[\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, \([\text{Cu}_2(\text{C}_6\text{H}_4\text{N}_2\text{O}_2)(\text{ClO}_4)_2(\text{C}_6\text{H}_8\text{N}_2\text{O}_2)]\)·2\(\text{C}_2\text{H}_5\text{H}_2\text{O}\), contains a dinuclear copper(II) complex which lies about a twofold axis at the mid-point of the \(\text{C} \cdots \text{C}\) bond of the oxamide ligand that bridges the two CuII atoms. The Cu···Cu distance is 5.215 (2) Å and the Cu atoms have distorted octahedral coordination geometry. Intramolecular hydrogen bonds and intermolecular 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 oxamide bridges. \(N,N'-\)Disubstituted oxamidates are multifunctional ligands. Coordination complexes of copper(II) with oxamide are known to act as paramagnetic ligands towards other metal ions (Mathioniere et al., 1993). The crystal structures and magnetic properties of many polynuclear complexes have been previously reported, in which the bridging ligand is the oxamide 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\(L\) [oxen is \(N,N'-\)bis(2-aminoethyl)oxamide 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 \([\text{Cu}_2(\text{oxen})(\text{ClO}_4)_2(L)]\) complex, which lies about the mid-point of the \(\text{C} \cdots \text{C}\) 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 CuII 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 \([\text{Cu}_2(\text{oxen})(\text{ClO}_4)_2(\text{4-APy})_2]\) (5.24 Å; 4-APy is 4-aminopyridine; Zhang et al., 1999). The two CuII 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 O3i of the oxen group [symmetry code: (ii) 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 \([\text{Cu}_2(\text{oxen})(\text{ClO}_4)_2(\text{4-APy})_2]\).

The angle between the \(L\) plane (atoms C1–C11/N1/N2/O1) and the plane of atoms Cu/N5/C25/O3/Cu/N5/C25/O3 is 91.20 (7)°, which shows the planes to be approximately perpendicular. The main structural features of the \([\text{Cu}_2(\text{oxen})(\text{ClO}_4)_2]\) component are similar to those of the reported complexes \([\text{Cu}_2(\text{oxen})(\text{ClO}_4)_2(\text{4-APy})_2]\) 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 \([\text{Cu}_2(\text{oxen})(\text{ClO}_4)_2(\text{4-APy})_2]\) 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 CuII atoms exhibiting square-pyramidal geometries. Although it may be thought that the CuII atoms in \([\text{Cu}_2(\text{oxen})(\text{ClO}_4)_2(\text{4-APy})_2]\) are in a distorted octahedral environment, the sixth coordinated atom is very weakly linked to the CuII atom (Cu···N4 = 3.077 Å). By contrast, in (I), the second ligand is 4,5-diazafluorenen-9-one and this is bidentate, with the result that the CuII 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 \([\text{Cu}_2(\text{oxen})(\text{ClO}_4)_2(L)]\) 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 \([\text{Cu}_2(\text{oxen})(\text{ClO}_4)_2(L)]\) components are interleaved regularly to form a chain along the \(c\) axis via \(\pi\)–\(\pi\) stacking interactions and intermolecular \(\text{C} \cdots \text{H} \cdots \text{O}\) hydrogen bonds. Planes 1 (atoms C1–C11/N1/N2) and 3 [atoms C1II–C1II′/N1II/N2II; symmetry code: (ii) \(-x, y, -z\)] 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...
interstices between the \([\text{Cu}_2(\text{oxen})(\text{ClO}_4)_2] \) components along the \(a\) axis via \(\pi-\pi\) stacking interactions and N-H \(\cdots\) N hydrogen bonds. The \(L\) planes 2 (atoms C12-C22/N3/N4) and 4 (atoms C12iii-C22iii/N3iii/N4iii) are also in a parallel arrangement, the distance between the two planes being 3.3040 (8) \(\text{Å}\).

The interatomic distance 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 \(\text{Å}\); 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 \(\text{Cu}((\text{ClO}_4)_2\cdot6\text{H}_2\text{O} (3.71 \text{ g}, 10 \text{ mmol})\) 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 \(M\) \(\text{NaOH} (10 \text{ ml})\) 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 \(\text{L} (0.36 \text{ g}, 2 \text{ mmol}; \text{Henderson et al., 1984}) \) was added to a methanol solution (25 ml) of \([\text{Cu}_2(\text{oxen})(\text{ClO}_4)_2] (0.50 \text{ g}, 1 \text{ mmol}) \) 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**

\[
[\text{Cu}_2(\text{C}_6\text{H}_{12}\text{N}_4\text{O}_2)(\text{ClO}_4)_2]-2\text{C}_1\text{H}_4\text{N}_2\text{O} \\
M_r = 1226.89 \\
\text{Monoclinic, } C2/c \\
a = 26.5955 (1) \text{ Å} \\
b = 11.4267 (3) \text{ Å} \\
c = 16.5915 (4) \text{ Å} \\
\beta = 92.0530 (10) \\
V = 5038.90 (18) \text{ Å}^3 \\
Z = 4
\]

