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Syntheses, Structure, and Properties of Several Bis{(alkylthio)acetato}copper(II)-Amine Adducts[1)]

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The crystal and molecular structure of tetrakis{(isopropylthio)acetato}bis(quinoline)dicopper(II) (**1**), bis(dibenzylamine)bis{(ethylthio)acetato}copper(II) (**2**), and bis{(isopropylthio)acetato}tris(isoquinoline)copper(II) (**3**) were determined by the X-ray diffraction method. The final R values obtained are 0.041, 0.055, and 0.078 for **1**, **2**, and **3** respectively. **1** is green in color and is orthorhombic with the space group Pcab. It has a dimer structure similar to that of the copper(II) acetate hydrate, where four (alkylthio)acetate liagnds bridge both copper(II) atoms. **2** is violet in color and is monoclinic with the space group A2/a. It has a square-palnar geometry, and no atoms are coordinated to the copper(II) atom from the axial direction, probably because of the steric effect of the large dibenzylamine molecules. **3** is blue in color and is triclinic with the space group P$\bar{1}$. It has potentially a hepta-coordinate geometry, where one nitrogen atom and two oxygen atoms ligate from the axial direction of the CuN_2O_2 plane.

(Alkylthio)acetic acids are interesting ligands, as they have a carboxyl group as well as a sulfide sulfur atom which can be coordinated to a metal atom. In the cases of cobalt(II) or copper(II) (alkylthio)acetate dihydrates, the ligand is bidentate, forming a five-membered chelate ring by the coordination of its oxygen and sulfur atoms.[2—4)] On the other hand, in the anhydrous cobalt(II) (propylthio)acetate hexamer, it was found that the ligands bridge the metal atoms; half of them bridge two cobalt atoms by both of the carboxyl oxygen atoms, while the other half bridge three cobalt atoms with both of carboxyl oxygen and the sulfide sulfur atoms.[5)]

This time, the authors planned the synthesis of the anhydrous copper(II) (alkylthio)acetate. However, the dehydration of the hydrated copper(II) (alkylthio)acetates by the azeotropic method, *i.e.*, evaporating the benzene–alcohol solution to dryness as in the cases of cobalt(II) or nickel(II) salts, was not successful; the copper(II) salts were destroyed during the process. On the other hand, when quinoline or some such kind of amine was added to the solution before the evaporation process, the water in the complex was completely replaced by the amine, and their mono-, bis-, and tris(amine) adducts were obtained without decomposing the (alkylthio)acetate ligand. They are easily soluble in nonpolar solvents such as benzene, and they are stable in air. Each of them has a characteristic color; *i.e.*, the mono(amine) adducts are green; the bis(amine) adducts, violet, and the tris(amine) adducts, blue. The absorption coefficients of their benzene solution (containing excess of amine) are rather high (about 150—200 cm^{-1} mol^{-1} dm^3) compared with those of the common copper(II) salts. Therefore, it seems that it would be interesting to clarify their geometries around the copper(II) atom, and so we began to study their structures by means of the X-ray diffraction technique.

Experimental

Synthesis of Tetrakis{(isopropylthio)acetato}bis(quinoline)dicopper(II) (1) and the Related Mono(amine) Adduct Dimers. The ligand, (isopropylthio)acetic acid, was obtained by a condensation reaction between 2-bromopropane and mercaptoacetic acid (Larsson's method).[6)] The copper(II) (isopropylthio)acetate dihydrate was obtained according to the method described in early papers.[7)] (The other ligands and the starting copper(II) salts were obtained similarly.) The hydrated copper(II) salt (violet isomer) (0.55 g, 1.5 mmol) and quinoline (0.40 g, 3.1 mmol) were boiled with about 10 cm^3 of benzene for several minutes, and then cooled. Then the supernatant fluid was separated into another open vessel; the water in the hydrate remained on the wall of the original vessel. About 10 cm^3 of petroleum benzine was then added, and the mixture was left standing for several hours. The deposited crystals were filtered off, washed with a small portion of benzene–petroleum ether mixture (1 : 1=v/v), and dried in a vacuum desiccator (yield, 0.47 g, 68%). They were purified by reprecipitation: the product was dissolved into benzene containing an excess of quinoline, and the solution in an open vessel was left standing in petroleum benzine vapor (in a desiccator) for several days to obtain the crystals.

The other mono(amine) adduct dimers with the formula of $[Cu_2(RSCH_2CO_2)_4(amine)_2]$ (where $R=CH_3$, C_2H_5, or $(CH_3)_2CH$, and amine=quinoline, isoquinoline, or pyridine) were obtained similarly; their yields were comparable to that of **1**.

Synthesis of Bis(dibenzylamine)bis{(ethylthio)acetato}copper(II) (2). Diaquabis{(ethylthio)acetato}copper(II) (0.50 g, 1.5 mmol) and dibenzylamine (1.2 g, 6.0 mmol) were boiled in 5 cm^3 of benzene, and they dissolved. The supernatant fluid was mixed with 5 cm^3 of petroleum benzine in a beaker, after which the mixture was left standing overnight in petroleum benzine vapor (in a desiccator). A deep violet product was thus precipitated (yield, 0.73 g, 70%). It was purified by the reprecipitation process (see the process for **1**). The same type of adducts were similarly obtained using (methylthio)- or (isopropylthio)acetate of copper(II) in place of the (ethylthio)acetate mentioned above.

Synthesis of Bis{(isopropylthio)acetato}bis(isoquinoline)copper(II). Bis{(isopropylthio)acetato}copper(II) dihydrate (violet isomer) (0.55 g, 1.5 mmol) and isoquinoline (0.40 g, 3.1 mmol), were dissolved into about 5 cm^3 of a benzene–ligroine mixture (1 : 1=v/v) by heating them. To the supernatant fluid, about 15 cm^3 of ligroine was then added. After the mixture had been left standing for several hours, a violet precipitate was deposited; the precipitate was filtered off and washed with

