Synthesis and Spectroscopic Characterization of Organometallic Cluster Macrocycles Containing Functionally Bridged Dicyclopentadienyl Ligands. Crystal Structures of $[Mo_2Fe(\mu_3\text{-}S)(CO)_7][\eta^5\text{-}C_5H_4C(O)CH_2]_2$, $[W_2Fe(\mu_3\text{-}S)(CO)_7]_2\{[\eta^5\text{-}C_5H_4C(O)CH_2]_2\}_2$, and $[Mo_2Fe(\mu_3\text{-}S)(CO)_7][\eta^5\text{-}C_5H_4CH(OH)CH_2]_2$

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The self-assembly cyclization reactions of the diketo-containing carbon chain-bridged dicyclopentadienyl M/Na salts $[NaM(CO)_3]_2[\eta^5\text{-}C_5H_4\ C(O)CH_2]_2$ (**I**, M = Mo, W) with the same chain-bridged dicyclopentadienyl double clusters $[MCoFe(\mu_3\text{-}S)(CO)_8]_2[\eta^5\text{-}C_5H_4C(O)CH_2]_2$ (**II**, M = Mo, W) were studied. While the reaction of **I** (M = Mo) with **II** (M = Mo) gave organometallic macrocycles containing a single and double $[Mo_2Fe(\mu_3\text{-}S)]$ cluster core, $[Mo_2Fe(\mu_3\text{-}S)(CO)_7]_n\{[\eta^5\text{-}C_5H_4C(O)CH_2]_2\}_n$ (**IIIa**, $n = 1$; **IVa**, $n = 2$), **I** (M = W) reacted with **II** (M = W) to afford the macrocycles with a single and double $[W_2Fe(\mu_3\text{-}S)]$ cluster core $[W_2Fe(\mu_3\text{-}S)(CO)_7]_n\{[\eta^5\text{-}C_5H_4C(O)CH_2]_2\}_n$ (**IIIb**, $n = 1$; **IVb**, $n = 2$). Further study on functional transformation reactions of these diketo-containing macrocycles indicated that **IIIa,b** and **IVa,b** could react with $NaBH_4$ to give dihydroxy-containing macrocycles having a single and double $[M_2Fe(\mu_3\text{-}S)]$ cluster core $[M_2Fe(\mu_3\text{-}S)(CO)_7][\eta^5\text{-}C_5H_4CH(OH)CH_2]_2$ (**Va**, M = Mo; **Vb**, M = W) and $[M_2Fe(\mu_3\text{-}S)(CO)_7]_2\{[\eta^5\text{-}C_5H_4CH(OH)CH_2]_2\}_2$ (**VIa**, M = Mo; **VIb**, M = W). The structures of all the new macrocycles **IIIa,b**−**VIa,b** were characterized by elemental analyses and IR and ^1H NMR spectroscopy, whereas those of the representative clusters **IIIa**, **IVb**, and **Va** were unambiguously confirmed by X-ray diffraction techniques.

Introduction

During recent years, macrocyclic compounds have been receiving considerable attention in view of their great importance in theory and practical applications.[1−8] We are interested in synthesis and structural characterization of the macrocycles containing organometallic cluster cores, largely because of such macrocycles being expected to display novel properties and specific features that could not be found in macrocyclic systems without metal cluster cores. Recently, we have reported a series of new types of organometallic macrocycles that contain tetrahedral and butterfly cluster cores linked by ether chain structural units or ether chain-bridged dicyclopentadienyl moieties.[9−12] In this paper, we wish to report another new type of organometallic cluster macrocycles, which contain tetrahedral $M_2Fe(\mu_3\text{-}S)$ (M = Mo, W) cluster cores and diketo- or dihydroxy-containing carbon chain-bridged dicyclopentadienyl ligands, namely, $[M_2Fe(\mu_3\text{-}S)(CO)_7][\eta^5\text{-}C_5H_4C(O)CH_2]_2$ (**IIIa**, M = Mo; **IIIb**, M = W), $[M_2Fe(\mu_3\text{-}S)(CO)_7]_2\{[\eta^5\text{-}C_5H_4C(O)CH_2]_2\}_2$ (**IVa**, M = Mo; **IVb**, M = W), $[M_2Fe(\mu_3\text{-}S)(CO)_7][\eta^5\text{-}C_5H_4CH(OH)CH_2]_2$ (**Va**, M = Mo; **Vb**, M = W), and $[M_2Fe(\mu_3\text{-}S)(CO)_7]_2\{[\eta^5\text{-}C_5H_4CH(OH)CH_2]_2\}_2$ (**VIa**, M = Mo; **VIb**, M = W), which were synthesized by self-assembly cyclization and functional transformation reactions.

