Preparation and Structural Characterization of the Isostructural Dichromium(II) and Dimolybdenum(II) Complexes, $M_2(O_2CCH_3)_2[o\text{-}(NMe_2)C_6H_4CH_2]_2$, Containing Two Four Atom Bridging Ligands and Surprisingly Short M≡M Quadruple Bonds

F. Albert Cotton* and Graham N. Mott

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

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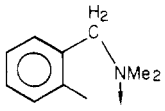
The title compounds have been prepared in good yields by reactions of $Cr_2(O_2CCH_3)_4$ and $Mo_2(O_2CCH_3)_4$ with $Li[o\text{-}(NMe_2)C_6H_4CH_2]$ in THF. Although the molecules of the two compounds are isostructural, each compound was obtained in a different crystal form. For $Cr_2(O_2CCH_3)_2[o\text{-}(NMe_2)C_6H_4CH_2]_2$: space group, *Pbca* with a = 12.478 (2) Å, b = 19.048 (2) Å, c = 9.795 (2) Å, V = 2328 (1) Å^3, and Z = 4. The molecules reside on inversion centers and all of the ligands are bridging. With the $Me_2NC_6H_4CH_2$ ligands oppositely oriented, the inversion center is the only symmetry element possessed by the molecule. The phenyl ring planes make dihedral angles of 55.0° with the central $Cr_2C_2N_2$ plane. The Cr–Cr distance is in the "supershort" range, viz., 1.870 (1) Å. The molybdenum compound crystallizes in space group $P2_1/c$ with a = 8.577 (2) Å, b = 8.685 (1) Å, c = 15.663 (2) Å, β = 101.72 (1)°, V = 1142 (1) Å^3, and Z = 2. The molecular structure is qualitatively the same as that of the chromium homologue with an Mo–Mo distance of 2.065 (1) Å, which is among the shortest Mo–Mo quadruple bond distances known, and the dihedral angle corresponding to the one quoted above is 57.6°.

Introduction

Several years ago Manzer[1] studied the ability of the isomeric chelating ligands 1 and 2 to improve the stability



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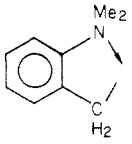

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of M–C σ bonds in organometallic compounds of the early transition elements. He found that significant enhancements of stability did occur for mononuclear complexes of Ti^{III}, V^{III}, and Cr^{III}. Whether the increased stability is entirely a result of the chelate effect is not certain since the bulky NMe_2 groups may contribute by sterically restricting the reactivity of the M–C bonds. Whatever may be the detailed explanation for the stabilization effect, the empirical fact that there is such an effect prompted us to examine the usefulness of these ligands in preparing stable organo derivatives of multiply bonded dimetal units such as Cr_2^{4+} and Mo_2^{4+}.

We have previously reported our studies of the reactions of the lithium derivative of 1 with $Cr_2(O_2CCH_3)_4$[2] and $Mo_2(O_2CCH_3)_4$.[3] All of the products obtained contained the chelating form of 1 but with chromium no simple compound of Cr_2^{4+} was obtained. With Mo_2^{4+} we did get the expected tetrakis-chelate species, albeit with a few unexpected structural details.

We turned then to ligand 2, which we thought would be even more likely to give products that (1) would retain the M_2^{4+} units and (2) would contain four chelating bidentate ligands. As we show in this report, expectation 1 proved correct but 2 has not been fulfilled. Ligand 2 assumes a bidentate bridging role with respect to the Cr_2^{4+} and Mo_2^{4+} species. Moreover, expectation 2 was unfulfilled also in that no more than two of these ligands could be induced to enter the products as replacements for acetate groups. Finally, the products, $M_2(O_2CCH_3)_2[o\text{-}(NMe_2)C_6H_4CH_2]_2$, both have very short M–M quadruple bonds.

For convenience in subsequent discussions in this paper, we shall use DMAB as a code for the *o*-(dimethylamino)benzyl ligand.

