Structural and Magnetic Studies of Dimeric Copper(II) 2,2-Diphenylpropanoato and Triphenylacetato Complexes with Oxygen-Donor Ligands. The Cage Geometry of Dimeric α-Phenyl Substituted Copper(II) Carboxylates[1)]

Omar W. Steward,* Brian S. Johnston, Shih-Chi Chang,† Akihiko Harada,†† Shigeru Ohba,*,†† Tadashi Tokii,††† and Michinobu Kato,††††

Department of Chemistry and Biochemistry, Duquesne University, Pittsburgh, Pennsylvania, 15282, U.S.A.

†Department of Physics, Duquesne University, Pittsburgh, Pennsylvania, 15282, U.S.A.

††Department of Chemistry, Faculty of Science and Technology, Keio University, Hiyoshi 3-14-1, Kohoku-ku, Yokohama 223

†††Department of Chemistry, Faculty of Science and Engineering, Saga University, Saga 840

††††5-603, 4-Chome 6, Kamezaki, Asakita-ku, Hiroshima 739-17

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The syntheses, structures, and magnetic properties of copper(II) carboxylates with bridging α-phenyl substituted carboxylato ligands and unidentate oxygen-donor ligands are reported: $Cu_2(O_2CCPh_2Me)_4(acetone)_2$ (**1**), triclinic $P\bar{1}$, $a = 15.441(4)$, $b = 15.602(4)$, $c = 12.790(2)$ Å, $\alpha = 106.52(2)$, $\beta = 92.11(2)$, $\gamma = 96.38(2)°$, $V = 2928(1)$ Å^3, $Z = 2$, $-2J = 352$ cm^{-1}; $[Cu_2(O_2CCPh_2Me)_4(H_2O)_2]\cdot H_2O$ (**2**), triclinic $P\bar{1}$, $a = 13.895(2)$, $b = 14.717(2)$, $c = 7.318(1)$ Å, $\alpha = 95.67(1)$, $\beta = 101.71(1)$, $\gamma = 68.12(1)°$, $V = 1359.3(4)$ Å^3, $Z = 1$, $-2J = 344$ cm^{-1}; $[Cu_2(O_2CCPh_2Me)_4(EtOH)_2]\cdot EtOH$ (**3**), monoclinic $P2_1/c$, $a = 26.927(5)$, $b = 9.152(3)$, $c = 26.881(5)$ Å, $\beta = 115.02(1)°$, $V = 6003(2)$ Å^3, $Z = 4$, $-2J = 347$ cm^{-1}; $[Cu_2(O_2CCPh_3)_4(Ph_3CCO_2H)_2]\cdot CH_2Cl_2$ (**4**), monoclinic $P2_1/c$, $a = 18.133(8)$, $b = 23.046(7)$, $c = 25.013(7)$ Å, $\beta = 101.01(3)°$, $V = 10268(5)$ Å^3, $Z = 4$; $[Cu_2(O_2CCPh_3)_4(H_2O)_2]\cdot 4H_2O$ (**5a**), tetragonal $I\bar{4}$, $a = 18.451(6)$, $c = 10.703(7)$ Å, $V = 3643(3)$ Å^3, $Z = 2$; $[Cu_2(O_2CCPh_3)_4(H_2O)_2]\cdot 2H_2O$ (**5b**), tetragonal $I\bar{4}$, $a = 18.224(2)$, $c = 10.776(5)$ Å, $V = 3578(1)$ Å^3, $Z = 2$, $-2J = 292$ cm^{-1}; and $Cu_2(O_2CSiPh_3)_4(EtOH)_2$ (**6**), monoclinic $C2/c$, $a = 21.811(3)$, $b = 17.366(3)$, $c = 21.221(4)$ Å, $\beta = 91.19(1)°$, $V = 8036(2)$ Å^3, $Z = 4$, $-2J = 1193$ cm^{-1}. The factors which influence the cage and coordination sphere geometry in dimeric α-phenyl substituted copper(II) carboxylates are discussed based on the above structures and the reported structures with unidentate nitrogen- and oxygen-donor ligands. In **4** and **5**, intramolecular steric effects between the bulky triphenylacetato ligands result in a considerable distortion of the cage geometry. The distortion of the coordination sphere geometry around copper(II) in the complexes from square pyramidal toward trigonal bipyramidal reduces the spin-exchange interaction.

A number of dimeric copper(II) carboxylates have been observed to have a variation of the classical copper(II) acetate monohydrate-type structure in which the arrangement of the atoms in the coordination sphere about each copper(II) in the dimer can best be described as distorted trigonal bipyramidal (DTB).[2—11)] To date, those dimeric complexes found to have a DTB ligand arrangement about copper(II) can be divided into two groups: complexes with bridging α-phenyl substituted carboxylato ligands[2—4,9,11)] and complexes with bridging trichloroacetato ligands.[5—11)] The cause(s) of the change in geometry about copper(II), from square pyramidal (SP) toward trigonal bipyramidal (TB), has been discussed briefly.

The present paper reports on an investigation of the factors which influence the coordination geometry about copper(II) in α-phenyl substituted carboxylato complexes ($[Cu_2(O_2CMR_3)_4(L)_2]\cdot n$S (where M = C or Si, R = Me and Ph, L = a unidentate ligand, and nS = the number and type of solvent molecule(s) of crystallization)). During this study, the structures of the following seven complexes with oxygen-donor unidentate ligands were determined: $Cu_2(O_2CCPh_2Me)_4(acetone)_2$ (**1**), $[Cu_2(O_2CCPh_2Me)_4(H_2O)_2]\cdot H_2O$ (**2**), $[Cu_2(O_2CCPh_2Me)_4(EtOH)_2]\cdot EtOH$ (**3**), $[Cu_2(O_2CCPh_3)_4(Ph_3CCO_2H)_2]\cdot CH_2Cl_2$ (**4**), $[Cu_2(O_2CCPh_3)_4(H_2O)_2]\cdot 4H_2O$ (**5a**), $[Cu_2(O_2CCPh_3)_4(H_2O)_2]\cdot 2H_2O$ (**5b**), and $Cu_2(O_2CSiPh_3)_4(EtOH)_2$ (**6**). The structures of the above complexes along with the previously reported structures of seven complexes with oxygen- and nitrogen-donor unidentate ligands ($Cu_2(O_2CCPhMe_2)_4(H_2O)_2$ (**7**),[4)] $Cu_2(O_2CCPhMe_2)_4$(quin-

oline)$_2$ (**8**),[12] $[Cu_2(O_2CCPhMe_2)_4(2,6\text{-lutidine})_2]$·benzene (**9**),[4] $Cu_2(O_2CCPh_2Me)_4(quinoline)_2$ (**10**),[12] $[Cu_2(O_2CCPh_3)_4(4\text{-picoline})_2]$·2toluene (**11**),[3] $[Cu_2(O_2CCPh_3)_4(4\text{-picoline})_2]$·2benzene (**12**),[3] and $[Cu_2(O_2CCPh_3)_4(pyridine)_2]$·benzene (**13**),[2]) are used to elucidate the factors which produce the change in geometry about copper(II) from SP toward TB.

Experimental

Starting Materials. Triphenylacetic acid, 99%, (Aldrich), 2,2-diphenylpropionic acid, 95%, (Aldrich), copper(II) acetate 1-hydrate (Fisher) and copper(II) nitrate 2.5-hydrate (Fisher) were used without further purification. Pentaphenyldisilanecarboxylic acid was synthesized as previously reported.[13] Unless indicated below, all copper(II) carboxylato complexes were synthesized as described previously.[14] All of the products were characterized by infrared (see Table 1).

Crystal Preparations. (a) $Cu_2(O_2CCPh_2Me)_4(acetone)_2$ (1). $Cu_2(O_2CCPh_2Me)_4(H_2O)_2$ (0.20 g) was dissolved in 25 mL of water/acetone (25 v/v%), yielding a blue solution. After filtering, the solution was placed in a vial, which was covered with Parafilm in which small holes were punched, and placed in a hood. After 10 days, blue prismatic crystals of **1** had formed.

Anal. Calcd for $C_{66}H_{64}Cu_2O_{10}$: C, 69.27; H, 5.67%. Found: C, 69.09; H, 5.67%.

(b) $[Cu_2(O_2CCPh_2Me)_4(H_2O)_2]$·$H_2O$ (2). $Cu_2(O_2CCPh_2Me)_4(H_2O)_2$ (0.16 g) was dissolved in 25 mL of methylene chloride, yielding a blue-green solution. After adding 10 mL of heptane, the solution was filtered, placed in a flask, and stored in a hood. After 4 d, blue-green crystals of **2** had formed.

Anal. Calcd for $C_{60}H_{58}Cu_2O_{11}$: C, 66.59; H, 5.40%. Found: C, 66.83; H, 5.28%.

(c) $[Cu_2(O_2CCPh_2Me)_4(EtOH)_2]$·EtOH (3). 2,2-Diphenylpropionic acid (0.24 g, 1.06 mmol) was dissolved in absolute alcohol (25 mL). Copper(II) nitrate 2.5-hydrate (0.12 g, 0.52 mmol) was dissolved in absolute alcohol (20 mL) yielding a blue solution. Upon mixing, a small change in the color occurred. Alcoholic potassium hydroxide (0.49 mmol mL^{-1}, 2.5 mL) was added dropwise, and the cloudy solution was filtered. The solution was placed in a flask and stored in a hood. After 44 d, bluish-green needles had formed. The crystals were separated by filtration, washed with 50% ethanol/water, and allowed to air dry, yielding 0.04 g of **3**.

Anal. Calcd for $C_{66}H_{70}Cu_2O_{11}$: C, 67.96; H, 6.05%. Found: C, 67.96; H, 5.83%.

A similar reaction carried out in 70 v/v% alcohol/water yielded crystals of **3**. A crystal formed by this method had the same unit cell dimensions within the experimental error.

(d) $[Cu_2(O_2CCPh_3)_4(Ph_3CCO_2H)_2]$·$CH_2Cl_2$ (4) and $[Cu_2(O_2CCPh_3)_4(H_2O)_2]$·$4H_2O$ (5a). The complex $[Cu_2(O_2CCPh_3)_3(O_2CSiPh_2SiPh_3)]$·$4H_2O$ was prepared by the procedure reported by C. E. Taylor.[15] Pentaphenyldisilanecarboxylic acid (1.00 g, 2.05 mmol) was dissolved in 95% ethanol, and $[Cu_2(O_2CCPh_3)_4(H_2O)_2]$·$2H_2O$ (**5b**) (0.67 g, 0.50 mmol (powder)) was dissolved with stirring and heating, yielding a blue suspension. The acid solution was filtered and added to the above mixture, yielding a green suspension. After stirring for 9 d, a green solid had formed, which was separated by filtration, washed with 95% ethanol, and allowed to air dry. The green complex, $[Cu_2(O_2CCPh_3)_3(O_2CSiPh_2SiPh_3)]$·$4H_2O$ (in 76% yield) was characterized by IR: (KBr), 1586 (ν_{asym} CCO_2^-), 1546 (ν_{asym} $SiCO_2^-$), 1376 cm^{-1} (ν_{sym} CO_2^-).

Anal. Calcd for $C_{91}H_{78}Cu_2O_{12}Si_2$: C, 70.65; H, 5.08; Cu, 8.22%. Found: C, 70.65; H, 5.08; Cu, 8.79%.

$[Cu_2(O_2CCPh_3)_3(O_2CSiPh_2SiPh_3)]$·$4H_2O$ (ca.0.2 g) was dissolved in 3 mL of methylene chloride with warming on a steam bath yielding a green solution. After heptane (2 mL) was added, the solution was again heated on the steam bath. After cooling, the solvent was allowed to slowly evaporate. After 4 d, light green needles of **4**, blue-green dichroic tetragonal crystals of **5a**, and colorless crystals of triphenylacetic acid had formed. Immediately after the remaining liquid was decanted, crystals of **4** and **5a** were washed with heptane, coated with epoxy, and mounted.

Crystals of **5a** can also be obtained directly by the crystallization of **5b** (powder) from methylene chloride.

(e) $[Cu_2(O_2CCPh_3)_4(H_2O)_2]$·$2H_2O$ (5b). Crystals of **5b** were obtained by allowing crystals of **5a** to air dry for several days. Elemental analyses indicated that two waters of crystallization were lost upon standing.

Anal. Calcd for $C_{80}H_{68}Cu_2O_{12}$: C, 71.25; H, 5.12%. Found: C, 71.30; H, 5.21%.

(f) $Cu_2(O_2CSiPh_3)_4(EtOH)_2$ (6). Triphenylsilanecarboxylic acid (0.31 g, 1.02 mmol) was dissolved in absolute alcohol (25 mL). Copper(II) nitrate 2.5 hydrate (0.12 g, 0.50 mmol) was dissolved in absolute alcohol (25 mL), yielding a blue solution. After both solutions had been filtered, upon mixing a dark green solution was obtained. This solution was placed in a 125-mL Erlenmeyer flask, which was covered with Parafilm. After a few minutes, dark green crystals started to form. After standing overnight, dark green prismatic crystals of **6**, suitable for structural studies, had formed.

In a subsequent preparation, the crystals were separated by filtration, washed with 40 mL of 75% alcohol/water, and allowed to air dry, yielding 0.11 g (32%) of **6**.

Anal. Calcd for $C_{80}H_{72}Cu_2O_{10}Si_4$: C, 67.06; H, 5.07; Cu, 8.87%. Found: C, 66.41; H, 4.96; Cu, 8.48%.

Triphenylsilanecarboxylic acid, 0.20 g (64%) was recovered from the filtrate.

Physical Measurements. The IR spectra were recorded on a Perkin–Elmer 1430 ratio recording spectrophotometer, polystyrene standard. The magnetic susceptibilities over the temperature range of 80—300 K were determined by one of the authors (T.T.) by the Faraday Method.[2]

X-Ray Crystal Structure Determinations. All of the crystals were mounted on glass fibers and coated with epoxy, except for **6**, which was mounted in a capillary. Crystallographic data, experimental conditions, and refinement information are listed in Table 2.

Table 1. Carbon–Oxygen Stretching Frequencies of the Carboxylato Ligands for the $[Cu_2(O_2CMR_3)_4(L)_2]$·nS Complexes[a]

Complex	$\bar{\nu}_{asym}$/cm^{-1}	$\bar{\nu}_{sym}$/cm^{-1}	$\Delta\bar{\nu}$/cm^{-1}
1[b]	1618	1388	228
2	1594	1387	207
3	1610	1386	224
4[c]	1620	1369	251
5a	1617	1369	248
5b	1626	1373	253
6	1542	1360	182
13[d]	1639	1369	270

a) KBr disk. b) Acetone: (C=O) 1695 cm^{-1} in complex (KBr); (C=O) 1720 cm^{-1} in mineral oil. c) Chloroform: (C–Cl) 731 and (CH_2) 1261 cm^{-1}. Triphenylacetic acid: (C=O) 1695 cm^{-1} in complex; (C=O) 1696 cm^{-1} in acid dimer (KBr). d) Ref. 2.

