

Tetraamminediaquacopper(II) 4-amino-2,5-dichlorobenzenesulfonate

Wen-Li Zhang, Jian-Fang Ma* and Hui Jiang

Department of Chemistry, Northeast Normal University, Changchun 130024, People's Republic of China

Correspondence e-mail: jianfangma@yahoo.com.cn

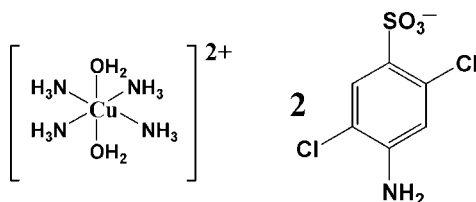
Received 21 June 2007; accepted 24 June 2007

Key indicators: single-crystal X-ray study; $T = 293$ K; mean $\sigma(\text{C}-\text{C}) = 0.003$ Å; R factor = 0.029; wR factor = 0.076; data-to-parameter ratio = 18.0.

In the title compound, $[\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4](\text{C}_6\text{H}_4\text{Cl}_2\text{NO}_3\text{S})_2$, the Cu^{II} cation lies on an inversion centre and is six-coordinated by four NH_3 molecules and two water molecules in an elongated octahedral coordination geometry. The anion is free from coordination but is linked to the Cu^{II} complex cation *via* $\text{O}-\text{H}\cdots\text{O}$ and $\text{N}-\text{H}\cdots\text{O}$ hydrogen bonding.

Related literature

For general background, see: Côté & Shimizu (2003); Markku & Reijo (1993); Yang *et al.* (2006).



Experimental

Crystal data

$[\text{Cu}(\text{H}_2\text{O})_2(\text{NH}_3)_4](\text{C}_6\text{H}_4\text{Cl}_2\text{NO}_3\text{S})_2$

$M_r = 649.83$

Triclinic, $P\bar{1}$

$a = 7.367$ (6) Å

$b = 7.380$ (5) Å

$c = 12.689$ (10) Å

$\alpha = 96.22$ (4)°

$\beta = 94.62$ (4)°

$\gamma = 118.33$ (3)°

$V = 596.8$ (8) Å³

$Z = 1$

Mo $K\alpha$ radiation

$\mu = 1.59$ mm⁻¹

$T = 293$ (2) K

$0.44 \times 0.37 \times 0.27$ mm

Data collection

Rigaku R-AXIS RAPID IP diffractometer

Absorption correction: multi-scan (ABSCOR; Higashi, 1995)

$T_{\text{min}} = 0.521$, $T_{\text{max}} = 0.650$

5849 measured reflections

2715 independent reflections

2518 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.020$

Refinement

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.076$

$S = 1.10$

2715 reflections

151 parameters

H-atom parameters constrained

$\Delta\rho_{\text{max}} = 0.43$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.42$ e Å⁻³

Table 1

Selected bond lengths (Å).

Cu1—N2	2.024 (2)	Cu1—O1W	2.580 (2)
Cu1—N3	2.025 (2)		

Table 2

Hydrogen-bond geometry (Å, °).

$D-\text{H}\cdots A$	$D-\text{H}$	$\text{H}\cdots A$	$D\cdots A$	$D-\text{H}\cdots A$
O1W—H1A ⁱ ⋯O2 ⁱ	0.88	2.07	2.900 (3)	156
O1W—H1B ⁱ ⋯O1 ⁱⁱ	0.83	2.14	2.925 (3)	159
N1—H1N ⁱ ⋯O1W ⁱⁱⁱ	0.86	2.34	3.179 (4)	166
N1—H2N ⁱ ⋯Cl2	0.82	2.56	2.967 (3)	112
N2—H2A ⁱ ⋯O1	0.86	2.32	3.134 (3)	157
N2—H2B ⁱ ⋯O1 ^{iv}	0.91	2.22	3.108 (3)	166
N2—H2C ⁱ ⋯O3 ⁱ	0.85	2.19	3.038 (3)	174
N3—H3A ⁱ ⋯O2	0.82	2.23	3.033 (3)	164
N3—H3B ⁱ ⋯O2 ^v	0.84	2.59	3.412 (3)	166
N3—H3B ⁱ ⋯O3 ^v	0.84	2.59	3.226 (3)	133
N3—H3C ⁱ ⋯O3 ⁱⁱ	0.85	2.33	3.157 (3)	164

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

Data collection: *PROCESS-AUTO* (Rigaku, 1998); cell refinement: *PROCESS-AUTO*; data reduction: *PROCESS-AUTO*; program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL-Plus* (Sheldrick, 1990); software used to prepare material for publication: *SHELXL97*.

