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Dichromium and Dimolybdenum Compounds of 2,6-Dimethoxyphenyl and 2,4,6-Trimethoxyphenyl Ligands

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The three compounds $Cr_2(DMP)_4$ (**1**), $Mo_2(DMP)_4$ (**2**), and $Cr_2(TMP)_4$ (**3**), where DMP represents 2,6-dimethoxyphenyl and TMP represents 2,4,6-trimethoxyphenyl, have been prepared by the reactions of the appropriate di- or trimethoxyphenyllithiums with $Cr_2(O_2CCH_3)_4$ or $Mo_2(O_2CCH_3)_4$. Each of the three compounds has been fully characterized by X-ray crystallography. **1** and **2** are isomorphous, crystallizing in the acentric space group $Pn2_1a$ with the following cell dimensions in Å, where those of $Cr_2(DMP)_4$ are listed first: $a = 16.266$ (3), 16.575 (2); $b = 16.560$ (3), 16.444 (3); $c = 11.350$ (1), 11.545 (2). With $Z = 4$, no crystallographic symmetry is imposed on the molecule, though it has approximately C_{2h} symmetry. In each case both enantiomorphs were refined and the correct one was selected based on its lower residuals. $Cr_2(TMP)_4$ forms monoclinic crystals in the space group $P2_1/n$ with $a = 11.075$ (3) Å, $b = 14.279$ (3) Å, $c = 11.748$ (2) Å, $\beta = 91.07$ (2) Å, and $Z = 2$; each molecule lies at an inversion center but approximates closely to C_{2h} symmetry. The two most significant structural features are (1) the extremely short M–M bonds, which are 1.847 (1) Å in $Cr_2(DMP)_4$, 1.849 (2) Å in $Cr_2(TMP)_4$, and 2.064 (1) Å in $Mo_2(DMP)_4$, and (2) the absence of any significant axial bonding to the metal atoms.

Introduction

Recent work in this laboratory[1-6] has opened a wholly new chapter in the chemistry of divalent chromium. An extensive series of dinuclear compounds with Cr–Cr bonds shorter than 1.90 Å has been discovered and a number of them have been described in structural detail. The compound that initiated this series of investigations, tetrakis(2,6-dimethoxyphenyl)dichromium, $Cr_2(DMP)_4$, has been the subject of a brief, preliminary report, as have its molybdenum analogue and the closely similar 2,4,6-trimethoxyphenyl compound, $Cr_2(TMP)_4$.

The purpose of this paper is to provide a detailed account of the preparation, structural characterization, and general properties of these three substances and to discuss critically the available data concerning the conditions under which exceedingly short Cr–Cr bonds, i.e., those <1.90 Å, are observed.

Experimental Section

Preparations. All manipulations were conducted in an atmosphere of nitrogen. Solvents were dried and deoxygenated prior to use.

2,6-Dimethoxyphenyllithium (LiDMP). A modification of a published method[7] was used. To a solution of 34.5 g (0.25 mol) of 1,3-dimethoxybenzene in 150 mL of diethyl ether was slowly added by syringe 156 mL (0.25 mol) of 1.6 M *n*-butyllithium in hexane. The mixture was refluxed for 12 h and then approximately half of the solvent was removed by evaporation under reduced pressure. The precipitate was collected by filtration, washed with hexane (2 × 100 mL), and dried to give 22.7 g (0.16 mol, 63% yield) of crystalline product.

2,4,6-Trimethoxyphenyllithium (LiTMP). This compound[8] was prepared in 52% yield by a procedure essentially the same as that just described for the preparation of LiDMP.

$Cr_2(DMP)_4$. Approximately 200 mL of THF was added to a flask containing 5.0 g (14.7 mmol) of anhydrous chromium(II) acetate and 8.5 g (59.0 mmol) of LiDMP. After stirring for 3 h, the reaction mixture was filtered through Celite. The remaining orange precipitate, if any, was extracted with hot THF, and the extracts were combined with the filtrate. Crystalline product (3.9 g, 6.0 mmol, 41% yield) was obtained by gently placing a layer of hexane (ca. 200 mL) over the concentrated THF filtrate (ca. 250 mL) and allowing the layers to mix by slow diffusion over a period of 5 days. Solutions of $Cr_2(DMP)_4$ are oxygen sensitive, but crystals can be handled in air for several minutes without visual indication of decomposition.

$Mo_2(DMP)_4$. An immediate reaction ensued when THF (200 mL) was added to a flask containing molybdenum(II) acetate (5.0 g, 11.7 mmol) and LiDMP (6.7 g, 46.7 mmol). The mixture was stirred for 30 min and then filtered through Celite. Dark red crystalline product (3.2 g, 4.3 mmol, 37% yield) was obtained by gently placing a layer of hexane (ca. 250 mL) over the concentrated THF filtrate (ca. 150 mL) and allowing the layers to combine by diffusion over a period of 7 days. Both solutions and crystals of $Mo_2(DMP)_4$ are extremely sensitive to oxygen.

$Cr_2(TMP)_4$. Anhydrous chromium(II) acetate (5.0 g, 14.7 mmol) and LiTMP (10.2 g, 58.8 mmol) were allowed to react in 100 mL of THF for 4 h. The mixture was filtered and the red-orange residue extracted with hot THF. A 46% yield of a crystalline red-orange product was obtained by addition of a layer of hexane as described above.

Crystal Structure Determinations.[9] In each case the crystal was sealed in a capillary tube, in a nitrogen atmosphere, with epoxy cement and mounted on a Syntex $P\bar{1}$ diffractometer. All work was done at 22 ± 2 °C using Mo Kα radiation monochromated by a graphite crystal in the incident beam. For collection of intensity data, the $\theta/2\theta$ method was used with scan rates varying from 4 to 24°/min depending on intensity, and backgrounds were counted at 2θ(Mo Kα_1) + 1.0 and 2θ(Mo Kα_2) − 1.0°. Data were processed and all calculations required to solve and refine the structures were carried out on a PDP 11/45 computer at the Molecular Structure Corp., College Station, Texas. Tables of observed and calculated structure factors for all three compounds are available as supplementary material.

Structure of $Mo_2(DMP)_4$. A crystal with approximate dimensions 0.4 × 0.6 × 0.3 mm was used. Axial photographs and unit cell constants indicated the orthorhombic system with unit cell dimensions of $a = 16.575$ (2), $b = 16.444$ (3), and $c = 11.545$ (2) Å. The cell volume of 3147 (1) Å^3 is consistent with $Z = 4$. Intensities were measured in the range $0 < \theta 2 \leq 55°$ giving 2769 independent reflections with $I > 3\sigma(I)$.

The systematic absences ($0kl$, $k + l = 2n + 1$; $hk0$, $h = 2n + 1$) limited the choice of space groups to the centric *Pnma* (No. 62) and the acentric $Pn2_1a$, a nonstandard setting of $Pna2_1$ (No. 33). The three-dimensional Patterson function was only solvable using the acentric space group. Least-squares refinement of the coordinates of the two molybdenum atoms followed by a difference Fourier synthesis revealed the remaining atoms. The structure was refined to convergence using isotropic thermal parameters for the methoxy carbon atoms and anisotropic ones for the remaining atoms. The final discrepancy indices were $R_1 = 0.0448$, $R_2 = 0.0575$ with the error in an observation of unit weight equal to 1.29. Because of the acentric space group the coordinates of the atoms were inverted and the resultant entantiomorphic structure was also refined to convergence. The residuals were slightly reduced, $R_1 = 0.0445$, $R_2 = 0.0573$, and the esd of an observation of unit weight was again 1.29. This second enantiomorph is used in the tabulations of results.

