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A Molybdenum-Molybdenum Quadruple Bond Bridged by Four Carboxyl Groups but Entirely Isolated from Axial Coordination

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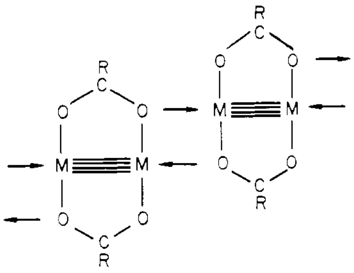
The compound $Mo_2(O_2Cbiph)_4$, where $biphCO_2H$ is 2-phenylbenzoic acid, has been prepared and structurally characterized by X-ray crystallography. In this case the steric properties of the $biphCO_2^-$ ligands prevent intermolecular association, and the crystal structure consists of a simple van der Waals packing of the molecules with no axial ligation, intermolecular or otherwise. The Mo–Mo bond length is 2.082 (1) Å, which is 0.014 (2) Å shorter than that in the benzoate where there is intermolecular association with Mo···O distances of 2.876 (2) Å. The compound crystallizes in space group $P\bar{1}$ with $Z = 1$ and the following unit cell dimensions: $a = 10.169$ (1) Å, $b = 14.812$ (3) Å, $c = 7.563$ (1) Å, $\alpha = 98.59$ (1)°, $\beta = 103.93$ (1)°, $\gamma = 102.58$ (1)°, $V = 1054.4$ (6) Å^3. The structure was refined with the use of 352 variables to $R_1 = 0.034$ and $R_2 = 0.044$ with those 2243 measured reflections having intensities $>3\sigma$.

Introduction

All types of compounds containing quadruple bonds evidently have some inherent tendency to bind ligands in their axial positions, but the strength of this tendency varies greatly. For dichromium tetracarboxylates it is very great, and $Cr_2(O_2CR)_4$ molecules are very difficult to obtain without axial ligation. Virtually all solid compounds known contain $Cr_2(O_2CR)_4L_2$ molecules. In the two cases where a crystalline $Cr_2(O_2CR)_4$ compound has been obtained, namely, with R = CH_3 and $C(CH_3)_3$, the molecules are linked into infinite chains[1,2] in which the $Cr_2(O_2CR)_4$ molecules serve as axial donors to one another, as indicated in the partial schematic diagram I. Qualitatively similar though weaker intramolecular associations occur in five $Mo_2(O_2CR)_4$ compounds.[3-6]



I

From a theoretical point of view, it is easier to discuss the quadruple bond in isolation, i.e., to consider just the $M_2(O_2CR)_4$ unit, uncomplicated by either axial ligands or the intermolecular bonds. As a basis for such theoretical study, it is necessary to have structural data and other experimental results on the isolated $M_2(O_2CR)_4$ molecules. The problem, in view of their propensity to bind axial ligands or to associate, is how to isolate them under conditions where the desired structural and other data can be measured. The use of R groups with the size and shape necessary to ensure isolation is something more easily said than done, and we have previously reported that using 2-phenylbenzoate ($biphCO_2^-$) ligands with Cr_2^{4+} we still obtained a "dimer of dimers" structure rather than the desired $Cr_2(O_2Cbiph)_4$ molecules.[7]

Table I. Crystallographic Parameters

formula	$Mo_2O_8C_{52}H_{36}$
space group	$P\bar{1}$
a, Å	10.169 (1)
b, Å	14.812 (3)
c, Å	7.563 (1)
α, deg	98.59 (1)
β, deg	103.93 (1)
γ, deg	102.58 (1)
V, Å^3	1054.4 (6)
d_{calcd}, g/cm^3	1.544
Z	1
fw	980.74
crystal size, mm	0.10 × 0.30 × 0.40
μ(Mo Kα), cm^{-1}	6.461
range 2θ, deg	$0° < 2\theta < 50°$
no. of unique data	2261
no. of data with $F_o^2 > 3\sigma(F_o^2)$	2243
no. of variables	352
R_1	0.034
R_2	0.044
goodness of fit (esd)	0.979
largest shift	0.03
largest peak, e/Å^3	0.674

In view of the fact that the $Mo_2(O_2CR)_4$ compounds show a much lower tendency to bind axial ligands and to associate with one another,[5] we wondered if the $biphCO_2^-$ ligand might succeed in giving isolated $Mo_2(O_2Cbiph)_4$ molecules even though it had failed to enforce complete isolation of $Cr_2(O_2Cbiph)_4$ molecules. In this paper we report the preparation and structural characterization of $Mo_2(O_2Cbiph)_4$ and show that the crystalline compound does, in fact, consist of a van der Waals packing of isolated molecules.