The authors thank the National Natural Science Foundation of China (grant No. 20471014), the Programme for New Century Excellent Talents in Chinese Universities (grant No. NCET-05-0320), the Fok Ying Tung Education Foundation, and the Analysis and Testing Foundation of Northeast Normal University, China, for supporting this work.

Supplementary data and figures for this paper are available from the IUCr electronic archives (Reference: XU2281).

References

- Côté, A. P. & Shimizu, G. K. H. (2003). *Chem. Eur. J.* **9**, 5361–5370.
- Higashi, T. (1995). *ABSCOR*. Rigaku Corporation, Tokyo, Japan.
- Markku, R. S. & Reijo, S. (1993). *Acta Chem. Scand.* **47**, 1173–1178.
- Rigaku (1998). *PROCESS-AUTO*. Rigaku Corporation, Tokyo, Japan.
- Sheldrick, G. M. (1990). *SHELXTL-Plus*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.
- Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.
- Yang, J., Li, L., Ma, J.-F., Liu, Y.-Y. & Ma, J.-C. (2006). *J. Mol. Struct.* **788**, 43–48.

supplementary materials

Acta Cryst. (2007). E63, m2001 [doi:10.1107/S1600536807030711]

Tetraamminediaquacopper(II) 4-amino-2,5-dichlorobenzenesulfonate

W.-L. Zhang, J.-F. Ma and H. Jiang

Comment

As metal sulfonates are a class of novel materials showing interesting properties, such as exchange, guest sorption (Côté & Shimizu, 2003; Yang *et al.*, 2006), several studies on the coordination chemistry of transition metal sulfonates and their solid-state properties have been reported. In some cases, sulfonate group can compete with water molecule and coordinate to metal ion (Markku & Reijo, 1993). As part of an investigation of the structure of transition metal sulfonate compounds, we present here the structure of the title compound.

The crystal of the compound is composed of $[\text{Cu}(\text{NH}_3)_4(\text{H}_2\text{O})_2]^{2+}$ cations and 4-amino-2,5-dichlorobenzenesulfonate anions (Fig. 1). The Cu^{II} cation lies on an inversion center and is six-coordinated by four NH_3 molecules and two water molecules. The $\text{Cu}-\text{O1W}$ bond in the axial direction is much longer than $\text{Cu}-\text{N}$ bonds in the equatorial plane (Table 1), showing the typical Jahn-Teller distortion. The anions act as counterions and are hydrogen-bonded to the complex cations, forming a three dimensional supra-molecular structure (Fig. 2).

Experimental

A mixture of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.171 g, 1 mmol) and NaOH (0.080 g, 2 mmol) in water (10 ml) was stirred for 10 min at room temperature, then the $\text{Cu}(\text{OH})_2$ precipitate was collected by filtration and washed with water. 4-Amino-2,5-dichlorobenzenesulfonic acid (0.484 g, 2 mmol) was added to the $\text{Cu}(\text{OH})_2$ suspension in water (10 ml) with stirring, and a blue precipitate was obtained. A minimum amount of ammonia solution (14 M) was added to give a blue, clear solution. Suitable crystals of the title compound were obtained after several days.

Refinement

H atoms bonded to N and O atoms were located in a difference Fourier map and refined as riding in their as-found relative positions, $U_{\text{iso}}(\text{H}) = 1.5U_{\text{eq}}(\text{N}, \text{O})$. Aromatic H atoms were positioned geometrically and refined as riding atoms, with $\text{C}-\text{H} = 0.93 \text{ \AA}$ and $U_{\text{iso}}(\text{H}) = 1.2U_{\text{eq}}(\text{C})$.

