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Diaquabis[μ_2-3-(1*H*-imidazol-5-yl)-2-(3-iminopropionamido)propionato-$\kappa^4N{:}N',N'',O$]dicopper(II) dihydrate

Jie Shen,[a] Yi-Zhi Li,[b] Dong-Mei Zhang[a] and Jun-Hui Chen[a]*

[a]State Key Laboratory of Pharmaceutical Biotechnology, Nanjing University, Nanjing 210093, People's Republic of China, and [b]State Key Laboratory of Coordination Chemistry, School of Chemistry and Chemical Engineering, Nanjing University, Nanjing, 210093, People's Republic of China
Correspondence e-mail: llyyjz@nju.edu.cn

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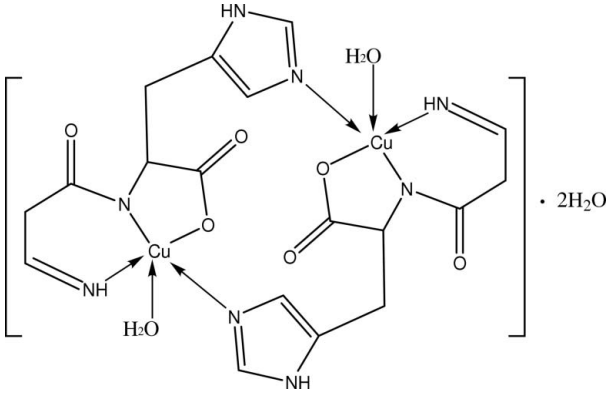
Key indicators: single-crystal X-ray study; T = 291 K; mean σ(C–C) = 0.009 Å; R factor = 0.055; wR factor = 0.109; data-to-parameter ratio = 11.9.

In the crystal structure of the title compound, $[Cu_2(C_9H_{10}N_4O_3)_2(H_2O)_2]\cdot 2H_2O$, there are one and a half dicopper complexes in the asymmetric unit. One dicopper complex is located on a twofold rotation axis, while the other is in a general position. Each ligand bridges a pair Cu^{II} atoms, rendering the complex circular in form. Each Cu^{II} atom has a square-pyramidal coordination geometry. The basal positions are occupied by two N atoms and one O atom from one ligand and one N atom from another ligand, while the apical position is occupied by a coordinated water molecule. All chiral C atoms have an *S* configuration. In the crystal structure, there are uncoordinated water molecules that bridge neighboring complex molecules by hydrogen bonds, forming a three-dimensional structure.

Related literature

For related literature, see: Pang & Chau (1999); Hobart *et al.* (2004); Babizhayev *et al.* (1994).



Experimental

Crystal data

$[Cu_2(C_9H_{10}N_4O_3)_2(H_2O)_2]\cdot 2H_2O$
M_r = 643.56
Monoclinic, $C2$
a = 14.598 (9) Å
b = 8.627 (5) Å
c = 30.508 (19) Å
β = 90.322 (3)°
V = 3842 (4) Å^3
Z = 6
Mo $K\alpha$ radiation
μ = 1.73 mm^{-1}
T = 291 (2) K
0.30 × 0.26 × 0.24 mm

Data collection

Bruker SMART APEX CCD diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.61, T_{max} = 0.67
10436 measured reflections
6743 independent reflections
5342 reflections with $I > 2\sigma(I)$
R_{int} = 0.030

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.055
$wR(F^2)$ = 0.109
S = 1.07
6743 reflections
568 parameters
1 restraint
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max}$ = 0.42 e Å^{-3}
$\Delta\rho_{min}$ = −0.77 e Å^{-3}
Absolute structure: Flack (1983), with 2717 Friedel pairs
Flack parameter: 0.020 (15)

Table 1
Hydrogen-bond geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2B···O8^{i}	0.85 (8)	2.18 (8)	2.945 (7)	149 (7)
N4—H4B···O3^{ii}	0.86 (7)	1.84 (7)	2.692 (8)	168 (7)
N6—H6C···O7^{iii}	0.87 (7)	2.19 (7)	2.950 (8)	147 (7)
N8—H8B···O11	0.85 (7)	1.80 (7)	2.650 (6)	173 (7)
N10—H10A···O12^{iv}	0.87 (8)	2.23 (8)	3.061 (9)	160 (7)
N12—H12E···O6^{i}	0.86 (7)	1.80 (8)	2.652 (7)	168 (7)
O7—H7B···O4^{i}	0.86 (8)	2.15 (8)	2.998 (7)	170 (7)
O7—H7A···O15^{v}	0.83 (8)	1.85 (8)	2.678 (7)	170 (8)
O8—H8C···O14^{iii}	0.96 (7)	1.83 (7)	2.734 (6)	158 (6)
O8—H8D···O1^{iii}	0.95 (7)	2.05 (7)	2.988 (6)	166 (6)
O8—H8D···O2^{iii}	0.95 (7)	2.57 (7)	3.317 (6)	135 (5)
O12—H12C···O9^{iv}	0.85 (8)	2.40 (8)	3.032 (7)	131 (7)
O12—H12C···O10^{iv}	0.85 (8)	2.40 (8)	3.223 (6)	162 (7)
O12—H12B···O13	0.85 (8)	2.03 (8)	2.698 (7)	134 (7)
O13—H13B···O10^{vi}	0.84 (8)	1.92 (9)	2.661 (7)	147 (9)
O13—H13D···O6	0.85 (9)	1.94 (9)	2.734 (7)	155 (8)
O14—H14B···O5	0.85 (8)	1.92 (9)	2.701 (8)	153 (8)
O14—H14D···O11^{vi}	0.84 (8)	1.97 (8)	2.757 (7)	155 (8)
O15—H15C···O2^{vii}	0.86 (7)	1.92 (7)	2.722 (7)	154 (7)
O15—H15E···O3^{ii}	0.85 (8)	1.93 (8)	2.718 (6)	155 (7)

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

Data collection: *SMART* (Bruker, 2000); cell refinement: *SAINT* (Bruker, 2000); data reduction: *SAINT*; program(s) used to solve structure: *SHELXTL* (Bruker, 2000); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: IS2204).