Results and Discussion

Synthesis and Characterization of Diketo-Containing Macrocycles IIIa,b and IVa,b. We have

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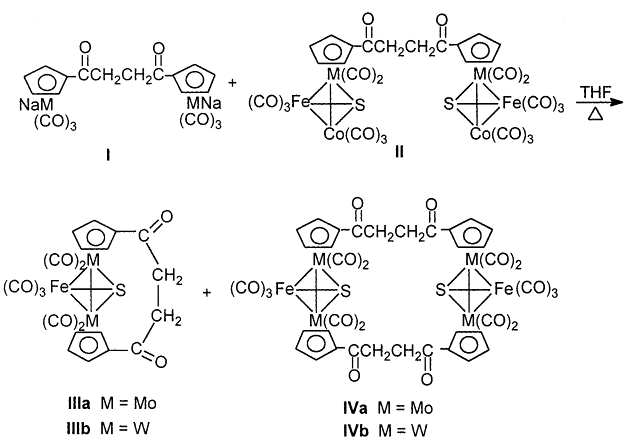
Scheme 1



found that the diketo-containing carbon chain-bridged dicyclopentadienyl M/Na salts (**I**, M = Mo, W), formed from $[\eta^5\text{-}C_5H_4C(O)CH_2]_2Na_2$ and $M(CO)_6$ (M = Mo, W),[13] reacted with the same chain-bridged double clusters $[MCoFe(\mu_3\text{-}S)(CO)_8]_2[\eta^5\text{-}C_5H_4C(O)CH_2]_2$ (**II**, M = Mo, W) in THF at reflux to afford two types of organometallic macrocycles containing a single and double tetrahedral $M_2Fe(\mu_3\text{-}S)$ cluster core $[M_2Fe(\mu_3\text{-}S)(CO)_7][\eta^5\text{-}C_5H_4C(O)CH_2]_2$ (**IIIa**, M = Mo; **IIIb**, M = W) and $[M_2Fe(\mu_3\text{-}S)(CO)_7]_2\{[\eta^5\text{-}C_5H_4C(O)CH_2]_2\}_2$ (**IVa**, M = Mo; **IVb**, M = W), respectively (Scheme 1).

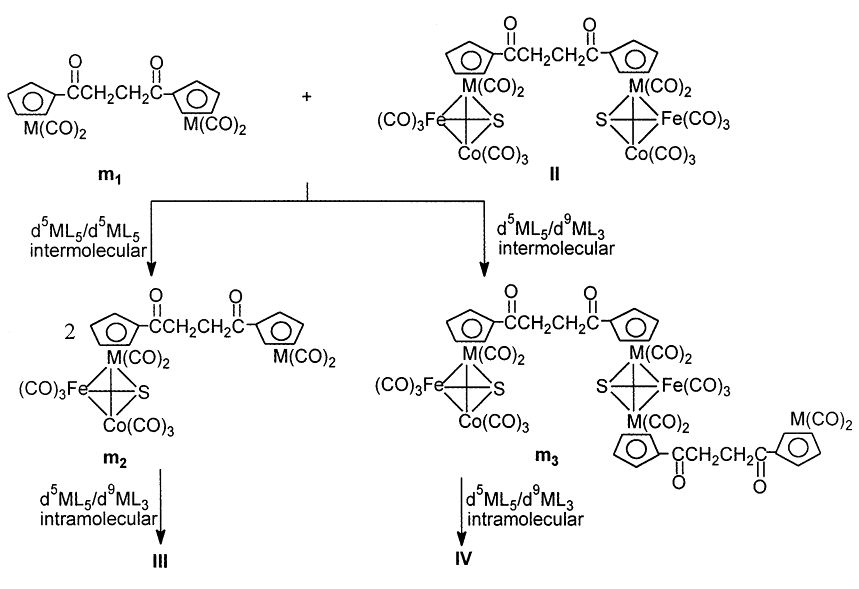
Products **IIIa,b** and **IVa,b** are air-stable brown solids, which were characterized by elemental analysis and IR and ^1H NMR spectroscopy. The IR spectra of **IIIa,b** and **IVa,b** showed several absorption bands in the range 2050−1847 cm^{-1} for their carbonyls attached to transition metals and one absorption band in the region 1661−1684 cm^{-1} for their diketo functional groups. The ^1H NMR spectra of **IIIa,b** and **IVa,b** displayed two sets of signals in the range 5.40−5.81 ppm for their substituted Cp protons, the downfield singlet being assigned to H^2/H^5 close to the diketo chain substituent and the upfield doublet to H^3/H^4 remote from the substituent.[14,15] In addition, the ^1H NMR spectra of **IIIa,b** and **IVa,b** also exhibit one singlet at ca. 3 ppm for their ethylene groups.

The possible pathway for the formation of **IIIa,b** and **IVa,b** is shown in Scheme 2, which is similar to that for the formation of their analogues containing the ether chain-bridged dicyclopentadienyl ligands.[9,11] According to this pathway, the M/Na salts of type **I** can be converted into their decarbonylated intermediates $\mathbf{m_1}$. Then, while these intermediates react further with double clusters of type **II** through intermolecular single isolobal d^5ML_5/d^5ML_5 displacement to give two molecules of intermediates $\mathbf{m_2}$, their reactions with **II** via intermolecular single isolobal d^5ML_5/d^9ML_3 displacement give intermediates $\mathbf{m_3}$. Furthermore, while $\mathbf{m_2}$ undergoes an intramolecular d^5ML_5/d^9ML_3 single isolobal displacement to give single cluster macrocycles of type **III**, the intramolecular single isolobal d^5ML_5/d^9ML_3 displacement of $\mathbf{m_3}$ affords double cluster macrocycles of type **IV**.

It is evident that the successful synthesis of products **IIIa,b** and **IVa,b** has further demonstrated that such a type of self-assembly cyclization reaction based on the principle of isolobal analogy[16] is independent of the nature of the bridged dicyclopentadienyl ligands to produce organometallic cluster macrocycles. In addition, it is worth pointing out that the diketo functionality in such macrocycles may undergo functional transformation reactions to give their derivatives, which cannot be easily prepared by conventional methods (vide infra).

