

**(2,2'-Bipyridyl- $\kappa^2N,N'$ )(chloranilato- $\kappa^2O,O'$ )-copper(II)****Santiago Reinoso, Pablo Vitoria,\*  
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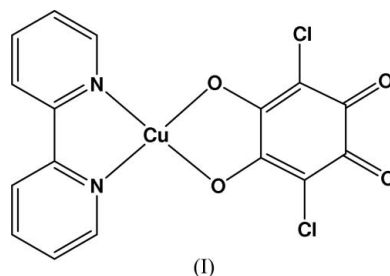
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**Key indicators**Single-crystal X-ray study  
 $T = 295$  K  
Mean  $\sigma(C-C) = 0.004$  Å  
 $R$  factor = 0.035  
 $wR$  factor = 0.065  
Data-to-parameter ratio = 19.9For details of how these key indicators were  
automatically derived from the article, see  
<http://journals.iucr.org/e>.

The Cu atom in the title complex,  $[Cu(C_6Cl_2O_4)(C_{10}H_8N_2)]$ , has a square-planar  $CuN_2O_2$  environment. The structure is built of monomeric neutral, essentially planar, molecules stacked along the  $b$  axis, with the stacks held together by means of weak  $\pi-\pi$ ,  $\pi \cdots Cl$ , and  $\pi \cdots Cu$  interactions. The molecules of neighbouring stacks are linked *via*  $C-H \cdots O$  hydrogen bonds.

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To date, there is only one structurally characterized  $Cu^{II}$  complex in the literature with both 2,2-bipyridine (bpy) and the chloranilate dianion (chl) as ligands, namely the dimeric cation of  $[[Cu(C_{10}H_8N_2)(CH_3OH)]_2(chl)](PF_6)_2$  (Fujii *et al.*, 1994). The title monomeric neutral complex, (I), was obtained in an attempt to prepare a hybrid inorganic-metal-organic material based on the auto-assembly of the above-mentioned dimer and Keggin-type polyoxometallates.

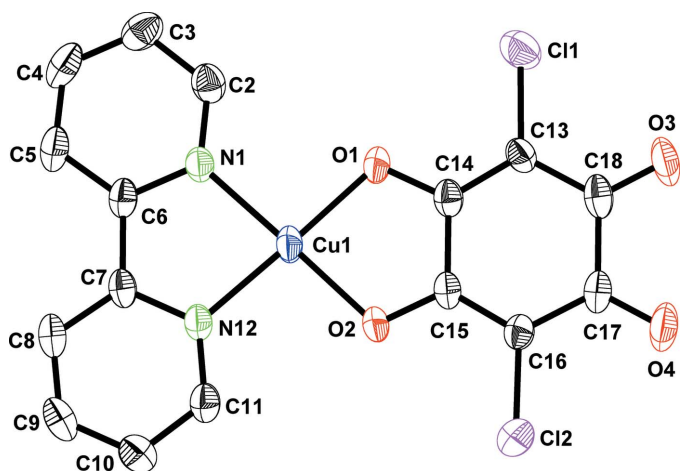


The Cu atom in the title compound is coordinated by both the neutral bpy and the dianionic chl ligands in a chelating bidentate fashion, leading to a square-planar  $CuN_2O_2$  coordination environment (Fig. 1).

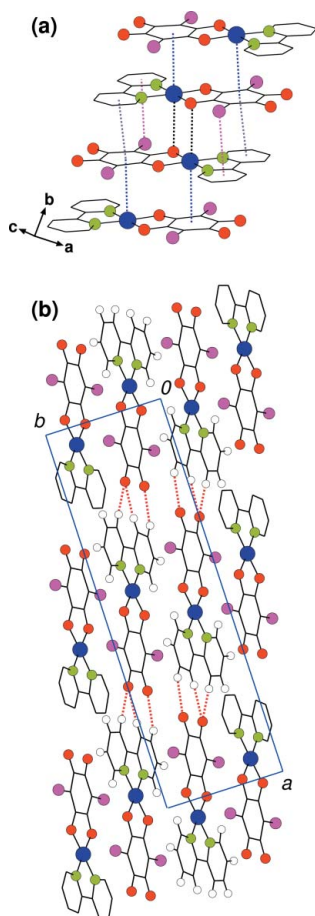
The crystal structure shows infinite ladder-like columns of monomeric complexes stacked along the  $b$  axis (Fig. 2). In addition to intermolecular  $Cu1 \cdots O2^i$  contacts [ $3.210(2)$  Å], the stacks are held together by means of an alternating sequence of  $\pi(C7-N12) \cdots \pi(chl)^i$ ,  $\pi(N1-C6) \cdots Cl2^i$  and  $\pi(chl) \cdots Cu1^{ii}$  interactions [symmetry codes: (i)  $-x, -y, -z$ ; (ii)  $-x, 1-y, -z$ ], the centroid-centroid or centroid-atom distances being  $3.416(2)$ ,  $3.558(1)$  and  $3.451(1)$  Å, respectively. The stacks are connected to each other through an extended network of  $C-H \cdots O$  hydrogen bonds (Table 2), involving those O atoms which are not coordinated to the Cu atom. These  $C-H \cdots O$  interactions give rise to layers parallel to the  $ab$  plane.

