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Molybdenum-Tungsten Mixed-Metal Trinuclear Clusters with Two Capping Oxides and Six Bridging Acetates, and Other Mixed Molybdenum-Tungsten Clusters

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MOLYBDENUM-TUNGSTEN MIXED-METAL TRINUCLEAR CLUSTERS WITH
TWO CAPPING OXIDES AND SIX BRIDGING ACETATES, AND OTHER
MIXED MOLYBDENUM-TUNGSTEN CLUSTERS

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Abstract Mixed molybdenum-tungsten clusters of di-, tri-, tetra- and pentavalent metal ions are reviewed. Those having strong π -accepting and/or σ -donating ligands such as CO are not included. The complexes which have been prepared by the authors' group are described in more detail. These are trinuclear complexes ($[\text{Mo}_n\text{W}_{3-n}(\mu_3\text{-O})_2(\mu\text{-CH}_3\text{COO})_6(\text{H}_2\text{O})_3]^{2+}$) with the oxidation state four and dinuclear complex ($[\text{MoW}(\mu\text{-O})_2(\text{O})_2(\mu\text{-N,N'-edta})]^{2-}$) with the oxidation state five. Other complexes described are dinuclear complexes of divalent metal ions ("Mo-W quadruple bond") and of trivalent metal ions ("Mo-W triple bond"), and trinuclear complexes with *i*-propoxide ligands.

Keywords: Molybdenum-tungsten cluster, trinuclear complexes

INTRODUCTION

Molybdenum and tungsten, both belonging to 6 family in the periodic table, form various di- and poly-nuclear coordination compounds with similar structures.¹⁻⁴ Except for the hexavalent state, their di-, tri-, tetra- and penta-valent states give compounds with direct metal-metal bonds. These compounds are useful for studying mixed-metal clusters, and they provide us some insights into the metal-metal interactions as well as systems having characteristic reactivities such as new regioselective reactions. Structures of corresponding molybdenum and tungsten compounds are very similar to each other and often almost identical.⁵ Thus it is expected that the electronic structure and the reactivity of mixed Mo-W

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TABLE I Known mixed molybdenum-tungsten clusters

complex	oxid. state	d(Mo-W) Å	data	ref.
[MoW(Me ₃ CCOO) ₄]	2	2.081(1)	b,c,e,l	8,21
[MoW(mhp) ₄] ⁿ	2	2.091(1)	a,c,d,j	9,10
[MoWCl ₄ (PMe ₂ Ph) ₄]	2		a,b,d,e,g	17
[MoWCl ₄ (PMePh ₂) ₄]	2	2.210(4) 2.207(4)	a,b,c,d,e,g	11,17
[Cl ₂ (PMe ₃) ₂ MoWCl ₂ (PMePh ₂) ₂]	2	2.207(1)	a,b,c,d,e,g	17
[MoWCl ₄ (PMe ₃) ₄]	2	2.209(1)	a,b,c,d,e,g,l	11,15 17
[MoW(Me ₃ CCOO) ₄ I(CH ₃ CN)]	2.5	2.194(2)	b,c,j	6
[MoWCl ₈ H] ³⁻	3	2.445(3)	a,c	7,8
[MoW(O- <i>t</i> -Br) ₆] ^m	3		(e)	12
[Mo ₂ W(O)(O- <i>i</i> -Pr) ₁₀]	4		b,d,e	12
[Mo ₂ W(CMe)(O- <i>i</i> -Pr) ₉]	(4)		e	13
[Mo ₂ W(O) ₂ (CH ₃ COO) ₆ (H ₂ O) ₃] ²⁺	4	2.723(3)	b,c,e,h,i,k	14,18 19
[MoW ₂ (O) ₂ (CH ₃ COO) ₆ (H ₂ O) ₃] ²⁺	4		b,c,e,h,i,k	14,18 19
[MoW(O) ₄ (edta)] ²⁻ _o	5	2.55(1)	b,c,d,e,f,h,i,k	19,20

a.vibrational spectroscopy, b.electronic absorption spectroscopy, c.X-ray crystal structure, d.cyclic voltammetry, e.¹H NMR, f.¹³C NMR, g.³¹P NMR, h.⁹⁵Mo NMR, i.¹⁸³W NMR, j.ESR, k.X-ray photoelectron spectroscopy, l.He(I) photoelectron spectroscopy, m.identified in solution only, n.mhp=2-hydroxy-6-methylpyridine anion, o.edta=ethylenediaminetetraacetate.

