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Structures of Aqua and Pyridine Adducts of Dimeric Copper(II) 2-Chlorobenzoate

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Abstract. Tetrakis(μ-2-chlorobenzoato-*O*,*O*′)-bis[aquacopper(II)], [$Cu_2(C_7H_4ClO_2)_4(H_2O)_2$], (I), $M_r = 785.4$, monoclinic, $P2_1/n$, $a = 7.214\,(2)$, $b = 19.554\,(4)$, $c = 10.877\,(4)$ Å, $\beta = 103.82\,(3)°$, $V = 1489.9\,(7)$ Å^3, $Z = 2$, $D_m = 1.75\,(2)$, $D_x = 1.75$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.848$ mm^{-1}, $F(000) = 788$, $T = 298\,(2)$ K, $R = 0.032$ for 2536 observed reflections. Tetrakis(μ-2-chlorobenzoato-*O*,*O*′)-bis[pyridinecopper(II)] di(tetrachloromethane), [$Cu_2(C_7H_4ClO_2)_4(C_5H_5N)_2$].2$CCl_4$, (II), $M_r = 1215.2$, monoclinic, $P2_1/a$, $a = 23.365\,(3)$, $b = 10.688\,(1)$, $c = 20.542\,(2)$ Å, $\beta = 100.03\,(1)°$, $V = 5051.5\,(9)$ Å^3, $Z = 4$, $D_x = 1.60$ Mg m^{-3}, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 1.533$ mm^{-1}, $F(000) = 2424$, $T = 299\,(2)$ K, $R = 0.074$ for 5124 reflections. The $-2J$ value of (I) observed by magnetic susceptibility measurement is abnormally small (262 cm^{-1}) among the copper benzoate complexes. This may be mainly a result of the bent structure of the Cu—O—C—O—Cu bridges.

Introduction. The exchange interaction in dimeric copper(II) carboxylates, [$Cu(RCOO)_2L$]$_2$, is antiferromagnetic. Quite recently, correlations between the $-2J$ value (the energy separation between the singlet and triplet states) and the molecular structure have been extensively studied, yielding a number of conclusions. The important factors which determine

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the exchange properties in the dimeric systems are the electronic structure of the carboxylate groups, which depends on the substituent R (Yamanaka, Uekusa, Ohba, Saito, Iwata, Kato, Tokii, Muto & Steward, 1991), deformation of the coordination geometry around the Cu atoms from square pyramidal toward trigonal bipyramidal (Uekusa, Ohba, Tokii, Muto, Kato, Husebye, Steward, Chang, Rose, Pletcher & Suzuki, 1992), and coplanarity of the Cu—O—C—O—Cu bridges (Kawata, Uekusa, Ohba, Furukawa, Tokii, Muto & Kato, 1992). Of the dimeric copper(II) benzoates, the quinoline adduct has an unusually smaller $-2J$ value (267 cm^{-1}) than the other adducts (316–350 cm^{-1}). The reduction of $-2J$ in this compound was attributed to the bent structure of the Cu—O—C—O—Cu bridges (Kawata *et al.*, 1992). Certain aqua adducts of substituted benzoate copper dimers show smaller $-2J$ values than the corresponding pyridine adducts, by 60–90 cm^{-1}, suggesting bent structures of the bridges in the former. In order to confirm this expectation, we determined the crystal structures of aqua and pyridine adducts of copper(II) 2-chlorobenzoate.

Experimental. *Complex* (I). A green prismatic crystal, 0.5 × 0.3 × 0.2 mm, was used for data collection with a Rigaku AFC-5 four-circle diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Cell parameters were refined by least squares for 25 2θ values ($20 < 2\theta < 30°$). Intensity data were collected up to $2\theta = 55°$ (h: $0\rightarrow 9$, k: $0\rightarrow 25$, l: $-14\rightarrow 14$) by ω scan. The intensity variation of five standard reflections was monitored; $0.997 < \Sigma(|F_o|/|F_o|_{\rm initial})/5 < 1.004$. 3686 reflections were measured, of which 2731 were observed with $|F_o| > 3\sigma(|F_o|)$, and 2536 were unique [$R_{\rm int}(|F|) = 0.010$] after absorption correction by the Gaussian numerical integration method [Busing & Levy (1957); transmission factor, A, 0.51–0.74]. The structure was solved by Patterson and Fourier methods. Eight of the ten H atoms were found from difference syntheses and the others were calculated theoretically. Coordinates of all the atoms, anisotropic thermal parameters of the non-H atoms and isotropic thermal parameters of the H atoms were refined by block-diagonal least squares to minimize the function $\Sigma w(|F_o| - |F_c|)^2$, with $w^{-1} = \sigma^2(|F_o|) + (0.015|F_c|)^2$. $R(F) = 0.032$, $wR = 0.039$, $S = 1.60$ for 240 variable parameters and 2536 unique reflections. Reflection/parameter (r/p) ratio = 10.6, $\Delta/\sigma < 0.15$, $-0.57 < \Delta\rho < 0.56$ e Å^{-3}. The complex neutral-atom scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). The calculations were carried out using the *UNICS*III computation program system (Sakurai & Kobayashi, 1979) on a FACOM M-780/10 computer at Keio University.

