Acta Crystallographica Section E
Structure Reports Online
ISSN 1600-5368

Triaquabis(1*H*-imidazole)bis[μ_2-2-(oxaloamino)benzoato(3−)]dicopper(II)-calcium(II) heptahydrate

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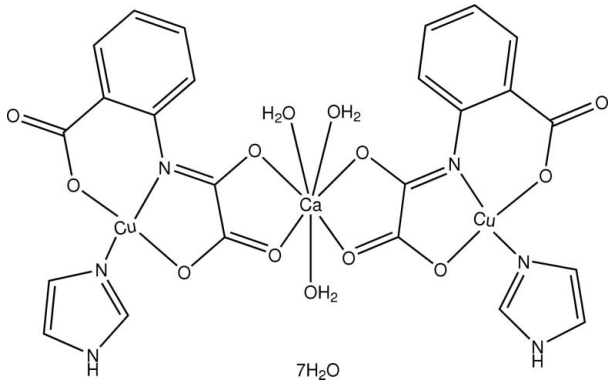
Received 19 November 2007; accepted 18 December 2007

Key indicators: single-crystal X-ray study; T = 293 K; mean σ(C–C) = 0.009 Å; R factor = 0.063; wR factor = 0.122; data-to-parameter ratio = 12.8.

In the title heterotrinuclear coordination compound, $[CaCu_2(C_9H_4NO_5)_2(C_3H_4N_2)_2(H_2O)_3]\cdot 7H_2O$, the Ca^{2+} cation is in a pentagonal–bipyramidal geometry and bridges two (1*H*-imidazole)[2-(oxaloamino)benzoato(3−)]copper(II) units in its equatorial plane. Each Cu^{II} atom has a normal square-planar geometry. The molecule has approximate local (non-crystallographic) mirror symmetry and 23 classical hydrogen bonds are found in the crystal structure.

Related literature

For related literature, see: Zang *et al.* (2003).



Experimental

Crystal data

$[CaCu_2(C_9H_4NO_5)_2(C_3H_4N_2)_2(H_2O)_3]\cdot 7H_2O$
M_r = 895.75
Monoclinic, $P2_1/n$
a = 6.8988 (9) Å
b = 24.011 (3) Å
c = 21.161 (3) Å
β = 93.511 (3)°
V = 3498.7 (8) Å^3
Z = 4
Mo $K\alpha$ radiation
μ = 1.45 mm^{-1}
T = 293 (2) K
0.2 × 0.2 × 0.2 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
T_{min} = 0.75, T_{max} = 0.76
17203 measured reflections
6119 independent reflections
3486 reflections with $I > 2\sigma(I)$
R_{int} = 0.093

Refinement

$R[F^2 > 2\sigma(F^2)]$ = 0.063
$wR(F^2)$ = 0.122
S = 0.99
6119 reflections
478 parameters
7 restraints
H-atom parameters constrained
$\Delta\rho_{max}$ = 0.59 e Å^{-3}
$\Delta\rho_{min}$ = −0.48 e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
O20—H20*D*···O2^{i}	0.85	2.11	2.950 (7)	172
O20—H20*C*···O19	0.85	2.09	2.749 (11)	134
O19—H19*D*···O18	0.85	2.34	2.887 (12)	123
O19—H19*C*···O17^{ii}	0.85	1.91	2.758 (11)	180
O18—H18*D*···O6	0.85	2.50	3.070 (7)	125
O18—H18*D*···O7	0.85	2.20	3.049 (7)	179
O18—H18*C*···O14^{iii}	0.85	2.04	2.887 (10)	178
O17—H17*C*···O14^{iv}	0.85	2.17	2.974 (12)	158
O16—H16*A*···O10	0.85	2.10	2.850 (6)	148
O15—H15*D*···O16	0.85	2.01	2.845 (7)	167
O15—H15*A*···O9	0.85	2.42	3.131 (6)	141
O15—H15*A*···O4	0.85	2.38	3.121 (7)	146
O14—H14*D*···O15	0.85	2.08	2.798 (7)	142
O14—H14*C*···O3	0.85	2.21	3.045 (7)	169
O13—H13*B*···O19^{v}	0.85	2.15	2.963 (9)	160
O13—H13*A*···O6^{vi}	0.85	1.95	2.780 (6)	164
O12—H12*B*···O1^{vii}	0.85	1.86	2.706 (6)	180
O12—H12*A*···O6^{v}	0.85	1.87	2.725 (5)	180
O11—H11*C*···O15^{ii}	0.85	2.37	2.778 (6)	110
O11—H11*A*···O1^{viii}	0.85	1.96	2.780 (6)	163
N6—H6*A*···O9^{iii}	0.86	2.13	2.958 (7)	161
N6—H6*A*···O4^{iii}	0.86	2.48	3.018 (6)	122
N4—H4*A*···O20^{iii}	0.86	2.03	2.888 (9)	178

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

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: *publCIF* (Westrip, 2008).

