Stereochemistry and Bonding in Bis[pentacarbonylmanganese]mercury, Hg[Mn(CO)₅]₂. A Linear, Mercury-Bridged Derivative of Dimanganese Decacarbonyl with an Eclipsed Conformation

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The crystal and molecular structure of bis[pentacarbonylmanganese]mercury, $Hg[Mn(CO)_5]_2$, has been determined by a single-crystal X-ray analysis using three-dimensional X-ray data collected by counter methods. The compound crystallizes in the triclinic system with one molecule in a centrosymmetric unit cell of lattice parameters a = 6.3296 (11) Å, b = 9.4837 (15) Å, c = 6.3332 (11) Å, α = 97.478 (6)°, β = 81.668 (6)°, and γ = 90.816 (6)°. The calculated density of 2.63 g/cm³ agrees well with the experimental density of 2.61 g/cm³. Structural refinement by full-matrix least-squares yielded a final unweighted R factor of 5.5% for 1295 independent observed reflections. $Hg[Mn(CO)_5]_2$ consists of discrete molecules which are required crystallographically to have C_i-$\bar{1}$ symmetry. The coordination of the $Mn(CO)_5$ groups about the mercury atom is linear, and each manganese atom is octahedrally coordinated to five carbonyl groups and the mercury atom. The four equatorial carbonyls in each half of the molecule are bent toward the mercury atom with an average $Hg-Mn-C_{eq}$ angle of 84.3 (2)°. The molecule possesses approximate point group symmetry of D_{4h}-$4/m2/m2/m$; the equatorial carbonyls on one of the manganese atoms are approximately eclipsed with respect to those on the other manganese. The Hg–Mn bond length is 2.610 (2) Å, slightly shorter than that expected from the sum of the covalent radii. This shortening is attributed to $d\pi$–$p\pi$ bonding and/or to direct interaction of the Hg atom with the equatorial carbonyls on the adjacent Mn atom. The axial Mn–C distance is 1.810 (14) Å and the average equatorial distance is 1.848 (8) Å. The mean C–O distance is 1.154 (10) Å. Complete mass spectral data are presented.

Introduction

There has been much interest in the chemistry and structure of the group IIb derivatives of transition metal carbonyls. Several syntheses,[1-8] infrared and Raman spectral studies,[8-14] and crystal structure analyses[2,15-18] have been reported. During the years immediately following the discovery of $Hg[Co(CO)_4]_2$, compounds of this type were thought to contain bridging carbonyl groups.[1-3] More recently, studies by Bor and Markó[9] led to the conclusions (1) that bridging carbonyl groups were absent and (2) that there exists a fairly high molecular symmetry compatible with a D_{3h} or D_{3d} conformation. A complete Raman study of $Cd[Co(CO)_4]_2$ and a partial study of $Hg[Co(CO)_4]_2$ established the staggered D_{3d} configuration for these compounds.[10] This was verified by an X-ray structural study of the latter compound.[15] Structural studies of other molecules of this type[16,17] have shown that all possess nonbridged metal–metal bonds, with linear coordination about the mercury atom. The similarity of these compounds to the

organomercurials, both in structure and reactivity,[4,8] makes them potentially useful tools in the fields of catalysis[19] and organometallic synthesis.

The synthesis of bis(pentacarbonylmanganese)-mercury, $Hg[Mn(CO)_5]_2$, was first reported by Hieber and Schropp in 1960.[5] Shortly thereafter, King[6] reported the formation of this compound as a by-product in the preparation of the $Mn(CO)_5^-$ anion *via* the sodium amalgam route. More recently, Burlitch and Ferrari[4] have reported an improved synthesis of this compound. There have been several studies of the infrared and Raman spectra of $Hg[Mn(CO)_5]_2$.[8,11-13] All of the data are consistent with a linear Mn–Hg–Mn framework and a molecular symmetry of D_{4h} or D_{4d}.[20] In a more recent infrared study of substituted derivatives of the type $Hg[Mn(CO)_4L]_2$, the author proposed a bent Mn–Hg–Mn framework based on solution spectral data.[14]

Because there has been interest in the structure and reactivity of this compound and since there have been no X-ray structural studies of compounds containing mercury–manganese bonds,[21,22] we have undertaken this study to gain further insight into the stereochemistry and bonding in this type of compound.

Experimental Section

Infrared and Mass Spectral Characterization.—Yellow needle-like crystals of $Hg[Mn(CO)_5]_2$ were generously supplied to us by Dr. J. J. Benedict. Their composition was confirmed by infrared and mass spectral analysis. An expanded-scale spectrum taken on a Perkin-Elmer Model 421 infrared spectrometer with CsI plates showed bands at 2059 (s), 2006 (s, sh), 1969 (vs), and 633 (s) cm⁻¹ which were in good agreement with the values previously reported.[5,7,8] Mass spectral data were obtained on an AEI MS902 instrument by direct insertion at 70 eV with a source temperature of 180°. These data are tabulated in Table I.

(1) W. Hieber in "FIAT—Review of German Science, 1939-1946," Vol. 24, Part II, Dieterich'sche Verlagsbuchhandlung, Wiesbaden, Germany, 1948, p 125.

(2) W. Hieber and U. Teller, *Z. Anorg. Allg. Chem.*, **249**, 43 (1942).

(3) J. S. Anderson, *Quart. Rev., Chem. Soc.*, **1**, 331 (1947).

(4) J. M. Burlitch and A. Ferrari, *Inorg. Chem.*, **9**, 563 (1970).

(5) W. Hieber and W. Schropp Jr., *Chem. Ber.*, **93**, 455 (1960).

(6) R. B. King, *J. Inorg. Nucl. Chem.*, **25**, 1296 (1963).

(7) J. M. Burlitch, *Chem. Commun.*, 887 (1968).

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(10) H. Stammreich, K. Kawai, O. Sala, and P. Krumholz, *J. Chem. Phys.*, **35**, 2175 (1961).

(11) D. M. Adams and A. Squire, *J. Chem. Soc. A*, 2817 (1968).

(12) P. N. Brier, A. A. Chalmers, J. Lewis, and S. B. Wild, *ibid.*, 1889 (1967).

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(14) D. J. Parker, *J. Chem. Soc. A*, 246 (1969).

(15) G. M. Sheldrick and R. N. F. Simpson, *ibid.*, 1005 (1968).

(16) R. F. Bryan and H. P. Weber, *Acta Crystallogr., Sect. A*, **21**, 138 (1966).

(17) R. F. Bryan and A. R. Manning, *Chem. Commun.*, 1316 (1968).

(18) B. Lee, J. M. Burlitch, and J. L. Hoard, *J. Amer. Chem. Soc.*, **89**, 6362 (1967).

(19) G. N. Schrauzer, B. N. Bastian, and G. A. Fosselius, *ibid.*, **88**, 4890 (1966).

(20) Although the point group symmetry for this molecule was stated to be D_{4d} in one of these studies,[12] there is no spectral evidence for this choice over that of D_{4h}.