Crystal Structures of IIIa and IVb. To further confirm the structures of **IIIa,b** and **IVa,b**, the X-ray crystal diffraction analyses for **IIIa** and **IVb** were carried out. The molecular structure of **IIIa** is shown in Figure 1, whereas its selected bond lengths and angles are given in Table 1. As seen in Figure 1, **IIIa** is composed of a tetrahedral $Mo_2Fe(\mu_3\text{-}S)$ cluster core, which carries one 1,1′-succinyldicyclopentadienyl ligand coordinated to two Mo atoms, one set of three CO ligands bonded to the Fe atom, and two sets of two CO ligands attached to two Mo atoms, respectively. It is worthy of note that since the five carbon atoms from C(8) to C(12) of the Cp ring and the two atoms of the ketone carbonyl C(13)=O(8), or the two atoms of C(16)=O(9) and those carbon atoms from C(17) to C(21) of the Cp ring, are basically coplanar (the mean deviations are

Scheme 2



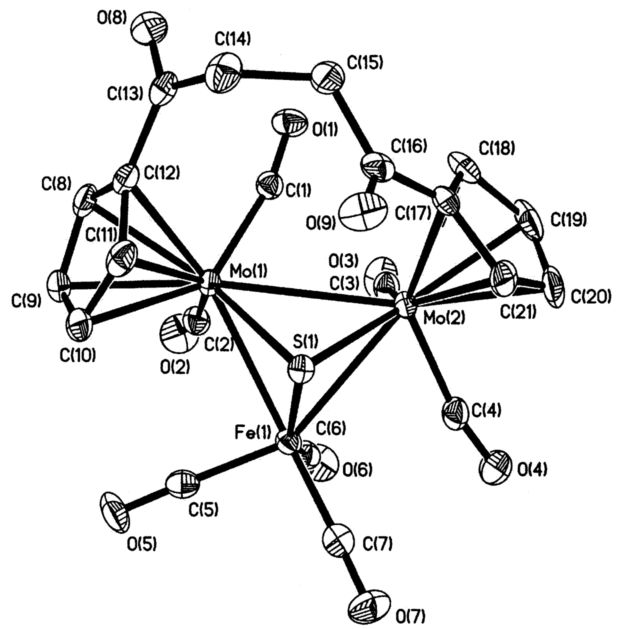


Figure 1. ORTEP drawing of **IIIa** with atom-labeling scheme.

Table 1. Selected Bond Lengths (Å) and Angles (deg) for IIIa

Mo(1)−C(1)	1.956(5)	S(1)−Mo(1)	2.3595(12)
Mo(1)−Fe(1)	2.7983(9)	Mo(2)−Mo(1)	3.0527(7)
Mo(2)−C(3)	2.006(5)	Mo(2)−S(1)	2.3481(12)
Mo(2)−Fe(1)	2.8347(9)	Fe(1)−S(1)	2.1797(13)
C(12)−C(13)	1.480(7)	C(16)−C(17)	1.483(6)
C(13)−O(8)	1.206(6)	C(16)−O(9)	1.205(5)
S(1)−Mo(1)−Mo(2)	49.41(3)	Fe(1)−Mo(1)−Mo(2)	57.760(19)
S(1)−Mo(2)−Fe(1)	48.63(3)	S(1)−Mo(2)−Mo(1)	49.74(3)
S(1)−Fe(1)−Mo(1)	54.90(3)	S(1)−Mo(1)−Fe(1)	49.10(3)
Fe(1)−Mo(2)−Mo(1)	56.611(19)	S(1)−Fe(1)−Mo(2)	53.95(3)
Mo(1)−Fe(1)−Mo(2)	65.628(19)	Fe(1)−S(1)−Mo(2)	77.42(4)
Fe(1)−S(1)−Mo(1)	76.00(4)	Mo(2)−S(1)−Mo(1)	80.85(3)

0.02 and 0.04 Å, respectively), the π systems of the two C═O double bonds would be quite well conjugated with the two Cp rings, respectively. So, the C−C single bond lengths of C(12)−C(13) (1.480(7) Å) and C(16)−C(17) (1.483(6) Å) become much shorter than a normal C−C single bond.

In addition, while the three CO attached to Fe(1), one CO attached to Mo(1) (C(1)O(1)), and one CO attached to Mo(2) (C(3)O(3)) are terminal, the other two CO attached to Mo(1) and Mo(2), i.e., C(2)O(2) and C(4)O(4), are semibridging. This is because the asymmetric parameters of the latter two carbonyls (0.41 and 0.36, respectively) fall within the range of α values (0.1 ≤ α ≤ 0.6) typical for semibridging carbonyls.[17] This is consistent with the IR spectrum of **IIIa** showing absorption bands ranging from 1866 to 2043 cm^{-1}. In fact, this molecule is a polycyclic system, which can be regarded as an 18-membered macrocycle, if all the carbon atoms of the bridged dicyclopentadienyl ligand from C(8) to C(21) and all the cluster core atoms Mo(2)Fe(1)S(1)-Mo(1) are involved in counting the ring size. In addition, the structure of **IIIa** is very similar to that of its analogues containing ether chain-bridged dicyclopentadienyl ligands.[9,11]