Experimental Section

All preparations and other operations were carried out under a dry and oxygen-free argon atmosphere, using standard Schlenk techniques. Solvents were dried and purged of molecular oxygen by distillation from sodium–potassium amalgam. $Li[o\text{-}(NMe_2)C_6H_4CH_2]$ was prepared by a literature procedure.[1]

Preparation of $Cr_2(O_2CCH_3)_2[o\text{-}(NMe_2)C_6H_4CH_2]_2$. The (*o*-(dimethylamino)benzyl)lithium reagent (0.83 g, 5.8 mmol) was dissolved in 30 mL of THF. Dichromium tetraacetate (1.0 g, 2.9 mmol) was added and the resulting dark orange solution stirred overnight. The amorphous precipitate of lithium acetate was removed by filtration, and the resultant solution was cooled to −10 °C to afford orange-red, air-sensitive crystals. Yield: 0.95 g (64%).

Preparation of $Mo_2(O_2CCH_3)_2[o\text{-}(NMe_2)C_6H_4CH_2]_2$. The molybdenum compound was prepared in a similar manner to that for the chromium compound using 1.0 g (2.3 mmol) of dimolybdenum tetraacetate and 0.66 g (4.6 mmol) of the benzyllithium reagent. After filtration the dark yellow THF solution was reduced to a volume of about 10 mL. Overnight cooling at −10 °C afforded bright yellow, air-stable crystals. Yield: 1.1 g (80%).

Several attempts were made to replace all four acetate moieties with $o\text{-}(NMe_2)C_6H_4CH_2$ groups, first by using a 1:4 dimetal tetraacetate to $o\text{-}(NMe_2)C_6H_4CH_2Li$ ratio at room temperature and then a tenfold excess of ligand with refluxing for several days in THF, but in no case was there evidence for the introduction of more than two of the DMAB ligands.

Collection and Reduction of X-ray Data. Suitable crystals of the title compounds were transferred to capillaries and sealed under a stream of argon by using epoxy cement. The crystallographic studies were conducted in the same manner for both compounds. Crystallographic data are collected in Table I. The crystal class, cell dimensions, and space groups were established in a routine manner by examination on an Enraf-Nonius CAD-4 diffractometer, operating at room temperature, and the same

(1) Manzer, L. E. *J. Am. Chem. Soc.* **1978**, *100*, 8068.
(2) Cotton, F. A.; Mott, G. N. *Organometallics* **1982**, 1, 38.
(3) Cotton, F. A.; Mott, G. N. *Inorg. Chem.* **1981**, *20*, 3896.

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Table I. Crystallographic Data and Data Collection Procedures

	$Cr_2O_4N_2C_{22}H_{30}$ (1)	$Mo_2O_4N_2C_{22}H_{30}$ (2)
M	490.49	578.38
space group	$Pbca$	$P2_1/c$
a, Å	12.478 (2)	8.5766 (17)
b, Å	19.048 (2)	8.6849 (9)
c, Å	9.795 (2)	15.6631 (20)
β, deg	90.00	101.723 (14)
V, Å^3	2328 (1)	1142 (1)
Z	4	2
ρ_{calcd}, g/cm^3	1.399	1.68
μ (Mo Kα), cm^{-1}	7.177	6.687
cryst size, mm	0.35 × 0.30 × 0.30	0.15 × 0.20 × 0.20
diffractometer	Enraf Nonius CAD-4	
radiation	graphite-monochromated Mo Kα ($\lambda(\alpha)$ = 0.710 73 Å)	
collection range	$+h,+k,+l$; $0 < 2\theta \leq 50°$	$+h,+k,\pm l$; $0 < 2\theta \leq 50°$
aperture width, mm	1.50 + 1.0 tan θ	1.50 + 1.0 tan θ
prescan rejection limit	2.0	2.0
max counting time, s	30	30
prescan acceptance limit	0.02	0.02
X-ray exposure time, h	24	16
no. of unique data	2035	1993
no. of data with $I \geq 3\sigma(I)$	1363	1505
p	0.05	0.05
no. of variables	184	184
R_1	0.033	0.023
R_2	0.043	0.031
esd	1.29	0.97
largest shift/error ratio	0.01	0.05
largest peak, e/Å^3	0.43	0.24

