complex is closely similar to that reported for $FeRu_2(\mu\text{-}Cl)_2(CO)_8(PR_3)_2$.[32]

Interestingly, abstraction of the gold atom can be also realized upon nucleophilic attack: simple addition of tetraethylammonium chloride at ambiant temperature is sufficient to induce degradation of the mixed-metal cluster, yielding a mixture of anionic and neutral complexes among which we were able to again isolate $Ru_3(\mu\text{-}Cl)_2(CO)_8(PPh_3)_2$.[33]

While a number of hydrido cluster complexes have now their gold analogue,[2–16] it should be of interest to know whether a gold–phosphine group can be designed to stabilize complexes for which the corresponding postulated hydrido derivative is unstable. Such studies are currently under investigation in this laboratory.

Registry No. $Ru_3(\mu\text{-}AuPPh_3)(\mu\text{-}Cl)(CO)_{10}$, 88181-31-1; $Ru_3(\mu\text{-}Cl)_2(CO)_8(PPh_3)_2$, 88181-32-2; $Ru_3(CO)_{12}$, 15243-33-1; $AuPPh_3Cl$, 14243-64-2; Au, 7440-57-5; Ru, 7440-18-8.

Supplementary Material Available: Anisotropic thermal parameters for independent atoms (Table S1), rigid-group parameters (Table S2), root-mean-square amplitudes of vibration (Table S3), and a complete listing of observed and calculated structure factor amplitudes (20 pages). Ordering information is given on any current masthead page.

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Contribution from the Department of Chemistry and Molecular Structure Center,
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The Molybdenum–Molybdenum Triple Bond. 13.[1] Preparations and Characterization of Bis(β-diketonato)tetraalkoxydimolybdenum and -ditungsten Compounds

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Dinuclear tungsten and molybdenum alkoxides of formula $M_2(OR)_6$ ($M{\equiv}M$) react in hydrocarbon solvents at room temperature with β-diketones, $R'COCH_2COR''$, to give mixed alkoxide-β-diketonate complexes of formula $M_2(OR)_4(R'COCHCOR'')_2$. Various combinations of R = *t*-Bu, *i*-Pr, and CH_2-*t*-Bu and R′, R″ = Me, *t*-Bu, and Ph have been made in order to elucidate structures and dynamic solution behavior of this class of compounds. The molecular structure of $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2$, determined from a single-crystal X-ray diffraction study, provides the basis for a discussion of the above. There are unbridged $Mo{\equiv}Mo$ bonds united by four ligated metal atoms. The Mo—O bonds, two to OR ligands and two to the didentate acac ligand, lie roughly in a plane. In solution, there is rapid rotation about the $M{\equiv}M$ bonds. From variable-temperature NMR studies of compounds with R′ = Me and R″ = Ph, the bidentate nature of the β-diketonate ligand is established. Only at +110 °C for M = Mo is there evidence for rapid reversible chelate $\rightleftharpoons$ monodentate behavior for the β-diketonate ligands. Crystal data for $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2$ at −143 °C: $a = 14.008$ (4) Å, $b = 11.462$ (3) Å, $c = 11.497$ (3) Å, $\alpha = 87.84$ (1)°, $\beta = 92.94$ (1)°, $\gamma = 88.82$ (1)°, $Z = 2$, $d_{calcd} = 1.332$ g cm^{-3} in space group $P\bar{1}$.

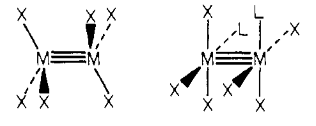
Introduction

The compound $M_2(OR)_6$, where M = Mo[2] and W[3] and R = *t*-Bu, *i*-Pr, and CH_2-*t*-Bu, are coordinatively unsaturated and provide good starting materials for the exploration of dinuclear molybdenum and tungsten chemistry.[4] They react reversibly with neutral donor ligands, L, such as amines or tertiary phosphines according to eq 1. The position of

$$M_2(OR)_6 + 2L \rightleftharpoons M_2(OR)_6L_2 \quad K \qquad (1)$$

equilibrium is sensitive to the steric constraints imposed by R and L, and for related compounds $K_W > K_{Mo}$. Indeed the compounds $W_2(OR)_6$, where R = *i*-Pr and CH_2-*t*-Bu, are not known in the absence of coordinating ligands (L = $HNMe_2$, py, or PMe_3) though UV–visible spectra recorded at dilute concentrations (ca. 10^{-4} M) support their free existence according to (1).[4–6]

In reaction 1, ethane-like dimers (I) are converted to compounds where metal atoms are each coordinated to four ligand atoms and are united by unbridged M–M triple bonds (II). The four σ bonds formed to each metal atom in II lie roughly in a plane, and the conformation of the dinuclear species reflects the interactions of the ligands across the Mo–Mo triple bonds. In general, steric repulsive interactions favor staggered conformations, though hydrogen bonding (e.g. L = $HNMe_2$, R = *i*-Pr, and M = W) may cause an eclipsed conformation.[4,5]



I II

X = OR

The M–M triple bond of configuration $\sigma^2\pi^4$ provides a reservoir of electrons for oxidative-addition reactions[7–9] and also for reactions with π-acid ligands.[4] $M_2(OR)_6$ compounds have been shown to react with CO,[10,11] NO,[12,13] and alkyl and aryl isocyanides[14] to give products in which the $M{\equiv}M$ bond has been cleaved. Similarly, $W_2(O\text{-}t\text{-}Bu)_6$ has been found to