Table 2. Selected Bond Lengths (Å) and Angles (deg) for IVb

W(1)−C(1)	2.03(2)	S(1)−W(1)	2.360(4)
W(1)−Fe(1)	2.848(2)	W(2)−W(1)	3.0520(11)
W(2)−C(3)	1.913(18)	W(2)−S(1)	2.384(4)
W(2)−Fe(1)	2.809(2)	Fe(1)−S(1)	2.198(5)
C(12)−C(13)	1.50(2)	C(16)−C(17)	1.49(2)
S(1)−W(2)−Fe(1)	49.25(11)	S(1)−W(2)−W(1)	49.62(10)
Fe(1)−W(2)−W(1)	57.97(5)	S(1)−Fe(1)−W(2)	55.24(11)
S(1)−Fe(1)−W(1)	53.92(12)	W(2)−Fe(1)−W(1)	65.29(5)
Fe(1)−S(1)−W(1)	77.25(15)	Fe(1)−S(1)−W(2)	75.51(14)
W(1)−S(1)−W(2)	80.08(13)	S(1)−W(1)−Fe(1)	48.83(12)
S(1)−W(1)−W(2)	50.30(9)	Fe(1)−W(1)−W(2)	56.74(5)

Figure 2 shows the molecular structure of **IVb**, whereas the selected bond lengths and angles are listed in Table 2. As can be seen intuitively from Figure 2, **IVb** consists of two identical tetrahedral $W_2Fe(\mu_3\text{-}S)$ cluster cores, which are connected by two identical 1,1′-succinyldicyclopentadienyl ligands. In addition, each of the two cluster cores carries one set of three CO ligands coordinated to Fe atom and two sets of two CO ligands to two W atoms, respectively. Similar to **IIIa**, the two ketone carbonyls C(13)−O(8) and C(16A)−O(9A) or C(16)−O(9) and C(13A)−O(8A) in the bridged dicyclopentadienyl ligand are well conjugated with their attached two Cp rings. So, the C−C single bond lengths C(12)−C(13) (1.50(2) Å) and C(16)−C(17) (1.49(2) Å) are shorter than a normal C−C single bond. Furthermore, in **IVb** the carbonyls C(1)−O(1), C(1A)−O(1A), C(3)−O(3), C(3A)−O(3A), C(4)−O(4), and C(4A)−O(4A) attached to W atoms are semibridging (their asymmetric parameters are in the range 0.37−0.53)[17] and the others terminal.

It is worth pointing out that this is the first reported macrocyclic compound that consists of two tetrahedral cluster cores and two bridged dicyclopentadienyl ligands characterized by X-ray crystal diffraction techniques. In addition, just like **IIIa** mentioned above, **IVb** is also a polycyclic system, which can be viewed as a size-varied macrocycle, depending on which carbon atoms of the Cp rings and which atoms of the cluster cores are involved in counting the ring size.

Synthesis and Characterization of Dihydroxy-Containing Macrocycles Va,b and VIa,b. Crystal Structure of Va. We have further found that the diketo-containing macrocycles **IIIa,b** and **IVa,b** could react with excess $NaBH_4$ in MeOH at room temperature, through reduction of the diketo functional group, to give dihydroxyl derivatives $[M_2Fe(\mu_3\text{-}S)(CO)_7][\eta^5\text{-}C_5H_4CH(OH)CH_2]_2$ (**Va**, M = Mo; **Vb**, M = W) and $[M_2Fe(\mu_3\text{-}S)(CO)_7]_2\{[\eta^5\text{-}C_5H_4CH(OH)CH_2]_2\}_2$ (**VIa**, M = Mo; **VIb**, M = W) in quite high yields (Scheme 3).

Products **Va,b** and **VIa,b** are air-stable brown solids, which have been characterized by elemental analysis and IR and ^1H NMR spectroscopy. For example, the IR spectra of **Va,b** and **VIa,b** showed several absorption bands in the range 2046−1847 cm^{-1} for their carbonyls attached to metals and one absorption band in the region 3382−3416 cm^{-1} for their hydroxy groups. In addition, the ^1H NMR spectra of these derivatives

