

## **[ $\mu$ -*N,N'*-Bis(2-aminoethyl)oxamidato(2-)]bis[(4,5-diazafluoren-9-one)-perchloratocopper(II)] 4,5-diazafluoren-9-one disolvate**

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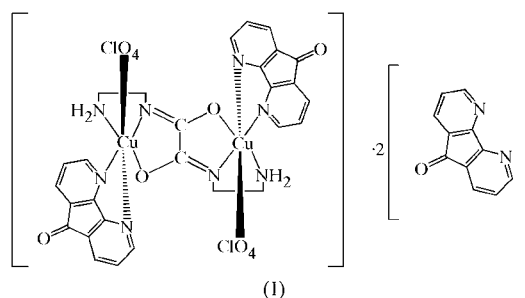
The title compound,  $[\text{Cu}_2(\text{C}_6\text{H}_{12}\text{N}_4\text{O}_2)(\text{ClO}_4)_2(\text{C}_{11}\text{H}_6\text{N}_2\text{O})_2] \cdot 2\text{C}_{11}\text{H}_6\text{N}_2\text{O}$ , contains a dinuclear copper(II) complex which lies about a twofold axis at the mid-point of the C—C bond of the oxamide ligand that bridges the two  $\text{Cu}^{\text{II}}$  atoms. The Cu··Cu distance is 5.215 (2) Å and the Cu atoms have distorted octahedral coordination geometry. Intramolecular N—H··O and N—H··N hydrogen bonds and intermolecular C—H··O hydrogen bonds, together with  $\pi$ – $\pi$  stacking interactions, dominate throughout the crystal structure.

### 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 the 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). As part of our work in this area, we have designed and synthesized the title novel binuclear complex  $[\text{Cu}_2(\text{oxen})(\text{ClO}_4)_2(L)_2] \cdot 2L$  [oxen is *N,N'*-bis(2-aminoethyl)oxamidate and *L* is 4,5-diazafluorenen-9-one], (I), for which we have undertaken the present crystal structure determination.

Details of the molecular geometry of (I) are given in Table 1 and the complex is shown in Fig. 1. The structure consists of a  $[\text{Cu}_2(\text{oxen})(\text{ClO}_4)_2(L)_2]$  complex, which lies about the mid-point of the C—C bond of the oxen ligand on a twofold axis,

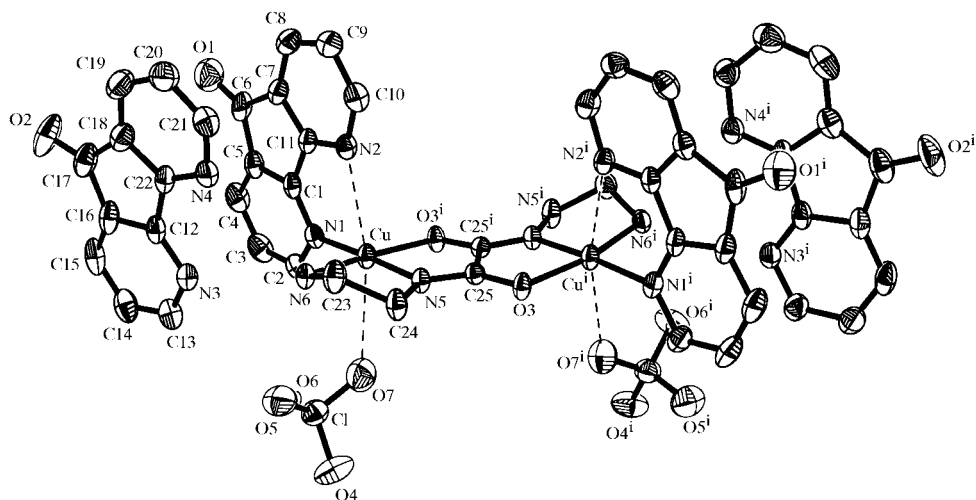
and two free *L* molecules. The oxen group adopts the *trans* conformation and acts as a bis-tridentate ligand connecting the two  $\text{Cu}^{\text{II}}$  atoms and forming a dinuclear complex with a distance between the two Cu atoms of 5.215 (2) Å (without direct interaction), slightly shorter than that in  $[\text{Cu}_2(\text{oxen})(\text{ClO}_4)_2(4\text{-APy})_2]$  (5.24 Å; 4-APy is 4-aminopyridine; Zhang *et al.*, 1999). The two  $\text{Cu}^{\text{II}}$  atoms have the same coordination environment, namely a distorted octahedron, the meridional plane of which is composed of atom N1 of *L* and atoms N5, N6 and O3<sup>i</sup> of the oxen group [symmetry code: (i)  $1 - x, y, \frac{1}{2} - z$ ]. One of the apical positions is occupied by an O atom of the perchlorate group and the other site is weakly linked to atom N2 of *L*, with typical Jahn–Teller elongated distances comparable with the values reported in  $[\text{Cu}_2(\text{oxen})(\text{ClO}_4)_2(4\text{-APy})_2]$ .



