The Crystal Structures of Chloro Mercury(II) Salts Found for some CrN_6^{3+} Cations and their Cr–N Bond-ruptured Hydrolysis Products

DONALD A. HOUSE, VICKIE McKEE and WARD T. ROBINSON

Department of Chemistry, University of Canterbury, Christchurch, New Zealand

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Abstract

$Cr(en)_3^{3+}$ and isomeric forms of $Cr(dien)_2^{3+}$ produce yellow or orange–yellow chloro mercury(II) salts on crystallisation from 6 M HCl containing excess $HgCl_2$. The salt formed by $[Cr(en)_3]Cl_3$ has the stoichiometric composition $[Cr(en)_3]_2[Hg_3Cl_{12}]$ whereas the $Cr(dien)_2^{3+}$ salts are associated with various anions of empirical stoichiometry $Hg_2Cl_7^{3-}$. With $Cr(en)_3^{3+}$ and *u-fac*-$Cr(dien)_2^{3+}$, red Cr–N bond ruptured products, such as *cis*-$[CrCl(en)_2(Hen,N)^{3+}]$-$[HgCl_5^{3-}]$ are formed at long reaction times. The crystal structures of $[Cr(en)_3]_2[Hg_3Cl_{12}]$ (**1**) (triclinic; $a = 11.25, b = 11.245, c = 17.421$ Å, $\alpha = 81.66$, $\beta = 72.25$, $\gamma = 90.01°$; $V = 2074.31$ Å^3; $Z = 2$), $[CrCl(en)_2(Hen,N)][HgCl_5]$ (**2**) (monoclinic; $a = 13.304$, $b = 11.717$, $c = 14.040$ Å; $\alpha = 90$, $\beta = 119.05$, $\gamma = 90°$; $V = 1915.71$ Å^3; $Z = 4$), *mer*-$[Cr(dien)_2]$-$[HgCl_5]\cdot[DMSO]_2$ (**3**) (monoclinic; $a = 11.007$, $b = 8.696$, $c = 14.305$ Å; $\alpha = 90$, $\beta = 91.85$, $\gamma = 90°$; $V = 1368.52$; $Z = 2$), *s-fac*-$[Cr(dien)_2][Hg_2Cl_7]$ (**4**) (triclinic; $a = 11.011$, $b = 11.922$, $c = 17.588$ Å; $\alpha = 77.295$, $\beta = 78.739$, $\gamma = 83.553°$; $V = 2201.00$ Å^3; $Z = 4$), *u-fac*-$[Cr(dien)_2][Hg_2Cl_7]$ (**5**) (orthorhombic; $a = 8.521$, $b = 16.175$, $c = 31.914$ Å; $\alpha = 90$, $\beta = 90$, $\gamma = 90°$; $V = 4398.76$; $Z = 8$) and *s-fac*-$[CrCl(dien)(Hdien,N,N)][Hg_2Cl_7]$ (**6**) (monoclinic; $a = 7.885$, $b = 18.21$, $c = 16.926$ Å; $\alpha = 90$, $\beta = 101.37$, $\gamma = 90°$; $V = 2382.55$; $Z = 4$) have been determined by X-ray analyses. In **2** and **3**, the $HgCl_5^{3-}$ stoichiometry comes from isolated $HgCl_4^{2-}$ and Cl^- units and in **1** the $Hg_3Cl_{12}^{6-}$ stoichiometry from three $HgCl_4^{2-}$ units. The $Hg_2Cl_7^{2-}$ anions are more diverse, with linear $(Hg_2Cl_7)_n^{3n-}$ chains in **6**, $(HgCl_3)_n^{n-}$ chains closely associated with $HgCl_4^{2-}$ anions in **5** and *s-fac*-$Cr(dien)_2^{3+}$ cations associated with distinguishable $Hg_2Cl_6^{2-}$, $Hg_4Cl_{14}^{6-}$ and $HgCl_4^{2-}$ anions in **4**.

Introduction

In a recent publication [1], we described the preparation of isomeric forms of the $Cr(dien)_2^{3+}$ cations where the *mer*-, *u-fac*- and *s-fac*-forms were isolated as $Hg_2Cl_7^{3-}$ salts*. This paper describes the single crystal X-ray structural data for the latter two salts. Numerous attempts to produce single crystals of *mer*-$[Cr(dien)_2][Hg_2Cl_7]$ were unsuccessful and our solution of the structure of this complex using twinned crystals will be described later. We were, however, successful in isolating single crystals of *mer*-$[Cr(dien)_2][HgCl_5][DMSO]_2$ suitable for X-ray structure determination, using similar methods to those described previously for *mer*-$[Cr(dien)_2][Hg_2Cl_7]$ [1] but in 50:50 DMSO:6 M HCl media.

It is well known that Cr(III) amine complexes are susceptible to Cr–N bond rupture [1, 2] and Garner and coworkers described the separation of several partially dechelated Cr(III) polyamine systems by ion exchange chromatography [2]. The rate of Cr–N bond rupture in $Cr(en)_3^{3+}$ and $Cr(dien)_2^{3+}$ has also been investigated [1–3]. Partially dechelated systems such as $Cr(en)_2(Hen,N)(OH_2)^{4+}$ have been postulated as intermediates [4].

In an investigation of the $[Cr(en)_3Cl_3]/HgCl_2/HCl$ system (from which $[Cr(en)_3]_2[Hg_3Cl_{12}]$ can be isolated), we observed the deposition of red crystals of *cis*-$[CrCl(en)_2(Hen,N)][HgCl_5]$ from the mother liquor. Similarly, red crystals of *s-fac*-$[CrCl(dien)(Hdien,N,N)][Hg_2Cl_7]$ can be obtained from the mother liquor of the *u-fac*-$Cr(dien)_2^{3+}/HgCl_2/HCl$ system [1]. Both these complexes contain partially dechelated polyamine ligands as confirmed by their crystal structure analysis.

Experimental

$[Cr(en)_3]Cl_3\cdot xH_2O$ [5] and *mer*-/*u-fac*-$[Cr(dien)_2](ClO_4)_3$ [1] were prepared according to the literature procedures.

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*Abbreviations used: en = $NH_2(CH_2)_2NH_2$, Hen = $NH_2(CH_2)_2NH_3^+$, dien = $NH_2(CH_2)_2NH(CH_2)_2NH_2$, Hdien = $NH_2(CH_2)_2NH(CH_2)_2NH_3^+$, H3dien = $NH_3(CH_2)_2NH_2(CH_2)_2NH_3^{3+}$, H3dpt = $NH_3(CH_2)_3NH_2(CH_2)_3NH_3^{3+}$, DMSO = dimethylsulfoxide.

0020-1693/89/$3.50

TABLE 1. Crystal Data

Complex	1	2	3	4	5	6
Molecular formula	$C_{12}H_{48}N_{12}Cl_{12}Cr_2Hg_3$	$C_6H_{25}N_6Cl_6CrHg$	$C_{12}H_{38}N_6O_2S_2Cl_5CrHg$	$C_8H_{26}N_6Cl_7CrHg_2$	$C_8H_{26}N_6Cl_7CrHg_2$	$C_8H_{27}N_6Cl_8CrHg_2$
Formula weight	1347.7	730.65	792.45	907.7	907.7	942.6
	triclinic	monoclinic	monoclinic	triclinic	orthorhombic	monoclinic
Space group	$P\bar{1}$	$P2_1/c$	$P2/n$	$P\bar{1}$	$Pbca$	$P2_1/c$
a (Å)	11.250(2)	13.304(2)	11.007(2)	11.011(3)	8.521(2)	7.885(3)
b (Å)	11.245(1)	11.732(2)	8.696(2)	11.922(3)	16.175(5)	18.210(4)
c (Å)	17.421(4)	14.040(2)	14.305(3)	17.588(4)	31.914(9)	16.926(7)
α (°)	81.66(1)	90	90	77.30(2)	90	90
β (°)	72.25(1)	119.05(1)	91.85(1)	78.74(2)	90	101.37(3)
γ(°)	90.01(1)	90	90	83.55(2)	90	90
V (Å^3)	2074.31	1915.71	1368.52	2201.00	4398.76	2382.55
Z	2	4	2	4	8	4
Temperature (℃)	23	–80	–135	23	23	–140
D_{meas} (g/cc)	2.26		1.88	2.71		
D_{calc} (g/cc)	2.16	2.54	1.92	2.74	2.74	2.36
F(000)	1391.57	1235.66	777.81	1675.48	3310.94	1747.48
Absorption coefficient (cm^{-1})	123.66	22.20	66.50	152.42	152.66	142.07
Transmission	0.973	0.914	0.971	0.997	0.268	0.994
factors	0.235	0.657	0.317	0.266	0.056	0.253
Scan mode	0.5°, ω	1.2°, ω	1.2°, ω	1.2°, ω	1.4°, ω	0.8°, ω
Octants	13, ±13, ±19	17, 15, ±18	17, 14, ±22	12, ±13, ±19	10, 18, 35	10, 22, ±21
$2\theta_{\mathrm{max}}$ (°)	45	52	65	45	50	50
Reflections measured	5684	4186	4929	4460	4512	4369
Reflections used	4568	3796	3473	3687	3889	3531
Parameters refined	371	181	139	296	147	229
Weighting, g × 10^3	5.00	0.6	1.55	0.77	1.00	2.00
R	4.11	6.49	3.96	3.31	6.50	5.01
R_{w}	5.47	4.94	6.03	4.35	7.73	5.87