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supplementary materials

Acta Cryst. (2007). E**63**, m2569-m2570 [**doi:10.1107/S160053680704473X**]

Diaquabis[μ_2-3-(1*H*-imidazol-5-yl)-2-(3-iminopropionamido)propionato-κ^4N:*N*',*N*'',*O*]dicopper(II) dihydrate

J. Shen, Y.-Z. Li, D.-M. Zhang and J.-H. Chen

Comment

It has been reported that organic copper complexes can induce apoptosis in tumor tissues (Pang & Chau, 1999). Carnosine has been extensively investigated as a physiological buffer, an antioxidant, a metal chelator and a radical scavenger (Hobart *et al.*, 2004; Babizhayev *et al.*, 1994). To study the antioxidant activity and the copper-chelating capability of carnosine, the title compound was synthesized and characterized.

There are one and half dicopper complex molecules in the asymmetric unit (Fig. 1). The dicopper complex consists of two copper atoms, two ligand molecules and two coordinated water molecules. Two ligands bridge and form a circular configuration with two copper atoms. Each copper atom adopts a square pyramidal coordination with the copper atom in the center of the square. The square is formed by two N atoms and one O atom from one ligand and one N atom from another ligand, while the axial position is occupied by a coordinated water molecule. There are three chiral carbon atoms, C2, C11 and C20 in the molecules, which are in S configuration. In the crystal packing there are uncoordinated water molecules that bridge neighboring complex molecules by hydrogen bonds and are important for the 3-D structure (Fig. 2).

Experimental

Carnosine (67.8 mg, 0.3 mmol) dissolved in 10 ml deionized water and $Cu(Ac)_2{\cdot}H_20$ (0.3 mmol) dissolved in 1 ml deionized water were mixed. To the solution ethanol (4.2 ml) was added. The purple block crystal was formed after one week.

Refinement

H atoms bonded to N and O atoms were located in a difference map and their positional parameters were refined, with U_{iso}(H) = 1.2U_{eq}(N,*O*). The refined distances are O—H = 0.83 (8)–0.96 (7) Å and N—H = 0.85 (8)–0.87 (7) Å. Other H atoms were positioned geometrically and refined using a riding model, with C—H = 0.93–0.98 Å, and with U_{iso}(H) = 1.2U_{eq}(C).

Figures

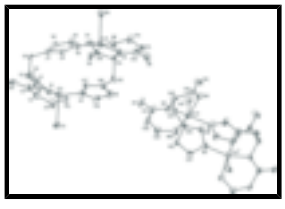

Fig. 1. The molecular structure of the dicopper complex, showing the labeling of the non-H atoms and 30% probability ellipsoids. H atoms and free water molecules have been omitted for clarity [symmetry code: (i) 2 − *x*, *y*, −*z*].

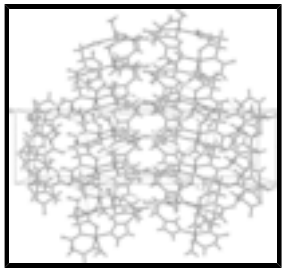

Fig. 2. A packing diagram of the title compound viewed down the *a* axis. Dashed lines indicate hydrogen bounds.

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Crystal data

$[Cu_2(C_9H_{10}N_4O_3)_2(H_2O)_2]\cdot 2H_2O$	F_{000} = 1980
M_r = 643.56	D_x = 1.669 Mg m^{-3}
Monoclinic, *C*2	Mo *K*α radiation λ = 0.71073 Å
Hall symbol: C 2y	Cell parameters from 2360 reflections
a = 14.598 (9) Å	θ = 2.7–24.8º
b = 8.627 (5) Å	μ = 1.73 mm^{-1}
c = 30.508 (19) Å	*T* = 291 (2) K
β = 90.322 (3)º	Block, purple
V = 3842 (4) Å^3	0.30 × 0.26 × 0.24 mm
Z = 6	

Data collection

Bruker SMART APEX CCD diffractometer	6743 independent reflections
Radiation source: sealed tube	5342 reflections with $I > 2\sigma(I)$
Monochromator: graphite	R_{int} = 0.030
T = 291(2) K	θ_{max} = 26.0º
φ and ω scans	θ_{min} = 2.0º
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)	*h* = −18→15
T_{min} = 0.61, T_{max} = 0.67	*k* = −7→10
10436 measured reflections	*l* = −36→37

Refinement

Refinement on F^2	Hydrogen site location: inferred from neighbouring sites
Least-squares matrix: full	H atoms treated by a mixture of independent and constrained refinement
$R[F^2 > 2\sigma(F^2)]$ = 0.055	$w = 1/[\sigma^2(F_o^2) + (0.0545P)^2 + 1.22P]$ where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2)$ = 0.109	$(\Delta/\sigma)_{max} < 0.001$
S = 1.07	$\Delta\rho_{max}$ = 0.42 e Å^{-3}

