Cryst. Struct. Comm. (1978), 7, 565.

DIAQUAETHYLENEDIAMINESULPHATOCOPPER(II) [$C_2H_{12}CuN_2O_6S$]

Peter C. Healy*

School of Science, Griffith University, Brisbane, Australia 4109.

Colin H.L. Kennard

Department of Chemistry, University of Queensland, Brisbane, Australia 4067.

Graham Smith

Department of Chemistry, Queensland Institute of Technology, Brisbane, Australia 4000.

Alan H. White

Department of Physical and Inorganic Chemistry, University of Western Australia, Nedlands, Western Australia 6009.

Preliminary information. The crystal structure of the title compound, $[Cu(OH_2)_2(en)SO_4]$, was completed to ascertain the molecular configuration and the possible effect of distortion on the coordination sphere about the copper(II) atom.

Crystal data. a = 723.3(1), b = 1172.3(3), c = 1048.5(3) pm, β = 116.13(2)°, V = 0.798 nm^3, D_m = 2.13, Z = 4, D_c = 2.13 g cm^{-3}, space group $C2/c$, (Mo $K\alpha$, λ=71.07 pm), μ(Mo $K\alpha$)=30.9 cm^{-1}, $F(000)$=524.

Intensity data and refinement. The complex was prepared using Baldwin's (1963) method. Intensity data were collected from a crystal (0.20 , 0.50 , 0.08 mm) with a Syntex $P\bar{1}$ four-circle diffractometer. A unique set of data were gathered in the range $2\theta < 55^{\circ}$, yielding 2084 independent reflections of which 1559 with $I > 2.5\sigma(I)$ were considered observed and used in the subsequent structure solution and refinement. Although intensity statistics ($|E^2-1|=0.82$) did not convincingly indicate the space group $C2/c$, the centrosymmetric direct methods approach of SHELX (Sheldrick, 1976) was used to locate the position of the copper, and subsequent structure factor electron density syntheses in the space group Cc gave the positions of the remaining non-hydrogen atoms. The R value reduced from 0.67 (copper only) to 0.05 (all non-hydrogens). A difference electron density synthesis at this stage revealed the hydrogen atoms, which were included in calculations but not refined. This gave a final R 0.040 and Rw 0.042. A weighting scheme with $w = 1.527/(\sigma^2F+5.21\times10^{-4}F^2)$ was found suitable.

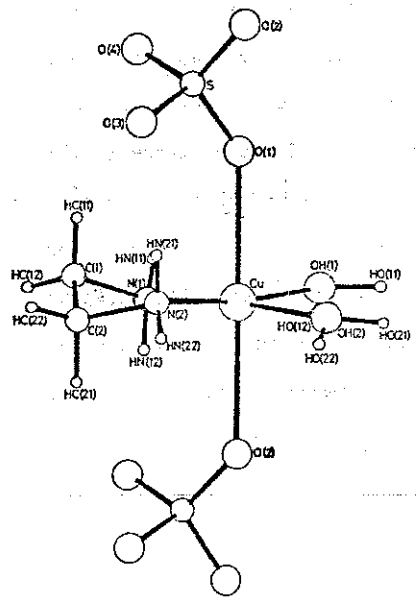
Because the molecule possessed a potential two-fold rotation axis, it was decided to test the refinement in the space group $C2/c$ with the molecular two-fold axis coincident with a crystallographic two-fold axis at $z = \frac{1}{4}$. Accommodating the change in origin, a difference-Fourier synthesis calculated in $C2/c$ located the hydrogen atoms. With all non-hydrogen atoms being refined anisotropically, the hydrogen atom positions fixed, reflections (002) and (020) omitted because of extinction, and an appropriate weighting scheme $w = 1.677/(\sigma^2F+5.63\times10^{-4}F^2)$, the structure refined to R 0.042 and Rw 0.044. A final difference-electron density synthesis did not show any electron density greater than 0.19e Å^{-3}. No corrections were made for absorption.

Although agreement for both structures is similar, the e.s.d's for the centric model are smaller (σ(centric), 0.2pm; σ (acentric), 0.9pm) and may be strongly accepted on the basis of the Hamilton R-Ration test at the 5% level (1.063 *cf* 1.01185).

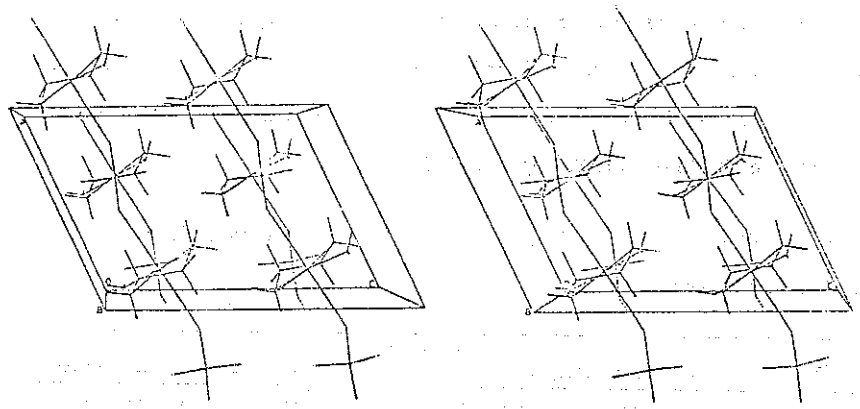
Table 1. Comparative M-L,M-S,S-O and M-M distances (pm) for a series of $ML_4(SO_4)$ complexes.