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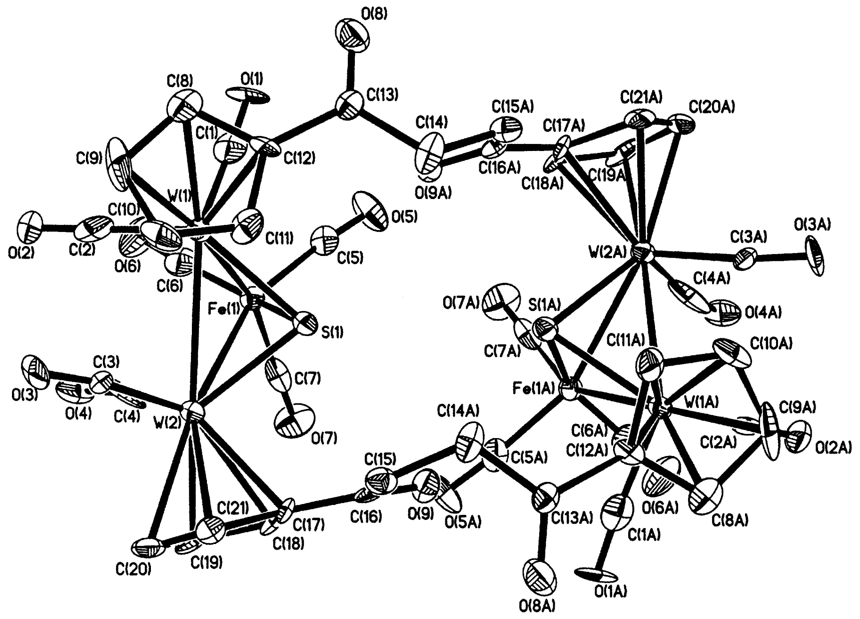
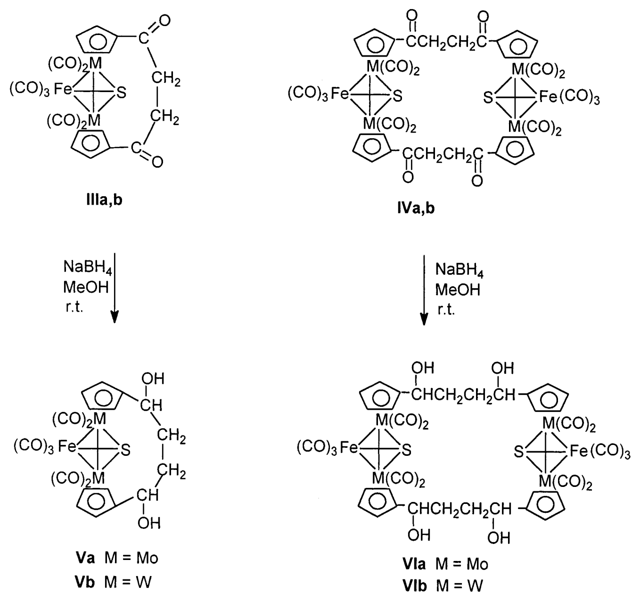


Figure 2. ORTEP drawing of **IVb** with atom-labeling scheme.

Scheme 3



displayed resonance signals assignable to their ethylene, CH, OH, and C_5H_4 groups.

To confirm the functional transformation of the diketo carbon chain-bridged dicyclopentadienyl ligands in **IIIa,b** and **IVa,b**, the crystal X-ray diffraction analysis for **Va** was undertaken. While Figure 3 presents its molecular structure, Table 3 lists its selected bond lengths and angles. It can be seen from Figure 3 and Table 3 that **Va** is very similar to **IIIa**. This is consistent with the fact that **Va** is simply the dihydroxy derivative of the parent diketo compound **IIIa**. That is, C(13)−O(8) (1.206(6) Å) and C(16)−O(9) (1.205(5) Å) in **IIIa** are C═O double bonds, whereas C(16)−O(12) (1.431(18) Å) and C(19)−O(11) (1.441(15) Å) in **Va** are C−O single bonds. In addition, the two carbonyls attached to Mo(1) and Mo(2), i.e., C(1)−O(1) and C(7)−O(7), are semibridging (their α values are 0.42 and 0.46, respectively)[17] and the others terminal. This coincides very well with the IR spectrum of **Va** showing absorption bands ranging from 2034 to 1847 cm^{-1}.

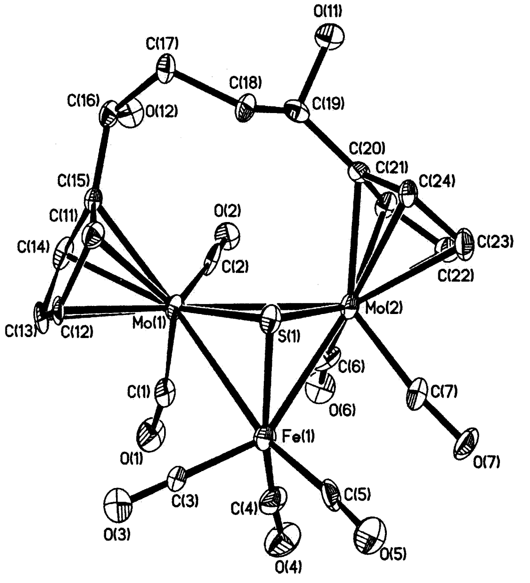


Figure 3. ORTEP drawing of **Va** with atom-labeling scheme.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Va

Mo(1)−C(1)	1.951(16)	S(1)−Mo(1)	2.383(4)
Mo(1)−Fe(1)	2.812(3)	Mo(2)−Mo(1)	3.057(2)
Mo(2)−C(6)	2.003(19)	Mo(2)−S(1)	2.361(4)
Mo(2)−Fe(1)	2.856(3)	Fe(1)−S(1)	2.195(4)
C(16)−O(12)	1.431(18)	C(19)−O(11)	1.441(15)
S(1)−Mo(1)−Fe(1)	49.14(11)	S(1)−Mo(2)−Mo(1)	50.18(9)
Fe(1)−Mo(2)−Mo(1)	56.67(6)	S(1)−Fe(1)−Mo(1)	55.17(11)
S(1)−Fe(1)−Mo(2)	53.83(11)	Mo(1)−Fe(1)−Mo(2)	65.28(6)
Fe(1)−S(1)−Mo(2)	77.54(13)	Fe(1)−S(1)−Mo(1)	75.68(12)
Mo(2)−S(1)−Mo(1)	80.26(12)	S(1)−Mo(1)−Mo(2)	49.57(10)
Fe(1)−Mo(1)−Mo(2)	58.06(7)	S(1)−Mo(2)−Fe(1)	48.63(11)

