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Bis(N-oxidonicotinamidium-κ^2O,O')-diperchloratocopper(II)

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Key indicators

Single-crystal X-ray study
T = 120 K
Mean σ(C–C) = 0.003 Å
Disorder in main residue
R factor = 0.032
wR factor = 0.091
Data-to-parameter ratio = 11.6

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

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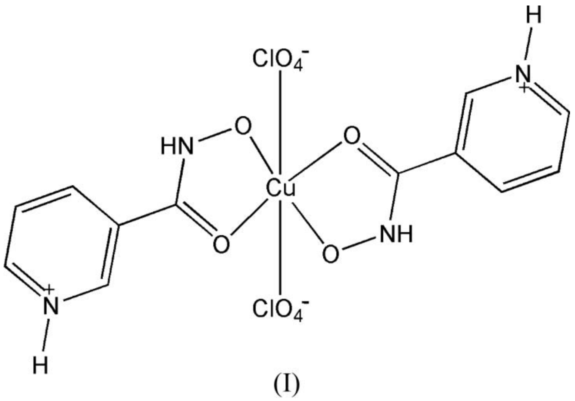
The title compound, $[Cu(ClO_4)_2(C_6H_6N_2O_2)_2]$, contains neutral molecules of a centrosymmetric mononuclear copper(II) complex, in which the zwitterionic hydroxamic acid ligand is O,O'-chelated to the Cu^{II} atom. The Cu^{II} atom lies on an inversion centre and has a distorted tetragonal-bipyramidal environment, being coordinated by four O atoms of the two N-hydroxynicotinamide molecules forming the equatorial plane, and by two O atoms of the perchlorate anions occupying the axial positions.

Comment

Hydroxamic acids are a traditional class of ligands widely used in coordination and analytical chemistry and are efficient inhibitors of a series of metalloenzymes, *e.g.* urease or histone deacetylase (Kaczka *et al.*, 1962; Hershko *et al.*, 1992; Ghio *et al.*, 1992; Shao *et al.*, 2004). During the past decade, hydroxamic acids have been found to exhibit a remarkable ability to form oligonuclear compounds containing large numbers of metal ions, and also coordination polymers (Bodwin *et al.*, 2001; Cutland-Van Noord *et al.*, 2002; Gaynor *et al.*, 2002). The present investigation is aimed at the study of the molecular structure of the title compound, (I), which is a suitable mononuclear precursor for the preparation of coordination polymers (Mulcahy *et al.*, 2005).



(I)

The structure of (I) comprises neutral centrosymmetric molecules (Fig. 1). The Cu^{II} ion is situated in a distorted tetragonal–bipyramidal environment consisting of six O atoms. The equatorial plane is formed by the four O atoms of the two hydroxamic acid ligands, while the axial positions are occupied by two perchlorate anions. The organic ligand exists in a zwitterionic form due to intramolecular proton transfer from the hydroxamic O atom to the pyridine N atom, and is coordinated in a classical O,O'-chelating mode. The proto-

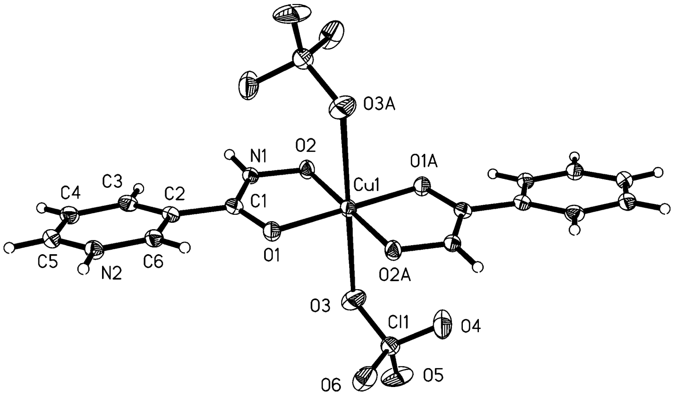


Figure 1
The molecular structure of compound (I), with displacement ellipsoids drawn at the 50% probability level. H atoms are shown as spheres of arbitrary radius. The minor disordered component is not shown. Unlabelled atoms and atoms labelled with the suffix A are generated by the symmetry operation ($-x + \frac{1}{2}, -y + \frac{3}{2}, -z + 1$).

