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catena-[Cd{ μ -S(CH₂)₃NHMe₂}Br₂]

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Abstract

The title complex, *catena*-poly[dibromocadmium- μ -3-dimethylamino-1-propanethiolato], contains polymeric chains of alternating Cd and S atoms with Cd—S bond lengths of 2.515(3) and 2.520(3) Å. Distorted tetrahedral coordination of Cd [with a wide S—Cd—S angle of 126.95(5)°] is completed by two Br ligands [Cd—Br 2.5834(15) and 2.6400(14) Å]. The longer Cd—Br bond is to a Br atom involved in inter-chain hydrogen bonding with the ammonium group of a mercaptoamine ligand of an adjacent chain, to give two-dimensional sheets.

Comment

Interest in cadmium-thiolate coordination chemistry centres mainly on structural and bioinorganic objectives (Dance, 1986; Blower & Dilworth, 1987). Cadmium-cysteine coordination in several metallothioneins has

been established by solution ¹¹³Cd NMR studies and by X-ray diffraction measurements (Robbins, McRee, Williamson, Collett, Xuong, Furey, Wang & Stout, 1991). As part of our extensive studies of the coordination chemistry of mercaptoamine ligands (Capdevila, Clegg, González-Duarte, Harris, Mira, Sola & Taylor, 1992, and references therein), and with the specific aim of correlating ¹¹³Cd solid-state NMR data with the coordination of Cd in different environments, we have determined the structure of *catena*-[Cd{ μ -S(CH₂)₃NHMe₂}Br₂].

The complex (Fig. 1) is isostructural with the corresponding chloride (Casals, González-Duarte, Sola, Font-Bardía, Solans & Solans, 1987) and with the analogous mercury chloride complex (Casals, González-Duarte, Sola, Miravittles & Molins, 1988). It consists of polymeric chains of alternating Cd and S atoms. The mercaptoamine ligands are doubly bridging through the S atom only, the protonated amine group playing no part in the metal coordination. The tetrahedral coordination of Cd by two thiolate and two Br ligands shows slightly more distortion than in the corresponding chloride, but less than in the analogous Hg complex; the correlation between such geometrical variations and solid-state ¹¹³Cd NMR parameters will be the subject of a separate publication.

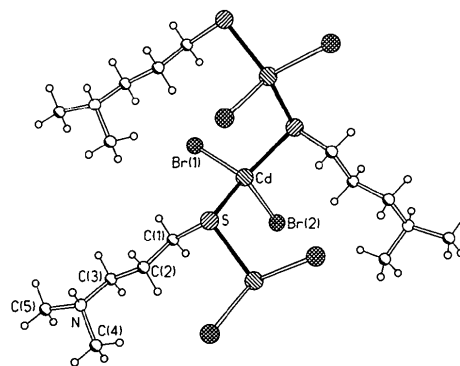


Fig. 1. Part of the polymeric chain structure, showing the labelling of the independent atoms.

The chains are held together in extended two-dimensional sheets by hydrogen bonding between ammonium groups and Br ligands. The H...Br and N...Br distances are 2.52(2) and 3.35(2) Å respectively, with an angle of 148(2)° at the H atom (these values are calculated from the refinement results, whereby the H atom was made to ride on its N atom with a fixed bond length of 0.93 Å). The Br ligand involved in hydrogen bonding forms a longer bond to the Cd atom.

Previous attempts to synthesize this complex gave no pure product, but a mixture containing also the salt [Me₂NH(CH₂)₃S]₂[CdBr₄] (Casals *et al.*, 1987). Comparable synthetic procedures with halides of Zn, Cd and Hg, and with the 4-mercapto-1-methylpiperidine ligand (a cyclic instead of linear γ -mercaptoamine) give dimeric [M₂(μ -SR)₂X₄] (Bayón, Casals, Gaete, González-Duarte

& Ros, 1982). Cationic chains with pairs of mercaptoamine bridging ligands are also known (Bayón, Briansó, Briansó & González-Duarte, 1979; Casals, Clegg & González-Duarte, 1991).

