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^{183}W NMR Spectra of Some Di- and Tri-nuclear Clusters of Tungsten(III), (IV), and (V)

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^{183}W chemical shifts of $[W^{III}{}_2Cl_9]^{3-}$, $[W^{IV}{}_3(O)_4(NCS)_9]^{5-}$, $[M^{IV}{}_3(O)_2(CH_3COO)_6(H_2O)_3]^{2+}$ (M_3 = Mo_3, Mo_2W, MoW_2, and W_3), and $[M^{V}{}_2(O)_4(edta)]^{2-}$ (M = Mo and W) show clear trends that the shielding at W atom increases, with an increase in the oxidation state, and upon replacement of W with Mo in a series of the mixed-metal(IV) complexes.

Chemistry of molybdenum and tungsten is very complicated since they occur in a wide range of oxidation states with preference of formation of bi- and poly-nuclear compounds.1) ^{95}Mo NMR spectroscopy has been used as a powerful tool for the investigation of electronic, structural and dynamic aspects of such a variety of molybdenum compounds.2) On the other hand, information on ^{183}W NMR spectra is scarce and limited to various monomeric W^{VI} species, W^{VI} polyacids, and monomeric carbonyl compounds of W^{0} and W^{II}.2a) In this paper, we report ^{183}W NMR data on several W^{III}, W^{IV}, and W^{V} compounds given in Table 1,3-12) along with ^{95}Mo NMR chemical shifts for relevant molybdenum complexes. All the compounds studied herein are di- or tri-nuclear complexes, and have formally metal-metal single bond(s) except for $[W_2Cl_9]^{3-}$ which is claimed to have a higher-order W-W bond.13) To our knowledge, ^{183}W NMR data on tungsten compounds with formal oxidation state +III, +IV, and +V have been reported on only few systems: $[W^{III}{}_2(t\text{-BuO})_6]$ (+4408 ppm in toluene),14) $[(C_5H_5)_2W^{IV}H_2]$ (-4663 ppm in CH_2Cl_2),15) $[W^{V}{}_2S_4(S_4)_2]^{2-}$ (+2132 ppm in $(CH_3)_2NCHO$),16) $[W^{V}{}_2OS_3(S_2CN(i\text{-Bu})_2)_2]$ (+2240 and +882 ppm in CD_2Cl_2),16) and $[W^{V}{}_2S_4(S_2CN(i\text{-Bu})_2)_2]$ (+2271 ppm in CD_2Cl_2).16)

Examples of ^{183}W and ^{95}Mo NMR spectra are shown in Fig.1.17) Table 1 lists ^{183}W and ^{95}Mo chemical shifts (δ) of the eight complexes together with the metal-metal bond distances. The ^{183}W chemical shifts are at considerably lower field (less shielded) than those of most compounds with no W-W bond.2) This is the case with dinuclear complexes having much lower oxidation states, i.e. $[W^{III}{}_2(t\text{-BuO})_6]$,14) and $[W^{II}{}_2(CF_3COO)_4]$ (+6760 ppm in tetrahydrofuran)18) with triple and quadruple metal-metal bonds, respectively.10) The same trend has been reported for ^{95}Mo chemical shifts of molybdenum complexes with Mo-Mo bond.2) The presence of metal-metal bond may have a significant effect on the chemical shift. Table 1 shows a clear trend between the oxidation state and the ^{183}W chemical shift: the shielding increases (NMR signal shifts to upfield) with an increase in

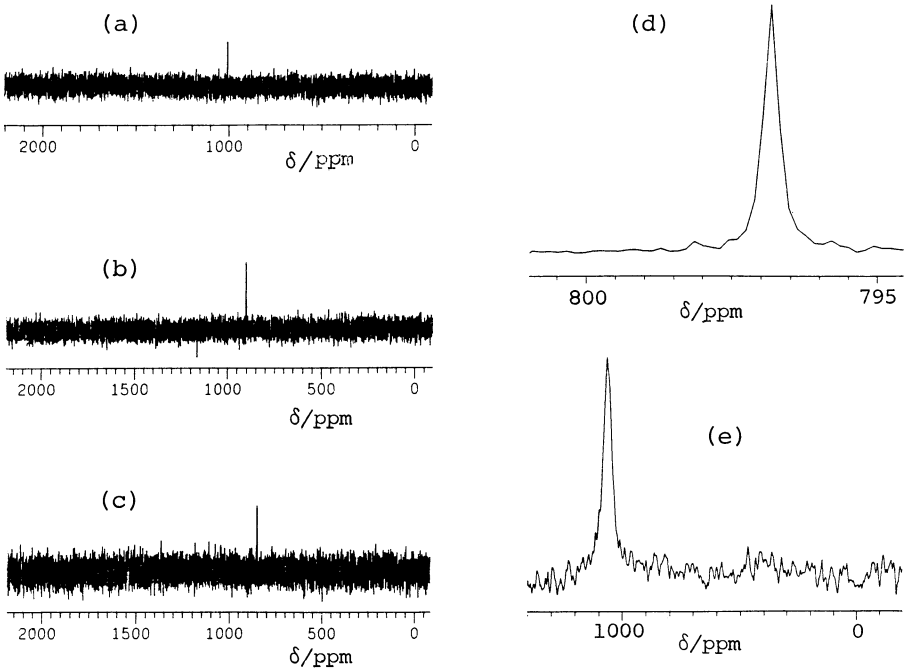

Fig.1. ^{183}W NMR at 20.84 MHz in D_2O: (a) $[W_3(\mu_3\text{-}O)_2(\mu\text{-}CH_3COO)_6(H_2O)_3]Br_2\cdot H_2O$; (b) $[MoW_2(\mu_3\text{-}O)_2(\mu\text{-}CH_3COO)_6(H_2O)_3]Br_2\cdot H_2O$; (c) $[Mo_2W(\mu_3\text{-}O)_2(\mu\text{-}CH_3COO)_6(H_2O)_3]Br_2\cdot H_2O$; (d) $Na_2[W_2(\mu\text{-}O)_2O_2(\mu\text{-}edta)]\cdot 2H_2O$. ^{95}Mo NMR at 32.59 MHz in D_2O: (e) $[Mo_3(\mu_3\text{-}O)_2(\mu\text{-}CH_3COO)_6(H_2O)_3]Br_2\cdot H_2O$.

