217 parameters	Atomic scattering factors from Cromer & Waber (1974)
H-atom parameters not refined	

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

$B_{\rm iso}$ for C(15); $B_{\rm eq} = (8\pi^2/3)\sum_i\sum_j U_{ij}a_i^*a_j^*\mathbf{a}_i.\mathbf{a}_j$ for all others.

	x	y	z	$B_{\rm eq}/B_{\rm iso}$
Cu(1)	0.55216 (9)	0.23527 (10)	0.61531 (5)	2.70 (3)
Cu(2)	1/2	0.3301 (1)	3/4	2.54 (4)
Cl	0.6455 (2)	0.3695 (3)	0.5814 (1)	5.23 (10)
O(1)	0.5081 (6)	0.1151 (5)	0.6604 (3)	4.4 (2)
O(2)	0.4868 (5)	0.3292 (5)	0.6698 (3)	2.8 (2)
O(3)†	0.4300 (7)	0.1858 (10)	0.7473 (7)	3.8 (4)
N(1)	0.4814 (7)	−0.1739 (7)	0.6273 (4)	3.6 (3)
N(2)	0.6258 (7)	0.1193 (7)	0.5728 (4)	3.5 (3)
N(3)	0.3735 (6)	0.4266 (7)	0.7460 (4)	3.5 (2)
N(4)	0.4257 (8)	0.2833 (9)	0.5582 (4)	4.4 (3)
C(1)	0.5710 (8)	0.0211 (9)	0.5810 (5)	4.0 (3)
C(2)	0.5413 (8)	0.0120 (10)	0.6431 (5)	3.8 (3)
C(3)	0.4641 (8)	−0.0691 (10)	0.6521 (5)	4.4 (4)
C(4)	0.3998 (10)	−0.241 (1)	0.6305 (5)	6.8 (4)
C(5)	0.562 (1)	−0.227 (1)	0.6541 (5)	7.1 (5)
C(6)	0.6373 (9)	0.1348 (10)	0.5133 (5)	5.4 (4)
C(7)	0.7161 (8)	0.1135 (10)	0.5998 (5)	5.2 (4)
C(8)	0.3940 (9)	0.377 (1)	0.5916 (5)	4.4 (4)
C(9)	0.3964 (9)	0.3517 (9)	0.6528 (5)	3.5 (3)
C(10)	0.3628 (9)	0.4486 (9)	0.6867 (5)	4.6 (4)
C(11)	0.2925 (8)	0.3645 (10)	0.7660 (5)	5.5 (4)
C(12)	0.3755 (9)	0.5272 (10)	0.7804 (5)	5.6 (4)
C(13)	0.4453 (10)	0.320 (1)	0.5011 (5)	7.8 (5)
C(14)	0.3548 (10)	0.197 (1)	0.5585 (5)	6.8 (5)
C(15)†	0.355 (1)	0.114 (2)	0.7342 (9)	3.1 (5)

† 50% occupancy.