Experimental

Crystal data

[CdBr₂(C₅H₁₃NS)]

$M_r = 391.44$

Monoclinic

$P2_1/n$

$a = 9.993$ (1) Å

$b = 6.8236$ (6) Å

$c = 16.398$ (2) Å

$\beta = 96.00$ (1)°

$V = 1112.0$ (2) Å³

$Z = 4$

$D_x = 2.338$ Mg m⁻³

Data collection

Stoe-Siemens diffractometer
 ω/θ scans with on-line profile fitting (Clegg, 1981)

Absorption correction:

empirical (SHELXTL/PC; Sheldrick, 1990)

$T_{\min} = 0.074$, $T_{\max} = 0.117$

5481 measured reflections

1940 independent reflections

Refinement

Refinement on F^2

Final R (all data) = 0.0548

wR (all data) = 0.1412

S (all data) = 1.132

1934 reflections

94 parameters

Calculated weights

$w = 1/[\sigma^2(F_o^2) + (0.0100P)^2 + 24.2500P]$,
where $P = (F_o^2 + 2F_c^2)/3$

$(\Delta/\sigma)_{\max} = 0.001$

$\Delta\rho_{\max} = 1.184$ e Å⁻³

Data collection: Stoe DIF4. Cell refinement: Stoe DIF4. Data reduction: local programs. Program(s) used to solve structure: SHELXTL/PC (Sheldrick, 1990). Program(s) used to refine structure: SHELXL92 (Sheldrick, 1992). Molecular graphics: SHELXTL/PC. Software used to prepare material for publication: local programs.

Table 1. Fractional atomic coordinates and equivalent isotropic thermal parameters (Å²)

| | x | y | z | U_{eq} |
|-----|--------------|--------------|-------------|------------|
| Cd | 0.35841 (8) | 0.52127 (11) | 0.23959 (5) | 0.0344 (5) |
| Br1 | 0.49686 (13) | 0.6731 (2) | 0.13100 (8) | 0.0528 (7) |
| Br2 | 0.52522 (12) | 0.2874 (2) | 0.32915 (7) | 0.0408 (7) |

| | | | | |
|----|-------------|--------------|-------------|-------------|
| S | 0.1909 (3) | 0.2932 (4) | 0.1640 (2) | 0.0328 (14) |
| N | 0.2035 (10) | -0.1672 (15) | -0.0891 (6) | 0.046 (6) |
| C1 | 0.2964 (11) | 0.1765 (16) | 0.0930 (7) | 0.038 (6) |
| C2 | 0.2154 (11) | 0.0380 (18) | 0.0355 (6) | 0.042 (6) |
| C3 | 0.2914 (11) | -0.0417 (17) | -0.0316 (6) | 0.040 (6) |
| C4 | 0.1601 (15) | -0.3495 (19) | -0.0507 (9) | 0.063 (9) |
| C5 | 0.2677 (16) | -0.2124 (24) | -0.1649 (7) | 0.070 (11) |

Table 2. Geometric parameters (Å, °)

| | | | |
|------------------------|-------------|-----------------------|------------|
| Cd—S | 2.515 (3) | N—C4 | 1.479 (17) |
| Cd—S ⁱ | 2.520 (3) | N—C3 | 1.490 (14) |
| Cd—Br1 | 2.5834 (15) | N—C5 | 1.489 (15) |
| Cd—Br2 | 2.6400 (14) | C1—C2 | 1.509 (15) |
| S—C1 | 1.833 (11) | C2—C3 | 1.503 (14) |
| S—Cd—S ⁱ | 126.95 (5) | Cd—S—Cd ⁱⁱ | 108.08 (9) |
| S—Cd—Br1 | 106.57 (7) | C4—N—C3 | 113.2 (9) |
| S ⁱ —Cd—Br1 | 106.92 (7) | C4—N—C5 | 110.6 (11) |
| S—Cd—Br2 | 104.43 (7) | C3—N—C5 | 111.7 (10) |
| S ⁱ —Cd—Br2 | 104.47 (7) | C2—C1—S | 111.3 (7) |
| Br1—Cd—Br2 | 105.86 (5) | C3—C2—C1 | 113.9 (9) |
| C1—S—Cd | 100.7 (3) | N—C3—C2 | 111.2 (9) |
| C1—S—Cd ⁱⁱ | 104.0 (4) | | |

Symmetry code: (i) $\frac{1}{2} - x, \frac{1}{2} + y, \frac{1}{2} - z$; (ii) $\frac{1}{2} - x, y - \frac{1}{2}, \frac{1}{2} - z$.

Reaction of stoichiometric amounts of CdBr₂·4H₂O and HS—(CH₂)₃NMe₂ in water-methanol (4:1) under nitrogen yielded a white powder, from which colourless crystals of the title complex were obtained by cooling a solution in a water-ethanol-DMSO mixed solvent. Satisfactory chemical analyses were found.

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Lists of structure factors, anisotropic thermal parameters, H-atom coordinates and complete geometry have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55593 (9 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: AL1022]

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