The authors express their thanks to the Natural Science Foundation of Henan Province for financial support.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: SI2057).

References

Bruker (2000). *SADABS*, *SMART*, *SAINT* and *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
Westrip, S. P. (2008). *publCIF*. In preparation.
Zang, S.-Q., Tao, R.-J., Wang, Q.-L., Hu, N.-H., Cheng, Y.-X., Niu, J.-Y. & Liao, D.-Z. (2003). *Inorg. Chem.* **42**, 761–766.

  doi:10.1107/S1600536807067517

supporting information

Acta Cryst. (2008). E**64**, m278 [doi:10.1107/S1600536807067517]

Triaquabis(1*H*-imidazole)bis[μ_2-2-(oxaloamino)-benzoato(3−)]dicopper(II)calcium(II) heptahydrate

Chongzhen Mei, Kaihui Li and Peng Zhang

S1. Comment

The "complex as ligand" approach, *i.e.* using metal cations to link reactively stable coordination compounds that contain potential bridging blocks, is particularly suitable for designing heteropolymetallic compounds.

In the title compound, Cu^{II} adopts square planar geometry, coordinating to the oxamato-N-benzoate and the imidazole ligand to afford a Cu-containing "ligand". Ca^{II} then bridges two Cu-ligands together.

The molecule has a local (non-crystallographic) mirror plane containing Ca and three aqueous ligands O11, O12 and O13. In addition, 23 classic hydrogen bonds are found in the structure (Table 1).

S2. Experimental

2-(Oxaloamino)benzoic acid (0.232 g, 1 mmol; Zang *et al.*, 2003) and ? (0.12 g, 3 mmol) were dissolved in water (20 ml). To this solution, $CuCl_2.2H_2O$ (0.17 g, 1 mmol) and imidazole (0.068 g, 1 mmol) were added. After stirring for an hour, $CaCl_2$ (0.111 g, 1 mmol) was added. The solution was filtered after stirring for another hour. Evaporation of the filtrate gave green single crystals of the title compound after one week. Elemental analysis found (calculatedd) for $C_{24}H_{36}CaCu_2N_6O_{20}$ (%): C 32.26 (32.18); H, 3.92 (4.05); N 9.52 (9.38); Ca 4.45 (4.47); Cu 14.14 (14.19). The analyses were performed on a Perkin–Elmer 240 C elemental analyzer. The abundance of Cu is determined by spectrophotometry while the abundance of Ca is obtained from edta titration.

S3. Refinement

The structure was solved by direct methods. All the H atoms were fixed geometrically and constrained with a riding model. d(C—H) = 0.93 Å, U_{iso}=1.2U_{eq} (C) for aromatic 0.97 Å, U_{iso} = 1.2U_{eq} (C) for CH_2 and 0.96 Å, U_{iso} = 1.5U_{eq} (C) for CH_3 atoms; 0.85 Å, U_{iso} = 1.5U_{eq} (O) for H_2O atoms.

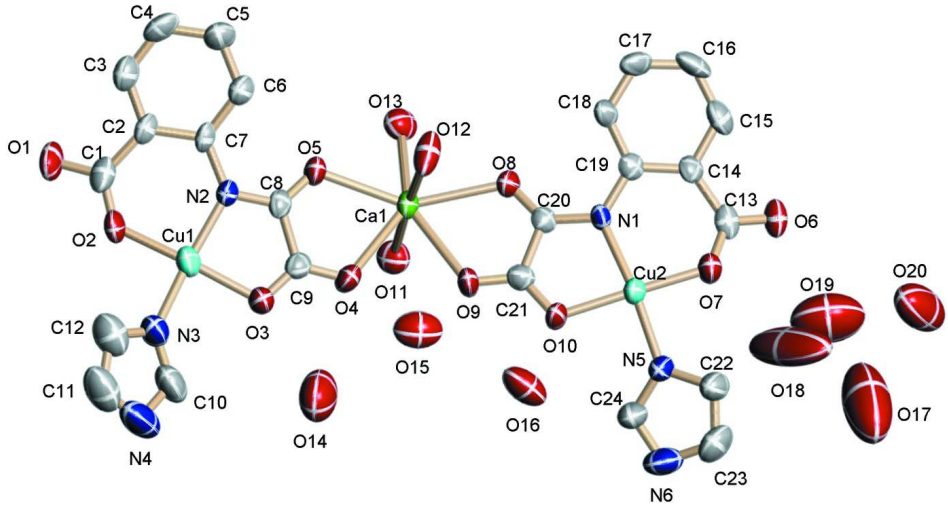


Figure 1

Asymmetric unit of the title compound. Hydrogen atoms are omitted for clarity. Displacement ellipsoids are drawn at the 50% probability level.

