Synthesis and Structures of Tetranuclear 2-(Dimethylamino)ethanethiolato Complexes of Zinc, Cadmium and Mercury involving both Primary and Secondary Metal–Halogen Bonding

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Two series of complexes of Zn, Cd and Hg with 2-(dimethylamino)ethanethiolate (L) ligands have been prepared. Complexes $[M_4L_4X_4]$ (series **I**) (X = Cl or Br) are obtained from anhydrous MX_2, HL·HX and triethylamine in acetonitrile, and also from the metal acetate, HL·HX and sodium hydroxide in aqueous solution. Treatment of $[Cd_4L_4X_4]$ with NaL in acetonitrile–methanol gives $[Cd_4L_6X_2]$ (series **II**, Cd only). The structures of two complexes of series **I**, $[Cd_4L_4Br_4]$ **1** and $[Hg_4L_4Cl_4]$ **2**, and of the series **II** complex $[Cd_4L_6Cl_2]$ **3**, have been determined crystallographically, and are probably representative of the two series. All have a central centrosymmetric M_4S_4 eight-membered ring in an extended-chair conformation with two opposite M atoms disposed one on each side of the M'_2S_4 plane, and with aminothiolate ligands which are both S,N-chelating to M′ atoms and S-bridging between M and M′ atoms. The additional L ligands in **3** chelate the out-of-plane M atoms. The halogen atoms in **1** and **2** are terminally bonded to the M atoms, but two of them are also weakly bonded to both M′ atoms to give incipient triple bridging. In complex **3** the Cl atoms bridge the two M′ atoms and are only weakly bonded to one M atom each. These patterns of primary and secondary M–X bonding are compared with those in other structures having a similar central $X_2M_2M'_2S_4$ core.

As part of our continuing interest in the fundamental chemistry of metal thiolate complexes, and because of the special relevance of zinc,[1] cadmium[2] and mercury[3] in biological systems, we have extended our previous work on the structural characterization[4] and solution equilibria studies[5] of complexes of Zn^{II}, Cd^{II} and Hg^{II} with aliphatic γ-mercaptoamine ligands to those with β-mercaptoamines. The main difference between these two types of ligand is that, while the former often co-ordinate through the sulphur atom exclusively,[4] nitrogen tends to participate in metal binding in the case of the latter.[6]

We have recently described the electrochemical synthesis and structure of a mononuclear zinc(II) complex of 2-(dimethylamino)ethanethiol[7] which closely resembles models proposed for zinc(II) co-ordination in Transcription Factor IIIA.[1] We now report the synthesis of complexes of formula $[M_4\{S(CH_2)_2NMe_2\}_4X_4]$ **I** for M = Zn, Cd or Hg and X = Cl or Br, and of related complexes $[M_4\{S(CH_2)_2NMe_2\}_6X_2]$ **II** for M = Cd, X = Cl or Br. The crystal structures of **I** for M = Cd, X = Br (**1**) and for M = Hg, X = Cl (**2**), as well as that of **II** for M = Cd, X = Cl (**3**), are also described.

Experimental

Synthesis.—2-(Dimethylamino)ethanethiol hydrochloride was obtained commercially. As it is a hygroscopic and easily oxidized material, however, its purity was always checked before use by iodometric determination of the SH content. It was converted into the hydrobromide by means of an anionic exchange resin, Dowex 11, which was first treated several times with 2 mol dm^{-3} sodium hydroxide solution at 60 °C and washed with distilled water; then the same procedure was repeated with 2 mol dm^{-3} hydrobromic acid solution. A solution of 2-(dimethylamino)ethanethiol hydrochloride (2 g) in distilled water (25 cm^3) was slowly eluted and the resin washed with distilled water (20 cm^3). Vacuum evaporation of the solvent and drying the solid residue with diethyl ether yielded a white solid whose SH and halide contents were determined: SH, 88.0% of theoretical; Br, 41.6%; Cl, 3.2% of total mass. Calculated for $HS(CH_2)_2NMe_2{\cdot}HBr$: Br, 42.9; Cl, 0%.

Anhydrous halides of zinc, cadmium and mercury were commercial samples, as were the corresponding acetates, which were dihydrates in the case of zinc and cadmium. Solvents were stored over molecular sieves before use. Other reagents were research grade and were not further purified.

Preparation of Complexes.—All complexes of formula $[M_4\{S(CH_2)_2NMe_2\}_4X_4]$ **I**, with M = Zn, Cd or Hg and X = Cl or Br, were obtained by the same general procedures. Reagents and their quantities used in each case are given in Table 1. The amount of the ligand is given only in mmol because this refers to the pure material; the corresponding weight used depended on its previously determined SH content.

(*i*) 2-(Dimethylamino)ethanethiol hydrohalide was dispersed in acetonitrile (40 cm^3). Triethylamine and the anhydrous metal halide were successively added with stirring under a nitrogen atmosphere. Stirring was continued for 24 h. The resulting

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† *Supplementary data available:* see Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1991, Issue 1, pp. xviii–xxii.

Table 1 Reagents used in the syntheses

Complex $[M_4\{S(CH_2)_2NMe_2\}_4X_4]$		Reagents					
		$HS(CH_2)_2NMe_2{\cdot}HX$	NEt_3		MX_2		
M	X	(mmol)	cm^3	mmol	g	mmol	Yield (%)
Zn	Cl	10	2.8	20	1.35	10	52
Zn	Br	5	1.4	10	1.40	5	52
Cd	Cl	10	2.8	20	1.83	10	58
Cd	Br	5	1.4	10	1.36	5	61
Hg	Cl	10	2.8	20	2.71	10	62
Hg	Br	5	1.4	10	1.80	5	59
$[M_4\{S(CH_2)_2NMe_2\}_6X_2]$		$[M_4\{S(CH_2)_2NMe_2\}_4X_4]$	$HS(CH_2)_2NMe_2{\cdot}HX$		NaOMe		
M	X	(mmol)	(mmol)		g	mmol	Yield (%)
Cd	Cl	0.32	1.4		0.22	4	16
Cd	Br	0.31	1.4		0.22	4	15

