

$$a = \sigma D < 1, E_s = \frac{4}{\pi a} - \frac{2}{a^2} + \frac{8}{\pi a^2 (1-a^2)^{1/2}} \tan^{-1} \left(\frac{1-a}{1+a} \right)^{1/2}$$

$$a = D = 1, E_s = \frac{8}{\pi} - 2$$

$$a = \sigma D > 1, E_s = \frac{4}{\pi a} - \frac{2}{a^2} + \frac{4}{\pi a^2 (a^2-1)^{1/2}} \log \frac{(1+a)^{1/2} + (a-1)^{1/2}}{(1+a)^{1/2} - (a-1)^{1/2}}$$

The results are accumulated in Table 1. The quantity tabulated is $1/E_s$, i.e. I_c/I_o . To obtain an estimate of the accuracy of these numbers, calculations were made of a few pure absorption corrections, with the results compared in Table 2 with values from Vol. II of the *International Tables for X-ray Crystallography* (1959). For $\mu D=3$, the errors are no more than a few tenths of 1%. These increase to 2-3% at $\mu D=30$. This should be a tolerable error for any practical work where extinction or absorption is this severe.

Table 1 is extended to values of σD where the reflected intensity is becoming independent of the

Table 2. Comparison of calculated pure absorption corrections with those tabulated in the *International Tables for X-ray Crystallography*

μR	θ	Calc.	Table	Relative error
1.5	15	9.843	9.88	0.0037
	25	8.766	8.79	0.0027
	35	7.668	7.68	0.0015
	45	6.722	6.74	0.0027
	55	6.000	6.00	—
	65	5.453	5.45	0.0006
15.0	75	5.083	5.08	0.0006
	15	711.5	731	0.027
	25	321.3	313	0.027
	35	179.9	176	0.022
	45	117.6	115	0.023
	55	84.95	82.7	0.027
	65	65.86	64.8	0.016
	75	54.43	54.1	0.006

structure factor, and the limiting values of $1/E_s$ are also included in the table. The limiting values for $2\theta=0^\circ$ and $2\theta=180^\circ$ are exact; the others were obtained by extrapolation.

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Crystal Structure of $[\text{BrMn}(\text{CO})_4]_2$

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(Received 18 September 1962)

A three-dimensional structural analysis of $[\text{BrMn}(\text{CO})_4]_2$, a typical member of the group VII metal tetracarbonyl halides, has been carried out. Crystals of $[\text{BrMn}(\text{CO})_4]_2$ possess space group symmetry $P2_1/c$ and contain four dimeric molecules in a monoclinic unit cell of dimensions

$$a = 9.57 \pm 0.01, b = 11.79 \pm 0.02, c = 12.91 \pm 0.02 \text{ \AA}, \beta = 109^\circ 30' \pm 10'.$$

Isotropic least-squares refinement of all twenty atoms has yielded final discrepancy factors of $R_1=10.0\%$ and $R_2=10.9\%$. The structure consists of discrete dimeric molecules formed by two octahedra joined at a common edge with bridging bromines equally shared between the manganese atoms. Within experimental error each molecular unit is of D_{2h} symmetry. The mean bond length for the four equivalent Mn-Br bonds is $2.526 \pm 0.005 \text{ \AA}$.

Introduction

Although a large number of metal carbonyl halides are known, to date the structures of only two of them, $[\text{ClRh}(\text{CO})_2]_2$ (Dahl, Martell & Wampler, 1961) and $\text{I}_2\text{Ru}(\text{CO})_4$ (Dahl & Wampler, 1962), have been determined by X-ray diffraction. This paper reports the results of a three-dimensional X-ray investigation of a third such compound, $[\text{BrMn}(\text{CO})_4]_2$, which is a

representative member of the tetracarbonyl halides of the group VII transition metals.