compounds can be discussed without considering serious influence of steric factors. Some mixed molybdenum-tungsten clusters are known and various new aspects are revealed.⁶⁻²¹ The known mixed Mo-W clusters are summarized in Table I. In this review, we wish to summarize the field of Mo-W mixed-metal clusters, and to show what can be seen by mixing two metal ions and what should be done further. The complexes prepared in our laboratory, [Mo_nW_{3-n}(μ⁻O)₂(μ-CH₃COO)₆(H₂O)₃]²⁺¹⁸ and [MoW(μ-O)₂(O)₂(μ-N,N'-edta)]²⁻₂₀ will be treated in more detail than other complexes in the earlier part of the review. The latter part deals with the complexes prepared by other groups in the order of the increasing oxidation number.

TRINUCLEAR CLUSTERS WITH TWO CAPPING OXIDES AND SIX BRIDGING ACETATES

Trinuclear clusters of this type (Figure 1) are known for the tetravalent state of molybdenum and tungsten.²² Cotton and his coworkers first prepared such homonuclear complexes,²³⁻²⁵ and extended the field.²² Mixed molybdenum-tungsten clusters of this type, dimolybdenum-tungsten and molybdenum-ditungsten compounds, have recently been prepared by us.¹⁴ This preparation provided a first complete series of four compounds of trinuclear system, Mo_3 , Mo_2W , MoW_2 , and W_3 .

Preparation

Preparation methods¹⁴ are briefly given here, which involved refluxing of MoO_4^{2-} , WO_4^{2-} , and zinc dust in acetic anhydride for 24 h, and subsequent purification by column chromatography. It was important to add Na_2MoO_4 15 min after the initiation of the reflux of tungstate in acetic anhydride. Mixture of the dicationic trinuclear species was collected by preliminary chromatography, and separated into their components by the use of an SP-Sephadex C-25 cation exchange column (successive three columns of 4 cm in diameter and 140 cm in length) with 0.1 M HBr as eluting reagent. It took nearly a month to achieve complete separation. Two new complexes, $[\text{Mo}_2\text{W}(\text{O})_2(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{Br}_2 \cdot \text{H}_2\text{O}$ and $[\text{MoW}_2(\text{O})_2(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{Br}_2 \cdot \text{H}_2\text{O}$ were obtained by this method as well as the known 'W₃' complex.²⁵

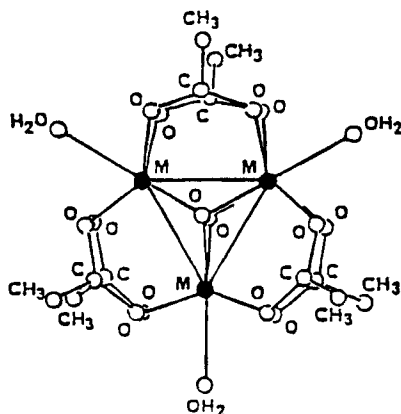


FIGURE 1 Structure of $[\text{M}_3(\mu_3\text{-O})(\mu\text{-CH}_3\text{COO})_6(\text{H}_2\text{O})_3]^{2+}$ ($\text{M}_3 = \text{Mo}_3, \text{Mo}_2\text{W}, \text{MoW}_2, \text{and W}_3$).

Crystal Structure

Bromide salts of the four complexes crystallize in rhombohedral space group R3m. Table II compares the crystallographic data of the four compounds. Except for the crystal densities, the corresponding parameters are almost identical to one another. The data

TABLE II Crystallographic data of $[\text{Mo}_n\text{W}_{3-n}(\mu_3\text{-O})_2(\mu\text{-CH}_3\text{COO})_6(\text{H}_2\text{O})_3]\text{Br}_2 \cdot \text{H}_2\text{O}$.

