Polymeric Thiolate Complexes of Group 12† Metals. Crystal and Molecular Structures of *catena*-[μ-(3-Dimethylammonio-1-propanethiolate)]-dichlorocadmium(II) and Bis[3-(dimethylammonio)propyl] Disulphide Tetrabromocadmate(II)‡

Isidre Casals, Pilar González-Duarte,* and Joan Sola
Departament de Química, Universitat Autònoma de Barcelona, Bellaterra, 08193 Barcelona, Catalunya, Spain
Mercè Font-Bardía, Joaquim Solans, and Xavier Solans
Departament de Cristal.lografia i Mineralogia, Universitat de Barcelona, Gran Via 585, 08007 Barcelona, Catalunya, Spain

---

The complexes $[MX_2\{\mu\text{-}S(CH_2)_3NH(CH_3)_2\}]$ and corresponding disulphides $[\{(CH_3)_2HN(CH_2)_3S\}_2][MX_4]$ (M = Zn^{II}, Cd^{II}, or Hg^{II}; X = Cl or Br) have been prepared or characterized. Both families of compounds are isostructural with $[CdCl_2\{\mu\text{-}S(CH_2)_3NH(CH_3)_2\}]$ and $[\{(CH_3)_2HN(CH_2)_3S\}_2][CdBr_4]$ respectively. Crystals of the former are monoclinic, space group $P2_1/n$, with a = 15.995(3), b = 6.532(2), c = 10.237(2) Å, and β = 95.66(2)°. The crystal structure consists of infinite chains of alternating cadmium and sulphur atoms. Each cadmium atom is tetrahedrally co-ordinated to two terminal chlorine atoms and two bridging sulphur atoms. Crystals of the second compound are orthorhombic, space group $Pbn2_1$, with a = 23.406(3), b = 13.531(2), and c = 6.738(1) Å. The crystal structure consists of discrete bis[3-(dimethylammonio)propyl] disulphide dications and tetrabromocadmate(II) anions linked by hydrogen-bond interactions that give rise to a staircase-like framework.

Based on the results obtained in our systematic study of metal complexes of γ-mercaptoamine ligands we have shown that while 3-amino-1-propanethiol behaves as a chelating agent,[1–3] analogously to β-mercaptoethylamine, 3-dimethylamino-1-propanethiol, 3-(mercaptomethyl)-1-methylpiperidine, 2-(2-mercaptoethyl)-1-methylpiperidine, and 4-mercapto-1-methylpiperidine tend to co-ordinate exclusively *via* the thiolate group.[4–12] The last ligand has given rise to molecular structures ranging in size from discrete units, as with mercury(II),[6] through dimers and tetranuclear rings, as with zinc(II)[9] and nickel(II)[8] respectively, to one-dimensional polymeric chains, as with cadmium(II).[7] These γ-mercaptoamine ligands which behave as simple thiols furnish however a good solubility to the complexes owing to the presence of the amine group. A striking difference has been found when the metal atom is Pd^{II} or Pt^{II}, which undoubtedly enhance the chelating ability of these ligands. The molecular structures are either dimers[4,13,14] or trinuclear species.[13,15]

To provide a deeper insight into the behaviour of γ-mercaptoamine ligands and to contribute to the understanding of the chemistry of cadmium(II) thiolate complexes because of their biological interest,[16] we have undertaken a study of zinc(II), cadmium(II), and mercury(II) complexes of 3-dimethylamino-1-propanethiol. Published results for 4-mercapto-1-methylpiperidine and zinc(II),[9,10] cadmium(II),[7,10] and mercury(II)[6,10] include dimeric and polymeric compounds depending on the solvent composition of the reaction mixture. With 3-amino-1-propanethiol, formation of trinuclear species involving co-ordination through sulphur and nitrogen has been proposed.[17]

Experimental

All reagents and solvents were research grade (≥98%) and were not further purified. The ligand was obtained according to a previously published procedure,[18] its purity being always ≥95%.

It was necessary to change the conditions for the syntheses of the complexes several times in order to avoid the formation of intractable highly viscous or plastic precipitates. Trials at different temperatures were made with different solvents (dimethyl sulphoxide, CH_3CN, several alcohols), and at different water:organic solvent or metal:ligand ratios (but keeping the latter close to one), and also by changing the addition time of the hydrohalic acid.

