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Mo_2(β-diketonate)$_4$ Complexes. Preparations, Properties, and Solid-State and Molecular Structure of Tetrakis(2,2,6,6-tetramethyl-3,5-heptanedionato)dimolybdenum

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The β-diketonates of dimolybdenum $Mo_2(OCR^2CR^1CR^2O)_4$ (R^1 = H, R^2 = Me; $R^1 = R^2$ = Me; R^1 = H, $R^2 = (CH_2)_6CH_3$; R^1 = H, R^2 = *t*-Bu) have been prepared from the reaction between Mo_2(O-*i*-Pr)$_4$(*i*-PrOH)$_4$ and the appropriate β-diketone (4 equiv) in pentane at −18 °C. The compounds are dark pink or red, hydrocarbon-soluble, air-sensitive crystalline solids at room temperature. The compound where R^1 = H and R^2 = *t*-Bu has been characterized by single-crystal X-ray crystallography. Crystal data at −169 °C: a = 10.397 (1) Å, b = 9.985 (1) Å, c = 23.133 (4) Å, β = 94.08 (1)°, Z = 2, d_{calcd} = 1.28 g cm^{-3}, space group $P2_1/n$. The molecule contains a Mo–Mo quadruple bond, Mo–Mo = 2.1467 (5) Å, and each molybdenum atom is ligated by two chelating β-diketonate ligands with Mo–O = 2.08 (1) Å (average). The central Mo_2O_8 skeleton is eclipsed with Mo–Mo–O = 104 (1)° (average). The Mo chelate rings are also eclipsed in the centrosymmetric molecule. The new compounds have been characterized by NMR, IR, and UV–visible spectroscopy.

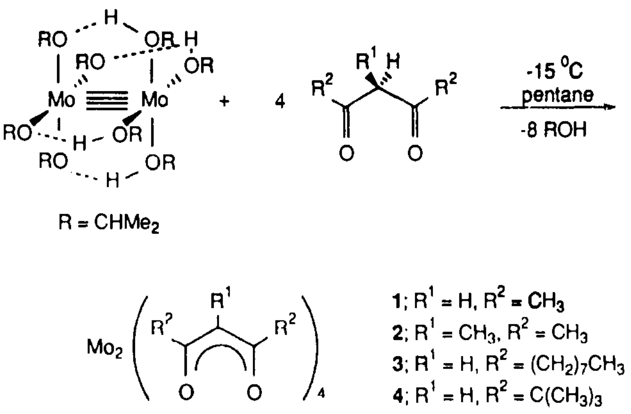
Introduction

Metal diketonates of formula $M(OCR^2CR^1CR^2O)_2$ where M = Cu, Cr, and Pd are planar molecules and tend to stack in the solid state.[1] For long-chain R^2 derivatives, Japanese workers have shown that the Cu complexes show thermotropic discotic mesophases.[2] It seemed to us that the molecular architecture of the Mo_2^{4+} unit ($M\overset{4}{-}M$) might also allow for similar packing and thus related liquid crystalline behavior. Surprisingly, in view of the extensive coordination chemistry of the Mo_2^{4+} unit, compounds of the type Mo_2(β-diketonate)$_4$ were unknown. We report here what we believe to be a general synthetic route to compounds of this formula, together with our characterization of four specific compounds along with the solid-state and molecular structure of the 2,2,6,6-tetramethyl-3,5-heptanedionate derivative.

Results and Discussion

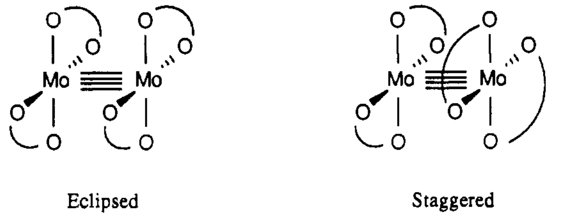
Synthesis. The general synthetic procedure involves the use of the substitutionally labile molecule Mo_2(O-*i*-Pr)$_4$(*i*-PrOH)$_4$[3] as shown in Scheme I.

