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Synthesis and Crystal and Molecular Structure of {Bis[4-N-Methylpiperidinium]-disulfide} tetrachlorocuprate(II)

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The X-ray structure of {Bis[4-N-methylpiperidinium] disulfide}tetrachlorocuprate(II), $(C_5H_9NH(CH_3)S)_2CuCl_4$*, was determined by X-ray diffraction methods. The yellow crystals are orthorhombic, Iba2, with* a = *12.583(12)* Å, b = *26.550(18)* Å, *and* c = *12.437(12)* Å. *With Z = 8, the calculated density is 1.502 g cm*$^{-3}$ *(observed density = 1.48 g cm*$^{-3}$*). Solution of the structure by direct methods led to a final weighted R factor of 0.100 for 1476 independent reflections. The crystal structure consists of* $CuCl_4^{2-}$ *anions and {Bis[4-N-methylpiperidinium]-disulfide}cations. The* $CuCl_4^{2-}$ *anions show a flattened tetrahedral geometry, the two largest Cl–Cu–Cl angles being 133.8° (1.1) and 136.3° (1.2); the dihedral angle is 60.7°. The Cu–Cl distances range from 2.21 to 2.29 Å. Two chlorine atoms are involved in Cl···N interactions, which may be responsible for the distortion of the* $CuCl_4^{2-}$ *ions from the tetrahedral configuration. The two piperidine rings show the usual 'chair' configuration. The S–S bond length is 2.03(2) Å and the CSSC dihedral angle is 79°. The far IR and electronic spectra are in agreement with the distortion from tetrahedral symmetry.*

Introduction

There has been considerable interest in ambidentate ligands, *i.e.*, ligands with more than one mode of coordination. In particular, ligands which may, in principle, coordinate through either nitrogen or sulfur have been of especial concern [1]. The metal complexes of several β-mercaptoamine ligands have been widely studied in the solid state as well as in solution. However metal complexes of γ-mercaptoamine ligands have had much less attention up to now. In our laboratory we are studying the ligand ability of the N-methyl-4-mercaptopiperidine as a first part of a more extensive project. The product of the reaction of the named ligand with cadmium perchlorate [2] and with zinc chloride [3] have been reported recently. During efforts to prepare copper(II) complexes of this ligand, a reduction of the Cu^{2+} to Cu^{+} occurred, concomitant with the oxidation of the mercaptopiperidine to disulfide. With an excess of copper(II) chloride in acidic medium, the product isolated was $[C_5H_9NH(CH_3)S]_2CuCl_4$.

It was of interest to determine the structure of this compound because of current interest in the geometry and environment of the $CuCl_4^{2-}$ anion. The configuration of the tetrachlorocuprate(II) ions has aroused great interest since it was first reported in Cs_2CuCl_4 [4] for the great ease with which this species assumed various geometries, ranging from square planar through tetrahedral to trigonal bipyramidal [5]. A flattened tetrahedral geometry is expected for M_2CuCl_4 and $MCuCl_4$ when M is a large bulky cation [6], as in the present case.

Experimental Section

N-methyl-4-mercaptopiperidine and its hydrochloride were synthesized according to Barrera *et al.* [7].

Preparation of $[C_5H_9NH(CH_3)S]_2CuCl_4$

Dry HCl was bubbled through a solution of 4 g of $CuCl_2 \cdot 2H_2O$ in 100 ml of 99% ethanol until the initial blue solution turned yellow. To the stirred solution was added slowly 50 ml of an ethanolic solution of 2 g of N-methyl-4-mercaptopiperidinium

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TABLE I. Experimental Data for the X-ray Diffraction Study of $(SC_5H_9NH(CH_3))_2CuCl_4$.

(A) *Crystal Data*

Crystal system: Orthorhombic
Space group: *Iba*2
a = 12.583(12) A
b = 26.550(18) A
c = 12.437(12) A
V = 4155 A^3
Z = 8
density (calc) = 1.50 g cm^{-3}
density (obs.)[a] = 1.48 g cm^{-3}

(B) *Measurement of Intensity Data*

Diffractometer: Philips PW 1100
Radiation: CuK_α (λ = 1.5418 A)
Monochromator: graphite
Scan type, scan speed: $\theta-2\theta$, 2°/min in 2θ
Scan range: symmetrical 2°/min
Background measurement: stationary of scan time at each of the scan time
Data collected: 1476 independent F_{hkl}
Standard reflections: three remeasured after each 50 reflections
Reflections measured: (hkl)

[a] Flotation in acetone–carbon tetrachloride.

