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Crystal and Molecular Structure of Rhenium Manganese Decacarbonyl, $ReMn(CO)_{10}$, Containing an Unexpectedly Short Re-Mn Bond

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Heterobimetallic complexes have been prepared in increasing profusion in the last decade in a search for new catalytic properties.[1] In many instances these preparative studies include the first crystallographic characterization of a new metal-metal bond. Only four structures containing a Mn-Re bond have been reported (see Results and Discussion). The earliest is that of the decacarbonyl $MnRe(CO)_{10}$,[2] which could reasonably serve as the reference structure for other Mn-Re bonded systems. This structure, reported in 1967, was apparently carried out in the wrong space group (*Ia*, instead of *I2/a*) with unit cell esd's 1 order of magnitude greater than commonly available today. Additionally, no crystallographic methodology was reported and the Mn-Re bond distance, 2.96 Å, is given without an estimate of error. Churchill et al. recently accurately redetermined the homoatomic structures of $Mn_2(CO)_{10}$ and $Re_2(CO)_{10}$,[3] and Martin et al. reported a low-temperature structure for $Mn_2(CO)_{10}$.[4] We now report the redetermination of the $MnRe(CO)_{10}$ structure.

Experimental Section

$MnRe(CO)_{10}$ was prepared by published procedures[5] and purified by sublimation. Mass spectral characterization of the sample used for crystallographic work showed no peaks corresponding to Mn_2 or Re_2 fragments. A well-formed brick-shaped specimen was selected for data collection and found to diffract strongly. Crystal mounting and the measurement of unit cell parameters were accomplished by procedures previously employed.[6] Table I provides crystal data as well as details of the data collection and refinement. Corrections were applied to the intensity data for *Lp* effects and absorption (empirical, ψ-scan, fitted to six-parameter ellipsoidal model, seven reflections, 252 data, $9° \leq 2\theta \leq 36°$; R(int,before) = 4.2%, R(int,after) = 1.7%). An initial phasing of the data was obtained by using the metal atom coordinates from the $Re_2(CO)_{10}$ isomorph.[3]

As required, the structure is disordered in metal atom identity, and the asymmetric unit consists of an $M^*(CO)_5$ fragment, M* = an Mn/Re composite, with the fragments related by a crystallographic twofold rotational axis. Four strategies for dealing with the metal atom disorder were refined to convergence with all atoms anisotropic: (1) half-occupancy Mn and Re atoms without positional or temperature factor constraint; (2) one Re atom with a refined occupancy of 0.657 (compared to a theoretical $[(Z_{Re} + Z_{Mn}/2)/Z_{Re} = 0.667]$ "occupancy"); (3) one "rhenganese" atom with linearly interpolated composite scattering factors at full-occupancy; (4) half-occupancy Mn and Re atoms with all positional and thermal parameters refined as single, linked variables. Some comparative results of the four strategies are given in Table II, which reveal that, with the exception of strategy 1, there are only insignificant differences in the final parameters and no differences in the chemical information obtained from the results. Electron density plots, Figure 2, show a tightly and essentially spherically contoured metal atom, invalidating strategy 1 at the available "resolution", $d = \lambda/2 \sin\theta = 0.8$ Å. Although strategies 2, 3, and 4 yielded chemically identical results, we report the detailed results of strategy 4 because of the lower residuals and the use of unapproximated atomic form factors. Atomic coordinates and temperature factors are given in Table III and bond distances and angles in Table IV.

Results and Discussion

Figure 1 shows the expected approximate D_{4d} symmetry of $MnRe(CO)_{10}$. $MnRe(CO)_{10}$ is isomorphous with the three group 7 homometallic decacarbonyls. A crystallographic twofold rotational axis is perpendicular to the midpoint of the M-M′ vector. The crystallographic results appear indistinguishable from those expected for a homometallic decacarbonyl with metal atom scattering power intermediate between Mn and Re. Figure 2a shows the metal atom core electron density for $MnRe(CO)_{10}$ with carbonyl group contributions deleted. The nearly spherical shape (identical in two other views perpendicular to the one shown) of the composite atom core electron density contours argues against

Table I. Crystal, Data Collection, and Refinement Parameters for $MnRe(CO)_{10}$

(a) Crystal Parameters

formula	$MnReC_{10}O_{10}$	Z	4
fw	521.2	V, Å^3	1454.9 (7)
cryst syst	monoclinic	D(calcd), g cm^{-3}	2.379
space group	*I2/a*	μ(Mo Kα), cm^{-1}	97.7
a, Å	14.390 (4)	temp, K	295
b, Å	7.112 (2)	cryst dim., mm	0.30 × 0.35 × 0.39
c, Å	14.736 (3)	cryst color	pale yellow
β, deg	105.54 (2)		