Table 2 Analytical data with calculated values in parentheses

Complex	Analysis (%) C	N	S	X
$[Zn_4\{S(CH_2)_2NMe_2\}_4Cl_4]$	23.35 (23.45)	6.75 (6.85)	15.40 (15.65)	17.40 (17.30)
$[Zn_4\{S(CH_2)_2NMe_2\}_4Br_4]$	19.85 (19.25)	5.85 (5.60)	12.90 (12.85)	31.15 (32.00)
$[Cd_4\{S(CH_2)_2NMe_2\}_4Cl_4]$	19.30 (19.05)	5.70 (5.55)	12.70 (12.70)	14.25 (14.05)
$[Cd_4\{S(CH_2)_2NMe_2\}_4Br_4]$	16.45 (16.20)	4.75 (4.70)	11.00 (10.80)	26.90 (26.95)
$[Hg_4\{S(CH_2)_2NMe_2\}_4Cl_4]$	14.15 (14.10)	4.20 (4.10)	9.45 (9.40)	* (10.40)
$[Hg_4\{S(CH_2)_2NMe_2\}_4Br_4]$	12.45 (12.50)	3.70 (3.65)	8.45 (8.35)	* (20.75)
$[Cd_4\{S(CH_2)_2NMe_2\}_6Cl_2]$	24.85 (25.15)	7.35 (7.35)	17.00 (16.80)	6.25 (6.20)
$[Cd_4\{S(CH_2)_2NMe_2\}_6Br_2]$	23.10 (23.35)	6.50 (6.80)	15.65 (15.60)	13.00 (12.95)

* Could not be determined by electrochemical titration.

suspension was filtered in the open atmosphere, washed with copious cold distilled water, then with methanol and diethyl ether, and vacuum dried. Yields were always greater than 50% (Table 1). Analytical data are given in Table 2.

(*ii*) Alternatively, complexes with the same empirical formulae were obtained by adding an aqueous solution of equimolar amounts of 2-(dimethylamino)ethanethiol hydrohalide and sodium hydroxide to an aqueous solution of the metal acetate, the metal:ligand molar ratio being always 1:1. Manipulations were carried out under an inert atmosphere. A white powder formed immediately. The mixture was stirred for several hours, the solid was filtered off, washed with cold water and then methanol, and dried under vacuum. Analytical results and infrared spectra were essentially identical to those of the corresponding complexes obtained in organic media.

The complexes are very stable in the open atmosphere and highly insoluble in water and common organic solvents. Crystals suitable for X-ray diffraction were obtained by refluxing each product in dimethyl sulphoxide (dmso), filtering off the undissolved solid, letting the solution cool to 60 °C, and maintaining it at this temperature for 24 h. All these manipulations were performed under a nitrogen atmosphere.

For the preparation of complexes of formula $[Cd_4\{S(CH_2)_2NMe_2\}_6X_2]$ **II** with X = Cl or Br, a solution of the sodium thiolate $NaS(CH_2)_2NMe_2$ (freshly prepared by mixing the corresponding hydrochloride with sodium methoxide in a 1:2 ratio in methanol) was added to a suspension of an equimolar amount of $[Cd\{S(CH_2)_2NMe_2\}X]$ in acetonitrile under an inert atmosphere. The reaction mixture was stirred under nitrogen overnight. The filtered solution was concentrated until a colourless solid separated out. This was filtered off, washed with acetonitrile, dried under vacuum, and then recrystallized from methanol. To increase the overall yield, the filtrate from the reaction was evaporated to dryness and the solid residue recrystallized from methanol; several crops of crystals could be obtained in this way. Analytical data for both complexes (X = Cl or Br) are given in Table 2.

These complexes are soluble in methanol, ethanol and dmso, but decompose in water. Suitable crystals for X-ray diffraction (X = Cl) were obtained by slow evaporation of methanol solutions under an inert atmosphere.

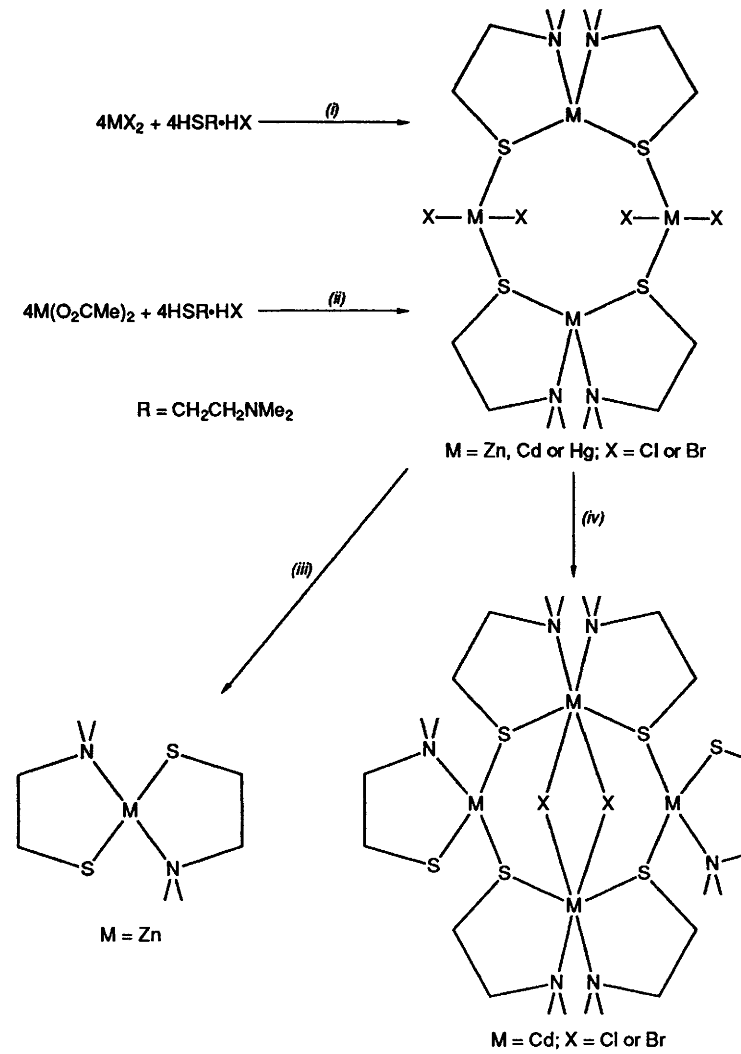
Instrumentation.—Microanalyses were performed with a Carlo Erba NA-1500 analyser. Halide content was determined electrochemically by the Servei de Microanàlisi del CID (CSIC), Barçelona. Infrared spectra in the range 4000–400 cm^{-1} were recorded from KBr discs on a Perkin-Elmer 1710 spectrophotometer. X-Ray powder diffraction traces were obtained on a Siemens D-500 diffractometer with graphite-monochromated Cu-Kα radiation.

