

# Crystal Structures and Significance of Complexes formed Between Cadmium Bromide and Dimethyl Sulfoxide\*

Mark Nieuwenhuyzen and Cuthbert J. Wilkins

Chemistry Department, University of Canterbury, Christchurch, New Zealand

Cadmium bromide reacts with dimethyl sulfoxide (dmsO) in increasing proportion to produce a series of complexes ranging from a layer-lattice type, through slab and chain structures to ionic derivatives, as shown by X-ray analysis. The layer lattice  $[\{\text{CdBr}_2(\text{dmsO})\}_n]$  is converted into hydrates  $[\{\text{CdBr}_2(\text{dmsO})\}_n \cdot n\text{H}_2\text{O}]$  and  $[\{(\text{CdBr}_2)_3(\text{dmsO})_2(\text{H}_2\text{O})\}_n \cdot n\text{H}_2\text{O}]$ , both of which have 'slab' structures with a  $\text{CdBr}_2$  core having the same connectivity as in  $\text{CdBr}_2$  itself. Crystalline products  $[\{(\text{CdX}_2)_3(\text{dmsO})_4\}_n]$ ,  $[\{(\text{CdX}_2)_2(\text{dmsO})_3\}_n]$ ,  $\text{X} = \text{Cl}$  or  $\text{Br}$ , contain two separate chains of compositions  $(\text{CdX}_2)_3(\text{dmsO})_4$  and  $(\text{CdX}_2)_2(\text{dmsO})_3$ . The former has a condensed chain and the latter a single-chain structure. Single-chain structures are varied, with differing combinations of cadmium centres in six- and five-co-ordination. With potentially cationic and anionic centres, they can be seen as precursors of ionic derivatives  $[\text{Cd}(\text{dmsO})_6]^{2+} 2[\text{CdBr}_3(\text{dmsO})]^-$ , and  $[\text{Cd}(\text{dmsO})_6]^{2+} [\text{CdBr}_4]^{2-}$ . With the ready development of chain structures, Cd differs from Zn (with its strong tetrahedral preference), and also from Hg in showing no tendency towards strong digonal bonding.

We have recently shown that the products from the reactions of cadmium halides with simple oxo-ligands (L) are highly dependent upon the  $\text{L}:\text{CdX}_2$  ratio,<sup>1,2</sup> the work having been developed originally with the use of pyridine *N*-oxide (pyo). With low ratios there are products having layer lattices closely relating to that of the parent  $\text{CdX}_2$  structure. Higher ratios produce polymeric chain structures, and finally ionic compounds. The chain derivatives extend the variety of single-chain structures which have been described.<sup>3-5</sup> As might be expected from progressive weakening of the Cd-X bonds, the products obtained under particular conditions suggest that the ease of degradation of the parent halide lattices increases from chloride to iodide.

In exploratory work with dimethyl sulfoxide (dmsO) it became clear that, while its ligand field is similar to that of pyo,<sup>6</sup> it showed a significant difference in behaviour. It is less inclined to play a bridging role, probably through its larger steric demand close to the co-ordination centre. One consequence proved to be the facility with which dmsO, reacting with  $\text{CdBr}_2$ , produced derivatives having a ribbon-like structure where the two-dimensional cadmium halide lattice has in effect been cut into slabs. The development of the slab structures is assisted by controlled access of water, which can function as an auxiliary ligand as well as providing inter-slab hydrogen bonding. The appearance of such core structures was not unexpected, for they carry features which already appear in several double-chain structures:  $\text{CdCl}_2 \cdot \text{H}_2\text{O}$ ,<sup>7</sup>  $[\{\text{CdCl}_2(\mu)\}_n]$ <sup>8</sup> from methylurea ( $\mu$ ), and  $[\{(\text{CdCl}_2)_4\text{L}(\text{H}_2\text{O})\}_n]$ <sup>9</sup> from a crown ether (L). Such structures have been reported individually, but their collective significance does not seem to have been discussed.

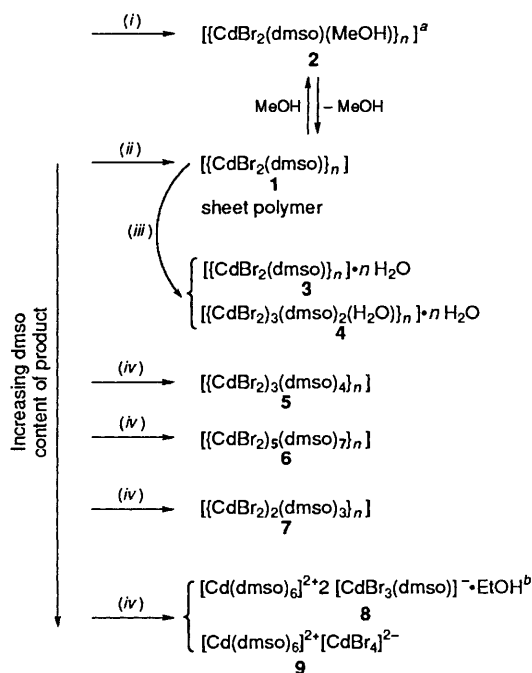
It becomes clear also that, with the availability of the structures now reported, cadmium halides differ sharply from the halides of both zinc and mercury in co-ordination behaviour.

## Results and Discussion

*Survey of Structures.*—The succession of phases obtainable from dmsO and  $\text{CdBr}_2$ , with generally increasing dmsO :  $\text{CdBr}_2$  ratio, and through use of water or methanol as auxiliary ligands, is summarised in Scheme 1. The structure of compound **2** has

been reported,<sup>10</sup> that of **8** is known through its isomorphism with the iodide,<sup>1</sup> and the constitution of **9** as  $[\text{Cd}(\text{dmsO})_6]^{2+} [\text{CdBr}_4]^{2-}$  has now been established, although we have not refined its structure due to extensive disorder of the dmsO ligands.

Compound **1** with its sheet structure (Fig. 1) is the first derivative obtainable at low dmsO :  $\text{CdBr}_2$  ratio (without intervention of other ligands). Unlike the sheet structures from pyo,<sup>1</sup> where that ligand plays only a bridging role, it does not relate directly to the original  $\text{CdBr}_2$  lattice.<sup>11</sup> The structure contains chains running through the centres  $\text{Cd}(1'')$ ,  $\text{Cd}(1)$ ,  $\text{Cd}(2)$ ,  $\text{Cd}(2')$ ,  $\text{Cd}(1')$ ,  $\text{Cd}(1''')$ , and cross-linked through  $\text{Br}(1)$  atoms. It is of interest that individual chains having this connectivity, with the same 5,5,6,6 cadmium co-ordination sequence appear in the single-chain structure of **7** (Fig. 6). There,



**Scheme 1** (i) dmsO : Cd = 1 : 1, MeOH; (ii) dmsO : Cd = 1 : 1, EtOH; (iii) controlled access of atmospheric moisture; (iv) see Experimental section. <sup>a</sup> A zigzag chain structure with interchain hydrogen bonding between the *cis* ligands. <sup>b</sup> Isomorphous with the iodide.<sup>2</sup>

\* Supplementary data available: see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

