Contribution from the Division of Inorganic Chemistry, Department of Chemistry,
University of Helsinki, SF-00100 Helsinki 10, Finland

Exchange Interaction through Hydrogen-Bond Bridges and the Effect of a Single-Oxygen Bridge. Crystal Structures and Magnetic Susceptibilities of Two Binuclear Copper(II) Complexes of 2-Amino-2-methyl-1-propanol

Heikki Muhonen

The structures and magnetic properties of [{Cu($C_4H_{10}NO$)($C_4H_{11}NO$)(H_2O)}{Cu($C_4H_{10}NO$)($C_4H_{11}NO$)(SO_4)}]·CH_3OH (**1**) and [Cu_2($C_4H_{10}NO$)$_2$($C_4H_{11}NO$)$_2$(H_2O)]($ClC_7H_4O_2$)$_2$·$2C_3H_7OH$ (**2**) have been investigated as part of a study to determine the kinds of complexes 2-amino-2-methyl-1-propanol (=MepH) forms with copper(II). Crystal data for **1**: triclinic, space group $P\bar{1}$, a = 10.808 (4) Å, b = 10.958 (4) Å, c = 12.738 (5) Å, α = 78.27 (3)°, β = 86.61 (3)°, γ = 77.07 (3)°, and Z = 2. Crystal data for **2**: triclinic, space group $P\bar{1}$, a = 11.919 (7) Å, b = 15.063 (4) Å, c = 15.648 (9) Å, α = 117.82 (3)°, β = 98.95 (4)°, γ = 97.48 (4)°, and Z = 2. The structures were refined by least-squares methods to R values of 0.041 for **1** and 0.053 for **2**. The structure of **1** is built up of cationic and anionic copper(II) complexes, both of which have the metal atom in a square-pyramidal environment, and of one solvate methanol molecule. The basal corners of each square pyramid are occupied by the oxygen and nitrogen atoms of a MepH-Mep ligand pair arranged in a cis configuration around the metal atom. There are two independent ligand pairs, one coordinated in the cation and the other in the anion. The basal planes of the cation and anion are joined edge to edge by two hydrogen bonds (oxygen-oxygen distances of 2.417 (4) and 2.475 (4) Å) to form a binuclear cluster molecule. A water molecule occupies the apical position in the cation and a sulfate molecule in the anion. The structure of **2** contains a binuclear complex cation, two *o*-chlorobenzoate anions, and two solvate 2-propanol molecules. The binuclear complex cation comprises two very similar building blocks, each of which has copper in square-pyramidal coordination with a MepH-Mep ligand pair defining the basal plane in the same manner as in **1**. The basal planes of the building blocks are joined, as in **1**, by two hydrogen bonds (oxygen-oxygen distances of 2.446 (7) and 2.494 (8) Å), but here the building blocks share a water ligand at the apexes of their square pyramids. In **1** the dihedral angle between the basal planes is 26.7 (1)°, whereas in **2**, owing to the presence of the single-atom bridge, it is 80.1 (2)°. Both compounds show antiferromagnetic coupling, with $2J$ values of -49 cm^{-1} in **1** and -27 cm^{-1} in **2** obtained from the temperature dependences of the magnetic susceptibilities. Reasons for the difference in the $2J$ values are considered.

Introduction

Dimer formation between monomeric transition-metal fragments through hydrogen bonding was first suggested by Yoneda and Kida[1] for the series of compounds [Co_2(Eta)$_3$(EtaH)$_3$]X_3, where EtaH represents 2-aminoethanol and Eta the corresponding anion. Two different structures for the cation were considered: one containing a singly bridged corner-to-corner hydrogen bonding and the other a triply bridged face-to-face hydrogen bonding. With the purpose of investigating polynuclear complexes with hydrogen-bond bridges more throughly, Bertrand and co-workers prepared complexes by using Cu^{2+}, Ni^{2+}, and Co^{3+} as central atoms and a few amino alcohols and an imino alcohol as ligands and determined the structures by X-ray diffraction.[2-6] The compounds were found to be made up of monomeric fragments associated into binuclear units by cooperative hydrogen bonding. In conjunction with the studies, the cation of the compound [Co_2(Eta)$_3$(EtaH)$_3$](ClO$_4$)$_3$·$^1/_2H_2O$ was confirmed to contain a triply bridged face-to-face hydrogen bonding.[5] In all the complexes studied by Bertrand and co-workers the O···O distances of the hydrogen-bond bridges were much shorter than normal hydrogen-bonding O···O distances, the shortest of them only 2.31 (1) Å.[3] The exchange interactions between metal ions were therefore investigated by magnetic susceptibility measurements, with the finding of an unusually strong antiferromagnetic interaction, and a singlet-triplet separation, $2J$, varying up to about -100 cm^{-1} in the copper-copper dimers. Analyses of the structural and magnetic properties did not yield any correlations between structure and magnetism even though specific structural parameters were observed to affect the magnitude of the exchange coupling.

As part of our study to determine what kind of complexes the N-unsubstituted amino alcohol MepH will form with copper(II),

we have prepared two new binuclear hydrogen-bridged copper(II) complexes. In one of these we succeeded in constructing a single oxygen atom bridge between metal atoms, thereby creating a new type of multibridged network. The syntheses, results of X-ray structural determinations, and studies of exchange interactions by magnetic susceptibility measurements are now reported for these two complexes.

Experimental Section

Preparation of [{Cu($C_4H_{10}NO$)($C_4H_{11}NO$)(H_2O)}{Cu($C_4H_{10}NO$)($C_4H_{11}NO$)(SO_4)}]·CH_3OH (1). A 0.02-mol sample of anhydrous $CuSO_4$ was added in small portions to 0.06 mol of $C_4H_{11}NO$ in about 250 mL of a hot methanol–ethanol (4:1) mixed solvent. After 1 day the solution was filtered to remove the formed precipitate. The filtrate was left to stand at room temperature in an Erlenmeyer flask closed with a filter paper stopper. Within a few days blue, rectangular-shaped crystals were precipitated. Copper was analyzed electrolytically. Anal. Calcd for $Cu_2C_{17}H_{48}N_4O_{10}S$: Cu, 20.24. Found: Cu, 20.28.

Preparation of [Cu_2($C_4H_{10}NO$)$_2$($C_4H_{11}NO$)$_2$(H_2O)]($ClC_7H_4O_2$)$_2$·$2C_3$-H_7OH (2). The copper(II) *o*-chlorobenzoate used as starting material in the complex preparation was prepared from $CuSO_4$·$5H_2O$ and *o*-chlorobenzoic acid. The title complex was synthesized by dissolving 0.01 mol of copper(II) *o*-chlorobenzoate, used without prior analysis, in a solution of 0.02 mol of $C_4H_{11}NO$ in about 100 mL of ethanol. The solution was allowed to evaporate to dryness at room temperature, yielding a noncrystalline precipitate. This was redissolved by heating in 2-propanol, and the solution was allowed to concentrate at room temperature by slow evaporation of the solvent through the filter paper stopper of an Erlenmeyer flask. Moving of the flask appeared to disturb the crystallization. Blue, rectangular-shaped crystals, which gradually decomposed in air, were obtained.

