Polynuclear chloromercurate(II) systems in their chloropyridinium salts

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Abstract

The chloromercurate(II) salts of 2-, 3- and 4-chloropyridine display a variety of anion stoichiometries and structures, including the rare $[Hg_3Cl_{10}]^{4-}$ stoichiometry. 2-Chloropyridinium trichloromercurate(II), (I), $(C_5H_5ClN)[HgCl_3]$, monoclinic, $P2_1/n$, $a = 9.094$ (8), $b = 18.143$ (4), $c = 12.902$ (3) Å, $\beta = 106.13$ (4)° with $Z = 8$, has the $[HgCl_3]^-$ stoichiometry, but the anions are infinite chains composed of $[HgCl_3]^-$, $HgCl_2$ and Cl^- moieties linked by longer $Hg\cdots Cl$ contacts. Hydrogen bonds link the cations to the formal Cl^- ions. Tetrakis-(3-chloropyridinium) decachlorotrimercurate(II), (II), $(C_5H_5ClN)_4[Hg_3Cl_{10}]$, monoclinic, $P2_1/n$, $a = 7.522$ (2), $b = 28.046$ (3), $c = 9.165$ (2) Å, $\beta = 105.78$ (2)° with $Z = 2$, has the rare $[Hg_3Cl_{10}]^{4-}$ stoichiometry and contains infinite one-dimensional double-stranded $\{([HgCl_4]^{2-})_2 [HgCl_2]\}_n$ anionic chains made up of linear $HgCl_2$ and distorted $[HgCl_4]^{2-}$ entities linked together by longer $Hg\cdots Cl$ contacts. The $HgCl_2$ moieties are joined by double $[HgCl_4]^{2-}$ bridges. Hydrogen bonds link the cations to the sides of the anionic columns. Tetrakis-(4-chloropyridinium) decachlorotrimercurate(II), (III), $(C_5H_5ClN)_4[Hg_3Cl_{10}]$, triclinic, $P\bar{1}$, $a = 9.907$ (3), $b = 13.226$ (2), $c = 7.282$ (2) Å, $\alpha = 84.41$ (2), $\beta = 74.81$ (2), $\gamma = 87.34$ (2)° with $Z = 1$, also has the $[Hg_3Cl_{10}]^{4-}$ stoichiometry and the same type of $\{([HgCl_4]^{2-})_2 [HgCl_2]\}_n$ anionic chains that were found in compound (II), but the formal $HgCl_2$ and $[HgCl_4]^{2-}$ moieties are more discrete with much weaker contacts linking the individual units. Bifurcated hydrogen bonds with the cations cross-link the anionic chains to form an infinite two-dimensional network. Second forms of the 3- and 4-chloropyridinium salts were also obtained. 3-Chloropyridinium trichloromercurate(II), (IV), $(C_5H_5ClN)[HgCl_3]$, monoclinic, $P2_1/c$, $a = 7.243$ (5), $b = 22.145$ (8), $c = 12.320$ (3) Å, $\beta = 99.52$ (3)° with $Z = 8$, has the $[HgCl_3]^-$ stoichiometry, but the anions are infinite chains composed of distorted $[Hg_2Cl_6]^{2-}$ moieties. Bifurcated hydrogen bonds from the cations cross-link the anionic chains to form infinite two-dimensional layers. Bis(4-chloropyridinium) hexachlorodimercurate(II), (V), $(C_5H_5ClN)_2[Hg_2Cl_6]$, monoclinic, $C2/m$, $a = 13.447$ (3), $b = 7.534$ (2), $c = 9.939$ (2) Å, $\beta = 97.48$ (2)° with $Z = 2$, contains highly symmetrical discrete $[Hg_2Cl_6]^{2-}$ anions. Bifurcated hydrogen bonds from the cations interconnect the anions to form infinite one-dimensional chains.

1. Introduction

A number of chloromercurate(II) complexes have been shown to exhibit ferroelectric behaviour (Mitsui & Nakamura, 1990) and interest has focused on the mechanism of the ferroelectric–paraelectric phase transition (White, 1963; Körfer *et al.*, 1988; Jiang *et al.*, 1995; Liesegang *et al.*, 1995) for which structural information is crucial. In addition, the ability of the anions in this class of compounds to exhibit a wide range of geometry, stoichiometry and connectivity has long been known (Grdenic, 1965). This flexibility is a result of the large volume and spherical charge distribution of the Hg^{2+} ion, which are a consequence of the filled $4f$ and $5d$ electron shells.

An early attempt at generalization suggested that small cations tend to give chloromercurates with Hg in (distorted) octahedral sites, while larger cations produced structures with Hg atoms in trigonal bipyramidal sites (Goggin *et al.*, 1982), but later investigations showed a greater variety of anion types. A recent review of chloromercurate(II) compounds (House *et al.*, 1994) describes a prolific range of anionic structures from the simple $[HgCl_3]^-$ ion right through to very complex species, such as $[Hg_6Cl_{13}]^-$ and $[Hg_4Cl_{14}]^{6-}$. Both infinite chain structures and discrete anions are common, but complex networks have also been observed. Although a wide range of complex anionic structures exists, their make-up is often derived from simple subunits linked by longer $Hg\cdots Cl$ contacts. The usual subunits are $HgCl_2$, Cl^-, $[HgCl_3]^-$ and $[HgCl_4]^{2-}$. For example, two $HgCl_2$ subunits and an $[HgCl_4]^{2-}$ anion combine to make up $[Hg_3Cl_8]^{2-}$ (Terzis *et al.*, 1985). The linear $HgCl_2$ subunit, distorted by $Hg\cdots Cl$ contacts, is probably the most frequently occurring of the primary building blocks. Sometimes the overall anion stoichiometry does not reflect the actual species present. In one notable example, the compound with stoichiometry *s-fac*-$[Cr(dien)_2][Hg_2Cl_7]$ contains an amazing combi-

Table 1. *The chloromercurate(II) complexes investigated in this study*

Compound	Cation	Anion stoichiometry	Form of the anion
(I)	$(2\text{-ClpyH})^+$	$[HgCl_3]^-$	$\{[HgCl_3]^-\,[HgCl_2]\,Cl^-\}_n$ chains
(II)	$(3\text{-ClpyH})^+$	$[Hg_3Cl_{10}]^{4-}$	$\{([HgCl_4]^{2-})_2\,[HgCl_2]\}_n$ chains
(III)	$(4\text{-ClpyH})^+$	$[Hg_3Cl_{10}]^{4-}$	$\{([HgCl_4]^{2-})_2\,[HgCl_2]\}_n$ chains
(IV)	$(3\text{-ClpyH})^+$	$[HgCl_3]^-$	$\{[Hg_2Cl_6]^{2-}\}_n$ chains
(V)	$(4\text{-ClpyH})^+$	$[HgCl_3]^-$	Discrete $[Hg_2Cl_6]^{2-}$ anions

nation of discrete $[HgCl_4]^{2-}$, $[Hg_2Cl_6]^{2-}$ and $[Hg_4Cl_{14}]^{6-}$ ions (House *et al.*, 1989).

In compounds with $[HgCl_3]^-$ stoichiometry, the isolated trigonal planar $[HgCl_3]^-$ unit is actually very rare and chains of $[HgCl_3]^-$ units are much more prevalent. The isolated dimeric $[Hg_2Cl_6]^{2-}$ version is also somewhat more familiar (Kistenmacher *et al.*, 1980; Goggin *et al.*, 1982; Chaari *et al.*, 1989). While there are reports of structures said to contain isolated $[HgCl_3]^-$ ions (for example, Larock *et al.*, 1987; Lobana *et al.*, 1990; Sobhia *et al.*, 1992), closer examination of the structures usually reveals the presence of additional coordination by long Hg$\cdots$Cl contacts which have either been overlooked or discarded as being too long to be significant.

Currently, there is no explanation available which allows the Hg coordination geometry in any particular structure to be predicted and the Hg—Cl distances are found to vary significantly from one structure to the next. Hg—Cl distances of 2.3–2.6 Å are clearly formal bonding interactions, while Hg$\cdots$Cl contacts right up to 3.35 Å, and maybe even longer, are considered to be significant interactions (House *et al.*, 1994). A large variety of intermediate distances have been observed, and there is no clear definition as to where the border between a formal bond and a long contact lies.

In experiments designed to extend the range of trichloromercurate(II) compounds that might display ferroelectric properties, the simple, but related, organic base cations from 2-, 3- and 4-chloropyridine have been combined with $HgCl_2$ in concentrated HCl and the structures of the resulting crystalline salts have been determined. It was expected that the moderately sized and flat chloropyridinium cations $[(n\text{-ClpyH})^+]$ would lead to one consistent chloromercurate type, but with some steric influences arising from the relative positions of the substituent Cl atoms. Cation–anion (N—H$\cdots$Cl) hydrogen bonds were also expected to influence the structure, but only slightly. That these modest expectations were generally not met will be discussed below. The forms of the anions and the stoichiometries of the salts obtained are summarized in Table 1.

2. Experimental

2.1. Syntheses

Starting materials were obtained from the Aldrich Chemical Company and used without further purifica-

tion. For compounds (I)–(V), colourless prismatic crystals were obtained by slow dehydration of concentrated HCl solutions containing equimolar quantities of mercury(II) chloride and the appropriate chloropyridine (the hydrochloride salt for 4-chloropyridine). It was found that product formation was somewhat inconsistent in that those crystals isolated from the body of the mother liquor often became opaque rapidly on exposure to air (especially the 3-chloropyridinium samples), while others which formed at the air–mother liquor interface remained transparent and stable (often for months under ambient conditions). For compound (I): m.p. 377–379 K; analysis calculated for $C_5H_5Cl_4HgN$: C 14.25, H 1.20, N 3.32, Cl 33.64%; found: C 14.20, H 0.88, N 3.48, Cl 33.47%. For compound (III): m.p. 373–375 K; analysis calculated for $C_{20}H_{20}Cl_{14}Hg_3N_4$: C 16.98, H 1.43, N 3.96, Cl 35.09%; found: C 17.46, H 1.25, N 3.93, Cl 33.85%. For compound (IV): m.p. 367–370 K; analysis calculated values are as for compound (I); found: C 14.32, H 0.60, N 3.21, Cl 33.30%. For compound (V): m.p. 385 K; analysis calculated values are as for compound (I); found: C 14.32, H 0.93, N 3.28, Cl 33.00%. Although a transparent crystal of compound (II) was isolated for the crystal structure determination, the bulk sample rapidly became opaque and had an m.p. of 354–355 K and analysis C 13.97, H 1.93, N 3.28, Cl 33.18%, which does not correspond with that expected from the formula obtained from the crystal structure analysis. This material might be a hydrated variant of a compound with $[HgCl_3]^-$ stoichiometry, since for $2[C_5H_5Cl_4HgN]\cdot H_2O$, the calculated values would be C 13.95, H 1.17, N 3.25, Cl 35.09%.