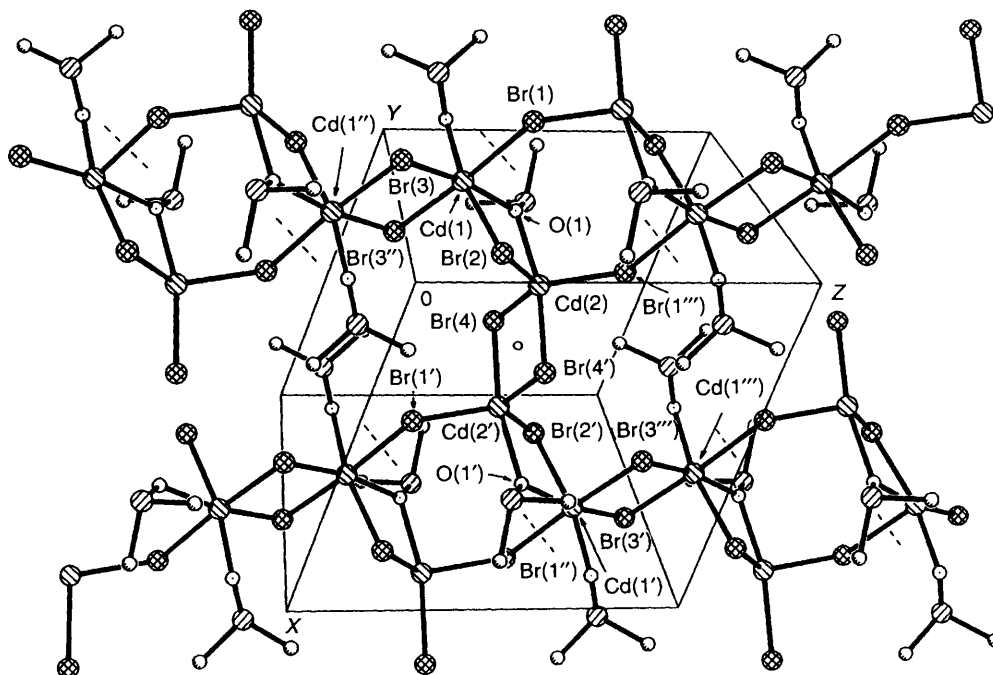


Fig. 1 The layer structure of  $[\{\text{CdBr}_2(\text{dmsO})\}_n]$  **1**. The Cd(1)–Br(1) bonds which would be broken to give the chains present in **7**, are indicated. Symmetry codes are: Cd(1), Br(1), Br(3), O(1),  $-x, \frac{1}{2} + y, \frac{1}{2} - z$ ; Cd(2), Br(4), Br(1''),  $x, \frac{1}{2} + y, \frac{1}{2} - z$ ; Cd(1'), Br(1'), Br(2'), Br(3'), O(1),  $1 + x, \frac{1}{2} - y, \frac{1}{2} + z$ ; Cd(2'), Br(1'), Br(4'),  $1 - x, \frac{1}{2} - y, \frac{1}{2} + z$ ; Cd(2''), Br(3''),  $x, \frac{1}{2} - y, z - \frac{1}{2}$ ; Cd(3''), Br(3''),  $1 - x, \frac{1}{2} + y, \frac{3}{2} - z$

the chains are separated through breaking of the Cd(1)–Br(1) linkages, with insertion of a dmsO molecule on the Cd(1) centres to preserve their six-co-ordination.

With methanol, compound **1** converts into the methanol solvate **2**, and with controlled access of atmospheric moisture it gives the hydrates **3** (Fig. 2) and **4** (Fig. 3). Here, lattice water provides inter-slab hydrogen bonding to the dmsO ligands, and in **4** there is co-ordinated water as well. Both hydrates illustrate slab formation, through what must be a rather delicate balance between redevelopment (from solution) of bromide bridging as exists in  $\text{CdBr}_2$  itself and the terminal co-ordination of dmsO. An end-on view of the slabs (Fig. 2) confirms the complete correspondence of the connectivity within the slabs with that pre-existing in the parent lattice, although there is some asymmetry of bromide bridging in the fragmented lattice. The slab packing gives interlayer  $\text{S} \cdots \text{Br}$  approaches of 3.8 Å. These reinforce  $\text{CH}_3 \cdots \text{Br}$  approaches, and reflect the existence of a resultant positive charge on the S atom in the free dmsO molecule as indicated by theoretical calculations.<sup>12</sup>

The isomorphous crystalline derivatives **6** (bromide) and **6a** (chloride, on which the structure determination was done) have chain structures which require particular comment. First there is a most unusual feature of two independent chains, of compositions  $(\text{CdBr}_2)_3(\text{dmsO})_4$  and  $(\text{CdBr}_2)_2(\text{dmsO})_3$ , which keep in step through no more than van der Waals interactions. However, as accords with their simultaneous appearance from solution, they are closely related (Fig. 4). If the atoms on the left-hand side of the broken line drawn through the bulkier chain **1** are notionally removed, and the two loose ends converging on the Cl(4) position be satisfied by a bridging dmsO ligand, then the smaller chain **2** arises. Chain **1** is comprised of 'link-blocks'\* extending in line between Cd(3) and Cd(3') centres. In isolation, these segments would have the composition  $\text{Cd}_4\text{X}_6$ , but there is atom sharing in accordance

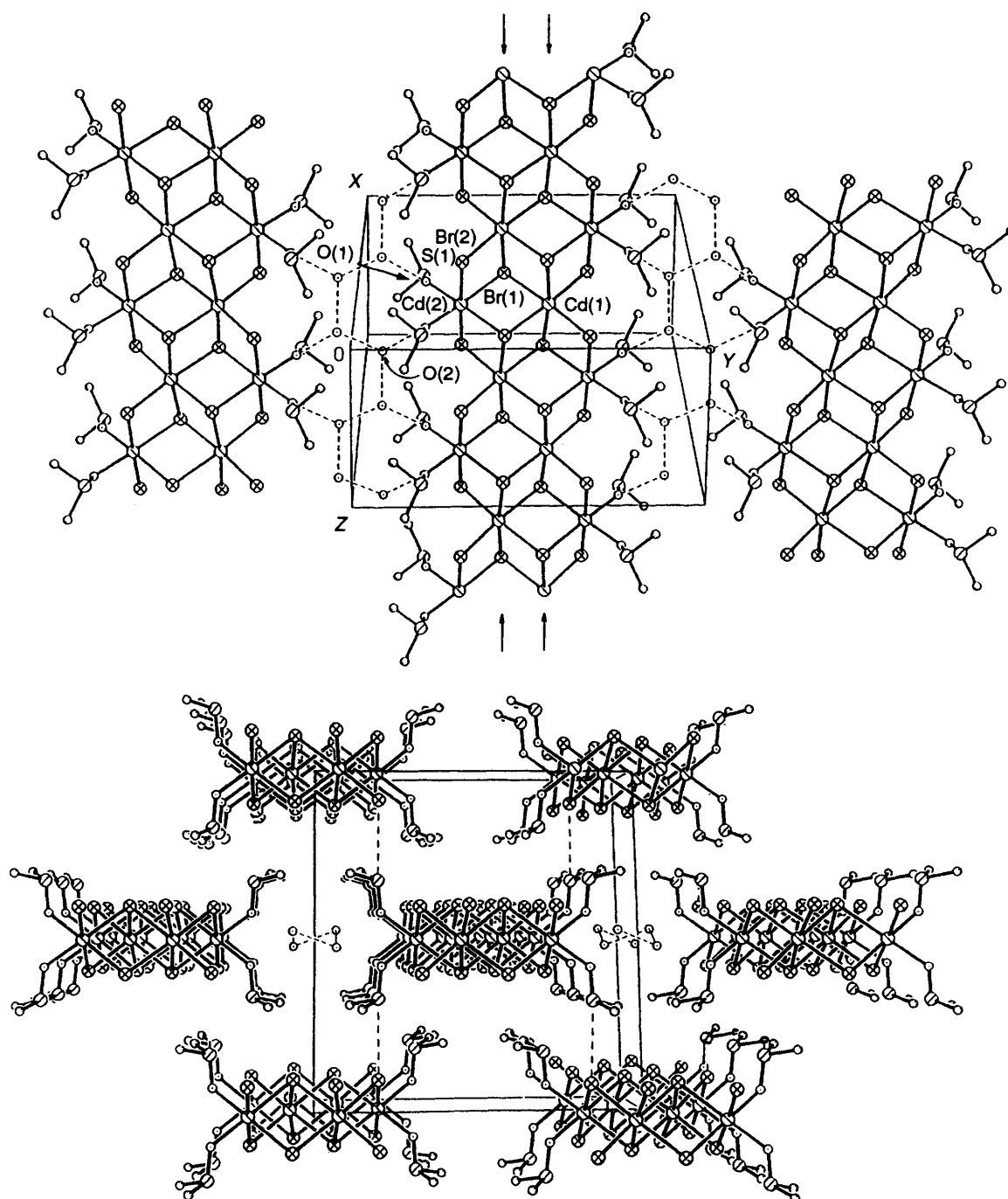
with the  $\text{CdX}_2$  stoichiometry. The common feature provided by these link-blocks within condensed structures is discussed below.