X-ray Structure Determinations. For compound **1** accurate unit cell parameters and the orientation matrix were obtained by a least-squares fit of 14 centered and indexed reflections in the range 12 < 2θ < 34°; for compound **2**, 16 reflections in the range 6.5 < 2θ < 14.5° were utilized. For intensity measurement a crystal of **2** was coated with epoxy glue. Details of the crystallographic data collections and the results for both compounds are summarized in Table I. Intensities were corrected for Lorentz and polarization effects, but not for extinction. The positions of copper atoms in both compounds were determined by MULTAN80,[7] and

(1) Yoneda, H.; Kida, S. *J. Am. Chem. Soc.* **1960**, *82*, 2139.
(2) Bertrand, J. A.; Howard, W. J.; Kalyanaraman, A. R. *Chem. Commun.* **1971**, 437.
(3) Bertrand, J. A.; Black, T. D.; Eller, P. G.; Helm, F. T.; Mahmood, R. *Inorg. Chem.* **1976**, *15*, 2965.
(4) Bertrand, J. A.; Eller, P. G. *Prog. Inorg. Chem.* **1976**, *21*, 29.
(5) Bertrand, J. A.; Eller, P. G.; Fujita, E.; Lively, M. O.; VanDerveer, D. G. *Inorg. Chem.* **1979**, *18*, 2419.
(6) Bertrand, J. A.; Fujita, E.; VanDerveer, D. G. *Inorg. Chem.* **1980**, *19*, 2022.

(7) Main, P.; Fiske, S. J.; Hull, S. E.; Lessinger, L.; Germain, G.; Declercq, J. P.; Woolfson, M. M. "MULTAN80, a System of Computer Programs for Automatic Solution of Crystal Structures from X-ray Diffraction Data"; Universities of York and Louvain: York, England, and Louvain, Belgium, 1980.

Table I. Crystal Data and Details of the Structure Determinations

mol formula	[{Cu(C$_4$H$_{10}$NO)(C$_4$H$_{11}$NO)(H$_2$O)}- {Cu(C$_4$H$_{10}$NO)(C$_4$H$_{11}$NO)(SO$_4$)}]·CH$_3$OH (1)	[Cu$_2$(C$_4$H$_{10}$NO)$_2$(C$_4$H$_{11}$NO)$_2$(H$_2$O)]- (ClC$_7$H$_4$O$_2$)$_2$·2C$_3$H$_7$OH (2)
fw	627.7	930.9
cryst syst	triclinic	triclinic
a, Å	10.808 (4)	11.919 (7)
b, Å	10.958 (4)	15.063 (4)
c, Å	12.738 (5)	15.648 (9)
α, deg	78.27 (3)	117.82 (3)
β, deg	86.61 (3)	98.95 (4)
γ, deg	77.07 (3)	97.48 (4)
space group	$P\bar{1}$	$P\bar{1}$
V, Å^3	1440 (1)	2387 (2)
Z	2	2
d_{calcd}, g cm^{-3}	1.45	1.29
d_{obsd}, g cm^{-3}	1.45	1.29
diffractometer	Nicolet P3	Nicolet P3
cryst dimens, mm	0.16 × 0.20 × 0.55	0.10 × 0.19 × 0.49
radiation, Å	graphite-monochromatized Mo Kα λ = 0.7107	graphite-monochromatized Mo Kα λ = 0.7107
temp, °C	20 (1)	20 (1)
abs coeff, cm^{-1}	16.6	10.9
data collected	4.0 < 2θ < 54.0°	4.0 < 2θ < 48.0°
scan type	ω	ω
scan speed, deg min^{-1}	2.0–29.3	2.4–29.3
scan range, deg	[2θ(Mo Kα_1) − 1.0]–[2θ(Mo Kα_2) + 1.0]	[2θ(Mo Kα_1) − 1.0]–[2θ(Mo Kα_2) + 1.0]
bkgd time/scan time	0.5	0.5
no. of std reflecns	2 (no signif variation)	1 (no signif variation)
abs cor	not made	not made
no. of reflecns collected	6294	7921
no.of obsd reflecns	4386 [$F > 6\sigma(F)$]	3121 [$F > 6\sigma(F)$]
function minimized	$\sum w(|F_o| − |F_c|)^2$	$\sum w(|F_o| − |F_c|)^2$
weighting scheme	$w = 1.0/[\sigma^2(F_o) + 0.0003F^2]$	$w = 1.0/[\sigma^2(F_o) + 0.0003F^2]$
no. of parameters refined	500	506
$R = \sum(|F_o| − |F_c|)/\sum|F_o|$	0.041	0.053
$R_w = [\sum w(|F_o| − |F_c|)^2/\sum w|F_o|^2]^{1/2}$	0.053	0.049

these were used in the first step of the Fourier syntheses. The structures were developed by successive least-squares refinements and Fourier syntheses.

For compound **1**, difference syntheses calculated during the refinement provided the locations of all the hydrogen atoms. The final refinement by the full-matrix least-squares method with anisotropic temperature factors for the non-hydrogen atoms and isotropic temperature factors for the hydrogen atoms and with hydrogen atom coordinates and temperature factors allowed to vary, converged to the R value of 0.042. The highest peaks in the difference Fourier map calculated at the end of the refinement were 0.65 e Å^{-3} in the copper atom environments near Cu1, and 0.36 e Å^{-3} elsewhere.

One of the *o*-chlorobenzoate anions of compound **2** exhibits disorder: the substituted phenyl ring has two orientations that are about 180° apart with respect to rotation around the line passing through the ring carbon atom (C25) to which the carboxylate group is attached and through the ring carbon atom (C28) opposite to it. Because of the extensive coalescence of the two sets of the ring carbon atoms, the positions of the ring atoms could be resolved for only one set. However, both positions of the chlorine substituent were located, and on the basis of the electron density maxima population parameters of 0.8 and 0.2 were assigned to the positions. The nature of the disorder is treated in greater detail in Description of the Structures. Most of the hydrogen atom positions of compound **2** were located from a difference Fourier map, but the positions of some methyl hydrogen atoms of the amino alcohol and solvate molecules and the positions of some hydrogen atoms in the disordered phenyl ring had to be determined by calculation. A C–H distance of 1.00 Å was used in calculating hydrogen atom positions. The final refinement, which was carried out by the full-matrix least-squares method with anisotropic temperature factors for the non-hydrogen atoms and fixed coordinates and isotropic thermal parameters of U_{iso} = 0.06 Å^2 for the hydrogen atoms, converged to the R value of 0.053. The highest peaks in the final difference Fourier map calculated at the end of the refinement were less than 0.34 e Å^{-3}.

All crystallographic calculations except the phase determination were carried out with the programs of the X-RAY 76 system.[8] The atomic scattering factors were those of the program system, and dispersion

correction was applied for copper and sulfur atoms in the sulfate compound and for copper and chlorine atoms in the *o*-chlorobenzoate compound.[9] A Univac 1100 computer was used for calculations, and figures were drawn by the PLUTO[10] and ORTEP[11] programs.