Table 2. Crystallographic Data, Experimental Conditions, and Refinement Information

	1	2	3	4	5a	5b	6
Formula	$C_{66}H_{64}Cu_2O_{10}$	$C_{60}H_{58}Cu_2O_{11}$	$C_{66}H_{70}Cu_2O_{11}$	$C_{121}H_{94}Cl_2Cu_2O_{12}$	$C_{80}H_{72}Cu_2O_{14}$	$C_{80}H_{68}Cu_2O_{12}$	$C_{80}H_{72}Cu_2O_{10}Si_4$
F. W.	1144.32	1082.20	1166.37	1938.06	1384.53	1348.50	1432.88
Crystal system	Triclinic	Triclinic	Monoclinic	Monoclinic	Tetragonal	Tetragonal	Monoclinic
Space group	$P\bar{1}$(#2)	$P\bar{1}$(#2)	$P2_1/c$(#14)	$P2_1/c$(#14)	$I\bar{4}$(#82)	$I\bar{4}$(#82)	$C2/c$(#15)
a/Å	15.441(4)	13.895(2)	26.927(5)	18.133(8)	18.451(6)	18.224(2)	21.811(3)
b/Å	15.602(4)	14.717(2)	9.152(3)	23.046(7)			17.366(3)
c/Å	12.790(2)	7.318(1)	26.881(5)	25.013(7)	10.703(7)	10.776(5)	21.221(4)
α/°	106.52(2)	95.67(1)					
β/°	92.11(2)	101.71(1)	115.02(1)	101.01(3)			91.19(1)
γ/°	96.38(2)	68.12(1)					
V/Å^3	2928(1)	1359.3(4)	6003(2)	10268(5)	3643(3)	3578(1)	8036(2)
Z	2	1	4	4	2	2	4
D_x/Mg m^{-3}	1.298	1.322	1.290	1.254	1.262	1.251	1.184
μ(Mo $K\alpha$)/cm^{-1}	7.84	8.43	7.67	5.28	6.47	6.55	6.41
Crystal size/mm	0.40 × 0.20 × 0.70	0.50 × 0.40 × 0.20	0.60 × 0.30 × 0.30	0.40 × 0.30 × 0.25	0.80 × 0.70 × 0.70	0.60 × 0.50 × 0.30	0.30 × 0.20 × 0.20
Scan range 2Θ/°	4—60	4—65	4—45	4—45	4—65	4—65	4—50
h	0 to 21	0 to 15	−29 to 29	0 to 24	0 to 24	0 to 24	0 to 23
k	−21 to 21	−16 to 16	0 to 9	0 to 24	0 to 24	0 to 24	0 to 20
l	−17 to 17	−10 to 10	0 to 28	−26 to 26	0 to 14	0 to 14	−25 to 25
No. of measured reflections	17657	8527	8042	14386	3413	3382	5768
No. of observed reflections [$I > 3\sigma(I)$]	9186	5888	5498	6568	1977	1784	1690
Relative transmission factors	0.91—1.00	0.34—1.00	0.99—1.00	0.59—1.00	0.97—1. 00	0.94—1.00	0.90—1.00
R	0.054	0.096	0.073	0.067	0.076	0.066	0.078
R_w	0.055	0.094	0.083	0.092	0.078	0.046	0.071
$(\Delta/\sigma)_{max}$ for non-hydrogen atoms	0.04	0.01	0.38	0.38	0.08	0.06	0.06
$\Delta\rho$/eÅ^{-3}	(−1.08)—(1.26)	(−1.35)—(1.75)	(−0.62)—(0.60)	(−0.59)—(1.11)	(−0.72)—(0.95)	(−0.87)—(0.89)	(−0.38)—(0.66)

Table 3. Positional Parameters and Isotropic Thermal Parameters[a] and Their Standard Deviations for the Complexes $[Cu_2(O_2CMR_3)_4(L)_2]\cdot nS$

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
	$Cu_2(O_2CCPh_2Me)_4(acetone)_2$ (**1**)				C(56)	1.3074(3)	0.6690(3)	0.6205(4)	3.3(1)
Cu(1)	0.48983 (4)	0.06543 (3)	0.08675(4)	2.45(1)	C(57)	1.3367(3)	0.7602(3)	0.6508(5)	4.2(1)
Cu(2)	0.98721(3)	0.47892 (3)	0.39401(4)	2.25(1)	C(58)	1.3569(4)	0.8027(4)	0.5723(6)	5.2(2)
O(1)	0.4097(2)	−0.0321(2)	0.1125(2)	3.54(8)	C(59)	1.3475(4)	0.7532(4)	0.4650(6)	5.7(2)
O(2)	0.4237(2)	−0.1441(2)	−0.0371(2)	3.18(7)	C(60)	1.3183(4)	0.6622(4)	0.4340(4)	4.5(1)
O(3)	0.5868(2)	0.0260(2)	0.1547(2)	3.59(8)	C(61)	1.3095(3)	0.4685(3)	0.5548(3)	2.59(9)
O(4)	0.5998(2)	−0.0907(2)	0.0085(2)	3.33(7)	C(62)	1.2652(3)	0.3968(3)	0.5821(4)	3.6(1)
O(5)	0.4554(2)	0.1548(2)	0.2391(3)	4.16(8)	C(63)	1.3092(4)	0.3495(4)	0.6401(5)	4.6(1)
O(6)	0.9787(2)	0.3526(2)	0.3928(2)	3.15(7)	C(64)	1.3958(4)	0.3730(4)	0.6705(5)	4.8(2)
O(7)	1.0076(2)	0.3899(2)	0.5737(2)	3.22(7)	C(65)	1.4407(3)	0.4443 (4)	0.6444(5)	4.6(1)
O(8)	1.1150(2)	0.4899(2)	0.4067(2)	3.18(7)	C(66)	1.3969(3)	0.4908(3)	0.5854(4)	3.7(1)
O(9)	1.1386(2)	0.5304(2)	0.5888(2)	2.83(7)					
O(10)	0.9853(2)	0.4471(2)	0.2158(3)	4.29(9)		$[Cu_2(O_2CCPh_2Me)_4(H_2O)_2]\cdot H_2O$ (**2**)			
C(1)	0.3922(3)	−0.1121(3)	0.0535(4)	2.76(10)	Cu	0.04708(8)	0.49424(9)	0.1731(2)	2.39(2)
C(2)	0.3242(3)	−0.1734(3)	0.0931(3)	2.76(10)	O(1)	0.1533(4)	0.3746(4)	0.0860(8)	3.4(1)
C(3)	0.6214(3)	−0.0433(3)	0.1048(4)	3.0(1)	O(2)	0.0785(4)	0.3903(5)	−0.2132(9)	4.4(2)
C(4)	0.6993(3)	−0.0645(3)	0.1678(4)	2.9(1)	O(3)	−0.0360(4)	0.4155(5)	0.2058(8)	3.6(2)
C(5)	0.4438(3)	0.2338(3)	0.2701(4)	4.0(1)	O(4)	−0.1156(4)	0.4240(4)	−0.0955(8)	3.2(2)
C(6)	0.4458(5)	0.2905(4)	0.1950(5)	7.8(2)	O(5)	0.1195(4)	0.4831(5)	0.4616(8)	4.1(2)
C(7)	0.4281(4)	0.2757(4)	0.3870(5)	6.1(2)	O(6)	0.4020(4)	−0.0057(4)	0.4624(8)	3.7(2)
C(8)	0.3102(3)	−0.1278(3)	0.2148(4)	3.7(1)	C(1)	0.1487(7)	0.3505(6)	−0.081(1)	2.9(2)
C(9)	0.3545(3)	−0.2666(3)	0.0875(4)	3.1(1)	C(2)	0.2376(6)	0.2551(7)	−0.138(1)	3.4(2)
C(10)	0.4400(3)	−0.2829(3)	0.0752(4)	4.1(1)	C(3)	−0.0969(6)	0.3946(6)	0.067(1)	2.7(2)
C(11)	0.4636(4)	−0.3670(4)	0.0788(5)	5.5(2)	C(4)	−0.1536(6)	0.3283(6)	0.113(1)	2.7(2)
C(12)	0.4025(5)	−0.4310(4)	0.0942(5)	5.7(2)	C(5)	0.2471(8)	0.2672(8)	−0.340(1)	5.7(3)
C(13)	0.3176(5)	−0.4154(4)	0.1072(5)	5.6(2)	C(6)	0.3484(7)	0.2360(7)	−0.011(1)	3.6(2)
C(14)	0.2938(4)	−0.3322(3)	0.1051(4)	4.4(1)	C(7)	0.3753(8)	0.2980(9)	0.123(2)	6.2(3)
C(15)	0.2419(3)	−0.1859(3)	0.0174(3)	2.78(10)	C(8)	0.479(1)	0.278(1)	0.210(2)	7.6(4)
C(16)	0.2354(3)	−0.2448(3)	−0.0883(4)	3.2(1)	C(9)	0.5577(10)	0.195(1)	0.166(2)	7.2(4)
C(17)	0.1632(4)	−0.2550(4)	−0.1587(4)	4.0(1)	C(10)	0.5337(9)	0.1319(10)	0.039(2)	7.1(4)
C(18)	0.0940(3)	−0.2067(4)	−0.1269(4)	4.3(1)	C(11)	0.4298(8)	0.1512(8)	−0.052(2)	6.4(3)
C(19)	0.0990(4)	−0.1481(4)	−0.0242(5)	4.6(1)	C(12)	0.2020(7)	0.1664(7)	−0.109(2)	4.2(3)
C(20)	0.1717(4)	−0.1375(3)	0.0470(4)	3.9(1)	C(13)	0.1701(8)	0.1118(10)	−0.259(2)	6.5(4)
C(21)	0.7707(3)	0.0149(3)	0.1773(5)	4.4(1)	C(14)	0.143(1)	0.0317(10)	−0.214(2)	7.4(4)
C(22)	0.6755(4)	−0.0678(3)	0.2820(4)	3.6(1)	C(15)	0.145(1)	0.013(1)	−0.043(2)	8.2(5)
C(23)	0.5912(4)	−0.0839(4)	0.3074(5)	5.1(2)	C(16)	0.1741(10)	0.0649(10)	0.091(2)	6.7(4)
C(24)	0.5715(5)	−0.0860(5)	0.4128(6)	7.1(2)	C(17)	0.2033(8)	0.1414(8)	0.065(2)	4.8(3)
C(25)	0.6379(7)	−0.0730(5)	0.4908(6)	8.2(3)	C(18)	−0.0727(7)	0.2490(7)	0.246(1)	4.3(3)
C(26)	0.7217(6)	−0.0574(6)	0.4678(6)	8.0(2)	C(19)	−0.1879(7)	O.2741(7)	−0.063(1)	3.2(2)
C(27)	0.7410(4)	−0.0552(4)	0.3636(5)	5.8(2)	C(20)	−0.1150(7)	0.2176(7)	−0.174(1)	3.7(3)
C(28)	0.7271(3)	−0.1561(3)	0.1013(4)	3.3(1)	C(21)	−0.1429(8)	0.1657(8)	−0.319(1)	4.8(3)
C(29)	0.7878(4)	−0.1599(4)	0.0230(5)	5.2(2)	C(22)	−0.2413(10)	0.1630(8)	−0.358(2)	5.6(3)
C(30)	0.8127(5)	−0.2422(5)	−0.0361(5)	6.2(2)	C(23)	−0.3145(8)	0.2148(9)	−0.255(2)	5.4(3)
C(31)	0.7768(5)	−0.3200(4)	−0.0189(6)	6.2(2)	C(24)	−0.2880(7)	0.2694(7)	−0.101(1)	4.5(3)
C(32)	0.7170(4)	−0.3185(4)	0.0578(6)	5.7(2)	C(25)	−0.2451(7)	0.3985(7)	0.200(1)	3.1(2)
C(33)	0.6924(3)	−0.2357(3)	0.1173(4)	4.2(1)	C(26)	−0.3164(8)	0.4783(8)	0.104(2)	4.5(3)
C(34)	0.9902(3)	0.3338(3)	0.4817(4)	2.62(9)	C(27)	−0.4001(9)	0.5419(9)	0.177(2)	6.1(4)
C(35)	0.9780(3)	0.2324(3)	0.4740(3)	2.76(10)	C(28)	−0.4158(10)	0.532(1)	0.348(2)	6.9(4)
C(36)	1.1647(3)	0.5107(3)	0.4914(4)	2.55(10)	C(29)	−0.346(1)	0.452(1)	0.451(2)	6.8(4)
C(37)	1.2642(3)	0.5168(3)	0.4810(3)	2.58(9)	C(30)	−0.2617(8)	0.3850(8)	0.367(2)	4.9(3)
C(38)	0.9365(4)	0.4567(4)	0.1457(4)	4.3(1)					
C(39)	0.8671(5)	0.5160(6)	0.1703(5)	8.6(3)		$[Cu_2(O_2CCPh_2Me)_4(EtOH)_2]\cdot EtOH$ (**3**)			
C(40)	0.9431(5)	0.4041(4)	0.0280(4)	6.4(2)	Cu(1)	0.25957(3)	0.29120(9)	0.25527(3)	2.9(3)
C(41)	0.8839(3)	0.1967(3)	0.4271(4)	4.2(1)	Cu(2)	0.24404(3)	0.00788(8)	0.25619(3)	3.1(3)
C(42)	0.9934(3)	0.2225(3)	0.5889(4)	2.89(10)	O(3)	0.2617(2)	0.2319(5)	0.1849(2)	3.8(2)
C(43)	0.9279(4)	0.2323(4)	0.6604(4)	4.6(1)	O(4)	0.2412(2)	−0.0064(5)	0.1830(2)	4.2(2)
C(44)	0.9428(4)	0.2296(4)	0.7665(5)	5.6(2)	O(5)	0.3379(2)	0.2478(5)	0.2943(2)	3.4(2)
C(45)	1.0218(4)	0.2163(4)	0.8038(4)	5.0(2)	O(6)	0.3257(2)	0.0058(5)	0.2859(2)	3.8(2)
C(46)	1.0876(4)	0.2075(4)	0.7357(5)	5.6(2)	O(7)	0.2528(2)	0.2896(5)	0.3259(2)	3.9(2)
C(47)	1.0738(3)	0.2102(4)	0.6285(4)	4.5(1)	O(8)	0.2484(2)	0.0465(5)	0.3290(2)	4.1(2)
C(48)	1.0427(4)	0.1827(3)	0.3961(4)	3.6(1)	O(9)	0.1808(2)	0.3153(5)	0.2172(2)	3.7(2)
C(49)	1.1117(4)	0.2263(3)	0.3607(4)	4.4(1)	O(10)	0.1668(2)	0.0776(5)	0.2232(2)	4.0(2)
C(50)	1.1712(4)	0.1795(4)	0.2927(5)	6.0(2)	O(11)	0.2802(2)	0.5288(5)	0.2477(2)	4.8(2)
C(51)	1.1593(6)	0.0883(5)	0.2616(6)	7.9(2)	O(12)	0.2274(2)	−0.2214(5)	0.2642(2)	6.5(2)
C(52)	1.0916(6)	0.0427(4)	0.2955(6)	8.2(2)	C(13)	0.2514(3)	0.1084(9)	0.1627(3)	3.5(3)
C(53)	1.0331(5)	0.0891(4)	0.3645(5)	6.3(2)	C(14)	0.2506(3)	0.0949(8)	0.1049(3)	3.9(3)
C(54)	1.2809(3)	0.4662(3)	0.3614(4)	3.8(1)	C(15)	0.2784(3)	0.2297(9)	0.0939(3)	5.4(3)
C(55)	1.2982(3)	0.6170(3)	0.5116(4)	2.9(1)	C(16)	0.1899(3)	0.083(1)	0.0637(3)	4.8(3)

a) $B_{eq}=(8\pi^2/3)[U_{11}(aa^*)^2+U_{22}(bb^*)^2+U_{33}(cc^*)^2+2U_{12}(aa^*bb^*\cos\gamma)+2U_{13}(aa^*cc^*\cos\beta)+2U_{23}(bb^*cc^*\cos\alpha)]$ for atoms refined anisotropically. b) Occupancy = 0.5.