Table 1. *Positional parameters and equivalent isotropic temperature factors* (Å^2) (*Hamilton*, 1959)

$$U_{\rm eq} = (1/3)\Sigma_i\Sigma_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	$U_{\rm eq}$
(I)				
Cu	−0.14737 (4)	−0.01692 (2)	0.04251 (3)	0.0255
Cl(1)	0.6074 (1)	0.10152 (5)	0.28666 (9)	0.0593
Cl(2)	0.0153 (1)	−0.19709 (5)	0.2826 (1)	0.0663
O(1)	0.0135 (3)	0.0153 (1)	0.2024 (2)	0.0422
O(2)	−0.2689 (3)	−0.0425 (1)	−0.1332 (2)	0.0406
O(3)	−0.0244 (3)	−0.1070 (1)	0.0688 (2)	0.0426
O(4)	−0.2348 (3)	0.0781 (1)	−0.0047 (2)	0.0389
O(5)	−0.3825 (3)	−0.0425 (1)	0.1219 (2)	0.0374
C(1)	0.1804 (4)	0.0382 (1)	0.2183 (3)	0.0282
C(2)	0.2735 (4)	0.0615 (1)	0.3502 (2)	0.0288
C(3)	0.4568 (4)	0.0904 (2)	0.3880 (3)	0.0363
C(4)	0.5248 (5)	0.1133 (2)	0.5099 (3)	0.0551
C(5)	0.4164 (6)	0.1072 (2)	0.5974 (3)	0.0585
C(6)	0.2378 (5)	0.0778 (2)	0.5637 (3)	0.0508
C(7)	0.1689 (4)	0.0556 (2)	0.4412 (3)	0.0372
C(8)	0.1412 (4)	−0.1180 (1)	0.0582 (3)	0.0313
C(9)	0.2437 (4)	−0.1822 (1)	0.1144 (3)	0.0332
C(10)	0.2036 (4)	−0.2179 (2)	0.2153 (3)	0.0382
C(11)	0.3185 (5)	−0.2716 (2)	0.2722 (3)	0.0511
C(12)	0.4715 (5)	−0.2908 (2)	0.2263 (3)	0.0547
C(13)	0.5124 (5)	−0.2582 (2)	0.1252 (4)	0.0571
C(14)	0.3977 (5)	−0.2042 (2)	0.0687 (3)	0.0460
(II)				
Cu(1)	0.24066 (4)	0.22499 (9)	0.27069 (5)	0.0341
Cu(2)	0.26599 (4)	−0.00077 (9)	0.22672 (5)	0.0342
Cl(1)	0.3959 (1)	0.0727 (3)	0.4443 (1)	0.0953
Cl(2)	0.3864 (1)	0.1404 (3)	0.0906 (2)	0.1044
Cl(3)	0.1136 (1)	0.1735 (3)	0.0548 (1)	0.0860
Cl(4)	0.1170 (1)	0.0375 (3)	0.3975 (1)	0.0900
O(1)	0.3242 (2)	0.2330 (5)	0.3090 (2)	0.0461
O(2)	0.2597 (2)	0.2842 (5)	0.1859 (2)	0.0495
O(3)	0.1608 (2)	0.1864 (5)	0.2256 (3)	0.0503
O(4)	0.2274 (2)	0.1229 (4)	0.3478 (2)	0.0424
O(5)	0.3458 (2)	0.0488 (5)	0.2690 (3)	0.0513
O(6)	0.2761 (2)	0.0922 (5)	0.1478 (2)	0.0485
O(7)	0.1814 (2)	−0.0069 (5)	0.1920 (2)	0.0456
O(8)	0.2518 (2)	−0.0630 (5)	0.3120 (2)	0.0490
N(1)	0.2178 (3)	0.4026 (6)	0.3083 (3)	0.0428
