Crystal Structure of the Dimeric 1:2 Addition Complex of Tricarbonylmesitylenemolybdenum with Mercury(II) Chloride

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Crystals of the title compound $[\{(C_6H_3Me_3)(CO)_3Mo(HgCl_2)_2\}_2]$ are monoclinic, space group *C*2/*c*, *a* = 17.049(4), *b* = 13.599(3), *c* = 17.249(7) Å, β = 102.54°, *Z* = 8. The structure was determined from diffractometer data by the heavy-atom method and refined by full-matrix least-squares to *R* 0.035 (on F) for 1 598 reflections. The structure consists of centrosymmetric dimers in which the tricarbonylmesitylenemolybdenum groups are bonded to mercury [Mo–Hg 2.745(1) Å]; the central Hg_2Cl_2 four-membered ring has one molybdenum bonded to each mercury. All the mercury atoms are four-co-ordinate; the mercury atoms not bonded to molybdenum are halogen-bridged to the four-membered ring, extending the mercury–halogen network. The mercury–chloride distances range widely from 2.317(5) to 3.038(5) Å.

The upwards shift of 58 cm^{-1} of the averaged i.r. CO stretching frequencies on complex formation is due to this Lewis acid–base bonding.

A NUMBER of compounds of mercury(II) chloride with substituted metal carbonyls, which can be formulated as Lewis base–acid addition complexes have been prepared by Lewis *et al.*[1] They suggested that the 1 : 1 adducts of the type $[(arene)(CO)_3M(HgX_2)_n]$ are neutral and seven-co-ordinate with $[(arene)(CO)_3M]$ acting as a Lewis base, a situation which is similar to that observed in $[(\pi\text{-}C_5H_5)(CO)_2Co(HgCl_2)]$ where the Cl–Hg–Cl group is bent and a definite Co–Hg bond formed.[2]

For the 1 : 2 complexes their suggestion was that either both mercury atoms could be co-ordinated to the metal or an anionic complex such as $[(arene)(CO)_3Mo(HgX)][HgX_3]$ could form. The lability and low solubility of these complexes make measurements of conductance of limited utility in deciding between these formulations. The structure of the 1 : 3 adduct of $[(\pi\text{-}C_5H_5)(CO)_2Co]$ is known to be of this type, $[(\pi\text{-}C_5H_5)(CO)_2Co(HgCl)]^+Cl^-\cdot 2HgCl_2$, with the halide ion dissociated from the co-ordinated mercury.[3] More recently it was confirmed that adducts such as $[(bipy)(CO)_4Mo(HgX_2)_n]$ (bipy = 2,2′-bipyridyl) can decompose by oxidative elimination to produce stable tricarbonyls,[4] $[(bipy)(CO)_3Mo(HgX)X]$, in which both HgX and X are co-ordinated to molybdenum. The structure of $[(mesitylene)(CO)_3Mo(HgCl_2)_2]$ was undertaken to decide between these possibilities.

EXPERIMENTAL

Crystals suitable for structure analysis were prepared by reaction of excess of mercury(II) chloride in acetone with acetone solutions of $[(mesitylene)(CO)_3Mo]$ under nitrogen. The yellow prismatic needles were stable in air and in the dark for up to 6 months and gave the same i.r. ν(CO) frequencies as did the product obtained from dichloromethane.[1]

Preliminary precession photographs (Mo-K_α radiation, Zr filter) established the crystals to be monoclinic, space group *C*2/*c* or *Cc*. Successful analysis showed the former to be correct. The cell parameters were obtained from the ω scans of *h*00, 0*k*0, and 00*l* reflections on a Stoe automatic Weissenberg diffractometer fitted with a graphite monochromator.

Crystal Data.—$C_{12}H_{12}Cl_4Hg_2Mo$, *M* = 843.2, Monoclinic, *a* = 17.049(4), *b* = 13.599(3), *c* = 17.249(7) Å, β = 102.54(5)°, *U* = 3 903.8 Å^3, D_m = 2.96(3), *Z* = 8, D_c = 2.873 g cm^{-3}, *F*(000) = 3 024. λ(Mo-K_α) = 0.7107 Å; μ(Mo-K_α) = 171.8 cm^{-1}. Space group *C*2/*c*.

Intensities were measured on the diffractometer by use of Mo-K_α radiation and the ω-scan technique, with variable scan and scan-time routines previously described.[5] Data about two axes with separate crystals were recorded out to 2θ 45°: crystal (1) was mounted along *b* (0.3 × 0.9 × 2 mm^3) and was used for the *h*0–12*l* data, and crystal (2), of similar size, was used for *hk*0–8 data. Absorption, Lorentz, and polarization corrections were applied, and data from both axes were scaled together by a non-iterative least-squares procedure to give 1 598 unique reflections.