Figures

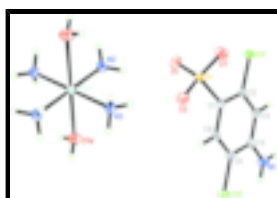


Fig. 1. A view of the structure of the title compound. Displacement ellipsoids are drawn at the 30% probability level [symmetry code: (i) $-x + 2, -y, -z + 2$].

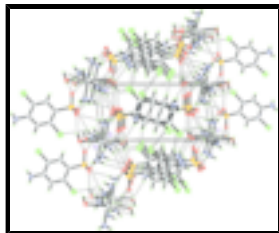


Fig. 2. View of the two-dimensional network formed by the L^- anions and $[Cu(NH_3)_4(H_2O)_2]^{2+}$ cations. The hydrogen bonds are drawn as dashed lines.

Tetraamminediaquacopper(II) 4-amino-2,5-dichlorobenzenesulfonate

Crystal data

$[Cu(H_2O)_2(NH_3)_4](C_6H_4Cl_2NO_3S)_2$

$M_r = 649.83$

Triclinic, $P\bar{1}$

Hall symbol: -P 1

$a = 7.367$ (6) Å

$b = 7.380$ (5) Å

$c = 12.689$ (10) Å

$\alpha = 96.22$ (4)°

$\beta = 94.62$ (4)°

$\gamma = 118.33$ (3)°

$V = 596.8$ (8) Å³

$Z = 1$

$F_{000} = 331$

$D_x = 1.808$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 5673 reflections

$\theta = 3.2$ – 27.5 °

$\mu = 1.59$ mm⁻¹

$T = 293$ (2) K

Block, blue

$0.44 \times 0.37 \times 0.27$ mm

Data collection

Rigaku R-Axis RAPID IP
diffractometer

Radiation source: rotor target

Monochromator: graphite

Detector resolution: 10.0 pixels mm⁻¹

$T = 293$ (2) K

ω scans

Absorption correction: multi-scan
(ABSCOR; Higashi, 1995)

$T_{\min} = 0.521$, $T_{\max} = 0.650$

5849 measured reflections

2715 independent reflections

2518 reflections with $I > 2\sigma(I)$

$R_{\text{int}} = 0.020$

$\theta_{\max} = 27.5$ °

$\theta_{\min} = 3.1$ °

$h = -9 \rightarrow 9$

$k = -9 \rightarrow 9$

$l = -16 \rightarrow 16$

Refinement

Refinement on F^2

Least-squares matrix: full

$R[F^2 > 2\sigma(F^2)] = 0.029$

$wR(F^2) = 0.076$

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0461P)^2 + 0.1532P]$

where $P = (F_o^2 + 2F_c^2)/3$

$S = 1.10$ $(\Delta/\sigma)_{\max} = 0.001$
 2715 reflections $\Delta\rho_{\max} = 0.43 \text{ e } \text{\AA}^{-3}$
 151 parameters $\Delta\rho_{\min} = -0.42 \text{ e } \text{\AA}^{-3}$
 Primary atom site location: structure-invariant direct methods Extinction correction: none