Experimental Section

Molybdenum(II) acetate was prepared by established procedures.[8] A mixture of 0.110 g of $Mo_2(O_2CCH_3)_4$ and 0.25 g of 2-phenylbenzoic acid ($biphCO_2H$) was heated at 120 °C under an argon atmosphere for 12 h. The molten mixture solidified to a bright yellow solid, which was slightly soluble in toluene, giving crystals of $Mo_2(O_2Cbiph)_4$ upon cooling.

A crystal of dimensions of 0.10 × 0.30 × 0.40 mm was coated with epoxy cement and then attached to the end of a glass fiber. Data were collected on a Syntex $P\bar{1}$ automated four-circle diffractometer using Mo Kα ($\lambda = 0.710730$ Å) radiation with a graphite crystal monochromator in the incident beam. Unit cell constants were obtained from indexing on 15 intense centered reflections in the range $25° \leq 2\theta \leq 32°$. Unit cell constants are given in Table I with other data

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0020-1669/81/1320-3887$01.25/0

Table II. Table of Positional and Thermal Parameters and Their Estimated Standard Deviations[a, b]

atom	*x*	*y*	*z*	*B*(1,1)	*B*(2,2)	*B*(3,3)	*B*(1,2)	*B*(1,3)	*B*(2,3)
Mo	0.45930 (4)	0.45033 (3)	0.07013 (6)	1.23 (1)	1.91 (1)	1.76 (1)	0.36 (1)	0.29 (1)	0.43 (1)
O(1)	0.4098 (3)	0.3390 (2)	−0.1604 (4)	2.1 (1)	1.9 (1)	1.9 (1)	0.2 (1)	0.7 (1)	0.6 (1)
O(2)	0.4937 (3)	0.4453 (2)	−0.3123 (4)	2.0 (1)	1.8 (1)	2.0 (1)	0.2 (1)	0.5 (1)	0.4 (1)
O(3)	0.6555 (3)	0.4234 (2)	0.1667 (4)	1.4 (1)	2.3 (1)	2.3 (1)	0.5 (1)	0.6 (1)	0.8 (1)
O(4)	0.7439 (3)	0.5315 (2)	0.0233 (4)	1.5 (1)	2.2 (1)	2.5 (1)	0.3 (1)	0.6 (1)	0.9 (1)
C(1)	0.4331 (4)	0.3602 (3)	−0.3084 (7)	1.4 (2)	2.5 (2)	2.1 (2)	0.8 (1)	0.3 (1)	0.0 (2)
C(2)	0.7569 (5)	0.4694 (3)	0.1207 (7)	1.8 (2)	2.3 (2)	2.3 (2)	0.5 (1)	0.5 (2)	0.1 (2)
C(11)	0.3950 (5)	0.2862 (3)	−0.4803 (7)	1.8 (2)	2.2 (2)	2.1 (2)	0.8 (1)	0.2 (1)	0.4 (2)
C(12)	0.2942 (5)	0.1986 (3)	−0.5144 (7)	2.0 (2)	2.5 (2)	2.3 (2)	0.4 (2)	0.4 (2)	0.2 (2)
