Structures of Mercury(II) Halide Adducts with Transition-metal Lewis Bases. Part I. Crystal Structure of the Dicarbonyl-π-cyclopentadienylcobalt Complex with Mercury(II) Chloride

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Crystals of $(\pi\text{-}C_5H_5)(CO)_2Cl,HgCl_2$ are monoclinic, $P2_1/n$, $a = 7{\cdot}85$, $b = 13{\cdot}90$, $c = 9{\cdot}38$ Å, $\beta = 91{\cdot}1°$, $Z = 4$. The structure was solved from photographic data by Patterson and Fourier methods and refined by block-diagonal least-squares analysis to a final R 0·093 for 1002 non-equivalent reflexions. The complex is a 1 :1 Lewis acid–base adduct bonded through the metal atoms, the resulting Hg–Co bond length of 2·578 ± 0·004 Å is that expected for a covalent single bond. The idealised co-ordination about mercury is trigonal planar, but two long intermolecular Hg–Cl distances raise the effective co-ordination to trigonal bipyramidal.

EQUIMOLAR amounts of mercuric chloride and dicarbonyl-(π-cyclopentadienyl)cobalt react to give the red crystalline complex $(\pi\text{-}C_5H_5)(CO)_2Co,HgCl_2$. Cook and Kemmitt found [1] that the i.r. spectrum of the complex in nitrobenzene or *o*-chloroaniline solutions contains carbonyl bands due both to the complex and starting material, and postulated dissociation in solution [equation (1)]. The complex may be considered as either a

$$(\pi\text{-}C_5H_5)(CO)_2Co,HgCl_2 \rightleftharpoons (\pi\text{-}C_5H_5)Co(CO)_2 + HgCl_2 \quad (1)$$

salt, $[(\pi\text{-}C_5H_5)(CO)_2Co(HgCl)]^+Cl^-$ or a 1 : 1 adduct, $(\pi\text{-}C_5H_5)(CO)_2Co,HgCl_2$. Conductivity measurements are inconclusive [2] and we have undertaken an *X*-ray analysis to determine the structure of the complex. A preliminary report of the structure has already appeared.[3]

EXPERIMENTAL

Accurate unit-cell dimensions were measured from precession photographs taken with Zr filtered Mo-K_α radiation.

Crystal Data.—$C_7H_5Cl_2CoHgO_2$, $M = 451{\cdot}6$, Monoclinic, $a = 7{\cdot}85 \pm 0{\cdot}01$, $b = 13{\cdot}90 \pm 0{\cdot}02$, $c = 9{\cdot}38 \pm 0{\cdot}01$ Å, $\beta = 91{\cdot}1 \pm 0{\cdot}1°$, $U = 1023$ Å^3, D_m (by flotation) = 2·94, $Z = 4$, $D_c = 2{\cdot}90$, $F(000) = 816$. Mo-K_α radiation, $\lambda = 0{\cdot}7107$ Å; $\mu(\text{Mo-}K_\alpha) = 176$ cm^{-1}. Space group $P2_1/n$ (a nonstandard setting of C_{2h}^5, No. 14) from systematic absences: $h0l$ for $h + l$ odd, $0k0$ for k odd.

Data Collection.—Integrated equi-inclination Weissenberg data was collected on a Nonius camera from a crystal of dimensions 0·06 × 0·08 × 0·1 mm. Zr filtered Mo-K_α radiation was used to collect the reciprocal layers $hk0$—6 by the multiple-film technique. A Supper precession camera was used to collect a further 5 reciprocal layers ($0kl$, $1kl$, $2kl$, $h0l$, $h1l$), from a second crystal of dimensions 0·06 × 0·08 × 0·01 mm. The reciprocal layers $hk0$, $0kl$, were estimated visually, while the remaining 10 layers were measured with a Joyce-Loebl integrating microdensitometer. Intensities were corrected for Lorentz and polarisation factors, and different layers were scaled together by common reflections [4] to give 1002 independent reflections.