**Experimental**

Upon addition of a solution containing  $Cu(NO_3)_2 \cdot 3H_2O$  (96 mg), 2,2'-bipyridine (62 mg) and chloranilic acid (42 mg) in methanol (40 ml)



**Figure 1**  
A plot of (I), with 50% probability displacement ellipsoids. H atoms have been omitted for clarity.



**Figure 2**  
(a) The ladder-like column, highlighting the intermolecular Cu—O,  $\pi$ – $\pi$ ,  $\pi$ ...Cl and  $\pi$ ...Cu interactions. (b) A projection of a layer on the *ab* plane, together with a detail of the C—H...O network. Intermolecular interactions are shown as dotted lines.

to a solution of  $\text{K}_4\text{SiW}_{12}\text{O}_{40}$  (667 mg) in water (50 ml), a green precipitate was formed. The title compound was obtained as prismatic dark-red crystals by recrystallization of the precipitate from a 1:2 mixture of water and dimethylformamide. Elemental analysis,

found: C 44.92, H 1.97, N 6.51%; calculated for  $\text{C}_{16}\text{CuCl}_2\text{H}_8\text{N}_2\text{O}_4$ : C 45.04, H 1.89, N 6.57%. Spectroscopic analysis: IR (KBr pellet,  $\nu$ ,  $\text{cm}^{-1}$ ): 1643, 1533, 1368, 845, 774, 604, 565. Axial electron paramagnetic resonance signal:  $g_{\text{parallel}} = 2.205$ ,  $g_{\text{perpendicular}} = 2.052$ .

#### Crystal data

$[\text{Cu}(\text{C}_6\text{Cl}_2\text{O}_4)(\text{C}_{10}\text{H}_8\text{N}_2)]$   
 $M_r = 426.68$   
 Monoclinic,  $C2/c$   
 $a = 24.987$  (3) Å  
 $b = 7.438$  (1) Å  
 $c = 17.215$  (2) Å  
 $\beta = 104.57$  (1)°  
 $V = 3096.6$  (7) Å<sup>3</sup>  
 $Z = 8$

$D_x = 1.831$  Mg m<sup>-3</sup>  
 Mo  $K\alpha$  radiation  
 Cell parameters from 6500 reflections  
 $\theta = 3.5$ – $25^\circ$   
 $\mu = 1.78$  mm<sup>-1</sup>  
 $T = 295$  (2) K  
 Prism, dark red  
 0.14 × 0.11 × 0.06 mm

#### Data collection

Oxford Diffraction Xcalibur diffractometer  
 $\omega$  scans  
 Absorption correction: analytical (*CrysAlisRED*; Oxford Diffraction, 2003)  
 $T_{\text{min}} = 0.802$ ,  $T_{\text{max}} = 0.903$   
 14006 measured reflections

4506 independent reflections  
 2120 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.045$   
 $\theta_{\text{max}} = 30.0^\circ$   
 $h = -33 \rightarrow 35$   
 $k = -8 \rightarrow 10$   
 $l = -24 \rightarrow 23$

#### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.035$   
 $wR(F^2) = 0.065$   
 $S = 0.74$   
 4506 reflections  
 226 parameters

H-atom parameters constrained  
 $w = 1/[\sigma^2(F_o^2) + (0.0227P)^2]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\text{max}} < 0.001$   
 $\Delta\rho_{\text{max}} = 0.57$  e Å<sup>-3</sup>  
 $\Delta\rho_{\text{min}} = -0.31$  e Å<sup>-3</sup>

**Table 1**

Selected geometric parameters (Å, °).

Cu1—O1	1.9128 (17)	Cu1—N1	1.956 (2)
Cu1—O2	1.9176 (17)	Cu1—N12	1.947 (2)
O1—Cu1—O2	85.14 (7)	O1—Cu1—N1	96.00 (8)
O1—Cu1—N12	177.54 (8)	O2—Cu1—N1	178.79 (8)
O2—Cu1—N12	96.23 (8)	N12—Cu1—N1	82.65 (9)

**Table 2**

Hydrogen-bond geometry (Å, °).

<i>D</i> —H... <i>A</i>	<i>D</i> —H	H... <i>A</i>	<i>D</i> ... <i>A</i>	<i>D</i> —H... <i>A</i>
C5—H5...O3 <sup>i</sup>	0.93	2.54	3.465 (3)	173
C8—H8...O3 <sup>i</sup>	0.93	2.40	3.330 (3)	177
C9—H9...O4 <sup>i</sup>	0.93	2.49	3.171 (4)	130

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

The positions of all H atoms were calculated geometrically and refined as riding, with C—H = 0.93 Å and with  $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$ .

Data collection: *CrysAlis CCD* (Oxford Diffraction, 2003); cell refinement: *CrysAlis RED* (Oxford Diffraction, 2003); data reduction: *CrysAlis RED*; program(s) used to solve structure: *DIRDIF99.2* (Beurskens *et al.*, 1999); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP3 for Windows* (Farrugia, 1997); software used to prepare material for publication: *WinGX* (Farrugia, 1999).

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