F36	0.0853 (8)	0.4159 (4)	0.5900 (2)	0.120 (6)
N11	0.5954 (7)	0.4787 (3)	0.7401 (2)	0.0272 (16)
N12	0.6023 (7)	0.3304 (3)	0.7427 (2)	0.0247 (15)
N13	0.5998 (7)	0.4074 (3)	0.8401 (2)	0.0254 (15)
N14	0.2764 (7)	0.4047 (3)	0.7738 (2)	0.0274 (16)
N21	0.2115 (7)	0.2599 (3)	0.4306 (2)	0.0262 (15)
N22	−0.1078 (7)	0.2576 (3)	0.3612 (2)	0.0249 (15)
N23	−0.1203 (7)	0.3269 (3)	0.4636 (2)	0.0256 (16)
N24	−0.1054 (7)	0.1811 (3)	0.4606 (2)	0.0231 (15)
N31	0.0353 (7)	0.4987 (3)	1.0890 (2)	0.0322 (17)
N32	0.0941 (6)	0.4183 (3)	0.9891 (2)	0.0263 (15)
N33	0.0265 (7)	0.3475 (3)	1.0937 (2)	0.0353 (17)
N34	−0.2503 (7)	0.4213 (3)	1.0457 (2)	0.0281 (16)
C11	0.6631 (9)	0.5155 (4)	0.7206 (3)	0.0290 (20)
C12	0.7538 (10)	0.5630 (4)	0.6957 (3)	0.0428 (25)
C13	0.6771 (8)	0.2958 (3)	0.7251 (3)	0.0220 (18)
C14	0.7784 (9)	0.2496 (4)	0.7007 (3)	0.0322 (20)
C15	0.6681 (8)	0.4099 (4)	0.8745 (3)	0.0211 (17)
C16	0.7599 (8)	0.4130 (4)	0.9192 (3)	0.0316 (21)
C17	0.1437 (8)	0.4053 (4)	0.7762 (3)	0.0227 (18)
C18	−0.0287 (9)	0.4047 (4)	0.7825 (3)	0.0335 (20)
C21	0.3424 (8)	0.2595 (3)	0.4311 (3)	0.0231 (18)
C22	0.5136 (9)	0.2576 (3)	0.4312 (2)	0.0291 (18)
C23	−0.1697 (8)	0.2588 (4)	0.3252 (3)	0.0230 (17)
C24	−0.2475 (9)	0.2605 (4)	0.2773 (3)	0.0405 (23)
C25	−0.1855 (8)	0.3668 (4)	0.4804 (3)	0.0242 (18)
C26	−0.2686 (9)	0.4192 (4)	0.5010 (3)	0.0343 (22)
C27	−0.1599 (8)	0.1413 (3)	0.4794 (3)	0.0211 (18)
C28	−0.2334 (9)	0.0901 (4)	0.5068 (3)	0.0364 (22)
C31	0.0442 (8)	0.5406 (4)	1.1130 (3)	0.0301 (20)
C32	0.0554 (9)	0.5972 (4)	1.1427 (3)	0.0372 (22)
C33	0.1478 (8)	0.4148 (3)	0.9520 (3)	0.0239 (18)
C34	0.2148 (9)	0.4106 (4)	0.9032 (3)	0.0328 (21)
C35	0.0260 (9)	0.3055 (3)	1.1170 (3)	0.0267 (18)
C36	0.0310 (9)	0.2510 (4)	1.1470 (3)	0.0369 (21)
C37	−0.3771 (9)	0.4240 (4)	1.0491 (3)	0.0310 (21)
C38	−0.5554 (9)	0.4282 (4)	1.0533 (3)	0.0321 (20)
N41*S*	0.0115 (8)	0.4833 (3)	0.4332 (2)	0.0423 (18)
N42*S*	0.0609 (8)	0.3543 (3)	0.2408 (3)	0.0425 (20)
N43*S*	0.4704 (9)	0.3241 (3)	0.9621 (3)	0.0489 (20)
C41*S*	0.0102 (9)	0.4585 (4)	0.3977 (3)	0.0334 (19)
C42*S*	0.0136 (10)	0.4264 (4)	0.3509 (3)	0.0413 (21)
C43*S*	0.1529 (9)	0.3849 (4)	0.2249 (3)	0.0359 (22)
C44*S*	0.2782 (11)	0.4258 (5)	0.2047 (4)	0.0548 (28)
C45*S*	0.4032 (9)	0.2863 (4)	0.9804 (3)	0.0370 (22)
C46*S*	0.3225 (11)	0.2345 (5)	1.0051 (4)	0.0588 (29)