(21) The structure of the alloy Mn_2Hg_5 has been elucidated,[22] but it is regarded as alternate layers of mercury and manganese atoms.

(22) J. F. deWet, *Acta Crystallogr.*, **14**, 733 (1961).

<div style="text-align:center">

TABLE I

MASS SPECTRAL DATA FOR $Hg[Mn(CO)_5]_2$

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Ion	m/e	Intens[a,b]	Ion	m/e	Intens[a,b]
$HgMn_2(CO)_{10}^+$	592	23.5	$Mn_2(CO)_4^+$	222	100
$HgMn_2(CO)_7^+$	508	<0.5	$Mn_2(CO)_3^+$	194	40
$HgMn_2(CO)_6^+$	480	0.9	$Mn_2(CO)_2^+$	166	40
$HgMn_2(CO)_5^+$	452	36.2	Mn_2CO^+	138	3.7
$HgMn_2(CO)_4^+$	424	<0.5	Mn_2C^+	122	2
$HgMn(CO)_5^+$	397	48.6	Mn_2^+	110	47
$HgMn_2(CO)_2^+$	368	8.7	$Mn_2(CO_3)^{2+}$	97	1.3
$HgMn_2CO^+$	340	2	$Mn(CO)_5^+$	195	17.8
$HgMn_2^+$	312	48.6	$Mn(CO)_4^+$	167	4.3
$HgMnCO^+$	285	3.4	$Mn(CO)_3^+$	139	13.4
$HgMn^+$	257	34	$Mn(CO)_2^+$	111	7.1
Hg^+	202	45.3	$Mn(CO)C^+$	95	2.2
Hg^{2+}	101	4.4	$MnCO^+$	83	12
$Mn_2(CO)_{10}^+$	390	<0.1	MnC^+	67	2.7
$Mn_2(CO)_9^+$	362	0.15	$Mn(CO)_2^{2+}$	55.5	0.5
$Mn_2(CO)_7^+$	306	1.7	Mn^+	55	72
$Mn_2(CO)_6^+$	278	1.9	$Mn(CO)^{2+}$	41.5	1.0
$Mn_2(CO)_5^+$	250	78			

[a] Intensity values refer to all elements being monoisotopic, and are presented as relative ion abundances with respect to the base peak at m/e 222. The per cent of the total ionization, σ, for a given fragment, may be calculated by multiplying the intensity value given by 0.474 for all mercury-containing peaks and by 0.141 for all other peaks. [b] Values within 1% accuracy were conveniently obtained by use of a variable scale which was designed in these laboratories and is described elsewhere: M. L. Katcher, *J. Chem. Educ.*, in press.

A high-resolution measurement of the exact mass of the molecular ion was used to verify the elemental composition of the compound. m/e: calculated for $^{202}Hg^{55}Mn_2{}^{12}C_{10}{}^{16}O_{10}$, 591.7959; found, 591.7955 ± 0.0029. The molecular ion cluster and all fragment ion clusters with m/e greater than 390 showed the characteristic isotopic distribution of mercury (Figure 1).

X-Ray Data Collection.—The crystals of $Hg[Mn(CO)_5]_2$ are triclinic parallelepipeds elongated in the direction of the c axis. For the X-ray investigation a crystal of dimensions 0.28 × 0.22 × 0.09 mm along the [001], [100], and [010] directions, respectively, was cemented to the end of a thin glass fiber. Preliminary Weissenberg and precession photographs indicated a triclinic cell of either $P1$ or $P\bar{1}$ symmetry. The choice of $P\bar{1}$ as the probable space group was confirmed by the satisfactory refinement of the structure. After optical and X-ray alignment on a Datex-automated General Electric XRD-5 diffractometer,[23] 18 reflections were carefully centered with Mo Kα radiation (λ 0.7107 Å). The angle settings obtained were used in the least-squares program ANGSET[24] to calculate the following lattice parameters: a = 6.3296 (11) Å, b = 9.4837 (15) Å, c = 6.3332 (11) Å, α = 97.478 (6)°, β = 81.668 (6)°, γ = 90.816 (6)°.[25,26] The volume of the unit cell is 372.08 Å³. The experimental density of 2.61 ± 0.02 g/cm³ obtained by flotation methods agrees well with a calculated density of 2.629 g/cm³ based on one molecule per unit cell.

Intensity data were collected on the same diffractometer equipped with a scintillation counter and pulse-height analyzer designed to admit 90% of the Zr-filtered Mo Kα radiation. The intensity of all independent reflections within the sphere θ < 25.0° was measured *via* a θ-2θ scan technique with (stationary-crystal, stationary-counter) background measurements on both sides of the peak. Symmetric scans of 1.50° were employed for reflections with $2\theta \geq 16°$, and a scan width of 1.80° was used for $2\theta < 16°$. The scan speed was 2°/min, and 12.5-sec background counts were taken before and after each scan. All reflections were sampled at least twice. Prime evidence that the

resultant data are of high quality is given by the overall excellent agreement in the intensities ($<2\sigma(I)$) for a given independent reflection.

Four reflections were sampled approximately every 3 hr and were used as standards for crystal alignment, decay, and instrument stability. No significant changes (>3%) in the intensities of these standard reflections were observed throughout the data collection. The criterion used for considering a reflection to be statistically observed was that the integrated intensity (I) should be greater than twice the standard deviation of the intensity, $\sigma(I)$. The integrated intensity is calculated by the formula $I = S - B(T/t)$, where S is the total scan count measured for time T and B is the total background count measured for time t. The standard deviations of the intensities are given by $\sigma(I) = [S + B(T/t)^2 + (\rho I)^2]^{1/2}$, where ρ, the conventional ignorance factor, has the value of 0.05. All data were corrected for Lorentz and polarization effects, reduced to F_o's,[27] and merged.[28] Thus, a set of 1295 independent reflections was obtained. The linear absorption coefficient for Mo Kα radiation is 122.71 cm⁻¹. Since the transmission factors varied from 0.10 to 0.34, an absorption correction was also applied to the individual F_o's.[29] No corrections for extinction were made since the strong reflections at low (sin θ)/λ showed no systematic deviations from the calculated values.

Solution of the Structure

A three-dimensional Patterson map[30] calculated from the observed structure factors yielded two collinear vectors of 2.6 and 5.2 Å in length with approximate intensity ratio of 3:1. These were readily interpreted as corresponding to Hg–Mn and Mn–Mn vectors, respectively, which indicated a linear Mn–Hg–Mn framework. A Fourier synthesis[30] based on this model, which gave reliability indices of R_1 = 45.1% and R_2 = 68.1%, indicated the location of the ten carbonyls. Refinement[31,32] by full-matrix isotropic least squares resulted in reliability indices of R_1 = 10.2% and R_2 = 12.6%. The thermal parameters of all atoms were varied anistropically in the subsequent refinements. This latter thermal model resulted, at convergence, in final

Figure 1.—Approximate isotopic distribution of mercury as exemplified by the parent peak cluster in the mass spectrum of $Hg[Mn(CO)_5]_2$.