6743 reflections	$\Delta\rho_{min} = -0.77$ e Å^{-3}
568 parameters	Extinction correction: none
1 restraint	Absolute structure: Flack (1983), 2717 Friedel pairs
Primary atom site location: structure-invariant direct methods	Flack parameter: 0.020 (15)
Secondary atom site location: difference Fourier map	

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted *R*-factor *wR* and goodness of fit *S* are based on F^2, conventional *R*-factors *R* are based on *F*, with *F* set to zero for negative F^2. The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating *R*-factors(gt) *etc*. and is not relevant to the choice of reflections for refinement. *R*-factors based on F^2 are statistically about twice as large as those based on *F*, and *R*- factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å^2)

	x	*y*	*z*	U_{iso}*/U_{eq}
C1	0.5715 (4)	0.2703 (7)	0.40534 (19)	0.0465 (15)
C2	0.6209 (4)	0.3479 (8)	0.4437 (2)	0.0526 (16)
H2A	0.6138	0.2817	0.4696	0.063*
C3	0.7769 (5)	0.3748 (9)	0.4668 (2)	0.0620 (19)
C4	0.8756 (4)	0.4282 (9)	0.4619 (2)	0.0590 (18)
H4A	0.8796	0.5377	0.4688	0.071*
H4C	0.9140	0.3722	0.4825	0.071*
C5	0.9097 (5)	0.4023 (9)	0.4170 (2)	0.0614 (19)
H5A	0.9665	0.3544	0.4144	0.074*
C6	0.5815 (4)	0.5047 (7)	0.45415 (15)	0.0374 (13)
H6A	0.5162	0.4940	0.4591	0.045*
H6B	0.6091	0.5426	0.4811	0.045*
C7	0.5963 (4)	0.6198 (7)	0.41921 (17)	0.0403 (13)
C8	0.5681 (4)	0.6289 (6)	0.37706 (16)	0.0357 (12)
H8A	0.5298	0.5569	0.3636	0.043*
C9	0.6537 (4)	0.8302 (8)	0.38718 (17)	0.0483 (14)
H9A	0.6853	0.9227	0.3830	0.058*
C10	0.4564 (4)	0.6099 (8)	0.26138 (19)	0.0459 (14)
C11	0.5162 (4)	0.6449 (7)	0.22274 (18)	0.0429 (14)
H11A	0.4775	0.6679	0.1972	0.051*
C12	0.6075 (4)	0.8534 (8)	0.19779 (19)	0.0484 (15)
C13	0.6801 (4)	0.9761 (8)	0.20578 (18)	0.0460 (14)
H13A	0.7394	0.9311	0.1993	0.055*
H13C	0.6700	1.0599	0.1851	0.055*
C14	0.6843 (4)	1.0421 (9)	0.24954 (19)	0.0532 (17)
H14A	0.6828	1.1495	0.2520	0.064*
C15	0.5762 (4)	0.5020 (7)	0.21278 (17)	0.0412 (13)

H15A	0.5367	0.4125	0.2092	0.049*
H15B	0.6073	0.5189	0.1852	0.049*
C16	0.6435 (4)	0.4680 (7)	0.24593 (17)	0.0379 (12)
C17	0.6350 (4)	0.4175 (6)	0.28876 (18)	0.0364 (12)
H17A	0.5795	0.3958	0.3023	0.044*
C18	0.7772 (4)	0.4421 (8)	0.27869 (18)	0.0461 (15)
H18A	0.8403	0.4390	0.2831	0.055*
C19	0.8858 (3)	0.8743 (7)	0.06998 (18)	0.0393 (13)
C20	0.8977 (4)	0.7637 (7)	0.1103 (2)	0.0421 (14)
H20A	0.8676	0.8099	0.1358	0.051*
C21	0.8262 (4)	0.5350 (8)	0.13383 (19)	0.0507 (16)
C22	0.7617 (5)	0.4025 (9)	0.1221 (2)	0.065 (2)
H22A	0.7556	0.3365	0.1476	0.078*
H22B	0.7018	0.4461	0.1158	0.078*
C23	0.7884 (4)	0.3043 (8)	0.08456 (19)	0.0517 (14)
H23A	0.7858	0.1970	0.0871	0.062*
C24	0.9974 (4)	0.7407 (7)	0.12051 (19)	0.0417 (13)
H24A	1.0030	0.6802	0.1472	0.050*
H24B	1.0252	0.8411	0.1260	0.050*
C25	1.0500 (4)	0.6603 (7)	0.0845 (2)	0.0428 (13)
C26	1.0739 (4)	0.6996 (8)	0.0440 (2)	0.0532 (16)
H26A	1.0608	0.7951	0.0313	0.064*
C27	1.1294 (5)	0.4756 (8)	0.0539 (2)	0.0515 (16)
H27A	1.1604	0.3828	0.0495	0.062*
Cu1	0.73812 (5)	0.34830 (9)	0.37106 (3)	0.0537 (2)
Cu2	0.58071 (5)	0.81489 (9)	0.29434 (2)	0.0490 (2)
Cu3	0.84047 (5)	0.58662 (8)	0.03755 (2)	0.04530 (19)
N1	0.7178 (3)	0.3560 (7)	0.43345 (17)	0.0523 (14)
N2	0.8651 (4)	0.4428 (8)	0.37829 (19)	0.0587 (16)
H2B	0.889 (5)	0.502 (10)	0.359 (3)	0.070*
N3	0.6032 (4)	0.7577 (6)	0.35642 (17)	0.0517 (13)
N4	0.6521 (4)	0.7493 (7)	0.42513 (19)	0.0541 (14)
H4B	0.681 (5)	0.774 (9)	0.449 (2)	0.065*
N5	0.5722 (4)	0.7789 (6)	0.23280 (16)	0.0516 (14)
N6	0.6904 (4)	0.9567 (7)	0.28788 (18)	0.0533 (14)
H6C	0.735 (5)	0.962 (9)	0.307 (2)	0.064*
N7	0.7169 (3)	0.4038 (6)	0.30806 (17)	0.0467 (12)
N8	0.7368 (4)	0.4864 (7)	0.24148 (18)	0.0527 (14)
H8B	0.764 (5)	0.520 (9)	0.219 (2)	0.063*
N9	0.8545 (3)	0.6177 (6)	0.10018 (16)	0.0500 (14)
N10	0.8176 (4)	0.3722 (7)	0.04501 (18)	0.0611 (16)
H10A	0.826 (5)	0.311 (10)	0.023 (3)	0.073*
N11	1.1189 (4)	0.5860 (8)	0.02374 (18)	0.0619 (15)
N12	1.0886 (4)	0.5171 (7)	0.09179 (17)	0.0522 (14)
H12E	1.087 (5)	0.465 (9)	0.116 (2)	0.063*
O1	0.6181 (3)	0.2441 (5)	0.37014 (15)	0.0526 (11)
O2	0.4888 (3)	0.2400 (5)	0.40683 (14)	0.0533 (11)
O3	0.7501 (3)	0.3606 (6)	0.50674 (16)	0.0597 (13)
O4	0.4667 (3)	0.6957 (6)	0.29549 (15)	0.0547 (11)