Table 2. *Selected geometric parameters* (Å, °)

Cu1—N11	2.019 (6)	Cu2—N23	2.006 (6)
Cu1—N12	2.018 (6)	Cu2—N24	2.019 (6)
Cu1—N13	2.004 (6)	Cu3—N31	2.004 (7)
Cu1—N14	1.968 (6)	Cu3—N32	1.994 (6)
Cu2—N21	1.997 (6)	Cu3—N33	2.017 (7)
Cu2—N22	1.999 (6)	Cu3—N34	2.030 (6)
N11—Cu1—N12	106.9 (3)	N22—Cu2—N23	107.0 (3)
N11—Cu1—N13	104.6 (3)	N22—Cu2—N24	106.7 (3)
N11—Cu1—N14	112.3 (3)	N23—Cu2—N24	105.0 (2)
N12—Cu1—N13	104.6 (3)	N31—Cu3—N32	112.3 (3)
N12—Cu1—N14	114.0 (3)	N31—Cu3—N33	110.9 (3)
N13—Cu1—N14	113.7 (3)	N31—Cu3—N34	105.3 (3)
N21—Cu2—N22	113.5 (2)	N32—Cu3—N33	112.7 (3)
N21—Cu2—N23	112.4 (2)	N32—Cu3—N34	112.2 (3)
N21—Cu2—N24	111.6 (2)	N33—Cu3—N34	102.7 (3)

The Cu-atom positions were located by direct methods (Sheldrick, 1985) and the remaining non-H atoms were found by repeated structure-factor and electron density calculations (Sheldrick, 1976).

Data collection: Enraf–Nonius software. Cell refinement: Enraf–Nonius software. Data reduction: Enraf–Nonius software. Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELX*76 (Sheldrick, 1976). Molecular graphics: *ORTEP*II (Johnson, 1976), *PLUTO* (Motherwell & Clegg, 1978).

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Lists of structure factors, anisotropic displacement parameters and complete geometry have been deposited with the IUCr (Reference: HU1132). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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μ-Aqua-bis(μ-trichloroacetato-*O*:*O*′)bis[(3-cyanopyridine)(trichloroacetato)copper(II)] Dichloroform Solvate

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Abstract

The crystal structure of the title compound, $[Cu_2(C_2Cl_3O_2)_4(C_6H_4N_2)_2(H_2O)].2CHCl_3$, was determined by single-crystal X-ray diffraction. Two Cu

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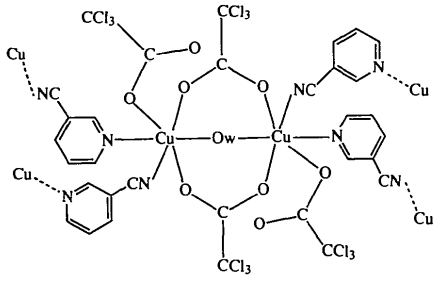
atoms, separated by a distance of 3.567 (2) Å, are bridged by a water molecule and two trichloroacetate ions to form a local binuclear unit. The binuclear units are linked by 3-cyanopyridine molecules to form a two-dimensional network. The coordination geometry around Cu is tetragonally elongated octahedral. The spin-exchange interaction between the Cu atoms in the local binuclear unit is weakly antiferromagnetic.

Comment

Magneto–structural correlations of dimeric copper(II) trichloroacetates have been investigated (Uekusa *et al.*, 1992). The title compound, (I), was obtained unexpectedly along with the usual cage-structure complex, $[Cu(Cl_3CCOO)_2(3\text{-CN-py})]_2$, during synthesis using 3-cyanopyridine (3-CN-py) as a ligand.