C(13)	0.2776 (6)	0.1333 (4)	−0.6763 (8)	3.2 (2)	2.4 (2)	3.9 (3)	−0.7 (2)	0.8 (2)	−0.9 (2)
C(14)	0.3544 (7)	0.1524 (4)	−0.8004 (8)	4.7 (3)	3.9 (3)	2.6 (2)	0.4 (2)	1.1 (2)	−0.7 (2)
C(15)	0.4528 (6)	0.2383 (4)	−0.7662 (7)	3.6 (2)	3.1 (2)	2.7 (2)	0.9 (2)	1.4 (2)	0.6 (2)
C(16)	0.4709 (5)	0.3042 (3)	−0.6078 (7)	2.0 (2)	2.3 (2)	2.3 (2)	0.3 (1)	0.5 (2)	0.6 (2)
C(21)	0.2012 (5)	0.1721 (4)	−0.3963 (7)	1.9 (2)	2.8 (2)	2.7 (2)	0.1 (2)	0.5 (2)	0.3 (2)
C(22)	0.1232 (6)	0.2309 (4)	−0.3396 (8)	2.7 (2)	3.3 (2)	4.2 (3)	0.5 (2)	1.6 (2)	0.8 (2)
C(23)	0.0314 (6)	0.2034 (5)	−0.2385 (9)	3.6 (2)	4.6 (3)	6.0 (3)	1.0 (2)	2.9 (2)	0.7 (3)
C(24)	0.0172 (7)	0.1173 (5)	−0.1887 (9)	3.8 (3)	5.4 (3)	5.0 (3)	−0.2 (2)	2.3 (2)	1.1 (3)
C(25)	0.0911 (7)	0.0581 (5)	−0.2455 (10)	4.4 (3)	4.0 (3)	5.6 (3)	0.3 (2)	2.0 (2)	1.9 (2)
C(26)	0.1829 (6)	0.0853 (4)	−0.3463 (9)	3.0 (2)	3.4 (2)	5.2 (3)	0.8 (2)	1.4 (2)	1.0 (2)
C(31)	0.9007 (5)	0.4553 (3)	0.1898 (1)	1.7 (2)	3.2 (2)	2.2 (2)	1.0 (1)	0.8 (1)	1.1 (2)
C(32)	0.9255 (5)	0.3666 (3)	0.1854 (7)	2.1 (2)	3.3 (2)	2.9 (2)	1.3 (1)	1.2 (2)	1.3 (2)
C(33)	1.0621 (5)	0.3630 (4)	0.2659 (8)	2.6 (2)	4.8 (2)	4.1 (2)	2.3 (2)	1.3 (2)	2.4 (2)
C(34)	1.1693 (5)	0.4431 (4)	0.3524 (8)	1.7 (2)	5.6 (3)	3.2 (2)	1.3 (2)	0.6 (2)	1.8 (2)
C(35)	1.1435 (5)	0.5308 (4)	0.3562 (8)	1.3 (2)	4.6 (3)	3.7 (2)	0.1 (2)	0.4 (2)	1.3 (2)
C(36)	1.0106 (5)	0.5375 (4)	0.2741 (8)	1.5 (2)	3.3 (2)	3.4 (2)	0.5 (2)	0.6 (2)	0.9 (2)
C(41)	0.8147 (5)	0.2769 (4)	0.0888 (8)	2.2 (2)	3.1 (2)	4.5 (3)	1.4 (2)	1.3 (2)	0.9 (2)
C(42)	0.7309 (6)	0.2654 (4)	−0.0912 (8)	3.4 (2)	3.2 (2)	3.9 (3)	1.3 (2)	1.0 (2)	0.5 (2)
C(43)	0.6331 (6)	0.1808 (4)	−0.1843 (10)	3.2 (2)	3.5 (3)	6.2 (4)	1.3 (2)	−0.1 (2)	−0.6 (3)
C(44)	0.6191 (7)	0.1057 (5)	−0.0999 (13)	3.1 (3)	3.7 (3)	9.9 (5)	0.7 (2)	0.6 (3)	0.1 (3)
C(45)	0.6986 (8)	0.1151 (4)	0.0753 (12)	5.3 (3)	3.1 (2)	10.3 (5)	1.3 (2)	2.6 (3)	3.0 (3)
C(46)	0.7989 (7)	0.2000 (4)	0.1727 (9)	4.0 (3)	3.4 (2)	5.5 (3)	1.3 (2)	1.0 (2)	1.6 (2)