O5	0.3989 (3)	0.5042 (5)	0.25906 (13)	0.0527 (11)
O6	0.5853 (3)	0.8218 (7)	0.15888 (15)	0.0660 (13)
O7	0.8104 (3)	0.1061 (7)	0.35354 (17)	0.0590 (13)
H7B	0.860 (5)	0.126 (9)	0.339 (3)	0.071*
H7A	0.824 (5)	0.050 (10)	0.375 (3)	0.071*
O8	0.4985 (3)	1.0486 (5)	0.31269 (14)	0.0478 (10)
H8C	0.493 (4)	1.112 (9)	0.287 (2)	0.057*
H8D	0.531 (4)	1.104 (8)	0.335 (2)	0.057*
O9	0.8477 (2)	0.8128 (5)	0.03590 (13)	0.0486 (10)
O10	0.9102 (3)	1.0069 (5)	0.07319 (15)	0.0545 (11)
O11	0.8329 (3)	0.5820 (7)	0.17319 (12)	0.0581 (12)
O12	0.6810 (3)	0.6007 (6)	0.01956 (18)	0.0618 (13)
H12C	0.670 (5)	0.569 (10)	−0.006 (3)	0.074*
H12B	0.653 (6)	0.550 (10)	0.039 (3)	0.074*
O13	0.5775 (4)	0.6092 (6)	0.09253 (17)	0.0668 (15)
H13B	0.522 (6)	0.616 (11)	0.086 (3)	0.080*
H13D	0.592 (6)	0.687 (11)	0.108 (3)	0.080*
O14	0.4370 (4)	0.2051 (7)	0.24037 (17)	0.0623 (14)
H14B	0.409 (5)	0.286 (10)	0.249 (3)	0.075*
H14D	0.401 (5)	0.149 (10)	0.226 (3)	0.075*
O15	0.8596 (3)	0.9559 (6)	0.42679 (14)	0.0502 (11)
H15C	0.885 (5)	0.871 (9)	0.419 (2)	0.060*
H15E	0.813 (5)	0.936 (9)	0.442 (2)	0.060*

Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C1	0.043 (3)	0.061 (4)	0.036 (3)	0.016 (3)	−0.002 (2)	0.007 (3)
C2	0.038 (3)	0.060 (4)	0.059 (4)	0.018 (3)	−0.003 (3)	0.000 (3)
C3	0.057 (4)	0.081 (5)	0.048 (4)	0.023 (4)	0.011 (3)	0.016 (3)
C4	0.045 (4)	0.076 (5)	0.056 (4)	0.017 (3)	0.004 (3)	0.013 (3)
C5	0.067 (4)	0.068 (5)	0.049 (4)	−0.031 (4)	−0.005 (3)	0.008 (3)
C6	0.036 (3)	0.058 (4)	0.019 (2)	0.021 (2)	0.0077 (19)	0.000 (2)
C7	0.044 (3)	0.046 (4)	0.030 (3)	−0.008 (2)	0.005 (2)	−0.002 (2)
C8	0.038 (3)	0.036 (3)	0.033 (3)	−0.003 (2)	−0.001 (2)	0.002 (2)
C9	0.056 (3)	0.060 (4)	0.029 (3)	−0.012 (3)	0.000 (2)	0.001 (3)
C10	0.042 (3)	0.051 (4)	0.044 (3)	0.010 (3)	−0.009 (2)	0.015 (3)
C11	0.046 (3)	0.058 (4)	0.024 (3)	−0.006 (3)	−0.008 (2)	0.019 (2)
C12	0.045 (3)	0.061 (4)	0.039 (3)	−0.011 (3)	−0.009 (2)	0.005 (3)
C13	0.039 (3)	0.063 (4)	0.036 (3)	−0.006 (3)	0.011 (2)	0.010 (3)
C14	0.057 (4)	0.068 (5)	0.035 (3)	−0.016 (3)	0.004 (3)	−0.006 (3)
C15	0.045 (3)	0.047 (4)	0.032 (3)	−0.004 (3)	−0.007 (2)	0.018 (2)
C16	0.039 (3)	0.044 (3)	0.031 (3)	0.006 (2)	−0.001 (2)	0.006 (2)
C17	0.030 (3)	0.042 (3)	0.037 (3)	0.007 (2)	0.006 (2)	0.004 (2)
C18	0.035 (3)	0.072 (5)	0.031 (3)	−0.010 (3)	−0.003 (2)	−0.015 (3)
C19	0.034 (3)	0.042 (3)	0.041 (3)	0.010 (2)	0.007 (2)	−0.011 (2)
C20	0.045 (3)	0.038 (3)	0.044 (3)	0.004 (2)	0.003 (2)	−0.017 (2)
C21	0.040 (3)	0.070 (5)	0.043 (3)	−0.015 (3)	0.014 (3)	−0.014 (3)

