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An adduct of (1,10-phenanthroline)-diperchloratobis(pyridine-4-carboxaldehyde oxime-κN^1)copper(II) and pyridine-4-carboxaldehyde oxime

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In the structure of [Cu(ClO$_4$)$_2$(PA)$_2$(μ-phen)]·PA [PA = pyridine-4-carboxaldehyde oxime or 4-pyridinealdoxime ($C_6H_6N_2O$) and phen = 1,10-phenanthroline ($C_{12}H_8N_2$)], the coordination geometry around the Cu^{II} atom may be described as a distorted octahedron. Four N atoms, two from a phen ligand and two from PA ligands, occupy the equatorial positions, while two O atoms from two perchlorate groups occupy the axial positions. The PA molecules which are not involved in the Cu^{II} coordination link the complexes through O—H···N and O—H···O hydrogen bonds, forming layers parallel to the *ac* plane.

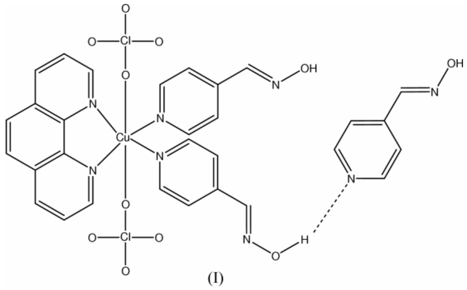
Key indicators

Single-crystal X-ray study
T = 293 K
Mean σ(C–C) = 0.009 Å
R factor = 0.069
wR factor = 0.122
Data-to-parameter ratio = 12.7

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

Comment

It is well known that the design of complexes of the copper ion with various organic ligands is an interesting field (Richards & Durrant, 2002; Melnik *et al.*, 2000) because of their diversity in coordination chemistry and model applications in biomolecules. As a strong bidentate ligand and a chromophoric group, 1,10-phenanthroline (phen) is involved in many copper complexes (Liu *et al.*, 2002; Chen *et al.*, 2003; Wang *et al.*, 2002; Devi & Zubieta, 2003; Clarke *et al.*, 2003; Guo *et al.*, 2002). 4-Pyridinealdoxime (PA) can be considered as a linear bridging ligand and few complexes of transition metals with PA have been reported (Allan & Paton, 1993). We report here, the structure of a coordination aggregate, (I), constructed by Cu(ClO$_4$)$_2$, phen and PA, in which the PA functions as a terminal ligand.



(I)

The asymmetric unit of (I) contains a discrete [Cu(PA)$_2$(μ-phen)(ClO$_4$)$_2$] complex and a PA molecule. A displacement ellipsoid plot of the complex is shown in Fig. 1 and selected bond distances and angles are given in Table 1.. The coordination environment of the central Cu^{II} atom can be described as a distorted octahadron with two N atoms (N1 and N2) from a phen ligand and two N atoms (N3 and N5) from PA ligands occupying the equatorial positions, and two O atoms (O1 and O6) from two perchlorate groups occupying the axial positions. The Cu^{II} atom is displaced from the equatorial plane by

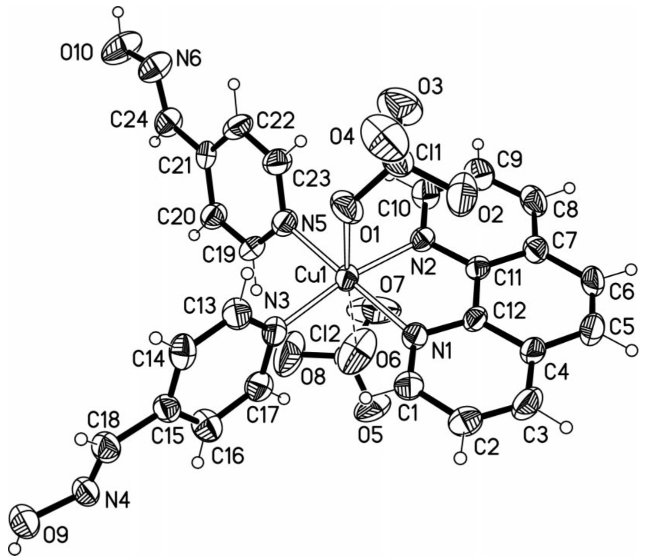


Figure 1
The structure of (I), showing 35% probability displacement ellipsoids and the atomic numbering scheme. The coordination bonds are shown as open lines and dashed line indicates a longer coordination bond.