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Table I. Some Characterization Data for $M_2(OR)_4(R'COCHCOR'')_2$ Compounds

		anal., %				
		calcd		found		
compd	color	C	H	C	H	IR ν(C=O), cm^{-1}
$Mo_2(OCH_2$-*t*-Bu$)_4$(acac$)_2$	red	48.77	7.93	48.80	7.53	1595, 1520
Mo_2(O-*i*-Pr$)_4$[PhC(O)CHC(O)Me$]_2$	red	51.20	6.19	51.23	5.99	1595, 1565, 1520
Mo_2(O-*t*-Bu$)_4$[*t*-BuC(O)CHC(O)-*t*-Bu$]_2$	red	53.63	8.78	52.68	7.86	1580, 1558, 1529
$W_2(OCH_2$-*t*-Bu$)_4$(acac$)_2$	black	39.39	6.40	39.56	6.29	1576, 1530
W_2(O-*i*-Pr$)_4$(acac$)_2$	red	32.93	5.29	32.74	5.23	1585, 1570, 1530
W_2(O-*t*-Bu$)_4$[*t*-BuC(O)CHC(O)-*t*-Bu$]_2$	red	44.45	7.28	43.97	5.06	1570, 1545, 1522
W_2(O-*t*-Bu$)_4$[PhC(O)CHC(O)Me$]_2$	purple	44.0	5.55	43.9	5.39	1580, 1560, 1522

Table II. Fractional Coordinates ($\times 10^4$) for the $Mo_2(OCH_2$-*t*-Bu$)_4$(MeCOCHCOMe$)_2$ Molecule

atom	*x*	*y*	*z*
Mo(1)	1540.9 (2)	1462.8 (3)	1076.0 (3)
Mo(2)	3104.5 (2)	1207.5 (3)	1535.7 (3)
O(3)	1510 (2)	611 (2)	−526 (2)
C(4)	1243 (3)	−399 (4)	−836 (4)
C(5)	906 (3)	−1251 (4)	−76 (4)
C(6)	835 (3)	−1102 (3)	1108 (4)
O(7)	1053 (2)	−159 (2)	1605 (2)
C(8)	1310 (3)	−625 (4)	−2102 (4)
C(9)	471 (3)	−2044 (4)	1878 (4)
O(10)	1086 (2)	2062 (2)	2472 (2)
C(11)	1528 (3)	2512 (4)	3496 (4)
C(12)	824 (3)	2635 (4)	4453 (4)
C(13)	−15 (4)	3426 (5)	4072 (4)
C(14)	458 (4)	1423 (4)	4797 (4)
C(15)	1369 (4)	3125 (5)	5503 (4)
O(16)	1470 (2)	2840 (2)	117 (2)
C(17)	2060 (3)	3450 (4)	−657 (4)
C(18)	1736 (3)	4728 (3)	−847 (4)
C(19)	701 (3)	4824 (4)	−1329 (4)
C(20)	1831 (3)	5323 (4)	316 (4)
C(21)	2383 (3)	5297 (4)	−1719 (4)
O(22)	3262 (2)	−468 (2)	856 (2)
C(23)	3562 (3)	−835 (4)	−96 (4)
C(24)	3887 (3)	−110 (4)	−969 (4)
C(25)	3955 (3)	1085 (4)	−903 (4)
O(26)	3731 (2)	1636 (2)	−5 (2)
C(27)	3540 (4)	−2124 (4)	−227 (5)
C(28)	4311 (4)	1826 (5)	−1876 (4)
O(29)	3332 (2)	2751 (2)	2064 (2)
C(30)	4213 (3)	2943 (4)	2700 (4)
C(31)	4450 (3)	4237 (4)	2683 (4)
C(32)	3646 (4)	4941 (4)	3173 (4)
C(33)	4609 (3)	4648 (4)	1437 (4)
C(34)	5367 (3)	4354 (4)	3447 (4)
O(35)	3168 (2)	371 (2)	2985 (2)
C(36)	2647 (3)	−523 (4)	3534 (4)
C(37)	3163 (3)	−963 (4)	4678 (4)
C(38)	3258 (4)	19 (5)	5510 (4)
C(39)	4142 (3)	−1453 (4)	4439 (4)
C(40)	2545 (3)	−1919 (5)	5204 (4)

Table III. Selected Bond Distances (Å) for the $Mo_2(OCH_2$-*t*-Bu$)_4$(MeCOCHCOMe$)_2$ Molecule

A	B	dist	A	B	dist
Mo(1)	Mo(2)	2.237 (1)	O(22)	C(23)	1.275 (5)
Mo(1)	O(3)	2.117 (3)	O(26)	C(25)	1.281 (5)
Mo(1)	O(7)	2.074 (3)	O(29)	C(30)	1.427 (5)
Mo(1)	O(10)	1.904 (3)	O(35)	C(36)	1.418 (5)
Mo(1)	O(16)	1.890 (3)	C(4)	C(5)	1.392 (6)
Mo(2)	O(22)	2.112 (3)	C(4)	C(8)	1.496 (6)
Mo(2)	O(26)	2.064 (3)	C(5)	C(6)	1.386 (6)
Mo(2)	O(29)	1.919 (3)	C(6)	C(9)	1.485 (6)
Mo(2)	O(35)	1.888 (3)	C(23)	C(24)	1.380 (6)
O(3)	C(4)	1.281 (5)	C(23)	C(27)	1.491 (6)
O(7)	C(6)	1.278 (5)	C(24)	C(25)	1.379 (6)
O(10)	C(11)	1.422 (5)	C(25)	C(28)	1.491 (6)
O(16)	C(17)	1.419 (5)	C	C	1.521 (1)[a]

[a] Averaged for *t*-Bu groups.

react with certain alkynes and nitriles to give metathesis products $(t\text{-BuO})_3W{\equiv}CR$ and $(t\text{-BuO})_3W{\equiv}N$.[15] In the presence of donor ligands such as pyridine, a number of adducts of formula $M_2(OR)_6L_2(\mu\text{-}X)$ have been isolated (X = CO,[16] R'C≡CR' where R' = H or Me[17]).

As part of a continuing program aimed at developing the coordination chemistry of compounds containing the central $(M{\equiv}M)^{6+}$ moiety (M = Mo, W), we have prepared several mixed β-diketonate–alkoxide complexes of formula $M_2(OR)_4(R'COCHCOR'')_2$. We describe here our syntheses and characterization of these compounds, and in the following paper,[14] we evaluate their reactivity toward the aforementioned π-acceptor ligands.