C22	0.076 (5)	0.088 (6)	0.032 (3)	−0.052 (4)	0.026 (3)	−0.017 (3)
C23	0.057 (3)	0.055 (4)	0.044 (3)	−0.009 (3)	0.001 (2)	−0.001 (3)
C24	0.034 (3)	0.046 (3)	0.045 (3)	0.003 (2)	0.001 (2)	−0.010 (3)
C25	0.033 (3)	0.040 (3)	0.055 (4)	0.001 (2)	0.010 (2)	0.001 (3)
C26	0.052 (4)	0.062 (4)	0.046 (3)	0.023 (3)	0.021 (3)	0.010 (3)
C27	0.060 (4)	0.040 (3)	0.055 (4)	0.003 (3)	0.023 (3)	0.008 (3)
Cu1	0.0456 (4)	0.0658 (6)	0.0497 (4)	0.0228 (4)	0.0038 (3)	0.0082 (4)
Cu2	0.0527 (4)	0.0620 (5)	0.0323 (3)	0.0025 (4)	−0.0052 (3)	0.0086 (3)
Cu3	0.0475 (4)	0.0476 (4)	0.0409 (4)	−0.0152 (3)	0.0141 (3)	−0.0183 (3)
N1	0.026 (2)	0.071 (4)	0.061 (3)	0.022 (2)	0.009 (2)	0.016 (3)
N2	0.064 (4)	0.068 (4)	0.044 (3)	−0.007 (3)	0.003 (3)	0.024 (3)
N3	0.062 (3)	0.054 (3)	0.039 (3)	−0.008 (2)	0.003 (2)	0.009 (2)
N4	0.052 (3)	0.066 (4)	0.045 (3)	−0.009 (3)	0.001 (2)	0.001 (3)
N5	0.071 (3)	0.050 (4)	0.034 (3)	−0.002 (3)	−0.009 (2)	0.007 (2)
N6	0.066 (4)	0.053 (3)	0.041 (3)	−0.005 (3)	−0.026 (2)	0.010 (2)
N7	0.032 (2)	0.064 (4)	0.044 (3)	0.003 (2)	0.003 (2)	−0.008 (2)
N8	0.044 (3)	0.070 (4)	0.044 (3)	−0.010 (3)	0.009 (2)	0.015 (3)
N9	0.053 (3)	0.051 (3)	0.046 (3)	−0.029 (2)	0.020 (2)	−0.020 (2)
N10	0.078 (4)	0.064 (4)	0.042 (3)	−0.025 (3)	0.017 (3)	−0.007 (3)
N11	0.055 (3)	0.072 (4)	0.058 (3)	0.027 (3)	0.016 (2)	0.023 (3)
N12	0.064 (4)	0.055 (3)	0.037 (3)	0.021 (3)	0.010 (2)	0.023 (2)
O1	0.055 (3)	0.058 (3)	0.045 (2)	0.012 (2)	0.0050 (19)	0.006 (2)
O2	0.053 (3)	0.066 (3)	0.041 (2)	−0.010 (2)	0.0113 (18)	−0.014 (2)
O3	0.049 (2)	0.066 (3)	0.064 (3)	0.033 (2)	0.007 (2)	0.002 (2)
O4	0.053 (2)	0.056 (3)	0.055 (3)	0.017 (2)	0.006 (2)	0.000 (2)
O5	0.068 (3)	0.053 (3)	0.037 (2)	−0.016 (2)	0.017 (2)	−0.0008 (19)
O6	0.083 (3)	0.058 (3)	0.057 (3)	−0.027 (3)	−0.018 (2)	0.010 (3)
O7	0.047 (2)	0.075 (4)	0.056 (3)	0.028 (2)	0.008 (2)	−0.001 (3)
O8	0.053 (2)	0.055 (3)	0.034 (2)	−0.010 (2)	−0.0091 (18)	0.0044 (19)
O9	0.042 (2)	0.053 (3)	0.051 (2)	0.001 (2)	0.0033 (17)	−0.018 (2)
O10	0.060 (3)	0.041 (3)	0.062 (3)	0.009 (2)	−0.031 (2)	−0.009 (2)
O11	0.073 (3)	0.076 (3)	0.026 (2)	−0.031 (3)	0.0172 (18)	−0.016 (2)
O12	0.064 (3)	0.064 (3)	0.058 (3)	−0.036 (3)	−0.004 (2)	−0.022 (3)
O13	0.081 (3)	0.056 (3)	0.064 (3)	−0.035 (3)	0.028 (3)	−0.029 (3)
O14	0.067 (3)	0.068 (4)	0.052 (3)	−0.027 (3)	−0.031 (2)	0.022 (3)
O15	0.042 (2)	0.070 (3)	0.038 (2)	−0.008 (2)	0.0117 (18)	0.002 (2)

Geometric parameters (Å, °)