TABLE 1. ANALYSES AND MAGNETIC MOMENTS OF THE COMPLEXES, $[Cu(RSCH_2CO_2)_2(amine)_n]$**

n	R	Amine		Cu(%)	C(%)	H(%)	N(%)	μ_{eff}[a] / BM
1	CH_3	Isoquinoline	Found	15.55	45.61	4.29	3.40	1.3_6
			Calcd	15.77	44.71	4.25	3.48	
1	CH_3	Quinoline	Found	15.59	45.03	4.28	3.56	1.3_2
			Calcd	15.77	44.71	4.25	3.48	
1	CH_3	Pyridine	Found	17.78	37.05	4.20	3.89	1.4_2
			Calcd	18.01	37.44	4.28	3.97	
1	C_2H_5	Isoquinoline	Found	14.89	47.52	4.98	3.14	1.3_5
			Calcd	14.74	47.37	4.91	3.25	
1	C_2H_5	Quinoline	Found	14.90	47.36	4.91	3.21	1.3_8
			Calcd	14.74	47.37	4.91	3.25	
1	C_2H_5	Pyridine	Found	16.63	41.20	5.08	3.64	1.4_1
			Calcd	16.68	40.99	5.03	3.68	
1	$(CH_3)_2CH$	Isoquinoline	Found	13.66	49.88	5.54	3.05	1.3_8
			Calcd	13.84	49.71	5.49	3.05	
1	$(CH_3)_2CH$	Quinoline	Found	13.61	50.00	5.56	3.08	1.3_3
			Calcd	13.84	49.71	5.49	3.05	
2	CH_3	Dibenzylamine	Found	9.30	61.36	6.07	4.18	1.7_3
			Calcd	9.51	61.10	6.03	4.19	
2	C_2H_5	Dibenzylamine	Found	9.19	61.70	6.35	4.02	1.7_6
			Calcd	9.12	62.09	6.37	4.02	
2	$(CH_3)_2CH$	Isoquinoline	Found	10.70	57.23	5.63	4.58	1.7_9
			Calcd	10.80	57.17	5.48	4.76	
2	$(CH_3)_2CH$	Dibenzylamine	Found	8.51	62.82	6.68	3.60	1.6_9
			Calcd	8.77	63.00	6.68	3.87	
3	CH_3	Isoquinoline	Found	10.00	57.63	4.60	6.08	1.8_2
			Calcd	9.61	57.94	4.73	6.35	
3	C_2H_5	Isoquinoline	Found	9.16	60.68	5.07	5.83	1.8_2
			Calcd	9.22	60.98	5.12	6.10	
3	$(CH_3)_2CH$	Isoquinoline	Found	9.09	62.07	5.46	5.84	1.8_5
			Calcd	8.86	61.95	5.48	5.86	

a) 1 BM$=9.274078(36)\times10^{-24}$ J T^{-1}.

** Mono (amine) adducts are shown by the experimental formula.

ligroine (yield 0.50 g, 57%). When isoquinoline is present in a large excess, and when the volume ratio of benzene to ligroine of the mixed solvent is high, only the blue tris(isoquinoline) adduct was obtained. On the other hand, when the amount of added isoquinoline was less than twice that of the starting copper(II) salt in mol/mol, only the green mono(isoquinoline) adduct was obtained. No bis(amine) adduct was obtained by using quinoline in place of isoquinoline.

Synthesis of Bis{(isopropylthio)acetato}tris(isoquinoline)copper(II) (3). Bis{(isopropylthio)acetato}copper(II) (violet isomer) (0.55 g, 1.5 mmol) and isoquinoline (1.0 g, 7.8 mmol) were boiled with 5 cm^3 of benzene, and they dissolved. The supernatant fluid was mixed with 8 cm^3 of ligroine, after which the mixture was left standing for several hours until blue crystals were precipitated (yield, 0.7 g, 65%). The crude product was recrystallized from toluene–ligroine (1 : 1.5=v/v) containing about 2 mol dm^{-3} of isoquinoline.

The same type of complexes were also obtained using (methylthio)- or (ethylthio)acetato of copper(II) and/or pyridine in place of the starting materials mentioned above, but the pyridine adducts were unstable and they lost pyridine even when they were washed with petroleum benzine, changing into green mono(amine) adduct dimers. Even when the blue pyridine adduct crystals obtained without washing were kept in a bottle at room temperature, they decomposed within several days. The same type of adducts were not obtained using quinoline.

Their analyses and the magnetic moments as measured by means of Gouy balance at room temperature (15—20 °C), are shown in Table 1. The yields of the complexes were between 55 and 68%.

Single-crystal X-Ray Analyses. The crystals used were in the shape of parallelepipeds (**1**, 0.3×0.3×0.2 mm^3; **2**, 0.3×0.3×0.3 mm^3; and **3**, 0.3×0.3×0.4 mm^3). All their edges were ground off, though they were not shaped into perfect spheres. The reflections within the range of $2\theta<55°$ were collected on a Philips PW 1100 automated four-circle diffractometer with graphite monochromated Mo $K\alpha$ radiation (0.7107 Å), the θ-2θ scan technique being employed (scan speed 4° min^{-1}; scan width, $1.0+0.3\tan\theta°$). The intensities were corrected for Lorentz and polarization factors, but no correction was made for absorption and extinction. As a representative bis(amine) adduct, bis(dibenzylamine)bis{(isopropylthio)acetato}copper(II) had been studied first, because **1** and **3** are the adducts of (isopropylthio)acetates and it was thought to be convenient to compare its data with those of the other types of adducts. However, the attempt was not successful, because the complex was decomposed under the X-ray radiation within several hours. On the other hand, the crystals of **2** did not decompose even under X-ray radiation for several weeks.

The crystallographic and X-ray measurement data of **1**, **2**, and **3** are as follows:

1. $Cu_2C_{38}H_{50}S_4O_8N_2$, F.W.=918.17; orthorhombic; space group Pcab (The systematic absences of the reflections were those of $kk0(k=\text{odd})$, $0kl(l=\text{odd})$, and $h0l(h=\text{odd})$; $a=17.525(6)$, $b=28.068(18)$, $c=8.870(4)$ Å, $Z=4$,[8] $D_m=1.40(3)$, $D_x=1.38$ g cm^{-3}, $\mu(\text{Mo } K\alpha)=1.24$ mm^{-1}. In total, 2323 independent reflections with $|F_o|>3\sigma(|F_o|)$ among the 2485 measured ones were used for the structure refinement.

2. $CuC_{36}H_{44}S_2O_4N_2$, F.W.=696.43; monoclinic; space group A2/a (the systematic absences of the reflections were $hkl(k+l=\text{odd})$ and $h0l(h=\text{odd})$; $a=19.235(8)$, $b=11.944(2)$, $c=17.137(5)$ Å, $\beta=111.13(3)°$, $Z=4$, $D_m=1.26(2)$, $D_x=1.25$ g cm^{-3}, $\mu(\text{Mo } K\alpha)=0.592$ mm^{-1}. In total, 2090 independent reflections with $|F_o|>3\sigma(|F_o|)$ among the 2188 measured ones were used for the structure determination.