X-Ray Crystallography.—Three structures were determined from single-crystal X-ray diffraction data, collected at room temperature on four-circle diffractometers with graphite-monochromated radiation. Crystallographic data are summarized in Table 3. Empirical[11] or semiempirical[12] absorption corrections were applied in each case. Refinement was by least-squares methods,[12–14] to minimize $\Sigma w\Delta^2$, $\Delta = |F_o| - |F_c|$. Anisotropic thermal parameters were refined for non-H atoms, H atoms were included in calculated positions with isotropic thermal parameters. Extinction effects were negligible. Atomic scattering factors were taken from ref. 15. The weighting schemes were empirical, based on an analysis of the variances for each structure: for **1**, $w^{-1} = (a + b|F_o|)^2(c + d\sin\theta/\lambda)$ with different values for a, b, c and d for various ranges of $|F_o|$ and $\sin\theta/\lambda$; for **2**, $w^{-1} = \sigma^2(F) + 0.0063F_o^2$; for **3**, $w^{-1} = \sigma^2(F) = \sigma_c^2(F) + 70 - 94G + 677G^2 - 166H + 106H^2 - 88GH$ ($G = F_o/F_{max}$, $H = \sin\theta/\sin\theta_{max}$, σ_c from counting statistics only).[16] Refined coordinates are given in Tables 4–6, bond lengths and angles in Tables 7–9.

Additional material available from the Cambridge Crystallographic Data Centre comprises thermal parameters and H-atom coordinates.

Results and Discussion

Synthesis.—Reactions which have given pure, characterized products are summarized in Scheme 1. Two different synthetic



Scheme 1 (*i*) NEt_3, MeCN; (*ii*) NaOH, water; (*iii*) excess of NaSR, MeCN–MeOH; (*iv*) 4NaSR, MeCN–MeOH

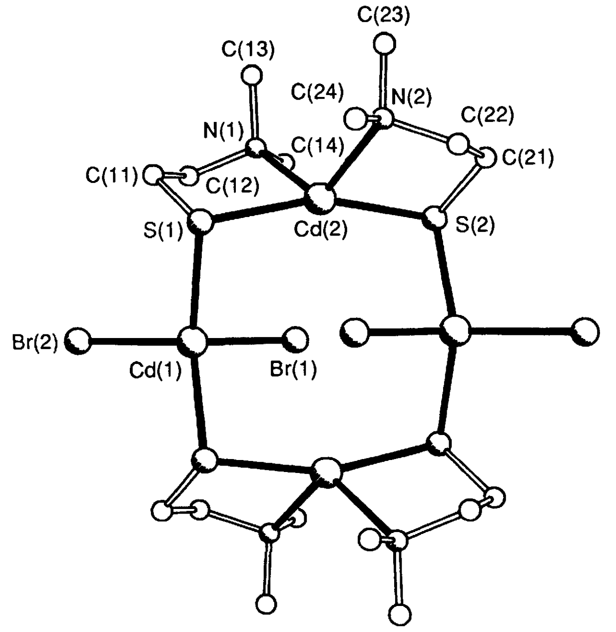


Fig. 1 Molecular structure of complex **1**, with the labelling of the independent atoms; H atoms are omitted

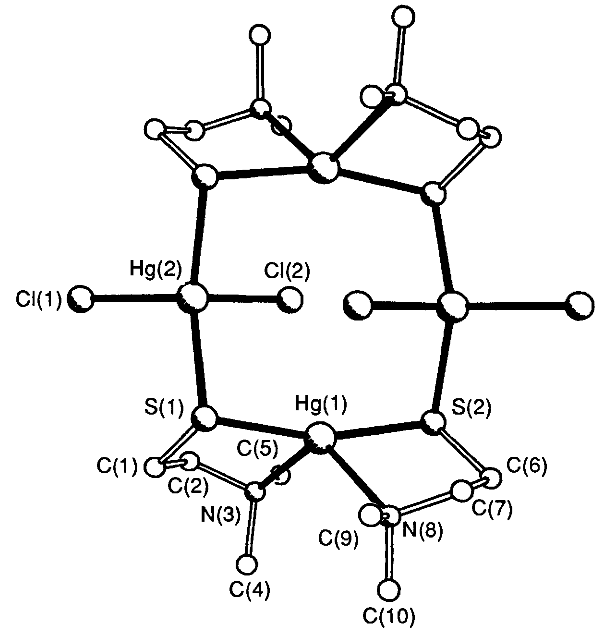


Fig. 2 Molecular structure of complex **2**, with the labelling of the independent atoms; H atoms are omitted

routes which differed in the reaction medium (organic or aqueous) have led to the same family of complexes of empirical formula $[M\{S(CH_2)_2NMe_2\}X]$, where M = Zn, Cd or Hg, X = Cl or Br. Their high insolubility, independent of the metal or halide used, suggested an oligomeric or polymeric structure.

Treatment of the above cadmium complexes in organic

Table 3 Crystallographic data

Complex	**1**	**2**	**3**
Formula	$C_{16}H_{40}Br_4Cd_4N_4S_4$	$C_{16}H_{40}Cl_4Hg_4N_4S_4$	$C_{24}H_{60}Cd_4Cl_4Cl_2N_6S_6$
M	1186.0	1360.9	1145.6
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/n$	$P2_1/c$
a/Å	9.3977(4)	13.960(3)	12.846(1)
b/Å	13.4993(11)	13.107(3)	13.109(1)
c/Å	13.9005(12)	9.563(2)	13.456(1)
β/°	108.675(4)	110.60(2)	109.130(7)
U/Å^3	1670.6	1637.9	2140.8
Z	2	2	2
D_c/g cm^{-3}	2.357	2.759	1.777
Radiation, λ/Å	Cu-Kα, 1.541 84	Mo-Kα, 0.710 69	Mo-Kα, 0.710 73
μ/mm^{-1}	28.83	19.28	2.39
F(000)	1120	1232	1136
Crystal size/mm	0.07 × 0.07 × 0.33	0.08 × 0.08 × 0.15	0.16 × 0.48 × 0.54
Diffractometer	Philips PW1100	Philips PW1100	Stoe-Siemens
Laboratory	Madrid	Barcelona	Newcastle[8]
No. reflections for cell, 2θ range/°	27, 4–90	25, 8–24	32, 20–25
Scan type	ω–2θ	ω	ω–θ
$2\theta_{max}$/°	130	50	50
Transmission factors	0.56–1.26*	0.81–0.94	0.30–0.47
Reflections measured	2847	1947	9097
Unique reflections	2847	1723	3748
Observed reflections	2638	1286	3444
Observation criterion	$I > 2\sigma(I)$	$I > 2.5\sigma(I)$	$F > 4\sigma_c(F)$
R_{int}	—	0.034	0.027
Solution method	Direct methods[9]	Patterson[10]	Patterson[10]
R	0.048	0.036	0.039
$R' = (\Sigma w\Delta^2/\Sigma wF_o^2)^{\frac{1}{2}}$	0.055	0.037	0.031
No. of parameters	145	146	209
Mean, max. shift/e.s.d.	0.01, 0.05	0.1, 0.3	0.006, 0.09
Max., min. electron density/e Å^{-3}	0.93, −0.72	0.4, −0.4	1.30, −0.70

* Relative, not absolute values.

