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The Crystal and Molecular Structure of *cis*-(Diethylenetriamine)molybdenum Tricarbonyl; the Dependence of Mo–C Bond Length on Bond Order[1]

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The structure of *cis*-(diethylenetriamine)molybdenum tricarbonyl has been determined by the single crystal X-ray diffraction method using counter-diffractometer data. The crystals are orthorhomic, space group $P2_12_12_1$, with $a = 8.55 \pm 0.01$, $b = 11.90 \pm 0.01$, $c = 10.08 \pm 0.01$ Å. There are four molecules per unit cell. The coordination about each molybdenum is distorted octahedral, the distortion arising as a result of the bridging ethylene groups in the diethylenetriamine ligands restricting the freedom of the coordinating nitrogens. Hydrogen bonding appears to be very weak in the crystal, the shortest intermolecular O···N distance being 3.20 Å. A relationship between metal–carbon bond lengths and bond order is given, and it is shown that it correlates well with carbon–oxygen bond orders in metal carbonyls as derived from carbon–oxygen stretching force constants.

Introduction

It has been shown that carbon–oxygen stretching force constants, estimated in an approximate but consistent way, can be extremely useful in making and checking infrared assignments[2-4] for substituted metal carbonyls with essentially octahedral coordination and also for estimating carbon–oxygen and hence metal–carbon bond orders.[4]

In order to test and extend the bond order estimates, it was considered desirable to see how well they would correlate with bond length data. For this purpose the lengths of single and double bonds from molybdenum to carbon were required, and it appeared that both of these could be observed or deduced from the structure of *cis*-Mo(dien)$(CO)_3$, where dien stands for diethylenetriamine, $H_2NCH_2CH_2NHCH_2CH_2NH_2$. In order to secure relatively high accuracy it seemed advisable to collect a large amount of data using a counter-diffractometer.

Experimental

The Mo(dien)$(CO)_3$ was prepared by direct reaction at 150° between molybdenum hexacarbonyl and an excess of the freshly distilled diethylenetriamine as described previously.[3] The product crystallized from the excess diethylenetriamine upon slow cooling (3–4 hr.) to room temperature. The yellow crystals were washed with water and ethanol before drying overnight in a vacuum desiccator.

The rhombohedra were found to belong to the orthorhombic system, with the cell dimensions: $a = 8.55 \pm 0.01$, $b = 11.90 \pm 0.01$, $c = 10.08 \pm 0.01$ Å. The density, as determined by flotation in iodobenzene, was 1.83 g./cm.^{3}. Using the molecular weight of 283 a.m.u. the number of molecules per unit cell was calculated to be 3.99. The systematic absences $h00$ for $h \neq 2n$, $0k0$ for $k \neq 2n$, $00l$ for $l \neq 2n$ observed on precession and Weissenberg photographs uniquely determined the space group as $P\,2_12_12_1$ (No. 19).

The intensities of 1500 reflections $0 < 2\theta \leqslant 59°$ were collected using a General Electric Furnas-Harker eucentric goniometer equipped with a scintillation counter and Mo Kα radiation. The crystal, of approximate dimensions 0.2 mm. on an edge, was mounted with the c axis vertical and parallel to the spindle. The intensities were measured using a modification of the moving crystal–moving counter method of Furnas.[5,6]

No corrections were made for absorption, the linear coefficient, μ, being 12 cm.$^{-1}$. The settings required to observe reflections as well as the reciprocal Lorentz and polarization factors were computed as described previously.[6]

Determination of the Structure

A three-dimensional Patterson synthesis was computed[7] using about 500 of the low-angle reflections. From the large peak in each of the Harker sections, $(^1/_2, y, z)$, $(x, {}^1/_2, z)$, and $(x, y, {}^1/_2)$, the fractional coordinates of the molybdenum atom were estimated to be: $x = 0.317$; $y = 0.400$; $z = 0.817$. No other interatomic vectors could be identified on the Patterson map.

A Fourier summation was computed with all phases the same as those given by the molybdenum atoms, and this revealed a clear image of the molecule except for the carbon atoms of the ethylene bridges. One cycle of least-squares refinement[8] of Mo, C, O, and N atom coordinates was carried out, followed by two additional cycles of refinement of the isotropic temperature factors along with the coordinates; these reduced the residual[9] from 33% (Mo only) to 17%.