The structure was solved by the heavy-atom method assuming the higher-frequency[6] space group *C*2/*c* to be correct. Full-matrix least-squares refinement employing anisotropic temperature factors for all atoms converged at 0.035 on *F*. The function minimised was $\Sigma w(|F_o| - |F_c|)^2$, where weights *w* were taken as $1/(\sigma^2(|F_o|) + (0.09|F_o|)^2)$.

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TABLE 1

Final positional and thermal * parameters ($\times 10^5$, those for O and C $\times 10^4$)

	X	Y	Z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg(1)	23 987(4)	14 057(4)	−7 358(4)	453(4)	511(4)	450(4)	114(3)	111(3)	−81(3)
Hg(2)	43 674(4)	38 724(5)	−4 157(5)	535(5)	645(5)	728(6)	14(3)	212(4)	−125(4)
Mo	33 148(8)	−359(8)	−12 166(8)	329(6)	357(7)	294(7)	14(5)	49(5)	−18(6)
Cl(1)	41 223(26)	34 766(30)	10 038(28)	339(20)	755(31)	447(24)	−24(19)	34(17)	86(22)
Cl(2)	60 011(27)	44 272(30)	5 873(32)	390(21)	565(27)	651(29)	−4(18)	131(19)	92(22)
Cl(3)	25 895(25)	33 276(25)	−8 391(26)	494(22)	397(23)	381(22)	−43(17)	123(18)	20(18)
Cl(4)	48 711(33)	26 430(31)	−11 000(33)	705(29)	637(30)	617(28)	136(24)	178(23)	−42(25)
O(1)	2 867(9)	1 487(9)	−2 588(9)	91(9)	98(10)	55(8)	20(7)	17(6)	20(7)
O(2)	4 986(8)	256(9)	−1 676(8)	63(7)	110(10)	65(8)	3(7)	33(6)	6(7)
O(3)	4 355(8)	1 023(8)	266(8)	65(7)	75(8)	44(7)	−18(6)	−6(5)	−9(6)
C(1)	2 723(10)	−1 355(10)	−2 042(11)	36(8)	44(9)	57(10)	−13(7)	3(8)	−6(8)
C(2)	3 443(10)	−1 727(10)	−1 580(10)	57(10)	46(10)	26(8)	23(8)	9(7)	−16(7)
C(3)	3 574(9)	−1 657(10)	−743(11)	36(8)	32(9)	45(10)	−33(6)	5(7)	−2(7)
C(4)	2 958(11)	−1 275(10)	−346(11)	56(10)	29(9)	50(10)	−73(7)	12(9)	6(8)
C(5)	2 236(10)	−952(11)	−838(11)	47(9)	51(10)	32(10)	−23(7)	−6(8)	−9(8)
C(6)	2 107(11)	−971(11)	−1 678(13)	43(9)	54(11)	67(14)	−21(8)	8(9)	−25(10)
C(7)	1 291(11)	−655(13)	−2 209(11)	50(9)	84(13)	48(10)	8(9)	−20(8)	−5(9)
C(8)	3 115(12)	−1 248(12)	558(10)	72(11)	90(13)	21(8)	1(9)	5(7)	8(8)
C(9)	4 070(11)	−2 208(13)	−1 982(11)	68(11)	85(13)	51(10)	21(9)	26(9)	−9(9)
C(10)	3 024(11)	964(11)	−2 025(12)	67(11)	56(11)	36(10)	10(8)	9(8)	6(8)
C(11)	4 366(13)	159(12)	−1 522(11)	65(11)	66(12)	31(9)	4(10)	11(8)	8(8)
C(12)	3 943(11)	686(11)	−2 776(12)	47(9)	39(10)	51(11)	1(7)	15(8)	−2(8)

* The form of the anisotropic thermal ellipsoid is $\exp - [\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + 2\beta_{12}hk + 2\beta_{13}hl + 2\beta_{23}kl]$.

TABLE 2

Bond lengths (Å) and angles (°)

(*a*) Bond lengths

Hg(1)–Mo	2.745(1)	C(2)–C(3)	1.412(2)
Hg(1)–Cl(3)	2.645(4)	C(3)–C(4)	1.47(2)
Hg(1)–Cl(3′)	2.736(4)	C(4)–C(5)	1.41(2)
Hg(1)–Cl(1′)	2.538(4)	C(5)–C(6)	1.42(2)
Hg(2)–Cl(1)	2.628(5)	C(6)–C(1)	1.43(2)
Hg(2)–Cl(2)	3.038(5)	C(2)–C(9)	1.54(2)
Hg(2)–Cl(3)	3.051(4)	C(4)–C(8)	1.53(2)
Hg(2)–Cl(4)	2.317(5)	C(6)–C(7)	1.55(2)
Mo–C(10)	1.93(2)	C(10)–O(1)	1.19(2)
Mo–C(11)	1.99(2)	C(11)–O(2)	1.15(2)
Mo–C(12)	1.99(2)	C(12)–O(3)	1.14(2)
C(1)–C(2)	1.41(2)		