Table 4 Atomic coordinates (× 10^4) for complex **1**

Atom	*x*	*y*	*z*
Cd(1)	2868.2(9)	−28.6(6)	3321.9(6)
Cd(2)	4193.4(8)	−1764.2(6)	5491.8(5)
Br(1)	3173(1)	638(1)	5194(1)
Br(2)	192(2)	164(1)	2072(1)
S(1)	3224(3)	−1868(2)	3596(2)
S(2)	5455(3)	−1123(2)	7241(2)
N(1)	1659(9)	−2079(7)	5354(6)
N(2)	5873(10)	−3115(6)	6057(7)
C(11)	1297(13)	−2199(9)	3487(8)
C(12)	744(12)	−1779(10)	4328(9)
C(13)	1385(18)	−3123(12)	5512(11)
C(14)	1198(14)	−1494(11)	6091(10)
C(21)	6714(12)	−2168(8)	7715(8)
C(22)	7147(13)	−2720(9)	6894(9)
C(23)	5302(17)	−3972(10)	6452(11)
C(24)	6465(17)	−3473(11)	5254(10)

Table 5 Atomic coordinates (× 10^4) for complex **2**

Atom	*x*	*y*	*z*
Hg(1)	512.8(1)	1763.5(1)	1301.0(1)
Hg(2)	−1669.8(1)	45.5(1)	406.0(1)
S(1)	−1328(1)	1910(1)	445(1)
S(2)	2233(1)	1175(1)	1745(1)
Cl(1)	−2872(1)	−183(1)	1807(1)
Cl(2)	157(1)	−677(1)	2017(1)
C(1)	−1457(2)	2276(2)	2232(3)
C(2)	−616(2)	1731(2)	3663(3)
N(3)	399(1)	2092(2)	3775(3)
C(4)	509(2)	3190(3)	4222(5)
C(5)	1120(2)	1432(2)	5023(3)
C(6)	2779(2)	2201(2)	946(3)
C(7)	1940(3)	2774(2)	−250(3)
N(8)	1103(1)	3194(1)	63(3)
C(9)	356(2)	3581(3)	−1419(3)
C(10)	1504(2)	4049(2)	1093(3)

medium with sufficient additional thiolate to substitute all the halide ions has always led to displacement of only half of them. The complexes thus obtained have a stoichiometric empirical formula of $[Cd_2\{S(CH_2)_2NMe_2\}_3X]$ (X = Cl or Br), and show a greater solubility in polar organic solvents than their precursors. The corresponding substitution reactions for zinc and mercury complexes were not successful, yielding only intractable oily products.

The addition of a great excess of sodium thiolate to $[Zn\{S(CH_2)_2NMe_2\}X]$ (X = Cl or Br) produced a previously reported zinc thiolate complex, $[Zn\{S(CH_2)_2NMe_2\}_2]$.[7] In the case of cadmium and mercury no pure products could be isolated.

Infrared Spectra.—The infrared spectra of complexes **I** compare very well. The most significant feature common to them all is the appearance of only one broad (3000–2800 cm^{-1}) band in the region 3000–2500 cm^{-1}, with well resolved vibrational structure. On comparison of these spectra with that of free 2-(dimethylamino)ethanethiol, the absence of an intense absorption at 2780 cm^{-1}, assigned to ν(CH_3–N), indicates clearly that the complexed ligands behave as chelates. The relationship between infrared absorptions in the region 3000–2500 cm^{-1} and ligand-bonding behaviour has already been discussed for complexes of β-[7] and γ-mercaptoamines.[17,18]

The S,N-chelating behaviour of 2-(dimethylamino)ethanethiolate and the stoichiometric ratio in complexes **I** would be compatible with a structure consisting of discrete species of formula [XM(μ-SR)$_2$MX], already found for square-planar Pd^{II} and Pt^{II} with chelating γ-mercaptoamine ligands,[18] but unreported yet for such ligands with metals preferring tetrahedral co-ordination. However, nitrogen binding, as evidenced

Table 6 Atomic coordinates (× 10^4) for complex **3**

Atom	*x*	*y*	*z*
Cd(1)	2331.7(2)	1042.2(3)	1257.8(2)
Cd(2)	699.9(2)	−727.4(2)	−990.2(2)
Cl	760.6(7)	−809.8(7)	1057.4(7)
S(1)	3710.4(13)	218.4(16)	2767.7(15)
S(2)	2285.6(7)	555.5(7)	−585.8(8)
S(3)	781.3(7)	2110.6(7)	1480.5(8)
N(1)	3734(3)	2444(5)	1618(4)
C(11)	4737(7)	1195(10)	3125(9)
C(12)	4793(5)	1842(9)	2210(9)
C(13)	3910(10)	2834(11)	696(9)
C(14)	3547(7)	3185(8)	2315(13)
N(2)	2356(3)	−1935(3)	−460(3)
C(21)	3456(3)	−337(4)	−293(5)
C(22)	3289(3)	−1321(3)	192(4)
C(23)	2627(4)	−2425(4)	−1315(5)
C(24)	2114(4)	−2765(4)	191(5)
N(3)	−144(3)	662(3)	2964(3)
C(31)	1154(5)	2079(4)	2925(4)
C(32)	202(5)	1693(4)	3311(4)
C(33)	−1083(7)	379(6)	3299(6)
C(34)	746(7)	−89(5)	3413(4)

