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# Crystal Structures and Magnetic Properties of Binuclear Copper(II) Complexes with Alkoxo and Benzoato or Silanecarboxylato Bridges

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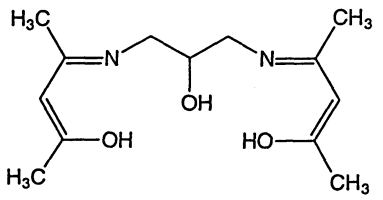
The crystal structures of the binuclear copper(II) complexes $[Cu_2(L\text{-}ac)(PhCOO)]$ (**1**), $[Cu_2(L\text{-}ac)(2\text{-}Me\text{-}PhCOO)\cdot 1/2MeOH$ (**2**), $[Cu_2(L\text{-}ac)(2,6\text{-}Me_2\text{-}PhCOO)]$ (**3**), $[Cu_2(L\text{-}ac)(2,6\text{-}Cl_2\text{-}PhCOO)]\cdot 0.7DMF$ (**4**), and $[Cu_2(L\text{-}ac)(Ph_2MeSiCOO)]$ (**5**) were determined by X-ray diffraction. The ligand $H_3(L\text{-}ac)$ is a 1:2 Schiff base derived from 1,3-diaminopropan-2-ol and acetylacetone. These complexes are antiferromagnetic and their $-2J$ values are (**1**) 183, (**2**) 188, (**3**) 133, (**4**) 207, and (**5**) 95 $cm^{-1}$, respectively. A rough positive correlation between the Cu···Cu distance and the $-2J$ value was observed except for **5**. The smaller $-2J$ value of the triorganosilanecarboxylato complex, **5**, than the benzoato complexes, **1**—**4**, indicates a stronger orbital countercomplementary effect in **5**. The geometrical parameters in the benzoato bridge have a minor effect on the magnitude of the antiferromagnetic interaction.

The structures and magnetism of the binuclear Cu(II) complexes with both $\mu$-alkoxo and $\mu$-carboxylato bridges were studied by Nishida & Kida to determine the importance of orbital countercomplementarity in spin coupling through the two different bridging groups.[1] Very recently, the remarkable effect of the silanecarboxylato bridge on the spin exchange interaction was revealed for dimeric copper(II) carboxylates, $[Cu(R_3XCOO)_2L]_2$ ($R_3X$=substitute group, $L$=monodentate ligand).[2] The $-2J$ values of the dimeric copper(II) carboxylates have been observed to be ca. 300, 500, and 1000 $cm^{-1}$ for $X$=C, H, and Si, respectively, which results from the variation of the electronic structure of the central C atom on the OCO bridges.[3] Furthermore, a magneto-structural study for the dimeric copper(II) benzoates revealed that the $-2J$ value decreases as the structure of the Cu-OCO-Cu bridge is bent.[4] These characteristics of the carboxylato bridge were examined in the heterobridged systems.

## Experimental

**Syntheses.** $H_3(L\text{-}ac)$ is a 1:2 Shiff base derived from 1,3-diaminopropan-2-ol and acetylacetone. Compounds **1**, **2**, and **3** were prepared by reacting the copper(II) carboxylate and $H_3(L\text{-}ac)$.[1] The complexes **4** and **5** were prepared through the precursor, $[Cu_2(L\text{-}ac)Cl(H_2O)]$, in order to reduce the amount of the carboxylato ligand required. X-Ray structural analyses revealed that chlorine atoms were introduced into the L-ac ligand by this procedure. Compound **4** (Found: C, 41.64; H, 3.98; N, 5.83 %. Calcd for $C_{20}H_{21.5}Cl_{2.5}Cu_2N_2O_5\cdot 0.7C_3H_7NO$: C, 41.68; H, 4.18; N, 5.94%). Compound **5** (Found: C, 51.46; H, 4.99; N, 4.49%. Calcd for $C_{27}H_{31.7}Cl_{0.3}Cu_2N_2O_5Si$: C, 51.47; H, 5.07; N, 4.45%).




$H_3(L\text{-}ac)$

**X-Ray Crystal Structure Determination.** Crystallographic data, experimental conditions, and refinement information are listed in Table 1. X-Ray intensities were measured on a Rigaku AFC-5 four-circle diffractometer with graphite monochromatized Mo $K\alpha$ radiation ($\lambda$=0.71073 Å). Five standard reflections were measured every 100 reflections, and a correction for radiation damage was made. The cut-off limit of the reflection data was $|F_o|=3\sigma(|F_o|)$. The absorption correction was made by the numerical integration method. Cell parameters were refined by least squares based on 25—50 $2\theta$ values ($20<2\theta<30°$). The structures were solved by the Patterson-Fourier method or direct methods.[5] The coordinates and anisotropic thermal parameters of the non-H atoms were refined by block-diagonal least squares to minimize the function, $\sum w(|F_o|-|F_c|)^2$ with weight $w^{-1}=\sigma^2(|F_o|)+(0.015|F_o|)^2$ in **1**—**3** or $w^{-1}=\sigma(|F_o|)$ in **4** and **5**. Hydrogen atoms were either located in difference syntheses or calculated theoretically. The hydrogen parameters were refined for **1**, **4**, and **5**, but were fixed for **2** and **3**. The calculations were carried out on a FACOM M-780/10 computer with a UNICSIII program system[6] or a MIPS 3230 workstation with XTAL3.0[7] at Keio University. Complex neutral-atom scattering factors were used.[8] The atomic coordinates are listed in Table 2 and selected bond lengths and angles in Table 3.[9] Some experimental details are given below.

**2:** There are two possible positions for the methyl carbon atom, labeled C(8) and C(8′), indicating a rotational disorder

Table 1. Crystallographic Data, Experimental Conditions, and Refinement Information

| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| Formula | $C_{20}H_{24}Cu_2N_2O_5$ | $C_{21}H_{26}Cu_2N_2O_5 \cdot 0.5CH_3OH$ | $C_{22}H_{28}Cu_2N_2O_5$ | $C_{20}H_{21.5}Cl_{2.5}Cu_2N_2O_5 \cdot 0.7C_3H_7NO$ | $C_{27}H_{31.7}Cl_{0.3}Cu_2N_2O_5Si$ |
| F.W. | 499.52 | 529.57 | 527.57 | 636.79 | 630.07 |
| Space group | $P2_1/a$ | $P2_1/n$ | $Pbca$ | $P\bar{1}$ | $Pbca$ |
| $a$/Å | 20.778(7) | 26.431(1) | 16.427(3) | 11.205(2) | 16.444(2) |
| $b$/Å | 7.486(2) | 7.574(1) | 13.920(2) | 13.285(2) | 27.558(3) |
| $c$/Å | 14.137(4) | 11.356(2) | 20.333(3) | 9.722(2) | 12.485(2) |
| $\alpha$/° | | | | 108.66(1) | |
| $\beta$/° | 109.60(3) | 94.39(2) | | 95.40(1) | |
| $\gamma$/° | | | | 94.59(2) | |
| $V$/Å$^3$ | 2072(1) | 2266.7(6) | 4649(1) | 1355.7(4) | 5658(1) |
| $Z$ | 4 | 4 | 8 | 2 | 8 |
| $D_x$/Mg m$^{-3}$ | 1.60 | 1.54 | 1.51 | 1.56 | 1.48 |
| $\mu$(Mo $K\alpha$)/mm$^{-1}$ | 2.09 | 1.92 | 1.87 | 1.86 | 1.62 |
| Crystal dimensions/mm | 0.60×0.40×0.20 | 0.40×0.15×0.05 | 0.45×0.35×0.30 | 0.35×0.15×0.15 | 0.60×0.40×0.30 |
| Scan mode | $\omega$ | $\omega$ | $\theta$-$2\theta$ | $\omega$ | $\omega$ |
| Scan range of $2\theta$/° | 4—55 | 4—45 | 4—50 | 4—50 | 4—55 |
| Ranges of | | | | | |
| $h$ | −27 to 27[a)] | −29 to 31[a)] | 0 to 19 | −13 to 13 | 0 to 21 |
| $k$ | 0 to 9 | 0 to 8 | 0 to 16 | 0 to 15 | 0 to 35 |
| $l$ | −13 to 18 | −5 to 12 | 0 to 25 | −11 to 11 | 0 to 16 |
| Variation of $\lvert F_o \rvert$ of standard reflections | 0.995—1.002 | 0.974—1.003 | 0.993—1.004 | 0.767—1.000 | 0.993—1.005 |
| No. of measured reflections | 6795 | 3953 | 4914 | 5145 | 6499 |
| No. of observed reflections $\lvert F_o \rvert > 3\sigma(\lvert F_o \rvert)$ | 3356 | 1614 | 2063 | 2283 | 3736 |
| No. of independent reflections | 2022 | 1318 | 2063 | 2155 | 3736 |
| Transmission factor, $A$ | 0.618—0.663 | 0.747—0.910 | 0.524—0.609 | 0.703—0.839 | 0.510—0.694 |
| $R$ | 0.047 | 0.057 | 0.060 | 0.082 | 0.059 |
| $R_w$ | 0.060 | 0.060 | 0.060 | 0.071 | 0.032 |
| $(\Delta/\sigma)_{max}$ for nonhydrogen atoms | 0.29 | 0.41 | 0.37 | 0.33 | 0.38 |
| $\Delta\rho$/eÅ$^{-3}$ | −0.76—0.74 | −0.40—0.40 | −0.50—1.23 | −0.87—0.96 | −0.78—0.50 |

a) A semisphere of the reciprocal space was measured for **1**; $2\theta < 40°$ and **2**; $2\theta < 20°$, and the independent reflections were measured in the high angle region.

Table 2. Positional Parameters and Equivalent Isotropic Temperature Factors

| Atom | $x$ | $y$ | $z$ | $U_{eq}$/Å$^2$ [a] | $PP$ [b] | Atom | $x$ | $y$ | $z$ | $U_{eq}$/Å$^2$ | $PP$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **1** | | | | | | **2** | | | | | |
| Cu(1) | 0.22602(4) | 0.4143(1) | 0.05058(6) | 0.049 | | Cu(1) | 0.12027(6) | 0.1220(3) | 0.3639(2) | 0.052 | |
| Cu(2) | 0.38284(4) | 0.3776(1) | 0.24254(6) | 0.052 | | Cu(2) | 0.01305(6) | 0.2739(3) | 0.4980(2) | 0.056 | |
| O(1) | 0.2130(2) | 0.4542(8) | 0.1778(3) | 0.078 | | O(1) | 0.1417(3) | 0.235(1) | 0.5095(7) | 0.067 | |
| O(2) | 0.3131(2) | 0.4343(7) | 0.3005(3) | 0.071 | | O(2) | 0.0735(3) | 0.321(1) | 0.6019(7) | 0.056 | |
| O(3) | 0.3226(2) | 0.4119(6) | 0.1080(3) | 0.056 | | O(3) | 0.0512(3) | 0.174(1) | 0.3780(7) | 0.052 | |
| O(4) | 0.1295(2) | 0.3934(7) | −0.0066(3) | 0.063 | | O(4) | 0.1897(3) | 0.061(1) | 0.3536(7) | 0.054 | |
| O(5) | 0.4401(2) | 0.3117(7) | 0.3735(3) | 0.064 | | O(5) | −0.0259(3) | 0.374(1) | 0.6172(7) | 0.061 | |
| N(1) | 0.2422(3) | 0.4178(7) | −0.0751(4) | 0.050 | | N(1) | 0.1003(4) | 0.046(1) | 0.2070(8) | 0.045 | |
| N(2) | 0.4537(3) | 0.3748(7) | 0.1848(4) | 0.051 | | N(2) | −0.0457(4) | 0.205(1) | 0.3994(9) | 0.050 | |
| C(1) | 0.2507(3) | 0.473(1) | 0.2671(5) | 0.055 | | C(1) | 0.1212(4) | 0.306(2) | 0.595(1) | 0.046 | |
| C(2) | 0.2189(3) | 0.546(1) | 0.3397(4) | 0.050 | | C(2) | 0.1537(5) | 0.379(2) | 0.698(1) | 0.052 | |
| C(3) | 0.1514(3) | 0.589(1) | 0.3092(5) | 0.067 | | C(3) | 0.1354(5) | 0.378(2) | 0.810(1) | 0.073 | |
| C(4) | 0.1223(4) | 0.650(1) | 0.3761(6) | 0.085 | | C(4) | 0.1676(7) | 0.440(3) | 0.904(1) | 0.112 | |
| C(5) | 0.1599(4) | 0.671(1) | 0.4759(6) | 0.073 | | C(5) | 0.2162(6) | 0.503(2) | 0.888(1) | 0.108 | |
| C(6) | 0.2280(4) | 0.626(1) | 0.5063(5) | 0.072 | | C(6) | 0.2322(5) | 0.504(2) | 0.779(1) | 0.090 | |
| C(7) | 0.2577(3) | 0.567(1) | 0.4394(5) | 0.057 | | C(7) | 0.2031(5) | 0.438(2) | 0.678(1) | 0.065 | |
| C(8) | 0.0955(3) | 0.4051(9) | −0.1026(5) | 0.052 | | C(9) | 0.2089(5) | −0.006(2) | 0.261(1) | 0.063 | |
| C(9) | 0.1236(3) | 0.4193(9) | −0.1778(5) | 0.055 | | C(10) | 0.1813(5) | −0.040(2) | 0.158(1) | 0.060 | |
| C(10) | 0.1935(3) | 0.4298(9) | −0.1655(4) | 0.053 | | C(11) | 0.1282(5) | −0.012(2) | 0.130(1) | 0.064 | |
| C(11) | 0.3137(3) | 0.4262(9) | −0.0643(5) | 0.052 | | C(12) | 0.0450(5) | 0.058(2) | 0.183(1) | 0.070 | |
| C(12) | 0.3537(3) | 0.369(1) | 0.0408(5) | 0.076 | | C(13) | 0.0207(5) | 0.115(3) | 0.285(1) | 0.131 | |
| C(13) | 0.4284(3) | 0.403(1) | 0.0768(5) | 0.056 | | C(14) | −0.0326(5) | 0.147(2) | 0.285(1) | 0.063 | |
| C(14) | 0.5202(3) | 0.358(1) | 0.2364(5) | 0.059 | | C(15) | −0.0929(5) | 0.209(2) | 0.430(1) | 0.053 | |
| C(15) | 0.5431(3) | 0.320(1) | 0.3390(5) | 0.061 | | C(16) | −0.1065(4) | 0.276(2) | 0.539(1) | 0.056 | |
| C(16) | 0.5061(3) | 0.299(1) | 0.3998(5) | 0.057 | | C(17) | −0.0739(5) | 0.352(2) | 0.623(1) | 0.059 | |
| C(17) | 0.0199(4) | 0.397(1) | −0.1281(6) | 0.076 | | C(18) | 0.2644(5) | −0.038(2) | 0.275(1) | 0.088 | |
| C(18) | 0.2122(4) | 0.454(1) | −0.2583(5) | 0.070 | | C(19) | 0.1076(6) | −0.066(2) | 0.007(1) | 0.080 | |
| C(19) | 0.5717(4) | 0.374(1) | 0.1821(6) | 0.083 | | C(20) | −0.1356(5) | 0.150(2) | 0.344(1) | 0.072 | |
| C(20) | 0.5396(4) | 0.253(1) | 0.5096(5) | 0.077 | | C(21) | −0.0940(5) | 0.423(2) | 0.736(1) | 0.064 | |
| | | | | | | C(8) | 0.081(1) | 0.378(6) | 0.834(3) | 0.051[c] | 0.33 |
| | | | | | | C(8′) | 0.2268(7) | 0.460(3) | 0.567(2) | 0.060[c] | 0.67 |
| | | | | | | O(6) | 0.0192(8) | 0.305(3) | 0.877(2) | 0.109[c] | 0.50 |
| | | | | | | C(22) | 0.025(1) | 0.453(6) | 0.958(3) | 0.137[c] | 0.50 |

