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## Spermine Copper(II) Perchlorate

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## Abstract.

$H_2N(CH_2)_3NH(CH_2)_4NH(CH_2)_3NH_2Cu(ClO_4)_2$ , monoclinic,  $P2_1/n$ ,  $a = 16.003$  (3),  $b = 14.701$  (4),  $c = 7.849$  (1) Å,  $\beta = 91.66$  (1)°,  $Z = 4$ ,  $D_c = 1.67$  g cm<sup>-3</sup>. Full-matrix least-squares refinement gave a final  $R$  of 8.2%. The coordination about the copper ions is square planar of four nitrogen atoms of the same spermine molecule.

**Introduction.** The high level of spermine and spermidine in some human cancer sera has been demonstrated (Tsou, Lo, Selzer, Weinstein & Bender, 1973) with a cupric-cuprous sulfite method. To explore the physiological meaning of this *in vitro* reaction copper(II)-spermine chelates were prepared by Tsou, Lo & Miller (1973). Further studies by them indicated that whereas spermine stimulated growth in tissue culture systems of two tumor cell lines, the copper(II) chelate inhibited growth, suggesting a plausible non-immunogenic mechanism for retardation of tumor growth through ligand exchange of copper(II)-containing proteins with spermine. The X-ray structure determination was undertaken to confirm the nature of the chelate.

Lilac crystals, obtained by evaporation from 25% isopropanol in methanol, were supplied by Dr K. C. Tsou and Dr K. W. Lo. Precession photography indicated that they are monoclinic with the space group  $P2_1/n$  uniquely determined by the systematic absences  $h0l$ ,  $h + l = 2n + 1$  and  $0k0$ ,  $k = 2n + 1$ .

Data were collected on a Picker Nuclear FACS-I automated diffractometer using monochromatic Cu  $K\alpha$  radiation. The  $\theta-2\theta$  scan technique was used out to a maximum  $\sin \theta/\lambda$  of 0.52 with a scan rate of 1° min<sup>-1</sup>, a base width of 1.5° and a background time of 20 s. The data set consisted of 2804 reflections of which 858 were unobserved. All reflections having intensities less than  $2.33\sigma(I)$  were considered to be unobserved.

The coordinates of the copper(II) ion as well as those of the two chlorine atoms of the perchlorate ions

were determined through three-dimensional Patterson synthesis and atomic superposition methods. For the latter the superposition programs by Hubbard & Jacobson (1969) were used. The remaining atoms were located through successive Fourier maps. The structure was isotropically refined with the UCLA full-matrix least-squares program to an  $R$  value of 10.9% and anisotropically refined to a final  $R$  value of 8.2%. Hydrogen atoms were not located. The function minimized was  $\sum w[|F_o| - (1/k)|F_c|]^2$  where  $k$  is the scale factor for the observed structure factors. The data were given weights inversely proportional to the standard errors of the observed structure amplitudes, where  $\sigma[F_o(\mathbf{h})] = \{|F_o(\mathbf{h})|^2 + \sigma[I(\mathbf{h})]\}^{1/2} - |F_o(\mathbf{h})|$ . The final positional parameters and anisotropic temperature factors,

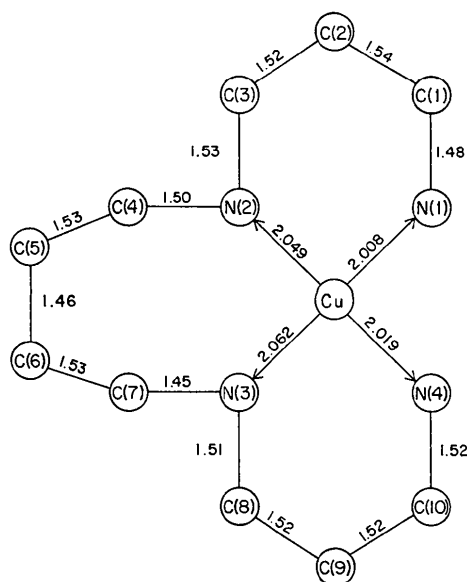


Fig. 1. Bond lengths in spermine copper(II) perchlorate.

with their estimated standard deviations, are given in Tables 1 and 2.\*

**Discussion.** Bond lengths and angles are shown in Figs. 1 and 2. The square planar coordination of the copper

\* A list of structure amplitudes has been deposited with the British Library Lending Division as Supplementary No. SUP 30672 (23 pp., 1 microfiche). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

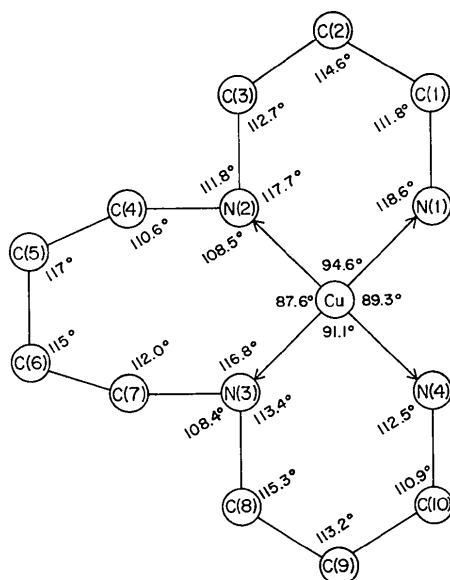


Fig. 2. Bond angles in spermine copper(II) perchlorate.