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

Cu(1)—Cl	2.289 (3)	Cu(1)—O(1)	1.948 (7)
Cu(1)—O(2)	1.984 (6)	Cu(1)—N(2)	2.057 (9)
Cu(1)—N(4)	2.35 (1)	Cu(2)—O(2)	1.924 (6)
Cu(2)—O(3)	2.06 (1)	Cu(2)—N(3)	2.178 (9)
O(1)—C(2)	1.43 (1)	O(2)—C(9)	1.39 (1)
O(3)—C(15)	1.43 (2)		
Cl—Cu(1)—O(1)	161.0 (3)	Cu(2)—O(3)—C(15)	157 (1)
Cl—Cu(1)—O(2)	94.4 (2)	O(1)—Cu(1)—N(2)	84.3 (3)
Cl—Cu(1)—N(2)	92.2 (3)	O(2)—Cu(1)—N(2)	168.5 (4)
Cl—Cu(1)—N(4)	93.5 (3)	O(2)—Cu(1)—N(4)	82.2 (3)
O(1)—Cu(1)—O(2)	86.4 (3)	N(2)—Cu(1)—N(4)	106.8 (4)
O(1)—Cu(1)—N(4)	105.4 (4)	O(2)—Cu(2)—O(2′)	179.3 (4)
Cu(1)—N(2)—C(1)	104.2 (6)	O(2)—Cu(2)—O(3′)	94.3 (5)
Cu(1)—N(2)—C(6)	116.8 (8)	Cu(2)—N(3)—C(10)	103.6 (7)
Cu(1)—N(2)—C(7)	105.9 (8)	Cu(2)—N(3)—C(11)	110.7 (6)
O(2)—Cu(2)—O(3)	85.1 (5)	Cu(2)—N(3)—C(12)	114.9 (8)
O(2)—Cu(2)—N(3)	83.0 (3)	O(3)—Cu(2)—N(3′)	152.7 (4)
O(2)—Cu(2)—N(3′)	97.4 (3)	N(3)—Cu(2)—N(3′)	113.1 (5)
O(3)—Cu(2)—O(3′)	58.5 (6)	Cu(1)—N(4)—C(13)	118.1 (8)
O(3)—Cu(2)—N(3)	94.2 (4)	Cu(1)—O(1)—C(2)	115.0 (6)
Cu(1)—O(2)—Cu(2)	127.5 (4)	Cu(1)—N(4)—C(8)	97.2 (7)
Cu(1)—O(2)—C(9)	111.6 (6)	Cu(1)—N(4)—C(14)	110.1 (7)
Cu(2)—O(2)—C(9)	112.5 (6)		

The metal-atom positions were determined by direct methods. The methanol ligand was disordered over two sites related by a twofold rotation axis. The occupancy factor of the methanol ligand for each site is 50%. All non-H atoms except C(15) of the disordered methanol were refined anisotropically. The positions of H atoms except H(38) were calculated and their isotropic displacement factors were tied to the corresponding C atom's isotropic displacement factor (multiplied by 1.2). H(38) was located directly from the difference Fourier map and its position was not refined.

Data collection: *MSC/AFC Diffractometer Control Software* (Molecular Structure Corporation, 1988). Cell refinement: *MSC/AFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992). Program(s) used to solve structure: *TEXSAN*. Program(s) used to refine structure: *TEXSAN*. Molecular graphics: *TEXSAN*.

These studies were supported by the Natural Science and Engineering Research Council of Canada.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: CF1030). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Cromer, D. T. & Waber. J. T. (1974). *International Tables for X-ray Crystallography*, Vol. IV, Table 2.2A. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

Molecular Structure Corporation (1988). *MSC/AFC Diffractometer Control Software*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Molecular Structure Corporation (1992). *TEXSAN. Single Crystal Structure Analysis Package*. MSC, 3200 Research Forest Drive, The Woodlands, TX 77381, USA.

Waltz, L., Paulus, H. & Haase, W. (1985). *J. Chem. Soc. Dalton Trans.* pp. 913–920.

Wang, S., Pang, Z., Smith, K. D. L. & Wagner, M. J. (1994). *J. Chem. Soc. Dalton Trans.* pp. 955–964.

Wang, S., Pang, Z., Zheng, J. C. & Wagner, M. J. (1993). *Inorg. Chem.* **32**, 5975–5980.

Wang, S., Trepanier, S. J. & Wagner, M. J. (1993). *Inorg. Chem.* **32**, 833–840.

