Registry No. $Cr(H_2O)HEDTA$, 76582-41-7.

Supplementary Material Available: A list of structure factor amplitudes, supplementary Tables I–III (deviations from least-squares planes, angles between least-squares planes, and distances and angles involving hydrogen bonds), and supplementary Figure 1 (unit cell packing and hydrogen bonding in $[Cr(H_2O)HEDTA]$) (15 pages). Ordering information is given on any current masthead page.

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Redetermination of the Crystal Structure of Dimanganese Decacarbonyl and Determination of the Crystal Structure of Dirhenium Decacarbonyl. Revised Values for the Mn–Mn and Re–Re Bond Lengths in $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$

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and Harvey J. Wasserman

Received July 2, 1980

While relatively accurate room-temperature X-ray diffraction studies have been carried out on the tetranuclear "binary" carbonyls of the cobalt subgroup ($Co_4(CO)_{12}$,[1] $Rh_4(CO)_{12}$,[2] $Ir_4(CO)_{12}$[3]),on the trinuclear binary carbonyls of the iron subgroup ($Fe_3(CO)_{12}$,[4] $Ru_3(CO)_{12}$,[5] $Os_3(CO)_{12}$[6]) and on the dinuclear species $Fe_2(CO)_9$,[7] there have been no correspondingly accurate studies on the neutral binary carbonyls of the group 7 transition metals.

The species $M_2(CO)_{10}$ (M = Mn,[8] Tc,[9] Re[10]) have previously been shown to be isomorphous. Completed structural studies of $Mn_2(CO)_{10}$[8] and $Tc_2(CO)_{10}$[9] show the molecules to have approximate D_{4d} symmetry. Although there is no question that these structures were correctly determined, each was reported more than 15 years ago, the determination was based on film data and is (by current standards) of limited precision. Thus, the structural study of $Mn_2(CO)_{10}$ was based on 614 visually estimated X-ray diffraction data, and the model was refined to R_F = 7.0%. The resulting Mn–Mn bond length of 2.923 (3) Å has been quoted widely throughout the chemical literature. No complete study of $Re_2(CO)_{10}$ has been reported, although a Re–Re distance of 3.02 Å (from a partial structure)[10] has, again, been quoted frequently.

We now report accurate room-temperature X-ray diffraction studies of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$. The metal–metal bond lengths thus obtained (along with other geometric features) will be of value in comparison with results from other room-temperature studies of substituted $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ complexes. While a case can be made for carrying out structural studies on this type of molecule only at low temperature (and, in fact, a study of the distribution of bonding electrons in $Mn_2(CO)_{10}$ is currently under way)[11], most structural studies will continue to be carried out under ambient conditions and require comparisons with fundamental structures studied under similar conditions.

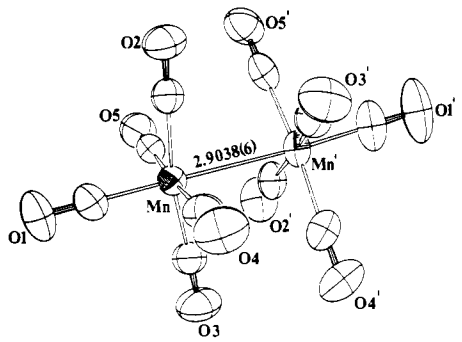

Figure 1. Geometry of the $Mn_2(CO)_{10}$ molecule (ORTEP-II diagram; 30% ellipsoids).

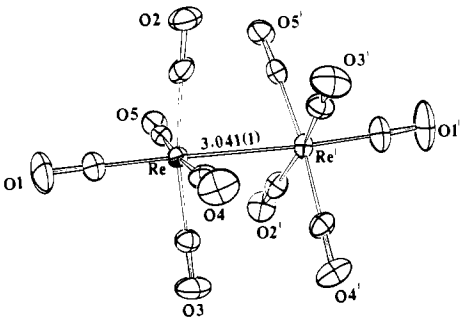

Figure 2. $Re_2(CO)_{10}$ molecule (ORTEP-II diagram; 30% ellipsoids).

