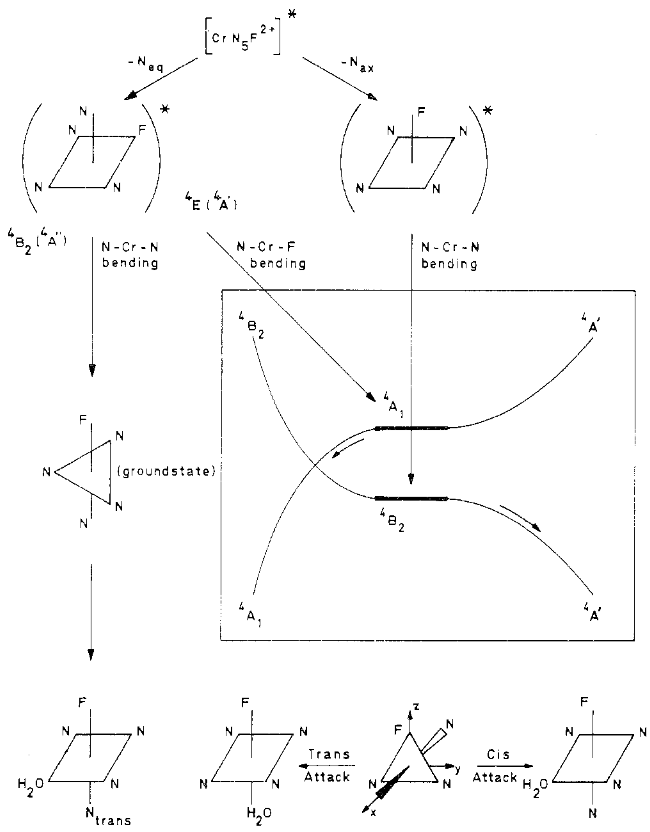

**Figure 3.** Schematic pattern of the photosubstitutions in fluoropentaaminechromium(III). "$N_{trans}$" in the final product of TBP (F ax) stands for the amine that was trans to F in the initial complex (for instance $NH_3$ in *trans*-$Cr(en)_2(NH_3)F^{2+}$). The insert in the figure shows the relevant part of the correlation diagram[7] for the association reactions of the TBP (F eq); the reaction paths can be inferred from the bottom part of the figure.

reochemical behavior of the TBP (F eq) is mainly determined by the properties of the $^4A_1$ state, in which it is produced.

In summary, equatorial labilization appears to be structurally different from the earlier considered axial labilization. In future experimental work along these lines, such as for instance the stereochemistry of difluorotetraamines, due attention should be paid to the appearance of branching schemes, similar to the one introduced in Figure 3.

**Acknowledgment.** The authors acknowledge helpful discussions with Dr. Adamson and Dr. Kirk. They are especially grateful to Dr. Kirk for making available a more elaborate preprint related to ref 15.

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(16) It should be stressed that the electronically allowed N–Cr–N bending can be expected—at least in a dissociative mechanism—to be sterically hindered for a bidentate ligand such as *trans*-$Cr(en)_2(NH_3)F^{2+}$, where the five-coordinated fragment still contains one bidentate bridge in the $(x,y)$ plane.
(17) The forbidden (a″,a″) crossover in Figure 1 (N–Cr–N bending) is quasi-allowed, due to a holohedron effect: in the $C_{2v}$ holohedron, $d_{xz}$ and $d_{yz}$ belong to different irreducible representations.
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Departement de Mineralogie et Cristallographie, Université Pierre et Marie Curie, Paris, France

# Synthesis and Crystal and Molecular Structure of *catena*-Bis[μ-(*N*-methylpiperidinium-4-thiolato)]-cadmium(II) Perchlorate Dihydrate

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The reaction of cadmium perchlorate hexahydrate with *N*-methyl-4-mercaptopiperidine in aqueous methanol gives *catena*-bis[μ-(*N*-methylpiperidinium-4-thiolato)]-cadmium(II) perchlorate dihydrate. Crystallization occurs in the tetragonal space group $I\bar{4}$ in a unit cell of dimensions $a = 18.78\ (2)$ Å and $c = 6.66\ (1)$ Å. Solution of the structure by direct methods led to a final weighted $R$ factor of 0.055 for 796 independent reflections. The crystal structure consists of infinite chains of cadmium atoms, each of them tetrahedrally coordinated to four sulfur atoms of four different *N*-methylpiperidinium-4-thiolato groups. Each sulfur atom acts as a bridge between two consecutive cadmium atoms. The four cadmium–sulfur bond distances average 2.548 (9) Å. The coordination geometry around the chlorine atom of each perchlorate anion is that of a distorted tetrahedron due to hydrogen bonding with a water molecule. The compound represents the first polymeric cadmium complex of γ-mercaptoamine ligands reported.

