Structures of Mercury(II) Halide Adducts with Transition-metal Lewis Bases. Part II.[1] Crystal Structure of the 1 : 3 Complex between Dicarbonyl-π-cyclopentadienylcobalt and Mercury(II) Chloride

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Crystals of $(\pi\text{-}C_5H_5)(CO)_2Co,3HgCl_2$ are triclinic, $a = 10{\cdot}080$, $b = 12{\cdot}572$, $c = 7{\cdot}144$ Å, $\alpha = 87{\cdot}82$, $\beta = 95{\cdot}67$, $\gamma = 108{\cdot}7°$, and $Z = 2$ in space group $P\bar{1}$. The structure was solved from photographic data by Patterson and Fourier methods and refined by least squares to R 0·095 for 1354 observed reflections. Unlike $(\pi\text{-}C_5H_5)(CO)_2Co,HgCl_2$ which is an adduct, this complex is best formulated as a salt, $[(\pi\text{-}C_5H_5)Co(CO)_2(HgCl)]^+Cl^-$, with two additional molecules of mercury(II) chloride. The cation contains an Hg–Co bond (2·504 ± 0·009 Å) which is significantly shorter than that found in the 1 : 1 adduct (2·578 ± 0·004 Å).

EQUIMOLAR amounts of dicarbonyl-π-cyclopentadienylcobalt and mercury(II) chloride react to give the complex $(\pi\text{-}C_5H_5)(CO)_2Co,HgCl_2$. X-Ray analysis shows[1] the latter to be a true 1 : 1 adduct containing a metal donor Co–Hg bond. By the reaction of excess of mercury(II) chloride with either the 1 : 1 adduct or $Co(\pi\text{-}C_5H_5)(CO)_2$, Cook and Kemmitt obtained[2] a yellow compound, with analysis corresponding to $(\pi\text{-}C_5H_5)(CO)_2Co,2{\cdot}7HgCl_2$. In view of this rather unsatisfactory formulation, a crystal structure determination was undertaken to establish whether the complex is a 1 : 1 adduct containing additional mercury(II) chloride molecules in the lattice, or a salt as in the ruthenium and osmium complexes:[3] $[M^{II}(CO)_3(PPh_3)_2(HgCl)]^+[HgCl_3]^-$.

In the event, the X-ray results show that the crystals selected for study correspond to $[(\pi\text{-}C_5H_5)(CO)_2Co(HgCl)]^+Cl^-$ with two additional molecules of mercury(II) chloride in the crystal lattice. The vibration parameters of the atoms provide no evidence that the additional $HgCl_2$ sites are occupied in a non-stoicheiometric manner, and it is possible that the discordance with the chemical analysis can be accounted for by the presence of some 1 : 1 adduct in the bulk sample.

EXPERIMENTAL

Crystals were prepared by the reaction of an excess of mercury(II) chloride with $(\pi\text{-}C_5H_5)(CO)_2Co,HgCl_2$. The yellow precipitate was recrystallised from acetone [containing mercury(II) chloride to prevent dissociation of the compound] by the addition of petroleum ether (b.p. 40—60 °C). Analysis of the product was still unsatisfactory, but the ratio of Co : C : H and Hg : Cl was in agreement with the formulations $Co(\pi\text{-}C_5H_5)(CO)_2$ and $HgCl_2$ respectively. Thus the complex was regarded as having the stoicheiometry $(\pi\text{-}C_5H_5)(CO)_2Co,nHgCl_2$ and the unsatisfactory analysis was attributed to variations in the value of n. Crystals selected for X-ray analysis proved to have the value $n = 3$. Accurate unit-cell dimensions were measured from precession photographs, by use of Zr filtered Mo-K_α radiation.