2.2. Data collection, structure solution and refinement

Details of the crystal data, data collections and refinements are summarized in Table 2. Crystals were mounted on glass fibres and a 12 kW rotating-anode generator was used. The space groups for (I), (II) and (IV) were uniquely determined by the systematic absences and for (III) and (V) by the successful analysis. An analytical absorption correction (de Meulenaer & Tompa, 1965) was applied in the case of (III) and (V), while an empirical absorption correction based on ψ scans (North *et al.*, 1968) was applied for (I), (II) and (IV). Attempts to apply analytical absorption corrections for these latter compounds produced inferior results. This may be attributed, in part, to the lumpy and

Table 2. *Experimental details*

	(I)	(II)	(III)	(IV)	(V)
Crystal data					
Chemical formula	$(C_5H_5ClN)[HgCl_3]$	$(C_5H_5ClN)_4$-$[Hg_3Cl_{10}]$	$(C_5H_5ClN)_4$-$[Hg_3Cl_{10}]$	$(C_5H_5ClN)[HgCl_3]$	$(C_5H_5ClN)_2$-$[Hg_2Cl_6]$
Chemical formula weight	421.49	1414.52	1414.52	421.49	842.98
Cell setting	Monoclinic	Monoclinic	Triclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/n$	$P\bar{1}$	$P2_1/c$	$C2/m$
a (Å)	9.094 (8)	7.522 (2)	9.907 (3)	7.243 (5)	13.447 (3)
b (Å)	18.143 (4)	28.046 (3)	13.226 (2)	22.145 (8)	7.534 (2)
c (Å)	12.902 (3)	9.165 (2)	7.282 (2)	12.320 (3)	9.939 (2)
α (°)	90	90	84.41 (2)	90	90
β (°)	106.13 (4)	105.78 (2)	74.81 (2)	99.52 (3)	97.48 (2)
γ (°)	90	90	87.34 (2)	90	90
V (Å^3)	2045 (2)	1860.5 (7)	916.2 (4)	1948.8 (13)	998.3 (3)
Z	8	2	1	8	2
D_x (Mg m^{-3})	2.738	2.524	2.564	2.873	2.804
Radiation type	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$	Mo $K\alpha$
Wavelength (Å)	0.71069	0.71069	0.71069	0.71069	0.71069
No. of reflections for cell parameters	25	25	25	25	25
θ range (°)	19.5–20.0	19.5–20.0	19.5–20.0	19.0–20.0	19.0–20.0
μ (mm^{-1})	16.04	13.37	13.58	16.83	16.46
Temperature (K)	173 (1)	173 (1)	173 (1)	173 (1)	173 (1)
Crystal form	Prism	Prism	Prism	Prism	Prism
Crystal size (mm)	0.40 × 0.25 × 0.15	0.37 × 0.35 × 0.28	0.43 × 0.27 × 0.11	0.38 × 0.30 × 0.28	0.35 × 0.25 × 0.15
Crystal colour	Colourless	Colourless	Colourless	Colourless	Colourless
Data collection					
Diffractometer	Rigaku AFC-5R	Rigaku AFC-5R	Rigaku AFC-5R	Rigaku AFC-5R	Rigaku AFC-5R
Data collection method	ω–2θ scans	ω scans	ω–2θ scans	ω–2θ scans	ω–2θ scans
Absorption correction	Empirical *via* ψ scans (North *et al.*, 1968)	Empirical *via* ψ scans (North *et al.*, 1968)	Analytical (de Meulenaer & Tompa, 1965)	Empirical *via* ψ scans (North *et al.*, 1968)	Analytical (de Meulenaer & Tompa, 1965)
T_{min}	0.026	0.010	0.055	0.004	0.034
T_{max}	0.090	0.024	0.270	0.009	0.200
No. of measured reflections	5129	5915	5621	6239	1618
No. of independent reflections	4679	5426	5337	5681	1557
No. of observed reflections	3153	4337	4398	4100	1329
Criterion for observed reflections	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$	$I > 2\sigma(I)$
R_{int}	0.273	0.046	0.019	0.073	0.088
θ_{max} (°)	27.5	30	30	30	30
Range of h, k, l	$0 \rightarrow h \rightarrow 11$	$0 \rightarrow h \rightarrow 10$	$-13 \rightarrow h \rightarrow 0$	$0 \rightarrow h \rightarrow 10$	$0 \rightarrow h \rightarrow 18$
	$0 \rightarrow k \rightarrow 23$	$0 \rightarrow k \rightarrow 39$	$-18 \rightarrow k \rightarrow 18$	$0 \rightarrow k \rightarrow 31$	$0 \rightarrow k \rightarrow 10$
	$-16 \rightarrow l \rightarrow 16$	$-12 \rightarrow l \rightarrow 12$	$-10 \rightarrow l \rightarrow 9$	$-17 \rightarrow l \rightarrow 17$	$-13 \rightarrow l \rightarrow 13$
No. of standard reflections	3	3	3	3	3
Frequency of standard reflections	Every 150 reflections	Every 150 reflections	Every 150 reflections	Every 150 reflections	Every 150 reflections
Intensity decay	None	None	None	None	None
Refinement					
Refinement on	F	F	F	F	F
R	0.0437	0.0357	0.0383	0.0486	0.0528
wR	0.0358	0.0375	0.0386	0.0489	0.0641
S	1.684	1.950	2.200	2.014	2.187
No. of reflections used in refinement	3153	4337	4398	4100	1328
No. of parameters used	200	188	198	200	61

Table 2 (*cont.*)

	(I)	(II)	(III)	(IV)	(V)
Weighting scheme	$w = 1/[\sigma^2(F_o)$ $+ (0.005F_o)^2]$	$w = 1/[\sigma^2(F_o)$ $+ (0.005F_o)^2]$	$w = 1/[\sigma^2(F_o)$ $+ (0.005F_o)^2]$	$w = 1/[\sigma^2(F_o)$ $+ (0.005F_o)^2]$	$w = 1/[\sigma^2(F_o)$ $+ (0.015F_o)^2]$
$(\Delta/\sigma)_{max}$	0.0002	0.0005	0.003	0.001	0.0007
$\Delta\rho_{max}$ (e Å^{-3})	1.66	2.15	2.31	4.06	2.81
$\Delta\rho_{min}$ (e Å^{-3})	−2.33	−2.32	−2.12	−2.79	−3.16
Extinction method	Isotropic (Zachar-iasen, 1963)	Isotropic (Zachar-iasen, 1963)	Isotropic (Zachar-iasen, 1963)	Isotropic (Zachar-iasen, 1963)	Isotropic (Zachar-iasen, 1963)
Extinction coeffi-cient	$9.3 (8) \times 10^{-8}$	$1.3 (2) \times 10^{-7}$	$1.8 (1) \times 10^{-6}$	$1.9 (1) \times 10^{-7}$	$1.6 (3) \times 10^{-6}$
Source of atomic scattering factors	*International Tables for Crystallo-graphy* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.1)	*International Tables for Crystallo-graphy* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.1)	*International Tables for Crystallo-graphy* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.1)	*International Tables for Crystallo-graphy* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.1)	*International Tables for Crystallo-graphy* (1992, Vol. C, Tables 4.2.6.8 and 6.1.1.1)
Computer programs					
Data collection and cell refinement	*MSC/AFC Diffract-ometer Control Software* (Mole-cular Structure Corporation, 1991)	*MSC/AFC Diffract-ometer Control Software* (Mole-cular Structure Corporation, 1991)	*MSC/AFC Diffract-ometer Control Software* (Mole-cular Structure Corporation, 1991)	*MSC/AFC Diffract-ometer Control Software* (Mole-cular Structure Corporation, 1991)	*MSC/AFC Diffract-ometer Control Software* (Mole-cular Structure Corporation, 1991)
Data reduction	*TEXSAN PROCESS* (Molecular Struc-ture Corporation, 1989)	*TEXSAN PROCESS* (Molecular Struc-ture Corporation, 1989)	*TEXSAN PROCESS* (Molecular Struc-ture Corporation, 1989)	*TEXSAN PROCESS* (Molecular Struc-ture Corporation, 1989)	*TEXSAN PROCESS* (Molecular Struc-ture Corporation, 1989)
Structure solution	*SHELXS*86 Patterson (Shel-drick, 1990)	*DIRDIF*92 Patterson (Beurskens *et al.*, 1992)	*DIRDIF*92 Patterson (Beurskens *et al.*, 1992)	*DIRDIF*92 Patterson (Beurskens *et al.*, 1992)	*DIRDIF*92 Patterson (Beurskens *et al.*, 1992)
Structure refinement	*TEXSAN LS*	*TEXSAN LS*	*TEXSAN LS*	*TEXSAN LS*	*TEXSAN LS*
Preparation of mate-rial for publication	*TEXSAN FINISH* and local programs	*TEXSAN FINISH* and local programs	*TEXSAN FINISH* and local programs	*TEXSAN FINISH* and local programs	*TEXSAN FINISH* and local programs

irregular nature of some of the crystal faces, which hindered the accurate indexing of the faces. The crystals generally grew as larger masses which were very brittle when cut. R_{int} is very large for compound (I), but this is owing only to a few inconsistent equivalences. Each structure was solved by the Patterson method which revealed the positions of the Hg atoms. All remaining non-H atoms were located in subsequent difference electron density maps. In (II) and (III), one Hg atom lies on a centre of inversion. In (V), the Hg and terminal Cl atoms of the anion lie on a mirror plane, while the bridging Cl atoms lie on a twofold axis and the cation lies perpendicular to the mirror plane passing through the atoms N1, C4 and Cl4. The non-H atoms were refined anisotropically. All H atoms were fixed in geometrically calculated positions (C—H and N—H = 0.95 Å) and, except in the case of compound (III), were assigned isotropic displacement parameters with values equal to $1.2U_{eq}$ of the parent atom. Individual isotropic displacement parameters were refined for the H atoms of compound (III). Corrections for secondary extinction were applied. For (V), reflection 400 was excluded from the final refinement cycles because of suspected extreme extinction effects. The four largest peaks of residual electron density were always within 1.2 Å of the Hg

atoms. There is no evidence of disorder in any of the structures. Examination of each structure using *PLATON* (Spek, 1997) showed that there were no solvent-accessible regions in the crystal structures. The diagrams were prepared using *ORTEP*III (Burnett & Johnson, 1996). Final fractional atomic coordinates and equivalent isotropic displacement parameters are given in Tables 3–7†.

