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The Structures of [Co(en)$_3$][HgCl$_4$I] and *cis*-[Co(en)$_2$(NH$_3$)(py)][Hg$_2$Cl$_7$] – Complexes Containing Novel Halo-mercury(II) Anions

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Abstract

The single crystal X-ray structures of the title complexes have been determined. Racemic [Co(en)$_3$][HgCl$_4$I] (monoclinic, $P2_1/a$, $a = 13.488$, $b = 11.716$, $c = 11.910$ Å, $\beta = 109.82°$, $V = 1770.6$ Å^3, $Z = 4$, $D_{calc} = 2.67$ g/cc) consists of lel ob$_2$ cations associated with [HgCl$_3$I]$^{2-}$ and Cl$^-$ anions. Halo-mercury(II) distances within the irregular tetrahedral [HgCl$_3$I]$^{2-}$ anion are Hg–I = 2.65 Å and Hg–Cl varies from 2.46 to 2.63 Å. Racemic-*cis*-[Co(en)$_2$(NH$_3$)(py)][Hg$_2$Cl$_7$] (orthorhombic, *Pbcn*, $a = 22.663$, $b = 14.137$, $c = 14.459$ Å, $V = 4632$ Å^3, $Z = 8$, $D_{calc} = 2.66$ g/cc) consists of isolated $\delta\lambda$ cations and weakly interacting dibridged [Hg$_2$Cl$_7$]$^{3-}$ anions. Within each [Hg$_2$Cl$_7$]$^{3-}$ unit, Hg–Cl distances vary from 2.34–2.97 Å, and the closest Hg–Cl approach between two adjacent [Hg$_2$Cl$_7$]$^{3-}$ units is 3.36 Å.

Introduction

We have recently been interested in structures adopted by chloro-mercury(II) anions with trivalent cations, [1, 2] as the stoichiometry of the salt rarely reflects the nature of the anions in the crystal lattice [3].

This paper reports the nature of the anions formed when *rac*-[Co(en)$_3$]I$_3$ or *rac-cis*-[Co(en)$_2$(NH$_3$)(py)](ClO$_4$)$_3$ [4] are crystallized from 3 M HCl containing excess HgCl$_2$. In the case of [Co(en)$_3$]I$_3$, the first product to form was [Co(en)$_3$][HgCl$_5$]* (as needles) which were unsuitable for single crystal X-ray analysis. The mother liquor subsequently deposited [Co(en)$_3$][HgCl$_4$I]* (**1**) as large irregular blocks. With *cis*-[Co(en)$_2$(NH$_3$)(py)](ClO$_4$)$_3$, the only product isolated was *cis*-[Co(en)$_2$(NH$_3$)(py)][Hg$_2$Cl$_7$]* (**2**).

We report here the results of single crystal X-ray structural analyses of **1** and **2**.

Experimental

Racemic [Co(en)$_3$]Cl$_3$·xH$_2$O was prepared according to literature procedures [5] and converted to the triodide by metathesis (with NaI).

[Co(en)$_3$]I$_3$ (2 g) was dissolved in 3 M HCl (100 ml) at 50 °C and a solution of HgCl$_2$ (5 g) in 3 M HCl (50 ml), also at 50 °C, was added. On spontaneous cooling to room temperature a considerable quantity (~2 g) of [Co(en)$_3$][HgCl$_5$]* deposited as needles and these were removed by filtration after five hours. *Anal.* Calc. for C$_6$H$_{24}$N$_6$Cl$_5$CoHg: C, 11.68; H, 3.92; N, 13.62. Found: C, 11.80; H, 4.28; N, 13.61%. The still yellow mother liquor was allowed to evaporate spontaneously at room temperature in an open beaker for 7–10 days, during which time crystals of [Co(en)$_3$][HgCl$_4$I]* (**1**) suitable for single crystal X-ray structural analysis, slowly deposited.