instrument was then used to collect intensity data. The centering, autoindexing, and data collection procedures have been described previously.[4] The intensity data were collected to $2\theta = 50°$ by using the ω–2θ method and a scan range determined by $\Delta\omega = (0.54 + 0.35 \tan \theta)°$ for the Cr compound and $\Delta\omega = (0.50 + 0.35 \tan \theta)°$ for the Mo compound with a 25% extension at either end for background determination in each case. The data were monitored by measuring three standard reflections every 100 reflections. Only the reflections having intensities, I, greater than $3\sigma(I)$ were retained as observed and, after correction for Lorentz and polarization effects, were used to solve and refine the structures. With $\mu < 8$ cm^{-1} for both compounds no absorption corrections were deemed necessary.

Solution and Refinement of the Structures. $Cr_2(O_2CCH_3)_2[o\text{-}(NMe_2)C_6H_4CH_2]_2$. This compound crystallizes in the space group $Pbca$ with each molecule residing on an inversion center and half of the molecule constituting the asymmetric unit. The structure was solved by Patterson and Fourier methods and refined[5] by the full-matrix least-squares procedure. The position of the chromium atom was obtained through a three-dimensional Patterson synthesis. Three cycles of isotropic least-squares refinement gave values of $R_1 = 0.41$ and $R_2 = 0.50$ where the R_i are defined as follows: $R_1 = \sum(||F_o| - |F_c||)/\sum|F_o|$; $R_2 = [\sum w(|F_o| - |F_c|)^2/\sum w(|F_o|)^2]^{1/2}$. Subsequent least-squares cycles and difference Fourier maps located all nonhydrogen atoms, and after anisotropic refinement the discrepancy indices were $R_1 = 0.045$ and $R_2 = 0.063$. Hydrogen atoms were then located at all expected positions except for those of the acetate ion, but these three were introduced at calculated positions. With inclusion of the hydrogen atoms, the refinement proceeded to convergence at $R_1 = 0.033$ and $R_2 = 0.043$.

(4) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.
(5) All crystallographic computing was performed on a PDP 11/60 computer at the Molecular Structure Corp., College Station, TX, using a modified version of the Enraf-Nonius Structure Determination Package.

Table II. Positional Parameters and Their Estimated Standard Deviations for $Cr_2(O_2CCH_3)_2[o\text{-}(NMe_2)C_6H_4CH_2]_2$[a]

atom	x	y	z
Cr(1)	0.03741 (4)	0.05598 (5)	0.03132 (2)
O(1)	−0.1529 (2)	−0.1064 (2)	0.0361 (1)
O(2)	−0.0627 (2)	0.0223 (2)	0.1114 (1)
N	−0.1567 (2)	0.0607 (3)	−0.0933 (1)
C(1)	−0.1387 (3)	−0.0590 (3)	0.0969 (2)
C(2)	−0.2149 (3)	−0.0993 (5)	0.1547 (2)
C(3)	−0.0441 (3)	0.2359 (3)	0.0039 (2)
C(4)	−0.0533 (2)	0.2701 (3)	−0.0713 (2)
C(5)	−0.0011 (3)	0.3851 (4)	−0.0995 (2)
C(6)	−0.0039 (3)	0.4161 (4)	−0.1700 (2)
C(7)	−0.0578 (3)	0.3339 (4)	−0.2162 (2)
C(8)	−0.1087 (3)	0.2195 (4)	−0.1907 (2)
C(9)	−0.1068 (2)	0.1862 (3)	−0.1201 (2)
C(10)	−0.2611 (13)	0.0950 (4)	−0.0583 (2)
C(11)	−0.1795 (3)	−0.0407 (4)	−0.1483 (2)
H(3A)	−0.104 (2)	0.231 (3)	0.023 (1)
H(3B)	−0.008 (3)	0.308 (3)	0.028 (1)
H(5)	0.033 (2)	0.437 (3)	−0.072 (1)
H(6)	0.026 (3)	0.479 (3)	−0.188 (2)
H(7)	−0.058 (3)	0.361 (4)	−0.266 (2)
H(8)	−0.147 (2)	0.168 (3)	−0.220 (1)
H(10A)	−0.251 (2)	0.166 (3)	−0.018 (1)
H(10B)	−0.310 (3)	0.131 (4)	−0.095 (2)
H(10C)	−0.291 (3)	0.012 (4)	−0.038 (1)
H(11A)	−0.228 (3)	−0.010 (4)	−0.187 (2)
H(11B)	−0.206 (3)	−0.123 (3)	−0.123 (1)
H(11C)	−0.116 (3)	−0.062 (3)	−0.177 (2)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