In all our previous experience of working with γ-mercaptoamines in air, oxidation of the ligand has occurred only in the presence of Cu^{II}.[19] None of the dry crystalline products obtained decomposes detectably on exposure to laboratory air during 24 h. The following procedures gave the best results.

catena-$[ZnCl_2\{\mu\text{-}S(CH_2)_3NH(CH_3)_2\}]$ (**1**) *and* $[\{(CH_3)_2HN(CH_2)_3S\}_2][ZnCl_4]$ (**2**).—A solution of 3-dimethylamino-1-propanethiol (0.38 g, 3.23 mmol) in methanol (10 cm^3) and water (40 cm^3), at room temperature, was added slowly with stirring to a solution of $ZnCl_2$ (0.44 g, 3.23 mmol) in the same solvent previously acidified with 4.0 mol dm^{-3} hydrochloric acid in order to keep the solution clear. A flocculent white precipitate formed which did not redissolve and was filtered off just before completion of the addition. The clear solution was then allowed to crystallize at room temperature over a few days. After 48 h crystalline agglomerates began to appear on the walls and bottom of the beaker and also some flakes in the liquid. Colourless crystals of complex (**1**) grew together with a small number of long needles of (**2**) accompanied by some $Zn(OH)_2$ which could be filtered off owing to its jellied nature. After filtration it was possible to separate manually crystals of the main product [Found: C, 23.15; Cl, 27.2; N, 5.40; S, 12.35. Calc. for $C_5H_{13}Cl_2NSZn$ (**1**): C, 23.50; Cl, 27.75; N, 5.50; S, 12.55. Calc. for $C_{10}H_{26}Cl_4N_2S_2Zn$ (**2**): C, 26.95; Cl, 31.85; N, 6.30; S, 14.4%]. *X*-Ray powder analyses of the solid obtained (Table 1) indicate that it includes a mixture of (**1**) and (**2**). Attempts to purify the sample by recrystallization were unsuccessful.

---

† Refers to the 18-group format of the Periodic Table.

‡ *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1987, Issue 1, pp. xvii—xx

Table 1. Compounds identified in *X*-ray powder analyses and their cell parameters

Compound	a/Å	b/Å	c/Å	β/°	Maxima used
$[\{ZnCl_2[\mu\text{-}S(CH_2)_3NH(CH_3)_2]\}_2]$	15.81	6.44	10.23	94.65	16
$[\{(CH_3)_2HN(CH_2)_3S\}_2][ZnCl_4]$	23.34	13.58	6.70	90.00	15
$[\{ZnBr_2[\mu\text{-}S(CH_2)_3NH(CH_3)_2]\}_2]$	15.91	6.57	10.20	95.36	38
$[\{(CH_3)_2HN(CH_2)_3S\}_2][ZnBr_4]$	23.46	13.57	6.71	90.00	33
$[\{CdCl_2[\mu\text{-}S(CH_2)_3NH(CH_3)_2]\}_2]$*	15.995(3)	6.532(2)	10.237(2)	95.66(2)	—
$[\{(CH_3)_2HN(CH_2)_3S\}_2][CdCl_4]$	23.44	13.56	6.70	90.00	20
$[\{CdBr_2[\mu\text{-}S(CH_2)_3NH(CH_3)_2]\}_2]$	15.94	6.56	10.21	95.14	32
$[\{(CH_3)_2HN(CH_2)_3S\}_2][CdBr_4]$*	23.406(3)	13.531(2)	6.738(1)	90.00	—
$[\{HgCl_2[\mu\text{-}S(CH_2)_3NH(CH_3)_2]\}_2]$	15.89	6.58	10.21	95.57	29
$[\{(CH_3)_2HN(CH_2)_3S\}_2][HgCl_4]$	23.49	13.62	6.67	90.00	27
$[\{HgBr_2[\mu\text{-}S(CH_2)_3NH(CH_3)_2]\}_2]$	15.85	6.60	10.20	95.53	34
$[\{(CH_3)_2HN(CH_2)_3S\}_2][HgBr_4]$	23.48	13.63	6.69	90.00	33

* Experimental data from single-crystal *X*-ray diffraction.

catena-$[ZnBr_2\{\mu\text{-}S(CH_2)_3NH(CH_3)_2\}]$ (**3**) *and* $[\{(CH_3)_2HN(CH_2)_3S\}_2][ZnBr_4]$ (**4**).—A solution of 3-dimethylamino-1-propanethiol (0.30 g, 2.50 mmol) in methanol (10 cm^3) and water (40 cm^3), at room temperature, was added dropwise with stirring to a solution of $ZnBr_2$ (0.56 g, 2.50 mmol) in the same solvent that contained sufficient 4.0 mol dm^{-3} bromine-free hydrobromic acid to keep the solution clear. Soon after completion of the addition some turbidity developed which was eliminated by centrifuging and decanting. The clear solution was then allowed to crystallize at room temperature. After 2 weeks colourless needles appeared while the bottom of the beaker was encrusted with a white paste. By decanting the liquid, filtering, washing with water, and vacuum drying, crystals of essentially complex (**3**) were separated [Found: C, 17.55; Br, 45.6; N, 4.15; S, 9.20. Calc. for $C_5H_{13}Br_2NSZn$ (**3**): C, 17.45; Br, 46.40; N, 4.05; S, 9.30. Calc. for $C_{10}H_{26}Br_4N_2S_2Zn$ (**4**): C, 19.25; Br, 51.25; N, 4.50; S, 10.3%]. *X*-Ray powder analyses of the reaction product (Table 1) indicate that this solid includes a mixture of (**3**) and (**4**).