Crystal Data.—$C_7H_5Cl_6CoHg_3O_2$, $M = 994{\cdot}5$, Triclinic, $a = 10{\cdot}08 \pm 0{\cdot}02$, $b = 12{\cdot}57 \pm 0{\cdot}03$, $c = 7{\cdot}144 \pm 0{\cdot}010$ Å, $\alpha = 87{\cdot}8 \pm 0{\cdot}1$, $\beta = 95{\cdot}6 \pm 0{\cdot}1$, $\gamma = 108{\cdot}7 \pm 0{\cdot}1°$, $U = 887{\cdot}3$ Å^3, $Z = 2$, $D_c = 3{\cdot}72$,† $F(000) = 864$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; $\mu(\text{Mo-}K_\alpha) = 284$ cm^{-1}. Space group $P\bar{1}$ confirmed by successful refinement.

Data Collection.—Ten reciprocal levels were collected photographically by use of Zr filtered Mo-K_α radiation. Six layers (hk0—5) were collected by the equi-inclination technique using an integrating Nonius camera from a crystal of dimensions 0·05 × 13 × 0·43 mm. A further four reciprocal levels (0kl, 1kl, h0l, h1l) were collected from a second crystal of dimensions 0·08 × 0·18 × 0·25 mm by use of a Supper precession camera. All intensities were measured with a Joyce–Loebl integrating microdensitometer and corrected for Lorentz and polarisation factors. An absorption correction[4] was applied to all data giving, after suitable inter-film and inter-layer scaling, a total of 1354 independent reflections.

Structure Analysis.—Positions of the three mercury atoms were found from a three-dimensional sharpened Patterson map. Structure factors ‡ for these three atoms were calculated and three cycles of block-diagonal least-squares refinement gave R 0·28. A difference-Fourier map enabled the position of six chlorine atoms and cobalt to be found. The atomic scattering factors of mercury, cobalt, and chlorine were corrected for anomalous dispersion[6] and refinement of all ten atoms reduced R to 0·17. A further difference-Fourier synthesis revealed the remaining carbon and oxygen atoms, along with electron-density distributed anisotropically about the heavy atoms. Consequently the mercury, cobalt, and chlorine atoms were given anisotropic temperature factors and refinement of all atoms for several cycles, initially with oxygens having isotropic temperature factors but finally with anisotropic values, gave R 0·098. Further refinement was carried out with the weighting scheme $w = 1/(a + b|KF_o| + c|KF_o|^2)$ (where a, b, c were 0·935, 0·125, and 0·00408) to give a final R value of 0·095. Structure factors are listed in Supplementary Publication No. SUP 20490 (6 pp., 1 microfiche).§ The final positional parameters, with their standard deviations, are listed in Table 1. The final temperature factors are given in Table 2, and relevant bond distances and angles are listed in Table 3.

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† No suitable flotation medium could be found to measure the density of the crystals used for the structure determination.

‡ Scattering factors for all atoms were taken from ref. 5.

§ For details see Notice to Authors No. 7 in *J. Chem. Soc.* (*A*), 1970, Issue No. 20 (items less than 10 pp. are sent as full size copies).

[1] Part I, I. W. Nowell and D. R. Russell, preceding paper.

[2] D. J. Cook and R. D. W. Kemmitt, *Chem. and Ind.*, 1966, 946.

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[4] N. W. Alcock's ABSCOR programme, based on the method of J. De Meulenaer and H. Tompa, *Acta Cryst.*, 1965, **19**, 1014.

[5] 'International Tables for X-Ray Crystallography,' vol. **3**, Kynoch Press, Birmingham, 1962, p. 201.

[6] Ref. 5, p. 203.