Structure Analysis. Positions of the mercury and cobalt atoms were readily found from Patterson projections. Structure factors (scattering factors for all atoms and $\Delta f'$ for mercury, cobalt, and chlorine were taken from ref. 5) were calculated for these two atoms and two cycles of block-diagonal least-squares refinement gave R 0·22. A difference-Fourier map enabled the two chlorine atoms to be located. Inclusion of these in the least-squares refinement reduced R to 0·17, and the positions of all carbon and oxygen atoms were found from a further difference-Fourier synthesis. All atoms were then refined for several least-squares cycles, initially with only mercury and cobalt treated anisotropically but finally with all atoms anisotropic. Absorption corrections [6] were applied to all reflections and final refinement was carried out by use of the weighting scheme $\omega = 1/(a + b|KF_0| + c|KF_0|^2)$; a, b, c, were given the values 1600, 1·0, 1·22 × 10^{-4} respectively. The matrix associated with the anisotropic temperature factors of C(2) was found to be non-positive definite, even after several cycles of refinement. A difference-Fourier synthesis, using values of F_c calculated without any contribution from this carbon atom, confirmed the position refined by the least-squares process. Consequently, an isotropic temperature factor was used for this atom during the last few cycles of refinement and a final R value of 0·093 was obtained. Observed and calculated structure factors have been deposited with the National Lending Library as Supplementary Publication No. SUP 20489 (6 pp., 1 microfiche).† The final positional parameters, with their estimated standard deviations are given

TABLE 1

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

	x	*y*	*z*
Hg	0·25266(2)	0·03715(1)	0·05749(2)
Co	0·24152(6)	0·14486(3)	0·28084(4)
Cl(1)	0·09984(14)	−0·11879(7)	0·04661(12)
Cl(2)	0·41086(15)	0·07514(8)	−0·15817(11)
O(1)	0·6009(4)	0·1687(2)	0·2677(3)
O(2)	0·1663(5)	0·3036(2)	0·0877(3)
C(1)	0·4452(5)	0·1561(3)	0·2660(4)
C(2)	0·2030(5)	0·2318(3)	0·1561(3)
C(3)	0·0013(6)	0·1021(5)	0·3374(4)
C(4)	0·0616(6)	0·1697(4)	0·4268(5)
C(5)	0·1213(7)	0·0160(4)	0·3566(6)
C(6)	0·2403(7)	0·0672(4)	0·4618(5)
C(7)	0·1992(6)	0·1438(3)	0·4984(4)

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

[2] D. J. Cook, J. L. Dawes, and R. D. W. Kemmitt, *J. Chem. Soc.* (*A*), 1967, 1547.

[3] I. W. Nowell and D. R. Russell, *Chem. Comm.*, 1967, 817.

[4] W. C. Hamilton, J. S. Rollett, and R. A. Sparks, *Acta Cryst.*, 1965, **18**, 129.

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

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

in Table 1, anisotropic temperature factors in Table 2, and some bond distances and angles in Table 3.

TABLE 2

Anisotropic temperature factors (Å^2) *

Atom	B_{11}	B_{22}	B_{33}	B_{23}	B_{13}	B_{12}
Hg	3·69	2·81	2·38	−0·80	0·74	−1·10
Co	1·53	2·27	1·66	−0·06	0·17	0·06
Cl(1)	3·04	2·09	5·97	0·02	−1·51	−0·24
Cl(2)	4·82	4·00	3·38	0·86	0·88	1·29
O(1)	2·2	3·6	6·3	−0·1	−0·2	−2·0
O(2)	7·3	2·5	5·8	3·0	−3·9	−1·7
C(1)	1·9	5·7	3·9	−3·6	−1·6	2·1
C(2) †	2·9					
C(3)	2·5	14·8	2·7	0·5	0·7	−4·2
C(4)	4·9	7·5	6·2	4·6	3·8	4·0
C(5)	5·1	7·0	5·3	0·9	3·0	4·2
C(6)	7·5	7·3	5·8	6·1	3·9	2·8
C(7)	5·2	2·8	0·7	−1·0	0·6	−0·6

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

† C(2) was given an isotropic temperature factor. Estimated errors, based on shifts from the last two cycles of refinement are 0·08 for Hg, 0·20 for Co, 0·35 for Cl, and 0·8 Å^2 for C and O atoms.