By contrast with this composite chain structure, two single-chain structures have been identified in derivatives **5** and **7**. Their compositions,  $\text{CdBr}_2:\text{dmsO}$ , are again 3:4 and 2:3, but the chains are of quite different connectivity from those of the same compositions which are paired in **6** and **6a** (see Figs. 5 and 6). This full sequence of derivatives, as shown in Scheme 1, is specific to the bromide. From the chloride, only a methanol solvate  $[\{\text{CdCl}_2(\text{dmsO})(\text{MeOH})\}_n]$  and **6a** could be isolated in a pure state. With the iodide, no sheet or slab structures could be obtained.<sup>2</sup>

*Unifying Features of the Structures.*—The  $\text{Cd}_4\text{X}_6$  blocks carry the connectivity existing in a  $\text{CdX}_2$  layer lattice, although here the units are fully condensed, so that any link-block description would be artificial. However, within derivative structures where there is still condensation of octahedra the connectivity they represent becomes significant. Their frequent occurrence suggests that such aggregates may exist in solution. They are present in  $\text{CdCl}_2 \cdot 2.5\text{H}_2\text{O}$ <sup>13</sup> as well separated units, though interconnected through chloride bridges. In **6a** they are linked linearly along chain **1**. In the hydrates **3** and **4** there is again this linear linking, but now with broadening through the sideways overlap of two such chains, the directions of which are marked by arrows in Figs. 2 and 3. It is noticeable that the cut (of a parent  $\text{CdX}_2$  lattice) to give the chains differs in the two cases, with the chains in **4** inclined to the length of the slab. Then the remaining variant of link-block condensation through repeated sharing of atoms in positions designated by the double arrows in Fig. 3, describes the double-chain structures of  $\text{CdX}_2 \cdot \text{L}$  derivatives<sup>7–9</sup> in relation to the  $\text{CdX}_2$  lattice.

*Single-chain Structures.*—Three distinct dmsO/ $\text{CdBr}_2$  single-chain types, as in compounds **5**, **6(2)** and **7** appear. They differ from any reported with other ligands, including that in  $[\{\text{CdI}_2(\text{pyo})_3\}_n]$ <sup>1</sup> of the same composition type as **6** (chain 2) and **7**. Structural features are summarised in Table 1. The variety of these chains is determined in part by the L: $\text{CdX}_2$  reactant ratios, but also by the differing abilities of dmsO and

\* These 'link-blocks' are shown throughout as projections of centre-and-spoke representations. However, equally, they can be described as blocks arising from condensation of four octahedra, as in refs. 8 and 13. These blocks then provide the basis for further condensation.

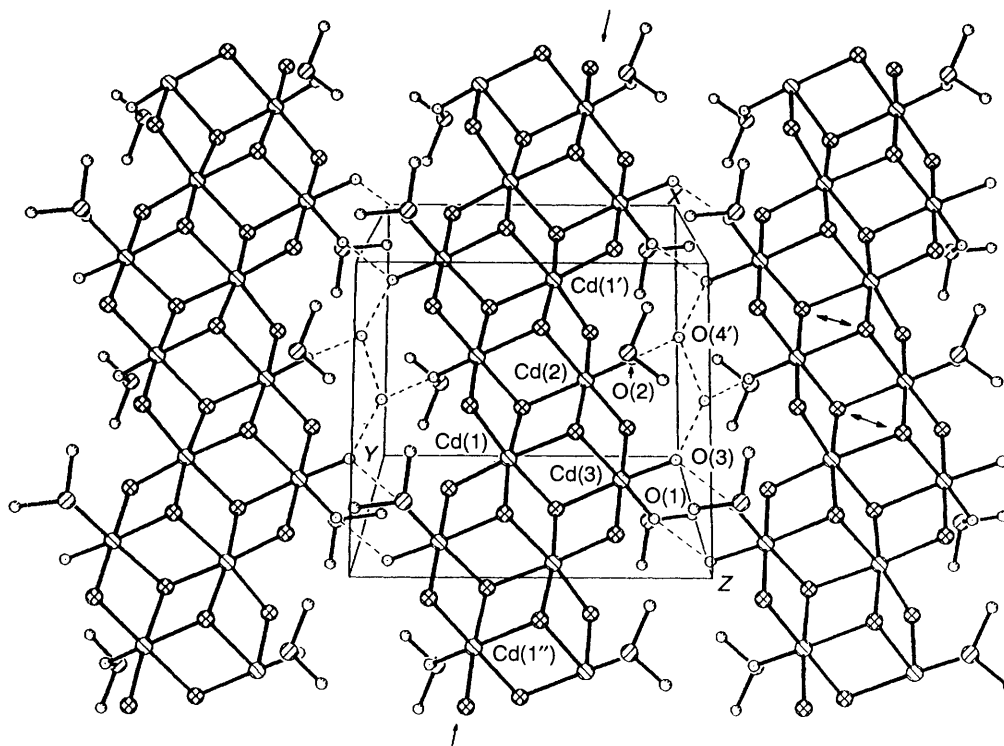


**Fig. 2** Upper: the connectivity within the slab structure of the hydrate 3. The arrows point to the two overlapping chains of link-blocks extending along the slab. Water molecules, O(2), provide weak interlayer hydrogen bonding to ligand O(1), with  $O(1) \cdots O(2)$  2.92 Å and  $O(2) \cdots O(2)$  2.56, 2.60 Å. Lower: a view looking along the chains in the [001] direction, showing the structural relationship to a  $CdBr_2$  layer lattice. Typical interlayer  $S \cdots Br$  approaches (3.8 Å) are shown by the broken lines

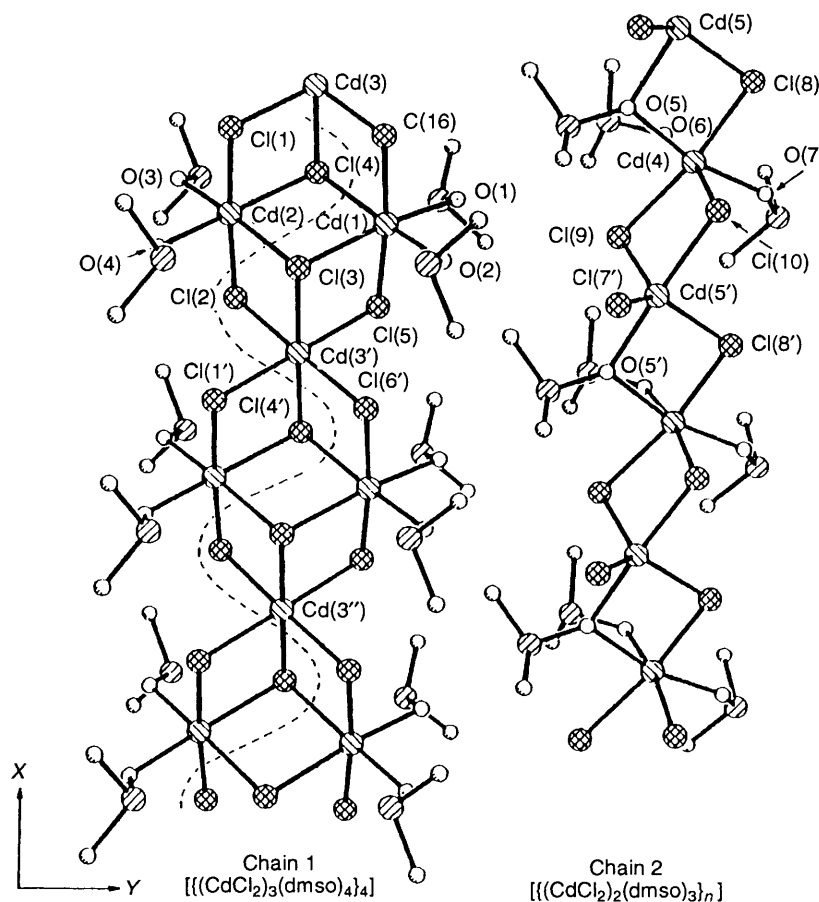
pyo towards terminal and bridging roles. The varying demands of chain development are met by the Cd switching between five- and six-co-ordination, with such centres in different combinations along the chains (Table 1). In delicately balanced situations, chain packing may control chain type, as with the differing  $(CdBr_2)_2(dmsO)_3$  chains which appear in **6** (chain 2) and **7**. It would seem that the chain 2 in **6** which does not appear elsewhere is stabilised through its lattice relationships. In most cases both dmsO and pyo single-chain structures show paired bridging (by O,O or X,X) between equivalent centres, but mixed (O,X) bridging between non-equivalent centres. However, chain 2 in **6/6a** is exceptional in having paired bridging between non-equivalent centres.