N(2)	0.2910 (3)	−0.1752 (5)	0.1881 (3)	0.0369
C(1)	0.3588 (3)	0.1465 (7)	0.3003 (3)	0.0403
C(2)	0.4213 (4)	0.1660 (8)	0.3295 (4)	0.0465
C(3)	0.4433 (4)	0.1302 (8)	0.3950 (4)	0.0562
C(4)	0.5011 (4)	0.1404 (9)	0.4220 (5)	0.0726
C(5)	0.5382 (4)	0.186 (1)	0.3846 (5)	0.0887
C(6)	0.5182 (4)	0.221 (1)	0.3187 (5)	0.0807
C(7)	0.4601 (3)	0.2099 (9)	0.2909 (4)	0.0693
C(8)	0.2729 (3)	0.2089 (7)	0.1424 (3)	0.0430
C(9)	0.2843 (3)	0.2690 (8)	0.0798 (3)	0.0405
C(10)	0.3319 (4)	0.2404 (8)	0.0528 (4)	0.0592
C(11)	0.3422 (4)	0.297 (1)	−0.0061 (4)	0.0791
C(12)	0.3011 (5)	0.378 (1)	−0.0360 (4)	0.0888
C(13)	0.2550 (5)	0.4103 (9)	−0.0089 (4)	0.0788
C(14)	0.2439 (4)	0.3567 (8)	0.0483 (4)	0.0627
C(15)	0.1477 (3)	0.0844 (8)	0.1958 (3)	0.0444
C(16)	0.0856 (3)	0.0722 (8)	0.1658 (4)	0.0447
C(17)	0.0663 (4)	0.1091 (8)	0.1000 (4)	0.0592
C(18)	0.0079 (4)	0.0992 (9)	0.0701 (4)	0.0700
C(19)	−0.0304 (4)	0.046 (1)	0.1068 (5)	0.0841
C(20)	−0.0125 (4)	0.008 (1)	0.1719 (5)	0.0941
C(21)	0.0457 (4)	0.018 (1)	0.1993 (4)	0.0716
C(22)	0.2354 (3)	0.0093 (7)	0.3537 (3)	0.0349
C(23)	0.2272 (3)	−0.0528 (7)	0.4173 (3)	0.0399
C(24)	0.1755 (4)	−0.0476 (7)	0.4404 (4)	0.0479
C(25)	0.1671 (4)	−0.1135 (8)	0.4972 (4)	0.0630
C(26)	0.2111 (4)	−0.1814 (9)	0.5309 (4)	0.0643
C(27)	0.2635 (4)	−0.1878 (9)	0.5100 (4)	0.0676
C(28)	0.2721 (4)	−0.1278 (8)	0.4520 (4)	0.0532
C(29)	0.2571 (4)	0.4901 (8)	0.3265 (5)	0.0657
C(30)	0.2421 (4)	0.6036 (9)	0.3543 (5)	0.0927
C(31)	0.1868 (5)	0.6216 (9)	0.3620 (5)	0.0934
C(32)	0.1468 (4)	0.533 (1)	0.3434 (6)	0.1039
C(33)	0.1641 (4)	0.4232 (9)	0.3174 (5)	0.0771
C(34)	0.2615 (3)	−0.2806 (8)	0.1914 (4)	0.0548
C(35)	0.2762 (4)	−0.3917 (8)	0.1652 (5)	0.0821
C(36)	0.3223 (4)	−0.3933 (9)	0.1338 (5)	0.0877
C(37)	0.3537 (4)	−0.2892 (9)	0.1298 (5)	0.0744
C(38)	0.3366 (3)	−0.1804 (8)	0.1584 (4)	0.0511
Cl(5)	0.3970 (2)	−0.2265 (5)	0.3296 (2)	0.1898
Cl(6)	0.4225 (2)	−0.3426 (4)	0.4485 (2)	0.2137
Cl(7)	0.4412 (2)	−0.4739 (5)	0.3417 (3)	0.2332