(23) T. C. Furnas, "Single Crystal Orienter Instructuion Manual," General Electric Co., Milwaukee, Wis., 1957.

(24) A. S. Foust, Ph.D. Thesis, University of Wisconsin, Madison, Wis., Jan 1970.

(25) The conventional reduced cell has parameters a' = 6.3296 (11) Å, b' = 9.4837 (15) Å, c' = 8.2798 (14) Å, α' = 95.0866 (6)°, β' = 130.8151 (8)°, γ' = 90.8160 (6)°.[26]

(26) The matrix used in the transormation is

$$\begin{pmatrix} a' \\ b' \\ c' \end{pmatrix} = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ -1 & 0 & 1 \end{pmatrix} \begin{pmatrix} a \\ b \\ c \end{pmatrix}$$
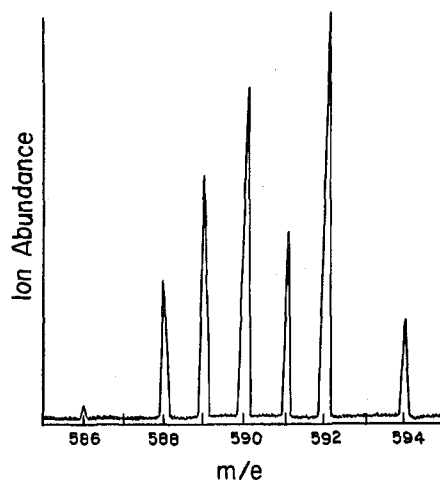
(27) DREDGE, a local Fortran program for diffractometry data reduction, University of Wisconsin, Madison, Wis., 1968.

(28) J. Calabrese, SORTMEROE, Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1971.

(29) J. F. Blount, DEAR, an absorption correction program based on the methods of W. R. Busing and H. A. Levy, *Acta Crystallogr.*, **10**, 180 (1957).

(30) J. F. Blount, "A Three Dimensional Crystallographic Fourier Summation Program for the CDC Computers," Ph.D. Thesis (Appendix), University of Wisconsin, Madison, Wis., 1965.

(31) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFLS, A Fortran Crystallographic Least-Squares Program," ORNL-TM-305, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1963.

(32) The function minimized was $\Sigma w_i(\Delta F_i)^2$ where the weights were assigned according to the estimated standard deviation of the structure factors. The unweighted and weighted residuals are defined respectively as follows: $R_1 = 100[\Sigma||F_o| - |F_c||/\Sigma|F_o|]$ and $R_2 = 100[\Sigma w||F_o| - |F_c||^2/\Sigma w|F_o|^2]^{1/2}$.

TABLE II

FINAL POSITIONAL AND ANISOTROPIC THERMAL ($\times 10^3$) PARAMETERS FOR Hg[Mn(CO)$_5$]$_2$[a,b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Hg[c]	0	0	0	19.5 (2)	4.7 (1)	19.7 (2)	−0.7 (1)	−3.5 (1)	−1.4 (1)
Mn	0.1330 (3)	0.2406 (2)	0.1840 (3)	17.7 (5)	4.5 (2)	18.6 (6)	0.0 (2)	−3.1 (4)	−0.7 (3)
C(1)	0.2266 (22)	0.4064 (14)	0.3140 (22)	25 (3)	6 (1)	20 (4)	−1 (2)	−1 (3)	−2 (2)
O(1)	0.2810 (22)	0.5133 (13)	0.4000 (22)	41 (4)	9 (1)	39 (4)	−5 (2)	−10 (3)	−4 (2)
C(2)	−0.1099 (22)	0.3178 (15)	0.1110 (25)	21 (3)	7 (2)	30 (5)	0 (2)	−2 (3)	2 (2)
O(2)	−0.2588 (20)	0.3689 (15)	0.0691 (24)	32 (4)	15 (2)	47 (5)	8 (2)	−10 (3)	5 (2)
C(3)	0.3592 (22)	0.1334 (15)	0.2325 (24)	23 (4)	7 (2)	26 (4)	1 (2)	−1 (3)	0 (2)
O(3)	0.5007 (18)	0.0704 (14)	0.2624 (22)	26 (3)	14 (1)	43 (5)	5 (2)	−8 (3)	4 (2)
C(4)	−0.0268 (21)	0.1876 (14)	0.4272 (25)	20 (3)	7 (1)	29 (5)	2 (2)	−7 (3)	−1 (2)
O(4)	−0.1240 (19)	0.1575 (14)	0.5867 (19)	35 (3)	14 (2)	26 (3)	0 (2)	5 (3)	3 (2)
C(5)	0.2715 (23)	0.2577 (16)	−0.0891 (29)	23 (4)	8 (2)	35 (6)	0 (2)	−9 (4)	−3 (2)
O(5)	0.3599 (20)	0.2719 (15)	−0.2582 (18)	38 (4)	19 (2)	20 (3)	−6 (2)	0 (3)	4 (2)

a In this and subsequent tables, the estimated standard deviations of the last significant figure(s) are given in parentheses. *b* Anisotropic thermal parameters are of the form $\exp[-(h^2\beta_{11} + k^2\beta_{22} + l^2\beta_{33} + 2hk\beta_{12} + 2hl\beta_{13} + 2kl\beta_{23})]$. *c* The positional parameters for the Hg atom are fixed by the C_i-$\bar{1}$ symmetry.
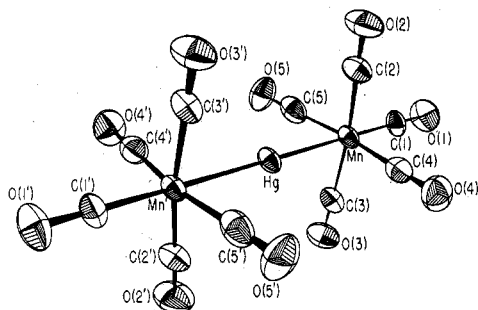

Figure 2.—The 50% probability ellipsoids of Hg[Mn(CO)$_5$]$_2$ which has idealized D_{4h}-$4/m2/m2/m$ geometry and C_i-$\bar{1}$ crystallographic site symmetry.

residuals of $R_1 = 5.5\%$ and $R_2 = 7.6\%$. In the last least-squares cycle no parameter shifted by more than $1/20$th of its standard deviation ($\Delta/\sigma = 0.05$). The final goodness of fit parameter was 2.68 which indicates an underestimation in the standard deviations of the intensity data.

The scattering factor tables used throughout the refinement were those of Hanson, *et al.*[33] Corrections for real and imaginary anomalous dispersion for Hg ($\Delta f' = -2.6$, $\Delta f'' = 10.6$) and for Mn ($\Delta f' = 0.4$, $\Delta f'' = 0.9$) were included in the structure factor calculation.[34]

Table II contains the positional and thermal parameters along with estimated standard deviations from the output of the last cycle.[35] The molecular structure is shown[36] in Figure 2 where the numbering system can be found. Interatomic distances and angles with estimated standard deviations[37] are given in Table III, while in Table IV the equations and parameters of interest for some least-squares planes are listed.[38]

Discussion

The mass spectral data of Hg[Mn(CO)$_5$]$_2$ (Table I) show a moderately intense molecular ion with the

(33) H. P. Hanson, F. Herman, J. D. Lea, and S. Skillman, *Acta Crystallogr.*, **17**, 1040 (1964).