Structure of $Cr_2(DMP)_4$. A crystal of dimensions 0.65 × 0.53 × 0.48 mm was selected. Preliminary examination showed it to be isomorphous with the molybdenum compound. Unit cell parameters were found to be $a = 16.266$ (3) Å, $b = 16.560$ (3) Å, $c = 11.350$ (1) Å, and $V = 3057$ (1) Å^3. Data were collected in the range $0 < 2\theta \leq 55°$ to give 2438 reflections with $I > 3\sigma(I)$. The coordinates and thermal parameters from the $Mo_2(DMP)_4$ structure were used to commence refinement, which converged to given $R_1 = 0.0590$, $R_2 = 0.0801$ and the esd of an observation of unit weight equal to 1.726, with all nonhydrogen atoms except the methoxy carbon atoms treated anisotropically. The other enantiomorph was then tested and found to refine less satisfactorily, giving $R_1 = 0.0596$, $R_2 = 0.0806$ and the error in an observation of unit weight equal to 1.747. The coordinates

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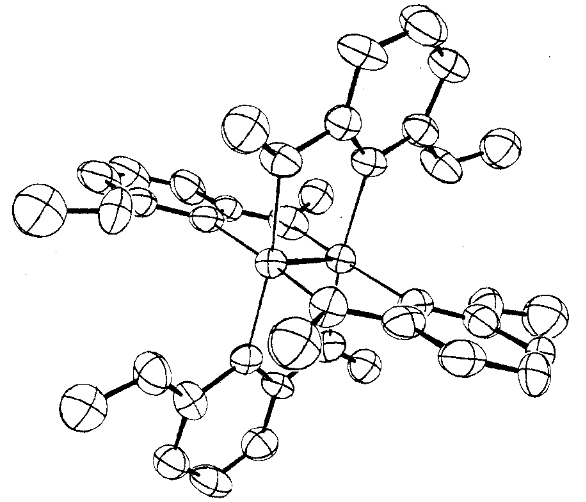

Figure 1. ORTEP drawing of the $M_2(DMP)_4$ type structure (with dimensions for M = Cr) in which atoms are represented by their ellipsoids of thermal vibration contoured to enclose 50% of the electron density.

of the first enantiomorph are reported.

Structure of $Cr_2(TMP)_4$. A crystal 0.4 × 0.4 × 0.3 mm was mounted. Preliminary examination showed that it belonged to the monoclinic system, and the unit cell dimensions were found to be a = 11.075 (3) Å, b = 14.279 (3) Å, c = 11.748 (2) Å, β = 91.07 (2)°; the volume, 1857.6 (7) Å^3, is consistent with $Z = 2$. Data were measured in the range $0 < 2\theta \leq 45°$, giving 1688 reflections with $I > 3\sigma(I)$. Systematic absences were those for the space group $P2_1/n$, a nonstandard setting of $P2_1/c$.

The coordinates of the unique chromium atom were determined from the Patterson map. All remaining nonhydrogen atoms were located by a sequence of refinement and difference Fourier maps. The final refinement, in which the methoxy carbon atoms were treated isotropically while all the other atoms were treated anisotropically, gave residuals R_1 = 0.066 and R_2 = 0.091.

Mass Spectrum. The high-resolution mass spectrum of $Cr_2(DMP)_4$ was run on a CEC21-110B mass spectrometer using a probe temperature of 200 °C and an ionizing electron beam of 70 eV. We thank Professor R. D. Grigsby for running the spectrum and Dr. M. W. Extine for the calculated parent ion mass pattern.

Results

The positional and thermal vibration parameters for the three structures are given in Tables I–III, and the bond lengths and angles are listed in Tables IV–VI. Figure 1 shows the structure of the $M_2(DMP)_4$ molecules and Figure 2 defines the atom numbering scheme for $Cr_2(DMP)_4$ (which is the same, mutatis mutandis, in the molybdenum compound). Only one pair of ligands is shown; for the other two, analogous numbers from 30 to 39 and 40 to 49 are used. Figure 3 shows the numbering scheme for $Cr_2(TMP)_4$.

All three molecules have virtual C_{2h} symmetry although this amount of symmetry is not demanded crystallographically. For the $M_2(DMP)_4$ molecules the entire molecule is the crystallographic asymmetric unit and therefore no crystallographic symmetry is imposed. Indeed the crystals themselves are chiral and it was necessary in each case to test both enantiomers in order to achieve optimum refinement of the molecular structures. $Cr_2(TMP)_4$ molecules reside upon crystallographic centers of inversion.

The existence of virtual C_{2h} symmetry means the following things in practical chemical terms. On each metal atom the arrangement of M–C and M–O bonds is such that the different kinds of bond are trans to each other. The C_2 axis of symmetry is a perpendicular bisector of the M–M bond and the plane of symmetry contains the M–M bond but does not contain any ligand atoms. The four ligands in the molecule are equivalent under the combined action of the symmetry operations of the group C_{2h}. Inspection of the data in Tables IV–VI will show that this is true within the experimental uncertainties.

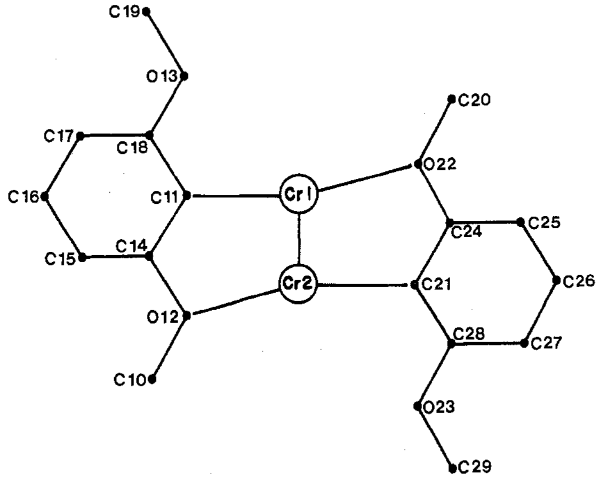

Figure 2. Schematic representation of two of the ligands and the metal atoms in $Cr_2(DMP)_4$, showing how the atom numbering scheme is defined.

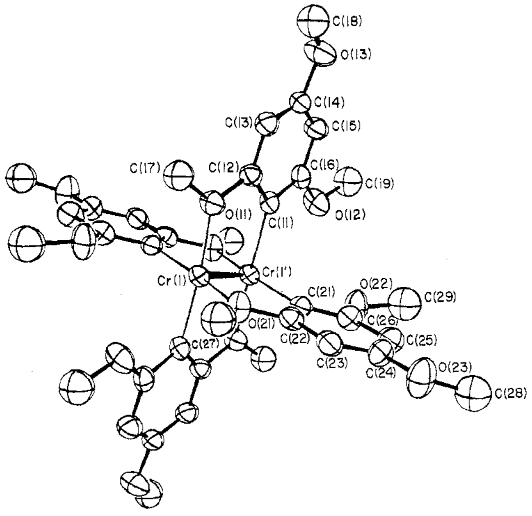

Figure 3. ORTEP drawing of the $Cr_2(TMP)_4$ molecule in which the atom numbering scheme is defined; unlabeled atoms are related by a center of inversion to numbered atoms and bear the corresponding primed labels. Atoms are represented by thermal vibration ellipsoids contoured to enclose 50% of the electron density.

Within the individual ligand, the C–C distances show no significant variation and the average of all C–C distances in all these molecules is 1.40 ± 0.03 Å. The two methoxy groups of each DMP ligand have essentially equal dimensions, even though one is coordinated and the other not. Each ligand is essentially planar, although some of the methyl groups are tipped slightly (ca. 10°) out of the plane defined by the phenyl ring and the oxygen atoms.

As is typical of all M_2(*o*-oxyphenyl)$_4$ molecules thus far examined, the M–M–C angles are just slightly greater than 90°, whereas the M–M–O angles are distinctly obtuse, averaging around 102° for the chromium compounds, but considerably less, 96.1 (3)°, in the molybdenum case because of the greater M–M distance.