Triaquabis(1*H*-imidazole)bis[μ_2-2- (oxaloamino)benzoato(3-)]dicopper(II)calcium(II) heptahydrate

Crystal data

$[CaCu_2(C_9H_4NO_5)_2(C_3H_4N_2)_2(H_2O)_3]\cdot 7H_2O$
$M_r = 895.75$
Monoclinic, $P2_1/n$
Hall symbol: -P 2yn
$a = 6.8988$ (9) Å
$b = 24.011$ (3) Å
$c = 21.161$ (3) Å
$\beta = 93.511$ (3)°
$V = 3498.7$ (8) Å^3
$Z = 4$
$F(000) = 1840$
$D_x = 1.701$ Mg m^{-3}
Mo $K\alpha$ radiation, $\lambda = 0.71073$ Å
Cell parameters from 1959 reflections
$\theta = 2.7$–$20.5°$
$\mu = 1.45$ mm^{-1}
$T = 293$ K
Block, green
0.2 × 0.2 × 0.2 mm

Data collection

Bruker SMART CCD area-detector diffractometer
Radiation source: fine-focus sealed tube
Graphite monochromator
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 2000)
$T_{min} = 0.75$, $T_{max} = 0.76$
17203 measured reflections
6119 independent reflections
3486 reflections with $I > 2\sigma(I)$
$R_{int} = 0.093$
$\theta_{max} = 25.0°$, $\theta_{min} = 2.0°$
$h = -8\rightarrow 8$
$k = -28\rightarrow 28$
$l = -15\rightarrow 25$

Refinement

Refinement on F^2
Least-squares matrix: full
$R[F^2 > 2\sigma(F^2)] = 0.063$
$wR(F^2) = 0.122$
$S = 1.00$
6119 reflections
478 parameters
7 restraints
Primary atom site location: structure-invariant direct methods
Secondary atom site location: difference Fourier map
Hydrogen site location: inferred from neighbouring sites
H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.03P)^2]$
where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} = 0.018$

$\Delta\rho_{max} = 0.59$ e Å^{-3}
$\Delta\rho_{min} = -0.48$ e Å^{-3}

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}
Ca1	0.57052 (19)	0.21723 (5)	0.36790 (5)	0.0305 (3)
Cu1	0.42034 (12)	0.15913 (3)	0.10945 (3)	0.0365 (2)
Cu2	0.40057 (12)	0.12870 (3)	0.60805 (3)	0.0303 (2)
N1	0.4528 (7)	0.20197 (17)	0.57516 (19)	0.0223 (12)
N2	0.4559 (7)	0.22668 (18)	0.1570 (2)	0.0275 (12)
C1	0.4976 (10)	0.2460 (3)	0.0207 (3)	0.0400 (17)
C2	0.4626 (8)	0.2899 (2)	0.0672 (3)	0.0273 (15)
C3	0.4444 (9)	0.3438 (3)	0.0446 (3)	0.0405 (17)
H3	0.4611	0.3502	0.0019	0.049*
C4	0.4034 (10)	0.3877 (3)	0.0816 (3)	0.0460 (19)
H4	0.3903	0.4232	0.0645	0.055*
C5	0.3812 (10)	0.3788 (3)	0.1455 (3)	0.0422 (18)
H5	0.3532	0.4085	0.1716	0.051*
C6	0.4004 (9)	0.3262 (2)	0.1701 (3)	0.0326 (16)
H6	0.3856	0.3206	0.2131	0.039*
C7	0.4416 (8)	0.2810 (2)	0.1321 (2)	0.0260 (14)
C8	0.4955 (9)	0.2169 (2)	0.2188 (3)	0.0278 (15)
C9	0.4692 (9)	0.1558 (2)	0.2362 (3)	0.0294 (15)
N3	0.3548 (9)	0.0899 (2)	0.0656 (3)	0.0497 (16)
C10	0.3866 (13)	0.0390 (3)	0.0854 (4)	0.070 (3)
H10	0.4524	0.0299	0.1236	0.084*
N4	0.3135 (12)	0.0024 (3)	0.0442 (4)	0.091 (3)
H4A	0.3211	−0.0332	0.0478	0.109*
C11	0.2251 (14)	0.0305 (4)	−0.0043 (4)	0.083 (3)
H11	0.1579	0.0154	−0.0397	0.099*
C12	0.2529 (12)	0.0841 (4)	0.0084 (4)	0.070 (2)
H12	0.2098	0.1133	−0.0177	0.084*
C13	0.4628 (9)	0.1977 (3)	0.7176 (3)	0.0309 (16)
C14	0.4633 (8)	0.2491 (2)	0.6780 (3)	0.0268 (15)
C15	0.4633 (9)	0.2996 (3)	0.7113 (3)	0.0417 (18)
H15	0.4738	0.2986	0.7553	0.050*
C16	0.4481 (10)	0.3508 (3)	0.6814 (3)	0.0451 (19)

