Structure of Tetrakis(pyridine)sulfatocopper(II) Monohydrate

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Abstract. $|Cu(C_5H_5N)_4SO_4|.H_2O$, $M_r = 494.03$, monoclinic, Cc, $a = 15.354$ (4), $b = 10.929$ (3), $c = 14.407$ (3) Å, $\beta = 117.33$ (2)°, $V = 2147.7$ (9) Å^3, $Z = 4$, $D_m = 1.51$, $D_x = 1.53$ Mg m^{-3}, $\lambda(Cu K\alpha) = 1.54178$ Å, $\mu = 2.58$ mm^{-1}, $F(000) = 1020$, room temperature, $R = 0.020$ for 1145 unique reflections with $F > 4\sigma(F)$. The copper(II) ion has distorted square-pyramidal coordination with the four pyridine ligands in basal sites and a sulfato O atom occupying the axial position.

Introduction. This work is concerned with the factors which determine whether the water molecule in $CuL_4SO_4.H_2O$ complexes is directly attached to the metal atom. When L is H_2O one water molecule is not directly attached to the Cu atom although it is linked by hydrogen bonds to the O atoms of the sulfato group and the coordinated H_2O molecules (Varghese & Maslen, 1985). The fifth and sixth coordination positions are occupied by sulfato O atoms. When L is NH_3 the water molecule occupies the fifth coordination site, and forms bridges to the next Cu atom, so that the coordination number may be expressed as $4 + 1 + 1$ (Morosin, 1969). It was therefore of interest to determine the role of the water molecule when the relatively small ligands H_2O or NH_3 are replaced by bulkier pyridine (py) molecules. The existence of $|Cu(py)_4SO_4|.H_2O$ was known previously (*Gmelins Handbuch der Anorganischen Chemie*, 1952), but no crystal data were available.

Experimental. Hot, freshly distilled pyridine in a large excess was added to a boiling aqueous solution of $CuSO_4$, saturated at 293 K. The compound crystallizes readily from the hot solution. The crystals were filtered from the hot solution and washed several times with cold ether. Recrystallization was carried out from a 3:1 mixture of pyridine and water at room temperature. Dark-blue needle {found: Cu, 12.99; C, 48.80; N, 11.10; H, 4.42%; $|Cu(py)_4SO_4|.H_2O$ requires: Cu, 12.86; C, 48.58; N, 11.33; H, 4.48%}, highly unstable due to pyridine loss. The crystal was sealed in a 0.5 mm glass capillary. Crystal system and approximate cell dimensions determined from Weissenberg and oscillation photographs; density measured by flotation in a mixture of $CHBr_3$ and $C_6H_5.CH_3$; crystal specimen

Table 1. *Atomic coordinates* ($\times 10^4$) *and equivalent isotropic thermal parameters* (Å^2 $\times 10^4$)

$U_{eq} = \frac{1}{3}$ (trace of orthogonalized U_{ij} matrix).

	x	y	z	U_{eq}
Cu	3085*	2229 (1)	4554*	269 (3)
S	4811 (1)	−210 (1)	5390 (1)	265 (5)
O(1)	4074 (3)	752 (3)	4967 (3)	548 (18)
O(2)	5396 (3)	7 (4)	6513 (3)	577 (15)
O(3)	4290 (5)	−1359 (3)	5173 (4)	707 (26)
O(4)	5427 (3)	−138 (5)	4863 (3)	674 (20)
O(5)	6349 (4)	191 (9)	3671 (4)	1319 (39)
N(1)	2971 (3)	2297 (3)	5900 (3)	306 (20)
N(2)	3009 (3)	2459 (4)	3123 (3)	312 (20)
N(3)	1847 (3)	1158 (4)	3925 (3)	335 (21)
N(4)	4084 (3)	3613 (3)	5084 (3)	295 (17)
C(11)	2372 (4)	3086 (5)	6021 (4)	386 (24)
C(12)	2279 (4)	3167 (6)	6917 (4)	411 (24)
C(13)	2834 (5)	2407 (6)	7735 (6)	454 (30)
C(14)	3467 (5)	1587 (5)	7629 (5)	508 (29)
C(15)	3513 (4)	1559 (5)	6698 (4)	445 (27)
C(21)	2374 (4)	3217 (5)	2423 (4)	392 (23)
C(22)	2303 (4)	3375 (6)	1433 (4)	466 (25)
C(23)	2928 (5)	2707 (6)	1177 (6)	511 (32)
C(24)	3599 (5)	1944 (6)	1898 (5)	491 (29)
C(25)	3630 (4)	1823 (5)	2867 (4)	397 (22)
C(31)	1932 (5)	56 (5)	3982 (5)	435 (27)
C(32)	1117 (5)	−830 (6)	3602 (5)	536 (31)
C(33)	205 (5)	−331 (6)	3151 (5)	577 (31)
C(34)	102 (4)	926 (7)	3089 (5)	578 (32)
C(35)	935 (4)	1617 (5)	3481 (4)	451 (27)
C(41)	3823 (5)	4795 (5)	4915 (5)	403 (28)
C(42)	4475 (5)	5720 (6)	5227 (5)	465 (27)
C(43)	5476 (5)	5468 (6)	5765 (5)	488 (29)
C(44)	5759 (5)	4270 (5)	5942 (5)	488 (28)
C(45)	5053 (4)	3376 (5)	5604 (4)	406 (26)

* Parameter fixed.

