to the $^2\Sigma_g^+ \rightarrow {}^2\Pi_g$ transition and the higher energy absorption to the $^2\Sigma_g^+ \rightarrow {}^2\Delta_g$ transition. This assignment was later supported by Smith.[3] However, DeKock and Gruen,[2] and subsequently Lever and Hollebone,[4] proposed that the higher energy band is due to a charge-transfer transition, as is suggested by its high intensity (ϵ 3200 L mol^{-1} cm^{-1}), and that the absorption at 0.9 μm^{-1} be assigned to the transition $^2\Sigma_g^+ \rightarrow {}^2\Delta_g$. Using ligand field arguments, the transition $^2\Sigma_g^+ \rightarrow {}^2\Pi_g$ would then lie below 0.5 μm^{-1} where it would not be observed. In each of the $3d^9$ states of $CuCl_2$ the valence Cu d orbitals are lower in energy than the predominantly Cl MOs $7\sigma_u$, $4\pi_u$, and $3\pi_g$, with the largest contribution to the bonding in the $^2\Sigma_g^+$ state from the $8\sigma_g$ orbital with approximately 28% metal character (Table VI). The calculated configurations of the copper atom obtained from a Mulliken population analysis of the SCF wave functions of each state are $3d^94s^{0.5}$.

Our proposed assignment of the electronic spectrum of $CuCl_2$(g) using the admittedly rather unsatisfactory results of Table VII is that the band at 1.9 μm^{-1} is due to the excitation $^2\Sigma_g^+ \rightarrow {}^2\Pi_u$ and that the transition energy for $^2\Sigma_g^+ \rightarrow {}^2\Delta_g$ occurs in the region 0.7–1.1 μm^{-1}. The $^2\Sigma_g^+ \rightarrow {}^2\Pi_g$ transition may also occur within this latter spectral region which is highly structured[2] and therefore may derive from more than one electronic excitation.

Acknowledgment. We thank the Science Research Council for financial support including the award of a studentship (C.W.).

Registry No. $CrCl_2$, 10049-05-5; $CoCl_2$, 7646-79-9; $CuCl_2$, 7447-39-4.

References and Notes

(1) J. T. Hougen, G. E. Leroi, and T. C. James, *J. Chem. Phys.*, **34**, 1670 (1961).
(2) C. W. DeKock and D. M. Gruen, *J. Chem. Phys.*, **44**, 4387 (1966).
(3) D. W. Smith, *Inorg. Chim. Acta.*, **5**, 231 (1971).
(4) A. B. P. Lever and B. R. Hollebone, *Inorg. Chem.*, **11**, 2183 (1972).
(5) P. A. Akishin and V. P. Spiridonov, *Kristallografiya*, **2**, 475 (1957).
(6) A. Büchler, J. L. Stauffer, and W. Klemperer, *J. Chem. Phys.*, **40**, 3471 (1964).
(7) D. E. Milligan, M. E. Jacox, and J. D. McKinley, *J. Chem. Phys.*, **42**, 902 (1965).
(8) G. E. Leroi, T. C. James, J. T. Hougen, and W. Klemperer, *J. Chem. Phys.*, **36**, 2879 (1962).
(9) H. Basch, C. J. Hornback, and J. W. Moskowitz, *J. Chem. Phys.*, **51**, 1311 (1969).
(10) I. H. Hillier, J. Kendrick, F. E. Mabbs, and C. D. Garner, *J. Am. Chem. Soc.*, **98**, 395 (1976).
(11) A. J. H. Wachters, IBM Research Report RJ 584 (1969).
(12) T. H. Dunning, Jr., *Chem. Phys. Lett.*, **7**, 423 (1970).

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

Insensitivity of the Molybdenum-to-Molybdenum Quadruple Bond in the Dimolybdenum Tetracarboxylates to Axial Coordination and Changes in Inductive Effects

F. ALBERT COTTON,* MICHAEL EXTINE, and LARRY D. GAGE

Received June 28, 1977

Several x-ray crytallographic studies have been conducted to determine the response of the Mo–Mo quadruple bond, as that response is evidenced in the bond length, to (a) the presence or absence of axial ligands and (b) changes in the inductive strength of the R group in compounds of the general formula $Mo_2(O_2CR)_4L_2$. The new structures reported here are those of **1**, $Mo_2(O_2CC_6H_5)_4$, and **2**, $Mo_2(O_2CCMe_3)_4$. They are compared with a number of other previously reported structures. Crystal data and some results for **1**: space group $P2_1/c$ with unit cell dimensions a = 5.676 (1) Å, b = 10.339 (2) Å, c = 21.964 (3) Å, β = 94.38 (1)°, V = 1285.3 (3) Å^3, and Z = 2. The $Mo_2(O_2CPh)_4$ molecule has crystallographic C_i symmetry and virtual symmetry which deviates only slightly from D_{4h}. The Mo–Mo distance is 2.096 (1) Å and the mean Mo–O distance is 2.11 (1) Å. The closest intermolecular Mo–O contact is 2.876 (2) Å with an Mo—Mo—O angle of 115.66 (6) °. The structure was refined to R_1 = 0.030 and R_2 = 0.050 using 1476 reflections having $I > 3\sigma(I)$. Crystal data for compound **2**: space group $P\bar{1}$ with unit cell dimensions a = 11.793 (3) Å, b = 12.154 (4) Å, c = 10.403 (4) Å, α = 90.07 (3)°, β = 104.61 (3)°, γ = 71.33 (2)°, V = 1361.8 (7) Å^3, and Z = 2. The $Mo_2(O_2CCMe_3)_4$ molecule has a Mo–Mo distance of 2.088 (1) Å. The mean intramolecular Mo–O distances lie in the range 2.098 to 2.135 Å and the mean axial intermolecular contacts are 2.870 (5) and 2.926 (5) Å. The structure was refined to R_1 = 0.060 and R_2 = 0.085 using 2916 reflections having $I > 3\sigma(I)$.