Acta Cryst. (1996). C**52**, 43–45

A Tetracarboxylatobenzene-Bridged Binuclear Copper(II) Complex

WEI CHEN,[a] NGEE HENG TIOH,[a] JIAN-ZHONG ZOU,[b] ZHENG XU[b] AND XIAO-ZENG YOU[b]

[a]*Department of Chemistry, University of Malaya, 59100 Kuala Lumpur, Malaysia, and* [b]*Coordination Chemistry Institute, National Key Laboratory of Coordination Chemistry, Nanjing University, Nanjing 210093, People's Republic of China*

(*Received 4 April 1995; accepted 25 July 1995*)

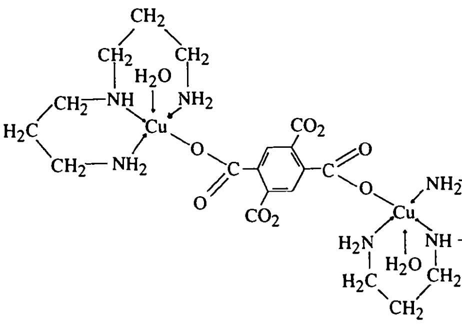
Abstract

The tetracarboxylatobenzene tetraanion in μ-(1,2,4,5-benzenetetracarboxylato-O^1:O^4)bis[aqua(4-azaheptane-1,7-diamine-N,N',N'')copper(II)] octahydrate, [{Cu-

$(C_6H_{17}N_3)(H_2O)\}_2(\mu\text{-}C_{10}H_2O_8)].8H_2O$, bridges two N,N',N''-chelated aquacopper entities in a monodentate manner to give rise to square-pyramidal coordination at the metal centres. Hydrogen bonding involving the three N atoms, the four carboxyl O atoms and the five water molecules gives rise to a three-dimensional network structure.

Comment

The title complex, (I), was synthesized for a study on long-range magnetic interactions between Cu atoms.



(I)

The terephthalato dianion, an appropriate bridging unit with a separation of 11–12 Å between the two magnetic centres, has been used for studies of magnetic interactions (Francesconi, Corbin, Clauss, Hendrickson & Stucky, 1981; Tinti, Verdaguer, Kahn & Savariault, 1987). Strong magnetic interactions propagated through the bridging ligand were observed in the bis(1,4,7-trimethyl-1,4,7-triazacyclononane)diaquadicopper(II) perchlorate derivative (Chaudhuri *et al.*, 1988), which has a Cu···Cu distance of 11.25 Å. The corresponding distance in the present complex (11.19 Å) compares well with the previously reported distance.

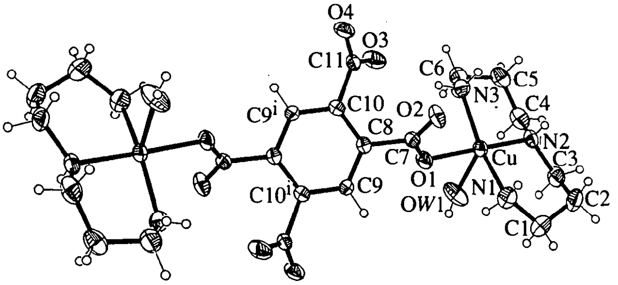


Fig. 1. Atomic labelling scheme for title complex. Displacement ellipsoids are drawn at the 50% probability level.

The complex also adopts square-pyramidal geometry at the metal; the three N atoms of the triamine and one O atom of the tetraanion comprise the basal plane. The water molecule occupies the apical position.

The eight lattice water molecules form hydrogen bonds (Table 3) with one another to give rise to a distorted cube structure (Fig. 2). *OW*2 and *OW*5, however, are not linked by a hydrogen bond (Fig. 2) (*OW*2···*OW*5 3.693 Å).

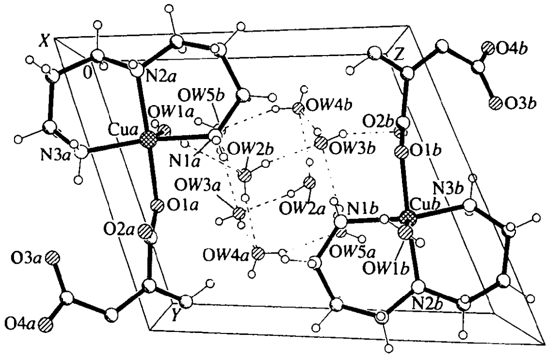


Fig. 2. Packing diagram projected down the *a* axis.