Table 1 (*cont.*)

	x	y	z	U_{eq}
Cl(8)	0.5105 (2)	−0.2641 (5)	0.3874 (3)	0.2599
Cl(9)	0.5931 (2)	−0.2081 (5)	0.1659 (2)	0.1969
Cl(10)	0.5013 (2)	−0.1278 (5)	0.0704 (2)	0.2120
Cl(11)	0.5022 (2)	−0.0734 (5)	0.2024 (2)	0.2196
Cl(12)	0.5796 (3)	0.0425 (6)	0.1370 (3)	0.3564
C(39)	0.4448 (5)	−0.329 (1)	0.3730 (5)	0.1102
C(40)	0.5456 (6)	−0.086 (1)	0.1426 (5)	0.1378

Table 2. *Selected bond lengths* (Å) *and angles* (°)

(I)

Cu···Cu^{i}	2.599 (1)	C(4)—C(5)	1.373 (6)
Cu—O(1)	1.950 (2)	C(5)—C(6)	1.378 (5)
Cu—O(2)	1.967 (2)	C(6)—C(7)	1.376 (5)
Cu—O(3)	1.960 (2)	C(8)—C(9)	1.512 (3)
Cu—O(4)	1.990 (2)	C(9)—C(10)	1.388 (5)
Cu—O(5)	2.138 (2)	C(9)—C(14)	1.389 (5)
Cl(1)—C(3)	1.736 (4)	C(10)—C(11)	1.388 (4)
Cl(2)—C(10)	1.738 (4)	C(11)—C(12)	1.368 (6)
O(1)—C(1)	1.257 (4)	C(12)—C(13)	1.363 (6)
O(2^{i})—C(1)	1.247 (4)	C(13)—C(14)	1.392 (5)
O(3)—C(8)	1.246 (4)		
O(4^{i})—C(8)	1.260 (4)	Cl(1)···O(2^{i})	2.852 (2)
C(1)—C(2)	1.502 (3)	Cl(2)···O(3)	2.876 (3)
C(2)—C(3)	1.406 (4)	O(5)···O(2^{ii})	3.042 (3)
C(2)—C(7)	1.385 (4)	O(5)···O(4^{ii})	2.837 (3)
C(3)—C(4)	1.374 (5)		

Cu^{i}—Cu—O(1)	82.6 (1)	C(1)—C(2)—C(7)	117.5 (2)
Cu^{i}—Cu—O(2)	86.1 (1)	C(3)—C(2)—C(7)	117.3 (2)
Cu^{i}—Cu—O(3)	84.3 (1)	Cl(1)—C(3)—C(2)	123.5 (2)
Cu^{i}—Cu—O(4)	84.6 (1)	Cl(1)—C(3)—C(4)	116.0 (2)
Cu^{i}—Cu—O(5)	177.0 (1)	C(2)—C(3)—C(4)	120.5 (3)
O(1)—Cu—O(2)	168.6 (1)	C(3)—C(4)—C(5)	120.6 (3)
O(1)—Cu—O(3)	90.4 (1)	C(4)—C(5)—C(6)	120.2 (3)
O(1)—Cu—O(4)	90.7 (1)	C(5)—C(6)—C(7)	119.1 (3)
O(1)—Cu—O(5)	94.4 (1)	C(2)—C(7)—C(6)	122.2 (3)
O(2)—Cu—O(3)	89.7 (1)	O(3)—C(8)—O(4^{i})	124.6 (2)
O(2)—Cu—O(4)	86.9 (1)	O(3)—C(8)—C(9)	119.6 (2)
O(2)—Cu—O(5)	96.9 (1)	O(4^{i})—C(8)—C(9)	115.9 (2)
O(3)—Cu—O(4)	168.6 (1)	C(8)—C(9)—C(10)	124.3 (3)
O(3)—Cu—O(5)	96.1 (1)	C(8)—C(9)—C(14)	117.9 (3)
O(4)—Cu—O(5)	95.1 (1)	C(10)—C(9)—C(14)	117.6 (3)
Cu—O(1)—C(1)	125.8 (2)	Cl(2)—C(10)—C(9)	123.1 (3)
Cu^{i}—O(2^{i})—C(1)	121.0 (2)	Cl(2)—C(10)—C(11)	115.7 (3)
Cu—O(3)—C(8)	123.5 (2)	C(9)—C(10)—C(11)	121.2 (3)
Cu^{i}—O(4^{i})—C(8)	121.6 (2)	C(10)—C(11)—C(12)	119.5 (3)
O(1)—C(1)—O(2^{i})	124.4 (2)	C(11)—C(12)—C(13)	121.0 (4)
O(1)—C(1)—C(2)	115.8 (2)	C(12)—C(13)—C(14)	119.4 (4)
O(2^{i})—C(1)—C(2)	119.8 (2)	C(9)—C(14)—C(13)	121.2 (3)
C(1)—C(2)—C(3)	125.2 (2)		