3. $CuC_{37}H_{39}S_2O_4N_2$, F.W.=717.41; triclinic; space group $P\bar{1}$; $a=11.550(10)$, $b=16.912(6)$, $c=9.792$ Å, $\alpha=100.32(5)$, $\beta=109.96(13)$, $\gamma=79.50(5)°$, $Z=2$, $D_m=1.36(2)$, $D_x=1.34$ g cm^{-3}, $\mu(\text{Mo } K\alpha)=0.553$ mm^{-1}. In total, 3404 independent reflections with $|F_o|>3\sigma(|F_o|)$ among the 3832 measured ones were used for the structure refinement.

The Structure Determination. The calculations were carried out on a HITAC M200H computer at the Computer Center of The University of Tokyo, using the local version of the UNICS program.[9]

The atomic scattering factors were taken from the tables.[10] The structure was solved by the heavy-atom method. The positional and thermal parameters were refined by the block-diagonal least-squares method. The positions of several hydrogen atoms were obtained from a difference Fourier synthesis, and some others, by calculation on the assumption of C–H=1.0 Å; they were also refined assuming $B_{iso}=8.0$. In the last cycle of the refinement, all the parameter shifts were less than $\sigma/3$'s. The final R values[11] were 0.041, 0.055, and 0.078 for **1**,**2**, and **3** respectively.

The Spectroscopic Measurements. The infrared absorption spectra of the samples were obtained by means of a JASCO 403G infrared spectrophotometer, using nujol and hexachloro-1,3-butadiene mull.

The visible absorption spectra in a benzene solution, and the reflectance spectra of their solids, were measured by means of a Hitachi 124 spectrophotometer.

Results and Discussion

The final atomic parameters of non-hydrogen atoms are listed in Table 2, while their interactomic distances and bond angles are tabulated in Table 3.[12] A perspective drawing of each complex and the numbering scheme are shown in Figs. 1, 2, and 3.

No abnormal intermolecular contact is found in the crystal structures of **1**—**3**.

As is shown in Fig. 1, the **1** complex has a dimer structure, in which four (isopropylthio)acetate ions bridge two copper atoms. The complex has a center of symmetry at the middle point of the Cu–Cu bond (2.676(4) Å).

All of the Cu–O bond lengths are normal (1.964(5)—1.981(5) Å).[13] The average plane of the CuO_4 is shown by this equation:

$$-0.651x - 0.729y - 0.211z + 1.164 = 0$$

(where x, y, z, are taken in the a-, b-, and c-axis directions respectively and are shown in Å units), and the distances from the average plane are: Cu, −0.174; O(12), 0.051; O(22), 0.052; O(11$^{\text{I}}$), 0.050; and O(21$^{\text{I}}$), 0.052 Å. Thus, the Cu atom deviates a little to the N(31) side from the plane. The ∠Cu$^{\text{I}}$–Cu–N(31) is about 8° less than 180°, and ∠O–Cu–N(31) are in the 90.84(12)—102.18(13)° range. The Cu–N(31) (2.222(6) Å) is a little longer than the common Cu–N bond (2.00 Å).[13] The dihedral angle between the CuO_4 plane and the quinoline one is 81.5°. Both of the carboxyl groups of the carboxylate ligands are almost symmetric. Neither of the sulfur atoms, S(1) and S(2), is coordinated. Thus, the structure is similar to that of tetrakis(acetato)-diaquadicopper(II) or some such bis(amine)tetrakis-(carboxylato)copper(II) dimers;[14] and the bond lengths and bond angles of **1** are comparable to those of the dimers.

The complexes with the same chemical formula, $[Cu(RSCH_2CO_2)_4(\text{amine})_2]$, where amine=isoquinoline or pyridine, are expected to have similar structures, though those of some aromatic amines are expected to have different structures, as has been shown for bis-(propionato)-*p*-toluidinecopper(II).[15]

TABLE 2. FINAL ATOMIC COORDINATES (× 10 ^{4}) AND EQUIVALENT ISOTROPIC TEMPERATURE FACTORS (B/Å^2) OF NON-HYDROGEN ATOMS, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(1) Tetrakis{(isopropylthio)acetato}bis(quinoline)dicopper(II)

Atom	x	y	z	B_{eq}/Å^2 [a]	Atom	x	y	z	B_{eq}/Å^2 [a]
Cu	493.5(3)	352.9(2)	279.9(6)	2.8	C(23)	−1417(3)	1554(2)	521(6)	4.6
S(1)	545(1)	−1322(1)	3920(2)	4.9	C(24)	−1740(4)	1877(2)	−686(6)	6.0
S(2)	−2114(1)	1088(1)	898(2)	4.4	C(25)	−1206(4)	1830(2)	1899(7)	5.7
O(11)	−65(2)	−648(1)	1540(4)	4.2	N(31)	1418(2)	859(1)	897(4)	3.0
O(12)	755(2)	−60(1)	2014(3)	3.6	C(32)	2011(3)	659(2)	1564(5)	3.6
O(21)	−1187(2)	29(1)	988(4)	4.2	C(33)	2604(3)	910(2)	2269(6)	4.4
O(22)	−369(2)	620(1)	1415(4)	3.8	C(34)	2580(3)	1387(2)	2249(6)	4.6
C(11)	465(2)	−458(2)	2276(5)	3.4	C(35)	1931(3)	2126(2)	1409(7)	5.4
C(12)	801(3)	−713(2)	3630(6)	4.9	C(36)	1363(4)	2337(2)	673(7)	5.6
C(13)	−469(3)	−1309(2)	4293(5)	4.4	C(37)	787(3)	2062(2)	−22(6)	5.0
C(14)	−688(4)	−1806(3)	4840(9)	8.4	C(38)	811(3)	1575(2)	78(5)	3.6
C(15)	−703(4)	−931(3)	5393(8)	8.1	C(39)	1405(2)	1346(2)	836(5)	3.0
C(21)	−1013(3)	428(2)	1515(5)	3.3	C(30)	1986(3)	1628(2)	1511(5)	3.8
C(22)	−1634(3)	714(2)	2265(6)	4.1					

a) The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the following expression: $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2)$. The B_{ij}'s are defined by: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hlB_{13}+2hkB_{12})]$.