H16	0.4443	0.3836	0.7046	0.054*
C17	0.4390 (10)	0.3517 (2)	0.6165 (3)	0.0422 (18)
H17	0.4291	0.3857	0.5954	0.051*
C18	0.4441 (9)	0.3035 (2)	0.5821 (3)	0.0352 (17)
H18	0.4390	0.3057	0.5382	0.042*
C19	0.4568 (8)	0.2516 (2)	0.6106 (3)	0.0258 (15)
C20	0.4908 (8)	0.2006 (2)	0.5142 (3)	0.0247 (14)
C21	0.4483 (9)	0.1434 (2)	0.4842 (3)	0.0305 (16)
N5	0.3638 (8)	0.05199 (19)	0.6339 (2)	0.0339 (14)
C22	0.2829 (10)	0.0326 (3)	0.6870 (3)	0.0466 (19)
H22	0.2244	0.0544	0.7169	0.056*
C23	0.3020 (12)	−0.0230 (3)	0.6888 (4)	0.061 (2)
H23	0.2597	−0.0466	0.7199	0.074*
N6	0.3947 (9)	−0.0383 (2)	0.6367 (3)	0.0591 (18)
H6A	0.4251	−0.0716	0.6261	0.071*
C24	0.4289 (10)	0.0077 (3)	0.6058 (3)	0.0468 (19)
H24	0.4919	0.0088	0.5682	0.056*
O1	0.5537 (7)	0.26049 (18)	−0.03227 (19)	0.0528 (13)
O2	0.4690 (7)	0.19479 (18)	0.03125 (17)	0.0415 (12)
O3	0.4352 (7)	0.12114 (15)	0.19170 (18)	0.0423 (12)
O4	0.4854 (7)	0.14343 (15)	0.29325 (19)	0.0436 (13)
O5	0.5407 (6)	0.24986 (15)	0.26216 (17)	0.0347 (11)
O6	0.5085 (6)	0.20180 (16)	0.77547 (17)	0.0420 (12)
O7	0.4140 (7)	0.15086 (16)	0.69376 (17)	0.0418 (12)
O8	0.5517 (6)	0.23713 (15)	0.47962 (17)	0.0315 (10)
O9	0.4621 (7)	0.13889 (15)	0.42624 (17)	0.0401 (12)
O10	0.4020 (6)	0.10426 (15)	0.51994 (17)	0.0372 (12)
O11	0.8768 (6)	0.17246 (16)	0.37391 (18)	0.0466 (12)
H11A	0.9524	0.1891	0.4009	0.070*
H11C	0.8666	0.1385	0.3846	0.070*
O12	0.2690 (6)	0.26068 (18)	0.36776 (18)	0.0590 (14)
H12A	0.1876	0.2723	0.3390	0.089*
H12B	0.2011	0.2541	0.3991	0.089*
O13	0.7663 (6)	0.29991 (15)	0.37573 (18)	0.0492 (13)
H13A	0.8576	0.2976	0.3507	0.074*
H13B	0.6965	0.3282	0.3663	0.074*
O14	0.2004 (10)	0.0229 (2)	0.2365 (3)	0.117 (2)
H14C	0.2560	0.0500	0.2192	0.175*
H14D	0.1710	0.0263	0.2747	0.175*
O15	0.1196 (7)	0.08557 (18)	0.3431 (2)	0.0766 (17)
H15A	0.2257	0.1036	0.3467	0.115*
H15D	0.1356	0.0662	0.3767	0.115*
O16	0.1226 (8)	0.02987 (18)	0.4619 (2)	0.0818 (18)
H16A	0.1659	0.0551	0.4871	0.123*
H16B	0.2171	0.0074	0.4592	0.123*
O17	0.1399 (16)	0.0127 (4)	0.8469 (4)	0.252 (5)
H17C	0.0609	−0.0057	0.8226	0.378*
H17D	0.2441	0.0153	0.8276	0.378*

O18	0.6065 (16)	0.0784 (2)	0.7980 (4)	0.265 (7)
H18C	0.6615	0.0481	0.7884	0.397*
H18D	0.5511	0.0987	0.7693	0.397*
O19	0.9605 (13)	0.1133 (3)	0.8665 (4)	0.198 (4)
H19C	1.0155	0.0822	0.8607	0.296*
H19D	0.9021	0.1202	0.8308	0.296*
O20	0.6630 (11)	0.1175 (2)	0.9470 (3)	0.149 (3)
H20C	0.7636	0.1334	0.9343	0.224*
H20D	0.5978	0.1372	0.9715	0.224*