Table III. Positional Parameters and Their Estimated Standard Deviations for $Mo_2(O_2CCH_3)_2[o\text{-}(NMe_2)C_6H_4CH_2]_2$[a]

atom	x	y	z
Mo(1)	0.07968 (3)	0.09014 (3)	0.01345 (2)
O(1)	0.2533 (2)	−0.0262 (3)	−0.0386 (1)
O(2)	0.0855 (3)	−0.2236 (3)	−0.0666 (1)
N	0.0378 (3)	0.2430 (3)	−0.1133 (2)
C(1)	0.2201 (4)	−0.1614 (5)	−0.0666 (2)
C(2)	0.3457 (5)	−0.2502 (5)	−0.0989 (3)
C(3)	−0.2065 (4)	−0.0021 (5)	−0.1417 (2)
C(4)	−0.2464 (4)	0.1654 (4)	−0.1478 (2)
C(5)	−0.4057 (4)	0.2130 (5)	−0.1625 (2)
C(6)	−0.4508 (5)	0.3663 (6)	−0.1663 (3)
C(7)	−0.3370 (5)	0.4774 (5)	−0.1562 (3)
C(8)	−0.1771 (5)	0.4381 (4)	−0.1404 (2)
C(9)	−0.1323 (4)	0.2838 (4)	−0.1352 (2)
C(10)	0.0914 (4)	0.1768 (5)	−0.1895 (2)
C(11)	0.1445 (5)	0.3730 (4)	−0.0818 (3)
H(3A)	−0.293 (4)	−0.056 (4)	−0.153 (2)
H(3B)	−0.140 (4)	−0.025 (4)	−0.179 (2)
H(5)	−0.468 (4)	0.129 (4)	−0.159 (2)
H(6)	−0.552 (4)	0.382 (4)	−0.173 (2)
H(7)	−0.363 (4)	0.568 (4)	−0.152 (2)
H(8)	−0.103 (3)	0.505 (4)	−0.132 (2)
H(10A)	0.200 (4)	0.351 (4)	0.327 (2)
H(10B)	0.080 (4)	0.257 (5)	0.266 (2)
H(10C)	0.038 (5)	0.423 (5)	0.291 (3)
H(11A)	0.100 (4)	0.417 (4)	0.957 (3)
H(11B)	0.246 (4)	0.329 (4)	0.929 (2)
H(11C)	0.142 (4)	0.454 (4)	0.867 (2)

[a] Estimated standard deviations in the least significant digits are shown in parentheses.

$Mo_2(O_2CCH_3)_2[o\text{-}(NMe_2)C_6H_4CH_2]_2$. This compound crystallizes in the space group $P2_1/c$, again with the molecule on an inversion center and half of the molecule per asymmetric unit. The position of the molybdenum atom was located through a Patterson synthesis. Three cycles of isotropic least-squares refinement gave values of $R_1 = 0.29$ and $R_2 = 0.38$. Subsequent least-squares cycles and difference Fourier maps located all atoms

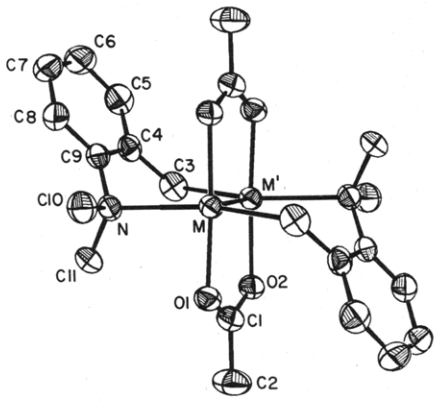

Figure 1. The molecular structure of the $Cr_2(O_2CCH_3)_2[o\text{-}(NMe_2)C_6H_4CH_2]_2$ molecule. The structure of the molybdenum homologue is virtually identical and the same atom numbering scheme applies to both molecules.