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > 2\text{sigma}(F^2)$ is used only for calculating R -factors(gt) *etc.* and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$
Cu1	1.0000	0.0000	1.0000	0.02605 (10)
Cl1	0.12744 (6)	0.22744 (8)	0.68358 (3)	0.03803 (12)
Cl2	0.80402 (7)	0.27818 (7)	0.40904 (3)	0.03640 (12)
S1	0.57643 (6)	0.30274 (6)	0.80181 (3)	0.02445 (11)
C1	0.5153 (2)	0.2819 (2)	0.66165 (12)	0.0231 (3)
C2	0.3236 (2)	0.2471 (2)	0.61119 (13)	0.0248 (3)
C3	0.2789 (2)	0.2209 (3)	0.50137 (13)	0.0279 (3)
H3	0.1496	0.1983	0.4704	0.033*
C4	0.4238 (3)	0.2275 (3)	0.43586 (12)	0.0270 (3)
C5	0.6171 (2)	0.2647 (2)	0.48716 (13)	0.0256 (3)
C6	0.6623 (2)	0.2912 (2)	0.59713 (12)	0.0246 (3)
H6	0.7921	0.3155	0.6284	0.030*
N1	0.3790 (3)	0.1971 (3)	0.32678 (12)	0.0384 (4)
H1N	0.2620	0.1798	0.2962	0.058*
H2N	0.4689	0.2039	0.2910	0.058*
O1	0.4554 (2)	0.0939 (2)	0.82788 (10)	0.0357 (3)
O2	0.79984 (18)	0.3761 (2)	0.82209 (10)	0.0357 (3)
O1W	1.0063 (2)	-0.1798 (2)	0.81528 (12)	0.0445 (3)
H1A	0.9705	-0.3136	0.8054	0.067*
H1B	1.1262	-0.1150	0.8014	0.067*
N2	0.6962 (2)	-0.0932 (2)	0.95054 (12)	0.0317 (3)
H2A	0.6650	-0.0215	0.9104	0.048*
H2B	0.6300	-0.1033	1.0089	0.048*
H2C	0.6394	-0.2209	0.9211	0.048*
O3	0.5222 (2)	0.4502 (2)	0.85509 (10)	0.0362 (3)
N3	1.0992 (2)	0.2790 (2)	0.95026 (11)	0.0314 (3)
H3A	1.0038	0.2791	0.9115	0.047*

supplementary materials

H3B	1.1447	0.3759	1.0025	0.047*
H3C	1.1979	0.3035	0.9140	0.047*

Atomic displacement parameters (\AA^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
Cu1	0.02468 (15)	0.02976 (17)	0.02568 (15)	0.01440 (12)	0.00308 (11)	0.00729 (11)
Cl1	0.0261 (2)	0.0597 (3)	0.0322 (2)	0.0231 (2)	0.00693 (16)	0.01044 (19)
Cl2	0.0330 (2)	0.0446 (3)	0.0305 (2)	0.01790 (19)	0.01035 (16)	0.00277 (17)
S1	0.02302 (18)	0.0277 (2)	0.02057 (18)	0.01111 (15)	0.00088 (14)	0.00409 (14)
C1	0.0238 (7)	0.0231 (7)	0.0216 (7)	0.0110 (6)	0.0017 (6)	0.0046 (5)
C2	0.0227 (7)	0.0256 (8)	0.0270 (7)	0.0116 (6)	0.0045 (6)	0.0074 (6)
C3	0.0238 (7)	0.0302 (8)	0.0286 (8)	0.0127 (6)	-0.0011 (6)	0.0062 (6)
C4	0.0301 (8)	0.0242 (8)	0.0236 (7)	0.0110 (6)	0.0015 (6)	0.0047 (6)
C5	0.0264 (7)	0.0242 (8)	0.0256 (7)	0.0115 (6)	0.0065 (6)	0.0045 (6)
C6	0.0220 (6)	0.0251 (7)	0.0264 (7)	0.0115 (6)	0.0015 (6)	0.0046 (6)
N1	0.0371 (8)	0.0530 (10)	0.0225 (7)	0.0205 (7)	0.0008 (6)	0.0062 (6)
O1	0.0392 (7)	0.0336 (7)	0.0297 (6)	0.0128 (5)	0.0042 (5)	0.0122 (5)
O2	0.0250 (6)	0.0494 (8)	0.0300 (6)	0.0167 (5)	-0.0017 (5)	0.0074 (5)
O1W	0.0394 (7)	0.0418 (8)	0.0477 (8)	0.0143 (6)	0.0165 (6)	0.0087 (6)
N2	0.0298 (7)	0.0364 (8)	0.0317 (7)	0.0185 (6)	0.0024 (6)	0.0062 (6)
O3	0.0378 (6)	0.0382 (7)	0.0310 (6)	0.0198 (6)	0.0014 (5)	-0.0042 (5)
N3	0.0328 (7)	0.0339 (8)	0.0286 (7)	0.0169 (6)	0.0028 (6)	0.0073 (6)

Geometric parameters (\AA , $^\circ$)