## Introduction

The metal complexes of several β-mercaptoamine ligands have been widely studied in the solid state as well as in solution. Ligands such as 2-aminoethanethiol, 2-aminobenzenethiol, and 8-mercaptoquinoline form stable chelates with many metal ions.[2] However metal complexes of γ-mercaptoamine ligands have had much less attention up to now. Complexes of 4-pyridinethiol with Co(II), Ni(II), Zn(II), Cd(II), Hg(II), Pt(II), Sn(IV), and Bi(III) have been reported. In all these cases bonding appears to be through sulfur rather than nitro-

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gen.[3] 2-(2-Mercaptoethyl)pyridine forms solid complexes with Co, Ni, Pd, and Pt in which the ambidentate ligand is a chelating agent.[4]

The ligand studied in this work, 1-methyl-4-mercaptopiperidine, is a cyclic γ-mercaptoamine that cannot have the flexibility of 2-(2-mercaptoethyl)pyridine, thus allowing a metal atom bonding to only one of the two functional groups, depending on its tendency to interact with sulfur or with nitrogen. Only when the metal atom interacts with both groups very strongly will the ligand change its more stable conformation and so behave as a chelating agent. This is not a possibility for the 4-pyridinethiol because of the planarity of the ring.

Several solid metal complexes, either mono- or polynuclear, of 3-amino-1-propanethiol, 2-(2-mercaptoethyl)-*N*-methylpiperidine, 3-(mercaptomethyl)-*N*-methylpiperidine, 1-methyl-4,4-dimercaptopiperidine, and the ligand studied in this work have been prepared in this laboratory recently.[5] There is evidence that all these γ-mercaptoamines behave quite similarly to β-mercaptoamines and that formation of metal chelates implies the presence of proton acceptors in the reaction mixture.

The elements of the group 2B of the periodic table take part in several biological processes, though Cd and Hg resemble each other more than they do Zn from a toxicological point of view. $Cd^{2+}$ and $Hg^{2+}$ salts are extremely toxic, and it has been suggested that poisoning by $Cd^{2+}$ may involve a metal-sulfur (cysteine) bonding similar to that postulated to account for protein and enzyme inactivation by $Hg^{2+}$.[6]

As a first part of extensive work that should enable us to understand and to compare the behavior of $Zn^{2+}$, $Cd^{2+}$, and $Hg^{2+}$ toward 1-methyl-4-mercaptopiperidine ligand in the solid state and in solution, a single-crystal X-ray diffraction study has been undertaken on the cadmium complex. Along this line the synthesis and structure of the cadmium bromide complex of DL-penicillamine have been reported recently.[7]

## Experimental Section

1-Methyl-4-mercaptopiperidine was synthesized according to Barrera et al.[8] and purified by distillation under reduced pressure. Cadmium perchlorate hexahydrate in 99.9% purity was purchased from Pierce Inorganics.

**Preparation of $\{Cd[SC_5H_9NH(CH_3)]_2\}(ClO_4){\cdot}2H_2O$.** Cadmium perchlorate hexahydrate (7.0 g) dissolved in 50 mL of 90:10 aqueous methanol was added slowly to 1-methyl-4-mercaptopiperidine (4.5 g) in about 50 mL of the same solvent. The reaction mixture did not show any change upon the addition of metal ion solution. A stream of $N_2$ was passed through the reaction mixture during the addition, and crystallization took place under $N_2$ atmosphere. The crystalline white product was isolated by filtration after 48 h, washed with cold water and then with methanol, and dried in vacuo (water pump) over silica gel. Anal. Calcd for $\{Cd[SC_5H_9NH(CH_3)]_2\}(ClO_4)_2{\cdot}2H_2O$: C, 23.63; H, 4.95; N, 4.59; S, 10.52; Cd, 18.43; $ClO_4^-$, 32.62. Found: C, 24.22; H, 4.93; N, 4.52; S, 10.49; Cd, 18.49; $ClO_4^-$, 33.15.

Carbon, hydrogen, and nitrogen analyses were performed in the laboratories of the Instituto de Quimica Orgânica "Juan de la Cierva" (Barcelona).

