Chloromercury(II) anions

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ABSTRACT

The nature of $Hg_xCl_y^{n-}$ anions, characterized by single-crystal X-ray structural analysis, is reviewed. Only compounds with Hg in the 2+ oxidation state are considered and the range of compounds has

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been restricted to those with two or more Hg–Cl bonds. The problem of weak Hg····Cl interactions is considered using "structure-correlation" concepts and a value of 3.35 Å is regarded as an upper limit for Hg····Cl bonding. The anions are considered in terms of $Hg_xCl_y^{n-}$ units, rather than in terms of classical "coordination numbers". Four features emerge: (i) the configuration of the anion cannot be determined from the analytical stoichiometry; (ii) $Hg_xCl_y^{n-}$ stoichiometries show a marked propensity for multi-anion combinations; (iii) some of the $Hg_xCl_y^{n-}$ formulations, such as $Hg_6Cl_{13}^-$, proposed at the turn of the century, have been fully justified; and (iv) it is still not possible to predict, even for simple stoichiometries such as $HgCl_3^-$, the form that will be adopted in the solid state.

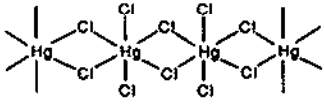
LIST OF ABBREVIATIONS

BEDTT-TTF	bis(ethylenedithio)tetrathiafulvalene [233]
bis-L-trypt	bis(L-tryptophanium) [189]
Br_2pyNO	3,5-dibromopyridine N-oxide [95]
bpy	2,2-bipyridyl
Bu^n	$CH_3CH_2CH_2^-$
bzpipNH	*n*-benzylpiperazium [127]
18-crown-6	1,4,7,10,13,16-hexaoxacyclooctadecane [108]
cyclam	1,4,8,11-tetraazacyclotetradecane [15]
dan	naphthalene-1,8-diamine [153]
dapmp	2,6-diacetylpyridine bis[*N*-methyl-*N*-(2′-pyridyl)hydrazone] [193]
diditet	*N*,*N*′-diethyl-imidazolidine-2-thione [112]
dien	$NH_2(CH_2)_2NH(CH_2)_2NH_2$
dienH	$[NH_2(CH_2)_2NH(CH_2)NH_3]^+$
dienH$_3$	$[NH_3(CH_2)_2NH_2(CH_2)_2NH_3]^{3+}$
ditet	*N*-ethyl-imidazolidine-2-thione [112]
DMSO	dimethylsulphoxide
dpm (=dppm)	$Ph_2P(CH_2)PPh_2$ [135,154]
dpmp	bis(diphenylphosphinomethyl)phenylphosphine [156]
dppeS$_2$	$Ph_2P(S)(CH_2)_2(S)PPh_2$ [116]
dppmS$_2$	$Ph_2P(S)(CH_2)(S)PPh_2$ [117]
dpt	$NH_2(CH_2)_3NH(CH_2)_3NH_2$
dptH$_3$	$[NH_3(CH_2)_3NH_2(CH_2)_3NH_3]^{3+}$
DTO	$[CH_2S(CH_2)_2OH]_2$ [147]
en	$NH_2(CH_2)_2NH_2$
enH	$[NH_2(CH_2)NH_3]^+$
enH$_2$	$[NH_3(CH_2)_2NH_3]^{2+}$
Et	$CH_3CH_2^-$
HBTN	2-(α-hydroxybenzyl)thiamin [128]
H$_2$dapp	2,6-diacetylpyridine bis(2′-pyridylhydrazone) [28]
hist	histidine [109]
H$_4$ttf	tetrahydrotetrathiafulvalene [74,84,185]
IR	infrared
Me	CH_3^-
9Mehyp	9-methylhypoxanthine [165]
mes (=mesitylene)	1,3,5-Me$_3$-benzene [149]
NQR	nuclear quadrupole resonance
pen	D,L-penicillamine [150]
Ph	$C_6H_5^-$
Pr^i	$(CH_3)_2CH^-$

Pr^n	$CH_3CH_2CH_2^-$
py	pyridine
pyNO	pyridine N-oxide
R	alkyl group
T	thiamine [10]
333-tet	$NH_2(CH_2)_3NH(CH_2)_3NH(CH_2)_3NH_2$ [14]
tet*b*	*rac*-5,5,7,12,12,14-Me_6cyclam [16]
TMTTF	tetramethyltetrathiafulvalene [187]
TPP	1,2,5-triphenylphosphole [137]
trienH_4	$[NH_3(CH_2)_2NH_2(CH_2)NH_2(CH_2)NH_3]^{4+}$
ttp	1,4,8,11-tetrathiacyclotetradecane [120]

A. INTRODUCTION

Compounds containing $Hg_xCl_y^{n-}$ anions are of interest to structural chemists, theoretical chemists and vibrational spectroscopists [1]. Of the generalizations that have been made with regard to these salts, one is outstanding in its significance, namely "the configuration of the anion does not follow from the stoichiometry" [2]. Thus $K_2HgCl_4 \cdot H_2O$ does not contain discrete $HgCl_4^{2-}$ anions, but distorted $HgCl_6$ octahedra forming columns which share two opposite edges [3,4] (Scheme 1).



Scheme 1. $(HgCl_4^{2-})_n$ in $K_2HgCl_4 \cdot H_2O$ [3–6].

Nevertheless, there are now many examples where more or less tetrahedral $HgCl_4^{2-}$ anions are formed (Table 1), despite the fact that these were considered (in 1965) to be exceptions to the generalization that "the characteristic coordination for chloromercury complexes is generally digonal" [2].

Another, frequently unsuspected characteristic of $Hg_xCl_y^{n-}$ salts is the propensity to form multi-anionic combinations from relatively simple stoichiometries. In one case [18], "$Hg_2Cl_7^{3-}$" is found to be an $[HgCl_4^{2-}]_2[Hg_2Cl_6^{2-}][Hg_4Cl_{14}^{6-}]$ combination and the "double salt" $2CaCl_2 \cdot 11HgCl_2 \cdot 16H_2O$ is shown to contain the $[Hg_6Cl_{13}^{-}][Hg_5Cl_{13}^{3-}]$ combination [31]. This multi-anion phenomenon is also observed in $Hg_xI_y^{n-}$ systems [32].

It is some time since the topic of chloromercury(II) systems has been reviewed [2,33,37] and several interesting structural units have recently been characterized.

Here we concentrate on charge-type relationships, and the number of Hg atoms in the anion, rather than on the coordination number [2,37], because the distinction between bonded and non-bonded chloride ions surrounding Hg(II) is not always clear. The sum of the van der Waals' radii (a normally accepted cut-off point) is not

TABLE 1

Salts containing discrete pseudo-tetrahedral $HgCl_4^{2-}$ anions

Salt	Cl–Hg–Cl bond angles (°) Hg–Cl bond lengths (Å)						Reference
$[MeNH_3^+]_2[HgCl_4^{2-}]$	103.9 2.464	108.9 2.467	109.4 2.470	109.4 2.478	110.8	114.2	7
$[Me_2NH_2^+]_2[HgCl_4^{2-}]$	101.73 2.424	108.38 2.457	108.49 2.479	108.89 2.530	113.75	114.70	8
$[Me_3NH^+]_2[HgCl_4^{2-}]$	103.07 2.427	104.34 2.437	104.60 2.481	109.19 2.574	114.62	119.08	9
$[ThH^{2+}][HgCl_4^{2-}].H_2O$	102.5 2.359	102.8 2.477	103.0 2.514	109.4 2.553	117.0	120.1	10
$[C_{30}H_{22}S_4^{2+}][HgCl_4^{2-}]^a$	100.9 2.441	101.9 2.462	104.2 2.476	110.1 2.523	118.4	122.1	11
	102.5 2.448	107.6 2.465	109.6 2.474	109.8 2.535	111.4	115.8	
$[C_6H_{16}N_2O^{2+}][HgCl_4^{2-}]$	98.2 2.439	105.5 2.461	106.4 2.468	111.6 2.559	113.0	119.4	12
$[C_6H_{14}NO^+]_2[HgCl_4^{2-}]$	92.6 2.395	104.9 2.460	113.1 2.500	113.2 2.562	113.7	117.1	12
$Cs_2[HgCl_4^{2-}]$	103.1 2.386	103.1 2.453	104.8 2.453	112.9 2.458	112.9	118.6	13
$[HgCl(333\text{-}tet)^+]_2[HgCl_4^{2-}]$	108.8 (×6) 2.503 (×4)						14
$[HgCl(cyclam)^+]_2[HgCl_4^{2-}]$	107.8 (×2) 2.50 (×4)	108.2 (×2)	116.0 (×2)				15
$[Hg(tet\,b)^{2+}][HgCl_4^{2-}]^d$	95.0 2.421	106.4 2.421	106.4 2.529	113.8 2.529	117.1	117.1	16

$[Et_4N^+]_2[HgCl_4^{2-}]$[c]	—	—	—	—	—	—	17
	—	—	—	—			
u-fac-$[Cr(dien)_2][HgCl_4^{2-}][HgCl_3^-]$	96.9	106.5	108.3	109.7	117.5	118.3	18
	2.431	2.479	2.528	2.557			
mer-$[Cr(dien)_2][HgCl_4^{2-}][Cl^-][DMSO]_2$	101.8	105.7	105.7	111.2	111.2	119.8	18
	2.454	2.454	2.518	2.518			
cis-$[CrCl(en)_2(Hen)^{3+}][HgCl_4^{2-}][Cl^-]$	99.0	103.0	111.3	113.0	113.3	116.2	18
	2.443	2.446	2.477	2.543			
(±)-$[Cr(en)_3]_2[HgCl_4^{2-}]_3$[b]	108.9	108.9	109.0	109.4	109.9	110.5	19
	2.466	2.469	2.475	2.476			
	94.7	98.2	102.2	106.1	121.1	136.5	
	2.457	2.485	2.496	2.612			
	92.8	97.7	104.5	106.3	121.4	135.6	
	2.452	2.486	2.511	2.612			
$[C_6H_{18}N_3^{3+}][HgCl_4^{2-}][Cl^-]$	92.0	99.6	103.4	116.4	121.0	121.4	20
	2.434	2.445	2.535	2.477			
s-fac-$[Cr(dien)_2^{3+}]_4[HgCl_4^{2-}]_2.[Hg_2Cl_6^{2-}].[Hg_4Cl_{14}^{6-}]$	99.8	100.6	103.3	114.2	118.4	120.6	18
	2.432	2.444	2.516	2.544			
$[Cs^+]_3[HgCl_4^{2-}][Cl^-]$	100.8	100.8	105.9	105.9	111.7	123.1	21
	2.438	2.438	2.441	2.540			
$[C_9H_{22}N_2^{2+}][HgCl_4^{2-}]$[e]	103.1	105.5	106.0	108.5	115.3	118.9	22
	2.457	2.503	2.516	2.520			
	103.0	105.6	105.8	108.6	115.7	118.7	
	2.454	2.501	2.516	2.523			
$[C_6H_{14}N_2^{2+}][HgCl_4^{2-}].H_2O$	100.5	—	—	—	—	121.1	23
	2.438	2.444	2.529	2.531			

TABLE 1 (*continued*)

Salt	Cl–Hg–Cl bond angles (°) Hg–Cl bond lengths (Å)						Reference
$[C^{2+}][HgCl_4^{2-}].2H_2O$	98	102	102	110	110	119	24,25
	2.48	2.48	2.51	2.51			
$[Me_4N^+]_2[HgCl_4^{2-}]$[c,e,g]	105.9	107.8	108.2	110.2	110.9	114.1	26,27
	2.463	2.472	2.476	2.480			
$[Hg(H_2dapp)^{2+}][HgCl_4^{2-}]$	96.0	104.8	109.2	110.4	110.5	124.4	28
	2.454	2.412	2.624	2.500			
$[ClHgNC_6H_{12}Cl^+]_2[HgCl_4^{2-}].[C_6H_6].H_2O$[f]	96.5	105.2	100.5	141.1			29
	2.387	2.387	2.643	2.643			
$[C_{10}H_{22}N_8O_4^+]_2[HgCl_4^{2-}].2H_2O$	103.2	106.7	106.7	113.0	113.0	113.9	30
	2.462	2.463	2.481	2.482			

[a]Two independent anions.
[b]One independent $HgCl_4^{2-}$ anion and a possible $Hg_2Cl_8^{4-}$ unit (see Section D.(ii)(b)).
[c]Isomorphous with $[Me_4N^+]_2[HgBr_4^{2-}]$ [26].
[d]*cis*-$Hg(tet\,b)^{2+}$ cation weakly interacting with the $HgCl_4^{2-}$ anion [16].
[e]Isomorphous with the corresponding Ni^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+} salts [17].
[f]This anion may be distorted by close association with a chloro ligand from the cation [29].
[g]Structural data at −70°C (see Table 9).

well defined [38], and estimates range from 3.17 to 3.53 Å [2,39]. Indeed, the covalent radius of Hg(II) (1.48 Å [2] to 1.73 Å [40]) may well depend on the stereochemistry adopted.

Statements such as "fifth and sixth Hg–Cl contacts are found for some of the atoms, but these distances are of the order 3.37–3.47 Å and are no longer considered to contribute to the bonding" or "this chlorine completes the environment about the Hg but does not contribute to the bonding", frequently occur.

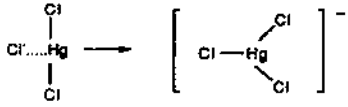
This difficulty has led to concepts such as "effective coordination number" defined as the number of atoms that, in the solid state, approach the mercury at distances less than the sum of the van der Waals' radii (3.30 Å) [2], or "secondary interactions" [36].

Even adhering to this criterion causes problems, e.g. "the distances are at the limit of the van der Waals' contact distance and, as a result, the influence of these Hg–Cl interactions is difficult to ascertain completely".

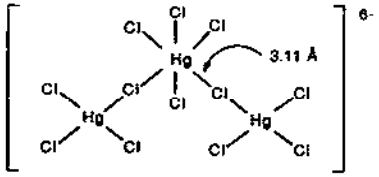
In view of these uncertainties, and with a considerable quantity of crystallographic data now available, a more quantitative approach to the question of the limit of Hg–Cl interaction has been investigated. In this approach, the concept of the "structure-correlation method", as developed by Burgi and Dunitz [41,43], is applied to Cl–Hg–Cl + Cl^- interactions. Thus the observed Cl–Hg–Cl angle is plotted against the approaching Hg–Cl distance for structural fragments containing one distorting chloro ligand (Scheme 2). In most cases it is easy to recognize two short and one long Hg–Cl bonds and thus the distorting angle is easily identified. However, in nearly regular $HgCl_3^-$ units the choice is sometimes not quite so clear.