catena-$[CdCl_2\{\mu\text{-}S(CH_2)_3NH(CH_3)_2\}]$ (**5**) *and* $[\{(CH_3)_2HN(CH_2)_3S\}_2][CdCl_4]$ (**6**).—A solution of 3-dimethylamino-1-propanethiol (0.60 g, 5 mmol) in methanol (2 cm^3) and water (18 cm^3), at room temperature, was added dropwise with stirring to a solution of $CdCl_2 \cdot 2H_2O$ (1.10 g, 5 mmol) in the same solvent. The white dusty precipitate immediately formed was filtered off and the solution allowed to crystallize at room temperature. Colourless crystals and a microcrystalline solid appeared after 48 h and were both collected after a further 24 h by filtration, washing with water, and vacuum drying. Then it was possible to separate manually the crystals of complex (**5**) whose structure was determined by *X*-ray diffraction [Found: C, 19.9; Cl, 23.4; N, 4.50; S, 10.35. Calc. for $C_5H_{13}CdCl_2NS$ (**5**): C, 19.85; Cl, 23.45; N, 4.65; S, 10.6. Calc. for $C_{10}H_{26}CdCl_4N_2S_2$ (**6**): C, 24.4; Cl, 28.8; N, 5.70; S, 13.0%]. *X*-Ray powder analyses of the mixture of solids (Table 1) show that it includes (**5**) and (**6**).

catena-$[CdBr_2\{\mu\text{-}S(CH_2)_3NH(CH_3)_2\}]$ (**7**) *and* $[\{(CH_3)_2HN(CH_2)_3S\}_2][CdBr_4]$ (**8**).—A solution of 3-dimethylamino-1-propanethiol (0.30 g, 2.5 mmol) in methanol (10 cm^3) and water (40 cm^3), at room temperature, was added slowly with stirring to a solution of $CdBr_2 \cdot 4H_2O$ (0.86 g, 2.50 mmol) in the same solvent. Soon after completion of the addition some white flakes developed and eventually settled at the bottom of the beaker while small colourless crystals appeared on the walls. After 48 h the flakes were separated by filtration through a 2-μm nylon mesh and the crystals were washed with water and vacuum dried. It was then possible to separate manually a very few crystals of complex (**8**) with the aid of a magnifying glass. One of these was good enough for single-crystal *X*-ray analysis. A selection of crystals whose shape was different to that of (**8**) were analyzed [Found: C, 15.0; Br, 39.35; N, 3.40; S, 8.0. Calc. for $C_5H_{13}Br_2CdNS$ (**7**): C, 15.35; Br, 40.85; N, 3.60; S, 8.20. Calc. for $C_{10}H_{26}Br_4CdN_2S_2$ (**8**): C, 17.9; Br, 47.65; N, 4.20; S, 9.55%]. *X*-Ray powder analyses of the mixture of crystalline solids (Table 1) indicate the presence of (**7**) and (**8**).

catena-$[HgCl_2\{\mu\text{-}S(CH_2)_3NH(CH_3)_2\}]$ (**9**) *and* $[\{(CH_3)_2HN(CH_2)_3S\}_2][HgCl_4]$ (**10**).—A solution of 3-dimethylamino-1-propanethiol (0.60 g, 5 mmol) in water (12.5 cm^3) and ethanol (12.5 mmol), at room temperature, was slowly added with stirring to 25 cm^3 of a solution of $HgCl_2$ (1.36 g, 5 mmol) in the same solvent. Just before completion of the addition very small colourless crystals started to develop. After 1 week crystals of regular size were filtered off, washed with water, and vacuum dried [Found: C, 15.3; N, 3.50; S, 8.0. Calc. for $C_5H_{13}Cl_2HgNS$ (**9**): C, 15.35; N, 3.60; S, 8.20. Calc. for $C_{10}H_{26}Cl_4HgN_2S_2$ (**10**): C, 20.7; N, 4.80; S, 11.05%]. *X*-Ray powder analyses of these crystals (Table 1) indicate that they include a mixture of (**9**) and (**10**).

catena-$[HgBr_2\{\mu\text{-}S(CH_2)_3NH(CH_3)_2\}]$ (**11**) *and* $[\{(CH_3)_2HN(CH_2)_3S\}_2][HgBr_4]$ (**12**).—A solution of 3-dimethylamino-1-propanethiol (0.60 g, 5 mmol) in water (18 cm^3) and ethanol (2 cm^3), at room temperature, was added very slowly to a solution of $HgBr_2$ (1.80 g, 5 mmol) in 20 cm^3 of the same solvent. During the first minutes of the addition a white precipitate developed and it eventually became a white mass that adhered to the walls of the beaker. Meanwhile a white microcrystalline solid started to appear. These crystals were separated by decanting and then filtering, washing with water, and vacuum drying (Found: C, 12.5; N, 2.80; S, 6.50. Calc. for $C_5H_{13}Br_2HgNS$ (**11**): C, 12.5; N, 2.90; S, 6.70. Calc. for $C_{10}H_{26}Br_4HgN_2S_2$ (**12**): C, 15.85; N, 3.70; S, 8.45%]. *X*-Ray powder analyses (Table 1) show that these crystals are a mixture of (**11**) and (**12**).

