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Charge Shift along the Metal-Metal Bond in Molybdenum-Tungsten Mixed-metal Complexes, $[M_3(\mu_3\text{-}O)_2(\mu\text{-}CH_3COO)_6(H_2O)_3]^{2+}$ (M_3 = Mo_2W and MoW_2) and $[MoW(O)_2(\mu\text{-}O)_2(\mu\text{-}N,N'\text{-edta})]^{2-}$

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An XPS study for series of dinuclear and trinuclear complexes of Mo and W including titled mixed-metal complexes and their parent homo-metal analogs shows that, in the mixed metal complexes, oxidation states of Mo and W shift to some extent toward lower and higher states than the formal ones, respectively. This is a result of charge shift along the metal-metal bond in the mixed metal clusters.

Recently, we prepared successfully Mo^{IV}-W^{IV} 1) and Mo^{V}-W^{V} 2) mixed-metal tri- or di-nuclear complexes with structures, **a** and **b**, respectively. Since the corresponding homo-nuclear complexes (Mo_3,3) W_3,4) Mo_2,5) and $W_2$6)) have been known, two series of compounds shown in Table 1 are now available (see Table 1 for abbreviation). Such a series of compounds is useful in studying fundamental aspects of metal cluster chemistry such as nature of metal-metal bonding or site selective reaction. Both series of compounds involve metal-metal bonding. Metal ions in structures **a** and **b** are in the formal oxidation state of 4+ and 5+, respectively. We wish to report here X-ray photoelectron spectra (XPS)7) of the

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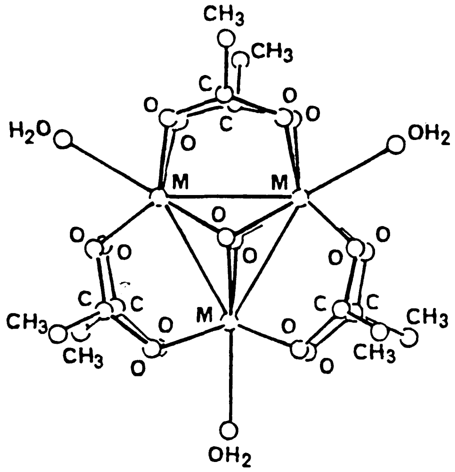
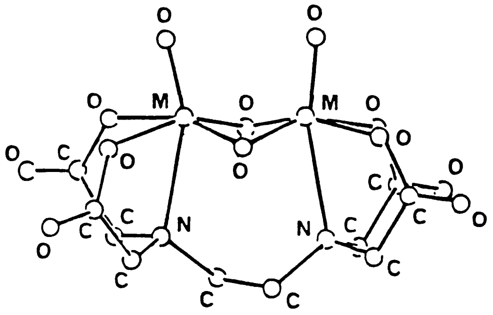


a

M_3 = Mo_3
Mo_2W
MoW_2
W_3



b

M_2 = Mo_2
MoW
W_2

Table 1. Relevant Binding Energies (eV)[a]

Structure **a** : $[M_3(\mu_3\text{-}O)_2(\mu\text{-}CH_3COO)_6(H_2O)_3]^{2+}$,[b]

M_3	Mo-$3d_{3/2}$	Mo-$3d_{5/2}$	W-$4d_{3/2}$	W-$4d_{5/2}$	W-$4f_{5/2}$	W-$4f_{7/2}$
Mo_3	234.1	231.1	—	—	—	—
Mo_2W	233.8	230.6	258.4	245.9	36.7	34.8
MoW_2	233.5	230.4	258.0	245.5	36.2	34.2
W_3	—	—	257.5	245.0	36.1	34.0

Structure **b** : $[M_2(O)_2(\mu\text{-}O)_2(\mu\text{-}N,N'\text{-edta})]^{2-}$,[c]

M_2	Mo-$3d_{3/2}$	Mo-$3d_{5/2}$	W-$4d_{3/2}$	W-$4d_{5/2}$	W-$4f_{5/2}$	W-$4f_{7/2}$
Mo_2	234.7	231.5	—	—	—	—
MoW	234.2	231.1	259.0	246.4	36.7	34.6
W_2	—	—	258.7	246.0	36.0	33.9

[a] Estimated error ± 0.15 eV. [b] Bromide mono-hydrate salt. [c] Sodium salt.

two series of cluster compounds, which provide evidence for a systematic charge shift along the metal-metal bond in the mixed metal complexes.

