

# Aquachloro(1,10-phenanthroline- $\kappa^2N,N'$ )(*p*-toluenesulfonato- $\kappa O$ )-copper(II)

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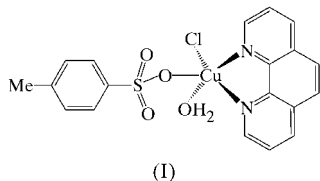
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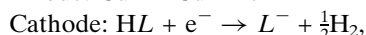
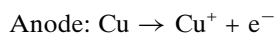
In the title compound, [CuCl(C<sub>7</sub>H<sub>7</sub>O<sub>3</sub>S)(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)(H<sub>2</sub>O)], the central Cu atom is coordinated by a water molecule, a chloride ion, an *O*-monodentate *p*-toluenesulfonate anion and an *N,N'*-bidentate 1,10-phenanthroline ligand. The copper environment is best described as a slightly distorted square pyramid, with bond distances Cu–Cl 2.2282 (9) Å, Cu–OW 1.984 (3) Å, and Cu–N 2.006 (3) and 2.028 (3) Å; the apical Cu–O distance is 2.281 (2) Å. In the supramolecular structure,  $\pi$ – $\pi$ -stacking stabilization is observed, and classical and non-classical hydrogen bonds also play an important role.

## Comment

In recent years, an important research topic of our group has been the electrochemical synthesis of neutral metal sulfonamide complexes. Neutral complexes can be easily obtained when a sacrificial anode is oxidized in a cell containing an appropriate proligand with a weak acidic character (García-Vázquez *et al.*, 1999), *e.g.* sulfonamides (Cabaleiro *et al.*, 2000). The title compound, (I), was obtained using this general method (see *Experimental* for details).

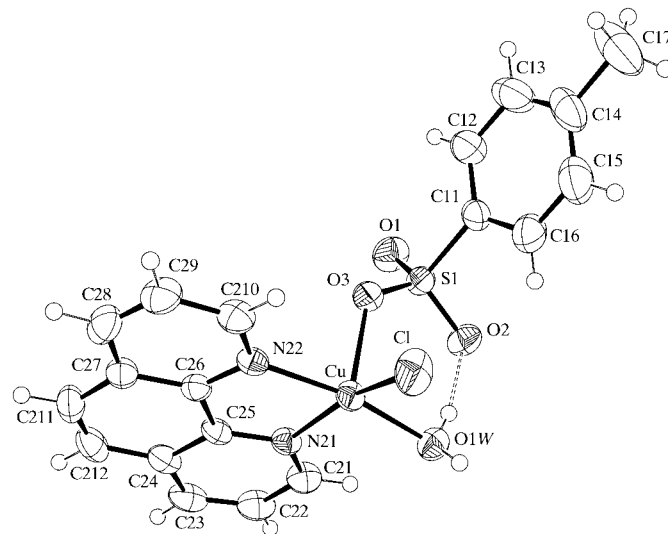


The electrochemical efficiency, defined as the molar amount of metal dissolved per Faraday, was close to 1.0. This, together with the formation of H<sub>2</sub> gas at the cathode, is compatible with a reaction mechanism involving anodic oxidation to copper(I) and deprotonation of the ligand at the cathode.



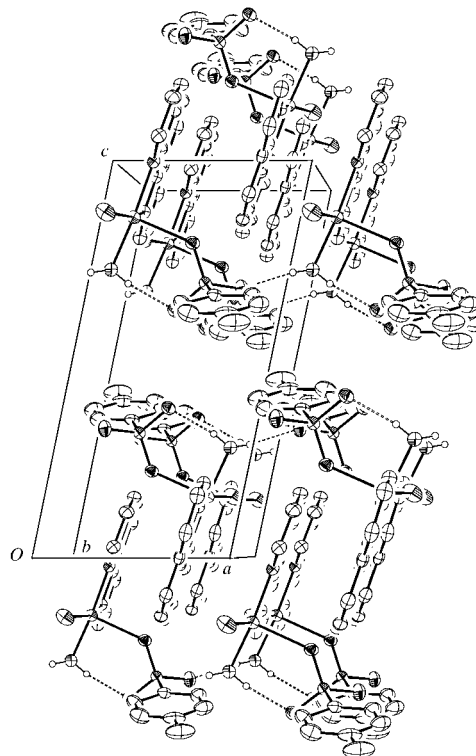
where HL and L<sup>−</sup> are *p*-toluenesulfonic acid and its anion, respectively.

The Cu<sup>+</sup> compound initially formed during the electrochemical process is further oxidized in solution to give the Cu<sup>2+</sup> product. The presence of the chloride ligand is probably



**Figure 1**

View of the title molecule, including the atomic numbering scheme, drawn using ORTEP-3 (Farrugia, 1998). H atoms are represented as circles of arbitrary radii, with the non-H atoms as displacement ellipsoids drawn at the 50% probability level.