(34) D. H. Templeton in "International Tables for X-Ray Crystallography," Vol. III, Kynoch Press, Birmingham, England, 1962, p 215.

(35) A listing of observed and calculated structure factor amplitudes derived from the final least squares cycle will appear following these pages in the microfilm edition of this volume of the journal. Single copies may be obtained from the Business Operations Office, Books and Journals Division, American Chemical Society, 1155 Sixteenth St., N.W., Washington, D. C. 20036, by referring to code number INORG-72-1651. Remit check or money order for $3.00 for photocopy or $2.00 for microfiche.

(36) C. K. Johnson, "ORTEP, A Fortran Thermal-Ellipsoid Plot Program for Crystal Structure Illustration," ORNL-3794, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1965.

(37) W. R. Busing, K. O. Martin, and H. A. Levy, "ORFFE, A Fortran Crystallographic Function and Error Program," ORNL-TM-306, Oak Ridge National Laboratory, Oak Ridge, Tenn., 1964.

(38) D. L. Smith, "A Least-Square Planes Program for the CDC 1604 Computer," Ph.D. Thesis (Appendix IV), University of Wisconsin, Madison, Wis., 1962.

expected isotopic distribution (Figure 1). The outstanding feature of the high-mass portion of the spectrum is a trimetallic series which shows successive loss of ten carbonyls. In addition to the molecular ion, the most abundant fragments in this series were HgMn$_2$(CO)$_5$$^+$ and HgMn$_2$$^+$. The base peak was that of the Mn$_2$(CO)$_4$$^+$ fragment, and no metastable ions were observed. This fragmentation pattern is very similar to those indicated for other molecules of this type.[4,7]

Three bands were present in the infrared spectrum in the terminal carbonyl stretching region, *ca.* 2000 cm^{-1}. The close resemblance of this spectrum to those of Zn[Mn(CO)$_5$]$_2$ and Cd[Mn(CO)$_5$]$_2$ suggested that all three molecules are isosteric.[7] Although in M[Co(CO)$_4$]$_2$ (M = Zn, Cd, Hg) it is possible to differentiate between an eclipsed D_{3h} and a staggered D_{3d} conformation by Raman spectroscopy (the former symmetry has four Raman-active carbonyl stretching vibrations, while the latter has three), it is not possible to determine in this manner whether Hg[Mn(CO)$_5$]$_2$ has D_{4h} or D_{4d} geometry.[39] Thus, it was necessary to perform an X-ray structural analysis in order to elucidate the stereochemical conformation of Hg[Mn(CO)$_5$]$_2$.

The structure of bis(pentacarbonylmanganese)-mercury (Figure 2) consists of discrete molecules of geometry approximately corresponding to point group symmetry D_{4h}-$4/m2/m2/m$. Since the mercury atom is located on a crystallographic center of symmetry, the Mn–Hg–Mn bond angle is required to be 180°. Each manganese atom is octahedrally coordinated to five carbonyl groups and the mercury atom such that the two sets of four equatorial carbonyl groups are in an eclipsed conformation. The distortion of the molecule from D_{4h} geometry is small. This is evident not only from a comparison of the chemically equivalent molecular parameters (Table III) but also from the dihedral angle between the two mean least-squares vertical planes containing the molecular axis (Table IV, planes 3 and 4) which deviates only slightly (*viz.*, 0.3°) from the value of 90° required for perfect fourfold symmetry.

The eclipsed D_{4h} conformation of this molecule is similar to that found in the [Cr$_2$(CO)$_{10}$H]$^-$ anion[40] but differs from the staggered D_{4d}-$\bar{8}2m$ symmetry

(39) For a complete discussion and normal vibrational analysis, see M. L. Katcher, Ph.D. Thesis, University of Wisconsin, Madison, Wis., 1972.

(40) L. B. Handy, J. K. Ruff, and L. F. Dahl, *J. Amer. Chem. Soc.*, **92**, 7312 (1970).

TABLE III

INTERATOMIC DISTANCES (Å) AND ANGLES (DEG)

FOR Hg[Mn(CO)₅]₂

A. Bond Lengths

Mercury to Manganese		Manganese to Axial Carbonyl Carbon	
Hg–Mn	2.610 (2)	Mn–C(1)	1.810 (14)

Manganese to Equatorial Carbonyl Carbon		Carbonyl Carbon to Oxygen	
Mn–C(2)	1.854 (14)	C(1)–O(1)	1.159 (18)
Mn–C(3)	1.852 (15)	C(2)–O(2)	1.146 (19)
Mn–C(4)	1.839 (16)	C(3)–O(3)	1.135 (18)
Mn–C(5)	1.848 (19)	C(4)–O(4)	1.171 (19)
Av	1.848 (8)	C(5)–O(5)	1.157 (21)
		Av	1.154 (10)

B. Interatomic Angles

Manganese–Mercury–Manganese

Mn–Hg–Mn 180.0 (required by symmetry)

Mercury-Manganese- Equatorial Carbonyl Carbon		Equatorial Carbon- Manganese-Equatorial Carbon	
Hg–Mn–C(2)	85.1 (5)	C(2)–Mn–C(4)	89.6 (6)
Hg–Mn–C(3)	84.6 (4)	C(4)–Mn–C(3)	89.5 (6)
Hg–Mn–C(4)	83.7 (4)	C(3)–Mn–C(5)	89.8 (7)
Hg–Mn–C(5)	83.9 (5)	C(5)–Mn–C(2)	88.9 (7)
Av	84.3 (2)	Av	89.4 (4)

Mercury-Manganese- Equatorial Carbonyl Oxygen		C(2)–Mn–C(3)	169.8 (7)
Hg–Mn···O(2)	85.8 (3)	C(4)–Mn–C(5)	167.6 (6)
Hg–Mn···O(3)	85.2 (3)	Av	168.7 (5)
Hg–Mn···O(4)	84.6 (3)		
Hg–Mn···O(5)	84.6 (3)	Equatorial Carbon- Manganese-Axial Carbon	
Av	85.0 (2)	C(2)–Mn–C(1)	95.5 (6)
		C(3)–Mn–C(1)	94.8 (6)
Mercury-Manganese- Axial Carbonyl Carbon		C(4)–Mn–C(1)	95.9 (6)
Hg–Mn–C(1)	179.3 (5)	C(5)–Mn–C(1)	96.5 (6)
		Av	95.7 (3)

Mercury-Manganese- Axial Carbonyl Oxygen		Manganese-Carbon-Oxygen	
Hg–Mn···O(1)	179.1 (3)	Mn–C(1)–O(1)	178.1 (13)
		Mn–C(2)–O(2)	178.1 (14)
		Mn–C(3)–O(3)	178.4 (13)
		Mn–C(4)–O(4)	177.4 (13)
		Mn–C(5)–O(5)	178.2 (14)
		Av	178.0 (7)