As a result of angle deformation analysis for $Cl^- + HgCl_2 \rightarrow HgCl_3^-$, $HgCl_4^{2-} + HgCl_2 \rightarrow Hg_2Cl_6^{2-}$ and $2Cl^- + HgCl_2 \rightarrow HgCl_4^{2-}$ (see Appendix), we find an upper limit for the $Cl^- + Hg_xCl_y^{n-}$ interaction of 3.02 Å. Ben Salah et al. [9] have attempted a similar correlation using $HgCl_2 + 2Cl^- \rightarrow HgCl_4^{2-}$ data where the average of the two longer Hg–Cl bonds is plotted against the average of the two shorter Hg–Cl bonds. Unfortunately, their plot has considerable scatter and is distinctly curved. They conclude that "Hg–Cl bond lengths of the order of 3.0–3.2 Å appear to give non-negligible contribution to the bonding in these complexes", and an upper limit was not established. Despite this internal consistency, the fact remains that there are associations of structural units with Hg–Cl distances of greater than 3.03 Å (Schemes 3 and 4), which are examples of isolated clusters, as well as infinite linking of $(HgCl_3)_n^{n-}$ chains (Scheme 5).

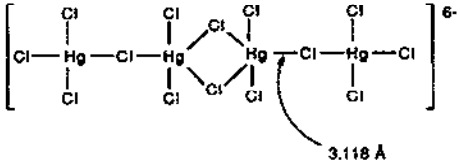
As a working definition, and from the considerable structural data now available, we will regard Hg–Cl distances of up to 3.35 Å as being part of the coordination sphere about the Hg(II) atom. Hg–Cl distances greater than 3.35 Å are not considered as part of the Hg(II) structural unit. This is equivalent to using the "effective coordination number" concept with a cut-off at 3.35 Å, a value slightly greater than the sum of the estimated van der Waals' radii (1.48 Å (Hg) + 1.77 Å (Cl)) [2]. Even this value may be conservative and an upper limit for the Hg···Cl interaction of



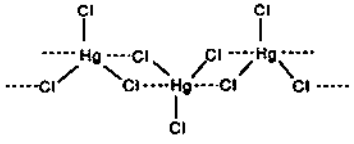
Scheme 2.



Scheme 3. $Hg_3Cl_{12}^{6-}$ [44].



Scheme 4. $Hg_4Cl_{14}^{6-}$ [18].



Scheme 5. $(HgCl_3^-)_n$.

3.55 Å would be possible of 1.73 Å were used for the Hg(II) radius [40]. There are, however, relatively few systems where Hg·····Cl distances of this magnitude are observed [38,45]. In this regard, we note that all the Hg·····Cl cross-linking distances in polymeric $HgCl_3^-$ anions (Scheme 5, Table 2) are less than 3.3 Å.

B. EARLY WORK

A survey of the "classical" inorganic literature [58,59] reveals that chloromercury(II) anions of extremely diverse composition had been discovered by the mid to late 18th century. Daniel Strömholm [60] describes a whole host of $Hg_xCl_y^{n-}$ salts using $R_3S^+Cl^- + HgCl_2$, $R_4N^+Cl^- + HgCl_2$ and $[PtN_4]^{2+}(Cl^-)_2 + HgCl_2$ (N≡monoamine) as model systems. It is obvious from his work that the size of the cation (by varying R or N≡monoamine) is critical in determining the value of x (≤ 6) in the $Hg_xCl_y^{n-}$ anion. It is also apparent that, due to the uncertain nature of the anions, this work has never appeared in contemporary

TABLE 2
Association of $HgCl_3^-$ units in $(HgCl_3)_n^{n-}$ chains (Scheme 5)

Hg···Cl interanion distances (Å)	Reference
2.851, 3.248	46
2.883, 2.888	47
2.901, ?	48
2.92, 3.22	49
2.922, ?	48
2.93, 3.27	49
2.982, 3.112	50
2.997, 3.145	51
3.017, 3.054	52
3.022, 3.204	53
3.030, 3.030	54
3.040, 3.049	39

Structural data for isolated $HgCl_3^-$ anions

Hg–Cl distances (Å)	Cl–Hg–Cl angles (°)	Reference
2.35(1)	101.0(4)	29
2.42(1)	120.2(4)	
2.46(1)	137.7(4)	
2.29(1)	103.2(4)	29
2.40(1)	114.0(4)	
2.54(1)	142.1(4)	
2.371(5)	108(1)	55
2.431(4)	120(1)	
2.503(4)	130(1)	
2.400(8)	114.2(3)	56
2.406(10)	120.5(3)	
2.434(10)	124.9(3)	
2.391(4)	105.30(14)	57
2.432(4)	115.78(15)	
2.504(4)	138.34(14)	

text books and is missing from a modern compilation [37], although in this publication the authors' terms of reference were restricted.

Nevertheless, isomorphous rhombohedral salts of $Hg_6Cl_{13}^-$ with R_4N^+ and R_3S^+ (R ≡ Me, Et) had been isolated by about 1900 [60], were "rediscovered" in about 1968 [61,62], and were structurally characterized [63] 90 years after their isolation. Similarly "forgotten" have been the alkali metal salts of $Hg_5Cl_{11}^-$ [63–69].

(i) Structural predictions based on spectroscopic studies

Several papers have described the IR, Raman or NQR spectra of $[M_x^+][Hg_xCl_y^{n-}]$ salts [1,70,71] and, using these data, predictions have been made as to the structural

units involved in the anion. In one or two cases, subsequent single-crystal X-ray data have appeared, and it is interesting to compare the predictions with those found in the structural studies.

For example, as a result of far IR spectroscopy, Barr and Goldstein [72] conclude that α-$[Et_4N^+][HgCl_3^-]$ consists of "essentially monomeric anionic units. If halogen bridging is present, it is so weak that it has little influence on the vibrational spectrum". The subsequent crystal structure [52] indicates that potential chloride bridging contacts occur at 3.054 and 3.017 Å.

In the same paper [72], IR studies indicate that $[Me_4N^+][HgCl_3^-]$ is "in the same structural category" as α-$[Et_4N^+][HgCl_3^-]$. Subsequent single-crystal X-ray structural analysis [48] indicates bridging chloro ligands at 2.901–2.922 Å.

In contrast, for $[Pr^n_4N^+][HgCl_3^-]$, Hg–Cl–Hg bridges are strongly implied from IR spectral data, and while the structure of this complex has not yet been determined, the structure of $[Bu^n_4N^+][HgCl_3^-]$ [73] clearly demonstrates the formation of $Hg_2Cl_6^{2-}$ units.

The structure of $[Et_4N^+][HgCl_3^-]$ has also been predicted [61] as "an infinite chain of $HgCl_4$ tetrahedra sharing chloride ion corners ... Dimeric $Hg_2Cl_6^{2-}$ units, however, cannot be excluded". This is certainly not the structure adopted by the α-isomer [52], but bridging chlorides are proposed [72] for the β-form.

The present situation can be summarized according to Konovalov and Davarski [74] who conclude that, while Hg–X distances can be estimated to ±0.05 Å from IR data, it is not possible to predict the coordination environment or structural units from such measurements.

C. $HgCl_2$ AND ITS ADDUCTS

$HgCl_2$ in the gas phase [45,75] is strictly linear (180(16)°) [45] with equal Hg–Cl distances (2.252(5) Å) [45], but in the solid state the Hg–Cl bonds are not exactly equal and there are small distortions from 180.0° (Table 3). If the upper limit of Hg····Cl = 3.55 Å is allowed, then Hg is essentially six-coordinate in $HgCl_2$(s), as there are four (previously considered non-bonding [80]) additional Hg····Cl distances of 3.37, 3.39, 3.44 and 3.48 Å. The $HgCl_2$ molecule appears to have some flexibility, as symmetrical structures are adopted when required by crystal symmetry [83], but distorted arrangements result when this restriction is relaxed [81].

(i) $HgCl_2$ adducts [34]

Neutral molecules or salts can often crystallize with $HgCl_2$. These can be called "adducts" or "coordination compounds" [74] and examples where structural information is available are listed in Table 4. In general, as the strength of the interaction between donor atoms from the adduct and Hg increases, the Hg–Cl bond distance increases. For non-octahedral geometries, the Cl–Hg–Cl angle also distorts from

TABLE 3
Hg–Cl distances in $HgCl_2$[a,b]

Compound	Hg–Cl (Å)	Hg····Cl (Å)	Cl–Hg–Cl (°)	Reference
$HgCl_2$(g)	2.29(2) × 2		180(40)	75
$HgCl_2$(g)	2.252(5) × 2		180(16)	45
$HgCl_2$(s)	2.23		180	76
	2.27			
$HgCl_2$(s)	2.25 × 2	3.34 × 2	180	77
		3.63 × 2		
$HgCl_2$(s)	2.25	3.23		78
$HgCl_2$(s)	2.24			79
	2.26			
$HgCl_2$(s)	2.284(12)	3.37	178.9(5)	80
	2.301(14)			
Mean	2.262(21)			
$HgCl_2$(s)[c]	2.327(7)		172.7(2)	81
	2.304(7)			

[a] $HgCl_2$ in dimethylsulphoxide (DMSO) solution [82]: 2.350(4) × 2; $HgCl_2$ in MeOH solution [82]: 2.308(3) × 2.
[b] $HgCl_2$, $M_R = 271.50$, orthorhombic, *Pnma*, $a = 12.765(6)$, $b = 5.972(3)$, $c = 4.330(2)$ (at 298 K), $\rho_{calc} = 5.464$ g cm^{-3}, $Z = 4$ [80], m.p. 277°C, b.p. 302°C, 6.9 g dissolves in 100 ml H_2O at 293 K.
[c] Encapsulated in a ruthenocenophane thio-oxa macrocycle.

linearity as the Hg–donor atom strength increases. A plot of Hg–X distance vs. Cl–Hg–Cl angle has considerable scatter as donor atoms include O, N, S, P and Se as well as Cl.

D. INDIVIDUAL ANIONS

Table 5 presents a compilation of the known $Hg_xCl_y^{n-}$ anions. In the following sections we will discuss the occurrence and nature of these species.

(i) Monomercury(II) chloride ions, $HgCl_3^-$, $HgCl_4^{2-}$, $HgCl_5^{3-}$ and $HgCl_6^{4-}$

(a) $HgCl_3^-$ anions

There is much confusion in the literature with regard to the nature of salts such as $[NH_4^+][HgCl_3^-]$ or $[Na^+][HgCl_3^-]$. This partly arises from the method of preparation and partly due to polymorph formation [173]. Thus $[NH_4^+][HgCl_3^-]$, when obtained from a melt of NH_4Cl and $HgCl_2$, is the tetragonal α-form [174–176] isomorphous with $[Rb^+][HgCl_3^-]$ [174], but when obtained from aqueous solution is the orthorhombic β-form (*Pnam*) isomorphous with

TABLE 4

Hg–Cl distances in $HgCl_2$ adducts

Monomeric adducts: Hg·····Cl systems Compound	Hg–Cl (Å)	Hg·····Cl (Å)	Cl–Hg–Cl (°)	Reference
$(H_4ttf)\cdot(HgCl_2)_3$ [2+2+2]	2.309(5) × 2	2.989(6) × 2 3.235(5) × 2	180	84
$(DMSO)_2\cdot(HgCl_2)_3$ [2+2+2]	2.306(6) × 2	3.004(5) × 2 3.081(6) × 2	180	85,86
$(Et_2S)\cdot(HgCl_2)_2$ [2+4]	2.30 2.33	2.88, 3.06, 3.00, 3.16	180(?)	87–89
$(C_8H_{12}S_2)\cdot(HgCl_2)_2$ [2+4]	2.30 × 2	2.93, 3.21, 3.02, 4.44	168	90

Hg·····O systems Compound	Hg–Cl (Å)	Hg·····Cl (Å)	Hg·····O (Å)	Cl–Hg–Cl (°)	Reference
$(K_2Cr_2O_7)\cdot HgCl_2$ t-[2+2+2(O)]	2.349(2) × 2 2.343(2) × 2	3.029(2) × 2 3.034(2) × 2	2.636(7) × 2 2.663(7) × 2	180 180	91
$(Uracil)_2\cdot HgCl_2$ t-[2+2+2(O)]	2.299(6) × 2	3.067(6) × 2	2.71(x) × 2	180(?)	92
$(Dihydrouracil)_2\cdot HgCl_2$ t-[2+2+2(O)]	2.284(8) × 2	3.053(9) × 2	2.88(3) × 2	180(?)	92
$(Quinoline\text{-}N\text{-}oxide)\cdot HgCl_2$?-[2+2+2(O)]	2.299 2.304	3.12 3.25	2.56 2.61	174	93
$(DMSO)_2\cdot(HgCl_2)_3$ c-[2+2+2(O)]	2.309(6) 2.320(6)	3.372(7) 3.302(6)	2.56(1) 2.52(1)	166.0(2)	85
$(MeOH)_2\cdot HgCl_2$ [2+2+2(O)]	2.31 × 2	3.07 × 2	2.82 × 2	180(?)	94
$(Br_2pyNO)\cdot HgCl_2$	2.29	3.12	2.51	173.5	95

[2+2+1(O)]	2.31	3.21			
$(Bu^n_2SO)\cdot HgCl_2$	2.33(1)	3.13(1)	2.59(3)	167.0(5)	86
[2+2+1(O)]	2.35(1)	3.16(1)			
$(Ph_2SO)\cdot HgCl_2$	2.291(4)	3.284(5)	2.58(1)	172.4(1)	96
[2+2+1(O)+1(Ph)(?)]	2.289(4)	3.230(6)			
(Azoxyanisol)·$HgCl_2$	2.285	3.10, 3.15,	2.60	175	93
[2+3+1(O)]	2.304	3.18			
$(C_9H_6O_2)\cdot HgCl_2$	2.33 × 2	2.94, 3.18,	2.38	180	97
[2+3+1(O)]		3.34			
(1,4-Cyclohexanedione)·$HgCl_2$	2.30 × 2	—	2.79 × 2	173	98
[2+2(O)]					
(Dioxane)·$HgCl_2$	2.34 × 2	—	2.66 × 2		99
[2+2(O)]					
(Polyethyleneoxide)·$HgCl_2$	2.30 × 2	—	2.62 × 2	176.6	100,101
Type I [2+2(O)]					
(Polyethyleneoxide)·$HgCl_2$	2.23	—	2.79	171.7	100
Type II [2+2(O)]	2.25				
$(EtOH)_2\cdot HgCl_2$	2.31 × 2	—	3.07 × 2		78
[2+2(O)]					
$(Ph_3AsO)_2\cdot HgCl_2$	2.33(1)	—	2.32(3)	146.5(4)	89,93,102
[2+2(O)]	2.32(1)		2.37(3)		
$(Testosterone)_2\cdot HgCl_2$	2.296(6) × 2	—	2.48(2) × 2	165	103
[2+2(O)]					
(Cyclononanone)·$HgCl_2$	2.27[c]		2.87[c]	177.3	104
[2+2(O)]					
μ-$Hg(C_4H_6NO)_2\cdot HgCl_2$	2.320(5)	3.33	2.56(2)	166.8(2)	105
[2+2(O)]	2.314(5)		2.58(1)		
$[Cu_4(damp)_2(AcO)_2(OH)_2][HgCl_2(AcO)]_2[HgCl_2]$	2.355(8)		2.43(2)	154.2(4)	106
	2.298(9)		2.45(1)		
[2+2(O)]					
[2+2(O)]	2.300(7) × 2		2.76(2) × 2	180.00	

TABLE 4 (*continued*)