Table 3. (Continued)

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
C(17)	0.1652(4)	0.186(1)	0.0230(4)	6.5(4)	O(1)	0.2024(4)	0.6188(3)	0.1511(3)	4.1(2)
C(18)	0.1120(6)	0.172(2)	−0.0147(5)	9.7(6)	O(2)	0.3222(4)	0.6079(3)	0.1446(3)	4.2(2)
C(19)	0.0816(5)	0.055(2)	−0.0123(5)	9.6(6)	O(3)	0.2144(4)	0.4977(3)	0.1685(3)	4.0(2)
C(20)	0.1047(5)	−0.049(1)	0.0273(5)	8.8(5)	O(4)	0.3371(4)	0.4918(3)	0.1717(3)	4.6(2)
C(21)	0.1590(4)	−0.038(1)	0.0659(3)	6.1(3)	O(5)	0.2248(4)	0.5200(3)	0.2780(3)	4.0(2)
C(22)	0.2831(3)	−0.0386(8)	0.1014(3)	4.1(3)	O(6)	0.3483(4)	0.5181(3)	0.2846(3)	3.9(2)
C(23)	0.2716(4)	−0.106(1)	0.0518(3)	6.3(3)	O(7)	0.2524(4)	0.6381(3)	0.2592(3)	3.8(2)
C(24)	0.3038(5)	−0.221(1)	0.0475(4)	8.2(4)	O(8)	0.3726(4)	0.6328(3)	0.2538(3)	3.7(2)
C(25)	0.3479(4)	−0.268(1)	0.0932(5)	7.8(4)	O(9)	0.0965(4)	0.5784(3)	0.2160(3)	4.8(2)
C(26)	0.3605(4)	−0.202(1)	0.1427(4)	6.8(4)	O(10)	0.0781(4)	0.5238(4)	0.2842(4)	6.6(3)
C(27)	0.3289(4)	−0.0873(9)	0.1461(3)	5.3(3)	O(11)	0.4724(4)	0.5534(3)	0.2150(3)	4.8(2)
C(28)	0.3561(3)	0.1188(9)	0.2986(3)	3.4(3)	O(12)	0.5205(4)	0.6339(4)	0.2543(4)	6.3(3)
C(29)	0.4174(3)	0.0982(8)	0.3176(3)	3.9(3)	C(1)	0.2558(6)	0.6248(5)	0.1277(5)	3.9(3)
C(30)	0.4329(3)	−0.0595(9)	0.3400(4)	5.9(3)	C(2)	0.2353(6)	0.6535(5)	0.0690(4)	3.8(3)
C(31)	0.4311(3)	0.1268(9)	0.2682(3)	4.5(3)	C(3)	0.2721(6)	0.4718(5)	0.1592(4)	3.6(3)
C(32)	0.4103(3)	0.246(1)	0.2355(4)	6.5(4)	C(4)	0.2633(5)	0.4114(4)	0.1308(4)	3.5(3)
C(33)	0.4244(4)	0.277(1)	0.1917(4)	8.1(4)	C(5)	0.2913(6)	0.5079(4)	0.3026(5)	3.5(3)
C(34)	0.4601(5)	0.187(2)	0.1822(4)	7.8(5)	C(6)	0.2948(6)	0.4787(5)	0.3592(5)	4.2(3)
C(35)	0.4801(5)	0.070(1)	0.2146(5)	10.0(6)	C(7)	0.3166(6)	0.6583(5)	0.2657(4)	3.5(3)
C(36)	0.4666(4)	0.039(1)	0.2570(4)	7.5(4)	C(8)	0.3317(6)	0.7193(5)	0.2929(5)	4.1(3)
C(37)	0.4510(3)	0.2021(8)	0.3652(3)	3.6(2)	C(9)	0.0554(6)	0.5621(5)	0.2440(5)	4.6(3)
C(38)	0.4381(3)	0.214(1)	0.4086(3)	6.1(3)	C(10)	−0.0285(6)	0.5786(5)	0.2404(5)	4.3(3)
C(39)	0.4708(4)	0.292(1)	0.4548(4)	8.3(4)	C(11)	0.5229(7)	0.5844(5)	0.2258(5)	4.5(3)
C(40)	0.5163(4)	0.366(1)	0.4564(4)	6.8(4)	C(12)	0.6020(6)	0.5784(5)	0.2123(5)	4.3(3)
C(41)	0.5280(3)	0.353(1)	0.4122(4)	5.9(3)	C(13)	0.3067(6)	0.6731(5)	0.0496(4)	4.3(3)
C(42)	0.4967(3)	0.2731(9)	0.3673(3)	4.7(3)	C(14)	0.3657(7)	0.6343(6)	0.0460(5)	5.3(4)
C(43)	0.2493(3)	0.1716(9)	0.3486(3)	3.6(2)	C(15)	0.4283(7)	0.6519(7)	0.0259(6)	6.5(4)
C(44)	0.2468(3)	0.1802(8)	0.4051(3)	4.4(3)	C(16)	0.4354(8)	0.7074(9)	0.0083(6)	8.0(5)
C(45)	0.2280(4)	0.3329(9)	0.4128(3)	5.9(3)	C(17)	0.3794(8)	0.7457(7)	0.0120(6)	7.1(4)
C(46)	0.2056(3)	0.0701(8)	0.4085(3)	4.2(3)	C(18)	0.3150(7)	0.7309(5)	0.0324(5)	5.5(4)
C(47)	0.1561(4)	0.0456(9)	0.3633(3)	5.6(3)	C(19)	0.1936(6)	0.6055(5)	0.0313(5)	4.1(3)
C(48)	0.1165(3)	−0.044(1)	0.3671(4)	6.9(4)	C(20)	0.2095(6)	0.5949(5)	−0.0203(5)	5.1(3)
C(49)	0.1248(4)	−0.109(1)	0.4162(5)	7.7(4)	C(21)	0.1683(8)	0.5529(6)	−0.0549(5)	6.4(4)
C(50)	0.1731(4)	−0.084(1)	0.4610(4)	7.3(4)	C(22)	0.1114(8)	0.5227(6)	−0.0366(7)	6.8(4)
C(51)	0.2142(3)	0.0062(9)	0.4578(3)	5.5(3)	C(23)	0.0956(7)	0.5321(6)	0.0128(6)	6.5(4)
C(52)	0.3057(3)	0.144(1)	0.4479(3)	4.4(3)	C(24)	0.1348(6)	0.5739(5)	0.0462(5)	5.2(3)
C(53)	0.3277(3)	0.008(1)	0.4462(3)	5.6(3)	C(25)	0.1823(6)	0.7051(5)	0.0733(5)	4.2(3)
C(54)	0.3802(4)	−0.030(1)	0.4855(4)	7.3(4)	C(26)	0.1944(7)	0.7422(6)	0.1171(6)	6.1(4)
C(55)	0.4084(5)	0.071(2)	0.5266(5)	9.7(6)	C(27)	0.1512(9)	0.7900(7)	0.1173(7)	8.1(5)
C(56)	0.3878(6)	0.204(2)	0.5271(5)	10.3(6)	C(28)	0.0933(10)	0.8034(7)	0.0748(8)	8.6(6)
C(57)	0.3356(4)	0.244(1)	0.4879(4)	6.7(4)	C(29)	0.0794(8)	0.7670(7)	0.0323(7)	7.7(5)
C(58)	0.1502(3)	0.2057(9)	0.2085(3)	3.4(2)	C(30)	0.1234(7)	0.7170(6)	0.0295(5)	5.7(4)
C(59)	0.0878(3)	0.2292(8)	0.1806(3)	3.9(2)	C(31)	0.3054(6)	0.3659(5)	0.1700(5)	4.5(3)
C(60)	0.0602(3)	0.0927(9)	0.1458(3)	5.8(3)	C(32)	0.3738(8)	0.3759(6)	0.2013(6)	7.2(4)
C(61)	0.0702(3)	0.2580(8)	0.2266(3)	4.2(3)	C(33)	0.4105(9)	0.3306(9)	0.2345(7)	9.5(5)
C(62)	0.0958(3)	0.3655(9)	0.2654(4)	5.2(3)	C(34)	0.373(1)	0.2780(9)	0.2322(9)	12.0(7)
C(63)	0.0795(4)	0.395(1)	0.3072(4)	6.3(4)	C(35)	0.308(1)	0.2690(10)	0.198(1)	14.1(9)
C(64)	0.0375(5)	0.318(1)	0.3100(5)	8.7(5)	C(36)	0.2743(8)	0.3123(6)	0.1704(7)	8.9(5)
C(65)	0.0112(4)	0.212(1)	0.2712(6)	9.8(6)	C(37)	0.1796(6)	0.3964(4)	0.1169(5)	3.6(3)
C(66)	0.0275(4)	0.183(1)	0.2306(4)	7.1(4)	C(38)	0.1425(6)	0.3888(5)	0.0630(5)	5.2(3)
C(67)	0.0730(3)	0.3574(9)	0.1407(3)	4.1(3)	C(39)	0.0656(7)	0.3757(6)	0.0528(6)	6.4(4)
C(68)	0.0966(3)	0.374(1)	0.1044(4)	6.4(4)	C(40)	0.0260(7)	0.3706(6)	0.0926(7)	6.4(4)
C(69)	0.0801(4)	0.485(1)	0.0652(4)	8.4(4)	C(41)	0.0635(7)	0.3768(6)	0.1463(6)	6.0(4)
C(70)	0.0408(5)	0.582(1)	0.0626(5)	8.2(5)	C(42)	0.1387(6)	0.3909(5)	0.1566(5)	5.0(3)
C(71)	0.0158(4)	0.564(1)	0.0971(5)	9.2(5)	C(43)	0.2994(5)	0.4146(5)	0.0796(5)	3.9(3)
C(72)	0.0328(4)	0.456(1)	0.1364(4)	7.4(4)	C(44)	0.3292(7)	0.3664(5)	0.0606(6)	6.1(4)
C(73)	0.2883(4)	0.575(1)	0.1987(4)	7.8(4)	C(45)	0.3590(8)	0.3679(7)	0.0118(7)	7.4(5)
C(74)	0.2354(4)	0.591(1)	0.1506(4)	6.9(4)	C(46)	0.3598(7)	0.4179(7)	−0.0162(6)	6.6(4)
C(75)	0.1761(7)	−0.259(1)	0.2706(7)	11.8(8)	C(47)	0.3296(7)	0.4662(6)	0.0021(6)	6.1(4)
C(76)[b]	0.190(1)	−0.309(3)	0.319(1)	11(1)	C(48)	0.2996(7)	0.4642(5)	0.0496(6)	5.4(4)
C(77)[b]	0.1360(9)	−0.277(3)	0.228(2)	15(2)	C(49)	0.3754(6)	0.4572(5)	0.3835(5)	4.7(3)
O(78)	0.3781(3)	0.9536(8)	0.8370(3)	10.5(3)	C(50)	0.4332(7)	0.4962(6)	0.3911(5)	5.9(4)
C(79)	0.3799(8)	0.876(2)	0.8836(6)	16.1(9)	C(51)	0.5054(7)	0.4799(7)	0.4172(7)	7.5(5)
C(80)	0.3442(6)	0.925(2)	0.9020(6)	14.6(8)	C(52)	0.5183(8)	0.4240(8)	0.4358(6)	8.6(5)
					C(53)	0.4617(9)	0.3849(7)	0.4285(6)	8.0(5)
	$[Cu_2(O_2CCPh_3)_4(Ph_3CCO_2H)_2]\cdot CH_2Cl_2$ (**4**)				C(54)	0.3894(7)	0.4013(6)	0.4029(6)	6.8(4)
Cu(1)	0.21202(7)	0.56853(6)	0.21298(5)	3.49(3)	C(55)	0.2364(6)	0.4286(5)	0.3478(5)	4.5(3)
Cu(2)	0.35570(7)	0.56111(6)	0.21353 (5)	3.60(3)	C(56)	0.2477(7)	0.3844(6)	0.3130(6)	6.2(4)
Cl(1)[b]	0.257(1)	0.226(1)	1.010(1)	26.6(9)	C(57)	0.1967(10)	0.3391(6)	0.3016(6)	7.7(5)
Cl(2)[b]	0.129(1)	0.1591(9)	1.0094(9)	22.5(7)	C(58)	0.133(1)	0.3386(8)	0.3223(9)	10.2(6)
Cl(3)[b]	0.2776(8)	0.1686(7)	0.9987(7)	17.3(5)	C(59)	0.1190(9)	0.3836(8)	0.3554(8)	10.0(6)
Cl(4)[b]	0.156(1)	0.2181(9)	1.0288(9)	23.6(8)	C(60)	0.1712(8)	0.4281(6)	0.3690(6)	6.7(4)