$0.2 \times 0.2 \times 0.5$ mm; Syntex $P2_1$ four-circle diffractometer, graphite-monochromated Cu $K\alpha$ radiation, θ–2θ scan mode with a variable scan rate ranging from 4.88 to 29.30° min^{-1}; accurate cell parameters refined from setting angles of 12 reflections with $5° < \theta < 13°$; max.$(\sin\theta)/\lambda = 0.4969$ Å^{-1}; index range h 0/15, k 0/10, l −12/12; two check reflections measured every 98 reflections, no significant systematic fluctuation; 1159 unique reflections measured, 1153 considered observed $|F > 4\sigma(F)|$, $R_{int} = 0.023$ for 57 reflections, Lp correction, empirical absorption correction based on reflection intensity measurements at different azimuthal angles, transmission range 0.609–0.926. Position of Cu atom derived from Patterson synthesis, other non-hydrogen atoms from subsequent Fourier syntheses. H atoms located from difference synthesis in positions consistent with those expected on geometrical grounds (C–H 1.080 Å, sp^2 hybridization). Full-matrix least-

squares refinement on F, $w^{-1} = k|\sigma^2(F) + gF^2|$, k = 1·00, g = 0·0004, anisotropic thermal parameters for all non-H atoms, isotropic for H with freely refined coordinates except for those of water H atoms H(51) and H(52) which could not be successfully refined. These atoms were included in the refinement with fixed positional parameters obtained from a difference synthesis and variable isotropic thermal parameters. Isotropic extinction correction $F_c^* = F_c(1 - xF_c^2/\sin\theta)$, $x = 1·45$ (7) × 10^{-6}. Eight of the strongest reflections (20$\bar{6}$, 40$\bar{6}$, 20$\bar{4}$, 00$\bar{2}$, 20$\bar{2}$, 11$\bar{1}$, 220, 002) were considered to be poorly measured and were excluded from the refinement. 361 parameters, R =0·020 and wR=0·021 (clearly superior to the model of opposite chirality which converged with R = 0·024, wR = 0·026), max.Δ/σ = 0·27, mean = 0·04, max.$\Delta\rho$ = +0·14, min. = −0·19 e Å^{-3}, slope of normal probability plot 0·91. Scattering factors and anomalous-dispersion corrections from *International Tables for X-ray Crystallography* (1974); *SHELX76* programs (Sheldrick, 1976).

Discussion. The atomic coordinates and equivalent isotropic temperature factors are listed in Table 1, and bond lengths and angles in Table 2.† An *ORTEP* plot of the molecule and the atom numbering are shown in Fig. 1, and the packing of the molecules is shown in Fig. 2 (Johnson, 1976).

The structure consists of polymeric one-dimensional chains, formed from sulfato groups and water molecules linked together by hydrogen bonds. The penta-coordinated Cu^{II} complex is attached to this chain through O(1) of the sulfato group.

The Cu^{II} coordination polyhedron is a tetragonal pyramid. The basal plane is defined by the N atoms of four pyridine molecules. The axial position is occupied by O(1). Cu—N distances are in the range 2·026 (5)–2·055 (5) Å, *cis* N—Cu—N angles 88·5 (2)–90·7 (2)° and O—Cu—N angles 94·6 (2)–98·3 (2)°. The four equatorial N atoms are coplanar to within ±0·016 (5) Å with the Cu atom displaced by 0·222 Å out of their mean plane towards the apical O atom. All pyridine rings are planar, with no atom deviating from the least-squares planes through six pyridine non-H atoms by more than 0·011 (8) Å. The pyridine rings have C—C and C—N distances in the ranges 1·35 (1) to 1·40 (1) Å and 1·32 (1) to 1·36 (1) Å. Angles of planes formed by pyridine rings to the N$_4$ basal plane are in the range 91·8 (1)–96·8 (1)°. S—O bond distances are from 1·444 (4) to 1·465 (4) Å and O—S—O angles from 106·9 (3) to 112·1 (2)°. An interesting feature of

† Lists of structure factors, anisotropic thermal parameters, H-atom parameters and least-squares planes have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 51692 (15 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