This same product can be obtained more easily by dissolving [Co(en)$_3$][HgCl$_5$]* (2 g) in 3 M HCl (150 ml, 80 °C) and adding NaI (~1 g). If too much iodide is added, a floculant yellow precipitate deposits (at 80 °C). This can be redissolved by addition of sufficient HgCl$_2$ (~1 g) to give a clear yellow solution. [Co(en)$_3$][HgICl$_4$]* deposits (irregular blocks) on slow cooling to room temperature.

[Co(en)$_2$(NH$_3$)(py)][Hg$_2$Cl$_7$] (**2**) deposits slowly from a room temperature solution prepared from 1.5 g of the perchlorate salt [4] in 50 ml of 3 M HCl followed by the addition of 5 g of HgCl$_2$ in 50 ml of 3 M HCl.

X-ray Structural Analyses

Crystal parameters and data collection details (Nicolet R3m diffractometer) for **1** and **2** are presented in Table 1. The non-unique data were averaged and the data corrected for Lorentz, polarization and absorption effects and check reflection fluctuations. The structures were solved using Patterson calculations and conventional difference Fourier synthesis methods (SHELXTL) [6]. In the final cycles, hydrogen atoms were included in idealized calculated positions. For **1**, all Hg, halogen and Co atoms were refined using anisotropic thermal

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*This represents the stoichiometric formula only and it would be unwise to assume the existence of any particular anionic structural unit in the lattice.

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TABLE 1. Crystal data for (±)-$[Co(en)_3][HgICl_4]$ (1) and (±)-$[Co(en)_2(NH_3)(py)][Hg_2Cl_7]$ (2)

Molecular formula	$C_6H_{24}N_6ICoCl_4Hg$ (1)	$C_9H_{24}N_6Cl_7CoHg_2$ (2)
Formula weight	708.2	924.4
Space group	$P2_1/a$	$Pbcn$
a (Å)	13.488(6)	22.663(8)
b (Å)	11.716(4)	14.137(4)
c (Å)	11.910(4)	14.459(4)
α (°)	90	90
β (°)	109.82(3)	90
γ (°)	90	90
V (Å^3)	1771(1)	4632(2)
Z	4	8
Temperature (°C)	−130	−135
D_{calc} (g cm^{-3})	2.67	2.66
D_{meas} (g cm^{-3})	2.60	2.62
$F(000)$	1320	3407
Absorption coefficient, μ (cm^{-1})	119	148
Absorption correction	empirical	empirical
Transmission factors	max. 0.964	max. 0.432
	min. 0.443	min. 0.192
Mo Kα (λ) (Å)	0.71069	0.71069
Scan mode	ω scans	ω scans
	6° min^{-1}	var. 2.93–29.3° min^{-1}
Octants	h 0–17, k 0–14, l 0–±15	h 0–25, k 0–16, l 0–16
$2\theta_{max}$ (°)	50	45
Reflections measured	3418	3366
Reflections used	2509	2255
Parameters refined	109	111
Weighting, g	8.8×10^{-4}	10×10^{-4}
R	0.0411	0.0492
R_2	0.0536	0.0665

parameters and for 2 all non-hydrogen atoms were refined similarly. Non-hydrogen atom coordinates are listed in Tables 2 and 3. See also 'Supplementary Material'.

Results and Discussion

$[Co(en)_3][HgCl_4I]$ consists of Δ- plus Λ-$[Co(en)_3]^{3+}$ cations and isolated Cl^- and $[HgCl_3I]^{2-}$ anions (Fig. 1). The three chelate rings in the $[Co(en)_3]^{3+}$ cations adopt the lel ob$_2$ configuration (Fig. 2) as does the racemic triiodide salt [7–9]. While salts containing more or less tetrahedral $[HgCl_4]^{2-}$ or $[HgI_4]^{2-}$ anions are known [1, 10–12], the above is the first characterized [13] example of the $[HgCl_3I]^-$ anion (Fig. 2, Table 4). The mean Hg–Cl distance of 2.53 Å is quite comparable to that observed (~2.49 Å) [10, 11] in isolated tetrahedral $[HgCl_4]^{2-}$ anions. However, the Hg–I distance of 2.651(1) Å is considerably shorter than those observed in tetrahedral $[HgI_4]^{2-}$ anions (2.75–2.80 Å) [12], and is similar to the distance observed in various forms of HgI_2 (~2.62 Å) [14, 15].