C1—O2	1.237 (7)	C20—H20A	0.9800
C1—O1	1.294 (7)	C21—O11	1.271 (7)
C1—C2	1.526 (9)	C21—N9	1.319 (8)
C2—N1	1.452 (7)	C21—C22	1.522 (9)
C2—C6	1.505 (8)	C22—C23	1.478 (9)
C2—H2A	0.9800	C22—H22A	0.9700
C3—O3	1.289 (8)	C22—H22B	0.9700
C3—N1	1.339 (9)	C23—N10	1.410 (8)
C3—C4	1.519 (10)	C23—H23A	0.9300
C4—C5	1.476 (10)	C24—C25	1.511 (8)

C4—H4A	0.9700	C24—H24A	0.9700
C4—H4C	0.9700	C24—H24B	0.9700
C5—N2	1.390 (9)	C25—C26	1.331 (8)
C5—H5A	0.9300	C25—N12	1.375 (8)
C6—C7	1.474 (8)	C26—N11	1.334 (8)
C6—H6A	0.9700	C26—H26A	0.9300
C6—H6B	0.9700	C27—N11	1.333 (8)
C7—C8	1.350 (7)	C27—N12	1.352 (8)
C7—N4	1.393 (8)	C27—H27A	0.9300
C8—N3	1.377 (7)	Cu1—N1	1.929 (5)
C8—H8A	0.9300	Cu1—O1	1.970 (5)
C9—N3	1.345 (8)	Cu1—N7	2.003 (5)
C9—N4	1.352 (8)	Cu1—N2	2.036 (6)
C9—H9A	0.9300	Cu1—O7	2.402 (5)
C10—O5	1.242 (7)	Cu2—N5	1.906 (5)
C10—O4	1.285 (8)	Cu2—O4	1.956 (5)
C10—C11	1.501 (8)	Cu2—N3	1.983 (5)
C11—N5	1.448 (8)	Cu2—N6	2.026 (6)
C11—C15	1.544 (9)	Cu2—O8	2.414 (5)
C11—H11A	0.9800	Cu3—N10	1.893 (6)
C12—O6	1.258 (7)	Cu3—N9	1.939 (5)
C12—N5	1.351 (8)	Cu3—O9	1.955 (5)
C12—C13	1.517 (8)	Cu3—N11^{i}	1.965 (5)
C13—C14	1.452 (8)	Cu3—O12	2.392 (5)
C13—H13A	0.9700	N2—H2B	0.85 (8)
C13—H13C	0.9700	N4—H4B	0.86 (7)
C14—N6	1.385 (8)	N6—H6C	0.87 (7)
C14—H14A	0.9300	N8—H8B	0.85 (7)
C15—C16	1.436 (7)	N10—H10A	0.87 (8)
C15—H15A	0.9700	N11—Cu3^{i}	1.965 (5)
C15—H15B	0.9700	N12—H12E	0.86 (7)
C16—N8	1.379 (7)	O7—H7B	0.86 (8)
C16—C17	1.383 (7)	O7—H7A	0.83 (8)
C17—N7	1.335 (7)	O8—H8C	0.96 (7)
C17—H17A	0.9300	O8—H8D	0.95 (7)
C18—N7	1.303 (8)	O12—H12C	0.85 (8)
C18—N8	1.332 (8)	O12—H12B	0.85 (8)
C18—H18A	0.9300	O13—H13B	0.84 (8)
C19—O10	1.202 (7)	O13—H13D	0.85 (9)
C19—O9	1.290 (7)	O14—H14B	0.85 (8)
C19—C20	1.565 (9)	O14—H14D	0.84 (8)
C20—N9	1.441 (7)	O15—H15C	0.86 (7)
C20—C24	1.500 (8)	O15—H15E	0.85 (8)
O2—C1—O1	120.7 (6)	C25—C24—H24A	108.8
O2—C1—C2	121.5 (5)	C20—C24—H24B	108.8
O1—C1—C2	117.7 (5)	C25—C24—H24B	108.8
N1—C2—C6	112.1 (6)	H24A—C24—H24B	107.7
N1—C2—C1	108.2 (5)	C26—C25—N12	105.6 (5)