The final atomic positional parameters for non-hydrogen and bridging hydrogen atoms, together with the U_{eq} values for the former atoms and U_{iso} values for the latter, are listed in Table II for compound **1** and in Table III for compound **2**. For compound **1**, anisotropic temperature factor coefficients of non-hydrogen atoms and fractional coordinates and U_{iso} values of hydrogen atoms are listed in Tables SI and SII, respectively.[12] The corresponding structural parameters for **2** are listed in Tables SIII and SIV. Listings of the observed and calculated structure factors are available.[12]

Magnetic Measurements. Magnetic susceptibility measurements in the range 77–300 K were performed on powdered samples weighing about 15 mg with use of a Faraday type balance consisting of a Cahn 2000 electrobalance equipped with an Anac 3472 HA electromagnet and Lewis 502 coils from George Associates, Berkeley, CA. Automatic data collection was controlled with a Tektronix 4052A graphic computing system as has been described elsewhere.[13] At low temperatures, from 4.2 to 100 K, magnetic susceptibility data were collected at 10 kOe on powdered samples weighing about 150 mg with a PAR Model 155 vibrating-sample magnetometer (VSM). The procedures have been described earlier.[14] Both instruments were calibrated with HgCo(NCS)$_4$. Susceptibilities were corrected for the diamagnetism of the constituent atoms, which was estimated to be −177 × 10^{-6} cgsu/Cu atom for **1** and −273 × 10^{-6} cgsu/Cu atom for **2**, and for the temperature-independent paramagnetism, $N\alpha$, of copper(II), which was estimated to be 60 × 10^{-6} cgsu/Cu atom.
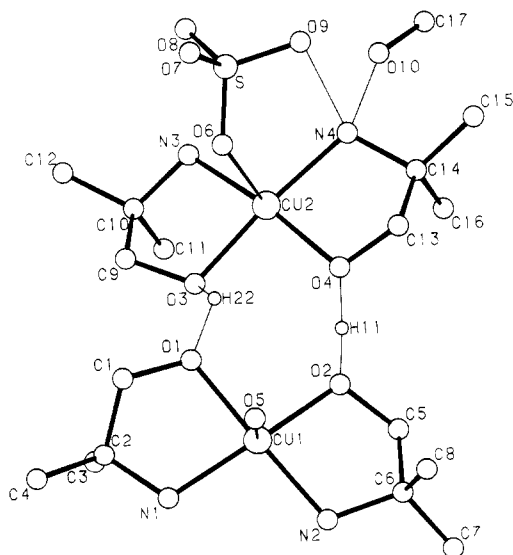
(8) Steward, J. M., Ed. "The X-ray System, Version of 1976"; Technical Report TR-446; Computer Science Center, University of Maryland: College Park, MD, 1976.

(9) *International Tables for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV, p 149.

(10) Motherwell, W. D. S.; Clegg, W. "PLUTO 1978: Program for Plotting Molecular and Crystal Structures"; University of Cambridge: Cambridge, England.

(11) ORTEP was used as a part of the X-RAY 76 system.

(12) Supplementary material.

(13) Weller, R. R. Dissertation, The University of North Carolina at Chapel Hill, 1980.

(14) Corvan, P. J.; Estes, W. E.; Weller, R. R.; Hatfield, W. E. *Inorg. Chem.* **1980**, *19*, 1297.

Table II. Final Fractional Coordinates, and U_{eq} ($\times 10^2$) and U_{iso} ($\times 10^2$) Values for Non-Hydrogen and Bridging Hydrogen Atoms, Respectively, in [{Cu(C$_4$H$_{10}$NO)(C$_4$H$_{11}$NO)(H$_2$O)}-{Cu(C$_4$H$_{10}$NO)(C$_4$H$_{11}$NO)(SO$_4$)}]·CH$_3$OH (**1**)^a

atom	x	y	z	U_{eq} or U_{iso}, Å^2
Cu1	0.01551 (5)	−0.18516 (4)	0.39491 (4)	2.65 (3)
Cu2	0.07126 (5)	0.20606 (5)	0.13594 (4)	3.03 (3)
S	−0.01261 (11)	0.46414 (10)	0.26407 (9)	3.42 (7)
N1	−0.1476 (3)	−0.2471 (3)	0.4196 (3)	3.4 (2)
N2	0.1318 (3)	−0.3555 (3)	0.4295 (3)	3.1 (2)
N3	−0.0504 (3)	0.3242 (3)	0.0279 (3)	3.0 (2)
N4	0.2198 (4)	0.2923 (3)	0.1112 (3)	3.8 (3)
O1	−0.0922 (3)	−0.0192 (2)	0.3402 (2)	3.0 (2)
O2	0.1697 (3)	−0.1276 (3)	0.3426 (3)	4.0 (2)
O3	−0.0602 (3)	0.1047 (3)	0.1591 (2)	3.3 (2)
O4	0.1876 (3)	0.0701 (3)	0.2239 (3)	4.2 (2)
O5	−0.0097 (4)	−0.1419 (3)	0.5628 (3)	4.8 (3)
O6	−0.0203 (4)	0.3325 (3)	0.2624 (2)	4.6 (2)
O7	−0.0869 (4)	0.5067 (3)	0.3546 (3)	5.7 (3)
O8	−0.0691 (4)	0.5442 (4)	0.1625 (3)	6.7 (3)
O9	0.1198 (4)	0.4729 (4)	0.2677 (4)	7.7 (4)
O10	0.3058 (7)	0.4078 (7)	−0.1101 (4)	9.7 (6)
C1	−0.2179 (4)	−0.0198 (4)	0.3757 (3)	3.5 (3)
C2	−0.2529 (4)	−0.1441 (4)	0.3662 (4)	3.7 (3)
C3	−0.2547 (6)	−0.1552 (5)	0.2493 (5)	5.9 (5)
C4	−0.3806 (5)	−0.1548 (5)	0.4253 (6)	6.5 (5)
C5	0.2729 (4)	−0.2310 (4)	0.3308 (4)	4.0 (3)
C6	0.2671 (4)	−0.3418 (4)	0.4248 (3)	3.1 (3)
C7	0.3576 (5)	−0.4633 (5)	0.4046 (5)	5.1 (4)
C8	0.2967 (5)	−0.3093 (5)	0.5298 (4)	4.8 (4)
C9	−0.1753 (4)	0.1773 (4)	0.1102 (4)	3.9 (3)
C10	−0.1459 (4)	0.2566 (4)	0.0025 (3)	3.3 (3)
C11	−0.0835 (5)	0.1722 (4)	−0.0752 (4)	4.8 (4)
C12	−0.2649 (5)	0.3485 (5)	−0.0447 (4)	5.0 (4)
C13	0.2886 (5)	0.1159 (5)	0.2528 (4)	4.7 (4)
C14	0.3346 (4)	0.1989 (4)	0.1542 (4)	4.6 (4)
C15	0.4330 (6)	0.2653 (6)	0.1867 (6)	7.6 (6)
C16	0.3918 (6)	0.1195 (6)	0.0705 (6)	7.6 (6)
C17	0.3964 (7)	0.4388 (8)	−0.1858 (6)	9.8 (7)
H11	0.182 (6)	−0.034 (6)	0.281 (5)	9 (2)
H22	−0.036 (7)	0.073 (7)	0.242 (6)	12 (3)

$^a U_{eq} = {}^1\!/_3 \sum_i \sum_j U_{ij} a_i{}^* a_j{}^* a_i a_j \cos \alpha_{ij}$.

Table III. Final Fractional Coordinates for Non-Hydrogen and Bridging Hydrogen Atoms and U_{eq} ($\times 10^2$) Values for Non-Hydrogen Atoms in [Cu$_2$(C$_4$H$_{10}$NO)$_2$(C$_4$H$_{11}$NO)$_2$(H$_2$O)](ClC$_7$H$_4$O$_2$)$_2$·2C$_3$H$_7$OH (**2**)^a