TABLE 1

Atomic positional parameters (fractional) with their estimated standard deviations in parentheses

	x	y	z
Hg(1)	−0·01662(3)	0·05557(3)	0·24624(5)
Hg(2)	0·08142(3)	0·35370(3)	−0·01950(5)
Hg(3)	−0·13999(3)	0·30647(3)	0·47038(5)
Co	−0·39982(9)	0·26199(8)	0·48141(12)
Cl(1)	0·17763(20)	0·11338(18)	0·07566(30)
Cl(2)	−0·21316(21)	−0·01164(19)	0·41228(27)
Cl(3)	−0·13743(19)	0·21793(20)	0·00554(36)
Cl(4)	0·32635(17)	0·42405(18)	−0·00055(28)
Cl(5)	0·07157(15)	0·26437(16)	0·51901(29)
Cl(6)	−0·00251(16)	0·49726(15)	0·25429(23)
O(1)	−0·4400(6)	0·1809(2)	0·1174(8)
O(2)	−0·4095(6)	0·0567(2)	0·6964(8)
C(1)	−0·4298(8)	0·1968(6)	0·2583(10)
C(2)	−0·4039(6)	0·1386(5)	0·6057(9)
C(3)	−0·4537(8)	0·3996(7)	0·3698(10)
C(4)	−0·5855(5)	0·3054(4)	0·4650(7)
C(5)	−0·3425(8)	0·4383(7)	0·5678(10)
C(6)	−0·5490(7)	0·2927(6)	0·6257(10)
C(7)	−0·3736(8)	0·3678(6)	0·7072(10)

TABLE 2

Final temperature factors, with estimated standard deviations in parentheses

(a) Anisotropic temperature factors (Å^2) *

Atom	B_{11}	B_{22}	B_{33}
Hg(1)	3·02(14)	3·47(16)	3·78(15)
Hg(2)	1·80(12)	3·94(18)	4·49(16)
Hg(3)	1·03(11)	4·84(19)	4·62(16)
Co	1·33(33)	2·55(45)	2·54(39)
Cl(1)	3·7(9)	4·0(1·1)	4·5(1·0)
Cl(2)	3·9(9)	4·8(1·2)	3·4(9)
Cl(3)	2·4(8)	5·0(1·2)	6·6(1·3)
Cl(4)	1·1(6)	3·9(1·0)	4·3(9)
Cl(5)	1·8(7)	2·9(9)	6·6(1·2)
Cl(6)	2·4(6)	3·2(9)	2·1(7)
O(1)	1·6(1·6)	10·1(3·0)	3·6(2·7)
O(2)	5·2(3·0)	2·2(2·9)	5·9(3·1)

Atom	B_{23}	B_{13}	B_{12}
Hg(1)	0·09(11)	0·98(11)	0·36(12)
Hg(2)	0·81(12)	−0·22(10)	−0·27(12)
Hg(3)	−0·24(13)	0·24(9)	0·87(11)
Co	0·32(33)	0·56(29)	0·66(34)
Cl(1)	−0·6(8)	0·9(8)	−0·4(9)
Cl(2)	−0·2(8)	1·2(7)	0·3(9)
Cl(3)	0·5(1·0)	0·4(8)	0·0(9)
Cl(4)	−0·3(7)	0·4(6)	−0·3(7)
Cl(5)	−1·8(8)	−0·3(7)	0·6(7)
Cl(6)	0·7(6)	0·4(6)	0·8(7)
O(1)	−0·0(2·7)	0·4(1·7)	1·4(2·2)
O(2)	−0·0(2·4)	0·4(2·7)	1·4(2·7)

(b) Isotropic temperature factors (A^2) †

Atom	B	Atom	B
C(1)	2·0(9)	C(5)	4·4(1·2)
C(2)	1·3(8)	C(6)	2·5(9)
C(3)	3·3(1·1)	C(7)	4·3(1·2)
C(4)	0·7(7)		

* In the form $\exp\{-\tfrac{1}{4}(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{23}klb^*c^* + 2B_{13}hla^*c^* + 2B_{12}hka^*b^*)\}$.

† In the form $\exp\{-B\sin^2\theta/\lambda^2\}$.