atom	*x*	*y*	*z*	*B*, Å^2	atom	*x*	*y*	*z*	*B*, Å^2
H(13)	0.213 (5)	0.074 (3)	−0.708 (6)	2.2 (10)	H(33)	1.077 (4)	0.306 (3)	0.264 (6)	1.8 (10)
H(14)	0.339 (5)	0.109 (4)	−0.904 (7)	3.7 (13)	H(34)	1.262 (6)	0.439 (4)	0.408 (8)	4.6 (15)
H(15)	0.499 (5)	0.250 (3)	−0.854 (6)	2.4 (11)	H(35)	1.216 (5)	0.594 (3)	0.418 (7)	2.9 (12)
H(16)	0.534 (4)	0.362 (3)	−0.590 (5)	1.1 (9)	H(36)	0.989 (6)	0.599 (4)	0.272 (7)	3.9 (13)
H(22)	0.132 (5)	0.292 (3)	−0.376 (7)	3.3 (12)	H(42)	0.744 (6)	0.312 (4)	−0.153 (8)	4.4 (14)
H(23)	−0.018 (6)	0.247 (4)	−0.190 (8)	5.2 (16)	H(43)	0.577 (5)	0.171 (4)	−0.321 (7)	3.6 (13)
H(24)	−0.049 (7)	0.090 (5)	−0.137 (10)	7.3 (20)	H(44)	0.545 (5)	0.044 (4)	−0.166 (7)	3.7 (13)
H(25)	0.072 (6)	0.000 (4)	−0.226 (8)	4.5 (14)	H(45)	0.690 (5)	0.071 (3)	0.123 (6)	2.3 (11)
H(26)	0.227 (5)	0.049 (3)	−0.374 (7)	3.3 (12)	H(46)	0.842 (5)	0.209 (3)	0.296 (6)	2.1 (10)

[a] The form of the anisotropic thermal parameter is $\exp[-0.25\{h^2a^2B(1,1) + k^2b^2B(2,2) + l^2c^2B(3,3) + 2hkabB(1,2) + 2hlacB(1,3) + 2klbcB(2,3)\}]$, where *a*, *b*, and *c* are reciprocal lattice constants. [b] Estimated standard deviations in the least significant digits are shown in parentheses.

collection parameters. A $\theta/2\theta$ scan technique with a variable scan rate from 4.0 to 24.0°/min was used in collection of data. Other general procedures for data collection are described elsewhere.[9] Diffraction data were corrected for Lorentz and polarization effects, but the small absorption coefficient (Table I) made an absorption correction unnecessary.

Solution and refinement[10] were undertaken in the triclinic space group $P\bar{1}$. The position of the Mo atom was obtained from a three-dimensional Patterson function. Initial refinement on this position gave discrepancy indices of

$$R_1 = \sum||F_o| - |F_c||/\sum|F_o| = 0.31$$

$$R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w|F_o|^2]^{1/2} = 0.39$$

The remaining four oxygen atoms and 26 carbon atoms were found by subsequent difference Fourier maps and least-square refinements. Refinement of positional and anisotropic thermal parameters gave discrepancy indices of $R_1 = 0.045$ and $R_2 = 0.064$. A difference Fourier map revealed the positions of the hydrogen atoms which were then included in the refinement with isotropic thermal parameters to give final discrepancy indices of $R_1 = 0.034$ and $R_2 = 0.044$. The largest peak in the final difference Fourier map was 0.674 e/Å^3.

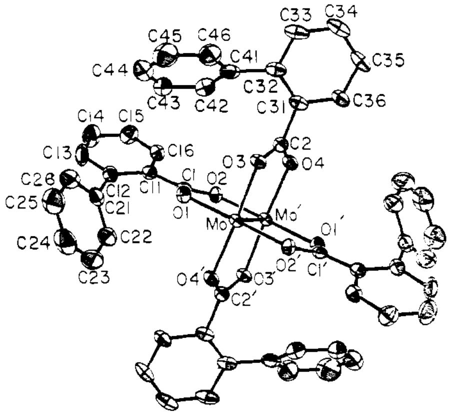

Figure 1. ORTEP drawing of $Mo_2(O_2Cbiph)_4$ with 50% probability thermal ellipsoids.

Results

The positional and thermal parameters are recorded in Table II. Tables III and IV present the bond distances and angles following the numbering scheme as shown in Figure 1. Figure 2 shows the packing in the unit cell. A list of least-squares planes and dihedral angles for the phenyl rings and the dimolybdenum carboxylate units is given in Table V, which is

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[9] Cotton, F. A.; Frenz, B. A.; Deganello, G.; Shaver, A. *J. Organomet. Chem.* **1973**, *50*, 227. Adams, R. D.; Collins, D. M.; Cotton, F. A. *J. Am. Chem. Soc.* **1974**, *96*, 749.

[10] All crystallographic computing was done on a PDP 11/60 computer at the Molecular Structure Corporation, College Station, Texas, using the Enraf-Nonius structure determination package.