	a/Å	α	V/Å ³	Z	$\frac{\rho_{\text{obs}}}{\text{g cm}^{-3}}$	$\frac{\rho_{\text{calcd}}}{\text{g cm}^{-3}}$
Mo ₃ ^a	11.784	106.34°	1386.58	2	2.18	2.17
Mo ₂ W	11.809	106.37°	1394.5	2	2.33	2.35
MoW ₂	11.812	106.74°	1346.5	2	2.54	2.57
W ₃	11.787	106.30°	1388.93	2	>2.7	2.80

a. M. Ardon, A. Bino, F. A. Cotton, Z. Dori, M. Kaftory, G. Reisner, Inorg. Chem., **21**, 1912 (1982).

indicate that four complex cations, $[\text{M}_3(\mu_3\text{-O})_2(\mu\text{-CH}_3\text{COO})_6(\text{H}_2\text{O})_3]^{2+}$ ($\text{M}_3 = \text{Mo}_3, \text{Mo}_2\text{W}, \text{MoW}_2,$ and W_3), should have almost identical structural parameters. In fact, metal-metal bond distances of the Mo₂W cation are 2.73 Å, which is compared with those of the Mo₃ (2.759 Å)²⁶ and the W₃ complex cation (2.746 Å).²⁷ The metal ions in the mixed-metal clusters are statistically disordered in the crystal lattice. Various properties of the mixed-metal clusters can be discussed without considering serious influence of steric factors.

¹H and Metal NMR Spectra

¹H NMR spectra of the four complexes (Figure 2) provide the most conclusive evidence for the mixed-metal structures. The acetate methyl signal splits into two peaks with a 1:2 integrated intensity ratio. It is seen that the chemical shift appears at lower magnetic field as the molybdenum atom is replaced by tungsten.

¹⁸³W NMR spectra of the three clusters, Mo₂W, MoW₂, and W₃, are shown in Figure 3.¹⁸ The chemical shifts are summarized in

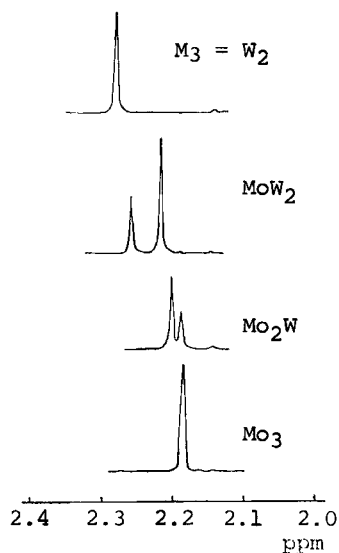


FIGURE 2 ^1H NMR spectra of $[\text{M}_3(\mu_3\text{-O})_2(\mu\text{-CH}_3\text{COO})_6(\text{H}_2\text{O})_3]^{2+}$ in aqueous solution (from ref.14).

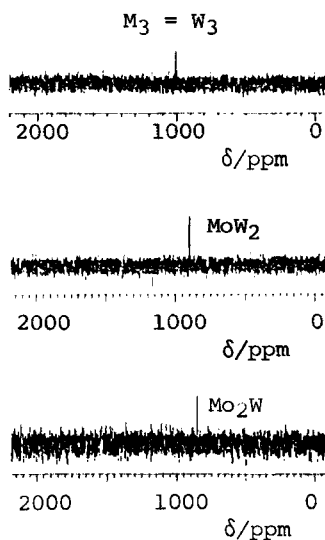


FIGURE 3 ^{183}W NMR spectra of $[\text{M}_3(\mu_3\text{-O})_2(\mu\text{-CH}_3\text{COO})_6(\text{H}_2\text{O})_3]^{2+}$ in aqueous solution (from ref.18).

Table III, together with those of some other clusters of Mo and W.^{18,28} It is known for ^{95}Mo NMR that the chemical shift of di- and poly-nuclear clusters appears at lower field as the oxidation number becomes lower.²⁹ Similar trend is also observed for the ^{183}W NMR (Table III). When these facts are taken into consideration, it is concluded that Mo in the mixed-metal trinuclear clusters is in somewhat lower oxidation state and W in somewhat higher oxidation state than the oxidation states of these metal ions in the Mo_3 and W_3 complexes.¹⁸ The same conclusion is derived for the dimeric complex of pentavalent metal ions (vide infra).