Results and Discussion

Preparations. Addition of β-diketones to hydrocarbon solutions of $M_2(OR)_6$ compounds or their pyridine adducts (M = W) leads to the rapid stoichiometric reaction at room temperature shown in eq 2.

$$M_2(OR)_6 + 2R'COCH_2COR'' \rightarrow M_2(OR)_4(R'COCHCOR'')_2 + 2ROH \quad (2)$$

Even in the presence of excess β-diketones (R', R'' = alkyl or phenyl), substitution is limited to two alkoxy groups under these mild conditions. Such partial substitution is typical of the reactions of mononuclear alkoxides.[18] The new compounds are red or purple, air-sensitive crystalline solids. They are soluble in hydrocarbon solvents and appear indefinitely stable when stored under a nitrogen atmosphere at ambient temperatures. Our choice of various R, R', and R'' groups is taken to be representative of the possibilities and is not exhaustive. It is believed to provide a sufficient basis for elucidation of structure, dynamic solution behavior, and reactivity toward π acids of this new class of compounds. Analytical and other characterization data for the new compounds are given in Table I. Further data (IR and NMR) are given in the Experimental Section.

Solid-State and Molecular Structure of $Mo_2(OCH_2$-*t*-Bu$)_4$(MeCOCHCOMe$)_2$. Fractional coordinates are given in Table II; selected bond distances and angles are given in Tables III and IV, respectively. An ORTEP view of the molecule giving the atomic numbering scheme and looking down the Mo–Mo bond is given in Figure 1, and a view of the molecule perpendicular to the Mo–Mo bond is given in Figure 2.

The molecule has virtual C_2 symmetry and confirms what could now be "reasonably expected" from our knowledge of the coordination chemistry of $(M{\equiv}M)^{6+}$-containing com-

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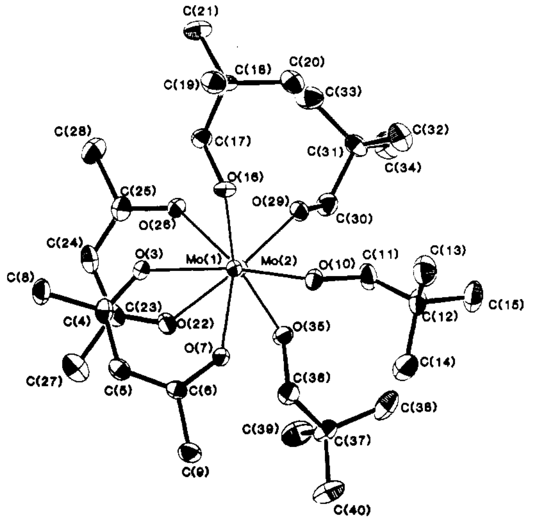


Figure 1. ORTEP diagram of the $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2$ molecule viewed down the Mo–Mo bond and giving the atomic numbering scheme used in the tables.

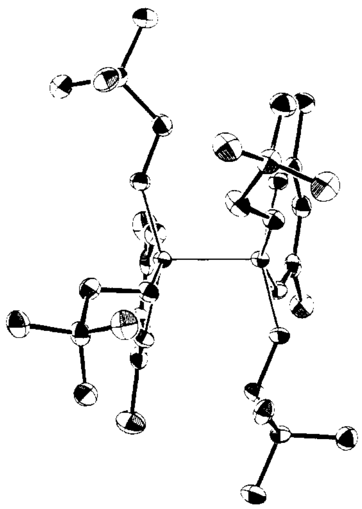


Figure 2. ORTEP diagram of the $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2$ molecule viewed perpendicular to the Mo–Mo bond.

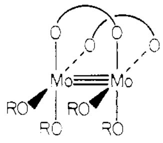
Table IV. Selected Bond Angles (deg) for the $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2$ Molecule

A	B	C	angle
Mo(2)	Mo(1)	O(3)	97.5 (1)
Mo(2)	Mo(1)	O(7)	100.0 (1)
Mo(2)	Mo(1)	O(10)	101.9 (1)
Mo(2)	Mo(1)	O(16)	104.0 (1)
O(3)	Mo(1)	O(7)	79.7 (1)
O(3)	Mo(1)	O(10)	158.6 (1)
O(3)	Mo(1)	O(16)	84.1 (1)
O(7)	Mo(1)	O(10)	88.1 (1)
O(7)	Mo(1)	O(16)	152.6 (1)
O(10)	Mo(1)	O(16)	99.7 (1)
Mo(1)	Mo(2)	O(22)	97.2 (1)
Mo(1)	Mo(2)	O(26)	103.3 (1)
Mo(1)	Mo(2)	O(29)	97.1 (1)
Mo(1)	Mo(2)	O(35)	104.9 (1)
O(22)	Mo(2)	O(26)	79.8 (1)
O(22)	Mo(2)	O(29)	164.0 (1)
O(22)	Mo(2)	O(35)	83.6 (1)
O(26)	Mo(2)	O(29)	90.0 (1)
O(26)	Mo(2)	O(35)	148.8 (1)
O(29)	Mo(2)	O(35)	99.5 (1)
Mo(1)	O(3)	C(4)	133.6 (3)
Mo(1)	O(7)	C(6)	135.9 (3)
Mo(1)	O(10)	C(11)	134.6 (3)
Mo(1)	O(16)	C(17)	137.8 (2)
Mo(2)	O(22)	C(23)	133.6 (3)
Mo(2)	O(26)	C(25)	135.5 (3)
Mo(2)	O(29)	C(30)	117.8 (2)
Mo(2)	O(35)	C(36)	136.9 (2)
O(3)	C(4)	C(5)	124.0 (4)
O(3)	C(4)	C(8)	115.5 (4)
C(5)	C(4)	C(8)	120.5 (4)
C(4)	C(5)	C(6)	123.4 (4)
O(7)	C(6)	C(5)	123.3 (4)
O(7)	C(6)	C(9)	115.6 (4)
C(5)	C(6)	C(9)	121.1 (4)
O(10)	C(11)	C(12)	111.7 (4)
C(11)	C(12)	C(13)	112.0 (4)
O(22)	C(23)	C(24)	123.6 (4)
O(22)	C(23)	C(27)	115.7 (4)
C(24)	C(23)	C(27)	120.8 (4)
C(23)	C(24)	C(25)	124.4 (4)
O(26)	C(25)	C(24)	122.8 (4)
O(26)	C(25)	C(28)	115.2 (4)
C(24)	C(25)	C(28)	122.0 (4)
O(29)	C(30)	C(31)	111.4 (3)
O(35)	C(36)	C(37)	110.9 (3)