Table 7 Bond lengths (Å) and angles (°) for complex **1**

Cd(1)–Br(1)	2.681(2)	Cd(1)–Br(2)	2.572(1)
Cd(1)–S(1)	2.518(3)	Cd(1)–S(2′)	2.510(3)
Cd(2)–S(1)	2.501(2)	Cd(2)–S(2)	2.494(2)
Cd(2)–N(1)	2.366(9)	Cd(2)–N(2)	2.375(9)
S(1)–C(11)	1.824(12)	S(2)–C(21)	1.823(11)
N(1)–C(12)	1.467(13)	N(1)–C(13)	1.463(19)
N(1)–C(14)	1.465(18)	N(2)–C(22)	1.476(13)
N(2)–C(23)	1.455(18)	N(2)–C(24)	1.480(20)
C(11)–C(12)	1.533(18)	C(21)–C(22)	1.524(18)
Br(2)–Cd(1)–S(1)	104.8(1)	Br(1)–Cd(1)–S(1)	102.5(1)
Br(1)–Cd(1)–Br(2)	113.5(1)	Br(1)–Cd(1)–S(2′)	102.3(1)
Br(2)–Cd(1)–S(2′)	107.6(1)	S(1)–Cd(1)–S(2′)	126.3(1)
S(1)–Cd(2)–S(2)	161.0(1)	S(1)–Cd(2)–N(1)	83.5(2)
S(2)–Cd(2)–N(1)	106.1(2)	S(1)–Cd(2)–N(2)	106.6(2)
S(2)–Cd(2)–N(2)	83.4(2)	N(1)–Cd(2)–N(2)	115.7(3)
Cd(1)–S(1)–Cd(2)	95.2(1)	Cd(1)–S(1)–C(11)	98.6(4)
Cd(2)–S(1)–C(11)	96.8(4)	Cd(2)–S(2)–Cd(1′)	93.5(1)
Cd(2)–S(2)–C(21)	97.7(4)	Cd(1′)–S(2)–C(21)	101.1(4)
Cd(2)–N(1)–C(12)	106.9(7)	Cd(2)–N(1)–C(13)	112.5(8)
Cd(2)–N(1)–C(14)	111.2(7)	C(12)–N(1)–C(13)	109.6(9)
C(12)–N(1)–C(14)	108.6(9)	C(13)–N(1)–C(14)	108.0(10)
Cd(2)–N(2)–C(22)	105.6(6)	Cd(2)–N(2)–C(23)	116.7(9)
Cd(2)–N(2)–C(24)	111.8(7)	C(22)–N(2)–C(23)	107.1(9)
C(22)–N(2)–C(24)	107.8(10)	C(23)–N(2)–C(24)	107.3(10)
S(1)–C(11)–C(12)	114.6(8)	C(11)–C(12)–N(1)	113.8(9)
S(2)–C(21)–C(22)	114.0(8)	C(21)–C(22)–N(2)	115.0(10)

Symmetry operator for primed atoms: $1 - x, -y, 1 - z$.

Table 8 Bond lengths (Å) and angles (°) for complex **2**

Hg(1)–S(1)	2.415(1)	Hg(1)–S(2)	2.414(1)
Hg(1)–N(3)	2.464(2)	Hg(1)–N(8)	2.506(2)
Hg(2)–S(1)	2.487(1)	Hg(2)–S(2′)	2.504(1)
Hg(2)–Cl(1)	2.506(1)	Hg(2)–Cl(2)	2.648(1)
S(1)–C(1)	1.844(3)	S(2)–C(6)	1.839(3)
N(3)–C(2)	1.462(3)	N(3)–C(4)	1.494(3)
N(3)–C(5)	1.529(3)	N(8)–C(7)	1.414(4)
N(8)–C(9)	1.521(3)	N(8)–C(10)	1.467(3)
C(1)–C(2)	1.621(4)	C(6)–C(7)	1.517(4)
S(2)–Hg(1)–S(1)	163.6(1)	N(3)–Hg(1)–S(1)	83.8(1)
N(3)–Hg(1)–S(2)	106.4(1)	N(8)–Hg(1)–S(1)	105.6(1)
N(8)–Hg(1)–S(2)	81.4(1)	N(8)–Hg(1)–N(3)	117.8(1)
Cl(1)–Hg(2)–S(1)	105.7(1)	Cl(2)–Hg(2)–S(1)	101.7(1)
Cl(2)–Hg(2)–Cl(1)	109.6(1)	S(2′)–Hg(2)–S(1)	130.0(1)
S(2′)–Hg(2)–Cl(1)	106.7(1)	S(2′)–Hg(2)–Cl(2)	102.1(1)
Hg(1)–S(1)–Hg(2)	95.9(1)	Hg(1)–S(1)–C(1)	98.4(1)
Hg(2)–S(1)–C(1)	100.9(1)	Hg(1)–S(2)–Hg(2′)	93.1(1)
Hg(1)–S(2)–C(6)	103.0(1)	Hg(2′)–S(2)–C(6)	100.5(1)
Hg(1)–N(3)–C(2)	105.2(1)	Hg(1)–N(3)–C(4)	114.1(1)
Hg(1)–N(3)–C(5)	113.8(1)	C(2)–N(3)–C(4)	109.4(2)
C(2)–N(3)–C(5)	103.2(2)	C(4)–N(3)–C(5)	110.4(2)
Hg(1)–N(8)–C(7)	104.0(2)	Hg(1)–N(8)–C(9)	117.3(2)
Hg(1)–N(8)–C(10)	111.4(2)	C(7)–N(8)–C(9)	106.2(2)
C(7)–N(8)–C(10)	106.9(2)	C(9)–N(8)–C(10)	110.2(2)
S(1)–C(1)–C(2)	113.0(2)	C(1)–C(2)–N(3)	108.3(2)
S(2)–C(6)–C(7)	110.6(2)	C(6)–C(7)–N(8)	120.6(2)

Symmetry operator for primed atoms: $-x, -y, -z$.

by the infrared data, precludes the possibility of a cubane structure, $[\{MX(\mu_3\text{-}SR)\}_4]$, which is also unknown to date for zinc, cadmium and mercury thiolate complexes.

Infrared spectra for the cadmium complexes **II** resemble those of **I**, the chelating character of the ligands being the only information thus supplied about their possible structure.

Description of the Structures.—A common feature of complexes **1**–**3** is that they all crystallize as discrete centrosymmetric tetranuclear molecules with eight-membered rings of alternating metal and sulphur atoms. The four metal atoms lie rigorously in a plane, as is required by the crystallographic centrosymmetry of the molecules, two of them being crystallographically independent and having different co-ordination geometries. In the case of the non-isomorphous complexes **1** (Fig. 1) and **2** (Fig. 2), two metal atoms in each case are tetrahedrally co-ordinated to two terminal halogen and two bridging sulphur atoms (MS_2X_2), while the other two are co-ordinated to two bridging sulphur and two nitrogen atoms ($M'N_2S_2$). The latter show a marked distortion from tetrahedral towards octahedral co-ordination, with secondary interactions with two halogen atoms, which thus become triply bridging, as shown in Fig. 4. X-Ray powder diffraction patterns have been recorded and compared for all six complexes of series **I**. The complex with M = Hg, X = Br is isomorphous with **1**, so it is probably isostructural. The similarities in properties and spectra of the whole series of complexes **I** suggest that they all have the same basic molecular structure, although only two are isomorphous and only two structures have been determined in detail.