3. Results and discussion

In the 2-, 3- and 4-chloropyridinium [$(n$-ClpyH)$^+$] systems reported here, diversity of anion geometry and stoichiometry was observed once again, although the cations were all deliberately chosen to be similar. Surprisingly, even under apparently similar conditions, two preparations of the 3- and 4-chloropyridinium salts yielded crystals with different anion stoichiometries [compounds (II) and (IV) and compounds (III) and (V), respectively; see Table 1]. Compound (I) contains the 2-chloropyridinium cation.

Table 3. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (I)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Hg1	0.13401 (6)	0.04692 (3)	0.13608 (4)	0.03324 (18)
Hg2	0.26398 (6)	0.00416 (3)	0.46822 (3)	0.03023 (17)
Cl1	0.1802 (3)	−0.05881 (15)	0.0335 (2)	0.0248 (10)
Cl2	0.0080 (3)	0.03031 (16)	0.2800 (2)	0.0276 (10)
Cl3	0.2063 (4)	0.17045 (16)	0.1019 (2)	0.0279 (10)
Cl4	0.2795 (4)	0.12691 (17)	0.5241 (2)	0.0347 (11)
Cl5	0.4371 (3)	0.01605 (15)	0.3200 (2)	0.0264 (10)
Cl6	0.2392 (4)	−0.12373 (17)	0.4683 (2)	0.0369 (12)
Cl7	0.6412 (4)	−0.05774 (17)	0.1025 (3)	0.0425 (13)
N1	0.4981 (11)	−0.1340 (5)	0.2147 (7)	0.026 (4)
C2	0.5716 (12)	−0.1372 (6)	0.1377 (8)	0.022 (4)
C3	0.5874 (13)	−0.2044 (7)	0.0922 (8)	0.024 (4)
C4	0.5298 (14)	−0.2665 (7)	0.1280 (8)	0.025 (4)
C5	0.4548 (15)	−0.2609 (7)	0.2069 (9)	0.030 (5)
C6	0.4387 (15)	−0.1935 (7)	0.2499 (8)	0.030 (5)
Cl8	0.6674 (4)	0.1408 (2)	0.1466 (3)	0.0599 (16)
N21	0.5387 (11)	0.1780 (5)	0.2937 (7)	0.025 (4)
C22	0.5934 (13)	0.2036 (7)	0.2158 (8)	0.024 (4)
C23	0.5908 (16)	0.2777 (7)	0.1946 (9)	0.035 (5)
C24	0.5280 (18)	0.3256 (8)	0.2562 (12)	0.057 (7)
C25	0.4776 (16)	0.2969 (10)	0.3378 (11)	0.052 (6)
C26	0.4813 (16)	0.2231 (9)	0.3554 (9)	0.046 (6)

Table 4. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (II)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Hg1	0	0	0	0.02077 (13)
Hg2	0.44770 (4)	0.12603 (1)	−0.21367 (3)	0.02059 (9)
Cl1	−0.0673 (3)	−0.04381 (6)	−0.2260 (2)	0.0243 (6)
Cl2	0.2445 (3)	0.06871 (6)	−0.0959 (2)	0.0238 (6)
Cl3	0.3173 (3)	0.12483 (8)	−0.4810 (2)	0.0368 (7)
Cl4	0.4927 (3)	0.18989 (7)	−0.0298 (2)	0.0326 (7)
Cl5	0.7291 (3)	0.07370 (7)	−0.1353 (3)	0.0315 (7)
Cl6	−0.0203 (3)	0.25279 (8)	−0.2269 (3)	0.0408 (8)
N1	0.0286 (10)	0.1501 (2)	0.0704 (8)	0.031 (2)
C2	0.0188 (11)	0.1736 (3)	−0.0608 (9)	0.026 (3)
C3	−0.0109 (10)	0.2217 (3)	−0.0638 (9)	0.023 (2)
C4	−0.0348 (12)	0.2441 (3)	0.0637 (11)	0.033 (3)
C5	−0.0191 (13)	0.2187 (3)	0.1975 (10)	0.036 (3)
C6	0.0113 (11)	0.1704 (3)	0.1980 (9)	0.028 (3)
Cl7	0.8257 (3)	0.15591 (8)	0.5247 (3)	0.0384 (8)
N21	0.5482 (9)	0.0657 (3)	0.2230 (7)	0.031 (2)
C22	0.6193 (12)	0.1067 (3)	0.2914 (9)	0.028 (3)
C23	0.7391 (11)	0.1037 (3)	0.4323 (9)	0.025 (3)
C24	0.7860 (12)	0.0592 (3)	0.5012 (10)	0.033 (3)
C25	0.7089 (12)	0.0196 (3)	0.4243 (10)	0.034 (3)
C26	0.5876 (12)	0.0236 (3)	0.2864 (10)	0.032 (3)

3.1. (2-ClpyH)[HgCl₃], (I): an {[HgCl₃]⁻ [HgCl₂] Cl⁻}ₙ chain structure

The anion in the 2-chloropyridinium salt, (I), has overall [HgCl$_3$]$^-$ stoichiometry, but the structure contains infinite one-dimensional {[HgCl$_3$]$^-$ [HgCl$_2$] Cl$^-$}$_n$ anionic chains made up of virtually undistorted [HgCl$_3$]$^-$, slightly distorted HgCl$_2$, and Cl$^-$ moieties linked by longer Hg···Cl contacts (Fig. 1). There are two independent Hg centres which have quite distinct coordination environments (Table 8). A schematic representation of the chloromercurate(II) chain structure is given below.

(I)
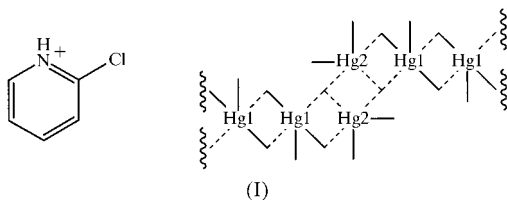
Hg1 has three short Hg—Cl bonds (2.41–2.46 Å) forming a regular trigonal arrangement. Two long, axially disposed Hg···Cl contacts [3.086 (4) and 3.148 (4) Å] complete a quite regular but axially stretched trigonal bipyramid. Only one of the short Hg—Cl bonds is a terminal bond; all other Cl atoms are bridging. The dimensions of the coordination about Hg1 are very similar to those about the unique Hg centre in [Et$_4$N][HgCl$_3$] (Sandström & Liem, 1978). Hg2 has two short, nearly linear [Cl4—Hg2—Cl6 161.35 (11)°] terminal Hg—Cl bonds [2.331 (3) and 2.333 (3) Å] with a longer contact [2.803 (3) Å] to a Cl$^-$ ion. This can be

Table 5. *Fractional atomic coordinates and equivalent isotropic displacement parameters (Å²) for (III)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^i a^j \mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Hg1	0	0	0	0.03401 (15)
Hg2	0.21586 (3)	−0.21696 (2)	0.36228 (4)	0.02723 (10)
Cl1	−0.22481 (19)	−0.05156 (16)	0.0342 (3)	0.0339 (6)
Cl2	0.0786 (2)	−0.23234 (16)	0.1300 (3)	0.0418 (8)
Cl3	0.45688 (19)	−0.15944 (14)	0.2166 (3)	0.0308 (6)
Cl4	0.2307 (2)	−0.39314 (15)	0.5343 (3)	0.0330 (6)
Cl5	0.0895 (2)	−0.11267 (15)	0.6232 (3)	0.0354 (6)
Cl6	0.2874 (2)	0.36338 (16)	0.4862 (3)	0.0389 (7)
N1	0.4770 (8)	0.0724 (5)	0.2840 (9)	0.039 (3)
C2	0.3415 (10)	0.0747 (6)	0.3784 (12)	0.042 (3)
C3	0.2802 (9)	0.1644 (7)	0.4447 (11)	0.036 (3)
C4	0.3625 (8)	0.2487 (6)	0.4119 (9)	0.025 (2)
C5	0.5014 (9)	0.2444 (6)	0.3187 (10)	0.031 (3)
C6	0.5590 (10)	0.1536 (7)	0.2530 (11)	0.041 (3)
Cl7	−0.4724 (2)	−0.45326 (18)	1.2083 (3)	0.0378 (7)
N21	−0.0582 (6)	−0.3942 (6)	0.8109 (8)	0.031 (2)
C22	−0.1042 (8)	−0.4889 (7)	0.8448 (10)	0.033 (3)
C23	−0.2321 (8)	−0.5115 (6)	0.9670 (10)	0.030 (3)
C24	−0.3116 (7)	−0.4303 (6)	1.0525 (9)	0.026 (2)
C25	−0.2618 (8)	−0.3331 (6)	1.0169 (10)	0.028 (2)
C26	−0.1333 (8)	−0.3164 (7)	0.8931 (10)	0.032 (3)

considered as an HgCl$_2$ + Cl$^-$ grouping distorted towards an [HgCl$_3$]$^-$ unit, which is a phenomenon that has been observed frequently (House *et al.*, 1994). As a result, the short Hg—Cl bond lengths are slightly longer than those in solid HgCl$_2$ (see §3.2). Two long diametrically opposed Hg···Cl contacts [2.898 (3) and 3.296 (3) Å] complete an almost square-pyramidal arrangement about Hg2 with the formal Cl$^-$ ion, Cl5,