TABLE 3

Bond lengths (Å) and angles (°) with estimated standard deviations in parentheses (relevant intermolecular bond lengths and angles are included)

(*a*) Distances

Hg–Co	2·578(4)	Co–C(5)	2·15(6)
Hg–Cl(1)	2·479(9)	Co–C(6)	2·01(4)
Hg–Cl(2)	2·451(10)	Co–C(7)	2·08(4)
Co–C(1)	1·615(39)	C(3)–C(4)	1·34(8)
Co–C(2)	1·705(28)	C(3)–C(5)	1·53(8)
C(1)–O(1)	1·24(5)	C(4)–C(7)	1·31(7)
C(2)–O(2)	1·22(4)	C(5)–C(6)	1·52(9)
Co–C(3)	2·06(4)	C(6)–C(7)	1·16(6)
Co–C(4)	2·02(4)	Hg–Cl(1′)	3·129(9)
		Hg–Cl(2′)	3·195(10)

(*b*) Angles

Co–Hg–Cl(1)	121·2(1)	C(1)–Co–C(7)	105(1)
Co–Hg–Cl(2)	124·8(2)	C(1)–Co–C(6)	98(1)
Cl(1)–Hg–Cl(2)	114·0(2)	C(1)–Co–C(5)	123(1)
Co–C(1)–O(1)	173(6)	C(1)–Co–C(4)	138(1)
Co–C(2)–O(2)	168(9)	C(1)–Co–C(3)	164(3)
C(2)–Co–C(1)	92(1)	C(2)–Co–C(7)	130(1)
C(2)–Co–Hg	86·4(4)	C(2)–Co–C(6)	162(4)
C(1)–Co–Hg	82·1(5)	C(2)–Co–C(5)	138(2)
C(5)–C(3)–C(4)	105(2)	C(2)–Co–C(4)	103(1)
C(3)–C(4)–C(7)	114(4)	C(2)–Co–C(3)	103(1)
C(4)–C(7)–C(6)	109(3)	Co–Hg–Cl(1′)	90·0(1)
C(7)–C(6)–C(5)	116(3)	Cl(1′)–Hg–Cl(1)	83·1(2)
C(6)–C(5)–C(3)	94(3)	Cl(1′)–Hg–Cl(2′)	172·0(5)
Hg–Co–C(7)	143(1)	Cl(2′)–Hg–Cl(2)	85·4(1)
Hg–Co–C(6)	112(1)	Co–Hg–Cl(2′)	94·8(2)
Hg–Co–C(5)	78·9(2)	Cl(1′)–Hg–Cl(2)	97·1(2)
Hg–Co–C(4)	133(2)	Cl(2′)–Hg–Cl(1)	88·9(2)
Hg–Co–C(3)	95·0(5)		

Cl(1′) is at −*x*, −*y*, −*z*, and Cl(2′) is at 1 − *x*, −*y*, −*z*.

DISCUSSION

The complex $(\pi\text{-}C_5H_5)(CO)_2Co,HgCl_2$ is best considered as a 1 : 1 Lewis acid–base adduct (Figure 1) containing a Co–Hg bond, in which mercury(II) chloride behaves as a Lewis acid and dicarbonyl-(π-cyclopentadienyl)cobalt as a Lewis base. The Hg–Co bond length in the present complex, 2·578(4) Å, lies close to the sum of Pauling's single-bond metallic radii[7] (2·55 Å) and the sum of the covalent radii obtained by the method of Bennett and Mason,[8] [2·58 Å taking 1·29 Å for Co, this being the mean Co–C$(\pi\text{-}C_5H_5)$ distance in the present structure, and 1·29 Å for mercury from methylmercury(II) chloride[9]]. The length of this donor–acceptor metal–metal bond is similar to that found in other cobalt–mercury complexes where covalent metal–metal bonding is involved (Table 4).