A three-dimensional Fourier map computed at this point showed the entire molecule. Two more cycles of refinement, including now all 1500 observed reflections, varying coordinates of all atoms in the first cycle and an isotropic temperature factor for each atom in addition in the second cycle, lowered the residual to 13%. A difference Fourier was computed, which indicated a need for anisotropic temperature factors and gave reasonable, although not distinct, positions for 7 of 13 hydrogen atoms.

Three more cycles of refinement of all atom coordinates and anisotropic temperature factors for each

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[1] Supported by the U. S. Atomic Energy Commission.

[2] F. A. Cotton and C. S. Kraihanzel, *J. Am. Chem. Soc.*, **84**, 4432 (1962).

[3] C. S. Kraihanzel and F. A. Cotton, *Inorg. Chem.*, **2**, 533 (1963).

[4] F. A. Cotton, *ibid.*, **3**, 702 (1964).

[5] T. C. Furnas, Jr., "Single Crystal Orienter Instruction Manual," General Electric X-Ray Department, 1957.

[6] F. A. Cotton and R. C. Elder, *Inorg. Chem.*, **3**, 397 (1964).

[7] Using ERFR-2, a two- and three-dimensional Fourier program for the IBM 709/7090 by W. G. Sly, D. P. Shoemaker, and J. H. Van den Hende.

[8] Using C. T. Prewitt's full-matrix crystallographic least-squares program for the IBM 709/7090. This program minimizes the function $(\Sigma w||F_o| - |F_c||^2)/\Sigma w|F_o|^2$.

[9] The residual is defined here as $(\Sigma||F_o| - |F_c||)/\Sigma|F_o|$.

TABLE I

FINAL ATOM PARAMETERS AND THEIR STANDARD DEVIATIONS[a]

	Coordinates			$\sigma \times 10^3$		
Atom	x/a	y/b	z/c	σ_x	σ_y	σ_z
Mo	0.3178	0.3957	0.8108	0.2	0.1	0.2
C_1	0.482	0.428	0.684	2	1	3
C_2	0.483	0.408	0.945	2	1	2
C_3	0.301	0.558	0.815	2	2	2
O_1	0.582	0.454	0.613	2	1	2
O_2	0.587	0.417	0.014	2	1	2
O_3	0.305	0.656	0.817	2	1	2
N_1	0.105	0.360	0.947	2	1	2
N_2	0.111	0.358	0.669	2	1	2
N_3	0.327	0.202	0.768	2	1	2
C_4	0.957	0.343	0.873	3	2	3
C_5	0.963	0.392	0.741	2	2	3
C_6	0.102	0.238	0.622	3	2	3
C_7	0.265	0.180	0.641	3	2	2

[a] The numbering of the atoms in this and the following tables coincides with that in Figure 1.

TABLE II

ANISOTROPIC THERMAL PARAMETERS[a] ($\times 10^3$)

Atom	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	7.3	3.7	7.2	0.1	0.2	0.2
C_1	9	4	10	1	−2	0.4
C_2	10	4	9	−1	−0.5	0
C_3	6	5	16	−2	−8	2
O_1	15	5	11	−0.4	2	0
O_2	12	5	18	−1	−9	0.8
O_3	13	3	44	0.3	2	−2
N_1	9	4	8	1	0.2	−1.
N_2	5	6	11	−0.1	−2	0.1
N_3	11	5	11	−0.8	0	0.4
C_4	8	8	12	0.1	0.8	1
C_5	7	6	19	0.7	−1	−3
C_6	14	7	11	2	0.1	3
C_7	15	7	8	0.7	0	−5

[a] Standard deviations: for Mo, 1–2 × 10^{-4}; for all other atoms, 1–4 × 10^{-3}.

TABLE III

BOND LENGTHS

Bond	Length, Å.	Bond	Length, Å.
Mo–C_1	1.933 ± 0.021	C_1–O_1	1.158 ± 0.027
Mo–C_2	1.953 ± 0.019	C_2–O_2	1.135 ± 0.026
Mo–C_3	1.942 ± 0.021	C_3–O_3	1.166 ± 0.030
Mo–N_1	2.311 ± 0.019	N_1–C_4	1.48 ± 0.03
Mo–N_2	2.310 ± 0.019	N_2–C_5	1.51 ± 0.03
Mo–N_3	2.348 ± 0.018	N_2–C_6	1.51 ± 0.03
C_4–C_5	1.45 ± 0.04	N_3–C_7	1.41 ± 0.03
C_6–C_7	1.56 ± 0.04		

atom lowered the residual to a final value of 0.095. In these final cycles all reflections were given equal weights and the hydrogen atoms were omitted. In the final cycle the changes in all positional and thermal parameters were less than the standard deviations. A final difference Fourier showed no peaks greater than ~0.7 electron/Å.^{3}.