C6—C2—C1	112.1 (5)	C26—C25—C24	134.0 (6)
N1—C2—H2A	108.1	N12—C25—C24	120.3 (5)
C6—C2—H2A	108.1	C25—C26—N11	112.1 (6)
C1—C2—H2A	108.1	C25—C26—H26A	124.0
O3—C3—N1	120.5 (6)	N11—C26—H26A	124.0
O3—C3—C4	114.5 (6)	N11—C27—N12	110.6 (6)
N1—C3—C4	124.7 (6)	N11—C27—H27A	124.7
C5—C4—C3	111.7 (6)	N12—C27—H27A	124.7
C5—C4—H4A	109.3	N1—Cu1—O1	83.6 (2)
C3—C4—H4A	109.3	N1—Cu1—N7	156.1 (2)
C5—C4—H4C	109.3	O1—Cu1—N7	87.86 (19)
C3—C4—H4C	109.3	N1—Cu1—N2	91.4 (2)
H4A—C4—H4C	107.9	O1—Cu1—N2	173.6 (2)
N2—C5—C4	126.2 (7)	N7—Cu1—N2	98.3 (2)
N2—C5—H5A	116.9	N1—Cu1—O7	108.6 (2)
C4—C5—H5A	116.9	O1—Cu1—O7	89.52 (19)
C7—C6—C2	113.3 (4)	N7—Cu1—O7	93.47 (19)
C7—C6—H6A	108.9	N2—Cu1—O7	88.4 (2)
C2—C6—H6A	108.9	N5—Cu2—O4	83.2 (2)
C7—C6—H6B	108.9	N5—Cu2—N3	155.5 (2)
C2—C6—H6B	108.9	O4—Cu2—N3	89.3 (2)
H6A—C6—H6B	107.7	N5—Cu2—N6	92.8 (2)
C8—C7—N4	104.6 (5)	O4—Cu2—N6	172.8 (2)
C8—C7—C6	133.1 (5)	N3—Cu2—N6	96.7 (2)
N4—C7—C6	122.3 (5)	N5—Cu2—O8	109.57 (19)
C7—C8—N3	111.7 (5)	O4—Cu2—O8	90.63 (18)
C7—C8—H8A	124.1	N3—Cu2—O8	93.8 (2)
N3—C8—H8A	124.1	N6—Cu2—O8	85.0 (2)
N3—C9—N4	110.1 (6)	N10—Cu3—N9	92.0 (2)
N3—C9—H9A	124.9	N10—Cu3—O9	171.0 (2)
N4—C9—H9A	124.9	N9—Cu3—O9	83.2 (2)
O5—C10—O4	123.0 (6)	N10—Cu3—N11^{i}	99.6 (3)
O5—C10—C11	119.9 (6)	N9—Cu3—N11^{i}	155.1 (2)
O4—C10—C11	117.0 (6)	O9—Cu3—N11^{i}	87.8 (2)
N5—C11—C10	108.9 (5)	N10—Cu3—O12	84.6 (2)
N5—C11—C15	111.0 (5)	N9—Cu3—O12	108.4 (2)
C10—C11—C15	109.1 (4)	O9—Cu3—O12	89.78 (17)
N5—C11—H11A	109.3	N11^{i}—Cu3—O12	94.6 (2)
C10—C11—H11A	109.3	C3—N1—C2	117.8 (5)
C15—C11—H11A	109.3	C3—N1—Cu1	130.6 (4)
O6—C12—N5	123.1 (6)	C2—N1—Cu1	111.5 (4)
O6—C12—C13	118.6 (5)	C5—N2—Cu1	114.4 (4)
N5—C12—C13	118.3 (5)	C5—N2—H2B	123 (5)
C14—C13—C12	116.6 (5)	Cu1—N2—H2B	123 (5)
C14—C13—H13A	108.2	C9—N3—C8	105.1 (5)
C12—C13—H13A	108.2	C9—N3—Cu2	129.6 (4)
C14—C13—H13C	108.2	C8—N3—Cu2	125.3 (4)
C12—C13—H13C	108.2	C9—N4—C7	108.5 (5)

H13A—C13—H13C	107.3	C9—N4—H4B	126 (5)
N6—C14—C13	124.7 (6)	C7—N4—H4B	126 (5)
N6—C14—H14A	117.6	C12—N5—C11	115.4 (5)
C13—C14—H14A	117.6	C12—N5—Cu2	132.7 (4)
C16—C15—C11	114.3 (5)	C11—N5—Cu2	111.8 (4)
C16—C15—H15A	108.7	C14—N6—Cu2	110.9 (4)
C11—C15—H15A	108.7	C14—N6—H6C	125 (5)
C16—C15—H15B	108.7	Cu2—N6—H6C	124 (5)
C11—C15—H15B	108.7	C18—N7—C17	106.4 (5)
H15A—C15—H15B	107.6	C18—N7—Cu1	128.2 (4)
N8—C16—C17	102.9 (5)	C17—N7—Cu1	125.3 (4)
N8—C16—C15	125.4 (5)	C18—N8—C16	108.4 (5)
C17—C16—C15	131.7 (5)	C18—N8—H8B	126 (5)
N7—C17—C16	111.1 (5)	C16—N8—H8B	125 (5)
N7—C17—H17A	124.5	C21—N9—C20	116.4 (5)
C16—C17—H17A	124.5	C21—N9—Cu3	131.3 (4)
N7—C18—N8	111.1 (5)	C20—N9—Cu3	112.1 (4)
N7—C18—H18A	124.4	C23—N10—Cu3	124.3 (5)
N8—C18—H18A	124.4	C23—N10—H10A	117 (5)
O10—C19—O9	125.6 (6)	Cu3—N10—H10A	118 (5)
O10—C19—C20	119.0 (5)	C27—N11—C26	105.1 (5)
O9—C19—C20	115.3 (5)	C27—N11—Cu3^{i}	128.7 (5)
N9—C20—C24	110.6 (5)	C26—N11—Cu3^{i}	126.2 (5)
N9—C20—C19	108.6 (5)	C27—N12—C25	106.4 (5)
C24—C20—C19	110.3 (5)	C27—N12—H12E	127 (5)
N9—C20—H20A	109.1	C25—N12—H12E	126 (5)
C24—C20—H20A	109.1	C1—O1—Cu1	112.3 (4)
C19—C20—H20A	109.1	C10—O4—Cu2	112.6 (4)
O11—C21—N9	122.7 (6)	Cu1—O7—H7B	108 (5)
O11—C21—C22	120.4 (5)	Cu1—O7—H7A	116 (6)
N9—C21—C22	114.8 (5)	H7B—O7—H7A	108 (7)
C23—C22—C21	116.6 (5)	Cu2—O8—H8C	109 (4)
C23—C22—H22A	108.1	Cu2—O8—H8D	109 (4)
C21—C22—H22A	108.1	H8C—O8—H8D	110 (6)
C23—C22—H22B	108.1	C19—O9—Cu3	114.4 (4)
C21—C22—H22B	108.1	Cu3—O12—H12C	112 (5)
H22A—C22—H22B	107.3	Cu3—O12—H12B	107 (5)
N10—C23—C22	120.5 (6)	H12C—O12—H12B	113 (7)
N10—C23—H23A	119.8	H13B—O13—H13D	109 (9)
C22—C23—H23A	119.8	H14B—O14—H14D	109 (8)
C20—C24—C25	113.9 (5)	H15C—O15—H15E	110 (7)
C20—C24—H24A	108.8		

Symmetry codes: (i) −*x*+2, *y*, −*z*.