Table 3. (Continued)

Atom	x	y	z	B_{eq}/Å^2
C(61)	0.2733(6)	0.5216(5)	0.4001(5)	4.8(3)
C(62)	0.2878(8)	0.5092(7)	0.4559(6)	7.0(4)
C(63)	0.2691(9)	0.5461(9)	0.4946(6)	9.1(6)
C(64)	0.2345(9)	0.5988(8)	0.4802(6)	8.0(5)
C(65)	0.2197(7)	0.6138(6)	0.4257(7)	6.9(4)
C(66)	0.2387(7)	0.5756(6)	0.3864(5)	5.5(4)
C(67)	0.4037(6)	0.7124(6)	0.3391(5)	4.9(3)
C(68)	0.4060(7)	0.6668(6)	0.3748(6)	6.5(4)
C(69)	0.4696(9)	0.6570(7)	0.4172(6)	8.3(5)
C(70)	0.5295(9)	0.694(1)	0.4186(8)	10.6(7)
C(71)	0.527(1)	0.738(1)	0.3841(9)	14.0(8)
C(72)	0.4632(8)	0.7479(7)	0.3437(6)	8.6(5)
C(73)	0.2644(6)	0.7401(5)	0.3167(5)	4.4(3)
C(74)	0.2703(7)	0.7579(5)	0.3707(5)	5.6(4)
C(75)	0.2059(8)	0.7755(6)	0.3890(6)	6.7(4)
C(76)	0.1362(8)	0.7779(6)	0.3552(8)	7.5(5)
C(77)	0.1303(7)	0.7616(6)	0.3011(7)	6.3(4)
C(78)	0.1931(7)	0.7445(5)	0.2813(5)	5.4(4)
C(79)	0.3467(6)	0.7624(5)	0.2501(5)	4.7(3)
C(80)	0.3773(7)	0.7478(5)	0.2058(6)	5.2(4)
C(81)	0.3947(7)	0.7893(7)	0.1690(6)	6.3(4)
C(82)	0.3793(9)	0.8477(7)	0.1771(8)	9.1(6)
C(83)	0.348(1)	0.8617(7)	0.2198(10)	11.8(7)
C(84)	0.3309(9)	0.8204(6)	0.2561(7)	8.9(5)
C(85)	−0.0348(6)	0.6242(5)	0.2837(5)	5.0(3)
C(86)	0.0102(8)	0.6243(7)	0.3345(6)	8.1(5)
C(87)	−0.002(1)	0.6671(9)	0.3729(7)	10.8(6)
C(88)	−0.056(1)	0.7085(7)	0.3605(9)	9.0(6)
C(89)	−0.0996(9)	0.7080(8)	0.3128(8)	9.3(6)
C(90)	−0.0894(7)	0.6666(7)	0.2743(6)	7.1(4)
C(91)	−0.0718(6)	0.5230(5)	0.2478(5)	4.5(3)
C(92)	−0.1176(7)	0.5176(6)	0.2841(6)	5.8(4)
C(93)	−0.1552(8)	0.4670(8)	0.2890(7)	7.6(5)
C(94)	−0.1469(8)	0.4195(7)	0.2574(8)	8.3(5)
C(95)	−0.1008(8)	0.4241(6)	0.2203(7)	7.9(5)
C(96)	−0.0635(7)	0.4762(6)	0.2162(6)	6.4(4)
C(97)	−0.0553(6)	0.6066(6)	0.1835(5)	5.1(3)
C(98)	−0.0174(7)	0.6543(6)	0.1689(6)	6.8(4)
C(99)	−0.0411(9)	0.6828(7)	0.1188(8)	8.8(6)
C(100)	−0.103(1)	0.6614(8)	0.0850(7)	9.1(6)
C(101)	−0.1431(9)	0.6175(8)	0.0972(7)	9.0(6)
C(102)	−0.1196(7)	0.5877(6)	0.1480(6)	6.7(4)
C(103)	0.6233(6)	0.6312(5)	0.1799(5)	4.5(3)
C(104)	0.6971(7)	0.6414(6)	0.1745(6)	6.2(4)
C(105)	0.7159(8)	0.6875(6)	0.1451(7)	7.1(5)
C(106)	0.6610(10)	0.7248(6)	0.1203(6)	7.2(5)
C(107)	0.5888(9)	0.7147(6)	0.1230(6)	7.1(4)
C(108)	0.5704(7)	0.6694(6)	0.1511(6)	6.4(4)
C(109)	0.6501(6)	0.5684(6)	0.2705(5)	5.1(3)
C(110)	0.6380(7)	0.5204(5)	0.3007(6)	5.7(4)
C(111)	0.6747(8)	0.5123(6)	0.3533(6)	7.0(4)
C(112)	0.7259(10)	0.5526(7)	0.3761(6)	8.9(5)
C(113)	0.7411(9)	0.5995(8)	0.3492(7)	9.9(6)
C(114)	0.7030(8)	0.6095(6)	0.2958(6)	7.7(5)
C(115)	0.6049(6)	0.5254(5)	0.1767(5)	4.8(3)
C(116)	0.5453(7)	0.5106(6)	0.1330(6)	6.7(4)
C(117)	0.5522(9)	0.4617(7)	0.1013(6)	8.0(5)
C(118)	0.6160(10)	0.4285(7)	0.1069(6)	7.6(5)
C(119)	0.6745(8)	0.4442 (6)	0.1474(6)	7.1(4)
C(120)	0.6701(7)	0.4910(6)	0.1816(5)	5.7(4)
C(121)	0.197(3)	0.186(3)	0.981(3)	43(3)
	$[Cu_2(O_2CCPh_3)_4(H_2O)_2]\cdot 4H_2O$ (**5a**)			
Cu	0.0000	0.0000	0.1209(1)	3.04(4)
O(1)	−0.1045(4)	0.0245(5)	0.0917(7)	4.2(2)
O(2)	−0.1007(4)	0.0245(5)	−0.1155(9)	4.4(2)
O(3)[b]	0.004(2)	0.039(1)	0.338(2)	13(1)
O(4)[b]	−0.093(1)	0.087(1)	0.490(5)	17(1)
O(5)	0.0000	0.5000	−0.616(1)	5.8(3)
C(1)	−0.1337(5)	0.0303(5)	−0.010(2)	3.5(2)
C(2)	−0.2146(5)	0.0504(5)	−0.022(1)	3.1(2)
C(3)	−0.2164(5)	0.1351(5)	−0.027(1)	3.9(3)
C(4)	−0.1750(5)	0.1727(6)	−0.110(1)	4.3(3)
C(5)	−0.1781(6)	0.2464(6)	−0.116(1)	5.3(3)
C(6)	−0.2221(8)	0.2863(6)	−0.047(1)	5.9(4)
C(7)	−0.2631(8)	0.2523(7)	0.035(2)	7.5(5)
C(8)	−0.2626(6)	0.1753(6)	0.046(1)	5.5(3)
C(9)	−0.2442(6)	0.0159(6)	−0.136(1)	3.9(3)
C(10)	−0.2850(6)	0.0578(7)	−0.229(1)	5.0(3)
C(11)	−0.3114(7)	0.0218(8)	−0.331(2)	6.5(4)
C(12)	−0.3011(8)	−0.0522(8)	−0.350(2)	7.7(5)
C(13)	−0.2630(7)	−0.0899(7)	−0.262(1)	6.4(4)
C(14)	−0.2348(6)	−0.0563(6)	−0.159(1)	4.4(3)
C(15)	−0.2623(6)	0.0221(7)	0.090(1)	4.4(3)
C(16)	−0.3284(6)	−0.0063(7)	0.074(1)	4.9(3)
C(17)	−0.3714(7)	−0.0292(7)	0.166(1)	5.8(4)
C(18)	−0.3467(7)	−0.0255(7)	0.285(1)	6.2(4)
C(19)	−0.2764(8)	0.0085(10)	0.314(2)	7.9(5)
C(20)	−0.2366(6)	0.0298(7)	0.209(1)	5.1(3)
	$[Cu_2(O_2CCPh_3)_4(H_2O)_2]\cdot 2H_2O$ (**5b**)			
Cu	0.0000	0.0000	0.1198(1)	3.12 (3)
O(1)	−0.0236(4)	−0.1068(3)	0.0926(7)	4.6(2)
O(2)	−0.0211(3)	−0.1021(3)	−0.1108(7)	4.1(2)
O(3)	0.0000	0.0000	0.3309(9)	20.6(7)
O(4)[b]	0.080(2)	0.096(1)	0.503(4)	32(1)
C(1)	−0.0288(3)	−0.1350(4)	−0.007(1)	3.5(2)
C(2)	−0.0481(4)	−0.2179(4)	−0.0202(9)	3.4(2)
C(3)	−0.1351(4)	−0.2211(4)	−0.018(1)	4.2(2)
C(4)	−0.1745(4)	−0.1808(4)	−0.1032(8)	4.0(2)
C(5)	−0.2496(4)	−0.1844(4)	−0.1061(9)	4.5(2)
C(6)	−0.2872(4)	−0.2277(5)	−0.0373(9)	5.1(3)
C(7)	−0.2509(5)	−0.2676(6)	0.0465(10)	6.0(3)
C(8)	−0.1748(4)	−0.2661(4)	0.0562(8)	4.7(2)
C(9)	−0.0176(5)	−0.2647(6)	0.0873(10)	4.6(3)
C(10)	−0.0238(6)	−0.2437(5)	0.204(1)	5.4(3)
C(11)	0.0030(7)	−0.2820(6)	0.312(1)	7.6(4)
C(12)	0.0338(6)	−0.3538(6)	0.280(1)	6.2(3)
C(13)	0.0354(5)	−0.3777(5)	0.1630(10)	5.9(3)
C(14)	0.0109(5)	−0.3334(4)	0.0718(8)	4.9(2)
C(15)	−0.0153(5)	−0.2493(5)	−0.134(1)	4.3(2)
C(16)	0.0576(4)	−0.2390(4)	−0.1653(8)	4.3(2)
C(17)	0.0892(5)	−0.2704(5)	−0.270(1)	6.0(3)
C(18)	0.0492(6)	−0.3148(6)	−0.346(1)	7.0(3)
C(19)	−0.0222(6)	−0.3251(6)	−0.3242(10)	6.4(3)
C(20)	−0.0560(5)	−0.2941(5)	−0.2245(9)	4.9(2)
	$Cu_2(O_2CSiPh_3)_4(EtOH)_2$ (**6**)			
Cu(1)	0.0000	0.3177(3)	0.2500	4.0(1)
Cu(2)	0.0000	0.1680(3)	0.2500	4.3(1)
Si(1)	0.1574(3)	0.2407(5)	0.3867(3)	4.4(2)
Si(2)	0.1303(3)	0.2471(6)	0.0907(3)	4.7(2)
O(1)	0.0698(8)	0.3058(10)	0.3066(8)	5.8(6)
O(2)	0.0702(8)	0.1764(10)	0.3085(8)	5.0(5)
O(3)	0.0564(8)	0.3071(10)	0.1814(7)	5.2(5)
O(4)	0.0540(9)	0.178(1)	0.1789(9)	6.5(6)
O(5)	0.0000	0.448(1)	0.2500	7.0(9)
O(6)	0.0000	0.036(1)	0.2500	9(1)
C(1)	0.0910(10)	0.240(2)	0.324(1)	4.8(7)
C(2)	0.0711(9)	0.242(2)	0.1604(9)	4.1(6)
C(3)[b]	−0.036(3)	0.527(4)	0.243(4)	13(2)
C(4)[b]	−0.105(2)	0.479(3)	0.226(2)	6(1)
C(5)[b]	−0.028(4)	−0.047(4)	0.267(4)	15(3)
C(6)[b]	−0.061(2)	0.009(3)	0.341(2)	5(1)
C(7)	0.120(1)	0.241(2)	0.464(1)	4.8(7)
C(8)	0.075(1)	0.293(1)	0.480(1)	6.4(9)
C(9)	0.045(1)	0.293(2)	0.541(1)	7.3(9)
C(10)	0.069(1)	0.238(2)	0.583(1)	10(1)
C(11)	0.112(2)	0.191(2)	0.568(2)	10(1)
C(12)	0.137(1)	0.190(2)	0.510(1)	6.3(8)
C(13)	0.207(1)	0.156(1)	0.3770(10)	3.5(7)
C(14)	0.190(1)	0.087(2)	0.346(1)	5.2(8)
C(15)	0.225(1)	0.023(1)	0.342(2)	7.0(10)
C(16)	0.282(1)	0.030(2)	0.362(1)	6.5(10)

Table 3. (Continued)

Atom	x	y	z	B_{eq}/Å^2	Atom	x	y	z	B_{eq}/Å^2
C(17)	0.305(1)	0.094(2)	0.390(1)	8(1)	C(30)	0.253(1)	0.296(1)	0.117(1)	6.2(9)
C(18)	0.267(1)	0.158(2)	0.401(1)	7.9(10)	C(31)	0.117(1)	0.335(1)	0.043(1)	4.1(8)
C(19)	0.201(1)	0.329(2)	0.374(1)	6.1(10)	C(32)	0.137(1)	0.335(2)	−0.021(1)	7.3(9)
C(20)	0.212(1)	0.386(2)	0.414(1)	6.3(9)	C(33)	0.125(2)	0.400(2)	−0.061(2)	10(1)
C(21)	0.248(2)	0.457(2)	0.401(2)	9(1)	C(34)	0.096(2)	0.462(2)	−0.034(2)	7(1)
C(22)	0.271(2)	0.459(2)	0.345(2)	16(1)	C(35)	0.080(1)	0.465(2)	0.027(1)	6.2(9)
C(23)	0.271(2)	0.409(2)	0.312(2)	13(1)	C(36)	0.089(1)	0.403(1)	0.062(1)	6.2(9)
C(24)	0.238(2)	0.342(2)	0.322(2)	9(1)	C(37)	0.122(1)	0.159(1)	0.040(1)	5.1(9)
C(25)	0.2079(9)	0.244(2)	0.1314(10)	4.3(6)	C(38)	0.168(1)	0.115(2)	0.022(1)	6.4(9)
C(26)	0.223(1)	0.189(2)	0.176(1)	6.2(9)	C(39)	0.157(2)	0.051(2)	−0.018(2)	10(1)
C(27)	0.280(1)	0.188(2)	0.206(1)	7.7(10)	C(40)	0.104(2)	0.032(2)	−0.043(2)	9(1)
C(28)	0.324(1)	0.239(2)	0.192(1)	9(1)	C(41)	0.055(1)	0.074(2)	−0.024(1)	9(1)
C(29)	0.310(1)	0.296(2)	0.147(1)	6.8(9)	C(42)	0.062(1)	0.140(2)	0.013(1)	7(1)