Hg·····O systems Compound	Hg–Cl (Å)	Hg·····Cl (Å)		Cl–Hg–Cl (°)	Reference
$(biuret)_2 \cdot HgCl_2$ [2+4(O)]	2.30 × 2	—	2.76 × 2 2.95 × 2	180	107
(Hexaethyleneglycoldiethylether)·$HgCl_2$ [2+4(O)]	2.298 2.319	—	2.66–2.91	175.9	100
(Tetraethyleneglycoldimethylether)·$HgCl_2$ [2+5(O)]	2.311(13) 2.291(13)	—	2.78–2.96	174.2	100
(Tetraethyleneglycoldiethylether)·$HgCl_2$ [2+5(O)]	2.35	—	(?)	180(?)	100
(18-crown-6)·$HgCl_2$ [2+6(O)]	2.314(1) × 2	—	2.825(4) × 6	180	108
(Macro O_5N)·$HgCl_2$ [2+5(O)+1(N)]	2.327(2) × 2		2.887(9) × 2 2.826(7) × 2	180	57
(Macro O_5MeN)·$HgCl_2$ [2+5(O)+1(N)]	2.327(2) × 2		2.753(6) 2.767(5) 2.922(6) 2.961(6) 2.968(6) 2.739(6) (Hg–N)	174.07(8)	57
(hist)·$HgCl_2$ [3+1+1(O)]	2.34 × 2 2.53	3.25	2.54	126	109
(pyNO)·$HgCl_2$ [2+2+2(O)]	2.316(16) 2.339(15)	3.185(18) 3.318(17)	2.59(5) 2.60(5)	163.1(19)	110

Hg·····S systems Compound	Hg–Cl (Å)	Hg·····Cl (Å)	Hg·····S (Å)	Cl–Hg–Cl (°)	Reference
$(Et_2S)_2 \cdot HgCl_2$ [1+4+1(S)]	2.35	2.70, 2.85, 3.55, 3.64	2.41	—	89,111

$(C_4H_8S)\cdot HgCl_2$	2.30	2.62, 2.83,	2.40	—	89
[1+4+1(S)]		3.07, 3.89			
(dioditet)·$HgCl_2$	2.36(2)	2.58(2)	2.42(2)	110.9(5)	112
[1+2+1(S)]		2.70(2)			
$(Thiourea)_2\cdot HgCl_2$[f]	2.57(1)×2	3.22	2.416(6)×2	180(?)	113,114
[2+1+2(S)]					
$(H_4ttf)\cdot(HgCl_2)_3$	2.307(5)	3.294(5)	3.131(4)	169.7	84
[2+3+2(S)]	2.319(5)	3.349(6)	3.124(6)		
		3.336(5)			
[(Me)S(Et)]·$HgCl_2$	2.37(1)	2.61(1)	2.47(1)	110(1)	115
[1+2+1+1(S)]		2.71(1)			
		3.36(1)			
$(dppmS_2)\cdot HgCl_2$	2.445(2)	—	2.557(2)	111.1(1)	116
[2+2(S)]	2.455(2)	—	2.613(2)		
$(dppeS_2)\cdot HgCl_2$	2.447(3)		2.559(3)		117
[2+2(S)]	2.442(3)		2.546(3)		
$(C_3H_6S_3)\cdot HgCl_2$	2.44(1)×2	—	2.61(1)×2	117(4)	118
[2+2(S)]					
$(C_8H_{12}S_2)\cdot HgCl_2$	2.51	—	2.53×2	99	90, 114
[2+2(S)]	2.50				
$(ditet)_2\cdot HgCl_2$	2.51(1)	—	2.49(1)	107.6(3)	112
[2+2(S)]	2.52(1)	—	2.50(1)		
$(C_4H_8SO)_2\cdot HgCl_2$	2.43	—	2.54	114	119
[2+2(S)]	2.52	—	2.59		
(ttp)·$(HgCl_2)_2$	2.407	—	2.580	117.5	120
[2+2(S)]	2.419	—	2.699		

TABLE 4 (*continued*)

Hg·····S systems Compound	Hg–Cl (Å)	Hg·····Cl (Å)		Cl–Hg–Cl (°)	Reference
$(Thiourea)_3 \cdot HgCl_2$	2.24	—	2.37, 2.61,	168(?)	121
[2+3(S)]	2.36		3.10		
(Dithiapropellane)$\cdot HgCl_2$	2.395		2.540	122.8	122
[2+2(S)]	2.486		2.754		
[2+4(S)]	2.330 × 2		3.212 × 4		
$(Thiourea)_2 \cdot HgCl_2$		3.067(4) × 2	2.394(4) × 2		123
[0+4+2(S)]		3.071(4) × 2			

Hg·····N systems Compound	Hg–Cl (Å)	Hg·····Cl (Å)	Hg·····N (Å)	Cl–Hg–Cl (°)	Reference
$(py)_2 \cdot HgCl_2$	2.34 × 2	3.25 × 2	2.60 × 2	180(?)	124,125
[2+2+2(N)]					
[0+4+2(N)]		2.765(2) × 2	2.266(6) × 2	180	126
		2.764(2) × 2			
$(bzpipNH)Hg_2Cl_5$	2.40 × 2	3.13	2.41(5)	136.2	127
[2+1+1(N)]					
[3+1]	2.28, 2.24, 2.69	3.04		168.2	
$(HBTN)HgCl_3$	2.425(3)		2.23(1)	105.8(1)	128
[3+1(N)]	2.484(3)			99.0(1)	
	2.588(3)			106.4(1)	

Hg·····P systems Compound	Hg–Cl (Å)	Hg·····Cl (Å)	Hg·····P (Å)	Cl–Hg–Cl (°)	Reference
$[(C_4H_3S)_3P]_2 \cdot HgCl_2$	2.539(2)	—	2.472(2)	107.3(1)	129
[2+2(P)]	2.519(2)		2.513(2)		

$(Ph_3P)_2 \cdot HgCl_2$	2.559(2)	—	2.478(2)	110.7(1)	130
[2+2(P)]	2.545(3)		2.462(2)		
$(Et_3P)_2 \cdot HgCl_2$	2.68(1)×2	—	2.39(1)×2	105.5(5)	131
[2+2(P)]					
$[(Ph)_2P(CH_2)_2N(Et)_2] \cdot HgCl_2$	2.443(3)	3.522(4)	2.417(3) Hg–P	109.0(1)	132
[2+1(P)+1(N)]	2.445(3)		2.641(11) Hg–N		
$[R_2PC(S)N(H)Ph]_2 \cdot HgCl_2$	2.594(5)	—	2.452(6)	102.7(2)	133
[2+2(P)]	2.598(8)		2.457(7)		
$[(N{\equiv}C{-}CH_2CH_2)_3P]_2 \cdot HgCl_2$	2.608(10)	—	2.450(12)	95.0(3)	134
[2+2(P)+2(CN)?] (I)	2.622(10)	—	2.452(10)		
[2+2(P)+1(CN)?] (II)	2.669(11)	—	2.411(7)	98.1(3)	134
	2.603(10)	—	2.450(6)		

Miscellaneous Hg·····X systems

Compound	Hg–Cl (Å)	Hg·····Cl (Å)	Hg·····X (Å)	Cl–Hg–Cl (°)	Reference
$Pt_2Cl_2(dppm)_2 \cdot HgCl_2$[b]	2.440(4)		2.7122(8)	106.0(1)	135
[2+2(Pt)]	2.417(4)		2.7153(7)		
	2.445(4)		2.6991(8)	103.7(1)	
	2.448(5)		2.7097(8)		

Dimeric adducts[a]

Compound	Hg–Cl (Å)	Hg·····Cl (Å)	Hg·····X (Å)	Cl–Hg–Cl (°)	Reference
$[(NH_4)_2Cr_2O_7] \cdot HgCl_2$	2.325(2)	3.300(6)	2.677(5), 3.100(5)	(?)	91
[2+1+4(O)]	2.316(2)		2.669(5)×2		
β-$(Bu^n_3P) \cdot HgCl_2$	2.348(8)	2.720(6)	2.377(6)	97.3(3)	136
[1+2+1(P)]		2.736(6)			
$(TPP) \cdot HgCl_2$	2.404(11)	2.747(14)	2.438(10)	107.4(5)	137

TABLE 4 (*continued*)

Dimeric adducts[a] Compound	Hg–Cl (Å)	Hg····Cl (Å)		Cl–Hg–Cl (°)	Reference
[1+2+1(P)]		2.542(12)			
$(Ph_3P)\cdot HgCl_2$[g]	2.370(10)	2.623(8)	2.406(7)	103.8(3)	137
[1+2+1(P)]		2.658(8)			
$[(C_6H_{11})_3P]\cdot HgCl_2$[h]	2.391(5)	2.641(4)	2.416(3)	95.2(2)	138
[1+2+1(P)]		2.665(4)			
	2.413(3)	2.602(4)	2.412(3)	101.4(1)	
		2.779(4)			
$Pr^i_3P\cdot HgCl_2$	2.348(5)	2.638(4)	2.358(4)	96.5(2)	139
[1+2+1(P)][a]		2.780(4)		90.6(2)	
$(2,4,6\text{-}Me_3\text{-}py)\cdot HgCl_2$	2.455	2.956	2.181	85.8	140
[2+2+1(N)]	2.542	2.948			
$[(Ph_3C_3P)_2Hg_2Cl_4]$	2.342	2.651	2.389	89.8	141
(1+2+1P)		2.673			
(1+2+1P)	2.339	2.732	2.381	91.4	
		2.712			
$(C_{13}H_{10}N_4S)\cdot HgCl_2$	2.34(1)		2.40(1)	111.5(4)	142
[2+3(S)]	2.57(1)		3.28(2)×2		
$(C_6H_{11}NS_2)\cdot HgCl_2$	2.37(1)	2.57(1)	2.42(1)	107.5(4)	143
[1+2+1(S)]		2.78(1)			
$(Ph_3PSe)\cdot HgCl_2$	2.332(7)	2.596(7)	2.527(3)	103.5	144
[1+2+1(Se)]		2.781(7)			
$[(CH_3)_3Si(CH_2)Se(CH_3)]\cdot HgCl_2$	2.354(5)	2.698(5)	2.528(2)	101.5(2)	145
[1+2+1(Se)]		2.707(5)			
(Me-cytosine)·$HgCl_2$	2.322(3)	2.745(3)	2.17(1) Hg–N	100.4(1)	146
[1+2+1(N)+1(O)]		2.719(2)	2.84(1) Hg–O		
(DTO)·$[HgCl_2]_2$[e]	2.354(3)	2.763(3)	2.756(11) Hg–O	96.1(1)	147
[1+3+1(S)+1(O)]		2.795(3)	2.478(3) Hg–S		
		3.134(3)			

Dithiamacrocycle·$[HgCl_2]_2$	2.427(6)		2.522(6)		148
[2+2(S)]	2.460(6)		2.672(7)		
[2+1]	2.315(7)	2.900(6)		166.8(2)	
	2.313(7)				
$[(mes)(CO)_3Mo]\cdot[HgCl_2]_2$	2.538(4)	2.645(4)	2.745(1)		149
[1+2+1(Mo)]		2.736(4)			
[2+2]	2.317(5)	3.038(5)		118.6	
	2.628(5)	3.051(4)			
pen.$[HgCl_2]_2\cdot 2H_2O$[b]	2.380(5)	2.687(5)	2.822(5)	142.1(1)	150
[2+1+1(S)]	2.348(5)				
[1+2+1(S)]	2.356(5)	2.780(5)	2.356(5)		
		3.091(4)			
Dithiapropellane·$HgCl_2$	2.326	2.659	2.438		122
[1+2+1(S)]		2.789			
[1+2+1(S)]	2.332	2.764	2.430		
		2.729			
$[R_2PC(S)N(H)Ph]\cdot HgCl_2.CH_2Cl_2$[b]	2.352(8)	2.748(7)	2.400(7)		133
[1+2+1(P)]		2.715(7)			
	2.348(8)	2.719(7)	2.393(7)		
		2.690(7)			
$[C_{18}H_{24}O_5Ru]\cdot HgCl_2$	2.451(9)	2.943(9)	2.683(3)	103.7(3)	151
[2+1+1(Ru)]	2.528(9)				
$[C_{18}H_{24}O_2S_3Ru]\cdot HgCl_2$	2.430(5)	2.885(4)	2.704(1)	104.6(2)	151
[2+1+1(Ru)]	2.574(4)				
$[C_{20}H_{28}O_6Ru]\cdot HgCl_2$	2.466(6)	2.697(6)	2.696(2)	99.8(2)	151
[2+1+1(Ru)]	2.670(6)				
$[C_6H_5NCH_2CH_2CO_2\cdot HgCl_2]_2$	2.358(4)		2.191(9)	114.6(1)	152
[3+2(O)]	2.578(4)		2.679(9)		
	2.743(3)				
$[Ru_2(dan)(CO)_4(PPr^i)_2Hg_2Cl_4]$	2.301(9)	2.652(5)	2.537(4)		153

TABLE 4 (*continued*)

Dimeric adducts[a]

Compound	Hg–Cl (Å)	Hg···Cl (Å)		Cl–Hg–Cl (°)	Reference
[2+2+2(Ru)]	2.427(6)	2.685(5)	2.834(6)		
$[IrCl(CO)(dpm)(dpmAuCl)\cdot Hg_2Cl_4]$	2.330(9)	2.623(8)		142.9(3)	154
[2+2]	2.370(9)	2.779(9)			
[1+1+1(Ir)]	2.463(9)	2.985(8)	2.618(3)	82.9(3)	
$(ClC_6H_4C_5H_9SO)_2\cdot HgCl_2$	2.284(10)		2.48(2) br.	164.0(3)	155
[2+3(O)]	2.295(10)		2.97(2) br.		
			2.70(2) term.		