The water content was determined by thermal gravimetric analysis and differential thermal analysis in the Departament de Termologia de la Universitat Autõnoma de Barcelona with a Netzch S.T.A. Model 429 apparatus, under air atmosphere and with a porcelain crucible. The heating rate was 2 °C/min. The weight of the sample ranged between 30 and 120 mg. The loss of 1 mol of water/mol of complex starts at 40 °C and proceeds up to 85 °C. At this temperature the loss of the second water molecule begins, and it is completed at 120 °C. If heating is continued, no loss of mass is detected up to 266 °C, where the anhydrous complex decomposes. At this temperature the loss of mass corresponds to 2 mol of $H_2S$/mol of complex. This fact can only be seen if the heating is stopped just before reaching the decomposition temperature; otherwise the perchlorate explodes.

The other elements were analyzed in this laboratory. Cadmium content was determined gravimetrically as the anthranilate, sulfur content iodometrically according the Leussing et al.[9] method, and perchlorate content by means of ionic exchange resins.

**Table I.** Experimental Data for the X-ray Diffraction Study of $\{Cd[SC_5H_9NH(CH_3)]_2\}(ClO_4)_2{\cdot}2H_2O$

(A) Crystal Data

cryst system: tetragonal
space group $I\bar{4}$
$a = b = 18.76$ (2) Å[a]
$c = 6.66$ (1) Å
$V = 2347.7$ Å$^3$
$Z = 4$
$d$(obsd)[b] = 1.70 g cm$^{-3}$
$d$(calcd) = 1.725 g cm$^{-3}$

(B) Measurement of Intensity Data

diffractometer: Philips PW 1100
radiation: Cu Kα
monochromator: graphite crystal
scan type, scan speed: θ–2θ, 2°/min in 2θ
scan range: symmetrical, 2°/min
bkgd measurement: stationary of scan time at each of the scan limits.
data collected: 1328 $|F_{hkl}|$, 1233 independent
data with $F_o^2 > 2\sigma(F_o^2) > 1046$
2θ max: 60°
std reflctns: three remeasured after each 50 reflections; linear decay of ca. 10% was observed over the period data collection
reflctn measd: *hkl*

[a] Accurate centering of 20 reflections well distributed in reciprocal space resulted in unit cell dimensions. [b] Flotation in bromoform–carbon tetrachloride.

**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 a thin film. The spectra were calibrated by using the polystyrene absorption bands at 1602 and 907 cm$^{-1}$. The infrared spectrum of the cadmium complex after being heated at 140 °C shows that 2 mol of water/mol of complex is gone and only the anhydrous complex remains.

**X-ray Data Collection and Reduction.** Preliminary Weissenberg photographs indicated that the complex crystallizes in the tetragonal space group $I4$ or $I\bar{4}$ according to the observed conditions for reflection. A small crystal was chosen and mounted on a Philips four-circle diffractometer, PW1100 (Department of Mineralogy and Crystallography of Paris VI University). The intensities were corrected for Lorentz-polarization factors. Details appropiate to the current analysis appear in Table I.

**Structure Solution and Refinement.** The structure was solved by direct methods. The 150 reflections with $|E| \geq 1.431$ were used with the program MULTAN.[10] The $|E|$ maps computed from the best set of phases led to the coordinates of all the atoms, except hydrogen atoms and the water molecule. The crystal structure solution was solved in the space group $I\bar{4}$. Isotropic refinement was by full-matrix least-squares calculation using the program AFFINE.[11] Positional parameters, except those for Cd atoms, individual isotropic thermal parameters, and an overall scale factor were varied; $R$ based on 798 reflections converged to 0.127, after five cycles. Refinement with anisotropic temperature factors (seven cycles) gave $R = 0.085$ with all independent reflections (Cd atoms refined isotropically). The water molecule was located on a difference map and included in the anisotropic refinement. The final $R$ value was 0.076 for all the reflections and 0.055 with only 796 reflections. A final difference Fourier synthesis showed no anomalies. All the calculations were made on the IBM 370-168 System of C.I.R.C.E. (Orsay University). The final positional parameters are listed in Table II. Distances and angles are given in Tables III and IV. Mean planes are shown in Table V. The crystallographic study was supported by the Comisiõn Asesora Cientifica y Tẽcnica (C.A.C.T. Grant 1642).