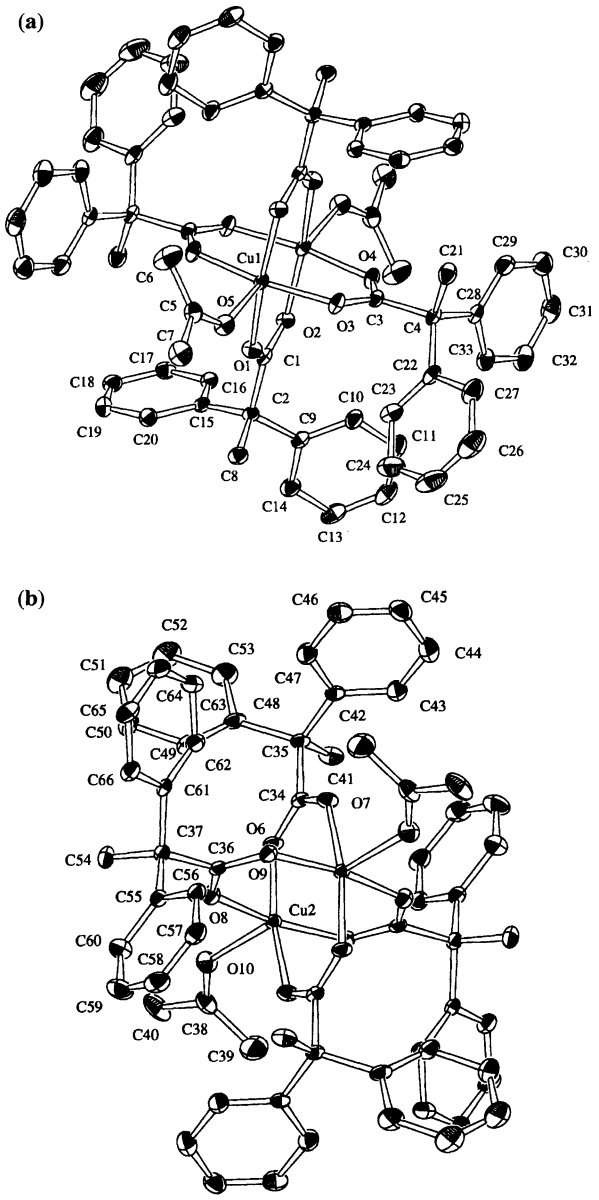

Fig. 1. ORTEP drawings of the molecular structures of $Cu_2(O_2CCPh_2Me)_4(acetone)_2$ (**1**), dimer 1 (a, top) and dimer 2 (b, bottom) showing 20% thermal ellipsoids. The hydrogen atoms are omitted for clarity.

X-Ray intensities were measured on a Rigaku AFC7R four-cycle diffractometer using graphite-monochromatized Mo $K\alpha$ radiation ($\lambda = 0.71069$ Å) at 21±1 °C using the ω–2θ scan technique. The cut-off limit of the reflection was $I > 3\sigma(I)$. Three standard reflections were measured every 150 reflections; a linear correction factor was applied.

The structures were solved by direct methods[16] and expanded using Fourier techniques.[17] The non-hydrogen atoms were refined anisotropically using a full-matrix least-squares program to minimize the function, $\Sigma w(|F_o| - |F_c|)^2$ with $w^{-1} = \sigma^2(F_o)$, with the exceptions of some disordered atoms in the unidentate ligands and solvents of crystallization, which were refined isotropically. Hydrogen atoms bonded to carbon were included. The methylene chloride of crystallization in **4** is disordered, and was modeled as being oriented in two positions with each chlorine atom having an occupancy of 0.5. Calculations were carried out using the teXsan crystallographic software package of Molecular Structure Corporation.[18] Complex neutral-atom scattering factors were used.[19] The R values for **2**, **3**, **5a**, and **6** are larger than 0.07 as a result of the disorder of the monodentate ligands or the solvent molecules of crystallization. Positional parameters are given in Table 3, and selected bond distances and angles in Table 4.[20]

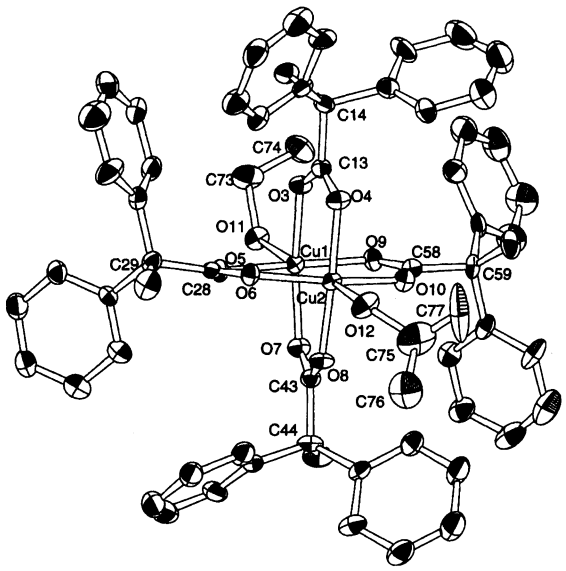

Fig. 2. ORTEP drawing of the molecular structure of $[Cu_2(O_2CCPh_2Me)_4(EtOH)_2]\cdot EtOH$ (**3**), showing 15% thermal ellipsoids. The hydrogen atoms are omitted for clarity.

Table 4. Selected Bond Distances (Å) and Angles (°) for the Complexes $[Cu_2(O_2CMR_3)_4(L)_2]\cdot nS$

$Cu_2(O_2CCPh_2Me)_4(acetone)_2$ (**1**)

Distances

Cu(1)–O(1)	1.962(3)	Cu(2)–O(6)	1.956(3)
Cu(1)–O(2)$^{i)}$	1.959(3)	Cu(2)–O(7)$^{i)}$	1.961(3)
Cu(1)–O(3)	1.948(3)	Cu(2)–O(8)	1.958(3)
Cu(1)–O(4)$^{i)}$	1.956(3)	Cu(2)–O(9)$^{i)}$	1.958(3)
Cu(1)–O(5)	2.172(3)	Cu(2)–O(10)	2.189(3)
O(1)–C(1)	1.254(5)	O(6)–C(34)	1.264(5)
O(2)–C(1)	1.262(5)	O(7)–C(34)	1.249(5)
O(3)–C(3)	1.273(5)	O(8)–C(36)	1.246(5)
O(4)–C(3)	1.253(5)	O(9)–C(36)	1.288(5)
O(5)–C(5)	1.219(5)	O(10)–C(38)	1.203(6)
C(1)–C(2)	1.538(6)	C(34)–C(35)	1.548(6)
C(3)–C(4)	1.542(6)	C(36)–C(37)	1.541(6)
C(5)–C(6)	1.478(8)	C(38)–C(39)	1.477(8)
C(5)–C(7)	1.493(7)	C(38)–C(40)	1.509(7)

Angles

O(1)–Cu(1)–O(2)$^{i)}$	168.8(1)	O(6)–Cu(2)–O(7)$^{i)}$	168.6(1)
O(1)–Cu(1)–O(3)	90.1(1)	O(6)–Cu(2)–O(8)	91.0(1)
O(1)–Cu(1)–O(4)$^{i)}$	91.1(1)	O(6)–Cu(2)–O(9)$^{i)}$	86.5(1)
O(1)–Cu(1)–O(5)	88.9(1)	O(6)–Cu(2)–O(10)	93.8(1)
O(2)–Cu(1)–O(3)	87.6(1)	O(7)$^{i)}$–Cu(2)–O(8)	90.3(1)
O(2)–Cu(1)–O(4)$^{i)}$	89.1(1)	O(7)$^{i)}$–Cu(2)–O(9)$^{i)}$	90.0(1)
O(2)$^{i)}$–Cu(1)–O(5)	102.3(1)	O(7)$^{i)}$–Cu(2)–O(10)	97.4(1)
O(3)–Cu(1)–O(4)$^{i)}$	168.7(1)	O(8)–Cu(2)–O(9)$^{i)}$	169.0(1)
O(3)–Cu(1)–O(5)	94.4(1)	O(8)–Cu(2)–O(10)	91.4(1)
O(4)$^{i)}$–Cu(1)–O(5)	96.9(1)	O(9)$^{i)}$–Cu(2)–O(10)	99.5(1)
Cu(1)–O(1)–C(1)	128.3(3)	Cu(2)–O(6)–C(34)	119.4(3)
Cu(1)$^{i)}$–O(2)–C(1)	118.0(3)	Cu(2)$^{i)}$–O(7)–C(34)	125.8(3)
Cu(1)–O(3)–C(3)	121.6(3)	Cu(2)–O(8)–C(36)	128.3(3)
Cu(1)$^{i)}$–O(4)–C(3)	124.1(3)	Cu(2)$^{i)}$–O(9)–C(36)	118.4(3)
Cu(1)–O(5)–C(5)	134.9(4)	Cu(2)–O(10)–C(38)	134.9(4)
O(1)–C(1)–O(2)	124.8(4)	O(6)–C(34)–O(7)	125.5(4)
O(1)–C(1)–C(2)	116.9(4)	O(6)–C(34)–C(35)	116.0(4)
O(2)–C(1)–C(2)	118.3(4)	O(7)–C(34)–C(35)	118.5(4)
O(3)–C(3)–O(4)	125.0(4)	O(8)–C(36)–O(9)	124.1(4)
O(3)–C(3)–C(4)	115.6(4)	O(8)–C(36)–C(37)	119.0(4)
O(4)–C(3)–C(4)	119.3(4)	O(9)–C(36)–C(37)	116.9(4)
O(5)–C(5)–C(6)	121.8(5)	O(10)–C(38)–C(39)	122.5(5)
O(5)–C(5)–C(7)	119.8(5)	O(10)–C(38)–C(40)	119.5(6)
C(6)–C(5)–C(7)	118.5(5)	C(39)–C(38)–C(40)	117.9(5)

$[Cu_2(O_2CCPh_2Me)_4(H_2O)_2]\cdot H_2O$ (**2**)

Distances

Cu–O(1)	1.977(6)	Cu–O(4)$^{i)}$	1.970(5)
Cu–O(2)$^{i)}$	1.980(6)	Cu–O(5)	2.140(5)
Cu–O(3)	1.974(5)	O(1)–C(1)	1.231(9)
O(2)–C(1)	1.24(1)	O(3)–C(3)	1.277(9)
O(4)–C(3)	1.247(9)	C(1)–C(2)	1.57(1)
C(3)–C(4)	1.56(1)		

Angles

O(1)–Cu–O(2)$^{i)}$	168.2(3)	O(2)$^{i)}$–Cu–O(4)$^{i)}$	92.4(3)
O(1)–Cu–O(3)	89.2(3)	O(2)$^{i)}$–Cu–O(5)	94.5(3)
O(1)–Cu–O(4)$^{i)}$	90.7(3)	O(3)–Cu–O(4)$^{i)}$	169.9(2)
O(1)–Cu–O(5)	96.3(2)	O(3)–Cu–O(5)	91.9(2)
O(2)$^{i)}$–Cu–O(3)	85.8(3)	O(4)$^{i)}$–Cu–O(5)	98.1(2)
Cu–O(1)–C(1)	121.6(6)	Cu–O(3)–C(3)	120.6(5)
Cu$^{i)}$–O(2)–C(1)	121.3(6)	Cu$^{i)}$–O(4)–C(3)	123.3(5)
O(1)–C(1)–O(2)	127.8(8)	O(3)–C(3)–O(4)	126.1(8)
O(1)–C(1)–C(2)	118.3(8)	O(3)–C(3)–C(4)	114.6(7)
O(2)–C(1)–C(2)	113.9(8)	O(4)–C(3)–C(4)	119.3(7)

$[Cu_2(O_2CCPh_2Me)_4(EtOH)_2]\cdot EtOH$ (**3**)

Distances

Cu(1)–O(3)	1.992 (5)	Cu(1)–O(5)	1.959(4)
Cu(1)–O(7)	1.982 (5)	Cu(1)–0(9)	1.938(4)
Cu(1)–O(11)	2.274(5)	Cu(2)–O(4)	1.942(5)
Cu(2)–O(6)	1.998(4)	Cu(2)–O(8)	1.942(5)
Cu(2)–O(10)	1.988(4)	Cu(2)–O(12)	2.175(5)
O(3)–C(13)	1.253(9)	O(5)–C(28)	1.264(9)
O(4)–C(13)	1.26(1)	O(6)–C(28)	1.272(9)
C(13)–C(14)	1.55(1)	C(28)–C(29)	1.52(1)
O(7)–C(43)	1.263(9)	O(8)–C(43)	1.257(9)
C(43)–C(44)	1.55(1)	O(9)–C(58)	1.256(9)
O(10)–C(58)	1.257(9)	C(58)–C(59)	1.538(9)

Angles

O(9)–Cu(1)–O(5)	174.8(2)	O(9)–Cu(1)–O(7)	89.0(2)
O(9)–Cu(1)–O(3)	89.7(2)	O(9)–Cu(1)–O(11)	95.6(2)
O(5)–Cu(1)–O(7)	90.0(2)	O(5)–Cu(1)–O(3)	89.8(2)
O(5)–Cu(1)–O(11)	89.6(2)	O(7)–Cu(1)–O(3)	163.5(2)
O(7)–Cu(1)–O(11)	102.6(2)	O(3)–Cu(1)–O(11)	94.0(2)
O(8)–Cu(2)–O(4)	173.2(2)	O(8)–Cu(2)–O(10)	89.9(2)
O(8)–Cu(2)–O(6)	90.6(2)	O(8)–Cu(2)–O(12)	90.2(2)
O(4)–Cu(2)–O(10)	89.1(2)	O(4)–Cu(2)–O(6)	88.2(2)
O(4)–Cu(2)–O(12)	96.5(2)	O(10)–Cu(2)–O(6)	161.4(2)
O(10)–Cu(2)–O(12)	97.6(2)	O(6)–Cu(2)–O(12)	100.9(2)
Cu(2)–O(12)–C(76)	125.1(7)	Cu(2)–O(12)–C(77)	113.8(8)
C(13)–O(3)–Cu(1)	127.5(5)	C(13)–O(4)–Cu(2)	117.2(5)
C(13)–O(4)–Cu(2)	117.2(5)	C(28)–O(5)–Cu(1)	121.7(4)
C(28)–O(6)–Cu(2)	125.0(5)	C(43)–O(7)–Cu(1)	121.6(5)
C(43)–O(8)–Cu(2)	124.8(5)	C(58)–O(9)–Cu(1)	119.5(4)
C(58)–O(10)–Cu(2)	127.2(5)	O(3)–C(13)–O(4)	126.0(7)
O(5)–C(28)–O(6)	123.7(7)	O(7)–C(43)–O(8)	124.7(7)
O(9)–C(58)–O(10)	124.6(6)	O(3)–C(13)–C(14)	117.1(7)
O(4)–C(13)–C(14)	116.8(6)	O(5)–C(28)–C(29)	118.0(6)
O(6)–C(28)–C(29)	118.2(7)	O(7)–C(43)–C(44)	118.2(6)
O(8)–C(43)–C(44)	117.1(7)	O(9)–C(58)–C(59)	118.3(6)
O(10)–C(58)–C(59)	117.0(6)		