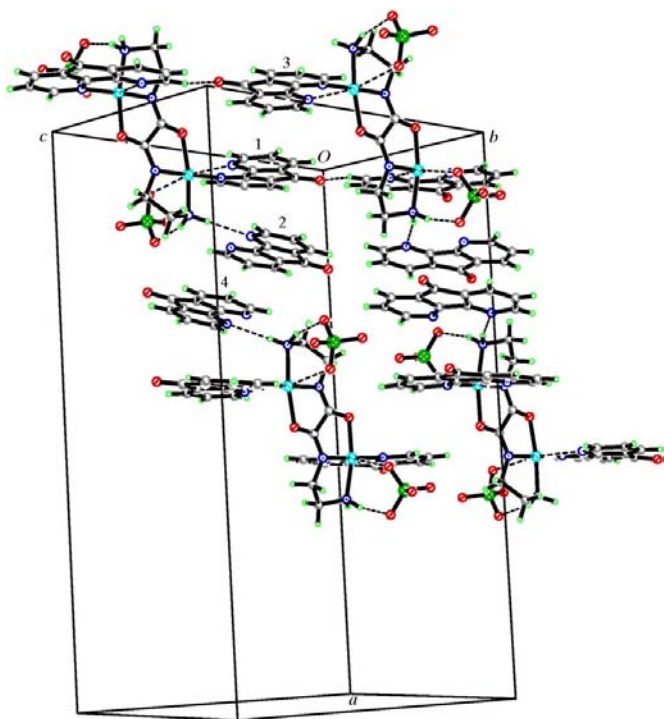
The angle between the *L* plane (atoms C1–C11/N1/N2/O1) and the plane of atoms Cu/N5/C25/O3/Cu<sup>i</sup>/N5<sup>i</sup>/C25<sup>i</sup>/O3<sup>i</sup> is 91.20 (7)°, which shows the planes to be approximately perpendicular. The main structural features of the  $[\text{Cu}_2(\text{oxen})L_2(\text{ClO}_4)_2]$  component are similar to those of the reported complexes  $[\text{Cu}_2(\text{oxen})(\text{ClO}_4)_2(4\text{-APy})_2]$  and  $[\text{Cu}_2\text{Br}_2(\text{oxen})(\text{DAPM})_2]$  (DAPM is 4,4'-diaminodiphenylmethane; Zhang *et al.*, 1999), in that they all contain the oxen group. Their second ligands, however, are different. In  $[\text{Cu}_2(\text{oxen})(\text{ClO}_4)_2(4\text{-APy})_2]$  and  $[\text{Cu}_2\text{Br}_2(\text{oxen})(\text{DAPM})_2]$ , the second ligands are 4-APy and DAPM, respectively, and these are both monodentate, which results in the  $\text{Cu}^{\text{II}}$  atoms exhibiting square-pyramidal geometries. Although it may be thought that the  $\text{Cu}^{\text{II}}$  atoms in  $[\text{Cu}_2(\text{oxen})(\text{ClO}_4)_2(4\text{-APy})_2]$  are in a distorted octahedral environment, the sixth coordinated atom is very weakly linked to the  $\text{Cu}^{\text{II}}$  atom (Cu··N4 = 3.077 Å). By contrast, in (I), the second ligand is 4,5-diazafluoren-9-one and this is bidentate, with the result that the  $\text{Cu}^{\text{II}}$  atoms exhibit a Jahn–Teller-distorted octahedral geometry.