Analyses.—Microanalyses were performed by one of the authors (I. C.) with a Carlo Erba NA-1500 analyzer.

Physical Measurements.—Infrared spectra from 250 to 4 000 cm^{-1} were recorded (KBr pellets) on a Beckman IR-20A spectrophotometer.

X-*Ray Powder Analyses.*—The samples were mounted on a Siemens D500-DACOMP diffractometer. Nickel-filtered Cu-K_α radiation was used with scan speed of 1/20 min^{-1} and θ = 4—30°. The indexation was based on the two single-crystal analyses. Cell parameters in each case were refined by the full-matrix least-squares method, using the AFFMAIL computer program.[20] The function minimized was $|d_o - d_c|^2$, and overlapped peaks were not used in the refinement. The compounds identified and their cell parameters are listed in Table 1.

X-Ray Data Collection, Structure Determination, and Refinement.—*For* $[\{CdCl_2[\mu\text{-}S(CH_2)_3NH(CH_3)_2]\}_2]$. *Crystal data.* $C_{10}H_{26}Cd_2Cl_4N_2S_2$, M = 532.1, monoclinic, a = 15.995(3), b = 6.532(2), c = 10.237(2) Å, β = 95.66(2)°, U = 1 064.3(6) Å^3, D_m = 1.68, Z = 2, D_c = 1.660 g cm^{-3}, $F(000)$ = 260, space group $P2_1/n$, $\lambda(\text{Mo-}K_\alpha)$ = 0.710 69 Å, $\mu(\text{Mo-}K_\alpha)$ = 24.06 cm^{-1}, room temperature.

A prismatic crystal (0.07 × 0.08 × 0.12 mm) was mounted on a Philips PW-1100 four-circle diffractometer. The unit-cell parameters were determined from 25 reflections ($4 \leqslant \theta \leqslant 12°$) and refined by least squares. Intensities were collected with graphite-monochromated Mo-K_α radiation, using the ω-scan technique, scan width 1°, and scan speed 0.03° s^{-1}. 2 411 Reflections were measured in the range $2 \leqslant \theta \leqslant 25°$, 2 353 of which taken as observed [$I \geqslant 2.5\sigma(I)$]. Three reflections were measured every 2 h as orientation and intensity controls, but significant intensity decay was not observed. Lorentz-polarization, but not absorption, corrections were made.

The Cd was located from a Patterson synthesis and the remaining non-hydrogen atoms using the DIRDIF computer system.[21] The structure was isotropically and anisotropically refined by full-matrix least squares using the SHELX 76 computer program.[22] The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = [\sigma^2(F_o) + 0.0102|F_o|^2]^{-1}$; f, f', and f'' were taken from ref. 23. A difference synthesis revealed the position of all hydrogen atoms which were refined with an overall isotropic thermal parameter; the remaining atoms were assigned anisotropic thermal parameters. The final R was 0.052 for all observed reflections (R' = 0.057). Atomic co-ordinates are given in Table 2.

For $[\{(CH_3)_2HN(CH_2)_3S\}_2][CdBr_4]$. *Crystal data.* $C_{10}H_{26}Br_4CdN_2S_2$, M = 668.5, orthorhombic, a = 23.406(3), b = 13.531(2), c = 6.738(1) Å, U = 2 134.0(9) Å^3, D_m = 2.04, Z = 4, D_c = 2.080 g cm^{-3}, $F(000)$ = 1 272, space group = $Pbn2_1$, $\lambda(\text{Mo-}K_\alpha)$ = 0.71 069 Å, $\mu(\text{Mo-}K_\alpha)$ = 91.23 cm^{-1}, room temperature.

A prismatic crystal (0.07 × 0.07 × 0.1 mm) was mounted on a Philips four-circle diffractometer. Unit-cell parameters were determined and refined and intensities collected as above, except that the scan width was 0.8°. 1 703 Reflections were measured in the range $2 \leqslant \theta \leqslant 25°$, 1 497 of which taken as observed [$I \geqslant 2.5\sigma(I)$]. Standard reflections as before. Lorentz-polarization and absorption corrections were made. The Cd atom was located from a Patterson synthesis and the remaining atoms from a weighted Fourier synthesis. The structure was refined by least squares using SHELX 76. The function minimized was $\Sigma w(|F_o| - |F_c|)^2$, where $w = \sigma^{-2}(F_o)$. The hydrogen atom positions were calculated and refined with an overall isotropic thermal parameter and the bond length constrained to 1.080 Å; the remaining atoms were refined anistropically. The final R was 0.020 (R' = 0.021) for all observed reflections. Atomic co-ordinates are given in Table 2.