C. Intramolecular Nonbonding Distances

Manganese to Equatorial Carbonyl Oxygen		Within the Mn(CO)₅ Fragment	
Mn···O(2)	3.000 (11)	C(1)···C(2)	2.712 (20)
Mn···O(3)	2.987 (11)	C(1)···C(3)	2.695 (19)
Mn···O(4)	3.010 (11)	C(1)···C(4)	2.711 (20)
Mn···O(5)	3.005 (11)	C(1)···C(5)	2.730 (21)
Av	3.000 (6)	Av	2.712 (10)

Manganese to Axial Carbonyl Oxygen		C(2)···C(4)	2.603 (21)
		C(2)···C(5)	2.593 (21)
Mn···O(1)	2.969 (11)	C(3)···C(4)	2.599 (20)
		C(3)···C(5)	2.612 (24)
Mercury to Equatorial Carbonyl Carbon		Av	2.602 (11)
Hg···C(2)	3.070 (14)		
Hg···C(3)	3.056 (15)		
Hg···C(4)	3.023 (14)		
Hg···C(5)	3.034 (16)		
Av	3.046 (7)		

D. Selected Intermolecular Nonbonding Distances

Hg···O(3)	x − 1, y, z	3.383 (12)
Hg···O(4)	x, y, z − 1	3.368 (12)
O(1)···O(4)	x̄, 1 − y, 1 − z	3.277 (18)
O(1)···C(4)	x̄, 1 − y, 1 − z	3.262 (18)
O(1)···O(1)	1 − x, 1 − y, 1 − z	3.237 (27)
O(1)···O(5)	1 − x, 1 − y, z̄	3.143 (17)

TABLE IV

LEAST-SQUARES PLANES, PERPENDICULAR DISTANCES

(Å) OF SELECTED ATOMS FROM THESE PLANES, AND

DIHEDRAL ANGLES (DEG) BETWEEN NORMALS TO

THE PLANES FOR Hg[Mn(CO)₅]₂[a]

Plane 1: Equatorial Carbonyl Carbons

Equation of the Plane:

$$-0.378X - 0.815Y - 0.440Z + 2.428 = 0$$

Defining atoms	Δ	Other atoms	Δ
C(2)	−0.017	Hg	2.428
C(3)	−0.017	Mn	−0.182
C(4)	0.017	O(2)	0.048
C(5)	0.017	O(3)	0.056
		O(4)	0.094
		O(5)	0.107

Plane 2: Equatorial Carbonyl Oxygens

Equation of the Plane:

$$-0.380X - 0.814Y - 0.439Z + 2.351 = 0$$

Defining atoms	Δ	Other atoms	Δ
O(2)	−0.024	Hg	2.351
O(3)	−0.024	Mn	−0.259
O(4)	0.024	C(2)	−0.091
O(5)	0.024	C(3)	−0.096
		C(4)	−0.055
		C(5)	−0.063

Plane 3: Approximate Vertical Mirror Plane 1

along the Molecular Axis

Equation of the Plane: $0.387X + 0.293Y - 0.875Z = 0$

Atoms	Δ	Atoms	Δ
Hg	0.000	C(2)	0.006
Mn	0.002	C(2)′	−0.006
Mn′	−0.002	C(3)	0.006
C(1)	−0.008	C(3)′	−0.006
C(1)′	0.008		

Plane 4: Approximate Verticle Mirror Plane 2

along the Molecular Axis

Equation of the Plane: $-0.844X + 0.497Y - 0.202Z = 0$

Atoms	Δ	Atoms	Δ
Hg	0.000	C(4)	0.010
Mn	0.004	C(4)′	−0.010
Mn′	−0.004	C(5)	0.010
C(1)	−0.013	C(5)′	−0.010
C(1)′	0.013		

Dihedral Angles between Normals to Planes

Planes	Angle	Planes	Angle	Planes	Angle
1–3	90.8	2–3	90.1	3–4	90.3
1–4	89.8	2–4	89.8		

[a] The equation of the plane is expressed in orthogonal ångström coordinates (X, Y, Z) which are related to the fractional triclinic crystallographic coordinates (x, y, z) by the transformation: $X = ax + b(\cos \gamma)y + c(\cos \beta)z$; $Y = b(\sin \gamma)y + [c(\cos \alpha - \cos \beta \cos \gamma)/\sin \gamma]z$; $Z = c[\sin^2 \beta - (\cos \alpha - \cos \beta \cos \gamma)^2/\sin^2 \gamma]^{1/2}z$. All atoms were assigned unit weights in the calculations.

of Mn₂(CO)₁₀,[41,42] Tc₂(CO)₁₀,[43] [Cr₂(CO)₁₀]²⁻,[40] [Mo₂(CO)₁₀]²⁻,[40] [Co₂(CN)₁₀]⁶⁻,[44] and [Co₂(CNCH₃)₁₀]⁴⁺.[45] The staggered conformation of the [M₂L₁₀]ᶻ species has been attributed to intramolecular repulsion between the equatorial ligands of the two halves of the molecule. Insertion of an atom in the metal–metal bond of these bimetallic metal carbonyls results in separation of the halves of the molecule, thereby

(41) L. F. Dahl and R. E. Rundle, *Acta Crystallogr.*, **16**, 419 (1963).

(42) A. Almenninger, G. G. Jacobsen, and H. M. Seip, *Acta Chem. Scand.*, **23**, 685 (1969).

(43) M. F. Bailey and L. F. Dahl, *Inorg. Chem.*, **4**, 1140 (1965).

(44) G. L. Simon, A. W. Adamson, and L. F. Dahl, *J. Amer. Chem. Soc.*, in press.

(45) F. A. Cotton, T. G. Dunne, and J. S. Wood, *Inorg. Chem.*, **3**, 1495 (1964).