Trimeric and tetrameric adducts

Compound	Hg–Cl (Å)	Hg···Cl (Å)	Hg···X (Å)	Cl–Hg–Cl (°)	Reference
α-$(Bu^n_3P)\cdot HgCl_2$	2.289(21)	2.709(20)	2.363(21)	98.4(7)	137
[1+2+1(P)]		2.626(19)			
$[Hg_3(dpmp)_2Cl_4]Cl\cdot HCO_3$	2.488(9)		2.454(9)	95.6(3)	156
[2+2P]	2.674(8)		2.442(9)		
[2+2P]	2.484(9)		2.450(9)	102.3(3)	
	2.626(9)		2.453(8)		
[2+2P]	2.667(9)		2.461(8)	90.2(3)	
	2.691(9)		2.449(9)		
$[Hg_4\{S(CH_2)_2NMe_2\}_4Cl_4]$	2.506(1)		2.487(1)	109.6(1)	157
[2+2S]	2.648(1)		2.504(1)		

Polymeric adducts

Compound	Hg–Cl (Å)	Hg···Cl (Å)	Hg···X (Å)	Cl–Hg–Cl (°)	Reference
$[\{(CNCH_2CH_2)_3P\}\cdot\{HgCl_2\}]_n$	2.331(7)	2.780(7)	2.393(5)	99.0(3)	158
[1+2+1(P)]		2.714(7)			

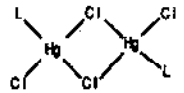
$[(Me_3P)\cdot HgCl_2]_n$	2.355(4)	2.782(4)	2.365(3)	98.2(1)	136,159
[1+2+1(P)]		2.941(4) [3.489(4)]			
$[(Et_3P)\cdot HgCl_2]_n$	2.42(1)	3.04(1)	2.35(1)	98.9(3)	159,160
[2+2+1(P)]	2.56(1)	3.21(1)			
$[L\cdot HgCl_2]_n$[d]	2.398(6)	2.779(5)	2.410(6)	94.5(2)	161
[1+2+1(S)]		2.628(6)			
$\{[(Me)\{CH_2C(H)(Ph)(Et)\}S]\cdot HgCl_2\}_n$	2.315(5)	2.677(5)	2.433(4)	94.2	88
[1+3+1(S)+Ph]		2.838(10)			
		2.995(10)			
$\{[Guanosine]\cdot HgCl_2\}_n$	2.339(7)	2.761(7)	2.16(1)	105.0	162
[1+2+1(N)]		2.659(7)			
$\{[C_3H_6N_2O]_2\cdot HgCl_2\}_n$	2.309(4)×2	—	2.953(11) Hg–N	180.0	163
[2+2(O)+2(N)]			2.673(9) Hg–O		
$\{(Nicotine)\cdot HgCl_2\}_n$	2.384(5)	—	2.454(13) Hg–N(py)	137.0(2)	164
[2+2(N)]	2.364(6)	—	2.397(14) Hg–N(pyro)		
$\{(9Mehyp)\cdot HgCl_2\}_n$	2.353(3)	2.979(3)	2.299(7)	140.5(1)	165
[2+2+1(N)]	2.401(2)	2.925(3)			
$\{(Me_2PPMe_2)\cdot HgCl_2\}_n$	2.51	—	2.49	?	166
[2+2(P)]	2.55	—	2.19		
$[(pen)\cdot HgCl_2\cdot H_2O]_n$		2.850(5)	2.335(5)		150
[0+2+2(S)]		3.323(5)	2.357(4)		
$\{(Me_2EtP)_3[HgCl_2]_2\}_n$	2.69(1)	3.07(1)	2.40(1)		167
[1+2+2(P)]		3.25(1)	2.40(1)		
[3+1(P)]	2.45(1), 2.52(1)		2.40(1)	103.1(5)	
	2.62(1)				
$[(Thiourea)_2(HgCl_2)_3]_n$	2.39(2)	2.84(2)	2.40		168
[1+2+1(S)]		2.94(2)			
[2+2]	2.23(2)×2	3.15(2)		180.0	
		3.13(2)			
$[(C_4H_4Se)\cdot HgCl_2]_n$	2.352(2)	2.634(2)	2.535(1)		169

TABLE 4 (*continued*)

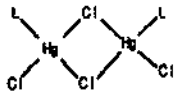
Polymeric adducts Compound	Hg–Cl (Å)	Hg⋯Cl (Å)		Cl–Hg–Cl (°)	Reference
[1+3+1(Se)]		2.842(2)			
		3.165(2)			
$[(C_9H_8N_2)\cdot HgCl_2]_n$	2.326(7)	3.070(7)	2.61(3)	168.56	170
[2+3+1(N)]	2.348(7)	3.081(7)			
		3.328(7)			
$[\{\mu\text{-}S(CH_3)_3NH(CH_3)_2\}\cdot HgCl_2]_n$	—	2.513(6)	2.464(6)	99.0(2)	171
[0+2+μ(S)]	—	2.634(5)			
$[(cis\text{-}PtCl_2(NH_3)_2)\cdot 3HgCl_2]_n$	2.301(5)	2.979(2)		178.8	83
[2+1] Hg(2)×2	2.308(5)	3.25			
[2+2] Hg(1)	2.308(5)×2	3.004(4)×2		180.0	
$[Hg(O_4N)Cl_2\cdot HgCl_2]_n$	2.291(4)	3.129(4)	2.664(10)	102.37(13)	57
[1+1+4(O)+1(N)]			2.756(9)		
			2.777(9)		
			2.806(9)		
			2.145(10)(Hg–N)		
[3+2]	2.391(4)	2.930(4)		138.34(14)	
	2.432(4)	2.989(4)		115.78(15)	
	2.504(4)			105.30(14)	
$\{[Me_3NCH_2CO_2\cdot HgCl_2]_2\cdot HgCl_2\}_n$	2.348(5)		2.26(2)	157.9(2)	152
[2+2(O)]	2.346(5)		2.45(2)		
[2+3+1(O)]	2.276(5)	3.083(5)	2.78(2)	174.0(2)	
	2.312(4)	3.177(6)			
		3.199(6)			

$\{[C_6H_5NCH_2CO_2 \cdot HgCl_2]_2 \cdot HgCl_2\}_n$	2.311(7)		2.59(1)	156.2(2)	152
[2+3(O)]	2.318(5)		2.60(1)		
			2.66(1)		
[2+2+2(O)]	2.295(5)×2	3.141(7)×2	2.74(1)×2	180.00	

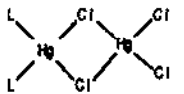
[a]There are potentially three isomers for a simple dimeric adduct, namely



(A)



(B)

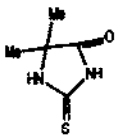


(C)

Those listed here are of the centrosymmetric (A) type, but (C) types are also known for other HgX_2 adducts [172].

[b]Two independent molecules.

[c]Mean data.



[d]DTO = CH_2–S–$(CH_2)_2$OH
|
CH_2–S–$(CH_2)_2$OH

[f]This species is better represented as (thiourea)$_2HgCl^+Cl^-$. [g]$(Ph_3As) \cdot HgCl_2$ is isostructural [137]. [h]Bridging S atom.

TABLE 5

Summary of known $Hg_xCl_y^{n-}$ anions classified in terms of x, y and n

Increasing x			Increasing y			Increasing n		
$x=1$	$x=2$	$x=3$	$y=2$	$y=3$	$y=4$	$n=0$	$n=-1$	$n=-2$
$HgCl_2$	$Hg_2Cl_5^-$	$Hg_3Cl_7^-$	$HgCl_2$	$HgCl_3^-$	$HgCl_4^{2-}$	$HgCl_2$	$HgCl_3^-$	$HgCl_4^{2-}$
$HgCl_3^-$	$Hg_2Cl_6^{2-}$	$Hg_3Cl_8^{2-}$	$y=5$	$y=6$	$y=7$		$Hg_2Cl_5^-$	$Hg_2Cl_6^{2-}$
$HgCl_4^{2-}$	$Hg_2Cl_7^{3-}$	$Hg_3Cl_9^{3-}$	$HgCl_5^{3-}$	$Hg_2Cl_6^{2-}$	$Hg_2Cl_7^{3-}$		$Hg_3Cl_7^-$	$Hg_3Cl_8^{2-}$
$HgCl_5^{3-}$	$Hg_2Cl_8^{4-}$	$Hg_3Cl_{10}^{4}$	$Hg_2Cl_5^-$	$HgCl_64-$	$Hg_3Cl_7^-$		$Hg_5Cl_{11}^-$	
$HgCl_6^{4-}$		$Hg_3Cl_{12}^{6-}$					$Hg_6Cl_{13}^-$	
$x=4$	$x=5$	$x=6$	$y=8$	$y=9$	$y=10$	$n=-3$	$n=-4$	$n=-6$
$Hg_4Cl_{14}^{6-}$	$Hg_5Cl_{11}^-$	$Hg_6Cl_{13}^-$	$Hg_2Cl_8^{4-}$	$Hg_3Cl_9^{3-}$	$Hg_3Cl_{10}^{4-}$	$HgCl_5^{3-}$	$Hg_3Cl_{10}^{4-}$	$Hg_3Cl_{12}^{6-}$
	$Hg_5Cl_{13}^{3-}$		$Hg_3Cl_8^{2-}$			$Hg_2Cl_7^{3-}$	$Hg_2Cl_8^{4-}$	$Hg_4Cl_{14}^{6-}$
			$y=11$	$y=12$	$y=13$	$Hg_3Cl_9^{3-}$	$HgCl_6^{4-}$	
			$Hg_5Cl_{11}^-$	$Hg_3Cl_{12}^{6-}$	$Hg_6Cl_{13}^-$	$Hg_5Cl_{13}^{3-}$		
			$y=14$		$Hg_5Cl_{13}^{3-}$			
			$Hg_4Cl_{14}^{6-}$					

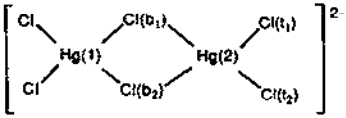
$[M^+][CdCl_3^-]$ (M≡K, Rb, NH_4) [173]. $[NH_4^+][HgCl_3^-]$. H_2O (orthorhombic, *Pnma*) has also been obtained from aqueous solution [177].

Similar problems arise with $[Na^+][HgCl_3^-]$. A structural investigation of the anhydrous salt has been reported [178], but only the dihydrate could be isolated by subsequent investigators [174,177,179,180], and the validity of the original structure and its isomorphism with $[NH_4^+][XCl_3^-]$ (X≡Hg, Cd) has been questioned [174]. Indeed, the cell dimensions (Table 6) of the alleged anhydrous salt and the dihydrate are effectively the same. Similar conclusions could also be made with respect to the hydrated and anhydrous forms of β-$[NH_4^+][HgCl_3^-]$.

The $HgCl_3^-$ anion commonly forms $[3+2]_n$ chains (Scheme 5) (Tables 2 and 7), but $[2+4]_n$ chains are also described. Isolated $HgCl_3^-$ anions are very rare (Table 2) and there is also one example of $HgCl_3^-$ as $[3+2]_n$ chains associated with $HgCl_4^{2-}$ anions to give the $Hg_2Cl_7^{3-}$ stoichiometry. The other major structural isomer adopted by $HgCl_3^-$ is $Hg_2Cl_6^{2-}$ (Table 8) as dimeric edge-shared bitetrahedra.

We cannot, at the moment, predict which anion arrangement will be adopted for a particular unipositive cation.

Some generalizations are: (i) relatively small, spherical cations allow pseudo-octahedral structural units, [2+2+2] or [2+4] associations; (ii) moderate sized cations without extensive hydrogen bonding networks allow $[3+2]_n$ chains, i.e. $[HgCl_3^-]_n$ chains (Scheme 5); (iii) moderate sized cations with extensive hydrogen bonding networks develop complex Hg–Cl structural patterns; (iv) large cations, especially those forming layers, result in the development of $Hg_2Cl_6^{2-}$ units (Scheme 6).



Scheme 6. $Hg_2Cl_6^{2-}$.

The above generalizations are made on the basis of an assessment of the space available for Hg–Cl bonding after cation sites are fixed. Chains appear to penetrate the cation lattice if space is available, but, if not, the $HgCl_3^-$ units are constrained to form $Hg_2Cl_6^{2-}$.

Additional difficulties often arise due to variation in the nature of the anion, and salts of differing stoichiometry can form. Thus $CsHgCl_3$ [3,17,181], Cs_2HgCl_4 [13,202,203] and Cs_3HgCl_5 [21] have been characterized, and the work of Daoud and co-workers [7–9,204] illustrates the complexity when protonated amines are used as cations [205].

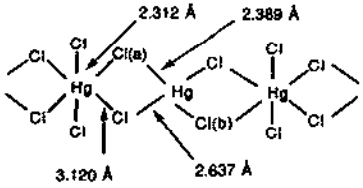
TABLE 6
Cell dimensions of $[M^+][HgCl_3^-].xH_2O$ salts

M^+	x	Space group	a (Å)	b (Å)	c (Å)	Reference
α-NH_4^+	0	*P4/mmm*[a]	4.20	4.20	7.90	174
			4.19	4.19	7.94	175
			4.198	4.198	7.935	176
			4.20	4.20	7.94	181
β-NH_4^+	0	*Pnam*[b]	9.20	14.90	4.30	173,174
β(?)-NH_4^+	1[b]	*Pnma*	8.727	4.344	17.73	177
Na^+	0	*Pnma*	9.48	4.16	18.35	178
Na^+	2	*Pnma*	9.327	4.037	18.71	180
K^+	0	Not isomorphous with other $[M^+][XCl_3^-]$ salts				17,174
Cs^+	0	Cubic	5.42	5.42	5.42	181
			5.41	5.41	5.41	3, 17
Rb^+	0	*P4/mmm*	4.21	4.21	8.01	174,181
Tl^+	0	Not isomorphous with α-$[NH_4^+][HgCl_3^-]$				17

[a]From the melt.
[b]From aqueous solution.

Reedijk and Groenveld [61] describe $[M^+]HgCl_3$ ($M^+ \equiv Et_4N^+$) (and there are α- and β-forms of this [72]), $[M^+]_2HgCl_4$, $[M^+]Hg_3Cl_7$, $[M^+]_2Hg_3Cl_8$ and $[M^+]Hg_5Cl_{11}$ as stoichiometrically distinguishable species, and $[Et_4N]Hg_2Cl_5$ is reported by Scaife [17]. Until recently (see Table 9), the only single-crystal X-ray data available in this series were for α-$[Et_4N^+][HgCl_3^-]$ [52], but the anion in $[Et_4N^+]_2[HgCl_4^{2-}]$ is almost certainly tetrahedral [17,61] as this salt is isomorphous with the corresponding Ni^{2+}, Co^{2+}, Zn^{2+} and Cd^{2+} salts [17].

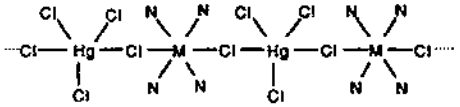
Among the more complex $HgCl_3^-$ systems are chains of alternate four- and six-coordinate Hg atoms as in $[Me_3NH^+][HgCl_3^-]$ [9] (Scheme 7).



Scheme 7. Cl(a)–Hg–Cl(b) = 143.35° [9].

Relatively inert M(III) dichloro complex ions from sparingly soluble salts of the type *trans*-$[M(III)Cl_2(N_4)^+][HgCl_3^-]$ [207] with bridges (Scheme 8) [208] or isolated $Hg_2Cl_6^{2-}$ anions, e.g. in *trans*-$[CoCl_2(en)_2]_2[Hg_2Cl_6]$ [44].

The *cis*-isomers [209] can form complexes shown in Scheme 9. Simpler structures can be obtained for inert square planar M(II) complexes [16,210,22]



Scheme 8.