## Description and Discussion of the Structure

The crystal structure of $\{Cd[SC_5H_9NH(CH_3)]_2\}(ClO_4)_2{\cdot}2H_2O$ shows that it is polymeric, consisting of central infinite chains of cadmium atoms, each being coordinated with four ligand molecules (Figure 1). Cadmium atoms are linked by sulfur atoms so that each ligand molecule is a bridge between two cadmium atoms such as Cd(1) and Cd(2). Cd(1) is linked to four sulfur atoms with Cd(1)–S distances equal to 2.546 (9) Å. Analogously Cd(2) is linked to four sulfur atoms (2.550 (9) Å), the bond lengths being very close but not equal to those

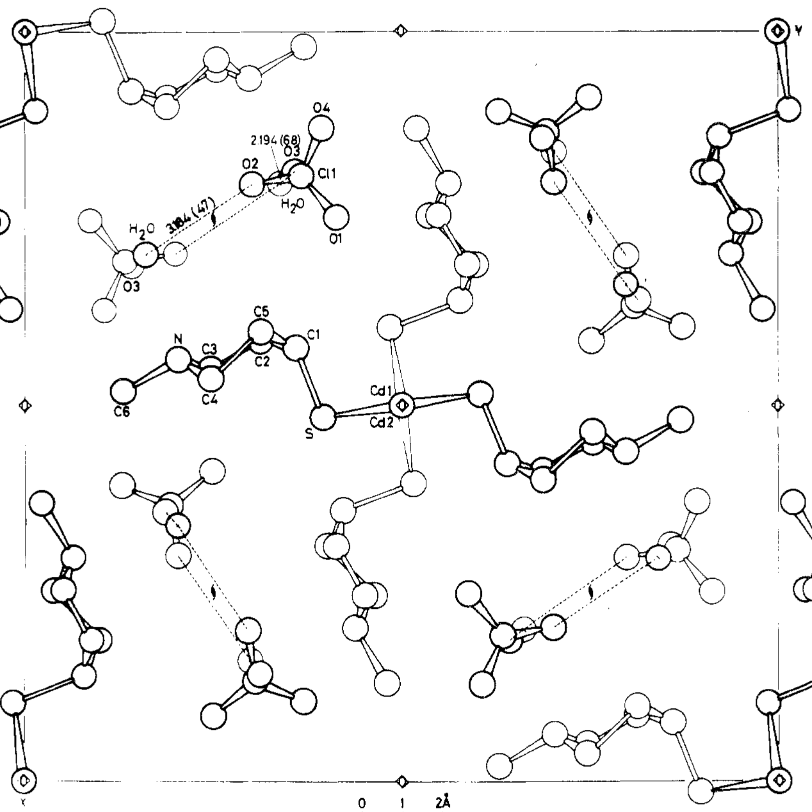

**Figure 1.** Crystal structure of $\{Cd[SC_5H_9NH(CH_3)]_2\}(ClO_4)_2{\cdot}2H_2O$ viewed down *c*.

**Table II.** Atomic Coordinates ($\times 10^4$) and Anisotropic Thermal Factors ($\times 10^4$) for $\{Cd[SC_5H_9NH(CH_3)]_2\}(ClO_4)_2{\cdot}2H_2O$[a]

| atom | *x* | *y* | *z* | $B_{11}$ | $B_{22}$ | $B_{33}$ | $B_{12}$ | $B_{13}$ | $B_{23}$ |
|---|---|---|---|---|---|---|---|---|---|
| Cd(1) | 10 000 (0) | 10000 (0) | 10000 (0) | 34 (1) | 34 (0) | 213 (7) | 0 (0) | 0 (0) | 0 (0) |
| Cd(2) | 10 000 (0) | 10000 (0) | 5000 (0) | 32 (1) | 32 (0) | 211 (7) | 0 (0) | 0 (0) | 0 (0) |
| S | 11 023 (2) | 10092 (2) | 7505 (13) | 25 (1) | 30 (1) | 262 (8) | 0 (1) | −11 (7) | −4 (7) |
| C(1) | 11 388 (7) | 9175 (7) | 7530 (72) | 31 (4) | 30 (4) | 411 (54) | 7 (4) | 33 (35) | 13 (33) |
| C(2) | 11 848 (15) | 9098 (15) | 9331 (46) | 40 (9) | 54 (10) | 484 (117) | 29 (8) | 53 (26) | 60 (27) |
| C(3) | 12 515 (15) | 9476 (13) | 9453 (42) | 49 (11) | 41 (8) | 359 (93) | 23 (8) | −8 (24) | −21 (23) |
| C(4) | 12 523 (14) | 9575 (18) | 5713 (43) | 30 (9) | 94 (14) | 330 (84) | −10 (9) | 24 (22) | −4 (30) |
| C(5) | 11 845 (16) | 9003 (16) | 5623 (46) | 46 (11) | 60 (11) | 393 (113) | −6 (9) | 36 (27) | −41 (28) |
| C(6) | 13 657 (9) | 9765 (9) | 7670 (90) | 37 (6) | 40 (6) | 1085 (145) | −4 (5) | 49 (54) | 45 (53) |
| N | 12 949 (6) | 9349 (7) | 7400 (48) | 31 (4) | 46 (5) | 491 (50) | 1 (3) | 3 (33) | −4 (33) |
| Cl(1) | 6 316 (3) | 1926 (3) | 2810 (22) | 49 (2) | 43 (2) | 1032 (46) | 10 (1) | 9 (13) | −2 (13) |
| O(1) | 5 859 (8) | 2483 (7) | 2688 (45) | 70 (6) | 57 (6) | 611 (65) | 9 (5) | 57 (31) | −35 (30) |
| O(2) | 6 983 (9) | 2034 (11) | 2944 (32) | 63 (7) | 110 (11) | 570 (95) | 11 (7) | −20 (23) | 41 (28) |
| O(3) | 6 384 (17) | 1875 (17) | 4966 (32) | 194 (21) | 211 (23) | 288 (53) | 85 (18) | −78 (36) | −55 (37) |
| O(4) | 6 062 (11) | 1284 (9) | 2613 (74) | 128 (13) | 62 (7) | 928 (96) | −12 (8) | 49 (74) | 54 (54) |
| $H_2O$ | 6 600 (13) | 2038 (13) | 8170 (50) | 92 (12) | 115 (13) | 1385 (215) | −22 (10) | −81 (41) | 116 (44) |