pounds.[19] (1) There is an unbridged Mo≡Mo bond of length 2.237 (1) Å, which is typical of Mo–Mo distances in $Mo_2(OR)_6L_2$ compounds;[4] cf. Mo–Mo = 2.242 (1) Å in $Mo_2(OSiMe_3)_6(HNMe_2)_2$.[20] (2) Each molybdenum atom is coordinated to four ligands, which lie roughly in a plane. (3) The nearly perfectly staggered conformation of the Mo_2O_8 moiety (Figure 1) may be understood in terms of the minimization of steric repulsive interactions. The Mo–Mo–O angles span a range 97–104°, reflecting little internal crowding of the molecule. (4) The Mo–O(acac) distances, 2.08 Å (averaged), are what is anticipated for Mo–O single bonds in $(M{\equiv}M)^{6+}$-containing compounds.[4] The Mo–O(OR) distances, 1.90 Å (averaged), are significantly shorter, indicative of RO→Mo π bonding.[4] This must involve the one in-plane molybdenum atomic orbital (d_{xy}) not used in forming Mo–O σ bonds (s, p_x, p_y, $d_{x^2-y^2}$). (5) The presence of bidentate acac ligands is expected, on the basis of the desire of the metal atoms to become four-ligated (eq 1). That the acac ligand behaves as a chelate to each metal atom and does not bridge the Mo–Mo bond is understandable in terms of the preference for the formation of six- rather than seven-membered rings. Only bidentate ligands such as carboxylates or triazines have a marked preference for bridging the M–M bond, since five-membered rings are so produced and these are more stable than four-membered rings.[21]

Finally, we note that the C–O and C–C distances within the acac ring are typical of those seen in related compounds; e.g. C–O = 1.28 (1) Å and C–C = 1.38 (2) Å in $MoO_2(PhCOCHCOPh)_2$.[21,23]

NMR Studies. The ^1H NMR spectrum of $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2$ recorded in toluene-d_8 at +16 °C and 220 MHz is shown in Figure 3. The appearance of only one acac methyl resonance and only one type of OR ligand implies either that some dynamic process is occurring or that the structure in solution is cis bridged as depicted in III.



III

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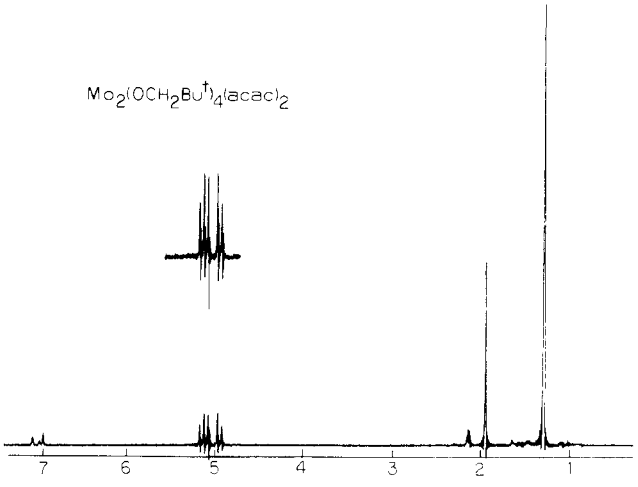
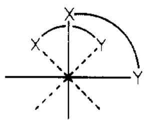


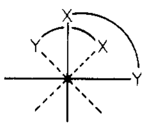
Figure 3. ^{1}H NMR spectrum of $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(MeCOCHCOMe)_2$ recorded in toluene-d_8 at +16 °C and 220 MHz. The β-diketonate methyne signal is flanked by the AB quartet signals of the methylene protons of the neopentoxide ligands at ca. 5 ppm.

Although structures of type III are seen for $Mo_2(OR)_4(O_2CX)_2$ compounds, where X = OR[24] or Ph,[8] we do not believe that the seven-membered ring would be preferred over the six-membered chelate ring found in the solid-state structure. We propose that the fortuitously simple spectrum results from rapid rotation about the Mo$\equiv$Mo bond.[25] Even at low temperatures, −80 °C, ^{1}H and ^{13}C NMR spectra are consistent with rapid rotation about the Mo$\equiv$Mo bond. This is also true when bulky alkyl substituents are present, as in $W_2(O\text{-}t\text{-}Bu)_4(t\text{-}BuCOCHCO\text{-}t\text{-}Bu)_2$. Apparently steric factors do not impose a sufficient barrier to restrict rotation on the NMR time scale. The β-diketonate ligands are judged to be bidentate in solution from solution IR spectra that show $\nu(\mathrm{C}\overset{\cdots}{-}\mathrm{O})$ at ca. 1590 cm^{-1}, essentially the same as found in the Nujol mull spectra. Moreover, we discount a rapid reversible Mo–O(acac) bond cleavage (bidentate $\rightleftharpoons$ monodentate) from studies of the solution behavior of $M_2(O\text{-}i\text{-}Pr)_4(PhCOCHCOMe)_2$ described below.

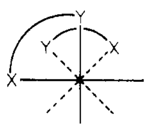
On the basis of considerations of the molecular structure of $Mo_2(OCH_2\text{-}t\text{-}Bu)_4(acac)_2$, an unsymmetrically substituted β-diketone would be expected to adopt one of three structures shown in IVA–C (other rotamers are also possible). Note in



IVA



IVB



IVC

IVA–C, the two alkoxy ligands at each molybdenum are different: one is trans to X; the other trans to Y. Rotations about the M$\equiv$M bond interconvert IVB and IVC but do not interconvert IVB or IVC with IVA.