DISCUSSION

The structure consists basically of $[(\pi\text{-}C_5H_5)Co(CO)_2(HgCl)]^+$ cations, Cl^- anions, and two distinct mercury(II) chloride molecules, linked together by Hg–Cl interactions to give what is essentially a layer structure. Figure 1 shows the arrangement within each layer, neighbouring layers are held together by weak CH · · · Cl interactions (Figure 2 and Table 3).

TABLE 3

Interatomic distances (Å) and angles (°) with estimated standard deviations of the last figure in parentheses

(a) Distances

Hg(1)–Cl(1)	2·309(20)	Co–C(1)	1·76(7)
Hg(1)–Cl(2)	2·314(18)	Co–C(2)	1·76(6)
Hg(1)–Cl(3)	3·086(25)	Co–C(3)	2·09(8)
Hg(1)–Cl(1^{I})	3·141(20)	Co–C(4)	2·11(5)
Hg(1)–Cl(5)	3·168(16)	Co–C(5)	2·23(8)
Hg(1)–Cl(2^{II})	3·352(18)	Co–C(6)	2·05(7)
Hg(2)–Cl(3)	2·335(18)	Co–C(7)	2·08(8)
Hg(2)–Cl(4)	2·332(16)	C(1)–O(1)	1·04(9)
Hg(2)–Cl(6)	3·061(19)	C(2)–O(2)	1·17(8)
Hg(2)–Cl(6^{III})	2·722(19)	C(3)–C(4)	1·64(9)
Hg(2)–Cl(1)	3·481(20)	C(3)–C(5)	1·74(10)
Hg(2)–Cl(5^{IV})	3·506(17)	C(4)–C(6)	1·17(8)
Hg(3)–Co	2·504(9)	C(5)–C(7)	1·32(11)
Hg(3)–Cl(5)	2·348(16)	C(6)–C(7)	1·75(10)
Hg(3)–Cl(6)	2·839(17)		
Hg(3)–Cl(6^{V})	3·093(17)	C(3)–Cl(4^{VI})	3·41
Hg(3)–Cl(3)	3·548(27)	C(4)–Cl(5^{VI})	3·46
		(Sum of CH and Cl van der Waals radii 3·65)	

(b) Angles

Cl(1)–Hg(1)–Cl(1^{I})	89·3(2)	Co–Hg(3)–Cl(3)	99·3(1)
Cl(1)–Hg(1)–Cl(2)	177·2(1·5)	Co–Hg(3)–Cl(5)	153·5(5)
Cl(1)–Hg(1)–Cl(2^{II})	83·4(2)	Co–Hg(3)–Cl(6)	116·7(2)
Cl(1)–Hg(1)–Cl(3)	88·1(2)	Co–Hg(3)–Cl(6^{V})	106·2(2)
Cl(1)–Hg(1)–Cl(5)	97·3(2)	Cl(3)–Hg(3)–Cl(5)	83·1(2)
Cl(1^{I})–Hg(1)–Cl(2)	88·7(2)	Cl(3)–Hg(3)–Cl(6)	71·3(2)
Cl(1^{I})–Hg(1)–Cl(2^{II})	83·4(2)	Cl(3)–Hg(3)–Cl(6^{V})	142·0(4)
Cl(1)–Hg(1)–Cl(3)	88·3(2)	Cl(5)–Hg(3)–Cl(6)	89·2(2)
Cl(2)–Hg(1)–Cl(2^{II})	96·1(2)	Cl(5)–Hg(3)–Cl(6^{V})	106·2(3)
Cl(2)–Hg(1)–Cl(3)	93·4(2)	Cl(6)–Hg(3)–Cl(6^{V})	72·7(3)
Cl(2)–Hg(1)–Cl(5)	85·5(2)		
Cl(2^{II})–Hg(1)–Cl(5)	73·3(3)	Hg(1)–Cl(1)–Hg(2)	85·1(2)
Cl(3)–Hg(1)–Cl(5)	79·7(2)	Hg(1)–Cl(3)–Hg(2)	94·4(2)
		Hg(2)–Cl(5)–Hg(3)	85·0(2)
Cl(1)–Hg(2)–Cl(3)	78·8(2)	Hg(2)–Cl(6)–Hg(2^{III})	102·6(3)
Cl(1)–Hg(2)–Cl(4)	77·7(2)	Hg(2)–Cl(6)–Hg(3)	92·4(2)
Cl(1)–Hg(2)–Cl(5)	80·9(2)	Hg(3)–Cl(6)–Hg(3^{V})	107·3(2)
Cl(1)–Hg(2)–Cl(6)	128·5(3)		
Cl(3)–Hg(2)–Cl(4)	156·2(7)	Co–C(1)–O(1)	164(3)
Cl(3)–Hg(2)–Cl(5)	80·9(2)	Co–C(2)–O(2)	177(4)
Cl(3)–Hg(2)–Cl(6)	87·6(3)	C(3)–C(4)–C(6)	110(4)
Cl(3)–Hg(2)–Cl(6^{III})	99·7(3)	C(4)–C(3)–C(5)	98(3)
Cl(4)–Hg(2)–Cl(5)	90·3(2)	C(4)–C(6)–C(7)	118(4)
Cl(4)–Hg(2)–Cl(6)	104·7(2)	C(5)–C(7)–C(6)	100(3)
Cl(4)–Hg(2)–Cl(6^{III})	102·7(3)		
Cl(5)–Hg(2)–Cl(6)	85·7(2)		
Cl(6)–Hg(2)–Cl(6^{III})	77·4(3)		