TABLE II. Atomic Coordinates ($\times 10^4$) (standard deviations in parentheses).

Atom	x	y	z
Cu(1)	3326(2)	3738(1)	4039(0)
Cl(1)	4435(2)	4384(2)	3993(8)
Cl(2)	1825(5)	4178(2)	4471(6)
Cl(3)	3072(5)	3071(2)	5092(7)
Cl(4)	3894(5)	3338(2)	2523(7)
S(1)	1344(6)	6153(3)	5615(7)
C(1)	2016(19)	5668(8)	6400(24)
C(2)	1328(19)	5220(8)	6700(28)
C(3)	1944(22)	4812(9)	7285(26)
N(1)	2888(17)	4662(7)	6506(21)
C(4)	3570(18)	5097(10)	6218(30)
C(5)	2951(21)	5502(10)	5662(26)
C(6)	3453(24)	4223(10)	7074(26)
S(2)	5087(6)	1353(2)	1534(8)
C(7)	5688(17)	1776(8)	2552(25)
C(8)	6048(21)	2262(8)	2036(22)
C(9)	6498(21)	2605(8)	2921(22)
N(2)	5658(15)	2711(6)	3745(16)
C(10)	5259(20)	2236(8)	4231(25)
C(11)	4820(19)	1885(8)	3374(19)
C(12)	6092(24)	3043(10)	4649(25)

TABLE III. Interatomic Distances (Å) and Angles (deg.) (standard deviations are given in parentheses).

	Bond Distances
Cu(1)–Cl(1)	2.21(1)
Cu(1)–Cl(2)	2.28(1)
Cu(1)–Cl(3)	2.22(1)
Cu(1)–Cl(4)	2.28(1)
S(1)–S(2)	2.02(2)
S(1)–C(1)	1.82(4)
C(1)–C(2)	1.52(6)
C(1)–C(5)	1.56(6)
C(2)–C(3)	1.52(6)
C(3)–N(1)	1.58(6)
N(1)–C(4)	1.48(6)
N(1)–C(6)	1.54(6)
C(4)–C(5)	1.50(7)
S(2)–C(7)	1.86(4)
C(7)–C(8)	1.51(6)
C(7)–C(11)	1.52(6)
C(8)–C(9)	1.54(6)
C(9)–N(2)	1.50(5)
N(2)–C(12)	1.53(6)
N(2)–C(10)	1.49(5)
C(10)–C(11)	1.52(6)
	Bond Angles
Cl(1)–Cu(1)–Cl(2)	97.5(0.8)
Cl(1)–Cu(1)–Cl(3)	136(1)
Cl(2)–Cu(1)–Cl(3)	98.6(0.8)
Cl(1)–Cu(1)–Cl(4)	98.2(0.9)
Cl(3)–Cu(1)–Cl(4)	99.3(0.8)
Cl(2)–Cu(1)–Cl(4)	133.8(1.1)
S(1)–C(1)–C(2)	115(6)
S(1)–C(1)–C(5)	104(5)
C(2)–C(1)–C(5)	111(7)
C(1)–C(2)–C(3)	113(7)
C(2)–C(3)–N(1)	106(7)
C(3)–N(1)–C(6)	105(6)
C(4)–N(1)–C(6)	116(7)
N(1)–C(4)–C(5)	112(8)
C(4)–C(5)–C(1)	109(7)
S(2)–C(7)–C(8)	111(6)
S(2)–C(7)–C(11)	106(5)
C(8)–C(7)–C(11)	110(7)
C(7)–C(8)–C(9)	108(7)
C(8)–C(9)–N(2)	110(6)
C(9)–N(2)–C(10)	111(6)
C(9)–N(2)–C(12)	111(6)
C(10)–N(2)–C(12)	108(6)
N(2)–C(10)–C(11)	111(7)
C(10)–C(11)–C(7)	109(7)

chloride. Some precipitate was formed. The bubbling of dry HCl through the reaction mixture caused dissolution of the solid. The solution was then filtered and placed in a refrigerator at 5 °C for several days. The product, which slowly deposited as yellow crystals, was collected by filtration, washed with absolute ethanol previously saturated with dry hydrogen