(2) Bis(dibenzylamine)bis{(ethylthio)acetato}copper(II)

Atom	*x*	*y*	*z*	B_{eq}/Å^2 [b)]	Atom	*x*	*y*	*z*	B_{eq}/Å^2 [b)]
Cu	0.0	0.0	0.0	3.9	C(13)	−3174(3)	1419(5)	−2999(4)	6.7
S	1485(1)	−2958(2)	−678(1)	8.9	C(14)	−3219(3)	630(6)	−3591(4)	6.9
O(1)	479(2)	−1029(3)	−502(2)	6.0	C(15)	−2743(3)	−240(5)	−3400(4)	7.5
O(2)	−372(2)	−1528(3)	−1706(2)	6.4	C(16)	−2217(3)	−340(5)	−2621(4)	6.4
N	−796(2)	455(3)	−1098(2)	4.0	C(20)	−655(3)	1596(4)	−1341(3)	4.9
C(1)	266(3)	−1509(4)	−1200(3)	4.5	C(21)	133(3)	1694(4)	−1310(3)	4.9
C(2)	889(3)	−2020(5)	−1427(3)	6.3	C(22)	669(3)	2203(5)	−640(4)	7.3
C(3)	1005(5)	−4298(7)	−1024(6)	12.7	C(23)	1408(3)	2279(7)	−615(5)	9.8
C(4)	342(5)	−4355(8)	−827(7)	14.9	C(24)	1592(3)	1827(6)	−1227(5)	9.4
C(10)	−1574(3)	305(4)	−1137(3)	4.9	C(25)	1083(4)	1324(6)	−1879(4)	8.1
C(11)	−2148(2)	433(4)	−1997(3)	4.4	C(26)	351(3)	1256(5)	−1923(3)	6.5
C(12)	−2636(3)	1324(5)	−2204(3)	5.4					

b) The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the following expression : $B_{eq}=4/3(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{13}ac\cos\beta)$. The B_{ij}'s are defined by: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hlB_{13}+2hkB_{12})]$.

(3) Bis{(isopropylthio)acetato}tris(isoquinoline)copper(II)

Atom	*x*	*y*	*z*	B_{eq}/Å^2 [c)]	Atom	*x*	*y*	*z*	B_{eq}/Å^2 [c)]
Cu	5852(1)	2552(1)	3396(1)	2.8	C(36)	2860(9)	116(6)	5840(11)	4.6
S(1)	1776(2)	4455(2)	4081(3)	4.4	C(37)	2589(9)	−36(6)	4327(11)	4.4
S(2)	8243(3)	388(2)	1091(3)	4.6	C(38)	3087(8)	365(5)	3613(10)	3.7
O(11)	5298(5)	3551(3)	4575(6)	3.3	C(39)	3905(7)	936(5)	4425(9)	2.7
O(12)	3565(6)	3324(4)	2749(6)	4.0	C(30)	4186(7)	1093(5)	5965(9)	2.7
O(21)	6428(5)	1572(3)	2272(6)	3.0	C(41)	6737(8)	3775(5)	2325(9)	3.5
O(22)	4704(6)	1291(4)	468(7)	4.5	C(43)	5248(8)	3094(6)	519(10)	3.9
N(32)	5223(6)	1889(4)	4494(7)	2.7	C(44)	5293(9)	3517(6)	−542(10)	4.4
N(42)	5964(6)	3234(4)	1932(7)	3.1	C(45)	6246(10)	4551(6)	−1212(11)	4.6
N(52)	7872(7)	2502(4)	5104(7)	3.5	C(46)	7047(11)	5128(6)	−686(13)	6.1
C(11)	4129(8)	3698(5)	3934(9)	3.2	C(47)	7730(11)	5267(6)	739(12)	5.5
C(12)	3442(9)	4377(6)	4711(11)	4.3	C(48)	7644(11)	4839(6)	1777(11)	5.0
C(13)	1508(9)	3450(7)	4211(12)	5.2	C(49)	6834(9)	4251(5)	1303(10)	3.7
C(14)	120(11)	3457(8)	3803(16)	7.7	C(40)	6128(9)	4093(5)	−170(10)	3.8
C(15)	2167(14)	3185(8)	5723(16)	8.2	C(51)	8205(8)	3011(5)	6308(10)	3.6
C(21)	5850(8)	1180(5)	1076(9)	3.2	C(53)	8698(8)	1824(5)	4962(10)	3.7
C(22)	6583(9)	524(5)	321(10)	4.2	C(54)	9787(9)	1647(6)	6024(11)	4.4
C(23)	8715(9)	1337(6)	976(11)	4.7	C(55)	11290(9)	2030(7)	8522(11)	5.1
C(24)	10080(11)	1276(8)	1697(13)	6.5	C(56)	11554(11)	2557(7)	9760(11)	5.8
C(25)	8358(13)	1503(10)	−593(16)	9.6	C(57)	10745(11)	3265(7)	9891(12)	6.2
C(31)	4465(8)	1364(5)	3757(8)	3.0	C(58)	9636(10)	3435(6)	8805(11)	4.5
C(33)	5498(8)	2037(5)	5964(9)	3.2	C(59)	9339(8)	2878(6)	7477(9)	3.8
C(34)	5010(8)	1659(5)	6725(9)	3.2	C(50)	10147(8)	2177(6)	7337(9)	3.7
C(35)	3642(9)	659(5)	6671(10)	4.1					

c) The equivalent isotropic temperature factors for non-hydrogen atoms were computed using the following expression: $B_{eq} = 4/3\,(B_{11}a^2+B_{22}b^2+B_{33}c^2+B_{12}ab\cos\gamma+B_{13}ac\cos\beta+B_{23}bc\cos\alpha)$. The B_{ij}'s are defined by: $\exp[-(h^2B_{11}+k^2B_{22}+l^2B_{33}+2klB_{23}+2hlB_{13}+2hkB_{12})]$.

As is shown in Fig. 2, the copper atom of **2** lies at the center of symmetry, forming a N_2O_2 tetra-coordinate square-planar complex. Both the Cu–O and Cu–N bond lengths are normal,[13] but the ∠O–Cu–N angle is 4.6° more than the right angle. Although the axially elongated octahedral geometry is the most common coordination site around a copper(II) ion, there are not many complexes with the pure square-planar configuration. In the case of bis(oxalato)copper(II), two oxygen atoms of other chelates are coordinated weakly from both the axial directions,[16] while in the cases of β-diketonates,[17–21] which are typical square-planar complexes, weak Cu–C bondings between the copper(II) and the γ-carbon atoms of other chelates were found. Recently, a long-distance interaction of the type was also reported in copper(II) metalaacetylacetonate.[22]

Especially in crystaline state, copper(II) complexes coordinated to four unidentate ligands arer are, although $Na_4[Cu^{II}(NH_3)_4][Cu^I(S_2O_3)_2]_2$,[23] $Cu(C_5H_5NO)_4X_2$ (where $X=BF_4$ or ClO_4),[24] and $Cu(diazepam)_2Cl_2\cdot 2H_2O\cdot 1/3\,CHCl_3$ (where diazepam=7-chloro-1,3-dihydro-1-methyl-5-phenyl-3*H*-1,4-benzodiazepin-2-one)[25] have been reported.