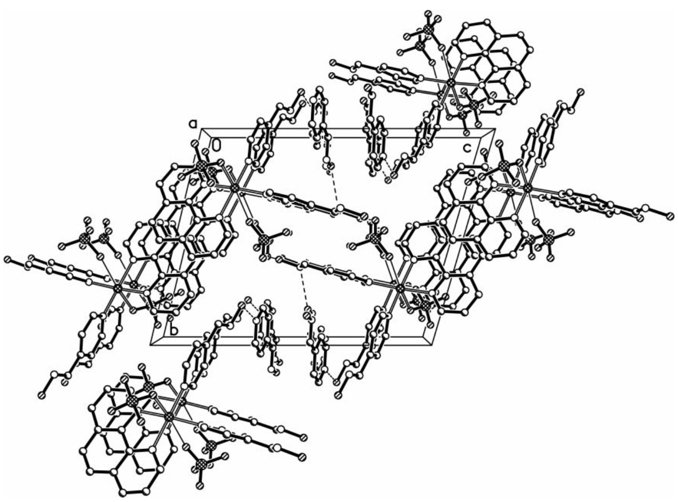


Figure 2
A view of the molecular packing down the *a* axis.

0.095 (3) Å, in the direction of O1. The average Cu—N distance of 2.005 (4) Å is comparable to that [2.020 (3) Å] found in $[Cu(phen)_2py(ClO_4)]^+$ (py = pyridine; Niu *et al.*, 2001). The length of the two axial Cu—O coordination bonds are not equal. The Cu1—O6 bond length [2.960 (5) Å] is considerably longer than Cu1—O1 bond length [2.357 (4) Å]. The shorter Cu—O length is slightly longer than that found between Cu^{II} and the O atom of a water molecule (2.274 Å; Liu *et al.*, 2002). The longer Cu—O distance suggests a very weak bonding. However, it is still shorter than that found in $[Cu(phen)_2py(ClO_4)]^+$ (Niu *et al.*, 2001). The fact that atoms O1 and O6 have smaller displacement parameters compared to those of the other O atoms of perchlorate groups confirms the interactions between Cu^{II} and perchlorate groups.

The phen ligand is planar and makes a dihedral angle of 4.0 (2)° with the equatorial plane. The coordinated PA molecules play a role of terminal ligand instead of the expected linear bridging ligand. However, the PA molecules which are not involved in the Cu^{II} coordination connect the complexes through hydrogen bondings. As can be seen from Fig. 2, the O—H⋯N and O—H⋯O hydrogen bonds (Table 2) between the complexes and uncoordinated PA molecules, as well as O—H⋯O hydrogen bonds between coordinated PA molecules and perchlorate groups, result in the formation of thick layers parallel to the *ac* plane.

Experimental

To a methanol solution (20 ml) of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.5 mmol) and phen (0.5 mmol), 4-pyridinealdoxime (1.0 mmol) was added. The mixture was stirred for 2 h in air before being left at room temperature for 30 min. The resulting dark-blue solution was filtered and allowed to evaporate at room temperature. After 2 d, blue crystals of the complex suitable for X-ray analysis were obtained. They were collected by suction filtration and air-dried. All chemicals were purchased commercially and used without further purification.