X-Ray Photoelectron Spectra (XPS)

The XPS spectra were taken in the form of either the BN disk or

TABLE III ^{183}W and ^{95}Mo chemical shifts of some di- and tri-nuclear cluster complexes.

complex	oxid. state	$\delta(^{183}\text{W})$ ppm	$\delta(^{95}\text{Mo})$ ppm	solvent
$[\text{W}_2\text{Cl}_9]^{3-}$	3	3539	—	CD_3CN
$[\text{W}_3(\text{O})_4(\text{NCS})_9]^{5-}$	4	2063	—	CH_3CN
$[\text{W}_3(\text{O})_4(\text{H}_2\text{O})_9]^{4+}$ ^a	4	1138	—	D_2O
$[\text{W}_3(\text{O})_2(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]^{2+}$	4	1005	—	D_2O
$[\text{Mo}_2(\text{O})_2(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]^{2+}$	4	897	1360	D_2O
$[\text{Mo}_2\text{W}(\text{O})_2(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]^{2+}$	4	848	1224	D_2O
$[\text{Mo}_3(\text{O})_2(\text{CH}_3\text{COO})_6(\text{H}_2\text{O})_3]^{2+}$	4	—	1061	D_2O
$[\text{W}_2(\text{O})_4(\text{edta})]^{2-}$	5	798	—	D_2O
$[\text{MoW}(\text{O})_4(\text{edta})]^{2-}$	5	549	877	D_2O
$[\text{Mo}_2(\text{O})_4(\text{edta})]^{2-}$	5	—	612	D_2O

a. ref.28

TABLE IV Binding energies of Mo and W in some di- and tri-nuclear cluster complexes (unit in eV).

complex	Mo-3d _{3/2}	Mo-3d _{5/2}	W-4f _{5/2}	W-4f _{7/2}	W-4d _{3/2}	w-4d _{5/2}
(a) $[\text{M}_3(\mu_3\text{-O})_2(\mu\text{-CH}_3\text{COO})_6(\text{H}_2\text{O})_3]^{2+}$						
Mo_3	234.1	231.1	—	—	—	—
Mo_2W	233.8	230.6	36.7	34.8	258.4	245.9
MoW_2	233.5	230.4	36.2	34.2	258.0	245.5
W_3	—	—	36.1	34.0	257.5	245.0
(b) $[\text{M}_2(\mu\text{-O})_2(\text{O})_2(\mu\text{-edta})]^{2-}$						
Mo_2	234.7	231.5	—	—	—	—
MoW	234.2	231.1	36.7	34.6	259.0	246.4
W_2	—	—	36.0	33.9	258.7	246.0

the thin film on Ni or Al metal. The thin film was prepared by evaporating acetonitrile solution. The Mo-3d and W-4d and 4f binding energies are summarized in Table IV.¹⁹ The mixed-metal clusters clearly show shifts of binding energies from those of the homonuclear Mo₃ and W₃ complexes. The Mo-3d binding energies of the mixed-metal complexes are smaller than those of the Mo₃ complex, while the W-4d and -4f binding energies of the mixed-metal clusters are larger than those of the W₃ cluster. Thus the same conclusion as described in the metal NMR section is derived.¹⁹

The metal NMR and the XPS data indicate that negative charge shift takes place from W to Mo through the metal-metal bond. Thus the results reenforced the fact that Mo(IV) is more electronegative than W(IV). The XPS spectrum of the mixed Ru^{III}-Rh^{III} complex, [Ru₂Rh(μ₃-O)(μ-CH₃COO)₆(H₂O)₃]⁺, does not show significant difference in Ru-3d and Rh-3d binding energies from those of the homonuclear Ru₃ and Rh₃ trimers.³⁰ Their metal-metal bond distances are considerably large (ca. 3.3 Å), and direct metal-metal bond is reckoned to be absent.³⁰ Direct metal-metal bonding interaction seems essential for the observed charge shift.

Electronic Absorption Spectra

Electronic absorption spectra of the four complexes in aqueous solution are given in Figure 4.¹⁴ Except for the Mo₂W complex, two peaks are observed in the visible region. The spectra of the three compounds, Mo₃, Mo₂W, and W₃, show systematic trend that the corresponding transitions shift to shorter wavelength with an increase in intensity as the molybdenum is