TABLE 2. Non-hydrogen atom coordinates (×10^4) for (±)-$[Co(en)_3][HgICl_4]$ (1)

Atom	x	y	z
Hg(1)	3634(1)	5245(1)	7369(1)
I	1777(1)	6262(1)	6453(1)
Cl(1)	5252(2)	6385(2)	7536(3)
Cl(2)	4251(2)	3917(2)	9069(2)
Cl(3)	3727(2)	3702(2)	5799(2)
Cl(4)[a]	9073(2)	6167(2)	943(2)
Co	7499(1)	4024(1)	7787(1)
N(1)	6362(7)	4293(7)	6250(8)
C(1)	6192(9)	3226(9)	5521(10)
C(2)	6251(9)	2255(9)	6354(10)
N(2)	7229(7)	2402(7)	7394(8)
C(3)	7069(9)	3943(9)	9965(10)
N(3)	6497(7)	3999(7)	8655(8)
C(4)	8059(8)	3260(9)	10181(10)
N(4)	8579(7)	3704(7)	9345(8)
N(5)	7767(7)	5662(8)	8071(9)
C(5)	8705(9)	6014(10)	7754(11)
C(6)	8717(9)	5318(9)	6701(11)
N(6)	8574(7)	4090(7)	7016(9)

[a] Isolated chloride ion.

TABLE 3. Non-hydrogen atom coordinates ($\times 10^4$) for (±)-*cis*-$[Co(en)_2(NH_3)(py)][Hg_2Cl_7]$ (**2**)

Atom	*x*	*y*	*z*
Hg(1)	1407(1)	2213(1)	4423(1)
Hg(2)	1853(1)	4656(1)	3068(1)
Co	1188(1)	1818(1)	338(1)
Cl(11)	1138(1)	3019(2)	2914(2)
Cl(12)	852(1)	2579(2)	5776(2)
Cl(13)	2268(1)	1263(2)	4107(3)
Cl(21)	2160(1)	3896(2)	4638(2)
Cl(22)	1091(1)	5774(2)	3220(2)
Cl(23)	2566(2)	4111(4)	2013(3)
Cl(0)	535(1)	737(2)	3909(2)
N(1)	823(4)	1335(6)	1471(6)
N(2)	1487(4)	519(7)	197(7)
N(3)	503(4)	1483(6)	−426(6)
N(4)	1555(4)	2181(7)	−848(6)
N(5)	879(4)	3106(7)	556(5)
N(6)	1902(4)	2144(8)	1051(7)
C(1)	1104(6)	467(9)	1762(9)
C(2)	1206(7)	−116(9)	906(8)
C(3)	570(5)	1871(9)	−1355(8)
C(4)	1210(5)	1773(9)	−1625(8)
C(5)	1218(5)	3893(9)	504(8)
C(6)	1027(5)	4771(8)	752(7)
C(7)	463(5)	4874(9)	1058(8)
C(8)	100(5)	4112(8)	1095(8)
C(9)	316(4)	3231(8)	863(7)