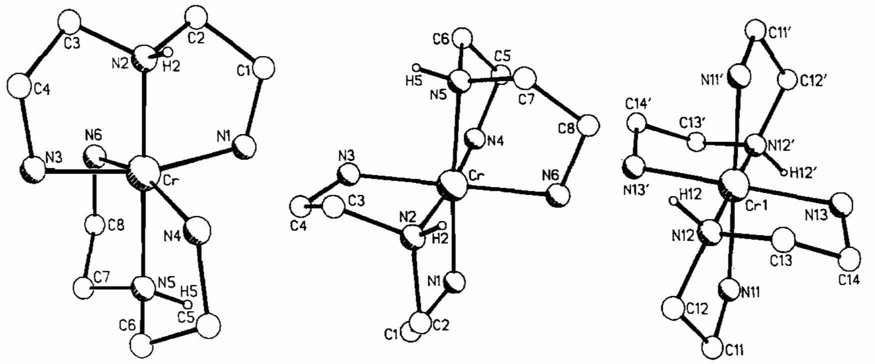

Fig. 1. A perspective view of the cation configurations for λ-NH-*mer*, Λ-*u*-*fac*- and *s*-*fac*-$Cr(dien)_2^{3+}$ (left to right) showing the numbering scheme adopted in Tables 4–6 and 11–13. For the first and second cations, the lattice consists of equivalent amounts of the δ-NH- and Δ-isomers, respectively.

Chloro Bis(1,2-diaminoethane)(2-aminoethylammonium)chromium(III) Heptachlorodimercurated(II)

A 6 M solution of HCl (50 ml) was heated to 90 °C and 1.5 g $[Cr(en)_3]Cl_3 \cdot xH_2O$ stirred in. The yellow solution was maintained at 90 ± 2 °C for 10 ± 0.5 min when 4.0 g of $HgCl_2$ were stirred in. Some $[Cr(en)_3]_2[HgCl_4]_3$ may deposit (yellow plates) but the solution is left to cool to room temperature and then a further 24 h. During this time, small amounts of the desired chloropentaamine (red crystals) deposit along with a residue of yellow $[Cr(en)_3]_2[HgCl_4]_3$.

The two forms may be hand separated, or partially separated by flotation in a *ca.* 1:1 bromoform:carbon tetrachloride mixture, the hexaamine (yellow) being the less dense (Table 1).

The above synthesis and separation was repeated two or three times to accumulate sufficient quantities of enriched chloropentaamine fractions before a final recrystallisation from hot (80 °C) 1 M HCl by addition of $HgCl_2$.

X-ray Structure Determinations

Intensity data for the complexes listed in Table 1 were collected with a Nicolet R3m four-circle diffractometer in either room temperature (**1**, **4**, **5**) or *ca.* –140 °C (**2**, **3**, **6**). Graphite monochromated Mo Kα radiation (0.71069 Å) was used, with fixed speed ω scans. Cell parameters were determined by least-squares refinement of 25 accurately centred reflections. During the data collections the intensities of three standard reflections were monitored at regular intervals and these indicated no significant crystal decomposition. The collected intensities were corrected for Lorentz, polarisation and absorption effects (Table 1).

The structures were solved by conventional Patterson and Fourier methods, and refined by blocked cascade least-squares procedures. For structures **4** and **5**, only Cr, Cl and Hg were refined with anisotropic thermal parameters, but for **1**, **2**, **3** and **6**, satisfactory refinement was obtained with anisotropic thermal parameters for all non-hydrogen atoms. In the last cycles of refinement, hydrogen atoms were included in their calculated positions. All calculations were performed on Nova 4X or DG30 computers using the SHELXTL [6] suite of programs. See also 'Supplementary Material'.

Results and Discussion

The initial aim of this work was to characterise structurally the three geometric isomers of the $Cr(dien)_2^{3+}$ cation [1, 7] (Fig. 1). Two problems were immediately apparent in that one isomer (*u*-*fac*) was only present at the 2–5% level and that a second isomer (*s*-*fac*) has a half-life of about 10 min with respect to Cr–N bond rupture in aqueous solution at room temperature [1, 7]. Thus, the choice of anion was critical in trying to obtain single crystals suitable for X-ray structure analysis.

We decided to explore the use of chloro mercury(II) anions, as Clegg [8, 9] has shown that $Cr(NH_3)_6^{3+}$ forms $[Cr(NH_3)_6][HgCl_5]$ when using this cation and $HgCl_2/HCl$ mixtures.

Our investigations showed that all three $Cr(dien)_2^{3+}$ isomers could be obtained as $[Cr(dien)_2][Hg_2Cl_7]$ salts [1]. The crystals obtained for the *s*-*fac* (triclinic) (**4**) and *u*-*fac* (orthorhombic) (**5**) were suitable for X-ray structural analysis, but those for the *mer*-(monoclinic?) were always twinned. We were, however, able to obtain X-ray quality crystals of monoclinic *mer*-$[Cr(dien)_2][HgCl_5][DMSO]_2$ (**3**).

During the course of crystal preparation of $Cr(dien)_2^{3+}$ samples enriched with the *u*-*fac* isomer, we observed the deposition of red crystals at long reaction times. These subsequently proved to be *s*-*fac*-$[CrCl(dien)(Hdien,N,N)][Hg_2Cl_7]$ (**6**) (Fig. 2) containing a Cr–Cl bond and a dechelated (and protonated) polyamine 'arm'. Analogous complexes of Pd(II) are also known [10].

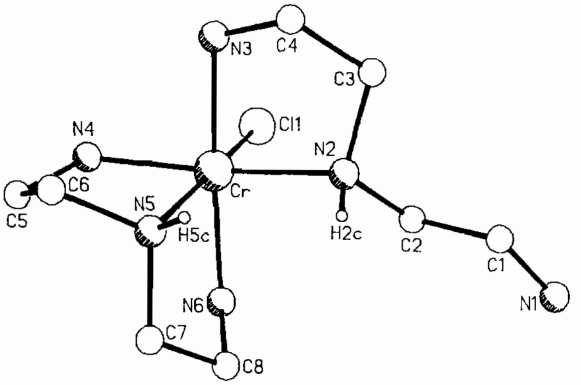

Fig. 2. A perspective view of the (*S*)-*s*-*fac*-CrCl(dien)(Hdien,*N*,*N*)$^{3+}$ cation showing the numbering scheme adopted in Tables 7 and 14. The lattice contains an equivalent amount of the (*R*)-isomer.

Although extensive Cr–N bond rupture also occurs with the *mer*- and *s*-*fac*-isomers, no analogous dechelated species were obtained. It is obvious that if Cr–N bond rupture is rapid, there will be insufficient build up of material in solution to cause crystallisation of these intermediates.

We were aware that related dechelated species had been postulated as intermediates [11] in the acid decomposition of Cr(en)$_3^{3+}$ and a study of the Cr(en)$_3^{3+}$/HgCl$_2$/HCl system showed that if the initially formed [Cr(en)$_3$]$_2$[Hg$_3$Cl$_{12}$] (1) (Fig. 3) is allowed to remain in contact with the mother liquor for several days at room temperature, red crystals of *cis*-[CrCl(en)$_2$(Hen,*N*)][HgCl$_5$] (2) (Fig. 3), containing half protonated monodentate ethylendiamine, are formed. Analogous complexes of Co(III) have previously been characterised [12, 13].