Scheme I



1; R^1 = H, R^2 = CH_3
2; R^1 = CH_3, R^2 = CH_3
3; R^1 = H, R^2 = $(CH_2)_7CH_3$
4; R^1 = H, R^2 = $C(CH_3)_3$

The acetylacetonate derivative **1** (R^1 = H, R^2 = Me) is insoluble in pentane and precipitate within a few minutes. The more bulky substituents, e.g. R^2 = *t*-Bu and *n*-octyl, impart greater solubility, and the reactions are complete within 2 h. The new compounds range in color from dark pink (**1**) to dark red (**2**, **3**, **4**). They are air-sensitive and diamagnetic. The NMR spectra are simple and reveal only one type of ligand. This does not allow us to distinguish between chelate structures that are eclipsed or staggered as shown in I. Moreover, one cannot rule out the possibility of a quadruply bridged structure involving seven-membered rings, although the formation of a chelate structure of type I would seem more likely on the basis of the known preference for six- relative to seven-membered rings.



I

Solid-State and Molecular Structure. A ball-and-stick drawing of the molecular structure of **4** is shown in Figure 1, and a view down the Mo–Mo bond is given in Figure 2. Each metal is ligated by two chelating β-diketonates. The central Mo_2O_8 skeleton is eclipsed, as are the sets of chelate ligands. The molecule has a

Table I. Selected Bond Distances (Å) and Bond Angles (deg) for Mo_2(*t*-BuC(O)CHC(O)-*t*-Bu)$_4$

	Distances		
Mo(1)–Mo(1)′	2.1467 (5)	O(2)–C(3)	1.272 (3)
Mo(1)–O(2)	2.0949 (17)	O(6)–C(5)	1.281 (3)
Mo(1)–O(6)	2.0882 (17)	O(15)–C(16)	1.276 (3)
Mo(1)–O(15)	2.0783 (17)	O(19)–C(18)	1.271 (3)
Mo(1)–O(19)	2.0844 (17)		
	Angles		
Mo(1)′–Mo(1)–O(2)	104.43 (5)	O(6)–Mo(1)–O(15)	87.81 (7)
Mo(1)′–Mo(1)–O(6)	10[illegible]1 (5)	O(6)–Mo(1)–O(19)	152.05 (7)
Mo(1)′–Mo(1)–O(15)	102.34 (5)	O(15)–Mo(1)–O(19)	86.03 (7)
Mo(1)′–Mo(1)–O(19)	103.74 (5)	Mo(1)–O(2)–C(3)	128.63 (16)
O(2)–Mo(1)–O(6)	85.81 (7)	Mo(1)–O(6)–C(5)	128.64 (16)
O(2)–Mo(1)–O(15)	153.23 (7)	Mo(1)–O(15)–C(16)	129.29 (17)
O(2)–Mo(1)–O(19)	87.53 (7)	Mo(1)–O(19)–C(18)	128.52 (16)

Table II. Summary of Crystal Data for Mo_2(*t*-BuC(O)CHC(O)-*t*-Bu)$_4$

empirical formula	$C_{44}H_{76}Mo_2O_8$
cryst dimens, mm	0.16 × 0.32 × 0.40
space group	$P2_1/n$
temp, °C	−169
a, Å	10.397 (1)
b, Å	9.985 (1)
c, Å	23.133 (4)
β, deg	94.08 (1)
Z (molecules/cell)	2
V, Å^3	2395.56
calcd density, g/cm^3	1.282
wavelength, Å	0.71069
mol wt	924.96
linear abs coeff, cm^{-1}	5.337
no. of reflns with $F > \sigma 3.0(F)$	2852
$R(F)$	0.0244
$R_w(F)$	0.0285

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0020-1669/92/1331-1510$03.00/0