The M_4S_4 rings can also be viewed (as in Fig. 4) as containing a central planar M'_2S_4 arrangement with one additional M metal atom on each side of the plane, to give an extended chair-shaped eight-membered ring. The six M'_2S_4 atoms lie practically in a plane which is nearly perpendicular to the planes defined by MX_2 atoms; dihedral angles between selected planes are given in Table 10, together with other geometrical parameters for these and related structures.

Substitution of two chloride ions in $[Cd_4\{S(CH_2)_2NMe_2\}_4Cl_4]$ by additional thiolate ligands gives rise to the centrosymmetric complex $[Cd_4\{S(CH_2)_2NMe_2\}_6Cl_2]$ **3**. In this case, one of the crystallographically independent cadmium atoms is octahedrally co-ordinated to two bridging sulphur, two bridging chlorine and two terminal nitrogen atoms ($Cd'S_2N_2Cl_2$) as shown in Fig. 3. The other is bonded to two bridging sulphur atoms and to a chelating ligand, to give a highly distorted CdS_3N co-ordination; there is a secondary interaction with a chlorine atom, to produce distorted trigonal-bipyramidal co-ordination and, as in the two other structures, triply bridging halogen (Fig. 4). The analogous bromide complex is shown, by X-ray powder diffraction, to be non-isomorphous with the chloride complex, but spectroscopy and other properties indicate that the molecular structure is probably essentially the same.

An analogous M_4S_4 ring, together with metal–halide bonding to give a central $X_2M_4S_4$ core, has been found in the following complexes: $[Zn_4\{S(CH_2)_2NMe(CH_2)_2NMe(CH_2)_2S\}_2Cl_4]$ **4**,[19] $[Cd_4(SCMe_2CH_2NH_2)_4Cl_4]\cdot 2H_2O$ **5**,[20] and

$[Hg_4(SBu^t)_4Cl_4(py)_2]$ (py = pyridine) **6**.[21] Complexes **4** and **5** also contain chelating aminothiolate ligands (tetradentate in the case of **4**), while **6** has simple thiolate ligands.

Selected geometrical details for all the complexes **1**–**6** are given in Table 10, and Fig. 5 shows the central core of each structure (C, H and N atoms are omitted) viewed along the M′M′ line. All the molecules are strictly centrosymmetric, and the essential coplanarity of the six M'_2S_4 atoms is clearly seen: the largest root-mean-square deviation for this plane is 0.04 Å, in **6**, the least precisely determined of these structures. Planes were also calculated for the following sets of atoms: plane 1, M_2X_2 involving the core X atoms; plane 2, M'_2X_2; plane 3, M'_2S_4 as already described; plane 4, MS_2 (the end-flap of the $M_2M'_2S_4$ ring). In each case except plane 3 the atoms concerned are all strictly coplanar. Dihedral angles between planes 1 and 2, and between planes 1 and 3, demonstrate the essential C_{2h} symmetry of all the molecules (C_2 axis along M′M′, σ_h mirror plane containing the M_2X_2 atoms): these angles are all within 3° of 90°. Dihedral angles between planes 3 and 4 are a measure of the degree of folding of the $M_2M'_2S_4$ extended-chair ring.

Table 9 Bond lengths (Å) and angles (°) for complex **3**

Cd(1)–S(1)	2.464(2)	Cd(1)–N(1)	2.507(5)
Cd(1)–S(2)	2.543(1)	Cd(1)–S(3)	2.532(1)
Cd(2)–Cl	2.733(1)	Cd(2)–S(2)	2.559(1)
Cd(2)–N(2)	2.558(3)	Cd(2)–Cl′	2.735(1)
Cd(2)–S(3′)	2.554(1)	Cd(2)–N(3′)	2.516(3)
S(1)–C(11)	1.787(11)	N(1)–C(12)	1.549(9)
N(1)–C(13)	1.427(15)	N(1)–C(14)	1.424(16)
C(11)–C(12)	1.516(18)	S(2)–C(21)	1.843(5)
N(2)–C(22)	1.471(5)	N(2)–C(23)	1.457(8)
N(2)–C(24)	1.492(7)	C(21)–C(22)	1.494(8)
S(3)–C(31)	1.844(6)	N(3)–C(32)	1.451(7)
N(3)–C(33)	1.468(11)	N(3)–C(34)	1.479(8)
C(31)–C(32)	1.561(9)		
S(1)–Cd(1)–N(1)	83.4(1)	S(1)–Cd(1)–S(2)	118.4(1)
N(1)–Cd(1)–S(2)	99.1(1)	S(1)–Cd(1)–S(3)	121.7(1)
N(1)–Cd(1)–S(3)	96.6(1)	S(2)–Cd(1)–S(3)	119.1(1)
Cl–Cd(2)–S(2)	93.1(1)	Cl–Cd(2)–N(2)	87.0(1)
S(2)–Cd(2)–N(2)	79.4(1)	Cl–Cd(2)–Cl′	81.7(1)
S(2)–Cd(2)–Cl′	90.7(1)	N(2)–Cd(2)–Cl′	164.6(1)
Cl–Cd(2)–S(3′)	90.3(1)	S(2)–Cd(2)–S(3′)	174.6(1)
N(2)–Cd(2)–S(3′)	96.5(1)	Cl′–Cd(2)–S(3′)	94.0(1)
Cl–Cd(2)–N(3′)	166.0(1)	S(2)–Cd(2)–N(3′)	97.6(1)
N(2)–Cd(2)–N(3′)	103.8(1)	Cl′–Cd(2)–N(3′)	89.2(1)
S(3′)–Cd(2)–N(3′)	79.7(1)	Cd(2)–Cl–Cd(2′)	98.3(1)
Cd(1)–S(1)–C(11)	100.1(4)	Cd(1)–N(1)–C(12)	100.4(5)
Cd(1)–N(1)–C(13)	113.8(6)	C(12)–N(1)–C(13)	105.4(8)
Cd(1)–N(1)–C(14)	111.2(5)	C(12)–N(1)–C(14)	108.6(7)
C(13)–N(1)–C(14)	115.9(9)	S(1)–C(11)–C(12)	114.2(7)
N(1)–C(12)–C(11)	115.7(7)	Cd(1)–S(2)–Cd(2)	97.7(1)
Cd(1)–S(2)–C(21)	101.2(2)	Cd(2)–S(2)–C(21)	99.5(2)
Cd(2)–N(2)–C(22)	105.5(3)	Cd(2)–N(2)–C(23)	116.4(3)
C(22)–N(2)–C(23)	110.7(4)	Cd(2)–N(2)–C(24)	107.5(3)
C(22)–N(2)–C(24)	109.5(4)	C(23)–N(2)–C(24)	107.0(4)
S(2)–C(21)–C(22)	114.6(4)	N(2)–C(22)–C(21)	114.7(4)
Cd(1)–S(3)–C(31)	99.8(2)	Cd(1)–S(3)–Cd(2′)	97.2(1)
C(31)–S(3)–Cd(2′)	99.8(2)	C(32)–N(3)–C(33)	109.4(5)
C(32)–N(3)–C(34)	112.0(4)	C(33)–N(3)–C(34)	108.0(5)
C(32)–N(3)–Cd(2′)	105.0(3)	C(33)–N(3)–Cd(2′)	110.8(3)
C(34)–N(3)–Cd(2′)	111.6(3)	S(3)–C(31)–C(32)	113.4(3)
N(3)–C(32)–C(31)	112.7(5)		

Symmetry operator for primed atoms: $-x, -y, -z$.