Crystal data

$[Cu(ClO_4)_2(C_6H_6N_2O)_2(C_{12}H_8N_2)]{\cdot}C_6H_6N_2O$
$M_r = 809.03$
Triclinic, $P\overline{1}$
$a = 8.2981$ (7) Å
$b = 13.525$ (2) Å
$c = 16.5280$ (13) Å
$\alpha = 104.16$ (2)°
$\beta = 90.05$ (2)°
$\gamma = 107.34$ (2)°
$V = 1711.3$ (4) Å^3
$Z = 2$
$D_x = 1.570$ Mg m^{-3}
Mo *Kα* radiation
Cell parameters from 3143 reflections
$\theta = 2.3$–20.4°
$\mu = 0.87$ mm^{-1}
$T = 293$ (2) K
Plate, blue
0.30 × 0.10 × 0.08 mm

Data collection

Bruker SMART APEX CCD diffractometer
φ and ω scans
Absorption correction: multi-scan (*SADABS*; Bruker, 1999)
$T_{min} = 0.726$, $T_{max} = 0.933$
7700 measured reflections
5970 independent reflections
3289 reflections with $I > 2\sigma(I)$
$R_{int} = 0.048$
$\theta_{max} = 25.0$°
$h = -9 \rightarrow 9$
$k = -15 \rightarrow 16$
$l = -19 \rightarrow 19$

Refinement

Refinement on F^2
$R[F^2 > 2\sigma(F^2)] = 0.069$
$wR(F^2) = 0.122$
$S = 1.02$
5970 reflections
469 parameters
H-atom parameters constrained
$w = 1/[\sigma^2(F_o^2) + (0.001P)^2 + 0.5P]$ where $P = (F_o^2 + 2F_c^2)/3$
$(\Delta/\sigma)_{max} < 0.001$
$\Delta\rho_{max} = 0.48$ e Å^{-3}
$\Delta\rho_{min} = -0.33$ e Å^{-3}

Table 1
Selected geometric parameters (Å, °).

Cu1—N3	1.986 (5)	Cu1—N5	2.026 (4)
Cu1—N2	1.993 (4)	Cu1—O1	2.357 (4)
Cu1—N1	2.014 (4)	Cu1—O6	2.960 (5)
N3—Cu1—N2	170.4 (2)	N1—Cu1—O1	90.40 (15)
N3—Cu1—N1	91.45 (18)	N5—Cu1—O1	92.76 (17)
N2—Cu1—N1	82.81 (18)	N3—Cu1—O6	93.53 (19)
N3—Cu1—N5	90.61 (17)	N2—Cu1—O6	78.72 (15)
N2—Cu1—N5	94.71 (17)	N1—Cu1—O6	88.83 (14)
N1—Cu1—N5	176.18 (18)	N5—Cu1—O6	87.83 (16)
N3—Cu1—O1	91.59 (18)	O1—Cu1—O6	174.84 (14)
N2—Cu1—O1	96.12 (15)		

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

D—H$\cdots A$	D—H	H$\cdots A$	$D\cdots A$	D—H$\cdots A$
O9—H9$B\cdots$N7^{i}	0.82	1.88	2.660 (7)	160
O10—H10$B\cdots$O7^{ii}	0.82	2.01	2.823 (7)	169
O11—H11$A\cdots$N6	0.82	2.05	2.816 (7)	156

Symmetry codes: (i) $x-2, y, z$; (ii) $1-x, 1-y, 1-z$.

H atoms were placed in geometrical positions and allowed for using a riding model [C—H = 0.93 Å, O—H = 0.82 Å and $U_{\rm iso}$(H) = $1.2U_{\rm eq}$(parent C) and $1.5U_{\rm eq}$(parent N)].

Data collection: *SMART* (Bruker, 1997); cell refinement: *SMART*; data reduction: *SAINT* (Bruker, 1997); program(s) used to solve structure: *SHELXTL* (Bruker, 1997); program(s) used to refine structure: *SHELXTL*; molecular graphics: *SHELXTL*; software used to prepare material for publication: *SHELXTL*.

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