Table 6. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$) for (IV)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^ia^j\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Hg1	−0.05411 (7)	0.57150 (3)	0.36436 (4)	0.02636 (17)
Hg2	0.38188 (7)	0.60230 (2)	0.21518 (3)	0.01930 (14)
Cl1	−0.1703 (4)	0.51782 (13)	0.2032 (2)	0.0214 (9)
Cl2	−0.0229 (5)	0.58621 (14)	0.5531 (2)	0.0247 (10)
Cl3	0.1175 (4)	0.66586 (12)	0.2803 (2)	0.0180 (8)
Cl4	0.6411 (4)	0.66852 (12)	0.2927 (2)	0.0178 (8)
Cl5	0.3091 (5)	0.56245 (14)	0.0324 (2)	0.0268 (10)
Cl6	0.3566 (4)	0.52641 (13)	0.3688 (2)	0.0207 (9)
Cl7	0.1227 (5)	0.23839 (14)	−0.0429 (3)	0.0291 (10)
N1	0.1987 (14)	0.4106 (5)	0.0256 (8)	0.022 (3)
C2	0.1859 (18)	0.3567 (6)	−0.0270 (9)	0.022 (4)
C3	0.1413 (15)	0.3066 (5)	0.0255 (8)	0.016 (3)
C4	0.1031 (16)	0.3099 (6)	0.1328 (9)	0.021 (4)
C5	0.1121 (19)	0.3651 (7)	0.1814 (10)	0.029 (4)
C6	0.1569 (18)	0.4175 (6)	0.1280 (10)	0.026 (4)
Cl8	0.6317 (5)	0.22561 (14)	0.4759 (3)	0.0258 (10)
N21	0.5419 (15)	0.3964 (4)	0.4002 (8)	0.024 (3)
C22	0.5583 (18)	0.3430 (6)	0.4581 (9)	0.022 (4)
C23	0.6106 (15)	0.2930 (5)	0.4051 (9)	0.015 (3)
C24	0.6498 (15)	0.2970 (5)	0.3008 (9)	0.017 (4)
C25	0.6319 (18)	0.3536 (6)	0.2450 (10)	0.024 (4)
C26	0.5820 (16)	0.4024 (6)	0.2989 (10)	0.022 (4)

Table 7. *Fractional atomic coordinates and equivalent isotropic displacement parameters ($\mathring{A}^2$) for (V)*

$$U_{eq} = (1/3)\Sigma_i\Sigma_j U^{ij}a^ia^j\mathbf{a}_i.\mathbf{a}_j.$$

	x	y	z	U_{eq}
Hg1	0.13306 (5)	0	0.10021 (6)	0.0285 (2)
Cl1	0.0973 (4)	0	0.3259 (4)	0.0346 (12)
Cl2	0.2412 (3)	0	−0.0668 (4)	0.0337 (12)
Cl3	0	0.2556 (4)	0	0.0233 (9)
Cl4	−0.1695 (4)	1/2	0.6409 (4)	0.0365 (13)
N1	−0.0926 (11)	1/2	0.2258 (14)	0.034 (4)
C2	−0.1031 (9)	0.3417 (14)	0.2835 (11)	0.031 (3)
C3	−0.1292 (9)	0.3398 (14)	0.4131 (12)	0.033 (3)
C4	−0.1415 (11)	1/2	0.4790 (14)	0.023 (4)

Table 8. *Selected geometric parameters ($\mathring{A}$, °) for (I)*

Hg1—Cl1	2.432 (3)	Hg2—Cl2	2.898 (3)
Hg1—Cl1^i	3.086 (4)	Hg2—Cl6	2.331 (3)
Hg1—Cl2	2.456 (3)	Hg2—Cl4	2.333 (3)
Hg1—Cl3	2.411 (3)	Hg2—Cl5	2.803 (3)
Hg1—Cl5	3.148 (4)	Hg2—Cl5^{ii}	3.296 (3)
Cl1—Hg1—Cl1^i	86.28 (9)	Cl2—Hg2—Cl6	96.21 (9)
Cl1—Hg1—Cl2	120.13 (9)	Cl4—Hg2—Cl5	98.04 (10)
Cl1—Hg1—Cl3	122.45 (10)	Cl4—Hg2—Cl5^{ii}	83.39 (9)
Cl1—Hg1—Cl5	91.29 (9)	Cl4—Hg2—Cl6	161.35 (11)
Cl2—Hg1—Cl1^i	90.57 (10)	Cl5—Hg2—Cl5^{ii}	94.81 (8)
Cl2—Hg1—Cl3	117.42 (10)	Cl5—Hg2—Cl6	98.62 (10)
Cl2—Hg1—Cl5	84.44 (10)	Cl6—Hg2—Cl5^{ii}	86.93 (9)
Cl3—Hg1—Cl1^i	92.92 (9)	Hg1—Cl1—Hg1^i	93.72 (9)
Cl3—Hg1—Cl5	94.43 (9)	Hg1—Cl2—Hg2	102.63 (12)
Cl1^i—Hg1—Cl5	172.43 (8)	Hg2—Cl5—Hg1	89.30 (10)
Cl2—Hg2—Cl4	93.91 (9)	Hg1—Cl5—Hg2^{ii}	173.03 (10)
Cl2—Hg2—Cl5	83.59 (10)	Hg2—Cl5—Hg2^{ii}	85.19 (8)
Cl2—Hg2—Cl5^{ii}	176.65 (8)		

Symmetry codes: (i) $-x, -y, -z$; (ii) $1 - x, -y, 1 - z$.

occupying the apical position. The three longer contacts are all to bridging Cl atoms. The formal Cl$^−$ ion has T-shaped coordination and bridges one Hg1 and two Hg2 atoms, although the Hg···Cl distances vary greatly. This Cl atom is closely associated [2.803 (3) Å] with one HgCl$_2$ unit and has two long diametrically opposed contacts [3.148 (4) and 3.296 (3) Å] to neighbouring HgCl$_2$ and [HgCl$_3$]$^−$ units.

The Hg coordination polyhedra form infinite anionic chains by edge sharing. The trigonal bipyramidal Hg1 unit shares one edge across a centre of inversion with another Hg1 and a second edge with the square-pyramidal Hg2 unit. The Hg2 unit then shares a second edge across a centre of inversion with another Hg2 unit. Thus each Hg centre is linked by two Cl bridges to each of two adjacent Hg centres and the chains are made up of the sequence ···Hg1^i···Hg1···Hg2^{ii}···Hg2^{ii}···Hg1^{ii}···Hg1^{iii}··· [symmetry codes: (i) $-x, -y, -z$; (ii) $1 - x, -y, 1 - z$; (iii) $1 + x, y, 1 + z$].
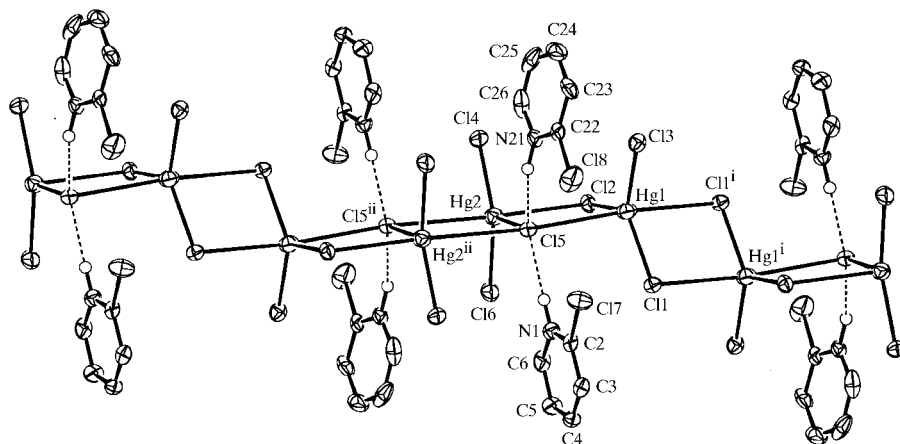

Fig. 1. A segment of the anionic chain and hydrogen-bonded cationic 'wings' in compound (I), showing the atom-numbering scheme. Anisotropic displacement ellipsoids are drawn at the 50% probability level. Pyridinium H atoms are represented by circles of arbitrary size and all other H atoms have been omitted for clarity. Symmetry codes are given in Table 8.

Both of the symmetry-independent cations in the asymmetric unit hydrogen-bond to the formal Cl$^-$ ion, Cl5 (Table 9). This completes a trigonal bipyramidal coordination about Cl5. The hydrogen bonds are reasonably linear and the H$\cdots$Cl and N$\cdots$Cl distances are in close agreement with the mean distances of 2.221 (7) and 3.181 (6) Å, respectively, deduced from an analysis of all reported $>Nsp^2-$H$\cdots$Cl interactions with angles $> 140°$ conducted recently by Steiner (1998). The hydrogen bonds do not cross-link the anionic chains, so the whole structure consists of infinite one-dimensional columns made up of anionic chains with cationic 'wings' (Fig. 1). These chains proceed in the [101] direction and are stacked in the [010] direction with the cations from adjacent chains interlocking next to each other. The entire crystal packing thereby consists of alternating layers of anionic chains and cations (Fig. 2).

3.2. (3-ClpyH)$_4$[Hg$_3$Cl$_{10}$] (II): looped {([HgCl$_4$]$^{2-}$)$_2$ [HgCl$_2$]}$_n$ chains

The anion in the first form of the 3-chloropyridinium salt, (II), has the overall [Hg$_3$Cl$_{10}$]$^{4-}$ stoichiometry, which is quite rare, there being only one previous report of a mercury(II) complex having this stoichiometry (House *et al.*, 1988, 1994). The structure does not consist of discrete [Hg$_3$Cl$_{10}$]$^{4-}$ anions, but contains infinite one-dimensional, double-stranded {([HgCl$_4$]$^{2-}$)$_2$ [HgCl$_2$]}$_n$ anionic chains made up of linear HgCl$_2$ and distorted [HgCl$_4$]$^{2-}$ entities linked together by longer Hg$\cdots$Cl
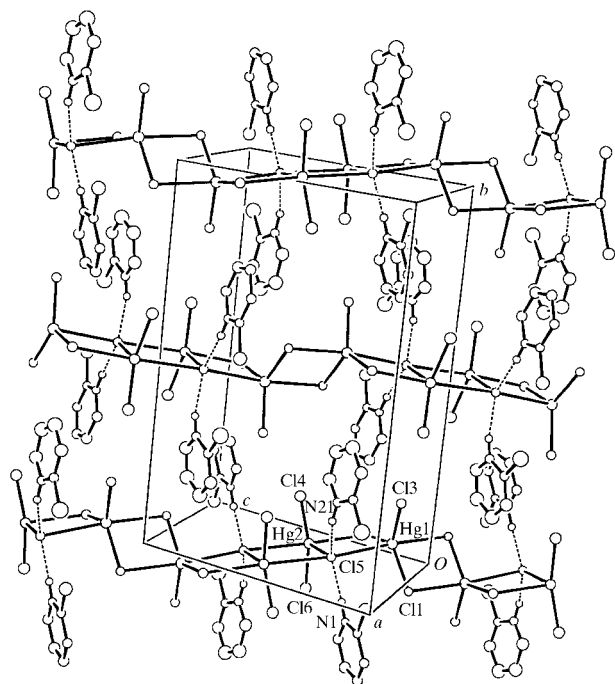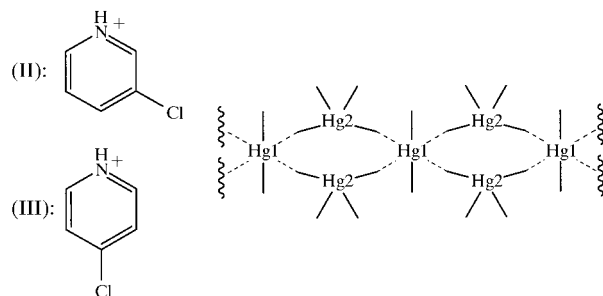

Fig. 2. The crystal packing of compound (I), showing the alternating layers of cations and anionic chains. H atoms bonded to C have been omitted for clarity.