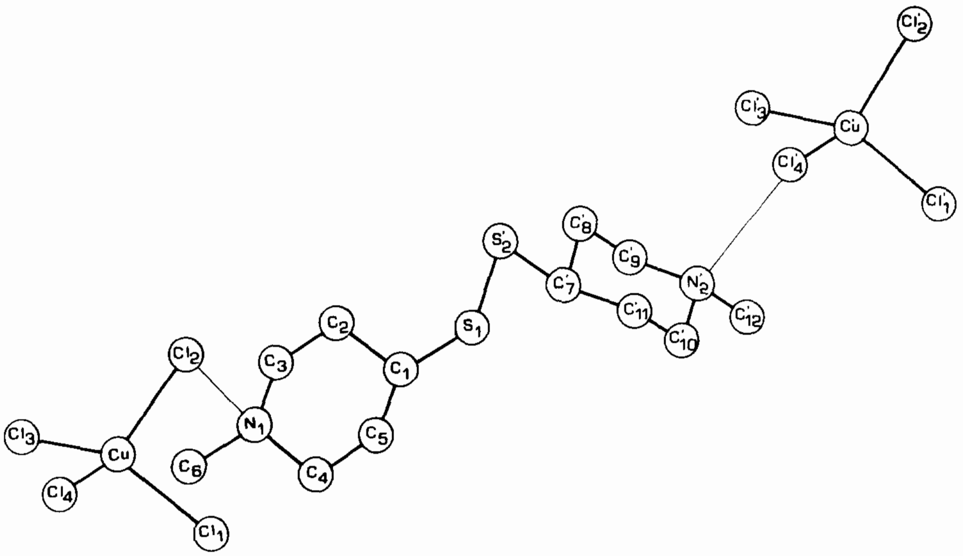

Fig. 1. Molecular structure of $(SC_5H_9NH(CH_3))_2CuCl_4$ showing the labelling of the atoms. Prime denotes atoms in the equivalent positions x – ½, y + ½, z + ½ relative to the reference atoms x, y, z in Table II. Light lines indicate hydrogen bonds.

chloride and then with diethyl ether, and dried *in vacuo* over silical gel. This method yielded crystals of suitable size and quality for X-ray analysis. *Anal.* Calcd.: Cu: 13.6; Cl: 30.3; S: 13.7; C: 30.8; N: 5.99; H: 5.60. Found: Cu: 13.6; Cl: 30.6; S: 13.9; C: 30.6; N: 6.02; H: 5.35.

Analyses

Carbon, hydrogen and nitrogen analyses were performed in the laboratories of the Instituto de Química Orgánica 'Juan de la Cierva' (Barcelona). The other elements were analyzed in this laboratory. Sulfur and chlorine contents were determined gravimetrically as $BaSO_4$ and AgCl respectively. Copper was determined volumetrically using thiosulfate.

Physical Measurements

Infrared spectra from 4000 to 250 cm^{-1} were recorded on a Beckman IR-20A spectrophotometer. The samples were either pressed in a potassium bromide pellet or run as Nujol mulls between polyethylene plates. Electronic diffuse reflectance spectra at room temperature were recorded on a Beckman MVII spectrophotometer (Departament de Química Analítica, Universitat Central de Barcelona).

X-Ray Data Collection and Reduction

Approximate cell parameters were determined from Weissenberg photographs and refined by least squares from a four-circle diffractometer. Systematic absences identified the space group as I*ba*2 or I*bam* (orthorhombic). The collection of intensity data was carried out on a PW 1100 Philips four-circle diffractometer. With graphite-monochromated CuK_α radiation (λ = 1.5418 Å) 1476 independent reflections were measured, satisfying the condition $|F_o|^2 > 2\sigma|F_o|^2$. The intensities were corrected for Lorentz and polarization factors, but absorption effects were ignored, and used for the structural determination. The lattice parameters refined from single-crystal data are: a = 12.583(12) Å, b = 26.550(18) Å, c = 12.437(12) Å, V = 4155 Å^3. The calculated density was 1.50 g cm^{-3} (See Table I).