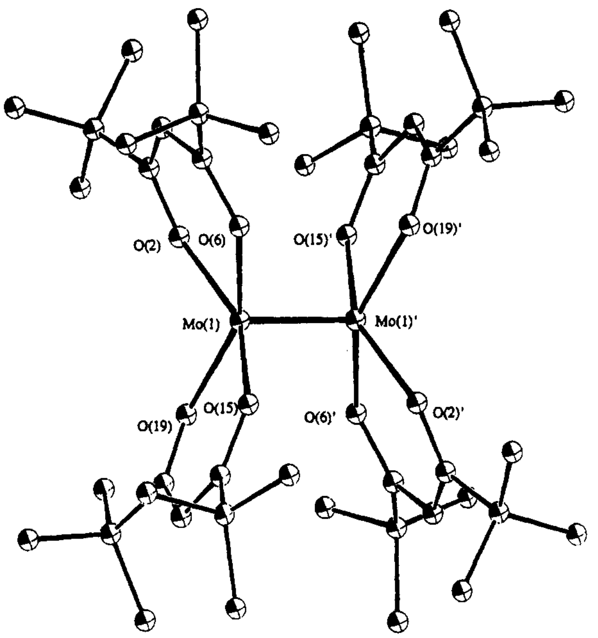

Figure 1. Ball-and-stick drawing of the molecular structure of $Mo_2((CH_3)_3CC(O)CHC(O)C(CH_3)_3)_4$ (**4**).

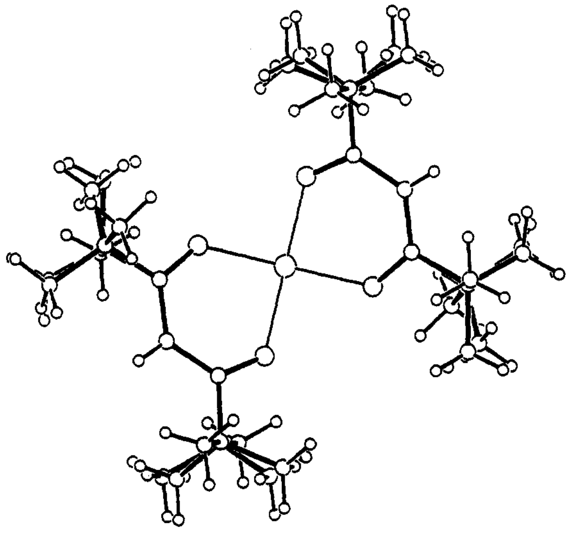

Figure 2. Molecular structure of $Mo_2((CH_3)_3CC(O)CHC(O)C(CH_3)_3)_4$ (**4**) viewed down the Mo–Mo bond.

crystallographically imposed center of inversion.

Selected bond distances and bond angles are given in Table I, and a summary of crystal data is given in Table II. The Mo–Mo distance of 2.1467 (5) Å is in the typical range for Mo–Mo quadruple bonds, and the Mo–Mo–O angle of 104 (1)° is also typical of M_2X_8 structures where there are no ligand bridges; e.g., Mo–Mo–Cl = 105° in $Mo_2Cl_8^{4-}$.[4] The Mo–O distances, 2.08 (1) Å (average), are comparable to those in $Mo_2(O_2CR)_4$ compounds.[5] The presence of the bulky *tert*-butyl groups and the eclipsed nature of the chelates result in the bending outward of the rings away from the Mo_2 center and a slight displacement of the Mo atom from the plane containing the other five atoms in each six-membered ring.

Pertinent to the design of metallomesogens is knowledge of the extended molecular architecture within the lattice. That is to say, we should examine how one dinuclear center is related to its neighbors. In Figure 3 we show a drawing of the unit cell. Each unit cell shares four Mo_2 units with its neighbors such that Z = 2. In Figure 4 we show the unit cells viewed roughly parallel to the *b* axis. This reveals that the extended architecture involves