Atomic displacement parameters (Å²)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Ca1	0.0384 (9)	0.0344 (7)	0.0194 (7)	−0.0010 (7)	0.0075 (6)	0.0025 (6)
Cu1	0.0455 (6)	0.0401 (5)	0.0245 (4)	−0.0008 (4)	0.0074 (4)	−0.0051 (4)
Cu2	0.0427 (5)	0.0282 (4)	0.0208 (4)	−0.0017 (4)	0.0095 (4)	0.0012 (4)
N1	0.028 (3)	0.025 (3)	0.015 (3)	−0.007 (2)	0.004 (2)	−0.004 (2)
N2	0.035 (3)	0.028 (3)	0.020 (3)	0.000 (3)	0.007 (2)	0.004 (2)
C1	0.035 (5)	0.059 (5)	0.026 (4)	0.007 (4)	0.003 (3)	0.012 (4)
C2	0.021 (4)	0.039 (4)	0.022 (3)	−0.002 (3)	0.003 (3)	0.011 (3)
C3	0.038 (5)	0.055 (5)	0.030 (4)	−0.006 (4)	0.009 (3)	0.007 (4)
C4	0.050 (5)	0.033 (4)	0.055 (5)	−0.015 (4)	0.001 (4)	0.020 (4)
C5	0.053 (5)	0.029 (4)	0.046 (4)	−0.013 (4)	0.009 (4)	0.001 (3)
C6	0.033 (4)	0.036 (4)	0.029 (4)	−0.004 (3)	0.006 (3)	0.007 (3)
C7	0.025 (4)	0.037 (4)	0.016 (3)	−0.008 (3)	0.005 (3)	0.006 (3)
C8	0.026 (4)	0.037 (4)	0.022 (4)	0.006 (3)	0.008 (3)	0.003 (3)
C9	0.030 (4)	0.029 (4)	0.031 (4)	0.003 (3)	0.009 (3)	0.004 (3)
N3	0.074 (5)	0.041 (4)	0.035 (3)	−0.012 (4)	0.010 (3)	−0.009 (3)
C10	0.101 (8)	0.063 (6)	0.049 (5)	−0.011 (6)	0.022 (5)	−0.025 (5)
N4	0.126 (8)	0.059 (5)	0.092 (6)	−0.026 (5)	0.052 (6)	−0.033 (5)
C11	0.088 (8)	0.096 (8)	0.065 (6)	−0.028 (6)	0.015 (6)	−0.036 (6)
C12	0.067 (6)	0.086 (6)	0.057 (5)	−0.005 (5)	0.001 (4)	−0.022 (5)
C13	0.015 (4)	0.054 (5)	0.024 (4)	0.001 (3)	0.003 (3)	−0.005 (3)
C14	0.025 (4)	0.031 (4)	0.026 (3)	0.005 (3)	0.009 (3)	−0.003 (3)
C15	0.039 (5)	0.053 (5)	0.034 (4)	−0.002 (4)	0.013 (3)	−0.018 (4)
C16	0.048 (5)	0.028 (4)	0.061 (5)	−0.006 (4)	0.018 (4)	−0.026 (4)
C17	0.052 (5)	0.021 (3)	0.056 (5)	−0.005 (3)	0.023 (4)	0.006 (3)
C18	0.049 (5)	0.030 (4)	0.029 (4)	−0.005 (3)	0.022 (3)	−0.004 (3)
C19	0.019 (4)	0.030 (3)	0.029 (3)	−0.002 (3)	0.008 (3)	−0.001 (3)
C20	0.020 (4)	0.028 (4)	0.027 (4)	0.002 (3)	0.005 (3)	−0.002 (3)
C21	0.032 (4)	0.027 (4)	0.033 (4)	−0.001 (3)	0.003 (3)	−0.002 (3)
N5	0.047 (4)	0.026 (3)	0.029 (3)	0.002 (3)	0.010 (3)	0.005 (2)
C22	0.063 (6)	0.034 (4)	0.044 (5)	0.000 (4)	0.023 (4)	0.003 (4)
C23	0.069 (6)	0.060 (6)	0.057 (5)	−0.012 (5)	0.015 (5)	0.025 (4)
N6	0.075 (5)	0.030 (3)	0.072 (5)	0.002 (3)	0.000 (4)	0.009 (3)
C24	0.070 (6)	0.030 (4)	0.042 (4)	0.006 (4)	0.012 (4)	0.006 (4)
O1	0.059 (3)	0.071 (3)	0.031 (2)	0.014 (2)	0.025 (2)	0.010 (2)
O2	0.056 (3)	0.049 (3)	0.020 (2)	0.004 (3)	0.014 (2)	−0.003 (2)