Table 1. Final positional parameters ( $\times 10^4$ ) for spermine copper(II) perchlorate

	<i>x</i>	<i>y</i>	<i>z</i>
Cu	4427.6 (0.7)	2315.1 (0.8)	2473 (2)
Cl(1)	4918 (2)	2606 (2)	8039 (3)
Cl(2)	2138 (2)	4433 (2)	8941 (3)
O(1)	2195 (8)	3499 (9)	9064 (19)
O(2)	2500 (9)	4697 (8)	7423 (13)
O(3)	1424 (6)	4772 (10)	9464 (16)
O(4)	2721 (6)	4685 (9)	201 (14)
O(5)	4138 (5)	3045 (6)	8377 (10)
O(6)	5201 (4)	2211 (5)	9579 (8)
O(7)	4804 (5)	1932 (5)	6754 (8)
O(8)	5484 (5)	3283 (5)	7480 (10)
N(3)	3308 (4)	1926 (5)	1330 (9)
N(1)	5584 (4)	2660 (5)	3300 (9)
N(4)	4626 (4)	1042 (4)	3360 (8)
N(2)	3997 (5)	3627 (5)	2373 (10)
C(4)	3592 (7)	3840 (7)	4020 (13)
C(5)	3039 (7)	3050 (10)	4566 (14)
C(6)	2403 (8)	2739 (10)	3333 (17)
C(7)	2597 (6)	1842 (8)	2428 (14)
C(8)	3370 (6)	1070 (6)	292 (11)
C(9)	3680 (6)	236 (6)	1267 (12)
C(10)	4573 (6)	333 (6)	1960 (13)
C(3)	4612 (7)	4370 (7)	1871 (14)
C(2)	5424 (7)	4340 (7)	2918 (14)
C(1)	5967 (6)	3490 (7)	2612 (13)

is evident in the ORTEP drawing of the molecule, Fig. 3. The bond distances and angles compare well with those found in other polyamine complexes of copper.

The thermal motion of atoms C(5) and C(6), see Fig. 3, suggests that there may be disorder present; this could account for the abnormally short C(5)–C(6) bond length of 1.46 Å. The torsion angle at the bond C(5)–C(6) is also anomalous: The value found, 105°,

Table 2. Final thermal parameters ( $\times 10^4$ ) for spermine copper(II) perchlorate

The temperature factors are of the form  $\exp [-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + hk\beta_{12} + hl\beta_{13} + kl\beta_{23})]$ .

	$\beta_{11}$	$\beta_{22}$	$\beta_{33}$	$\beta_{12}$	$\beta_{13}$	$\beta_{23}$
Cu	34.8 (0.5)	41.9 (0.6)	1357 (2)	0 (1)	0 (2)	-16 (2)
Cl(1)	45 (1)	40 (1)	92 (4)	-7 (2)	9 (3)	1 (4)
Cl(2)	46 (1)	64 (2)	111 (5)	9 (2)	-8 (4)	-8 (5)
O(1)	157 (10)	110 (10)	812 (52)	-45 (16)	335 (38)	51 (36)
O(2)	208 (11)	143 (10)	280 (24)	162 (17)	78 (26)	152 (25)
O(3)	49 (5)	311 (17)	618 (39)	130 (15)	-43 (22)	-476 (41)
O(4)	79 (6)	190 (12)	488 (33)	5 (14)	-120 (23)	-79 (32)
O(5)	61 (4)	93 (6)	272 (20)	39 (8)	49 (15)	-5 (17)
O(6)	64 (4)	75 (5)	145 (14)	-18 (7)	-50 (12)	83 (14)
O(7)	85 (5)	66 (5)	124 (13)	17 (8)	-14 (13)	-66 (13)
O(8)	62 (4)	62 (5)	325 (21)	-11 (8)	40 (15)	76 (17)
N(3)	38 (4)	49 (5)	1416 (15)	-9 (7)	-8 (12)	-39 (14)
N(1)	33 (3)	44 (4)	1542 (15)	-22 (7)	-16 (11)	33 (14)
N(4)	46 (4)	28 (4)	1003 (13)	10 (6)	-15 (11)	-33 (11)
N(2)	46 (4)	32 (4)	2189 (19)	10 (7)	7 (14)	-30 (15)
C(4)	61 (6)	56 (7)	1794 (22)	13 (10)	70 (19)	-83 (20)
C(5)	45 (6)	143 (12)	1449 (22)	-31 (13)	64 (18)	-126 (26)
C(6)	53 (6)	107 (10)	2944 (32)	22 (14)	99 (23)	-31 (30)
C(7)	28 (4)	68 (7)	2388 (24)	-22 (9)	88 (17)	-52 (21)
C(8)	50 (5)	44 (6)	1311 (18)	-16 (9)	-44 (15)	-40 (16)
C(9)	47 (5)	37 (5)	1636 (20)	-7 (8)	-40 (16)	-40 (16)
C(10)	51 (5)	23 (5)	2265 (23)	-4 (8)	-27 (18)	-47 (16)
C(1)	59 (6)	43 (6)	2699 (27)	-35 (10)	-34 (20)	61 (21)
C(3)	56 (6)	49 (6)	2385 (25)	-33 (10)	6 (19)	-24 (20)
C(2)	38 (5)	51 (6)	1905 (22)	-21 (9)	-4 (16)	11 (19)