atom	x	y	z	U_{eq}, Å^2
Cu1	0.18340 (9)	0.45540 (8)	0.14746 (8)	4.24 (5)
Cu2	0.23088 (9)	0.17645 (8)	0.04477 (8)	4.36 (5)
Cl1	−0.0807 (2)	0.2253 (2)	0.3416 (2)	8.7 (2)
Cl21^b	−0.1888 (4)	0.1145 (3)	−0.3411 (3)	12.7 (5)
Cl22^b	0.2072 (18)	0.3033 (17)	−0.2798 (17)	11.3 (13)
N1	0.0504 (6)	0.4902 (5)	0.2110 (5)	4.5 (3)
N2	0.1548 (6)	0.5177 (5)	0.0596 (5)	4.6 (3)
N3	0.1395 (5)	0.0810 (5)	0.0757 (5)	4.4 (3)
N4	0.2013 (6)	0.0832 (5)	−0.1023 (5)	4.9 (3)
O1	0.2429 (4)	0.4302 (4)	0.2559 (4)	4.7 (3)
O2	0.3273 (4)	0.4395 (4)	0.1006 (4)	4.5 (3)
O3	0.2910 (4)	0.2577 (3)	0.1921 (4)	4.1 (3)
O4	0.3514 (4)	0.2620 (4)	0.0256 (4)	4.8 (3)
O5	0.0999 (4)	0.2779 (4)	0.0399 (4)	4.1 (3)
O6	−0.0910 (5)	0.1104 (4)	0.1097 (4)	5.6 (3)
O7	−0.0876 (6)	0.2670 (4)	0.1076 (5)	6.8 (3)
O8	0.0539 (6)	0.2137 (4)	−0.1529 (4)	7.7 (4)
O9	0.0184 (5)	0.3565 (4)	−0.1489 (4)	6.5 (3)
O10	0.5057 (10)	0.7592 (6)	0.5381 (6)	16.1 (7)
O11	0.4594 (6)	0.5618 (5)	0.3766 (6)	11.6 (4)
C1	0.1615 (8)	0.4387 (6)	0.3139 (6)	5.4 (4)
C2	0.0928 (8)	0.5184 (7)	0.3173 (6)	5.2 (5)
C3	0.1701 (9)	0.6258 (7)	0.3720 (6)	7.3 (5)
C4	−0.0092 (9)	0.5163 (7)	0.3654 (7)	7.8 (6)
C5	0.3372 (8)	0.4794 (6)	0.0359 (7)	6.2 (5)
C6	0.2707 (8)	0.5632 (6)	0.0561 (6)	5.7 (5)
C7	0.2581 (9)	0.5907 (7)	−0.0269 (8)	8.0 (6)
C8	0.3265 (9)	0.6586 (7)	0.1555 (7)	8.1 (6)
C9	0.2454 (8)	0.2068 (6)	0.2416 (6)	5.2 (4)
C10	0.2072 (8)	0.0907 (7)	0.1691 (6)	5.2 (5)
C11	0.3104 (8)	0.0425 (7)	0.1464 (7)	6.7 (5)
C12	0.1343 (9)	0.0389 (7)	0.2124 (7)	7.2 (6)
C13	0.3486 (8)	0.2214 (6)	−0.0773 (7)	6.1 (5)
C14	0.3101 (8)	0.1034 (6)	−0.1335 (6)	5.7 (5)
C15	0.2853 (6)	0.0641 (7)	−0.2445 (7)	7.9 (6)
C16	0.3981 (9)	0.0533 (7)	−0.1026 (7)	7.1 (5)
C17	−0.1242 (7)	0.2007 (7)	0.1296 (6)	3.7 (4)
C18	−0.2196 (7)	0.2209 (5)	0.1851 (6)	3.7 (4)
C19	−0.2118 (8)	0.2280 (6)	0.2762 (7)	5.0 (5)
C20	−0.3058 (11)	0.2423 (7)	0.3221 (7)	6.5 (6)
C21	−0.4064 (10)	0.2468 (8)	0.2722 (10)	7.6 (6)
C22	−0.4181 (9)	0.2423 (7)	0.1816 (9)	6.7 (6)
C23	−0.3242 (9)	0.2285 (6)	0.1391 (6)	5.2 (5)
C24	0.0294 (7)	0.2667 (6)	−0.1919 (6)	5.2 (4)
C25	0.0223 (13)	0.2166 (8)	−0.3034 (8)	7.3 (6)
C26	−0.0715 (15)	0.1456 (10)	−0.3737 (11)	10.0 (9)
C27	−0.0879 (27)	0.0967 (18)	−0.4778 (16)	17.8 (17)
C28	0.0025 (34)	0.1281 (25)	−0.4964 (25)	20.8 (36)
C29	0.1085 (23)	0.1923 (22)	−0.4419 (20)	17.9 (23)
C30	0.1180 (20)	0.2434 (14)	−0.3369 (12)	12.6 (14)
C31	0.5101 (30)	0.8290 (14)	0.5088 (16)	30.4 (24)
C32	0.4956 (21)	0.9182 (14)	0.5825 (16)	21.7 (16)
C33	0.5424 (21)	0.8239 (13)	0.4338 (16)	21.7 (16)
C34	0.5475 (11)	0.5061 (10)	0.3563 (11)	10.5 (7)
C35	0.6414 (14)	0.5425 (13)	0.4425 (13)	17.1 (12)
C36	0.5934 (13)	0.5212 (12)	0.2771 (12)	15.2 (10)
H11^c	0.320	0.357	0.077	
H22^c	0.292	0.333	0.219	

^{a}See footnote a of Table II. ^{b} Population parameters of 0.8 and 0.2 were assigned to Cl21 and Cl22, respectively. ^{c} Hydrogen atom coordinates were not refined, and an isotropic thermal parameter, U_{iso} = 0.06 Å^2, was assigned to all hydrogen atoms.

Figure 1. View of the [{Cu(C$_4$H$_{10}$NO)(C$_4$H$_{11}$NO)(H$_2$O)}{Cu(C$_4$H$_{10}$NO)(C$_4$H$_{11}$NO)(SO$_4$)}]·CH$_3$OH (**1**) molecule.

Description of the Structures

[{Cu(C$_4$H$_{10}$NO)(C$_4$H$_{11}$NO)(H$_2$O)}{Cu(C$_4$H$_{10}$NO)(C$_4$H$_{11}$NO)-(SO$_4$)}]·CH$_3$OH (**1**). The molecular structure consists of a cationic and an anionic copper(II) complex joined cooperatively by two hydrogen bonds to form a binuclear metal cluster entity and of one solvate methanol molecule. A view of the molecule is shown in Figure 1, where it may be seen that both copper atoms have square-pyramidal coordination. The basal plane of the square pyramid comprises two oxygen and two nitrogen atoms arranged in a cis configuration around the metal atom. The basal atoms coordinated to the Cu1 atom come from one MepH–Mep ligand pair and those coordinated to the Cu2 atom from the other similar but independent pair. The apical coordination positions are occupied by a water molecule in the cation and by a sulfate oxygen atom in the anion. The basal coordination bond lengths in the
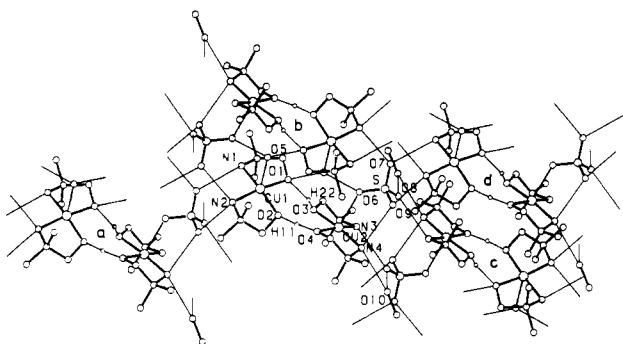
Figure 2. Two-dimensional packing pattern for compound **1**. The figure also displays the twist of the coordination planes in the binuclear molecules with respect to one another.