O3	0.073 (4)	0.029 (2)	0.026 (2)	−0.004 (2)	0.008 (2)	−0.003 (2)
O4	0.075 (4)	0.031 (3)	0.026 (2)	−0.006 (2)	0.004 (2)	0.009 (2)
O5	0.054 (3)	0.033 (2)	0.017 (2)	−0.005 (2)	0.004 (2)	0.002 (2)
O6	0.042 (3)	0.066 (3)	0.018 (2)	−0.003 (2)	−0.001 (2)	−0.002 (2)
O7	0.066 (4)	0.038 (3)	0.022 (2)	−0.007 (3)	0.007 (2)	−0.002 (2)
O8	0.043 (3)	0.029 (2)	0.024 (2)	−0.003 (2)	0.012 (2)	0.0015 (19)
O9	0.069 (4)	0.034 (3)	0.018 (2)	−0.009 (2)	0.014 (2)	−0.0050 (19)
O10	0.065 (3)	0.027 (2)	0.022 (2)	−0.013 (2)	0.017 (2)	0.0012 (19)
O11	0.046 (3)	0.049 (3)	0.043 (3)	0.000 (2)	−0.005 (2)	−0.003 (2)
O12	0.046 (3)	0.100 (4)	0.032 (3)	0.019 (3)	0.009 (2)	0.023 (3)
O13	0.050 (3)	0.046 (3)	0.053 (3)	0.003 (2)	0.016 (2)	−0.005 (2)
O14	0.143 (7)	0.134 (5)	0.076 (4)	0.021 (5)	0.033 (4)	0.015 (4)
O15	0.054 (4)	0.061 (3)	0.114 (5)	−0.002 (3)	0.003 (3)	−0.003 (3)
O16	0.085 (5)	0.069 (3)	0.092 (4)	−0.007 (3)	0.014 (3)	−0.041 (3)
O17	0.297 (13)	0.352 (13)	0.105 (6)	0.155 (11)	0.000 (7)	−0.011 (8)
O18	0.451 (18)	0.077 (5)	0.236 (10)	0.052 (7)	−0.226 (11)	−0.008 (6)
O19	0.199 (10)	0.115 (6)	0.277 (12)	−0.027 (7)	0.002 (8)	0.010 (7)
O20	0.194 (8)	0.105 (5)	0.160 (7)	−0.032 (5)	0.098 (6)	−0.042 (5)

Geometric parameters (Å, º)

Ca1—O12	2.327 (4)	C13—O6	1.250 (6)
Ca1—O11	2.367 (4)	C13—O7	1.269 (6)
Ca1—O5	2.368 (4)	C13—C14	1.492 (8)
Ca1—O9	2.395 (4)	C14—C15	1.403 (7)
Ca1—O13	2.401 (4)	C14—C19	1.425 (7)
Ca1—O4	2.422 (4)	C15—C16	1.384 (8)
Ca1—O8	2.423 (4)	C15—H15	0.93
Ca1—H11A	2.7672	C16—C17	1.372 (8)
Ca1—H11C	2.7894	C16—H16	0.93
Cu1—O2	1.911 (4)	C17—C18	1.368 (7)
Cu1—N2	1.917 (4)	C17—H17	0.93
Cu1—N3	1.943 (5)	C18—C19	1.384 (7)
Cu1—O3	1.962 (4)	C18—H18	0.93
Cu2—O7	1.887 (4)	C20—O8	1.234 (6)
Cu2—N1	1.934 (4)	C20—C21	1.533 (7)
Cu2—N5	1.943 (5)	C21—O9	1.240 (6)
Cu2—O10	1.955 (4)	C21—O10	1.260 (6)
N1—C20	1.332 (6)	N5—C24	1.311 (7)
N1—C19	1.409 (6)	N5—C22	1.367 (7)
N2—C8	1.340 (6)	C22—C23	1.342 (8)
N2—C7	1.409 (6)	C22—H22	0.93
C1—O1	1.257 (7)	C23—N6	1.358 (8)
C1—O2	1.266 (7)	C23—H23	0.93
C1—C2	1.473 (8)	N6—C24	1.313 (7)
C2—C3	1.383 (7)	N6—H6A	0.86
C2—C7	1.406 (7)	C24—H24	0.93
C3—C4	1.352 (8)	O11—H11A	0.85

C3—H3	0.93	O11—H11C	0.85
C4—C5	1.385 (8)	O12—H12A	0.85
C4—H4	0.93	O12—H12B	0.85
C5—C6	1.369 (7)	O13—H13A	0.85
C5—H5	0.93	O13—H13B	0.85
C6—C7	1.390 (7)	O14—H14C	0.85
C6—H6	0.93	O14—H14D	0.85
C8—O5	1.237 (6)	O15—H15A	0.85
C8—C9	1.526 (7)	O15—H15D	0.85
C9—O4	1.241 (6)	O16—H16A	0.85
C9—O3	1.268 (6)	O16—H16B	0.85
N3—C10	1.305 (8)	O17—H17C	0.85
N3—C12	1.371 (8)	O17—H17D	0.85
C10—N4	1.316 (8)	O18—H18C	0.85
C10—H10	0.93	O18—H18D	0.85
N4—C11	1.344 (10)	O19—H19C	0.85
N4—H4A	0.86	O19—H19D	0.85
C11—C12	1.326 (10)	O20—H20C	0.85
C11—H11	0.93	O20—H20D	0.85
C12—H12	0.93		