Introduction

In a compound of the general structure shown in Figure 1 there are three convenient variables: (1) the metal atoms, M and M′; (2) the R group; (3) the axial ligands (which may, of course, be absent). In order to understand the nature of metal–metal quadruple bonds it is useful to study a range of such molecules in which these three variables are altered systematically. In this report we are concerned with systems in which M = M′ = Mo. A forthcoming report will discuss analogous dichromium compounds.

There is already evidence[1] that for Mo_2 systems the M–M bond is very strong, shows little attraction for axial ligands, and is only slightly weakened when axial ligands are present. However, there has been only one simple comparison of an $Mo_2(O_2CR)_4$–$Mo_2(O_2CR)_4L_2$ pair, namely, that in which R = CF_3 and L = pyridine.[2] Since this involves an extremely electron-withdrawing R group, we sought a comparison in which the R group is of intermediate character. For this purpose we have chosen the case where R = C_6H_5 and L = $CH_3OCH_2CH_2OCH_3$. The structure of the $Mo_2(O_2CR)_4L_2$ member of this pair has already been reported[3] and we supply here the data for the corresponding $Mo_2(O_2CR)_4$ compound.

With respect to the effect of the inductive character of R, there are data already available for R = CF_3,[2a] H,[4] and CH_3,[5] that is for R groups ranging from the most strongly electron withdrawing to those of intermediate character. To complete the picture we have examined $Mo_2(O_2CCMe_3)_4$, in which we have the very highly electron-donating *tert*-butyl group, $(CH_3)_3C$.

Experimental Section

The preparations of $Mo_2(O_2CR)_4$, R = CMe_3 and C_6H_5, were done by reaction of $Mo(CO)_6$ with RCO_2H in refluxing *o*-$C_6H_4Cl_2$.[6]

0020-1669/78/1317-0172$01.00/0 © 1978 American Chemical Society

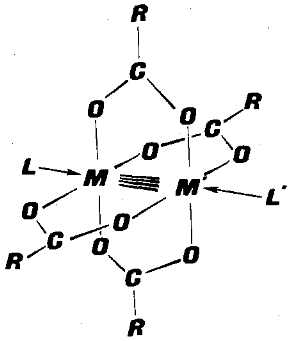

Figure 1. General structural formula for the tetracarboxylato-bridged, quadruply bonded dimetal compounds, in which the metal atoms may be dissimilar and the terminal ligands L and L′ may be identical or different, or may even be absent.

Suitable crystals of $Mo_2(O_2CPh)_4$ were isolated from the reaction solution. Crystals of $Mo_2(O_2CCMe_3)_4$ were grown by sublimation of a small sample in an evacuated sealed glass tube at ca. 100 °C.

X-Ray Crystallography of $Mo_2(O_2CPh)_4$. A yellow crystal of $Mo_2(O_2CPh)_4$ measuring ca. $0.15 \times 0.20 \times 0.60$ mm was mounted in a thin-walled glass capillary. The crystal was shown to be of good quality by ω scans of several intense reflections which had peak widths at half-height of ca. 0.20°.

Preliminary lattice parameters and the orientation matrix used for data collection were obtained from the least-squares refinement of diffractometer settings for 15 intense reflections having $4° < 2\theta$ (Mo $K\alpha$) $< 24°$.

Cell constants and axial photographs indicated that the crystal belongs to the monoclinic system. Final lattice parameters, determined using 15 reflections having $20° < 2\theta(\text{Mo } K\alpha) < 25°$, are as follows: $a = 5.676$ (1) Å, $b = 10.339$ (2) Å, $c = 21.964$ (3) Å, $\beta = 94.38$ (1)°, and $V = 1285.3$ (3) Å^3. The observed volume is consistent with expectation for $Z = 2$.

Data were collected at 22 ± 2 °C using a Syntex $P\bar{1}$ autodiffractometer, with graphite-monochromatized Mo $K\alpha$ radiation and the θ–2θ scan technique. Variable scan rates from 4 to 24°/min were used, depending upon the intensity of the reflection. The scan ranges were from Mo $K\alpha_1 - 1.0°$ to Mo $K\alpha_2 + 1.0°$. The systematic absences $0k0$, $k = 2n + 1$, and $h0l$, $l = 2n + 1$, indicated that the space group was $P2_1/c$ (No. 14).[7] A total of 1991 reflections having $0° < 2\theta(\text{Mo } K\alpha) < 45°$ were collected. Three standard reflections measured every 100 reflections showed no decrease in intensity. The intensities were reduced to a set of relative $|F_o|^2$ values for use in structure refinement[8] and systematically absent and nonunique data were rejected. Only the 1476 reflections having $I > 3\sigma(I)$ were utilized in the subsequent structure solution and least-squares refinement.

Solution and Refinement of the Structure[8] of $Mo_2(O_2CPh)_4$. The space group $P2_1/c$ and $Z = 2$ require that the molecules lie on inversion centers.