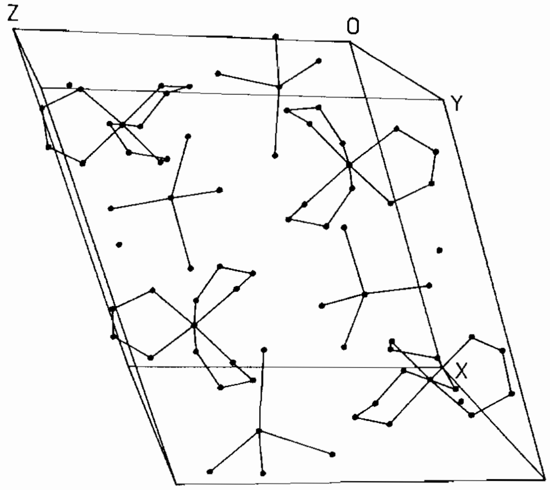

Fig. 1. A packing diagram for (lel ob$_2$)-(±)-$[Co(en)_3][HgCl_4I]$ (**1**) showing the Δ-(λδδ) plus Λ-(δλλ) cations and the Cl^- and $[HgCl_3I]^{2-}$ anions.

The other cobalt(III) complex, of formal stoichiometry, $[Co(en)_2(NH_3)(py)][Hg_2Cl_7]$, consists of Δ- plus Λ-*cis*-$[Co(en)_2(NH_3)(py)]^{3+}$ cations and $[Hg_2Cl_7]^{3-}$ anions. In the cations, the two chelate rings adopt the δλ conformation (Fig. 3, Tables 5 and 6) and the Co–N(py) distance [1.971(9) Å] is not significantly different from the other

TABLE 4. Selected bond lengths (Å) and bond angles (°) for (±)-$[Co(en)_3][HgICl_4]$ (**1**)

Cation			
Co–N(1)	1.974(8)	Co–N(2)	1.962(9)
Co–N(3)	1.960(11)	Co–N(4)	1.968(8)
Co–N(5)	1.960(9)	Co–N(6)	1.964(12)
	Co–N (mean) = 1.965(5)		
N(1)–C(1)	1.494(14)	C(1)–C(2)	1.493(16)
N(2)–C(2)	1.482(12)	C(3)–C(4)	1.502(16)
N(3)–C(3)	1.489(13)	C(5)–C(6)	1.500(18)
N(4)–C(4)	1.492(17)		
N(5)–C(5)	1.496(17)		
N(6)–C(6)	1.515(14)		
N(1)–Co–N(4)	176.9(4)		
N(2)–Co–N(5)	176.2(4)		
N(3)–Co–N(6)	176.1(3)		
N(1)–C(1)–C(2)–N(2)	−50.1(1.2)		
N(3)–C(3)–C(4)–N(4)	47.5(1.0)		
N(5)–C(5)–C(6)–N(6)	−49.2(1.0)		
Anion, $HgCl_3I^{2-}$			
Hg–Cl(1)	2.508(3)	Hg–Cl(2)	2.464(3)
Hg–Cl(3)	2.634(3)	Hg–I	2.651(1)
I–Hg–Cl(1)	118.0(1)		
I–Hg–Cl(2)	129.1(1)		
I–Hg–Cl(3)	106.4(1)		
Cl(1)–Hg–Cl(2)	103.2(1)		
Cl(1)–Hg–Cl(3)	99.9(1)		
Cl(2)–Hg–Cl(3)	93.8(1)		