Table 2. (Continued)

| Atom | $x$ | $y$ | $z$ | $U_{eq}$/Å$^2$ | $PP$ | Atom | $x$ | $y$ | $z$ | $U_{eq}$/Å$^2$ | $PP$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **3** | | | | | | **4** | | | | | |
| Cu(1) | 0.22237(7) | 0.11268(8) | −0.03315(6) | 0.047 | | Cu(1) | 0.0359(2) | 0.4234(2) | 0.6850(2) | 0.055 | |
| Cu(2) | 0.09435(7) | 0.07009(8) | 0.09939(6) | 0.049 | | Cu(2) | 0.2622(2) | 0.4324(2) | 0.4604(2) | 0.052 | |
| O(1) | 0.2093(4) | 0.2324(4) | 0.0158(3) | 0.058 | | Cl(1) | 0.0051(5) | 0.0786(5) | 0.2321(6) | 0.104 | |
| O(2) | 0.1213(4) | 0.2047(4) | 0.0989(3) | 0.069 | | Cl(2) | 0.3019(5) | 0.1815(5) | 0.7378(5) | 0.095 | |
| O(3) | 0.1375(3) | 0.0486(4) | 0.0136(3) | 0.045 | | O(1) | 0.072(1) | 0.2790(9) | 0.589(1) | 0.076 | |
| O(4) | 0.3095(4) | 0.1742(4) | −0.0779(3) | 0.065 | | O(2) | 0.218(1) | 0.2836(8) | 0.445(1) | 0.069 | |
| O(5) | 0.0545(4) | 0.0909(5) | 0.1857(3) | 0.069 | | O(3) | 0.1571(9) | 0.4862(8) | 0.600(1) | 0.057 | |
| N(1) | 0.2246(4) | −0.0001(5) | −0.0877(3) | 0.048 | | O(4) | −0.0872(8) | 0.3588(8) | 0.755(1) | 0.058 | |
| N(2) | 0.0518(4) | −0.0586(5) | 0.0938(4) | 0.051 | | O(5) | 0.3503(9) | 0.3759(9) | 0.304(1) | 0.060 | |
| C(1) | 0.1667(6) | 0.2578(6) | 0.0648(5) | 0.046 | | N(1) | 0.005(1) | 0.566(1) | 0.783(1) | 0.050 | |
| C(2) | 0.1712(6) | 0.3621(6) | 0.0837(5) | 0.050 | | N(2) | 0.315(1) | 0.578(1) | 0.493(1) | 0.041 | |
| C(3) | 0.2176(7) | 0.3871(8) | 0.1403(5) | 0.075 | | C(1) | 0.146(1) | 0.244(1) | 0.508(2) | 0.057 | |
| C(4) | 0.2274(8) | 0.4836(8) | 0.1537(6) | 0.091 | | C(2) | 0.154(1) | 0.128(1) | 0.481(1) | 0.064 | |
| C(5) | 0.1917(7) | 0.5500(7) | 0.1145(6) | 0.091 | | C(3) | 0.094(1) | 0.046(1) | 0.365(2) | 0.058 | |
| C(6) | 0.1445(7) | 0.5268(7) | 0.0608(6) | 0.078 | | C(4) | 0.093(1) | −0.064(1) | 0.339(2) | 0.070 | |
| C(7) | 0.1343(6) | 0.4305(7) | 0.0448(5) | 0.062 | | C(5) | 0.157(2) | −0.097(1) | 0.441(2) | 0.080 | |
| C(8) | 0.2579(9) | 0.3140(9) | 0.1829(6) | 0.106 | | C(6) | 0.224(1) | −0.020(1) | 0.563(2) | 0.070 | |
| C(9) | 0.0863(7) | 0.4019(8) | −0.0126(6) | 0.081 | | C(7) | 0.219(1) | 0.090(1) | 0.575(2) | 0.060 | |
| C(10) | 0.3491(6) | 0.1380(6) | −0.1268(5) | 0.053 | | C(8) | −0.155(1) | 0.411(1) | 0.849(2) | 0.070 | |
| C(11) | 0.3318(7) | 0.0530(7) | −0.1560(5) | 0.061 | | C(9) | −0.148(1) | 0.524(1) | 0.908(1) | 0.056 | |
| C(12) | 0.2728(6) | −0.0136(6) | −0.1381(5) | 0.055 | | C(10) | −0.074(1) | 0.598(1) | 0.878(2) | 0.053 | |
| C(13) | 0.1638(6) | −0.0718(7) | −0.0674(5) | 0.053 | | C(11) | 0.079(1) | 0.645(1) | 0.740(2) | 0.053 | |
| C(14) | 0.1448(6) | −0.0530(6) | 0.0040(5) | 0.048 | | C(12) | 0.168(2) | 0.587(1) | 0.658(2) | 0.120 | |
| C(15) | 0.0722(6) | −0.1024(6) | 0.0314(5) | 0.055 | | C(13) | 0.243(1) | 0.651(1) | 0.595(1) | 0.057 | |
| C(16) | 0.0013(6) | −0.0978(7) | 0.1361(5) | 0.059 | | C(14) | 0.402(1) | 0.610(1) | 0.432(2) | 0.052 | |