The final positional parameters[10] are listed in Table I and the components of the anisotropic temperature factor tensors are listed in Table II.

TABLE IV

BOND ANGLES ABOUT MOLYBDENUM

C_1MoC_2	85.6 ± 0.8
C_2MoC_3	87.8 ± 0.9
C_1MoC_3	82.4 ± 0.9
N_1MoN_2	74.7 ± 0.7
N_2MoN_3	73.8 ± 0.6
N_1MoN_3	87.5 ± 0.6
N_1MoC_2	99.5 ± 0.7
N_1MoC_3	96.3 ± 0.8
N_2MoC_1	100.3 ± 0.8
N_2MoC_3	98.6 ± 0.8
N_3MoC_1	93.0 ± 0.8
N_3MoC_2	100.4 ± 0.7
N_1MoC_1	174.7 ± 0.7
N_2MoC_2	171.8 ± 0.7
N_3MoC_3	170.3 ± 0.8
Other Angles	
MoC_1O_1	175.5 ± 1.8
MoC_2O_2	174.2 ± 1.8
MoC_3O_3	173.9 ± 2.0
MoNC (av.)	111 ± 4
NCC (av.)	111 ± 2

The atomic scattering factors used in the refinements were: for Mo^+ that tabulated by Eichhorn[11]; and for carbon, nitrogen, and oxygen those tabulated by Hoerni and Ibers.[12]

A table of the observed and calculated structure factors has been deposited with the American Documentation Institute.[13]

Discussion

The Structure of *cis*-Mo(dien)(CO)$_3$.—The bond lengths and angles of the molecule[14] are listed in Tables III and IV. Standard deviations are estimated by Cruickshank's method.[15]

The shape of the coordination polyhedron about the molybdenum atom is that of a distorted octahedron, as shown in Figure 1. There are no crystallographic symmetry elements for the molecule, but the coordination polyhedron comes close to having C_{3v} symmetry. The average of the three C–Mo–C angles is 85.3°. The N–Mo–N bond angles seem to be influenced by the presence of the connecting ethylene groups across two of them, but not the third. The mean angle for the connected pairs of N atoms is 74.3 ± 0.4°, while that for the angle between the bonds to the unconnected pair is 87.5 ± 0.6°, a difference which is decidedly significant.

The three Mo–N bonds do not differ significantly in length, the mean and its standard deviation being 2.323 ± 0.011 Å. The three crystallographically independent Mo–C distances are also equal, within the

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[10] The standard deviations were estimated by the least-squares program using the formula $\sigma^2(j) = a_{jj}(\Sigma w\Delta^2)/(m - n)$, where a_{jj} is the appropriate element of the matrix inverse to the normal equation matrix.

[11] E. L. Eichhorn, *Acta Cryst.*, **10**, 717 (1957).

[12] J. A. Hoerni and J. A. Ibers, *ibid.*, **7**, 744 (1954).

[13] A table of observed and calculated structure factors has been deposited as Document No. 8218 with the American Documentation Institute, Auxiliary Publications Project, Photoduplication Service, Library of Congress, Washington 25, D. C. A copy may be secured by citing the document number and remitting in advance $3.75 for photoprints or $2.00 for 35-mm. microfilm, payable to Chief, Photoduplication Service, Library of Congress.

[14] Computed using J. S. Wood's MGPROG, a molecular geometry program for the IBM 7090, 1963.

[15] D. W. J. Cruickshank and A. P. Robertson, *Acta Cryst.*, **6**, 698 (1949).