The dimeric character of these compounds was first determined (Abel, Hargreaves & Wilkinson, 1958) from molecular weight measurements of the rhenium carbonyl halides. A structure of D_{2h} symmetry involving the connection of two octahedra at an edge with bridging halogen atoms was suggested as a most reasonable configuration. Other structures with

metal-metal bonds also were considered as possibilities. The similarity of the IR spectra of the rhenium (Abel, Hargreaves & Wilkinson, 1958) and manganese (Abel & Wilkinson, 1959) analogues led Abel & Wilkinson (1959) to postulate an identical molecular structure for the compounds. The preparation of the corresponding technetium derivatives (Hileman, Huggins & Kaesz, 1961) has resulted in a detailed, systematic study of the infrared spectra of the complete series of tetracarbonyl halides, $[\text{XM}(\text{CO})_4]_2$, where $M = \text{Mn, Tc, Re}$, and $X = \text{Cl, Br, I}$ (El-Sayed & Kaesz, 1963). An interpretation of the spectra of all these compounds is found to be consistent with the halogen-bridged structure of D_{2h} symmetry, in agreement with the preliminary X-ray results reported for $[\text{BrMn}(\text{CO})_4]_2$ (Dahl, 1961).

Experimental procedure

A sample of $[\text{BrMn}(\text{CO})_4]_2$ was kindly furnished to us by Drs Clossen and Coffield of the Ethyl Corporation. Yellow-orange single crystals suitable for X-ray examination were obtained by recrystallization from CCl_4 solution and loaded into thin-walled glass capillaries which were then sealed. Under prolonged exposure to the X-ray beam the crystals decomposed. A cylindrical needle crystal of length 0.15 mm and of thickness 0.08 mm was used for obtaining intensity data with Mo $K\alpha$ radiation; the crystal was sufficiently small (μR was estimated to be 0.33) that no absorption correction was applied. The lattice parameter a was determined initially from $h0l$ and $hk0$ precession photographs and then finally by the method reported by Weisz, Cochran & Cole (1948). The b and c lattice parameters were obtained from both Weissenberg and precession photographs which were internally calibrated; β was determined from precession photographs. The density of the crystal was measured by the flotation method. Three-dimensional intensity data were collected from multiple-film equi-inclination Weissenberg photographs. A total of 800 independent diffraction maxima, obtained for ten reciprocal layers from rotation of the crystal about b , were estimated visually by comparison with a set of standard intensity strips prepared from the same single crystal. The intensities were first corrected for Lorentz and polarization effects and then were put on a common scale with the aid of the corrected $hk0$ Weissenberg intensity data obtained from another crystal. Final adjustment of scale factors for the derived structure factors for different layers was made by least-squares refinement.

Crystal data

$[\text{BrMn}(\text{CO})_4]_2$; mol. wt. 493.8; sublimes at *ca.* 150 °C. Monoclinic, with

$$a = 9.57 \pm 0.01, \quad b = 11.79 \pm 0.02, \\ c = 12.91 \pm 0.02 \text{ \AA}; \quad \beta = 109^\circ 30' \pm 10'.$$

Volume of unit cell = 1,373 \AA^3 , $D_m = 2.39 \text{ g.cm}^{-3}$ (by flotation), $Z = 4$, $D_c = 2.35 \text{ g.cm}^{-3}$; $F(000) = 928$. Linear absorption coefficient for Mo $K\alpha$ radiation, 83 cm^{-1} . Systematic absences: $\{h0l\}$ for l odd, $\{0k0\}$ for k odd. The probable space group, $P2_1/c(C_{2h}^5)$, was confirmed by the structural analysis. All atoms are in the general 4-fold set of positions (4e): $\pm(x, y, z; x, \frac{1}{2} - y, \frac{1}{2} + z)$ (*International Tables for X-ray Crystallography*, 1952).

Determination of the structure

Two-dimensional Patterson projections were computed for the three principal zones. Since attempts to formulate a trial structure for the heavy atoms which would be consistent with these Patterson maps were unsuccessful, a three-dimensional Patterson function was calculated at intervals of 1/30 along each axis. The interpretation of the Patterson synthesis yielded trial coordinates for both the manganese and bromine atoms. Two manganese and two bromine atoms appeared to be located on alternate corners of a rhombus plane. The trial parameters of these four heavy atoms were refined by an essentially diagonal least-squares program (Senko & Templeton, 1956) on an IBM 650 computer with individual isotropic temperature factors and constant weighting. After three cycles a final discrepancy value of $R_1 = [\sum ||F_o| - |F_c|| / \sum |F_o|] \times 100 = 21.3\%$ was obtained. A three-dimensional Fourier synthesis was next carried out in order to locate the positions of the carbon and oxygen atoms. The resulting synthesis clearly revealed the positions of the light atoms. Final refinement of all parameters including individual isotropic temperature factors as well as ten scale factors was carried out on an IBM 704 computer with the Busing & Levy (1959a) full matrix least-squares program. After six cycles final discrepancy values of $R_1 = 10.0\%$ and $R_2 = [\sum w ||F_o| - |F_c||^2 / \sum w |F_o|^2]^{1/2} \times 100 = 10.9\%$ were obtained, the maximum positional parameter shift for the final cycle being 46% of its standard deviation. Variable weights (Hughes, 1941; Lavine & Lipscomb, 1954) were assigned for the observed structure factors as follows:

$$\sqrt{w} = 10/F_o \quad \text{if } F_o \geq 4F_o \text{ min}; \\ \sqrt{w} = F_o / 1.6F_o^2 \text{ min} \quad \text{if } F_o < 4F_o \text{ min}.$$

For manganese and bromine the scattering factors used were those of Thomas & Umeda (1957), while for carbon and oxygen the values used were those of Berghuis *et al.* (1955). Verification of the structural determination was made by calculation of a three-dimensional difference map which showed no residual values greater than 1.8 $e.\text{\AA}^{-3}$ or less than $-2.5 e.\text{\AA}^{-3}$. The observed and calculated structure factors from the last cycle of the isotropic least-squares refinement are listed in Table 1. The final positional and thermal parameters and their standard deviations are given

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Table 1. Observed and calculated structure factors

Table with columns labeled H, K, L, Fo, Fc, H, K, L, Fo, Fc. It contains a large grid of numerical data representing structure factors for various Miller indices (HKL).

Table 2. *Final atomic parameters, with standard deviations*

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i>	$10^4 \sigma(x)$	$10^4 \sigma(y)$	$10^4 \sigma(z)$	σB
Br ₁	0.3938	0.7432	0.1950	1.69 Å ²	5	6	4	0.09 Å ²
Br ₂	0.3900	0.5082	0.3456	1.95	5	5	4	0.10
Mn ₃	0.1856	0.6270	0.2191	1.71	7	7	5	0.13
Mn ₄	0.6005	0.6230	0.3210	1.31	6	8	5	0.13
C ₅	0.0496	0.5391	0.2403	1.21	40	41	28	0.73
O ₆	-0.0483	0.4880	0.2572	6.43	47	52	35	1.13
C ₇	0.0541	0.7096	0.1290	1.61	44	40	31	0.77
O ₈	-0.0457	0.7691	0.0642	6.44	49	53	39	1.13
C ₉	0.1908	0.5332	0.1076	1.61	40	40	32	0.75
O ₁₀	0.1998	0.4746	0.0315	3.76	39	36	29	0.77
C ₁₁	0.1936	0.7156	0.3336	2.20	48	46	36	0.91
O ₁₂	0.1924	0.7789	0.4174	5.70	47	47	38	1.05
C ₁₃	0.7407	0.7033	0.2976	3.10	56	50	40	1.03
O ₁₄	0.8372	0.7699	0.2892	3.57	39	44	28	0.82
C ₁₅	0.5908	0.5350	0.1950	1.49	41	40	32	0.73
O ₁₆	0.5775	0.4848	0.1203	4.15	41	42	33	0.82
C ₁₇	0.5968	0.7218	0.4392	2.33	47	46	38	0.87
O ₁₈	0.5997	0.7671	0.5144	4.69	41	45	32	0.89
C ₁₉	0.7401	0.5274	0.4101	2.76	50	47	39	0.94
O ₂₀	0.8250	0.4679	0.4703	3.24	37	33	29	0.71

in Table 2. Average standard deviations of the coordinates are 0.0072 Å for manganese atoms, 0.0055 Å for bromine atoms, 0.047 Å for carbon atoms, and 0.045 Å for oxygen atoms.

Interatomic distances and bond angles and their standard deviations were calculated with the Busing-Levy Function and Error Program (Busing & Levy, 1959b). The intramolecular distances and bond angles are given in Tables 3 and 4, respectively. The intermolecular distances of the nearest neighbors (less than 3.5 Å) are tabulated in Table 5.