Results and Discussion

Description of the Structures of $[CdCl_2\{\mu\text{-}S(CH_2)_3NH(CH_3)_2\}]$ *and Isomorphous Complexes* $[MX_2\{\mu\text{-}S(CH_2)_3NH(CH_3)_2\}]$ (M = Zn^{II}, Cd^{II}, *or* Hg^{II}; X = Cl *or* Br).—The crystal structure of $[CdCl_2\{S(CH_2)_3NH(CH_3)_2\}]$ shows that it is polymeric, consisting of infinite chains of cadmium atoms, each being tetrahedrally co-ordinated to two terminal chlorine atoms

Table 2. Final atomic co-ordinates (× 10^4)

Atom	X/a	Y/b	Z/c
(*a*) $[CdCl_2\{\mu\text{-}S(CH_2)_3NH(CH_3)_2\}]$ (Cd, Cl, and S × 10^5)			
Cd	24 299(2)	104 491(5)	36 945(3)
Cl(1)	33 284(8)	81 784(19)	52 279(7)
Cl(2)	14 011(11)	118 996(25)	50 643(9)
S	16 193(7)	82 131(18)	20 226(12)
C(1)	949(3)	6 820(8)	3 071(5)
C(2)	364(4)	5 412(10)	2 243(6)
C(3)	−288(4)	4 450(9)	3 031(6)
N(4)	−941(3)	3 323(8)	2 158(5)
C(5)	−604(7)	1 456(13)	1 590(9)
C(6)	−1 693(4)	2 860(13)	2 879(9)
(*b*) $[\{(CH_3)_2NH(CH_2)_3S\}_2][CdBr_4]$ (Cd and Br × 10^5)			
C(1)	2 620(4)	−724(8)	9 445(9)
C(2)	1 967(6)	−1 390(7)	11 615(11)
N(3)	2 557(4)	−1 115(9)	11 308(20)
C(4)	2 837(3)	−592(5)	13 320(12)
C(5)	3 441(4)	−282(7)	12 669(15)
C(6)	3 466(4)	864(5)	12 151(16)
S(7)	4 216(1)	1 291(2)	2 021(4)
S(8)	4 564(1)	462(1)	−146(3)
C(9)	4 283(2)	981(4)	−2 371(9)
C(10)	4 472(2)	2 051(4)	−2 830(15)
C(11)	5 087(2)	2 083(4)	−3 265(10)
N(12)	5 334(2)	3 076(4)	6 419(10)
C(13)	5 069(4)	3 534(5)	4 401(16)
C(14)	5 270(3)	3 829(7)	−2 029(20)
Cd	67 075(2)	33 861(3)	10 730
Br(1)	60 682(3)	19 289(4)	21 024(16)
Br(2)	77 593(2)	31 647(5)	20 149(17)
Br(3)	62 467(3)	50 715(5)	18 694(17)
Br(4)	67 299(2)	33 413(4)	70 906(11)

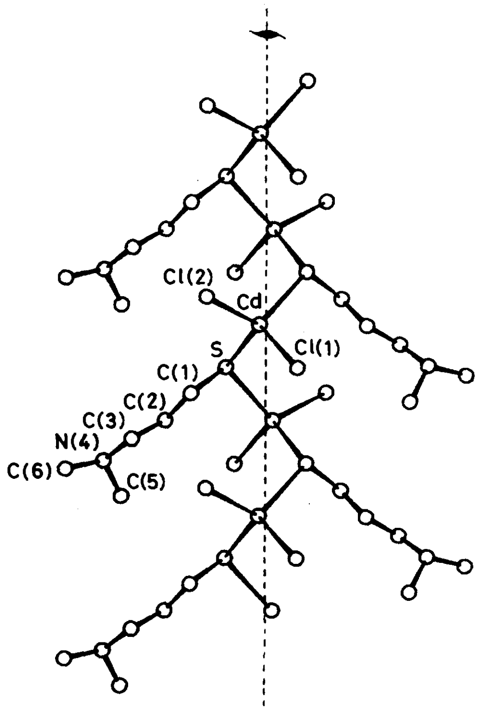

Figure 1. A view of the structure of $[CdCl_2\{\mu\text{-}S(CH_2)_3NH(CH_3)_2\}]$, with the atom numbering scheme

Table 3. Bond distances (Å) and bond angles (°) with estimated standard deviations in parentheses