Table 2. (Continued)

| Atom | $x$ | $y$ | $z$ | $U_{eq}$/Å$^2$ | $PP$ | Atom | $x$ | $y$ | $z$ | $U_{eq}$/Å$^2$ | $PP$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| C(17) | −0.0187(7) | −0.0542(7) | 0.1954(5) | 0.068 | | C(15) | 0.458(1) | 0.543(1) | 0.322(2) | 0.056 | |
| C(18) | 0.0063(6) | 0.0331(8) | 0.2161(5) | 0.067 | | C(16) | 0.425(1) | 0.434(1) | 0.263(1) | 0.057 | |
| C(19) | 0.4205(7) | 0.1979(8) | −0.1489(6) | 0.082 | | C(17) | −0.248(2) | 0.339(1) | 0.889(2) | 0.070 | |
| C(20) | 0.2666(8) | −0.1050(8) | −0.1781(5) | 0.077 | | C(18) | −0.090(2) | 0.709(1) | 0.951(2) | 0.070 | |
| C(21) | −0.0371(7) | −0.1927(8) | 0.1194(6) | 0.086 | | C(19) | 0.448(1) | 0.723(2) | 0.481(2) | 0.090 | |
| C(22) | −0.0222(7) | 0.0733(8) | 0.2826(5) | 0.084 | | C(20) | 0.486(1) | 0.373(2) | 0.135(2) | 0.080 | |
| | | | | | | Cl(3) | −0.236(1) | 0.561(1) | 1.049(2) | 0.112[c] | 0.35 |
| | | | | | | Cl(4) | 0.557(3) | 0.578(3) | 0.252(4) | 0.100[c] | 0.15 |
| | | | | | | O(6) | 0.323(2) | −0.119(2) | −0.100(2) | 0.104[c] | 0.70 |
| | | | | | | N(3) | 0.355(1) | −0.003(1) | 0.102(2) | 0.028[c] | 0.70 |
| | | | | | | C(21)A | 0.372(3) | −0.102(3) | 0.020(4) | 0.030[c] | 0.35 |
| | | | | | | C(21)B | 0.307(4) | −0.018(4) | 0.000(5) | 0.070[c] | 0.35 |
| | | | | | | C(22)A | 0.410(3) | −0.004(3) | 0.238(3) | 0.030[c] | 0.35 |
| | | | | | | C(22)B | 0.347(4) | 0.106(4) | 0.156(4) | 0.040[c] | 0.35 |
| | | | | | | C(23)A | 0.306(4) | 0.079(3) | 0.085(4) | 0.040[c] | 0.35 |
| | | | | | | C(23)B | 0.401(4) | −0.047(3) | 0.149(4) | 0.030[c] | 0.35 |

Table 2. (Continued)

| Atom | $x$ | $y$ | $z$ | $U_{eq}$/Å$^2$ | $PP$ | Atom | $x$ | $y$ | $z$ | $U_{eq}$/Å$^2$ | $PP$ |
|---|---|---|---|---|---|---|---|---|---|---|---|
| **5** | | | | | | | | | | | |
| Cu(1) | 0.61755(4) | 0.69386(2) | −0.00401(5) | 0.051 | | C(10) | 0.5813(4) | 0.5515(2) | 0.5243(4) | 0.104 | |
| Cu(2) | 0.72413(3) | 0.74347(2) | 0.21279(4) | 0.049 | | C(11) | 0.5032(4) | 0.5635(2) | 0.4980(5) | 0.108 | |
| Si | 0.7076(1) | 0.57654(4) | 0.2421(1) | 0.064 | | C(12) | 0.4842(4) | 0.5792(2) | 0.3975(5) | 0.113 | |
| O(1) | 0.6543(2) | 0.6405(1) | 0.0898(2) | 0.064 | | C(13) | 0.5474(3) | 0.5841(2) | 0.3217(4) | 0.086 | |
| O(2) | 0.7222(2) | 0.67420(9) | 0.2248(2) | 0.081 | | C(14) | 0.6961(4) | 0.5289(2) | 0.1380(4) | 0.109 | |
| O(3) | 0.6620(2) | 0.7438(1) | 0.0842(2) | 0.054 | | C(15) | 0.5151(3) | 0.6536(2) | −0.1649(3) | 0.062 | |
| O(4) | 0.5670(2) | 0.6450(1) | −0.0883(2) | 0.064 | | C(16) | 0.4931(3) | 0.6976(2) | −0.2042(3) | 0.061 | |
| O(5) | 0.7928(2) | 0.7423(1) | 0.3350(2) | 0.054 | | C(17) | 0.5229(2) | 0.7429(2) | −0.1679(3) | 0.055 | |
| N(1) | 0.5742(2) | 0.7470(1) | −0.0873(3) | 0.050 | | C(18) | 0.6011(3) | 0.7939(2) | −0.0482(3) | 0.061 | |
| N(2) | 0.7181(2) | 0.8127(1) | 0.2062(3) | 0.051 | | C(19) | 0.6380(4) | 0.7890(2) | 0.0553(4) | 0.129 | |
| C(1) | 0.6935(3) | 0.6387(1) | 0.1750(3) | 0.054 | | C(20) | 0.6760(3) | 0.8294(1) | 0.1088(4) | 0.061 | |
| C(2) | 0.8069(3) | 0.5735(1) | 0.3123(3) | 0.060 | | C(21) | 0.7444(3) | 0.8428(1) | 0.2784(3) | 0.055 | |
| C(3) | 0.8417(3) | 0.6139(2) | 0.3620(4) | 0.074 | | C(22) | 0.7872(3) | 0.8265(1) | 0.3707(3) | 0.057 | |
| C(4) | 0.9128(3) | 0.6108(2) | 0.4224(4) | 0.081 | | C(23) | 0.8100(3) | 0.7799(1) | 0.3919(3) | 0.051 | |
| C(5) | 0.9496(3) | 0.5671(2) | 0.4327(4) | 0.092 | | C(24) | 0.4780(4) | 0.6083(2) | −0.2123(4) | 0.094 | |
| C(6) | 0.9189(4) | 0.5265(2) | 0.3838(4) | 0.105 | | C(25) | 0.4921(3) | 0.7876(2) | −0.2257(4) | 0.073 | |
| C(7) | 0.8482(3) | 0.5300(2) | 0.3246(4) | 0.086 | | C(26) | 0.7328(3) | 0.8970(2) | 0.2692(4) | 0.090 | |
| C(8) | 0.6255(3) | 0.5718(1) | 0.3448(4) | 0.064 | | C(27) | 0.8627(3) | 0.7685(2) | 0.4890(4) | 0.075 | |
| C(9) | 0.6429(3) | 0.5553(2) | 0.4484(4) | 0.082 | | Cl | 0.8254(4) | 0.8697(2) | 0.4509(5) | 0.160[c] | 0.30 |

