-C(9)	113.2(3)	111.9(5)
C(4)-C(5)	1.425(8)	1.438(13)	C(1)-N(1)-C(9)	118.0(4)	120.8(7)
C(4)-C(9)	1.386(7)	1.407(12)	Cu-N(2)-C(8)	113.3(3)	112.4(5)
C(5)-C(6)	1.356(9)	1.370(14)	Cu-N(2)-C(12)	129.4(4)	129.4(6)
C(6)-C(7)	1.439(8)	1.410(13)	C(8)-N(2)-C(12)	117.3(4)	118.1(7)
C(7)-C(8)	1.372(7)	1.353(11)	N(1)-C(1)-C(2)	121.4(5)	119.8(8)
C(7)-C(10)	1.406(8)	1.364(14)	C(1)-C(2)-C(3)	120.7(6)	122.5(9)
C(8)-C(9)	1.458(7)	1.413(10)	C(2)-C(3)-C(4)	119.6(5)	118.2(8)
C(10)-C(11)	1.370(10)	1.346(14)	C(3)-C(4)-C(5)	124.8(5)	125.4(8)
C(11)-C(12)	1.393(9)	1.379(13)	C(3)-C(4)-C(9)	115.8(5)	117.7(8)
C(13)-C(14)		1.487(13)	C(5)-C(4)-C(9)	119.4(5)	116.9(8)
N(3)-O(4)	1.246(9)	1.236(11)	C(4)-C(5)-C(6)	121.4(5)	120.6(8)
N(3)-O(5)	1.228(8)	1.193(11)	C(5)-C(6)-C(7)	120.4(6)	121.0(9)
N(3)-O(6)	1.253(8)	1.158(14)	C(6)-C(7)-C(8)	119.4(5)	119.8(8)
Cu···Cu^{i}	3.103(2)	3.063(3)	C(6)-C(7)-C(10)	123.6(5)	122.8(9)
C(13)-O(2^{i})	1.235(7)	1.273(10)	C(8)-C(7)-C(10)	117.1(5)	117.4(8)
			N(2)-C(8)-C(7)	124.5(5)	123.2(7)
			N(2)-C(8)-C(9)	115.3(4)	116.2(7)
			C(7)-C(8)-C(9)	120.2(5)	120.6(7)
			N(1)-C(9)-C(4)	124.5(5)	121.1(7)
			N(1)-C(9)-C(8)	116.2(4)	117.7(7)
			C(4)-C(9)-C(8)	119.3(4)	121.0(7)
			C(7)-C(10)-C(11)	118.8(6)	119.8(9)
			C(10)-C(11)-C(12)	120.0(6)	119.1(9)
			N(2)-C(12)-C(11)	122.2(5)	122.2(8)
			O(1)-C(13)-C(14)		119.1(5)
			O(4)-N(3)-O(5)	121.1(6)	122.7(9)
			O(4)-N(3)-O(6)	117.9(6)	120.2(9)
			O(5)-N(3)-O(6)	121.0(6)	116.8(10)
			Cu-O(2)-C(13^{i})	132.1(4)	130.2(6)
			O(1)-C(13)-O(2^{i})	127.7(5)	126.1(8)
			O(2)-C(13^{i})-C(14^{i})		114.9(8)

Symmetry code: (i) (**1**) 1/2−x, y, −z, (**2**) −x, y, 1/2−z.



(**1**)



(**2**)

Fig. 2. Views of the complex cations approximately perpendicular to the two phenanthroline molecules.

The projections of the structures along the Cu···Cu direction are shown in Fig. 2. The stacking of the phen ligands differs from each other reflecting the effect of molecular packing in the crystals. The shortest C···C distance between the two phen moieties in **1** is 3.48(1) Å, which is approximately twice of the Van der Waals radius of aromatic carbon atoms (1.77 Å).[20]

Electronic Spectra. The reflectance spectra of the complexes are similar to one another, giving a band maximum at ca. 15200 cm^{-1} and a low-energy shoulder at ca. 11500 cm^{-1} (Fig. 3 and Table 3). The separation between these two peaks, $\Delta\tilde{\nu}$=3650—3980 cm^{-1}, is relatively small as compared with those observed for $[Cu(CH_3COO)_2(py)]_2$ (5000 cm^{-1})[21,22] and $[Cu(HCOO)_2(urea)]_2$ (5170 cm^{-1}) with a distorted square-pyramidal copper(II) geometry. Hathaway et al.[23] demonstrated in their study on $[Cu(bpy)_2Cl]X$ that copper(II) complexes with the metal geometry close to a regular trigonal bipyramid show a single broad peak in their electronic spectra at 12500 cm^{-1}, 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 $\Delta\tilde{\nu}$ value can be taken as a measure of the degree of distortion in metal geometry from square pyramidal to trigonal bipyram-

Table 3. Reflectance Spectral Data of $[Cu(RCOO)(phen)(H_2O)]_2(NO_3)_2\cdot 4H_2O$

R	$\tilde{\nu}/10^3$ cm^{-1}		$\Delta\tilde{\nu}/10^3$ cm^{-1}
H	15.20	11.3	3.90
CH_3	15.48	11.5	3.98
$(CH_3)_3C$	15.15	11.5	3.65