Discussion of the structure

The structure is composed of discrete dimeric molecules. Each molecular unit (Fig. 1) is made up of two

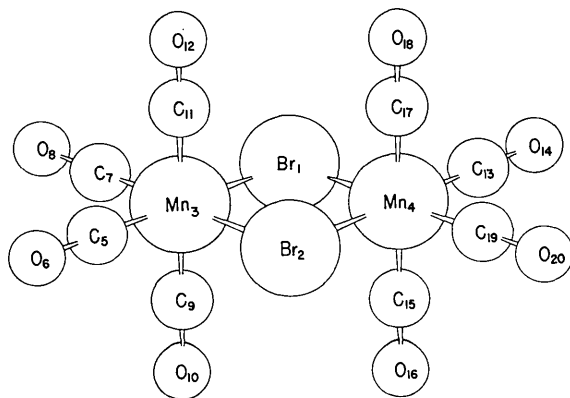


Fig. 1. The molecular configuration of $[\text{BrMn}(\text{CO})_4]_2$.

octahedra which are joined at a common edge with bridging bromine atoms equally shared between the manganese atoms. Within limits of accuracy as indicated by the standard deviations of bond lengths and bond angles (Tables 3 and 4), the molecular point symmetry is $D_{2h}-mmm$.

Table 3. *Intramolecular distances, with standard deviations*

Bond	Distance	Bond	Distance
Mn ₃ -Br ₁	2.521 ± 0.009 Å	C ₅ -O ₆	1.19 ± 0.05 Å
Mn ₃ -Br ₂	2.514 ± 0.009	C ₇ -O ₈	1.25 ± 0.06
Mn ₄ -Br ₁	2.534 ± 0.010	C ₁₃ -O ₁₄	1.24 ± 0.06
Mn ₄ -Br ₂	2.533 ± 0.010	C ₁₉ -O ₂₀	1.16 ± 0.05
Mn ₃ ...Mn ₄	3.743 ± 0.008	C ₉ -O ₁₀	1.23 ± 0.05
Br ₁ ...Br ₂	3.392 ± 0.008	C ₁₁ -O ₁₂	1.32 ± 0.06
Mn ₃ -C ₅	1.76 ± 0.04	C ₁₅ -O ₁₆	1.10 ± 0.05
Mn ₃ -C ₇	1.71 ± 0.04	C ₁₇ -O ₁₈	1.10 ± 0.05
Mn ₄ -C ₁₃	1.75 ± 0.05		
Mn ₄ -C ₁₉	1.83 ± 0.05		
Mn ₃ -C ₉	1.83 ± 0.04		
Mn ₃ -C ₁₁	1.79 ± 0.05		
Mn ₄ -C ₁₅	1.91 ± 0.04		
Mn ₄ -C ₁₇	1.93 ± 0.05		

The *mean* bond length of the four equivalent Mn-Br bonds is 2.526 ± 0.005 Å. Although the individual Mn-C and C-O bond distances vary considerably and possess relatively high standard deviations, the *mean* Mn-C and C-O bond lengths for the eight Mn-CO groups of 1.81 ± 0.02 and 1.20 ± 0.02 Å, respectively, are reasonably close to the *mean* Mn-C and C-O values of 1.82 ± 0.01 and 1.16 ± 0.01 Å, respectively, found for $\text{Mn}_2(\text{CO})_{10}$ (Dahl & Rundle, 1963). The *mean* length of the four Mn-C bonds essentially coplanar with the Mn_2Br_2 rhombus is 1.76 ± 0.02 Å; the *mean* length of the other four Mn-C bonds approximately perpendicular to the rhombus plane is 1.87 ± 0.02 Å. The difference in the *mean* bond lengths for these non-equivalent Mn-C bonds is possibly significant and perhaps may be attributed to greater M-C π -bonding for the carbonyls *trans* to the bromine atoms in accord with the reported *trans*-effect for these compounds (Abel, Hargreaves & Wilkinson, 1958).