The position of the unique Mo atom was determined from the solution of the three-dimensional Patterson function. Following refinement of the positional parameters of the Mo atom, a difference Fourier map revealed the positions of the 18 remaining unique nonhydrogen atoms. Positional and isotropic thermal parameters of the atoms were refined in three cycles of least-squares refinement to give discrepancy indices of

$$R_1 = \Sigma ||F_o| - |F_c|| / \Sigma |F_o| = 0.071$$

$$R_2 = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma |F_o|^2]^{1/2} = 0.104$$

The function minimized during least-squares refinement was $\sum w(|F_o| - |F_c|)^2$, where w, the weighting factor, is equal to $4F_o^2/\sigma(F_o^2)^2$. Atomic scattering factors used in all stages of the structure refinement were those of Cromer and Waber.[7] Anomalous dispersion effects were included in the calculation of the scattering factors for all atoms.[9] The structure was refined to convergence, utilizing anisotropic thermal parameters for all atoms, in four cycles of least-squares refinement yielding final values of $R_1 = 0.030$ and $R_2 = 0.050$. The estimated standard deviation of an observation of unit weight was 1.273. During the final refinement cycle no parameter shifted by more than 0.17σ. A final difference Fourier map revealed no features of structural significance.

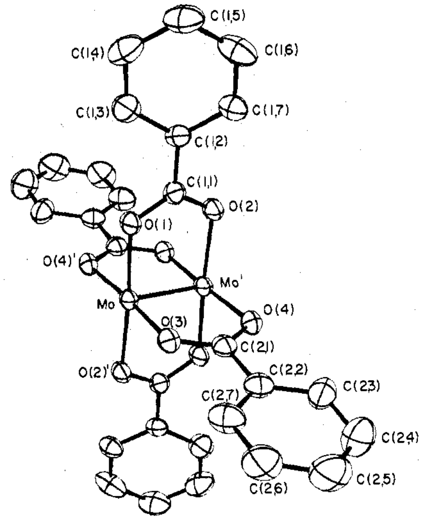

Figure 2. Molecular structure of dimolybdenum tetrabenzoate. Atoms are represented by their ellipsoids of thermal vibration scaled to enclose 50% of the electron density, and the numbering scheme used in Tables I, III, and IV is defined.

X-Ray Crystallography of $Mo_2[O_2CC(CH_3)_3]_4$. A yellow crystal of $Mo_2[O_2CC(CH_3)_3]_4$ having approximate dimensions $0.10 \times 0.11 \times 0.44$ mm was inspected under a polarizing microscope and sealed in a capillary previously flushed with N_2. The ω scans of several of the most intense reflections had widths at half-height of ca. 0.20°.

Cell constants for the triclinic crystal are as follows: $a = 11.793$ (3) Å, $b = 12.154$ (4) Å, $c = 10.403$ (4) Å, $\alpha = 90.07$ (3)°, $\beta = 104.61$ (3)°, $\gamma = 71.33$ (2)°, and $V = 1361.8$ (7) Å^3 as determined from 15 intense reflections having $20° < 2\theta(\text{Mo } K\alpha) < 30°$.

A total of 4798 reflections were collected as above. The 2916 reflections having $I > 3\sigma(I)$ were used in subsequent structure solution and refinement.

Solution and Refinement[8] of the Structure of $Mo_2[O_2CC(CH_3)_3]_4$. The unit cell parameters indicated that $Z = 2$. The space group $P\bar{1}$ was assumed from the outset. The similarity of the unit cell parameters of $Mo_2[O_2CC(CH_3)_3]_4$ and the previously examined $Cr_2[O_2CC(CH_3)_3]_4$[10] suggested that the compounds were isostructural.

A least-squares refinement of the positions of the two Mo atoms, with initial positions drawn from the analogous Cr species, and a subsequent difference Fourier map revealed 25 additional unique nonhydrogen atoms. A difference map after refining the positions of the 27 atoms revealed substantial rotational disorder of the *tert*-butyl group about C8. The three largest peaks about C8 were treated as carbon atoms with a 0.5 occupancy factor. This produced an acceptable reduction in the discrepancy indices, $R_1 = 0.092$ and $R_2 = 0.118$, after two cycles of least-squares refinement on the positional and isotropic thermal parameters. In spite of persistent efforts to do so no other refineable carbon atom positions were found.

Anisotropic refinement for the two Mo and eight O atoms with the remaining atoms refined isotropically produced discrepancy indices of $R_1 = 0.060$ and $R_2 = 0.085$. The final error in an observation of unit weight was 1.738. A difference map revealed numerous peaks around C8 with magnitudes of 1.3–2.34 e/Å^3. In addition several diffuse peaks, assumed to be hydrogen atoms, were located about each *tert*-butyl group, but no attempt was made to locate systematically or to refine any hydrogen atoms.

Results

The structures of **1** and **2** are shown in Figures 2 and 3, respectively. The atomic positional and thermal parameters are listed in Tables I and II. Bond distances and angles in the benzoate are listed in Tables III and IV and the molecular dimensions of the pivalate in Tables V and VI.