Experimental Section

Samples of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ were obtained from the Strem Chemical Co. An approximately ellipsoidal crystal of $Mn_2(CO)_{10}$ (dimensions 0.23 × 0.30 × 0.30 mm) was obtained from the original sample. Crystals of $Re_2(CO)_{10}$ were grown from a cyclohexane/carbon tetrachloride solution (70:30 v/v); the crystal selected for the X-ray structural study had dimensions of 0.20 × 0.20 × 0.23 mm. Each crystal was sealed into a thin-walled glass capillary under argon and was mounted on a Syntex $P2_1$ automated four-circle diffractometer as described previously;[12] details are presented in Table I.

Two complete asymmetric units of diffraction data were collected for each crystal. Following correction for Lorentz, polarization, and absorption effects, the data were (in each case) merged to a single averaged set. The statistics for averaging ($R(I)$ = 1.01% for 1260 averaged pairs for $Mn_2(CO)_{10}$ and $R(I)$ = 2.54% for 1316 averaged pairs for $Re_2(CO)_{10}$) indicate the satisfactory quality of the diffraction data.

Starting with the coordinates of Dahl and Rundle for $Mn_2(CO)_{10}$,[8] full-matrix least-squares refinement of the scale factor and positional and anisotropic thermal parameters for all atoms (100 parameters vs. 1260 independent reflections) led to final convergence [$(\Delta/\sigma)_{max}$ < 0.005] with R_F = 2.8%, R_{wF} = 3.7%, and GOF = 0.925. The discrepancy indices for those 1107 data with $|F_o| > 3\sigma(|F_o|)$ were R_F = 2.3% and R_{wF} = 3.6%. The highest feature on a final difference-Fourier synthesis was a peak of height 0.16 e Å^{-3}; tests of the weighting scheme indicated that it was satisfactory and that no correction for secondary extinction was necessary.

The structural analysis of $Re_2(CO)_{10}$ was begun with use of the coordinates obtained in our structure of $Mn_2(CO)_{10}$. Full-matrix least-squares refinement as before (100 parameters vs. 1330 independent reflections) led to final convergence with R_F = 2.9%, R_{wF} = 2.4%, and GOF = 1.203. For those 1207 data with $|F_o| > 3\sigma(|F_o|)$,

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Table I. X-Ray and Crystal Data for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$

(A) Crystal Parameters[a]

	$Mn_2(CO)_{10}$	$Re_2(CO)_{10}$
cryst system	monoclinic	monoclinic
space group[b]	*I2/a*	*I2/a*
a, Å	14.1350 (19)	14.6576 (38)
b, Å	7.0999 (9)	7.1188 (9)
c, Å	14.6277 (22)	14.8152 (53)
β, deg	105.167 (15)	105.799 (22)
V, Å^3	1416.9 (3)	1487.5 (6)
Z	4	4
ρ(calcd), g/cm^3	1.83	2.91
T, °C	23	23

(B) Collection of Intensity Data

diffractometer: Syntex $P2_1$
radiation: Mo K$\bar{\alpha}$ ($\bar{\lambda}$ = 0.710 730 Å)
monochromator: highly oriented graphite; equatorial mode; $2\theta_{mono} = 12.2°$
reflctns measd: $\pm h, +k, \pm l$ for each compound
scan type: coupled θ(crystal)-2θ(counter)
scan range: $[C + (K\alpha_2\text{-}K\alpha_1)]°$ (C = 18° for $Mn_2(CO)_{10}$ and 2.0° for $Re_2(CO)_{10}$)
scan speed: 2.5°/min in 2θ for $Mn_2(CO)_{10}$; 2.0°/min in 2θ for $Re_2(CO)_{10}$
2θ range: 4.0–50.0° for each compound
reflctns collctd: 2635 total, 1260 independent for $Mn_2(CO)_{10}$ (no crystal decomposition was observed—cf. ref 8); 2676 total, 1330 independent for $Re_2(CO)_{10}$
data av: $R(I)$ = 1.01% with 1260 multicontributors for $Mn_2(CO)_{10}$; $R(I)$ = 2.54% with 1316 multicontributors for $Re_2(CO)_{10}$
abs cor: μ = 19.2 cm^{-1} for $Mn_2(CO)_{10}$, data were corrected with use of 5 sets of ψ scans in which max/min transmission factors ranged from 1.04 to 1.09; μ = 172.5 cm^{-1} for $Re_2(CO)_{10}$, data were corrected via 7 sets of ψ scans in which max/min transmission factors were 1.32–1.39