Details of the hydrogen bonding in (I) are listed in Table 2. As illustrated in Fig. 2, the packing consists of a network of hydrogen bonds. These are mainly formed between atoms O1 and N6 of the  $[\text{Cu}_2(\text{oxen})(\text{ClO}_4)_2(L)_2]$  component, atom N4 of the free ligand and atom O6 of the  $\text{ClO}_4^-$  anion.

The  $\pi$ – $\pi$  stacking interactions in the structure of (I) are also shown in Fig. 2. The  $[\text{Cu}_2(\text{oxen})(\text{ClO}_4)_2(L)_2]$  components are interleaved regularly to form a chain along the *c* axis via  $\pi$ – $\pi$  stacking interactions and intermolecular C—H··O hydrogen bonds. Planes 1 (atoms C1–C11/N1/N2) and 3 [atoms C1<sup>ii</sup>–C11<sup>ii</sup>/N1<sup>ii</sup>/N2<sup>ii</sup>; symmetry code: (ii)  $x, -y, z - \frac{1}{2}$ ] of *L* are stacked in a parallel fashion, the distance between the two planes being 3.2816 (8) Å. The free ligands insert into the



**Figure 1**  
The structure of (I), showing the atom-numbering scheme. Displacement ellipsoids are drawn at the 30% probability level and H atoms have been omitted for clarity. [Symmetry code: (i)  $1 - x, y, \frac{1}{2} - z$ .]



**Figure 2**  
The hydrogen-bonding network and  $\pi$ - $\pi$  stacking interactions of (I). The numbers refer to planes defined in the *Comment*.

interstices between the  $[\text{Cu}_2(\text{oxen})(\text{ClO}_4)_2L_2]$  components along the  $a$  axis via  $\pi$ - $\pi$  stacking interactions and N-H...N hydrogen bonds. The  $L$  planes 2 (atoms C12-C22/N3/N4) and 4 [atoms C12<sup>iii</sup>-C22<sup>iii</sup>/N3<sup>iii</sup>/N4<sup>iii</sup>; symmetry code: (iii)  $\frac{1}{2} - x, y + \frac{1}{2}, \frac{3}{2} - z$ ] are also in a parallel arrangement, the distance between the two planes being 3.3040 (8) Å. The  $L$  plane 1 in  $[\text{Cu}_2(\text{oxen})(\text{ClO}_4)_2L_2]$  and the free ligand  $L$  plane 2 deviate somewhat from being parallel, the angle between them being 12.40 (5)°. The shortest interatomic distance between these planes is 3.3648 (8) Å, while the distance between the centres of the two planes is 3.7720 (8) Å. All these distances, *viz.* between  $L$  planes 1 and 2,  $L$  planes 1 and 3

and  $L$  planes 2 and 4, are shorter than the distance between neighbouring base pairs in DNA (3.4 Å; Neidle, 1999). Therefore, stacking interactions dominate throughout the crystal structure, stabilizing the crystal packing together with the hydrogen-bonding interactions.

### Experimental

All chemicals were of reagent grade, commercially available from the Beijing Chemical Reagents Company, China, and were used without further purification.  $[\text{Cu}_2(\text{oxen})](\text{ClO}_4)_2$  was synthesized according to the literature method of Zhang *et al.* (2000). To a methanol solution (30 ml) of  $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$  (3.71 g, 10 mmol) was added an 80% methanol solution (30 ml) of oxen (0.92 g, 5 mmol; Niu *et al.*, 1994) with stirring. After a few minutes, a solution of 1 M NaOH (10 ml) was added. The mixture was then refluxed for 2 h to give a green solid. The solid was filtered off, washed with methanol and recrystallized from an 80% methanol solution (yield 77%). For the preparation of (I), a methanol solution (5 ml) of  $L$  (0.36 g, 2 mmol; Henderson *et al.*, 1984) was added to a methanol solution (25 ml) of  $[\text{Cu}_2(\text{oxen})](\text{ClO}_4)_2$  (0.50 g, 1 mmol) with stirring. The mixture was refluxed for 1 h to give a clear blue solution and, after standing at room temperature for three weeks, blue single crystals of (I) were obtained by slow evaporation.