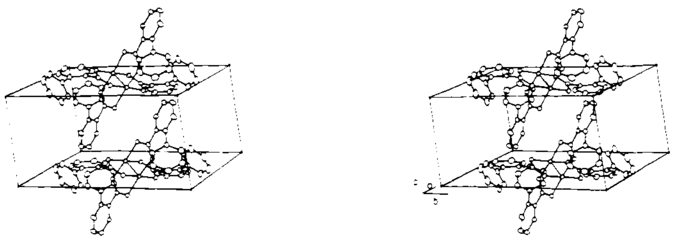

Figure 2. ORTEP stereographic view of the unit cell of $Mo_2(O_2Cbiph)_4$.

Table III. Bond Distances (Å) and Their Estimated Standard Deviations

Mo-Mo′	2.082 (1)	C(34)–C(35)	1.377 (9)
Mo–O(1)	2.090 (3)	C(35)–C(36)	1.377 (8)
Mo–O(2)′	2.094 (3)	C(41)–C(42)	1.385 (9)
Mo–O(3)	2.099 (3)	C(41)–C(46)	1.382 (9)
Mo–O(4)′	2.107 (3)	C(42)–C(43)	1.383 (9)
C(1)–O(1)	1.268 (6)	C(43)–C(44)	1.36 (1)
C(1)–O(2)	1.285 (6)	C(44)–C(45)	1.34 (1)
C(1)–C(11)	1.479 (7)	C(45)–C(46)	1.40 (1)
C(11)–C(12)	1.412 (7)	C(13)-H(13)	0.93 (5)
C(11)–C(16)	1.394 (8)	C(14)-H(14)	0.90 (6)
C(12)–C(13)	1.392 (8)	C(15)-H(15)	0.92 (6)
C(12)–C(21)	1.483 (8)	C(16)-H(16)	0.92 (5)
C(13)–C(14)	1.38 (1)	C(22)-H(22)	0.98 (6)
C(14)–C(15)	1.382 (9)	C(23)-H(23)	0.98 (7)
C(15)–C(16)	1.374 (8)	C(24)-H(24)	0.90 (9)
C(21)–C(22)	1.387 (8)	C(25)-H(25)	0.89 (7)
C(21)–C(26)	1.380 (9)	C(26)-H(26)	0.80 (6)
C(22)–C(23)	1.375 (9)	C(33)-H(33)	0.89 (5)
C(23)–C(24)	1.37 (1)	C(34)-H(34)	0.96 (7)
C(24)–C(25)	1.36 (1)	C(35)-H(35)	1.02 (6)
C(25)–C(26)	1.37 (1)	C(36)-H(36)	0.99 (6)
C(31)–C(32)	1.388 (8)	C(42)-H(42)	0.90 (7)
C(31)–C(36)	1.404 (8)	C(43)-H(43)	1.03 (6)
C(32)–C(33)	1.392 (8)	C(44)-H(44)	1.02 (6)
C(32)–C(41)	1.494 (8)	C(45)-H(45)	0.78 (6)
C(33)–C(34)	1.373 (9)	C(46)-H(46)	0.90 (6)

available as supplementary material.

The dimolybdenum unit is located on an inversion center, and the asymmetric unit consists of half of the molecule. The carboxylate groups are bonded in a regular fashion, imparting approximate D_{4h} symmetry to the central portion of the molecule. The Mo–Mo distance is 2.082 (1) Å, with the axial position unoccupied. The Mo–O distances average 2.098 (5) Å, which is equal to the average of the Mo–O distances to nonbridging oxygen atoms, 2.098 (4) Å in $Mo_2(O_2CC_6H_5)_4$.[4] The four O atoms are nearly planar, with the Mo atom lying 0.069 Å inside of the plane; the Mo–Mo–O angles have an average value of 91.9 (3)°.

Discussion

The steric hindrance to intermolecular association that is introduced by placing a *o*-phenyl group on each of the four benzoate ligands is variable because of rotational freedom about the $C-CO_2$ bond and, to a lesser extent, about the C–C bond between the two phenyl groups. Probably one of the least favorable configurations is that found in the chromium compound,[7] where all four *o*-phenyl groups are directed toward one end of the dinuclear unit. However, because of the relatively high strength of the axial interactions which are then possible at the other end, this configuration leads to the lowest *total* energy of the system. For molybdenum, where the energy of intermolecular association is small, the introduction of the four *o*-phenyl groups is sufficient to prevent it, even when these substituents adopt an arrangement that is very favorable to themselves.

