N(1)—C(2)—C(3)	110 (1)	C(1)—C(2)—C(3)	116 (1)
O(3)—C(3)—C(2)	110 (1)	O(4)—C(4)—O(5)	127 (2)
O(4)—C(4)—C(5)	121 (2)	C(5)—C(4)—O(5)	112 (2)
N(2)—C(5)—C(4)	115 (2)	N(2)—C(5)—C(6)	109 (2)
O(6)—C(6)—C(5)	105 (1)	C(4)—C(5)—C(6)	114 (1)

Symmetry code: (i) $1 + x, y, z$.

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Lists of structure factors, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55815 (22 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: SH1017]

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Structures of the Cadmium Halide Complexes [{$CdCl_2$(dmso)(MeOH)}$_n$] and [{$CdBr_2$(dmso)(MeOH)}$_n$] with Coordinated Dimethyl Sulfoxide and Methanol

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Abstract

Cadmium chloride and bromide form halogen-bridged polymeric chain complexes *catena*-poly[{(dimethyl sulfoxide)(methanol)cadmium}di-μ-chloro] [{$CdCl_2$(dmso)(MeOH)}$_n$] (dmso = dimethyl sulfoxide) and *catena*-poly[{(dimethyl sulfoxide)(methanol)cadmium}di-μ-bromo] [{$CdBr_2$(dmso)(MeOH)}$_n$] with Cd in octahedral coordination. With the chloride, the dmso and MeOH ligands are in *trans* positions. The hydroxylic proton of the coordinated methanol enters into hydrogen bonding with the O atom of a dmso ligand coordinated to an adjacent Cd centre in the same chain. The bromide differs in having the dmso and MeOH ligands in *cis* positions, with each chain now linked to its four neighbours through hydrogen bonding.

Comment

The two compounds have polymeric chain structures with six-coordinate cadmium centres bridged by halogen pairs. The chain simplicity distinguishes them from most of the other single-chain structures which cadmium chloride and bromide are found to produce (Nieuwenhuyzen, 1992). Each Cd carries a methanol and a dimethyl sulfoxide (dmso) ligand but whereas the two ligands are *trans* in the chloride (1), they are *cis* in the bromide (2). In (1), there is intrachain hydrogen bonding between the methanol and dmso ligands carried by adjacent Cd centres (Fig. 1) with the whole structure conforming to the 2_1 screw-axis relationship. Deviation from strict linearity is very slight with Cd···Cd···Cd angles of 179.3 (1)°. By contrast, the *cis* positioning in (2) means that there is chain zigzag, and the Cd···Cd···Cd angle is 130.2 (1)°. Both the zigzag and the linear chains can be related to the bonding within an original, but now degraded, CdX_2 layer lattice.

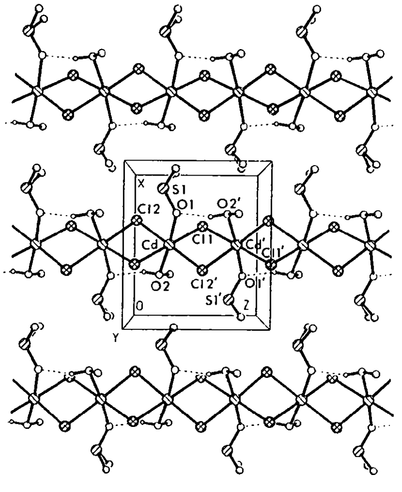

Fig. 1. Chain relationships for [{$CdCl_2$(dmso)(MeOH)}$_n$] (1) showing the intrachain hydrogen bonding. The coordinates of Cd are ($\frac{1}{2} - x$, $\frac{1}{2} + y$, $\frac{1}{2} + z$) and Cd' ($\frac{1}{2} + x$, $\frac{1}{2} - y$, $1 + z$); the x and y coordinates are therefore close to ($\frac{1}{2}$, $\frac{1}{2}$). In the extended structure, Cd atoms of the four neighbouring chains lie close to the cell edges parallel to the z axis.