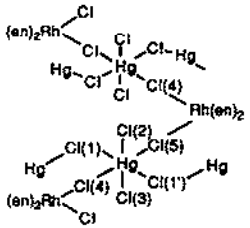
TABLE 7
Salts of $HgCl_3^-$

Stoichiometry	Structural units	Reference
$[Na^+][HgCl_3^-].2H_2O$	$[2+4]_n$ chains	177–179
$[NH_4^+][HgCl_3^-].2H_2O$	$[2+4]_n$ chains	175,177
$[Cs^+][HgCl_3^-]$	$HgCl_2.CsCl$ or $[2+4]_n$ chains	3
$[Me_4N^+][HgCl_3^-]$	$[3+2]_n$ chains, two independent Hg	48,49,234
$[Me_3NH^+][HgCl_3^-]$	Complex, two independent Hg	9
$[Me_2NH_2^+][HgCl_3^-]$	Complex, three independent Hg	8
$[MeNH_3^+][HgCl_3^-]$	$[3+2]_n$ chains	7
$[Me_3S^+][HgCl_3^-]$	$[3+2]_n$ chains	39
$[Et_4N^+][HgCl_3^-]$	$[3+2]_n$ chains	52
$[Et_3NH^+][HgCl_3^-]$	$[3+2]_n$ chains	51
$[Bu_4N^+][HgCl_3^-]$	$Hg_2Cl_6^{2-}$	73
$[Ph_4As^+][HgCl_3^-]$	$Hg_2Cl_6^{2-}$	182
$[PhCH_2NH_3^+][HgCl_3^-]$	Complex, two independent Hg	183
$[C_6H_{13}N_4^+][HgCl_3^-]$	$[3+2]_n$ chains	49
$[C_5H_6N_5^+][HgCl_3^-]$	Complex, two independent Hg	184
$[C_6H_4S_4^+][HgCl_3^-]$	$[3+2]_n$ chains plus $Hg_2Cl_6^{2-}$	47,185
$[Ph_3Te^+][HgCl_3^-]$	$Hg_2Cl_6^{2-}$	186
$[S_4N_3^+][HgCl_3^-]$	$[3+2]_n$ chains	53
A-$[C_{10}H_{12}S_4^+][HgCl_3^-]$	$Hg_2Cl_6^{2-}$	187,188
B-$[C_{10}H_{12}S_4^+][HgCl_3^-]$	$Hg_2Cl_6^{2-}$, two independent dimers	187,188
[bis-L-trypt$^+$][$HgCl_3^-$]	$[3+2]_n$ chains	189
[Sulphone$^+$][$HgCl_3^-$]	$Hg_2Cl_6^{2-}$	190
u-fac-$[Cr(dien)_2^{3+}][Hg_2Cl_7]$	$[3+2]_n$ chains plus $HgCl_4^{2-}$	18
$[ClC_6H_{12}NHgCl^+][HgCl_3^-]$	Isolated $HgCl_3^-$ anions	29
$[ClNC_5H_{10}HgCl^+][HgCl_3^-]$	Distorted $Hg_2Cl_6^{2-}$ anions	29
trans-$[CoCl_2(en)_2^+][HgCl_3^-]$	$Hg_2Cl_6^{2-}$	44
$[H_2en^{2+}][HgCl_3^-]_2$	$Hg_2Cl_6^{2-}$	44
$[HgCl(C_{11}H_{15}NS_3)^+][HgCl_3^-]$	Isolated $HgCl_3^-$ anions	55
$[C_{19}H_{17}NOTeCl^+][HgCl_3^-]$	Isolated $HgCl_3^-$ anions	56
$\{[Hg(L')Cl^+][HgCl_3^-]\}_n$	Complex polymeric	57

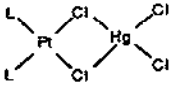
(Scheme 10). There is obviously considerable scope for further investigation in these areas [135,153,154].

(b) Tetraheral $HgCl_4^{2-}$ anions

While the majority of salts with stoichiometry $[M^{2+}][HgCl_4^{2-}]$ or $[M^+]_2[HgCl_4^{2-}]$ do contain discrete $HgCl_4^{2-}$ ions, this is not always the case, as

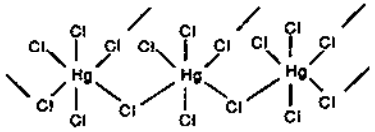


Scheme 9. Hg–Cl(2) = 2.33(3) Å; Hg–Cl(3) = 2.35(2) Å; Hg–Cl(1') = 2.98(2) Å; Hg–Cl(4) = 3.01(3) Å; Hg–Cl(1) = 3.05(2) Å; Hg–Cl(5) = 3.08(2) Å.



Scheme 10.

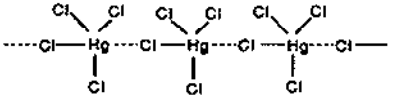
illustrated by $K_2HgCl_4 \cdot H_2O$ [3–5] (Scheme 1) or $[EtNH_3^+]_2[HgCl_4^{2-}]$ [212,213]. The latter exists in a two-dimensional polymeric form of vertex-shared chains of octahedral $HgCl_6$ units (Scheme 11).



Scheme 11. $(HgCl_4^{2-})_n$ in $[EtNH_3^+]_2[HgCl_4^{2-}]$ [212].

There are also examples of $HgCl_4^{2-}$ anions appearing in $HgCl_5^{3-}$ salts [20] (as $HgCl_4^{2-}$ plus Cl^- combinations) and in more complicated stoichiometric relationships [18]. Nevertheless, salts of large spherical divalent cations with $[M^{2+}][HgCl_4^{2-}]$ stoichiometry [23] are predicted to contain the more or less tetrahedral $HgCl_4^{2-}$ anion (Table 1).

Recently the salt of stoichiometry $[enH_2]_2HgCl_6$ has been investigated crystallographically [44]. The structure shows the salt contains two enH_2^{2+} cations, two isolated Cl^- anions and polymeric chains of $[HgCl_4^{2-}]_n$ units where each Hg is effectively five-coordinate (Scheme 12)



Scheme 12. Hg- - -Cl = 3.28 Å.

and the distorted $HgCl_4^{2-}$ units are corner shared. Thus for $HgCl_4^{2-}$ we can expect a whole range of interactions from isolated regular tetrahedra, through weakly

TABLE 8

Structural data for $Hg_2Cl_6^{2-}$ anions (Scheme 6)[a]

Complex	HG(2)–Cl(t) (Å)	Hg(2)–Cl(b1) (Å)	Hg(2)–Cl(b2) (Å)	Cl(t1)–Hg(2)–Cl(t2) (°)	Cl(b1)–Hg(2)–Cl(b2) (°)	Reference
[TMTTF][$HgCl_3$][b]	2.34, 2.45	2.70	2.55	119	85	187,233
$P2_1/b$	2.36 (×2)	2.76	2.67	140	90	
[TMTTF][$HgCl_3$]	2.387, 2.409	2.638	2.597	123.6	88.7	187
$P2_1/n$						
[$Cr(dien)_2$][Hg_2Cl_7][c,h]	2.344, 2.361	2.740	2.880	165.2	95.2	18
	2.383, 2.350	2.724	2.759	151.2	84.1	18
[NBu^n_4][$HgCl_3$][d]	2.390, 2.387	2.670	2.560	121.9	88.1	73
	2.370, 2.381	2.587	2.662	121.5	87.7	
[TFF][$HgCl_3$]	2.381, 2.368	2.600	2.696	132.2	90.1	47
[Ph_3Te][$HgCl_3$][e]	2.350 (×2)	2.684	2.717	141.34	89.63	186
trans-[$CoCl_2(en)_2$][$HgCl_3$][f]	2.368, 2.403	2.572	2.749	130.9	85.9	44
[enH_2^{2+}][$HgCl_3^-$]$_2$[i]	2.349, 2.353	2.751	2.811	165.1	89.6	44
[Ph_4As][$HgCl_3$]	2.365, 2.370	2.589	2.614	126.9	88.3	182
[RHgCl][$HgCl_3$][g]	2.32 (×2)	2.86	2.85	158.8	94.8	29
	2.30, 2.33	2.80	3.02	167.3	89.7	
$MgHg_3Cl_8.6H_2O$	2.351, 2.378	2.710	2.835	153.62	87.43	192
[Hg(dapmp)Cl]$_2$[Hg_2Cl_6]	2.370(3), 2.360(4)	2.584(4)	2.584(4)	131.7(1)	—	193
[$Ru(bpy)_3$][Hg_2Cl_6]						194

[a] See refs. 195–201 for other $Hg_2X_6^{2-}$ (X ≡ Br, I) structures.
[b] Two independent $Hg_2Cl_6^{2-}$ anions.
[c] Hg····Hg = 4.070 Å.
[d] Hg····Hg = 3.766 Å. The anion is not centrosymmetric.
[e] Hg····Hg = 3.831 Å.
[f] Hg····Hg = 3.897 Å.
[g] This anion may be distorted by close association of a chloro ligand from the cation [29].
[h] From the central Hg_2Cl_6 core of the $Hg_4Cl_{14}^{6-}$ anion [18].
[i] Hg····Hg = 3.946 Å.

TABLE 9

Salts of tetraalkylammonium chloride and mercury(II) chloride

Salt	Crystal lattice	Cell parameters (Å)	Reference
$[Me_4N]_2[HgCl_4]$[a]	Orthorhombic, *Pnma*	$a=12.30$, $b=9.02$, $c=15.59$	17
	Orthorhombic, *Pmcn*	$a=9.098(3)$, $b=15.685(7)$, $c=12.416(5)$ (23°C, disordered)	27
	Monoclinic, $P2_1/c$	$a=9.054(2)$, $b=15.554(2)$, $c=12.366(3)$, $\beta=90.15(2)°$ (−10°C)	27
		$a=9.019(2)$, $b=15.398(3)$, $c=12.311(3)$, $\beta=90.58(2)°$ (−70°C)	27
$[Me_4N][HgCl_3]$	Monoclinic, $P2_1$	$a=8.848$, $b=15.650$, $c=7.559$, $\beta=93.58°$	48,167,234
$[Me_4N][Hg_6Cl_{13}]$	Rhombohedral, $R\bar{3}$	$a=b=12.90$, $c=28.33$	60,63
$[Et_4N]_2[HgCl_4]$[b]	Tetragonal, $P4_2/nmc$	$a=b=8.93$, $c=15.49$	17
$[Et_4N][HgCl_3]$	Triclinic, $P\bar{1}$	$a=7.644$, $b=9.749$, $c=10.325$, $\alpha=62.78°$, $\beta=86.91°$, $\gamma=86.07°$	52,61,62,174
$[Et_4N]_2[Hg_3Cl_8]$	—	—	61,62
$[Et_4N][Hg_2Cl_5]$	Triclinic, $P\bar{1}$	$a=8.259$, $b=10.36$, $c=10.913$, $\alpha=105.679°$, $\beta=96.672°$, $\gamma=108.685°$	17,206
$[Et_4N][Hg_3Cl_7]$	Monoclinic, $C2/c$	$a=19.966$, $b=7.916$, $c=25.692$, $\beta=91.40°$	206
$[Et_4N][Hg_6Cl_{13}]$[c]	Rhombohedral, $R\bar{3}$	$a=b=13.59$, $c=28.50$	60,63
$[Bu^n_4N][HgCl_3]$	Triclinic, $P\bar{1}$	$a=11.011$, $b=11.267$, $c=19.341$, $\alpha=87.33$, $\beta=102.70$, $\gamma=96.45$	73

[a] Isomorphous with the corresponding Co(II) and Zn(II) salts [56], and with $[Me_4N]_2HgBr_4$ [26].

[b] Isomorphous with the corresponding Co(II), Ni(II), Zn(II) and Cd(II) salts [56].

[c] This compound was formulated as $[Et_4N^+][Hg_5Cl_{11}^-]$ [61].

associated dimers (see Section D.(ii) (b) for a discussion of $Hg_2Cl_8^{4-}$) to corner-shared polymeric chains and finally edge-shared polymeric chains.

(c) Trigonal bipyramidal $HgCl_5^{3-}$ anions

This type of anion (pentachloromercuriate (3−)) is rare, and until recently [17] was associated with small spherical $M(NH_3)_6^{3+}$ cations (M≡Co, Cr) (Table 10). It has now been found that the $[H_3dien^{3+}]_2[HgCl_8^{6-}]$ salt also contains an $HgCl_5^{3-}$ anion and three isolated chloride ions [217].

Two sets of $HgCl_5^{3-}$ anions can be distinguished, one with three short and two long Hg–Cl bonds, the other with two short and three long bonds (Table 10). We note that the series of salts $Cs_3[HgX_5]$ (X≡Cl, Br, I) contains the distorted tetrahedral HgX_4^{2-} plus X^- combination [21,218–220].

While the rarity of isolated $HgCl_5^{3-}$ ions has been commented on, five-coordinate Hg–Cl bridged systems are not unusual (Schemes 5, 12 and 15 and in $[Co(NH_3)_6][Hg_3Cl_9]\cdot H_2O$ [44]).

(d) Octahedral $HgCl_6^{4-}$ anions

This anion (together with $HgCl_4^{2-}$) appears in $[Tl^+]_{10}[Hg_3Cl_{16}^{10-}]$, i.e. $[Tl^+]_{10}[HgCl_6^{4-}]_2[HgCl_4^{2-}]$. The anion consists of a distorted [2+4] octahedral arrangement with Hg–Cl distances of 2.360 (×2) and 3.098 Å (×4) [221].

TABLE 10
Trigonal bipyramidal $HgCl_5^{3-}$ units

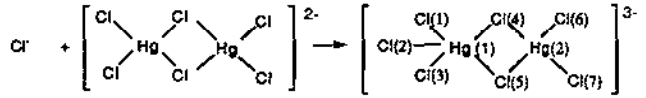
Cation	Space group	Hg–Cl (Å) (short)	Hg–Cl (Å) (long)	Reference
$Cr(NH_3)_6^{3+}$	Rhombohedral, *R3c*	2.417 (×3)	3.035 (×2)	214
$Cr(NH_3)_6^{3+}$	Cubic, *Fd3c*	2.518 (×2)	2.640 (×3)	215
$Co(NH_3)_6^{3+}$	Orthorhombic, *Pnma*	2.383	3.158	216
		2.447 (×2)	2.869	
$Co(NH_3)_6^{3+}$	Monoclinic, $P2_1/m$	2.418	3.038	214
		2.431 (×2)	2.817	
H_3dien^{3+}	Monoclinic, *P2/n*	2.327 (×2)	2.962 (×2)	217
			3.029	
$[CrCl(dien)(Hdien)][Hg_2Cl_7]$		2.335	3.109	18
		2.346	3.139	
			2.673	
s-fac-$[Cr(dien)_2][Hg_2Cl_7]$		2.344	2.881	18
		2.361	3.118	
			2.742	

(ii) Dimercury(II) chloride ions, $Hg_2Cl_5^-$, $Hg_2Cl_6^{2-}$, $Hg_2Cl_7^{3-}$ and $Hg_2Cl_8^{4-}$

We will discuss the $Hg_2Cl_5^-$ anion as the second member of the homologous series of $[Hg_xCl_{2x+1}^-]$ anions (see Section E) and the $Hg_2Cl_6^{2-}$ anion has been discussed in the previous section as the dimeric association of two $HgCl_3^-$ units.

(a) The $Hg_2Cl_7^{3-}$ anion

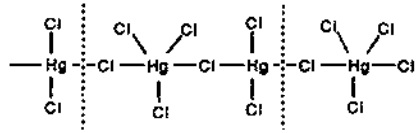
Salts with this anionic stoichiometry have only recently been characterized [18,19,216]. The anion is usually associated with tripositive $M(III)(N_6)^{3+}$ cations (Table 11), although Deacon [33] reports a $[C^+]_3[Hg_2Cl_7^{3-}]$ salt in his tabulation. Of the four examples examined structurally, only one contains the more or less isolated $Hg_2Cl_7^{3-}$ anion in the lattice (Scheme 13).