Table IV. Bond Angles (Deg) and Their Estimated Standard Deviations

Mo′-Mo–O(1)	92.5 (1)	C(22)–C(23)-H(23)	121 (4)
Mo′-Mo–O(2)′	91.4 (1)	C(24)–C(23)-H(23)	118 (4)
Mo′-Mo–O(3)	91.8 (1)	C(23)–C(24)–C(25)	119.4 (8)
Mo′-Mo–O(4)′	91.8 (1)	C(23)–C(24)-H(24)	126 (6)
O(1)-Mo–O(2)′	176.0 (2)	C(25)–C(24)-H(24)	114 (6)
O(1)-Mo–O(3)	89.3 (1)	C(24)–C(25)–C(26)	120.5 (8)
O(1)-Mo–O(4)′	89.2 (1)	C(24)–C(25)-H(25)	118 (5)
O(2)′-Mo–O(3)	89.7 (1)	C(26)–C(25)-H(25)	121 (5)
O(2)′-Mo–O(4)′	91.5 (1)	C(21)–C(26)–C(25)	121.5 (8)
O(3)-Mo–O(4)′	176.1 (1)	C(21)–C(26)-H(26)	121 (5)
Mo-O(1)–C(1)	117.0 (3)	C(25)–C(26)-H(26)	118 (5)
Mo′–O(2)–C(1)	117.6 (3)	C(32)–C(31)–C(36)	120.3 (5)
Mo-O(3)–C(2)	117.4 (3)	C(31)–C(32)–C(33)	117.6 (6)
Mo′–O(4)–C(2)	116.7 (3)	C(31)–C(32)–C(41)	122.7 (5)
O(1)-C(1)–O(2)	121.3 (5)	C(33)–C(32)–C(41)	119.6 (5)
O(1)–C(1)–C(11)	120.5 (5)	C(32)–C(33)–C(34)	122.4 (6)
O(2)–C(1)–C(11)	118.2 (5)	C(32)–C(33)-H(33)	117 (4)
O(3)–C(2)–O(4)	122.2 (5)	C(34)–C(33)-H(33)	120 (3)
O(3)–C(2)-C(31)	119.1 (5)	C(33)–C(34)–C(35)	119.6 (6)
O(4)–C(2)–C(31)	117.8 (5)	C(33)–C(34)-H(34)	121 (4)
C(1)–C(11)–C(12)	123.8 (5)	C(35)–C(34)-H(34)	119 (4)
C(1)–C(11)–C(16)	116.3 (5)	C(34)–C(35)–C(36)	119.9 (6)
C(12)–C(11)–C(16)	119.8 (5)	C(34)–C(35)-H(35)	125 (3)
C(11)–C(12)–C(13)	117.0 (5)	C(36)–C(35)-H(35)	115 (3)
C(11)–C(12)–C(21)	125.4 (5)	C(31)–C(36)–C(35)	120.2 (6)
C(13)–C(12)–C(21)	117.5 (5)	C(31)–C(36)-H(36)	118 (4)
C(12)–C(13)–C(14)	122.3 (6)	C(35)–C(36)-H(36)	122 (4)
C(12)–C(13)-H(13)	122 (4)	C(32)–C(41)–C(42)	121.6 (6)
C(14)–C(13)-H(13)	116 (3)	C(32)–C(41)–C(46)	120.6 (6)
C(13)–C(14)–C(15)	120.4 (6)	C(42)–C(41)–C(46)	117.7 (6)
C(13)-C(14)-H(14)	119 (4)	C(41)–C(42)–C(43)	121.7 (7)
C(15)–C(14)-H(14)	121 (4)	C(41)–C(42)-H(42)	120 (5)
C(14)–C(15)–C(16)	118.6 (6)	C(43)–C(42)-H(42)	118 (4)
C(14)–C(15)-H(15)	118 (3)	C(42)–C(43)–C(44)	119.9 (8)
C(16)–C(15)-H(15)	123 (4)	C(42)–C(43)-H(43)	122 (4)
C(11)–C(16)–C(15)	121.9 (6)	C(44)–C(43)-H(43)	118 (3)
C(11)–C(16)-H(16)	121 (3)	C(43)–C(44)–C(45)	119.6 (8)
C(15)–C(16)-H(16)	117 (3)	C(43)–C(44)-H(44)	120 (4)
C(12)–C(21)–C(22)	121.7 (6)	C(45)–C(44)-H(44)	120 (4)
C(12)–C(21)–C(26)	121.1 (6)	C(44)–C(45)-C(46)	121.7 (9)
C(22)–C(21)–C(26)	117.1 (6)	C(44)–C(45)-H(45)	119 (5)
C(21)–C(22)–C(23)	121.2 (7)	C(46)–C(45)-H(45)	119 (5)
C(21)–C(22)-H(22)	119 (4)	C(41)–C(46)–C(45)	119.4 (8)
C(23)–C(22)-H(22)	120 (4)	C(41)–C(46)-H(46)	118 (4)
C(22)–C(23)–C(24)	120.2 (8)	C(45)–C(46)-H(46)	121 (4)