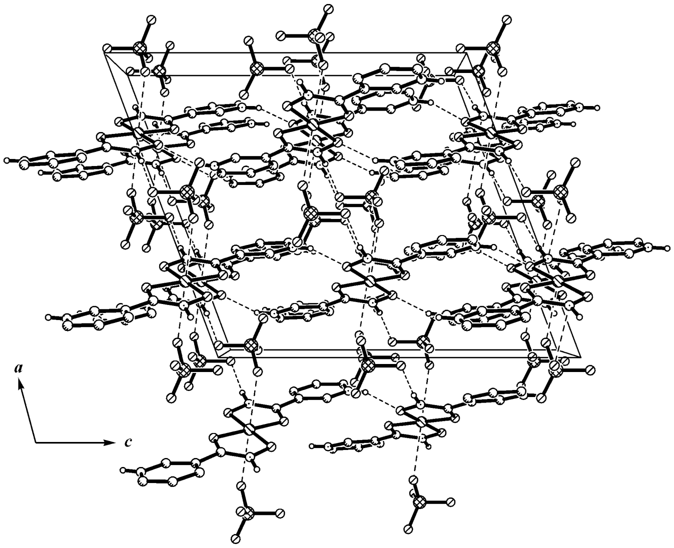


Figure 2
A packing diagram of the title compound. Hydrogen bonds are indicated by dashed lines. H atoms not involved in hydrogen bonding have been omitted for clarity.

nated state of the pyridine N atom makes it impossible for it to participate in coordination to the metal ion. The dihedral angle between the mean plane of the hydroxamic acid group defined by the four atoms O1/C1/N1/O2 and the pyridine ring is 15.85 (10)°.

The axial contact distance Cu—O [2.828 (2) Å] is noticeably longer than the equatorial Cu—O bond lengths [mean = 1.925 (2) Å], due to the Jahn–Teller effect. The angular distortions in the coordination environment are characterized by a diminishing of the O1—Cu1—O2 bite angle to 84.70 (6)°, and also by smaller deviations of the *cis* angles from 90° [87.63 (6)–92.37 (6)°].

The neutral molecules of the complex are connected by hydrogen bonds formed by the hydroxamic acid N—H H atoms and the perchlorate atoms O6, and also between the pyridinium N—H H atoms and the hydroxamic acid atom O2 of translationally related molecules (Table 1). As a result of interactions of the first type, translationally related complexes are arranged into stair-like columns, which are connected to form a two-dimensional network parallel to the *bc* plane (Fig. 2). Due to hydrogen bonds of the second type, the network along the *c* axis results in a three-dimensional structure.

Experimental

An aqueous solution of copper(II) perchlorate hexahydrate (1 *M*, 0.5 ml) was added to pyridine-3-hydroxamic acid [prepared according to the method of Mulcahy *et al.* (2005)] dissolved in methanol (5 ml, 0.138 g, 1 mmol). The resulting solution was left at room temperature to crystallize. Green crystals of (I) formed within 12 h, and these were separated by filtration, washed with cold water (10 ml) and air-dried.

Crystal data

$[Cu(ClO_4)_2(C_6H_6N_2O_2)_2]$
$M_r = 538.70$
Monoclinic, $C2/c$
$a = 14.1287$ (7) Å
$b = 8.6553$ (3) Å
$c = 15.7370$ (8) Å
$\beta = 110.535$ (2)°
$V = 1802.17$ (14) Å^3
$Z = 4$
Mo $K\alpha$ radiation
$\mu = 1.59$ mm^{-1}
$T = 120$ (2) K
0.23 × 0.15 × 0.12 mm

Data collection

Nonius KappaCCD area-detector diffractometer
Absorption correction: multi-scan (*SADABS*; Sheldrick, 2003*a*)
$T_{min} = 0.710$, $T_{max} = 0.832$
10729 measured reflections
2057 independent reflections
1746 reflections with $I > 2\sigma(I)$
$R_{int} = 0.037$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.032$
$wR(F^2) = 0.091$
$S = 1.06$
2057 reflections
178 parameters
3 restraints
H atoms treated by a mixture of independent and constrained refinement
$\Delta\rho_{max} = 0.46$ e Å^{-3}
$\Delta\rho_{min} = -0.63$ e Å^{-3}

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

D—H···A	D—H	H···A	D···A	D—H···A
N1—H1N···O6^{i}	0.86 (3)	2.02 (3)	2.868 (6)	169 (3)
N1—H1N···O6B^{i}	0.86 (3)	2.04 (3)	2.886 (7)	170 (3)
N2—H2N···O2^{ii}	0.84 (3)	1.90 (3)	2.704 (2)	158 (2)

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

Significant rotational disorder about the O3—Cl axis was found in the perchlorate anion, which was treated as a constrained regular tetrahedron. Three of the four O atoms were disordered over two positions, with occupancies of 0.52 (4):0.48 (4). The N-bound H atoms were located in a difference Fourier map and refined with isotropic displacement parameters. Other H atoms were positioned geometrically and constrained to ride on their parent atoms, with C—H = 0.95 Å and $U_{iso}(H) = 1.2U_{eq}(C)$.

Data collection: *COLLECT* (Nonius, 2000); cell refinement: *DENZO* and *SCALEPACK* (Otwinowski & Minor, 1997); data reduction: *DENZO* and *SCALEPACK*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine

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structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Sheldrick, 2003*b*); software used to prepare material for publication: *SHELXL97*.

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