Cu1—N2	2.024 (2)	C3—H3	0.9300
Cu1—N2 ⁱ	2.024 (2)	C4—N1	1.365 (2)
Cu1—N3	2.025 (2)	C4—C5	1.403 (3)
Cu1—N3 ⁱ	2.025 (2)	C5—C6	1.379 (2)
Cu1—O1W	2.580 (2)	C6—H6	0.9300
Cl1—C2	1.731 (2)	N1—H1N	0.8605
Cl2—C5	1.732 (2)	N1—H2N	0.8179
S1—O3	1.4482 (15)	O1W—H1A	0.8836
S1—O2	1.4574 (17)	O1W—H1B	0.8260
S1—O1	1.4608 (17)	N2—H2A	0.8642
S1—C1	1.771 (2)	N2—H2B	0.9089
C1—C6	1.390 (2)	N2—H2C	0.8531
C1—C2	1.395 (2)	N3—H3A	0.8251
C2—C3	1.377 (2)	N3—H3B	0.8346
C3—C4	1.391 (3)	N3—H3C	0.8488
N2—Cu1—N2 ⁱ	180.000 (1)	C3—C4—C5	116.84 (15)
N2—Cu1—N3	92.99 (7)	C6—C5—C4	122.08 (15)
N2 ⁱ —Cu1—N3	87.01 (7)	C6—C5—Cl2	119.39 (13)
N2—Cu1—N3 ⁱ	87.01 (7)	C4—C5—Cl2	118.53 (14)
N2 ⁱ —Cu1—N3 ⁱ	92.99 (7)	C5—C6—C1	120.52 (15)
N3—Cu1—N3 ⁱ	180.000 (1)	C5—C6—H6	119.7

O3—S1—O2	112.05 (9)	C1—C6—H6	119.7
O3—S1—O1	112.11 (10)	C4—N1—H1N	120.9
O2—S1—O1	111.67 (9)	C4—N1—H2N	118.6
O3—S1—C1	108.15 (8)	H1N—N1—H2N	120.3
O2—S1—C1	105.56 (8)	H1A—O1W—H1B	107.3
O1—S1—C1	106.89 (9)	Cu1—N2—H2A	119.1
C6—C1—C2	117.67 (15)	Cu1—N2—H2B	109.0
C6—C1—S1	118.57 (12)	H2A—N2—H2B	108.1
C2—C1—S1	123.70 (12)	Cu1—N2—H2C	106.8
C3—C2—C1	121.70 (15)	H2A—N2—H2C	111.0
C3—C2—C11	116.75 (13)	H2B—N2—H2C	101.4
C1—C2—C11	121.53 (13)	Cu1—N3—H3A	110.6
C2—C3—C4	121.18 (15)	Cu1—N3—H3B	110.9
C2—C3—H3	119.4	H3A—N3—H3B	109.9
C4—C3—H3	119.4	Cu1—N3—H3C	110.4
N1—C4—C3	121.51 (16)	H3A—N3—H3C	107.6
N1—C4—C5	121.65 (16)	H3B—N3—H3C	107.4
O3—S1—C1—C6	133.25 (13)	C11—C2—C3—C4	-178.05 (13)
O2—S1—C1—C6	13.16 (15)	C2—C3—C4—N1	178.56 (16)
O1—S1—C1—C6	-105.86 (14)	C2—C3—C4—C5	-0.8 (2)
O3—S1—C1—C2	-49.74 (16)	N1—C4—C5—C6	-178.61 (16)
O2—S1—C1—C2	-169.83 (14)	C3—C4—C5—C6	0.7 (2)
O1—S1—C1—C2	71.15 (16)	N1—C4—C5—C12	1.6 (2)
C6—C1—C2—C3	0.6 (2)	C3—C4—C5—C12	-179.06 (12)
S1—C1—C2—C3	-176.48 (13)	C4—C5—C6—C1	0.0 (3)
C6—C1—C2—C11	178.68 (12)	C12—C5—C6—C1	179.77 (12)
S1—C1—C2—C11	1.6 (2)	C2—C1—C6—C5	-0.6 (2)
C1—C2—C3—C4	0.2 (3)	S1—C1—C6—C5	176.58 (13)

Symmetry codes: (i) $-x+2, -y, -z+2$.