Co-ordination at the five-co-ordinate centres approximates to trigonal bipyramidal (*TBPY*), with bridging atoms always occupying the 'axial' positions to which there is weaker bonding (see Table 2). Ligand bridging distorts the angle between these axial bonds to 160–176°. In all chains the octahedral centres which alone bear terminally bonded dmsO are potentially cationic, and the *TBPY* centres with the higher proportion of Br/Cl are potentially anionic.

*Features of Cadmium Co-ordination.*—The octahedral co-ordination towards which a large  $Cd^{2+}$  centre tends is rather easily changed to five-co-ordination by constraints. There is six-co-ordination in the parent halides, and towards dmsO in the



**Fig. 3** The hydrate **4** containing both co-ordinated water, O(3), and interchain hydrogen-bonding water O(4). The interslab distances are shorter than those for **3**, with O(1)···O(3) 2.75, O(3)···O(4) 2.65 and O(2)···O(4) 2.85 Å. The link-block chains extending between Cd(1) centres are inclined at *ca.* 10.9° (ideally  $\tan^{-1} \sqrt{3/9}$ ) to the length of the slabs



**Fig. 4** The two chains existing in compounds **6** and **6a**. Two pairs of chains run through the cell in the direction of the *X* axis. In the extended structure there is hexagonal packing of chains, with each chain surrounded by two of the same kind and four of opposite kind

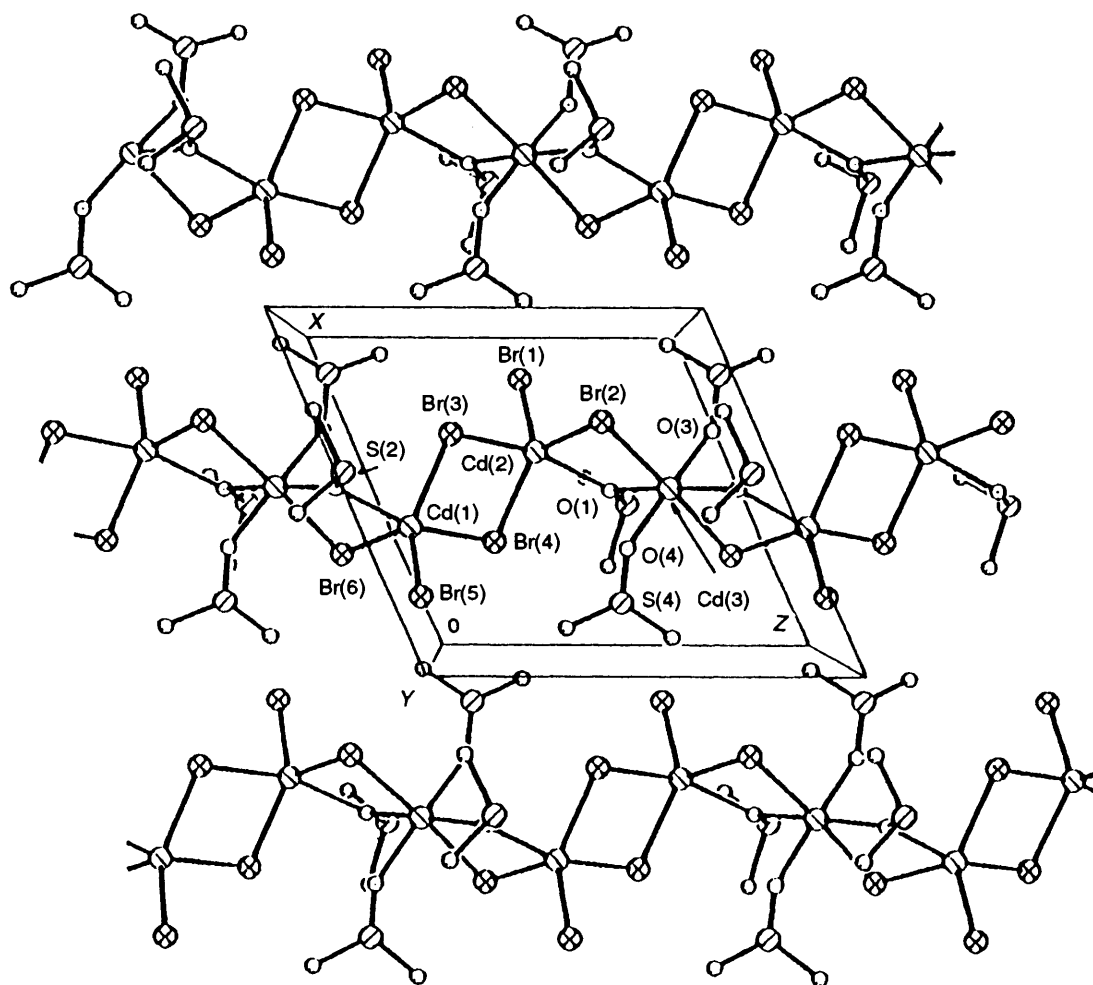


Fig. 5 The single-chain structure of  $[\{(CdBr_2)_3(dmsO)_4\}]_5$ . The differing environments provided by the bridging ligands towards the two five-coordinate cadmium centres are apparent

Table 1 Single-chain structures from cadmium halides

Chain composition	Cadmium co-ordination	Bridging pairs	TBPY axial atoms <sup>a</sup>
5 $(CdBr_2)_3(dmsO)_4$	5,5,6 <sup>b</sup>	Br, Br/O, Br	O, Br
6 $(CdX_2)_2(dmsO)_3$ <sup>c</sup>	5,6,5,6	X, X/O, X <sup>c</sup>	O, X
7 $(CdBr_2)_2(dmsO)_3$	5,5,6,6	Br, Br/O, Br	O, Br
$(CdI_2)_2(pyO)_3$ <sup>d</sup>	5,6,5,6	O, I	O, O
$CdI_2(pyO)$ <sup>e</sup>	5,5,5	I, I/O, O	O, I
$CdX_2 \cdot L_2$ <sup>f</sup>	6,6,6	X, X	—

<sup>a</sup> Atoms lying towards axial positions. They are always bridging atoms.

<sup>b</sup> The two five-co-ordination centres are non-equivalent. This is primarily due to the differing torsion angles around O-S in the two bridging ligands. <sup>c</sup> Chain 2 in 6 and 6a, which has X,X paired bridging between unlike centres. <sup>d</sup> Ref. 1. <sup>e</sup> Ref. 4. <sup>f</sup> Chains may be linear (ref. 3) or zigzag (ref. 5).

cation  $[Cd(dmsO)_6]^{2+}$  in 8 and 9, as also in the perchlorate.<sup>14</sup> However in the layer lattice of 1 the poorer bridging ability of dmsO than that of pyo causes half the cadmium centres to adopt five-co-ordination, cf.  $[\{(CdBr_2(pyO))_n\}]_n$  in which all cadmium centres are six-co-ordinate.<sup>1</sup> When 1 converts into the methanol solvate 2, or into the hydrates 3 and 4, all cadmium centres attain six-co-ordination and no dmsO bridging remains. The preferential bromide bridging in the hydrates contributes to the existence of the slab structures.