Hydrogen-bond geometry (Å, °)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
N2—H2B···O8^{ii}	0.85 (8)	2.18 (8)	2.945 (7)	149 (7)

N4—H4B···O3^{iii}	0.86 (7)	1.84 (7)	2.692 (8)	168 (7)
N6—H6C···O7^{iv}	0.87 (7)	2.19 (7)	2.950 (8)	147 (7)
N8—H8B···O11	0.85 (7)	1.80 (7)	2.650 (6)	173 (7)
N10—H10A···O12^{v}	0.87 (8)	2.23 (8)	3.061 (9)	160 (7)
N12—H12E···O6^{ii}	0.86 (7)	1.80 (8)	2.652 (7)	168 (7)
O7—H7B···O4^{ii}	0.86 (8)	2.15 (8)	2.998 (7)	170 (7)
O7—H7A···O15^{vi}	0.83 (8)	1.85 (8)	2.678 (7)	170 (8)
O8—H8C···O14^{iv}	0.96 (7)	1.83 (7)	2.734 (6)	158 (6)
O8—H8D···O1^{iv}	0.95 (7)	2.05 (7)	2.988 (6)	166 (6)
O8—H8D···O2^{iv}	0.95 (7)	2.57 (7)	3.317 (6)	135 (5)
O12—H12C···O9^{v}	0.85 (8)	2.40 (8)	3.032 (7)	131 (7)
O12—H12C···O10^{v}	0.85 (8)	2.40 (8)	3.223 (6)	162 (7)
O12—H12B···O13	0.85 (8)	2.03 (8)	2.698 (7)	134 (7)
O13—H13B···O10^{vii}	0.84 (8)	1.92 (9)	2.661 (7)	147 (9)
O13—H13D···O6	0.85 (9)	1.94 (9)	2.734 (7)	155 (8)
O14—H14B···O5	0.85 (8)	1.92 (9)	2.701 (8)	153 (8)
O14—H14D···O11^{vii}	0.84 (8)	1.97 (8)	2.757 (7)	155 (8)
O15—H15C···O2^{viii}	0.86 (7)	1.92 (7)	2.722 (7)	154 (7)
O15—H15E···O3^{iii}	0.85 (8)	1.93 (8)	2.718 (6)	155 (7)

Symmetry codes: (ii) $x+1/2, y-1/2, z$; (iii) $-x+3/2, y+1/2, -z+1$; (iv) $x, y+1, z$; (v) $-x+3/2, y-1/2, -z$; (vi) $x, y-1, z$; (vii) $x-1/2, y-1/2, z$; (viii) $x+1/2, y+1/2, z$.

Fig. 1

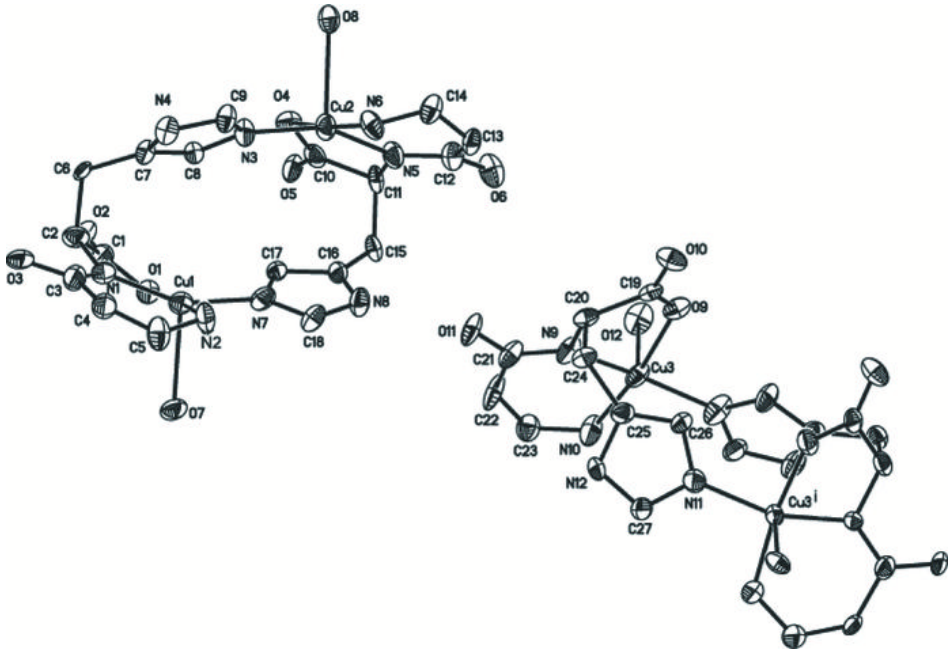
O8
N4
C9
O4
Cu2
N6
C14
C13
C6
C7
C8
N3
C10
N5
C12
O6
O5
C11
O2
C2
C1
C17
C16
C15
O3
C3
N1
O1
Cu1
N8
C4
N7
C5
N2
C18
O7
O10
C19
C20
O9
O11
N9
O12
C21
C24
Cu3
C22
C23
N10
C25
C26
N12
N11
Cu3i
C27

Fig. 2