Table IV. Bond Distances (Å) for the $M_2(O_2CCH_3)_2[o\text{-}(NMe_2)C_6H_4CH_2]_2$ Molecules

	M = Cr	M = Mo
M(1)-M(1)′	1.870 (1)	2.065 (1)
-O(1)	1.992 (2)	2.097 (2)
-O(2)	2.000 (2)	2.127 (2)
-N	2.217 (2)	2.355 (3)
-C(3)	2.101 (3)	2.217 (4)
O(1)-C(1)	1.261 (4)	1.265 (5)
O(2)-C(1)	1.268 (4)	1.274 (5)
N-C(9)	1.469 (3)	1.473 (4)
-C(10)	1.502 (4)	1.479 (5)
-C(11)	1.472 (4)	1.473 (5)
C(1)-C(2)	1.508 (4)	1.494 (6)
C(3)-C(4)	1.474 (4)	1.493 (6)
-H(3A)	0.83 (3)	0.87 (4)
-H(3B)	0.95 (4)	0.92 (4)
C(4)-C(5)	1.408 (4)	1.401 (5)
-C(9)	1.409 (4)	1.405 (5)
C(5)-C(6)	1.378 (5)	1.385 (7)
-H(5)	0.85 (3)	0.91 (4)
C(6)-C(7)	1.369 (6)	1.359 (8)
-H(6)	0.80 (4)	0.86 (4)
C(7)-C(8)	1.376 (5)	1.386 (6)
-H(7)	0.98 (3)	0.82 (4)
C(8)-C(9)	1.385 (4)	1.392 (6)
-H(8)	0.88 (3)	0.85 (4)
C(10)-H(10A)	1.05 (3)	0.95 (4)
-H(10B)	1.00 (4)	0.89 (5)
-H(10C)	0.97 (4)	1.00 (5)
C(11)-H(11A)	1.00 (4)	0.87 (5)
-H(11B)	0.99 (4)	0.94 (5)
-H(11C)	0.97 (4)	1.07 (4)

except for the acetate methyl hydrogen atoms. These were introduced at calculated positions and their contributions included in F_c values, but they were not refined. With all hydrogen atoms included refinement converged at $R_1 = 0.023$ and $R_2 = 0.031$.

The final atomic positional parameters for the chromium and molybdenum compounds are listed in Tables II and III, respectively. Tables of thermal vibration parameters and positional parameters for the hydrogen atoms that were included at calculated positions but not refined are available as supplementary material.

Results and Discussion

Figure 1 shows the molecular structure for the chromium compound and the numbering scheme for the atoms. This drawing will also serve to represent the molybdenum compound since the only differences are slight changes in some internuclear distances and the atom numbering schemes are parallel. This is possible, even though the crystals are different, because in each case the molecules reside on crystallographic inversion centers. The bond lengths and bond angles are listed in Tables IV and V for both compounds.

Table V. Bond Angles (Deg) for the $M_2(O_2CCH_3)_2[o\text{-}(NMe_2)C_6H_4CH_2]_2$