[a] Derived from a least-squares fit to the setting angles of the unresolved Mo K$\bar{\alpha}$ components of 25 reflections (2θ = 35–40° for $Mn_2(CO)_{10}$; 2θ = 21–30° for $Re_2(CO)_{10}$). [b] We followed ref 8 in using this setting.

the discrepancy indices were R_F = 2.2% and R_F = 2.4%. A correction for secondary extinction was found to be necessary for this structural study. The $|F_o|$ values were corrected with use of the approximation shown in eq 1. The value for k, obtained by a least-squares analysis

$$|F_o^{cor}| = |F_o^{uncor}|(1.0 + kI_o) \quad (1)$$

of those 29 reflections which had >3 × 10^5 counts, was 1.04 × 10^{-7}. A final difference-Fourier synthesis showed no significant features. Final positional and thermal parameters for the two structures appear in Table II.

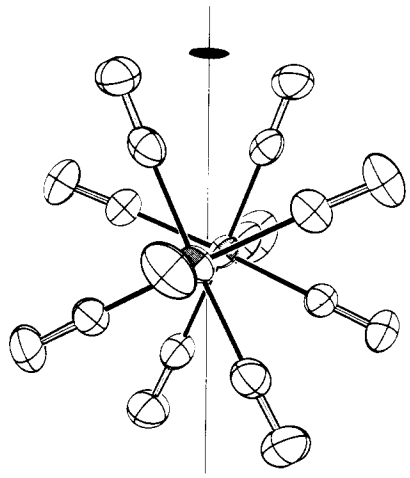

Figure 3. $Mn_2(CO)_{10}$ molecule, showing the crystallographic C_2 axis and the approximate D_{4d} symmetry of the molecule.

Discussion

Figures 1 and 2 show general views of the $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ molecules. Interatomic distances and angles are collected in Table III.

The redetermined structure of $Mn_2(CO)_{10}$ is in essential agreement with that reported by Dahl and Rundle in 1963;[8] esd's, however, are reduced to about one-tenth of their previous values. The geometry of $Re_2(CO)_{10}$ is, as expected, very similar to that of $Mn_2(CO)_{10}$. The following specific points may be noted.

(1) Our results reveal a Mn–Mn bond length of 2.9038 (6) Å, a distance substantially *shorter* than the previously reported

Table II. Positional and Anisotropic Thermal Parameters[a] for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$