**Figure 2**

The crystal packing of the title compound viewed parallel to the *y* axis.

attributable to the perchlorate used as the background electrolyte, through a process which is far from clear. Such behaviour has, however, been observed in the synthesis of other compounds by electrochemical procedures (Pérez-Lourido *et al.*, 1998).

The isolated title compound consists of discrete [CuCl(CH<sub>3</sub>C<sub>6</sub>H<sub>4</sub>SO<sub>3</sub>)(C<sub>12</sub>H<sub>8</sub>N<sub>2</sub>)(H<sub>2</sub>O)] molecules, where the Cu atom is coordinated by one water molecule, one chloride ion, one *p*-toluenesulfonate ion and one *N,N'*-bidentate 1,10-phenanthroline ligand (Fig. 1). The Cu atom is in a square-pyramidal environment. Bond distances in the basal positions are slightly shorter than the sum of the covalent radii [Cu—O1W 1.984 (3) Å, Cu—N21 2.028 (3) Å, Cu—N22 2.006 (3) Å and Cu—Cl 2.2282 (9) Å], but the length of the bond in the apical position is longer [Cu—O3 2.281 (2) Å]. This is, in part, because the fifth coordination position in square-pyramidal arrangements is usually longer (Murase *et al.*, 1991; Bailey *et al.*, 1980) and is also probably associated with the low coordination capability of the benzenesulfonate and toluenesulfonate anions, for which only eight entries were found in the Cambridge Structural Database (Version 5.22, October 2001; Allen & Kennard, 1993), coordinating to Cu<sup>II</sup> atoms (deviations: mean 2.443 Å, maximum 2.594 Å, minimum 2.153 Å). For comparison, a similar search for the trifluoromethanesulfonate ligand gave 44 hits (deviations: mean 2.359 Å, maximum 2.800 Å, minimum 1.948 Å).

The basal O1W/N21/N22/Cl plane is slightly distorted (r.m.s. deviation 0.105 Å), with a maximum deviation of 0.117 (1) Å for N21. The Cu atom lies 0.219 (1) Å out of the best plane formed by the four donor atoms, which subtends a small dihedral angle with the 1,10-phenanthroline best plane (r.m.s. deviation 0.020 Å) of 12.59 (8)°.

Some distortion is found around the tetrahedral S atom, with bond angles in the range 106.01 (16)–112.78 (16)°. In part, this distortion is probably associated with the hydrogen bond between the O2 atom of this SO<sub>3</sub> group and the coordinated water molecule (see Table 2); furthermore, the O1 atom interacts with another water molecule of a neighbouring complex. This hydrogen bond plays an important role in maintaining the supramolecular structure, as do some  $\pi$ – $\pi$ -stacking interactions and non-classical (Taylor & Kennard, 1982) hydrogen bonds between C29 and O3. In addition, the theoretical sixth coordination position of the Cu-atom environment is occupied by a  $\pi$ -cloud of the central benzene ring of 1,10-phenanthroline, with the centroid at 3.9648 (5) Å from the metal atom. Nevertheless, this distance is longer than the sum of the van der Waals radii, 3.10 Å, considering the phenyl group in a perpendicular fashion (Huheey *et al.*, 1993), so that this disposition could be due to geometrical constraints (see below).

$\pi$ – $\pi$  stacking (Janiak, 2001) is observed between the pyridine moieties of different 1,10-phenanthroline groups (Fig. 2), so alternating layers of 1,10-phenanthroline are found. Thus, the N21/C21–C25 ring is above the N22/C26–C29/C210 ring, with inter-centroid distances of 3.590 (2) and 4.343 (2) Å, and symmetry operators (2 – *x*, 1 – *y*, 1 – *z*) and (1 – *x*, 1 – *y*, 1 – *z*), respectively.

**Table 1**  
Selected geometric parameters (Å, °).

Cu—O1W	1.984 (3)	Cu—O3	2.281 (2)
Cu—N22	2.006 (3)	O2—S1	1.461 (3)
Cu—N21	2.028 (3)	O3—S1	1.467 (2)
Cu—Cl	2.2282 (9)	O1—S1	1.453 (3)
O1W—Cu—N22	169.20 (11)	N21—Cu—O3	94.19 (10)
O1W—Cu—N21	89.30 (11)	Cl—Cu—O3	103.62 (7)
N22—Cu—N21	81.22 (10)	O1—S1—O2	112.62 (15)
O1W—Cu—Cl	93.22 (8)	O1—S1—O3	112.78 (16)
N22—Cu—Cl	94.22 (8)	O2—S1—O3	111.06 (15)
N21—Cu—Cl	161.91 (8)	O1—S1—C11	107.22 (17)
O1W—Cu—O3	91.81 (10)	O2—S1—C11	106.01 (16)
N22—Cu—O3	94.03 (9)	O3—S1—C11	106.66 (15)

## Experimental

The electrochemical oxidation of a copper anode in an acetonitrile solution (50 ml) containing *p*-toluenesulfonic acid monohydrate (76.1 mg, 0.40 mmol), 1,10-phenanthroline monohydrate (70.5 mg, 0.40 mmol) and tetramethylammonium perchlorate (*ca* 10 mg) for 1 h at 8 V and 10 mA, resulted in a loss of 21.5 mg of copper from the anode and the formation of a green solution, which, after concentration by slow evaporation at room temperature, gave a crystalline solid.

