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[μ-*N*,*N*′-Bis(2-aminoethyl)ethanediamido(2−)-$\kappa^6N,N',O:O',N'',N'''$]bis[(1*H*-imidazole-$\kappa N^3$)-copper(II)] diperchlorate

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Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.004 Å
R factor = 0.029
wR factor = 0.077
Data-to-parameter ratio = 13.9

For details of how these key indicators were automatically derived from the article, see http://journals.iucr.org/e.

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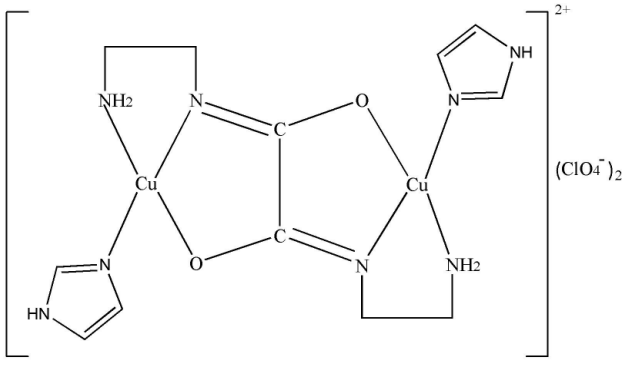
In the crystal structure of the title centrosymmetric binuclear copper(II) complex, $[Cu_2(C_6H_{12}N_4O_2)(C_3H_4N_2)_2](ClO_4)_2$ or $[Cu_2(oxen)(Him)_2](ClO_4)_2$ [oxen = *N*,*N*′-bis(2-aminoethyl)-ethanediamide(2−) and Him = imidazole], two Cu^{II} atoms are bridged by the oxen group. The Cu···Cu distance is 5.219 (2) Å and the Cu atoms have distorted square-planar coordination geometry. Molecules are connected by intermolecular N—H···O hydrogen bonds.

Comment

Bridging oxamidates have played a key role in the design of polynuclear systems, owing to their ability to facilitate strong exchange interactions (Ojima & Nonoyama, 1988). One of the most important properties of these ligands is a very easy *cis*–*trans* conformational change, affording symmetric and asymmetric oxamidate bridges. *N*,*N*′-Disubstituted oxamidates are multifunctional ligands. Coordination complexes of copper(II) with oxamidate are known to act as paramagnetic ligands towards other metal ions (Mathoniere *et al.*, 1993). The crystal structures and magnetic properties of many polynuclear complexes have been previously reported, in which the bridging ligand is the oxamidate group (*e.g.* Lloret *et al.*, 1992; Zhang *et al.*, 1999). We have synthesized a new binuclear complex $[Cu_2(oxen)(Him)_2](ClO_4)_2$, (I), for which we have undertaken the crystal-structure determination.



(I)

Details of the molecular geometry are given in Table 1 and the complex is shown in Fig. 1. The complex consists of a $[Cu_2(oxen)(Him)_2]^{2+}$ binuclear cation and two $(ClO_4)^-$ anions. In the centrosymmetric complex, the inversion center is located at the mid-point of the C1—C1^i [symmetry code: (i) $-x$, $-y$, $-z$] bond. The oxen group adopts the *trans* configuration and acts as a bis-bidentate ligand, connecting the two Cu^{II} atoms *via* five-membered chelate rings with a distance between the two Cu atoms of 5.219 (2) Å. The two Cu^{II} atoms

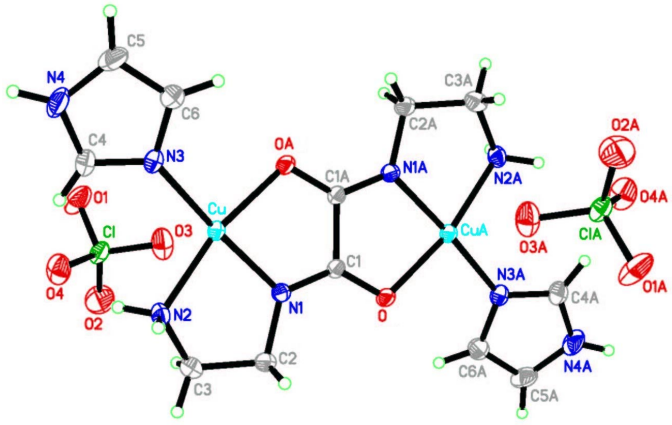


Figure 1
The structure of the title compound, with 30% probability displacement ellipsoids. H atoms are shown as small spheres of arbitrary radii and atoms with the suffix A are related by the symmetry operator $(-x, -y, -z)$.