Table 4. Bond angles, with standard deviations

Angle	Degrees	Angle	Degrees
Br ₁ -Mn ₃ -Br ₂	84.7 ± 0.3	C ₅ -Mn ₃ -C ₇	91.5 ± 1.9
Br ₁ -Mn ₄ -Br ₂	84.0 ± 0.2	C ₁₃ -Mn ₄ -C ₁₉	90.1 ± 2.3
Mn ₃ -Br ₁ -Mn ₄	95.5 ± 0.4	C ₉ -Mn ₃ -C ₅	89.0 ± 1.8
Mn ₃ -Br ₂ -Mn ₄	95.7 ± 0.3	C ₉ -Mn ₃ -C ₇	90.9 ± 1.9
Br ₁ -Mn ₃ -C ₇	92.2 ± 1.4	C ₁₁ -Mn ₃ -C ₅	92.6 ± 2.0
Br ₁ -Mn ₄ -C ₁₃	93.8 ± 1.8	C ₁₁ -Mn ₃ -C ₇	92.8 ± 2.0
Br ₂ -Mn ₃ -C ₅	91.5 ± 1.3	C ₁₅ -Mn ₄ -C ₁₉	91.1 ± 2.1
Br ₂ -Mn ₄ -C ₁₉	92.1 ± 1.5	C ₁₅ -Mn ₄ -C ₁₃	88.2 ± 2.2
Br ₁ -Mn ₃ -C ₁₁	88.1 ± 1.5	C ₁₇ -Mn ₄ -C ₁₉	94.4 ± 2.0
Br ₁ -Mn ₄ -C ₁₇	87.3 ± 1.4	C ₁₇ -Mn ₄ -C ₁₃	91.6 ± 2.3
Br ₁ -Mn ₃ -C ₉	90.1 ± 1.3	C ₉ -Mn ₃ -C ₁₁	175.9 ± 1.9
Br ₁ -Mn ₄ -C ₁₅	87.2 ± 1.2	C ₁₅ -Mn ₄ -C ₁₇	174.5 ± 1.9
Br ₂ -Mn ₃ -C ₁₁	88.8 ± 1.5	Mn ₃ -C ₆ -O ₆	174.1 ± 4.2
Br ₂ -Mn ₃ -C ₉	87.4 ± 1.3	Mn ₃ -C ₇ -O ₈	178.1 ± 4.0
Br ₂ -Mn ₄ -C ₁₇	89.9 ± 1.4	Mn ₃ -C ₉ -O ₁₀	176.3 ± 3.9
Br ₂ -Mn ₄ -C ₁₅	90.1 ± 1.3	Mn ₃ -C ₁₁ -O ₁₂	177.0 ± 4.0
Br ₁ -Mn ₃ -C ₅	176.1 ± 1.4	Mn ₄ -C ₁₃ -O ₁₄	172.4 ± 4.8
Br ₁ -Mn ₄ -C ₁₉	175.7 ± 1.7	Mn ₄ -C ₁₅ -O ₁₆	176.4 ± 3.6
Br ₂ -Mn ₃ -C ₇	176.5 ± 1.4	Mn ₄ -C ₁₇ -O ₁₈	171.6 ± 4.9
Br ₂ -Mn ₄ -C ₁₃	177.3 ± 1.6	Mn ₄ -C ₁₉ -O ₂₀	176.6 ± 4.0

The best plane through the Mn₂Br₂ rhombus and the four equivalent carbonyl groups *trans* to the bromines (*i.e.*, C₅-O₆, C₇-O₈, C₁₃-O₁₄, C₁₉-O₂₀) passes within 0.007 Å of the Mn and Br atoms and within 0.10 Å of the carbon and oxygen atoms. The equation of the plane was calculated by the method of least squares (Smith, 1962) in which the following weights were given to the individual atoms forming the plane:

Weight of atom = $1/(abc\sigma(x)\sigma(y)\sigma(z))^{\frac{2}{3}}$ where a , b , and c are cell constants; $\sigma(x)$, $\sigma(y)$, and $\sigma(z)$ are standard deviations of the atomic coordinates. The equation of this plane and the deviations of the atoms from the plane are:

$$0.264X - 0.577Y - 0.773Z + 6.112 = 0$$

[Br₁, 0.004; Br₂, 0.004; Mn₃, 0.007; Mn₄, 0.007;
C₅, 0.04; O₆, 0.04; C₇, 0.06; O₈, 0.09; C₁₃, 0.06;
O₁₄, 0.06; C₁₉, 0.07; O₂₀, 0.05 Å]

where X , Y , and Z are orthogonal coordinates expressed in Å units. These orthogonal directions are related to the axes of the monoclinic unit cell by the transformation $X = ax + cz \cos \beta$, $Y = by$, $Z = cz \sin \beta$. The variations of the atoms from the best plane are probably due to experimental error.