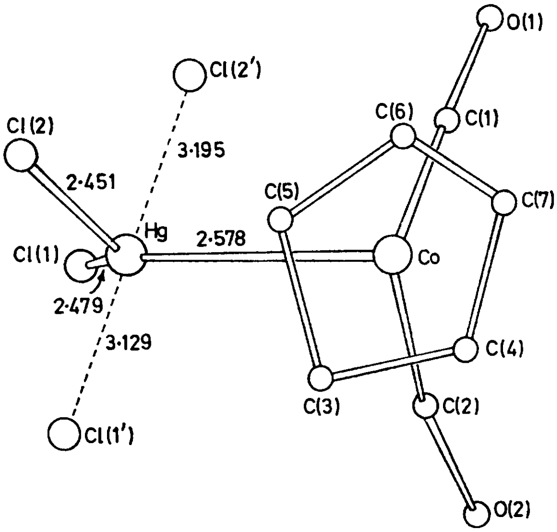

FIGURE 1 The structure projected in the plane of the C_5H_5 ring

TABLE 4

Complex	Hg–Co (Å)
$Hg[Co(CO)_4]_2$	2·498(7) [a] 2·500(7)
$Hg[Co(CO)_3(PEt_3)_2]_2$	2·499(5) [b]
$[\pi\text{-}C_5H_5)Fe(CO)_2HgCo(CO)_4$	2·56 [c]
$(\pi\text{-}C_5H_5)(CO)_2CoHgCl_2$	2·578(4)

[a] G. M. Sheldrick and R. N. F. Simpson, *J. Chem. Soc.* (*A*), 1968, 1005. [b] R. F. Bryan and A. R. Manning, *Chem. Comm.*, 1968, 1316. [c] R. F. Bryan and H. P. Weber, *Acta Cryst.*, 1966, **A21**, 138.

Structures of complexes containing donor–acceptor metal–metal bonds mainly involve d^8 metal systems.[10] The bond formed in the present complex presumably involves donation of formally non-bonding electrons of the cobalt into empty σ orbitals of the mercury. The resulting redistribution of electron density is mirrored by an increase in ν(CO) (from 2017, 1949 to 2074, 2042 cm^{-1}) and a decrease in ν(HgCl) [from 374, 331, 311 to 240(br) cm^{-1}] upon adduct formation.[2]

Mercury(II) chloride forms a large number of adducts with donor molecules[11] and it appears that increasing donor strength is accompanied by a lengthening of the Hg–Cl bond, reduction of the Cl–Hg–Cl bond angle from 180°, and a lowering of the effective co-ordination

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number of mercury.[12] The large distortion of mercury(II) chloride in the present complex indicates that dicarbonyl-(π-cyclopentadienyl)cobalt is behaving as a strong base. The Hg–Cl dstances are considerably increased from the value found in mercury(II) chloride (2·26 Å) [13] and there is a corresponding reduction of the Cl–Hg–Cl bond angle to 114°. The donor strength of dicarbonyl-(π-cyclopentadienyl)cobalt is also reflected in the low co-ordination number of mercury. The trigonal arrangement of atoms around mercury ($CoHgCl_2$) is almost planar (Table 5). The presence of two further chlorine atoms [Cl(1) and Cl(2)] from neighbouring molecules, both within the sum of the van der Waals radii of Hg and Cl (3·3 Å), increases the effective co-ordination number to five. The resulting co-ordination polyhedron is that of an elongated trigonal bipyramid with the neighbouring chlorines occupying axial positions, **3·129** and **3·195** Å from the mercury. Of the many known structures of mercury(II) chloride adducts with typical element bases, that of collidine,[14] $C_5H_2Me_3NHgCl_2$, compares most closely with the present complex. The $HgCl_2$ geometry in the collidine complex shows the greatest departure from that found in mercuric chloride; collidine is also one of the strongest bases. Mercury has a similar co-ordination geometry in the salt Me_3SHgI_3.[15] If the π-cyclopentadienyl ligand is assumed to occupy three co-ordination sites, cobalt has pseudo-octahedral geometry.