Mass Spectrum of $Cr_2(DMP)_4$. A strong parent ion multiplet, shown in Figure 4, was observed. The pattern is in quantitative agreement with expectation for a dinuclear ion of the assigned formula. Multiplets corresponding to $[Cr_2(DMP)_3{}^+]^+$, $[Cr_2(DMP)_2{}^+]^+$, $[Cr_2(DMP)_2 - CH_3]^+$, $[Cr_2(DMP)_2 - 2CH_3]^+$, $[Cr_2(DMP)_4]^{2+}$, $[Cr_2(DMP)_3]^{2+}$, and

Table I. Positional and Thermal Parameters for Tetrakis(2,6-dimethoxyphenyl)dimolybdenum[a,b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo(1)	−0.15623 (4)	−0.25000 (0)	−0.42878 (5)	0.00252 (2)	0.00240 (2)	0.00479 (4)	0.00046 (4)	0.00007 (6)	−0.00065 (6)
Mo(2)	−0.08071 (4)	−0.27591 (5)	−0.56610 (5)	0.00239 (2)	0.00248 (2)	0.00526 (4)	0.00040 (4)	0.00034 (6)	−0.00091 (7)
O(12)	−0.0244 (4)	−0.3887 (4)	−0.4844 (6)	0.0036 (3)	0.0029 (2)	0.0087 (5)	0.0009 (4)	−0.0005 (7)	−0.0004 (6)
O(13)	−0.1816 (5)	−0.3005 (5)	−0.1721 (5)	0.0061 (3)	0.0055 (4)	0.0064 (5)	0.0019 (6)	0.0033 (7)	0.0017 (7)
O(22)	−0.2105 (4)	−0.1367 (4)	−0.5068 (5)	0.0032 (2)	0.0030 (2)	0.0076 (5)	0.0021 (4)	0.0017 (6)	0.0000 (6)
O(23)	−0.0574 (5)	−0.2198 (5)	−0.8235 (5)	0.0060 (3)	0.0046 (3)	0.0073 (5)	0.0010 (6)	0.0024 (7)	−0.0004 (7)
O(32)	−0.0726 (4)	−0.1622 (4)	−0.3397 (5)	0.0040 (3)	0.0038 (3)	0.0063 (4)	−0.0004 (5)	0.0003 (6)	−0.0024 (6)
O(33)	0.0947 (4)	−0.2371 (5)	−0.6468 (6)	0.0033 (2)	0.0049 (3)	0.0118 (6)	−0.0013 (5)	0.0046 (6)	−0.0035 (8)
O(42)	−0.1654 (3)	−0.3657 (4)	−0.6564 (5)	0.0033 (2)	0.0030 (2)	0.0073 (5)	0.0003 (4)	0.0001 (6)	−0.0032 (5)
O(43)	−0.3323 (3)	−0.2831 (5)	−0.3515 (6)	0.0037 (2)	0.0044 (3)	0.0089 (5)	−0.0011 (5)	0.0035 (6)	−0.0021 (7)
C(11)	−0.1071 (5)	−0.3481 (5)	−0.3286 (8)	0.0023 (3)	0.0025 (3)	0.0085 (7)	−0.0002 (5)	−0.0031 (8)	0.0006 (8)
C(14)	−0.0502 (5)	−0.4044 (5)	−0.3734 (9)	0.0025 (3)	0.0025 (3)	0.0102 (8)	−0.0004 (5)	−0.0034 (9)	0.0012 (9)
C(15)	−0.0234 (6)	−0.4733 (6)	−0.3103 (10)	0.0034 (4)	0.0037 (4)	0.0162 (12)	0.0000 (7)	−0.0047 (11)	0.0068 (11)
C(16)	−0.0491 (7)	−0.4797 (7)	−0.1950 (10)	0.0040 (4)	0.0050 (4)	0.0117 (10)	−0.0010 (8)	−0.0018 (11)	0.0069 (10)
C(17)	−0.1044 (6)	−0.4226 (7)	−0.1469 (9)	0.0038 (4)	0.0060 (5)	0.0096 (8)	−0.0027 (8)	−0.0006 (11)	0.0063 (11)
C(18)	−0.1302 (5)	−0.3593 (5)	−0.2149 (8)	0.0032 (3)	0.0031 (3)	0.0063 (6)	−0.0011 (6)	−0.0012 (8)	0.0017 (8)
C(21)	−0.1324 (5)	−0.1743 (5)	−0.6646 (7)	0.0029 (3)	0.0028 (3)	0.0050 (5)	−0.0013 (5)	−0.0003 (7)	0.0003 (7)
C(24)	−0.1853 (5)	−0.1201 (5)	−0.6213 (8)	0.0030 (3)	0.0029 (3)	0.0073 (7)	−0.0003 (6)	−0.0007 (8)	0.0004 (8)
C(25)	−0.2162 (6)	−0.0527 (6)	−0.6798 (8)	0.0034 (3)	0.0030 (3)	0.0099 (8)	−0.0008 (6)	−0.0023 (9)	0.0026 (9)
C(26)	−0.1921 (6)	−0.0432 (6)	−0.7939 (9)	0.0037 (4)	0.0035 (4)	0.0118 (9)	−0.0020 (6)	−0.0026 (11)	0.0042 (10)
C(27)	−0.1389 (6)	−0.0974 (6)	−0.8461 (9)	0.0038 (4)	0.0042 (4)	0.0096 (8)	−0.0021 (7)	−0.0029 (10)	0.0056 (9)
C(28)	−0.1103 (5)	−0.1603 (6)	−0.7804 (8)	0.0030 (3)	0.0038 (4)	0.0080 (7)	−0.0016 (6)	−0.0003 (9)	0.0003 (9)
C(31)	0.0104 (5)	−0.1979 (5)	−0.4946 (7)	0.0028 (3)	0.0023 (3)	0.0065 (6)	−0.0002 (5)	−0.0018 (8)	0.0003 (7)
C(34)	0.0021 (6)	−0.1500 (6)	−0.3979 (8)	0.0035 (3)	0.0029 (3)	0.0076 (7)	0.0002 (6)	0.0003 (9)	0.0005 (8)
C(35)	0.0579 (7)	−0.0935 (7)	−0.3569 (10)	0.0047 (4)	0.0040 (4)	0.0102 (9)	−0.0014 (8)	−0.0003 (11)	−0.0034 (10)
C(36)	0.1300 (7)	−0.0864 (8)	−0.4186 (11)	0.0044 (4)	0.0046 (5)	0.0162 (13)	−0.0032 (8)	−0.0013 (14)	−0.0022 (14)
C(37)	0.1443 (6)	−0.1329 (7)	−0.5171 (11)	0.0032 (3)	0.0044 (4)	0.0135 (11)	−0.0025 (7)	−0.0020 (11)	0.0011 (13)
C(38)	0.0839 (5)	−0.1882 (6)	−0.5521 (8)	0.0031 (3)	0.0029 (3)	0.0085 (7)	−0.0004 (5)	0.0005 (9)	0.0005 (8)
C(41)	−0.2488 (5)	−0.3270 (5)	−0.5023 (7)	0.0027 (3)	0.0031 (3)	0.0059 (6)	0.0007 (5)	0.0001 (8)	0.0002 (8)
C(44)	−0.2410 (5)	−0.3723 (5)	−0.6027 (8)	0.0030 (3)	0.0025 (3)	0.0071 (6)	0.0001 (5)	−0.0017 (8)	0.0007 (8)
C(45)	−0.3001 (6)	−0.4226 (6)	−0.6476 (9)	0.0036 (4)	0.0032 (4)	0.0100 (8)	−0.0006 (6)	−0.0013 (10)	−0.0021 (9)
C(46)	−0.3743 (7)	−0.4255 (7)	−0.5900 (11)	0.0046 (5)	0.0038 (4)	0.0136 (12)	−0.0019 (8)	−0.0024 (12)	0.0011 (12)
C(47)	−0.3876 (6)	−0.3808 (6)	−0.4902 (9)	0.0034 (4)	0.0033 (4)	0.0098 (9)	−0.0013 (6)	−0.0004 (10)	0.0010 (10)
C(48)	−0.3239 (5)	−0.3313 (6)	−0.4493 (8)	0.0030 (3)	0.0026 (3)	0.0089 (8)	0.0003 (5)	0.0002 (9)	0.0011 (8)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
C(49)	−0.2250 (9)	−0.3151 (10)	−0.068 (1)	7.2 (3)	C(39)	0.1534 (8)	−0.2131 (9)	−0.730 (1)	6.8 (3)
C(10)	0.0502 (7)	−0.4233 (7)	−0.519 (1)	5.1 (2)	C(30)	−0.0902 (7)	−0.1185 (8)	−0.238 (1)	6.0 (3)
C(29)	−0.0242 (9)	−0.2079 (10)	−0.939 (1)	7.0 (3)	C(49)	−0.3987 (7)	−0.2968 (8)	−0.277 (1)	5.6 (2)
C(20)	−0.2805 (8)	−0.0938 (8)	−0.460 (1)	5.7 (3)	C(40)	−0.1543 (6)	−0.3936 (7)	−0.771 (1)	5.0 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Numbers in parentheses are esd's in the least significant digit.

$HDMP^+$, as well as others, were also seen.

Discussion

The significance of these molecules with respect to our understanding of multiple bonding between metal atoms cannot be too strongly emphasized. These were the first quadruply bonded dinuclear molecules containing the *o*-oxyphenyl type ligand to be structurally characterized[1] and they have clearly opened the door to an unforeseen field in which some of the formally shortest (vide infra) and, presumably, strongest of all chemical bonds will be found.