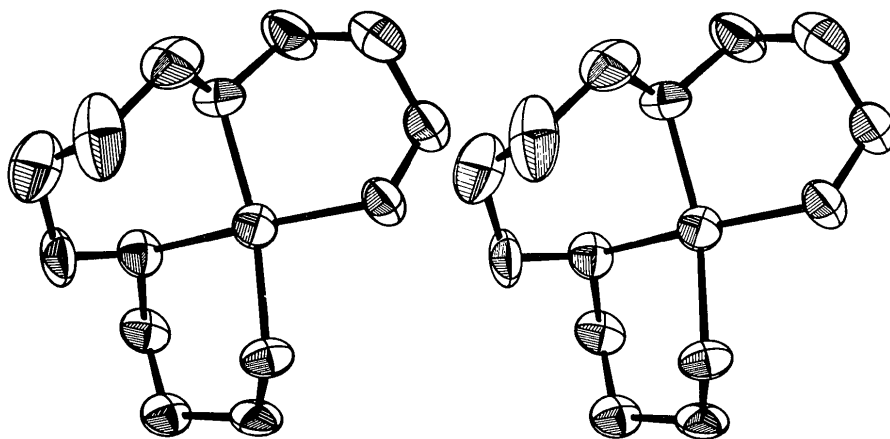


Fig. 3. Stereoscopic ORTEP drawing of spermine copper(II) perchlorate.

is markedly different from the average of  $65 \pm 5^\circ$  at the other six carbon-carbon single bonds. These distortions may result from the geometrical requirements of accommodating the seven-membered ring into the chelating system.

The bond lengths in the perchlorate ion of Cl(1) are 1.405 (7), 1.422 (7), 1.423 (8), and 1.436 (8), average  $1.422 \pm 0.011$  Å. Those in the second perchlorate ion are 1.32, 1.38, 1.39, and 1.40, average,  $1.37 \pm 0.03$  Å; the thermal parameters for these oxygen atoms are, however, all quite high, so that the positions of these atoms are much less certain.

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## Refinement of the Crystal Structure of Scorodite

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**Abstract.**  $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ , orthorhombic, *Pbca*,  $a = 10.325$  (6),  $b = 8.953$  (3),  $c = 10.038$  (2) Å,  $Z = 8$ ,  $D_m = 3.27$ ,  $D_x = 3.276$  g cm<sup>-3</sup>. Material from Kiura Mine, Oita, Japan. Each  $\text{AsO}_4$  tetrahedron shares its vertices with four  $\text{FeO}_4(\text{OH})_2$  octahedra and *vice versa*. With  $\text{Fe} \cdots \text{O}$  distances of 2.061 (5) and 2.125 (5) Å, the two water molecules coordinate to the metal ion in the *cis* position and donate two and one short hydrogen bonds, respectively, to arsenate oxygen atoms.

**Introduction.** Precession photographs exhibited orthorhombic symmetry. The systematic absences are  $hk0$  for  $h$  odd,  $0kl$  for  $k$  odd and  $h0l$  for  $l$  odd. Cell dimensions were determined from setting angles of a four-circle diffractometer. The intensity data of 1878 independent reflexions with  $2\theta \leq 60^\circ$  were collected from a

crystal of dimensions  $0.12 \times 0.11 \times 0.10$  mm on a Rigaku automatic four-circle diffractometer; a graphite monochromator, Mo  $K\alpha$  radiation and a  $\theta$ - $2\theta$  scan technique were used. Intensities of 183 reflexions smaller than  $2\sigma(F)$  were considered to be zero, where

Table 1. Final fractional atomic coordinates ( $\times 10^5$ ) with e.s.d.'s in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
As	34799 (6)	3556 (7)	-13618 (7)
Fe	37359 (9)	14651 (11)	18278 (10)
O(1)	19917 (42)	327 (51)	-19453 (46)
O(2)	35791 (45)	678 (50)	2939 (42)
O(3)	39294 (43)	21230 (50)	-16644 (47)
O(4)	44796 (45)	-8264 (51)	-21656 (46)
O(W1)	19851 (43)	23012 (54)	11835 (52)
O(W2)	44653 (47)	32843 (56)	6932 (47)