a) $U_{eq}=(1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\boldsymbol{a}_i\cdot\boldsymbol{a}_j$. b) Population parameters. c) Refined isotropically.

Table 3. Selected Bond Lengths (Å) and Angles (°)

| | **1** | **2** | **3** | **4** | **5** |
|---|---|---|---|---|---|
| Cu(1)···Cu(2) | 3.482(1) | 3.514(4) | 3.469(3) | 3.517(3) | 3.502(1) |
| Cu(1)–O(1) | 1.930(5) | 1.909(9) | 1.951(6) | 1.940(11) | 1.974(3) |
| Cu(1)–O(3) | 1.896(4) | 1.890(8) | 1.909(6) | 1.923(11) | 1.907(3) |
| Cu(1)–O(4) | 1.901(4) | 1.905(8) | 1.900(7) | 1.862(11) | 1.901(3) |
| Cu(1)–N(1) | 1.916(6) | 1.911(9) | 1.922(8) | 1.911(12) | 1.933(3) |
| Cu(2)–O(2) | 1.936(5) | 1.945(8) | 1.925(6) | 1.953(11) | 1.915(2) |
| Cu(2)–O(3) | 1.912(4) | 1.916(9) | 1.906(6) | 1.884(11) | 1.903(3) |
| Cu(2)–O(5) | 1.900(4) | 1.919(9) | 1.896(6) | 1.875(10) | 1.898(3) |
| Cu(2)–N(2) | 1.908(7) | 1.916(10) | 1.927(7) | 1.895(13) | 1.912(3) |
| O(1)–C(1) | 1.250(7) | 1.268(15) | 1.267(12) | 1.217(20) | 1.245(5) |
| O(2)–C(1) | 1.255(7) | 1.274(13) | 1.259(11) | 1.241(21) | 1.251(5) |
| O(3)–C[a] | 1.353(9) | 1.370(18) | 1.431(10) | 1.265(20) | 1.355(6) |
| O(1)–Cu(1)–O(3) | 93.6(2) | 93.6(4) | 93.7(2) | 93.1(5) | 94.4(1) |
| O(1)–Cu(1)–O(4) | 87.2(2) | 86.5(4) | 86.7(3) | 85.5(5) | 86.3(1) |
| O(1)–Cu(1)–N(1) | 170.0(2) | 170.5(4) | 173.1(3) | 178.4(5) | 175.2(1) |
| O(3)–Cu(1)–O(4) | 174.7(2) | 177.5(4) | 178.1(3) | 176.2(4) | 176.5(1) |

Table 3. (Continued)

| | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| O(3)-Cu(1)-N(1) | 84.6(2) | 86.3(4) | 85.4(3) | 86.4(5) | 84.6(1) |
| O(4)-Cu(1)-N(1) | 95.5(2) | 94.0(4) | 94.4(3) | 95.1(5) | 94.5(1) |
| O(2)-Cu(2)-O(3) | 93.4(2) | 93.1(4) | 93.5(3) | 94.0(5) | 93.5(1) |
| O(2)-Cu(2)-O(5) | 87.6(2) | 87.7(4) | 86.4(3) | 85.3(5) | 86.0(1) |
| O(2)-Cu(2)-N(2) | 168.0(3) | 174.7(4) | 171.1(3) | 174.3(5) | 175.6(1) |
| O(3)-Cu(2)-O(5) | 172.6(2) | 179.2(4) | 178.4(3) | 172.9(4) | 175.9(1) |
| O(3)-Cu(2)-N(2) | 85.2(2) | 85.4(4) | 86.3(3) | 85.0(5) | 86.1(1) |
| O(5)-Cu(2)-N(2) | 95.3(2) | 93.9(4) | 94.0(3) | 96.4(5) | 94.8(1) |
| Cu(1)-O(1)-C(1) | 136.2(4) | 137.4(8) | 134.3(6) | 132.4(12) | 134.0(3) |
| Cu(2)-O(2)-C(1) | 135.7(4) | 135.9(7) | 135.3(6) | 130.8(10) | 138.2(3) |
| Cu(1)-O(3)-Cu(2) | 132.2(3) | 134.8(4) | 130.8(3) | 135.0(5) | 133.6(2) |
| Cu(1)-O(3)-C[a] | 112.9(4) | 112.4(8) | 109.5(5) | 109.0(12) | 113.4(3) |
| Cu(2)-O(3)-C[a] | 111.0(4) | 112.3(8) | 108.0(5) | 116.0(13) | 112.6(3) |
| O(1)-C(1)-O(2) | 124.9(7) | 124.7(11) | 126.6(8) | 133.9(16) | 126.1(4) |

a) Carbon atom bonded to the alkoxide oxygen atom.

of the 2-methyl benzoato ligand. Their population parameters were estimated to be 33 and 67%, respectively. The occupation factor of the crystal methanol was assumed to be 50% based on the elemental analysis.