Experimental

Piperidinium 1,2,4,5-benzenetetracarboxylate was reacted with 4-azaheptane-1,7-diamine and copper perchlorate hexahydrate. The reactants, in a 1:2:2 molar stoichiometry, were heated in methanol for 2 h at 333 K. The solvent was evaporated and the product recrystallized from water.

Crystal data

$[Cu_2(C_{10}H_2O_8)(C_6H_{17}N_3)_2\text{-}(H_2O)_2].8H_2O$
$M_r = 819.81$
Triclinic
$P\bar{1}$
$a = 9.019\ (2)$ Å
$b = 9.986\ (1)$ Å
$c = 11.599\ (2)$ Å
$\alpha = 65.32\ (1)^\circ$
$\beta = 71.77\ (1)^\circ$
$\gamma = 71.57\ (1)^\circ$
$V = 880.5\ (3)$ Å^3
$Z = 1$
$D_x = 1.546$ Mg m^{-3}

Mo $K\alpha$ radiation
$\lambda = 0.71073$ Å
Cell parameters from 23 reflections
$\theta = 14\text{–}16^\circ$
$\mu = 1.289$ mm^{-1}
$T = 300\ (2)$ K
Parallelepiped
0.3 × 0.3 × 0.18 mm
Blue

Data collection

CAD-4 diffractometer
$\omega\text{–}2\theta$ scans
Absorption correction: ψ scan (North, Phillips & Mathews, 1968)
$T_{min} = 0.844$, $T_{max} = 0.998$
3251 measured reflections
3083 independent reflections

2776 observed reflections $[I > 2\sigma(I)]$
$R_{int} = 0.0192$
$\theta_{max} = 24.97^\circ$
$h = -10 \rightarrow 10$
$k = -10 \rightarrow 11$
$l = 0 \rightarrow 13$
3 standard reflections
frequency: 60 min
intensity decay: none

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.0323$
$wR(F^2) = 0.0836$

$(\Delta/\sigma)_{max} = 0.001$
$\Delta\rho_{max} = 0.670$ e Å^{-3}
$\Delta\rho_{min} = -0.298$ e Å^{-3}

$S = 1.154$
3083 reflections
301 parameters
H atoms located and refined with fixed $U = 0.05$ Å^2
$w = 1/[\sigma^2(F_o^2) + (0.0515P)^2 + 0.3500P]$ where $P = (F_o^2 + 2F_c^2)/3$

Extinction correction: none
Atomic scattering factors from *International Tables for Crystallography* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.4)

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

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

	x	*y*	*z*	$U_{\rm eq}$
Cu	0.19152 (3)	0.37030 (3)	0.19209 (3)	0.0256 (1)
O1	0.0872 (2)	0.5889 (2)	0.1458 (2)	0.034 (1)
O2	0.3097 (2)	0.6648 (2)	0.1081 (2)	0.039 (1)
O3	0.2811 (2)	0.7556 (2)	−0.1701 (2)	0.039 (1)
O4	0.3842 (2)	0.9537 (2)	−0.2283 (2)	0.038 (1)
O*W*1	−0.0621 (3)	0.3351 (3)	0.2284 (3)	0.052 (1)
O*W*2	0.2018 (3)	−0.4874 (3)	0.5925 (3)	0.066 (1)
O*W*3	0.3701 (4)	−0.3707 (4)	0.3388 (3)	0.067 (1)
O*W*4	0.5763 (3)	−0.2360 (3)	0.3599 (2)	0.045 (1)
O*W*5	0.4892 (3)	−0.3161 (3)	0.6225 (2)	0.056 (1)
N1	0.1542 (4)	0.3589 (3)	0.3752 (2)	0.039 (1)
N2	0.2741 (3)	0.1450 (2)	0.2319 (2)	0.029 (1)
N3	0.3114 (3)	0.4131 (3)	0.0073 (2)	0.041 (1)
C1	0.1198 (4)	0.2242 (4)	0.4878 (3)	0.049 (1)
C2	0.2288 (4)	0.0820 (4)	0.4712 (3)	0.049 (1)
C3	0.2053 (4)	0.0487 (3)	0.3635 (3)	0.040 (1)
C4	0.2591 (4)	0.0937 (3)	0.1342 (3)	0.041 (1)
C5	0.3497 (4)	0.1648 (3)	−0.0008 (3)	0.041 (1)
C6	0.2858 (4)	0.3305 (4)	−0.0623 (3)	0.044 (1)
C7	0.1675 (3)	0.6887 (3)	0.1044 (2)	0.025 (1)
C8	0.0788 (3)	0.8490 (2)	0.0478 (2)	0.021 (1)
C9	−0.0586 (3)	0.9083 (3)	0.1229 (2)	0.022 (1)
C10	0.1372 (3)	0.9417 (2)	−0.0769 (2)	0.020 (1)
C11	0.2790 (3)	0.8790 (3)	−0.1648 (2)	0.024 (1)