Table 9. *Hydrogen-bonding geometry (Å, °) in compounds (I)–(V)*

$D-$H$\cdots A$	$D-$H	H$\cdots A$	$D\cdots A$	$D-$H$\cdots A$
Compound (I)				
N1$-$H1$\cdots$Cl5	0.95	2.22	3.161 (10)	173
N21$-$H21$\cdots$Cl5	0.95	2.24	3.127 (10)	155
Compound (II)				
N1$-$H1$\cdots$Cl1^i	0.95	2.47	3.284 (7)	144
N1$-$H1$\cdots$Cl2	0.95	2.75	3.395 (7)	126
N21$-$H21$\cdots$Cl2	0.95	2.24	3.184 (7)	173
Compound (III)				
N1$-$H1$\cdots$Cl3	0.95	2.38	3.175 (7)	141
N1$-$H1$\cdots$Cl1^{ii}	0.95	2.73	3.469 (8)	135
N21$-$H21$\cdots$Cl4	0.95	2.11	3.037 (6)	166
Compound (IV)				
N1$-$H1$\cdots$Cl1^{iii}	0.95	2.48	3.210 (10)	134
N1$-$H1$\cdots$Cl5	0.95	2.69	3.455 (10)	138
N21$-$H21$\cdots$Cl6	0.95	2.43	3.173 (10)	135
N21$-$H21$\cdots$Cl6^{iv}	0.95	2.65	3.298 (10)	126
Compound (V)				
N1$-$H1$\cdots$Cl3	0.95	2.57	3.272 (11)	131

Symmetry codes: (i) $-x, -y, -z$; (ii) $1 + x, y, z$; (iii) $-x, 1 - y, -z$; (iv) $1 - x, 1 - y, 1 - z$.

contacts. The HgCl$_2$ moieties are joined by double [HgCl$_4$]$^{2-}$ bridges as in the schematic diagram below (see also Fig. 3 and Table 10).

Hg1 lies on a centre of inversion and is octahedrally coordinated by four bridging and two terminal Cl atoms. The terminal Hg$-$Cl bond lengths are short [2.3420 (18) Å] and form the formal HgCl$_2$ unit, while the longer bridging Hg$\cdots$Cl contacts are in the range 2.93–2.96 Å. The distortions of the octahedral angles are minimal. Hg2 is coordinated by two bridging Cl atoms and two terminal Cl atoms which form a distorted tetrahedron heavily distorted towards a trigonal pyramid and yield the formal [HgCl$_4$]$^{2-}$ unit. The terminal Hg$-$Cl bonds [2.379 (2) and 2.4193 (19) Å] are again shorter than the bridging Hg$-$Cl bonds [2.5148 (19) and 2.6427 (18) Å]. The latter are still short enough to be considered formal Hg$-$Cl bonds. The Cl bridges are therefore quite asymmetric, but they are relatively linear with the Hg$\cdots$Cl$-$Hg angles at Cl2 and Cl5 being 173.34 (8) and 165.22 (9)°, respectively.

Each Hg1 unit is linked to four Hg2 centres by vertex sharing of the respective coordination polyhedra. In turn, the Hg2 centres are linked to two different Hg1 units. In this way, the Hg atoms and the bridging Cl atoms form an almost planar square-loop arrangement with the Hg atoms at the corners and a Cl atom in the middle of each side (Fig. 3). The r.m.s. deviation from their mean plane of the eight atoms in the centrosymmetric Hg_4Cl_4 loop is only 0.067 Å with the maximum deviation being 0.110 (2) Å for atom Cl2. These Hg_4Cl_4 squares are joined to adjacent squares by sharing those vertices occupied by Hg1 and thereby form the infinite double-stranded, or looped, anionic chains. Alternatively, the form of the chain can be described as a row of $HgCl_2$ units linked by double $[HgCl_4]^{2-}$ bridges. The form of the Hg_4Cl_4 loops is reminiscent of the M_4F_4 squares formed by the M_4F_{20} tetramers in NbF_5 and TaF_5 (Edwards, 1964).

As the structure of the anionic chains is derived primarily from $HgCl_2$ and $[HgCl_4]^{2-}$ units, it is instructive to compare the geometries of these units with those of the corresponding ideal entities. The Hg—Cl bond length in gaseous $HgCl_2$ is 2.252 (5) Å (Kashiwabara *et al.*, 1973), while in the most recent of the solid-state structure determinations, the two unequal Hg—Cl distances are 2.284 (12) and 2.301 (14) Å (Subramanian & Seff, 1980). The slightly longer Hg—Cl bond lengths in the $HgCl_2$ moiety of compound (II) can be attributed to the additional relatively short Hg$\cdots$Cl contacts of *ca* 2.95 Å, compared with the long contacts of 3.37 Å in solid $HgCl_2$. One of the most ideal and undistorted isolated $[HgCl_4]^{2-}$ tetrahedra can be found in the

structure of $(CH_3NH_3)_2[HgCl_4]$ (Ben Salah *et al.*, 1982), where the Hg—Cl bond lengths range from 2.464 (4) to 2.478 (4) Å and the Cl—Hg—Cl bond angles range from

Table 10. *Selected geometric parameters (Å, °) for compounds (II) and (III)*

	Compound (II)	Compound (III)
Hg1—Cl1	2.3420 (18)	2.3032 (19)
Hg1—Cl2	2.9575 (18)	3.247 (2)
Hg1—Cl5^i	2.9303 (19)	3.1518 (19)
Hg2—Cl2	2.6427 (18)	2.4598 (18)
Hg2—Cl3	2.379 (2)	2.4677 (19)
Hg2—Cl4	2.4193 (19)	2.553 (2)
Hg2—Cl5	2.5148 (19)	2.4869 (19)
Cl1—Hg1—Cl1^{ii}	180	180
Cl1—Hg1—Cl2	94.66 (6)	88.07 (7)
Cl1—Hg1—Cl2^{ii}	85.34 (6)	91.93 (7)
Cl1—Hg1—Cl5^i	92.17 (6)	87.71 (6)
Cl1—Hg1—Cl5^{iii}	87.83 (6)	92.29 (6)
Cl2—Hg1—Cl2^{ii}	180	180
Cl2—Hg1—Cl5^i	80.31 (6)	73.91 (6)
Cl2—Hg1—Cl5^{iii}	99.69 (6)	106.09 (6)
Cl5^i—Hg1—Cl5^{iii}	180	180
Cl2—Hg2—Cl3	106.84 (7)	113.94 (7)
Cl2—Hg2—Cl4	98.77 (7)	107.15 (7)
Cl2—Hg2—Cl5	93.66 (7)	111.63 (8)
Cl3—Hg2—Cl4	131.94 (8)	107.82 (7)
Cl3—Hg2—Cl5	111.43 (8)	112.14 (7)
Cl4—Hg2—Cl5	106.60 (7)	103.41 (7)
Hg1—Cl2—Hg2	173.34 (8)	104.82 (7)
Hg1^{iii}—Cl5—Hg2	165.22 (9)	164.11 (9)

Symmetry codes for compound (II): (i) $x - 1, y, z$; (ii) $-x, -y, -z$; (iii) $1 - x, -y, -z$. Symmetry codes for compound (III): (i) $x, y, z - 1$; (ii) $-x, -y, -z$; (iii) $-x, -y, 1 - z$.
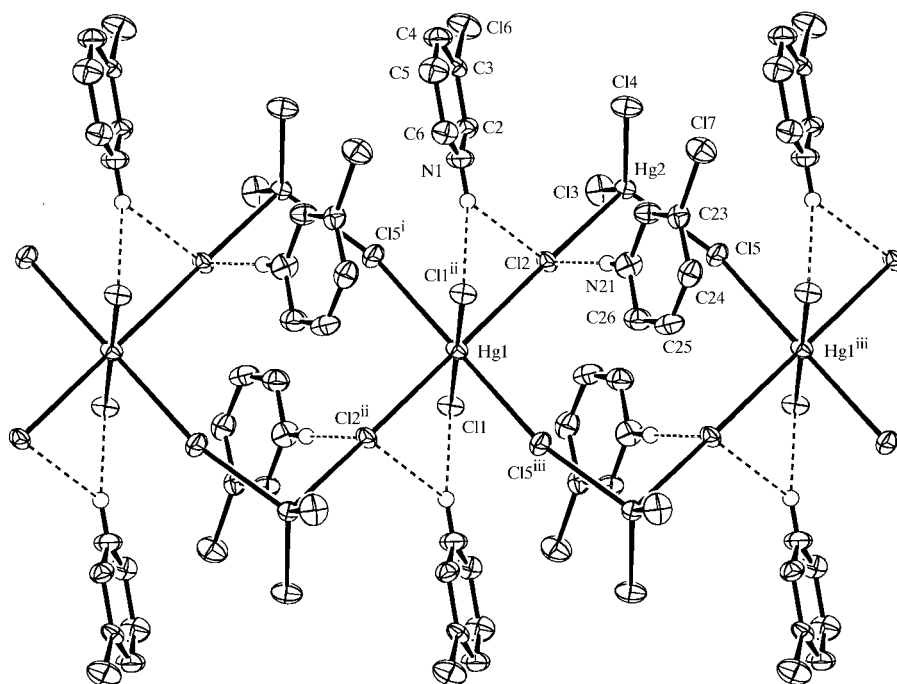

Fig. 3. A segment of the anionic chain and hydrogen-bonded cationic 'wings' in compound (II), showing the atom-numbering scheme and the nearly planar square-loop bridging system between the Hg centres. Anisotropic displacement ellipsoids are drawn at the 50% probability level. Pyridinium H atoms are represented by circles of arbitrary size and all other H atoms have been omitted for clarity. Symmetry codes are given in Table 10.