O12—Ca1—O11	176.97 (14)	C10—N3—C12	104.7 (6)
O12—Ca1—O5	79.88 (14)	C10—N3—Cu1	128.2 (5)
O11—Ca1—O5	103.11 (15)	C12—N3—Cu1	127.0 (6)
O12—Ca1—O9	92.60 (16)	N3—C10—N4	111.3 (8)
O11—Ca1—O9	85.50 (15)	N3—C10—H10	124.3
O5—Ca1—O9	137.32 (14)	N4—C10—H10	124.3
O12—Ca1—O13	97.38 (15)	C10—N4—C11	107.9 (7)
O11—Ca1—O13	82.84 (14)	C10—N4—H4A	126.0
O5—Ca1—O13	78.91 (14)	C11—N4—H4A	126.0
O9—Ca1—O13	143.71 (14)	C12—C11—N4	106.2 (8)
O12—Ca1—O4	98.41 (16)	C12—C11—H11	126.9
O11—Ca1—O4	83.26 (14)	N4—C11—H11	126.9
O5—Ca1—O4	67.80 (13)	C11—C12—N3	109.8 (8)
O9—Ca1—O4	71.98 (13)	C11—C12—H12	125.1
O13—Ca1—O4	139.70 (15)	N3—C12—H12	125.1
O12—Ca1—O8	79.15 (14)	O6—C13—O7	120.3 (6)
O11—Ca1—O8	97.93 (14)	O6—C13—C14	118.4 (6)
O5—Ca1—O8	148.21 (13)	O7—C13—C14	121.3 (5)
O9—Ca1—O8	67.35 (12)	C15—C14—C19	117.6 (5)
O13—Ca1—O8	80.40 (13)	C15—C14—C13	115.7 (5)
O4—Ca1—O8	139.05 (14)	C19—C14—C13	126.7 (5)
O12—Ca1—H11A	161.2	C16—C15—C14	122.7 (6)
O11—Ca1—H11A	16.8	C16—C15—H15	118.6
O5—Ca1—H11A	110.2	C14—C15—H15	118.6
O9—Ca1—H11A	90.1	C17—C16—C15	118.1 (6)
O13—Ca1—H11A	70.2	C17—C16—H16	121.0
O4—Ca1—H11A	100.1	C15—C16—H16	121.0

O8—Ca1—H11A	84.8	C18—C17—C16	121.1 (6)
O12—Ca1—H11C	162.1	C18—C17—H17	119.5
O11—Ca1—H11C	16.5	C16—C17—H17	119.5
O5—Ca1—H11C	111.4	C17—C18—C19	122.3 (6)
O9—Ca1—H11C	69.6	C17—C18—H18	118.9
O13—Ca1—H11C	98.5	C19—C18—H18	118.9
O4—Ca1—H11C	74.5	C18—C19—N1	122.1 (5)
O8—Ca1—H11C	95.3	C18—C19—C14	118.1 (5)
H11A—Ca1—H11C	28.9	N1—C19—C14	119.6 (5)
O2—Cu1—N2	92.99 (18)	O8—C20—N1	130.6 (5)
O2—Cu1—N3	91.0 (2)	O8—C20—C21	117.1 (5)
N2—Cu1—N3	173.2 (2)	N1—C20—C21	112.3 (5)
O2—Cu1—O3	166.89 (19)	O9—C21—O10	124.5 (5)
N2—Cu1—O3	85.94 (17)	O9—C21—C20	117.6 (5)
N3—Cu1—O3	91.3 (2)	O10—C21—C20	117.9 (5)
O7—Cu2—N1	95.17 (17)	C24—N5—C22	105.5 (5)
O7—Cu2—N5	89.76 (18)	C24—N5—Cu2	125.9 (4)
N1—Cu2—N5	173.9 (2)	C22—N5—Cu2	128.4 (4)
O7—Cu2—O10	176.73 (19)	C23—C22—N5	108.5 (6)
N1—Cu2—O10	85.29 (16)	C23—C22—H22	125.8
N5—Cu2—O10	89.59 (18)	N5—C22—H22	125.8
C20—N1—C19	122.6 (5)	C22—C23—N6	107.3 (6)
C20—N1—Cu2	112.2 (4)	C22—C23—H23	126.4
C19—N1—Cu2	125.2 (3)	N6—C23—H23	126.4
C8—N2—C7	122.2 (5)	C24—N6—C23	106.6 (6)
C8—N2—Cu1	112.1 (4)	C24—N6—H6A	126.7
C7—N2—Cu1	125.7 (4)	C23—N6—H6A	126.7
O1—C1—O2	119.1 (6)	N5—C24—N6	112.2 (6)
O1—C1—C2	118.0 (6)	N5—C24—H24	123.9
O2—C1—C2	122.9 (5)	N6—C24—H24	123.9
C3—C2—C7	117.9 (6)	C1—O2—Cu1	128.7 (4)
C3—C2—C1	117.0 (5)	C9—O3—Cu1	110.6 (3)
C7—C2—C1	125.1 (5)	C9—O4—Ca1	117.6 (4)
C4—C3—C2	123.1 (6)	C8—O5—Ca1	119.5 (3)
C4—C3—H3	118.5	C13—O7—Cu2	128.9 (4)
C2—C3—H3	118.5	C20—O8—Ca1	118.6 (3)
C3—C4—C5	119.0 (6)	C21—O9—Ca1	119.1 (4)
C3—C4—H4	120.5	C21—O10—Cu2	111.4 (3)
C5—C4—H4	120.5	Ca1—O11—H11A	109.4
C6—C5—C4	120.0 (6)	Ca1—O11—H11C	111.2
C6—C5—H5	120.0	H11A—O11—H11C	109.3
C4—C5—H5	120.0	Ca1—O12—H12A	134.4
C5—C6—C7	121.1 (6)	Ca1—O12—H12B	116.8
C5—C6—H6	119.4	H12A—O12—H12B	104.4
C7—C6—H6	119.4	Ca1—O13—H13A	109.8
C6—C7—C2	118.9 (5)	Ca1—O13—H13B	109.7
C6—C7—N2	121.2 (5)	H13A—O13—H13B	109.7
C2—C7—N2	119.8 (5)	H14C—O14—H14D	118.3