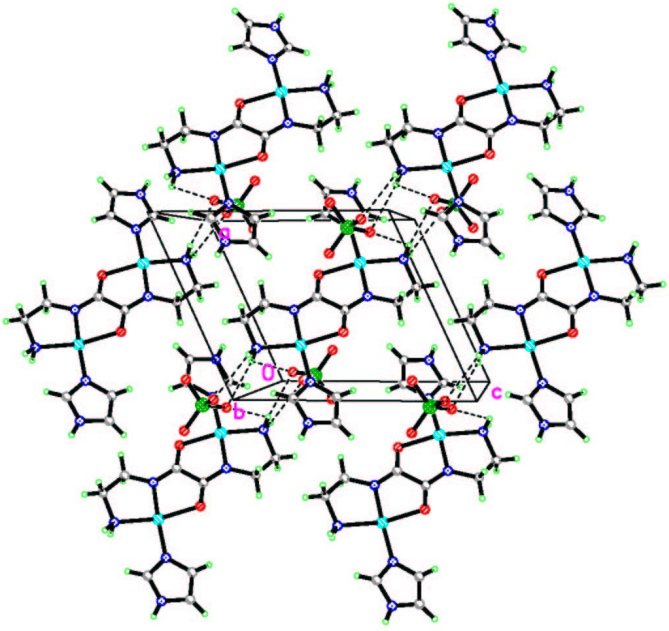


Figure 2
Packing of the title compound, with hydrogen bonds shown as dashed lines.

are four-coordinate, each displaying a distorted square-planar geometry. The Cu^{II} is coordinated by two N atoms [Cu—N1 = 1.9107 (19) Å and Cu—N2 = 2.020 (2) Å], one O atom [Cu—$O1^{i}$ = 2.0071 (16) Å] from the oxen ligand and one N atom [Cu—N3 = 1.942 (2) Å] from the Him group. The unique Cu atom deviates 0.0413 (10) Å from the plane of N1/N2/N3/$O1^{i}$. In the crystal structure, binuclear dications and perchlorate anions are connected by N—H···O hydrogen bonds to form chains along [101] (see Table 2 and Fig. 2).

Experimental

All chemicals were of reagent grade and commercially available from the Beijing Chemical Reagents Company of China, and were used without further purification. $[Cu_2(oxen)](ClO_4)_2$ was synthesized by a literature method (Zhang *et al.*, 2000). To a methanol solution (30 ml) of $Cu(ClO_4)_2·6H_2O$ (3.71 g, 10 mmol) was added a methanol solution (30 ml, 80%) of oxen (Niu *et al.*, 1994) (0.92 g, 5 mmol) with stirring. After a few minutes, 1 *M* NaOH (10 ml) was added. The mixture was then refluxed for 2 h. The resulting green solid was filtered, washed with methanol and recrystallized from a methanol solution (yield 77%). To a methanol solution (25 ml) of $[Cu_2(oxen)](ClO_4)_2$ (0.50 g, 1 mmol) was added a methanol solution (5 ml) of Him (0.14 g, 2 mmol) with stirring. The mixture was refluxed for 1 h, affording a clear blue solution. This was allowed to stand at room temperature for three weeks and well shaped blue single crystals were obtained by slow evaporation.

Crystal data

$[Cu_2(C_6H_{12}N_4O_2)(C_3H_4N_2)_2](ClO_4)_2$
M_r = 634.34
Monoclinic, $P2_1/n$
a = 8.7884 (15) Å
b = 13.765 (3) Å
c = 10.2773 (12) Å
β = 114.741 (12)°
V = 1129.1 (4) $Å^3$
Z = 2
D_x = 1.866 Mg m^{-3}
Mo $K\alpha$ radiation
Cell parameters from 25 reflections
θ = 13.6–18.9°
μ = 2.19 mm^{-1}
T = 293 (2) K
Block, blue
0.60 × 0.50 × 0.50 mm