(*a*) $[CdCl_2\{\mu\text{-}S(CH_2)_3NH(CH_3)_2\}]$

Cl(1)–Cd	2.507(1)	C(2)–C(1)	1.511(7)	Cl(2)–Cd–Cl(1)	104.2(1)	C(1)–S–Cd′	102.7(2)
Cl(2)–Cd	2.455(1)	C(3)–C(2)	1.516(8)	S–Cd–Cl(1)	108.0(1)	C(2)–C(1)–S	109.9(4)
S–Cd	2.511(1)	C(3)–N(4)	1.500(8)	S–Cd–Cl(2)	106.5(1)	C(3)–C(2)–C(1)	112.0(5)
S′–Cd	2.516(1)	C(5)–N(4)	1.478(9)	S′–Cd–Cl(1)	106.3(1)	N(4)–C(3)–C(2)	111.2(5)
C(1)–S	1.832(5)	C(6)–N(4)	1.501(9)	S′–Cd–Cl(2)	110.4(1)	C(5)–N(4)–C(3)	112.3(6)
				S′–Cd–S	120.3(1)	C(6)–N(4)–C(3)	110.6(6)
				Cd′–S–Cd	109.3(1)	C(6)–N(4)–C(5)	111.6(6)
				C(1)–S–Cd	100.5(2)		

(*b*) $[\{(CH_3)_2HN(CH_2)_3S\}_2][CdBr_4]$

N(3)–C(1)	1.370(14)	C(11)–C(10)	1.469(7)	C(2)–N(3)–C(1)	109.4(9)	N(12)–C(11)–C(10)	116.0(4)
N(3)–C(2)	1.445(14)	N(12)–C(11)	1.478(7)	C(4)–N(3)–C(1)	122.7(8)	C(13)–N(12)–C(11)	108.7(5)
C(4)–N(3)	1.664(14)	C(13)–N(12)	1.617(13)	C(4)–N(3)–C(2)	111.7(9)	C(14)–N(12)–C(11)	119.2(7)
C(5)–C(4)	1.537(11)	C(14)–N(12)	1.468(10)	C(5)–C(4)–N(3)	104.2(7)	C(14)–N(12)–C(13)	107.1(6)
C(6)–C(5)	1.590(9)	Br(1)–Cd	2.571(1)	C(6)–C(5)–C(4)	111.3(8)	Br(2)–Cd–Br(1)	113.8(1)
S(7)–C(6)	1.851(8)	Br(2)–Cd	2.560(1)	S(7)–C(6)–C(5)	110.5(6)	Br(3)–Cd–Br(1)	112.3(1)
S(8)–S(7)	2.013(3)	Br(3)–Cd	2.579(1)	S(8)–S(7)–C(6)	104.1(3)	Br(3)–Cd–Br(2)	117.0(1)
C(9)–S(8)	1.780(6)	Br(4)–Cd	2.685(1)	C(9)–S(8)–S(7)	104.0(2)	Br(4)–Cd–Br(1)	105.3(1)
C(10)–C(9)	1.546(7)			C(10)–C(9)–S(8)	115.6(5)	Br(4)–Cd–Br(2)	103.1(1)
				C(11)–C(10)–C(9)	110.3(4)	Br(4)–Cd–Br(3)	103.7(1)

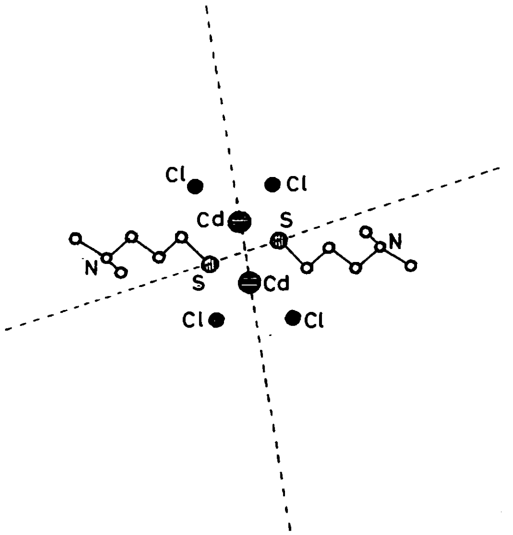

Figure 2. A chain of $[CdCl_2\{\mu\text{-}S(CH_2)_3NH(CH_3)_2\}]$ viewed down the two-fold screw axis. The dihedral angle (81.1°) formed by the planes of the sulphur and cadmium atoms respectively is shown