Both the Cr–Cr and Mo–Mo bond lengths found in these molecules were the shortest of their kind known when first reported.[1] That is still the case for the Mo–Mo bond; 2.064 (1) Å still is the shortest distance for any Mo–Mo bond, or indeed for any M–M bond at all formed by metal atoms other than Cr–Cr or Cr–Mo.[10] For Cr–Cr bonds, the one-time record of 1.847 (1) Å in $Cr_2(DMP)_4$ has since been eclipsed by the distances of 1.828 (2) Å in tetrakis(2-methoxy-5-methylphenyl)dichromium[5] and 1.830 (4) Å in $Li_6Cr_2(C_6H_4O)_4Br_2(Et_2O)_6$.[3]

In view of the formal similarity of the ligands used here to the many others found in quadruply bonded dimetal species[11,12] and the generally isoelectronic character of these and the other known quadruply bonded compounds, we assume that the assignment of quadruple Cr–Cr and Mo–Mo bonds to these molecules will not require detailed explanation. We turn then to two fascinating questions provoked by these results. First, why are the Cr–Cr and Mo–Mo bonds in these molecules—and others containing *o*-oxyphenyl type ligands—so short? Second, how short are they in comparison

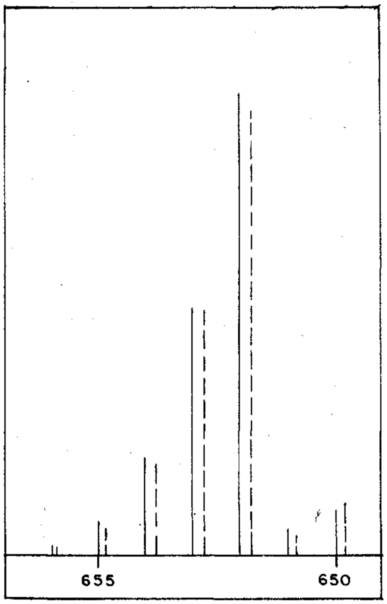

Figure 4. Structure of the parent ion multiplet in the mass spectrum of $Cr_2(DMP)_4$. Full lines represent the experimental spectrum and dashed lines the spectrum calculated from the normal-isotope abundances for the $[Cr_2(DMP)_4]^+$ ion.

Table II. Positional and Thermal Parameters for Tetrakis(2,6-dimethoxyphenyl)dichromium[a,b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr(1)	0.15319 (7)	0.25000 (0)	0.4360 (1)	0.00247 (4)	0.00236 (3)	0.00528 (7)	0.00032 (7)	−0.0000 (1)	−0.0009 (1)
Cr(2)	0.08449 (7)	0.27290 (8)	0.5612 (1)	0.00243 (4)	0.00244 (3)	0.00567 (8)	0.00031 (7)	0.0002 (1)	−0.0009 (1)
O(12)	0.0252 (3)	0.3806 (4)	0.4989 (6)	0.0034 (2)	0.0031 (2)	0.0128 (7)	0.0014 (4)	−0.0003 (8)	−0.0012 (7)
O(13)	0.1827 (4)	0.2989 (4)	0.1786 (5)	0.0062 (3)	0.0043 (3)	0.0062 (5)	0.0001 (5)	0.0023 (7)	0.0007 (6)
O(22)	0.2120 (3)	0.1423 (3)	0.4950 (5)	0.0032 (2)	0.0030 (2)	0.0071 (5)	0.0022 (4)	0.0013 (6)	−0.0003 (5)
O(23)	0.0585 (4)	0.2179 (5)	0.8210 (5)	0.0049 (3)	0.0060 (3)	0.0076 (5)	0.0011 (5)	0.0023 (7)	0.0024 (7)
O(32)	0.0812 (3)	0.1676 (3)	0.3353 (5)	0.0030 (2)	0.0034 (2)	0.0081 (5)	−0.0005 (4)	0.0011 (6)	−0.0041 (6)
O(33)	−0.0910 (3)	0.2369 (4)	0.6465 (7)	0.0035 (2)	0.0046 (3)	0.0129 (6)	−0.0023 (4)	0.0040 (7)	−0.0044 (8)
O(42)	0.1561 (4)	0.3569 (4)	0.6603 (5)	0.0035 (2)	0.0038 (2)	0.0071 (4)	0.0010 (4)	−0.0003 (6)	−0.0028 (6)
O(43)	0.3302 (4)	0.2838 (4)	0.3526 (5)	0.0041 (2)	0.0047 (3)	0.0078 (5)	−0.0007 (5)	0.0034 (6)	−0.0029 (7)
C(11)	0.1054 (5)	0.3447 (5)	0.3393 (7)	0.0025 (3)	0.0030 (3)	0.0081 (7)	−0.0006 (5)	−0.0027 (8)	0.0009 (8)
C(14)	0.0498 (5)	0.3990 (5)	0.3853 (7)	0.0022 (3)	0.0025 (3)	0.0081 (6)	0.0004 (5)	−0.0020 (8)	0.0017 (8)
C(15)	0.0206 (6)	0.4683 (6)	0.3234 (10)	0.0036 (4)	0.0040 (4)	0.0141 (11)	−0.0005 (7)	−0.0012 (11)	0.0050 (11)
C(16)	0.0476 (6)	0.4781 (6)	0.2124 (11)	0.0033 (3)	0.0041 (4)	0.0182 (13)	−0.0008 (7)	−0.0027 (13)	0.0055 (12)
C(17)	0.1019 (6)	0.4210 (7)	0.1539 (10)	0.0039 (4)	0.0050 (4)	0.0146 (11)	−0.0022 (7)	−0.0050 (12)	0.0057 (12)
C(18)	0.1293 (5)	0.3579 (5)	0.2232 (8)	0.0029 (3)	0.0033 (3)	0.0085 (7)	−0.0009 (5)	−0.0025 (8)	0.0029 (8)
C(21)	0.1315 (5)	0.1762 (5)	0.6577 (7)	0.0032 (3)	0.0024 (3)	0.0072 (7)	−0.0001 (5)	−0.0016 (8)	0.0003 (7)
C(24)	0.1868 (6)	0.1222 (5)	0.6088 (8)	0.0040 (3)	0.0023 (3)	0.0098 (7)	−0.0009 (6)	−0.0038 (9)	−0.0006 (8)
C(25)	0.2190 (6)	0.0543 (5)	0.6678 (9)	0.0038 (3)	0.0025 (3)	0.0128 (9)	−0.0004 (6)	−0.0050 (10)	0.0016 (9)
C(26)	0.1927 (6)	0.0447 (6)	0.7858 (9)	0.0048 (4)	0.0037 (3)	0.0125 (9)	−0.0020 (6)	−0.0023 (11)	0.0085 (9)
C(27)	0.1382 (5)	0.0969 (6)	0.8374 (8)	0.0036 (3)	0.0041 (3)	0.0088 (7)	−0.0022 (6)	−0.0026 (9)	0.0062 (8)
C(28)	0.1086 (5)	0.1620 (6)	0.7725 (8)	0.0031 (3)	0.0038 (3)	0.0089 (8)	−0.0014 (6)	0.0001 (9)	−0.0001 (9)
C(31)	−0.0060 (5)	0.1995 (5)	0.4917 (8)	0.0028 (3)	0.0026 (3)	0.0081 (7)	−0.0003 (5)	−0.0018 (8)	−0.0008 (8)
C(34)	0.0037 (5)	0.1528 (5)	0.3940 (7)	0.0031 (3)	0.0029 (3)	0.0076 (7)	0.0003 (5)	−0.0006 (8)	0.0000 (8)
C(35)	−0.0497 (6)	0.0988 (6)	0.3449 (10)	0.0032 (3)	0.0035 (3)	0.0145 (10)	−0.0015 (6)	−0.0027 (11)	−0.0019 (11)
C(36)	−0.1237 (7)	0.0893 (7)	0.4142 (10)	0.0055 (5)	0.0047 (4)	0.0132 (11)	−0.0043 (8)	0.0007 (13)	−0.0030 (12)
C(37)	−0.1394 (6)	0.1338 (6)	0.5116 (9)	0.0038 (3)	0.0033 (3)	0.0113 (9)	−0.0016 (6)	−0.0007 (11)	−0.0010 (10)
C(38)	−0.0790 (5)	0.1888 (5)	0.5485 (8)	0.0029 (3)	0.0030 (3)	0.0096 (8)	0.0001 (5)	−0.0002 (9)	−0.0002 (9)
C(41)	0.2433 (4)	0.3216 (4)	0.5068 (7)	0.0026 (3)	0.0022 (2)	0.0066 (6)	0.0013 (5)	−0.0007 (8)	0.0005 (7)
C(44)	0.2340 (4)	0.3669 (5)	0.6073 (7)	0.0019 (3)	0.0027 (3)	0.0079 (6)	−0.0002 (5)	−0.0007 (7)	−0.0004 (8)
C(45)	0.2952 (6)	0.4206 (6)	0.6546 (8)	0.0045 (4)	0.0040 (4)	0.0072 (7)	−0.0010 (7)	−0.0013 (9)	−0.0030 (9)
C(46)	0.3675 (6)	0.4239 (6)	0.5986 (9)	0.0031 (3)	0.0040 (4)	0.0137 (10)	−0.0022 (6)	−0.0020 (11)	−0.0006 (11)
C(47)	0.3823 (5)	0.3809 (6)	0.4939 (8)	0.0032 (3)	0.0040 (3)	0.0082 (8)	−0.0009 (6)	0.0002 (10)	−0.0010 (9)
C(48)	0.3208 (5)	0.3312 (5)	0.4530 (8)	0.0033 (3)	0.0024 (3)	0.0089 (7)	0.0004 (5)	0.0021 (8)	0.0004 (8)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
C(19)	0.2247 (9)	0.3165 (10)	0.0759 (12)	7.8 (3)	C(39)	−0.1524 (7)	0.2154 (7)	0.7301 (11)	6.0 (2)
C(10)	−0.0505 (7)	0.4128 (7)	0.5438 (9)	5.3 (2)	C(30)	0.1047 (6)	0.1192 (7)	0.2428 (10)	5.5 (2)
C(29)	0.0246 (8)	0.2072 (9)	0.9354 (11)	6.9 (3)	C(49)	0.3991 (7)	0.2967 (7)	0.2842 (10)	5.7 (2)
C(20)	0.2843 (8)	0.1031 (8)	0.4464 (10)	6.2 (2)	C(40)	0.1362 (6)	0.3909 (6)	0.7704 (9)	4.5 (2)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Numbers in parentheses are esd's in the least significant digit.