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

Cu—O1	1.994 (2)	N2—C4	1.480 (4)
Cu—O*W*1	2.306 (2)	N3—C6	1.476 (4)
Cu—N1	2.003 (3)	C1—C2	1.499 (5)
Cu—N3	2.006 (2)	C2—C3	1.507 (5)
Cu—N2	2.030 (2)	C4—C5	1.503 (5)
O1—C7	1.260 (3)	C5—C6	1.499 (4)
O2—C7	1.240 (3)	C7—C8	1.508 (3)
O3—C11	1.254 (3)	C8—C9	1.392 (3)
O4—C11	1.245 (3)	C8—C10	1.393 (3)
N1—C1	1.469 (4)	C9—C10^{i}	1.389 (3)
N2—C3	1.483 (3)	C10—C11	1.509 (3)
O1—Cu—O*W*1	84.90 (8)	N2—C3—C2	113.6 (2)
O1—Cu—N1	88.24 (9)	N2—C4—C5	114.2 (2)
O1—Cu—N2	172.52 (8)	C4—C5—C6	114.3 (3)
O1—Cu—N3	88.78 (9)	N3—C6—C5	109.6 (2)
N1—Cu—O*W*1	90.89 (11)	O1—C7—O2	125.3 (2)
N1—Cu—N3	154.41 (12)	O1—C7—C8	115.7 (2)
N1—Cu—N2	95.25 (10)	O2—C7—C8	119.0 (2)
N2—Cu—O*W*1	88.42 (9)	C7—C8—C9	119.9 (2)
N2—Cu—N3	90.88 (10)	C7—C8—C10	120.9 (2)
N3—Cu—O*W*1	114.14 (11)	C9—C8—C10	119.2 (2)
Cu—O1—C7	121.5 (2)	C8—C9—C10^{i}	121.4 (2)
Cu—N1—C1	122.6 (2)	C8—C10—C11	120.8 (2)
C3—N2—C4	109.4 (2)	C8—C10—C9^{i}	119.4 (2)
Cu—N2—C4	113.2 (2)	C9^{i}—C10—C11	119.8 (2)
Cu—N2—C3	114.9 (2)	O3—C11—O4	124.5 (2)
Cu—N3—C6	115.8 (2)	O3—C11—C10	117.3 (2)
N1—C1—C2	112.1 (3)	O4—C11—C10	118.2 (2)
C1—C2—C3	113.2 (3)		

Symmetry code: (i) $-x, 2-y, -z$.