(I)

The binuclear copper(II) unit is linked by 3-cyanopyridine molecules to form a two-dimensional network (Fig. 1). The tris-bridged binuclear unit is similar to that of $Os_2(\mu\text{-O})(\mu\text{-}CH_3COO)_2Cl_4(PPh_3)_2$ (Armstrong, Robinson & Walton, 1981). The bridging water molecule, O(13), lies on a crystallographic twofold axis and forms hydrogen bonds with the terminal O(15) and O(15^i) atoms of the monodentate trichloroacetate ions (Fig. 2). The coordination geometry around the copper(II) atom is tetragonally elongated octahedral and the magnetic orbital may consist predominantly of the $d_{x^2-y^2}$ orbital in the square plane formed by Cu, N(1), O(12), O(13) and O(14). Since the two square planes in the binuclear unit are approximately perpendicular to each other, the spin-exchange interaction seems to occur mainly through the Cu—O(13)—Cu bridge. The cryomagnetic data were fitted to the modified Bleaney–Bowers equation (1), taking into account the interactions between the binuclear units:

$$\chi_A = [Ng^2\beta^2/3k(T-\Theta)][1+\tfrac{1}{3}\exp(-2J/kT)]^{-1} + N\alpha \quad (1)$$

where Θ is the Curie temperature (Inoue, Kishita & Kubo, 1967). A least-squares refinement gave the following parameters: $-2J = 39\ cm^{-1}$ ($H = -2JS_1.S_2$), $g = 2.10$, $\Theta = -12.5$ K. This indicates that the spin-exchange interaction in and between the binuclear unit is weakly antiferromagnetic. In contrast, the μ-hydroxo-bis(μ-formato)-bridged binuclear copper(II) complex $[Cu_2(OH)(HCOO)_2(bpy)_2]BF_4$ (where bpy = 2,2′-bipyridine) shows a ferromagnetic interaction with $-2J = -99\ cm^{-1}$. In this complex, the coordination geometry at one of the Cu atoms is distorted trigonal bipyramidal and that at the other Cu is disorted square pyramidal with a Cu···Cu distance of 3.171 (1) Å (Tokii, Nagamatsu, Hamada & Nakashima, 1992).

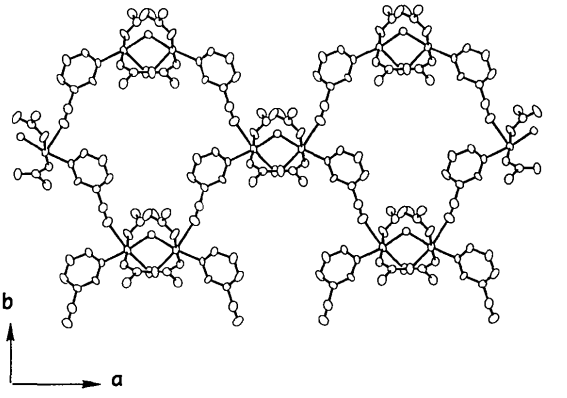


Fig. 1. The two-dimensional network parallel to the *ab* plane. The Cl and H atoms are omitted for clarity.

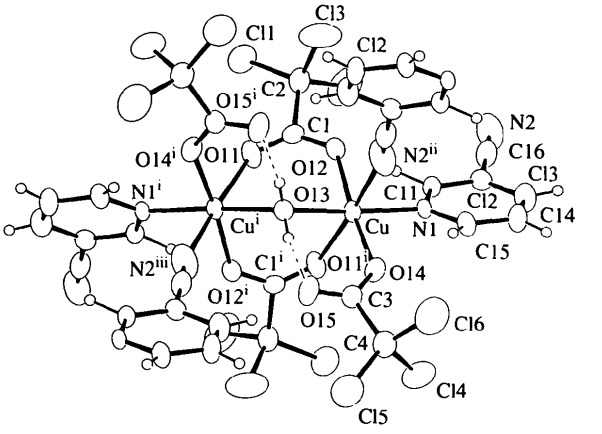


Fig. 2. *ORTEP* drawing (Johnson, 1965) of the local binuclear unit with the numbering scheme. The displacement ellipsoids are drawn at the 30% probability level. Symmetry codes: (i) $1-x, y, \frac{1}{2}-z$; (ii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; (iii) $-\frac{1}{2}+x, -\frac{1}{2}+y, z$.