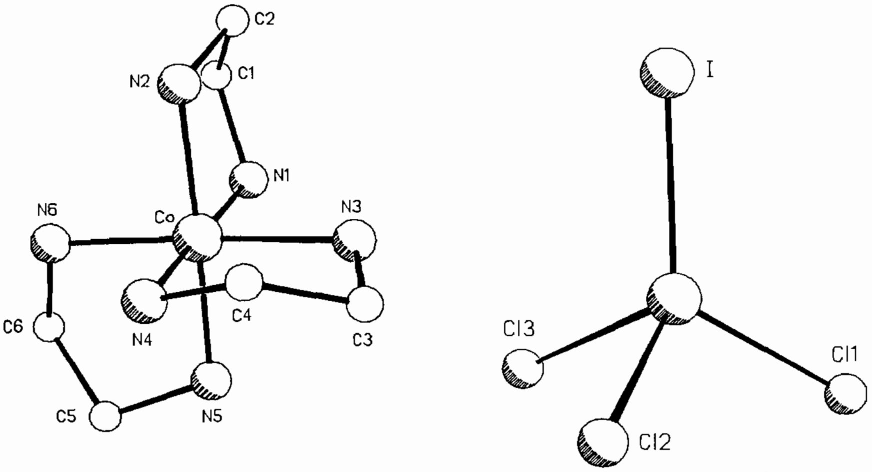

Fig. 2. Perspective views of the Λ-(δλλ)-$[Co(en)_3]^{3+}$ cation and the $[HgCl_3I]^{2-}$ anion. In the lattice there are equal amounts of the Δ-(λδδ) cation.

TABLE 5. Selected bond lengths (Å) and bond angles (°) for (±)-*cis*-$[Co(en)_2(NH_3)(py)]Hg_2Cl_7$ (**2**)

Cation			
Co–N(1)(en)	1.954(8)	N(1)–C(1)	1.443(16)
Co–N(2)(en)	1.964(10)	N(2)–C(2)	1.501(16)
Co–N(3)(en)	1.958(8)	N(3)–C(3)	1.456(14)
Co–N(4)(en)	1.970(9)	N(4)–C(4)	1.482(15)
Co–N(5)(py)	1.971(9)	C(1)–C(2)	1.502(18)
Co–N(6)(NH_3)	1.970(9)	C(3)–C(4)	1.506(15)
N(5)–C(5)	1.351(15)	C(6)–C(7)	1.359(17)
N(5)–C(9)	1.360(13)	C(7)–C(8)	1.354(17)
C(5)–C(6)	1.359(17)	C(8)–C(9)	1.377(16)
N(1)(en)–Co–N(4)(en)	174.6(4)		
N(2)(en)–Co–N(5)(py)	176.7(4)		
N(6)(NH_3)–Co–N(3)(en)	177.1(4)		
N(3)–C(3)–C(4)–N(4)	−50.8(1.2)		
N(1)–C(1)–C(2)–N(2)	48.3(1.3)		
Anion, $Hg_2Cl_7^{3-}$			
Hg(1)–Cl(0)	2.961(3)	Hg(2)–Cl(11)	2.828(3)
Hg(1)–Cl(12)	2.376(3)	Hg(2)–Cl(21)	2.601(3)
Hg(1)–Cl(13)	2.408(3)	Hg(2)–Cl(22)	2.346(3)
Hg(2) ···· Cl(13)′	3.36		
Hg(1) ···· Hg(2)	4.09		
Cl(11)–Hg(1)–Cl(0)	86.6(1)		
Cl(11)–Hg(1)–Cl(21)	82.4(1)		
Cl(11)–Hg(1)–Cl(13)	106.3(1)		
Cl(11)–Hg(1)–Cl(12)	118.8(1)		
Cl(12)–Hg(1)–Cl(0)	90.4(1)		
Cl(12)–Hg(1)–Cl(21)	92.5(1)		
Cl(12)–Hg(1)–Cl(13)	134.7(1)		
Cl(13)–Hg(1)–Cl(0)	95.7(1)		
Cl(13)–Hg(1)–Cl(21)	90.1(1)		
Cl(21)–Hg(1)–Cl(0)	168.6(1)		
Cl(11)–Hg(2)–Cl(23)	94.3(1)		
Cl(11)–Hg(2)–Cl(22)	97.8(1)		
Cl(11)–Hg(2)–Cl(21)	83.4(1)		
Cl(21)–Hg(2)–Cl(23)	104.3(1)		
Cl(21)–Hg(2)–Cl(22)	113.1(1)		
Cl(22)–Hg(2)–Cl(23)	141.8(1)		
Hg(1)–Cl(11)–Hg(2)	99.3(1)		
Hg(1)–Cl(21)–Hg(2)	94.9(1)		