In the case of **2**, the phenyl rings of the ligand effectively block the axial coordination site, as in the case of the diazepam complex.[25] In **2**, all distances between any carbon atoms of a phenyl ring and any one of the other phenyl rings of the same dibenzylamine ligand are over 4.0 Å. From the molecular-structure-model study of the **2** complex, using the HGS model and assuming that

TABLE 3. INTERATOMIC DISTANCES AND BOND ANGLES, WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

(1) Tetrakis{(isopropylthio)acetato}bis(quinoline)dicopper(II)

Bond length	l/Å	Bond length	l/Å
Cu–Cu$^{\rm I}$	2.676(4)	Cu–O(12)	1.981(5)
Cu–O(22)	1.964(5)	Cu–O(11$^{\rm I}$)	1.965(6)
Cu–O(21$^{\rm I}$)	1.971(6)	Cu–N(31)	2.222(6)
O(11)–C(11)	1.255(6)	O(12)–C(11)	1.248(6)
C(11)–C(12)	1.518(8)	C(12)–S(1)	1.786(6)
S(1)–C(13)	1.808(6)	C(13)–(14)	1.525(10)
C(13)–C(15)	1.498(10)	O(21)–C(21)	1.252(7)
O(22)–C(21)	1.254(6)	C(21)–C(22)	1.505(8)
C(22)–S(2)	1.812(7)	S(2)–C(23)	1.821(6)
C(23)C–(24)	1.515(9)	C(23)–C(25)	1.493(9)
N(31)–C(32)	1.323(7)	C(32)–C(33)	1.403(8)
C(33)–C(34)	1.338(8)	C(34)–C(30)	1.403(8)
C(30)–C(35)	1.403(8)	C(35)–C(36)	1.331(9)
C(36)–C(37)	1.411(9)	C(37)–C(38)	1.371(8)
C(38)–C(39)	1.397(7)	C(39)–C(30)	1.423(7)
C(39)–N(31)	1.368(6)		
Bond angle	ϕ/°	**Bond angle**	ϕ/°
Cu$^{\rm I}$–Cu–O(22)	83.09(9)	Cu$^{\rm I}$–Cu–O(12)	81.93(12)
Cu$_{\rm I}$–Cu–O(11$^{\rm I}$)	85.02(9)	Cu$^{\rm I}$–Cu–O(21$^{\rm I}$)	83.74(9)
Cu$^{\rm I}$–Cu–N(31)	171.74(9)	O(12)–Cu–O(22)	90.18(12)
O(12)–Cu–N(31)	90.84(12)	O(22)–Cu–O(11$^{\rm I}$)	88.06(13)
O(11$^{\rm I}$)–Cu–O(21$^{\rm I}$)	89.77(13)	Cu–O(12)–C(11)	125.1(3)
Cu$^{\rm I}$–O(11)–C(11)	122.1(3)	O(11)–C(11)–O(12)	125.8(4)
O(11)–C(11)–C(12)	119.9(4)	C(11)–C(12)–S(1)	118.0(4)
C(12)–S(1)–C(13)	104.7(2)	S(1)–C(13)–C(14)	106.8(4)
S(1)–C(13)–C(15)	113.7(4)	Cu–O(22)–C(21)	124.4(3)
Cu$^{\rm I}$–O(21)–C(21)	123.3(3)	O(21)–C(21)–O(22)	125.3(4)
O(21)–C(21)–C(22)	117.7(4)	C(21)–C(22)–S(2)	110.4(3)
C(22)–S(2)–C(23)	103.2(2)	S(2)–C(23)–C(24)	108.0(4)
S(2)–C(23)–C(25)	112.8(4)	Cu–N(31)–C(32)	114.3(3)
N(31)–C(32)–C(33)	124.6(4)	C(32)–C(33)–C(34)	118.3(5)
C(33)–C(34)–C(30)	120.9(5)	C(34)–C(30)–C(39)	117.2(4)
C(39)–C(30)–C(35)	118.5(4)	C(30)–C(35)–C(36)	121.9(5)
C(35)–C(36)–C(37)	120.3(5)	C(36)–C(37)–C(38)	119.7(5)
C(37)–C(38)–C(39)	120.87(4)	C(38)–C(39)–C(30)	118.7(4)
C(39)–N(31)–C(32)	117.1(4)	N(31)–C(39)–C(30)	121.9(4)

Key to symmetry operations: I. $-x$, $-y$, $-z$.

(2) Bis(dibenzylamine)bis{(ethylthio)acetato}copper(II)

Bond length	l/Å	Bond length	l/Å
Cu–O(1)	1.916(5)	Cu–N	2.026(6)
O(1)–C(1)	1.255(9)	O(2)–C(1)	1.221(7)
C(1)–C(2)	1.513(10)	C(2)–S	1.776(8)
S–C(3)	1.836(9)	C(3)–C(4)	1.434(20)
N–C(10)	1.483(10)	N–C(20)	1.479(7)
C(10)–C(11)	1.498(10)	C(11)–C(12)	1.377(7)
C(11)–C(16)	1.382(11)	C(12)–C(13)	1.386(12)
C(13)–C(14)	1.364(13)	C(14)–C(15)	1.345(9)
C(15)–C(16)	1.360(12)	C(20)–C(21)	1.502(9)
C(21)–C(22)	1.378(11)	C(21)–C(26)	1.367(13)
C(22)–C(23)	1.410(12)	C(23)–C(24)	1.334(18)
C(24)–C(25)	1.335(12)	C(25)–C(26)	1.384(11)
Cu···C(21)	3.100(9)	Cu···C(22)	3.286(9)
Cu···C(26)	3.985(11)	Cu···O(2)	3.300(7)
Bond angle	ϕ/°	**Bond angle**	ϕ/°
O(1)–Cu–N	94.6(2)	Cu–O(1)–C(1)	132.7(4)
O(1)–C(1)–O(2)	125.8(6)	O(1)–C(1)–C(2)	114.5(5)
C(2)–S–C(3)	101.4(4)	C(1)–C(2)–S	115.7(7)
Cu–N–C(10)	115.0(4)	S–C(3)–C(4)	110.6(9)

(Continued)