103.9 (2) to 114.2 (1)°. The distortions from ideality of the $[HgCl_4]^{2-}$ unit centred around Hg2 in the structure of compound (II) are therefore clearly evident and the longer bridging Hg—Cl bonds are countered by the shorter terminal bonds.

One of the bridging Cl atoms, Cl2, accepts two hydrogen bonds, one from each of the two symmetry-independent cations (Table 9). The terminal Cl atom of the $HgCl_2$ unit also accepts a hydrogen bond from one of the cations, so that one cation forms bifurcated hydrogen bonds. Some of the hydrogen-bonding interactions are considerably weaker than those in compound (I), but the increased H⋯Cl and N⋯Cl distances are consistent with the scatterplot for general N—H⋯Cl interactions whose angles are more acute
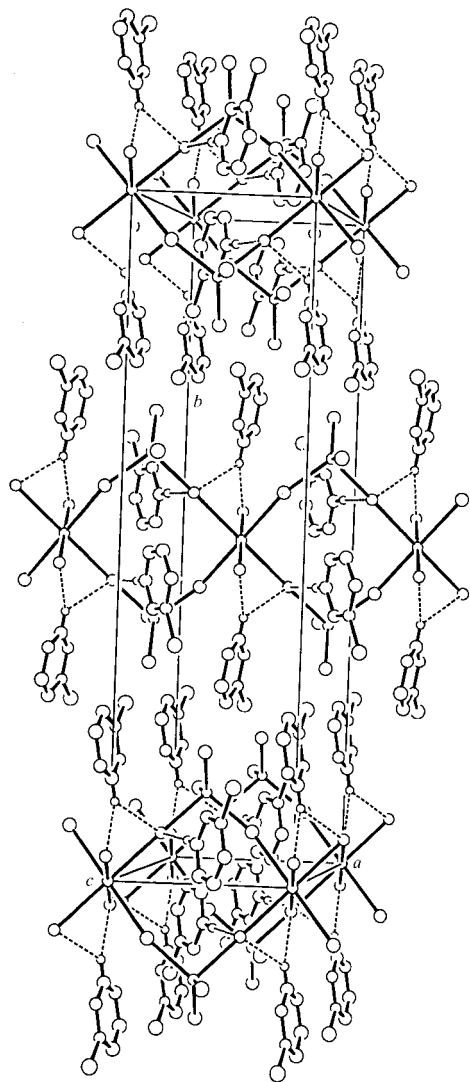
Fig. 4. The crystal packing of compound (II), showing how the two types of symmetry-independent cations are interspersed between the anionic chains in different directions. H atoms bonded to C have been omitted for clarity.

than 140° (Steiner, 1998). The hydrogen bonds do not cross-link the anionic chains and the whole structure again consists of infinite one-dimensional columns made up of anionic chains with cationic 'wings' (Fig. 4). These chains run in the [100] direction. In the crystal lattice, the chains are interspersed by the two types of symmetry-independent cations. One type of cation fills the spaces between the anionic chains in the [010] direction, while the other type of cation lies between the anionic chains in the [001] direction (Fig. 4).

3.3. (4-ClpyH)$_4$[Hg$_3$Cl$_{10}$] (III): puckered-loop {([HgCl$_4$]$^{2-}$)$_2$ [HgCl$_2$]}$_n$ chains

The anion in the first form of the 4-chloropyridinium salt, (III), also has the rare $[Hg_3Cl_{10}]^{4-}$ stoichiometry and consists of the same type of infinite one-dimensional, double-stranded $\{([HgCl_4]^{2-})_2 [HgCl_2]\}_n$ anionic chains that were found in compound (II). However, there are significant differences in the Hg—Cl distances and the distortions of the coordination polyhedra of the anion (Fig. 5 and Table 10).

As in compound (II), Hg1 lies on a centre of inversion, but the bridging Hg⋯Cl contacts [3.1518 (19) and 3.247 (2) Å] are much longer than previously. As a consequence, the terminal Hg—Cl bond lengths are shortened to 2.3032 (19) Å. The angles about Hg1 show that the long contacts significantly distort the octahedral geometry. In contrast, the coordination geometry about Hg2 is now a quite regular tetrahedron, there being no discernible trend among the Hg—Cl distances for the bridging and terminal Cl atoms (2.46–2.55 Å), and the angles about Hg2 closely approach the normal tetrahedral angle. Thus, in comparison with compound (II), the formal $HgCl_2$ and $[HgCl_4]^{2-}$ moieties making up the anionic chain in compound (III) are more discrete with much weaker contacts linking the individual units. These contacts are 0.2–0.3 Å longer than in compound (II). The discreteness of these moieties is further supported by the extreme similarities of their bonding and contact distances with those found in solid $HgCl_2$ (Subramanian
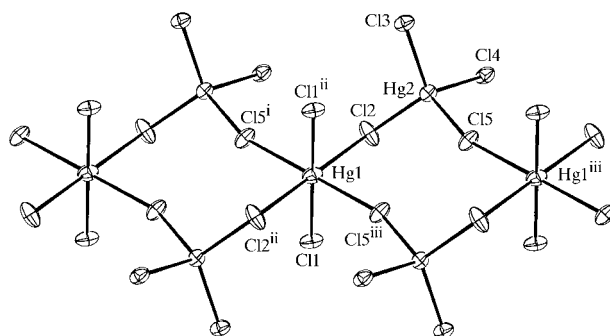

Fig. 5. A segment of the anionic chain in compound (III), showing the puckered-loop bridging system between the Hg centres. Anisotropic displacement ellipsoids are drawn at the 50% probability level. Symmetry codes are given in Table 10.

& Seff, 1980) and in the salts containing discrete $[HgCl_4]^{2-}$ anions, as summarized by House *et al.* (1994).

The Hg atoms and the bridging Cl atoms form centrosymmetric Hg_4Cl_4 square loops similar to those in compound (II), but the squares are highly distorted and the plane of each loop is significantly puckered (Fig. 6). The r.m.s. deviation from their mean plane of the eight atoms in the Hg_4Cl_4 loop is 0.361 Å with the maximum deviation being 0.557 (2) Å for atom Cl2. These deformations are caused by the angular distortions at Hg1 as well as the very acute angle at one of the bridging Cl atoms [Hg1···Cl2—Hg2 104.82 (7), Cl2···Hg1···Cl5^i 73.91 (6)°; symmetry code: (i) x, y, $z - 1$].

Each of the terminal Cl atoms accepts a hydrogen bond from a cation, with one of the two symmetry-independent cations forming bifurcated hydrogen bonds (Table 9). The bifurcated hydrogen bonds cross-link the infinite one-dimensional anionic chains to form an infinite two-dimensional network, which lies parallel to the xz plane (Fig. 7). These cross-links do not connect the same Cl atoms on adjacent chains, but each link involves Cl3 from an $[HgCl_4]^{2-}$ moiety in one chain and Cl1 from the $HgCl_2$ unit in the adjacent chain. The other symmetry-independent cation interacts solely with one of the terminal atoms, Cl4, from the $[HgCl_4]^{2-}$ moiety.

3.4. (3-ClpyH)[HgCl₃] (IV): an {[Hg₂Cl₆]²⁻}ₙ chain structure

The anion in the second form of the 3-chloropyridinium salt, (IV), has the overall $[HgCl_3]^-$ stoichiometry, but the structure contains infinite one-dimensional $\{[Hg_2Cl_6]^{2-}\}_n$ anionic chains made up of distorted double Cl-bridged $[Hg_2Cl_6]^{2-}$ units linked by single long Hg···Cl contacts of 3.103 (3) Å, as shown in the schematic diagram below. The two independent Hg centres have quite distinct coordination environments (Fig. 8 and Table 11).

(IV)
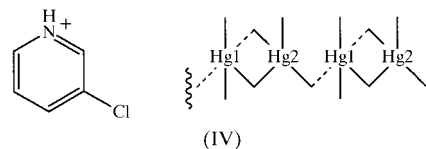
Hg1 has two short terminal Hg—Cl bonds [2.322 (3) and 2.348 (3) Å] arranged in a slightly bent geometry [Cl1—Hg1—Cl2 151.65 (11)°] with a longer contact [2.723 (3) Å] to atom Cl3, which bridges to Hg2. This is again the typical case of an $HgCl_2$ group being distorted towards an $[HgCl_3]^-$ unit by the close approach of a Cl^- ion, as observed in the structure of the (2-ClpyH)$^+$ salt, (I). Two long roughly opposed [Cl4^i···Hg1···Cl6 148.81 (8)°; symmetry code: (i) $x - 1$, y, z] Hg···Cl contacts [3.103 (3) and 3.130 (4) Å, respectively] to bridging Cl atoms complete a highly distorted square-pyramidal arrangement (distorted towards a trigonal bipyramid) about Hg1, with the nearest bridging Cl atom, Cl3, in the apical position. Hg2 has one terminal and three bridging Hg—Cl bonds (2.39–2.61 Å), which can all be designated as formal Hg—Cl bonds. The shortest Hg—Cl bond is the terminal bond. The coordination geometry about Hg2 lies between a highly
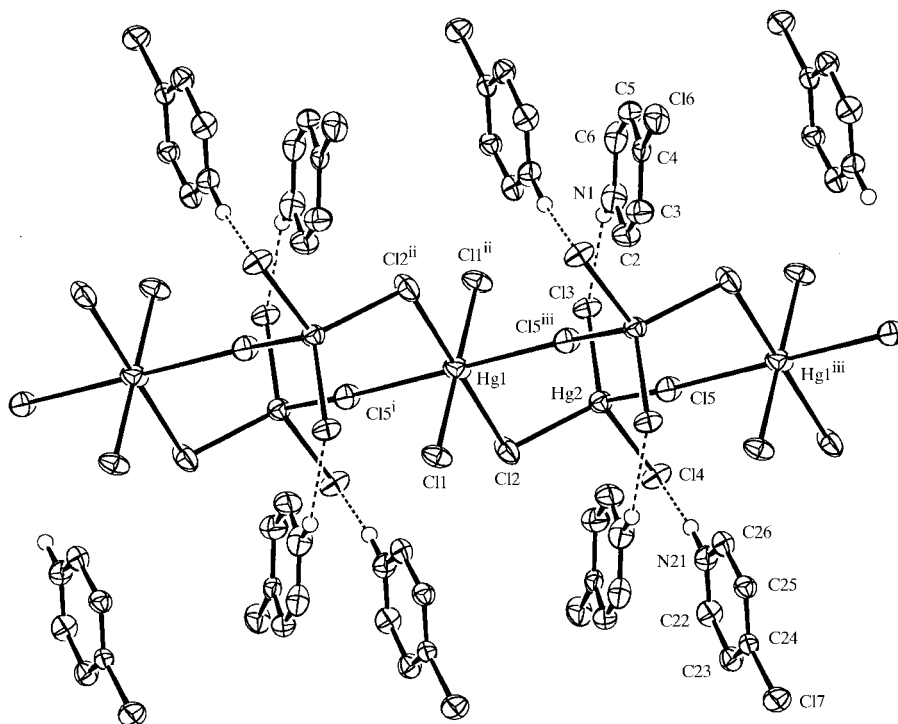

Fig. 6. A segment of the anionic chain in compound (III) with its hydrogen-bonded cations, showing the atom-numbering scheme. Anisotropic displacement ellipsoids are drawn at the 50% probability level. Pyridinium H atoms are represented by circles of arbitrary size and all other H atoms have been omitted for clarity. Symmetry codes are given in Table 10.

distorted tetrahedron and a trigonal pyramid in which Cl3 is again the apical atom.