(II)

Cu(1)···Cu(2)	2.679 (1)	Cl(4)—C(24)	1.747 (8)
Cu(1)—O(1)	1.975 (5)	O(1)—C(1)	1.26 (1)
Cu(1)—O(2)	1.975 (5)	O(2)—C(8)	1.280 (9)
Cu(1)—O(3)	1.978 (5)	O(3)—C(15)	1.260 (9)
Cu(1)—O(4)	1.991 (5)	O(4)—C(22)	1.230 (9)
Cu(1)—N(1)	2.151 (6)	O(5)—C(1)	1.236 (9)
Cu(2)—O(5)	1.987 (5)	O(6)—C(8)	1.253 (9)
Cu(2)—O(6)	1.950 (5)	O(7)—C(15)	1.26 (1)
Cu(2)—O(7)	1.982 (5)	O(8)—C(22)	1.261 (9)
Cu(2)—O(8)	1.956 (5)	C(1)—C(2)	1.49 (1)
Cu(2)—N(2)	2.146 (6)	C(8)—C(9)	1.50 (1)
Cl(1)—C(3)	1.74 (1)	C(15)—C(16)	1.48 (1)
Cl(2)—C(10)	1.739 (9)	C(22)—C(23)	1.51 (1)
Cl(3)—C(17)	1.71 (1)		

Cu(2)—Cu(1)—O(1)	85.0 (2)	Cu(2)—O(6)—C(8)	124.6 (5)
Cu(2)—Cu(1)—O(2)	83.9 (2)	Cu(2)—O(7)—C(15)	123.0 (5)
Cu(2)—Cu(1)—O(3)	84.2 (2)	Cu(2)—O(8)—C(22)	121.2 (5)
Cu(2)—Cu(1)—O(4)	81.3 (1)	O(1)—C(1)—O(5)	126.0 (7)
Cu(2)—Cu(1)—N(1)	177.6 (2)	O(1)—C(1)—C(2)	116.5 (7)
O(1)—Cu(1)—O(2)	88.8 (2)	O(5)—C(1)—C(2)	117.5 (7)
O(1)—Cu(1)—O(3)	169.2 (2)	C(1)—C(2)—C(3)	121.0 (7)
O(1)—Cu(1)—O(4)	89.2 (2)	C(1)—C(2)—C(7)	120.6 (7)
O(1)—Cu(1)—N(1)	96.2 (2)	C(3)—C(2)—C(7)	118.2 (7)
O(2)—Cu(1)—O(3)	89.6 (2)	Cl(1)—C(3)—C(2)	119.4 (6)
O(2)—Cu(1)—O(4)	165.2 (2)	Cl(1)—C(3)—C(4)	118.3 (7)
O(2)—Cu(1)—N(1)	98.2 (2)	O(2)—C(8)—O(6)	125.5 (7)
O(3)—Cu(1)—O(4)	89.7 (2)	O(2)—C(8)—C(9)	115.4 (7)
O(3)—Cu(1)—N(1)	94.6 (2)	O(6)—C(8)—C(9)	119.0 (7)
O(4)—Cu(1)—N(1)	96.6 (2)	C(8)—C(9)—C(10)	122.2 (7)

Table 2 (*cont.*)