The ^{1}H NMR spectra of $Mo_2(O\text{-}i\text{-}Pr)_4(PhCOCHCOMe)_2$ in toluene-d_8 from −80 to +60 °C show the presence of two isomers in roughly a 3:2 concentration ratio. Each isomer shows two types of OR ligands in the ratio 1:1. These observations are entirely consistent with the presence of IVA and rapidly interconverting IVB $\rightleftharpoons$ IVC. When the temperature is raised above 60 °C, the resonances begin to broaden and then sharpen until at +110 °C only one isopropoxy group and one type of β-diketonate ligand are seen. This high-temperature process requires OR group site exchange *and* interconversion of the two arrangements of the β-diketonate ligands. The most plausible interpretation of the high-temperature spectrum is that Mo–O(acac) bond breaking becomes rapid and reversible on the NMR time scale. The bond rupture is evidently of the bidentate $\rightleftharpoons$ monodentate type, commonly observed for metal chelate complexes,[26] and does not involve complete dissociation of the β-diketonate ligand since no exchange is observed with free β-diketone ligands in solution, even over prolonged periods.

Similar solution behavior is observed for the related tungsten compound $W_2(O\text{-}t\text{-}Bu)_4(PhCOCHCOMe)_2$ with the following important differences. At temperatures above +90 °C in toluene-d_8, thermal decomposition sets in, though it is still possible to observe, at +110 °C, the resonances ascribed to the NMR-distinct isomers IVA and IVB $\rightleftharpoons$ IVC. These differences are in keeping with expectations based on the known thermal stability and ligand binding of $M_2(OR)_6$ compounds. (1) $Mo_2(OR)_6$[3] compounds may be sublimed and are thermally stable to temperatures $\geq$120 °C, whereas $W_2(OR)_6$ compounds[4] cannot be sublimed and decompose above 80 °C. (2) Tungsten is found to bind donor ligands more tightly than molybdenum: $K_W > K_{Mo}$ in (1) for equivalent R and L.[4-6] Thus, for a related pair of $M_2(OR)_4(R'COCHCOR'')_2$ compounds, we would expect M–O(acac) bond rupture to occur more readily for molybdenum than for tungsten.

The reader may note that the observed ^{1}H NMR spectra of $M_2(O\text{-}i\text{-}Pr)_4(PhCOCHCOMe)_2$ compounds may also be interpreted in terms of head-to-head and head-to-tail isomers (on the basis of III) that, in the case of molybdenum, interconvert at high temperatures by a reversible Mo–O(acac) bond rupture. This situation was observed for $Mo_2(O\text{-}i\text{-}Pr)_4(2\text{-}O\text{-}6\text{-}MePy)_2$, where 2-O-6-Mepy is the anion derived from deprotonation of 2-hydroxy-6-methylpyridine.[27] In the present instance, however, we believe the six-membered ring chelate structure found in the solid is more likely present in solution.

Concluding Remarks. The reactions between $M_2(OR)_6$ compounds and β-diketones give $M_2(OR)_4(R'COCHCOR'')_2$ compounds that contain four-ligated metal atoms united by an unbridged M$\equiv$M bond. Solution NMR studies indicate that the chelate effect preserves the four-ligated metal atoms. Only at high temperatures for molybdenum is there evidence for rapid reversible bidentate $\rightleftharpoons$ monodentate behavior. At ambient temperatures (20 °C), the concentration of three-ligated metal atoms relative to four-ligated metal atoms must be very small. Recognition of this fact is important in terms of a comparison of the reactivities of $M_2(OR)_6$ and $M_2(OR)_4(R'COCHCOR'')_2$ compounds toward the π-acid ligands CO, RC$\equiv$CR, and RNC presented in the following paper.[14]

Experimental Section

General Procedures. All preparations and sampling operations were carried out under dry and oxygen-free atmospheres with standard Schlenk techniques or a Vacuum Atmospheres Co. Dri-Lab assembly.

^{1}H NMR spectra were recorded in toluene-d_8 as solvent on a Varian HR220 spectrometer. ^{13}C NMR data were recorded in toluene-d_8 on a Nicolet 360 spectrometer. All chemical shifts are recorded in δ relative to Me_4Si.

Infrared spectra were obtained from Nujol mulls between CsI plates or in hexane solutions with KBr cell windows by using a Perkin-Elmer 283 spectrometer.

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Table V. Summary of Crystallographic Data for the $\mathrm{Mo_2(OCH_2\text{-}\mathit{t}\text{-}Bu)_4(MeCOCHCOMe)_2}$ Molecule

formula	$\mathrm{C_{30}H_{58}Mo_2O_8}$
fw	738.66
space group	$P\bar{1}$
a, Å	14.008 (4)
b, Å	11.462 (3)
c, Å	11.497 (3)
α, deg	87.84 (1)
β, deg	92.94 (1)
γ, deg	88.82 (1)
Z	2
V, Å^3	1841.79
d_{calcd}, g/cm^3	1.332
cryst size, mm	0.20 × 0.18 × 0.18
cryst color	orange
radiation	Mo Kα ($\lambda = 0.71069$ Å); graphite monochromator
linear abs coeff, cm^{-1}	7.03
temp, °C	−143
instrument	Picker 4-circle diffractometer locally modified and interfaced
detector aperture	3.0 mm wide × 4.0 mm high; 22.5 cm from crystal
sample to source dist, cm	23.5
takeoff angle, deg	2.0
scan speed, deg/min	4.0
scan width, deg	$2.0 + 0.692 \tan\theta$
bkgd counts, s	3 at each end of scan
2θ range, deg	6–45
data collected	5158 total
unique data	4842
unique data with $F_o > 3\sigma(F_o)$	4177
$R(F)$	0.032
$R_w(F)$	0.033
goodness of fit	0.932
largest Δ/σ	0.05

Chemical analyses were performed by Alfred Bernhardt Microanalytisches Laboratorium, Elbach, West Germany.