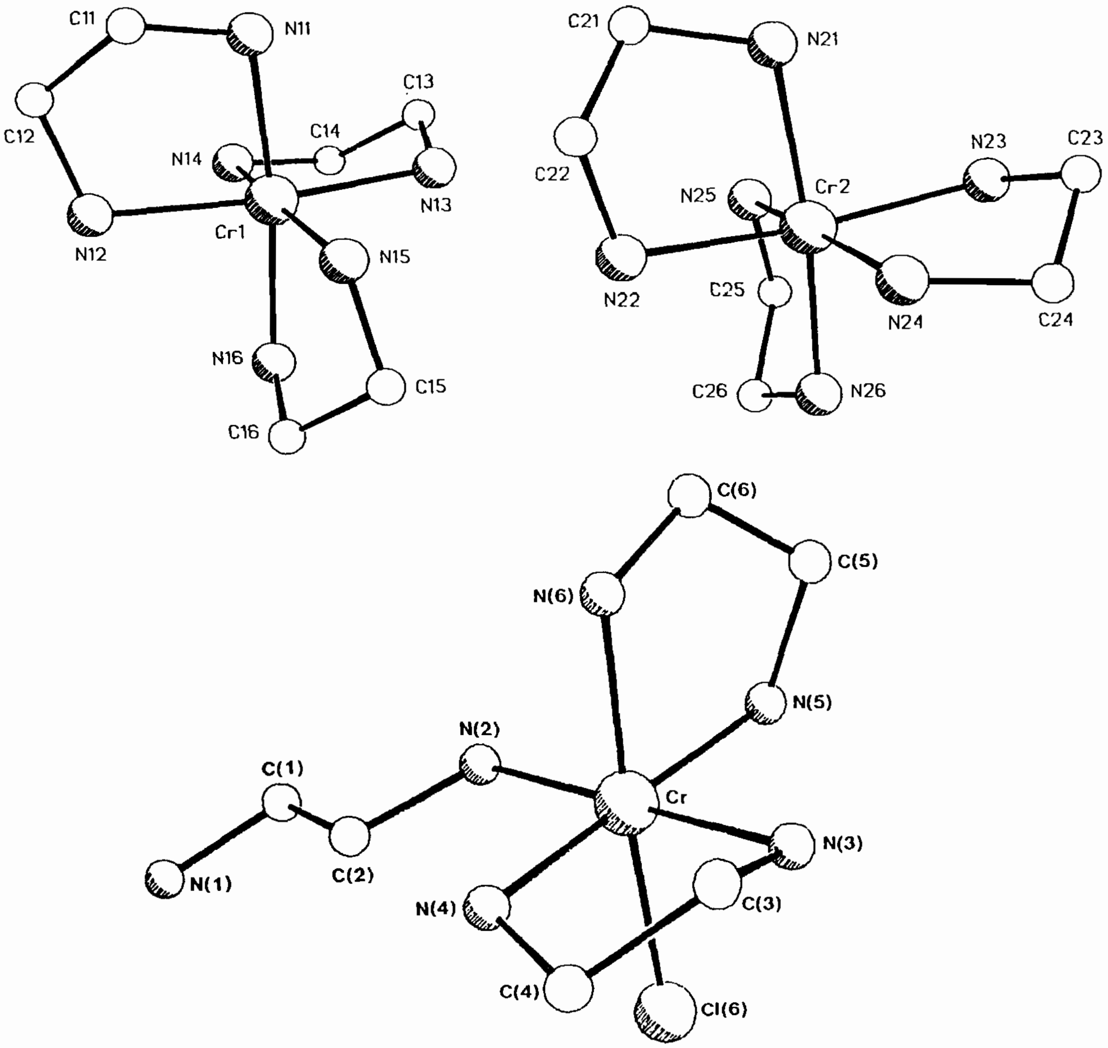

Fig. 3. Perspective views of the Λ(δδδ)[Cr(1)]- and Δ(λλλ)[Cr(2)]-Cr(en)$_3^{3+}$ cations in (±)-[Cr(en)$_3$]$_2$[HgCl$_4$]$_3$ (1) and the Λ(δλ)-*cis*-CrCl(en)$_2$(Hen)$^{3+}$ cation. For the latter, the lattice contains equivalent amounts of the Δ-*cis*-enantiomer.

TABLE 2. Non-hydrogen Atom Coordinates (×10^4) for $[Cr(en)_3]_2[HgCl_4]_3$ (1)

Atom	x	y	z
Hg(1)	9446(1)	6165(1)	2496(1)
Hg(2)	4009(1)	1019(1)	3590(1)
Hg(3)	5010(1)	1301(1)	1401(1)
Cr(1)	4707(1)	6332(1)	1931(1)
Cr(2)	9142(1)	1037(1)	3065(1)
Cl(11)	10817(3)	5949(2)	3376(2)
Cl(12)	9847(3)	8143(2)	1619(2)
Cl(13)	9833(3)	4568(2)	1621(2)
Cl(14)	7245(3)	5969(2)	3367(2)
Cl(21)	2802(3)	2637(2)	3090(2)
Cl(22)	2069(3)	-464(2)	4294(2)
Cl(23)	5521(2)	-465(2)	2978(2)
Cl(24)	5104(3)	1936(3)	4398(2)
Cl(31)	3080(3)	-22(2)	1989(2)
Cl(32)	6231(3)	2657(2)	1941(2)
Cl(33)	4040(3)	3108(2)	719(2)
Cl(34)	6534(3)	61(2)	580(2)
N(11)	6358(8)	7297(7)	1789(5)
C(11)	7311(10)	7039(9)	1013(7)
C(12)	7196(9)	5710(8)	972(7)
N(12)	5874(7)	5408(6)	1063(5)
N(13)	3705(8)	7182(7)	2875(6)
C(13)	3916(11)	6616(9)	3648(7)
C(14)	3924(10)	5282(9)	3664(7)
N(14)	4821(8)	5041(7)	2879(5)
N(15)	4294(8)	7637(7)	1082(6)
C(15)	3036(10)	7351(8)	1039(8)
C(16)	2937(10)	6012(9)	1073(7)
N(16)	3185(8)	5406(6)	1821(6)
N(21)	9839(8)	1609(6)	3932(5)
C(21)	9517(11)	2860(8)	4013(7)
C(22)	8219(10)	3014(9)	3967(7)
N(22)	8136(8)	2583(7)	3195(5)
N(23)	10030(8)	-569(7)	3190(6)
C(23)	9243(11)	-1369(8)	3916(7)
C(24)	7916(9)	-1230(8)	3951(7)
N(24)	7636(7)	57(7)	3906(5)
N(25)	10674(7)	1813(7)	2116(5)
C(25)	10641(10)	1453(9)	1332(7)
C(26)	9319(11)	1406(10)	1312(8)
N(26)	8537(7)	698(7)	2107(5)

Note that throughout this section we have used the empirical formula for the isolated chloro mercury(II) salts and the configuration of the anion does *not* follow from the stoichiometry.

Tables 2–7 list the non-hydrogen atom coordinates for (±)-$[Cr(en)_3]_2[Hg_3Cl_{12}]$ (1), (±)-*cis*-$[CrCl(en)_2(Hen,N)][HgCl_5]$ (2), (±)-*mer*-$[Cr(dien)_2][HgCl_5][DMSO]_2$ (3), *s-fac*-$[Cr(dien)_2][Hg_2Cl_7]$ (4), (±)-*u-fac*-$[Cr(dien)_2][Hg_2Cl_7]$ (5) and (±)-*s-fac*-$[CrCl(dien)(Hdien,N,N)][Hg_2Cl_7]$ (6).