The $Mo_2(O_2CPh)_4$ molecules occupy centers of symmetry and form chains in which each oxygen atom O(2) and the corresponding one on the other end, O(2)′, are located approximately in the axial coordination positions of adjacent molecules. These axial O···Mo contacts are at a distance of 2.876 (2) Å. That is to say, they are very weak in comparison

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Mo_2(O_2CPh)_4$[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo	−0.15791 (5)	−0.05168 (3)	0.00218 (2)	0.0124 (1)	0.00454 (4)	0.00156 (1)	−0.00265 (9)	0.00133 (6)	0.00024 (3)
O(1)	0.0265 (5)	−0.2179 (3)	0.0322 (1)	0.0142 (8)	0.0051 (3)	0.00208 (7)	−0.0039 (8)	0.0014 (4)	0.0009 (2)
O(2)	0.3658 (5)	−0.1102 (3)	0.0291 (1)	0.0136 (8)	0.0058 (3)	0.00178 (6)	−0.0018 (8)	0.0004 (4)	0.0006 (2)
O(3)	−0.1896 (5)	0.0116 (3)	0.0923 (1)	0.0166 (9)	0.0064 (3)	0.00177 (7)	−0.0034 (9)	0.0016 (4)	−0.0003 (3)
O(4)	0.1453 (5)	0.1206 (3)	0.0874 (1)	0.0157 (8)	0.0064 (3)	0.00177 (6)	−0.0043 (9)	0.0011 (4)	−0.0007 (2)
C(1,1)	0.2520 (7)	−0.2132 (4)	0.0406 (2)	0.016 (1)	0.0051 (4)	0.00150 (9)	−0.003 (1)	0.0027 (6)	0.0001 (3)
C(1,2)	0.3779 (7)	−0.3300 (4)	0.0650 (2)	0.018 (1)	0.0049 (4)	0.00153 (9)	0.001 (1)	0.0032 (5)	0.0007 (3)
C(1,3)	0.2706 (9)	−0.4499 (4)	0.0571 (2)	0.027 (2)	0.0080 (5)	0.00218 (12)	−0.001 (1)	0.0010 (8)	0.0006 (4)
C(1,4)	0.3818 (11)	−0.5609 (4)	0.0792 (3)	0.045 (2)	0.0059 (5)	0.00290 (15)	−0.001 (2)	0.0042 (10)	0.0006 (4)
C(1,5)	0.6065 (11)	−0.5512 (5)	0.1124 (3)	0.040 (2)	0.0081 (5)	0.00283 (14)	0.009 (2)	0.0048 (9)	0.0035 (4)
C(1,6)	0.7120 (9)	−0.4284 (5)	0.1203 (3)	0.023 (2)	0.0138 (6)	0.00266 (13)	0.009 (2)	0.0038 (8)	0.0042 (5)
C(1,7)	0.5996 (7)	−0.3199 (4)	0.0969 (2)	0.019 (1)	0.0077 (5)	0.00175 (10)	0.001 (1)	0.0032 (6)	0.0013 (4)
C(2,1)	−0.0357 (7)	0.0903 (4)	0.1150 (2)	0.019 (1)	0.0051 (4)	0.00157 (9)	0.001 (1)	0.0003 (6)	0.0008 (3)
C(2,2)	−0.0723 (8)	0.1523 (4)	0.1746 (2)	0.025 (1)	0.0063 (4)	0.00163 (9)	0.004 (1)	0.0004 (6)	0.0008 (4)
C(2,3)	0.0926 (9)	0.2397 (5)	0.2002 (2)	0.034 (2)	0.0083 (5)	0.00199 (11)	−0.003 (2)	−0.0014 (7)	−0.0012 (4)
C(2,4)	0.0480 (11)	0.3025 (6)	0.2544 (3)	0.049 (2)	0.0133 (7)	0.00210 (13)	−0.005 (2)	0.0002 (10)	−0.0025 (5)
C(2,5)	−0.1525 (11)	0.2753 (6)	0.2840 (3)	0.048 (2)	0.0159 (7)	0.00207 (13)	0.007 (2)	0.0035 (9)	−0.0023 (6)
C(2,6)	−0.3137 (10)	0.1856 (6)	0.2593 (3)	0.038 (2)	0.0161 (7)	0.00190 (12)	0.005 (2)	0.0042 (8)	−0.0018 (5)
C(2,7)	−0.2770 (9)	0.1248 (5)	0.2043 (2)	0.030 (2)	0.0103 (6)	0.00217 (11)	0.002 (2)	0.0055 (7)	0.0009 (4)

[a] The form of the anisotropic thermal parameters is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table II. Positional and Thermal Parameters and Their Estimated Standard Deviations for $Mo_2[O_2CC(CH_3)_3]_4$[a]

Atom	x	y	z	β_{11}	β_{22}	β_{33}	β_{12}	β_{13}	β_{23}
Mo1	0.51835 (8)	0.08615 (7)	0.85234 (8)	0.00780 (7)	0.00615 (6)	0.00558 (7)	−0.0054 (1)	0.0018 (1)	−0.0004 (1)
Mo2	0.46328 (8)	0.09895 (7)	0.64420 (8)	0.00766 (7)	0.00610 (6)	0.00541 (7)	−0.0040 (1)	0.0017 (1)	−0.0002 (1)
O1	0.3744 (6)	0.2409 (6)	0.8608 (7)	0.0101 (6)	0.0068 (5)	0.0075 (7)	−0.0042 (9)	0.004 (1)	−0.001 (1)
O2	0.4043 (6)	−0.0153 (5)	0.8674 (6)	0.0092 (6)	0.0078 (5)	0.0061 (6)	−0.0085 (8)	0.003 (1)	−0.002 (1)
O3	0.6692 (6)	−0.0645 (6)	0.8556 (7)	0.0074 (6)	0.0073 (5)	0.0076 (7)	−0.0032 (9)	0.001 (1)	0.001 (1)
O4	0.6302 (6)	0.1910 (6)	0.8509 (7)	0.0111 (6)	0.0091 (6)	0.0069 (7)	−0.0100 (9)	0.002 (1)	−0.002 (1)
O5	0.3154 (7)	0.2547 (6)	0.6372 (7)	0.0103 (7)	0.0072 (6)	0.0069 (7)	−0.0030 (10)	0.003 (1)	−0.001 (1)
O6	0.3457 (6)	0.0008 (6)	0.6448 (6)	0.0088 (6)	0.0088 (5)	0.0062 (6)	−0.0082 (8)	0.002 (1)	−0.001 (1)
O7	0.6118 (6)	−0.0552 (6)	0.6360 (6)	0.0083 (6)	0.0075 (5)	0.0063 (6)	−0.0036 (9)	0.003 (1)	−0.001 (1)
O8	0.5716 (6)	0.2037 (6)	0.6292 (7)	0.0105 (6)	0.0083 (5)	0.0072 (7)	−0.0087 (8)	0.004 (1)	0.001 (1)