	M = Cr	M = Mo
M(1)-M(1)′-O(1)	95.45 (6)	92.75 (7)
-O(2)	94.49 (7)	91.55 (7)
-N	111.88 (7)	105.92 (7)
-C(3)	95.2 (1)	96.1 (1)
O(1)-M(1)-O(2)	169.97 (8)	175.62 (9)
-N	89.18 (9)	86.7 (1)
-C(3)	89.0 (1)	86.0 (1)
O(2)-M(1)-N	85.87 (9)	91.3 (1)
-C(3)	91.5 (1)	94.4 (1)
N-M(1)-C(3)	125.9 (1)	157.1 (1)
M(1)-O(1)-C(1)	113.6 (2)	117.0 (2)
M(1)-O(2)-C(1)	113.8 (2)	116.4 (3)
M(1)-N-C(9)	109.4 (2)	107.8 (2)
-C(10)	117.4 (2)	116.2 (3)
-C(11)	99.3 (2)	99.9 (2)
C(9)-N-C(10)	109.5 (3)	111.2 (3)
-C(11)	113.6 (3)	114.4 (3)
C(10-N-C(11)	107.4 (3)	107.1 (3)
O(1)-C(1)-O(2)	122.4 (3)	122.2 (4)
-C(2)	119.1 (3)	118.0 (4)
O(2)-C(1)-C(2)	118.5 (3)	119.8 (4)
M(1)-C(3)-C(4)	118.0 (2)	117.3 (3)
-H(3A)	106 (2)	104 (3)
-H(3B)	106 (2)	104 (2)
C(4)-C(3)-H(3A)	112 (2)	110 (3)
-H(3B)	109 (2)	110 (3)
H(3A)-C(3)-H(3B)	105 (3)	111 (4)
C(3)-C(4)-C(5)	121.1 (3)	120.0 (4)
-C(9)	123.0 (3)	124.1 (4)
C(5)-C(4)-C(9)	115.7 (3)	115.8 (4)
C(4)-C(5)-C(6)	122.5 (4)	123.0 (5)
-H(5)	119 (2)	109 (3)
C(6)-C(5)-H(5)	119 (2)	127 (3)
C(5)-C(6)-C(7)	120.6 (4)	119.3 (5)
-H(6)	125 (3)	115 (3)
C(7)-C(6)-H(6)	114 (3)	126 (3)
C(6)-C(7)-C(8)	118.7 (4)	120.5 (5)
-H(7)	118 (2)	119 (4)
C(8)-C(7)-H(7)	124 (2)	120 (4)
C(7)-C(8)-C(9)	121.7 (4)	119.9 (5)
-H(8)	120 (2)	123 (3)
C(9)-C(8)-H(8)	119 (2)	117 (3)
N-C(9)-C(4)	117.4 (2)	119.1 (3)
-C(8)	121.8 (3)	119.6 (4)
C(4)-C(9)-C(8)	120.8 (3)	121.3 (4)
N-C(10)-H(10A)	112 (2)	109 (3)
-H(10B)	107 (2)	112 (3)
-H(10C)	109 (2)	112 (3)
H(10A)-C(10)-H(10B)	111 (3)	109 (4)
-H(10C)	108 (2)	103 (4)
H(10B)-C(10)-H(10C)	110 (3)	111 (4)
N-C(11)-H(11A)	116 (2)	104 (3)
-H(11B)	106 (2)	104 (3)
-H(11C)	113 (2)	110 (2)
H(11A)-C(11)-H(11B)	113 (3)	126 (4)
-H(11C)	97 (3)	107 (4)
H(11B)-C(11)-H(11C)	111 (3)	106 (3)

The molecular structure, common to both compounds even though they adopt different crystal packing patterns, is a neat and simple one, as can be clearly seen in Figure 1. The $M_2(O_2CCH_3)_2$ portion of the molecules forms a planar unit which has D_{2h} symmetry within the experimental errors. There are no significant inequalities among the M–O and C–O bond lengths. On either side of this plane the two DMAB ligands are placed so that all symmetry elements of D_{2h} are annulled except for the inversion center. The carbon atom of each DMAB ligand is trans to the nitrogen atom of the other one.

A ligand of the type of DMAB has a predilection to function as a chelating ligand with the coordinated metal

atom lying in the mean plane of the ring and the two donor atoms. In this configuration the substituents on each of the donor atoms are directed away from those on the other one. In order for the ligand-to-metal bonds to be directed towards two separate metal atoms, as they are here, it is necessary to rotate the Me_2N and H_2C groups around the ring–N and ring–C bonds, thus giving rise to the considerable dihedral angles (55.0° in the Cr compound and 57.6° in the Mo compound) between the M_2CN plane and the CC_6H_4N plane. This leads also to a relatively close approach of one of the NMe_2 methyl groups to one of the CH_2 hydrogen atoms (for M = Mo, Cr, H(3B)–H(10C) = 1.914 and 2.066 Å, respectively), and it is this which tends to disfavor the bridging role for this ligand. However, contrary to our initial expectation, this factor does not have the decisive role and the bridging arrangement is adopted. Very probably if it were not for the fact that one of the two groups that are forced to be close together is only a hydrogen atom, the bridging arrangement would not be tolerable. For example, the *diars* ligand, 1,2-bis(dimethylarsino)benzene, or others of that sort, presumably could not fulfill a bridging role.