Scheme 13. $[Hg_2Cl_7^{3-}]$.
Hg(1)–Cl(1)=2.38 Å; Hg(1)–Cl(2)=2.97 Å; Hg(1)–Cl(3)=2.41 Å; Hg(1)–Cl(4)=2.53 Å; Hg(1)–Cl(5)=2.94 Å; Hg(2)–Cl(6)=2.34 Å; Hg(2)–Cl(7)=2.35 Å; Hg(2)–Cl(4)=2.83 Å; Hg(2)–Cl(5)=2.60 Å. Angles: Cl(7)–Hg(2)–Cl(6)=141.8°; Cl(1)–Hg(1)–Cl(3)=134.7°; Cl(4)–Hg(1)–Cl(5)=82.4°; Cl(4)–Hg(2)–Cl(5)=83.4°; Hg(1)–Cl(4)–Hg(2)=99.3°; Hg(1)–Cl(5)–Hg(2)=94.9°.

This example can be regarded as either an $Hg_2Cl_6^{2-}$ unit with an extra chloro ligand on one Hg, or a trigonal bipyramidal $HgCl_5^{3-}$ unit (Hg(1)) associated with an $HgCl_2$ molecule (Hg(2)) (Scheme 13). If the latter concept is adopted, the $HgCl_5^{3-}$ unit is of the three short, two long Hg–Cl bond variety (Table 10). If the former view is taken, the "normal" Cl–Hg–Cl terminal angle of approximately 142° (Table 8) is observed at one end of the $Hg_2Cl_6^{2-}$ unit, but the other "terminal" angle is distorted to 135° by the approach (2.97 Å) of the additional chloro ligand (Cl(2)) (Scheme 13). The recently described $Hg_2I_7^{3-}$ is different again, with a single bridging iodine atom [32].

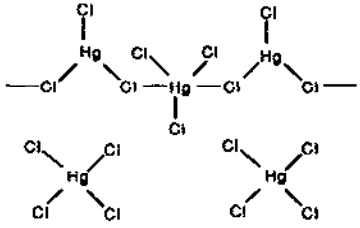
Two of the $Hg_2Cl_7^{3-}$ salts have chain structures. One consists of $(Hg_2Cl_7^{3-})_n$ strands (Scheme 14) with an –Hg–Cl–Hg–Cl–Hg– core and each alternate Hg atom with two or three additional chloro ligands.



Scheme 14. $(Hg_2Cl_7^{3-})_n$.

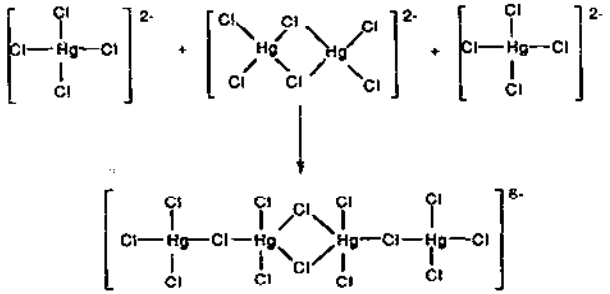
This system may also be regarded as tetrahedral $HgCl_4^{2-}$ units bridging to trigonal $HgCl_3^-$ units. Cations in the lattice separate the chains at an Hg····Cl distance of 3.21 Å.

The second structure consists of a more open $HgCl_3^-$ chain than is shown in Scheme 5 (with only one Hg–Cl–Hg bridge) together with associated (Hg····Cl = 3.3–3.4 Å) $HgCl_4^{2-}$ anions (Scheme 15).



Scheme 15. $\{(HgCl_3^-)_n(HgCl_4^{2-})_n\}$ "$[Hg_2Cl_7^{3-}]$".

Finally, we have the most remarkable structure in which the $HgCl_4^{2-}$ anions persist, but the $(HgCl_3^-)_n$ chain is now broken into $Hg_2Cl_6^{2-}$ and $Hg_4Cl_{14}^{6-}$ anionic fragments (Scheme 16).



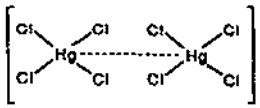
Scheme 16. $Hg_4Cl_{14}^{6-}$.

This salt has a total ionic composition of $[cation^{3+}]_4[HgCl_4^{2-}]_2[Hg_2Cl_6^{2-}]$-$[Hg_4Cl_{14}^{6-}]$ which reduces to "$[cation^{3+}][Hg_2Cl_7^{3-}]$".

We speculate on a core plus anion model resulting from a consideration of $Hg_2Cl_7^{3-}$ and $Hg_4Cl_{14}^{6-}$ in the Appendix.

(b) The $Hg_2Cl_8^{4-}$ anion

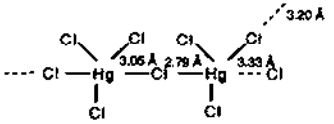
Trivalent cations frequently form sparingly soluble salts of stoichiometry $[C^{3+}]_2[HgX_4]_3$ [222]. The structure of one of these, $[Cr(en)_3]_2[HgCl_4]_3$ has been determined [19]. The lattice consists of two enantiomerically related cations and three distorted tetrahedral $HgCl_4^{2-}$ anions. Two of these anions are in close association (Scheme 17)



Scheme 17. $Hg_2Cl_8^{4-}$ (?).

in so far as the two tetrahedra have an eclipsed chloro ligand arrangement. The Hg····Hg distance of 3.60 Å between the units suggests that this may be a fortuitous packing consequence and it is doubtful that there is much justification for proposing an $Hg_2Cl_8^{4-}$ anion from this. However, the three $HgCl_4^{2-}$ anions have formal stoichiometry of $Hg_3Cl_{12}^{6-}$, and as this is shown to be a unique structural unit (Scheme 3), it cannot be assumed that all $[M^{3+}]_2[Hg_3X_{12}]$ salts will contain HgX_4^{2-} tetrahedra.

As mentioned earlier, the anion in $[enH_2]_2HgCl_6$ consists of polymeric chains of $[HgCl_4^{2-}]_n$ and (two) isolated chloride ions (Scheme 12). Alternate lengthening and shortening of the bridging Hg····Cl = 3.28 Å distance would result in a (polymeric) $Hg_2Cl_8^{4-}$ anion and this has now been realized [44] in $[trienH_4^{4+}][HgCl_4^{2-}]_2$, where $Hg_2Cl_8^{4-}$ can be recognized. The longest bridging distance in the dimer is decreased to 3.05 Å and cross-linking distances increased to 3.33 Å (along the chain), with Hg····Cl = 3.20 Å (between chains) (Scheme 18).



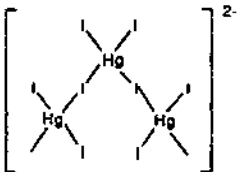
Scheme 18.

(iii) Trimercury(II) chloride ions, $Hg_3Cl_7^-$, $Hg_3Cl_8^{2-}$, $Hg_3Cl_9^{3-}$, $Hg_3Cl_{10}^{4-}$, $Hg_3Cl_{12}^{6-}$ and $Hg_3Cl_{16}^{10-}$

A discussion of the singly charged anion will be deferred to the $[Hg_xCl_{2x+1}^-]$ series.

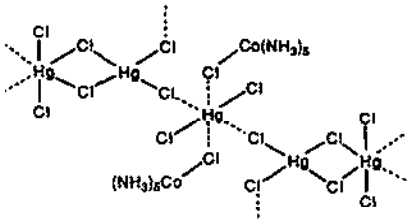
(a) The $Hg_3Cl_8^{2-}$ anion

This anion is perhaps more fully characterized for the iodo analogue [220,223] (vertex-sharing HgI_4 tetrahedra) (Scheme 19) than for the chloro [224]. The struc-

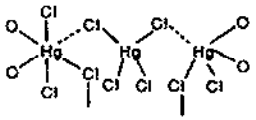


Scheme 19. $Hg_3I_8^{2-}$ [220].

tures of $[CoCl(NH_3)_5^{2+}][Hg_3Cl_8^{2-}]$ [225] and $[Co(HPO_4)(NH_3)_5^+]_2[Hg_3Cl_8^{2-}]$ have been determined and these are formulated as $\{[HgCl_2]_2HgCl_4]\}^{2-}$ salts [38] although both structures are described as "polymeric" (Schemes 20, 21). The chloro ligand in the chloropentaammine complex is also linked to an Hg atom.



Scheme 20. $\{[CoCl(NH_3)_5^{2+}][HgCl_4^{2-}][HgCl_2]_2\}_n$; Hg···Cl > 3.1 Å.



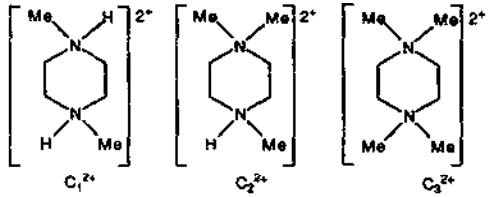
Scheme 21. $\{[Co(HPO_4)(NH_3)_5^{+}]_2[HgCl_4^{2-}][HgCl_2]_2\}_n$; Hg···Cl > 3.0 Å.

Another $Hg_3Cl_8^{2-}$ ion, associated with an ion-radical cation, is described as $\{[HgCl_2][Hg_2Cl_6]\}^{2-}$ with "chains of mercury chloromercurate anions lying in channels parallel to the *a* axis between the cation-radical layers" [191,224].

The only other salts where the $Hg_3Cl_8^{2-}$ stoichiometry appears with confidence are $[M^{2+}][Hg_3Cl_8^{2-}]\cdot 6H_2O$ ($M^{2+} \equiv Mg^{2+}$, Sr^{2+}, Ba^{2+}) [226]. The Mg^{2+} salt is shown to have the ionic composition $[Mg(OH_2)_6^{2+}][Hg_2Cl_6^{2-}][HgCl_2]$ with isolated $HgCl_2$ molecules in the lattice [192].

(b) Other $Hg_3Cl_y^{n-}$ anions

Three new $Hg_3Cl_y^{n-}$ anions have recently [22,44] been characterized in $[H_3dpt^{3+}]_2[Hg_3Cl_{12}^{6-}]$ ($H_3dpt^{3+} \equiv NH_3(CH_2)_3NH_2(CH_2)_3NH_3^{3+}$), $[Co(NH_3)_6^{3+}][Hg_3Cl_9^{3-}]\cdot H_2O$ and $[C_1^{2+}]_{1/2}[C_2^{2+}][C_3^{2+}]_{1/2}[Hg_3Cl_{10}^{4-}]$ (Scheme 22).



Scheme 22.

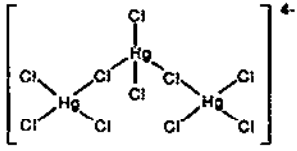
These are related anions containing the $Cl_3Hg–Cl–Hg–Cl–HgCl_3^{2-}$ structural unit. The $Hg_3Cl_9^{3-}$ and $Hg_3Cl_{10}^{4-}$ anions have two extra chloro ligands attached to the central Hg atom (Scheme 23)

with the $Hg_3Cl_9^{3-}$ being part of the $\cdots[\cdots HgCl_3^{-}\cdots HgCl_4^{2-}\cdots HgCl_2\cdots]\cdots HgCl_3^{-}\cdots$ chain. In $Hg_3Cl_{12}^{6-}$ there are four additional chloro ligands around the central Hg (Scheme 3). All three anions can be regarded as having the central Hg of an $HgCl_2$

TABLE 11

$[Hg_xCl_y^{n-}]$ compounds

Empirical formula	Cation type	Anionic units	Reference
cis-$PtCl_2(NH_3)_2.(HgCl_2)_3$	Zero	Polymeric	83
$[Et_4N][Hg_2Cl_5]$	1+	$[Cl.(HgCl_2)_2]^-$ chains	206
$[Et_4N][Hg_3Cl_7]$		Three-dimensional polymer	206
$[Et_4N][Hg_6Cl_{13}]$		$[Cl.(HgCl_2)_6]^-$ ions	63,206
$[M][Hg_5Cl_{11}]$ ($M \equiv NH_4^+$, Rb^+, Cs^+)		$[Cl.(HgCl_2)_4]^-$ anions and $HgCl_2$	63
$[Me_3S]_2[Hg_{13}Cl_{26}I_2]$		$Hg_6Cl_{13}^-$ and $Hg_6Cl_{11}I_2^-$ ions	208
[*trans*-$CoCl_2(en)_2$][$HgCl_3$]		Discrete $Hg_2Cl_6^{2-}$ ions	44
$[H_2en][HgCl_3]_2$	2+	Discrete $Hg_2Cl_6^{2-}$ ions	44
$[H_2en]_2[HgCl_6]$		Linear $HgCl_4^{2-}$ chains and Cl^- ions	44
$[C_1]_{1/2}[C_2][C_3]_{1/2}[Hg_3Cl_{10}]$ (Scheme 22)		Discrete $Hg_3Cl_{10}^{4-}$ ions	22
$[C_8H_{20}N_2][HgCl_4]$		Discrete $HgCl_4^{2-}$ ions	22
$[C_9H_{22}N_2][HgCl_4]$		Discrete $HgCl_4^{2-}$ ions	22
rac-mer-[Cr(dien)$_2$][Hg_2Cl_7]	3+	Unknown	18
s-fac-[Cr(dien)$_2$][Hg_2Cl_7]		Discrete $2HgCl_4^{2-}$, $Hg_2Cl_6^{2-}$ and $Hg_4Cl_{14}^{6-}$ ions	18
rac-u-fac-[Cr(dien)$_2$][Hg_2Cl_7]		Linear $(HgCl_3^-)_n$ chains and $HgCl_4^{2-}$ ions	18
rac-mer-[Cr(dien)$_2$][$HgCl_5$].2DMSO		Discrete $HgCl_4^{2-}$ and Cl^- ions	18
s-fac-[CrCl(dien)(Hdien,*N,N*)]Hg_2Cl_7		Linear $(Hg_2Cl_7^{3-})_n$ chains	18
rac-cis-[Co(en)$_2$(py)(NH_3)]Hg_2Cl_7		Discrete $Hg_2Cl_7^{3-}$ ions	19
$[H_3dpt]_2[Hg_3Cl_{12}]$		Discrete $Hg_3Cl_{12}^{6-}$ ions	44
rac-cis-[CrCl(en)$_2$(Hen,*N*)]$HgCl_5$		Discrete $HgCl_4^{2-}$ and Cl^- ions	18
rac-[Cr(en)$_3$]$_2$[$HgCl_4$]$_3$		$HgCl_4^{2-}$ ions and $Hg_2Cl_8^{4-}$ (?)	18
rac-[Co(en)$_3$]$HgCl_4I$		Discrete $HgCl_3I^{2-}$ and Cl^- ions	19
$[Co(NH_3)_6][Hg_3Cl_9].H_2O$		Linear $Hg_3C_9^{3-}$ chains	44
$[H_4trien][HgCl_4]_2$	4+	Linear $Hg_2Cl_8^{4-}$ chains	44



Scheme 23. $Hg_3Cl_{10}^{4-}$.

molecule coordinated to two $HgCl_4^{2-}$ units and two or four chloro ligands. There is a striking similarity between Schemes 23, 19 and 3.