Atom	x	y	z	B, Å	Atom	x	y	z	B, Å
C1	0.3050 (10)	0.2951 (9)	0.748 (1)	4.0 (2)	C11	0.1888 (15)	0.4916 (15)	0.624 (2)	8.3 (4)
C2	0.1999 (11)	0.4075 (11)	0.744 (1)	5.3 (3)	C12	0.8289 (14)	0.0525 (13)	0.144 (2)	7.2 (4)
C3	0.3390 (9)	−0.0341 (9)	0.755 (1)	3.7 (2)	C13	0.1711 (16)	−0.0525 (15)	0.856 (2)	8.7 (5)
C4	0.2526 (12)	−0.1027 (11)	0.755 (1)	5.5 (3)	C14	0.8320 (15)	0.0951 (14)	0.391 (2)	8.0 (4)
C5	0.6861 (8)	−0.1042 (8)	0.747 (1)	3.3 (2)	C15	0.1680 (11)	−0.0951 (11)	0.609 (1)	5.5 (3)
C6	0.7941 (10)	−0.2085 (10)	0.749 (1)	4.5 (2)	C16	0.8618 (14)	−0.1877 (13)	0.647 (2)	7.2 (4)
C7	0.6292 (10)	0.2349 (10)	0.738 (1)	4.5 (2)	C17	0.1167 (14)	0.2384 (14)	0.105 (2)	7.7 (4)
C8	0.8833 (15)	−0.2384 (14)	0.895 (2)	7.8 (4)	C18	0.6918 (21)	0.3648 (20)	0.600 (2)	4.8 (5)
C9	0.6936 (16)	0.3220 (15)	0.735 (2)	8.8 (5)	C19	0.7644 (29)	0.3460 (28)	0.861 (3)	8.0 (8)
C10	0.2235 (15)	0.4607 (15)	0.880 (2)	8.0 (4)	C20	0.8264 (39)	0.2429 (37)	0.753 (4)	11.3 (12)

[a] The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

Table III. Bond Distances (Å) in $Mo_2(O_2CC_6H_5)_4$[a,b]

Mo–Mo′	2.096 (1)	C(1,2)–C(1,3)	1.386 (6)
–O(1)	2.092 (3)	–C(1,7)	1.397 (6)
–O(2)	2.131 (3)	C(1,4)–C(1,3)	1.380 (7)
–O(3)	2.104 (3)	–C(1,5)	1.424 (8)
–O(4)	2.099 (3)	C(1,6)–C(1,5)	1.409 (7)
–O(2)′[c]	2.876 (2)	–C(1,7)	1.371 (6)
C(1,1)–O(1)	1.280 (4)	C(2,2)–C(2,1)	1.486 (6)
–O(2)	1.281 (5)	–C(2,3)	1.389 (6)
C(2,1)–O(3)	1.268 (5)	–C(2,7)	1.404 (6)
–O(4)	1.272 (5)	C(2,4)–C(2,3)	1.396 (7)
O(1)–O(2)	2.230 (3)	–C(2,5)	1.382 (8)
O(3)–O(4)	2.219 (3)	C(2,6)–C(2,5)	1.384 (8)
C(1,2)–C(1,1)	1.483 (5)	–C(2,7)	1.392 (7)

[a] Atoms are labeled as in Figure 2. [b] Figures in parentheses are estimated standard deviations. [c] Shortest axial intermolecular contact.

to the true Mo–O bonds, which have lengths in the range of 2.092–2.131 Å.

The $Mo_2(O_2CCMe_3)_4$ molecules are not subject to any crystallographic symmetry, but again, they are arranged in chains with one oxygen atom on each end of the molecule lying approximately along the direction for axial coordination to a

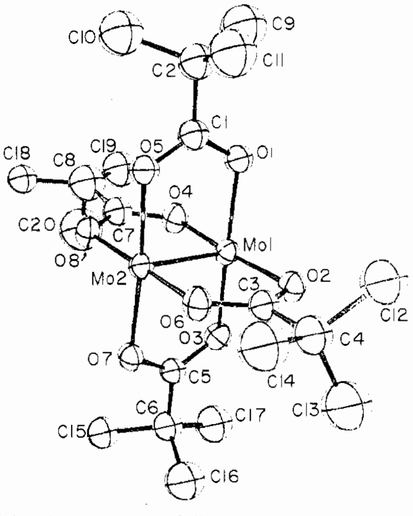

Figure 3. Molecular structure of dimolybdenum tetrapivalate. Atoms are represented by their ellipsoids of thermal vibration scaled to enclose 50% of the electron density. The numbering scheme used in Tables II, V, and VI is defined.