Table III. Positional and Thermal Parameters for Tetrakis(2,4,6-trimethoxyphenyl)dichromium[a,b]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Cr(1)	0.0069 (1)	0.06001 (8)	0.0289 (1)	0.00557 (9)	0.00276 (5)	0.00456 (8)	0.0004 (2)	0.0013 (1)	0.0003 (1)
O(11)	−0.1859 (4)	−0.0947 (3)	0.0182 (4)	0.0060 (4)	0.0027 (2)	0.0086 (5)	−0.0011 (6)	0.0015 (8)	−0.0025 (6)
O(12)	−0.1600 (5)	0.2207 (4)	0.1150 (5)	0.0098 (6)	0.0025 (3)	0.0103 (5)	−0.0001 (7)	0.0047 (9)	−0.0020 (6)
O(13)	−0.5327 (5)	0.0658 (4)	0.1793 (5)	0.0069 (5)	0.0054 (4)	0.0119 (6)	0.0013 (8)	0.0050 (9)	−0.0013 (8)
O(21)	0.0362 (5)	−0.1447 (3)	0.1153 (4)	0.0104 (6)	0.0019 (2)	0.0055 (4)	0.0003 (7)	−0.0003 (8)	0.0005 (5)
O(22)	0.0874 (6)	0.1585 (4)	0.2538 (5)	0.0158 (7)	0.0037 (3)	0.0066 (4)	0.0010 (9)	−0.0018 (10)	−0.0013 (7)
O(23)	0.1627 (6)	−0.1076 (4)	0.5027 (5)	0.0176 (8)	0.0051 (4)	0.0066 (5)	0.0026 (10)	−0.0037 (10)	0.0018 (7)
C(11)	−0.1732 (6)	0.0612 (5)	0.0720 (6)	0.0059 (6)	0.0027 (4)	0.0051 (5)	−0.0009 (9)	0.002 (1)	−0.0006 (8)
C(12)	−0.2453 (7)	−0.0164 (5)	0.0652 (6)	0.0054 (6)	0.0038 (4)	0.0047 (6)	0.0018 (9)	0.000 (1)	0.0008 (9)
C(13)	−0.3667 (7)	−0.0232 (6)	0.1025 (6)	0.0057 (6)	0.0050 (5)	0.0053 (6)	0.0009 (10)	−0.000 (1)	0.0006 (10)
C(14)	−0.4155 (7)	0.0581 (6)	0.1399 (6)	0.0053 (6)	0.0060 (5)	0.0049 (5)	0.0015 (11)	0.001 (1)	−0.0008 (10)
C(15)	−0.3527 (7)	0.1436 (6)	0.1423 (7)	0.0061 (7)	0.0049 (5)	0.0063 (6)	−0.0000 (10)	0.002 (1)	0.0003 (10)
C(16)	−0.2314 (7)	0.1421 (6)	0.1091 (6)	0.0079 (7)	0.0039 (4)	0.0042 (5)	0.0009 (10)	0.000 (1)	−0.0002 (8)
C(21)	0.0615 (6)	0.0080 (5)	0.1847 (6)	0.0051 (6)	0.0043 (4)	0.0048 (6)	0.0008 (10)	0.001 (1)	0.0004 (8)
C(22)	0.0675 (7)	−0.0886 (5)	0.2087 (6)	0.0061 (7)	0.0035 (4)	0.0053 (6)	0.0015 (9)	0.002 (1)	0.0013 (8)
C(23)	0.1026 (7)	−0.1269 (6)	0.3128 (6)	0.0072 (7)	0.0054 (5)	0.0058 (6)	0.0031 (11)	0.002 (1)	0.0001 (10)
C(24)	0.1311 (7)	−0.0656 (6)	0.4003 (6)	0.0085 (7)	0.0046 (4)	0.0042 (5)	0.0023 (11)	−0.001 (1)	0.0033 (9)
C(25)	0.1269 (8)	0.0302 (7)	0.3865 (7)	0.0086 (8)	0.0060 (5)	0.0059 (6)	0.0030 (11)	0.000 (1)	0.0030 (10)
C(26)	0.0921 (7)	0.0626 (6)	0.2778 (6)	0.0076 (7)	0.0037 (4)	0.0062 (6)	0.0011 (11)	0.001 (1)	0.0020 (9)

Atom	x	y	z	B, Å^2	Atom	x	y	z	B, Å^2
C(17)	−0.2537 (8)	−0.1768 (6)	−0.0133 (7)	4.5 (2)	C(27)	0.0405 (9)	−0.2433 (7)	0.1236 (8)	5.4 (2)
C(18)	−0.5972 (9)	−0.0182 (7)	0.1983 (8)	5.2 (2)	C(28)	0.2027 (9)	−0.0520 (8)	0.5950 (8)	6.2 (2)
C(19)	−0.2097 (9)	0.3034 (7)	0.1591 (9)	5.9 (2)	C(29)	0.0843 (10)	0.2237 (9)	0.3475 (9)	7.0 (3)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$. [b] Numbers in parentheses are esd's in the least significant digit.

with previously known short chemical bonds, including other M–M bonds?