[a] The form of the anisotropic thermal ellipsoid is given by $\exp[-(B_{11}h^2 + B_{22}k^2 + B_{33}l^2 + 2B_{12}hk + 2B_{13}hl + 2B_{23}kl)]$. Standard deviations are given in parentheses.

**Table III.** Bond Distances (Å)[a]

| | | | |
|---|---|---|---|
| Cd(1)-S | 2.546 (9) | Cl(1)-O(1) | 1.35 (4) |
| Cd(2)-S | 2.550 (9) | Cl(1)-O(2) | 1.27 (4) |
| S-C(1) | 1.85 (5) | Cl(1)-O(3) | 1.44 (5) |
| C(1)-C(2) | 1.48 (7) | Cl(1)-O(4) | 1.30 (6) |
| C(1)-C(5) | 1.56 (7) | $H_2O$-O(4) | 4.09 (7) |
| C(2)-C(3) | 1.44 (7) | $H_2O$-O(3) | 2.19 (7) |
| C(3)-N | 1.61 (6) | $H_2O$-O(2) | 3.55 (6) |
| N-C(6) | 1.55 (7) | $H_2O$-O(1) | 3.99 (6) |
| N-C(4) | 1.44 (6) | O(2P)-$H_2O$ | 3.18 (5) |
| C(4)-C(5) | 1.67 (7) | | |

[a] Standard deviations are given in parentheses.

**Table IV.** Bond Angles (deg)[a]

| | | | |
|---|---|---|---|
| Cd(2)-Cd(1)-S | 49.3 (2) | N-C(4)-C(5) | 105 (7) |
| S-Cd(2)-Cd(1) | 49.1 (2) | C(4)-C(5)-C(1) | 105 (7) |
| Cd(2)-S-Cd(1) | 81.6 (4) | O(1)-Cl(1)-O(3) | 100 (5) |
| Cd(1)-S-C(1) | 102 (3) | O(2)-Cl(1)-O(3) | 82 (4) |
| Cd(2)-S-C(1) | 103 (3) | O(1)-Cl(1)-O(2) | 120 (5) |
| S-C(1)-C(2) | 108 (7) | O(4)-Cl(1)-O(1) | 118 (6) |
| S-C(1)-C(5) | 113 (7) | O(4)-Cl(1)-O(3) | 94 (5) |
| Cd(2)-C(1)-C(5) | 96 (5) | O(4)-Cl(1)-O(2) | 121 (7) |
| C(1)-C(2)-C(3) | 120 (9) | S-Cd(1)-S(2) | 98.5 (4) |
| C(2)-C(3)-N | 109 (7) | S-Cd(2)-S(2) | 98.3 (4) |
| C(3)-N-C(4) | 110 (7) | S-Cd(2)-S(3) | 124.7 (5) |
| C(3)-N-C(6) | 105 (7) | S(2)-Cd(2)-S(3) | 132.8 (5) |
| C(4)-N-C(6) | 115 (8) | | |

[a] Standard deviations are given in parentheses.

between Cd(1) and S. Cd(1) and Cd(2) atoms alternate as is shown in Figure 2.