Table 2. *Selected lengths (Å) and angles (°) with their e.s.d.'s*

Cu–N(1)	2·026 (4)	N(1)–C(11)	1·329 (7)
Cu–N(2)	2·027 (4)	N(1)–C(15)	1·337 (7)
Cu–N(3)	2·055 (4)	N(2)–C(21)	1·323 (7)
Cu–N(4)	2·037 (4)	N(2)–C(25)	1·360 (7)
Cu–O(1)	2·105 (4)	N(3)–C(31)	1·332 (8)
Cu···O(5)^i	4·011 (9)	N(3)–C(35)	1·341 (7)
		N(4)–C(41)	1·342 (7)
		N(4)–C(45)	1·348 (7)
S–O(1)	1·457 (4)	O(5)–H(51)	0·955 (5)*
S–O(2)	1·465 (4)	O(5)–H(52)	1·089 (6)*
S–O(3)	1·444 (4)	O(2^{ii})···H(51)	1·817 (4)*
S–O(4)	1·462 (4)	O(4)···H(52)	1·819 (5)*
O(1)–Cu–N(1)	97·2 (2)	C(11)–N(1)–C(15)	118·2 (5)
O(1)–Cu–N(2)	94·6 (2)	C(21)–N(2)–C(25)	118·4 (5)
O(1)–Cu–N(3)	95·1 (2)	C(31)–N(3)–C(35)	117·0 (5)
O(1)–Cu–N(4)	98·2 (2)	C(41)–N(4)–C(45)	116·6 (5)
N(1)–Cu–N(2)	168·2 (2)		
N(1)–Cu–N(3)	88·5 (2)	O(5^i)···Cu–O(1)	175·1 (4)
N(1)–Cu–N(4)	89·7 (1)	O(5^i)···Cu–N(1)	86·4 (5)
N(2)–Cu–N(3)	90·7 (2)	O(5^i)···Cu–N(2)	81·8 (5)
N(2)–Cu–N(4)	88·3 (2)	O(5^i)···Cu–N(3)	88·8 (5)
N(3)–Cu–N(4)	166·7 (2)	O(5^i)···Cu–N(4)	78·1 (5)
H(51)–O(5)–H(52)	100·5 (5)*		
O(5)–H(51)···O(2^{ii})	175·3 (6)*		
O(5)–H(52)···O(4)	135·4 (4)*		

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

* Parameters x,y,z for H(51) and/or H(52) fixed.

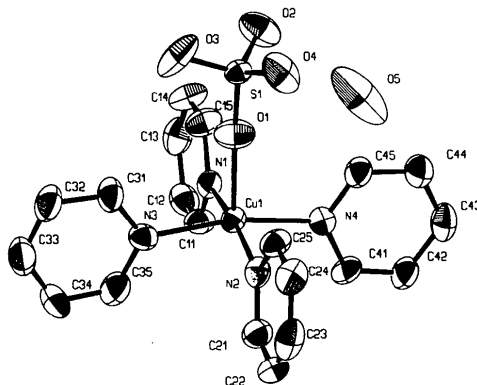Fig. 1. An *ORTEP* drawing of the molecular structure of [Cu(py)$_4$SO$_4$].H$_2$O. The thermal ellipsoids are drawn at the 50% probability level. The H atoms have been omitted.
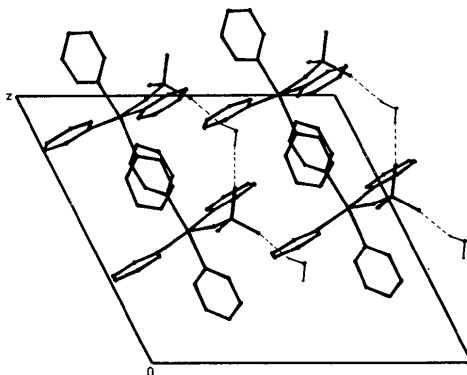
Fig. 2. Projection of the title complex down the b axis.

the structure is that O(5) completes a distorted octahedron about the Cu atom. The Cu···O(5) distance of 4·011 (9) Å is, however, too long to represent a chemical bond.

References

Gmelins Handbuch der Anorganischen Chemie (1952). Kupfer, Syst. No. 60, Teil B, Lief 1, p. 572. Weinheim: Verlag Chemie.

International Tables for X-ray Crystallography (1974). Vol. IV. Birmingham: Kynoch Press. (Present distributor Kluwer Academic Publishers, Dordrecht.)

JOHNSON, C. K. (1971). ORTEPII. Report ORNL-3794, revised. Oak Ridge National Laboratory, Tennessee, USA.

MOROSIN, B. (1969). Acta Cryst. B25, 19–30.

SHELDRICK, G. M. (1976). SHELX76. Program for crystal structure determination. Univ. of Cambridge, England.