### Crystal data

$[\text{Cu}_2(\text{C}_6\text{H}_{12}\text{N}_4\text{O}_2)(\text{ClO}_4)_2 \cdot (\text{C}_{11}\text{H}_6\text{N}_2\text{O}_2)_2] \cdot 2\text{C}_{11}\text{H}_6\text{N}_2\text{O}$   
 $M_r = 1226.89$   
 Monoclinic,  $C2/c$   
 $a = 26.5955$  (1) Å  
 $b = 11.4267$  (3) Å  
 $c = 16.5915$  (4) Å  
 $\beta = 92.0530$  (10)°  
 $V = 5038.90$  (18) Å<sup>3</sup>  
 $Z = 4$

$D_x = 1.617$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 4667 reflections  
 $\theta = 1.9$ -25.1°  
 $\mu = 1.03$  mm<sup>-1</sup>  
 $T = 293$  (2) K  
 Block, blue  
 $0.44 \times 0.40 \times 0.36$  mm

### Data collection

Siemens SMART CCD area-detector diffractometer  
 $\varphi$  and  $\omega$  scans  
 Absorption correction: empirical (*SADABS*; Sheldrick, 1996)  
 $T_{\min} = 0.659, T_{\max} = 0.708$   
 8436 measured reflections

4441 independent reflections  
 3294 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.040$   
 $\theta_{\text{max}} = 25.1^\circ$   
 $h = -25 \rightarrow 31$   
 $k = -10 \rightarrow 13$   
 $l = -19 \rightarrow 19$

## Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.069$   
 $wR(F^2) = 0.198$   
 $S = 1.09$   
 4441 reflections  
 355 parameters  
 H-atom parameters constrained

$$w = 1/[\sigma^2(F_o^2) + (0.0804P)^2 + 32.9042P]$$

where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} < 0.001$   
 $\Delta\rho_{\max} = 0.82 \text{ e } \text{\AA}^{-3}$   
 $\Delta\rho_{\min} = -0.58 \text{ e } \text{\AA}^{-3}$

Table 1

Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Cu—N5	1.914 (4)	Cu—O7	2.885 (7)
Cu—O3 <sup>i</sup>	2.002 (4)	Cl—O7	1.404 (6)
Cu—N1	2.009 (5)	Cl—O4	1.414 (6)
Cu—N6	2.017 (4)	Cl—O6	1.418 (6)
Cu—N2	2.619 (5)	Cl—O5	1.427 (6)
N5—Cu—O3 <sup>i</sup>	83.87 (16)	N1—Cu—N2	78.79 (18)
N5—Cu—N1	176.1 (2)	N6—Cu—N2	87.74 (18)
O3 <sup>i</sup> —Cu—N1	94.49 (17)	N5—Cu—O7	84.49 (19)
N5—Cu—N6	83.40 (18)	O3 <sup>i</sup> —Cu—O7	96.92 (18)
O3 <sup>i</sup> —Cu—N6	166.98 (16)	N1—Cu—O7	92.23 (19)
N1—Cu—N6	98.38 (19)	N6—Cu—O7	84.6 (2)
N5—Cu—N2	104.78 (18)	N2—Cu—O7	167.20 (16)
O3 <sup>i</sup> —Cu—N2	92.89 (16)		

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

Table 2

Hydrogen-bonding geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H\cdots A$	$D-H$	$H\cdots A$	$D\cdots A$	$D-H\cdots A$
N6—H6A $\cdots$ N4	0.90	2.31	3.195 (7)	169
N6—H6B $\cdots$ O6	0.90	2.17	3.037 (8)	163
C10—H10A $\cdots$ O1 <sup>ii</sup>	0.93	2.42	3.281 (9)	155

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

All H atoms were placed in geometrically idealized positions, with  $Csp^3-H = 0.97 \text{ \AA}$ ,  $Csp^2-H = 0.93 \text{ \AA}$  and  $Nsp^3-H = 0.90 \text{ \AA}$ , and constrained to ride on their parent atoms, with  $U_{iso}(H) = 1.2U_{eq}(C,N)$ .

Data collection: *SMART* (Siemens, 1996); cell refinement: *SAINTE* (Siemens, 1994); data reduction: *SAINTE*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXL97*; software used to prepare material for publication: *SHELXL97*.

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: SQ1182). Services for accessing these data are described at the back of the journal.

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