1-Methyl-4-mercaptopiperidine is an ambidentate ligand capable of coordinating via either sulfur or nitrogen. However in this cadmium complex it is not a chelating agent but coordination takes place only through sulfur. The same behavior is found in related ligands such as 4-pyridinethiols[3] and some

**Table V**

Least-Squares Planes

plane 1: C(1), C(2), C(5)
$0.2599X + 0.9630Y - 0.0707Z = 21.7939$
[S 1.4798][a]

plane 2: C(5), C(4), C(3), C(2)
$0.5810X - 0.8139Y - 0.0016Z = -0.9100$
[C(5) 0.0690, C(4) −0.0664, C(3) 0.0718, C(2) −0.0783]

plane 3: C(4), N, C(3)
$0.3875X + 0.9191Y + 0.0711Z = 25.9061$
[C(6) −1.2456]

Dihedral Angles between Planes
planes 1-2 = 50.75°   planes 1-3 = 11.23°
planes 2-3 = 58.46°

[a] Deviations (Å) of atoms from planes.

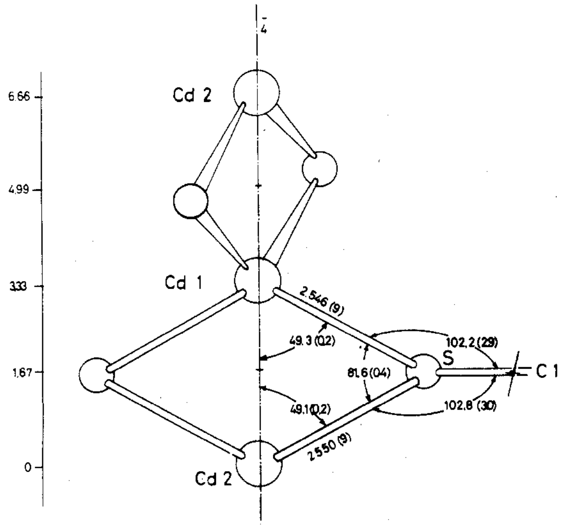

**Figure 2.** View of the immediate coordination sphere of cadmium atoms in $\{Cd[SC_5H_9NH(CH_3)]_2\}(ClO_4)_2 \cdot 2H_2O$ showing bond angles and distances.

N-substituted β-mercaptoethylamines.[12] On the other hand, other pyridinethiols such as 2-(2-mercaptoethyl)pyridine,[4] unsubstituted β-mercaptoethylamines, or N-substituted β-mercaptoethylamines, whose substituents have small steric requirements,[12] behave as chelating agents. All these facts lead to the conclusion that it is not the relative position, β or γ, of nitrogen and sulfur in the same molecule that determines its chelating behavior.

The coordination geometry about the cadmium atoms is essentially tetrahedral. The Cd(1)–S and Cd(2)–S distances are in good agreement with the value calculated from the sum of cadmium and sulfur tetrahedral covalent radii (2.52 Å).[13] The "pure" covalent Cd–S bond and the fact that each sulfur atom is coordinated to two cadmium atoms may cause the Cd(1)–S–Cd(2) angle to be much smaller than the Cd(1)–S–C(1) and Cd(2)–S–C(1) angles. The immediate coordination sphere of the cadmium is illustrated in Figure 2, which also shows the chain formed by the cadmium atoms.

Cadmium complexes similar to the one reported in this work have the following Cd–S distances: five cadmium–sulfur contacts ranging from 2.536 to 2.800 Å in cadmium(II) *N*,*N*-diethyldithiocarbamate, $Cd_2[(C_2H_5)_2CNS_2]_4$,[14] four cadmium–sulfur contacts ranging from 2.486 (7) to 2.590 (8) Å and a fifth one of 3.194 (8) Å in cadmium(II) *O*,*O*-diisopropylphosphorodithioate, $Cd_2[(i\text{-}C_3H_7O)_2PS_2]_4$,[15] and four cadmium–sulfur contacts ranging from 2.560 (9) to 2.619 (8) Å in the cadmium xanthate, $Cd[S_2COC_4H_9]_2$.[16]

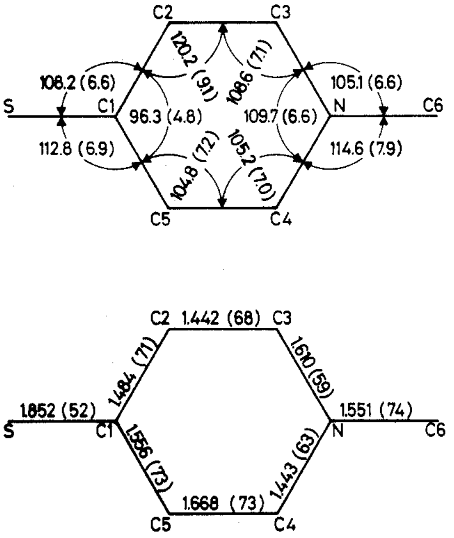

**Figure 3.** Bond lengths (angstroms) and angles (degrees) with their standard deviations in parentheses for the piperidine ring.