Finally, it should be pointed out that in the unit cell of **Va** there are eight molecules of **Va** and 16 molecules of solvent MeOH. In addition, between molecules of **Va** and MeOH, **Va** and **Va,** or MeOH and MeOH there possibly exist hydrogen-bonding interactions. This is because the distances, such as O(32A)···H···O(11A),

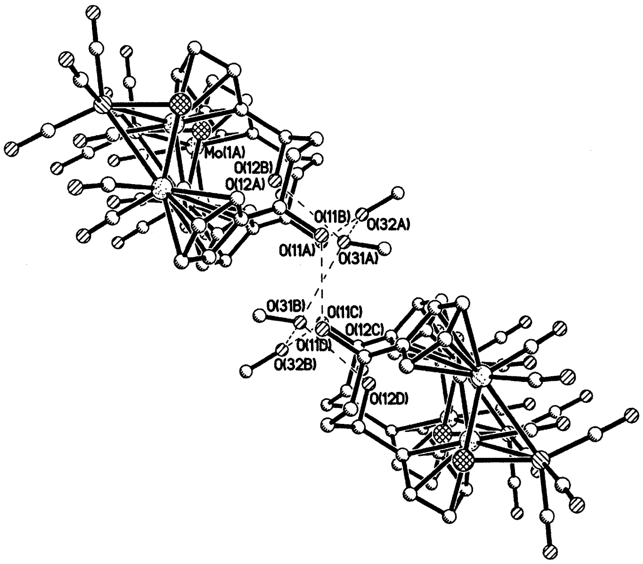


Figure 4. Part of an unit cell for **Va**.

O(31A)···H···O(12B), O(31A)···H···O(31B), O(31A)···H···O(32A), and O(11C)···H···(11A) (Figure 4), are within 2.697−2.846 Å, which fall into the range 2.0−3.0 Å, the values typical for the existence of hydrogen-bonding interactions.[18]

Experimental Section

General Comments. All reactions were carried out under an atmosphere of prepurified nitrogen using standard Schlenk and vacuum-line techniques. Tetrahydrofuran and diglyme were distilled from Na/benzophenone ketyl under nitrogen. M(CO)$_6$ (M = Mo, W) were purchased from Strem Chemicals, Inc. and used as received. [η^5-$C_5H_4C(O)CH_2$]$_2$Na$_2$[19] and [MFeCo(μ_3-S)(CO)$_8$]$_2$[η^5-$C_5H_4C(O)CH_2$]$_2$ (M = Mo, W)[20] were prepared according to literature procedures. Products were isolated by preparative TLC and were further recrystallized from CH_2Cl_2/hexane mixed solvent. IR spectra were recorded on a Nicolet Magna 560 FT-IR infrared spectrophotometer. ^{1}H NMR spectra were recorded on a Bruker AC-P200 NMR spectrometer. C/H analyses were performed on an Elementar Vario EL analyzer. Melting points were determined on a Yanaco MP-500 apparatus and were uncorrected.

Preparation of [$Mo_2Fe(\mu_3$-S)(CO)$_7$][η^5-$C_5H_4C(O)CH_2$]$_2$ (IIIa) and [$Mo_2Fe(\mu_3$-S) (CO)$_7$]$_2${[η^5-$C_5H_4C(O)CH_2$]$_2$ }$_2$ (IVa). A 100 mL three-necked flask equipped with a stir-bar, a serum cap, and a reflux condenser topped with a nitrogen inlet tube was charged with 0.792 g (3.0 mmol) of Mo(CO)$_6$, 0.412 g (1.6 mmol) of [η^5-$C_5H_4C(O)CH_2$]$_2$Na$_2$, and 20 mL of diglyme. The reaction mixture was stirred at reflux for 4 h. After removal of the solvent under vacuum, 1.134 g (1.0 mmol) of [MoFeCo(μ_3-S)(CO)$_8$]$_2$[η^5-$C_5H_4C(O)CH_2$]$_2$ and 30 mL of THF were added and the mixture was stirred at reflux for another 6 h. Solvent was removed under reduced pressure. The residue was subjected to preparative TLC separation using CH_2Cl_2/Et_2O (v/v = 25:1) as eluent. The first main brown band afforded 0.100 g (7.3%) of **IIIa** as a brown solid, mp 216 °C dec. Anal. Calcd for $C_{21}H_{12}FeMo_2O_9S$: C, 36.66; H, 1.76. Found: C, 36.61; H, 1.99. IR (KBr disk): $\nu_{C\equiv O}$ 2043(vs), 1998(vs), 1978(vs), 1922(s), 1866(vs); $\nu_{C=O}$ 1661(s) cm^{-1}. ^{1}H NMR (CDCl$_3$): 2.95 (br, s, 4H, 2CH$_2$), 5.41(d, 4H, 2H^3, 2H^4), 5.79 (s, 4H, 2H^2, 2H^5) ppm. The second main brown band afforded 0.134 g (9.7%) of **IVa** as a brown solid, mp 240 °C dec. Anal. Calcd for $C_{42}H_{24}Fe_2Mo_4O_{18}S_2$: C, 36.66; H, 1.76. Found: C, 36.41; H, 2.04. IR (KBr disk): $\nu_{C\equiv O}$ 2043(vs), 1998(vs), 1977(vs), 1922(s), 1866(vs); $\nu_{C=O}$ 1661(s) cm^{-1}. ^{1}H NMR (CDCl$_3$): 2.90 (br, s, 8H, 4CH$_2$), 5. 40 (d, 8H, 4H^3, 4H^4), 5.78 (s, 8H, 4H^2, 4H^5) ppm.