**4:** Chlorine atoms, Cl(3) and Cl(4), bonded to the L-ac ligand were detected in difference synthesis. The total of their occupation factors was estimated to be 0.5 based on the elemental analysis. It seems that the chlorine atoms were introduced into the L-ac ligand when the complex, $[Cu_2(L\text{-}ac)Cl(H_2O)]$ was reacted with 2,6-dichlorobenzoic acid. A

Table 4. A Comparison of the Coordination Geometry around the Cu Atoms and Their $-2J$ Values

| | 1 | 2 | 3 | 4 |
|---|---|---|---|---|
| Carboxylato ligand | PhCOO | 2-Me-PhCOO | 2,6-$Me_2$-PhCOO | 2,6-$Cl_2$-PhCOO |
| Cu(1)-O(3)-Cu(2)/° | 132.3(3) | 134.8(4) | 130.8(3) | 135.0(5) |
| Cu(1)···Cu(2)/Å | 3.482(2) | 3.514(4) | 3.469(3) | 3.517(3) |
| Cu-O(3)/Å | 1.896(4) | 1.890(8) | 1.909(6) | 1.923(11) |
| | 1.912(4) | 1.916(9) | 1.906(6) | 1.884(11) |
| Cu-O(carboxyl)/Å | 1.930(5) | 1.909(9) | 1.925(6) | 1.940(11) |
| | 1.936(5) | 1.945(8) | 1.951(6) | 1.953(11) |
| $\tau$/° [b] | 24.4(2) | 7.1(4) | 23.5(3) | 13.9(5) |
| $\phi_{rot}$/° [c] | 2.1(8) | 29.2(5) | 74.2(4) | 83.4(6) |
| $\phi_{bend}$/° [d] | 10.1(3) | 3.3(4) | 2.6(3) | 7.4(6) |
| $-2J/cm^{-1}$ | 183 | 188 | 133 | 207 |

Table 4. (Continued)

| | 5 | A[a] | B[a] | C[a] | D[a] |
|---|---|---|---|---|---|
| Carboxylato ligand | $Ph_2MeSiCOO$ | $CH_3COO$ | $CH_3COO$ | PhCOO | None |
| Cu(1)-O(3)-Cu(2)/° | 133.6(2) | 133.3(3) | 134.5(5) | 132.7(3) | 137.7(5) |
| Cu(1)···Cu(2)/Å | 3.502(1) | 3.502(2) | 3.495(3) | 3.482(2) | 3.644(2) |
| Cu-O(3)/Å | 1.907(3) | 1.902(6) | 1.877(9) | 1.917(6) | 1.944(9) |
| | 1.903(3) | 1.913(6) | 1.912(9) | 1.884(6) | 1.964(9) |
| Cu-O(carboxyl)/Å | 1.974(3) | 1.946(6) | 1.950(9) | 1.936(6) | 1.914(13) |
| | 1.915(2) | 1.930(6) | 1.919(9) | 1.953(6) | 1.915(9) |
| $\tau$/° [b] | 3.3(1) | 4.2(3) | 13.2(4) | 8.4(2) | 19.5(4) |
| $\phi_{rot}$/° [c] | — | — | — | 3.9(9) | — |
| $\phi_{bend}$/° [d] | 3.5(1) | 8.3(4) | 1.0(10) | 20.9(3) | — |
| $-2J/cm^{-1}$ | 95 | 165 | 170 | 160 | 635 |

a) The structures and $-2J$ values have been reported in Ref. 1: (**A**) $[Cu_2(L\text{-}ac)(CH_3COO)]\cdot H_2O$; (**B**) $[Cu_2(L\text{-}sal)(CH_3COO)]\cdot MeOH$; (**C**) $[Cu_2(L\text{-}sal)(PhCOO)]\cdot H_2O$; (**D**) $[Cu_2(L\text{-}mac)(MeO)(MeOH)]$, where the ligands $H_3L$ are 1 : 2 Schiff bases derived from 1,3-diaminopropan-2-ol and acetylacetone (for L-ac), salicylaldehyde (for L-sal), or methylacetoacetate (for L-mac). b) The dihedral angle between the coordinate planes, Cu(1)O(1)O(4)N(1) and Cu(2)O(2)O(5)N(2). c) The dihedral angle between the Ph ring and carboxyl moiety in the bridging benzoate ion. d) The dihedral angle between the best plane through the Cu(1)-O(1)···O(2)-Cu(2) moiety and the O(1)-C(1)-O(2) carboxyl bridge.

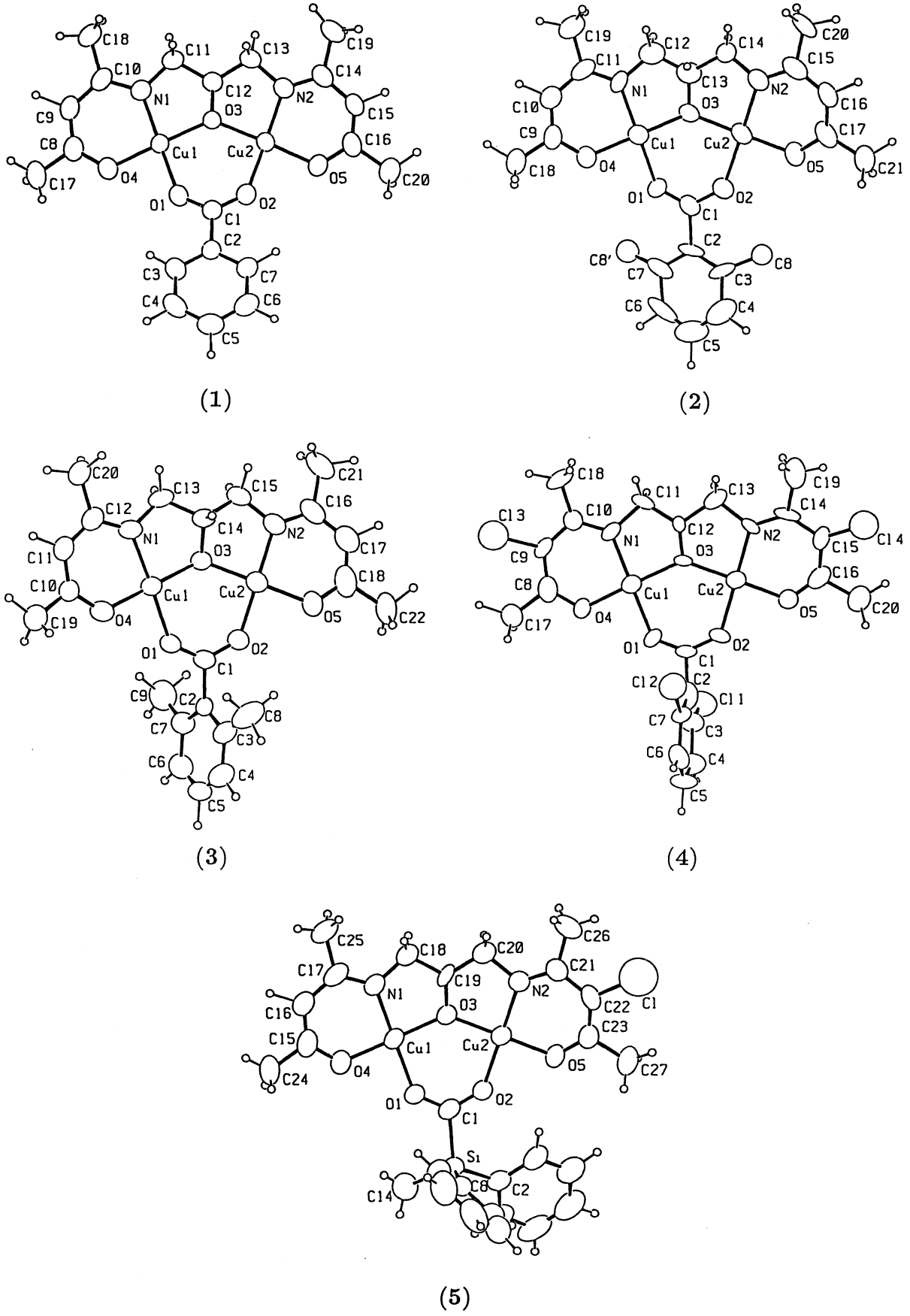



Fig. 1. ORTEPII drawing[10] of the molecules with the thermal ellipsoids scaled at 50% probability level. The H atoms are represented by circles of radius 0.08 Å. The methyl carbon atom of 2-Me-PhCOO in **2** has two possible positions, C(8) and C(8′), with 33 and 67% probability respectively.