Cu(1)—Cu(2)—O(5)	81.8 (2)	C(8)—C(9)—C(14)	118.3 (7)
Cu(1)—Cu(2)—O(6)	83.5 (2)	C(10)—C(9)—C(14)	119.5 (7)
Cu(1)—Cu(2)—O(7)	83.4 (2)	Cl(2)—C(10)—C(9)	122.9 (6)
Cu(1)—Cu(2)—O(8)	85.5 (2)	Cl(2)—C(10)—C(11)	115.1 (7)
Cu(1)—Cu(2)—N(2)	175.8 (2)	O(3)—C(15)—O(7)	126.6 (7)
O(5)—Cu(2)—O(6)	89.3 (2)	O(3)—C(15)—C(16)	114.5 (7)
O(5)—Cu(2)—O(7)	165.3 (2)	O(7)—C(15)—C(16)	118.8 (7)
O(5)—Cu(2)—O(8)	89.5 (2)	C(15)—C(16)—C(17)	120.3 (8)
O(5)—Cu(2)—N(2)	95.6 (2)	C(15)—C(16)—C(21)	121.8 (7)
O(6)—Cu(2)—O(7)	88.6 (2)	C(17)—C(16)—C(21)	117.8 (7)
O(6)—Cu(2)—O(8)	169.0 (2)	Cl(3)—C(17)—C(16)	120.4 (6)
O(6)—Cu(2)—N(2)	93.2 (2)	Cl(3)—C(17)—C(18)	117.8 (7)
O(7)—Cu(2)—O(8)	89.8 (2)	O(4)—C(22)—O(8)	126.6 (7)
O(7)—Cu(2)—N(2)	99.0 (2)	O(4)—C(22)—C(23)	118.7 (7)
O(8)—Cu(2)—N(2)	97.8 (2)	O(8)—C(22)—C(23)	114.7 (7)
Cu(1)—O(1)—C(1)	121.6 (5)	C(22)—C(23)—C(24)	122.3 (7)
Cu(1)—O(2)—C(8)	122.2 (5)	C(22)—C(23)—C(28)	119.4 (7)
Cu(1)—O(3)—C(15)	122.5 (5)	C(24)—C(23)—C(28)	118.1 (7)
Cu(1)—O(4)—C(22)	125.2 (5)	Cl(4)—C(24)—C(23)	120.3 (6)
Cu(2)—O(5)—C(1)	125.4 (5)	Cl(4)—C(24)—C(25)	118.0 (7)

Symmetry code: (i) $-x, -y, -z$; (ii) $-1-x, -y, -z$.

Complex (II). A green prismatic crystal, 0.5 × 0.3 × 0.1 mm, was used for data collection with the same diffractometer and experimental techniques used for complex (I): cell parameters refined by least squares for 34 2θ values ($20 < 2\theta < 28°$); $2\theta \leq 55°$ (h: $-30 \rightarrow 30$, k: $0 \rightarrow 13$, l: $0 \rightarrow 26$); θ–2θ scan; $0.973 < \sum(|F_o|/|F_o|_{\rm initial})/5 < 1.005$; 11921 reflections measured, 5253 reflections observed with $|F_o| > 3\sigma(|F_o|)$, 5124 unique [$R_{\rm int}(|F|) = 0.027$, $0.64 < A < 0.81$)]. Two independent CCl_4 molecules exist in the crystal with orientational disorder. All of the H atoms were calculated theoretically. $w = \sigma^{-1}(|F_o|)$, $R(F) = 0.074$, $wR = 0.049$, $S = 2.82$ for 682 variable parameters and 5124 unique reflections; $r/p = 7.5$, $\Delta/\sigma < 0.23$, $-0.98 < \Delta\rho < 0.91$ e Å^{-3}. The calculations were carried out using *XTAL*3.0 (Hall & Stewart, 1990) on a MIPS RS3230 computer at Keio University.

Atomic coordinates are listed in Table 1, and selected bond lengths and bond angles in Table 2.*

Magnetic susceptibilities over the temperature range of 80–300 K were determined by the Faraday method at Saga University. The procedure of deriving the $-2J$ value from the cryomagnetic data based on the Bleaney–Bowers equation is described elsewhere (Kawata *et al.*, 1992). An attempt to obtain crystals which do not effloresce under reduced pressure, by using several solvents, failed for the pyridine adduct.

Discussion. The molecular structures are shown in Fig. 1 with the atom-numbering schemes. The coordination geometry around the Cu atoms is

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* Lists of structure factors, anisotropic thermal parameters, bond lengths and bond angles and H-atom parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55097 (27 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AS0583]

square pyramidal for both complexes. (I) is isostructural with the 2-bromo substituted ligand (Harrison, Rettig & Trotter, 1972), and has a crystallographic centre of symmetry on the Cu···Cu axis. Projections of the molecular structures along the Cu···Cu axis are drawn in Fig. 2. Average bond distances and angles in the central cage structure, dihedral angles in the bridging benzoate groups and $-2J$ values of (I) and (II) are compared in Table 3. The $-2J$ value of the pyridine adduct may not correspond to the molecular structure of (II), because the magnetic susceptibilities were measured after the efflorescence of the crystals. For one of the two independent bridges of the aqua adduct, the bending angle of the OCO moiety to the Cu—O···O—Cu plane, φ_{bend}, is 12.5 (1)°. The abnormally small $-2J$ value of (I) (262 cm^{-1}) may be due to the bending in the bridge, which is unfavourable for the spin super-exchange interaction (Kawata *et al.*, 1992). Another factor which may reduce the $-2J$ value is the intermolecular hydrogen bonds of the aqua adduct. Distances between the O atoms of the hydrogen bonds in (I) are 2.837 (3) and 3.042 (3) Å. The $-2J$ values of aqua and pyridine adducts of copper(II) 2-nitrobenzoate are 328 and 340 cm^{-1}, respectively. The difference is only 12 cm^{-1}, although there exist inter-