TABLE 3. Non-hydrogen Atom Coordinates (×10^4) for *cis*-$[CrCl(en)_2(Hen,N)][HgCl_4][Cl]$ (2)

Atom	x	y	z
Hg(1)	2183(1)	4904(1)	6642(1)
Cl(1)	2010(2)	6796(2)	7274(2)
Cl(2)	3082(2)	5002(2)	5459(2)
Cl(3)	415(2)	3783(2)	5948(2)
Cl(4)	3526(2)	3590(2)	8174(2)
Cl(5)[a]	350(2)	4930(2)	1551(2)
Cl(6)[b]	4740(2)	3623(2)	1425(2)
Cr	3291(1)	4915(1)	1044(1)
N(1)	729(6)	1182(5)	-1310(5)
C(1)	1116(7)	2344(6)	-1398(7)
C(2)	1768(6)	2901(6)	-279(5)
N(2)	2207(5)	4029(5)	-371(5)
N(3)	4308(5)	5830(5)	2471(5)
C(3)	3933(7)	5576(7)	3277(7)
C(4)	3662(7)	4316(6)	3214(6)
N(4)	2835(5)	4040(5)	2059(5)
N(5)	3778(5)	5958(5)	154(5)
C(5)	3288(7)	7114(7)	85(7)
C(6)	2064(7)	6975(7)	-175(7)
N(6)	2007(5)	6143(5)	623(5)

[a] Isolated chloride ion. [b] Chloro ligand bound to Cr.

TABLE 4. Non-hydrogen Atom Coordinates (×10^4) for *mer*-$[Cr(dien)_2][HgCl_4][Cl][DMSO]_2$ (3)

Atom	x	y	z
Hg	2500	-625(1)	2500
Cl(1)	3643(1)	1201(1)	1483(1)
Cl(2)	4057(1)	-2040(2)	3416(1)
Cl(3)[a]	7500	6192(2)	2500
Cr	7500	1199(1)	2500
N(1)	6142(4)	2847(4)	2315(3)
C(1)	5548(5)	3157(5)	3216(3)
C(2)	5633(5)	1738(6)	3830(3)
N(2)	6899(4)	1232(4)	3845(3)
C(3)	7176(5)	-270(5)	4287(4)
C(4)	8488(5)	-621(5)	4084(4)
N(3)	8653(4)	-510(4)	3057(3)
S	8482(1)	5043(1)	5130(1)
O	8426(4)	3564(5)	4593(3)
C(12)	6950(6)	5702(6)	5208(4)
C(11)	8750(7)	4522(6)	6319(4)

[a] Isolated chloride ion.

Chromium(III) Cation Geometries

Figures 1–3 show perspective views of the Cr(III) cations and the atom labelling schemes adopted. Where appropriate, these schemes have been chosen to correspond to those used for the corresponding Co(III) cations [14–17].

All six cations contain five membered $-NH(CH_2)_2NH-$ chelate rings. These rings are puckered and can adopt either the δ or λ conformations. The observed conformations are listed in Table 8. We would have expected Cr(III)–dien conformations to correspond to those calculated [18] for Co(II) sys-

TABLE 5. Non-hydrogen Atom Coordinates ($\times10^4$) for *s-fac*-$[Cr(dien)_2]_4[HgCl_4]_2[Hg_2Cl_6][Hg_4Cl_{14}]$ (4)

Atom	*x*	*y*	*z*
Hg(1)	415(1)	14(1)	1076(1)
Hg(2)	5348(1)	5358(1)	3878(1)
Hg(3)	4585(1)	6331(1)	1839(1)
Hg(4)	9771(1)	1113(1)	3085(1)
Cl(0)	895(3)	−1398(2)	10(2)
Cl(1)	2043(3)	1288(2)	759(2)
Cl(2)	−1097(3)	−1050(2)	1997(2)
Cl(3)	6239(3)	6205(2)	4974(2)
Cl(4)	7082(3)	4135(2)	3511(2)
Cl(5)	3562(3)	6654(2)	3902(2)
Cl(6)	6191(3)	7183(2)	2351(2)
Cl(7)	3879(3)	4435(2)	2637(2)
Cl(8)	2922(4)	7716(2)	1482(2)
Cl(9)	5993(4)	5586(3)	721(2)
Cl(10)	10953(3)	2759(2)	3212(2)
Cl(11)	8080(4)	440(3)	4146(2)
Cl(12)	11496(3)	−333(2)	2887(2)
Cl(13)	8674(3)	2092(2)	1961(2)
Cr(1)	0	5000	0
N(11)	1557(10)	5847(7)	−80(5)
C(11)	2086(13)	5549(9)	679(6)
C(12)	1613(13)	4385(9)	1141(6)
N(12)	289(10)	4303(7)	1133(5)
C(13)	−580(14)	4918(10)	1690(7)
C(14)	−804(13)	6197(9)	1331(6)
N(13)	−1062(10)	6290(7)	519(5)
Cr(2)	0	5000	5000
N(21)	825(10)	6379(7)	5210(5)
C(21)	497(12)	7469(9)	4667(6)
C(22)	−756(13)	7422(10)	4473(7)
N(22)	−914(10)	6284(7)	4280(5)
C(23)	−459(12)	6194(10)	3435(6)
C(24)	950(12)	5913(9)	3294(6)
N(23)	1312(10)	5002(7)	3967(4)
Cr(3)	5075(2)	846(1)	2444(1)
N(31)	4483(10)	−345(7)	1929(4)
C(31)	5008(13)	−174(10)	1075(6)
C(32)	6334(12)	216(9)	961(6)
N(32)	6336(10)	1144(7)	1405(5)
C(33)	5998(12)	2342(9)	980(6)
C(34)	4649(12)	2602(9)	1013(6)
N(33)	3963(10)	2115(7)	1851(5)
N(36)	5688(10)	2040(7)	2954(4)
C(38)	5140(12)	1843(9)	3820(6)
C(37)	3840(11)	1491(9)	3921(6)
N(35)	3773(10)	584(7)	3473(5)
C(36)	4043(12)	−611(9)	3909(7)
C(35)	5385(12)	−899(9)	3900(6)
N(34)	6137(10)	−455(7)	3082(5)

tems (Co(II)–N = 2.12, Cr(III)–N = 2.10 Å) rather than for Co(III) (Co(III)–N = 1.97 Å) but this is not always the case. As with $M(en)_3^{3+}$ systems [19], the anion with its hydrogen bonding potential, may be of more importance in controlling the solid state conformation than the metal–N distance.

TABLE 6. Non-hydrogen Atom Coordinates ($\times10^4$) for *u-fac*-$[Cr(dien)_2]_n[HgCl_4]_n[HgCl_3]_n$ (5)

Atom	*x*	*y*	*z*
Hg(1)	7869(1)	9752(1)	1987(1)
Hg(2)	7256(1)	9537(1)	787(1)
Cl(1)	7930(8)	8292(4)	1935(2)
Cl(2)	8117(8)	11117(4)	1727(3)
Cl(3)	10622(8)	9898(4)	2450(3)
Cl(4)	7275(9)	10650(4)	275(3)
Cl(5)	4979(8)	9742(4)	1298(2)
Cl(6)	6508(9)	8132(5)	549(3)
Cl(7)	9994(8)	9468(4)	1090(2)
Cr	2908(5)	7072(3)	1210(1)
N(1)	4474(26)	6476(15)	806(8)
C(1)	3650(39)	6231(23)	415(12)
C(2)	2014(30)	5916(16)	529(9)
N(2)	1209(26)	6548(14)	832(8)
C(3)	360(31)	7256(16)	622(10)
C(4)	1473(33)	7863(17)	461(9)
N(3)	2620(25)	8057(14)	789(7)
N(4)	4542(26)	7719(14)	1539(8)
C(5)	3945(30)	7984(19)	1944(10)
C(6)	2255(30)	8249(16)	1880(9)
N(5)	1378(25)	7597(14)	1645(7)
C(7)	780(39)	6912(23)	1895(12)
C(8)	1953(31)	6251(17)	2001(9)
N(6)	2922(26)	6079(13)	1621(7)

TABLE 7. Non-hydrogen Atom Coordinates ($\times10^4$) for *s-fac*-$[CrCl(dien)(Hdien,N,N)]_n[Hg_2Cl_7]_n$ (6)

Atom	*x*	*y*	*z*
Hg(1)	−1536(1)	2042(1)	6560(1)
Hg(2)	−7121(1)	2266(1)	4305(1)
Cl(11)	310(4)	2036(2)	5538(2)
Cl(12)	−1730(3)	697(1)	6975(1)
Cl(13)	−140(4)	2676(2)	7789(2)
Cl(14)	−4358(3)	2515(1)	5867(1)
Cl(21)	−7150(3)	987(1)	4212(1)
Cl(22)	−4476(3)	2491(1)	3561(1)
Cl(23)	−7802(3)	3505(1)	4464(1)
Cl(1)	7635(4)	4584(1)	6186(1)
Cr	6490(2)	4781(1)	7325(1)
N(1)	1940(12)	6554(4)	5251(5)
C(1)	1957(13)	5914(5)	5802(6)
C(2)	3802(13)	5621(5)	6033(5)
N(2)	3967(11)	5069(4)	6696(4)
C(3)	3015(14)	4376(5)	6400(6)
C(4)	3469(14)	3805(5)	7039(6)
N(3)	5378(11)	3749(4)	7255(4)
N(4)	8741(11)	4389(5)	8061(5)
C(5)	8732(13)	4490(6)	8939(6)
C(6)	6863(14)	4501(5)	9052(6)
N(5)	5858(11)	5018(4)	8448(4)
C(7)	6278(14)	5808(5)	8666(6)
C(8)	6278(14)	6261(5)	7923(5)
N(6)	7322(11)	5868(4)	7418(4)