Table IV. Bond Lengths (Å) and Selected Angles (deg) for [{Cu(C₄H₁₀NO)(C₄H₁₁NO)(H₂O)}{Cu(C₄H₁₀NO)(C₄H₁₁NO)(SO₄)}]·CH₃OH (**1**)

Cu1–O1	1.944 (2)	C6–C7	1.523 (6)
Cu1–O2	1.945 (3)	C6–C8	1.521 (7)
Cu1–O5	2.271 (4)	C9–O3	1.420 (5)
Cu1–N1	2.013 (4)	C9–C10	1.524 (6)
Cu1–N2	1.985 (3)	C10–N3	1.482 (6)
Cu2–O3	1.965 (3)	C10–C11	1.519 (7)
Cu2–O4	1.925 (3)	C10–C12	1.516 (6)
Cu2–O6	2.366 (3)	C13–O4	1.395 (7)
Cu2–N3	2.006 (3)	C13–C14	1.521 (7)
Cu2–N4	2.017 (4)	C14–N4	1.473 (5)
C1–O1	1.408 (5)	C14–C15	1.533 (9)
C1–C2	1.522 (7)	C14–C16	1.528 (9)
C2–N1	1.495 (5)	S–O6	1.468 (3)
C2–C3	1.520 (8)	S–O7	1.461 (4)
C2–C4	1.549 (7)	S–O8	1.486 (4)
C5–O2	1.426 (5)	S–O9	1.460 (5)
C5–C6	1.532 (6)	C17–O10	1.381 (10)
C6–N2	1.500 (6)		

O1–Cu1–N1	85.3 (1)	O4–Cu2–N4	84.3 (1)
O2–Cu1–N2	83.9 (1)	O3–Cu2–N4	173.8 (1)
O1–Cu1–N2	172.0 (1)	O4–Cu2–N3	169.6 (1)
O2–Cu1–N1	169.0 (1)	O3–Cu2–O4	90.8 (1)
O1–Cu1–O2	92.6 (1)	N3–Cu2–N4	100.3 (1)
N1–Cu1–N2	96.7 (1)	O3–Cu2–O6	93.5 (1)
O1–Cu1–O5	89.5 (1)	O4–Cu2–O6	101.4 (1)
O2–Cu1–O5	103.2 (1)	N3–Cu2–O6	87.9 (1)
N1–Cu1–O5	87.6 (2)	N4–Cu2–O6	91.3 (1)
N2–Cu1–O5	98.4 (1)	Cu2–O3–C9	110.4 (2)
Cu1–O1–C1	109.1 (2)	Cu2–N3–C10	109.5 (2)
Cu1–N1–C2	108.8 (3)	Cu2–O4–C13	110.0 (2)
Cu1–O2–C5	112.4 (3)	Cu2–N4–C14	108.6 (3)
Cu1–N2–C6	110.3 (2)	Cu2–O6–S	128.0 (2)
O3–Cu2–N3	83.9 (1)		

cation vary in the range 1.944 (2)–2.013 (4) Å, the apical Cu1–O5 distance being 2.271 (4) Å. In the anion the basal bond lengths vary in the range 1.925 (3)–2.017 (4) Å, while the apical Cu2–O6 distance is 2.366 (3) Å. None of the coordinated atoms around Cu1 are more than 0.030 (3) Å from their least-squares plane, O1O2N1N2, nor are those around Cu2 more than 0.043 (3) Å from their least-squares plane, O3O4N3N4. The displacement of the Cu1 atom from its basal plane toward the apical O5 atom is 0.159 (2) Å, and that of the Cu2 atom from its basal plane toward the apical O6 atom is 0.116 (2) Å. The basal planes of the two square pyramids are twisted with respect to each other, forming a dihedral angle of 26.7 (1)°. Figure 2, which represents the packing of the molecules in the structure, clearly displays the twist of the planes. The coordination angles around the copper atoms have typical values for a slightly tetrahedrally distorted square-pyramidal geometry. The values, along with the bond lengths and angles for the compound, are given in Table IV.

For the cis arrangement that occurs in the present compound we have previously used the notation cis(b) to indicate that one of the amino alcohol ligands around a metal atom exists in neutral

Table V. Hydrogen-Bond Distances (Å) and Angles (deg) for [{Cu(C₄H₁₀NO)(C₄H₁₁NO)(H₂O)}{Cu(C₄H₁₀NO)(C₄H₁₁NO)-(SO₄)}]·CH₃OH (**1**)ᵃ

A–H⋯B	A–H	H⋯B	A⋯B	A–H⋯B
O2–H11⋯O4	1.19 (6)	1.23 (6)	2.417 (4)	174 (6)
O3–H22⋯O1	1.07 (8)	1.61 (8)	2.475 (4)	133 (7)
N4–H42⋯O9	1.02 (5)	2.10 (5)	3.073 (7)	159 (3)
N4–H41⋯O10	0.73 (5)	2.31 (5)	3.030 (6)	167 (5)
N1–H10⋯O7ⁱ	0.89 (5)	2.01 (5)	2.906 (5)	179 (5)
N2–H20⋯O9ⁱ	0.85 (6)	2.24 (6)	3.085 (7)	169 (4)
N2–H21⋯O7ʲ	0.73 (5)	2.30 (4)	2.982 (5)	156 (5)
N3–H32⋯O8ᵏ	0.83 (4)	2.11 (4)	2.944 (5)	173 (4)
O10–H45⋯O8ᵏ	0.75 (7)	1.87 (7)	2.594 (8)	162 (8)
O5–H44⋯O1ʲ	0.98 (6)	1.81 (6)	2.789 (5)	174 (4)
O5–H43⋯O6ʲ	0.77 (4)	1.97 (4)	2.705 (4)	162 (5)

ᵃThe symmetry codes are as follows: (i) $x, y - 1, z$; (j) $-x, -y, 1 - z$; (k) $-x, 1 - y, -z$.
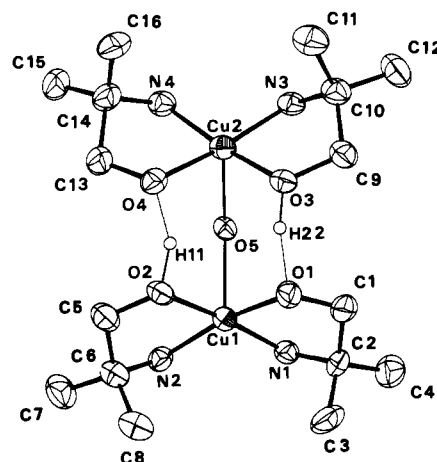

Figure 3. View of the complex cation [Cu₂(C₄H₁₀NO)₂(C₄H₁₁NO)₂-(H₂O)]²⁺ of compound **2**.

form and the other in deprotonated form.[15] We also noted that the cis(b) configuration will probably lead to the formation of polynuclear complexes with hydrogen-bond bridges. This is made possible by the mere simultaneous existence of both the neutral and deprotonated forms of the ligand in the bis chelate parts, [Cu(C₄H₁₀NO)(C₄H₁₁NO)]⁺, of the molecule and by the edge-to-edge orientation of the oxygen sides of these building blocks. The oxygen–oxygen distances of 2.475 (4) Å for O1⋯O3 and of 2.417 (4) Å for O2⋯O4 in the hydrogen bonds by which the cation and the anion are associated into a binuclear unit are much shorter than normal hydrogen-bonding oxygen–oxygen distances. The Cu1⋯Cu2 distance in the binuclear molecule is 4.979 (1) Å.

In the packing of molecules each of them forms hydrogen bonds with four neighboring molecules, a scheme that produces for the compound a two-dimensional packing pattern parallel to the (100) plane, as shown in Figure 2. All the hydrogen-bonding parameters for the compound are given in Table V. Inspection of the table indicates that the solvate methanol molecule, besides being bound to its own complex molecule by a hydrogen bond with a N⋯O distance of normal length, forms a fairly strong hydrogen bond to the sulfate oxygen atom O8 of a neighboring molecule. The coordinated water molecule takes part in two fairly strong hydrogen bonds, too, through its hydrogen atoms.