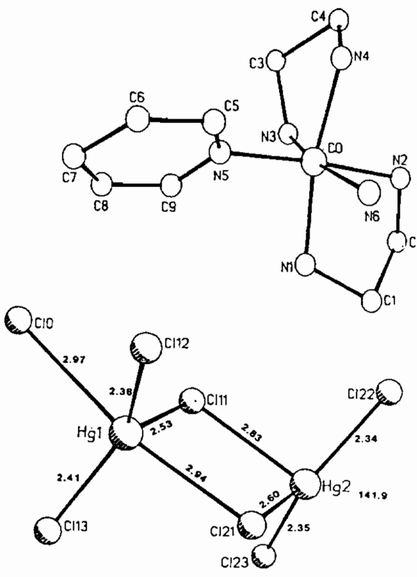

Fig. 3. Perspective views of the Δ-($\delta\lambda$)-$[Co(en)_2(NH_3)(py)]^{3+}$ cation and the $Hg_2Cl_7^{3-}$ anion. In the lattice, there are equal amounts of the Λ-($\lambda\delta$) cation.

Co–N bond lengths. This Co–N(py) distance is similar to the distance found in (±)-*cis*-$[CoCl(en)_2(py)]^{2+}$ [16], namely, 1.992(2) Å. Mean Co–N(en) distances in these Co(III) cations [1.965(5) for **1** and 1.961(7) Å for **2**] are remarkably consistent. As with $[M(en)_3]^{3+}$ systems [9], the ring conformation adopted in the solid state for *cis*-$[M(en)_2XY]Z$ systems appears to be anion dependent (Table 6).

Although various ionic or polymeric forms corresponding to $[Hg_2Cl_7]^{3-}$ have been reported previously [1, 17] (Table 7) we would regard the anion found in structure **2** to be an isolated dibridged $[Hg_2Cl_7]^{3-}$ unit (Fig. 3).

The next closest Cl atom to Hg(2) [Cl(13)] (Fig. 3) is at 3.36 Å, compared with a distance of 3.14 Å where linear singly bridged $[Hg_2Cl_7{}^{3-}]_n$ chains are proposed [1] and the Cl(23)–Hg–Cl(22) angle of 141.8° observed in the monomeric unit (Fig. 3), is opened to 165.3° in the chain structure [1].

Thus, this isolated $[Hg_2Cl_7]^{3-}$ anion can be regarded as a chloro adduct of the known dimeric, chloro-bridged, $Hg_2Cl_6{}^{2-}$ anion [36–38].