Table 3. *Hydrogen-bonding geometry (Å, °)*

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N1—H1···O*W*5^{i}	0.83 (4)	2.34	3.114 (4)	155
N1—H2···O1	0.79 (4)	2.46	2.783 (3)	106
N1—H2···O*W*2^{ii}	0.79 (4)	2.37	3.023 (4)	141
N2—H9···O4^{iii}	0.73 (4)	2.20	2.916 (3)	166
N3—H16···O2^{iii}	0.84 (4)	2.47	3.178 (3)	151
N3—H17···O1	0.81 (4)	2.52	2.798 (3)	102
N3—H17···O3	0.81 (4)	2.35	3.145 (3)	167
O*W*1—H18···O3^{iv}	0.77 (4)	2.01	2.767 (3)	170
O*W*1—H19···O*W*2^{ii}	0.74 (4)	2.12	2.829 (4)	162
O*W*2—H21···O*W*4^{v}	0.74 (4)	2.08	2.804 (3)	167
O*W*2—H22···O*W*3	0.80 (4)	2.00	2.790 (4)	172
O*W*3—H23···O*W*4	0.69 (4)	2.06	2.733 (4)	168
O*W*3—H24···O2^{vi}	0.81 (4)	1.98	2.753 (4)	161
O*W*4—H25···O4^{iii}	0.73 (4)	1.95	2.665 (3)	171
O*W*4—H26···O*W*5	0.77 (4)	1.98	2.721 (4)	161
O*W*5—H27···O3^{vii}	0.79 (4)	1.97	2.753 (3)	171
O*W*5—H28···O*W*3^{v}	0.69 (4)	2.23	2.876 (4)	158

Symmetry codes: (i) $1-x, -y, 1-z$; (ii) $-x, -y, 1-z$; (iii) $1-x, 1-y, -z$; (iv) $-x, 1-y, -z$; (v) $1-x, -1-y, 1-z$; (vi) $x, y-1, z$; (vii) $x, y-1, 1+z$.

Data collection: *CAD*-4 *VAX/PC* (Enraf–Nonius, 1988). Cell refinement: *CAD*-4 *VAX/PC*. Data reduction: *MolEN* (Fair, 1990). Program(s) used to solve structure: *SHELXS*86 (Sheldrick, 1985). Program(s) used to refine structure: *SHELXL*93 (Sheldrick, 1993). Molecular graphics: *SHELXTL-Plus* (Sheldrick, 1991). Software used to prepare material for publication: *SHELXL*93.

We thank the State Science and Technology Commission and the National Nature Science Foundation (People's Republic of China) and the University of Malaya for supporting this work.

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: KH1050). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

References

Bakalbassis, E. G., Mrozinski, J. & Tsipis, C. A. (1986). *Inorg. Chem.* **25**, 3684–3690.

Chaudhuri, P., Oder, K., Wieghardt, K., Gehring, S., Haase, W., Nuber, B. & Weiss, J. (1988). *J. Am. Chem. Soc.* **110**, 3657–3658.

Enraf–Nonius (1988). *CAD-4 VAX/PC Fortran System. Operator's Guide to the Enraf–Nonius CAD-4 Diffractometer Hardware, its Software and the Operating System.* Enraf–Nonius, Delft, The Netherlands.

Fair, C. K. (1990). *MolEN. An Interactive Intelligent System for Crystal Structure Analysis.* Enraf–Nonius, Delft, The Netherlands.

Francesconi, L. C., Corbin, D. R., Clauss, A. W., Hendrickson, D. N. & Stucky, G. D. (1981). *Inorg. Chem.* **20**, 2078–2083.

North, A. C. T., Phillips, D. C. & Mathews, F. S. (1968). *Acta Cryst.* A**24**, 351–359.

Sheldrick, G. M. (1985). *SHELXS86. Program for the Solution of Crystal Structures.* University of Göttingen, Germany.

Sheldrick, G. M. (1991). *SHELXTL-Plus.* Release 4.1. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.

Sheldrick, G. M. (1993). *SHELXL93. Program for the Refinement of Crystal Structures.* University of Göttingen, Germany.

Tinti, F., Verdaguer, M., Kahn, O. & Savariault, J. M. (1987). *Inorg. Chem.* **26**, 2380–2384.