[Cu₂(C₄H₁₀NO)₂(C₄H₁₁NO)₂(H₂O)](ClC₇H₄O₂)₂·2C₃H₇OH (2). The molecular structure consists of a binuclear complex cation, two *o*-chlorobenzoate anions, and two solvate 2-propanol molecules. The complex cation, which is shown in Figure 3, is made up of two mutually very similar bis chelate fragments, [Cu-(C₄H₁₀NO)(C₄H₁₁NO)]⁺, and a bridging water ligand. The structural similarity of the bis chelate parts is a consequence of the 2 pseudosymmetry that the binuclear cation has with the

(15) Muhonen, H.; Hatfield, W. E. *Acta Chem. Scand., Ser. A* **1986**, *A40*, 41.
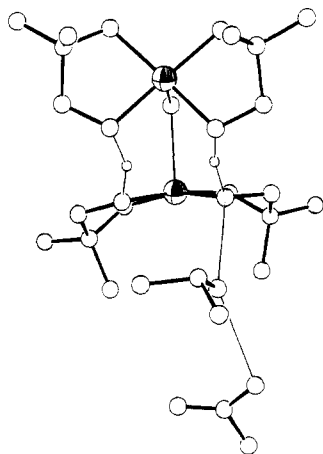
Figure 4. View of the bending with respect to one another of the coordination planes in the cation of compound **2**. Linking of solvate molecules to each other and to the cation is also shown.

Table VI. Selected Bond Lengths (Å) and Angles (deg) for $[Cu_2(C_4H_{10}NO)_2(C_4H_{11}NO)_2(H_2O)](ClC_7H_4O_2)_2 \cdot 2C_3H_7OH$ (**2**)^a

Cu1–O1	1.956 (7)	C10–N3	1.487 (13)
Cu1–O2	1.967 (6)	C10–C11	1.514 (14)
Cu1–O5	2.358 (4)	C10–C12	1.524 (17)
Cu1–N1	2.000 (7)	C13–O4	1.424 (11)
Cu1–N2	2.007 (9)	C13–C14	1.531 (11)
Cu2–O3	1.987 (5)	C14–N4	1.499 (13)
Cu2–O4	1.956 (6)	C14–C15	1.512 (4)
Cu2–O5	2.339 (6)	C14–C16	1.514 (16)
Cu2–N3	1.973 (8)	C17–O6	1.248 (10)
Cu2–N4	1.999 (6)	C17–O7	1.248 (12)
C1–O1	1.406 (12)	C17–C18	1.513 (13)
C1–C2	1.525 (15)	C19–C11	1.746 (10)
C2–N1	1.491 (12)	C24–O8	1.247 (14)
C2–C3	1.507 (12)	C24–O9	1.234 (10)
C2–C4	1.530 (16)	C24–C25	1.526 (15)
C5–O2	1.409 (14)	C26–Cl21	1.645 (19)
C5–C6	1.513 (14)	C31–O10	1.33 (3)
C6–N2	1.481 (12)	C31–C32	1.36 (3)
C6–C7	1.529 (18)	C31–C33	1.26 (4)
C6–C8	1.506 (10)	C34–O11	1.41 (2)
C9–O3	1.436 (13)	C34–C35	1.43 (2)
C9–C10	1.528 (11)	C34–C36	1.52 (3)
O1–Cu1–N1	85.5 (3)	O4–Cu2–N4	84.4 (3)
O2–Cu1–N2	83.1 (3)	O3–Cu2–N4	167.7 (3)
O1–Cu1–N2	164.4 (2)	O4–Cu2–N3	167.1 (3)
O2–Cu1–N1	172.1 (3)	O3–Cu2–O4	91.9 (2)
O1–Cu1–O2	92.1 (3)	N3–Cu2–N4	98.2 (3)
N1–Cu1–N2	97.2 (3)	O3–Cu2–O5	94.3 (2)
O1–Cu1–O5	90.9 (2)	O4–Cu2–O5	90.9 (2)
O2–Cu1–O5	90.4 (2)	N3–Cu2–O5	101.2 (2)
N1–Cu1–O5	97.2 (2)	N4–Cu2–O5	97.5 (2)
N2–Cu1–O5	103.9 (2)	Cu2–O3–C9	112.8 (3)
Cu1–O1–C1	110.4 (5)	Cu2–N3–C10	108.4 (5)
Cu1–N1–C2	106.7 (5)	Cu2–O4–C13	111.2 (4)
Cu1–O2–C5	112.1 (5)	Cu2–N4–C14	108.2 (4)
Cu1–N2–C6	106.9 (6)	Cu1–O5–Cu2	112.0 (2)
O3–Cu2–N3	82.8 (2)		

^{a} The C–C bonds for the C atoms C18, C19, C20, C21, C22, and C23 of the ordered benzene ring and for the C atoms C25, C26, C27, C28, C29, and C30 of the disordered benzene ring vary in the range 1.353 (18)–1.409 (17) and 1.25 (5)–1.43 (3), respectively.

twofold axis lying in the Cu1O5Cu2 plane bisecting the Cu1–O5–Cu2 angle. The symmetry of the cation is also not far from the higher *mm2* point symmetry. The coordination geometry at each copper atom is square pyramidal. Nitrogen and oxygen atoms of one MepH–Mep ligand pair define the basal plane for one copper atom, and those of the other pair do the same for the other copper atom. As in compound **1**, the chelate ligands adopt the cis(b) configuration around the metal atoms, which makes it possible for the two fragments to associate into a binuclear unit by cooperative hydrogen bonding. The oxygen–oxygen distances in the hydrogen-bond bridges, 2.494 (8) Å for O1···O3 and 2.446 (7) Å for O2···O4, are only 0.019 and 0.029 Å longer than the corresponding distances in **1**. Different from the case in compound **1**, the two square pyramids now share the oxygen atom of the water ligand at the axial positions. As far as we are aware, there is no other example of a binuclear metal cluster containing both cooperative hydrogen bonds and a single oxygen atom linking metal atoms.

Because of the 2 pseudosymmetry the basal coordination distances in the two square pyramids are very similar, varying between 1.956 (7) and 2.007 (9) Å. The apical bonds, which form the single-atom bridge between the metal atoms, have values of 2.358 (4) Å for Cu1–O5 and 2.339 (6) Å for Cu2–O5 and are equal within 3σ. The Cu1–O5–Cu2 bridge angle is 112.0 (2)°. Individual coordination bond length and angle values for the compound are listed in Table VI. The deviations of the basal atoms around Cu1 from their least-squares plane, O1O2N1N2, are less than 0.065 (7) Å, and those around Cu2 from their least-squares plane, O3O4N3N4, are less than 0.001 (7) Å. The displacements of the Cu1 and Cu2 atoms from their coordination planes toward the O5 atom are 0.198 (3) and 0.210 (3) Å, respectively. In contrast to the case for compound **1**, the coordination planes are bent rather than twisted with respect to each other, making a dihedral angle of 80.1 (2)° (Figure 4). Owing to the large bend angle the Cu1···Cu2 distance (3.893 (2) Å) is shortened by 1.1 Å from the value it has in **1**.