decreasing this repulsion. Molecules of this type may be compared by an examination of the calculated distance between the two mean least-squares planes each containing the four equatorial carbonyl carbons in half of the molecule. In the bimetallic metal carbonyls $[M_2(CO)_{10}]^z$ this distance is typically of the range 2.68–2.85 Å. In the protonated bimetallic carbonyl anion $[Cr_2(CO)_{10}H]^{-40}$ this distance is 3.35 Å, and in the μ-mercurio compound $Hg[Mn(CO)_5]_2$ this value is 4.85 Å. Handy, Ruff, and Dahl[40] have attributed the eclipsed conformation of the $[Cr_2(CO)_{10}H]^-$ anion to the proposition that the distance between the two $Cr(CO)_5$ groups places the equatorial carbons in the region in which the attractive van der Waals forces are dominant. This is not true in the case of $[M_2(CO)_{10}]^z$ where the $M(CO)_5$ moieties are sufficiently close together that the repulsive forces dominate and the molecule assumes a staggered conformation. By these considerations, the van der Waals forces in $Hg[Mn-(CO)_5]_2$ should be attractive, although less than in $[Cr_2(CO)_{10}H]^-$, due to the increased distance between the $Mn(CO)_5$ moieties. But consideration of these slight attractive forces alone cannot account for the eclipsed conformation in $Hg[Mn(CO)_5]_2$; for in both $Zn[Co(CO)_4]_2{}^{18}$ and $Hg[Co(CO)_4]_2{}^{15}$ the staggered $D_{3d}\text{-}\bar{3}2/m$ conformation is preferred over the eclipsed $D_{3h}\text{-}\bar{6}2m$. The corresponding distances between the mean least-squares planes (each containing the three equatorial carbonyl carbons in half of the molecule) in $Zn[Co(CO)_4]_2$ (4.06 Å[46]) and in $Hg[Co(CO)_4]_2$ (4.57 Å[47]) are intermediate between those in $[Cr_2(CO)_{10}H]^-$ and $Hg[Mn(CO)_5]_2$. It is possible that the charge distribution on the equatorial ligands in molecules possessing threefold symmetry is different from those possessing fourfold symmetry and that this difference is causing the drastic change in conformation. Regardless, it appears that minor changes in coulombic and van der Waals forces, both intramolecular and intermolecular, may be sufficient to cause a change in conformation. More structural data are needed in order to confirm which forces predominate in the determination of the molecular conformation in the solid state. From our data, we cannot speculate whether the molecule assumes D_{4d} or D_{4h} geometry or is freely rotating in solution.

The mercury–manganese bond length of 2.610 Å may be used to calculate the radius of the mercury atom in $Hg[Mn(CO)_5]_2$. If the radius of the manganese atom is taken to be 1.46 Å, which is half of the Mn–Mn bond length in $Mn_2(CO)_{10}$,[41] a mercury radius of 1.15 Å is obtained. Similarly, this can be done to find the mercury radius in $Hg[Co(CO)_4]_2{}^{15}$ and in $Hg[Co-(CO)_3P(C_2H_5)_3]_2$.[17] Although the structure of the nonbridged $Co_2(CO)_8$ molecule has not been determined, the Co–Co bond length for three nonbridged bis(phosphine)-substituted derivatives of $Co_2(CO)_8{}^{48-50}$ is found to be in the range of 2.66–2.67 Å. Likewise, in the $Mn_2(CO)_{10}$ series, phosphine substitution leaves the Mn–Mn bond length virtually unchanged[51,52]

from that in $Mn_2(CO)_{10}$, and consequently it is not unreasonable to assume that this invariance of metal–metal bond length also exists for the nonbridged stereoisomer. When the cobalt radius of 1.33 Å (corresponding to half the Co–Co distance) is subtracted from the mercury–cobalt bond length of 2.499 Å in $Hg[Co(CO)_4]_2{}^{15}$ and in $Hg[Co(CO)_3P(C_2H_5)_3]_2$,[17] a mercury radius of 1.17 Å is obtained. This agreement is encouraging, and thus the value of 1.16 ± 0.01 Å is proposed for the mercury radius in symmetric mercury–bis(transition metal carbonyl) derivatives. By comparison of this number with the covalent radius in the mercury compounds HgI_2 (1.28 Å), $HgBr_2$ (1.27 Å), $HgCl_2$ (1.29 Å), CH_3HgBr (1.30 Å), and CH_3HgCl (1.29 Å),[53] it is observed that there is a significant shortening of the metal–metal bond length in $Hg-[Mn(CO)_5]_2$ and $Hg[Co(CO)_4]_2$.[54,55] This shortening, of the order 0.10–0.15 Å, may be attributed to $d\pi$–$p\pi$ back-donation from the filled d_{xz} and d_{yz} orbitals on the manganese atom to the empty p_x and p_y orbitals, respectively, on the mercury atom which are of the proper symmetry for overlap. Burlitch and Ferrari[4] have found from infrared and Mössbauer data that the M–Fe bond in $M[Fe(h^5\text{-}C_5H_5)(CO)_2]_2$, where M = Zn, Cd, or Hg, is a combination of inductive M→Fe donation through the σ system and M$\rightleftarrows$Fe back-donation through the π system. A π contribution of this type would lead to a shortening and strengthening of the metal–metal bond and would be expected to increase in the series Hg < Cd < Zn from consideration of the relative size of the metal orbitals. Indeed, this effect has been noted in the mass spectra of the series $M[Co(CO)_4]_2$ and $M[Cr(h^5\text{-}C_5H_5)(CO)_3]_2$ where M = Zn, Cd, and Hg.[4] In order to investigate the shortening of the metal–metal bond in $Zn[Co(CO)_4]_2$, a procedure similar to that described above is used. From the zinc–cobalt bond length of 2.305 Å in $Zn[Co-(CO)_4]_2$,[18] the estimated value of the cobalt radius in nonbridged $Co_2(CO)_8$, 1.33 Å, is subtracted. Thus, the radius of zinc in this compound is taken to be 0.97 Å. This is 0.32–0.33 Å shorter than the value of the zinc radius in $ZnCl_2$ (1.29 Å), $ZnBr_2$ (1.29 Å), and ZnI_2 (1.30 Å).[56-58] The shortening of 0.32 Å in $Zn[Co-(CO)_4]_2$ compared to the shortening of 0.12 Å in $Hg-[Co(CO)_4]_2$ and $Hg[Mn(CO)_5]_2$ lends support to the notion that multiple bonding is more important in the zinc derivatives than in the mercury derivatives. An alternate explanation for metal–metal bond shortening in silylmetal carbonyls has been given by MacDiarmid and coworkers.[59] Their proposal of direct interaction between a metal and the carbonyl ligands on an adjacent metal atom is consistent with the calculation of Brown, *et al.*[60] This interaction will be discussed in

(46) Calculated from the data given in ref 18.
(47) Calculated from data given in ref 15.
(48) J. A. Ibers, *J. Organometal. Chem.*, **14**, 423 (1968).
(49) R. F. Bryan and A. R. Manning, *Chem. Commun.*, 1316 (1968).
(50) J. Molin-Case, A. S. Foust, Jr., and L. F. Dahl, submitted for publication.
(51) H. M. Powell, *et al.*, unpublished work cited in D. J. Parker and M. H. B. Stiddard, *J. Chem. Soc. A*, 695 (1966).
(52) M. J. Bennett and R. Mason, *ibid.*, 75 (1968).