In the co-ordination behaviour of their halides cadmium differs sharply from zinc, which shows an overriding preference

towards forming tetrahedral derivatives, e.g.  $[ZnCl_2(pyO)_2]$  and  $[ZnI_2(dmsO)_2]$ ,<sup>15</sup> rather than chain formation. Then again, cadmium has no tendency to develop the strong digonal bonding shown by mercury.<sup>16</sup> In the present compounds where octahedral and TBPY axial distances can be matched across a bridging atom, the latter are invariably longer. For example in 5, Cd(2)-O(1) (axial) is 2.429(13), while Cd(3)-O(1) is 2.316(12) Å. The relationship would be reversed if cadmium were developing strong digonal bonding. Therefore in these respects the behaviour of cadmium is such that zinc, cadmium and mercury all show distinctive behaviour.

### Experimental

**Preparation of Complexes.**—It was usually possible to use hydrated halides, with triethoxymethane (tem) to provide dehydration. For  $[\{(CdBr_2(dmsO))_n\}]_n$  1,  $CdBr_2 \cdot 4H_2O$  (0.34 g, 1 mmol) was dissolved in boiling ethanol (3 cm<sup>3</sup>) and tem (1.5 cm<sup>3</sup>), with dmsO (0.07 cm<sup>3</sup>, 1 mmol). Crystals of 1 (0.15 g) slowly separated as diamond-shaped blocks from the cold solution [Found (Calc.): C, 7.0 (6.85); H, 1.7 (1.7); S, 8.5 (9.1)%]. As seen from Scheme 1, 1 can be converted into the hydrates, 3 and 4, and reversibly into the methanol solvate 2.<sup>10</sup> The hydrates and the methanol solvate, as also the products 7-9 were not sufficiently stable for dry solvent-free crystals to be obtained for elemental analysis. The identities of these compounds were established from the crystal structure determinations made at low temperature.

**Hydrates 3 and 4.** These were obtained by allowing a solution of  $CdBr_2 \cdot 4H_2O$  (2 mmol) in methanol (4 cm<sup>3</sup>) and tem (1.5 cm<sup>3</sup>)

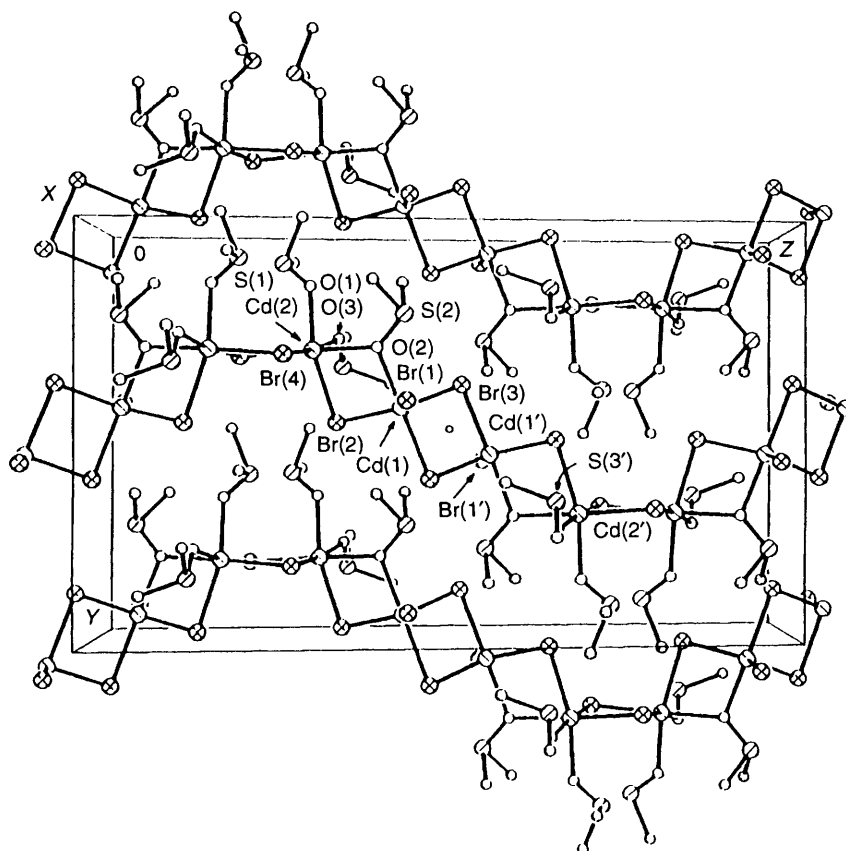


Fig. 6 The snake-like chains of  $[(\text{CdBr}_2)_2(\text{dmsO})_3]_n$  **7** within the cell. The co-ordination sequence is 5,5,6,6 as in the cross-linked chains in the layer lattice of **1**

Table 2 Bond lengths (Å) and angles (°) around five-co-ordinate centres<sup>a</sup>

$[(\text{CdBr}_2(\text{dmsO}))_n] \mathbf{1}$			
Cd(2)–Br(1')	2.583(2) <sup>b</sup>	Cd(2)–O(1)	2.414(6) <sup>c</sup>
Cd(2)–Br(2)	2.581(2) <sup>b</sup>	Br(4')–Cd(2)–O(1)	165.5(2)
Cd(2)–Br(4)	2.819(2) <sup>c</sup>		
Cd(2)–Br(4')	2.619(2) <sup>b</sup>		
$[(\text{CdBr}_2)_3(\text{dmsO})_4]_n \mathbf{5}$			
Cd(1)–Br(3)	2.653(2) <sup>b</sup>	Cd(2)–Br(3)	2.805(3) <sup>c</sup>
Cd(1)–Br(4)	2.806(3) <sup>c</sup>	Cd(2)–Br(4)	2.655(2) <sup>b</sup>
Cd(1)–Br(5)	2.537(3) <sup>d</sup>	Cd(2)–O(1)	2.429(13) <sup>c</sup>
Cd(1)–Br(6)	2.658(2) <sup>b</sup>		
Cd(1)–O(2)	2.402(14) <sup>c</sup>	O(2)–Cd(1)–Br(4)	161.4(3)
Cd(2)–Br(1)	2.563(3) <sup>d</sup>	O(1)–Cd(2)–Br(3)	159.8(3)
Cd(2)–Br(2)	2.627(3) <sup>b</sup>		
$[(\text{CdCl}_2)_5(\text{dmsO})_7]_n \mathbf{6a}$ (chain 2)			
Cd(5)–Cl(7)	2.439(3) <sup>d</sup>	Cd(5)–O(5)	2.422(7)
Cd(5)–Cl(8)	2.490(3) <sup>b</sup>		
Cd(5)–Cl(9')	2.524(3) <sup>b</sup>	O(5)–Cd(5)–Cl(10)	176.3(2)
Cd(5)–Cl(10')	2.634(3) <sup>c</sup>		
$[(\text{CdBr}_2)_2(\text{dmsO})_3]_n \mathbf{7}$			
Cd(1)–Br(1)	2.554(2) <sup>d</sup>	Cd(1)–O(2)	2.324(9) <sup>c</sup>
Cd(1)–Br(2)	2.632(2) <sup>b</sup>		
Cd(1)–Br(3)	2.668(2) <sup>b</sup>	O(2)–Cd(1)–Br(3')	169.5(3)
Cd(1)–Br(3')	2.770(2) <sup>c</sup>		

<sup>a</sup> Angles are given only for bonds between axial atoms. <sup>b</sup> Bridging atom in equatorial position. <sup>c</sup> Bridging atom in axial position. <sup>d</sup> Non-bridging atom; always equatorial.

with dmsO (0.15 cm<sup>3</sup>) to stand in a dish, loosely stoppered, so that methanol could slowly diffuse out and atmospheric

moisture gain access. Crystals of **2** and **1** formed first, but after a few weeks, depending on diffusion rates, they gave place to crystals of **7**, to be followed in turn by the hydrates **3** and **4**. The crystallisation of long needles of **3**, between the blocks of **7** and the prisms of **4**, served to indicate the progressive formation of these products. It did not prove possible to obtain the hydrates more directly from a water-containing solution.

**Crystallisation of Compound 5.** This was favoured by use of dmsO in 5 : 1 ligand : halide proportion, using CdBr<sub>2</sub>·4H<sub>2</sub>O (0.34 g) with dmsO (0.35 cm<sup>3</sup>) in ethanol (8 cm<sup>3</sup>) and tem (1.5 cm<sup>3</sup>). Monoclinic needles were obtained [Found (Calc.): C, 8.65 (8.5); H, 2.1 (2.1)%].