For the first of these questions, only a tentative, inconclusive discussion can be given. It may be noted that in every case

Table IV. Interatomic Distances (Å) and Bond Angles (deg) in Tetrakis(2,6-dimethoxyphenyl)dimolybdenum

A. Dimensions Involving the Molybdenum Atoms

Mo(1)–Mo(2)	2.064 (1)	Mo(2)–C(21)	2.195 (9)
Mo(1)–C(11)	2.146 (9)	Mo(2)–C(31)	2.147 (8)
Mo(1)–C(41)	2.164 (9)	Mo(2)–O(12)	2.281 (7)
Mo(1)–O(22)	2.256 (6)	Mo(2)–O(42)	2.288 (7)
Mo(1)–O(32)	2.251 (7)	Mo(2)–O(23)	3.135 (6)
Mo(1)–O(13)	3.105 (6)	Mo(2)–O(33)	3.119 (6)
Mo(1)–O(43)	3.101 (5)		

Mo(2)–Mo(1)–C(11)	91.6 (3)	Mo(1)–Mo(2)–C(21)	90.2 (2)
Mo(2)–Mo(1)–C(41)	90.5 (2)	Mo(1)–Mo(2)–C(31)	90.5 (2)
Mo(2)–Mo(1)–O(22)	96.1 (1)	Mo(1)–Mo(2)–O(12)	95.7 (2)
Mo(2)–Mo(1)–O(32)	96.3 (2)	Mo(1)–Mo(2)–O(42)	96.4 (2)
C(11)–Mo(1)–C(41)	92.3 (3)	C(21)–Mo(2)–C(31)	91.1 (3)
C(11)–Mo(1)–O(22)	170.9 (3)	C(21)–Mo(2)–O(12)	173.2 (3)
C(11)–Mo(1)–O(32)	90.1 (3)	C(21)–Mo(2)–O(42)	90.9 (3)
C(41)–Mo(1)–O(22)	92.5 (3)	C(31)–Mo(2)–O(12)	92.2 (3)
C(41)–Mo(1)–O(32)	172.7 (3)	C(31)–Mo(2)–O(42)	172.9 (3)
O(22)–Mo(1)–O(32)	84.2 (3)	O(12)–Mo(2)–O(42)	85.1 (3)
Mo(1)–O(22)–C(24)	114.6 (5)	Mo(2)–O(12)–C(14)	123.1 (7)
Mo(1)–O(32)–C(34)	114.2 (6)	Mo(2)–O(42)–C(44)	113.3 (5)
Mo(1)–C(11)–C(14)	123.1 (7)	Mo(2)–C(21)–C(24)	124.5 (6)
Mo(1)–C(41)–C(44)	125.2 (6)	Mo(2)–C(31)–C(34)	125.8 (6)

B. Dimensions within the Ligands

	Ligand 1	Ligand 2	Ligand 3	Ligand 4
C(1)–C(4)	1.42 (1)	1.35 (1)	1.37 (1)	1.38 (1)
C(4)–C(5)	1.42 (1)	1.40 (1)	1.39 (1)	1.38 (1)
C(5)–C(6)	1.40 (2)	1.39 (1)	1.40 (2)	1.40 (2)
C(6)–C(7)	1.42 (2)	1.39 (2)	1.39 (2)	1.38 (2)
C(7)–C(8)	1.37 (2)	1.37 (1)	1.41 (1)	1.42 (1)
C(8)–C(1)	1.38 (1)	1.41 (1)	1.40 (1)	1.39 (1)
O(2)–C(4)	1.38 (1)	1.41 (1)	1.42 (1)	1.40 (1)
O(2)–C(0)	1.42 (1)	1.46 (1)	1.40 (2)	1.42 (1)
O(3)–C(8)	1.38 (1)	1.41 (1)	1.37 (1)	1.39 (1)
O(3)–C(9)	1.42 (2)	1.46 (1)	1.43 (1)	1.41 (1)
C(1)–C(4)–C(5)	123 (1)	126 (1)	126 (1)	124.7 (9)
C(4)–C(5)–C(6)	117 (1)	116 (1)	117 (1)	117.7 (9)
C(5)–C(6)–C(7)	121 (1)	121.5 (9)	121 (1)	121 (1)
C(6)–C(7)–C(8)	119 (1)	118 (1)	118 (1)	117.6 (9)
C(7)–C(8)–C(1)	124 (1)	124 (1)	124 (1)	123.5 (9)
C(8)–C(1)–C(4)	116.3 (8)	114.4 (9)	114.1 (8)	115.3 (8)
C(1)–C(4)–O(2)	115.1 (8)	114.3 (8)	113.0 (8)	114.4 (7)
C(1)–C(8)–O(3)	114.7 (8)	112.6 (9)	115.3 (8)	114.9 (8)
C(4)–O(2)–C(0)	117.3 (8)	118.9 (7)	120.1 (8)	120.3 (8)
C(8)–O(3)–C(9)	120 (1)	118 (1)	117.9 (8)	118.9 (8)

Table V. Interatomic Distances (Å) and Bond Angles (deg) in Tetrakis(2,6-dimethoxyphenyl)dichromium

A. Dimensions Involving the Chromium Atoms

Cr(1)–Cr(2)	1.847 (1)	Cr(2)–C(21)	2.086
Cr(1)–C(11)	2.065 (8)	Cr(2)–C(31)	2.065
Cr(1)–C(41)	2.049 (7)	Cr(2)–O(12)	2.147
Cr(1)–O(22)	2.133 (5)	Cr(2)–O(42)	2.134
Cr(1)–O(32)	2.131 (5)	Cr(2)–O(23)	3.115 (5)
Cr(1)–O(13)	3.070 (5)	Cr(2)–O(33)	3.073 (5)
Cr(1)–O(43)	3.082 (5)		

Cr(2)–Cr(1)–C(11)	91.4 (2)	Cr(1)–Cr(2)–C(21)	91.4 (2)
Cr(2)–Cr(1)–C(41)	90.7 (2)	Cr(1)–Cr(2)–C(31)	90.4 (2)
Cr(2)–Cr(1)–O(22)	101.6 (1)	Cr(1)–Cr(2)–O(12)	100.9 (2)
Cr(2)–Cr(1)–O(32)	102.2 (2)	Cr(1)–Cr(2)–O(42)	102.1 (2)
C(11)–Cr(1)–C(41)	92.2 (3)	C(21)–Cr(2)–C(31)	90.6 (3)
C(11)–Cr(1)–O(22)	166.1 (3)	C(21)–Cr(2)–O(12)	167.3 (3)
C(11)–Cr(1)–O(32)	89.7 (3)	C(21)–Cr(2)–O(42)	91.3 (3)
C(41)–Cr(1)–O(22)	92.3 (2)	C(31)–Cr(2)–O(12)	92.5 (3)
C(41)–Cr(1)–O(32)	166.9 (2)	C(31)–Cr(2)–O(42)	166.8 (3)
O(22)–Cr(1)–O(32)	83.1 (2)	O(12)–Cr(2)–O(42)	83.0 (2)
Cr(1)–O(22)–C(24)	111.0 (4)	Cr(2)–O(12)–C(14)	111.1 (4)
Cr(1)–O(32)–C(34)	109.9 (4)	Cr(2)–O(42)–C(44)	110.0 (4)
Cr(1)–C(11)–C(14)	122.8 (6)	Cr(2)–C(21)–C(24)	121.6 (6)
Cr(1)–C(41)–C(44)	124.2 (5)	Cr(2)–C(31)–C(34)	124.3 (6)

B. Dimensions within the Ligands

	Ligand 1	Ligand 2	Ligand 3	Ligand 4
C(1)–C(4)	1.38 (1)	1.38 (1)	1.36 (1)	1.37 (1)
C(4)–C(5)	1.43 (1)	1.41 (1)	1.37 (1)	1.44 (1)
C(5)–C(6)	1.34 (1)	1.42 (1)	1.45 (1)	1.34 (1)
C(6)–C(7)	1.45 (2)	1.37 (1)	1.35 (1)	1.41 (1)
C(7)–C(8)	1.38 (1)	1.39 (1)	1.40 (1)	1.38 (1)
C(8)–C(1)	1.39 (1)	1.38 (1)	1.36 (1)	1.41 (1)
O(2)–C(4)	1.38 (1)	1.40 (1)	1.45 (1)	1.41 (1)
O(2)–C(0)	1.44 (1)	1.45 (1)	1.37 (1)	1.41 (1)
O(3)–C(8)	1.40 (1)	1.35 (1)	1.38 (1)	1.39 (1)
O(3)–C(9)	1.38 (1)	1.42 (1)	1.42 (1)	1.38 (1)
C(1)–C(4)–C(5)	123.8 (8)	124.5 (8)	129.2 (8)	124.9 (6)
C(4)–C(5)–C(6)	116.8 (9)	115.2 (8)	112.3 (8)	117.1 (7)
C(5)–C(6)–C(7)	123.3 (9)	122.0 (7)	122.8 (8)	122.1 (7)
C(6)–C(7)–C(8)	115 (1)	119.1 (8)	117.8 (8)	117.7 (7)
C(7)–C(8)–C(1)	124.6 (9)	122.7 (9)	123.6 (8)	124.8 (7)
C(8)–C(1)–C(4)	116.1 (7)	116.5 (8)	114.3 (7)	113.4 (6)
C(1)–C(4)–O(2)	113.5 (6)	114.1 (7)	112.3 (6)	112.9 (6)
C(1)–C(8)–O(3)	113.9 (7)	115.6 (8)	115.4 (7)	112.9 (6)
C(4)–O(2)–C(0)	119.8 (6)	118.9 (6)	119.7 (6)	122.5 (6)
C(8)–O(3)–C(9)	117.6 (8)	121.4 (8)	119.5 (7)	117.6 (6)

where these exceedingly short bonds have been found, there is an essentially complete absence of axial donor interaction with the metal atoms. We have previously commented on the fact that for heavier metals, that is, for Re–Re[13] and Mo–Mo[14,15] quadruple bonds, the M–M distance is a function of the strength of binding of axial ligands: The M–M bond becomes longer as axial ligands are more closely coordinated. With these heavier metals, however, the sensitivity of the M–M bond length to the strength of axial coordination is slight, on the order of a few hundreths of an angstrom, and the dinuclear systems do not appear to have the capacity to form strong bonds to axial ligands. The fact that the Mo–Mo distance in $Mo_2(DMP)_4$ is shorter, but only about 0.04 Å shorter, than those in the $Mo_2(O_2CR)_4$ compounds,[15] where there are weak axial bonds is not, therefore, surprising. It may well be that a distance of about 2.06 Å represents the shortest possible distance for a quadruple Mo–Mo bond in the type of compound that can be described formally as an Mo_2^{4+} unit coordinated by a square-prismatic set of eight two-electron donor atoms.