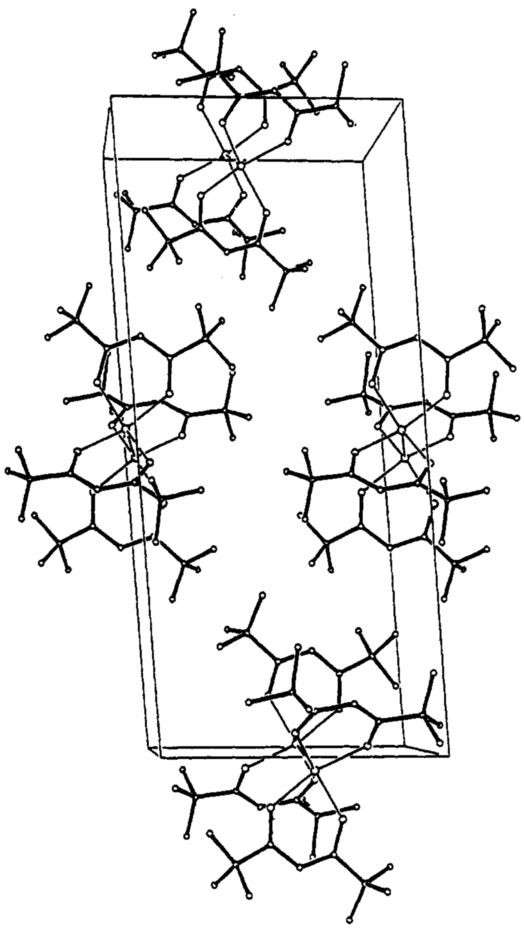

Figure 3. Unit cell of $Mo_2((CH_3)_3CC(O)CHC(O)C(CH_3)_3)_4$.

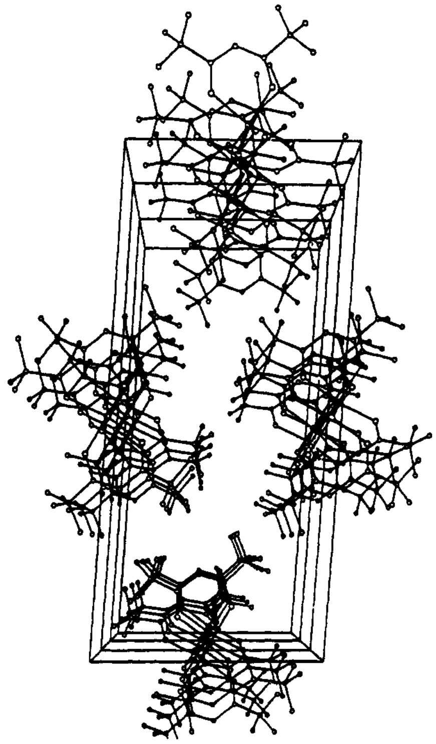

Figure 4. Three unit cells of $Mo_2((CH_3)_3C(O)CHC(O)C(CH_3)_3)_4$ viewed down the *b* axis.

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[4] Brencic, J. V.; Cotton, F. A. *Inorg. Chem.* **1969**, *8*, 7.

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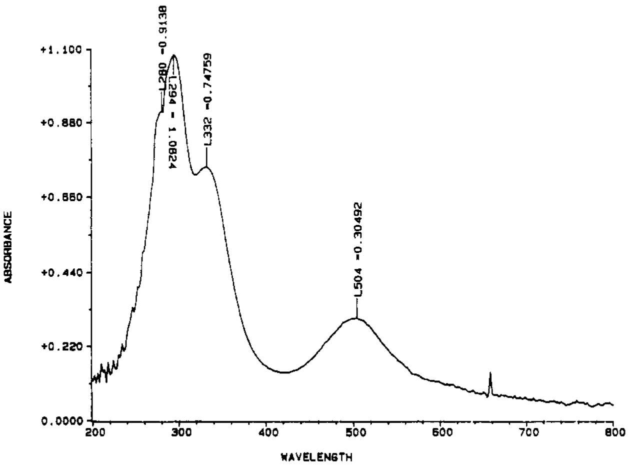


Figure 5. Electronic absorption spectrum of $Mo_2(OC(t\text{-}Bu)CHC(t\text{-}Bu)O)_4$. The "spike" at 660 nm is an instrumental glitch.