**Data collection**

\[
\begin{array}{ll}
\text{Siemens SMART CCD area-detector diffractometer} & \text{\(D_1 = 1.617 \text{ Mg m}^{-3}\)} \\
\text{4441 independent reflections} & \text{\(\text{Mo K\alpha radiation}\)} \\
\text{3294 reflections with } I > 2\sigma(I) & \text{Cell parameters from 4667} \\
\phi and \omega scans & \text{reflections} \\
\text{Absorption correction: empirical} & \theta = 1.9-25.1^\circ \\
\text{(SADABS; Sheldrick, 1996)} & \mu = 1.03 \text{ mm}^{-1} \\
T = 293 (2) \text{ K} & T = 293 (2) \text{ K} \\
\text{Block, blue} & \text{Block, blue} \\
0.44 \times 0.40 \times 0.36 \text{ mm} & \text{0.44 x 0.40 x 0.36 mm} \\
\end{array}
\]

**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.
Refinement

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

\[
\begin{align*}
 w & = [1 + 0.001F^2] / F^2 \quad \text{where} \quad P = (F^2 + 2F_i^2)/3 \\
(A/\sigma)_{	ext{max}} & < 0.001 \\
\Delta \rho_{	ext{max}} & = 0.82 \text{ e Å}^{-3} \\
\Delta \rho_{	ext{min}} & = -0.58 \text{ e Å}^{-3}
\end{align*}
\]

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1994); data reduction: SAINT; 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.

The Provincial Natural Science Foundation of Anhui is acknowledged for financial support for FXX (grant No. 29971001). The authors are indebted to Teacher Li-Ping Lu for helpful discussions.

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.

Table 1
Selected geometric parameters (Å, °).

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<tr>
<th>Bond</th>
<th>Distances</th>
<th>Angles</th>
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<tbody>
<tr>
<td>Cu–N5</td>
<td>1.914 (4)</td>
<td>Cu–O7 2.885 (7)</td>
</tr>
<tr>
<td>Cu–O3*</td>
<td>2.002 (4)</td>
<td>Cl–O7 1.404 (6)</td>
</tr>
<tr>
<td>Cu–N1</td>
<td>2.009 (5)</td>
<td>Cl–O4 1.414 (6)</td>
</tr>
<tr>
<td>Cu–N6</td>
<td>2.017 (4)</td>
<td>Cl–O6 1.418 (6)</td>
</tr>
<tr>
<td>Cu–N2</td>
<td>2.619 (5)</td>
<td>Cl–O5 1.427 (6)</td>
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<td>N3–Cu–O3*</td>
<td>83.87 (16)</td>
<td>N3–Cu–N1 78.79 (18)</td>
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<td>N5–Cu–N1</td>
<td>176.1 (2)</td>
<td>N5–Cu–O7 87.74 (18)</td>
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<td>O3*–Cu–N1</td>
<td>94.49 (17)</td>
<td>N5–Cu–O7 84.49 (19)</td>
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<tr>
<td>N5–Cu–N6</td>
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<td>O3*–Cu–N6</td>
<td>166.98 (16)</td>
<td>N5–Cu–N6 92.23 (19)</td>
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<td>N1–Cu–N6</td>
<td>98.38 (19)</td>
<td>N1–Cu–O7 84.6 (2)</td>
</tr>
<tr>
<td>N5–Cu–N2</td>
<td>104.78 (18)</td>
<td>N6–Cu–O7 167.20 (16)</td>
</tr>
<tr>
<td>O3*–Cu–N2</td>
<td>92.89 (16)</td>
<td>N5–Cu–N2 78.79 (18)</td>
</tr>
</tbody>
</table>

Symmetry code: (i) 1 − x, 1 − y, 1 − z.

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

<table>
<thead>
<tr>
<th>Bond</th>
<th>D–H ⋅⋅⋅A</th>
<th>D–H</th>
<th>H ⋅⋅⋅A</th>
<th>D ⋅⋅⋅A</th>
<th>D–H ⋅⋅⋅A</th>
</tr>
</thead>
<tbody>
<tr>
<td>N6–H6A⋯N4</td>
<td>0.90</td>
<td>2.31</td>
<td>3.195 (7)</td>
<td>169</td>
<td></td>
</tr>
<tr>
<td>N6–H6B⋯O6</td>
<td>0.90</td>
<td>2.17</td>
<td>3.037 (8)</td>
<td>163</td>
<td></td>
</tr>
<tr>
<td>C10–H10A⋯O1*</td>
<td>0.93</td>
<td>2.42</td>
<td>3.281 (9)</td>
<td>155</td>
<td></td>
</tr>
</tbody>
</table>

Symmetry code: (ii) x, −y, z − 1/2.

All H atoms were placed in geometrically idealized positions, with Csp²−H = 0.97 Å, Csp²−H = 0.93 Å and Nsp²−H = 0.90 Å, and constrained to ride on their parent atoms, with \( U_{	ext{iso}}(H) = 1.2U_{	ext{eq}}(C,N) \).

References