Complex **6**[21] has a very open $Hg_2Hg'_2S_4$ ring, with a dihedral angle of 148° between the Hg'_2S_4 'seat' and the HgS_2 'flap'. This complex has unidentate bridging Bu^tS^- ligands with no chelation, and there is no significant Hg ⋯ Cl interaction. Indeed, the very open form of the $Hg_2Hg'_2S_4$ ring and the pronounced inclination of the Hg'_2Cl_2 plane to this ring (dihedral angle 101°) are such that the Hg ⋯ Cl distance of 3.95 Å is slightly *longer* than the Hg ⋯ Cl distance to Cl on the *other* side of the ring, 3.89 Å, and far in excess of the genuine Hg–Cl bond lengths in the molecule. The sum of van der Waals radii for Hg and Cl atoms is estimated in the range 3.3–3.5 Å (corresponding approximate sums for other metal–halogen atom pairs relevant to this work are Zn ⋯ Cl 3.2, Cd ⋯ Cl 3.4, and Cd ⋯ Br 3.5 Å, while approximate normal single bond lengths may be estimated from typical covalent radii as Zn–Cl 2.35, Cd–Cl 2.55, Hg–Cl 2.50, and Cd–Br 2.70 Å).[22] Thus, this structure corresponds to the extreme form **B** (Scheme 2) in which there are doubly bridging halogen atoms with no secondary M ⋯ X interactions. An essentially identical structure is found for the analogous complex containing 4-methylpyridine in place of pyridine.[23]

The other extreme form **A**, with terminally bonded halides, most closely resembles the observed structure of complex **4**.[19] In this case, the difference between M–X and M′–X distances is almost exactly the same in magnitude as for **6**, but of opposite sign: Zn–Cl is essentially terminal in character (and hardly longer than the second and obviously terminal Zn–Cl bond), while Zn′ ⋯ Cl is too long to represent any significant interaction. The considerable degree of folding of the $Zn_2Zn'_2S_4$ ring, with a dihedral flap angle of only 84.5°, is, therefore, rather surprising, and is presumably dictated by other intramolecular (restrictions imposed by the tetradentate ligands) and intermolecular (crystal packing) factors rather than by direct Zn′ ⋯ Cl bonding. We note that the co-ordination of the 'flap' metal atom is almost ideal tetrahedral in this complex, while it is distorted to a moderate or high degree in the structures of **1**, **2** and **5**, which we consider to have significant M′ ⋯ X secondary interactions.

Bonds M–X and M′–X of comparable strength occur in complex **5**, which was described in the original report[20] as having triply bridging chloride and tetrahedrally and octahedrally co-ordinated Cd and Cd′ respectively. The dihedral flap angle of 88.6° is similar to that of **4**, but the additional M′–X bonding here (with concomitant weakening of M–X bonding) tips the $CdCl_2$ unit at each end of the molecule very much in towards the centre, giving a strong distortion of the Cd tetrahedral co-ordination. Complex **5** is thus of mixed **A**–**B** type.

Although complexes **1** and **2** are crystallographically non-isomorphous, the molecular structures are very similar. They are intermediate in character between those of **4** and **5**, with primary M–X and secondary M′ ⋯ X bonding. This combination results in comparatively minor distortions of the tetrahedral M co-ordination and in a M′ co-ordination inter-

Table 10 Selected geometrical parameters (in Å and °) for complexes **1**–**6**

Complex	M,M′	X	T^a	U^b	$V^{c,d}$	$U - V$	$W^{d,e}$	$X^{d,f}$	$W - X$	Y^g	Z^h	Ref.
1	Cd	Br	2.572	2.681	3.333	−0.652	2.514	2.498	+0.016	97.2	80.8	*i*
2	Hg	Cl	2.506	2.648	3.322	−0.674	2.496	2.415	+0.081	95.1	83.2	*i*
3	Cd	Cl	—	3.112	2.734	+0.378	2.538	2.559	−0.021	92.3	109.6	*i*
4	Zn	Cl	2.240	2.272	3.456	−1.184	2.350	2.285	+0.065	90.3	84.5	19
5	Cd	Cl	2.413	2.660	2.946	−0.286	2.513	2.558	−0.045	92.9	88.6	20
6	Hg	Cl	2.45	3.95	2.76	+1.19	2.50	2.39	+0.11	101	148	21

[a] T = Terminal M–X bond length. [b] U = M–X distance in the central core. [c] V = M–X distance. [d] Mean of two values. [e] W = M–S length. [f] X = M′–S bond length. [g] Y = Dihedral angle between planes 2 and 3. [h] Z = Dihedral angle between planes 3 and 4. [i] This work.

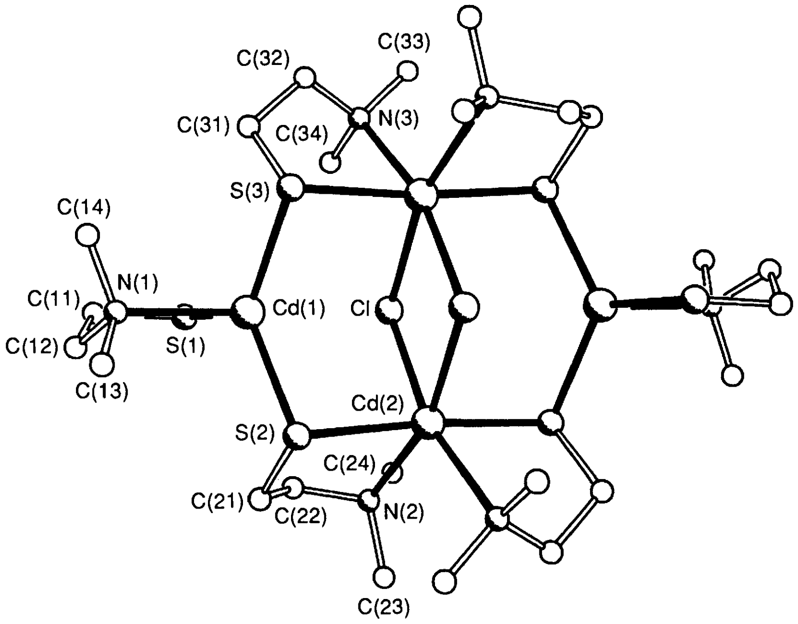


Fig. 3 Molecular structure of complex **3**, with the labelling of the independent atoms; H atoms are omitted