Roman numerals as superscripts refer to the following positions relative to the reference molecule at x, y, z:

I	$-x, -y, -z$	IV	$x, y, -1 + z$
II	$-x, -y, 1 - z$	V	$-x, 1 - y, 1 - z$
III	$-x, 1 - y, -z$	VI	$-1 + x, y, z$

The chemistry of the $(\pi\text{-}C_5H_5)(CO)_2Co,HgCl_2$ system can be understood if the following equilibria are assumed to exist in solution:

$$(\pi\text{-}C_5H_5)Co(CO)_2 + HgCl_2 \rightleftharpoons (\pi\text{-}C_5H_5)Co(CO)_2,HgCl_2 \rightleftharpoons [(\pi\text{-}C_5H_5)Co(CO)_2(HgCl)]^+Cl^-$$

(1) (adduct) (2) (salt)

Thus the reaction of equimolar amounts [2] of $Co(\pi\text{-}C_5H_5)(CO)_2$ and mercury(II) chloride gives only a low yield of the 1 : 1 adduct (1). To prevent dissociation of the latter upon recrystallisation, an acetone solution containing mercury(II) chloride must be used. The reaction of $Co(\pi\text{-}C_5H_5)(CO)_2$ or $(\pi\text{-}C_5H_5)(CO)_2Co,HgCl_2$ with excess of mercury(II) chloride forces the equilibria more to the right-hand side, thereby favouring formation of the salt (2) rather than the adduct. In the solid state the ionic species (2) is stabilised by an extensive network of Hg–Cl interaction. Although no discrete mercury-containing anion can be identified in the lattice, it is reasonable to suppose that such anions will exist in solutions containing an excess of mercury(II) chloride.

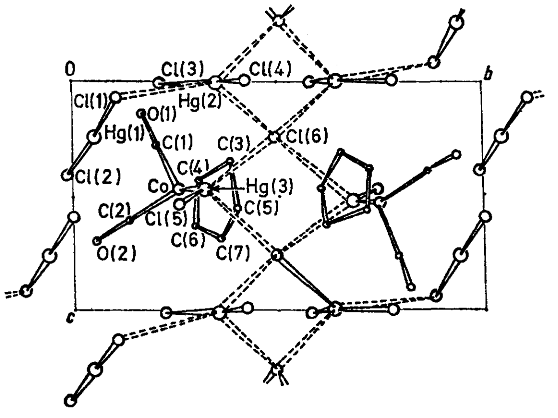

FIGURE 1 Projection of the unit cell along the a^* axis direction. Hg–Cl distances >2·6 Å are drawn with dashed lines. For clarity, not all Hg–Cl interactions are shown