(b) Data Collection

diffractometer	Nicolet R3	octants collcd	$\pm h,+k,+l$
radiation (λ, Å)	Mo Kα (0.71073)	no. of rflns collcd	1637
monochromator	graphite	no. of unique rflcns	1427
2θ range, deg	$4 \leq 2\theta \leq 53$	R(int), %	1.84
scan range, deg	[1.8 + (Kα_2 - Kα_1)]	no. of unique rflns, $F_o \geq 2\sigma(F_o)$	1203
scan type	θ-2θ	T max, T min	0.059, 0.033
scan speed deg min^{-1}	var, 4-10	stds/reflns	3/97 (<1% decay)

(c) Refinement[a]

R_F, %	3.26	highest peak, final diff map, e Å^{-3}	0.59
R_{wF}, %	3.67		
GOF	1.06	lowest trough, e Å^{-3}	-0.42
Δ/σ	0.004	slope, normal prob plot	0.901
data/param	11.8		

[a] Results from a model with colocated, half-occupancy Re and Mn atoms.

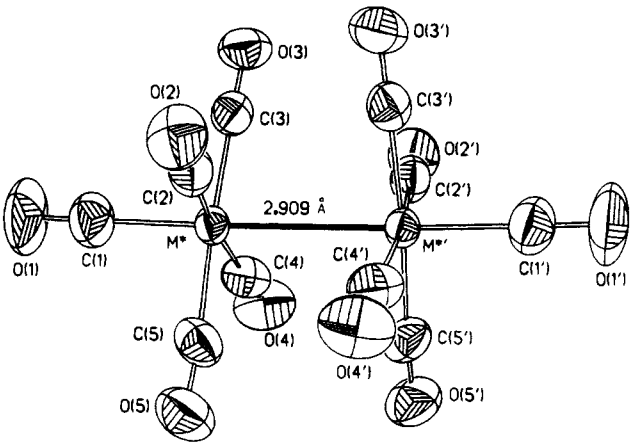

Figure 1. Thermal ellipsoid and labeling diagram for $MnRe(CO)_{10}$ (50% ellipsoids).

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Table II. Comparison of Selected Results of Four Refinement Strategies

	(1) independent atoms @ 0.5 sof	(2) Re atom with ref sof (66%)	(3) M atom with composite form factors	(4) colocated Re and Mn atoms @ 0.5 sof
R_F, %; R_{wF}, %	3.33; 3.69	3.52; 3.88	3.51; 3.88	3.26; 3.67
max e density, final diff map, e Å^{-3}	0.44	0.68	0.68	0.59
d(Re–Mn), Å	2.915 (30)	2.909 (1)	2.909 (1)	2.909 (1)
M–M sepn	0.177 (3)			
d[C(1)–O(1)], Å	1.12 (1)	1.13 (1)	1.12 (1)	1.12 (1)
U_{iso}, Å^2	Mn, 0.0454 (31) Re, 0.0478 (9)	0.0509 (2)	0.0309 (2)	0.0490 (2)

Table III. Atomic Coordinates (×10^4) for $MnRe(CO)_{10}$

atom	x	y	z
Mn/Re	1557.9 (3)	2320.9 (6)	9319.4 (3)
O(1)	−340 (6)	2454 (12)	7808 (6)
O(2)	775 (5)	3994 (10)	10877 (4)
O(3)	2090 (5)	6262 (7)	8777 (4)
O(4)	2602 (5)	468 (10)	8009 (4)
O(5)	1092 (5)	−1485 (9)	10025 (6)
C(1)	347 (7)	2397 (12)	8387 (7)
C(2)	1062 (5)	3407 (12)	10289 (6)
C(3)	1885 (6)	4792 (11)	8954 (5)
C(4)	2212 (6)	1160 (11)	8497 (6)
C(5)	1299 (5)	−90 (11)	9763 (6)

Table IV. Bond Distances and Angles for $MnRe(CO)_{10}$

(a) Bond Distances (Å)

M–M′	2.909 (1)	C(1)–O(1)	1.12 (1)
M–C(1)	1.909 (9)	C(2)–O(2)	1.14 (1)
M–C(2)	1.922 (9)	C(3)–O(3)	1.14 (1)
M–C(3)	1.935 (8)	C(4)–O(4)	1.14 (1)
M–C(4)	1.911 (9)	C(5)–O(5)	1.13 (1)
M–C(5)	1.909 (8)		

(b) Bond Angles (deg)

M′–M–C(1)	177.2 (3)	C(2)–M–C(4)	171.8 (3)
M′–M–C(2)	87.2 (2)	C(2)–M–C(5)	87.8 (4)
M′–M–C(3)	86.6 (2)	C(3)–M–C(4)	91.1 (3)
M′–M–C(4)	84.9 (2)	C(3)–M–C(5)	176.0 (3)
M′–M–C(5)	89.7 (2)	C(4)–M–C(5)	90.1 (4)
C(1)–M–C(2)	94.3 (4)	O(1)–C(1)–M	176.7 (9)
C(1)–M–C(3)	90.9 (3)	O(2)–C(2)–M	177.7 (7)
C(1)–M–C(4)	93.7 (4)	O(3)–C(3)–M	177.2 (6)
C(1)–M–C(5)	92.8 (3)	O(4)–C(4)–M	180.0 (9)
C(2)–M–C(3)	90.4 (4)	O(5)–C(5)–M	175.9 (7)