(53) D. Grdenic, *Quart. Rev., Chem. Soc.*, **19**, 303 (1965), and references cited therein.
(54) The degree of shortening due to ionic character in the HgX_2 and $CH_3Hg\text{-}X$ bonds should be similar to that in the Hg–Mn bond in $Hg[Mn-(CO)_5]_2$ since the electronegativity of the $Mn(CO)_5{}^-$ group as calculated by Stewart and Treichel[55] is similar to that of the bromide and iodide ions.
(55) R. P. Stewart and P. M. Treichel, *J. Amer. Chem. Soc.*, **92**, 2710 (1970).
(56) H. R. Oswald and H. Jaggi, *Helv. Chim. Acta*, **43**, 72 (1960).
(57) H. R. Oswald, *ibid.*, **43**, 77 (1960).
(58) L. Pauling, "The Nature of the Chemical Bond," 3rd ed, Cornell University Press, Ithaca, N. Y., 1960, p 225.
(59) A. D. Berry, E. R. Corey, A. P. Hagen, A. G. MacDiarmid, F. E. Saalfeld, and B. B. Wayland, *J. Amer. Chem. Soc.*, **92**, 1940 (1970).
(60) D. A. Brown, W. J. Chambers, N. J. Fitzpatrick, and R. M. Rawlinson, *J. Chem. Soc. A*, 720 (1971).

more detail below. From our data it is not possible to determine whether it is this kind of interaction or whether $d\pi-p\pi$ bonding is the major contributor to the shortening of the Hg–Mn bond.

Within a given $Mn(CO)_5$ group, the four equatorial Mn–CO bonds are bent toward the mercury atom and thus away from the axial carbonyl group. The manganese atom is thereby displaced 0.182 Å out of the mean least-squares plane defined by the four equatorial carbonyl carbon atoms. This value may be compared with 0.12 Å for $Mn_2(CO)_{10}$[41] and 0.21 Å for $Hg[Co(CO)_4]_2$.[47] The average value for the Hg–Mn–C_{eq} angle is 84.3 (2)°. A comparison of this value with those observed in the dinuclear metal carbonyls and other linear bridged dinuclear metal carbonyls is shown in Table V. The angular displace-

TABLE V

AVERAGE OUT-OF-PLANE ANGULAR DISPLACEMENT OF EQUATORIAL CARBONYL GROUPS IN DINUCLEAR METAL CARBONYLS AND DERIVATIVES

Compd	Av M′–M–C_{eq}, deg	Displacement β,[a] deg	Ref
$Zn[Co(CO)_4]_2$	81.1 (5)	8.9 (5)	18
$Hg[Co(CO)_4]_2$	83.3 (19)	6.7 (19)	15
$Hg[Mn(CO)_5]_2$	84.3 (2)	5.7 (2)	b
$[Cr_2(CO)_{10}H]^-$	89.0 (3)	1.0 (3)	40
$Mn_2(CO)_{10}$	86.2 (2)	3.8 (2)	41
	86.6 (5)	3.4 (5)	42
$Tc_2(CO)_{10}$	86.2 (2)	3.8 (2)	43
$[Cr_2(CO)_{10}]^{2-}$	87 (1)	3 (1)	40
$[Mo_2(CO)_{10}]^{2-}$	86 (1)	4 (1)	40

[a] The angle β is defined in Figure 3. [b] Value obtained in this work.

ment, β, is defined in Figure 3.

This inward bending of the carbonyl groups was first noted in $Mn_2(CO)_{10}$ and attributed[41] to apical, equatorial C$\cdots$C repulsion in half of the molecule. The fact that β is significantly smaller in the $[M_2(CO)_{10}]^z$ species ($\beta < 4°$) than in the $M^{II}[M(CO)_x]_2$ ($x = 4, 5$) species ($\beta > 5.7°$) suggests that the apical, equatorial $C_{ax}\cdots C_{eq}$ repulsion within half of the molecule is balanced by $C_{eq}\cdots C_{eq}$ repulsion between the halves of the molecule. Insertion of the Zn or Hg atom causes this latter force to be diminished, and β can thus achieve a higher value in the $M^{II}[M(CO)_x]_2$ derivatives. This explanation, however, does not account for the seemingly anomalous results ($\beta = 1°$) obtained for the linear hydrido-bridged anion $[Cr_2(CO)_{10}H]^-$.[40] In this anion, one would anticipate that β would be greater than 4° due to the separation of the $Cr(CO)_5$ moieties upon protonation of Cr–Cr bond. Recently, Brown and coworkers[60] have shown, *via* SCCC calculations, that in $Mn_2(CO)_{10}$ there exists a significant cross-interaction between one manganese atom and the carbonyl ligands directly bonded to the *other* manganese atom and that this cross-interaction may be an important stabilizing factor in forming metal–metal bonds. MacDiarmid and coworkers[59] have suggested that this interaction could, at least in part, be responsible for raising the equatorial carbonyl groups out of the molecular plane in $R_3Si-Co(CO)_4$ compounds. Recently, they have given mass spectral evidence for this interaction.[61] If this explanation of

M–L interaction is invoked, the smaller angular displacement in $[Cr_2(CO)_{10}H]^-$ is readily explained. In this anion there is no adjacent metal atom with which the carbonyl group can interact; thus there is a tendency for the M–CO bond to remain perpendicular to the molecular axis in order to maximize the Cr–C π overlap. In the μ-mercurio and μ-zincio compounds $M'[M(CO)_x]_2$, the tendency toward maximization of the M–C π overlap is overcome by the M′–CO cross-interaction; thus, the carbonyls are bent out of the plane perpendicular to the molecular axis. This latter effect also occurs in the unbridged dinuclear metal carbonyls $[M_2(CO)_{10}]^z$, but the out-of-plane bending is diminished because of the repulsion of the equatorial carbonyls on the adjacent metal atoms.
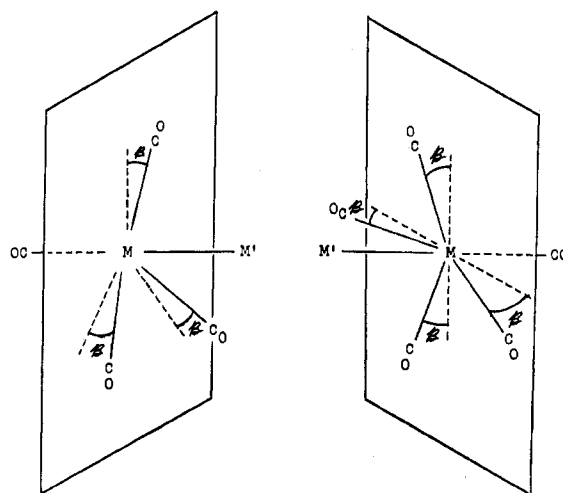

Figure 3.—Angular displacement, β, of the M–CO_{eq} bond out of a plane perpendicular to the molecular axis and passing through atom M for both $M'M(CO)_4$ and $M'M(CO)_5$.[59]

The axial Mn–C distance of 1.810 (14) Å is somewhat shorter than the average equatorial Mn–C distance of 1.848 (8) Å. Although the difference, 0.038 (16) Å, is not statistically significant, it is probably meaningful in light of the similar behavior observed for several compounds of the type $XM(CO)_5$[15,41,48,62-66] where X is a poorer charge acceptor than CO. In this case, more of the charge donated by X accumulates on the CO trans to X than on the CO groups which are cis to X. The increased M→C back-bonding to the trans carbonyl thus results in a stronger M–C bond.[67,68] These values may be compared with the corresponding axial and equatorial M–C distances of 1.792 (14) and 1.830 (8) Å, respectively, in $Mn_2(CO)_{10}$.[41] The consistent increase in both axial and equatorial metal–carbon bond distances in $Hg[Mn(CO)_5]_2$ compared to those in Mn_2-

(61) F. E. Saalfeld, M. V. McDowell, and A. G. MacDiarmid, *J. Amer. Chem. Soc.*, **92**, 2324 (1970).