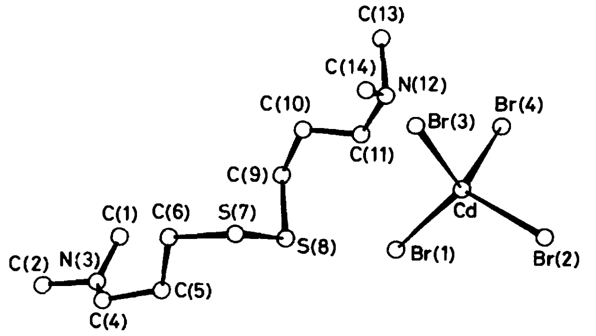

Figure 3. A view of the structure of $[\{(CH_3)_2HN(CH_2)_3S\}_2][CdBr_4]$ with the atom numbering scheme

and to two ligand molecules (Figure 1). Cadmium atoms are linked by sulphur atoms so that each ligand molecule is a bridge between two cadmium atoms. Cadmium and sulphur atoms within a chain are respectively coplanar (dihedral angle 81.1°) and placed alternately along four parallel straight lines because of a crystallographically imposed two-fold screw axis (Figure 2). The Cd–S distance [2.511(1) Å] (Table 3) is in good agreement with the value calculated from the sum of the cadmium and sulphur tetrahedral covalent radii (2.52 Å),[24] and with other values found with closely related ligands.[7,25] Both Cd–Cl(1) [2.507(1) Å] and Cd–Cl(2) [2.455(1) Å] are also in agreement with the value calculated from the sum of covalent radii (2.47 Å).[24]

Each chain is held together laterally by two other chains by means of hydrogen bonding between each ammonium group and Cl(1) atom, as is shown by the distance Cl(1) ··· N(4′) (3.17 Å).[26] Those chains joined through hydrogen bonds give rise to parallel layers which are not interconnected by any chemical forces.

Description of the Structures of $[\{(CH_3)_2HN(CH_2)_3S\}_2][CdBr_4]$ *and Isomorphous Compounds* $[\{(CH_3)_2HN(CH_2)_3S\}_2][MX_4]$ (M = Zn^{II}, Cd^{II}, *or* Hg^{II}; X = Cl *or* Br).—The crystal structure of $[\{(CH_3)_2HN(CH_2)_3S\}_2][CdBr_4]$ consists of discrete bis[3-(dimethylammonio)propyl] disulphide dications and tetrabromocadmate(II) anions as is shown in Figure 3, where the numbering system employed is also displayed.

The geometry about the cadmium atom in the anion is that of a distorted tetrahedron due to the formation of hydrogen bonds with the cations. Thus, while there are three very similar Cd–Br bond lengths [Cd–Br(1) 2.571(1), Cd–Br(2) 2.560(1), and Cd–Br(3) 2.579(1) Å], which agree well with the sum of covalent radii,[24] the fourth one is significantly longer [Cd–Br(4) 2.685(1) Å]. This trigonal distortion affects the Br–Cd–Br bond angles, Table 3, in the way expected when one of the ligands moves out.

The bis[3-(dimethylammonio)propyl] disulphide dication has positive charges located on the NH groups, thus enabling hydrogen-bond formation. Bond distances found for C–N, C–C, C–S, and S–S are close to those expected from the sum of the corresponding covalent radii and they are also in agreement with those in other previously reported disulphides of γ-mercaptoamine ligands.[19] The CSSC dihedral angle (74°85′) lies within the accepted ranges given in the literature.[19]

The only N–Br distances below 3.6 Å,[26] N(12) $\cdots$ Br(4) (3.32 Å) and N(3′) $\cdots$ Br(4) (3.48 Å), show that one $[CdBr_4]^{2-}$ anion links, through only Br(4), two disulphide cations by means of hydrogen bonding to two crystallographically independent nitrogen atoms belonging to different cations. These hydrogen-bond interactions result in an infinite chain structure. Each chain contains alternating cations and anions related through a two-fold screw axis thus giving rise to a staircase-like framework.

Infrared Data.—The i.r. spectra of the crystalline products obtained, analogously to the analytical data, do not reveal that $[MX_2\{\mu\text{-}S(CH_2)_3NH(CH_3)_2\}]$ complexes include the corresponding $[\{(CH_3)_2NH(CH_2)_3S\}_2][MX_4]$ salt in all cases, that is for M = Zn^{II}, Cd^{II}, or Hg^{II} and X = Cl or Br. However, the *X*-ray powder and single-crystal *X*-ray diffraction analysis confirm this. The i.r. spectra of the reaction products are very similar to that of the ligand, 3-dimethylamino-1-propanethiol, in its zwitterionic form, thus indicating that the amine group is protonated.

I.r. bands associated with the $\overset{+}{N}H$ group appear as broad peaks at 2 460—2 480 and 2 770—2 780 cm^{-1} and as a shoulder at *ca.* 2 980—3 000 cm^{-1}. The position of the latter indicates weak hydrogen bonds involving the $\overset{+}{N}H$ group,[27] in accord with the distances found in the single-crystal *X*-ray diffraction studies.