TABLE 8. Observed and Calculated Ring Conformations

Cation	Conformation		
	Co(II)[a]	Co(III)	Cr(III)[b]
(±)-$Cr(en)_3^{3+}$			Λ(δδδ) + Δ(λλλ)
(±)-*cis*-$CrCl(en)_2(Hen)^{3+}$			δλ
(±)-*mer*-$Cr(dien)_2^{3+}$	δλ, δλ	δλ, δλ	δλ, δλ
s-*fac*-$Cr(dien)_2^{3+}$	λλ, λλ	λδ, λδ	λδ, λδ
(±)-*u*-*fac*-$Cr(dien)_2^{3+}$	λλ, λλ	λδ, λδ[c]	λδ, λδ
(±)-*s*-*fac*-$CrCl(dien)(Hdien)^{3+}$			λλ, λ

[a] Calculated lowest energy conformation [18]. [b] This research, $Hg_xCl_y^{n-}$ salts. [c] δδ, δδ is also observed [17] and is calculated [18] to be 2.5 kJ mol^{-1} higher in energy than the λδ, λδ.

In 2 and 6, the nitrogen atoms on the dechelated 'arm' of the polyamine ligand adopt a *trans*-configuration with respect to the C–C bond [10, 20].

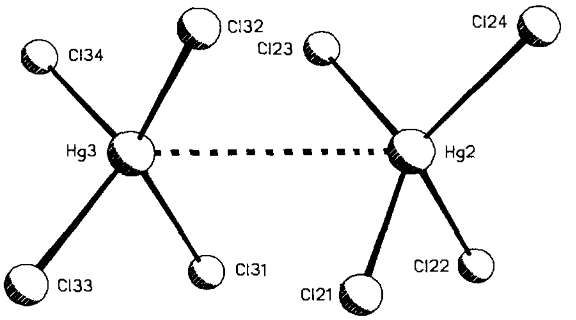

Fig. 4. The association of two eclipsed $HgCl_4^{2-}$ anions in $[Cr(en)_3]_2[Hg_3Cl_{12}]$ (1). The Hg(2)·····Hg(3) distance is 3.60 Å.

Chloro Mercury(II) Anion Geometries

The chloro mercury(II) anions in both '$HgCl_5^{3-}$' salts (2 and 3), are isolated $HgCl_4^{2-}$ tetrahedra and Cl^- ions, very similar to the situation found in Cs_3HgCl_5 [21] and $[H_3Q^{3+}][HgCl_5]$ [22]. Likewise, in $[Cr(en)_3]_2[Hg_3Cl_{12}]$ (1) two independent $Cr(en)_3^{3+}$ cations are associated with three $HgCl_4^{2-}$ units. Two of the $HgCl_4^{2-}$ anions are in close proximity with an Hg·····Hg distance of 3.46 Å and an eclipsed arrangement for the chloro ligands in the two tetrahedra (Fig. 4). A discussion of the possibility that this could be an $Hg_2Cl_8^{4-}$ unit will be incorporated in a future publication. We note that, under certain circumstances, discrete $Hg_3Cl_{12}^{6-}$ anions can exist as we have characterised these species in $[H_3dpt^{3+}]_2[Hg_3Cl_{12}^{6-}]$ [23] and they may also be present in $[H_3dien^{3+}]_2[Hg_3Cl_{12}^{6-}]$ [24].

Three different '$Hg_2Cl_7^{3-}$' anions are associated with the complex cations found in 4, 5 and 6, and

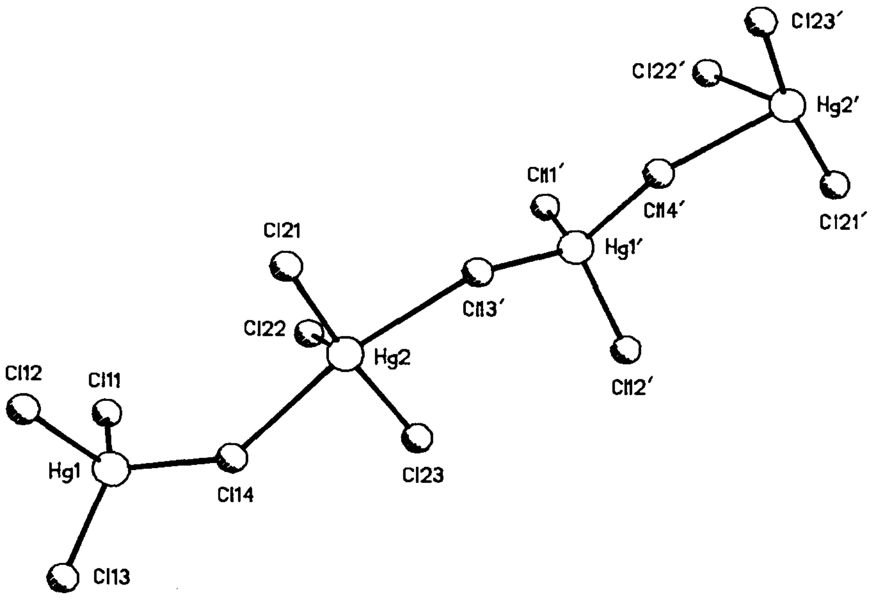

Fig. 5. The chloro mercury(II) anion arrangements in *s*-*fac*-[CrCl(dien)(Hdien,*N*,*N*)] $[Hg_2Cl_7]$ (6).

none of these correspond to the isolated $Hg_2Cl_7^{3-}$ unit found in *cis*-$[Co(en)_2(NH_3)(py)][Hg_2Cl_7]$ [25]. The above four $Hg_2Cl_7^{3-}$ salts are apparently the first to be characterised crystallographically, although $[Co(en)_3][Hg_2Cl_7]$ has been reported [26].

In **6** the anions combine into $(Hg_2Cl_7)_n^{3n-}$ polymeric chains (Fig. 5). These can be regarded as chains of alternate four and five coordinate Hg(II). The four coordinate Hg(1) is an irregular tetrahedron and the five coordinate Hg(2) can be regarded as having 3 + 2 coordination with the axial Hg(2)–Cl(14), Hg(2)–C(13′) bonds (3.110(2) and 3.139(3) Å) formed by bridges from adjacent $HgCl_4$ units.

Chains of singly bridged Hg–Cl–Hg atoms are again observed in **5**, but now each Hg atom has two reasonably short Hg–Cl bonds (2.38 Å), two longer bridging bonds (2.60, 2.83 Å) and two very long Hg–Cl interactions (3.3–3.4 Å) from adjacent tetrahedral $HgCl_4$ units (Fig. 6). In view of this latter distance the $Hg_2Cl_7^{3-}$ anion may be better regarded as isolated $HgCl_4^{2-}$ ions and singly chloro bridged $(HgCl_3)_n^{n-}$ chains [27, 28], and the salt as *u-fac*-$[Cr(dien)_2{}^{3+}]_n[HgCl_4{}^{2-}]_n[HgCl_3{}^{-}]_n$.

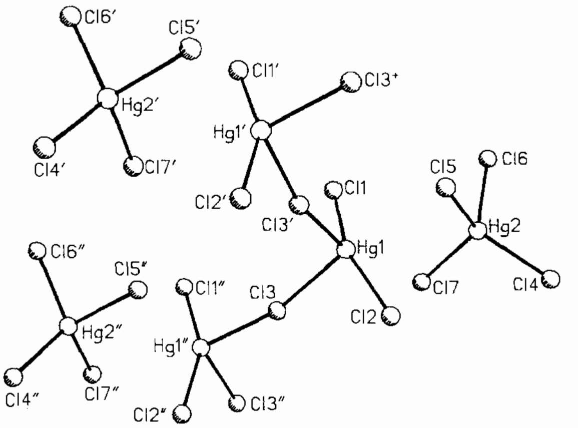

Fig. 6. The chloro mercury(II) anion arrangements in *u-fac*-$[Cr(dien)_2][Hg_2Cl_7]$ (**5**). The Hg(1)...Cl(5) and Hg(1)...Cl(7) distances are 3.30 and 3.42 Å, respectively.