VARGHESE, J. N. & MASLEN, E. N. (1985). Acta Cryst. B41, 184–190.

Structures of 1,8-Naphthyridine Silver(I) Perchlorate, Quinoxaline Silver(I) Perchlorate and Phthalazine Silver(I) Nitrate

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Abstract. Bis(μ-1,8-naphthyridine-N,N')-disilver(I)-(Ag–Ag) diperchlorate, $|Ag_2(C_8H_6N_2)_2|.2ClO_4$, (I), $M_r = 675 \cdot 0$, monoclinic, $P2_1/a$, $a = 16 \cdot 114$ (3), $b = 10 \cdot 462$ (2), $c = 5 \cdot 772$ (1) Å, $\beta = 100 \cdot 77$ (2)°, $V = 956 \cdot 0$ (3) Å^3, $Z = 2$, $D_x = 2 \cdot 36$ Mg m^{-3}, λ(Mo $K\alpha$) = 0·71073 Å, $\mu = 2 \cdot 38$ mm^{-1}, $F(000) = 164$, $T = 298$ (1) K, $R = 0 \cdot 026$ for 1586 unique reflections. catena-Poly|silver(I)-μ-quinoxaline-N,N')| perchlorate, $|Ag(C_8H_6N_2)|.ClO_4$, (II), $M_r = 337 \cdot 5$, orthorhombic, $Pmc2_1$, $a = 7 \cdot 211$ (2), $b = 6 \cdot 992$ (2), $c = 20 \cdot 375$ (5) Å, $V = 1027 \cdot 3$ (4) Å^3, $Z = 4$, $D_x = 2 \cdot 18$ Mg m^{-3}, $\mu = 2 \cdot 28$ mm^{-1}, $F(000) = 164$, $T = 297$ (1) K, $R = 0 \cdot 023$ for 1223 unique reflections. Bis(μ-phthalazine-N,N')-bis(phthalazine-N)disilver(I) dinitrate, $|Ag_2(C_8H_6N_2)_4|.2NO_3$, (III), $M_r = 860 \cdot 4$, monoclinic, $P2_1/a$, $a = 13 \cdot 603$ (2), $b = 15 \cdot 961$ (2), $c = 7 \cdot 328$ (1) Å, $\beta = 99 \cdot 10$ (2)°, $V = 1571 \cdot 1$ (5) Å^3, $Z = 2$, $D_x = 1 \cdot 83$ Mg m^{-3}, $\mu = 1 \cdot 30$ mm^{-1}, $F(000) = 214$, $T = 298$ (1) K, $R = 0 \cdot 034$ for 1526 unique reflections. In (I), a planar binuclear silver complex is formed with two 1,8-naphthyridine molecules as bridged ligands. In (II), Ag$^+$ cations and quinoxaline molecules are arranged alternately to form one-dimensional chains along **a**. In (III), each Ag atom is surrounded trigonally by the N atoms of one unidentate and two bridging phthalazine molecules to form a nearly planar binuclear silver complex. The binuclear silver complexes in (I) and (III) have a center of symmetry, the Ag—Ag distances being (I) 2·756 (1) and (III) 3·491 (1) Å.

Introduction. Although a number of techniques concerning surface analysis have been developed, it is quite difficult to elucidate the exact structure of adsorbate molecules on a metal surface. There is still controversy whether surface complexes formed by adsorption of molecules on a metal surface can be represented by metal complexes with the molecules as ligands (Rhodin & Ertl, 1979). Based on the many available data, there are good grounds for expecting metal complexes to be surface-structure models though no direct evidence for surface structure has been reported so far. We have recently reported the surface enhanced Raman scattering (SERS) results of azanaphthalene compounds on an Ag electrode surface (Takahashi, Furukawa, Fujita & Ito, 1987; Takahashi, Sakai, Fujita & Ito, 1986) and discussed the structure and orientation of the adsorbed molecules in relation to SER spectra. On the other hand, no structure data for azanaphthalene–silver complexes were available. In this study, we have determined the structures of the title complexes to investigate the correlation with the spectroscopic results.

Experimental. Colorless crystals were obtained by mixing AgClO$_4$ (or AgNO$_3$) and the diazanaphthalene in acetone. Rigaku AFC-5 diffractometer, graphite monochromator. Unit-cell parameters from 20–24 reflections ($20 < 2\theta < 31°$). $2\theta_{max} = 55°$, five standard reflections. After absorption correction, the structure was solved based on Patterson function or by direct methods with MULTAN78 (Main, Hull, Lessinger, Germain, Declercq & Woolfson, 1978). H atoms located in difference synthesis and refined isotropically. $\sum w(|F_o| - |F_c|)^2$ minimized, $w^{-1} =$