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The O1⋯O2 hydrogen-bonded distances in (1) and (2) are almost identical (2.78 and 2.73 Å), indicating near equal strength of the bonds. The Cd—*X*—Cd bridging angles are quite similar [92.2, 92.8° for (1), 91.4, 93.4 and 95.4° for (2)] so that Cd⋯Cd distances in the bromide (3.94, 4.08 Å) remain greater than for the chloride (3.75 Å). It can be suggested that the development of the alternative interchain hydrogen-bonding in the bromide is a consequence of the greater Cd⋯Cd separation, since this would reduce the strength of the alternative hydrogen-bonding along a chain. The *cis* positioning is suited to the development of interchain bonding between reciprocal sets of the two ligands in adjacent chains (see Fig. 2). This hydrogen bonding results in a three-dimensional network in the extended structure, with each chain linked to four equivalent neighbouring chains.

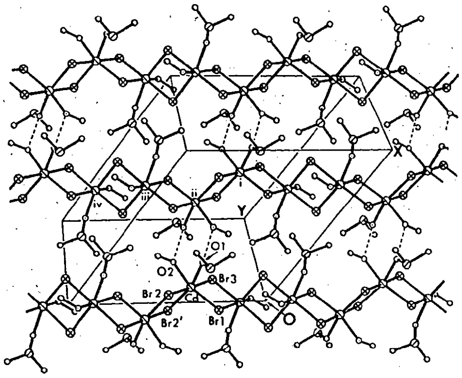

Fig. 2. The zigzag chains of [{CdBr$_2$(dmso)(MeOH)}$_n$] (2) with the interchain hydrogen bonding. Hydrogen bonding from the ligands centred on Cd^{iii} and Cd^{iv} extends to two other chains, respectively above and below the set shown. The labelled atoms Cd, Br1, Br2, Br3, O1, O2 have coordinates (*x*, *y*, *z*). The origin is at the lower front-right-hand corner of the cell.

The hydrogen bonding will lengthen the Cd—O bond from dmso, but shorten this bond from MeOH, a corresponding effect having been observed in [{CdI$_2$(pyo)$_2$(MeOH)}$_2$] (Nieuwenhuyzen, Robinson & Wilkins, 1991). For this reason, these bond lengths do not offer information on the relative ligand strengths. Methanol lies above dmso in the spectrochemical series of ligands, but other lines of evidence place its 'coordinating power' decisively below that of the sulfoxide (Munakata, Kitagawa & Miyazima, 1985, and references therein). Preparative experience with the present compounds is in line with this latter conclusion since they are only formed when the dmso:halide ratio is restricted to a low value, *e.g.* equimolecular in the case of (2). In these cadmium complexes, coordination of methanol will be promoted by its role in hydrogen bonding.

Experimental

Compound (1)

Crystal data

[CdCl$_2$(CH$_4$O)(C$_2$H$_6$OS)]
M_r = 293.5
Orthorhombic
$Pna2_1$
a = 8.402 (4) Å
b = 14.280 (10) Å
c = 7.498 (4) Å
V = 899.6 (9) Å^3
Z = 4
D_x = 2.167 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 6.5–20°
μ = 3.182 mm^{-1}
T = 150 K
Thick needle
0.7 × 0.17 × 0.15 mm
Colourless

Data collection

Nicolet *R3M* diffractometer
ω scans
Absorption correction: empirical (ψ scans)
T_{min} = 0.773, T_{max} = 0.779
968 measured reflections
968 independent reflections
609 observed reflections [$F > 6\sigma(F)$]

θ_{max} = 27.5°
$h = 0 \rightarrow 11$
$k = 0 \rightarrow 20$
$l = 0 \rightarrow 8$
3 standard reflections monitored every 100 reflections intensity variation: ±2.5%

Refinement

Refinement on F
Final R = 0.0268
wR = 0.0336
S = 0.97
609 reflections
74 parameters
$w = 1/[\sigma^2(F)+gF^2]$ where g = 0.0006

$(\Delta/\sigma)_{max}$ = 0.004
$\Delta\rho_{max}$ = 0.53 e Å^{-3}
$\Delta\rho_{min}$ = −0.55 e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Compound (2)