atom	*x*	*y*	*z*	B_{11}	B_{22}	B_{33}	B_{12}	B_{13}	B_{23}
				(A) $Mn_2(CO)_{12}$					
Mn	0.15449 (2)	0.23212 (4)	0.93204 (2)	3.21 (2)	4.01 (2)	3.59 (2)	0.15 (1)	0.45 (1)	−0.81 (1)
C1	0.03819 (20)	0.23874 (36)	0.84311 (21)	4.58 (11)	7.35 (15)	5.69 (13)	0.45 (9)	−0.28 (10)	−2.26 (10)
O1	−0.03415 (18)	0.24361 (38)	0.78664 (19)	5.67 (11)	13.22 (21)	8.34 (15)	0.81 (9)	−2.54 (10)	−3.44 (11)
C2	0.10768 (14)	0.33699 (32)	1.02774 (15)	3.48 (8)	5.00 (10)	4.74 (10)	0.20 (8)	0.61 (7)	−0.80 (8)
O2	0.07741 (13)	0.39707 (27)	1.08616 (13)	5.84 (8)	7.64 (10)	6.10 (9)	0.98 (8)	2.39 (7)	−1.93 (8)
C3	0.21966 (16)	0.11998 (29)	0.85186 (15)	5.37 (10)	4.04 (9)	4.09 (9)	0.30 (8)	1.33 (8)	−0.13 (7)
O3	0.25765 (16)	0.05020 (26)	0.80164 (12)	9.44 (12)	6.40 (10)	5.51 (9)	1.37 (8)	3.85 (8)	−0.57 (7)
C4	0.13046 (16)	−0.00332 (33)	0.97576 (16)	4.29 (10)	4.72 (10)	5.69 (11)	−0.62 (8)	1.88 (9)	−1.27 (9)
O4	0.11095 (14)	−0.14308 (26)	1.00194 (15)	7.54 (11)	5.03 (8)	9.21 (12)	−1.65 (8)	3.67 (9)	−0.49 (8)
C5	0.18855 (16)	0.47130 (31)	0.89865 (13)	4.70 (10)	4.59 (10)	3.19 (8)	1.01 (8)	0.18 (7)	−0.57 (7)
O5	0.20720 (14)	0.61729 (22)	0.87837 (11)	8.43 (11)	4.09 (7)	4.87 (7)	0.68 (7)	0.92 (7)	0.45 (6)
				(B) $Re_2(CO)_{10}$					
Re	0.15279 (1)	0.23214 (3)	0.92937 (1)	2.620 (12)	3.295 (13)	3.229 (11)	0.103 (7)	0.531 (8)	−0.626 (7)
C1	0.03285 (49)	0.24045 (90)	0.83424 (50)	4.12 (34)	7.10 (47)	5.18 (34)	0.54 (23)	−0.43 (26)	−1.57 (25)
O1	−0.03690 (48)	0.24882 (89)	0.77591 (55)	6.32 (40)	12.24 (65)	9.38 (50)	1.01 (25)	−4.00 (33)	−3.22 (32)
C2	0.10455 (34)	0.34368 (92)	1.02977 (45)	2.92 (23)	4.57 (32)	5.90 (36)	0.44 (21)	1.36 (21)	−0.33 (24)
O2	0.07825 (30)	0.40494 (65)	1.08922 (34)	5.31 (23)	7.15 (29)	6.47 (28)	0.76 (18)	3.04 (20)	−1.62 (20)
C3	0.22010 (42)	0.11321 (78)	0.84504 (41)	4.80 (31)	3.75 (31)	3.80 (28)	0.12 (23)	1.53 (23)	0.04 (20)
O3	0.25888 (36)	0.04355 (66)	0.79710 (35)	9.67 (34)	5.95 (28)	5.99 (27)	1.04 (21)	4.62 (23)	−0.77 (19)
C4	0.12682 (41)	−0.01661 (85)	0.97525 (42)	4.33 (29)	3.36 (32)	4.86 (30)	−0.50 (22)	1.70 (23)	−0.83 (23)
O4	0.10830 (33)	−0.15514 (76)	1.00260 (39)	7.22 (29)	4.57 (31)	9.45 (35)	−1.53 (21)	3.73 (25)	−0.11 (24)
C5	0.18941 (39)	0.4887 (10)	0.89459 (36)	3.92 (27)	3.91 (37)	2.88 (22)	0.55 (21)	0.46 (19)	−0.46 (19)
O5	0.21084 (31)	0.63243 (65)	0.87805 (29)	6.99 (27)	2.93 (27)	4.76 (22)	0.13 (18)	1.13 (18)	0.50 (15)

[a] These anisotropic thermal parameters are analogous to the usual form of the isotropic thermal parameter and have units of Å^2. They enter the expression for the structure factor in the form $\exp[-0.25(B_{11}h^2a^{*2} + B_{22}k^2b^{*2} + B_{33}l^2c^{*2} + 2B_{12}hka^*b^* + 2B_{13}hla^*c^* + 2B_{23}klb^*c^*)]$.