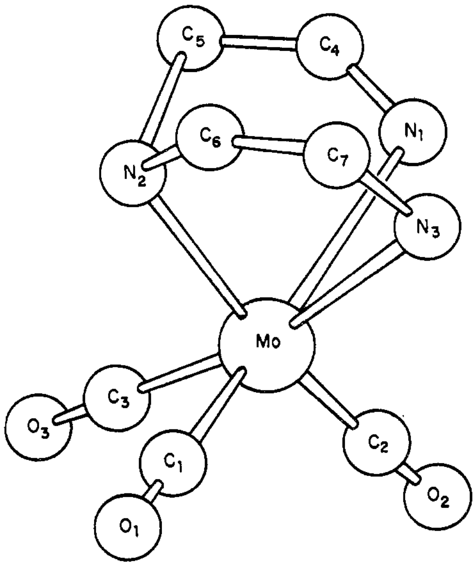

Figure 1.—A perspective view of the *cis*-(diethylenetriamine)-tricarbonylmolybdenum molecule.

significance of the results, with a mean value of 1.943 ± 0.012 Å.

The CO bonds are also of equal length within the significance of the results. The mean is 1.153 ± 0.016 Å. No correction has been made for "shortening" effects of thermal motions.

The distances and angles in the chelate rings are all normal. Thus the mean C–C bond length is 1.51 ± 0.03 Å., and the mean C–N bond length is 1.47 ± 0.02 Å. The puckering of the rings has been assessed by computing the mean planes of the two N–C–C portions of each ring. The dihedral angles (which correspond to the angle between projections of the C–N bonds down the C–C axis), of 48.8 ± 2° and 47.1 ± 2°, are approximately those to be expected for normal puckering.[6]

The Mo–C–O groups have a mean angle of 174.6 ± 1.2°. By the commonly used criterion of significance ($\Delta/\sigma > 3$), therefore, they deviate from 180° by an amount which is above the threshold of significance ($\Delta/\sigma = 4.5$). However, this may be due to intermolecular contacts.

Intermolecular distances are all normal. Those between N and O atoms were especially examined to see if hydrogen bonding occurs. The shortest ones are listed in Table V. Clearly, there are no strong intermolecular N–H···O bonds.

Table V

Shortest Intermolecular N to O Distances, Å.

$N_1 \cdots O_1$	3.20 ± 0.02
$N_1 \cdots O_2$	3.32 ± 0.02
$N_1 \cdots O_3$	3.81 ± 0.03
$N_2 \cdots O_2$	3.53 ± 0.03
$N_2 \cdots O_3$	3.63 ± 0.03
$N_3 \cdots O_1$	3.28 ± 0.02
$N_3 \cdots O_3$	3.29 ± 0.02

Mo–N Bond Length.—It is interesting, and perhaps remarkable, that the mean Mo–N bond length, 2.32 ± 0.01 Å., in this compound of formally zerovalent molybdenum is not significantly different from that found in dienMoO_3,[6] a compound in which molybdenum is formally in the oxidation state +6. In both cases, there is appreciable multiple bonding from Mo to the three ligand atoms or groups other than nitrogen. However, the nature or "sense" of the π-bonding is quite different in the two cases. In Mo(dien)$(CO)_3$ the CO groups accept dπ electron density from the metal atom so as to compensate for charge placed upon it by the six σ-donor bonds, thus tending to make the metal atom electrically neutral. In dienMoO_3, the shortness of the Mo–O bonds[6] indicates that they are approximately double bonds.[16] This can be viewed either in simple valence bond terms in which the bonds are symbolized as Mo═O, with partial positive charge on Mo and partial negative charge on O, or on a molecular orbital basis in which there is a σ-bond, $Mo^{+}\rightarrow O^{-}$, together with π-bonding, $Mo^{-}\leftarrow O^{+}$, the combination of which also leads to only a small positive charge on Mo. Thus, by rather different mechanisms in the two cases, the effective charges on the Mo atom in these two compounds are adjusted to values which probably differ very little. While the effective charge is probably higher in dienMoO_3 than in Mo(dien)$(CO)_3$, which would lessen the radius of the Mo atom, the tendency of bonds *trans* to multiply bonded oxygen atoms to be lengthened[17] would tend to compensate for this.

Relationship of Mo–C Bond Lengths to Bond Orders.—The results of this study, together with some data in the literature, provide a basis for discussing the relation between Mo–C bond lengths and bond orders.