TABLE 9. Selected Bond Lengths (Å), Bond Angles (°) and Dihedral Angles (°) for $[Cr(en)_3]_2[HgCl_4]_3$ (**1**)

Cations (Fig. 3)			
Cr(1)–N(11)	2.080(9)	Cr(1)–N(14)	2.070(9)
Cr(1)–N(12)	2.083(8)	Cr(1)–N(15)	2.085(9)
Cr(1)–N(13)	2.052(9)	Cr(1)–N(16)	2.076(10)
Cr(2)–N(21)	2.077(11)	Cr(2)–N(24)	2.062(7)
Cr(2)–N(22)	2.078(8)	Cr(2)–N(25)	2.075(7)
Cr(2)–N(23)	2.080(8)	Cr(2)–N(26)	2.066(10)
	Cr–N (mean) = 2.074(9)		
N(11)–C(11)	1.513(13)	N(21)–C(21)	1.469(12)
C(11)–C(12)	1.514(15)	C(21)–C(22)	1.496(17)
C(12)–N(12)	1.480(13)	C(22)–N(22)	1.522(17)
N(13)–C(13)	1.491(16)	N(23)–C(23)	1.476(12)
C(13)–C(14)	1.496(14)	C(23)–C(24)	1.484(17)
C(14)–N(14)	1.493(13)	C(24)–N(24)	1.477(12)
N(15)–C(15)	1.477(15)	N(25)–C(25)	1.490(16)
C(15)–C(16)	1.501(14)	C(25)–C(26)	1.499(18)
C(16)–N(16)	1.486(16)	C(26)–N(26)	1.504(13)
C–N (mean) = 1.490(16)		C–C (mean) = 1.498(9)	
N(11)–Cr(1)–N(16)		168.5(4)	
N(12)–Cr(1)–N(13)		172.7(4)	
N(14)–Cr(1)–N(15)		170.9(3)	
N(21)–Cr(2)–N(26)		172.0(3)	
N(22)–Cr(2)–N(23)		168.4(3)	
N(24)–Cr(2)–N(25)		171.3(4)	
N(11)–C(11)–C(12)–N(12)		53.7(1.2)	
N(13)–C(13)–C(14)–N(14)		51.4(1.2)	
N(15)–C(15)–C(16)–N(16)		56.2(1.1)	
N(21)–C(21)–C(22)–N(22)		−53.1(1.0)	
N(23)–C(23)–C(24)–N(24)		−52.9(1.2)	
N(25)–C(25)–C(26)–N(26)		−48.4(1.1)	
Anions (Fig. 4)			
Hg(1)–Cl(11)	2.476(5)	Hg(1)–Cl(13)	2.475(4)
Hg(1)–Cl(12)	2.466(4)	Hg(1)–Cl(14)	2.469(4)
Hg(2)–Cl(21)	2.485(4)	Hg(2)–Cl(23)	2.496(4)

(continued)

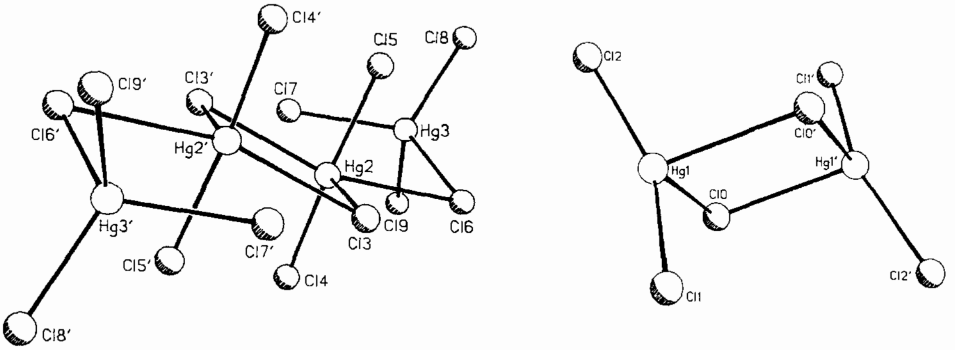

Fig. 7. The $Hg_2Cl_6^{2-}$ and $Hg_4Cl_{14}^{6-}$ anion arrangements in *s-fac*-$[Cr(dien)_2][Hg_2Cl_7]$ (**4**).

TABLE 9. *(continued)*

Anions (Fig. 4)			
Hg(2)–Cl(22)	2.612(4)	Hg(2)–Cl(24)	2.457(5)
Hg(3)–Cl(31)	2.486(3)	Hg(3)–Cl(33)	2.612(4)
Hg(3)–Cl(32)	2.511(4)	Hg(3)–Cl(34)	2.452(4)

Hg(1)–Cl (mean) = 2.499(6)
Hg(2)....Hg(3) = 3.598(4)
Hg(3)....Cl(23) = 3.461(4)
Hg(2)....Cl(32) = 3.349(4)

Cl(11)–Hg(1)–Cl(12)	110.6(1)
Cl(11)–Hg(1)–Cl(13)	109.9(1)
Cl(11)–Hg(1)–Cl(14)	108.9(1)
Cl(12)–Hg(1)–Cl(13)	108.9(1)
Cl(12)–Hg(1)–Cl(14)	109.4(1)
Cl(13)–Hg(1)–Cl(14)	109.0(1)
Cl(21)–Hg(2)–Cl(22)	94.7(1)
Cl(21)–Hg(2)–Cl(23)	136.5(1)
Cl(21)–Hg(2)–Cl(24)	106.1(1)
Cl(22)–Hg(2)–Cl(23)	98.2(1)
Cl(22)–Hg(2)–Cl(24)	121.1(1)
Cl(23)–Hg(2)–Cl(24)	102.2(1)
Cl(31)–Hg(3)–Cl(32)	135.6(1)
Cl(31)–Hg(3)–Cl(33)	97.7(1)
Cl(31)–Hg(3)–Cl(34)	104.5(1)
Cl(32)–Hg(3)–Cl(33)	92.8(1)
Cl(32)–Hg(3)–Cl(34)	106.3(1)
Cl(33)–Hg(3)–Cl(34)	121.4(1)

TABLE 10. Selected Bond Lengths (Å), Bond Angles (°) and Dihedral Angles (°) for *cis*-[CrCl(en)$_2$(Hen,*N*)][HgCl$_4$][Cl] (2)

Cations (Fig. 3)			
Cr–Cl(6)	2.302(3)	Cr–N(4)	2.072(8)
Cr–N(2)	2.080(6)	Cr–N(5)	2.065(8)
Cr–N(3)	2.090(6)	Cr–N(6)	2.089(7)
N(1)–C(1)	1.483(10)	C(1)–C(2)	1.525(10)
C(2)–N(2)	1.477(10)	N(3)–C(3)	1.472(14)
C(3)–C(4)	1.513(11)	C(4)–N(4)	1.487(9)
N(5)–C(5)	1.488(10)	C(5)–C(6)	1.495(14)
C(6)–N(6)	1.516(12)		

Cr–N (mean) = 2.079(11)
C–N (mean) = 1.490(19)
C–C (mean) = 1.511(15)

N(3)–C(3)–C(4)–N(4)	−53.1(9)
N(5)–C(5)–C(6)–N(6)	51.5(9)
N(1)–C(1)–C(2)–N(2)	176.7(7)
Cl(6)–Cr–N(6)	176.0(2)
N(2)–Cr–N(3)	177.1(3)
N(4)–Cr–N(5)	173.0(3)
N(1)–C(1)–C(2)	110.8(7)
C(1)–C(2)–N(2)	110.1(6)

(continued)

TABLE 10. *(continued)*

Anions HgCl$_4$$^{2-}$			
Hg(1)–Cl(1)	2.443(3)	Hg(1)–Cl(2)	2.477(4)
Hg(1)–Cl(3)	2.446(3)	Hg(1)–Cl(4)	2.543(3)

Hg–Cl (mean) = 2.477(46)