similar modification of the L-ac ligand was observed for **5**. The occupation factor of the DMF was assumed to be 70%. There exist two possible orientations, A and B, for the DMF molecule with the positions of O(6) and N(3) are common.

**5:** A chlorine atom bonded to the L-ac ligand was detected and the population was estimated to be 30%.

**Physical Measurements.** The magnetic susceptibilities over the temperature range of 80—300 K were determined by one of the authors (T.T.) by the Farady method. The $-2J$ values were determined from the cryomagnetic data based on the Bleany-Bowers equation which is described elsewhere.[4]

## Results and Discussion

**Molecular Structure.** The molecular structures are shown in Fig. 1. All of the compounds are binuclear complexes which have a mixed double-bridge consisting of alkoxo and carboxylato ligands. Coordination geometries around the Cu atoms and the $-2J$ values of the complexes are summarized in Table 4. Available data for related compounds also are included in Table 4. The coordination environment around the Cu atoms is approximately square-planar, and the dihedral angle of the two coordination planes varies from 3.3(1) to 24.4(2)°.

Positonal disorder was observed for the carbon atom bonded to the alkoxo O(3) with the exception of **3**. For example, the side view of the complex **5** is illustrated in Fig. 2. The elongated thermal ellipsoid of the C(19) atom suggests two possible positions of the $sp^3$ carbon atom. The short O(3)–C bond length and the large Cu–O(3)–C bond angles are artifacts resulting from the positional disorder of the C atom. The position of the O(3) atom seems to be ordered, judging from the normal Cu–O(3) bond distances. In $\mu$-alkoxo-$\mu$-pyrazolato-bridged binuclear metal complexes, a good correlation exists between the dihedral angle of the coordination planes and the metal–O–metal angle.[11] However, this relationship is not clear for the present complexes, which suggests a greater flexibility of the carboxylato bridge than the pyrazolato bridge.

**Magneto-Structural Correlation.** The singlet-triplet energy separation of the binuclear copper(II) complex with double hydroxo bridges correlates linearly with the Cu–O–Cu angle, and the spin-exchange interaction is antiferromagnetic for a Cu–O–Cu angle greater than 97.5°.[12] Alkoxo double-bridged compounds qualitatively follow this magneto-structural correlation, i.e., the antiferromagnetic interaction becomes stronger as the Cu–O–Cu angle increases.[13] However, the antiferromagnetic spin-exchange interaction is depressed by the so-called roof-shaped distortion, which is measured by the dihedral angle between the coordination planes, $\tau$ in Table 4.[14] The roof-shaped deformation of the $Cu_2O(OCO)$ core was observed in one of the compounds studied by Nishida and Kida with $\tau$=54.6°, Cu···Cu =3.129(2) Å and Cu–O–Cu=109.1(3)°,[1] and in a complex with 1,10-phenanthroline, $[Cu_2(OH)(CH_3COO)(phen)_2](NO_3)_2 \cdot H_2O$, $\tau$=57.3°, Cu···Cu=3.017(2) Å, and Cu–O–Cu=103.4(2)°.[15] The effective magnetic moments of these compounds at room temperature are larger than the spin-only value. Taking into account the effect of the roof-shaped distortion, the Cu···Cu distance is an alternative parameter to be used in place of the Cu–O–Cu angle, since a larger Cu–O–Cu angle, or a smaller $\tau$ yields a longer Cu···Cu distance.

In fact, among the benzoato- and acetato-bridged complexes (**1**—**4** and **A**—**C**), the $-2J$ value roughly correlates with the Cu···Cu distance as shown in Fig. 3. A single alkoxo-bridged complex $[Cu_2(L\text{-mac})(MeO)(MeOH)]$, compound **D**, shows a much stronger anti-

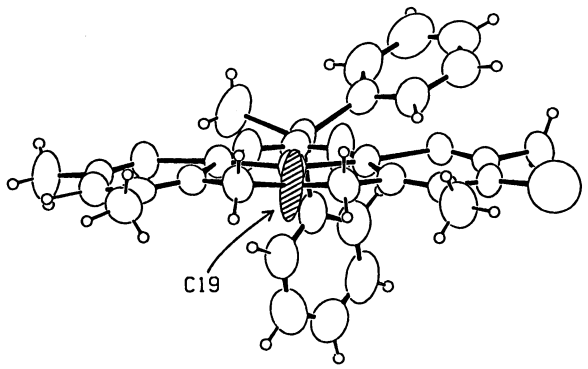



Fig. 2. The side view of $[Cu_2(L\text{-ac})(Ph_2MeSiCOO)]$ (**5**). The shaded atom is C(19), which is bonded to the alkoxo O(3) atom.

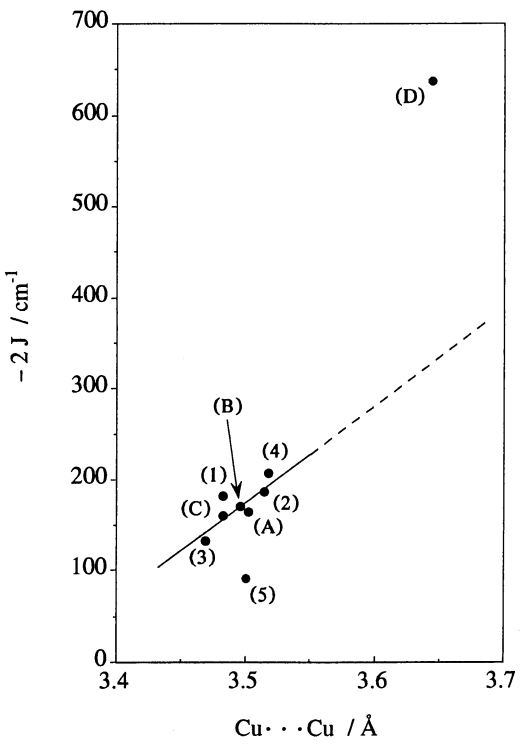



Fig. 3. The $-2J$ value of the complexes listed in Table 4 versus the Cu···Cu distance. The solid line shows the least-squares line calculated excluding the silanecarboxylate compound, **5**, and mono-bridged compound, **D**.