**The two-chain chloride**  $[(\text{CdCl}_2)_5(\text{dmsO})_7]_n$  **6a**. Conditions required the use of methanol in place of ethanol to enhance the solubility of cadmium chloride, but with dmsO in sufficient excess to avoid formation of the methanol solvate **2**. The compound CdCl<sub>2</sub>·2.5H<sub>2</sub>O (1 mmol) was dissolved with warming in methanol (3 cm<sup>3</sup>), tem (3 cm<sup>3</sup>) and dmsO (3 cm<sup>3</sup>). Needles of **6a** (0.17 g) crystallised after cooling. Unlike the methanol solvate, they were stable in air [Found (Calc.): C, 11.5 (11.5); H, 2.9 (2.9); S, 15.7 (15.3)%].

Needles of the isomorphous bromide **6** were obtained by careful addition of a lower layer of chloroform to a solution which would otherwise have produced only the ionic compound **8**. Cell parameters of **6**, which served to confirm its isomorphism with the chloride **6a** are  $a = 6.967(3)$ ,  $b = 35.345(24)$ ,  $c = 9.538(4)$  Å and  $\beta = 98.29(3)^\circ$ .

**The ionic compounds 8 and 9.** Crystals of  $[\text{Cd}(\text{dmsO})_6]^{2+} 2[\text{CdBr}_3(\text{dmsO})]^- \cdot \text{EtOH}$  **8** formed as poorly developed plates from a solution of CdBr<sub>2</sub>·4H<sub>2</sub>O (1 mmol) in an ethanol–tem–dmsO solvent mixture (1 cm<sup>3</sup> of each). The solubility of the compound is high, and some temperature reduction or addition of a few drops of diethyl ether was usually necessary to induce crystallisation. By adding an upper layer of ether to such a

Table 3 Crystal data, experimental conditions, and refinement

	$[(\text{CdBr}_2)(\text{dmsso})]_n$ 1	$[(\text{CdBr}_2)(\text{dmsso})]_n \cdot \text{H}_2\text{O}$ 3	$[(\text{CdBr}_2)_3(\text{dmsso})_2 \cdot (\text{H}_2\text{O})_n] \cdot n\text{H}_2\text{O}$ 4	$[(\text{CdBr}_2)_3(\text{dmsso})_4]_n$ 5	$[(\text{CdCl}_2)_5(\text{dmsso})_7]_n$ 6a	$[(\text{CdBr}_2)_2(\text{dmsso})_3]_n$ 7
<i>M</i>	350.4	368.4	1008.9	1129.1	1463.4	772.8
Crystal size (mm)	0.40 × 0.36 × 0.24	0.64 × 0.18 × 0.16	0.48 × 0.24 × 0.10	0.64 × 0.16 × 0.04	0.80 × 0.18 × 0.04	0.64 × 0.42 × 0.12
Crystal shape	Block	Needle	Block	Needle	Needle	Block
System	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic	Monoclinic
Space group ( <i>Z</i> )	$P2_1/c$ (8)	$C2/c$ (8)	$P2_1/c$ (4)	$P2_1/c$ (2)	$P2_1/c$ (2)	$C2/c$ (8)
<i>a</i> /Å	9.680(4)	16.484(5)	10.739(5)	9.590(4)	6.729(3)	10.499(6)
<i>b</i> /Å	16.307(9)	15.422(6)	11.757(6)	15.544(7)	34.948(16)	15.350(6)
<i>c</i> /Å	10.373(7)	6.941(3)	17.227(5)	10.264(4)	9.320(5)	25.411(14)
$\beta$ /°	109.15(4)	104.93(3)	101.52(4)	114.17(3)	97.89(4)	96.69(3)
<i>U</i> /Å <sup>3</sup>	1553.4(15)	1704.9(10)	2131.2(16)	1395.9(9)	2173(2)	4067(4)
<i>D<sub>c</sub></i> ( <i>D<sub>m</sub></i> )/g cm <sup>-3</sup>	3.015	2.854	3.145	2.687	2.237 (2.22, room temp.)	2.524
<i>F</i> (000)	1280	1344	1832	1044	1408	2848
$\mu$ (Mo-K $\alpha$ )/mm <sup>-1</sup>	13.25	12.01	14.30	11.06	3.39	10.17
Range <i>h</i>	0-11	-21 to 6	0-13	-11 to 11	0-7	-11 to 11
Range <i>k</i>	0-21	0-20	0-15	0-20	-41 to 41	0-16
Range <i>l</i>	-12 to 12	-9 to 9	-22 to 21	0-12	-11 to 10	0-27
Mode, $2\theta_{\text{max}}$	$\omega$ , 55°	$\omega$ , 55°	$\omega$ , 55°	$\omega$ , 50°	$\omega$ , 50°	$\omega$ , 45°
<i>R</i> <sub>int</sub>	0.0206	0.0160	0.0563	0.0083	0.0217	0.0477
Unique reflections	3046	1953	4878	3327	7536	2646
Reflections used	2136 ( <i>F</i> > 6 $\sigma$ ( <i>F</i> ))	1413 ( <i>F</i> > 6 $\sigma$ ( <i>F</i> ))	2714 ( <i>F</i> > 6 $\sigma$ ( <i>F</i> ))	2385 ( <i>I</i> > 3 $\sigma$ ( <i>I</i> ))	5959 ( <i>F</i> > 4 $\sigma$ ( <i>F</i> ) <sup>a</sup> )	2173 ( <i>F</i> > 6 $\sigma$ ( <i>F</i> ))
Transmission range	0.969-0.394	1.000-0.489	1.000-0.398	0.642-0.165	0.852-0.770	1.000-0.325
Parameters refined	122	74	172	222	387	161
Weighting, <i>g</i> ( <i>g</i> <sub>1</sub> <sup>a</sup> )	0.0006	0.0006	0.0004	0.0003	<i>g</i> <sub>1</sub> = 0.045 ( <i>g</i> <sub>2</sub> = 0) <sup>a</sup>	0.0009
$\Delta/\sigma$ (maximum)	0.001	0.002	0.020	0.020	< 0.001	0.001
Residual density <i>e</i> Å <sup>-3</sup>	1.93, -1.41	0.86, -0.95	1.32, -1.87	1.22, -1.12	0.73, -0.80	1.81, -2.22
<i>S</i>	1.22	1.01	1.44	1.18	1.01	2.07
<i>R</i> ( <i>R'</i> ) <sup>b</sup>	0.0386 (0.0433)	0.0251 (0.0342)	0.0453 (0.0515)	0.0400 (0.0378)	0.0385 (0.0898) <sup>a</sup>	0.0563 (0.0772)

<sup>a</sup> SHELX 93 was used for refinement of this structure to facilitate handling of a disordered dmsso ligand. Here *R'* is given by  $[\Sigma\{w(|F_o|^2 - |F_c|^2)\}]/\Sigma\{w|F_o|^2\}]^{1/2}$ , where  $w^{-1} = \sigma^2|F_o|^2 + (g_1P)^2 + g_2P$ , with  $P = (\text{max}|F_o|^2 + 2|F_c|^2)/3$ . <sup>b</sup>  $R = \Sigma|F_o| - |F_c|/\Sigma|F_o|$ ,  $R' = [\Sigma\{w|F_o| - |F_c|\}]/\Sigma\{w|F_o|\}]^{1/2}$ .