Table IV. Bond Angles (deg) in $Mo_2(O_2CC_6H_5)_4^{a,b}$

Mo′-Mo-O(1)	91.38 (7)	O(3)-C(2,1)-O(4)	121.8 (4)
-O(2)′	92.26 (7)	-C(2,2)	119.1 (4)
-O(3)	91.10 (7)	O(4)-C(2,1)-C(2,2)	119.1 (4)
-O(4)′	92.27 (7)	C(1,1)-C(1,2)-C(1,3)	119.2 (4)
-O(2)^c	159.66 (6)	-C(1,7)	120.8 (3)
O(1)-Mo-O(2)′	176.3 (1)	C(1,2)-C(1,3)-C(1,4)	121.0 (5)
O(3)	92.1 (1)	C(1,3)-C(1,4)-C(1,5)	119.3 (4)
-O(4)′	88.0 (1)	C(1,4)-C(1,5)-C(1,6)	118.8 (4)
O(2)′-Mo-O(3)	88.5 (1)	C(1,5)-C(1,6)-C(1,7)	120.7 (5)
-O(4)′	91.3 (1)	C(1,6)-C(1,7)-C(1,2)	120.2 (4)
O(3)-Mo-O(4)′	176.6 (1)	C(1,7)-C(1,2)-C(1,3)	120.0 (4)
Mo-O(1)-C(1,1)	119.0 (2)	C(2,1)-C(2,2)-C(2,3)	120.1 (4)
Mo′-O(2)-C(1,1)	116.2 (2)	-C(2,7)	119.9 (4)
Mo-O(3)-C(2,1)	117.7 (2)	C(2,2)-C(2,3)-C(2,4)	119.2 (4)
Mo′-O(4)-C(2,1)	116.8 (2)	C(2,3)-C(2,4)-C(2,5)	121.0 (5)
O(1)-C(1,1)-O(2)	121.1 (4)	C(2,4)-C(2,5)-C(2,6)	119.8 (5)
-C(1,2)	118.1 (3)	C(2,5)-C(2,6)-C(2,7)	120.3 (5)
O(2)-C(1,1)-C(1,2)	120.8 (3)	C(2,6)-C(2,7)-C(2,2)	119.7 (5)
		C(2,7)-C(2,2)-C(2,3)	120.0 (4)

[a] Atoms are labeled as in Figure 2. [b] Numbers in parentheses are estimated standard deviations of least significant digits. [c] Nearest intermolecular axial contact.

Table V. Bond Distances (A) in $Mo_2[O_2CC(CH_3)_3]_4^{a,b}$

Mo1-Mo2	2.088 (1)	C2-C1	1.54 (1)
-O1	2.111 (6)	-C9	1.55 (2)
-O2	2.126 (5)	-C10	1.57 (2)
-O3	2.098 (5)	-C11	1.55 (2)
-O4	2.109 (6)	C4-C3	1.51 (1)
-O2^c	2.870 (5)	-C12	1.59 (2)
Mo2-O5	2.110 (6)	-C13	1.55 (2)
-O6	2.100 (6)	-C14	1.57 (2)
-O7	2.135 (5)	C6-C5	1.48 (1)
-O8	2.103 (6)	-C15	1.54 (1)
-O7^c	2.926 (5)	-C16	1.57 (2)
C1-O1	1.28 (1)	-C17	1.58 (2)
-O5	1.276 (9)	C8-C7	1.49 (1)
C3-O2	1.29 (1)	-C18	1.50 (2)
-O6	1.26 (1)	-C19	1.44 (3)
C5-O3	1.265 (9)	-C20	1.52 (4)
-O7	1.270 (9)		
C7-O4	1.28 (1)		
-O8	1.29 (1)		

[a] Atoms labeled as in Figure 3. [b] Numbers in parentheses are estimated standard deviations of least significant digits. [c] Nearest intermolecular axial contact.

Table VI. Bond Angles (deg) in $Mo_2[O_2CC(CH_3)_3]_4^{a,b}$

Mo1-Mo2-O5	91.9 (2)	O1-Mo1-O2	90.8 (2)
-O6	91.6 (2)	-O3	176.0 (2)
-O7	92.2 (2)	-O4	87.1 (2)
-O8	92.4 (2)	O2-Mo1-O3	91.3 (2)
-O7^c	165.3 (3)	O4	175.9 (2)
Mo2-Mo1-O1	92.3 (2)	O3-Mo1-O4	90.5 (2)
-O2	92.3 (2)	O5-Mo2-O6	90.5 (2)
-O3	91.0 (2)	-O7	175.7 (2)
-O4	91.3 (2)	-O8	87.3 (2)
-O2^c	167.1 (3)	O6-Mo2-O7	90.8 (2)
Mo1-O1-C1	116.2 (3)	-O8	175.5 (2)
-O2-C3	115.3 (3)	C1-C2-C9	109.4 (9)
-O3-C5	119.6 (3)	-C10	108.8 (9)
-O4-C7	118.5 (4)	-C11	107.0 (9)
Mo2-O5-C1	116.8 (3)	C3-C4-C12	109.3 (9)
-O6-C3	118.2 (3)	-C13	108.6 (9)
-O7-C5	116.4 (3)	-C14	109.5 (9)
-O8-C7	117.8 (4)	C5-C6-C15	110.3 (8)
C2-C1-O1	120.2 (8)	-C16	106.8 (8)
-O5	117.0 (8)	-C17	109.0 (8)
C4-C3-O2	119.6 (7)	C7-C8-C18	116 (1)
-O6	117.8 (8)	-C19	118 (2)
C6-C5-O3	119.7 (8)	-C20	101 (2)
-O7	119.4 (8)	C9-C2-C10	113 (1)
C8-C7-O4	119.4 (9)	-C11	108 (1)
C8-C7-O8	121.2 (9)	C10-C2-C11	110 (1)
O7-Mo2-O8	91.2 (2)	C12-C4-C13	106 (1)
O1-C1-O5	122.6 (8)	-C14	111 (1)
O2-C3-O6	122.6 (8)	C13-C4-C14	112 (1)
O3-C5-O7	120.9 (7)	C15-C6-C16	110.1 (8)
O4-C7-O8	119.5 (9)	-C17	111.6 (9)
		C16-C6-C17	108.9 (9)
		C18-C8-C19	126 (2)
		-C20	90 (2)
		C19-C8-C20	74 (2)

[a] Atoms labeled as in Figure 3. [b] Numbers in parentheses are estimated standard deviations of least significant digits. [c] Nearest intermolecular axial contact.