Materials. The dimolybdenum and ditungsten hexaalkoxides and/or their amine adducts were prepared as described previously.[2,3,5] All solvents were dried by using standard procedures[28] and stored under nitrogen atmospheres as were the β-diketones ($\mathrm{R'COCH_2COR''}$, where R′ = R″ = Me, *t*-Bu and R′ = Me, R″ = Ph) purchased from Aldrich.

Preparations of $\mathbf{M_2(OR)_4(R'COCHCOR'')_2}$ Compounds. All the new compounds were prepared in similar manners. The $\mathrm{M_2(OR)_6}$ compounds or their amine adducts were allowed to react with the appropriate β-diketone at room temperature for 1–2 h. The solvent was then stripped, and the solids were redissolved and crystallized in a refrigerator at ca. −15 °C. The crystals so formed were collected by filtration and dried in vacuo. On the basis of eq 2, this procedure yielded ≥50% yield based on molybdenum. However, on the basis of reactions carried out in NMR tubes and monitored by ^{1}H NMR spectroscopy, formation of $\mathrm{M_2(OR)_4(R'COCHCOR'')_2}$ compounds is quantitative. The yield based on crystallization is thus limited by solubility factors and mechanical loss in collecting the crystalline products. A typical preparation is given below.

$\mathbf{Mo_2(O\text{-}\mathit{i}\text{-}Pr)_4(PhCOCHCOMe)_2}$. $\mathrm{Mo_2(O\text{-}\mathit{i}\text{-}Pr)_6}$ (0.650 g, 1.19 mmol) was dissolved in pentane (5 mL). A toluene solution of 1-phenyl-1,3-butanedione, $\mathrm{PhCOCH_2COMe}$ (3.0 mL, 0.76 M), was added by syringe. The solution immediately turned from yellow to red. The solution was stirred for 1 h. The solvent was then stripped, and the resultant powder was redissolved in hexane (5 mL) and the solution cooled to −15 °C in the freezer section of a refrigerator for 4 h, yielding red crystals, $\mathrm{Mo_2(O\text{-}\mathit{i}\text{-}Pr)_4(PhCOCHCOMe)_2}$, which were collected by filtration and dried in vacuo. Anal. Calcd (Found): C, 51.20 (51.23); H, 6.19 (5.99).

^{1} NMR data (+23 °C): δ 1.55, 1.72 (overlapping doublets, $J_{\mathrm{HH}} = 7$ Hz), OCH*Me*$_2$; δ 1.97 (s, 6 H), 2.0 (s, 6 H), β-diketonate methyls; δ 5.65 (s, 2 H), β-diketonate methynes δ 5.78, 5.9 (overlapping septets), 6.08 (overlapping septets), OC*H*Me$_2$; δ 7.0–7.2, 7.93 (multiplets), β-diketonate phenyls.

IR data: 2900 s, 1595 m, 1565 m, 1520 m, 1487 w, 1460 s, 1378 s, 1310 w, 1292 w, 1260 w, 1203 w, 1160 w, 1108 s, 1026 w, 977 s, 950 w, 850 m, 835 m, 795 w, 770 w, 765 w, 720 w, 710 m, 687 m, 640 m, 608 m, 600 m, 550 w, 461 w, 441 w, 428 w cm^{-1}.

$\mathbf{M_2(OCH_2\text{-}\mathit{t}\text{-}Bu)_4(MeCOCHCOMe)_2}$. ^{1}H NMR data (+16 °C): δ 1.33 (s, 36 H), *t*-Bu; δ 1.95 (s, 12 H), β-diketonate methyls; δ 5.08 (AB quartet, 8 H), OC*H*$_2$-*t*-Bu; δ 5.10 (s, 2 H), MeCOC*H*COMe.

IR data: 2710 s, 1595 s, 1520 s, 1450 s, 1372 s, 1280 m, 1241 w, 1212 w, 1185 w, 1131 w, 1061 s, 1035 w, 1021 m, 1010 m, 931 w, 901 w, 882 m, 800 w, 790 w, 766 m, 755 m, 722 s, 670 s cm^{-1}.

^{13}C NMR data (+16 °C): δ 25.88, *Me*COCHCO*Me*; δ 26.91, OCH$_2$C*Me*$_3$; δ 34.24, OCH$_2$*C*Me$_3$; δ 85.98, O*C*H$_2$CMe$_3$; δ 98.22, MeCO*C*HCOMe; δ 189.28, Me*C*OCH*C*OMe.

$\mathbf{Mo_2(O\text{-}\mathit{t}\text{-}Bu)_4(\mathit{t}\text{-}BuCOCHCO\text{-}\mathit{t}\text{-}Bu)_2}$. ^{1}H NMR data (+16 °C): δ 1.25 (s, 36 H), 1.57 (s, 36 H), 5.71 (s, 2 H).

IR data: 2900 s, 1580 w, 1558 s, 1529 s, 1460 s, 1375 s, 1352 s, 1241 w, 1225 m, 1175 s, 1148 m, 987 s, 922 s, 893 w, 859 m, 774 m, 768 m, 718 w, 612 m, 599 m, 541 w, 501 w, 488 w cm^{-1}.

$\mathbf{W_2(O\text{-}\mathit{i}\text{-}Pr)_4(MeCOCHCOMe)_2}$. ^{1}H NMR data (+16 °C): δ 1.60 (d, 12 H), 1.80 (d, 12 H, $J_{\mathrm{HH}} = 7$ Hz), OCH*Me*$_2$; δ 1.95 (s, 12 H), *Me*COCHCO*Me*; δ 5.05 (s, 2 H), MeCOC*H*COMe; δ 5.95 (septet, 4 H, $J_{\mathrm{HH}} = 7$ Hz), OC*H*Me$_2$.

IR data: 2900 s, 1585 s, 1570 m, 1530 s, 1470 s, 1380 s, 1370 s, 1331 m, 1289 m, 1214 w, 1185 w, 1162 m, 1130 w, 1120 s, 1102 m, 1015 w, 998 m, 988 s, 975 m, 951 m, 851 m, 839 m, 787 m, 762 w, 720 w, 640 m, 610 m, 602 m, 552 w, 466 w, 444 w cm^{-1}.