With Cr_2 systems the sensitivity of the M–M bond length to axial donors, and perhaps other factors, is enormously greater, as several recent studies[16,17] have shown. Thus, when axial coordination is totally absent, the shortest of all Cr–Cr quadruple bonds are present. The question that immediately arises, however, is *why* there is no axial coordination in these cases. One possibility is that some electronic, or electronic coupled with structural, characteristics of these ligands cause the metal atoms which are surrounded by them to form an extremely tight bond and that such a tight M–M bond, once formed, has little or no capacity to bind axial ligands. Another very different idea is that the Cr–Cr bonds are shut off from axial ligands and because no axial ligands reach them the metal orbitals are used with great effectiveness to form these exceptionally short bonds. Certainly in the present cases, $Cr_2(DMP)_4$ and $Cr_2(TMP)_4$, the axial positions are physically blocked so that the molecules can neither associate with each other nor bind separate donor molecules, which are the two things that the $Cr_2(O_2CR)_4$ molecules always do.[16,17] In the case of $Cr_2(2\text{-MeO-5-MePh})_4$, the case for purely steric prevention of axial coordination is not conclusive. Although intermolecular association seems impossible for purely steric reasons, as already shown,[5] and indeed the molecules do pack without the least hint of association, it is difficult to say whether the axial sites are entirely inaccessible to small, independent solvent molecules for purely steric reasons. All we know is that solvates have not been observed to form. In the case of the $Cr_2(C_6H_4O)_4^{4-}$ ion in $Li_6Cr_2(C_6H_4O)_4Br_2(Et_2O)_6$ there is no steric barrier to the approach of axial ligands.[3] It could, however, be argued that the 4– anion repels

Table VI. Interatomic Distances (Å) and Bond Angles (deg) in Tetrakis(2,4,6-trimethoxyphenyl)dichromium

A. Dimensions Involving the Chromium Atoms			
Cr(1)–Cr(1)′	1.849 (2)	Cr(1)–O(11)	2.127 (4)
Cr(1)–C(11)	2.067 (5)	Cr(1)–O(21)	2.129 (4)
Cr(1)–C(21)	2.055 (6)	Cr(1)–O(12)	3.126 (4)
		Cr(1)–O(22)	3.109 (4)
Cr(1)–Cr(1)′–C(11)	91.4 (2)	C(21)–Cr(1)–O(11)	93.2 (2)
Cr(1)–Cr(1)′–C(21)	90.7 (2)	C(21)–Cr(1)–O(21)	166.4 (2)
Cr(1)–Cr(1)′–O(11)	101.1 (1)	O(11)–Cr(1)–O(21)	103.3 (1)
Cr(1)–Cr(1)′–O(21)	102.6 (1)	Cr(1)–O(11)–C(12)	111.1 (3)
C(11)–Cr(1)–C(21)	93.1 (2)	Cr(1)–O(21)–C(22)	110.3 (3)
C(11)–Cr(1)–O(11)	90.0 (1)	Cr(1)–C(11)–C(12)	123.0 (4)
C(11)–Cr(1)–O(21)	98.8 (1)	Cr(1)–C(21)–C(22)	123.0 (4)
B. Dimensions within the Ligands			
C(11)–C(12)	1.367 (7)	C(21)–C(22)	1.409 (8)
C(12)–C(13)	1.425 (8)	C(22)–C(23)	1.389 (8)
C(13)–C(14)	1.356 (8)	C(23)–C(24)	1.381 (8)
C(14)–C(15)	1.405 (9)	C(24)–C(25)	1.378 (9)
C(15)–C(16)	1.406 (8)	C(25)–C(26)	1.405 (8)
C(16)–C(11)	1.397 (8)	C(26)–C(21)	1.381 (8)
C(12)–O(11)	1.415 (6)	C(22)–O(21)	1.397 (7)
C(14)–O(13)	1.390 (7)	C(24)–O(23)	1.383 (6)
C(16)–O(12)	1.374 (7)	C(26)–O(22)	1.399 (7)
O(11)–C(17)	1.436 (7)	O(21)–C(27)	1.412 (8)
O(12)–C(19)	1.406 (8)	O(22)–C(29)	1.442 (9)
O(13)–C(18)	1.416 (8)	C(23)–C(28)	1.409 (8)
C(16)–C(11)–C(12)	114.6 (5)	C(26)–C(21)–C(22)	112.6 (5)
C(11)–C(12)–C(13)	126.2 (5)	C(21)–C(22)–C(23)	125.0 (6)
C(12)–C(13)–C(14)	115.2 (5)	C(22)–C(23)–C(24)	117.6 (6)
C(13)–C(14)–C(15)	123.4 (5)	C(23)–C(24)–C(25)	122.3 (6)
C(14)–C(15)–C(16)	117.1 (6)	C(24)–C(25)–C(26)	116.2 (6)
C(15)–C(16)–C(11)	123.3 (6)	C(25)–C(26)–C(21)	126.4 (6)
C(12)–O(11)–C(17)	120.1 (4)	C(22)–O(21)–C(27)	120.7 (5)
C(16)–O(12)–C(19)	118.4 (5)	C(26)–O(22)–C(29)	118.6 (5)
C(14)–O(13)–C(18)	117.6 (5)	C(24)–O(23)–C(28)	119.7 (6)
C(11)–C(12)–O(11)	112.8 (5)	C(21)–C(22)–O(21)	113.2 (5)
C(11)–C(16)–O(12)	115.0 (5)	C(21)–C(26)–O(22)	112.6 (5)

them electrostatically. The fact that water molecules are coordinated to the $Cr_2(O_2CO)_4^{4-}$ anion in two of its compounds[17] lessens the force of this electrostatic argument but does not necessarily invalidate it, since the available ligands, Br^- and Et_2O, may well be poorer ones under the circumstances than H_2O.

In summary, the question of why the exceedingly short Cr–Cr bonds are exceedingly short is not one we can definitively answer at present. The fact that axial coordination is absent in all cases is significant but does not imply any unambiguous causal relationship.

Turning now to the other main question stated above, we propose that there is at least one way, perhaps a somewhat imperfect one, to express the idea of how short a given bond is relative to the shortness of other bonds *involving different elements*. Clearly, the shortness of a bond has meaning only in relation to the intrinsic size of the atoms that form it. It is not surprising, for example, that Si–Si bonds are longer than C–C bonds, because Si atoms are, predictably, larger than C atoms. If, however, we were to divide any given bond length, A–B, by the sum of some atomic parameters, one for A and one for B, that are proportional to (or equal to) the relative (or actual) sizes of the atoms, we should get a number that can be meaningfully compared to the corresponding figure for some other bond, say C–D. It might seem logical to call such quotients "scaled" or "reduced" bond lengths. In a previous paper, however, we have designated them "formal shortness ratios" because we wanted to draw attention to the shortness of certain bonds, and we shall continue to use that expression, abbreviated FSR, in this discussion.

We have chosen as a set of numbers to use as divisors a tabulation of radii for metallic elements, called R_1 values, that was made some years ago by Pauling.[18] These radii are available for all of the elements that possess any metallic character, and for entirely nonmetallic elements, like carbon, the comparable radii are the single-bond covalent radii. Thus, we have a convenient set of scaling factors with which to calculate FSR's from observed internuclear distances for all the elements.