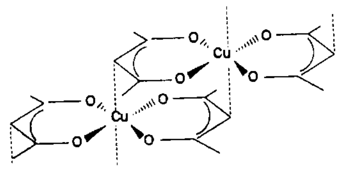
infinite stacks of Mo_2 units. Unlike the case of $[Mo_2(O_2CR)_4]$ compounds that form infinite chains in the solid state as a result of weak intermolecular $Mo_2\cdots O$ bonds,[6] the origin of the stacking in **4** is entirely determined by the ligand–ligand interaction. The shortest Mo-to-Mo nonbonding distance is 8.128 Å, and the closest Mo-to-O nonbonding distance is 6.75 Å in the stack.

Physicochemical Properties. The electronic absorption spectrum of **4** in toluene is shown in Figure 5. There are three intense bonds in the UV region of the spectrum, 35 700 cm^{-1} (ϵ = 17 600 M^{-1} cm^{-1}), 34 000 cm^{-1} (ϵ = 20 800 M^{-1} cm^{-1}), and 30 120 cm^{-1} (ϵ = 14 400 M^{-1} cm^{-1}), and a single broad transition in the visible region, 19 840 cm^{-1} with ϵ = 5900 M^{-1} cm^{-1}. The latter is in the region where we might expect to find a δ–δ^* singlet transition (c.f. δ–δ^* ca. 23 000 cm^{-1} for $Mo_2(O_2CR)_4$ complexes[7]), but the intensity is much too great for a d–d based electronic transition. Therefore we believe that the band at ca. 20 000 cm^{-1} arises from a fully allowed MLCT bond, most probably Mo_2 δ-to-ligand C–O π^*. This presumably masks the $\delta \rightarrow \delta^*$ transition.

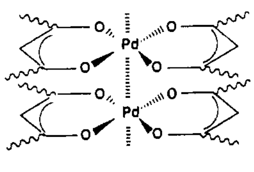
Compound **4** has been examined by cyclic voltammetric studies and found to show no reversible oxidation or reduction. In THF solution, there is an irreversible oxidation at –0.36 V (vs $Cp_2Fe^{0/+}$), which can most reasonably be assigned to removal of an electron from the Mo–Mo δ orbital. This can be contrasted with the reversible oxidation of $Mo_2(O_2C\text{-}t\text{-}Bu)_4$ at –0.04 V (vs $Cp_2Fe^{0/+}$).[8]

Concluding Remarks

This work provides, by the reaction shown in Scheme I, a general synthesis of $Mo_2(\beta\text{-diketonate})_4$ compounds. These compounds are members of the now extensive clan of $M\overset{4}{-}M$ containing compounds,[9] and the arrangement of the four chelating ligands in **4** is as found in the Rh_2 analogues.[10] Whereas for mononuclear $M(\beta\text{-diketonate})_2$ stacking in the solid state is known to arise from either weak $M\cdots M$ interactions (M = Pd^{II} or weak $M\cdots C$ interactions (M = Cr,[1a] Cu[13]) as shown in II and III, we find that the stacking in **4** arises solely from ligand–ligand interactions. This should allow thermotropic discotic mesomorphic behavior by suitable choice of ligands, providing, of course, the compounds are stable with respect to thermal decomposition. Suitable ligands will most likely be substituted porphyrins and phthalocyanines because of the favorable π–π interactions of the rings.



II



III

Experimental Section

Physical Techniques. ^1H NMR and ^{13}C NMR spectra were recorded on a Varian XL300 spectrometer at 300 MHz in dry and oxygen-free benzene-d_6, dimethyl-d_6 sulfoxide, and methanol-d_4.

Infrared spectra were recorded on a Nicolet 510P FT-IR spectrophotometer as KBr pellets in the region covering 4000–400 cm^{-1}.

Ultraviolet and visible absorption spectra were recorded on a Hewlett Packard 8452A diode array spectrophotometer using a 1.00-cm quartz cell. The spectrum was recorded in dry oxygen-free tetrahydrofuran from which a spectrum of the neat solvent in the same cell was subtracted.