Hydrogen-bond geometry ($\text{\AA}, ^\circ$)

<i>D</i> —H \cdots <i>A</i>	<i>D</i> —H	H \cdots <i>A</i>	<i>D</i> \cdots <i>A</i>	<i>D</i> —H \cdots <i>A</i>
O1W—H1A \cdots O2 ⁱⁱ	0.88	2.07	2.900 (3)	156
O1W—H1B \cdots O1 ⁱⁱⁱ	0.83	2.14	2.925 (3)	159
N1—H1N \cdots O1W ^{iv}	0.86	2.34	3.179 (4)	166
N1—H2N \cdots C12	0.82	2.56	2.967 (3)	112
N2—H2A \cdots O1	0.86	2.32	3.134 (3)	157
N2—H2B \cdots O1 ^v	0.91	2.22	3.108 (3)	166
N2—H2C \cdots O3 ⁱⁱ	0.85	2.19	3.038 (3)	174
N3—H3A \cdots O2	0.82	2.23	3.033 (3)	164
N3—H3B \cdots O2 ^{vi}	0.84	2.59	3.412 (3)	166
N3—H3B \cdots O3 ^{vi}	0.84	2.59	3.226 (3)	133
N3—H3C \cdots O3 ⁱⁱⁱ	0.85	2.33	3.157 (3)	164

Symmetry codes: (ii) $x, y-1, z$; (iii) $x+1, y, z$; (iv) $-x+1, -y, -z+1$; (v) $-x+1, -y, -z+2$; (vi) $-x+2, -y+1, -z+2$.

Fig. 1

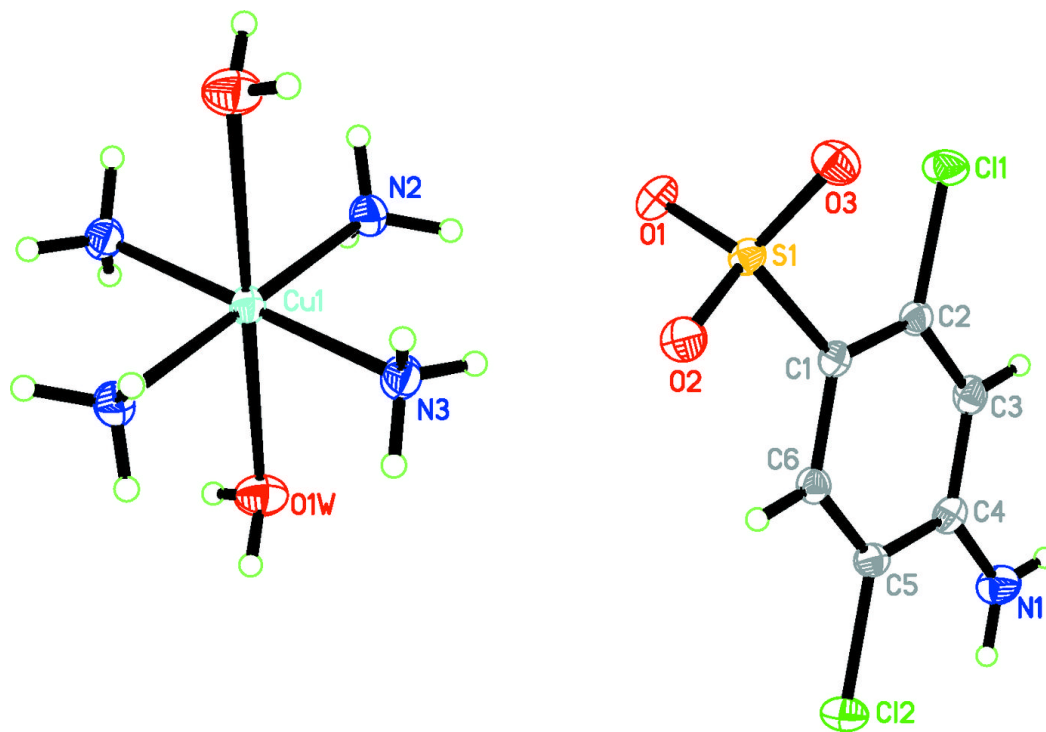


Fig. 2