Bond angle	ϕ/°	Bond angle	ϕ/°
C(10)-C(11)-C(12)	121.7(6)	N-C(10)-C(11)	114.0(6)
C(12)-C(11)-C(16)	116.8(6)	C(11)-C(12)-C(13)	121.0(7)
C(12)-C(13)-C(14)	119.9(6)	C(13)-C(14)-C(15)	119.9(8)
C(14)-C(15)-C(16)	120.4(8)	C(15)-C(16)C(11)	122.1(6)
Cu-N-C(20)	110.8(3)	N-C(20)-C(21)	110.3(4)
(C20)-C(21)-C(22)	120.4(7)	C(21)-C(22)-C(23)	119.9(9)
C(22)-C(21)-C(26)	117.7(7)	C(23)-C(24)-C(25)	121.2(9)
C(22)-C(23)-C(24)	120.0(9)	C(21)-C(26)-C(25)	121.5(7)
C(24)-C(25)-C(26)	119.8(10)	O(1)-Cu···C(21)	85.1(2)
O(1)-Cu···O(2)	39.9(2)	O(1)-Cu···C(26)	67.0(2)
O(1)-Cu···C(22)	93.1(2)	N-Cu···O(2)	58.4(2)

(3) Bis{(isopropylthio)acetato}tris(isoquinoline)copper(II)

Bond length	l/Å	Bond length	l/Å
Cu-O(11)	2.002(7)	Cu-O(12)	2.642(10)
Cu-O(21)	1.960(6)	Cu···O(22)	3.282(10)
Cu-N(32)	2.050(9)	Cu-N(42)	2.044(9)
Cu-N(52)	2.359(11)	O(11)-C(11)	1.278(12)
O(12)-C(11)	1.241(11)	C(11)-C(12)	1.515(14)
C(12)-S(1)	1.797(12)	S(1)-C(13)	1.815(13)
C(13)-C(14)	1.513(18)	C(13)-C(15)	1.522(20)
O(21)-C(21)	1.268(11)	O(22)-C(21)	1.246(12)
C(21)-C(22)	1.512(14)	C(22)-S(2)	1.792(12)
S(2)-C(23)	1.821(13)	C(23)-C(24)	1.483(16)
C(23)-C(25)	1.513(21)	C(31)-N(32)	1.303(11)
N(32)-C(33)	1.351(12)	C(33)-C(34)	1.368(16)
C(34)-C(30)	1.403(13)	C(30)-C(35)	1.435(17)
C(35)-C(36)	1.362(14)	C(36)-C(37)	1.391(16)
C(37)-C(38)	1.365(18)	C(38)-C(39)	1.415(13)
C(39)-C(30)	1.415(14)	C(39)-C(31)	1.415(15)
C(41)-N(42)	1.313(13)	N(42)-C(43)	1.352(12)
C(43)-C(44)	1.383(17)	C(44)-C(40)	1.408(16)
C(40)-C(45)	1.442(17)	C(45)-C(46)	1.377(17)
C(46)-C(47)	1.351(17)	C(47)-C(48)	1.387(19)
C(48)-C(49)	1.398(16)	C(49)-C(40)	1.398(14)
C(49)-C(41)	1.434(16)	C(51)-N(52)	1.315(11)
N(52)-C(53)	1.370(12)	C(53)-C(54)	1.354(14)
C(54)-C(50)	1.410(13)	C(50)-C(55)	1.446(14)
C(55)-C(56)	1.348(15)	C(56)-C(57)	1.393(17)
C(57)-C(58)	1.379(16)	C(58)-C(59)	1.439(13)
C(59)-C(50)	1.386(13)	C(59)-C(51)	1.427(13)
Bond angle	ϕ/°	Bond angle	ϕ/°
O(11)-Cu-O(12)	55.1(2)	O(11)-Cu-N(32)	88.0(3)
O(11)-Cu-N(42)	90.7(3)	O(11)-Cu-N(52)	90.2(2)
O(12)-Cu-N(52)	145.3(2)	O(21)-Cu-O(22)	41.4(2)
O(21)-Cu-N(32)	92.1(3)	O(21)-Cu-N(42)	89.6(3)
O(22)-Cu-N(52)	129.8(2)	Cu-O(11)-C(11)	104.7(5)
Cu-O(12)-C(11)	76.0(4)	O(11)-C(11)-O(12)	123.9(8)
O(11)-C(11)-C(12)	115.6(7)	C(11)-C(12)-S(1)	116.9(6)
C(12)-S(1)-C(13)	102.6(5)	S(1)-C(13)-C(14)	107.5(7)
S(1)-C(13)-C(14)	107.5(7)	S(1)-C(13)-C(15)	113.2(8)
Cu-O(21)-C(21)	130.1(5)	Cu···O(21)-C(21)	63.3(4)
O(21)-C(21)-O(22)	124.6(8)	O(21)-C(21)-C(22)	118.6(7)
C(21)-C(22)-S(2)	118.3(6)	C(22)-S(2)-C(23)	104.9(5)
S(2)-C(23)-C(24)	107.0(7)	S(2)-C(23)-C(25)	111.8(8)
Cu-N(32)-C(31)	119.6(6)	Cu-N(32)-C(33)	120.9(6)
C(31)-N(32)-C(33)	119.3(8)	N(32)-C(31)-C(39)	123.0(8)
N(32)-C(33)-C(34)	122.7(8)	C(33)-C(34)-C(30)	119.5(8)

(Continued)

Bond angle	$\phi/^{\circ}$	Bond angle	$\phi/^{\circ}$
C(30)-C(35)-C(36)	119.1(9)	C(35)-C(36)-C(37)	121.6(11)
C(36)-C(37)-C(38)	121.1(10)	C(37)-C(38)-C(39)	119.6(9)
C(30)-C(39)-C(31)	117.9(8)	C(38)-C(39)-C(30)	119.7(9)
C(34)-C(30)-C(39)	117.7(9)	C(35)-C(30)-C(39)	118.9(8)
Cu-N(42)-C(41)	121.7(6)	Cu-N(42)-C(43)	118.2(6)
C(41)-N(42)-C(43)	120.1(8)	N(42)-C(41)-C(49)	122.1(8)
N(42)-C(43)-C(44)	121.6(9)	C(43)-C(44)-C(40)	120.0(9)
C(40)-C(45)-C(46)	117.5(9)	C(45)-C(46)-C(47)	123.0(12)
C(46)-C(47)-C(48)	121.3(11)	C(47)-C(48)-C(49)	118.0(9)
C(40)-C(49)-C(41)	118.2(9)	C(48-(C(49)-C(40)	121.6(10)
C(44)-C(40)-C(49)	117.9(10)	C(45)-C(40)-C(49)	118.6(9)
Cu-N(52)-C(51)	124.5(5)	Cu-N(52)-C(53)	117.6(5)
C(51)-N(52)-C(53)	117.0(7)	N(52)-C(51)-C(59)	123.8(7)
N(52)-C(53)-(54)	123.1(8)	C(53)-C(54)-C(50)	120.7(8)
C(50)-C(55)-C(56)	120.5(9)	C(55)-C(56)-C(57)	120.3(10)
C(56)-C(57)-C(58)	121.9(10)	C(57)-C(58)-C(59)	118.6(9)
C(50)-C(59)-C(51)	118.6(7)	C(58)-C(59)-C(50)	119.7(7)
C(54)-C(50)-C(59)	116.9(7)	C(55)-C(50)-C(54)	119.1(8)