(*b*) Angles

Mo–Hg(1)–Cl(3)	110.7(1)	Hg(1)–Mo–C(11)	126.1(5)
Mo–Hg(1)–Cl(1′)	128.0(1)	Hg(1)–Mo–C(12)	69.1(5)
Mo–Hg(1)–Cl(3′)	120.8(1)	C(10)–Mo–C(11)	80(2)
Cl(3′)–Hg(1)–Cl(1′)	87.7(1)	C(10)–Mo–C(12)	104(2)
Cl(3)–Hg(1)–Cl(3′)	87.8(1)	C(11)–Mo–C(12)	78(2)
Cl(3)–Hg(1)–Cl(1′)	93.5(1)	Hg(2)–Cl(1)–Hg(1′)	100.4(2)
Cl(3)–Hg(2)–Cl(4)	99.3(2)	Hg(1)–Cl(3)–Hg(2)	110.7(1)
Cl(3)–Hg(2)–Cl(2)	159.6(1)	Hg(2)–Cl(3)–Hg(1′)	86.4(1)
Cl(3)–Hg(2)–Cl(1)	79.8(1)	Hg(1)–Cl(3)–Hg(1′)	92.2(1)
Cl(2)–Hg(2)–Cl(4)	94.2(2)	Mo–C(10)–O(1)	171(2)
Cl(2)–Hg(2)–Cl(1)	80.3(1)	Mo–C(11)–O(2)	178(2)
Cl(1)–Hg(2)–Cl(4)	118.6(2)	Mo–C(12)–O(3)	173(2)
Hg(1)–Mo–C(10)	69.0(5)		

Primed atoms are related to unprimed atoms by a centre of symmetry at ($\frac{1}{4}$, $\frac{1}{4}$, 0).

TABLE 3

Equation of the best least-squares plane associated with the mesitylene carbon atoms refered to orthogonal axes $X = xa + zc \cos\beta$, $Y = yb$ and $Z = zc \sin\beta$

$$0.41190X + 0.91100Y - 0.020462Z - 0.56060 = 0$$

Distances (Å) of atoms from the plane: C(1) 0.059, C(2) 0.016, C(3) 0.037, C(4), 0.003, C(5) −0.012, C(6) 0.033, C(7) −0.048, C(8) −0.024, C(9) −0.064, Mo 1.952

The numerical multiplier was chosen to give a flat distribution of the function $(\Sigma w(|F_o| - |F_c|)^2)$ averaged in ranges of $|F_o|$ *vs.* $|F_o|$. Hydrogen atoms were not included in the model and the final difference map showed no peaks of height >1.2 e Å^{-3}, which is *ca.* 25% the height of an average carbon peak in earlier difference maps. Scattering factors were taken from ref. 7, those for mercury, molybdenum, and chlorine being corrected for the effects of anomalous scattering ($\Delta f'$, $\Delta f''$).[8] All data processing was carried out on a CDC 6400 computer at the University of Adelaide with programs described previously.[5] Structure-factor tables are given in Supplementary Publication No. SUP 21501 (9 pp, 1 microfiche).* Results are shown in Tables 1—3 with estimated standard deviations in parentheses. Figure

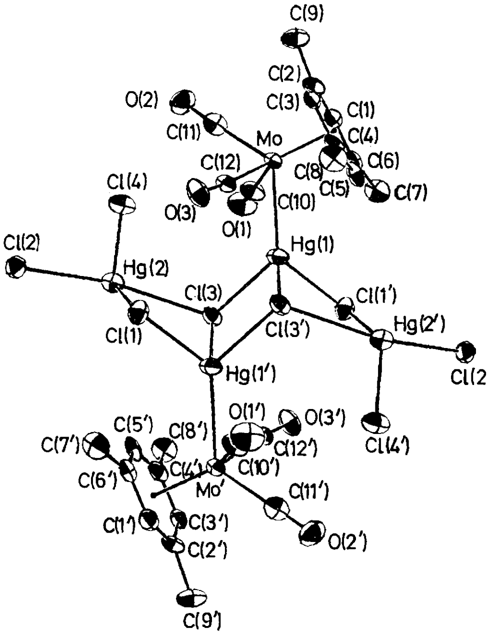

FIGURE 1 The structure showing atoms as 30% probability ellipsoids

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* See Notice to Authors No. 7 in *J.C.S. Dalton*, 1975, Index issue.