Electrochemical measurements were obtained with a PAR 173 potentiostat and 175 programmer along with a Houston Instruments 2000 X-Y recorder. The cyclic voltamogramm was recorded in an airless cell under an N_2 atmosphere in tetrahydrofuran, 2.0 M in tetra-*n*-butylammonium hexafluorophosphate as the supporting electrolyte. The working electrode was a platinum wire encased in a cobalt-tipped electrode. The counter electrode was a platinum-gauze electrode. All potentials reported are relative to the $(C_5H_5)_2Fe/(C_5H_5)_2Fe^+$ couple, which occurs at +0.89 V (ΔE_p = 70 mV) under the conditions specified above.

Elemental analyses were performed by Oneida Research Services, Whitesboro, NY, and all compounds were handled with inert-atmosphere techniques.

The melting points were measured with an Electrochemical melting point apparatus, and the DSC studies were performed on a Du Pont Thermal Analyst 2100.

Syntheses. Reactions were carried out using standard Schlenk techniques with dry, air-free solvents. Acetylacetone (2,4-dimethylpentanedione), 3-methyl-2,4-dimethylpentanedione, and 2,2,6,6-tetramethyl-3,5-heptanedione were purchased from commercial sources. $1,2\text{-}Mo_2(i\text{-}Bu)_2(NMe_2)_4$ and 9,11-nonadecanedione were prepared according to literature procedures.[14,15]

Preparation of $Mo_2(O\text{-}i\text{-}Pr)_4(i\text{-}PrOH)_4$. To a cold (–20 °C) solution of 0.190 g (0.394 mmol) of $1,2\text{-}Mo_2(i\text{-}Bu)_2(NMe_2)_4$ in 5 mL of hexane was added an excess of *i*-PrOH (5 mL). After 30 min of stirring, the reaction mixture was reduced in volume to 5 mL in order to remove dimethylamine, butane, and butene. Another 5 mL of *i*-PrOH was added, and the volume was reduced again. Cooling to –20 °C overnight gave dark purple temperature-sensitive crystals. The crystals were isolated and dried under vacuum. ^1H NMR (benzene-d_6, 20 °C): δ 1.35 (d, CH_3, 24 H), 4.49 (septet, CH, 4 H).

Preparation of $Mo_2(CH_3C(O)CHC(O)CH_3)_4$ (1). To a cold (–20 °C) solution of 0.280 g (0.419 mmol) of $Mo_2(O\text{-}i\text{-}Pr)_4(i\text{-}PrOH)_4$ in pentane was added an excess (0.20 mL, 2.05 mmol) of 2,4-dimethylpentanedione in a pentane solution. The volume was reduced to 5 mL under vacuum, and the mixture was cooled to –20 °C for 48 h. The mixture was filtered to yield 0.110 g (44.7%) of pink solid. Dark pink needles were obtained by recrystallization from 30 mL of THF at –20 °C. The compound melts at 262 °C. ^1H NMR (dimethyl-d_6 sulfoxide, 20 °C): δ 2.17 (s, CH_3, 24 H), 5.62 (s, CH, 4 H). IR (KBr, cm^{-1}): 2964 (w), 1570 (vs), 1524 (vs), 1420 (m), 1273 (s), 1192 (w), 937 (w), 908 (w). Anal. Calcd for $C_{20}H_{28}O_2Mo_2$: C, 40.83; H, 4.80; N, 0.00. Found: C, 40.66; H, 4.67; N, <0.05.