Experimental

Crystal data

$[Cu_2(C_2Cl_3O_2)_4(C_6H_4N_2)_2\text{-}(H_2O)].2CHCl_3$	Mo $K\alpha$ radiation $\lambda = 0.71073$ Å

M_r = 1241.56
Monoclinic
$C2/c$
a = 17.171 (2) Å
b = 13.309 (2) Å
c = 21.372 (3) Å
β = 112.45 (1)°
V = 4514 (4) Å^3
Z = 4
D_x = 1.83 Mg m^{-3}

Cell parameters from 32 reflections
θ = 10–14°
μ = 2.07 mm^{-1}
T = 298 K
Tabular
0.45 × 0.40 × 0.25 mm
Pale green

Data collection

Rigaku AFC-5 four-circle diffractometer
θ–2θ scans
Absorption correction: by integration from crystal shape
T_{min} = 0.480, T_{max} = 0.652
5356 measured reflections
5167 independent reflections

2710 observed reflections [$|F_o| > 3\sigma(|F_o|)$]
R_{int} = 0.017
θ_{max} = 27.5°
$h = 0 \rightarrow 22$
$k = 0 \rightarrow 17$
$l = -27 \rightarrow 27$
5 standard reflections monitored every 100 reflections
intensity decay: 19%

Refinement

Refinement on F
R = 0.077
wR = 0.066
S = 4.74
2710 reflections
273 parameters
All H-atom parameters refined
$w = 1/\sigma^2(F)$

$(\Delta/\sigma)_{max}$ = 0.11 (for non-H atoms)
$\Delta\rho_{max}$ = 1.66 e Å^{-3}
$\Delta\rho_{min}$ = −1.22 e Å^{-3}
Extinction correction: none
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic displacement parameters* (Å^2)

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

	x	y	z	U_{eq}
Cu	0.61231 (7)	0.29982 (9)	0.28748 (6)	0.0352 (4)
O(11)	0.4487 (4)	0.1888 (6)	0.1664 (3)	0.059 (3)
O(12)	0.5867 (4)	0.2266 (5)	0.2034 (3)	0.041 (3)
O(13)	1/2	0.3771 (7)	1/4	0.036 (4)
O(14)	0.6480 (4)	0.3775 (5)	0.3703 (3)	0.051 (3)
O(15)	0.5389 (4)	0.4735 (6)	0.3615 (4)	0.067 (4)
N(1)	0.7295 (4)	0.2395 (6)	0.3213 (3)	0.032 (3)
Cl(1)	0.4356 (2)	0.0827 (3)	0.0465 (2)	0.088 (2)
Cl(2)	0.6045 (3)	0.0410 (3)	0.1330 (2)	0.133 (2)
Cl(3)	0.5641 (3)	0.2236 (3)	0.0587 (2)	0.137 (2)
Cl(4)	0.7162 (2)	0.3818 (3)	0.5179 (2)	0.093 (2)
Cl(5)	0.6003 (2)	0.5411 (3)	0.5000 (2)	0.118 (2)
Cl(6)	0.7390 (2)	0.5607 (3)	0.4555 (2)	0.109 (2)
C(1)	0.5178 (6)	0.1892 (8)	0.1641 (4)	0.039 (4)
C(2)	0.5291 (6)	0.1345 (8)	0.1028 (5)	0.053 (5)
C(3)	0.6096 (7)	0.4385 (8)	0.3912 (5)	0.044 (5)
C(4)	0.6617 (6)	0.4788 (8)	0.4644 (5)	0.054 (5)
C(11)	0.7421 (6)	0.1491 (7)	0.2984 (5)	0.034 (4)
C(12)	0.8214 (6)	0.1099 (7)	0.3154 (5)	0.039 (4)
C(13)	0.8919 (8)	0.1602 (9)	0.3587 (6)	0.059 (6)
C(14)	0.8789 (7)	0.254 (1)	0.3800 (6)	0.059 (5)
C(15)	0.7969 (6)	0.2895 (9)	0.3609 (5)	0.044 (5)
C(16)	0.8308 (6)	0.0131 (9)	0.2871 (5)	0.054 (5)
N(2)	0.8369 (6)	−0.0594 (8)	0.2621 (5)	0.077 (5)
C(20)	0.877 (3)	0.347 (4)	0.184 (2)	0.39 (2)
Cl(7)	0.9025 (5)	0.3063 (7)	0.1114 (4)	0.285 (7)
Cl(8)	0.7828 (5)	0.3053 (7)	0.1677 (4)	0.274 (6)
Cl(9)†	0.9258 (8)	0.199 (1)	0.1991 (6)	0.210 (9)
Cl(10)‡	0.914 (1)	0.442 (2)	0.221 (1)	0.133 (7)
Cl(11)‡	0.880 (1)	0.449 (2)	0.169 (1)	0.130 (6)