We also note that in the "octahedral" Hg situation (Scheme 3), the $HgCl_4^{2-}$ "ligands" are in the cis configuration.

$[H_3dien^{3+}]_2[Hg_3Cl_{10}^{6-}]$ ($H_3dien^{3+} \equiv NH_3(CH_2)NH_2(CH_2)_2NH_3^{3+}$) has also been reported [217] but its structure has not been determined. From the same system $[H_3dien^{3+}][HgCl_8^{3-}]$ can be isolated. Here the anion consists of an $HgCl_5^{3-}$ unit (Table 10) and three isolated chloride ions [217].

E. THE $Hg_xCl_{2x+1}^-$ ANIONS ($x = 2$–6)

A perusal of the early literature [58–60] pertaining to the double salts of mercuric and alkali chlorides shows that a series of $[M^+][Hg_xCl_{2x+1}^-]$ salts can be prepared by crystallization of the appropriate mole ratios of MCl and $HgCl_2$ from aqueous solution.

These include $Tl^+[Hg_5Cl_{11}^-]$ [220], $Rb^+[Hg_5Cl_{11}^-]$ [64], $Cs^+[Hg_5Cl_{11}^-]$ [64,66,67], $NH_4^+[Hg_5Cl_{11}^-]$ [63] (rather than the alleged $(NH_4)_2[Hg_9Cl_{20}^{2-}]$ [67–69]), $Cs^+[Hg_2Cl_5^-]$ [19] and $NH_4^+[Hg_2Cl_5^-]$ [223]. A more extensive series (Table 9) was reported by Reedijk [61,62] using the appropriate mole ratios of Et_4NCl and $HgCl_2$ with acetonitrile as solvent. Single-crystal X-ray structural analysis of many of these salts has now been completed.

In terms of stoichiometry, $[Et_4N^+][Hg_5Cl_{11}^-]$ reported by Reedijk [61,62] is, in fact, $[Et_4N^+][Hg_6Cl_{13}^-]$, but $Hg_5Cl_{11}^-$ is a discrete anion for the K^+, NH_4^+, Rb^+, Cs^+ and Tl^+ salts which form an isomorphous series (Table 12) [65].

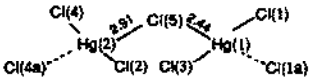
Structurally, the anions in the series of $MCl \cdot xHgCl_2$ ($x = 2$–6, $M \equiv Et_4N^+$) salts can be regarded as a chloride ion associated with varying molecules of $HgCl_2$. The analogy with a central metal ion surrounded by solvent (water) molecules is quite appealing as the chloride ion "coordination numbers" of two, four and six $HgCl_2$ molecules are well developed. Thus, in $[Et_4N^+][Hg_2Cl_5^-]$, the anion consists of a central chloride ion bound to two $HgCl_2$ molecules (Scheme 24) in a branched chain lattice [206].

Further chains [7,183] or polymers [8] of these units can occur and the association of the chloride ions distorts the $HgCl_2$ from linearity (to approximately 170°) (Schemes 24–26).

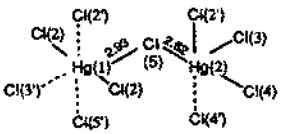
The ring structure in Scheme 26 produces a planar four-coordinate chloride

TABLE 12
$[M^+][Hg_xCl_{2x+1}^-]$ salts ($x = 2$–6)

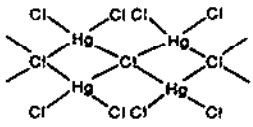
Salt	Anion structure	$Cl^-\cdots HgCl_2$ distance (Å)	Reference
$[C_5H_{12}ClN_2^+][Hg_2Cl_5^-]$	Polymeric	2.93, 2.62	227
$[Et_4N^+][Hg_2Cl_5^-]$	Polymeric chain	2.44, 2.91	61,216
$[CH_3NH_3^+][Hg_2C_5^-]$	Polymeric chain	2.92, 3.08	7
$[(CH_3)_2NH_2^+][Hg_2Cl_5^-]$	Polymeric chain	3.00	8
$[PhCH_2NH_3^+][Hg_2Cl_5^-]$	Polymeric	2.80, 2.90, 3.12, 2.76	183
$[Et_4N^+][Hg_3Cl_7^-]$	Polymeric		61,216
$[M^+][Hg_5Cl_{11}^-]$ $M^+ \equiv Rb^+$, Cs^+, NH_4^+, K^+, Tl^+	$[Hg_4Cl_9^-.HgCl_2]_n$	3.067	63,65
$[C^+][Hg_6Cl_{13}^-]$ $C^+ \equiv Me_4N^+$, Et_4N^+	$[Hg_6Cl_{13}^-]_n$	2.98	31,63,228



Scheme 24. $[Hg_2Cl_5^-]_n$.
Cl(2)–Hg(2)–Cl(4) = 170.8°; Cl(2)–Hg(2)–Cl(5) = 94.8°; Cl(2)–Hg(2)–Cl(4a) = 99.0°; Cl(4)–Hg(2)–Cl(5) = 94.4°; Cl(4)–Hg(2)–Cl(4a) = 83.9°; Cl(5)–Hg(2)–Cl(4a) = 76.8°; Hg(2)–Cl(2) = 2.33 Å; Hg(2)–Cl(4) = 2.32 Å; Hg(2)–Cl(4a) = 3.13 Å; Hg(2)–Cl(5) = 2.91 Å.
Cl(1)–Hg(1)–Cl(3) = 127.8°; Cl(1)–Hg(1)–Cl(5) = 118.7°; Cl(1)–Hg(1)–Cl(1a) = 85.5°; Cl(3)–Hg(1)–Cl(5) = 111.1°; Cl(3)–Hg(1)–Cl(1a) = 102.4°; Cl(5)–Hg(1)–Cl(1a) = 98.5°; Hg(1)–Cl(5) = 2.44 Å; Hg(1)–Cl(1) = 2.45 Å; Hg(1)–Cl(3) = 2.41 Å; Hg(1)–Cl(1a) = 2.81 Å.



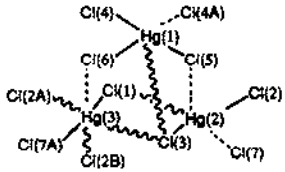
Scheme 25. $[Hg_2Cl_5^-]_n$ [227].
Cl(5)–Hg(1)–Cl(3') = 167.4°; Cl(1)–Hg(1)–Cl(2) = 168.3°; Cl(2')–Hg(1)–Cl(5') = 168.5°; Hg(1)–Cl(5) = 2.926(3) Å; Hg(1)–Cl(1) = 2.312(3) Å; Hg(1)–Cl(2) = 2.331(3) Å; Hg(1)–Cl(2') = 3.278(3) Å; Hg(1)–Cl(3') = 3.296(3) Å; Hg(1)–Cl(5') = 2.983(3) Å.
Cl(3)–Hg(2)–Cl(4) = 154.2°; Hg(2)–Cl(3) = 2.338(3) Å; Hg(2)–Cl(4) = 2.371(3) Å; Hg(2)–Cl(5) = 2.619(2) Å; Hg(2)–Cl(2') = 3.055(3) Å; Hg(2)–Cl(4') = 3.103(3) Å.



Scheme 26. $(Hg_2Cl_5^-)_n$ [7,183].

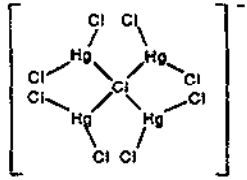
ion, which manifests itself again in the $Hg_5Cl_{11}^-$ structure (Scheme 28). The polymeric form found in $[PhCH_2NH_3^+][Hg_2Cl_5^-]$ [187] develops a ring system that is also found in the $Hg_3Cl_7^-$ anionic lattice (Scheme 27).

While some sort of "three-coordinate" central Cl^- may be expected in $[Et_4N^+][Hg_3Cl_7^-]$, this is not found, and a complicated three-dimensional lattice is developed (Scheme 27) with three different Hg atoms.



Scheme 27. [206].
Hg(1)–Cl(4) = 2.444(4) Å; Hg(1)–Cl(5) = 2.438(5) Å; Hg(1)–Cl(6) = 2.434(5) Å; Hg(1)–Cl(4A) = 2.770(5) Å; Hg(3)–Cl(1) = 2.341(5) Å; Hg(3)–Cl(7A) = 2.322(5) Å; Hg(3)–Cl(3) = 3.027(5) Å; Hg(3)–Cl(6) = 2.869(5) Å; Hg(3)–Cl(2A) = 3.016(5) Å; Hg(3)–Cl(2B) = 3.149(4) Å.
Hg(2)–Cl(1) = 3.120(5) Å; Hg(2)–Cl(2) = 2.339(5) Å; Hg(2)–Cl(3) = 2.319(5) Å; Hg(2)–Cl(5) = 2.864(5) Å; Hg(2)–Cl(7) = 2.943(5) Å; Cl(1)–Hg(3)–Cl(7A) = 173.0(2)°; Cl(2)–Hg(2)–Cl(3) = 167.1(2)°; Hg(1)–Cl(3) = 3.28 Å; ——, 2.3–2.5 Å; – – –, 2.5–3.0 Å; , 3.0–3.3 Å.

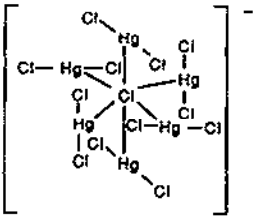
A series of isomorphous $[M^+][Hg_5Cl_{11}^-]$ salts ($M^+ \equiv Tl^+$, K^+, Cs^+, Rb^+, NH_4^+) can be prepared from aqueous solution [58,59,64,67–69]. The $Hg_5Cl_{11}^-$ anion [65] consists of a Cl^- ion surrounded by four $HgCl_2$ molecules in a square planar arrangement, with the cations occupying positions above and below the Cl^- ion in the square plane. These $Hg_4Cl_9^-$ units (Scheme 28) are held together in a polymeric lattice by an additional $HgCl_2$ molecule giving $Hg_5Cl_{11}^-$ as the overall stoichiometry.



Scheme 28. The "$Hg_4Cl_9^-$" unit in $Hg_5Cl_{11}^-$.

The final structure in this series occurs in the $[C^+][Hg_6Cl_{13}^-]$ ($C^+ \equiv Me_4N^+$, Et_4N^+) salts. These crystallize readily from acetonitrile solutions of $[C^+]Cl^-$ and $HgCl_2$ in a 1:6 mole ratio [61–63]. The related $[Et_4N^+][Hg_6Br_{13}^-]$ is isomorphous with the analogous chloride [63]. In these anions, the central halide is surrounded by six HgX_2 molecules in an octahedral arrangement to give a chloride-linked Hg(II) cluster (Scheme 29) with an extensive interlocking network of Hg–Cl and Cl–Hg interactions.

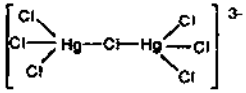
The $Hg_6Cl_{13}^-$ anion has also been characterized, together with $Hg_5Cl_{13}^{3-}$ in $Ca_2Hg_{11}Cl_{26}\cdot 16H_2O$ [31,228]. This calcium salt, which crystallizes from aqueous



Scheme 29. $Hg_6Cl_{13}^-$.

solution, has had an interesting history as it was first characterized by von Bonsdorf [46] as $CaHg_5Cl_{12}\cdot 8H_2O$ [$CaCl_2\cdot 5HgCl_2\cdot 8H_2O$], "corrected" to $CaHg_6Cl_{14}\cdot 6H_2O$ [$CaCl_2\cdot 6HgCl_2\cdot 6H_2O$] by Bassett et al. [226] and Strömholm [60], and is now shown to be $Ca_2Hg_{11}Cl_{26}\cdot 16H_2O$ [$2CaCl_2\cdot 11HgCl_2\cdot 16H_2O$] [31]. The bromide and iodide anologues of Ca^{2+} and Sr^{2+} are similar [228].

The $Hg_5Cl_{13}^{3-}$ anion can be regarded as $Hg_2Cl_7^{3-}$ (Scheme 30) plus three $HgCl_2$ in an icosahedral cluster [228].



Scheme 30. $Hg_2Cl_7^{3-}$ [31,228].

F. Hg(II)–Cl STEREOCHEMISTRY

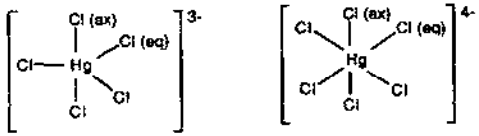
Much of the early work [2,229] has concentrated on the digonal influence of Hg(II) stereochemistry. While this coordination number is certainly important, we should draw attention to the other stereochemistries. Indeed, coordination numbers of two, three, four, five and six all reasonably common in $Hg_xCl_y^{4-}$ systems and it would be unwise to be dominated by the digonal influence. Particular examples of the higher coordination numbers three, four, five and six as found in $[ClC_6H_{12}NHgCl^+][HgCl_3^-]$ [29], $[Cs^+]_2[HgCl_4^{2-}]$ [13], $[Cr(NH_3)_6^{3+}][HgCl_5^{3-}$ (cubic form) [214,215] and $Tl_{10}Hg_3Cl_{16}$ [65,230] respectively are shown in Scheme 31.

Further examples of coordination number four are given in Tables 1 and 8 and those of coordination number six in Schemes 1, 3, 7, 9, 11, 20 and 27.

G. CONCLUSIONS

Unfortunately, we must conclude on a somewhat pessimistic note insofar as we are still a long way from any predictive generalizations. The change from

Scheme 31. Cl(5)–Hg = 2.36 Å; Cl(4)–Hg = 2.42 Å; Cl(3)–Hg = 2.46 Å; Cl(3)–Hg–Cl(4) = 101.0°; Cl(3)–Hg–Cl(5) = 120.2°; Cl(4)–Hg–Cl(5) = 137.7°.
Hg–Cl; Cl–Hg–Cl; 2.386 Å; 2.453 Å × 2; 2.458 Å; 103.1° (×2); 104.8°; 112.9° (×2); 118.6°.



Hg–Cl(ax) = 2.518 Å (×2); Hg–Cl(eq) = 2.640 Å (×3); Cl(eq)–Hg–Cl(eq) = 120°; Cl(ax)–Hg–Cl(ax) = 90°.
Hg–Cl(ax) = 2.360 Å (×2); Hg–Cl(eq) = 3.098 Å (×4); Cl–Hg–Cl = 90° or 180°.

$[HgCl_3^-]_n$ chains to $Hg_2Cl_6^{2-}$ dimers can be easily visualized (Scheme 5), but just what cationic influences are necessary are not yet defined.

On the more positive side, there is every good prospect that $Hg_xCl_y^{5-}$ anions will be eventually discovered, but whether the geometry adopted will follow Scheme 35 is speculative.

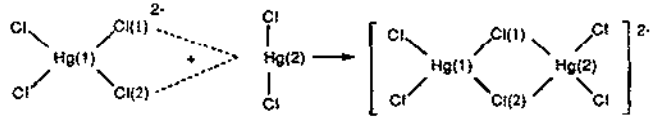
However, patterns are emerging [231] with an $HgCl_2$ core plus either $HgCl_4^{2-}$ or Cl^- "ligands" allowing some systematization in the $Hg_3Cl_y^{n-}$ anions (Schemes 3 and 23).