Compound	Bond or contact											
	Cu-O(1)	Cu-O(2)	Cu-N(1)	Cu-N(2)	Cu-OH	Cu-OH	S-O(1)	S-O(2)	S-O(3)	S-O(4)	Cu-Cu	Reference
$Cu(en)(H_2O)_2SO_4$ (I) Centric	197.6	197.6	199.0	199.0	249.2	249.2	146.7	146.7	149.9	149.9	723	*This work*
$Cu(en)(H_2O)_2SO_4$ (I) Acentric	200.9	195.4	193.2	203.8	250.6	248.6	143.2	150.2	151.9	148.3	723	
$Cu(bipy)(H_2O)_2SO_4$	197.5	197.5	200.5	200.5	244	244	146	146	149	149	699	*a*
$Cu(py)_2(H_2O)_2SO_4$	204	204	200	200	238	238	145	145	150	150	685	*b*

a Tedenac and Philippot, 1975. *b* Cannillo and Giuseppetti, 1964.



Stereochemistry and naming scheme for the complex $[Cu(OH_2)_2(en)SO_4]$ referred to the acentric model.



Stereoview perpendicular to ac

Comments. The complex coordination sphere consists of basic CuL_4SO_4 units with the neutral ligands (*en* and H_2O) occupying the equatorial positions in an approximate square plan.

The *en* ligand possesses the δ conformation on the basis of the positive torsion angle of the C-N bonds viewed down the C(1)-C(2) bond (Huheey, 1972). The sulphate ligands "semi-coordinate" in the fifth and sixth axial positions and form a bridge between adjacent copper atoms Cu-O, 249.2 pm . This results in formation of infinite linear chains consisting of [-Cu-O-(SO_2)-O-Cu-] with a Cu-Cu distance of 723 pm and a Cu-O-S bridge angle of 139.4°. The O-Cu-O (to sulphate) angle is 175.9°. The chains are held together by lateral hydrogen bonds between the ligated waters and the uncoordinated oxygens of the sulphate ligands. Preliminary magnetic susceptibility measurements at liquid helium temperature indicate a possible ferromagnetic intra-chain interaction with an eventual interchain antiferromagnetic interaction [P.C. Healy and A.J. Gregson, unpublished data].

A similar bridging system is reported for the CuL_4SO_4 system in

$Cu(bipy)(H_2O)_2SO_4$ (Tedenac and Philippot, 1975) where the interlinking hydrogen bonds also involve water and sulphate groups. However, in the analogous Ni complex $Ni(bipy)(H_2O)_2SO_4$ (Tedenac & Philippot (1974) the corresponding metal-oxygen distances are 206.8 and 215.6 pm compared with 198 pm ($Cu-OH_2$) and 244 pm ($Cu-OSO_3$) in the copper complex. The comparative bond distances and Cu-Cu distances for the series of CuL_4SO_4 complexes are listed in Table 1.

To S-O distance found for the sulphate group is longer for the S-O (uncoordinated) [149.9(2) pm] than for the S-O (coordinated), [146.7(2) pm]. This is also observed for the other members of the series and is not consistent with the bond distances expected for a polar SO_4 group.

Atomic coordinates (x 10⁴)

Atom	*x/a*	*y/b*	*z/c*	Atom	*x/a*	*y/b*	*z/c*
Cu	0	4782(0)	2500	HC(11)	1184	7071	1669
S	5000	5559(1)	2500	HC(12)	-953	7743	1219
O(1)	3148(3)	4858(2)	2100(2)	HN(11)	-1077	5933	365
O(3)	4738(3)	6321(2)	1284(2)	HN(12)	-2437	6023	971
OH(1)	-1023(3)	3596(2)	1010(2)	HO(11)	-909	2780	1041
N(1)	-1260(3)	6019(2)	1078(2)	HO(12)	-958	3696	416
C(1)	-0197(5)	7100(2)	1729(2)				

Bond distances (pm)

Cu - OH(1)	197.6(2)	OH(1) - HO(11)	96
Cu - N(1)	199.0(2)	OH(1) - HO(12)	67
Cu - O(1)	249.2(2)	N(1) - HN(11)	82
N(1) - C(1)	148.4(3)	N(1) - HN(12)	81
C(1) - C(2)	151.3(5)	C(1) - HC(11)	103
S - O(1)	146.7(2)	C(1) - HC(12)	95
S - O(3)	149.9(2)		

Bond angles (deg.)

O(1) - Cu - O(2)	175.90(1)	N(1) - C(1) - C(2)	107.89(2)
O(1) - Cu - OH(1)	86.78(1)	O(1) - S - O(2)	111.84(1)
O(1) - Cu - N(1)	87.09(1)	O(1) - S - O(3)	109.47(1)
OH(1) - Cu - N(1)	91.83(1)	O(3) - S - O(4)	106.83(1)
OH(1) - Cu - N(2)	173.63(2)	O(2) - S - O(4)	109.55(1)
OH(1) - Cu - OH(2)	90.54(1)	Cu - O(1) - S	139.4 (1)
N(1) - Cu - N(2)	86.43(2)		

Acknowledgements. The authors wish to thank the University of Western Australia for the use of their facilities and Griffith University for financial support. One of us (G.S.) thanks the Queensland Institute of Technology for the time to work on this project.

References.

Baldwin, M.E., (1963) *Spectrochimica Acta*, 19, 315.

Cannillo, E., and Giuseppetti, G., (1964) *Atti. Acad. Nazl. Lincei*, 36, 878.

Huheey, S.E., (1972) *Inorganic Chemistry*, Harper & Row, London p. 398.

Sheldrick, G., (1976) "SHELX", *System of computer programs*, University of Cambridge.

Tedenac, J.C., and Philippot, E., (1974) *Acta Cryst.*, B30, 2286.

Tedenac, J.C., and Philippot, E., (1975) *J. Inorg. Nucl. Chem.*, 37, 846.

Received: 21 April 1978