### Crystal data

[CuCl(C <sub>7</sub> H <sub>7</sub> O <sub>3</sub> S)(C <sub>12</sub> H <sub>8</sub> N <sub>2</sub> )(H <sub>2</sub> O)]	<i>Z</i> = 2
<i>M<sub>r</sub></i> = 468.40	<i>D<sub>x</sub></i> = 1.601 Mg m <sup>−3</sup>
Triclinic, <i>P</i> $\bar{1}$	Mo <i>K</i> $\alpha$ radiation
<i>a</i> = 7.0887 (7) Å	Cell parameters from 3380 reflections
<i>b</i> = 9.9723 (9) Å	$\theta$ = 2.5–27.8°
<i>c</i> = 14.4170 (13) Å	$\mu$ = 1.40 mm <sup>−1</sup>
$\alpha$ = 83.773 (2)°	<i>T</i> = 293 (2) K
$\beta$ = 78.629 (2)°	Prism, blue
$\gamma$ = 77.153 (2)°	0.55 × 0.36 × 0.18 mm
<i>V</i> = 971.90 (16) Å <sup>3</sup>	

### Data collection

Bruker SMART CCD area-detector diffractometer	3249 independent reflections
$\varphi$ and $\omega$ scans	2858 reflections with <i>I</i> > 2 $\sigma$ ( <i>I</i> )
Absorption correction: multi-scan (SADABS; Siemens, 1996)	<i>R</i> <sub>int</sub> = 0.036
<i>T</i> <sub>min</sub> = 0.506, <i>T</i> <sub>max</sub> = 0.778	$\theta$ <sub>max</sub> = 25.0°
5013 measured reflections	<i>h</i> = −8 → 7
	<i>k</i> = −11 → 11
	<i>l</i> = −17 → 16

### Refinement

Refinement on <i>F</i> <sup>2</sup>	H atoms treated by a mixture of independent and constrained refinement
<i>R</i> [ <i>F</i> <sup>2</sup> > 2 $\sigma$ ( <i>F</i> <sup>2</sup> )] = 0.047	<i>w</i> = 1/[ $\sigma^2(F_o^2) + (0.0943P)^2$ ]
<i>wR</i> ( <i>F</i> <sup>2</sup> ) = 0.126	where <i>P</i> = ( <i>F<sub>o</sub></i> <sup>2</sup> + 2 <i>F<sub>c</sub></i> <sup>2</sup> )/3
<i>S</i> = 1.03	( $\Delta/\sigma$ ) <sub>max</sub> < 0.001
3249 reflections	$\Delta\rho$ <sub>max</sub> = 1.09 e Å <sup>−3</sup>
262 parameters	$\Delta\rho$ <sub>min</sub> = −0.80 e Å <sup>−3</sup>

Aryl and rigid rotating-group methyl H atoms were placed in calculated positions and refined with a riding model, with C—H distances of 0.93 and 0.96 Å, and *U*<sub>iso</sub> values of 1.2*U*<sub>eq</sub> and 1.5*U*<sub>eq</sub>, respectively, of the C atoms to which they are attached. H atoms of the coordinated water molecule were located in a difference map and were refined isotropically with O—H distances restrained to 0.82 Å.

Data collection: SMART (Siemens, 1996); cell refinement: SAINT (Siemens, 1996); data reduction: SAINT; program(s) used to solve structure: SHELXS97 (Sheldrick, 1997); program(s) used to refine

**Table 2**

Hydrogen-bonding geometry (Å, °).

Cg1 is the centroid of the C11–C16 ring.

<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>
O1W–H1···O2	0.80 (2)	1.90 (2)	2.684 (4)	168 (5)
O1W–H2···O1 <sup>i</sup>	0.79 (2)	1.94 (2)	2.714 (4)	164 (5)
C21–H21···O1W	0.93	2.52	3.011 (4)	113
C210–H210···Cl	0.93	2.75	3.269 (4)	116
C29–H29···O3 <sup>ii</sup>	0.93	2.58	3.491 (4)	168
C28–H28···Cg1 <sup>ii</sup>	0.93	2.76	3.481 (4)	136
C29–H29···Cg1 <sup>ii</sup>	0.93	3.40	3.798 (4)	109

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

structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *ORTEP-3* (Farrugia, 1998); 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: JZ1489). Services for accessing these data are described at the back of the journal.

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