$\mathbf{W_2(O\text{-}\mathit{t}\text{-}Bu)_4(PhCOCHCOMe)_2}$. ^{1}H NMR data (+16 °C): δ 1.70 (s, 18 H), 1.74 (s, 18 H), 1.78 (s, 18 H), 1.82 (s, 18 H), OC*Me*$_3$; δ 1.84 (s, 6 H), 2.02 (s, 6 H), PhCOCHCO*Me*; δ 5.60 (s, 2 H), 5.72 (s, 2 H), PhCOC*H*COMe; δ 6.98–7.30, 7.90–8.05 (20 H, multiplets), *Ph*COCHCOMe.

IR data: 2900 s, 1580 m, 1560 w, 1522 m, 1460 s, 1372 s, 1350 m, 1308 w, 1292 w, 1258 m, 1170 s, 1020 m, 990 s, 920 s, 895 w, 785 m, 765 m, 758 w, 718 w, 702 m, 599 w cm^{-1}.

$\mathbf{W_2(O\text{-}\mathit{t}\text{-}Bu)_4(\mathit{t}\text{-}BuCOCHCO\text{-}\mathit{t}\text{-}Bu)_2}$. ^{1}H NMR data (+16 °C): δ 1.40 (s, 36 H), 1.70 (s, 36 H), 5.75 (s, 2 H).

IR data: 2900 s, 1570 m, 1545 m, 1522 s, 1487 w, 1460 s, 1375 s, 1350 m, 1220 m, 1170 s, 1145 m, 985 s, 960 w, 922 s, 892 w, 870 w, 784 w, 770 w, 718 m, 610 m, 590 w, 540 w, 482 w cm^{-1}.

$\mathbf{W_2(OCH_2\text{-}\mathit{t}\text{-}Bu)_4(MeCOCHCOMe)_2}$. ^{1}H NMR data (+16 °C): δ 1.30 (s, 36 H), *t*-Bu; δ 1.88 (s, 12 H), β-diketonate methyls; δ 5.10 (AB quartet, 8 H), OC*H*$_2$-*t*-Bu; δ 5.06 (s, 2 H), MeC(O)C*H*C(O)Me.

IR data: 2900 s, 1576 s, 1530 s, 1470 s, 1375 s, 1388 w, 1215 w, 1065 s, 1020 s, 930 w, 775 m, 750 m, 720 m, 668 s, 555 w, 442 m, 401 w cm^{-1}.

X-ray Structural Determinations. General operating procedures and computational techniques have been described.[29]

Structure of $\mathbf{Mo_2(OCH_2\text{-}\mathit{t}\text{-}Bu)_4(MeCOCHCOMe)_2}$. Crystal and experimental data are given in Table V. The crystals were rather large, and a suitable sample for X-ray diffraction was obtained by cleaving a small, almost equidimensional fragment from a larger crystal. The crystal was transferred to the goniostat and cooled to −143 °C. (The usual temperature for data collection is about −165 °C, but an initial crystal cooled to that temperature fragmented, possibly due to a phase transition; therefore, the higher temperature was chosen.) The crystal was characterized in the usual manner and the data collection proceeded normally.

The structure was solved by means of a Patterson function followed by standard heavy-atom Fourier techniques. Following refinement of all non-H atoms, a difference Fourier synthesis revealed the positions of the H atoms. The structure was refined by full-matrix least squares using anisotropic thermal parameters for all non-H atoms, while the H atoms were refined by using isotropic thermal parameters. The final difference map was essentially featureless. The largest peak was 0.45 e/Å^3.

Acknowledgment. We thank the National Science Foundation and the Wrubel Computing Center for support. A.L.R. is the 1982/1983 Indiana University SOHIO Fellow.

Registry No. $\mathrm{Mo_2(OCH_2\text{-}\mathit{t}\text{-}Bu)_4(acac)_2}$, 88393-48-0; $\mathrm{Mo_2(O\text{-}\mathit{i}\text{-}Pr)_4[PhC(O)CHC(O)Me]_2}$, 88393-49-1; $\mathrm{Mo_2(O\text{-}\mathit{t}\text{-}Bu)_4[\mathit{t}\text{-}BuC(O)CHC(O)\text{-}\mathit{t}\text{-}Bu]_2}$, 88393-50-4; $\mathrm{W_2(OCH_2\text{-}\mathit{t}\text{-}Bu)_4(acac)_2}$, 88393-51-5; $\mathrm{W_2(O\text{-}\mathit{i}\text{-}Pr)_4(acac)_2}$, 88412-21-9; $\mathrm{W_2(O\text{-}\mathit{t}\text{-}Bu)_4[\mathit{t}\text{-}BuC(O)CHC\text{-}}$

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(O)-*t*-Bu]$_2$, 88393-52-6; W_2(O-*t*-Bu)$_4$[PhC(O)CHC(O)Me]$_2$, 88393-53-7; Mo_2(O-*i*-Pr)$_6$, 62521-20-4; Mo, 7439-98-7; W, 7440-33-7.

Supplementary Material Available: Complete listings of atomic positional parameters, anisotropic thermal parameters, bond distances, bond angles, and structure factor amplitudes for $Mo_2(OCH_2$-*t*-Bu)$_4$(MeCOCHCOMe)$_2$ (37 pages). Ordering information is given on any current masthead page. The complete structural report, MSC No. 82080, is available from the Indiana University Library, in microfiche form only.