Cl(1)–Hg(1)–Cl(2)	111.3(1)
Cl(1)–Hg(1)–Cl(3)	113.0(1)
Cl(1)–Hg(1)–Cl(4)	113.3(1)
Cl(2)–Hg(1)–Cl(3)	116.2(1)
Cl(2)–Hg(1)–Cl(4)	103.0(1)
Cl(3)–Hg(1)–Cl(4)	99.0(1)

TABLE 11. Selected Bond Lengths (Å), Bond Angles (°) and Dihedral Angles (°) for *mer*-[Cr(dien)$_2$][HgCl$_4$][Cl]-[DMSO]$_2$ (3)

Cations (Fig. 1)	DMSO
Cr–N(1) = Cr–N(4) = 2.082(4)	S–O = 1.498(4)
Cr–N(2) = Cr–N(5) = 2.055(4)	S–C(11) = 1.776(6)
Cr–N(3) = Cr–N(6) = 2.095(4)	S–C(12) = 1.789(7)

Cr–N (mean) = 2.077(18)

N(1)–C(1) = N(4)–C(5) = 1.489(6)
C(1)–C(2) = C(5)–C(6) = 1.516(7)
C(2)–N(2) = C(6)–N(5) = 1.461(6)
N(2)–C(3) = N(5)–C(7) = 1.479(6)
C(3)–C(4) = C(7)–C(8) = 1.513(8)
C(4)–N(3) = C(8)–N(6) = 1.489(7)
N(1)–Cr–N(3) = 163.9(2)
N(2)–Cr–N(5) = 178.4(2)
N(4)–Cr–N(6) = 163.9(2)
N(1)–C(1)–C(2)–N(2) = 49.4(5)
N(2)–C(3)–C(4)–N(3) = 53.5(5)

HgCl$_4$$^{2-}$

Hg–Cl(1) = Hg–Cl(3) = 2.518(1)
Hg–Cl(2) = Hg–Cl(4) = 2.454(1)

Hg–Cl (mean) = 2.486(37)

Cl(1)–Hg–Cl(2) = 105.7(1) = Cl(3)–Hg–Cl(4)
Cl(1)–Hg–Cl(3) = 111.2(1) = Cl(2)–Hg–Cl(4)
Cl(1)–Hg–Cl(4) = 101.8(1)
Cl(2)–Hg–Cl(3) = 119.8(1)

Finally, in the *s-fac*-[Cr(dien)$_2$][Hg$_2$Cl$_7$] (4) salt, the infinite –Hg–Cl–Hg–Cl– chains are broken into smaller ionic fragments (Fig. 7) *viz.*, isolated tetrahedra, HgCl$_4$$^{2-}$; dimeric edge-shared bitetrahedra, Hg$_2$Cl$_6$$^{2-}$; and an Hg$_4Cl_{14}$$^{6-}$ unit where singly bridged HgCl$_4$ units are linked (3.118(3) Å) to each end of a dibridged Hg$_2$Cl$_6$ core, to give a salt of molecular formula *s-fac*-[Cr(dien)$_2$$^{3+}$]$_4$[HgCl$_4$$^{2-}$]$_2$[Hg$_2Cl_6$$^{2-}$]-[Hg$_4Cl_{14}$$^{6-}$].

TABLE 12. Selected Bond Lengths (Å), Bond Angles (°) and Dihedral Angles (°) for s-*fac*-$[Cr(dien)_2]_4[HgCl_4]_2[Hg_2Cl_6][Hg_4Cl_{14}]$, 's-*fac*-$[Cr(dien)_2][Hg_2Cl_7]$' (4)

Cations (Fig. 1)			
Cr(1)–N(11)	2.052(11)	Cr(2)–N(21)	2.097(10)
Cr(1)–N(12)	2.055(8)	Cr(2)–N(22)	2.064(9)
Cr(1)–N(13)	2.089(9)	Cr(2)–N(23)	2.089(8)
	Cr–N (mean) = 2.074(20)		
Cr(3)–N(31)	2.067(10)	Cr(3)–N(34)	2.091(9)
Cr(3)–N(32)	2.056(8)	Cr(3)–N(35)	2.066(9)
Cr(3)–N(33)	2.066(9)	Cr(3)–N(36)	2.072(10)
	Cr–N (mean) = 2.070(12)		
N(31)–C(31)	1.479(13)	N(36)–C(38)	1.502(13)
C(31)–C(32)	1.545(20)	C(38)–C(37)	1.503(18)
C(32)–N(32)	1.488(15)	C(37)–N(35)	1.485(15)
N(32)–C(33)	1.502(13)	N(35)–C(36)	1.490(13)
C(33)–C(34)	1.475(18)	C(36)–C(35)	1.476(19)
C(34)–N(33)	1.537(12)	C(35)–N(34)	1.528(13)
N(11)–C(11)	1.516(15)	N(21)–C(21)	1.488(13)
C(11)–C(12)	1.536(15)	C(21)–C(22)	1.495(21)
C(12)–N(12)	1.475(18)	C(22)–N(22)	1.504(16)
N(12)–C(13)	1.485(15)	N(22)–C(23)	1.497(14)
C(13)–C(14)	1.529(15)	C(23)–C(24)	1.532(18)
C(14)–N(13)	1.488(15)	C(24)–N(23)	1.503(13)
N(11)–C(11)–C(12)–N(12)	−42.8(1.2)		
N(12)–C(13)–C(14)–N(13)	47.1(1.5)		
N(21)–C(21)–C(22)–N(22)	−44.7(1.2)		
N(22)–C(23)–C(24)–N(23)	43.2(1.2)		
N(31)–C(31)–C(32)–N(32)	−46.8(1.1)		
N(32)–C(33)–C(34)–N(33)	41.8(1.3)		
N(34)–C(35)–C(36)–N(35)	47.0(1.0)		
N(35)–C(37)–C(38)–N(36)	−42.2(1.3)		
Anions			
$HgCl_4^{2-}$			
Hg(4)–Cl(10)	2.544(3)	Hg(4)–Cl(12)	2.444(3)
Hg(4)–Cl(11)	2.432(3)	Hg(4)–Cl(13)	2.516(3)
	Hg–Cl (mean) = 2.484(55)		
Cl(10)–Hg(4)–Cl(11)	118.4(1)	Cl(11)–Hg(4)–Cl(12)	114.2(1)
Cl(10)–Hg(4)–Cl(12)	99.8(1)	Cl(11)–Hg(4)–Cl(13)	103.3(1)
Cl(10)–Hg(4)–Cl(13)	100.6(1)	Cl(12)–Hg(4)–Cl(13)	120.6(1)
$Hg_2Cl_6^{2-}$ (Fig. 7)			
Hg(1)–Cl(0)	2.724(3)		
Hg(1)–Cl(0′)	2.759(3)		
Hg(1)–Cl(1)	2.383(3)		
Hg(1)–Cl(2)	2.350(3)		
Hg(1) .... Hg(1′)	4.070(5)		
Cl(1)–Hg(1)–Cl(2)	151.2(1)	Cl(0)–Hg(1)–Cl(1)	107.4(1)
Cl(1)–Hg(1)–Cl(0′)	92.4(1)	Cl(0)–Hg(1)–Cl(2)	97.6(1)
Cl(2)–Hg(1)–Cl(0′)	104.3(1)	Cl(0)–Hg(1)–Cl(0′)	84.1(1)

(continued)

TABLE 12. *(continued)*

Hg$_4$Cl$_{14}^{6-}$ (Fig. 7)			
Hg(2)–Cl(4)	2.344(3)	Hg(3)–Cl(6)	2.528(4)
Hg(2)–Cl(5)	2.361(3)	Hg(3)–Cl(7)	2.502(2)
Hg(2)–Cl(3)	2.740(3)	Hg(3)–Cl(8)	2.406(3)
Hg(2)–Cl(3′)	2.880(3)[a]	Hg(3)–Cl(9)	2.516(3)
Hg(2)–Cl(6)	3.118(2)		
	Hg(2)....Hg(2′)	3.790(4)	
	Hg(2)....Hg(3)	3.747(4)	
Cl(3)–Hg(2)–Cl(3′)	95.2(1)	Cl(5)–Hg(2)–Cl(3′)	84.7(1)
Cl(3)–Hg(2)–Cl(4)	98.6(1)	Cl(6)–Hg(2)–Cl(3′)	158.7(1)
Cl(3)–Hg(2)–Cl(5)	93.6(1)	Cl(6)–Hg(3)–Cl(7)	115.6(1)
Cl(3)–Hg(2)–Cl(6)	100.5(1)	Cl(6)–Hg(3)–Cl(8)	112.8(1)
Cl(4)–Hg(2)–Cl(5)	165.2(1)	Cl(6)–Hg(3)–Cl(9)	98.6(1)
Cl(4)–Hg(2)–Cl(6)	89.3(1)	Cl(7)–Hg(3)–Cl(8)	114.1(1)
Cl(4)–Hg(2)–Cl(3′)	102.4(1)	Cl(7)–Hg(3)–Cl(9)	97.7(1)
Cl(5)–Hg(2)–Cl(6)	80.2(1)	Cl(8)–Hg(3)–Cl(9)	116.2(1)

[a] Also equals Hg(2′)–Cl(3).