Crystal data

[CdBr$_2$(CH$_4$O)(C$_2$H$_6$OS)]
M_r = 382.4
Monoclinic
$C2/c$
a = 14.520 (6) Å
b = 10.692 (4) Å
c = 14.124 (5) Å
β = 121.38 (2)°
V = 1872.0 (1.2) Å^3
Z = 8
D_x = 2.714 Mg m^{-3}

Mo $K\alpha$ radiation
λ = 0.71073 Å
Cell parameters from 25 reflections
θ = 7–18°
μ = 10.92 mm^{-1}
T = 170 K
Cut (broken) from diamond-shaped block
0.56 × 0.48 × 0.46 mm
Colourless

Data collection

Absorption correction: empirical (ψ scans)
T_{min} = 0.218, T_{max} = 0.772
3590 measured reflections
2156 independent reflections
1764 observed reflections [$F > 6\sigma(F)$]
R_{int} = 0.0867 (see below)

θ_{max} = 27.5°
$h = -18 \rightarrow 18$
$k = 0 \rightarrow 13$
$l = -18 \rightarrow 9$
3 standard reflections monitored every 100 reflections intensity variation: ±2.5%

Refinement

Refinement on F
Final $R = 0.0563$
$wR = 0.0727$
$S = 1.83$
1764 reflections
83 parameters
$w = 1/[\sigma^2(F)+gF^2]$ where $g = 0.0006$
$(\Delta/\sigma)_{\max} = 0.001$
$\Delta\rho_{\max} = 1.92$ e Å^{-3}
$\Delta\rho_{\min} = -3.63$ e Å^{-3}
Atomic scattering factors from *International Tables for X-ray Crystallography* (1974, Vol. IV)

Table 1. *Fractional atomic coordinates and equivalent isotropic thermal parameters* (Å^2)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U_{eq}
(1)				
Cd(1)	−0.0007 (2)	0.0006 (1)	−0.2022	0.013 (1)
Cl(1)	−0.1260 (3)	−0.1023 (2)	0.0469 (7)	0.020 (1)
Cl(2)	−0.1641 (3)	−0.0793 (2)	−0.4568 (8)	0.016 (1)
O(1)	−0.2069 (10)	0.1072 (7)	−0.1497 (14)	0.016 (2)
S(1)	−0.3640 (3)	0.1044 (2)	−0.2497 (5)	0.018 (1)
C(11)	−0.4699 (11)	0.0090 (8)	−0.1648 (26)	0.027 (6)
C(12)	−0.4812 (13)	0.1966 (7)	−0.1583 (28)	0.040 (5)
O(2)	0.1979 (12)	−0.1098 (8)	−0.2790 (14)	0.022 (3)
C(2)	0.1998 (14)	−0.2019 (7)	−0.2044 (24)	0.032 (3)
(2)				
Cd(1)	0.0580 (1)	0.0819 (1)	0.4109 (1)	0.014 (1)
Br(1)	0.0	−0.0918 (1)	0.2500	0.018 (1)
Br(2)	0.1207 (1)	−0.1017 (1)	0.5766 (1)	0.017 (1)
Br(3)	0.0	0.2616 (1)	0.2500	0.018 (1)
S(1)	0.2812 (2)	−0.0723 (2)	0.4614 (2)	0.019 (1)
O(1)	0.2383 (4)	0.0604 (6)	0.4612 (4)	0.019 (2)
C(11)	0.3529 (7)	−0.0494 (9)	0.3917 (7)	0.025 (4)
C(12)	0.3936 (7)	−0.0935 (9)	0.5989 (7)	0.030 (4)
O(2)	0.1331 (4)	0.2489 (6)	0.5324 (4)	0.021 (2)
C(2)	0.1909 (7)	0.2245 (10)	0.6482 (6)	0.031 (4)

Table 2. *Selected bond lengths* (Å) *and angles* (°)