(62) S. J. La Placa, W. C. Hamilton, and J. A. Ibers, *Inorg. Chem.*, **3**, 1491 (1964).

(63) P. A. Agron, R. D. Ellison, and H. A. Levy, *Acta Crystallogr.*, **23**, 1079 (1967).

(64) E. H. Schubert and R. K. Sheline, *Z. Naturforsch. B*, **20**, 1306 (1965).

(65) H. D. Kaesz, R. Bau, and M. R. Churchill, *J. Amer. Chem. Soc.*, **89**, 2775 (1967).

(66) M. R. Churchill and R. Bau, *Inorg. Chem.*, **6**, 2086 (1967).

(67) This trend is in accord with the recent approximate MO calculations on the pentacarbonyl halides of Cr, Mn, and Fe by Hall and Fenske,[68] who were able to correlate both the cis and trans carbonyl force constants with the calculated occupancies of 5σ and π^* orbitals on the carbonyls.

(68) M. B. Hall and R. F. Fenske, *Inorg. Chem.*, **11**, 1619 (1972).

$(CO)_{10}$, although not statistically significant, is in accord with the aforementioned π acceptor capabilities of the mercury atom. Within each $Mn(CO)_5$ group, the average $C_{ax} \cdots C_{eq}$ nonbonding distance is 2.712 Å. This value is slightly longer than the corresponding value of 2.64 Å observed in $Mn_2(CO)_{10}{}^{41}$ but is in agreement with the greater angular distortion and greater metal–carbon bond lengths present in Hg-$[Mn(CO)_5]_2$.

The mean C–O distance of 1.154 (10) Å agrees well with the value of 1.156 Å in $Mn_2(CO)_{10}$ and also with values observed in other transition metal carbonyls. There is no significant difference between the axial and equatorial C–O distances in this compound, which is consistent with the known insensitivity of the C–O bond length to changes in bond order in the range 2–3. The Mn–C–O angles have an average value of 178°; thus there is no significant distortion from linearity due to intermolecular packing forces and/or electronic effects. The closest intermolecular contacts (Table III) of range 3.1–3.4 Å indicate no abnormal intermolecular forces.[69]

(69) NOTE ADDED IN PROOF.—Since acceptance of this article, a short paper has appeared by W. Clegg and P. J. Wheatly [*J. Chem. Soc. A*, 3572 (1971)] on the crystal structure of $Hg[Mn(CO)_5]_2$. As expected, their results which were obtained with film data are not quite so precise as ours which utilized diffractometry data. However, it is gratifying that a comparison of the molecular parameters shows no corresponding values deviating by more than three standard deviations. It is noteworthy that the value of the Hg–Mn bond length quoted in both the abstract and text of their paper is incorrect but that their correct value is listed in their Table 3.

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Out-of-Plane Interactions in Parallel-Planar Copper(II) Dimers. The Structure and Magnetic Properties of Dibromobis(2-methylpyridine)copper(II)

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The crystal and molecular structure of dibromobis(2-methylpyridine)copper(II), $Cu(NC_6H_7)_2Br_2$, has been determined from three-dimensional single-crystal X-ray data collected by counter methods on an automatic diffractometer. The material crystallizes in space group C_i-$P\bar{1}$ of the triclinic system with two formula units in a cell of dimensions $a = 8.777$ (5), $b = 11.738$ (13), and $c = 8.494$ (5) Å; $\alpha = 74.75$ (7), $\beta = 60.73$ (4), and $\gamma = 70.52$ (7)°. The observed and calculated densities are 1.90 (2) and 1.904 g cm^{-3}, respectively. Least-squares refinement of the structure has led to an R factor (on F) of 0.044 for 1481 independent reflections having $F^2 > 3\sigma(F^2)$. The structure consists of weakly bound bromine-bridged dimers, the bridging Cu–Br separation being 3.872 (5) Å. The coordination about the copper is tetragonal pyramidal, with two trans bromine atoms and two nitrogen atoms in the basal plane and the bridging bromine atom axial. The Cu–Cu separation in the dimer is 4.926 (6) Å. The structure is very similar to that of the corresponding dichloro complex. Despite the weakness of the bridging of the dimer the complex exhibits an antiferromagnetic transition with a Néel temperature of 4.5°K.

Introduction

There has been considerable interest in recent years in the role of out-of-plane copper–ligand interactions between parallel-planar copper(II) dimers.[1,2] One such system of potential importance is that formed by copper(II) halides with pyridine and substituted pyridines. The crystal structures of $Cu(py)_2Cl_2{}^3$ and $Cu(py)_2Br_2{}^4$ show distorted octahedral coordination around the copper atom with two halogen and two nitrogen atoms lying in the basal plane around the copper atom and two halogen atoms from neighboring molecules occupying the axial sites. On the basis of infrared spectroscopic measurements several possible structures have been proposed for the complexes $Cu(\alpha\text{-pic})_2X_2$

(where α-pic = α-picoline (2-methylpyridine) and X = Cl or Br). These include square planar,[5] where the α-methyl group completely blocks the axial sites, and five- or six-coordinate,[6] where the α-methyl group blocks only one or none of the axial coordination sites, respectively. The spectroscopic data of both groups[5,6] of authors, however, are in agreement in showing that the bromo series of complexes of pyridine and substituted pyridines exhibits a completely different trend than the chloro series. Thus, the copper–bromide asymmetric stretching frequencies of $Cu(\alpha\text{-pic})_2Br_2$ (233 cm^{-1}), $Cu(\gamma\text{-pic})_2Br_2$ (255), $Cu(2,6\text{-lut})_2Br_2$ (233), and $Cu(2,4,6\text{-coll})_2Br_2$ (228) (coll = collidine) are lower than or equal to that of $Cu(py)_2Br_2$ (255), whereas the copper–chloride asymmetric stretching frequencies

(1) B. J. Hathaway and A. A. G. Tomlinson, *Coord. Chem. Rev.*, **5**, 1 (1970).
(2) W. E. Hatfield, *Inorg. Chem.*, **11**, 216 (1972).
(3) J. D. Dunitz, *Acta Crystallogr.*, **10**, 307 (1957).
(4) V. Kupcik and S. Durovic, *Czech. J. Phys.*, **10**, 182 (1960).

(5) M. Goldstein, E. F. Mooney, A. Anderson, and H. A. Gebbie, *Spectrochim. Acta*, **21**, 105 (1965).
(6) J. R. Allen, D. H. Brown, R. H. Nuttall, and D. W. A. Sharp, *J. Chem. Soc., A*, 1031 (1966).