One of the *o*-chlorobenzoate anions exhibits disorder: the substituted phenyl ring has two orientations, which are approximately 180° apart with respect to rotation around the line that passes through the phenyl ring carbon atom (C25) to which the carboxylate group in the ring is attached and through the carbon atom (C28) opposite to it. The sites of the ring carbon atoms of the two sets overlap with one another and could not be distinguished, but the two sites of the chlorine substituent were successfully located. The disorder also manifests itself as high thermal motion of the ring carbon atoms C27, C28, C29, and C30 and as distorted bond length and angle values for the parameters associated with these atoms. Through the disorder, the less populated set of atomic positions acquires with the atomic positions of the ordered anion an arrangement that has approximately 2 symmetry, which is the pseudosymmetry possessed by the cation,

with the twofold axis lying in the Cu1O5Cu2 plane bisecting the Cu1–O5–Cu2 angle. Of the two positions for the chlorine substituent, it is Cl22, which has the minor population, that is generated from the twofold rotational symmetry. The distance of Cl22 from the nearest ring carbon atom, C30, of the resolved set is 1.20 (2) Å.

An impression of the accuracy of the twofold rotational symmetry when applied to the *o*-chlorobenzoate anion is provided by the mean displacement of the atoms from their symmetrically equivalent positions. This quantity has the value 0.61 (13) Å.

There are two 2-propanol molecules per structural formula unit, and these are joined together by a hydrogen bond, with one of the 2-propanol molecules linking them further to the O1 atom of the cation (Figure 4). The lack of another similar 2-propanol moiety in the molecular structure is the evident reason for the low structural symmetry. Inspection of the hydrogen-bonding parameters for the compound in Table VII shows that the bridging water molecule forms, through its hydrogen atoms, fairly strong hydrogen bonds to each of the anions, thereby linking them to the cation. Furthermore, the table shows that there are hydrogen-bonding connections from the nitrogen atoms to the carboxylate oxygen atoms O6 and O9 of adjacent molecules. These connections lead to the packing of molecules into infinite chains in the *b* direction, as depicted in the stereoview of Figure 5 for one of the chains.[12]
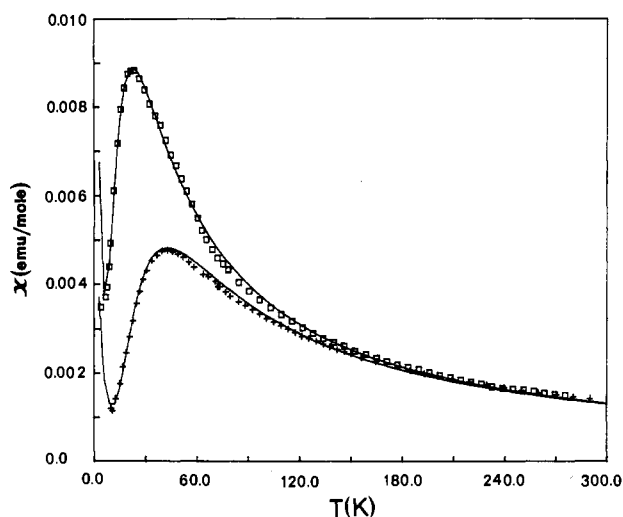
Magnetic Properties

Magnetic Data. Figure 6 displays χ_M^{cor} as a function of temperature for both of the compounds. The maxima in the χ_M^{cor} vs. *T* plots are indicative of antiferromagnetic intradimeric in-

Table VII. Hydrogen-Bond Distances (Å) and Angles (deg) for
$[Cu_2(C_4H_{10}NO)_2(C_4H_{11}NO)_2(H_2O)](ClC_7H_4O_2)_2 \cdot 2C_3H_7OH$ (2)^a

A–H···B	A–H	H···B	A···B	A–H···B
O2–H11···O4	1.11	1.41	2.446 (7)	152
O3–H22···O1	1.00	1.54	2.494 (8)	158
O10–H53···O11	1.02	1.78	2.766 (9)	161
O11–H61···O1	1.01	2.20	2.795 (8)	116
O5–H43···O8	1.10	1.54	2.639 (8)	177
O5–H44···O7	0.92	1.87	2.636 (9)	139
N1–H9···O7	0.99	2.13	3.047 (8)	153
N2–H20···O9	1.00	2.02	3.019 (7)	177
N3–H32···O6	0.99	1.97	2.959 (9)	177
N4–H42···O8	1.00	2.19	3.082 (11)	148
N1–H10···O9^i	1.00	2.08	3.048 (11)	162
N2–H21···O9^i	1.01	2.08	3.042 (9)	158
N3–H31···O6^j	1.02	1.96	2.953 (7)	164
N4–H41···O6^j	1.00	2.17	3.106 (10)	155

^{a} The symmetry codes are as follows: (i) x, $y + 1$, z; (j) x, $y - 1$, z.

Figure 7. Combinations of magnetic orbitals with hydrogen atom orbitals to give antibonding molecular orbitals. Note that the contributing p orbitals of nitrogen atoms, which point out away from the bridge, are not shown in the drawing.

Figure 6. Temperature dependences of the magnetic susceptibilities for **1** (+) and **2** (□). The solid curves represent theoretical values.
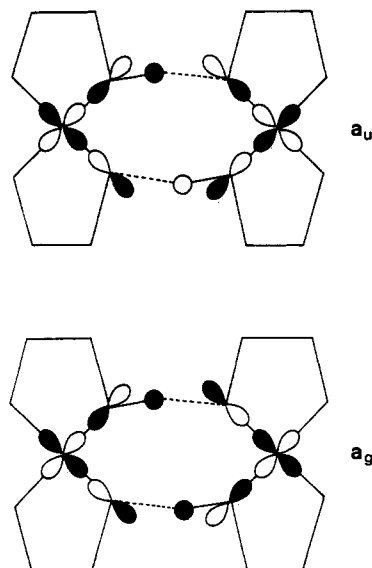
teractions. The rise in χ_M^{cor} as T decreases at low temperature is due to small amounts of paramagnetic impurities. The position of the susceptibility maximum for compound **2** is about 20 K lower than that for compound **1**, which suggests weaker antiferromagnetic interaction for **2**. At high temperatures, above 200 K, the susceptibility curves merge and the magnetic behaviors of the compounds are similar.

The fitting equation for the magnetic susceptibility data for the compounds was the well-known dimer equation

$$\chi_M^{cor} = \frac{Ng^2\beta^2}{kT}[3 + \exp(-2J/kT)]^{-1}(1 - \rho) + \rho\frac{Ng^2\beta^2S(S + 1)}{3kT}$$

where the susceptibility is expressed per copper atom. Here ρ is the mole fraction of the noncoupled paramagnetic impurity and the other symbols have their usual meaning. The calculated magnetic susceptibilities were fitted to the experimental data with the Simplex routine, where the criterion of best fit was the minimum value of the function $F = \sum[(\chi_i^{obsd} - \chi_i^{calcd})^2/(\chi_i^{obsd})^2]$. For **1** the best minimum was reached with values for the variables of $g = 2.070$, $2J = -49$ cm^{-1}, and $\rho = 1.38\%$ with R, defined as the square root of F, equaling 0.023. For **2** the best minimum yielded $g = 2.024$, $2J = -27$ cm^{-1}, $\rho = 2.63\%$, and $R = 0.038$.

Exchange Interactions. The calculated $2J$ values show that the interaction between the metal atoms in **1** is moderately strong antiferromagnetic with $2J = -49$ cm^{-1}, whereas the interaction in **2** is less by about half, with the energy gap between low-lying spin-singlet and spin-triplet states being now $2J = -27$ cm^{-1}. The relative magnitudes of the exchange coupling constants can be understood in terms of the structural details of the molecules and

the magnetic orbitals involved in the exchange processes. Kahn[16] has reported in several contexts that the energy gap between spin-singlet and spin-triplet states in antiferromagnetic binuclear metal complexes that contain extended bridges is essentially governed by the square of the overlap integral between the magnetic orbitals. A qualitative picture of the overlap between metal atoms and of the effect of structural details on it may be obtained by inspecting the orbitals that contribute to the overlap density in the bridges.

