Synthesis and Crystal and Molecular Structure of Di-μ-(*N*-methylpiperidinium-4-thiolate)-bis[dichlorozinc(II)] Monohydrate

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The reaction of zinc chloride with 4-mercapto-*N*-methylpiperidinium chloride in aqueous solution gives the title complex. Crystals of the compound are monoclinic, space group $P2_1/m$, with a = 10.988(12), b = 13.086(12), c = 7.476(9) Å, β = 91.99(1)°. With Z = 2, the calculated density is 1.71 g cm^{-3} (measured density 1.69 g cm^{-3}). Solution of the structure by direct methods led to a final weighted R factor of 0.072 for 2 028 independent reflections. The crystal structure of the zwitterionic complex consists of discrete dimeric molecules. Each sulphur atom of the ligand acts as a bridge between two zinc atoms. The crystallographic mirror plane passing through the zinc and chlorine atoms imposes a C_s symmetry on the molecule. The average Zn–Cl bond distance is 2.255(7) Å, while the Zn–S bond distances average 2.371(11) Å. The piperidine rings shows the usual ' chair ' configuration. The dimeric molecules are bridged by a network of hydrogen bonds involving –NH groups and the chlorine atoms.

We are presently studying the ligating ability of several γ-mercaptoamines. In particular we have focused our attention on the complexes formed by 4-mercapto-*N*-methylpiperidine [$HSC_5H_9N(CH_3)$] and several metal ions, in different conditions. The crystal and molecular structure [1] of $[Cd\{SC_5H_9NH(CH_3)\}_2][ClO_4]_2\cdot 2H_2O$ has been reported recently; a detailed introduction and justification for our interest can be found therein. As part of a more extensive study to understand and to compare the behaviour of Zn^{2+}, Cd^{2+}, and Hg^{2+} toward γ-mercaptoamines in the solid state and in solution, a single-crystal *X*-ray diffraction study has been undertaken on the zinc complex.

EXPERIMENTAL

4-Mercapto-*N*-methylpiperidine and its hydrochloride were synthesized according to Barrera and Lyle.[2]

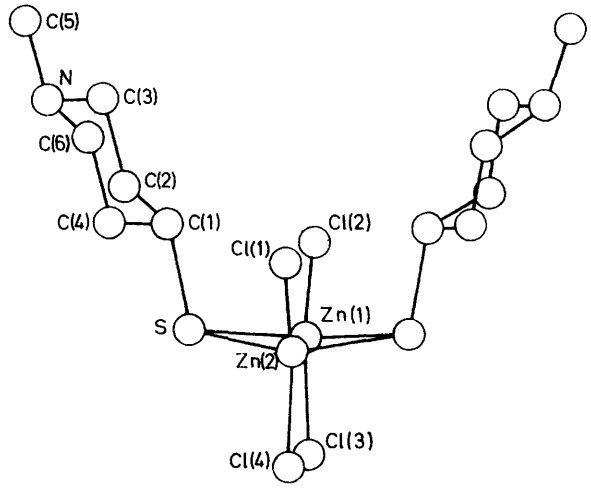
Preparation of $[\{Zn[SC_5H_9NH(CH_3)]Cl_2\}_2]\cdot H_2O$.—A filtered solution of $ZnCl_2$ (7.2 g, 52.8 mmol) in H_2O (50 cm^3) was added to a solution of 4-mercapto-*N*-methylpiperidinium chloride (2.1 g, 12.5 mmol) in H_2O (25 cm^3). The solution was placed in a refrigerator at 5 °C for several days. The white crystals were filtered off, washed with cold water, ethanol, and diethyl ether, and dried *in vacuo* over silica gel. Yield was *ca.* 60% (Found: C, 26.1; H, 5.00; Cl, 25.8; N, 5.00; S, 11.75; Zn, 23.45. Calc. for $C_{12}H_{28}Cl_4N_2OS_2Zn_2$: C, 26.05; H, 5.10; Cl, 25.65; N, 5.05; S, 11.6; Zn, 23.65%).

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. Zinc, sulphur, and chlorine contents were determined gravimetrically as the zinc anthranilate, $Ba[SO_4]$, and AgCl respectively.

The water content was determined by thermal gravimetric analysis and differential thermal analysis in the Department of Termology of this University with a Netzch S, TA. model 429 apparatus, under an air atmosphere and with a porcelain crucible at a heating rate of 2 °C min^{-1}. The loss of one mol of water per mol of complex starts at 130 °C and proceeds until 268 °C, where the anhydrous complex decomposes.

Physical Measurements.—Infrared spectra from 250 to 4 000 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.