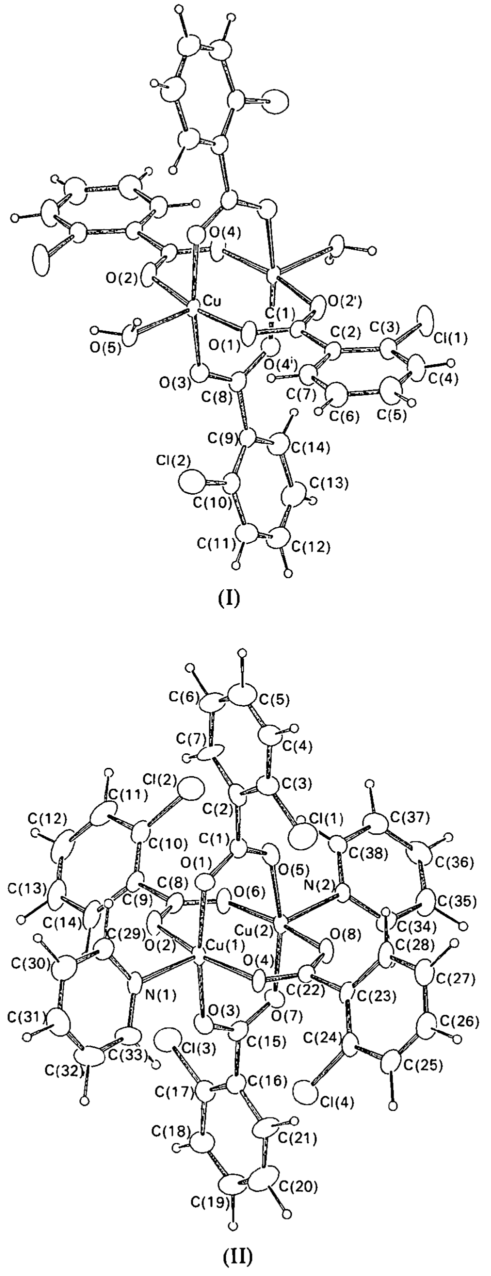

Fig. 1. *ORTEP*II drawing (Johnson, 1976) of dimeric complexes in (I) and (II) with thermal ellipsoids scaled at 35% in (I) and 25% in (II). H atoms are represented by circles of radius 0.08 Å.

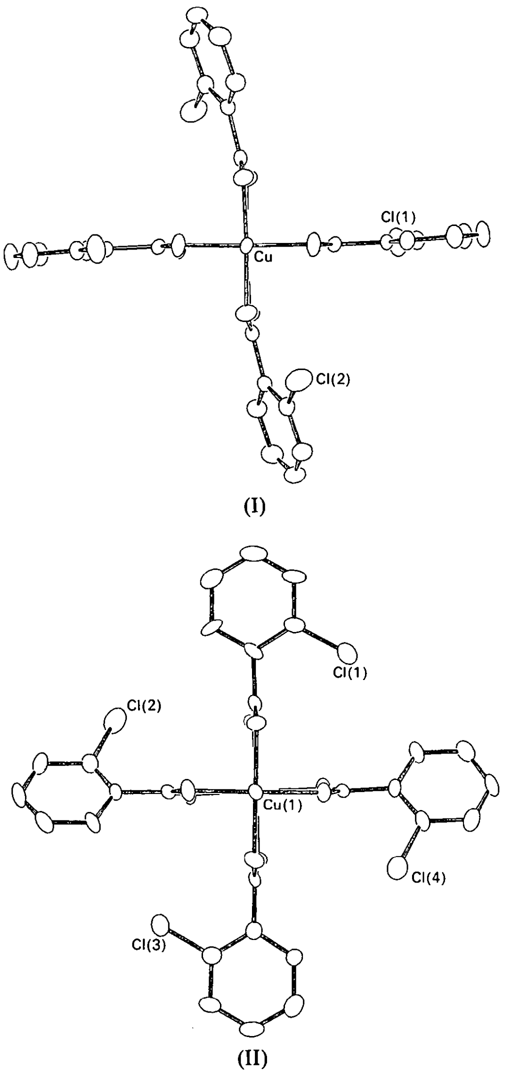

Fig. 2. Projection of the molecular structures of (I) and (II) along the Cu···Cu axis. The axial ligands are omitted for clarity.