$[Cu_2(O_2CCPh_3)_4(Ph_3CCO_2H)_2]\cdot CH_2Cl_2$ (**4**)

Distances

Cu(1)–O(1)	1.915(7)	Cu(2)–O(2)	2.026(7)
Cu(1)–O(3)	1.981(7)	Cu(2)–O(4)	1.906(7)
Cu(1)–O(5)	1.952(7)	Cu(2)–O(6)	2.063(7)
Cu(1)–O(7)	2.031(7)	Cu(2)–O(8)	1.930(7)
Cu(1)–O(9)	2.123(7)	Cu(2)–O(11)	2.117(7)
O(1)–C(1)	1.23(1)	O(7)–C(7)	1.24(1)
O(2)–C(1)	1.26(1)	O(8)–C(7)	1.26(1)
O(3)–C(3)	1.27(1)	O(9)–C(9)	1.18(1)
O(4)–C(3)	1.25(1)	O(10)–C(9)	1.34(1)
O(5)–C(5)	1.28(1)	O(11)–C(11)	1.15(1)
O(6)–C(5)	1.22(1)	O(12)–C(11)	1.35(1)
C(1)–C(2)	1.59(1)	C(7)–C(8)	1.56(1)
C(3)–C(4)	1.56(1)	C(9)–C(10)	1.55(1)
C(5)–C(6)	1.56(1)	C(11)–C(12)	1.54(1)

Angles

O(1)–Cu(1)–O(3)	93.1(3)	O(2)–Cu(2)–O(4)	89.3(3)
O(1)–Cu(1)–O(5)	177.4(3)	O(2)–Cu(2)–O(6)	158.6(3)
O(1)–Cu(1)–O(7)	87.1(3)	O(2)–Cu(2)–O(8)	88.8(3)
O(1)–Cu(1)–O(9)	91.5(3)	O(2)–Cu(2)–O(11)	101.3(3)
O(3)–Cu(1)–O(5)	89.0(3)	O(4)–Cu(2)–O(6)	92.0(3)
O(3)–Cu(1)–O(7)	158.0(3)	O(4)–Cu(2)–O(8)	178.0(3)
O(3)–Cu(1)–O(9)	103.6(3)	O(4)–Cu(2)–O(11)	90.6(3)
O(5)–Cu(1)–O(7)	90.4(3)	O(6)–Cu(2)–O(8)	89.6(3)
O(5)–Cu(1)–O(9)	89.6(3)	O(6)–Cu(2)–O(11)	100.0(3)
O(7)–Cu(1)–O(9)	98.4(3)	O(8)–Cu(2)–O(11)	90.3(3)
Cu(1)–O(1)–C(1)	119.6(7)	Cu(2)–O(2)–C(1)	124.3(7)
Cu(1)–O(3)–C(3)	126.9(7)	Cu(2)–O(4)–C(3)	120.5(7)
Cu(1)–O(5)–C(5)	118.5(7)	Cu(2)–O(6)–C(5)	127.4(7)
Cu(1)–O(7)–C(7)	126.9(7)	Cu(2)–O(8)–C(7)	117.9(6)
Cu(1)–O(9)–C(9)	136.7(8)	Cu(2)–O(11)–C(11)	134.3(8)
O(1)–C(1)–O(2)	126(1)	O(7)–C(7)–O(8)	125(1)
O(3)–C(3)–O(4)	123(1)	O(9)–C(9)–O(10)	121(1)
O(5)–C(5)–O(6)	124(1)	O(11)–C(11)–O(12)	122(1)
O(1)–C(1)–C(2)	114.8(9)	O(7)–C(7)–C(8)	118.6(10)
O(2)–C(1)–C(2)	118(1)	O(8)–C(7)–C(8)	116.2(9)
O(3)–C(3)–C(4)	119.3(9)	O(9)–C(9)–C(10)	128(1)

Symmetry code: i) $-x, -y, -z$; ii) $-x, -y, z$; iii) $y, -x, -z$; iv) $-y, x, -z$; v) $-x, y, 1/2-z$.

Table 4. (Continued).

O(4)–C(3)–C(4)	117(1)	O(10)–C(9)–C(10)	111(1)	O(1)–C(1)–O(2)	125.2(7)	O(1)–C(1)–C(2)	121(1)
O(5)–C(5)–C(6)	113.7(10)	O(11)–C(11)–C(12)	128(1)	O(2)–C(1)–C(2)	113(1)		
O(6)–C(5)–C(6)	121.7(9)	O(12)–C(11)–C(12)	108.5(10)				
		$[Cu_2(O_2CCPh_3)_4(H_2O)_2]\cdot 4H_2O$(**5a**)			$Cu_2(O_2CSiPh_3)_4(EtOH)_2$(**6**)		
		Distances			Distances		
Cu–O(1)	2.005(8)	Cu–O(2)$^{iii)}$	1.912(8)	Cu(1)–O(1)	1.93(2)	Si(1)–C(19)	1.83(3)
Cu–O(3)	2.43(2)	O(1)–C(1)	1.22(2)	Cu(1)–O(3)	1.93(2)	Si(2)–C(2)	1.99 (2)
O(2)–C(1)	1.29(2)	C(1)–C(2)	1.54(1)	Cu(1)–O(5)	2.26(2)	Si(2)–C(25)	1.89(2)
				Cu(2)–O(2)	1.96(2)	Si(2)–C(31)	1.86(3)
		Angles		Cu(2)–O(4)	1.94(2)	Si(2)–C(37)	1.87(3)
O(1)–Cu–O(1)$^{ii)}$	162.1(5)	O(2)$^{iii)}$–Cu–O(2)$^{iv)}$	176.6(6)	Cu(2)–O(6)	2.28(2)	O(1)–C(1)	1.28(3)
O(1)–Cu–O(2)$^{iii)}$	90.2(4)	O(1)–Cu–O(3)	96.5(9)	Si(1)–C(1)	1.95(2)	O(2)–C(1)	1.24(3)
O(1)–Cu–O(2)$^{iv)}$	89.2(4)	O(1)$^{ii)}$–Cu–O(3)	100.7(9)	Si(1)–C(7)	1.85(2)	O(3)–C(2)	1.27(3)
O(2)$^{iii)}$–Cu–O(3)	74.8(6)	O(2)$^{iv)}$–Cu–O(3)	108.7(6)	Si(1)–C(13)	1.85(3)	O(4)–C(2)	1.24(3)
Cu–O(1)–C(1)	125.7(7)	Cu–O(2)–C(1)	120.4(8)				
O(1)–C(1)–O(2)	124.5(8)	O(1)–C(1)–C(2)	121(1)		Angles		
O(2)–C(1)–C(2)	114(1)			O(1)–Cu(1)–O(1)$^{v)}$	168(1)	Cu(2)–O(2)–C(1)	121(2)
				O(1)–Cu(1)–O(3)	87.3(7)	Cu(2)–O(4)–C(2)	121(2)
		$[Cu_2(O_2CCPh_3)_4(H_2O)_2]\cdot 2H_2O$(**5b**)		O(1)–Cu(1)–O(3)$^{v)}$	91.6(7)	Cu(2)–O(6)–C(5)	154(3)
		Distances		O(1)–Cu(1)–O(5)	96.2(5)	C(1)–Si(1)–C(7)	106(1)
Cu–O(1)	2.014(7)	Cu–O(2)$^{iii)}$	1.902(7)	O(3)–Cu(1)–O(3)$^{v)}$	169(1)	C(1)–Si(1)–C(13)	110(1)
Cu–O(3)	2.27(1)	O(1)–C(1)	1.19(1)	O(3)–Cu(1)–O(5)	95.5(5)	C(1)–Si(1)–C(19)	107(1)
O(2)–C(1)	1.28(1)	C(1)–C(2)	1.56(1)	O(2)–Cu(2)–O(2)$^{v)}$	171(1)	C(2)–Si(2)–C(25)	104.4(9)
				O(2)–Cu(2)–O(4)	90.5(7)	C(2)–Si(2)–C(31)	110(1)
		Angles		O(2)–Cu(2)–O(4)$^{v)}$	88.8(7)	C(2)–Si(2)–C(37)	109(1)
O(1)–Cu–O(1)$^{ii)}$	163.3(5)	O(2)$^{iii)}$–Cu–O(2)$^{iv)}$	174.1(5)	O(2)–Cu(2)–O(6)	94.3(5)	Si(1)–C(1)–O(1)	117(2)
O(1)–Cu–O(2)$^{iii)}$	88.8(4)	O(1)–Cu–O(3)	98.4(3)	O(4)–Cu(2)–O(4)$^{v)}$	170(1)	Si(1)–C(1)–O(2)	116(2)
O(1)–Cu–O(2)$^{iv)}$	90.3(4)	O(1)$^{ii)}$–Cu–O(3)	98.4(3)	O(4)–Cu(2)–O(6)	94.9(5)	Si(2)–C(2)–O(3)	113(3)
O(2)$^{iii)}$–Cu–O(3)	92.9(3)	O(2)$^{iv)}$–Cu–O(3)	92.9(3)	Cu(1)–O(1)–C(1)	123(2)	Si(2)–C(2)–O(4)	120(3)
Cu–O(1)–C(1)	124.4(7)	Cu–O(2)–C(1)	121.7(7)	Cu(1)–O(3)–C(2)	121(2)	O(1)–C(1)–O(2)	126(3)
				Cu(1)–O(5)–C(3)	150(2)	O(3)–C(2)–O(4)	127(2)

Results and Discussion

Structures. The copper(II) complexes with two α-phenyl substituent groups on the bridging carboxylato ligands and oxygen-donor unidentate ligands, $[Cu_2(O_2CCPh_2Me)_4(L)_2]\cdot nS$ (complexes, **1**, **2**, and **3**) have cage structures similar to copper(II) acetate monohydrate in which the geometry of the coordination sphere around copper(II) is SP, or shows only small deviations from this arrangement.

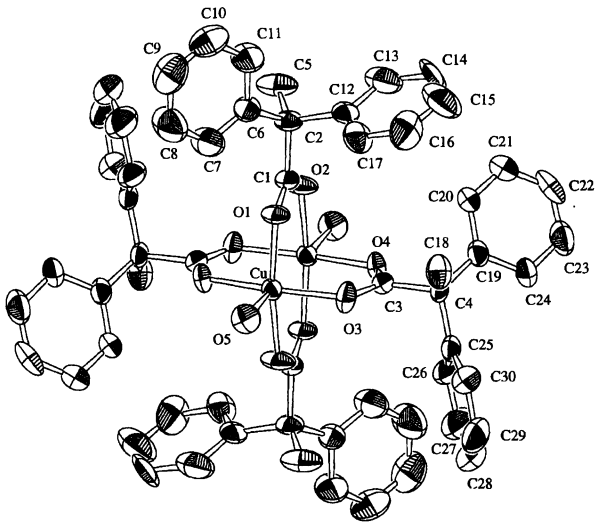

Fig. 3. ORTEP drawing of the molecular structure of $[Cu_2(O_2CCPh_2Me)_4(H_2O)_2]\cdot H_2O$ (**2**), showing 50% thermal ellipsoids. The hydrogen atoms are omitted for clarity.

Crystals of the complex, $Cu_2(O_2CCPh_2Me)_4(acetone)_2$ (**1**), form on slow evaporation of a solution of $Cu_2(O_2CCPh_2Me)_4(H_2O)_2$ in water/acetone (25 v/v%). The formation of **1** is unusual in that generally anhydrous conditions are required for preparing complexes with simple ketone ligands.[21,22] Smith, et al.[23] have reported on the formation of a dimeric copper(II) complex with axial acetone ligands when a complex formed by reacting (2,4-dichloro-5-methylphenylthio) acetic acid with $CuCO_3\cdot Cu(OH)_2$ in ethanol/water is crystallized from acetone. The structure of **1** contains two crystallographically independent dimer units (see Fig. 1). The axial acetone ligands in the two dimer units coordinate to copper(II) at the distances of 2.173(3) and 2.190(3) Å, forming Cu–O–C angles of 134.7(3) and 134.8(3)°, respectively. On coordination, the C=O bond in acetone is weakened, as indicated by a shift of the carbonyl stretching frequency to a lower energy by 25 cm^{-1} (see Table 1).

Crystals of $[Cu_2(O_2CCPh_2Me)_4(EtOH)_2]\cdot EtOH$ (**3**) were obtained on slow evaporation of the solvent, either absolute ethanol or 70 v/v% ethanol/water, from a solution of the copper(II) complex formed in situ. The structure of the dimer unit is shown in Fig. 2. One of the two ethanol ligands shows positional disorder of the terminal carbon atom; the disorder was modeled using an occupancy of 0.5 for each site [C(76) and C(77)].

As indicated above, dimeric 2,2-diphenylpropanoatocopper(II) complexes preferentially coordinate either acetone or ethanol to water in the axial positions when forming crystals from mixed solvent systems. Crystals of the aqua complex, $[Cu_2(O_2CCPh_2Me)_4(H_2O)_2]\cdot H_2O$ (**2**), were obtained using a methylene chloride–heptane solvent; the

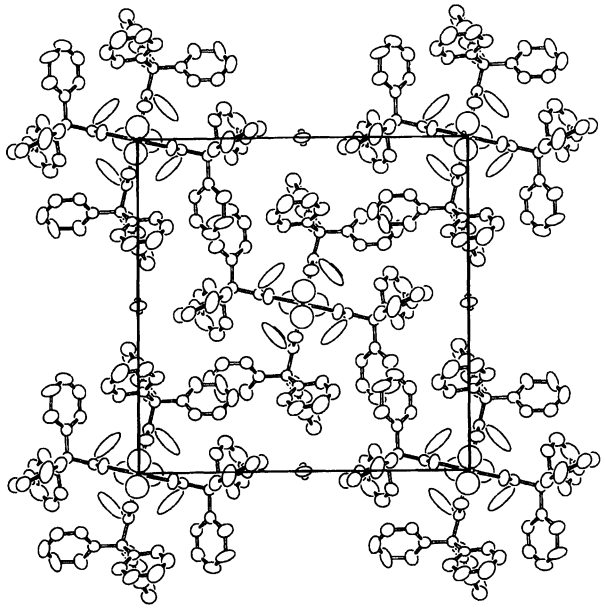

Fig. 4. Packing diagram of $[Cu_2(O_2CCPh_3)_4(H_2O)_2]\cdot 4H_2O$ (**5b**)(ORTEP drawing showing 20% thermal ellipsoids) viewed down the *c* axis. The oxygen atoms of the aqua ligands and the water molecules in the hydrogen-bonded network are shown around the central copper atoms. The hydrogen atoms are omitted for clarity.