(1)		(2)	
Cd(1)—Cl(1)	2.599 (5)	Cd(1)—Br(1)	2.708 (1)*
	2.604 (5)	Cd(1)—Br(2)	2.819 (2)*
Cd(1)—Cl(2)	2.614 (5)	Cd(1)—Br(2′)	2.699 (2)*
	2.562 (5)	Cd(1)—Br(3)	2.752 (1)*
Cd(1)—O(1)	2.338 (10)	Cd(1)—O(1)	2.339 (6)
Cd(1)—O(2)	2.367 (11)	Cd(1)—O(2)	2.317 (6)
O(1)—S(1)	1.519 (9)	O(1)—S(1)	1.548 (6)
O(2)—H(2)†	0.83 (12)		
Cd···Cd‡	3.75	Cd···Cd‡	3.94, 4.08
O···O‡	2.78	O···O‡	2.73
Cl(1)—Cd—Cl(1′)	179.4 (1)	Br(2)—Cd—Br(3)	179.2 (1)
C(2)—Cd—Cl(2′)	178.9 (2)	Cd—Br(1)—Cd	93.4 (1)
Cd—Cl(1)—Cd	92.2 (1)	Cd—Br(3)—Cd	91.4 (1)
O(1)—Cd—O(2)	175.1 (4)	O(1)—Cd—O(2)	80.3 (2)
Cd—O(1)—S(1)	122.9 (6)	Cd—O(1)—S(1)	118.5 (3)

* Bonds to Br(2) and Br(3), mutually in *trans* positions, are significantly longer than those to Br(1) and Br(2′) in *trans* positions to O(2) and O(1), respectively. This suggests that Br(2) and Br(3) are making demands on the same Cd orbital, *e.g.* a π-bonding 4*d* orbital.

† The refined position of the proton is 0.17(12) from the O(1)-O(2) vector.

‡ Non-bonded distance.

The chloride (1) was obtained by reacting the hydrate $CdCl_2.2.5H_2O$ (1 mmol) with dmso (1-3 mmol) in boiling methanol (10 cm^3) with triethoxymethane (tem, 2 cm^3) to provide for dehydration. The solution was filtered and crystals separated slowly after cooling. These were rinsed with tem and ether. They became opaque on exposure to air through hydrolysis and loss of methanol, but could be quickly mounted in the cold nitrogen stream of the diffractometer.

For the bromide (2), the hydrate $CdBr_2.4H_2O$ and dmso (2 mmol of each) were dissolved in methanol (5 cm^3) and tem (2 cm^3). Crystallization was promoted by careful addition of an upper layer of ether, or by standing at 273-278 K. This compound loses methanol more easily than the chloride, but is again stable for diffractometry at low temperature.

Space groups were determined from systematic absences. In the case of (1), counting statistics indicated *Pna*2$_1$ rather than *Pnma* and the absolute configuration was checked by chirality testing. For (2), the value of $|E^*E^{-1}|$ favoured *C*2/*c* over *Cc*; this was confirmed by successful refinement using the higher-symmetry space group. Atoms were located from the Patterson map and refined by full-matrix least-squares techniques minimizing $\Sigma w(|F_o| - |F_c|)^2$.

In both compounds, the methyl H atoms were inserted at idealized positions [C—H = 0.96 Å, $U = 0.030$ Å^2 (fixed)] and not refined. The hydroxylic H atom was located in (1) and its position refined with $U = 0.030$ Å^2 (fixed); in (2) it was probably located but was ignored. Atoms O(2) and C(2) of (1) were held isotropic because the comparatively low data:parameter ratio caused 'non-positive definites'.

The $R_{\rm int}$ value and electron-density results are high for the bromide. It is considered that the high $R_{\rm int}$ is the result of absorption. The crystal had to be 'cut' (in fact with irregular fragmentation). We did not wish to discard data from an 'over-run' beyond the minimum −18→0 scan requirement for *l*. As regards the overall quality of data, the final R and wR indices using all data retain quite low values ($R = 0.0639$, $wR = 0.0762$). It did not prove possible to obtain a crystal of suitable size for face-indexing. The electron-density residuals (maxima and minima) were all in the vicinity of the Cd and Br atoms. There was no evidence of ligand disorder.

We are indebted to Dr Vickie McKee for her interest in promoting this work.

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 55832 (13 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: MU1030]

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