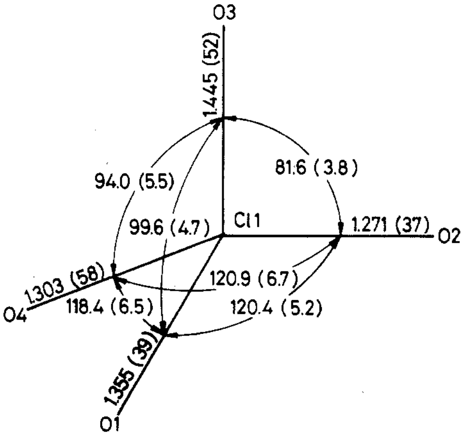

**Figure 4.** Bond lengths (angstroms) and angles (degrees) with their standard deviations in parentheses for the perchlorate anion.

The Cd(1)–Cd(2) distance in $\{Cd[SC_5H_9NH(CH_3)]_2\}(ClO_4)_2 \cdot 2H_2O$ is 3.330 (5) Å. The Cd–Cd distances are 3.58 Å in $Cd_2[(C_2H_5)_2CNS_2]_4$, 4.059 (4) Å in $Cd_2[(i\text{-}C_3H_7O)_2PS_2]_4$, and 5.817 Å in $Cd(S_2COC_4H_9)_2$. In the latter complex an infinite chain of cadmium atoms is linked by means of the ligand molecules, so that each cadmium atom is tetrahedrally coordinated to four sulfur atoms that belong to three different xanthine radicals. Despite the similarity between cadmium xanthate and the complex studied, the present structure shows the shortest Cd–Cd distance of two and also is the shortest that has been reported in the literature.

The piperidine groups in $\{Cd[SC_5H_9NH(CH_3)]_2\}(ClO_4)_2 \cdot 2H_2O$ are all identical and are in chair conformations. Bond angles and distances for these groups are shown in Figure 3. The sulfur atom in the cadmium complex has an axial position, and the methyl group on the protonated nitrogen atom has an equatorial one (Figure 1). The cause of the deviation from the theoretical "cyclohexane" bond angles and distances is not clear, for there is no evidence of overcrowding when the piperidine ring would have its normal shape. As it could be expected, thermal vibrations increase toward the amine end of each piperidine group (Table II), indicating that this side of the ligand can move more freely than the side bonded to the heavy atom.

The net positive charge of the complex species is compensated by perchlorate anions which are located close to the $NH^+$ groups. There is one $ClO_4^-$ anion for each ligand molecule. The geometry about the chlorine atom in the perchlorate anions is shown in Figure 4, and it is that of a distorted tetrahedron due to the formation of a hydrogen bond with a water molecule which is located next to each perchlorate anion. The