Figs. 2 and 3 illustrate the arrangement of the molecules in the unit cell viewed down the [100] and [001] directions, respectively. The intramolecular Mn-Mn directions in the four dimeric molecules are parallel to one another; the Mn-Mn direction is approximately perpendicular to the (100) plane. The mean Mn₂Br₂ rhombus planes are in two different orientations at angles of 54° 45' to the two (010) planes and are related to each other by a c glide plane (and a 2₁ axis). For clarity Fig. 3 shows the carbonyl

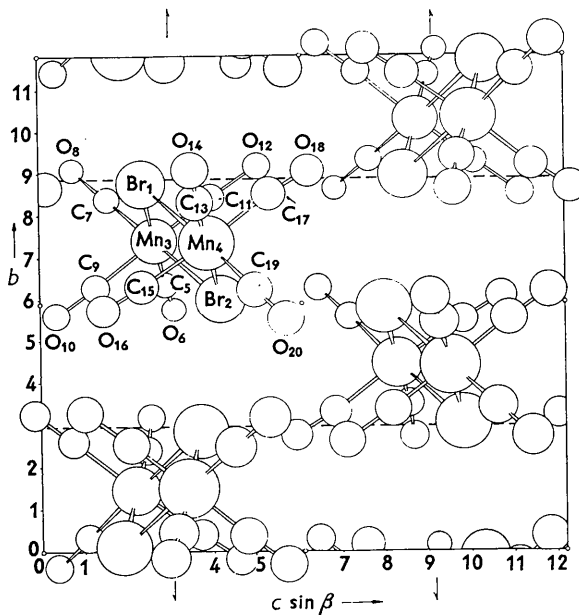


Fig. 2. [100] projection of the unit cell.

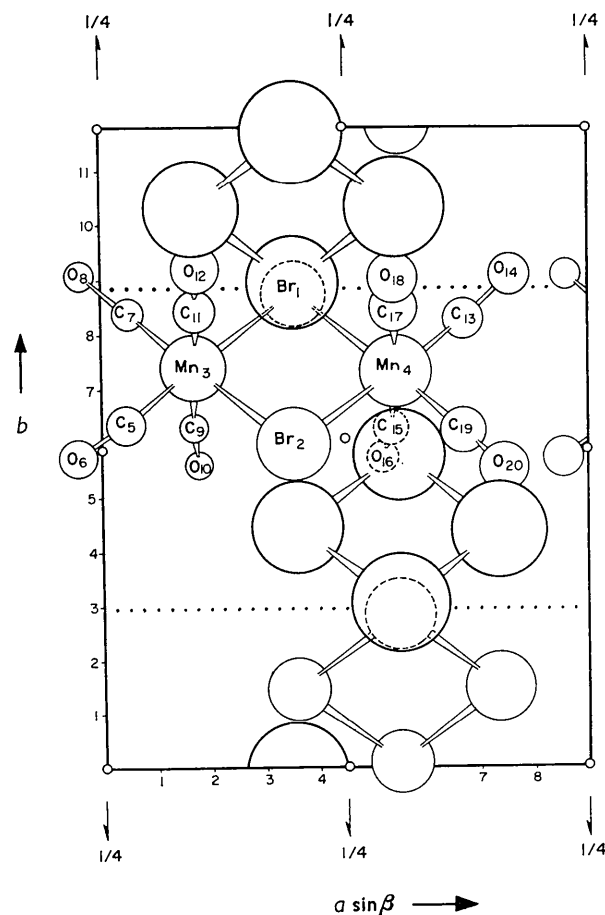


Fig. 3. [001] projection of the unit cell. The carbonyl positions for only the basic molecule are shown.

groups for only the one molecule corresponding to the positional parameters listed in Table 1. This [001] unit cell projection reveals the packing of all the bromine and manganese atoms in essentially four planes parallel to the (100) plane. The four pairs of bromines lie only in the equivalent inner planes, while the eight manganese atoms occupy all four planes in pairs. The closest intermolecular distances (Table 5) indicate that the primary interactions between molecules are only van der Waals forces. Each bridge halogen contributes three electrons in bonding with the two metals (or alternatively four electrons to the two Mn(I)) by utilization of two equivalent $s-p$ hybrid orbitals and one of its usually unshared electron pairs; the resulting formation of normal electron-pair metal-halide bonds provides each metal with the 'inert gas' configuration without the invoking of a metal-metal interaction. The non-bonding intramolecular Mn \cdots Mn distance of 3.74 Å (e.s.d. 0.008 Å) is much longer than the bonding Mn-Mn distance of 2.92 Å found in $\text{Mn}_2(\text{CO})_{10}$ (Dahl & Rundle, 1962). The unambiguous establishment of the D_{2h} molecular configuration for

1956), $[\text{C}_6\text{H}_5\text{SRe}(\text{CO})_4]_2$ (Hieber & Schuster, 1956), and $[(\text{C}_6\text{H}_5)_2\text{AsMn}(\text{CO})_4]_2$ (Lambert, 1961) should possess similar D_{2h} molecular configurations.