O5—C8—N2	129.7 (5)	H15A—O15—H15D	97.9
O5—C8—C9	117.7 (5)	H16A—O16—H16B	104.7
N2—C8—C9	112.6 (5)	H17C—O17—H17D	106.1
O4—C9—O3	124.6 (5)	H18C—O18—H18D	120.4
O4—C9—C8	117.4 (5)	H19C—O19—H19D	103.5
O3—C9—C8	118.1 (5)	H20C—O20—H20D	114.5

Hydrogen-bond geometry (Å, º)

D—H···*A*	*D*—H	H···*A*	*D*···*A*	*D*—H···*A*
O20—H20*D*···O2^{i}	0.85	2.11	2.950 (7)	172
O20—H20*C*···O19	0.85	2.09	2.749 (11)	134
O19—H19*D*···O18	0.85	2.34	2.887 (12)	123
O19—H19*C*···O17^{ii}	0.85	1.91	2.758 (11)	180
O18—H18*D*···O6	0.85	2.50	3.070 (7)	125
O18—H18*D*···O7	0.85	2.20	3.049 (7)	179
O18—H18*C*···O14^{iii}	0.85	2.04	2.887 (10)	178
O17—H17*C*···O14^{iv}	0.85	2.17	2.974 (12)	158
O16—H16*A*···O10	0.85	2.10	2.850 (6)	148
O15—H15*D*···O16	0.85	2.01	2.845 (7)	167
O15—H15*A*···O9	0.85	2.42	3.131 (6)	141
O15—H15*A*···O4	0.85	2.38	3.121 (7)	146
O14—H14*D*···O15	0.85	2.08	2.798 (7)	142
O14—H14*C*···O3	0.85	2.21	3.045 (7)	169
O13—H13*B*···O19^{v}	0.85	2.15	2.963 (9)	160
O13—H13*A*···O6^{vi}	0.85	1.95	2.780 (6)	164
O12—H12*B*···O1^{vii}	0.85	1.86	2.706 (6)	180
O12—H12*A*···O6^{v}	0.85	1.87	2.725 (5)	180
O11—H11*C*···O15^{ii}	0.85	2.37	2.778 (6)	110
O11—H11*A*···O1^{viii}	0.85	1.96	2.780 (6)	163
N6—H6*A*···O9^{iii}	0.86	2.13	2.958 (7)	161
N6—H6*A*···O4^{iii}	0.86	2.48	3.018 (6)	122
N4—H4*A*···O20^{iii}	0.86	2.03	2.888 (9)	178

Symmetry codes: (i) *x*, *y*, *z*+1; (ii) *x*+1, *y*, *z*; (iii) −*x*+1, −*y*, −*z*+1; (iv) −*x*, −*y*, −*z*+1; (v) *x*−1/2, −*y*+1/2, *z*−1/2; (vi) *x*+1/2, −*y*+1/2, *z*−1/2; (vii) *x*−1/2, −*y*+1/2, *z*+1/2; (viii) *x*+1/2, −*y*+1/2, *z*+1/2.