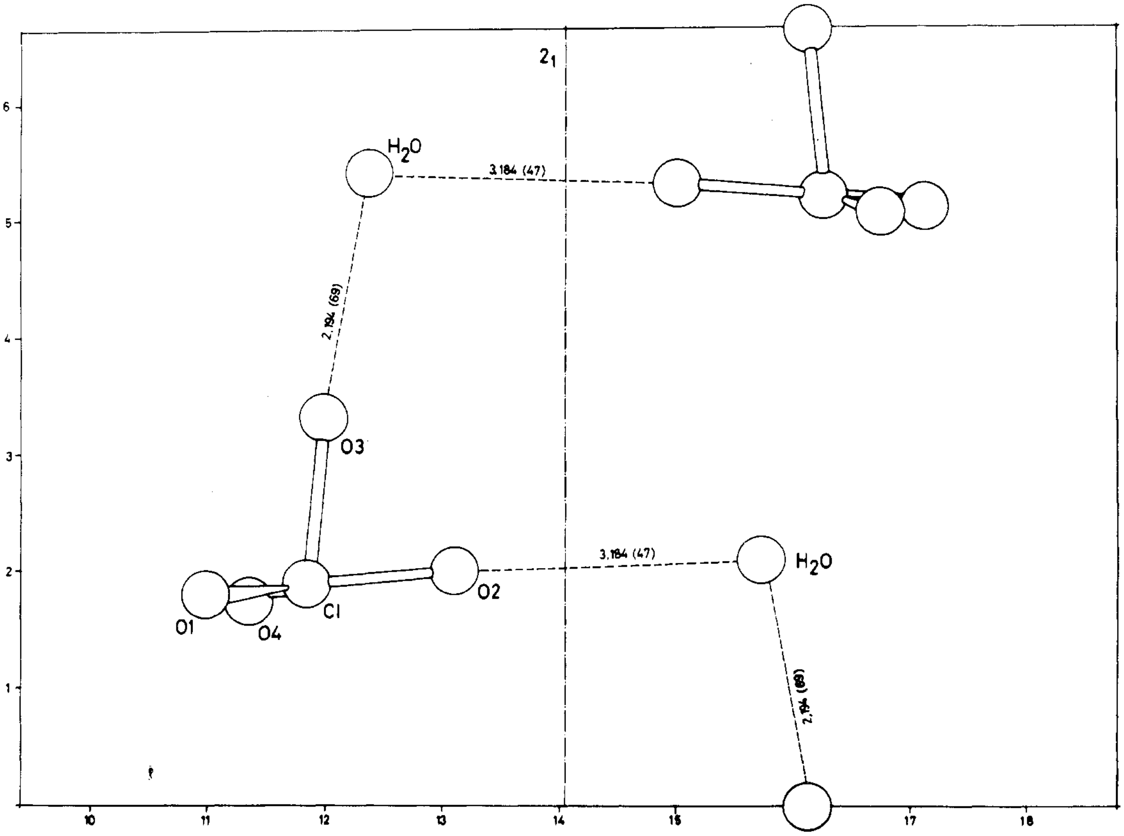

**Figure 5.** Hydrogen bonding with perchlorate anions.

Cl–O(3) distance is much longer than the other three Cl–O distances, and the angles O(1)–Cl–O(3), O(2)–Cl–O(3), and O(4)–Cl–O(3) are less than 100° while the angles O(1)–Cl–O(2), O(4)–Cl–O(1), and O(4)–Cl–O(2) are close to 120°. This is due to hydrogen bonding between O(3) and the water molecule. This is also in agreement with the fact that the O(3)–O($H_2O$) distance (2.19 (7) Å) is the shortest of all O($ClO_4^-$)–O($H_2O$) distances. However $\nu$(O–H), appearing at 3400 $cm^{-1}$ in the infrared spectrum of the complex, indicates that the interaction is not as strong as the crystallographic distance shows. In the same spectrum each of the bands (corresponding to $\nu_3$ and $\nu_4$ vibrations) of the perchlorate at 1160–1020 and 630 $cm^{-1}$ have split up into two bands (1085–1110, 1142, 625, and 635 $cm^{-1}$), which is consistent with a change in molecular geometry from $T_d$ to $C_{3v}$.[17] The infrared spectrum of the cadmium complex after being heated at 140 °C does not show splitting for $\nu_3$ and $\nu_4$ bands. Consequently the splittings may be due to hydrogen bonding of the $ClO_4^-$ and not to perturbations caused by the crystal field.

As is shown in Figure 5 another hydrogen bond between O(2) of the $ClO_4^-$ and a second water molecule can be postulated. The angle O(3)–O($H_2O$)–O(2) is 101 (6)°, and the O(2)–O($H_2O$) distance is 3.18 (5) Å. This suggests the existence of an infinite chain of perchlorate anions linked by water molecules or vice versa. The DTA and TGA show two different steps for the loss of water, each of the same altitude. During the first one, which occurs from 40 to 85 °C, half of the water molecules are gone and so the infinite chain mentioned is broken. Each of the remaining water molecules—one for two perchlorate anions—is now linked to two perchlorate anions strongly, and so now they need more energy to break these bonds and leave the structure, which happens between 85 and 120 °C.

The short N–O($H_2O$) distance (2.79 (6) Å) is in agreement with the existence of third hydrogen bond. This is clearly confirmed in the infrared spectrum of the complex where the absorption band corresponding to $\nu$(N–H) appears at 2700 $cm^{-1}$.

**Registry No.** $\{Cd[SC_5H_9NH(CH_3)]_2\}(ClO_4)_2\cdot 2H_2O$, 71359-32-5.

**Supplementary Material Available:** A listing of structure factor amplitudes (6 pages). Ordering information is given on any current masthead page.

## References and Notes

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