† Occupancy 0.5.
‡ Occupancy 0.25.

Table 2. *Selected geometric parameters* (Å, °)

Cu—O(12)	1.942 (6)	O(12)—C(1)	1.26 (1)
Cu—O(13)	2.059 (5)	O(14)—C(3)	1.23 (1)
Cu—O(14)	1.937 (6)	O(15)—C(3)	1.23 (1)
Cu—N(1)	2.027 (7)	N(1)—C(11)	1.35 (1)
Cu—O(11^i)	2.245 (8)	N(1)—C(15)	1.32 (1)
Cu—N(2^{ii})	2.469 (11)	O(13)—H(13)	0.84 (11)
O(11)—C(1)	1.21 (1)		
O(12)—Cu—O(13)	92.5 (2)	N(1)—Cu—N(2^{ii})	89.3 (3)
O(12)—Cu—O(14)	174.2 (3)	O(11^i)—Cu—N(2^{ii})	171.1 (3)
O(12)—Cu—N(1)	88.5 (3)	C(1)—O(11)—Cu^i	130.2 (6)
O(12)—Cu—O(11^i)	95.6 (3)	Cu—O(12)—C(1)	129.6 (7)
O(12)—Cu—N(2^{ii})	88.6 (3)	Cu—O(13)—Cu^i	120.0 (5)
O(13)—Cu—O(14)	90.7 (2)	Cu—O(14)—C(3)	131.0 (6)
O(13)—Cu—N(1)	172.6 (3)	Cu—N(1)—C(11)	119.9 (5)
O(13)—Cu—O(11^i)	88.6 (2)	Cu—N(1)—C(15)	122.4 (7)
O(13)—Cu—N(2^{ii})	83.4 (3)	Cu—N(2^{ii})—C(16^{ii})	164.8 (10)
O(14)—Cu—N(1)	87.8 (3)	Cu—O(13)—H(13)	97 (8)
O(14)—Cu—O(11^i)	89.3 (3)	Cu—O(13)—H(13^i)	112 (9)
O(14)—Cu—N(2^{ii})	87.0 (3)	H(13)—O(13)—H(13^i)	121 (11)
N(1)—Cu—O(11^i)	98.6 (3)		
Cu···Cu^i	3.567 (2)		
O(15)···H(13)	1.73 (11)	O(15)···H(13)—O(13)	169 (14)
O(13)···O(15)	2.561 (9)		

Symmetry codes: (i) $1-x, y, \frac{1}{2}-z$; (ii) $\frac{3}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$.

Rotational disorder is observed in the crystal solvent, $CHCl_3$. One of the Cl atoms was tentatively assumed to take three possible positions with site occupation factors of 50, 25 and 25%. The relatively large R value may be caused by the disorder. Decay of the crystal during the X-ray data collection was corrected based on the variation of standards (19%). Structure analysis was carried out on a FACOM M-780/10 computer using the *UNICS*III program system (Sakurai & Kobayashi, 1979). The magnetic susceptibilities over the temperature range of 80–300 K were determined by the Faraday method.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: HU1083). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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