(c) Torsion Angles (deg)

C(2)–M–M′–C(4′)	49.5	C(2)–M–M′–C(3′)	−41.9
C(3)–M–M′–C(3′)	48.7	C(4)–M–M′–C(5′)	−38.3
C(5)–M–M′–C(5′)	51.8		

a two-site metal atom disorder. Figure 2b is the reverse; the metal atom electron density is deleted and the differential carbonyl density plotted. (Full contouring is only seen for the carbonyl group in the view plane, C(1)–O(1).) Again the electron density reveals only the effects of thermal motion, not positional disorder (the positional disorder in the CO groups is, if it exists, of a magnitude small enough to be masked by thermal effects). The $MnRe(CO)_{10}$ average equatorial M–CO distance, 1.92 (1) Å, is the average of the equatorial distances found in $Mn_2(CO)_{10}$ (1.856 (7) Å) and $Re_2(CO)_{10}$ (1.987 (15) Å);[3] the axial M–CO distance in $MnRe(CO)_{10}$, 1.909 (9) Å, is between those found in $Mn_2(CO)_{10}$ (1.811 (3) Å) and $Re_2(CO)_{10}$ (1.929 (7) Å).[3]

The most striking feature in the structure of $MnRe(CO)_{10}$ is the short Re–Mn distance, 2.909 (1) Å (cf. Mn–Mn = 2.9038 (6) Å,[3] Mn–Mn = 2.895 (1) Å,[4] and Re–Re = 3.0413 (11) Å[3]). The Re–Mn value is considerably shorter than the 2.96-Å distance earlier determined.[2] Only three other Re–Mn distances have been reported:[8] $(CO)_5Re(H)Re(CO)_4Mn(CO)_5$, 2.960 (3) Å;[9] $(CO)_5MnRe(CO)_4(OCH_3)$, 2.972 (1) Å;[10] $ClMnRe(CO)_4(\mu\text{-}CO)(\mu\text{-}PhCCO)$, 2.817 (3) Å.[11] A bond order fractionally greater than 1 is proposed for the last entry.

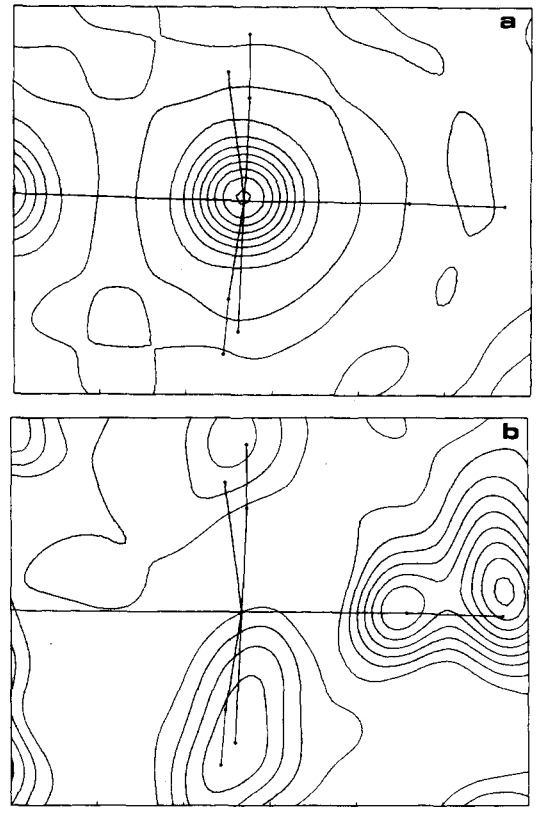

Figure 2. Equal interval difference electron density plots in the plane of the M–CO(axial) bond with heavy weighting of high-angle data to emphasize core densities: (a) metal atom (CO's deleted); (b) CO groups (metal atom deleted).

The unexpectedly short Re–Mn distance in $MnRe(CO)_{10}$ is consistent with the M–M bond dissociation energies obtained for $M_2(CO)_{10}$ structures, viz., D(Mn–Mn) = 94 (13) kJ mol^{-1}, D(Re–Re) = 187 (5) kJ mol^{-1}, and D(Mn–Re), 210 (10) kJ mol^{-1}.[12]

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Supplementary Material Available: Anisotropic temperature factors (Table 1S) (1 page); observed and calculated structure factors (Table 2S) (8 pages). Ordering information is given on any current masthead page.

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