Preparation of [$W_2Fe(\mu_3$-S)(CO)$_7$][η^5-$C_5H_4C(O)CH_2$]$_2$ (IIIb) and [$W_2Fe(\mu_3$-S)(CO)$_7$]$_2${[η^5-$C_5H_4C(O)CH_2$]$_2$}$_2$ (IVb). The flask described above was charged with 0.715 g (2.2 mmol) of W(CO)$_6$, 0.387 g (1.5 mmol) of [η^5-$C_5H_4C(O)CH_2$]$_2$Na$_2$, and 20 mL of diglyme. The reaction mixture was stirred at reflux for 6 h. After removal of the solvent under vacuum, 1.327 g (1.0 mmol) of [WFeCo(μ_3-S)(CO)$_8$]$_2$[η^5-$C_5H_4C(O)CH_2$]$_2$ and 30 mL of THF were added and the mixture was stirred at reflux for another 6 h. The same workup was used as that for **IIIa** and **IVa**. The first main brown band afforded 0.186 g (10.8%) of **IIIb** as a brown solid, mp 150 °C dec. Anal. Calcd for $C_{21}H_{12}FeO_9SW_2$: C, 29.20; H, 1.40. Found: C, 29.48; H, 1.52. IR (KBr disk): $\nu_{C\equiv O}$ 2042(vs), 1981(vs), 1890(s), 1851(s); $\nu_{C=O}$ 1684(s) cm^{-1}. ^{1}H NMR (CDCl$_3$): 2.96 (br, s, 4H, 2CH$_2$), 5.42 (d, 4H, 2H^3, 2H^4), 5.80 (s, 4H, 2H^2, 2H^5) ppm. The second main brown band afforded 0.090 g (5.2%) of **IVb** as a brown solid, mp 165 °C dec. Anal. Calcd for $C_{42}H_{24}Fe_2O_{18}S_2W_4$: C, 29.20; H, 1.40. Found: C, 29.20; H, 1.46. IR (KBr disk): $\nu_{C\equiv O}$ 2050(vs), 1977(vs), 1894(s), 1847(s); $\nu_{C=O}$ 1684(s) cm^{-1}. ^{1}H NMR (CDCl$_3$): 2.92 (br, s, 8H, 4CH$_2$), 5.41 (d, 8H, 4H^3, 4H^4), 5.81 (s, 8H, 4H^2, 4H^5) ppm.

Preparation of [$Mo_2Fe(\mu_3$-S)(CO)$_7$][η^5-$C_5H_4CH(OH)CH_2$]$_2$ (Va). The flask described above was charged with 0.103 g (0.15 mmol) of [$Mo_2Fe(\mu_3$-S)(CO)$_7$][η^5-$C_5H_4C(O)CH_2$]$_2$, 0.023 g (0.60 mmol) of NaBH$_4$, and 20 mL of MeOH. The reaction mixture was stirred at room temperature for 2 h. After evaporation of the solvent under vacuum, the residue was subjected to preparative TLC separation using CH_2Cl_2/Et_2O (v/v = 10:3) as eluent. The main brown band afforded 0.035 g (34.3%) of **Va** as a brown solid, mp >290 °C dec. Anal. Calcd for $C_{21}H_{16}FeMo_2O_9S$: C, 36.44; H, 2.33. Found: C, 36.34; H, 2.09. IR (KBr disk): ν_{O-H} 3382(br); $\nu_{C\equiv O}$ 2034(vs), 1985(vs), 1970(vs), 1890(s), 1847(m) cm^{-1}. ^{1}H NMR (CDCl$_3$): 1.53 (br, s, 4H, 2CH$_2$), 2.31 (s, 2H, 2OH), 3.46 (s, 2H, 2CH), 4.96−5.52 (m, 8H, 2C$_5$H$_4$) ppm.

Preparation of [$W_2Fe(\mu_3$-S)(CO)$_7$][η^5-$C_5H_4CH(OH)CH_2$]$_2$ (Vb). The same procedure as that for **Va** was followed, but 0.134 g (0.15 mmol) of [$W_2Fe(\mu_3$-S)(CO)$_7$][η^5-$C_5H_4C(O)CH_2$]$_2$ was used instead of [$Mo_2Fe(\mu_3$-S)(CO)$_7$][η^5-$C_5H_4C(O)CH_2$]$_2$. The main brown band afforded 0.051 g (39.1%) of **Vb** as a brown solid, mp >290 °C dec. Anal. Calcd for $C_{21}H_{16}FeO_9SW_2$: C, 29.06; H, 1.86. Found: C, 29.30; H, 1.97. IR (KBr disk): ν_{O-H} 3385(br); $\nu_{C\equiv O}$ 2046(vs), 1984(vs), 1969(vs), 1887(s), 1848(m) cm^{-1}. ^{1}H NMR (CDCl$_3$): 1.54 (br, s, 4H, 2CH$_2$), 2.32 (s, 2H, 2OH), 3.47 (s, 2H, 2CH), 4.98−5.53 (m, 8H, 2C$_5$H$_4$) ppm.