Notes

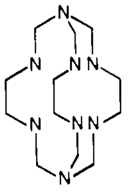
Contribution from the Departments of Chemistry
and Chemistry Education, Seoul National University,
Seoul 151, Korea

Preparation and Molecular Structure of the Nickel(II) Perchlorate Complex of a Hexadentate Macrobicyclic Ligand, 1,3,6,8,10,13,16,19-Octaazabicyclo[6.6.6]eicosane

Myunghyun Paik Suh,* Whanchul Shin,* Dooseop Kim, and Sangsoo Kim

Received December 20, 1982

Some macrocyclic ligands render extraordinary stability to metal complexes against ligand substitution or dissociation by effectively encapsulating the metal ions. Typical examples are the compounds classified as cryptates.[1,2] Condensation of amines with formaldehyde has often been employed for the synthesis of macrocyclic ligands.[3,4] We have isolated several Ni(II) complexes with different ligands (**1**–**3**) by the template condensation of ethylenediamine, formaldehyde, and ammonia.[5] The preparation and the molecular structure of the nickel(II) perchlorate complex of **1** (1,3,6,8,10,13,16,19-octaazabicyclo[6.6.6]eicosane; trivial name sepulchrate), a hexadentate cryptand-like ligand, are reported here. The Ni(II) complexes of **2** and **3** will be published separately.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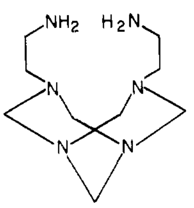
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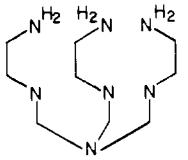
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Experimental Section

Synthesis. The Ni(II) complex of **1**, [Ni(sepulchrate)]$(ClO_4)_2$, was synthesized by refluxing ethylenediamine, formaldehyde, ammonia, and nickel chloride (3:6:2:1 mole ratio) in a 1:1 methanol–water mixture for 48 h, followed by precipitation with lithium perchlorate. The major product of the condensation reaction was the yellow Ni(II) complex of **2** (90% yield), and the second major product isolated was the Ni(II) complex of **3**. The pink title complex was obtained in low yield (<1%) by concentrating the filtrate, followed by fractional recrystallization of the resultant crude precipitates from warm water. Anal. Calcd for $NiC_{12}H_{30}N_8Cl_2O_8$: C, 26.47; H, 5.56; N, 20.61. Found: C, 26.04; H, 5.98; N, 21.08. Crystals of [Ni(**1**)]$(ClO_4)_2$, suitable for X-ray crystallographic work, were obtained by dissolving the pink precipitates in warm water followed by slow evaporation of the solvent.

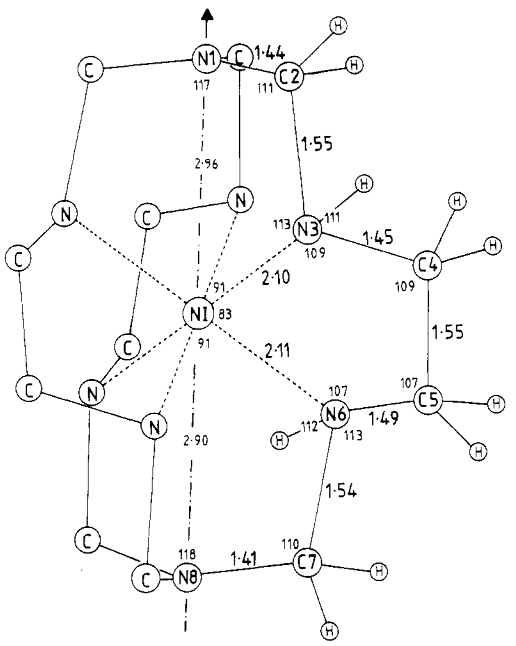

Figure 1. Schematic diagram of [Ni(sepulchrate)]$(ClO_4)_2$ showing the labeling scheme, bond distances (Å), and bond angles (deg). Estimated standard deviations are as follows: Ni–N, 0.01; N–C, C–C, 0.02–0.03; angles, 1–2.

Crystal Data Collection. Data were obtained at room temperature from a roughly spherical crystal of diameter 0.45 mm on a Rigaku AFC diffractometer equipped with Cu Kα radiation (λ = 1.5418 Å) and a graphite monochromator. The unique cell dimension was refined by a least-squares fit of 2θ angles for 15 accurately centered reflections having $30° \leq 2\theta \leq 40°$. Crystal data: $NiC_{12}H_{30}N_8 \cdot 2ClO_4$, mol wt 543.7, cubic space group $P2_13$, a = 12.707 (1) Å, V = 2051.9 (4) Å^3, Z = 4, d_{calcd} = 1.76 g cm^{-3}, d_{measd} = 1.74 g cm^{-3} in CH_3I-cyclohexanol, μ(Cu Kα) = 41.21 cm^{-1}. Intensity data were collected by the ω–2θ scan method over a range of $(1.1 + 0.4 \tan \theta)°$ in ω at a scan rate of 4° min^{-1} and by measuring background counts for 10 s at each end of the scan range. All data in the unique region of reciprocal space ($^1/_{24}$ of the reflecting sphere) were measured within $5° \leq 2\theta \leq 120°$ by keeping l greater than or equal to h and k indices. No decline in the intensities of three periodically remeasured reflections was noted. Of the 532 unique data measured, 497 had $I < 3\sigma(I)$ and were used in the refinement. Background, Lorentz, and polarization corrections were applied.[6] The variations in intensities of reflections near $\chi = 90°$ during ψ scans were less than 5%, and thus no absorption correction was applied.

Structure Determination and Refinement. Systematic absences $h00$ with h odd, $0k0$ with k odd, and $00l$ with l odd limit the space group to either $P2_13$ or $P4_232$. The space group was initially assumed to be $P2_13$ with 12 general positions since there were 4 formula units in the unit cell and both the cation and two anions have the potential for possessing molecular threefold axes that could coincide with

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[4] (a) Peng, S. M.; Goedken, V. L. *Inorg. Chem.* **1978**, *17*, 820. (b) Peng, S. M.; Gordon, G. C.; Goedken, V. L. *Ibid.* **1978**, *17*, 119.

[5] The preliminary results were reported in: (a) Suh, M. P.; Kim, D. S. "Abstracts of Papers", 45th Meeting of the Korean Chemical Society, 1980; p 214. (b) Shin, W.; Kim. S. S.; Suh, M. P. "Abstracts of Papers", Meeting of the American Crystallographic Association, Aug 1982; p C9.

[6] Data collection and data reduction were performed by using the Rigaku-Denki AFC software system for a PDP-8 computer.

0020-1669/84/1323-0618$01.50/0