Table VII. Structures of $Mo_2(O_2CR)_4L_2$ Compounds

Compd		Interatomic distances, A		
R	L	Mo···L	Mo–Mo	Ref
$C(CH_3)_3$	*a*	2.90	2.088 (1)	This work
CH_3	*a*	2.65	2.093 (1)	11
H	*a*	2.65	2.091 (2)	12
C_6H_5	*a*	2.88	2.096 (1)	This work
C_6H_5	Diglyme	2.66	2.100 (1)	13
$CH_2NH_3^+$	SO_4^{2-}	2.93	2.115 (1)	14
CF_3	*a*	2.72	2.090 (4)	15
CF_3	C_5H_5N	2.55	2.129 (2)	16

[a] In all cases where there is no separate ligand L, the crystal packing places oxygen atoms of neighboring molecules in axial positions.

neighboring molecule. In this case the axial contacts are at distances of 2.870 (5) and 2.926 (5) Å, i.e., quite similar to those in the benzoate.

There is another similarity between the two crystal structures. The intramolecular Mo–O distances to those oxygen atoms that form the weak axial bonds to neighboring molecules are all longer (2.126–2.135 Å) than the Mo–O bonds to the other, nonbridging oxygen atoms (2.092–2.111 Å). Apart from this distortion, and neglecting the rotational orientations of the R groups, in each case the molecules have virtual D_{4h} symmetry.

Discussion

The results of these two structure determinations provide further evidence, by means of particularly apt comparisons, for the already suspected insensitivity of the Mo–Mo quadruple bond in $Mo_2(O_2CR)_4L_2$ to the influence of changes in the inductive effect of the R groups as well as to variations in the nature or location of the axial ligands, L. Table VII gives a list of all reported structures of $Mo_2(O_2CR)_4L_2$ compounds.

There is no significant response to changes in the inductive effect of the group R of the carboxylic acid. In the set of four unsolvated compounds with R = CH_3, H, C_6H_5, and CF_3, in which the intermolecular axial interaction distances are all long (and for three of them substantially constant) and the inductive effect changes enormously, the Mo–Mo distances are invariant within experimental error. In the pivalate where the R group now provides us with the extreme in electron-donating ability, the Mo–Mo distance appears to be slightly shorter, but the difference from the others just mentioned does not exceed the uncertainty by enough to have more than marginal statistical validity. It is true that the difference between the Mo–Mo distances in the pivalate and the benzoate is statistically significant at a rather high confidence level (>95%), but the other three compounds do not fall in with any recognizable trend. We conclude that Mo–Mo quadruple bond lengths are essentially insensitive to the entire accessible range of variation in the inductive properties of R in $Mo_2(O_2CR)_4$ compounds and that the value is in the range 2.092 ± 0.004 Å.

With respect to the influence of axial ligand coordination, the evidence suggests a small but apparently real effect. The first,[16] and still the most persuasive, evidence that there is such an effect was provided by the comparison of the trifluoroacetate and its dipyridine adduct. Here, the replacement of weak intermolecular axial interactions (Mo···O, 2.72 Å) by considerably shorter bonds to a stronger base (Mo···N, 2.55 Å) is accompanied by an increase of 0.039 (4) Å in the Mo–Mo distance. It seems reasonable to presume a cause and effect relationship.

However, the effect seen in the case of the trifluoroacetate may well be atypically large in view of the result we now have in comparing the benzoate and its diglyme adduct. In the former the axial intermolecular contacts are rather weak (Mo···O, 2.88 Å) while in the latter a diglyme oxygen atom is coordinated in each molybdenum atom considerably more closely (2.66 Å) although still not so strongly as is the pyridine nitrogen atom in $Mo_2(O_2CCF_3)_4 \cdot 2C_5H_5N$. There is an apparent slight increase in the Mo–Mo quadruple bond distance, 0.004 (1.5) Å, but it is on the threshold of statistical or chemical significance.

Thus, we conclude that axial coordination can affect the strength of the Mo–Mo quadruple bond but that only in special cases, i.e., where R is very electron withdrawing and L is a very good donor (factors that should operate synergistically) will the lengthening of the Mo–Mo quadrupole bond be more than marginal.

As we shall show in a forthcoming paper[10] this rigidity or toughness of the Mo–Mo quadruple bond is in dramatic contrast to the ease with which the length of the Cr–Cr quadruple bond in analogous compounds can be altered.

Acknowledgment. We thank the National Science Foundation for financial support and Dr. D. M. Collins for helpful advice.

Registry No. 1, 24378-22-1; **2**, 55946-68-4.

Supplementary Material Available: Tables of observed and calculated structure factors for both $Mo_2[O_2CC(CH_3)_3]_4$ and $Mo_2(O_2CPh)_4$ (20 pages). Ordering information is given on any current masthead page.