TABLE 6. Ordered ring conformations in some *cis*-$[Co(XY)(en)_2]Z$ complexes

Complex	Enantiomer	Conformation[a]	Dihedral angles[b]	Reference
$[CoCl(en)_2(NH_3)]Cl_2$	(±)	($\delta\lambda$)	50.2, −49.5	16
$[CoCl(en)_2(py)]Cl_2 \cdot H_2O$	(±)	($\lambda\lambda$)	−49.9, −50.0	16
$Na_2[Co(SO_3)_2(en)_2]ClO_4 \cdot 3H_2O$	(±)	($\delta\delta$)	46.6, 49.2	18
$[Co(CN)_2(en)_2]Cl \cdot H_2O$	(+)	Λ ($\lambda\lambda$)	−47.2, −46.0	19
$[CoCl_2(en)_2]Cl \cdot H_2O$	(+)	Λ ($\delta\delta$)	48.1, 53.3	20
$[CoCl_2(en)_2]Cl \cdot H_2O$	(±)	($\delta\lambda$)		21
$[Co(NO_2)_2(en)_2]NO_3$	(±)	($\delta\lambda$)	44.9, −44.0	22
$[Co(NO_2)_2(en)_2][Co(mal)_2(en)] \cdot 2H_2O$	(−)	Δ ($\delta\delta$)	47.9, 45.9	23
$[Co(NO_2)_2(en)_2][Co(NO_2)_2(ox)(NH_3)_2] \cdot H_2O$	(−)	Δ ($\delta\lambda$)		24
$[Co(NO_2)_2(en)_2][Co(NO_2)_4(NH_3)_2]$	(+)[c]	Λ ($\delta\lambda$)	46.6, −46.6	25
$[Co(NO_2)_2(en)_2]Cl$	(+)[c]	Λ ($\delta\lambda$)	50.2, −48.1	26
$[Co(NCS)_2(en)_2]Cl \cdot H_2O$	(±)	($\delta\lambda$)	48.3, −47.6	27
$[Co(N_3)_2(en)_2]_2[Sb_2\text{-(+)-}(tart)_2]$	(+)	Λ		28
$[CoCl(en)_2(imid)]Cl_2$	(±)	($\lambda\lambda$)	−56.6, −45.9	29
$[CoCl(en)_2\{(S)\text{-}prol\}]ZnCl_4$	(−)	Δ ($\delta\lambda$)	45.2, −45.3	30
$[CoCl\{adenine(-1)\}(en)_2]Br \cdot H_2O$	(±)	$\lambda\lambda$		31
$[CoCl\{theophilline(-1)\}(en)_2]ClO_4$	(±)	$\lambda\lambda$		32
$[Co(en)_2(NH_3)(py)](Hg_2Cl_7)$	(±)	$\delta\lambda$	48.3, −50.8	d
$[CoBr(en)_2(py)](NO_3)_2$	(±)	$\delta\lambda$	42.9, −44.2	33
$[Co(NO_2)(SO_3)(en)_2]$	(±)	($\delta\lambda$)		34
$[Co(N_3)(SO_3)(en)_2]$	(±)	($\delta\delta$)		34
$[Co(NO_2)(SSO_3)(en)_2]$	(±)	($\delta\lambda$)	48.8, −50.7	35

[a]For a racemic crystal, the lattice will contain equal amounts of the $\Delta\lambda\lambda$ and $\Lambda\delta\delta$ *or* $\Delta\delta\lambda$ and $\Lambda\delta\lambda$ cations. The data reported in this Table are those assigned to the particular absolute configuration used in the structure analysis. [b]In many instances these have been calculated from the cited atom coordinates. Where numbers are not given, either the atom coordinates are not available to us, or unreasonable dihedral angles were calculated. [c]The sign of rotation reported in this work [25, 26] has been incorrectly assigned (I. Bernal, personal communication) and should be (+). [d]This research.

TABLE 7. Structures adopted by the '$Hg_2Cl_7^{3-}$' anion

Cation	Structure	Reference
u-fac-$[Cr(dien)_2]^{3+}$	$(HgCl_3^-)_n$ chains and weakly associated (Hg ····· Cl = 3.3–3.4 Å) $HgCl_4^{2-}$ anions	1
s-fac-$[Cr(dien)_2]^{3+}$	$2HgCl_4^{2-}$, $Hg_2Cl_6^{2-}$ and $Hg_4Cl_{14}^{6-}$ anions	1
s-fac-[CrCl(dien)(Hdien),*N*,*N*)]$^{3+}$	$[Hg_2Cl_7^{3-}]_n$ chains (Hg ····· Cl = 3.21 Å between chains)	1
cis-$[Co(en)_2(NH_3)(py)]^{3+}$	weakly associated (Hg ····· Cl = 3.36 Å) dibridged $Hg_2Cl_7^{3-}$ anions	this research
(±)-$[Co(en)_3]^{3+}$	unknown	17

We will discuss in detail, the whole question of bonding in chloro-mercury(II) anions in a subsequent review paper.

Supplementary Material

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

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