Preparation of $Mo_2(CH_3C(O)C(CH_3)C(O)CH_3)_4$ (2). To a cold (–20 °C) solution of 0.277 g (0.41 mmol) of $Mo_2(O\text{-}i\text{-}Pr)_4(i\text{-}PrOH)_4$ in pentane was added through a syringe an excess of 3-methyl-2,4-dimethylpentanedione (0.19 mL, 1.66 mmol) in a pentane solution. The volume was partially reduced under vacuum, and the reaction mixture was stirred at room temperature for 12 h. The mixture was filtered to yield 0.115 g (43.5%) of dark pink solid. Dark pink needles were recrystallized from 30 mL of EtOH/THF at –20 °C. The compound decomposes at 210 °C. ^1H NMR (methanol-d_4, 20 °C): δ 1.85 (s, CH_3, 12 H), 2.10 (s, CH_3, 6 H), 2.17 (m, THF), 3.72 (m, THF). IR (KBr, cm^{-1}): 3443 (s), 2361

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Table III. Fractional Coordinates and Isotropic Thermal Parameters for Compound **4**

atom	10^4x	10^4y	10^4z	$10B_{iso}$, Å^2
Mo(1)	4818.7 (2)	958.9 (2)	187.5 (1)	9
O(2)	6470 (2)	1347 (2)	734 (1)	13
C(3)	6578 (3)	1415 (3)	1284 (1)	14
C(4)	5612 (3)	1043 (3)	1646 (1)	18
C(5)	4362 (3)	669 (3)	1472 (1)	14
O(6)	3929 (2)	503 (2)	945 (1)	14
C(7)	7858 (3)	1975 (3)	1557 (1)	16
C(8)	8573 (3)	861 (4)	1899 (1)	25
C(9)	7599 (3)	3141 (4)	1964 (2)	28
C(10)	8695 (3)	2474 (4)	1083 (1)	25
C(11)	3336 (3)	540 (3)	1917 (1)	17
C(12)	3915 (4)	−19 (6)	2497 (2)	46
C(13)	2783 (5)	1920 (4)	1983 (2)	61
C(14)	2290 (3)	−418 (4)	1704 (1)	29
O(15)	3005 (2)	1436 (2)	−192 (1)	14
C(16)	2685 (2)	2333 (3)	−568 (1)	13
C(17)	3567 (3)	3127 (3)	−842 (1)	16
C(18)	4906 (2)	3125 (3)	−734 (1)	12
O(19)	5530 (2)	2315 (2)	−396 (1)	12
C(20)	1232 (2)	2590 (3)	−663 (1)	15
C(21)	923 (3)	3743 (4)	−259 (2)	28
C(22)	478 (3)	1358 (3)	−494 (1)	21
C(23)	831 (3)	2967 (4)	−1293 (1)	26
C(24)	5722 (3)	4194 (3)	−1020 (1)	15
C(25)	5379 (3)	5581 (3)	−785 (1)	19
C(26)	7157 (3)	3943 (3)	−875 (1)	19
C(27)	5433 (3)	4160 (3)	−1679 (1)	20

(m), 2336 (w), 1663 (w), 1576 (s), 1560 (vs), 1541 (w), 1473 (m), 1458 (m), 1419 (m), 1282 (s), 985 (w), 943 (w).

Preparation of $Mo_2(CH_3(CH_2)_7C(O)CHC(O)(CH_2)_7CH_3)_4$ (3). To a cold (−15 °C) solution of 0.031 g (0.046 mmol) of $Mo_2(O\text{-}i\text{-}Pr)_4(i\text{-}PrOH)_4$ in pentane was added a cold pentane solution containing 4 equiv (0.055 g, 0.18 mmol) of 9,11-nonadecanedione. The volume was reduced under vacuum, and the mixture was slowly warmed to room temperature. The volume was reduced again, and the mixture was left at −20 °C for 24 h. A dark red solid was isolated from the cold (−78 °C) solution and dried under vacuum. The compound melts at 36 °C. ^{1}H NMR (benzene-d_6, 20 °C): δ 0.92 (t, CH_3), 1.25 (m, CH_2), 5.76 (s, CH). IR (KBr, cm^{-1}): 2980 (s), 2912 (w), 2389 (w), 1585 (s), 1540 (s), 1485 (w), 1434 (s).