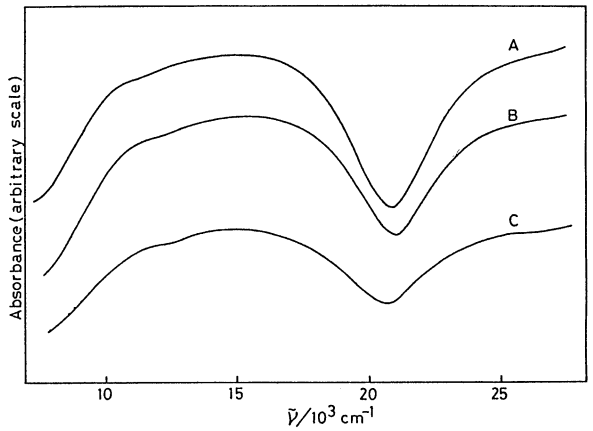


Fig. 3. Reflectance spectra of $[Cu(RCOO)(phen)(H_2O)]_2(NO_3)_2 \cdot 4H_2O$: (A) R=H, (B) $R=CH_3$, (C) $R=(CH_3)_3C$.

idal. Although the $\Delta\tilde{\nu}$ values observed for the present complexes are smaller than those of the distorted square-pyramidal copper(II) complexes, the values are much larger than those of the distorted trigonal-bipyramidal copper(II) complexes such as $[Cu(bpy)_2Cl]NO_3 \cdot 3H_2O$,[23] $[Cu(bpy)_2CN]NO_3 \cdot 2H_2O$,[24] and $[Cu(Ph_3CCOO)_2(py)]_2 \cdot$ benzene[25] ($\Delta\tilde{\nu}$=2000—2510 cm^{-1}). Therefore the present complexes have a slightly larger degree of distortion in the metal geometry from square pyramidal to trigonal bipyramidal than those of $[Cu(CH_3COO)_2(py)]_2$ and $[Cu(HCOO)_2(urea)]_2$.

Magnetic Susceptibilities. The magnetic susceptibility data of the present complexes are well represented by Eq. 1 (Fig. 4 and Table 4), indicating that an antiferromagnetic interaction is operative between the copper(II) ions in these complexes. These magnetic and spectral data clearly indicate that Compound **3** also have the same type of the binuclear structure as determined for **1** and **2**. The $-2J$ values (86—125 cm^{-1}) of the present complexes are much less than one third of those found for the corresponding tetra-μ-carboxylato-bridged complexes, $[Cu(RCOO)_2 \cdot L]_2$ ($-2J$=250—555 cm^{-1}).[2,3] Although the Cu···Cu distances of 3.103(2) Å for **1** and 3.063(3) Å for **2** are much longer than those in the $[Cu(RCOO)_2 \cdot L]_2$ complexes,[2,3] recent works have clearly demonstrated that the Cu···Cu separation is not the major factor in determining the $-2J$ value in these systems.[3,19] Therefore, such a decrease in antiferromagnetic interaction can be explained in terms of a decrease in the number of the bridging carboxylato ions, through which superexchange interaction is operative: from four to two in the present complexes. Moreover, the distortion of copper(II) geometry from square pyramidal to trigonal bipyramidal described above leads to a further weaker magnetic interaction in the present complexes. Such a decrease in the magnetic interaction with increasing the distortion has been observed for copper(II) trichroloacetate adducts with 3-substituted pyridines, $[Cu(Cl_3CCOO)_2(3\text{-}Xpy)]_2$.[26]

Table 4. Magnetic Data of $[Cu(RCOO)(phen)(H_2O)]_2(NO_3)_2 \cdot 4H_2O$

R	$-2J$/cm^{-1}	g	$\sigma_{dis}\times10^3$
H	125	2.18	5.61
CH_3	86	2.16	5.49
$(CH_3)_3C$	99	2.17	6.43

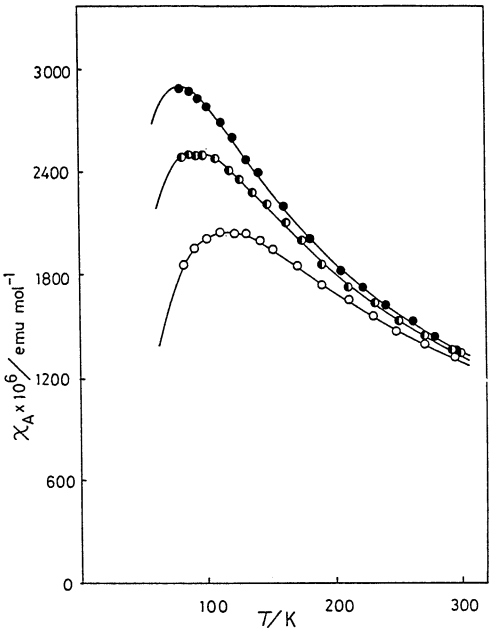


Fig. 4. Temperature dependence of magnetic susceptibilities for $[Cu(RCOO)(phen)(H_2O)]_2(NO_3)_2 \cdot 4H_2O$: (○) R=H, (●) $R=CH_3$, (◐) $R=(CH_3)_3C$. The solid curves were calculated from Eq. 1 using the parameters listed in Table 4.

The order of decrease in the $-2J$ values for the present complexes is the formate> the 2,2-dimethylpropanoate> the acetate. This is the same as that for the corresponding $[Cu(RCOO)_2 \cdot L]_2$ complexes: the order of decrease in $-2J$ is $[Cu(HCOO)_2 \cdot L]_2$ ($-2J$= 485—555 cm^{-1})[2]>$[Cu((CH_3)_3CCOO)_2 \cdot L]_2$ ($-2J$= 319—397 cm^{-1})[27]>$[Cu(CH_3COO)_2 \cdot L]_2$ ($-2J$=284—325 cm^{-1}).[2] Recently it has been shown that there are little magneto-structural correlation between $[Cu(HCOO)_2 \cdot L]_2$ and $[Cu(CH_3COO)_2 \cdot L]_2$,[19] though the copper(II) formates display much larger $-2J$ values than the copper(II) acetates and other alkanoates. The reason for the strongest magnetic interaction of the formate, **1**, among the present complexes also remains unclear because of no significant differences in structure between **1** and **2**.

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