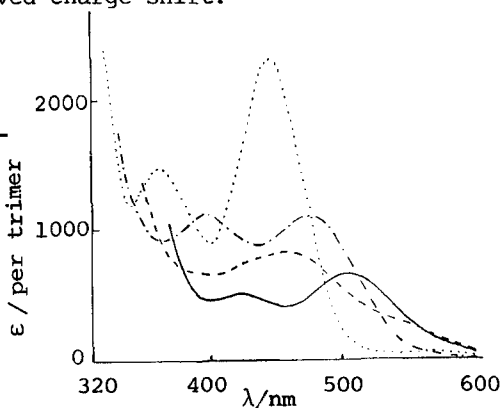


FIGURE 4 Electronic absorption spectra in 1 M HClO₄ of [M₃(O)₂-(CH₃COO)₆(H₂O)₃]²⁺ (— Mo₃, --- Mo₂W, -.- MoW₂, ··· W₃) (from ref. 14).

replaced by tungsten. Further studies should be necessary in order to interpret the nature of these transitions.³¹

MIXED Mo^V-W^V COMPLEX, [MoW(μ-O)₂(O)₂(edta)]²⁻

The dinuclear core, M₂(μ-O)₂(O)₂, is known for M = Mo^V and W^V. The complexes which were analyzed by the X-ray crystallography are those with a wide variety of ligands for molybdenum,^{3,32} and with edta⁴⁻³³ and F⁻³⁴ for tungsten. The edta complexes are the most stable

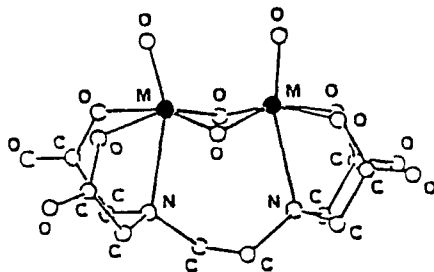


FIGURE 5 Structure of [MoW(μ-O)₂(O)₂(edta)]²⁻.

among those with this core (Figure 5). The mixed molybdenum-tungsten complex with edta ligand, [Mo^VW^V(μ-O)₂(O)₂(edta)]²⁻, has recently been prepared by neutralizing the acidic solutions containing EDTA, [MoOCl₅]²⁻ and [WOCl₅]²⁻.²⁰ The mixed-metal complex was separated from the two homonuclear complexes by the use of anion-exchange column chromatography after several weeks. X-Ray crystal structural analysis revealed that Mo and W atoms in the mixed-metal species are again statistically disordered. The Mo-W distance is 2.55 Å.²⁰ This is compared with the W-W distance (2.55 Å) in [W₂O₄(edta)]²⁻.³³ Corresponding bond distance is not available for [Mo₂O₄(edta)]²⁻, but the Mo-Mo distance (2.53 Å) of similar complex, [Mo₂O₄(R-pdta)]²⁻ (R-pdta = (R)-propylenediamine-N,N,N',N'-tetraacetate),³² would be referred to.

The metal NMR spectral (Table III) and the X-ray photoelectron spectral data (Table IV) indicate clearly that the molybdenum and tungsten in the mixed-metal dinuclear complex are somewhat lower and higher oxidation states, respectively, than those in the homonuclear dimers, Mo₂ and W₂.^{19,20} Similar conclusion was already derived for the trinuclear mixed Mo^{IV}-W^{IV} complexes (vide

supra).^{18,19} The difference in the NMR chemical shifts and the XPS binding energies between the mixed-metal and the homometal dinuclear clusters are larger than that for the trinuclear complexes. Somewhat shorter metal-metal bond distances of the dinuclear complexes may be relevant to the larger difference.

The pattern of the electronic absorption spectra is intermediate between those of the two homonuclear clusters.

DINUCLEAR COMPLEXES WITH Mo^{II}-W^{II} QUADRUPLE BONDS

Both Mo^{II} and W^{II} form various types of dinuclear complexes with metal-metal quadruple bond.³⁵ Several complexes containing Mo^{II}-W^{II} 6,8-11,15-17 and Cr^{II}-Mo^{II} 9,36 quadruple bonds have been reported. This area has recently been reviewed by Morris.¹⁶