The length of an Mo–C single bond has been estimated in two ways. It should be noted that the bond length figure we desire is that for a bond in which carbon uses an sp-hybrid orbital, as it does in M–CO bonds. First, we take the mean Mo–N bond length observed in dienMo$(CO)_3$, 2.32 ± 0.01 Å., as a starting point, since this seems certain to be essentially a single bond. The difference between the covalent radii of sp^3-hybridized C and N atoms is 0.07 Å.[18] Thus an Mo–C single bond might be expected to have a length of 2.39 Å. for sp^3 hybridization of the carbon atom. This should then be diminished by 0.07 Å. to make it applicable to sp-hybridized carbon, giving 2.32 Å. Second, we may take the Mo–C(ethyl) distance which has been observed by Bennett and Mason[19] in $(C_5H_5)Mo(CO)_3$-C_2H_5, 2.38 Å., and, after correcting for hybridization change, obtain 2.31 Å. for the Mo–C single bond for sp-hybridized carbon.[20]

For Mo–C bonds of orders 1.5 and 2.0 we turn to the Mo–C distances in $Mo(CO)_6$[21] and *cis*-Mo(dien)$(CO)_3$,

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(16) F. A. Cotton and R. M. Wing, *Inorg. Chem.*, in press.

(17) A. B. Blake, F. A. Cotton, and J. S. Wood, *J. Am. Chem. Soc.*, **86**, 3024 (1964); F. A. Cotton, S. M. Morehouse, and J. S. Wood, *Inorg. Chem.*, **3**, 1603 (1964).

(18) L. Pauling, "The Nature of the Chemical Bond," 3rd Ed., Cornell University Press, Ithaca, N. Y., 1960, p. 224.

(19) M. J. Bennett and R. Mason, *Proc. Chem. Soc.*, 273 (1963).

(20) The remarkably close agreement in the two estimates leads us to disagree with Bennett and Mason's suggestion that the Mo–C distance they have observed is indicative of an anomalously weak σ-bond.

which are 2.06 ± 0.02 and 1.94 ± 0.01 Å., respectively. The basis for assigning bond orders of 1.5 and 2.0 to the Mo–C bonds in these compounds has been presented previously.[4]

The figures discussed above are plotted in Figure 2. It may be seen that they define a curve which is physically reasonable. It is entirely comparable to the curves which are known for C–C, N–N, C–N, and C–O bonds[23] in being concave upward and it approaches the value of zero bond order asymptotically as the bond length goes to infinity. Also indicated on the plot are the probable limits of certainty in extrapolating the curve into the bond order range 2 to 3. In this range the curve is relatively flat and thus carbonyl compounds still more highly substituted with non-π-bonding ligands will not show particularly marked decreases in Mo–C bond lengths.

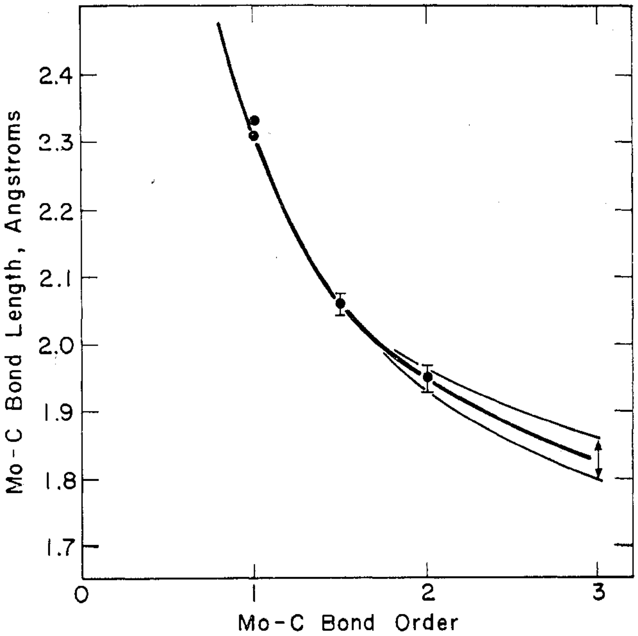

Figure 2.—A plot of Mo–C bond lengths against the Mo–C bond orders as estimated from the C–O force constants.[4] The upper points are derived from the Mo–N distance in Mo(dien)$(CO)_3$ and Mo–C(ethyl) in $C_6H_5Mo(CO)_3C_2H_5$. The middle point is the Mo–C distance in $Mo(CO)_6$. The lowest point is the Mo–C distance in Mo(dien)$(CO)_3$.