Structural Determination

The structure was solved by direct methods with the multiple-solution program MULTAN [8] using 200 reflections with $E_{hkl} \geqslant 1.435$. An E map calculated from the phases generated for the set with the highest figure of merit clearly showed the position of all the non-hydrogen atoms. The crystal structure was solved on a I*ba*2 space group. Refinement was made by full-matrix least squares techniques using first isotropic (R index reduced from 0.276 to 0.131) and then anisotropic thermal parameters to a final R = 0.100 for all data (1476 F_{hkl}). The refinement was carried out with the program AFFINE [9]. The calculations were carried out on the IBM 370-168 computer at the C.I.R.C.E. (Orsay University, France).

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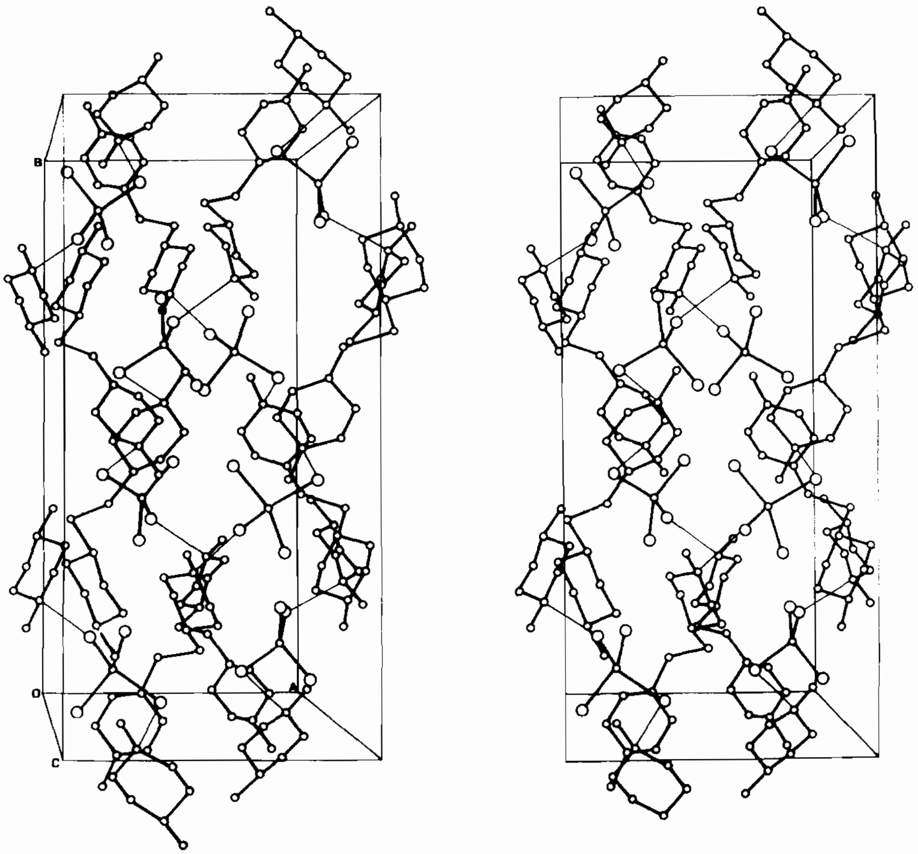

Fig. 2. Stereoview of the unit cell showing the molecular packing. Atoms are represented as spheres of arbitrary size. Chlorine atoms are of greater size. Hydrogen bonds are represented by light lines.