Table 4 Atomic coordinates

Atom	x	y	z	Atom	x	y	z
<b>[{CdBr<sub>2</sub>(dmsO)}<sub>n</sub>] 1</b>							
Cd(1)	403(1)	248(1)	3 324(1)	S(1)	-1 088(3)	1 856(2)	848(2)
Cd(2)	2 951(1)	-64(1)	-110(1)	C(11)	751(10)	2 168(7)	1 081(11)
Br(1)	2 638(1)	-316(1)	2 242(1)	C(12)	-1 422(11)	2 420(6)	2 177(11)
Br(2)	-1 331(1)	-969(1)	1 837(1)	O(2)	1 993(7)	1 281(4)	4 205(7)
Br(3)	1 568(1)	-775(1)	5 475(1)	S(2)	3 592(3)	1 070(2)	4 976(3)
Br(4)	5 227(1)	1 102(1)	619(1)	C(21)	4 609(11)	1 593(7)	4 097(11)
O(1)	-938(7)	949(4)	1 309(6)	C(22)	4 045(11)	1 715(7)	6 439(10)
<b>[{CdBr<sub>2</sub>(dmsO)}<sub>n</sub>·nH<sub>2</sub>O 3</b>							
Cd(1)	0	10 721(1)	2 500	S(1)	1 729(1)	6 897(1)	2 312(2)
Cd(2)	0	8 069(1)	2 500	C(11)	1 920(4)	6 020(4)	4 017(10)
Br(1)	991(1)	9 384(1)	1 415(1)	C(12)	1 960(4)	6 363(4)	267(9)
Br(2)	-965(1)	8 081(4)	-1 312(1)	O(2)	269(4)	5 708(3)	-4 103(11)
O(1)	776(2)	6 990(2)	1 693(5)				
<b>[{(CdBr<sub>2</sub>)<sub>3</sub>(dmsO)<sub>2</sub>(H<sub>2</sub>O)}<sub>n</sub>·nH<sub>2</sub>O 4</b>							
Cd(1)	3 208(1)	685(1)	5 009(1)	S(1)	4 183(3)	-3 767(3)	3 056(2)
Cd(2)	344(1)	-1 699(1)	4 883(1)	C(11)	5 556(13)	-3 617(14)	2 666(8)
Cd(3)	3 852(1)	-2 804(1)	4 844(1)	C(12)	3 749(18)	-5 178(14)	2 751(9)
Br(1)	2 807(1)	-1 349(1)	5 820(1)	O(2)	202(9)	-3 063(9)	5 781(5)
Br(2)	813(1)	276(1)	4 079(1)	S(2)	611(3)	-2 893(3)	6 684(2)
Br(3)	4 344(1)	-793(1)	4 023(1)	C(21)	-651(12)	-3 459(14)	7 097(9)
Br(4)	1 454(1)	-3 057(1)	3 944(1)	C(22)	1 761(14)	-3 998(15)	6 998(9)
Br(5)	3 765(1)	2 563(1)	4 264(1)	O(3)	3 635(9)	-4 411(8)	5 548(5)
Br(6)	2 012(1)	1 876(1)	6 004(1)	O(4)	1 385(11)	417(11)	262(8)
O(1)	4 653(8)	-3 875(8)	3 960(5)				
<b>[{(CdBr<sub>2</sub>)<sub>3</sub>(dmsO)<sub>4</sub>}<sub>n</sub>] 5</b>							
Cd(1)	3 958(1)	4 544	834(1)	O(1)	5 081(12)	3 074(8)	6 343(11)
Cd(2)	6 253(1)	3 661(1)	4 838(1)	O(4)	3 340(10)	4 940(8)	-3 934(10)
Cd(3)	5 148(1)	4 208(1)	-2 169(1)	O(3)	6 884(12)	3 461(9)	-395(11)
Br(4)	3 488(2)	3 434(2)	2 770(2)	O(2)	5 122(12)	5 239(8)	-561(12)
Br(6)	3 090(2)	3 419(1)	-1 300(2)	C(42)	936(17)	5 176(13)	-6 364(14)
Br(2)	7 115(2)	4 861(1)	6 811(2)	C(32)	9 516(18)	3 183(14)	-564(17)
Br(3)	6 745(2)	4 739(1)	2 876(2)	C(41)	662(18)	5 216(14)	3 849(19)
Br(1)	8 483(2)	2 631(2)	5 260(2)	C(22)	4 387(19)	6 760(14)	1 625(19)
Br(5)	1 913(2)	5 678(2)	392(2)	C(21)	7 360(21)	6 303(13)	-184(21)
S(3)	8 582(4)	3 687(4)	384(4)	C(31)	9 223(20)	3 007(14)	1 894(18)
S(4)	1 681(4)	4 623(3)	-4 684(4)	C(12)	2 692(19)	2 043(13)	5 450(18)
S(1)	4 629(4)	2 164(3)	6 661(4)	C(11)	5 509(20)	1 453(12)	5 886(17)
S(2)	5 583(5)	6 184(3)	-121(4)				
<b>[{(CdCl<sub>2</sub>)<sub>5</sub>(dmsO)<sub>7</sub>}<sub>n</sub>] 6a</b>							
Cd(1)	10 772(1)	0(1)	7 906(1)	O(4)	9 736(11)	-1 562(2)	9 160(7)
Cd(2)	11 164(1)	-989(1)	9 900(1)	S(4)	9 160(4)	-1 656(1)	7 552(3)
Cd(3)	15 980(1)	-500(1)	8 913(1)	C(41)	10 966(17)	-1 989(3)	7 140(13)
Cl(1)	14 102(4)	-1 152(1)	8 474(3)	C(42)	7 101(17)	-1 973(4)	7 529(14)
Cl(2)	8 180(3)	-784(1)	11 218(2)	Cd(4)	13 430(1)	2 171(1)	16 074(1)
Cl(3)	8 994(3)	-681(1)	7 486(2)	Cd(5)	18 194(1)	1 783(1)	14 904(1)
Cl(4)	12 957(3)	-305(1)	10 310(2)	Cl(7)	17 640(4)	1 246(1)	13 229(3)
Cl(5)	7 865(4)	149(1)	9 407(3)	Cl(8)	16 399(4)	2 407(1)	14 810(3)
Cl(6)	13 807(4)	-197(1)	6 624(3)	Cl(9)	10 597(3)	1 772(1)	17 234(2)
O(1)	11 906(12)	603(2)	8 460(8)	Cl(10)	11 239(4)	2 035(1)	13 671(3)
S(1)	12 099(6)	666(1)	10 146(4)	O(5)	15 334(10)	1 595(2)	16 060(7)
C(11)	14 522(27)	875(5)	10 533(17)	S(5)	14 592(4)	1 213(1)	16 638(3)
S(1)*	12 633(12)	928(2)	9 544(8)	C(51)	16 657(18)	897(3)	16 761(13)
C(11)*	13 900(49)	660(9)	11 034(32)	C(52)	13 104(17)	996(3)	15 153(13)
C(12)	10 584(18)	1 078(3)	10 306(13)	O(6)	14 889(11)	2 251(2)	18 410(7)
O(2)	9 246(11)	209(2)	5 749(7)	S(6)	15 487(4)	1 912(1)	19 417(3)
S(2)	8 971(4)	-57(1)	4 434(3)	C(61)	14 121(17)	1 972(4)	20 900(12)
C(21)	6 591(16)	68(4)	3 510(11)	C(62)	17 925(17)	2 034(3)	20 329(12)
C(22)	10 421(16)	144(3)	3 184(11)	O(7)	12 363(11)	2 788(2)	16 071(7)
O(3)	12 695(10)	-1 203(2)	12 079(7)	S(7)	11 634(5)	3 080(1)	17 095(3)
S(3)	13 014(4)	-925(1)	13 368(3)	C(71)	9 977(19)	2 830(4)	18 104(13)
C(31)	11 505(16)	-1 105(3)	14 660(11)	C(72)	13 637(18)	3 168(3)	18 508(11)
C(32)	15 398(16)	-1 047(4)	14 333(12)				
<b>[{(CdBr<sub>2</sub>)<sub>2</sub>(dmsO)<sub>3</sub>}<sub>n</sub>] 7</b>							
Cd(1)	637(1)	4 442(1)	4 398(1)	O(3)	-2 547(11)	2 811(10)	3 499(5)
Cd(2)	-625(1)	3 078(1)	3 183(1)	S(3)	-3 628(5)	3 426(4)	3 545(2)
Br(1)	3 074(2)	4 281(1)	4 487(1)	C(31)	-5 016(18)	2 715(17)	3 539(9)
Br(2)	-784(2)	4 795(1)	3 501(1)	C(32)	-3 516(23)	3 701(21)	4 226(8)
Br(3)	-509(2)	3 876(1)	5 217(1)	S(1)	-1 397(9)	977(6)	2 757(3)
Br(4)	-1 711(1)	3 205(1)	2 164(1)	C(12)	-927(34)	-101(24)	3 010(13)
O(1)	-755(10)	1 600(7)	3 146(4)	C(11)	-3 037(45)	1 013(29)	2 845(16)
O(2)	329(10)	2 994(6)	4 054(4)	C(11)*	-2 717(45)	680(30)	3 304(19)
S(2)	850(4)	2 268(2)	4 440(1)	S(1)*	-2 026(12)	1 268(8)	2 823(4)
C(21)	1 826(18)	1 621(12)	4 077(7)	C(12)*	-1 608(42)	399(29)	2 413(17)
C(22)	-488(16)	1 564(10)	4 437(6)				

\* Alternative position for atoms of disordered ligand.



solution, prismatic crystals of the alternative product **9** appeared at the interface.