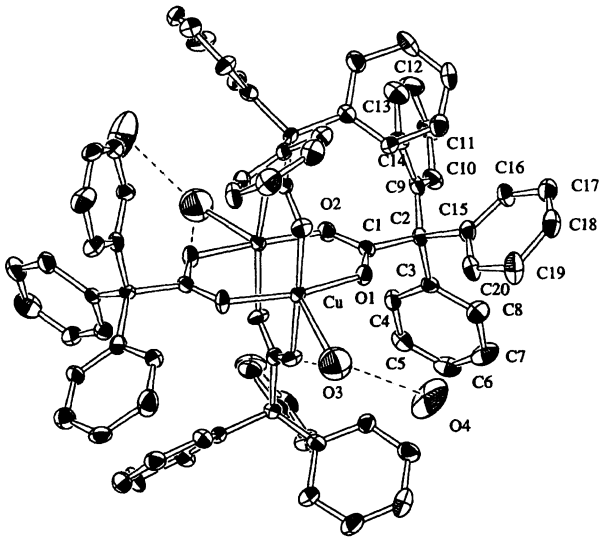

Fig. 5. ORTEP drawing of the molecular structure of $[Cu_2(O_2CCPh_3)_4(H_2O)_2]\cdot 4H_2O$ (**5a**) with the hydrogen-bonded waters, O(4), showing 20% thermal ellipsoids. The hydrogen bonds are shown as dashed lines. The aqua ligands, O(3), are hydrogen bonded to the water molecules, O(4), and bridging carboxylato ligands, O(2). The water molecules, O(4), form hydrogen-bonded bridges with the aqua ligands, O(3)′, on adjacent dimer units. The bridging waters, both ligands and molecules, are disordered (not shown) with respect to $\bar{4}$ symmetry. The hydrogen atoms are omitted for clarity.

structure of the dimer unit is given in Fig. 3. In **2**, the water of crystallization occurs as dimeric hydrogen-bonded units with an O···O distance of 2.732(9) Å.

The copper(II) complexes with three α-phenyl substituent groups on the carbon in the bridging carboxylato ligands and the oxygen-donor unidentate ligands, $[Cu_2(O_2CCPh_3)_4(L)_2]\cdot nS$, complexes **4**, **5a**, and **5b** have structures in which the geometry about each copper(II) is distorted from SP, forming a cage, which shows some changes in the bond distances and angles from those observed for the classical copper(II) acetate monohydrate-type structure (see Table 6). In particular, one *trans* O–Cu–O angle on each copper atom widens, 174 to 178° (vide infra).

The complex, $[Cu_2(O_2CCPh_3)_4(H_2O)_2]\cdot 4H_2O$ (**5a**), crystallizes from a methylene chloride-heptane solution of $[Cu_2(O_2CCPh_3)_3(O_2CSiPh_2SiPh_3)]\cdot 4H_2O$ on slow evaporation. A methylene chloride solution of **5b** also yields crystals of **5a**. The former procedure gave the best crystals for structure determination; the silanecarboxylato complex is more soluble in methylene chloride and yields crystals of **5a** on decomposition of the pentaphenyldisilanecarboxylato ligand.[13] The complex **5a** crystallizes in the tetragonal space group $I\bar{4}$. The crystals are dichroic, blue when viewed along the unique axis (*c* axis) and green along the *a* and *b* axes. Figure 4 shows a packing diagram of **5a** viewed down the *c* axis. The binuclear complex has crystallographic $\bar{4}$ symmetry, and the Cu–Cu axis is parallel to the *c* axis. The aqua ligand, O(3), is shifted from the Cu–Cu axis exhibiting positional disorder. The molecular structure of **5a** is shown in Fig. 5. The O(3) atoms on the adjacent copper(II) dimeric units along the *c* axis [O(3)–O(3)′ distance, 3.62(5) Å] form two hydrogen-bonded bridges around a twofold axis with

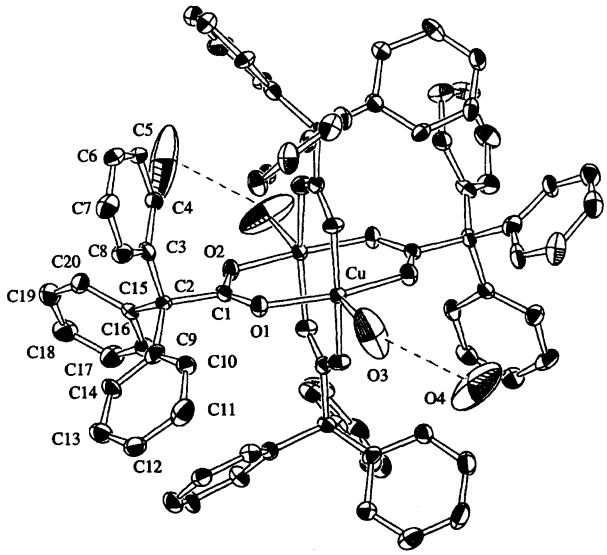

Fig. 6. ORTEP drawing of the molecular structure of $[Cu_2(O_2CCPh_3)_4(H_2O)_2]\cdot 2H_2O$ (**5b**) with the hydrogen-bonded waters, O(4), showing 20% thermal ellipsoids. The hydrogen bonds are shown as dashed lines. The aqua ligands, O(3), are hydrogen bonded to the water molecules, O(4). The water molecules, O(4), form hydrogen-bonded bridges with the aqua ligands, O(3)′, on adjacent dimer units. The bridging water molecules are disordered (not shown) with respect to $\bar{4}$ symmetry. The hydrogen atoms are omitted for clarity.

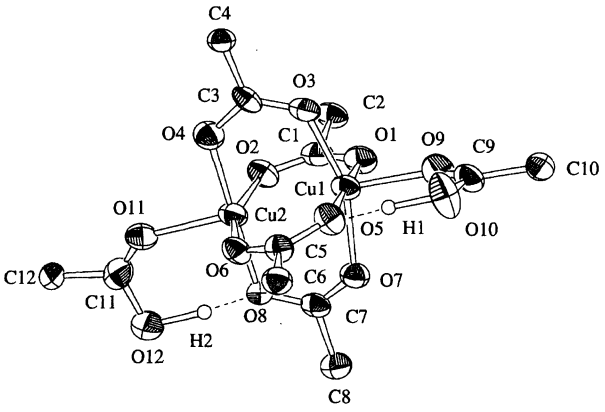

Fig. 7. ORTEP drawing of the molecular structure of $[Cu_2(O_2CCPh_3)_4(Ph_3CCO_2H)_2]\cdot CH_2Cl_2$ (**4**), showing 40% thermal ellipsoids. The hydrogen bonds between the triphenylacetic acid ligands and the bridging carboxylato ligands are shown as dashed lines. The phenyl groups are omitted for clarity.

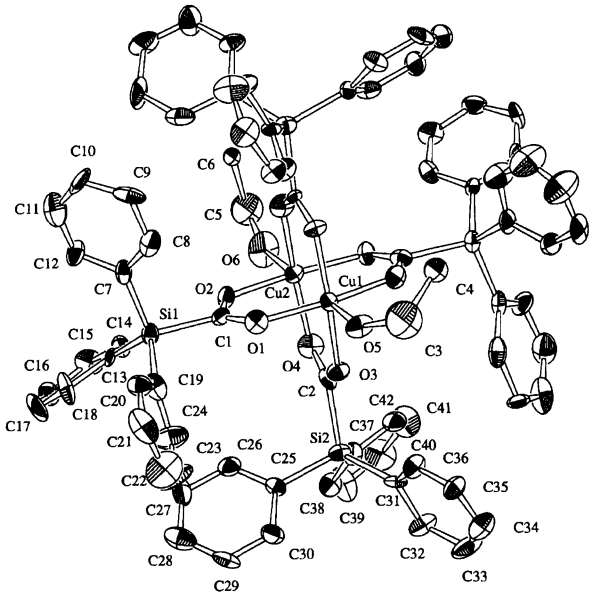

Fig. 8. ORTEP drawing of the molecular structure of $Cu_2(O_2CSiPh_3)_4(EtOH)_2$ (**6**), showing 20% thermal ellipsoids. The carbon atoms of the ethanol ligands are disordered (not shown) with respect to the C_2 axis. The hydrogen atoms are omitted for clarity.

the water molecules, O(4), at a distance of 2.59(5) Å. The intermolecular hydrogen-bonded bridges exhibit positional disorder with respect to the $\bar{4}$ symmetry. The aqua ligands, O(3), also have hydrogen bonds with the carboxylato groups, O(2), at a distance of 2.67(2) Å. These hydrogen-bonding interactions result in unusually long Cu–O(3) bonds of 2.43(2) Å. Two waters of crystallization per copper(II) dimer, which occur as dimeric hydrogen-bonded units with an O(5)···O(5′) distance of 2.88(3) Å, are located in the spaces between the complex molecules (see Fig. 4).

The complex, $[Cu_2(O_2CCPh_3)_4(H_2O)_2]\cdot 2H_2O$ (**5b**), is formed from **5a** on exposure to the atmosphere for several days. The crystals of **5b** retain the tetragonal space group $I\bar{4}$; however, the a axis decreases by about 0.23 Å. The structure of **5b** differs from **5a** in that the two waters of crystallization, O(5), are no longer present. The molecular structure of the dimer complex **5b** with the hydrogen-bonded waters is shown in Fig. 6. The structure of the dimer unit in **5b** is more symmetrical than in **5a** in that the oxygen atoms, O(3), of the aqua ligands approximately lie along a twofold axis which is coincident with the Cu–Cu axis. The O(3)–O(3)′ distances between adjacent copper(II) dimeric units along the *c* axis in **5b** and **5a** are the same within the experimental error. The distances between the oxygen atoms in the hydrogen-bonded bridges are O(3)···O(4), 2.94(3) and O(3)′···O(4), 2.89(3) Å.

Light green needles of $[Cu_2(O_2CCPh_3)_4(Ph_3CCO_2H)_2]\cdot CH_2Cl_2$ (**4**) were obtained as a by-product during the formation of the crystals of **5a**. The structure of the dimer unit of **4** is given in Fig. 7. In **4**, monodentate triphenylacetic acid ligands are bonded to the copper atoms through the carbonyl oxygen atoms, O(9) and O(11), at distances of 2.123(7) and 2.117(7) Å, respectively. Intramolecular hydrogen bonds occur between the O–H groups of the acid ligands and the oxygen atoms of two bridging carboxylato ligands, O(5)···O(10) 2.69(1) and O(8)···O(12) 2.68(1) Å. The structure of a closely related complex, $Cu_2(O_2CCH_3)_4(CH_3CO_2H)_2$, has been reported.[24] In this structure, the axial acetic acid ligands are bonded to the cage in a similar fashion. However, there is a difference in the stereochemistry of the monodentate carboxylic acid ligands in the two complexes. In **4**, the triphenylacetic acid ligands have a *cis* arrangement with respect to the cage, the dihedral angle between the planes of the carboxyl groups is 79.2°, while in $Cu_2(O_2CCH_3)_4(CH_3CO_2H)_2$ the arrangement is *trans*. In **4**, the intramolecular repulsions between the triphenylacetic acid and the bridging triphenylacetato ligands are expected to reach a minimum when the Cu–Cu–O(carbonyl) angles approach 180° [Cu(2)–Cu(1)–O(9), 176.7(2) and Cu(1)–Cu(2)–O(11), 178.7(2)°]. As a result of the cage distortion from SP toward TB in **4**, the closest carboxylato oxygens at the opposite ends of the cage to the triphenylacetic acid ligands have a *cis* relationship. For comparison purposes, the Cu–Cu–O(carbonyl) angles in $Cu_2(O_2CCH_3)_4(CH_3CO_2H)_2$, which has a SP structure, are 170.6°.

The complex, $Cu_2(O_2CSiPh_3)_4(EtOH)_2$ (**6**), crystallizes from an alcoholic solution of triphenylsilanecarboxylic acid and copper(II) nitrate 2.5-hydrate. As shown in Fig. 8, the cage structure is SP. The Cu–Cu dimer unit lies on a site with a two-fold axis of symmetry; the carbon atoms of the axially coordinated ethanol molecules are disordered (0.5 occupancy).

Cage Structure. The geometry of the cage in dimeric copper(II) carboxylates with bridging α-phenyl-substituted carboxylato ligands varies with the type of ligands present, producing changes in the coordination sphere around each copper(II). The arrangement of the ligands about copper(II) can vary from primarily SP to DTB. The factors which affect the geometry of the coordination sphere about copper(II) are

Table 5. Copper(II) Stereochemistry Parameters for the Complexes, $[Cu_2(O_2CMR_3)_4(L)_2]\cdot nS$[a)]

Compound	No.	R_{sp}[b)]	R_{tb}[b)]	R_{sp}/R_{tb}[c)]
$Cu_2(O_2CCPh_2Me)_4(quin)_2$[d)]	**10**	0.063	0.116	0.54
$Cu_2(O_2CCPhMe_2)_4(quin)_2$[d)]	**8**	0.066	0.117	0.56
$Cu_2(O_2CCH_3)_4(H_2O)_2$[e)]	—	0.074	0.115	0.64
$Cu_2(O_2CCPhMe_2)_4(H_2O)_2$[f)]	**7**	0.075	0.116	0.64
$Cu_2(O_2CCPh_2Me)_4(acetone)_2$	**1**	0.076	0.115	0.66
$Cu_2(O_2CSiPh_3)_4(EtOH)_2$	**6**	0.077	0.114	0.67
$[Cu_2(O_2CCPh_2Me)_4(H_2O)_2]\cdot H_2O$	**2**	0.079	0.116	0.68
$[Cu_2(O_2CCPh_3)_4(H_2O)_2]\cdot 4H_2O$	**5a**	0.086	0.115	0.75
$[Cu_2(O_2CCPh_2Me)_4(EtOH)_2]\cdot EtOH$	**3**	0.074	0.091	0.81
$[Cu_2(O_2CCPh_3)_4(H_2O)_2]\cdot 2H_2O$	**5b**	0.075	0.092	0.82
$[Cu_2(O_2CCPh_3)_4(Ph_3CCO_2H)_2]\cdot CH_2Cl_2$	**4**	0.074	0.080	0.92
$[Cu_2(O_2CCPh_3)_4(4\text{-pic})_2]\cdot 2$toluene[g)]	**11**	0.088	0.066	1.26
$[Cu_2(O_2CCPhMe_2)_4(2,6\text{-lut})_2]\cdot$ benzene[f)]	**9**	0.076	0.053	1.43
$[Cu_2(O_2CCPh_3)_4(4\text{-pic})_2]\cdot 2$benzene[g)]	**12**	0.091	0.060	1.52
$[Cu_2(O_2CCPh_3)_4(py)_2]\cdot$ benzene[h)]	**13**	0.125	0.075	1.67

a) M=C and Si; R=Me and Ph; L=unidentate ligand; *n*S=No. and type of solvent molecule(s) of crystallization. b) R_{sp} and R_{tb} measure the deviations of the angles in the complexes from the idealized square pyramidal and trigonal bipyramidal structures respectively: see text and Refs. 25 and 26 for definitions. c) Ratio of R_{sp} to R_{tb}. d) Quinoline complexes, Ref. 12. e) Ref. 27. f) Aqua and 2,6-lutidine complexes, Ref. 4. g) 4-Picoline complexes, Ref. 3. h) Pyridine complex, Ref. 2.