TABLE 13. Selected Bond Lengths (Å), Bond Angles (°) and Dihedral Angles (°) for *u-fac*-[Cr(dien)$_2$]$_n$[HgCl$_4$]$_n$[HgCl$_3$]$_n$, '*u-fac*-[Cr(dien)$_2$][Hg$_2$Cl$_7$]' (5)

Cations (Fig. 1)			
Cr–N(1)	2.091(25)	Cr–N(4)	2.034(24)
Cr–N(2)	2.066(24)	Cr–N(5)	2.084(23)
Cr–N(3)	2.097(23)	Cr–N(6)	2.076(23)
	Cr–N (mean) = 2.075(22)		
N(1)–C(1)	1.486(44)	C(1)–C(2)	1.529(43)
N(2)–C(2)	1.565(36)	C(3)–C(4)	1.459(39)
N(2)–C(3)	1.512(36)	C(5)–C(6)	1.517(36)
N(3)–C(4)	1.468(37)	C(7)–C(8)	1.502(45)
N(4)–C(5)	1.454(39)	N(5)–C(7)	1.457(44)
N(5)–C(6)	1.494(35)	N(6)–C(8)	1.491(36)
N(1)–Cr–N(5)	175.7(1.0)		
N(2)–Cr–N(4)	172.9(1.0)		
N(3)–Cr–N(6)	173.6(0.9)		
N(1)–C(1)–C(2)–N(2)	48.8(3.2)		
N(2)–C(3)–C(4)–N(3)	−48.2(3.0)		
N(4)–C(5)–C(6)–N(5)	49.7(2.9)		
N(5)–C(7)–C(8)–N(6)	−42.1(3.6)		

Anions (Fig. 6)			
Hg(1)–Cl(1)	2.367(7)	Hg(1)·····Hg(1′)	5.374
Hg(1)–Cl(2)	2.369(7)	Hg(1)·····Hg(2′)	3.880
Hg(1)–Cl(3)	2.783(7)	Hg(1)·····Cl(2′)	6.46
Hg(1)–Cl(3′)	2.636(7)		
Hg(2)–Cl(4)	2.431(8)	Hg(1)·····Cl(5)	3.300
Hg(2)–Cl(5)	2.557(7)	Hg(1)·····Cl(7)	3.417
Hg(2)–Cl(6)	2.479(8)		
Hg(2)–Cl(7)	2.528(7)		
	Hg(2)–Cl (mean) = 2.497(53)		

(continued)

TABLE 13. *(continued)*

Anions (Fig. 6)

Cl(1)-Hg(1)-Cl(2)	154.6(3)	Cl(4)-Hg(2)-Cl(5)	109.7(2)
Cl(1)-Hg(1)-Cl(3)	95.9(3)	Cl(4)-Hg(2)-Cl(6)	118.3(3)
Cl(1)-Hg(1)-Cl(3′)	98.8(3)	Cl(4)-Hg(2)-Cl(7)	106.5(3)
Cl(2)-Hg(1)-Cl(3)	91.8(2)	Cl(5)-Hg(2)-Cl(6)	96.9(3)
Cl(2)-Hg(1)-Cl(3′)	102.7(3)	Cl(5)-Hg(2)-Cl(7)	117.5(2)
Cl(3)-Hg(1)-Cl(3′)	104.0(1)	Cl(6)-Hg(2)-Cl(7)	108.3(2)

TABLE 14. Selected Bond Lengths (A), Bond Angles (°) and Dihedral Angles (°) for *s-fac*-[CrCl(dien)(Hdien,*N*,*N*)]$_n$[Hg_2Cl_7]$_n$ (6)

Cations (Fig. 2)

Cr-Cl(1)	2.313(3)	C(5)-C(6)	1.523(15)
Cr-N(2)	2.129(8)	C(6)-N(5)	1.496(12)
Cr-N(3)	2.066(8)	N(5)-C(7)	1.507(12)
Cr-N(4)	2.083(8)	C(7)-C(8)	1.504(14)
Cr-N(5)	2.102(8)	C(8)-N(6)	1.483(14)
Cr-N(6)	2.081(8)	N(2)-C(3)	1.503(12)
N(1)-C(1)	1.492(13)	C(3)-C(4)	1.493(13)
C(1)-C(2)	1.527(14)	C(4)-N(3)	1.481(13)
C(2)-N(2)	1.492(12)	N(4)-C(5)	1.498(13)
N(1)-C(1)-C(2)	108.9(8)	Cl(1)-Cr-N(5)	170.6(2)
C(1)-C(2)-N(2)	111.4(8)	N(2)-Cr-N(4)	170.3(3)
C(2)-N(2)-C(3)	110.6(7)	N(3)-Cr-N(6)	173.0(4)
C(6)-N(5)-C(7)	111.8(7)		
N(2)-C(3)-C(4)-N(3)	-53.3(1.0)		
N(4)-C(5)-C(6)-N(5)	-48.4(1.0)		
N(5)-C(7)-C(8)-N(6)	-48.2(1.0)		
N(1)-C(1)-C(2)-N(2)	169.8(0.7)		

Anions (Fig. 5)

Hg(1)-Cl(11)	2.470(3)	Hg(2)-Cl(21)	2.335(2)
Hg(1)-Cl(12)	2.562(2)	Hg(2)-Cl(22)	2.672(3)
Hg(1)-Cl(13)	2.443(3)	Hg(2)-Cl(23)	2.346(2)
Hg(1)-Cl(14)	2.457(2)	Hg(2)-Cl(14)	3.110(2)[a]
Hg(2″)....Cl(11)[d]	3.209(3)	Hg(2)-Cl(13′)	3.139(3)[a,b]
	Hg(1)....Hg(2)	5.244(4)	
Cl(11)-Hg(1)-Cl(12)	105.3(1)	Cl(14)-Hg(2)-Cl(13′)[b]	168.9(1)
Cl(11)-Hg(1)-Cl(13)	111.7(1)	Cl(21)-Hg(2)-Cl(22)	96.8(1)[c]
Cl(11)-Hg(1)-Cl(14)	105.7(1)	Cl(21)-Hg(2)-Cl(23)	165.4(1)[c]
Cl(12)-Hg(1)-Cl(13)	105.0(1)	Cl(21)-Hg(2)-Cl(13′)[b]	89.0(1)
Cl(12)-Hg(1)-Cl(14)	111.6(1)	Cl(22)-Hg(2)-Cl(23)	97.2(1)[c]
Cl(13)-Hg(1)-Cl(14)	117.0(1)	Cl(22)-Hg(2)-Cl(13′)[b]	98.4(1)
Cl(14)-Hg(2)-Cl(21)	101.5(1)	Cl(23)-Hg(2)-Cl(13′)[b]	84.7(1)
Cl(14)-Hg(2)-Cl(22)	84.1(1)	Hg(1)-Cl(11)-Hg(2″)d	140.5(1)
Cl(14)-Hg(2)-Cl(23)	84.3(1)	Hg(1)-Cl(11)-Hg(2″)[d]	171.6(1)
		Hg(2)-Cl(13′)-Hg(1′)	148.6(1)

[a] Axial Hg(2)-Cl bond lengths in the '$HgCl_5$' unit. [b] Cl(13′) is equivalent to Cl(13). [c] 'Trigonal Hg(2)-Cl' bond angles. [d] Hg(2″) is in an adjacent chain.

We will postpone a detailed discussion of bond lengths and angles in chloro mercury(II) anions for a further publication but important distances observed are listed in Tables 9–14.

Supplementary Material

Tables of structure factors, hydrogen atom coordinates and anisotropic thermal parameters are available from the authors.

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