Table III. Interatomic Distances (Å) and Angles (Deg) for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$

atoms	M = Mn	M = Re
	(A) Metal-Metal Bond Length	
M-M′	2.9038 (6)	3.0413 (11)
	(B) M-CO(axial) Distances	
M-C(1)	1.811 (3)	1.929 (7)
M···O(1)	2.945 (3)	3.075 (7)
	(C) M-CO(equatorial) Distances	
M-C(2)	1.854 (2)	1.981 (6)
M-C(3)	1.850 (2)	1.987 (6)
M-C(4)	1.853 (2)	1.973 (6)
M-C(5)	1.865 (2)	2.007 (6)
M···O(2)	2.988 (2)	3.116 (5)
M···O(3)	2.981 (2)	3.119 (5)
M···O(4)	2.975 (2)	3.096 (5)
M···O(5)	2.993 (2)	3.128 (4)
	(D) C-O Distances	
C(1)-O(1)	1.134 (4)	1.146 (10)
C(2)-O(2)	1.134 (4)	1.136 (7)
C(3)-O(3)	1.131 (3)	1.132 (8)
C(4)-O(4)	1.124 (3)	1.124 (8)
C(5)-O(5)	1.128 (3)	1.122 (7)
	(E) M′-M-CO(axial) Angle	
M′-M-C(1)	177.03 (9)	176.34 (21)
	(F) M′-M-CO(equatorial) Angles	
M′-M-C(2)	86.25 (7)	86.70 (17)
M′-M-C(3)	84.61 (7)	84.21 (17)
M′-M-C(4)	89.16 (7)	89.71 (17)
M′-M-C(5)	85.51 (7)	84.88 (16)
	(G) OC(axial)-M-CO(equatorial) Angles	
C(1)-M-C(2)	95.50 (11)	95.52 (27)
C(1)-M-C(3)	93.71 (11)	93.65 (27)
C(1)-M-C(4)	93.29 (12)	93.29 (27)
C(1)-M-C(5)	92.08 (11)	92.19 (26)
	(H) OC-M-CO(diequatorial) Angles	
C(2)-M-C(3)	170.67 (10)	170.75 (24)
C(2)-M-C(4)	88.16 (10)	87.76 (24)
C(2)-M-C(5)	89.98 (10)	90.08 (24)
C(4)-M-C(5)	174.46 (10)	174.29 (24)
C(3)-M-C(4)	89.84 (10)	90.49 (24)
C(3)-M-C(5)	91.17 (10)	90.80 (23)
	(I) M-C-O Angles	
M-C(1)-O(1)	179.21 (27)	177.54 (65)
M-C(2)-O(2)	178.14 (20)	178.10 (52)
M-C(3)-O(3)	178.54 (20)	179.46 (53)
M-C(4)-O(4)	176.34 (22)	176.60 (54)
M-C(5)-O(5)	178.53 (30)	177.86 (51)

value of 2.923 (3) Å. (Interestingly, the change in this distance arises principally from changes in the measured unit-cell dimensions rather than from major shifts in the fractional atomic coordinates.) The newly determined Re-Re bond length is 3.0413 (11) Å, somewhat *longer* than the previously accepted distance of 3.02 Å.[13]

(2) The axial manganese-carbonyl distance of 1.811 (3) Å is 0.045 Å shorter than the average equatorial manganese-carbonyl distance of 1.856 [7] Å.[14] Similarly, the Re-CO(axial) bond length of 1.929 (7) Å is 0.058 Å shorter than the average Re-CO(equatorial) bond length of 1.987 [15] Å. This result is in accordance with the accepted model for M-CO bonding and is the net result of competition for d_π electron density between mutually trans pairs of equatorial carbonyl ligands.