The two unique Hg coordination polyhedra share edges to form the $[Hg_2Cl_6]^{2-}$ units. One of the Cl bridges within this unit is reasonably symmetrical [Hg1—Cl3 2.723 (3) and Hg2—Cl3 2.607 (3) Å], while the other is highly asymmetric [Hg1···Cl6 3.130 (4) and Hg2—Cl6 2.560 (3) Å]. Vertex sharing between two adjacent $[Hg_2Cl_6]^{2-}$ units then forms the infinite one-dimensional anionic chain. This final interaction is quite weak and results in another highly asymmetric bridge [Hg2—Cl4

2.448 (3) and Hg1[ii]···Cl4 3.103 (3) Å; symmetry code: (ii) $1 + x, y, z$].

The nearly symmetrical Cl bridge within the $[Hg_2Cl_6]^{2-}$ moiety, with its relatively short Hg—Cl distances, makes it more appropriate to describe the anionic chains as consisting of $[Hg_2Cl_6]^{2-}$ units, rather than as a combination of distorted formal $HgCl_2$ and $[HgCl_4]^{2-}$ groups. The structure of the $[Hg_2Cl_6]^{2-}$ unit of the chain is much more distorted than those usually found for isolated $[Hg_2Cl_6]^{2-}$ units in which both Cl bridges are often more symmetrical and equivalent (Kistenmacher *et al.*, 1980; Goggin *et al.*, 1982).

Each of the two symmetry-independent cations forms bifurcated hydrogen bonds with two different $[Hg_2Cl_6]^{2-}$ units (Table 9). The acceptor atoms are one terminal Cl atom from each Hg centre plus the more asymmetric of the bridging Cl atoms within the dimer, which accepts two hydrogen bonds. The H···Cl and N···Cl distances and the N—H···Cl angles are again consistent with the general scatterplot for N—H···Cl interactions (Steiner, 1998). The hydrogen bonds cross-link the anionic chains to form infinite two-dimensional layers, which lie parallel to the *xz* plane (Fig. 9). This is similar to the cross-linking observed in the (4-ClpyH)[+] salt, (III). The spaces between these layers are filled with the chlorine 'tails' of the cations.

3.5. (4-ClpyH)$_2$[Hg$_2$Cl$_6$] (V): discrete [Hg$_2$Cl$_6$]$^{2-}$ anions

The anion in the second form of the 4-chloropyridinium salt, (V), has the overall $[HgCl_3]^-$ stoichiometry and its structure is essentially a variation on that in compound (IV). Both have the same core $[Hg_2Cl_6]^{2-}$ moiety, but differ markedly in the degree of symmetry and discreteness of this unit. Compound (V) contains symmetrical and discrete $[Hg_2Cl_6]^{2-}$ anions, as shown in Fig. 10. The anion is double Cl-bridged and has crys-
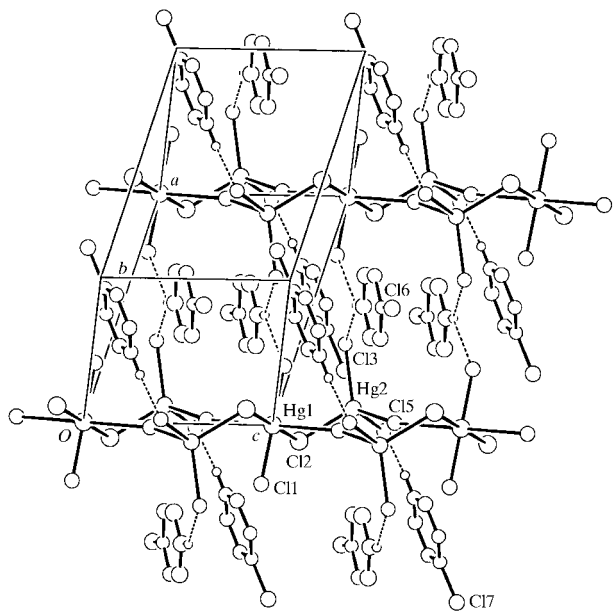

Fig. 7. A projection of a layer of compound (III) parallel to the (101) plane, showing the two-dimensional hydrogen-bonding network. H atoms bonded to C have been omitted for clarity.
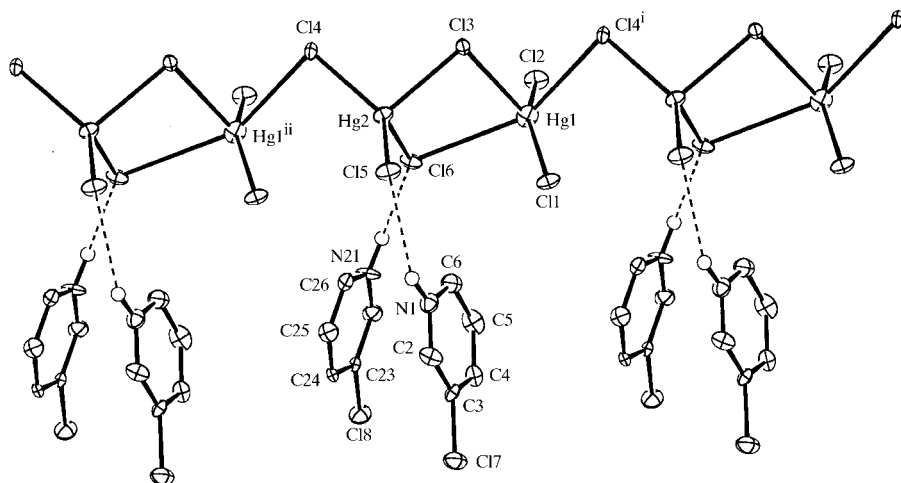

Fig. 8. A segment of the anionic chain in compound (IV) with its hydrogen-bonded cations, showing the atom-numbering scheme. Anisotropic displacement ellipsoids are drawn at the 50% probability level. Pyridinium H atoms are represented by circles of arbitrary size and all other H atoms have been omitted for clarity. Symmetry codes are given in Table 11.

tallographic 2/m symmetry with the Hg and terminal Cl atoms lying on a mirror plane and the bridging Cl atoms on a twofold axis. The two short terminal Hg—Cl bonds [average 2.350 (4) Å, Table 12] are arranged in a slightly bent geometry about the Hg atom [Cl1—Hg1—Cl2 153.72 (16)°]. This is very similar to the geometry about the Hg1 atom in compound (IV) and is again reminiscent of an $HgCl_2$ moiety being distorted by the longer Hg—Cl distances of 2.727 (2) Å to the two symmetrical Cl bridges. The Hg and bridging Cl atoms in the anion form an almost perfect square, as the bond angles are nearly 90° and all Hg—Cl bond lengths are equal by symmetry. The Hg···Hg distance is 3.8623 (16) Å. The anion is completely discrete as there are no additional Hg···Cl contacts shorter than 4.15 Å.

The structure of compound (V) appears to contain the most symmetrical $[Hg_2Cl_6]^{2-}$ anion reported so far. Theoretically, this anion could display *mmm* symmetry, but of the discrete anions of this type summarized by

Table 11. *Selected geometric parameters (Å, °) for (IV)*

Hg1—Cl1	2.348 (3)	Hg2—Cl3	2.607 (3)
Hg1—Cl2	2.322 (3)	Hg2—Cl4	2.448 (3)
Hg1—Cl3	2.723 (3)	Hg2—Cl5	2.395 (3)
Hg1—Cl4^i	3.103 (3)	Hg2—Cl6	2.560 (3)
Hg1—Cl6	3.130 (4)		
Cl1—Hg1—Cl2	151.65 (11)	Cl3—Hg2—Cl4	96.40 (10)
Cl1—Hg1—Cl3	100.90 (10)	Cl3—Hg2—Cl5	115.44 (11)
Cl1—Hg1—Cl4^i	88.36 (10)	Cl3—Hg2—Cl6	88.92 (9)
Cl1—Hg1—Cl6	93.42 (10)	Cl4—Hg2—Cl5	128.51 (11)
Cl2—Hg1—Cl3	107.37 (10)	Cl4—Hg2—Cl6	104.42 (10)
Cl2—Hg1—Cl4^i	97.75 (10)	Cl5—Hg2—Cl6	114.94 (10)
Cl2—Hg1—Cl6	95.31 (10)	Hg1—Cl3—Hg2	96.17 (9)
Cl3—Hg1—Cl4^i	73.05 (9)	Hg1^{ii}—Cl4—Hg2	99.20 (10)
Cl3—Hg1—Cl6	76.05 (8)	Hg1—Cl6—Hg2	87.81 (8)
Cl4^i—Hg1—Cl6	148.81 (8)		

Symmetry codes: (i) $x - 1, y, z$; (ii) $1 + x, y, z$.