As the $[(\pi\text{-}C_5H_5)(CO)_2Co(HgCl)]^+$ unit now carries a formal positive charge, one would expect a contraction of the mercury orbitals and a corresponding decrease in the Hg–Co and Hg–Cl bond lengths, compared with the values found in the 1 : 1 adduct. This is in agreement with the experimental results.

The Hg–Co bond length is similar to those found in $Hg[Co(CO)_4]_2$ (2·498 ± 0·007, 2·500 ± 0·007 Å)[7] and $Hg[Co(CO)_3(PEt_3)]_2$ (2·499 ± 0·005 Å).[8]

The presence of a formal positive charge on the mercury should facilitate a greater donation of electron density from the cobalt than in the 1 : 1 adduct. Any increase in electron-density donation will be accompanied by a decrease in back-donation from cobalt to the carbonyl groups, and the higher ν(CO) frequencies found by Cook and Kemmitt[2,9] are in agreement with this. The ν(CO) bands at 2069 and 2032 cm^{-1} for the complex formulated as $(\pi\text{-}C_5H_5)Co(CO)_2{,}2{\cdot}7HgCl_2$ may be due to the presence of a certain amount of the 1 : 1 adduct. This would also account for the poor analysis of the complex.

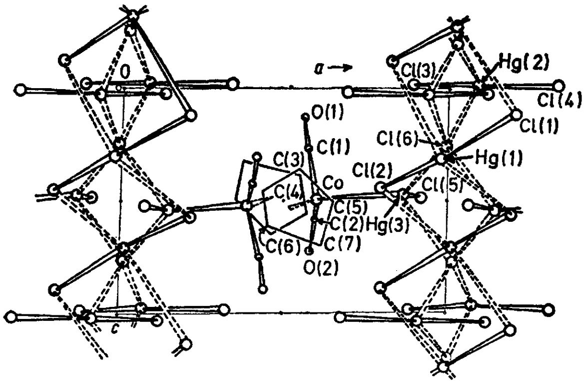

FIGURE 2 Projection of the unit cell along the b^* axis direction

The cyclopentadienyl ring is effectively planar. The equation of the best least-squares plane associated with the five carbon atoms together with distances are given in Table 4. The perpendicular distance of the cobalt atom from this plane (1·66 Å) is to be compared with the shorter value of 1·70 Å in the 1 : 1 adduct; this observation is also in keeping with the relative effective nuclear charges on the cobalt in the two complexes.

TABLE 4

Equation of the best least-squares plane associated with the five cyclopentadienyl carbon atoms, referred to the axis system a, b', c^*

$$-0{\cdot}65305X + 0{\cdot}69560Y + 0{\cdot}29945Z - 8{\cdot}47799 = 0{\cdot}0$$

Distances (Å) of atoms from the plane: C(3) −0·04, C(4) −0·02, C(5) 0·08, C(6) 0·06, C(7) 0·09, Co 1·66