The Mo-W complex with bridging ligands, (CH₃)₃CCOO⁻, was separated from its homonuclear analogue (Mo₂) by selective oxidation of the Mo-W complex with I₂.⁶ The pure crystalline solid of the one-electron oxidized species of the Mo-W complex was isolated and then reduced to give pure mixed Mo^{II}-W^{II} complex. Similar procedure was also used to obtain pure Mo^{II}-W^{II} complex of mhp (mhp⁻ = 2-hydroxy-6-methylpyridine anion).⁹ The metal-metal bond distance in [MoW((CH₃)₃CCOO)₄] (Figure 6)⁸ and [MoW(mhp)₄]⁹ were 2.080 and 2.091 Å, respectively. In the former case, the distance is shorter than the corresponding distance of the Mo₂ complex (2.088 Å)³⁷ despite the fact that W is expected to have a greater quadruple bond radius. The force constant of Mo-W bond

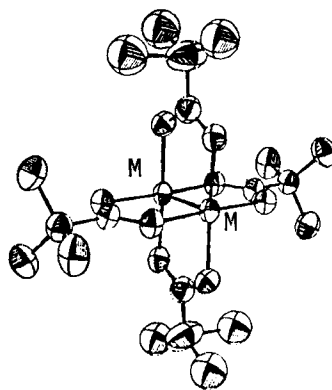


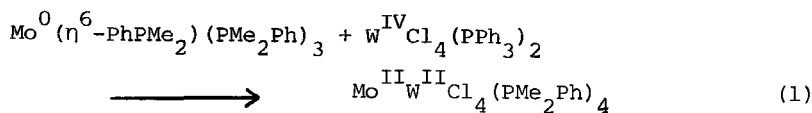
FIGURE 6 Structure of [MoW((CH₃)₃CCOO)₄] (from ref. 8).

based on Raman spectroscopy was stronger for $[\text{MoW}(\text{mhp})_4]$ (5.45 mdyn/Å) than those of Mo_2 and W_2 analogues.⁹ It was suggested that the Mo-W bond is more stabilized than the corresponding Mo-Mo bond in these complexes.^{8,9}

The one electron oxidized species, $[\text{MoW}((\text{CH}_3)_3\text{CCOO})_4]\text{I}\cdot\text{CH}_3\text{CN}$, was studied by the X-ray crystallographic analysis.⁶ This complex was suggested to have the Mo-W bond of order 3.5 on the basis of the total number (7) of d-electrons involved. The Mo-W distance was 2.194 Å.⁶ The metal ions were ordered as the iodine atom is bonded to W and the CH_3CN weakly to Mo. The selective bonding of I^- and CH_3CN was interpreted in terms of the 'polarization' of the Mo-W bond.

Cr-W dimer was also prepared with mhp as ligand.⁹ Cotton and his coworkers reported elegant work on the electronic structure of a series of compounds, Cr_2 , CrMo , Mo_2 , MoW , and W_2 ,³⁸ on the basis of the He(I) photoelectron spectra and the oxidation potential.¹⁰ It was reported that the first ionization energy, which was assigned to the metal-metal δ bonding electrons, decreases in the order from Cr_2 to W_2 (Figure 7). The reversible one-electron potentials shifted to negative direction in the order from CrMo (0.35 V vs. SCE) to W_2 (-0.35 V) in acetonitrile. An essentially linear correlation was found between the first ionization potentials and the one-electron oxidation potentials.¹⁰

Heteronuclear complexes without bridging ligands were prepared from the monomeric complexes without serious contamination by the homonuclear analogues (Reaction 1).^{11,17,39}



The ^{31}P NMR chemical shifts fell in the position far from the average position of the two homonuclear analogues. It was suggested that 'electron density' transfers from the tungsten to the molybdenum atom.¹⁷ The Mo-W distances without bridging ligands are