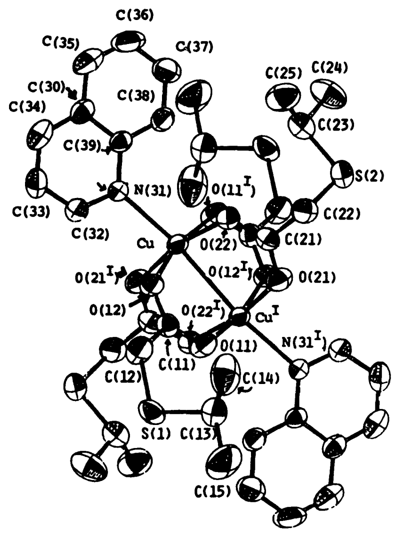

Fig. 1. A perspective drawing of tetrakis{(isopropylthio)-acetato}bis(quinoline)dicopper(II) (**1**), and the numbering scheme of atoms.

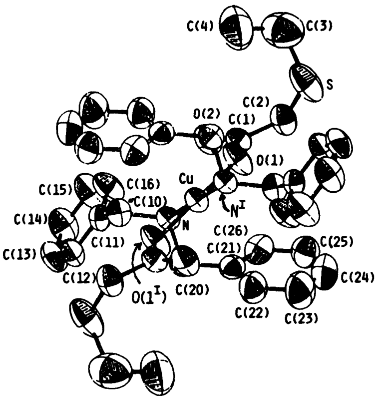

Fig. 2. A perspective drawing of bis(dibenzylamine)bis-{(ethylthio)acetato}copper(II) (**2**), and the numbering scheme of atoms.

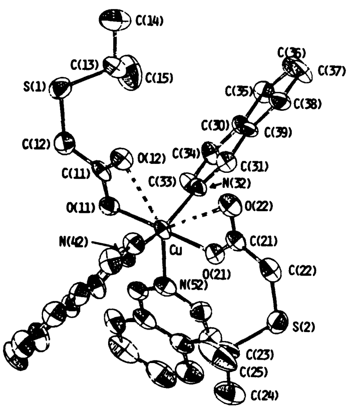

Fig. 3. A perspective drawing of bis{(isopropylthio)-acetato}tris(isoquinoline)copper(II) (**3**), and the numbering scheme of atoms.

each bond length is kept to the value shown by the X-ray analysis and that all sigle-bonded atoms can rotate freely around the axis, it was found that the phenyl groups of the amine ligand must approach each other when one more oxygen or sulfur atom of an (alkylthio)-acetate ligand bonds to the copper(II) atom. In the real structure, the intra-molecular interaction between phenyl groups of the amine is likely to be dominant, because the phenyl groups spread to prevent the bonding of the additional ligand atoms like a "*picket fence.*"[12]

As is shown in Fig. 3, the copper atom of **3** is coordinated to two oxygen and two nitrogen atoms in a O_2N_2 square planar geometry. These Cu-O as well as Cu-N bond lengths are normal compared with those of common copper(II) complexes.[13] The average plane of the CuO_2N_2 is shown by this equation:

$$-0.773x + 0.057y - 0.631z + 6.591 = 0$$

and the shifts from the plane are: Cu, −0.105; N(32), 0.201; N(42), 0.170; O(11), −0.135; and O(21), −0.117 Å. The ∠(Nor O)-Cu-N(or O) angles between side-by-side atoms in the plane are 88.0(3)—92.1(3)°.

The copper(II) atom is surrounded by seven atoms. Among them, the O(11), O(21), N(32), N(42), and N(52) atoms are situated in the axially elongated octahedral geometry, where one axially ligating atom is absent. While ∠O(11)-Cu-O(12) is 55.1°, and Cu-

O(12) is 2.642(10) Å, the deviation of the O(12) position from the octahedral environment is rather extreme compared with the positions of other five atoms mentioned above. Moreover, as ∠O(21)–Cu–O(22) is 41.4(2)° and Cu–O(22) is 3.282(10) Å, Cu–O(22) should not be considered as the common coordination bond. However, the three axial atoms, N(52), O(12), and O(22), together with the Cu, O(11), and O(21) atoms, are almost all on one plane, shown by the following plane equation:

$$0.552\,x + 0.631\,y - 0.545\,z + 3.301 = 0.$$

The shifts of the atoms are: Cu, 0.026; O(11), 0.001; O(12) −0.002; O(21), 0.047; O(22), −0.032; and N(52), −0.037 Å. An abnormally long-distance Cu–O bonding has already been reported in copper(II) oxalate[16] or in the nitrate.[26] In some carboxylate complexes of large metal ions, two oxygen atoms of a carboxylate ion are coordinated to the same metal ion.[27] Consequently, although both Cu–O(12) and Cu–O(22) are too long, and the bonds can be expected to be weak, it seems that both O(12) and O(22) atoms are coordinated to the copper atom, cooperating with each other. Therefore, the configuration of **3** is, tentatively, named the "*potentially hepta-coordinated configuration.*"