X-Ray Data Collection, Structure Determination, and Refinement for $[\{Zn[SC_5H_9NH(CH_3)]Cl_2\}_2]\cdot H_2O$.—*Crystal data.* $C_{12}H_{28}Cl_4N_2OS_2Zn_2$, M = 553.05, Monoclinic, a = 10.988(12), b = 13.086(12), c = 7.476(9) Å, β = 91.99(1)°,



Molecular structure of $[\{Zn[SC_5H_9NH(CH_3)]Cl_2\}_2]\cdot H_2O$ showing the labelling of the atoms. Unlabelled atoms are related to labelled ones by a mirror plane passing through the zinc and chlorine atoms. The water molecule of crystallization has been omitted

U = 1 074 Å^3, D_m = 1.69, Z = 2, D_c = 1.71 g cm^{-3}, $F(000)$ = 564, space group $P2_1/m$, Cu-K_α radiation, μ = 91·7 cm^{-1}, λ = 1.541 8 Å.

Preliminary Weissenberg photographs revealed the systematic absences $0k0$ ($k = 2n + 1$). This condition is consistent with space groups $P2_1$ and $P2_1/m$. As shown by subsequent solution of the structure, $P2_1/m$ is the correct space group. A small crystal was chosen and mounted on a Philips PW 1100 four-circle diffractometer with a graphite monochromator (Department of Mineralogy and Crystallography of Paris VI University, France). 2028 Independent intensity data satisfying the condition $|F_o|^2 > 2\sigma|F_o|^2$ were collected and used for the structural determination. The intensities were corrected for Lorentz and polarization factors.

The structure was solved by direct methods. The 200 reflections with $E|_{hkl}| \geqslant 1.634$ were used in the MULTAN [3] program. The Fourier $\pm E_{hkl}$ maps computed from the best set of phases led to the co-ordinates of all the non-hydrogen atoms. The crystal structure was refined by full-matrix least-squares calculations using the AFFINE [4] program. Positional parameters, except for the atoms with $y = 0.25$ (mirror plane), individual isotropic thermal parameters, and the overall scale factors were varied. After five isotropic cycles, the R value converged to 0.098 with 1 163 $\pm$ F_{hkl}. The anisotropic refinement was made with five cycles, and the final R value was 0.072 with all the crystal-structure factors. A final difference-Fourier map showed no anomalies. All the calculations were made on the IBM 370-168 system of the Centre Inter-Regional Calcul Electronique of Orsay University (France). Table 1 lists the final non-hydrogen atomic co-ordinates and Table 2 the bond lengths and angles. The final observed and calculated structure factors and thermal parameters are in Supplementary Publication No. SUP 22962 (11 pp.).*

* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1979, Index issue.

TABLE 1

Atomic co-ordinates ($\times 10^4$) with standard deviations in parentheses for $[\{Zn[SC_5H_9NH(CH_3)]Cl_2\}_2]\cdot H_2O$

Atom	x	y	z
Zn(1)	9 376(1)	2 500	6 186(2)
Zn(2)	6 623(1)	2 500	6 548(2)
Cl(1)	5 044(3)	2 500	4 520(4)
S	7 986(2)	1 121(1)	6 066(2)
Cl(2)	10 811(3)	2 500	4 113(4)
Cl(3)	10 191(3)	2 500	8 996(4)
Cl(4)	5 949(3)	2 500	9 358(4)
O	2 859(7)	2 500	7 066(10)
N	7 334(5)	−705(5)	868(8)
C(1)	7 642(6)	824(6)	3 692(9)
C(2)	8 743(7)	289(7)	2 871(11)
C(3)	8 426(7)	−19(7)	936(11)
C(4)	6 542(7)	119(7)	3 588(11)
C(5)	7 024(9)	−1 054(7)	−1 007(11)
C(6)	6 240(7)	−197(7)	1 636(12)

TABLE 2

Interatomic distances (Å) and angles (°) with estimated standard deviations in parentheses

(*a*) Bond distances

Zn(1)–S	2.363(3)	C(1)–C(4)	1.52(2)
Zn(1)–Cl(2)	2.249(4)	C(2)–C(3)	1.53(2)
Zn(1)–Cl(3)	2.255(4)	C(4)–C(6)	1.54(2)
Zn(2)–Cl(1)	2.264(4)	N–C(3)	1.50(2)
Zn(2)–Cl(4)	2.251(4)	N–C(5)	1.50(2)
Zn(2)–S	2.379(3)	N–C(6)	1.50(2)
Zn(1)–Zn(2)	3.046(2)	O · · · Cl(1)	3.155(10)
S–C(1)	1.843(12)	O · · · Cl(2)^{I,a}	3.097(10)
C(1)–C(2)	1.54(2)	O · · · N^{II,a}	2.824(14)

(*b*) Bond angles [b]

S–C(1)–C(2)	110(2)	S–Zn(2)–S′	98.6(2)
S–C(1)–C(4)	108(2)	S–Zn(1)–S′	99.5(2)
C(4)–C(1)–C(2)	110(2)	Cl(2)–Zn(1)–Cl(3)	112.1(3)
C(1)–C(2)–C(3)	110(2)	S–Zn(1)–Cl(2)	116.2(3)
C(2)–C(3)–N	110(2)	S–Zn(1)–Cl(3)	105.7(3)
C(3)–N–C(5)	112(2)	Cl(1)–Zn(2)–Cl(4)	110.8(3)
C(3)–N–C(6)	112(2)	S–Zn(2)–Cl(1)	111.7(3)
C(5)–N–C(6)	109(2)	S–Zn(2)–Cl(4)	111.7(3)
N–C(6)–C(4)	109(2)	Zn(1)–S–C(1)	108.8(8)
C(6)–C(4)–C(1)	111(2)	Zn(2)–S–C(1)	101.4(7)
Zn(1)–S–Zn(2)	79.9(2)		

[a] Superscripts refer to the following equivalent positions relative to the reference molecule at x, y, z: I $1 - x, y, z$; II $\bar{x}, \bar{y}, \bar{z}$. [b] Primed and unprimed symbols denote a pair of atoms related by the mirror plane.