(3) The axial manganese···oxygen and rhenium···oxygen distances (2.945 (3) and 3.075 (7) Å, respectively) are shorter than the appropriate equatorial metal···oxygen distances (Mn···O(equatorial, average) = 2.984 [8] Å and Re···O(equatorial, average) = 3.115 [13] Å).

(4) The Mn′-Mn-CO(equatorial) angles are all acute, ranging from 84.61 (7) to 89.16 (7)° and averaging 86.38°. The Re′-Re-CO(equatorial) angles show similar trends, ranging from 84.21 (17) to 89.71 (17)° and averaging 86.38°.

(5) The OC(axial)-M-CO(equatorial) angles are all obtuse, ranging from 92.08 (11) to 95.50 (11)° in $Mn_2(CO)_{10}$ and 92.19 (26) to 95.52 (27)° in $Re_2(CO)_{10}$.

(6) The carbon-oxygen distances are all equivalent within the limits of experimental error. Ranges are 1.124 (3)-1.134 (4) Å in $Mn_2(CO)_{10}$ and 1.122 (7)-1.146 (10) Å in $Re_2(CO)_{10}$.

(7) All M-C-O systems are close to linear; individual values range from 176.34 (22) to 179.21 (27)° in $Mn_2(CO)_{10}$ and 176.60 (54) to 179.46 (53)° in $Re_2(CO)_{10}$.

(8) The molecules have approximate D_{4d} symmetry in the solid state (see Figure 3). There are, however, numerous small deviations that are common to the two structures and presumably result from intermolecular interactions.

Acknowledgment. This work was supported by the National Science Foundation.

Registry No. $Mn_2(CO)_{10}$, 10170-69-1; $Re_2(CO)_{10}$, 14285-68-8.

Supplementary Material Available: Tables of observed and calculated structure factor amplitudes for $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$ and table of data-processing formulas (17 pages). Ordering information is given on any current masthead page.

(13) An electron diffraction study of $Re_2(CO)_{10}$ has revealed a Re-Re distance of 3.040 (5) Å: Gapotchenko, N. J.; Struchkov, Yu. T.; Alekseev, N. V.; Ronova, I. A. *J. Struct. Chem.* **1973**, *14*, 383.

(14) Esd's of average distances are enclosed in square brackets. They are calculated via the scatter formula $[\sigma]^2 = \sum_N (d_i - \bar{d})^2/(N-1)$.

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Mixed-Valence Pyrazine-Bridged Complexes of Ruthenium-Containing Substituted Phenanthrolines

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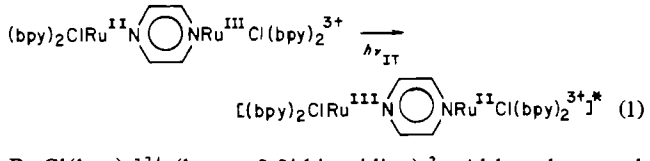
Mixed-valence transition-metal complexes continue to be of special interest, primarily because of the insight they provide into metal-metal interactions.[1] With the Hush model for mixed-valence complexes,[2] the extent of metal-metal interaction can be derived from the properties of the intervalence-transfer (IT) band (e.g., eq 1 for $[(bpy)_2ClRu(pyz)$-



$RuCl(bpy)_2]^{3+}$ (bpy = 2,2′-bipyridine).[3] Although several studies have focused on the effect of systematic changes in the *bridging* ligand on metal-metal interactions in these complexes,[4] few have examined the effect of a systematic change in the *nonbridging* ligands around the metal centers. Changes in the electronic environment about the metal could presumably lead to dramatic changes in the extent of metal-metal interaction. An understanding of such effects is essential if systems are to be designed in which the degree of metal-metal

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