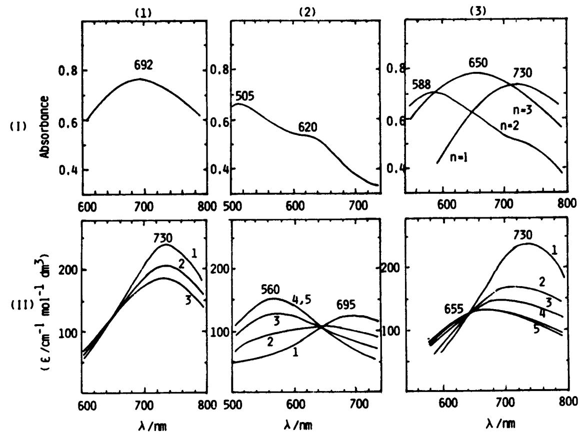

Fig. 4. Reflectance and absorption spectra of the complexes. (The wavelengths of absorption maxima are shown in figures.) (I): Diffuse reflectance spectra (upper figures). (II): Absorption spectra in benzene solution (lower figures). The concentration of Cu(II) in the solution: (1) 4.54×10^{-3}; (2) 4.72×10^{-3}, (3) 4.42×10^{-3} mol dm^{-3}.
(1) (Left figs.): tetrakis{(isopropylthio)acetato}bis(quinoline)dicopper(II). Amine: Cu(II) in the solution: 1, 6; 2, 175; 3, 406 (mol/mol). (2) (Middle figs.): bis(dibenzylamine)bis{(ethylthio)acetato}copper(II). Amine: Cu(II) in the solution: 1, 5; 2, 7; 3, 12; 4, 53; 5, 214 (mol/mol). (3) (Right figs.): $n=1$, tetrakis{(isopropylthio)acetato}bis(isoquinoline)dicopper(II); $n=2$, bis{(isopropylthio)acetato}bis(isoquinoline)copper(II); $n=3$, bis{(isopropylthio)acetato}tris(isoquinoline)copper(II). Amine: Cu(II) in the solution: 1, 6; 2, 45; 3, 80; 4, 150; 5, 400 (mol/mol). (For the absorption spectra in benzene solution, the same result was obtained when the mol ratio of Cu(II): amine in the solution is the same, when the $n=1$, $n=2$, or $n=3$ complex was used.)

A similar type of structure was found in tris(pyridine)copper(II) nitrate,[28] where two oxygen atoms of each nitrate ion are coordinated to the copper(II) atom, and where the geometry of the CuO_4N_3 configuration closely resembles that of **3**.

The diffuse reflectance spectra of the solid, and the absorption spectra in a benzene solution of **1**, **2**, and **3**, as well as those of mono- and bis(isoquinoline) adducts of copper (isopropylthio)acetate, are shown in Fig. 4. The reflectance spectra of **1** are characteristic of a copper(II) carboxylate dimer,[14,29,30] as the d-d band maximum appears at about 690—730 nm. Its benzene solution shows an absorption maximum of almost the same wavelength as that of the reflectance spectra of its solid. Consequently, their dimer structure is likely kept, even in the benzene solution.

When an excess of quinoline is added to the benzene solution of **1**, the absorption maximum does not move. On the other hand, when as excess of isoquinoline or pyridine is added to a solution of their adduct of the respective Type-**1** complex, the formation of Type-**3** complex is found by the change in color and in spectra. For example, as is shown in Fig. 4, in the case of the solution of Type-**1** isoquinoline adduct, the wavelength of the absorption maximum decreased from 730 to 655 nm depending on the increase in the isoquinoline concentration in the solution. The final wavelength, 655 nm, is almost the same as that of the maximum of the reflectance spectra of the solid **3**. During the process, as the minimum wavelength of the absorption maximum observed was 655 nm, its bis(amine) adduct is probably not the dominant species under these conditions, because the reflectance spectra of the solid bis(amine) adduct of the Type-**2**, bis{(isopropylthio)acetato}bis(isoquinoline)copper(II), has an absorption maximum at 588 nm. As has been shown in the experimental part, the solid Type-**2** adducts were obtained from a benzene–ligroine mixture solution containing both the starting copper(II) complex and the amine in higher concentrations.

The reflectance spectra of **2** shows an absorption maximum at about 505 nm, which is shorter than that of common copper complexes.[31] Such a short wavelength maximum is found only in D_{4h}-type complexes, where the axial atoms are bonded very weakly or where no axially ligating atoms exist.[32] (An additional shoulder appears at about 620 nm).

For example, bis{(isopropylthio)acetato}copper(II) dihydrate (violet isomer) shows a similar absorption maximum at 566 nm in its reflectance spectra of the solid, which has an axially elongated D_{4h} geometry.[2]

When a benzene solution of **2** is diluted, the change in the spectra and in the color of the solution shows the formation of the Type-**1** dimer complex. Therefore, in the solution, the amine ligand of **2** is in dissociation equilibrium, and a part of it is dissociated. Even when a large excess of dibenzylamine (about amine : Cu = 200, in mol/mol) is added to the solution, the absorption maximum shifts at most to 560 nm, not to 505 nm.

The reflectance spectra of **3** has an absorption maximum at about 650 nm, which is intermediate

Table 4. Infrared absorption spectral data of the complexes, $[Cu(RSCH_2CO_2)_2(amine)_n]$ (cm^{-1})[a]

		R=					
n	Amine	CH_3		C_2H_5		$(CH_3)_2CH$	
		ν_{as}	ν_s	ν_{as}	ν_s	ν_{as}	ν_s
1	Isoquinoline	1623	1393	1620	1390	1627	1393
1	Quinoline	1630	1393	1629	1393	1628	1391
1	Pyridine	1620 (1600)	1395	1620 (1597)	1395	1620 (1598)	1390
2	Dibenzylamine	1590	1353	1588	1352	1594	1352
2	Isoquinoline					1610	1365 1349
3	Isoquinoline	1623 1600	1388 1352	1618 1598	1390 1355	1619 1598	1388 1353

a) The $n=1$ complexes are shown by the experimental formula.

between those of **1** and **2**, probably because its axial atom bondings are of medium strength.

The wave numbers of the $\nu_{as}(COO)$ and $\nu_s(COO)$ of the adducts are shown in Table 4. As each of these complexes has Type-**1**, -**2**, or -**3** structure, the maximum wave numbers should also be classified into three groups.

In **1**, the carboxyl group of the ligand bridges the copper atoms with both of its oxygen atoms, and the group is almost completely symmetric. The $\nu_{as}(COO)$ of Type-**1** adducts is about 1600—1630 cm^{-1}, which is typical of the bridging carboxylate group of the copper(II) carboxylate dimer.[33,34]

In **2**, the carboxyl group bonds with the metal ion by only one oxygen atom, and the group is rather asymmetric. However, the $\nu_{as}(COO)$ of **2** appears in a relatively low wave number region, *i.e.*, at about 1590 cm^{-1}.

In **3**, as Cu–O(12) and Cu–O(22) are different in their bond lengths, the grades of asymmetry of the two carboxyl groups can be expected to be different, too. Therefore, two types of $\nu_{as}(COO)$ as well as $\nu_s(COO)$ bands overlap in its spectra.

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