Preparation of $Mo_2((CH_3)_3CC(O)CHC(O)C(CH_3)_3)_4$ (4). To a cold (−15 °C) solution of 0.134 g (0.2 mmol) of $Mo_2(O\text{-}i\text{-}Pr)_4(i\text{-}PrOH)_4$ in pentane was added an excess (0.17 mL, 0.8 mmol) of 2,2,6,6-tetramethyl-3,5-heptanedione. The reaction mixture was stirred for 12 h at room temperature. The dark red solid that formed was isolated by cannula removal of the solution and dried under vacuum. The compound was dissolved in toluene at 60 °C, and the mixture was slowly cooled down to room temperature to produce large dark red cubes. The compound decomposes at 73 °C. ^{1}H NMR (benzene-d_6, 20 °C): δ 1.38 (s, CH_3, 18 H), 8.35 (s, CH, 1 H). ^{13}C NMR (benzene-d_6): δ 29.3 (CH_3, 6 C), 39.1 (1 C). IR (KBr, cm^{-1}): 2950 (m), 2850 (w), 1595 (s), 1581 (s), 1522 (m). Anal. Calcd for $C_{44}H_{76}Mo_2O_8$: C, 57.13; H, 8.28; N, 0.00. Found: C, 57.33; H, 8.88; N, <0.05.

Single-Crystal X-ray Determination. General operating procedures and listings of programs have been given previously.[16] A summary of crystal data is given in Table II, and a listing of atomic coordinates is given in Table III. A suitable small fragment was cleaved from one of the very large crystals in the sample. Inert-atmosphere handling techniques (dry-nitrogen glovebag) were used. The crystal was transferred to the goniostat, where it was cooled to −169 °C for characterization and data collection. A systematic search of a limited hemisphere of reciprocal space yielded a set of reflections that exhibited monoclinic ($2/m$) symmetry. The systematic extinction of $h0l$ reflections for $h + l = 2n + 1$ and of $0k0$ for $k = 2n + 1$ uniquely identified the space group as $P2_1/n$. This choice was confirmed by the subsequent solution and refinement of the structure. Data collection was undertaken as detailed in Table II. Unit cell dimensions were determined using 50 reflections having 2θ values between 23 and 34°. A total of 4042 reflections (including space group extinctions and standard reflections) were collected within the given range. Following the usual data reduction and averaging of redundant data, a unique set of 3149 reflections was obtained. The R value for the averaging was 0.019 for 599 reflections measured more than once. A plot of the four standard reflections measured every 400 reflections showed no systematic trends. No correction for absorption was carried out.

The structure was solved by the usual combination of direct methods and difference Fourier techniques. The Mo atom was located in the best E map from MULTAN78, and the remaining non-hydrogen atoms were located in a difference map phased with the Mo atom. Following initial refinement, all but four of the hydrogen atoms were located in a difference Fourier map. The full-matrix least-squares refinement was completed using anisotropic thermal parameters on the non-hydrogen atoms and isotropic thermal parameters on the hydrogen atoms. The total number of parameters varied by 397, including the scale factor and an overall isotropic extinction parameter. The final $R(F)$ was 0.024; $R_w(F)$ was 0.029.

The final difference map was essentially featureless, the largest peak being 0.50 e/Å^3 in the immediate vicinity of the Mo atom.

The molecule possesses a crystallographic center of symmetry. Atoms related by the center of inversion are labeled with primes in the tables and figures.

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Registry No. **1**, 88589-09-7; **2**, 139428-44-7; **3**, 139428-45-8; **4**, 139428-46-9; $Mo_2(O\text{-}i\text{-}Pr)_4(i\text{-}PrOH)_4$, 88589-06-4; 1,2-$Mo_2(i\text{-}Bu)_2(NMe_2)_4$, 78274-35-8; Mo, 7439-98-7.

Supplementary Material Available: A table of anisotropic thermal parameters, complete listings of bond distances and angles, and VERSORT drawings and stereoviews (9 pages); a listing of F_o and F_c values (7 pages). Ordering information is given on any current masthead page.

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(16) Chisholm, M. H.; Folting, K.; Huffman, J. C.; Kirkpatric, C. C. *Inorg. Chem.* **1984**, *23*, 1021.