Results and Discussion

Description and Discussion of the Structure

The numbering system employed is displayed in Fig. 1. Figure 1 is a model in perspective of the molecule. Figure 2 is a stereoscopic view of the unit cell. Half $(C_5H_9NH(CH_3)S)_2$ of two different cations is hydrogen bonded to each tetrachlorocuprate anion. The remaining halves of each disulfide associate with different anions forming a polymeric chain following the [111] directions and those required by symmetry. The methyl substituents at each nitrogen atom are placed approximately between three chlorine atoms to minimize the Cl–CH_3 repulsions. It can be seen from Fig. 1 that C(6) is blocking approach to the trigonal face of the tetrahedron determined by Cl(1), Cl(2) and Cl(3), while C(12) is blocking approach to the face determined by Cl(1), Cl(3) and Cl(4). The following Cl–N distances are lesser than 3.5 Å indicating N–H···Cl hydrogen bonds: Cl(2)···N(1): 3.14(4) Å, and Cl(4)···N(2): 3.16(3) Å. These N–H···Cl interactions may explain the distortion of $CuCl_4^{2-}$ ions from T_d symmetry [10, 11]. Hydrogen bonding will reduce the effective charge on the chlorine atoms, thus allowing the square planar geometry favored by the crystal field stabilization [12]. The strongest interactions of the nitrogen atom N(1) are with Cl(2) and Cl(4) and this may be one of the reasons of the greater Cu–Cl(2) and Cu–Cl(4) bond lengths. The $CuCl_4^{2-}$ anions show a flattened tetrahedral geometry. The two δ' angles defined by Muetterties and Guggenberger [13] (the angle formed by the normals of the pair of triangular faces which become a square face in the square-planar limit) are 78.7 and 79.8°. The other four δ angles range from 126.0 to 126.7°.

The Cu–Cl distances range from 2.21 to 2.29 Å, as previously found on structural investigations of a number of compounds containing discrete $CuCl_4^{2-}$ anions. The cation consists of two piperidine rings joined through sulfur atoms. The rings are crystallographically independent and are both chair shaped as indicated by the puckering parameters [14].

Both sulfur atoms and the CH_3 groups are bonded to the piperidine rings in equatorial positions. The C–S bond lengths 1.86(4) and 1.82(4) Å are comparable with other reported disulfides [15]. The

TABLE IV. Puckering Coordinates of the Piperidine Rings.

	Ring I	*Ring II*
	N(1)·······C(4)	N(2)····C(9)
Q(A)	0.59	0.61
q_2(A)	0.01	0.03
q_3(A)	−0.59	0.61
ϕ_2 (degrees)	250.4	212.2
θ (degrees)	−1.3	3.2

CSSC dihedral angle is smaller than 90°, the angle at which the lone pair–lone pair repulsions within the sulfur moiety are at a minimum in free disulfides [16] but within the range found in most CSSC dihedral angles [17]. The S–S bond length is the same, within three times the standard deviation, as the value of 2.04 Å which is normally observed [16, 18] in aliphatic disulfides whose CSSC dihedral angles are close to 90°.

Far IR Spectrum

The observation of two absorptions at 300 and 262 cm^{-1} (the limit of our instrument is 250 cm^{-1}) is consistent with the lowering of symmetry when the tetrahedron is compressed along one of the S_4 axes to form a species with nearly D_{2d} symmetry. The triply degenerate t_2 mode in T_d splits into an e and a b_2 mode. The e Cu–Cl stretching mode remains at 300 cm^{-1}, a frequency typical of T_d ions [19], while the b_2 Cu–Cl stretching mode is shifted to lower frequencies. The amount of splitting is proportional to the extent of compression.

Electronic Spectrum

The following bands are observed at room temperature up to 45500 cm^{-1}: 16200(sh), 19400, 24400(sh) and 35700 cm^{-1}. These charge transfer bands are due to CuCl_4^{2-} and disulfide absorptions [20, 21]. A correlation has been found between the energy of the lowest energy UV transition and the dihedral angle about the S–S bond. As the CSSC dihedral angle is opened from 0 to 90°, the absorption maximum shifts from 27000 to about 40000 cm^{-1}. On this basis, the 37500 cm^{-1} band should be expected to be a $\sigma^* \leftarrow n_a$ disulfide absorption. A maximum with a broad tail extending to lower energies was observed at approximately 9800 cm^{-1}. Recently some attempts have been made to correlate empirically the maximum of the d–d transition for several CuCl_4^{2-} chromophores with the amount of distortion from the T_d symmetry. Harlow *et al.* [22] used the average of the two largest Cl–Cu–Cl angles, θ, and Battaglia *et al.* [11] used the Cl–Cu–Cl dihedral angle Δ. For 9800 cm^{-1} the calculated θ and Δ values using these empirical relationships are 135.5 and 60.9°, in good agreement with the observed values 135.1 and 60.7° respectively. However it should be pointed out that the spectrum has been fit to two gaussian bands centered at 7000 and 10300 cm^{-1}. Using the corrected 10300 cm^{-1} value, the agreement is not so good (θ_{calc} = 139.4 and Δ_{calc} = 55.6°).

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