House *et al.* (1994), centres of inversion are the most common symmetry elements found, and there are no other examples of these anions with 2/m symmetry. The Cl bridges in the anions with inversion centres vary from being almost symmetrical to the extreme asymmetric case in *trans*-[CoCl₂(en)₂]₂[Hg₂Cl₆] (en = ethylenediamine; Wen *et al.*, 1992) where the Hg—Cl bond lengths in the bridge differ by 0.18 Å. The lengths of the bridging Hg—Cl bonds vary in the range 2.55–2.88 Å and the longer bridges are associated with more linear Cl—Hg—Cl angles for the terminal Cl atoms (range 119–165°), as would be expected by considering the less distorting effect that the more distant bridging Cl atoms would have on a formally linear $HgCl_2$ moiety.
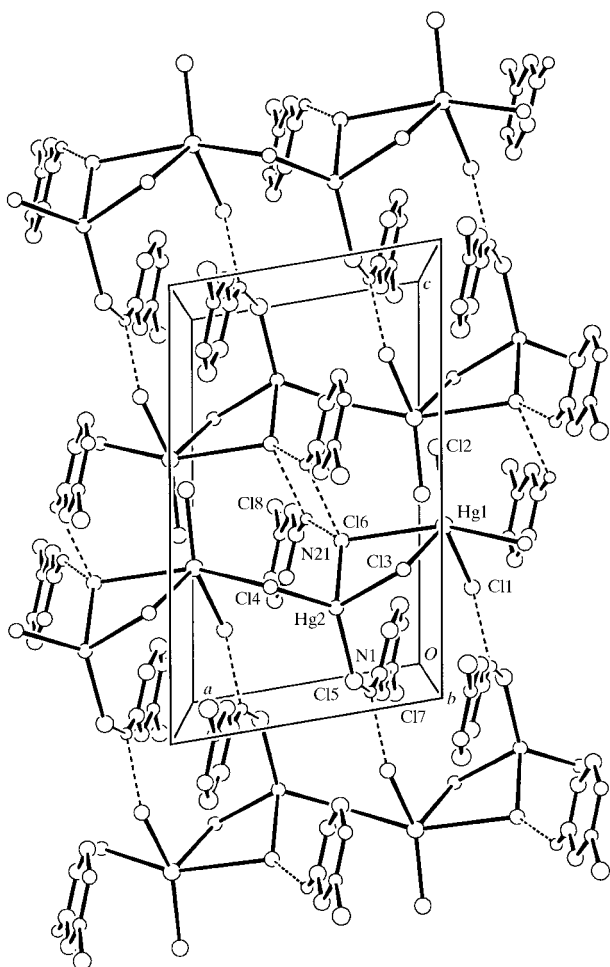

Fig. 9. A projection of a layer of compound (IV) parallel to the (101) plane, showing the two-dimensional hydrogen-bonding network. H atoms bonded to C have been omitted for clarity.
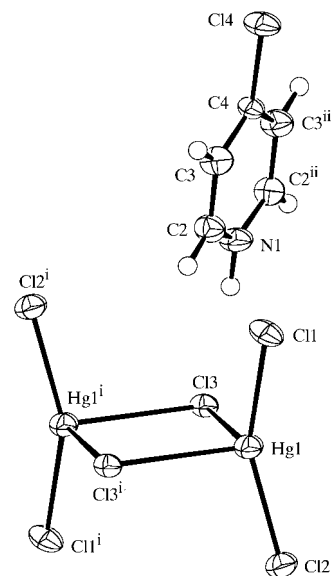

Fig. 10. The ions in compound (V), showing the atom-numbering scheme. Anisotropic displacement ellipsoids are drawn at the 50% probability level. H atoms are represented by circles of arbitrary size. Symmetry codes: (i) $-x, -y, -z$; (ii) $x, 1 - y, z$.

Compared with the other reported structures containing $[Hg_2Cl_6]^{2-}$ anions, the Hg—Cl bridging bonds in compound (V) lie towards the longer end of the range and the Cl1—Hg1—Cl2 angle is correspondingly large. The geometrically most similar anion is found in the structure of $(enH_2)[Hg_2Cl_6]$ (Wen *et al.*, 1992).

Each cation forms bifurcated hydrogen bonds with the bridging Cl atoms of two different $[Hg_2Cl_6]^{2-}$ anions (Table 9). Each of the bridging Cl atoms also accepts a hydrogen bond from each of two different cations, so that each anion is hydrogen-bonded to four cations. The geometry and dimensions of these interactions are normal and the Cl3···H1···Cl3[i] and H1···Cl3[i]···H1[i] [symmetry code: (i) −x, 1 − y, −z] angles are 92 and 88°, respectively. The hydrogen-bonding interactions link the ions into infinite one-dimensional chains which run in the [010] direction (Fig. 11). As both bridging Cl atoms are involved in hydrogen bonds, each anion forms a double cation bridge to the next neighbouring anion in the chain. These chains are arranged side-by-side so as to form layers which lie parallel to the (110) plane and the chlorine 'tails' of the cations are directed into the spaces between the layers. The terminal Cl atoms are not involved in any hydrogen bonds.

3.6. General remarks

While anionic chains with the stoichiometry $\{[HgCl_3]^-\}_n$ are quite common, the geometry and connectivity observed in the (2-ClpyH)⁺ salt, (I), is quite unusual. The discrete units making up the chains can be described as either $[HgCl_3]^- + HgCl_2 + Cl^-$ or a
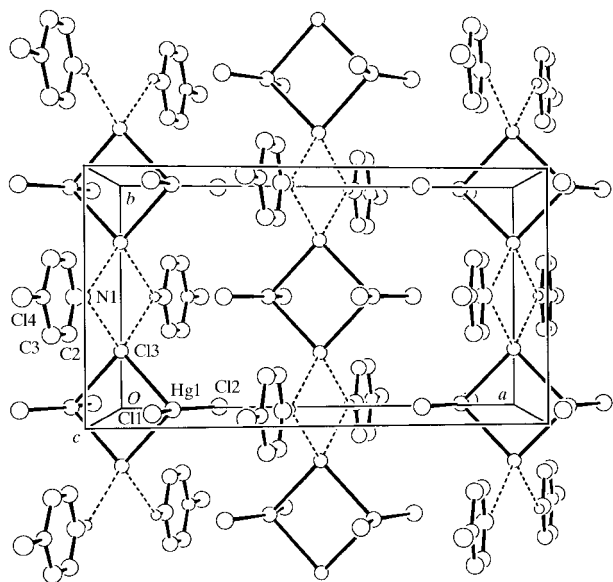

Fig. 11. A projection of a layer of compound (V) parallel to the (110) plane, showing the chains along [010] formed by the hydrogen-bonding interactions. H atoms bonded to C have been omitted for clarity.

Table 12. *Selected geometric parameters (Å, °) for (V)*

Hg1—Cl1	2.354 (4)	Hg1—Cl3	2.727 (2)
Hg1—Cl2	2.346 (4)	Hg1···Hg1[i]	3.8623 (16)
Cl1—Hg1—Cl2	153.72 (16)	Cl3—Hg1—Cl3[i]	89.84 (10)
Cl1—Hg1—Cl3	98.19 (8)	Hg1—Cl3—Hg1[i]	90.16 (10)
Cl2—Hg1—Cl3	100.33 (8)		

Symmetry code: (i) −x, −y, −z.

combination of regular and highly distorted $[HgCl_3]^-$ units. Compound (IV) also has the $\{[HgCl_3]^-\}_n$ stoichiometry, but the more frequently observed $[Hg_2Cl_6]^{2-}$ moieties constitute the primary components of the chains.

Compounds (II) and (III) both have the $\{[Hg_3Cl_{10}]^{4-}\}_n$ stoichiometry where $HgCl_2$ and $[HgCl_4]^{2-}$ units are linked by Hg···Cl contacts into infinite chains. In compound (II), the $HgCl_2$ and $[HgCl_4]^{2-}$ units interact quite closely, whereas the longer Hg···Cl contact distances in compound (III) result in the individual moieties being more discrete. The cross-linking of the anionic chains by hydrogen bonds in compound (III) is in sharp contrast to the unlinked chains in salt (II). The structures of compounds (IV) and (V) are both based on the $[Hg_2Cl_6]^{2-}$ moiety, yet they also manifest themselves in different ways. The distorted $\{[Hg_2Cl_6]^{2-}\}_n$ chains in compound (IV) give way to symmetrical and discrete $[Hg_2Cl_6]^{2-}$ anions in compound (V). Why this should occur is unclear, although it is conceivable that the more symmetrical nature of the 4-chloropyridinium cation allows the anion to adopt a much more symmetrical form. Indeed, the different crystal-packing effects introduced by the slightly different shapes of the 3- and 4-chloropyridinium cations are most probably the principal contributing factor to the geometrical differences between the structures of the anions in compounds (II) and (III) and in compounds (IV) and (V). That the coordination geometry about Hg centres can be so easily influenced by minor variations in packing requirements demonstrates the unusual flexibility of bonding interactions involving Hg atoms.

In the only other report of a complex having the $[Hg_3Cl_{10}]^{4-}$ stoichiometry (House *et al.*, 1988, 1994) the structure of the anion is quite different, yet subtly similar to those of the anions in compounds (II) and (III). It contains discrete $[Hg_3Cl_{10}]^{4-}$ anions which can be roughly described as being built from two independent $[HgCl_4]^{2-}$ units linked by Cl bridges to a central $HgCl_2$ moiety. The structures of compounds (II) and (III) also derive from the same entities, but they are combined in a different pattern.

At around 2.54 Mg m⁻³, the densities of compounds (II) and (III) are about 10% lower than those of compounds (I), (IV) and (V) (Table 2). Thus the $\{[Hg_3Cl_{10}]^{4-}\}_n$ chain structure has a more open

arrangement and its formation is probably not favoured if the cations allow a more efficient packing to be achieved. Interestingly, the previously reported structure involving discrete $[Hg_3Cl_{10}]^{4-}$ anions also has a similarly low density of 2.51 Mg m^{-3}. This may explain why the $[Hg_3Cl_{10}]^{4-}$ stoichiometry is so rare. This conclusion is consistent with the isolation procedures for the various compounds. Compounds (II) and (III) were obtained as crystals from the body of the mother liquor and rapidly turned opaque upon exposure to air, presumably due to the loss of the additional chloride ion to form the more dense and stable compounds (IV) and (V), respectively. Crystals of compounds (IV) and (V), which formed at the air–mother liquor interface, remained completely stable and transparent because they were already of the more stable form. The specific reason that crystals with differing anion stoichiometries were obtained from these solutions is unknown, even though polymorphism has been observed before in chloromercurate(II) salts (House *et al.*, 1994). If the energetics of either salt formation are very similar, small uncontrolled differences between the ratio of 3- or 4-chloropyridine to HgCl$_2$, or in the concentration of the hydrochloric acid in the body and at the surface of the solution could tip the balance in favour of either the $[Hg_3Cl_{10}]^{4-}$ or the $[Hg_2Cl_6]^{2-}$ salt.

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