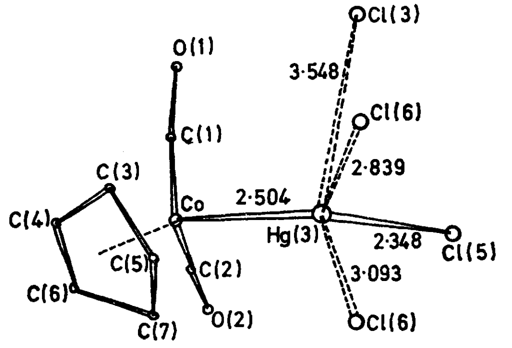

FIGURE 3 A view of the cation showing additional Hg(3)–Cl interactions

The co-ordination of Hg(3) in the structure is highly irregular (Figure 3) with an approximately trigonal bipyramidal geometry. The axial positions are occupied by the Cl^- anion [Cl(6′)] and a chlorine atom [Cl(3)], distance 3·11 and 3·54 Å respectively from the mercury, with a Cl(6′)–Hg(3)–Cl(3) bond angle of 142°. The sum of the van der Waals radii for mercury[10] and chlorine[11] is 3·3 Å ($R_{Hg} = 1{\cdot}5$, $R_{Cl} = 1{\cdot}8$ Å). Grdenic has suggested[10] that some interaction occurs up to a value of 1·73 Å for R_{Hg}, giving an upper limit of 3·53 Å for $R_{Hg} + R_{Cl}$. Even considering this value, the interaction between Hg(3) and Cl(3) must be very weak at 3·54 Å. The four closer chlorine atoms are in a very distorted tetrahedral arrangement around Hg(3), [Co–Hg(3)–Cl(5) and Cl(6)–Hg(3)–Cl(6′) bond

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angles are 153·5 and 72·7°]. This intermediate co-ordination around mercury is very similar to that found in the thiophene,[12] $[C_4H_8SHgCl]^+Cl^-$, and diethyl sulphide,[13] $[(Et_2S)HgCl]^+Cl^-,HgCl_2$, complexes of mercury(II)chloride, where salt formation also occurs.

The Cl^- ' anion ' is surrounded by a distorted tetrahedral arrangement of mercury atoms, such that each anion bridges two symmetry-related mercury(II) chloride molecules [Cl(3)–Hg(2)–Cl(4)]. Some covalent interaction exists between the Cl^- ' anion ' and the mercury(II) chloride molecules, evident from distortions induced in their molecular geometry. Hg(2) can be considered as having a distorted tetrahedral co-ordination of two chlorine atoms [Cl(3) and Cl(4)] and two chloride anions. Two further chlorines, Cl(5) and Cl(1), are within the upper limit of $R_{\text{Hg}} + R_{\text{Cl}}$ (3·53 Å) for Hg(2) and contribute to asymmetric bridging between Hg(2) and Hg(1), and Hg(2) and Hg(3).

Hg(1) is linked both to Hg(2) and other Hg(1) atoms by asymmetric chlorine bridges, and attains a distorted octahedral co-ordination of six chlorine atoms. The octahedral distortion is similar to that found in mercury(II) chloride itself,[14] and the Cl(1)–Hg(1)–Cl(2) molecules are linked together in zig-zag chains along the (001) direction (Figure 2). These mercury(II) chloride molecules, in contrast to the Cl(3)–Hg(2)–Cl(4) molecules, are only slightly distorted. The two short Hg–Cl distances are 2·31 Å, which although longer than that found in free mercury(II) chloride (2·26 Å) are similar to the values found[13] (2·30 and 2·33 Å) in the unsubstituted $HgCl_2$ of the diethyl sulphide adduct, $[(Et_2)SHgCl^+]Cl^-,HgCl_2$.

The formation of salts rather than discrete adducts may well occur in the reaction of other transition-metal complexes with mercury(II) chloride. Thus Collman and Roper[3] have formulated the ruthenium and osmium adducts, $M(CO)_3(PPh_3)_2,2HgX_2$ (X = Cl, Br, or I) as salts: $[M^{II}(CO)_3(PPh_3)_2(HgX)]^+[HgX_3]^-$. Complexes such as $Fe(CO)_3\{P(OPh)_3\}_2,2HgCl_2$[15] and $(\pi\text{-}C_6H_3Me_3)M(CO)_3,2HgCl_2$ (M = Cr or Mo)[16] may well be salts also. However, if similar equilibria are present as that postulated in the present system, detailed structural analysis would be necessary to confirm these formulations.

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