Table 6. Structural and Magnetic Data for the Complexes, $[Cu_2(O_2CMR_3)_4(L)_2]\cdot nS$

Compound	Cu–Cu Å	Cu–O_{av}/Å max[a)]	Dihedral angle/deg[b)]	O–Cu–O deg[c)]	Cu–Cu–L deg[d)]	$-2J$ cm^{-1} [e)]
$Cu_2(O_2CCH_3)_4(H_2O)_2$[f)]	2.616(1)	1.994(3)		168.9(2)	174.2(1)	284
1	2.609(1)	1.962(3)		168.7(1)	168.9(1)	352
	2.606(1)	1.961(3)		169.0(1)	172.1(1)	
2	2.594(2)	1.980(6)		169.9(2)	177.5(2)	344
3	2.628(1)	1.994(5)		173.2(2)	171.8(2)	347
				174.6(2)	173.3(2)	
4	2.609(2)	2.047(7)	86.7	177.4(3)	176.7(2)	
				178.0(3)	178.7(2)	
5a	2.588(3)	2.005(8)		176.6(6)	162.9(5)	
5b	2.583(3)	2.013(7)	90.0[g)]	174.1(5)	180.0[g)]	292
6	2.600(6)	1.95(2)		167(1)	180.0[g)]	1193
				171(1)		
7[h)]	2.589(1)	1.974(2)		168.9(1)	177.8(1)	348
8[i)]	2.683(1)	1.975(2)		166.8(1)	176.8(1)	353
9[h)]	2.907(1)	2.081(2)	88.1	178.0(1)	180.0[g)]	310
				178.2(1)		
10[i)]	2.696(1)	1.984(1)		166.2(1)	173.4(1)	339
11[j)]	2.793(3)	2.145(5)	84.9	176.8(2)	159.8(2)	326[k)]
				179.1(2)	166.6(2)	
12[j)]	2.835(4)	2.159(12)	87.5	178.0(6)	160.5(4)	326[k)]
				179.8(6)	166.7(4)	
13[l)]	3.086(1)	2.404(3)	88.8	178.0(1)	144.5(1)	187
				178.8(1)	146.3(1)	

a) Average of the two longest Cu–O bonds from each Cu atom to a bridging carboxylato ligand. b) Dihedral angle between the equatorial planes of the DTB Cu atoms in the dimer. c) Largest O–Cu–O angle for each Cu atom in the dimer structure. d) The angle formed by the donor atom of the unidentate ligand with the two Cu atoms in the dimer structure. e) $H=-2JS_1\cdot S_2$. f) Ref. 27. g) Required by symmetry. h) Ref. 4. i) Ref. 12. j) Ref. 3. k) Efflorescent sample. l) Ref. 2.

discussed below.

In order to quantify the geometry of the coordination sphere about copper(II), we used a method devised by Zemann.[25] Zemann defined a parameter (R) based on the central angles of a structure, which is a measure of the degree of correspondence of an observed structure to an ideal reference structure, SP or TB (the smaller the R value, the greater the correspondence).[26] In this paper, we have chosen to use both the individual R values, R_{sp} and R_{tb}, and the ratio of the R values, R_{sp}/R_{tb}. The ratio of the R values for a

complex allows one to compare the observed structure with reference structures using a single number: if $R_{sp}/R_{tb} < 1$, the complex more closely resembles an SP; if $R_{sp}/R_{tb} > 1$, the complex more closely resembles a TB.

The R_{sp}, R_{tb}, and R_{sp}/R_{tb} values for the complexes with bridging α-phenyl substituted carboxylato ligands (**1**—**13**) along with copper(II) acetate monohydrate for comparison purposes, are listed in Table 5. The data are arranged in the order of increasing R_{sp}/R_{tb} values. Structural and magnetic data for these complexes are listed in Table 6.

The transformation of the cage structure, which occurs during the rearrangement of the ligands about copper(II) from SP toward TB, can be visualized as occurring by staggering two adjacent bridging carboxylato ligands in such a way as to reduce the intramolecular repulsions between the bridging groups with respect to the equatorial plane (axial symmetry assumed) and/or between the unidentate ligand and the bridging groups. This simultaneous movement of two pairs of *trans* bridging ligands in the same direction results in a widening of one *trans* O–Cu–O angle on each copper(II) (174 to 180°) (see Table 6).

All dimeric copper(II) complexes with bridging 2-methyl-2-phenylpropanoato and 2,2-diphenylpropanoato ligands, with the exception of **9**, form complexes in which the cage geometry is similar to copper(II) acetate monohydrate, and the coordination sphere around copper(II) is primarily SP. Complex **9** is the only dimeric complex obtained when the bulky 2,6-lutidine ligand is reacted with the complexes, $Cu_2(O_2CCPh_nMe_{3-n})_4(H_2O)_2$, where $n = 1$—3.[4] In **9**, staggering of the bridging 2-methyl-2-phenylpropanoato ligands allows more room for the methyl groups of the 2,6-lutidine ligands. The most favorable orientations for the 2,6-lutidine ligands occur when the methyl groups lie in the proximity of opposite pairs of *trans* bridging carboxylato ligands, which are angled away from the 2,6-lutidine ligands. The DTP geometry cannot be attributed to intermolecular interactions between the 2,6-lutidine ligands in adjacent dimer units, since the N–Cu–Cu–N atoms lie along a twofold axis of the crystal.

All of the dimeric copper(II) complexes with bridging triphenylacetato ligands have structures which show a considerable distortion of the cage geometry with a concomitant change in the ligand arrangement about copper(II) from SP. These structural changes arise from intramolecular steric effects between the bulky triphenylacetato ligands (vide supra) and crystal packing effects.

Complexes **4**, **5a**, and **5b** have oxygen-donor unidentate ligands in addition to the bridging triphenylacetato ligands. These complexes show a widening of one *trans* O–Cu–O

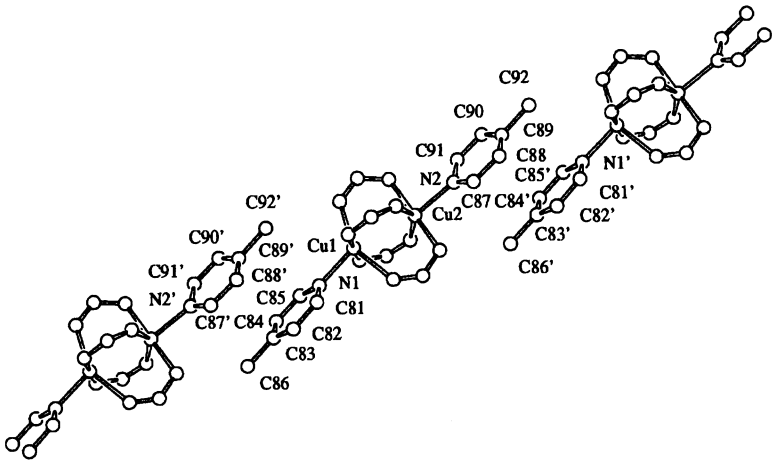

Fig. 9. Diagram showing the packing of the dimer units of $[Cu_2(O_2CCPh_3)_4(4\text{-pic})_2]\cdot 2$ toluene (**11**) along the *c* axis of the crystal. The triphenylmethyl groups and toluenes of crystallization are omitted for clarity.

Table 7. Intermolecular Distances (Å) between the Least-Squares Planes of the Heterocyclic Ligands and the Atoms of Adjacent Heterocyclic Ligands in the Complexes, $[Cu_2(O_2CCPh_3)_4(L)_2]\cdot n$S, (where L = Pyridine and 4-Picoline)[a]

11[b]				**12**[b]				**13**[c]			
Base I		Base II		Base I		Base II		Base I		Base II	
N(1′)	3.539	N(2′)	3.534	N(1′)	3.670	N(2′)	3.592	N(11′)	3.420	N(21′)	3.474
C(81′)	3.369	C(87′)	3.352	C(81′)	3.467	C(87′)	3.388	C(11′)	3.412	C(21′)	3.475
C(82′)	3.377	C(88′)	3.343	C(82′)	3.431	C(88′)	3.374	C(12′)	3.420	C(22′)	3.480
C(83′)	3.506	C(89′)	3.494	C(83′)	3.599	C(89′)	3.556	C(13′)	3.425	C(23′)	3.456
C(84′)	3.694	C(90′)	3.673	C(84′)	3.824	C(90′)	3.812	C(14′)	3.408	C(24′)	3.474
C(85′)	3.725	C(91′)	3.695	C(85′)	3.880	C(91′)	3.787	C(15′)	3.424	C(25′)	3.487
C(86′)	3.456	C(92′)	3.518	C(86′)	3.533	C(92′)	3.621				

a) The numbering systems are taken from Refs. 2 and 3. The prime refers to the atoms in adjacent dimer units (see Fig. 8). b) Calculated from data in Ref. 3. c) Calculated from data in Ref. 2.

angle on each copper(II), resulting from the intramolecular repulsion forces between the bulky triphenylacetato bridging ligands, which lead to the staggered arrangement described above. Complex **5b**, which has the smallest oxygen-donor unidentate ligands with the oxygen atoms collinear with the Cu–Cu axis, shows the smallest distortion from the SP arrangement around copper(II). Complex **4** shows a somewhat greater distortion from the SP arrangement. While the bulky triphenylacetic acid ligands increase the intramolecular repulsion forces, they prevent the close approach of an adjacent molecule and reduce the possibility that crystal packing forces are an important factor in determining the cage geometry. Complex **5a** is unique among the complexes studied in that the geometry around copper(II) shows a considerable distortion from the SP arrangement, but does not approach the TB arrangement. The position of the aqua ligand in **5a** yields a geometry around each copper(II), which shows a considerable deviation from both the SP and TB structures.

The cage structure of complex **6**, with bridging triphenylsilanecarboxylato ligands and the oxygen-donor unidentate ligand ethanol, does not show a staggered arrangement of the bridging ligands; the coordination geometry around each copper(II) is SP (see Table 5). Undoubtedly, the longer C–Si bonds increase the separation of the bridging ligands, and, thus, reduce the inter-ligand repulsion forces, which are responsible for the changes in geometry.

The three copper(II) complexes with bridging triphenylacetato ligands, which show the largest distortion from SP toward TP (**11**—**13**), have unidentate ligands which are bonded through the nitrogen atoms of the pyridine rings. Two types of forces are responsible for the changes in geometry in these complexes: intramolecular forces (vide supra) and intermolecular forces, i. e., crystal packing forces, which cause the pyridine rings to be skewed with respect to Cu–Cu axis (see Table 6). In these structures, the pyridine rings of the adjacent dimer units abut each other in the crystal, causing the pyridine-type ligands to be angled away from the apical positions (see the packing diagram, Fig. 9). The extent of molecular deformation is related to the molecular geometry via the spatial environment of, and around, the pyridine ring systems. In **13**, the tilt angles (Cu–Cu–N angles) are the smallest, the adjacent pyridine rings are parallel and related by a center of inversion, and the inter-ring distances approach the values reported by Pauling[28] for the effective thickness of an aromatic ring.[2] The 4-picoline rings in **11** and **12** are not parallel (see Fig. 9), and the tilt angles (Cu–Cu–N) are somewhat larger. The distances between the heterocyclic rings and the atoms of the heterocyclic rings of adjacent molecules are given in Table 7. Interestingly, the R values calculated for **13** indicate that the tilting of the pyridine rings by molecular packing in the crystal does not cause the coordination sphere around copper(II) to resemble a TB more than **11** and **12**, but causes a much larger deviation from the SP arrangement (see Table 5).

The effect of the cage geometry on the megnetic properties has been discussed.[2,10] The spin exchange is suppressed by a deformation toward a TB, since the bridges of the cage span axial to the equatorial positions in the TB structure. The $-2J$ values for the complexes with bridging α-phenyl substituted carboxylato ligands with SP geometry (**1**, **2**, **3**, **7**, **8**, and **10**) generally fall in a very narrow range, 339 to 353 cm^{-1} (see Table 6). Deformation through staggering bridging ligands, resulting from intramolecular forces between bulky ligands (complexes **5b** and **9**), leads to a lowering of the $-2J$ values, 292 and 310 cm^{-1}, respectively. Complex **13**, which shows the largest deformation from the SP arrangement, resulting from both intra- and intermolecular forces, has the smallest singlet triplet coupling, $-2J = 187$ cm^{-1}. The $-2J$ value obtained for **11** and **12** on efflorescent samples is 326 cm^{-1}, suggesting that the coordination geometry around copper changes from DTB toward SP on removal of the solvent of crystallization.[3]

The dimeric copper(II) complex with silanecarboxylato bridging ligands, **6**, has a much larger $-2J$ value (1193 cm^{-1}) than those complexes with bridging carbon–carboxylato ligands. The larger singlet–triplet splitting in **6** results from the effect of the silicon atoms bonded to the carboxyl groups on the energy of the magnetic orbitals of the complex.[11,12,14,29]

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$$R = \frac{\Sigma |D|}{\Sigma A},$$

where D is the deviation of the observed angle from the corresponding angle in a SP or TB structure and A is the angle for a SP or TB structure. The reference SP structure selected for comparison has apical atom-central atom-base atom angles of 104.1°.

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