In the final analysis it may well be that almost any $Hg_xCl_y^{n-}$ anion can be designed, given the appropriate charge and lattice-space considerations. Table II lists the $Hg_xCl_y^{n-}$ anion systems investigated in our laboratories.

H. APPENDIX

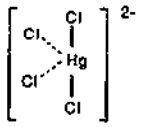
(i) Bond length–bond angle correlations

Bond length vs. bond angle correlation diagrams are presented for the systems: (i) $Cl^- + HgCl_2 \rightarrow HgCl_3$ (Scheme 2) (Table 13) (Fig. 1); (ii) $HgCl_4^{2-} + HgCl_2 \rightarrow Hg_2Cl_6^{2-}$ (Scheme 32) (Table 14) (Fig. 2); (iii) $2Cl^- + HgCl_2 \rightarrow HgCl_4^{2-}$ (Scheme 33) (Table 15) (Fig. 3).



Scheme 32.

For (i), extrapolation of the correlation to a Cl–Hg–Cl angle of 180° shows that an approach greater than 2.93 ± 0.02 Å will be effectively non-distorting.



Scheme 33.

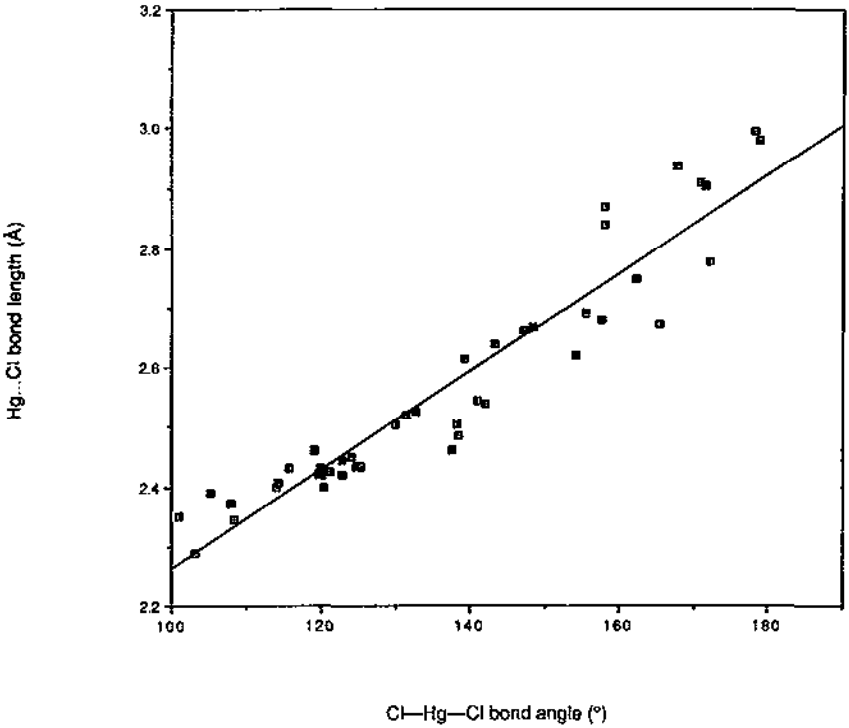


Fig. 1. Plot of Cl–Hg–Cl angle (°) vs. Hg–Cl distance (Å) for "$HgCl_3^-$" fragments.

For (ii) (Scheme 32), the majority of $Hg_2Cl_6^{2-}$ units have unequal Hg–Cl (bridge) and Hg–Cl (terminal) lengths and we have used the mean Hg–Cl (bridge) length vs. Cl–Hg–Cl (terminal) angle (Table 8). The best fit line through the data, constrained to 109° and 2.50 Å at the "tetrahedral" end, when extrapolated to 180° (i.e. no $HgCl_4^{2-}$–$HgCl_2$ interaction) gives values of 2.98 ± 0.02 Å as the upper limit.

There are only a small number of examples for (iii) (Scheme 33) (Table 15) where there are two long Cl–Hg interactions with a slightly bent Cl–Hg–Cl angle. The weakest interacting example is observed in $[Me_2NH_2^+][Hg_2Cl_5^-]$ [8] where the next-nearest Hg·····Cl interactions at 2.904 and 2.972 Å are able to cause an 8.4° bending of the Cl–Hg–Cl unit. The strongest interactions will be in the regular $HgCl_4^{2-}$ unit (Table 1). Our data selection is somewhat subjective, but we have

TABLE 13

Cl–Hg–Cl angle vs. Hg·····Cl distance in $HgCl_3^-$ fragments (Scheme 2)[a]

Cl–Hg–Cl angle (°)	Hg·····Cl distance (Å)	Reference
178.3	2.997	38
178.8	2.979	83
167.8	2.937	9
170.8	2.91	206
171.6	2.904	8
158.0	2.869	38
158.0	2.840	8
172.2	2.777	38
162.3	2.749	177
155.6	2.693	111
157.7	2.680	232
165.3	2.673	18
148.4	2.668	9
147.2	2.662	38
143.4	2.637	9
154.2	2.619	227
139.3	2.614	189
141.0	2.545	50
142.1	2.54	29
132.8	2.525	51
131.5	2.520	8
138.3	2.504	57
130.0	2.503	55
138.4	2.485	53
119.2	2.46	49
137.7	2.46	29
124.2	2.451	39
122.9	2.444	52
125.5	2.434	54
124.9	2.434	56
115.8	2.432	57
120.0	2.431	55
121.2	2.425	48
119.7	2.421	48
120.2	2.42	29
123.0	2.42	49
114.2	2.406	56
120.5	2.400	56
114.0	2.40	29
105.3	2.391	57
108.0	2.371	55
101.0	2.35	29
108.4	2.345	53
103.2	2.29	29

[a]See Fig. 1.

TABLE 14

Cl–Hg–Cl terminal angle in $Hg_2Cl_6^{2-}$ units vs. Hg–Cl····Hg bridging distance (Scheme 32)[a]

Cl–Hg–Cl terminal angle (°)	Hg–Cl bridge distance (Å)		Reference
	Short	Long	
167.3	2.80	3.02	29
165.2	2.742	2.881	18
164.7	2.780	2.812	44
160	2.71	2.82	7
158.8	2.85	2.86	29
158.0	2.750	2.840	8
156.5	2.732	2.846	2
153.6	2.710	2.835	192
151.1	2.725	2.759	18
148.0	2.668	2.736	8
143.3	2.637	2.637	9
141.3	2.648	2.717	186
140	2.67	2.76	187
132.2	2.60	2.696	47
130.9	2.572	2.749	44
123.6	2.597	2.638	187
121.9	2.56	2.67	73
119	2.55	2.70	187

[a]See Fig. 2.

difficulty describing the weak interaction cases (Scheme 33) — are they linear $HgCl_2$ molecules distorted by the close approach of the two chloride ions, or are they highly distorted $HgCl_4^{2-}$ units? Nevertheless, extrapolation of these data (Fig. 3) to 180° again shows that, at a (mean) distance of greater than 3.02 ± 0.01 Å, the chloride ions have no effect on the Cl–Hg–Cl angle. We would suggest that at distances of less than 3.02 Å Cl–Hg bonds are formed, and the structural unit is best described as a highly distorted $HgCl_4^{2-}$ species.

(ii) Structural units predicted on the core plus anion concepts

Schemes 13 and 16 show that the known $Hg_2Cl_7^{3-}$ and $Hg_4Cl_{14}^{6-}$ anions can be regarded as an $Hg_2Cl_6^{2-} + Cl^-$ unit and an $Hg_2Cl_6^{2-} + 2HgCl_4^{2-}$ unit respectively. This has led us to speculate on other potential $Hg_xCl_y^{n-}$ systems. Thus we could predict Schemes 34, 35 and 36 as possible structures based on the $Hg_2Cl_6^{2-}$ core plus Cl^- or $HgCl_4^{2-}$ combinations.

While there is evidence for $Hg_2Cl_8^{4-}$ (Section D. (ii) (b)), it is not of the type shown in Scheme 34, and the known $Hg_3Cl_{10}^{4-}$ anion (Scheme 23), while related to

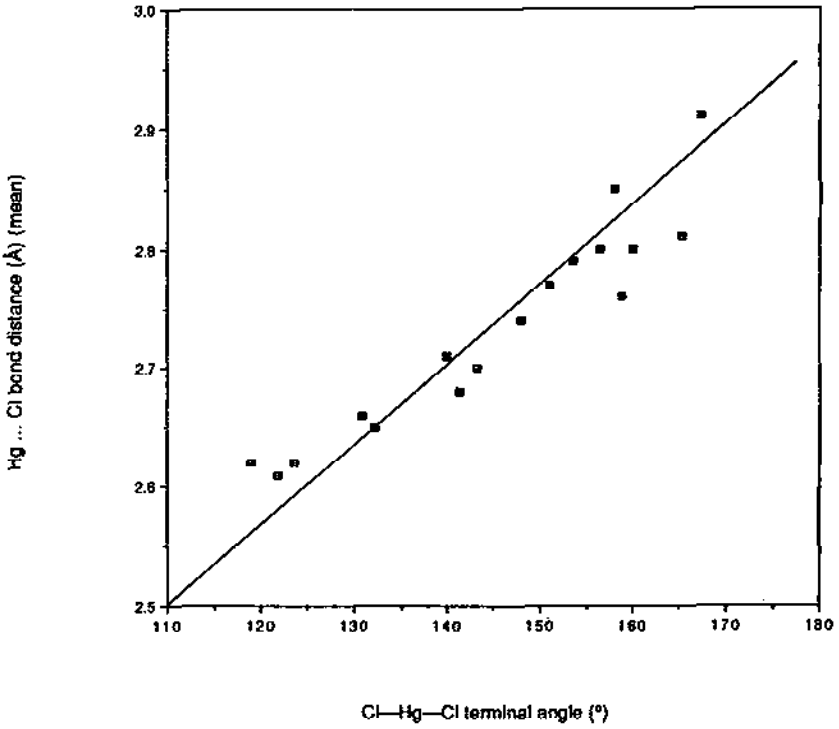


Fig. 2. Plot of Cl–Hg–Cl terminal angle (°) vs. mean Hg–Cl (bridge) distance (Å) in $Hg_2Cl_6^{2-}$ fragments.

TABLE 15

Data for $2Cl^- + HgCl_2$ interactions (Scheme 33)[a]

Compound	Angle (°)	Hg–Cl(long) (Å)	Hg–Cl(mean) (Å)	Reference
$[Co(NH_3)_6^{3+}].[Hg_3Cl_9^{3-}].H_2O$	175.9	2.949, 3.069	3.009	44
$[H_3dpt^{3+}]_2[Hg_3Cl_{12}^{6-}]$	172.6	2.810, 3.081	2.945	44
$[Me_2NH_2^+][Hg_2Cl_5^-]$	171.6	2.904, 2.972	2.938	8
	162	2.797, 2.760	2.778	8
$[MeNH_3^+][HgCl_3^-]$	160.1	2.712, 2.817	2.765	7
	157.7	2.680, 2.861	2.765	28
$[Me_2NH_2^+][HgCl_3^-]$	156.5	2.732, 2.846	2.789	8
	148.4	2.736, 2.668	2.702	8
$[Me_3NH^+][HgCl_3^-]$	143.3	2.637, 2.637	2.637	9

[a] See Fig. 3.

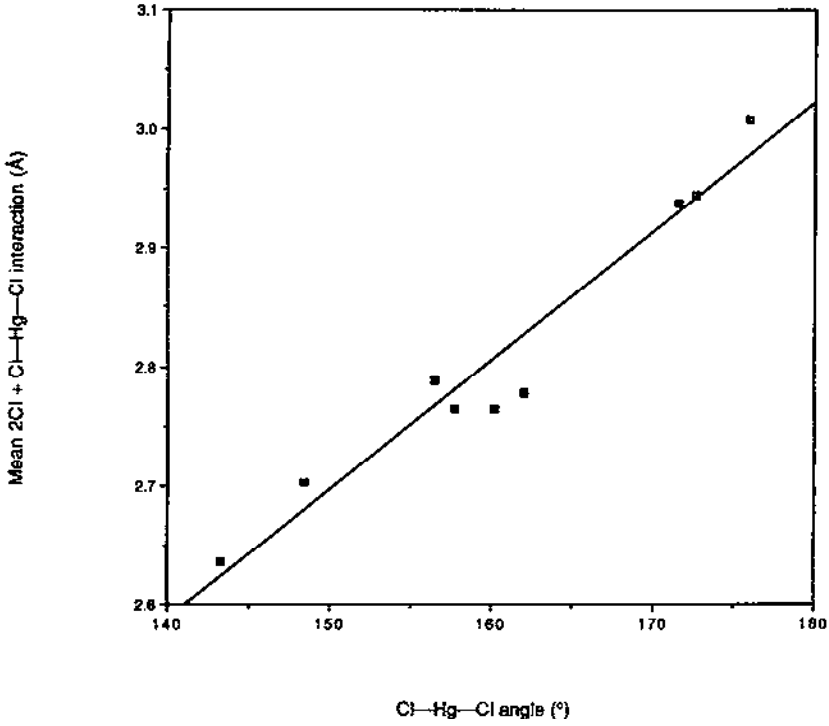
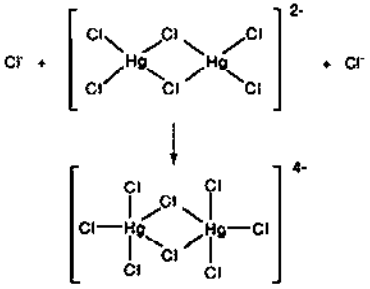


Fig. 3. Plot of Cl–Hg–Cl angle (°) vs. mean Hg–Cl distance (Å) in distorted $HgCl_4^{2-}$ fragments.



Scheme 34. Proposed $Hg_2Cl_8^{4-}$.

Scheme 36, has only single chloro bridges to the central Hg with more symmetry than in Scheme 36. $Hg_xCl_y^{5-}$ anions (Scheme 35) have not yet been characterized.

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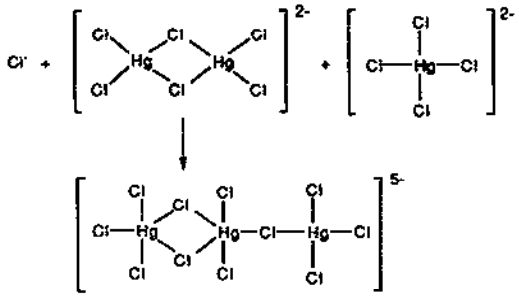
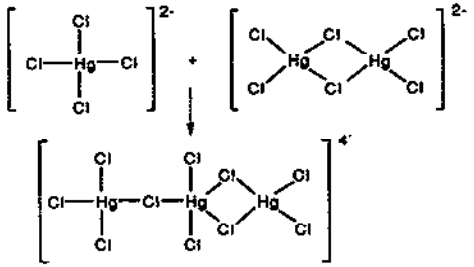


Scheme 35. Proposed $Hg_3Cl_{11}^{5-}$.



Scheme 36. Proposed $Hg_3Cl_{10}^{4-}$.

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