Table 1 collates binding energies of Mo-3d, W-4d, and W-4f for the series of compounds. It is clearly seen that there is a common systematic trend in each series of the binding energies. The binding energies of W-4d and W-4f increase as a tungsten ion is replaced successively by a molybdenum ion, that is, on going from W_3, W_2Mo to WMo_2, or on going from W_2 to WMo. On the other hand, the binding energies of Mo-3d decrease, as we go from Mo_3, Mo_2W to MoW_2 in series **a** or from Mo_2 to MoW in series **b**. The separations between Mo-$3d_{5/2}$ and Mo-$3d_{3/2}$, W-$4d_{5/2}$ and W-$4d_{3/2}$, and W-$4f_{7/2}$ and W-$4f_{5/2}$ remain essentially constant from compound to compound in each series. The observed shifts in the binding energies suggest changes in oxidation states of metal ions. In the mixed metal complexes, oxidation states of molybdenum and tungsten shift to some extent toward lower and higher states, respectively, than the formal ones.

Previous structural studies1,3,4) on the series of molybdenum-tungsten trinuclear compounds have revealed that metal-metal bond lengths are not much different in whatever combination of metal ions in triangular skelton is (W-W in W_3 2.746 Å,4) Mo-Mo in Mo_3 2.766 Å,3) W-Mo in MoW_2 2.725 Å,1) W-W in MoW_2 2.722 Å1)). Structural data of Mo_2,8) MoW,2) and $W_2$9) compounds also show very similar metal-metal bond lengths. Recently we observed similar systematic shifts in NMR chemical shifts of ^{183}W- and ^{95}Mo-nuclei for the present **a** series of complexes.10) As we go from Mo_3, Mo_2W to MoW_2 the resonance of the ^{95}Mo-nucleus shifts toward lower fields whereas the ^{183}W-nucleus resonates at higher fields on going from W_3, W_2Mo to WMo_2. There is no doubt that the behavior of the metal nuclear NMR is closely associated with the oxidation state of metal ion in the triangular skeleton.

In conclusion, it is most reasonable to consider all the present XPS observations to be a result of the charge shift along the metal-metal bond.11) Such a charge shift should be the reflection of the difference in electronegativity of the two metal ions. Thus the electronegativities of Mo(IV) and Mo(V) are higher than those of W(IV) and W(V), respectively, as far as the present series of compounds are concerned.

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7) XPS spectra were obtained on a VG ESCA LAB Mark II using Mg Kα exciting radiation at ambient temperature, the pressure being less than 10^{-9} Torr. The energy scale was calibrated by the emission from the C_{1s} (methyl or methylene carbon) line (284.6 eV).

8) The detailed crystal structural analysis of $[Mo_2(O)_2(\mu\text{-}O)_2(\mu\text{-}N,N'\text{-edta})]^{2-}$ is not available, but the closely related species, $[Mo_2(O)_2(\mu\text{-}O)_2(\mu\text{-}N,N'\text{-}R\text{-pdta})]^{2-}$ (R-pdta = (R)-propylenediaminetetraacetate) has been structurally characterized (A. Kojima, S. Ooi, Y. Sasaki, K. Z. Suzuki, K. Saito, and H. Kuroya, Bull. Chem. Soc. Jpn., 54, 2457 (1981)).

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11) We have carried out similar XPS studies on new Ru-Rh mixed metal trinuclear complex, $[Ru_2Rh(\mu_3\text{-}O)(\mu\text{-}CH_3COO)_6(\text{pyridien})_3]^{+}$.12) Data for the Ru_2Rh complex and its parent homo-metallic tri-nuclear complexes, $Ru_3$13) and Rh_3,14) suggest that the charge shift along the Rh-Ru bond is by far less, if any, in this Ru_2Rh complex.

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