The larger dihedral angle (57.6°) mentioned above for the molybdenum compounds as compared to that (55.0°) for the chromium compound can be attributed to the greater separation of the two molybdenum atoms.

An examination of the internal dimensions of the structure does not suggest that there would be any powerful steric opposition to the accommodation of four DMAB ligands around the M_2^{4+} unit, although one can, perhaps, envision minor steric problems. Thus, one remains uncertain as to why the formation of the $M_2(DMAB)_4$ molecules does not occur, even under forcing conditions.

The fact that the two $M_2(O_2CCH_3)_2(DMAB)_2$ compounds are molecularly isostructural but crystallize differently is mildly suprising but not alarming. Because of the selectively unequal changes in certain bond lengths and not others, the two molecules are not congruent. Thus, the M–M distances differ by ca. 0.20 Å, the various M-ligand distances differ by only 0.10–0.14 Å, and the intraligand distances are essentially unchanged. Also, the different dihedral angles between the DMAB ligand plane and the central CNMMCN plane, 55.0° in the chromium compound and 57.6° in the molybdenum compound, could also make a small difference in the energy of any given packing arrangement.

For $Mo_2(O_2CCH_3)_2(DMAB)_2$ it is interesting to compare the metal–ligand bond lengths with those found in $Mo_2[o\text{-}(CH_2NMe_2)C_6H_4]_4$, containing the ligand **1**, which is isomeric to DMAB, **2**. We noted in that earlier case[3] that the difference between the Mo–C (2.18 Å) and Mo–N (2.43 Å) distances was remarkably large and that this seemed to be due mainly to the fact that the Mo–N bonds were unusually long. The present results confirm these observations. Here we find an Mo–C bond length about 0.04 Å longer than in the previous case, but that can be attributed to the change from an sp^2 carbon atom to an sp^3 carbon atom. In the present case, we find an Mo–N bond length about 0.075 Å shorter than before. Even so, the difference between the Mo–C and Mo–N distances in the present case, 0.138 (5) Å, is quite large; it may be compared with the conventional difference in tetrahedral single-bond radii for C and N, which is 0.07 Å in the *other direction*. Evidently, the amine donor bond is weak compared to the Mo–C bond.

The structure of $Cr_2(O_2CCH_3)_2(DMAB)_2$ invites comparison with that of $Cr_2(O_2CCH_3)(o\text{-}(t\text{-Bu})OC_6H_4)_2$, which is the only other dichromium compound known with a supershort Cr–Cr bond that contains two carboxyl ligands.[6] The two structures are very similar in all the dimensions of the central portions of the molecules. Designating the two molecules A and B in the above order for convenience, we note that the Cr–O(acetate) distances, 1.996 (3) Å in A and 1.996 (2) Å in B, are identical and the Cr–C distances, 2.101 (3) Å in A and 2.064 (3) Å in B, differ by an amount that is about equal to the difference in covalent radii for sp^3 and sp^2 carbon atoms. The Cr–Cr distance in B, 1.862 (1) Å, is scarcely different from that found here for A, viz., 1.870 (1) Å. We have here another example of the fact that the retention of as many as two carboxylate ligands is not incompatible with the existence of a supershort Cr–Cr bond. It is also interesting that for A, even more than for B, the axial positions do not appear to be so severely hindered by the bridging ligands that coordination of the THF molecules available in the preparation is sterically impossible. Instead, the indication seems to be that the $Cr_2(O_2CCH_3)_2(DMAB)_2$ molecule simply has insufficient affinity for axial ligands to attract and hold the available THF molecules.

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Registry No. 1, 79803-01-3; 2, 79803-02-4; $Cr_2(O_2CCH_3)_4$, 15020-15-2; $Mo_2(O_2CCH_3)_4$, 14221-06-8.

Supplementary Material Available: Tables of structure factors for both compounds and tables of thermal parameters and positions of nonrefined hydrogen atoms (16 pages). Ordering information is given on any current masthead page.

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