As was discussed in Description of the Structures, both copper atoms of each compound have typical square-pyramidal coordination geometries, with the metal atoms being displaced only slightly from their basal planes. Furthermore, the oxygen–oxygen sides of the basal planes in the binuclear molecules are joined by hydrogen bonds, forming two O–H···O bridges between the metal atoms. In a square-pyramidal copper(II) environment the magnetic orbital centered on the Cu(II) ion is constructed from the $d_{x^2-y^2}$ metallic orbital and the orbitals of the four basal atoms toward which the metal orbital is delocalized. The contribution to the metal-based magnetic orbitals from the basal N and O atomic orbitals comes largely from their p orbitals, as these orbitals are relatively close in energy to the metallic $d_{x^2-y^2}$ orbitals. Combinations of the magnetic orbitals can interact with symmetrically similar combinations of s orbitals of the bridging hydrogen atoms to form σ^* molecular orbitals, as illustrated in Figure 7. The two orbitals shown differ in energy: the a_g orbital contains some degree of bonding character and is therefore the lower orbital. In a typical square-pyramidal coordination environment delocalization of the unpaired electron toward the apical direction is slight, so that the admixture of the d_{z^2} orbital in the singly occupied magnetic orbital is slight too. In compound **2** the two square pyramids share an oxygen atom at their apexes, and the oxygen forms a single-atom bridge between metal atoms. Because the bridging oxygen atom occupies exclusively the apical sites, its ability to propagate antiferromagnetic interaction is negligible. Ferromagnetic contribution through the oxygen bridge is vanishing for the same reason, i.e. because of the small spin density at the oxygen atom. Furthermore, the rather acute Cu1–O5–Cu2 bridge angle of 112.0 (2)° does not favor any appreciable ferromagnetic contribution. Thus, it is clear that in both compounds hydro-

(16) (a) Kahn, O. *Inorg. Chim. Acta* **1982**, *62*, 3. (b) Kahn, O. *Magneto-Structural Correlations in Exchange Coupled Systems*; Willet, R. D., Gatteschi, D., Kahn, O., Eds.; D. Reidel: Dordrecht, The Netherlands, 1984. (c) Julve, M.; Verdaguer, M.; Gleizes, A.; Philoche-Levisalles, M.; Kahn, O. *Inorg. Chem.* **1984**, *23*, 3808.

gen-bond bridges form the superexchange pathways, a conclusion that is supported by the experimentally observed lower numerical J value for compound **2**. The difference in the magnitudes of the J values in **1** and **2** can be understood by looking at the structural parameters that affect the overlap density in the hydrogen-bond bridges. This is discussed in the following.

Inspection of Figure 7 displays several structural parameters that in addition to the coordination geometry can control the distribution and magnitude of the overlap density in hydrogen-bond bridges. These include the oxygen–oxygen distance in the bridge, the copper–copper distance, the dihedral angle between the coordination planes and its existence as a twist or bend angle, in the case of parallel coordination planes their separation from each other, and the location of the bridging hydrogen atom. With such a large number of structural parameters, and these are probably interrelated as well, magneto–structural correlations are clearly going to be difficult to unravel. As for the dependence of the J value on the location of the bridging hydrogen atom, one can anticipate only rough estimates because of the low accuracy with which X-ray methods can provide hydrogen atom positions. Some studies have been directed at finding a relationship between the location of the hydrogen atom and its effect on the exchange interaction.[17] But all the studies have concerned cases where the hydrogen atom is itself nonbridging and is only bound to a bridging atom like oxygen in a hydroxo bridge. Even though the location of a hydrogen atom in a bridge is certainly one factor influencing the magnitude of the exchange interaction, presumably it is seldom the most important one, owing to the spherically symmetric s orbital the hydrogen atom has exclusively. Overlap of this kind of orbital with magnetic orbitals should depend less on location or orientation of the bridging atom than does the overlap of a nonspherical p orbital used by ordinary bridging atoms to form antibonding orbital pathways in extended bridges.

The reason for the different $2J$ values in **1** and **2** is the dihedral angles made by the basal coordination planes in the binuclear molecules. In **1** the planes are twisted with respect to each other, with a dihedral angle of 26.7 (1)°, whereas in **2** they are bent, with an angle of 80.1 (2)°. The large bend angle is a consequence of the presence of the bridging oxygen atom at the apexes of the square pyramids. Deviation of coordination planes from coplanarity leads to an unfavorable orientation of magnetic orbitals with regard to interaction, reducing the value of the overlap integral and thereby the numerical value of J. Twist and bend angles affect the overlap density in a different way, as is explained in the following. Bending of the coplanar coordination planes decreases the overlap density at both bridges, and this especially occurs strongly for the component of overlap in the copper–copper direction, i.e. in the direction perpendicular to the bending axis. But twisting of one of the coordination planes around one of the hydrogen-bond bridges while the other plane remains immobile

results in the twist angle taking up all values from 0 to 90° and significantly changes the overlap density only at one of the bridges, namely at that not functioning as the rotation axis. A propeller-shaped twist would, of course, change the overlap density at both bridges, as occurs in compound **1**. The bend angle in compound **2** is close to the right angle, so that the magnetic orbitals approach orthogonality. This situation leads to a dramatic drop in the numerical value of J relative to that in **1**. It is noteworthy that the copper–copper distance, which is much shorter in **2** than in **1** owing to the large bend angle in **2**, is in related compounds only of secondary importance as a parameter that can control the magnitude of the coupling.

All of the hydrogen-bridged copper–copper dimers described by Bertrand and co-workers[3,6] possess an intradimeric center of symmetry, and as a result, the two coordinatio planes of the dimers are parallel. The separation of the planes in the dimers varies from 0.22 to 1.65 Å.

Concluding Remarks

The present study has provided examples of hydrogen-bridged dimers of copper(II) where the coordination planes are not parallel. This is in contrast to all previously reported complexes, which are of structurally parallel planar type. Even though the occurrence of the single oxygen atom bridge along with hydrogen-bond bridges in **2** provides an interesting new structural detail, the significance of this bridge as a magnetic pathway is negligible owing to the apical connection it forms between the square pyramids. The task of the bridge is to function as a driving force for the large bend angle with the consequence that the antiferromagnetic exchange coupling propagated by the hydrogen-bond bridges is weakened. Other structural parameters besides interplanar angles have been surveyed for their potential to control the exchange coupling through hydrogen-bond bridges. In order to determine the ability of each of them to contribute to the coupling, more examples of hydrogen-bridged complexes are needed, preferably closely related ones displaying variation over only one or two parameters. Such a series of compounds might lead to the discovery of magneto–structural correlations. Even though such relations do not directly reflect the theoretical aspects of a problem, they can work as a probe, immediately either confirming predictions, or, in the case of unusual experimental observations, stimulating new theoretical expositions.

Supplementary Material Available: Anisotropic temperature factor coefficients of non-hydrogen atoms (Tables SI and SIII), fractional coordinates and isotropic thermal parameters for hydrogen atoms (Tables SII and SIV), and a packing diagram for compound **2** (Figure 5) (11 pages); listings of observed and calculated structure factors for **1** and **2** (54 pages). Ordering information is given on any current masthead page.

(17) (a) Glerup, J.; Hodgson, D. J.; Pedersen, E. *Acta Chem. Scand., Ser. A* **1983**, *A37*, 161. (b) Hodgson, D. J. *Magneto-Structural Correlations in Exchange Coupled Systems*; Willet, R. D., Gatteschi, D., Kahn, O., Eds.; D. Reidel: Dordrecht, The Netherlands, 1984.