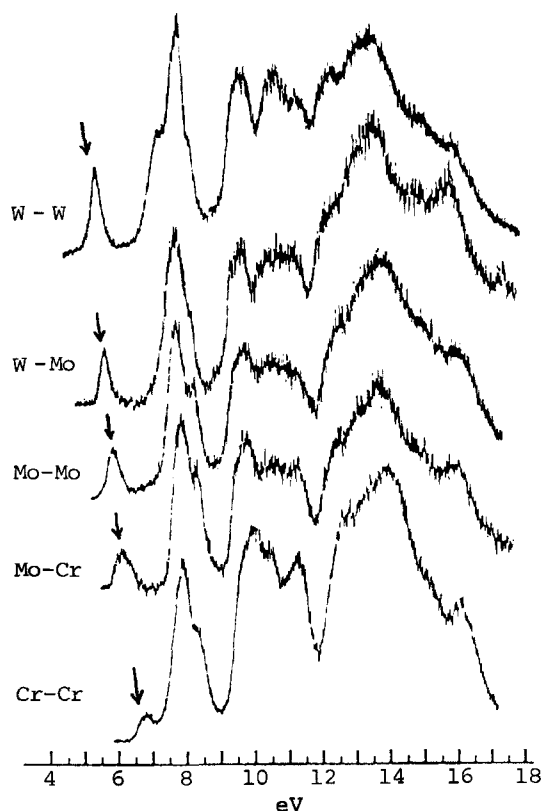


FIGURE 7 The He(I) photoelectron spectra of the series of the complexes, $[M_2(mhp)_4]$ ($M_2 = Cr_2, CrMo, Mo_2, MoW$ and W_2) (arrows indicate δ bonding electrons) (from ref.9).

close to the average of the two homonuclear metal-metal distances, in contrast to the observation for the complexes with bridging ligand.

For the non-bridging dinuclear complexes, the band assigned to $\delta - \delta^*$ transitions shifted to lower energy, and the one electron oxidizing and reducing potentials shifted to more negative as Mo was replaced by W. In these instances, the data of the Mo-W complexes were average of the two homonuclear counterparts.¹⁷

DINUCLEAR COMPLEXES WITH Mo^{III}-W^{III} TRIPLE BOND

The complex, [MoWCl₈H]³⁻ (Figure 8), may be classified as the compound with Mo-W triple bond in view of the number (6) of d-electrons involved.⁸ The bridging hydrogen is regarded as hydride ion, H⁻. The Mo-W distances (2.445 Å)⁸ is somewhat longer than the Mo-Mo

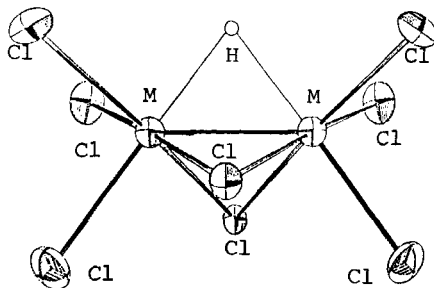


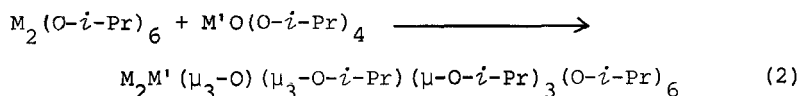
FIGURE 8 Structure of [MoWCl₈H]³⁻ (from ref. 8).

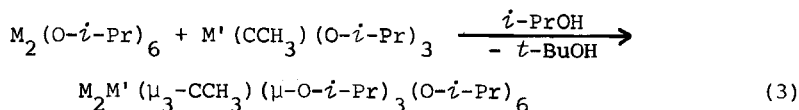
distance, 2.38 Å, in [Mo₂Cl₈H]³⁻.⁴⁰

The complexes, M₂L₆ (L = OR⁻, NR₂⁻, etc.)³⁵ have much stronger 'triple bond' with the metal-metal bond distances of around 2.1 Å. No Mo-W mixed-metal compound has been crystallographically analyzed, however. It was suggested that the reaction (2) (vide infra) with MoO(O-*i*-Pr)₄ and W₂(O-*i*-Pr)₆ gave MoW(O-*i*-Pr)₆ as intermediate.¹² This species was identified by ¹H NMR spectroscopy and by mass spectroscopy.

TRINUCLEAR COMPLEXES WITH ALKOXIDE LIGANDS

Trinuclear complexes of Mo^{IV} and W^{IV} containing alkoxide anions such as *i*-PrO⁻ ((CH₃)₂CHO⁻) as unidentate, bridging, and also capping ligands were studied by Chisholm and his coworkers.^{13,41,42} A typical example is Mo₃(μ₃-O)(μ₃-O-*i*-Pr)(μ-O-*i*-Pr)₃(O-*i*-Pr)₆ (Figure 9).¹² These compounds were prepared by the use of comproportionation reactions between the compounds with 'triple bond' (vide supra) and those of higher oxidation states (Reactions 2 and 3).^{12,13}