Conclusions

By treating 3-dimethylamino-1-propanethiol with Group 12 metal halides we have prepared polymeric complexes consisting of helicoidal chains of alternating metal and sulphur atoms. These chains are held together by hydrogen-bond interactions. The salt formed by the tetrahalogenometalate(II) and the protonated disulphide ions has been found as a side product and its structure determined by single-crystal *X*-ray diffraction.

Metal complexes with γ-mercaptoamine ligands give rise to a wide variety of structures[1–15,17] but that found in this case is the first of its type. Analogous reaction procedures to those followed in this case with 4-mercapto-1-methylpiperidine and zinc(II), cadmium(II), and mercury(II) halides have led to discrete dimeric molecules.[9]

Acknowledgements

We thank the Comisión Asesora de Investigación Científica y Técnica and the Comissió Interdepartmental de Recerca i Innovació Tecnològia for financial support.

References

1 H. Barrera, J. Suades, M. C. Perucaud, and J. L. Briansó, *Polyhedron*, 1984, **3**, 839.
2 J. Suades, X. Solans, M. Font-Altaba, and M. Aguiló, *Inorg. Chim. Acta*, 1985, **99**, 1.
3 J. Suades, X. Solans, and M. Font-Altaba, *Polyhedron*, 1984, **3**, 1227.
4 H. Barrera, J. C. Bayón, J. Suades, C. Germain, and J. P. Declerq, *Polyhedron*, 1984, **3**, 969.
5 H. Barrera, J. Sola, and J. Mª Viñas, *Transition Met. Chem.* (*Weinheim, Ger.*), 1985, **10**, 233.
6 H. Barrera, J. C. Bayón, P. González, J. Sola, J. Mª Viñas, M. C. Briansó, J. L. Briansó, and X. Solans, *Polyhedron*, 1982, **1**, 647.
7 J. C. Bayón, M. C. Briansó, J. L. Briansó, and P. González-Duarte, *Inorg. Chem.*, 1979, **18**, 3478.
8 W. Gaete, J. Ros, X. Solans, M. Font-Altaba, and J. L. Briansó, *Inorg. Chem.*, 1984, **23**, 39.
9 M. C. Briansó, J. L. Briansó, W. Gaete, J. Ros, and C. Suñer, *J. Chem. Soc., Dalton Trans.*, 1981, 852.
10 J. C. Bayón, I. Casals, W. Gaete, P. González-Duarte, and J. Ros, *Polyhedron*, 1982, **1**, 157.
11 W. Gaete and J. Ros, *Polyhedron*, 1985, **4**, 485.
12 R. M. Brunet, W. Gaete, P. González-Duarte, and J. Ros, *Transition Met. Chem.* (*Weinheim, Ger.*), 1984, **9**, 345.
13 X. Solans, M. Font-Altaba, J. L. Briansó, J. Sola, J. Suades, and H. Barrera, *Acta Crystallogr., Sect. C*, 1983, **39**, 1653.
14 H. Barrera and J. M. Viñas, *Polyhedron*, 1985, **4**, 2027.
15 J. Sola and R. Yáñez, *J. Chem. Soc., Dalton Trans.*, 1986, 2021.
16 I. G. Dance, *Inorg. Chim. Acta*, 1985, **108**, 227.
17 H. Barrera, J. Pons, and J. Suades, *An. Quim.*, 1984, **80**, 311.
18 B. C. Cossar, J. O. Fournier, D. L. Fields, and D. D. Reynolds, *J. Org. Chem.*, 1962, **27**, 93.
19 M. C. Briansó, J. L. Briansó, W. Gaete, and J. Ros, *Inorg. Chim. Acta*, 1981, **49**, 263 and refs. therein.
20 J. Stewart, AFFMAIL, A computer program for cell-parameters refinement, University of Bordeaux, 1970.
21 P. T. Beurskens, W. P. Bosman, H. M. Doesburg, R. O. Gould, Ch. E. M. Van den Hark, P. A. J. Prick, J. H. Noordik, G. Beurskens, and W. Parthasarathi, DIRDIF, an automatic procedure for phase extension and refinement of difference structure factor, Technical Report 1981/2, Crystallography Laboratory, Toernooiveld, Nijmegen, 1981.
22 G. M. Sheldrick, SHELX, a computer program for crystal structure determination, University of Cambridge, 1976.
23 'International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, 1974.
24 L. Pauling, 'The Nature of the Chemical Bond,' 3rd edn., Cornell University Press, Ithaca, 1960.
25 D. Craig, I. G. Dance, and R. Garbutt, *Angew. Chem., Int. Ed. Engl.*, 1986, **25**, 165.
26 G. C. Pimentel and A. L. McClelland, 'The Hydrogen Bond,' W. Freeman, San Francisco, 1960.
27 R. H. Nuttall, D. W. A. Sharp, and T. C. Waddington, *J. Chem. Soc.*, 1960, 4965.

Received 2nd December 1986; Paper 6/2329