Table VI. Structure Parameters (Å) for Five Infinite-Chain Associated Structures of $Mo_2(O_2CR)_4$ Compounds

	R	Mo–O(nb)[a]	Mo–O(b)[a]	Mo···O(b)[b]	Mo–Mo	ref
1	C_6H_5	2.098 (4)	2.131 (3)	2.876 (2)	2.096 (1)	5
2	H	2.101 (15)	2.131 (9)	2.645 (2)	2.091 (2)	6
3	CH_3	2.113 (6)	2.137 (4)	2.645 (2)	2.0934 (8)	3
4	C_4H_9	2.106 (5)	2.126 (5)	2.870 (5)	2.088 (1)	5
5	CF_3	2.03 (5)	2.14 (2)	2.71 (1)	2.090 (4)	4

[a] O(b) and O(nb) represent the carboxylate oxygen atoms that participate and do not participate, respectively, in intermolecular bridge bonding. [b] This distance is the intermolecular one.

The four *o*-phenyl groups in the present case are arranged so that two of them lie more or less in the equatorial region of the molecule, while each of the other two is directed toward one end of the molecule. This probably minimizes repulsive forces between the *o*-phenyl groups, but it also introduces only a slight interference with intermolecular association of the type shown in I. Evidently this slight interference is sufficient to preclude the weak association that would otherwise occur, as in the benzoate and the four compounds listed in Table VI. In short, weak association can be prevented by weak interference.

It is interesting to compare some of the structure parameters in this, the first isolated $Mo_2(O_2CR)_4$ molecule to be studied by X-ray crystallography, with those in the five associated $Mo_2(O_2CR)_4$ compounds previously studied crystallographically. The pertinent data on the latter are listed in Table VI. The only dimension that differs significantly from one of these associated compounds to another is the intermolecular Mo··O(b) distance, which is ca. 2.65 Å to two, ca. 2.87 Å in two others, and 2.71 Å in the fifth. However, this does not seem to induce, or correlate with, significant variations in any other distance. The Mo–Mo distances are all in the narrow range of 2.088–2.096 Å, with an average value of 2.092 Å. In each case the Mo–O(b) distances are ca. 0.03 Å longer than the Mo–O(nb) ones, and the latter, with the possible exception of the rather imprecise one in the CF_3 compound, are in the range 2.098–2.113 Å. In the present case, where all of the Mo–O distances are of the Mo–O(nb) type, the mean value is 2.098 ± 0.009 Å.

The only significantly different distance in the present case is the Mo–Mo distance, 2.082 (1) Å, which is 0.014 (2) Å shorter than that in the benzoate and 0.010 Å shorter than the average of all five listed in Table VI. Qualitatively, it is to be expected that the formation of weak intermolecular bonds would lengthen the Mo–Mo bond slightly, and a lengthening of 0.010–0.014 Å is indicated by the results reported here.

This present work is in excellent accord with the results of an electron diffraction study of the gaseous $Mo_2(O_2CCH_3)_4$ molecule,[11] where it was found that all bond lengths are essentially the same as those in the crystalline compound except for the Mo–Mo distance, which is 2.079 (3) Å. This is a decrease of 0.014 (3) Å from that in the crystalline compound, equal to the decrease we have found.