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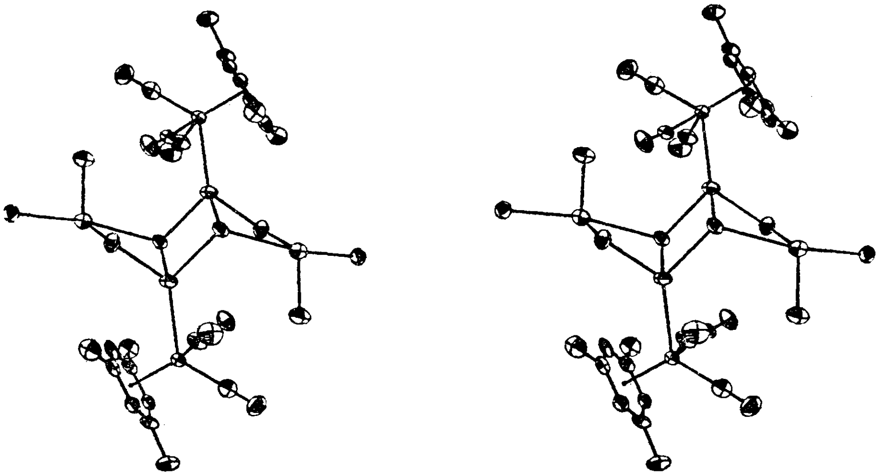

FIGURE 2 Stereoscopic view of the molecular structure viewed down the *z* axis

1 shows the atom labelling scheme and Figure 2 a stereoscopic view of the molecular structure.

DISCUSSION

The structure is comprised of discrete dimeric centrosymmetric molecules $[\{(C_6H_3Me_3)(CO)_3Mo\cdot 2HgCl_2\}_2]$, joined by a network of mercury–chloride bridges. Only one of the mercury atoms is directly bound to the molybdenum atom. The complex, therefore, can be considered as a 1 : 1 Lewis acid–base adduct in which the additional mercury chloride extends the bridge. The Mo–Hg distance [2.745(1) Å] is comparable to the sum of Pauling's single-bond metallic radii for the two atoms (2.736 Å),[9] but significantly longer than that found [2.700(7) Å] in the complex $[(bipy)(CO)_3Mo(HgCl)Cl]$,[4] where mercury has a co-ordination number of only 2. The average increase of 58 cm^{-1} in the i.r. ν(CO) (from 1 960, 1 948, and 1 880, to 2 032, 1 985, 1 946 cm^{-1}) on complex formation is consistent with a bonding model in which formally nonbonding electrons of the molybdenum are donated into empty σ orbitals of the mercury. A similar shift of 61 cm^{-1} was observed in the formation of the adduct $[(\pi\text{-}C_5H_5)Co(CO)_2\cdot HgCl_2]$ from its substrate.[2]

The 1 : 1 complex $[(C_6H_3Me_3)(CO)_3Mo\cdot HgCl_2]$ is reported[1] to be less stable than the 2 : 1 complex; we found it decomposed rapidly in air to a blue product within several hours. The average frequency shift for the 1 : 1 complex is only 33 cm^{-1} suggesting that the Mo–Hg bond is weaker here. It would appear, therefore, that the second mercury chloride in the 1 : 2 complex has a role to play in strengthening the Mo–Hg bond and inhibiting decomposition.

The arrangement of the mercury chloride bridge is unique in the structures of these addition complexes. Each mercury has a distorted tetrahedral co-ordination. Only one Hg–Cl distance approaches that in $HgCl_2$ (2.26 Å),[10] namely Hg(2)–Cl(4) 2.317(5) Å. The other distances vary up to 3.038(5) Å but remain within the sum of the relevant van der Waals radii (3.3 Å).

The co-ordination arrangement about molybdenum resembles that about tungsten in the complex $[(\text{hexamethylbenzene})(CO)_3WI]I_3$.[11] Both complexes have an approximate mirror plane, but in the present addition complex the two carbonyl groups closest together [C(12)–O(3) and C(10)–O(1)] lie under bonds of the benzene nucleus, whereas in the tungsten complex they lie under atoms of the benzene nucleus. The orientation of the benzene nucleus may be determined in part by packing requirements. Thus the orientation found here has no methyl group on C(5); if such a group were present, it would approach Hg(2′) to within *ca.* 3.2 Å. This value is equal to the sum of the van der Wall radii of a non-freely rotating methyl group and mercury.[12]

It can be seen from Table 3 that the methyl carbon atoms are slightly displaced from the average mesitylene plane in the direction away from the molybdenum. The mean displacement from the benzene nucleus plane of these methyl carbons is 0.07 Å. This distortion is statistically significant and can be rationalized by considering a rehybridization at the benzene carbon atoms on bonding to molybdenum.

[5/564 *Received, 24th March,* 1975]

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