Table VII. Bond Lengths and Formal Shortness Ratios (FSR's) for Some Multiple Bonds

Bond	Order	Molecule or ion	Length, Å	FSR
Cr–Cr	4	$Cr_2(2\text{-MeO-5-MePh})_4$	1.828 (2)[a]	0.771
		$Cr_2(DMP)_4$	1.847 (1)[b]	0.778
		$Cr_2(CH_3)_8^{4-}$	1.980 (5)[c]	0.835
		$Cr_2(O_2CO)_4^{4-}$	2.214 (1)[d]	0.933
Cr–Mo	4	$CrMo(O_2CCH_3)_4$	2.050 (1)[e]	0.826
Mo–Mo	4	$Mo_2(DMP)_4$	2.064 (1)[b]	0.796
		$Mo_2(O_2CCH_3)_4$	2.093 (1)[b]	0.807
		$Mo_2(CH_3)_8^{4-}$	2.148 (2)[g]	0.829
	3	$Mo_2(NMe_2)_6$	2.214 (2)[h]	0.854
W–W	4	$W_2(CH_3)_8^{4-}$	2.264 (1)[i]	0.868
	3	$W_2(NMe_2)_6$	2.293 (2)[j]	0.879
Re–Re	4	$Re_2(CH_3)_8^{2-}$	2.178 (1)[k]	0.837
N–N	3	N_2	1.098[l]	0.786
C–C	3	$HC\equiv CH$	1.206[l]	0.783
P–P	3	$P_2(g)$	1.893[l]	0.860

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We list in Table VII a number of FSR's, not only for M–M multiple bonds but also for a few other bonds with which interesting comparisons may be made.

It is seen that the shortest of the Cr–Cr quadruple bonds have the smallest FSR's of all chemical bonds in stable compounds. They are slightly smaller even than those for the N≡N, C≡C, and P≡P bonds which are the three strongest homonuclear bonds for which bond energy values (946, 813, and 490 kJ mol^{-1}, respectively) are known. All of the Mo–Mo quadruple bonds in compounds formally based on Mo_2^{4+} also have relatively low FSR's.

For third transition series metals, the quadruple bonds have still larger FSR's. This need not mean that the bonds become weaker as we descend in a homologous series, because the repulsive forces that result from inner-shell overlaps at these extremely short distances doubtless increase enormously from, say, Cr_2 to Mo_2 to W_2. This tends to lengthen the bonds in a way not really accounted for by the R_1 radii, which reflect relative atomic sizes in a regime where there are much weaker and longer bonds and inner-shell repulsions are much less severe.

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Registry No. **1**, 64836-05-1; **2**, 64836-04-0; **3**, 65745-31-5; $Cr_2(O_2CCH_3)_4$, 15020-15-2; $Mo_2(O_2CCH_3)_4$, 14221-06-8; LiDMP, 2785-97-9; LiTMP, 34425-71-3.

Supplementary Material Available: Listings of observed and calculated structure factors (31 pages). Ordering information is given on any current masthead page.

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Preparation and Structures of the Homologous Quadruply Bonded Tris(cyclooctatetraene)dimolybdenum and -ditungsten

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The methods of preparation and the crystal and molecular structures of $Mo_2(C_8H_8)_3$ and $W_2(C_8H_8)_3$ are reported. The crystalline compounds, which are air-stable for periods of several days, can be prepared by reaction of the metal tetrahalides with $K_2C_8H_8$ in tetrahydrofuran. The Mo and W compounds, crystallizing in the space group $I\bar{4}$, are isomorphous with each other but not with $Cr_2(C_8H_8)_3$. The unit cell dimensions at 21 ± 1 °C for $Mo_2(C_8H_8)_3$ are $a = 15.815$ (2) Å, $c = 15.014$ (2) Å, and $V = 3755$ (1) Å^3 and for $W_2(C_8H_8)_3$ are $a = 15.820$ (3) Å, $c = 15.041$ (3) Å, and $V = 3764$ (2) Å^3, with $Z = 8$. Both structures were determined by X-ray crystallography at 21 ± 1 °C and that of $W_2(C_8H_8)_3$ has also been determined by neutron diffraction at 110 K, where the cell dimensions are $a = 15.664$ (3) and $c = 14.980$ (3) Å. Each of these compounds has a molecular structure, essentially the same as that for the chromium homologue, in which the pair of closely bonded metal atoms (W–W = 2.375 (1) Å and Mo–Mo = 2.302 (2) Å) lies over one sharply folded ring which has all of its carbon atoms bonded to one or both metal atoms. Each metal atom also has attached to it a η^4-C_8H_8 ring. The M–M bonds can be construed as quadruple.

Introduction

Although the ability of transition metals to form compounds containing multiple M–M bonds (double,[2] triple,[3] and quadruple[4]) was recognized only recently, considerable progress has already been made[5] in exploring this new phase of transition-metal chemistry. One aspect of this development that has caused some consternation has been the apparent reluctance of the element tungsten to form quadruple bonds, even though (a) it forms triple bonds easily and abundantly,[6] (b) molybdenum forms both triple and quadruple bonds in abundance,[5] and (c) rhenium forms numerous quadruple[5] and some triple bonds.[7] Indeed the only documented cases of W–W quadruple bonds,[8] prior to the present work occur in $W_2(CH_3)_8^{4-}$ and the mixed-ligand ions $[W_2Cl_{8-x}(CH_3)_x]^{4-}$. In fact, the series $[Cr_2(CH_3)_8]^{4-}$, $[Mo_2(CH_3)_8]^{4-}$, and $[W_2(CH_3)_8]^{4-}$ represents the only proven set of three homologous quadruply bonded species aside from the one we are reporting here.[24]

The existence of several compounds with the formula $M_2(C_8H_8)_3$ (M = Ti, V, Cr, Mo, W) was first announced a number of years ago.[9] However, except for $Ti_2(C_8H_8)_3$ no preparative methods nor any identifying physical or chemical properties were revealed nor has there subsequently been any published account, however terse, of the methods of preparation of these substances. The structure of $Ti_2(C_8H_8)_3$, in which there is no M–M bond, was reported[10] in 1966. It was with the report last year by Brauer and Krüger,[11] of the structure of $Cr_2(C_8H_8)_3$ which indicates the presence of a quadruple Cr–Cr bond, that we became interested in the structures of $Mo_2(C_8H_8)_3$ and $W_2(C_8H_8)_3$. It was obvious, as Brauer and Krüger themselves stated, that the molybdenum and tungsten compounds are likely to have similar molecular structures. Our keen, long-standing[6,8,12] interest in the question of the stability of quadruple W–W bonds led us to examine the preparation and structure of $W_2(C_8H_8)_3$ and, in order to have a complete homologous series, the molybdenum compound.

Procedure

All reactions were done under nitrogen and solvents were carefully dried and degassed.

Preparation of $Mo_2(C_8H_8)_3$. Molybdenum(IV) chloride was prepared according to a published method.[13] A mixture of $MoCl_4$ (1.5 g, 6.3 mmol) and 12.5 mmol of $K_2C_8H_8$ in tetrahydrofuran was stirred for 24 h at room temperature, giving a brown solution. After filtration the solution was taken to dryness under vacuum and the brown-black residue then recrystallized from toluene, to give 0.9 g (35% yield) of black crystalline product.

Preparation of $W_2(C_8H_8)_3$. Tungsten(IV) chloride was prepared by reaction of WCl_6 with $W(CO)_6$ in refluxing chlorobenzene. It was collected by filtration, dried under vacuum, and used without further purification. The reaction of WCl_4 (2.0 g, 6.1 mmol) with $K_2C_8H_8$ (12.4 mmol) in tetrahydrofuran gave a green solution, which was filtered after 24 h. After solvent removal and recrystallization from hot toluene, green-black crystals, mp >360 °C, were obtained (0.4 g; 20% yield based on WCl_4).

Determination of the X-ray Crystal Structure of $W_2(C_8H_8)_3$. A crystal was ground to a sphere of radius 0.229 mm and was sealed in a thin-walled glass capillary under nitrogen. The crystal was examined on a Syntex $P\bar{1}$ automated diffractometer using Mo Kα radiation (λ 0.710 73 Å) with a graphite-crystal monochromator. A body-centered tetragonal cell was indicated and the cell parameters derived from the setting angles for 15 reflections are the following:

0020-1669/78/1317-2093$01.00/0