Table 3. *A comparison of the average dimensions* (Å, °) *of the* $[Cu_2(COO)_4]$ *cage and* $-2J$ *values* (cm^{-1})

	(I) $[Cu_2(2\text{-Cl-PhCOO})_4(H_2O)_2]$	(II) $[Cu_2(2\text{-Cl-PhCOO})_4(\text{pyridine})_2].2CCl_4$
Cu···Cu	2.599 (1)	2.679 (1)
Cu—O	1.966 (2)	1.974 (5)
Cu—*L*	2.138 (2)	2.149 (6)
C—O	1.253 (4)	1.26 (1)
Cu—O—C	123.0 (2)	123.2 (5)
O—C—O	124.5 (2)	126.2 (7)
$\varphi_{\rm rot}$*	2.6 (3), 24.0 (2)	84.5 (3), 48.8 (3), 88.7 (3), 55.1 (3)
$\varphi_{\rm bend}$†	2.2 (1), 12.5 (1)	2.1 (2), 2.8 (2), 2.6 (2), 2.5 (2)
$-2J$	262	351‡

* The dihedral angle between the Ph ring and carboxyl moiety in the bridging benzoate ions.

† The dihedral angle between the Cu—O···O—Cu plane and carboxyl moiety in the bridge.

‡ The $-2J$ value of (II) was measured after the removal of CCl_4 from crystals under reduced pressure.

molecular hydrogen bonds in the aqua adduct, the O···O distance being 2.847 (4) Å with $\varphi_{\rm bend}$ less than 2° (Furukawa, Nakashima, Tokii & Muto, 1992). These results suggest that the $-2J$ value is more sensitive to the $\varphi_{\rm bend}$ than the intermolecular hydrogen bonds. One more example supports this speculation. The aqua adduct of copper(II) 2-methoxybenzoate shows the small $-2J$ value, 284 cm^{-1} (Adelsköld, Eriksson, Werner, Westdahl, Lučanska, Krätsmár-Šmogrovič & Valent, 1989) in accordance with the large $\varphi_{\rm bend}$ angles of 8.1 (6)–12.7 (6)°, the O···O distances of intermolecular hydrogen bonds ranging from 2.92 (2) to 3.11 (2) Å.

Rotation angles of the phenyl group to the carboxyl moiety, $\varphi_{\rm rot}$, are 2.6 (3) and 24.0 (2)° in (I), and from 48.8 (3) to 88.7 (3)° in (II). However, the $\varphi_{\rm rot}$ angle does not correlate with the $-2J$ value (Kawata *et al.*, 1992).

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Structure of the Clathrate Compound Tris(2,4-pentanedionato)iron(III)–*trans*-1,2-Dichloroethene (1/1)

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Abstract. $[Fe(C_5H_7O_2)_3].C_2H_2Cl_2$, $M_r = 450.12$, orthorhombic, $P2_1ca$, $a = 7.8439$ (23), $b = 10.2444$ (19), $c = 26.550$ (5) Å, $V = 2133.5$ (8) Å^3, $Z = 4$, D_m(flotation in KI/H_2O) = 1.37, $D_x = 1.40$ Mg m^{-3}, λ(Mo $K\alpha$) = 0.70930 Å, $\mu = 0.98$ mm^{-1}, $F(000) = 931.89$, $T = 295$ K, final $R = 0.056$ and $wR = 0.054$ for 1008 reflections with $I > 2.5\sigma(I)$. The molecular structure of the Fe(acac)$_3$ in the Fe(acac)$_3$.$C_2H_2Cl_2$ (II) clathrate phase is not significantly different from that in the non-clathrated phase (I) or in the clathrate phase of Fe(acac)$_3$.CCl_4 (IV). The *trans*-CHCl=CHCl guest molecule is located at an ordered general position in the clathrate phase.

Introduction. Tris(acetylacetonato)iron(III), Fe(acac)$_3$, was observed to form 1/2 addition compounds with chloroform molecules over 30 years ago (Steinbach & Bruns, 1958). This chelate complex was recently shown to form clathrate compounds with

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