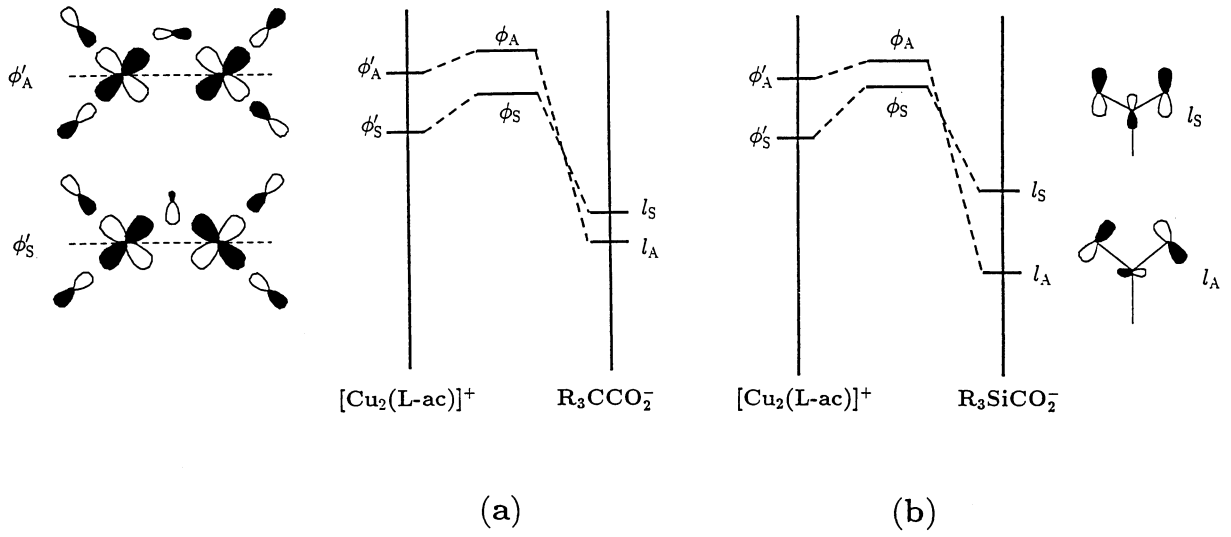



Fig. 4. Qualitative MO diagram of the magnetic orbitals of (a) $[Cu_2(L\text{-}ac)(R_3CCO_2)]$ and (b) $[Cu_2(L\text{-}ac)(R_3SiCO_2)]$, where $R$ stands for the organic group.

ferromagnetic coupling than the mixed bridged complexes, because there exists no orbital countercomplementary effect in this compound (see below). The point for the silanecarboxylato complex, **5**, shifts downward from the correlation line, indicating the presence of a stronger orbital countercomplementary effect in the silanecarboxylato-bridged complex than in the acetato- or benzoato-bridged complexes. The dimensions of the central double-bridged structure in **5** and those in $[Cu_2(L\text{-}ac)(CH_3COO)]$ compound **A**, are almost the same (see Table 4), although the $-2J$ values are quite different between them: (**5**) 95 and (**A**) 165 $cm^{-1}$.

The influence of the bent structure of the benzoato bridge ($\phi_{bend}$ in Table 4) on the orbital countercomplementary effect could not be clearly determined in the present work.

**Orbital Countercomplementary Effect.** The magnetic orbitals of the complex consist essentially of the copper $d_{x^2-y^2}$ orbitals (the local x and y axes are nearly parallel to the metal-ligand bonds) and the related orbitals on the bridge. The alkoxo bridge contributes to the spin-exchange interaction by an antisymmetric combination of the $d_{x^2-y^2}$ orbitals through a 2p orbital on oxygen. The carboxylato bridge provides a pathway for the spin-exchange by a symmetric combination through the symmetric HOMO. Therefore, the two bridges counteract against each other in the spin super-exchange interaction.[1]

The extent of the countercomplementary effect is explained in terms of the energy difference between the antisymmetric ($\phi_A$) and symmetric ($\phi_S$) combinations of the magnetic orbitals (see Fig. 4). According to Hay, Thibeault, and Hoffmann, the energy difference between $\phi_A$ and $\phi_S$ determines the magnitude of the antiferromagnetic interactions.[16] For a Cu–O–Cu angles greater than 97.5°, $\phi_A$ is higher in energy than $\phi_S$ for the di-$\mu$-hydroxo bridged copper(II) complexes. Likewise, the antisymmetric combination of the magnetic orbital ($\phi'_A$) is expected to be higher in energy than the symmetric combination ($\phi'_S$) in a single alkoxo-bridged $[Cu_2(L\text{-}ac)]^+$ system as illustrated in Fig. 4. The countercomplementary effect by the orbital interactions with a carboxylato ligand makes the energy difference between $\phi_A$ and $\phi_S$ smaller than that between $\phi'_A$ and $\phi'_S$. Therefore, the $-2J$ values of the $\mu$-alkoxo-$\mu$-carboxylato complexes are much smaller than that of the single alkoxo-bridged compound **D** as seen in Fig. 3.

Kuznesof, et al. has shown by MO calculations that the presence of Si in the carboxylato ligand raises the $\sigma_{a1}$ level ($l_S$) and lowers the $\sigma_{b1}$ level ($l_A$).[17] The distinguishing characteristic of the silanecarboxylato ligand is the larger contribution of the $2p_x$ orbital of the carboxylato C atom (x is parallel to the C–Si bond axis) in the symmetric HOMO than the carbon carboxylato ligand.[3] The larger contribution of the $2p_x$(C) may unstabilize the symmetric HOMO. The copper(II) $d_{x^2-y^2}$ orbitals are higher in energy than the ligand HOMO's.[16,18] Since the magnetic orbitals are antibonding in nature, on the principle of energy matching, the mixing of $\phi'_S$ with $l_S$ is enhanced and that of $\phi'_A$ with $l_A$ is diminished by the silanecarboxylato ligand in relation to the carbon carboxylato ligand, resulting in a larger increase in energy of $\phi_S$ as compared to $\phi_A$ and thus a smaller energy difference between these levels. Therefore, the $-2J$ value of the silanecarboxylato-bridged complex **5** is fairly smaller than those of the acetato- or benzoato-bridged complexes as seen in Fig. 3. The enhancement of the spin super-exchange interaction in the dimeric copper(II) silanecarboxylate is explained similarly by assumming that $\phi_S$ is higher in energy than $\phi_A$.

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