TABLE 5

Equations of least-squares planes referred to the orthogonal axis directions *a*, *b*, *c* * with distances (Å) of relevant atoms from the planes given in square brackets

Plane (*a*): $CoHgCl_2$ set of atoms

$$0{\cdot}79979X - 0{\cdot}46266Y + 0{\cdot}38247Z - 1{\cdot}54956 = 0$$

[Co 0·02, Hg −0·005, Cl(1) 0·002, Cl(2) 0·002]

Plane (*b*): C_5H_5 ring

$$-0{\cdot}56807X - 0{\cdot}36548Y + 0{\cdot}73737Z - 1{\cdot}85751 = 0$$

[C(3) −0·014, C(4) 0·000, C(5) 0·023, C(6) −0·030, C(7) 0·021]

The cyclopentadienyl ring is effectively planar (Table 5), all five Co–C(π-C_5H_5) distances are equal within their limits of error (mean 2·06, σ 0·05 Å which is similar to their individual σ values) and the cobalt atom lies 1·70 Å from the best least-squares plane through the cyclopentadienyl ring. This distance is similar to that found in other π-cyclopentadienylcobalt complexes, *e.g.* (π-C_5H_5)Co(MeC_2Me)$_2$(CO) (1·67 Å),[16] (π-C_5H_5)Co(PPh_2) (1·66 Å).[17] The mean Co–C(CO) and C–O distances (1·66 and 1·23 Å) lie within the range of values found for other cobalt complexes: $(CO)_6Co_2$-(PhC_2Ph) (1·75 and 1·23 Å),[18] $Co_3(CO)_5(SEt)_4$ (1·63 and 1·19 Å), and $Co_2(CO)_5(SEt)S_2$ (1·71 and 1·18 Å).[19] Unfortunately, the high standard deviations in the present determination preclude detailed discussion of the distances and angles within the Co(π-C_5H_5)(CO)$_2$ moiety.

Figure 2 shows the packing of the molecules in the unit cell as viewed along the *c* axis direction. Apart from the intermolecular Hg–Cl contacts discussed earlier, other intermolecular distances indicate normal van der Waals interactions.

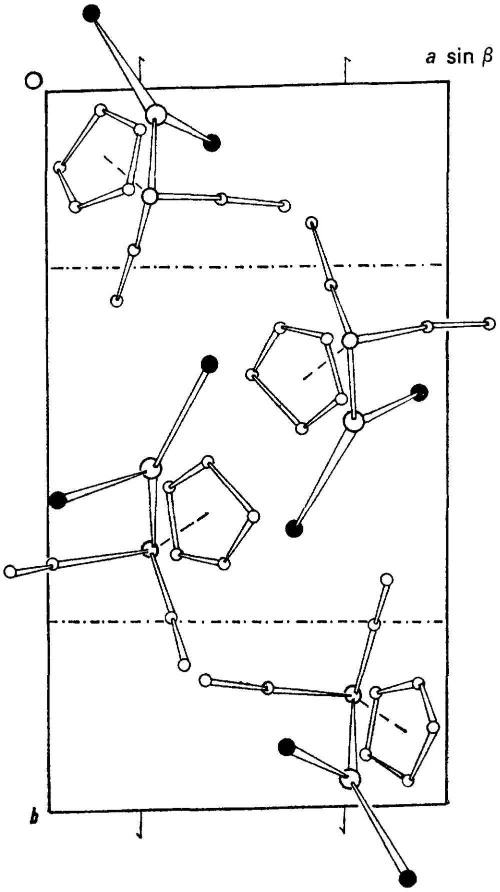

FIGURE 2 The (001) projection of the unit cell

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