Data collection

Enraf–Nonius CAD-4 diffractometer
$\omega/2\theta$ scans
Absorption correction: multi-scan (*SADABS*; Sheldrick, 1996)
T_{min} = 0.291, T_{max} = 0.335
2294 measured reflections
2154 independent reflections
2058 reflections with $I > 2\sigma(I)$
R_{int} = 0.038
θ_{max} = 26.0°
$h = 0 \rightarrow 10$
$k = 0 \rightarrow 16$
$l = -12 \rightarrow 11$
3 standard reflections
every 300 reflections
intensity decay: 1.0%

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)]$ = 0.029
$wR(F^2)$ = 0.077
S = 1.06
2154 reflections
155 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.0425P)^2 + 0.9241P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max}$ = 0.77 e $Å^{-3}$
$\Delta\rho_{min}$ = −0.41 e $Å^{-3}$
Extinction correction: *SHELXL*97
Extinction coefficient: 0.060 (4)

Table 1
Selected geometric parameters (Å, °).

Cu—N1	1.9107 (19)	Cl—O1	1.420 (2)
Cu—N3	1.942 (2)	Cl—O2	1.428 (3)
Cu—O^{i}	2.0071 (16)	Cl—O4	1.431 (2)
Cu—N2	2.020 (2)	Cl—O3	1.433 (2)
N1—Cu—N3	175.16 (9)	N1—Cu—N2	82.91 (8)
N1—Cu—O^{i}	83.63 (7)	N3—Cu—N2	100.18 (9)
N3—Cu—O^{i}	93.33 (8)	O^{i}—Cu—N2	166.48 (8)

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

Table 2
Hydrogen-bonding geometry (Å, °).

D—H···A	D—H	H···A	D···A	D—H···A
N2—H2D···O4	0.90	2.39	3.159 (3)	144
N2—H2A···$O1^{ii}$	0.90	2.44	3.212 (3)	144

Symmetry code: (ii) $\frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$.

H atoms attached to C atoms were placed in geometrically idealized positions, with Csp^3—H = 0.97 Å and Csp^2—H = 0.93 Å, and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(C). H atoms attached to N atoms were placed in geometrically idealized positions, with Nsp^3—H = 0.90 Å and Nsp^2—H = 0.86 Å, and constrained to ride on their parent atoms, with U_{iso}(H) = 1.2U_{eq}(N).

Data collection: *CAD*-4 *Software* (Enraf–Nonius, 1989); cell refinement: *CAD*-4 *Software*; data reduction: *MolEN* (Fair, 1990); program(s) used to solve structure: *SHELXS*97 (Sheldrick, 1997*a*); program(s) used to refine structure: *SHELXL*97 (Sheldrick, 1997*a*); molecular graphics: *SHELXTL* (Sheldrick, 1997*b*); software used to prepare material for publication: *SHELXTL*.

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References

Enraf–Nonius (1989). *CAD*-4 *Software*. Version 5.0. Enraf–Nonius, Delft, The Netherlands.
Fair, C. K. (1990). *MolEN*. Enraf–Nonius, Delft, The Netherlands.
Lloret, F., Julve, M., Faus, J., Ruiz, R., Castro, I., Mollar, M., & Philoche-Levisalles, M. (1992). *Inorg. Chem.* **31**, 784–791.
Mathoniere, C., Kahn, O., Daran, J. C., Hilbig, H. & Kohler, F. H. (1993). *Inorg. Chem.* **32**, 4057–4062.
Niu, D.-Z., Zhu, S. R. & Luo, Q. H. (1994). *Inorg. Chem.* **10**, 1–5.
Ojima, H. & Nonoyama, K. (1988). *Coord. Chem. Rev.* **92**, 85–97.
Sheldrick, G. M. (1996). *SADABS*. University of Göttingen, Germany.
Sheldrick, G. M. (1997*a*). *SHELXS*97 and *SHELXL*97. University of Göttingen, Germany.
Sheldrick, G. M. (1997*b*). *SHELXTL*. Bruker AXS Inc., Madison, Wisconsin, USA.
Zhang, C., Z, P., M. Z. & Y, D. (2000). *J. Coord. Chem.* **50**, 159–167.
Zhang, H.–X., Chen, Z.–N., Yu, K.–B., Kang, B.–S. (1999). *Inorg. Chem. Commun.* **2**, 223–226.