RESULTS AND DISCUSSION

Description of the Structure.—The numbering system employed is displayed in the Figure. 4-Mercapto-*N*-methylpiperidine is an ambidentate ligand capable of co-ordinating *via* sulphur or nitrogen. In $[Cd\{SC_5H_9NH(CH_3)\}][ClO_4]_2\cdot 2H_2O$ [1] the cadmium atoms are linked by sulphur atoms so that each ligand molecule is a bridge between two cadmium atoms. Certainly in this case, as in the present work, the ligand ability of the nitrogen is frustrated by being protonated. In the zwitterionic complex with zinc reported here the sulphur atom of the ligand is also acting as a bridge between two zinc atoms. Two chlorine atoms complete the co-ordination sphere around each zinc atom, forming discrete dimeric molecules. The zinc and chlorine atoms all lie in the symmetry plane of the unit cell. This mirror plane imposes a C_s symmetry on the molecule. The oxygen atom of the water molecule also lies on the mirror plane and is acting as a hydrogen-bond acceptor to the protons of the nitrogen atoms and as a hydrogen-bond donor to two chlorine atoms. The O–H · · · Cl distances (Table 2) are within the accepted ranges given in the literature.[5] The N–H · · · O distances are a little shorter than the common ranges of 2.87—3.07 Å. The angles Cl–O–Cl and N–O–N are 96.9(5) and 112.5(9)° respectively.

The same water molecule joins two molecules of the complex through the nitrogen atoms, forming infinite chains in [010] directions, and holding together parallel chains of molecules related to the former by the two-fold screw axis.

The co-ordination geometry around each zinc atom is a distorted tetrahedron, consisting of two equivalent sulphur atoms and two non-equivalent chlorine atoms. The S–Zn–S angles are constrained to 98.6(2) and 99.5(2)°. This distortion is compensated by an increase in the remaining angles around the zinc atoms. The mean Zn–Cl bond distance is 2.255(7) Å. Two chlorine atoms are hydrogen bonded but statistically it is difficult to argue that there is any real difference between the Zn–Cl lengths. The S–Zn(1)–Cl(2) angle is significantly larger [4.5° (10 σ)] than the S–Zn(2)–Cl(1) angle. The Zn–S bond distance averages 2.371(11) Å, greater than 2.35 Å, the sum of the covalent radii [6] and greater than the most common values found in zinc(II) complexes with sulphur-donor ligands.[7] Similar values for the Zn–S bond distance are found in some dithiocarbamate complexes.[8,9] The Zn(1)–S–Zn(2) angle is expanded from the idealized value of 70.5° for the interior bridge of two perfect tetrahedra sharing a common edge.[10] The dihedral angle between the SZn_2 planes is 14°, giving a slight **V** shape for the Zn_2S_2 unit.

The piperidine rings, related by the mirror plane, show the usual 'chair' conformation, as indicated by the 'puckering' parameters: [11] $q_2 = 0.005\ 0$ Å, $q_3 = -0.595$ Å, $Q = 0.595$ Å, $\phi_2 = 331°$. The puckering amplitudes describe a slightly distorted chair. The value of ϕ_2 indicates that the ring is slightly flattened at the nitrogen apex, allowing the C–N–C angle to increase to 112(2)°

while the other internal ring angles remain close to 109.5°.

Infrared Data.—Three strong and broad absorptions are observed at 3 340, 3 060, and 2 770 cm^{-1}. The i.r. spectrum of the deuteriated compound suggests the following assignments: the first band corresponds to the ν(OH) absorption and the other two probably to the ν(NH) vibration split by Fermi resonance with the first overtone of the $\delta(CH_2)$ vibration (1 465 cm^{-1}).

In the far-i.r. region (up to 250 cm^{-1}) the broad and strong absorptions at 293 and 280 cm^{-1} are assigned to Zn–Cl stretching vibrations, according to the reported values,[12] and according to the values observed in the isomorphous $[\{Zn[SC_5H_9NH(CH_3)]X_2\}_2]\cdot H_2O$ complexes (X = Br or I) [13] prepared in our laboratory. In accord with these data, the 290 cm^{-1} absorption could be assigned to the Zn–S stretching vibration.

We thank the Comisión Asesora Científica y Técnica for support.

[0/887 *Received*, 10*th June*, 1980]

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