Preparation of [$Mo_2Fe(\mu_3$-S)(CO)$_7$]$_2${[η^5-$C_5H_4CH(OH)CH_2$]$_2$}$_2$ (VIa). The same procedure as that for **Va** was followed, but 0.207 g (0.15 mmol) of [$Mo_2Fe(\mu_3$-S)(CO)$_7$]$_2${[η^5-$C_5H_4C(O)CH_2$]$_2$}$_2$ and 0.046 g (1.20 mmol) of NaBH$_4$ were employed, instead. The main brown band afforded 0.107 g (51.6%) of **VIa** as a brown solid, mp >290 °C dec. Anal. Calcd for $C_{42}H_{32}Fe_2Mo_4O_{18}S_2$: C, 36.44; H, 2.33. Found: C, 36.18; H, 2.52. IR (KBr disk): ν_{O-H} 3416(br); $\nu_{C\equiv O}$ 2046(vs), 1988(vs), 1969(vs), 1887(s), 1848(m) cm^{-1}. ^{1}H NMR (CDCl$_3$): 1.53 (br, s, 8H, 4CH$_2$), 2.33 (s, 4H, 4OH), 3.48 (s, 4H, 4CH), 4.97−5.53 (m, 16H, 4C$_5$H$_4$) ppm.

Preparation of [$W_2Fe(\mu_3$-S)(CO)$_7$]$_2${[η^5-$C_5H_4CH(OH)CH_2$]$_2$}$_2$ (VIb). The same procedure as that for **Va** was followed, but 0.259 g (0.15 mmol) of [$W_2Fe(\mu_3$-S)(CO)$_7$]$_2${[η^5-$C_5H_4C(O)CH_2$]$_2$}$_2$ and 0.046 g (1.20 mmol) of NaBH$_4$ were utilized, instead. The main brown band afforded 0.115 g (44.2%) of **VIb** as a brown solid, mp >290 °C dec. Anal. Calcd for $C_{42}H_{32}Fe_2O_{18}S_2W_4$: C, 29.06; H, 1.86. Found: C, 29.03; H, 1.59. IR (KBr disk): ν_{O-H} 3385(br); $\nu_{C\equiv O}$ 2046(vs), 1984(vs), 1965(vs), 1887(s), 1848(m) cm^{-1}. ^{1}H NMR (CDCl$_3$): 1.58 (br, s, 8H, 4CH$_2$), 2.32 (s, 4H, 4OH), 3.47 (s, 4H, 4CH), 4.99−5.53 (m, 16H, 4C$_5$H$_4$) ppm.

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Table 4. Crystal Data and Structural Refinements Details for IIIa, IVb, and Va

	IIIa	**IVb**	**Va**
mol formula	$C_{21}H_{12}FeMo_2O_9S$	$C_{42}H_{24}Fe_2O_{18}S_2W_4\cdot 2CH_2Cl_2$	$C_{21}H_{16}FeMo_2O_9S\cdot 2CH_3OH$
mol wt	688.10	1897.68	756.21
cryst syst	triclinic	orthorhombic	monoclinic
space group	$P\bar{1}$	$P2(1)2(1)2$	$C2/c$
a/Å	9.332(2)	10.532(3)	26.80(2)
b/Å	10.877(3)	26.028(9)	8.629(7)
c/Å	11.419(3)	9.359(3)	24.348(20)
α/deg	101.892(5)	90	90
β/deg	96.768(4)	90	107.544(15)
γ/deg	104.004(5)	90	90
V/Å^3	1083.2(4)	2565.6(15)	5368(7)
Z	2	4	8
D_c/g cm^{-3}	2.110	2.457	1.871
F(000)	672	1768	3008
abs coeff/mm^{-1}	1.950	9.483	1.589
temp/K	298(2)	293(2)	298(2)
scan type	$\omega-2\theta$	$\omega-2\theta$	ω-2θ
$2\theta_{max}$/deg	50.06	50.04	50.06
no. of reflns	3911	10 624	10 093
no. of indep reflns	3579	4482	4534
R_{int}	0.0190	0.0862	0.1322
no. of data/restraints/params	3579/0/307	4482/0/334	4534/0/338
R	0.0327	0.0429	0.0772
R_w	0.0800	0.0537	0.1378
goodness of fit	1.019	0.948	1.108
largest diff peak and hole/e Å^{-3}	0.675 and −0.655	1.396 and −1.050	0.849 and −0.958

X-ray Structure Determinations of IIIa, IVb, and Va. Single-crystals of **IIIa, IVb**, and **Va** suitable for X-ray diffraction analyses were grown by slow evaporation of the CH_2Cl_2/hexane solution of **IIIa** at about 4 °C and by diffusion of hexane and MeOH to the CH_2Cl_2 solutions of **IVb** and **Va** at room temperature, respectively. Each crystal was mounted on a Bruker SMART 1000 automated diffractometer with a graphite monochromator with Mo Kα radiation (λ = 0.71073 Å). Details of the crystal data, data collections, and structure refinements are summarized in Table 4.

The structures were solved by direct methods and expanded by Fourier techniques. The final refinements were accomplished by the full-matrix least-squares method with anisotropic thermal parameters for non-hydrogen atoms. The calculations were performed using the SHELXTL-97 program for **IIIa**, **IVb**, and **Va.** The Flack parameter[21] for **IVb** is zero, which indicated that the absolute structure of **IVb** is correct.

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Supporting Information Available: Full tables of crystal data, atomic coordinates and thermal parameters, and bond lengths and angles for **IIIa**, **IVb**, and **Va**. This material is available free of charge via the Internet at http://pubs.acs.org.

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