Relationship of C–O Bond Lengths to Bond Orders.—Figure 3 shows a plot of C–O bond lengths against C–O bond orders, with the bond lengths corrected where necessary for changes from the actual hybridization of the carbon to sp hybridization.[24] For a single bond the distance for aliphatic alcohols, 1.43 Å., diminished by 0.07 Å. was used. For bond order 1.33, the distance in the carbonate ion,[25] 1.29 Å., diminished by 0.03 Å. was used. For a bond order of 1.5, the distance 1.26 Å. diminished by 0.03 Å., typical of RCO_2^-, was used. For a bond order of 2.0, the values for CO_2, COS, COSe, $CH_2{=}C{=}O$, and isocyanates, uncorrected, were used. Finally, the distance in CO is taken as corresponding to a bond order of $\leqslant 3.0$.

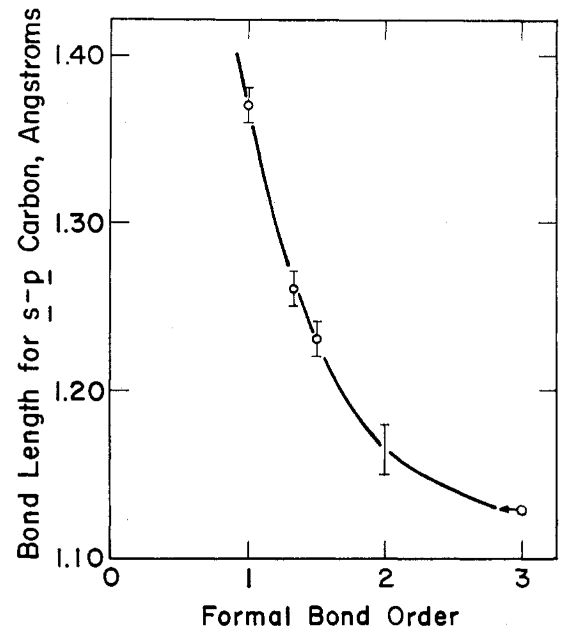

Figure 3.—A plot of carbon–oxygen bond lengths against bond orders for sp-hybridized carbon. See text for sources of data.

The significance of the plot for the present discussion lies in the fact that while there is a large over-all decrease in C–O bond lengths on going from bond orders of about 1 to about 3, very little of it occurs in the bond order range 2 to 3, which is that spanned by CO groups in practically all metal carbonyls and their derivatives. Thus, while changes in CO stretching force constants provide a good measure of CO bond order changes, CO bond lengths are virtually useless in this respect. For example, the change in Mo–C bond orders from 1.5 to 2.0, on going from $Mo(CO)_6$ to dien-$Mo(CO)_3$, would be expected, from Figure 3, to cause the CO bond lengths to change by only about 0.025 Å. Considering that the standard deviations in the observed values for CO bond lengths are generally about 0.02 Å. in the best of cases, the expected variations from one compound to another will not be significant.

Summary.—The preceeding discussion indicates that by using simple ideas about metal–CO bonding[2–4] it is possible to deduce from CO stretching frequencies the metal–carbon bond orders which then correlate in a reasonable manner with variations in metal–carbon bond lengths. Thus, the entire picture, which relates the physical observables, bond lengths, and CO stretching frequencies with one another and with the theoretical parameter, bond order, appears to be internally consistent. It is, then, presumably, reasonable to conclude that the actual magnitudes of the bond orders are approximately correct.

Acknowledgment.—We thank the M.I.T. Computation Center for access to the I.B.M. 7094 computer.

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(21) In unpublished electron diffraction work, in which due allowance was made for phase shifts due to discrepancies in the scattering factors for atoms of disparate size, G. M. Najarian [Ph.D. Thesis, California Institute of Technology, 1957] finds an Mo–C distance in $Mo(CO)_6$ of 2.06 ± 0.02 Å. This is used in preference to the older value of 2.08 ± 0.04 Å.[22]

(22) L. O. Brockway, R. V. G. Ewens, and M. W. Lister, *Trans. Faraday Soc.*, **34**, 1350 (1938).

(23) See ref. 18, p. 236, for the C–C curve.

(24) All bond lengths were taken from "Tables of Interatomic Distances and Configuration in Molecules and Ions," Special Publication No. 11, The Chemical Society, London, 1958, unless some other source is cited.

(25) R. L. Sass, *Acta Cryst.*, **10**, 567 (1957).