The authors wish to thank Prof. Kaesz of the University of California (Los Angeles) for supplying us with unpublished data. This work was supported by the National Science Foundation (Grant No. 86-3474), to whom grateful acknowledgment is made. We also wish to acknowledge the use of the computing facilities of the Numerical Analysis Laboratory of the University of Wisconsin.

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Table 5. Intermolecular distances less than 3.5 Å

Atoms	Distance	Atoms	Distance
$\text{O}_{16} \cdots \text{O}_{16}^{\text{V}}$	2.98 Å	$\text{C}_{11} \cdots \text{O}_{20}^{\text{I}}$	3.38 Å
$\text{O}_{18} \cdots \text{O}_{16}^{\text{II}}$	3.24	$\text{O}_6 \cdots \text{C}_{13}^{\text{III}}$	3.39
$\text{O}_{12} \cdots \text{O}_{14}^{\text{III}}$	3.25	$\text{C}_7 \cdots \text{O}_{10}^{\text{VI}}$	3.40
$\text{O}_8 \cdots \text{O}_{10}^{\text{VI}}$	3.28	$\text{O}_{14} \cdots \text{C}_5^{\text{II}}$	3.42
$\text{O}_{12} \cdots \text{O}_{20}^{\text{I}}$	3.28	$\text{O}_{12} \cdots \text{O}_{16}^{\text{II}}$	3.42
$\text{O}_8 \cdots \text{O}_{20}^{\text{II}}$	3.28	$\text{O}_{14} \cdots \text{C}_9^{\text{II}}$	3.42
$\text{O}_{18} \cdots \text{O}_{10}^{\text{II}}$	3.28	$\text{O}_6 \cdots \text{O}_{16}^{\text{III}}$	3.42
$\text{O}_6 \cdots \text{C}_{19}^{\text{III}}$	3.30	$\text{O}_{14} \cdots \text{O}_{10}^{\text{II}}$	3.44
$\text{O}_{12} \cdots \text{O}_6^{\text{IV}}$	3.32	$\text{O}_{14} \cdots \text{O}_6^{\text{II}}$	3.44
$\text{O}_6 \cdots \text{C}_{15}^{\text{III}}$	3.32	$\text{O}_8 \cdots \text{O}_{14}^{\text{III}}$	3.44
$\text{C}_{11} \cdots \text{O}_{14}^{\text{III}}$	3.33	$\text{C}_7 \cdots \text{O}_{14}^{\text{III}}$	3.46
$\text{O}_6 \cdots \text{O}_{20}^{\text{III}}$	3.36	$\text{C}_{17} \cdots \text{O}_{16}^{\text{II}}$	3.48
$\text{O}_8 \cdots \text{O}_6^{\text{IV}}$	3.38	$\text{O}_6 \cdots \text{O}_{20}^{\text{I}}$	3.49
$\text{O}_{10} \cdots \text{O}_{16}^{\text{V}}$	3.38		

Superscripts refer to the transformation of (x, y, z) into the following atomic positions:

I	$1-x$	$1-y$	$1-z$
II	$1-x$	$\frac{1}{2}+y$	$\frac{1}{2}-z$
III	$-1+x$	y	z
IV	$1-x$	$-\frac{1}{2}+y$	$\frac{1}{2}-z$
V	$1-x$	$1-y$	$-z$
VI	$-x$	$1-y$	$-z$

$[\text{BrMn}(\text{CO})_4]_2$, a typical member of the tetracarbonyl halide dimers of Mn, Tc, and Re, is completely compatible with magnetic susceptibility measurements (Hileman, Huggins & Kaesz, to be published) which show the compounds of Tc to be diamagnetic. These X-ray results definitely indicate that corresponding dinuclear metal carbonyls with other substituted ligands such as $\text{KH}[\text{ORe}(\text{CO})_4]_2$ (Hieber & Schuster,