Mixed-metal compounds with $M_2M' = Mo_2W$ were obtained as crystalline solid with $M = Mo$ and $M' = W$ as starting material. 1H NMR spectra in benzene- d_6 and toluene- d_8 for the μ_3-O and the μ_3-CCH_3 complexes, respectively, were consistent with the suggested mixed-metal structures.^{12,13} The MoW_2 compounds were only poorly characterized or not produced by the reactions 2 and 3 with $M = W$ and $M' = Mo$. Nevertheless, these reactions are important routes to reach mixed-metal compounds without serious contamination of the homonuclear analogues. Detailed crystal structure of $Mo_2W(O)(O-i-Pr)_{10}$ was not examined because of the statistical disorder of Mo and W atoms. The crystals were isomorphous with $Mo_3O(O-i-Pr)_{10}$ and $W_3O(O-i-Pr)_{10}$ and it was assumed that the Mo-W distances should be close to those of the homonuclear analogues, Mo_3 (Mo-Mo distance, 2.534 Å)⁴³ and W_3 (W-W distance, 2.540 Å).¹²

Quasireversible reduction and irreversible oxidation were observed on the cyclic voltammogram (CV) of the complexes, $M_3(O)(O-i-Pr)_{10}$ in THF. From the data in Table V, it was concluded that the reduction and the oxidation occur predominantly at Mo sites and at W site, respectively, and was suggested that the Mo-W bonds are polarized as $Mo^{\delta-}-W^{\delta+}$.¹²

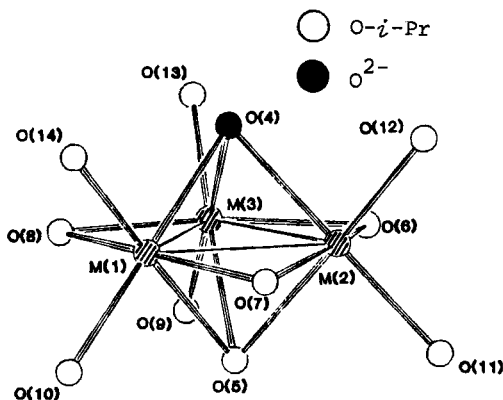


FIGURE 9 Structure of $M_3(\mu_3-O)(\mu_3-O-i-Pr)(\mu-O-i-Pr)_3(O-i-Pr)_6$ (from ref. 12).

TABLE V Redox potentials of $[M_3(O)(O-i-Pr)_{10}]$ in THF
(0.01 M $AgNO_3(CH_3CN)/Ag$ reference electrode)
(from ref. 12).

compound	$E_{1/2}$ (red)/V	E_p (oxid)/V
Mo_3	-1.46	0.48
Mo_2W	-1.57	0.20
W_3	-2.16	0.09

SUMMARY AND PROSPECTS

Known mixed molybdenum-tungsten clusters with Mo-W direct bond have been reviewed. The reported results give important information on the nature of metal-metal interactions which are not obtained from the homonuclear ones. UPS, XPS and metal NMR techniques played powerful role in this area. Charge shift (or called 'charge polarization' or 'electron density transfer') was frequently presumed for several Mo-W heteronuclear complexes. This was most clearly demonstrated for the tetravalent trinuclear and pentavalent dinuclear systems. No systematic study on the reactivities has been found so far. Our preliminary study on the terminal ligand (H_2O) substitution reactions of $[M_2M'(\mu_3-O)_2(\mu-CH_3COO)_6(H_2O)_3]^{2+}$ clearly shows some evidences for the significant regioselectivity.

Other type of clusters where both Mo and W give stable compounds may be as follows. Divalent Mo and W form stable hexanuclear clusters, $[M_6X_{14}]^{2-}$ ($X = Cl, Br$).^{1,44,45} They are luminescent⁴⁵⁻⁴⁷ and various new properties are expected on mixing two metal ions. Trinuclear species with one capping and three bridging oxides, $M_3-(\mu_3-O)(\mu-O)_3(L)_n$, are the most common complexes with tetravalent state in aqueous media.⁴⁸ Aqua ions of both molybdenum⁴⁸ and tungsten⁴⁹ are now known. Various attempts in our laboratory to mix the two different metal ions in one unit of the triangle have not been successful so far.⁵⁰ All these species should give stable heteronuclear complexes and certainly deserve further exploration of

their preparative approaches.

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