Cell parameters showing the isomorphous relationship of compound **8** to the corresponding iodide  $[\text{Cd}(\text{dmsO})_6]^{2+} 2[\text{CdI}_3(\text{dmsO})]^- \cdot \text{EtOH}$  (crystals could be handled with lesser difficulty)<sup>2</sup> are  $a = 16.272(9)$ ,  $b = 16.887(12)$ ,  $c = 17.622(14)$  Å,  $\alpha$ ,  $\beta$  and  $\gamma = 90^\circ$ .

The bromide **9** was shown to be  $[\text{Cd}(\text{dmsO})_6]^{2+} [\text{CdBr}_4]^{2-}$ , but its structure has not been fully refined due to extensive disorder of the co-ordinated dmsO. Cell parameters are  $a = 9.780(10)$ ,  $b = 9.670(8)$ ,  $c = 17.650(10)$  Å,  $\alpha = 89.07(9)$ ,  $\beta = 79.03(9)$  and  $\gamma = 88.50(9)^\circ$ . The ion packing differs from that in the iodide  $[\text{Cd}(\text{dmsO})_6]^{2+} [\text{CdI}_4]^{2-}$ .<sup>2</sup>

**Crystal Structure Determinations.**—These followed our usual procedure<sup>17</sup> using a Nicolet R3M diffractometer with the crystal at *ca.* 180 K in a cold nitrogen stream. At low temperature the crystals were stabilised against deterioration. Cell parameters were from 25 well centred reflections. Experimental data for the individual crystals are given in Table 3. Structure solutions were by way of Patterson mapping of heavy atoms, and Fourier difference maps for other atoms, excepting hydrogen. For methyl groups, the latter were inserted at C–H distances of 0.96 Å with fixed isotropic thermal parameters (0.030 Å<sup>2</sup>), but were not positionally refined. For the water molecules in compounds **3** and **4** the hydrogen atoms were neither located nor inserted.

Space groups were initially determined from systematic absences, and were confirmed by successful refinement. For compounds **3** and **7** the space group  $C2/c$  was preferred over the alternative  $Cc$  the mean of the  $|E^2 - 1|$  values pointed to a centrosymmetric structure.<sup>18</sup> For compounds **5** and **6a** with the space group  $P2_1$ , the absolute configuration giving the better refinement has been adopted, but in the case of **6a** there is the complication arising from racemic twinning.

Refinement of the structures of compounds **7** and **6a** showed that in each case one dmsO ligand was disordered. For **7** the disorder [due to rotation about the Cd–O(1) bond] was handled by usual procedures. With **6a** the two alternative positions, arising from reflection through a plane containing the O(1)–C(12) vector, placed the alternative positions of C(11) too close for resolution using SHELXTL PC.<sup>18</sup> While this disorder would exert only minimal effects on resulting bond lengths, use of SHELXL 93<sup>19</sup> (kindly provided by Professor Sheldrick during its trial introduction) enabled a clear refinement of the alternative positions of both the S(1) and C(11) atoms. At the same time, the incorporation of the Flack parameter<sup>20</sup> in this program revealed the racemic twinning. Refinement of these twinning components gave their contributions as 65 and 35%.

With use of the SHELXTL PC package, in all cases except for **6a**, the quantity minimised in refinement was  $\Sigma[w(|F_o| - |F_c|)^2]$ , with reflection weights  $w^{-1} = [\sigma^2|F_o| + gF_o^2]$ . However with SHELXL 93 the function minimised was  $\Sigma[w(|F_o|^2 - |F_c|^2)]$ ,

with  $w^{-1} = [\sigma^2|F_o|^2 + (g_1P)^2 + g_2P]$ , where  $P = [\text{max}|F_o|^2 + 2|F_c|^2]/3$  (see Table 3 footnotes). Atomic coordinates are listed in Table 4.

Additional material available from the Cambridge Crystallographic Data Centre comprises H-atom coordinates, thermal parameters and remaining bond lengths and angles.

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### References

- 1 M. Nieuwenhuyzen, W. T. Robinson and C. J. Wilkins, *Polyhedron*, 1991, **10**, 2121.
- 2 M. Nieuwenhuyzen, Huo Wen and C. J. Wilkins, *Z. Anorg. Allg. Chem.*, 1992, **615**, 143.
- 3 A. Mitschler, J. Fischer and R. Weiss, *Acta Crystallogr.*, 1967, **22**, 236.
- 4 G. Sawitski and H.-G. von Schnering, *Chem. Ber.*, 1974, **107**, 3266.
- 5 G. Linte, H. Nöth and M. Thomann, *Z. Naturforsch., Teil B*, 1990, **45**, 1463.
- 6 D. M. Meek, R. S. Drago and T. S. Piper, *Inorg. Chem.*, 1962, **1**, 285; J. Reedijk, *Recl. Trav. Chim. Pays-Bas*, 1969, **88**, 499; J. Reedijk, W. L. Driessen and W. L. Groeneveld, *Rec. Trav. Chim. Pays-Bas*, 1969, **88**, 1095.
- 7 H. Leligny and J. C. Monier, *Acta Crystallogr., Sect. B*, 1974, **30**, 305.
- 8 M. Nardelli, L. Coghi and G. Azzoni, *Gazz. Chim. Ital.*, 1958, **88**, 235; M. Nardelli and L. Coghi, *Ric. Sci.*, 1958, **28**, 379.
- 9 A. Hazell and R. G. Hazell, *Acta Crystallogr., Sect. C*, 1991, **47**, 730.
- 10 M. Nieuwenhuyzen, W. T. Robinson and C. J. Wilkins, *Acta Crystallogr., Sect. C*, 1993, **49**, 1173.
- 11 L. Pauling and J. Sherman, *Z. Kristallogr.*, 1937, **96**, 481.
- 12 W. J. Hehre, L. Radom, P. v. R. Schleyer and J. A. Pople, *Ab. Initio Molecular Orbital Theory*, Wiley, New York, 1986, pp. 182, 335.
- 13 H. Leligny and J. C. Monier, *Acta Crystallogr., Sect. B*, 1975, **31**, 728.
- 14 M. Sandström, *Acta Chem. Scand., Ser. A*, 1978, **32**, 519.
- 15 N. M. McConnell, R. O. Day and J. S. Wood, *Acta Crystallogr., Sect. C*, 1986, **42**, 1094; S. Jin, M. Nieuwenhuyzen, W. T. Robinson and C. J. Wilkins, *Acta Crystallogr., Sect. C*, 1992, **48**, 274.
- 16 L. E. Orgel, *An Introduction to Transition Metal Chemistry*, Methuen, London, 1960, p. 66; D. Grdenić, *Q. Rev. Chem. Soc.*, 1965, **19**, 303.
- 17 W. T. Robinson, C. J. Wilkins and Z. Zhang, *J. Chem. Soc., Dalton Trans.*, 1988, 2187.
- 18 G. M. Sheldrick, SHELXTL PC, An Integrated System for Data Collection, Processing, and Structure Solution and Refinement, Siemens Analytical X-Ray Instruments, Madison, WI, 1990.
- 19 G. M. Sheldrick, SHELX 93, Siemens Analytical X-Ray Instruments, Madison, WI, 1993.
- 20 H. D. Flack, *Acta Crystallogr., Sect. A*, 1983, **39**, 876.

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