References and Notes

(1) D. M. Collins, F. A. Cotton, and C. A. Murillo, *Inorg. Chem.*, **15**, 1861 (1976).
(2) (a) F. A. Cotton and J. G. Norman, Jr., *J. Coord. Chem.*, **1**, 161 (1971); (b) *J. Am. Chem. Soc.*, **94**, 5697 (1972).
(3) D. M. Collins, F. A. Cotton, and C. A. Murillo, *Inorg. Chem.*, **15**, 2950 (1976).
(4) F. A. Cotton, J. G. Norman, Jr., B. R. Stults, and T. R. Webb, *J. Coord. Chem.*, **5**, 217 (1976).
(5) F. A. Cotton, Z. C. Mester, and T. R. Webb, *Acta Crystallogr., Sect. B*, **30**, 2768 (1974).
(6) R. E. McCarley, J. L. Templeton, T. J. Colburn, V. Katovic, and R. J. Hoxmeier, *Adv. Chem. Ser.*, **No. 150**, 318 (1976).
(7) "International Tables for X-ray Crystallography", Kynoch Press, Birmingham, England: (a) Vol. I, 1969, Table 4.3; (b) Vol. IV, 1974, Table 2.3.1.
(8) All computations were performed on a PDP 11/45 computer at the Molecular Structure Corp., College Station, Tex. 77840, using software from the Enraf-Nonius structure determination package.
(9) D. T. Cromer and J. T. Liberman, *J. Chem. Phys.*, **53**, 1891 (1970).
(10) F. A. Cotton, M. Extine, and G. E. Rice, *Inorg. Chem.*, in press.
(11) F. A. Cotton, Z. C. Mester, and T. R. Webb, *Acta Crystallogr., Sect. B*, **30**, 2768 (1974).
(12) F. A. Cotton, J. G. Norman, Jr., B. R. Stults, and T. R. Webb, *J. Coord. Chem.*, **5**, 217 (1976).
(13) D. M. Collins, F. A. Cotton, and C. A. Murillo, *Inorg. Chem.*, **15**, 2950 (1976).
(14) F. A. Cotton and T. R. Webb, *Inorg. Chem.*, **15**, 68 (1976).
(15) F. A. Cotton and J. G. Norman, Jr., *J. Coord. Chem.*, **1**, 161 (1971).
(16) F. A. Cotton and J. G. Norman, Jr., *J. Am. Chem. Soc.*, **94**, 5697 (1972).

Contribution from the Department of Chemistry, Texas A&M University,
College Station, Texas 77843

Sensitivity of the Chromium–Chromium Quadruple Bond in Dichromium Tetracarboxylates to Axial Coordination and Changes in Inductive Effects

F. ALBERT COTTON,* MICHAEL W. EXTINE, and GARY W. RICE

Received July 18, 1977

X-ray crystallographic studies have been made of six $Cr_2(O_2CR)_4L_2$-type compounds to determine the response of the Cr–Cr quadruple bond, as that response is evidenced in the bond length, to (a) the closeness of axial ligand atoms and (b) the inductive character of the R groups. The new results together with others already in the literature (for a total of 8 compounds) show that the Cr–Cr quadruple bond is very sensitive to both of these factors and evidently to others as well, since no simple, qualitative trends are apparent. The new structures reported here are those of the following compounds, where the numbers in parentheses following each formula are the lengths in Å of the Cr–Cr and the Cr–(axial ligand) bonds: (I) $Cr_3(O_2CH)_6(H_2O)_2$ (2.451, 2.224); (II) $Cr_2(O_2CH)_4(C_5H_5N)_2$ (2.408, 2.308); (III) $Cr_2(O_2CCF_3)_4(Et_2O)_2$ (2.541, 2.244); (IV) $Cr_2(O_2CCMe_3)_4$ (2.388, 2.44); (V) $Cr_2(O_2CPh)_4(PhCO_2H)_2$ (2.352, 2.295); (VI) Cr_2(9-anthracenecarboxylate)$_4$-$(CH_3OCH_2CH_2OCH_3)$ (2.283, 2.283). It is concluded that the Cr–Cr quadruple bond interaction, within the tetra-μ-carboxylato environment, must be described by a very broad, relatively shallow potential function so that the Cr–Cr distance is easily varied over a broad range by a variety of additional factors. It is shown that the variations in Cr–Cr distance cannot be accounted for solely by postulating linear and independent dependences on the inductive effect of the R groups and the distances to the axial ligand atoms.

Introduction

The chemistry of compounds containing multiple bonds between metal atoms has developed rapidly since the recognition, in the early 1960s, of the first double bond,[1] the first triple bond,[2] and the first quadruple bond.[3] With several of the elements that have a consistent tendency to form such bonds, particularly molybdenum and rhenium, the structural patterns are relatively simple, especially with respect to the quadruple bonds. In these cases, the Mo_2^{4+} and Re_2^{6+} central units appear to be structurally rigid, and the observed variation in metal–metal distance is relatively slight. Thus the Mo–Mo quadruple bond lengths span a range from 2.088 (1) in $Mo_2(O_2CCMe_3)_4$[4] to 2.183 (2) Å in $Mo_2(C_3H_5)_4$,[5] and the known range of Re–Re quadruple bond lengths is from 2.178 (1) in the $Re_2Me_8^{2-}$ ion[6] to about 2.24 Å in several compounds,[7] e.g., $Re_2Cl_8^{2-}$ salts.

With chromium, however, the situation is not so simple. Prior to the work described here, Cr–Cr quadruple bond distances have been reported as low as about 1.98 Å in the $Cr_2Me_8^{4-}$ and $Cr_2(CH_2CH_2CH_2CH_2)_4^{4-}$ ions[8,9] and Cr_2(C$_3$-