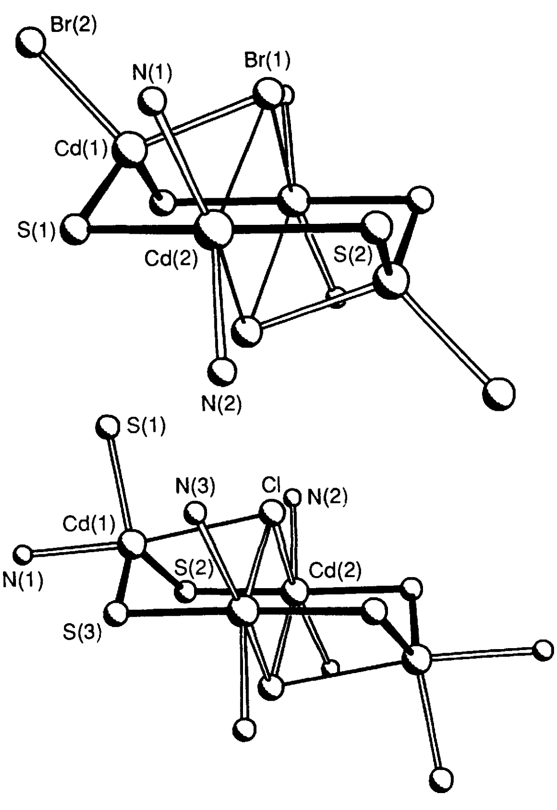


Fig. 4 Comparison of the structures of complexes **1** and **3**; C and H atoms are omitted. Bonds within the central $M_2M'_2S_4$ ring are shown filled, other primary bonds hollow, and secondary M ··· X or M′ ··· X interactions with narrow bonds

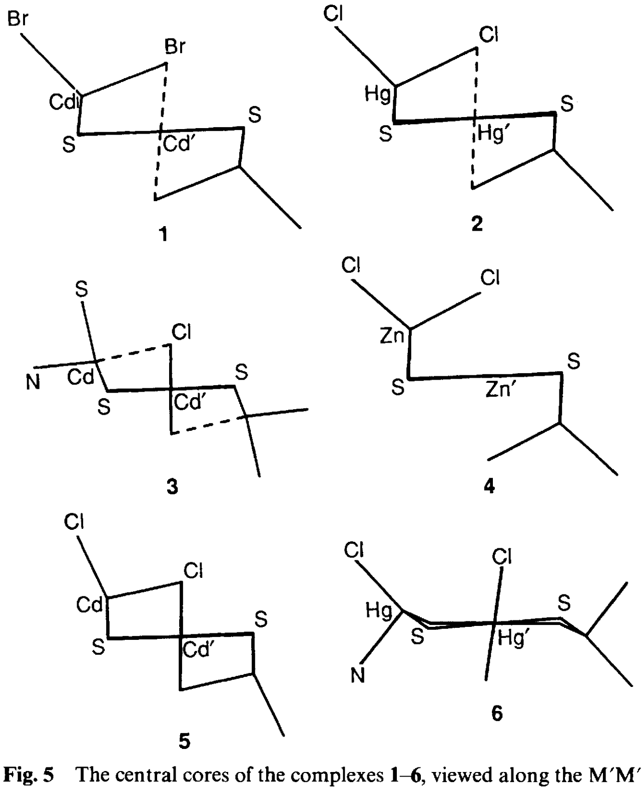


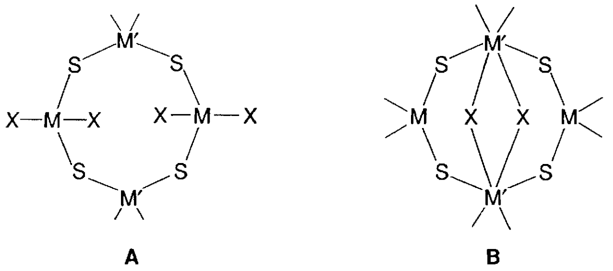
Fig. 5 The central cores of the complexes **1**–**6**, viewed along the M′M′ line in each case; C, H and most N atoms are omitted. Secondary bonding is shown dashed

mediate between highly distorted $M'S_2N_2$ and octahedral $M'S_2N_2X_2$. These structures are, therefore, largely of type **A** with a minor contribution of type **B** character.

By contrast, the structure of **3** has primary M′–X and secondary M ··· X bonding, and is largely of type **B**, intermediate in character between **5** and **6**. If the secondary Cd ··· Cl bonding is ignored, the co-ordination of Cd is highly distorted from tetrahedral, but inclusion of this secondary interaction gives a relatively undistorted trigonal-bipyramidal angular geometry, the axial positions being occupied by N and the weakly bonded Cl; Cd′ has somewhat distorted octahedral co-ordination. The intrachelate S–Cd–N angles at the Cd′ atom are significantly smaller than that subtended at the 'flap' Cd atom, where the thiolate is not involved in bridging and so is less subject to constraints on its preferred conformational geometry.

The six structures may hence be arranged in order of M–X bonding, to give the sequence $\mathbf{A} \approx \mathbf{4} > \mathbf{1} \approx \mathbf{2} > \mathbf{5} > \mathbf{3} > \mathbf{6} \approx \mathbf{B}$ with the M′–X bonding decreasing concomitantly across the sequence.

The conformation of the $M_2M'_2S_4$ ring in these structures and the nature of the M–X and M′–X bonding in the range of behaviour between the extremes of **A** and **B** are seen to depend on a number of factors, including the particular metal and halogen present, the exact nature of the thiolate ligands, and the number and type of other ligands bonded to the metal atoms.



Scheme 2

Differences in M–S and M′–S bond lengths in the various structures (see Table 10 for a summary) are generally small to moderate; the overall pattern is not just a simple reflection of the differences in effective co-ordination numbers of the metal atoms, although this is one of the factors involved.

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