There has also been a gas-phase electron diffraction study of $Mo_2(O_2CCF_3)_4$, but here the uncertainty in the Mo–Mo bond length, 2.105 (9) Å, together with that in the crystallographic value, 2.090 (4) Å, is such that the difference between them has an esd of ca. 0.010 Å, which is sufficient to obscure the sort of 0.010-Å difference in the other direction that might have been anticipated.

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Registry No. $Mo_2(O_2Cbiph)_4$, 78764-18-8; $Mo_2(O_2CCH_3)_4$, 14221-06-8.

Supplementary Material Available: Tables of observed and calculated structure factors and least-squares planes and dihedral angles (Table V) (11 pages). Ordering information is given on any current masthead page.

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[11] Fink, M.; Kelley, M., Department of Physics, University of Texas, Austin, TX, private communication.

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A Quadruply Bonded Dimolybdenum Compound Containing Only Chelating Ligands: Bis(diethyl-2-pyrazolylhydroxoborato)bis(diethyldi-2-pyrazolylborato)dimolybdenum

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Another of the reaction products of $[Et_2B(pz)_2]^-$ (pz = 2-pyrazolyl) with $Mo_2(O_2CCH_3)_4$ has been isolated and identified by X-ray crystallography. It is the first reported Mo_2^{4+} complex containing exclusively chelating ligands, two of which are $[Et_2B(pz)_2]^-$ ions and two are $[Et_2B(OH)pz]^-$ ions. One ligand of each type is coordinated to each molybdenum atom, and the arrangement is such that the $N_3OMo\overset{4}{-}MoON_3$ core is essentially eclipsed; there is no crystallographic symmetry, but the overall ligand arrangement conforms to virtual C_2 symmetry, with the twofold axis a perpendicular bisector of the Mo–Mo bond. This bond has a length of 2.156 (1) Å. The compound crystallizes in space group $P2_1/n$ with unit cell dimensions of $a = 10.176$ (5) Å, $b = 20.984$ (4) Å, $c = 22.892$ (5) Å, $\beta = 91.70$ (0)°, $V = 4886$ (5) Å^3, and $Z = 4$. The manner in which the dipyrazolyl ligand is partly converted to the pyrazolyl hydroxo ligand is not known, but the process occurs even under carefully anaerobic conditions.

Introduction

Several years ago reactions of $Mo_2(O_2CCH_3)_4$ with di- and tripyrazolylborate ligands were investigated.[1] The following three reactions were reported:

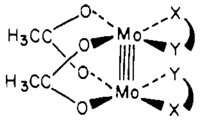
$$Mo_2(O_2CCH_3)_4 + 4Na[BEt_2(pz)_2] \rightarrow Mo_2(BEt_2(pz)_2)_4\ (\mathbf{1}) + 4CH_3CO_2Na \quad (1)$$

$$Mo_2(O_2CCH_3)_4 + 2Na[BEt_2(pz)_2] \rightarrow Mo_2(O_2CCH_3)_2(BEt_2(pz)_2)_2\ (\mathbf{2}) + 2CH_3CO_2Na \quad (2)$$

$$Mo_2(O_2CCH_3)_4 + 2K[BH(pz)_3] \rightarrow Mo(O_2CCH_3)_2(BH(pz)_3)_2\ (\mathbf{3}) + 2CH_3CO_2K \quad (3)$$

Products **2** and **3** were fully characterized by X-ray crystallography and shown to contain a cisoid $Mo_2(O_2CCH_3)_2$ unit with one chelating pyrazolylborate ligand on each metal atom. Attempts to obtain crystals of the blue compound, **1**, were unsuccessful, and at that time no further efforts were planned.

Since then two other reactions[2,3] of $Mo_2(O_2CCH_3)_4$ with chelating ligands have been examined, but in each case only two chelating ligands could be introduced, giving the products **4**[2] and **5**.[3]



4, X-Y = $[OC(CH_3)CHC(CH_3)O]^-$
5, X-Y = $[PhNC(CH_3)CHC(CH_3)O]^-$

We recently decided to reexamine the earlier work on the reaction of $Mo_2(O_2CCH_3)_4$ with $Na[Et_2B(pz)_2]$ in the hope

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[1] Collins, D. M.; Cotton, F. A.; Murillo, C. A. *Inorg. Chem.* **1976**, *15*, 1862.

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[3] Cotton, F. A.; Ilsley, W. H.; Kaim, W. *Inorg. Chim. Acta* **1979**, *37*, 267.