the oxidation state. The interrelation between an oxidation state and a chemical shift seems to hold almost only for compounds with metal-metal bond. In fact, monomeric complexes of molybdenum and tungsten show a different trend.$^{2)}$

It has been pointed out that the ratio of δ(W) vs. δ(Mo) for the same type of molybdenum and tungsten complexes is remarkably constant (1.7 ± 0.1) in the wide range of monomeric M^0, M^{II} and M^{VI} compounds, and dimeric $[M^{II}{}_2(CF_3COO)_4]$.$^{19)}$ However, the ratios for $[M_2(O)_4(edta)]^{2-}$ and $[M_3(O)_2(CH_3COO)_6(H_2O)_3]^{2+}$ were found to be 1.3 and 0.95, respectively, which are by far less than the constant value. It would be most reasonable to consider the variation in the ratios to be a result of difference between molybdenum and tungsten in the extent of participation of valence electrons in metal-metal bonding.

Of particular interest is a systematic change both in ^{183}W and ^{95}Mo chemical shifts within the series of di-μ_3-oxo-hexakis(μ-acetato) complexes, **3**, **4**, **5**, and **6**. The ^{183}W chemical shift decreases on going from W_3, MoW_2, to Mo_2W. On the other hand, the ^{95}Mo chemical shift increases as we go from Mo_3, Mo_2W, to MoW_2. Metal-metal bond lengths in these compounds show clearly the presence of metal-metal bonds (Table 1). Assuming that the "chemical shift-oxidation state relationship" holds within this particular series, the observed variation in the chemical shifts may be taken as a partial change in oxidation states upon metal substitution. The oxidation states of tungsten and molybdenum in the mixed metal complexes shift to some extent toward higher and lower states, respectively, than the formal oxidation state of +IV, i.e. those of homonuclear complexes. Such a shift in oxidation state would be due to the negative charge shift from tungsten

Table 1. ^{183}W Chemical Shifts and Relevant Data of Di- and Trinuclear Cluster Complexes

Compound a)	Oxidn. state	$\delta(^{183}\mathrm{W})$ b) ppm	$\delta(^{95}\mathrm{Mo})$ c) ppm	Solvent	Concn. $\mathrm{mol\ dm^{-3}}$	M-M Å
$[W_2Cl_9]^{3-}$ (**1**)	III	3539	-	CD_3CN d)	0.074	2.44 e)
$[W_3(O)_4(NCS)_9]^{5-}$ (**2**)	IV	2063	-	CH_3CN d,f)	ca.0.05	2.54 g)
$[W_3(O)_2(CH_3COO)_6(H_2O)_3]^{2+}$ (**3**)	IV	1005	-	D_2O	0.056	2.74 h)
$[MoW_2(O)_2(CH_3COO)_6(H_2O)_3]^{2+}$ (**4**)	IV	897	1360	D_2O	0.092	2.72 i)
$[Mo_2W(O)_2(CH_3COO)_6(H_2O)_3]^{2+}$ (**5**)	IV	848	1224	D_2O	0.089	-
$[Mo_3(O)_2(CH_3COO)_6(H_2O)_3]^{2+}$ (**6**)	IV	-	1061	D_2O	0.23	2.77 j)
$[W_2(O)_4(edta)]^{2-}$ (**7**)	V	798	-	D_2O	0.49	2.55 k)
$[Mo_2(O)_4(edta)]^{2-}$ (**8**)	V	-	612 l)	D_2O	0.31	(2.53) m)

a) Samples used are: **1**, $[(n\text{-}C_4H_9)_4N]_3[W_2(\mu\text{-}Cl)_3Cl_6]$ (Ref.3); **2**, $(NH_4)_2[(C_2H_5)_4N]_3[W_3(\mu_3\text{-}O)(\mu\text{-}O)_3(NCS)_9]$ (Ref.4); **3**, $[W_3(\mu_3\text{-}O)_2(\mu\text{-}CH_3COO)_6(H_2O)_3]Br_2\cdot H_2O$ (Ref.5); **4**, $[MoW_2(\mu_3\text{-}O)_2(\mu\text{-}CH_3COO)_6(H_2O)_3]Br_2\cdot H_2O$ (Ref.6); **5**, $[Mo_2W(\mu_3\text{-}O)_2(\mu\text{-}CH_3COO)_6(H_2O)_3]Br_2\cdot H_2O$ (Ref.6); **6**, $[Mo_3(\mu_3\text{-}O)_2(\mu\text{-}CH_3COO)_6(H_2O)_3]Br_2\cdot H_2O$ (Ref.7); **7**, $Na_2[W_2(\mu\text{-}O)_2O_2(\mu\text{-}edta)]\cdot 2H_2O$ ($edta^{4-}$ = ethylenediaminetetraacetate(4-), Ref.8); **8**, $Na_2[Mo_2(\mu\text{-}O)_2O_2(\mu\text{-}edta)]\cdot 2H_2O$ (Ref.9).
b) Relative to 1.0 M Na_2WO_4 in D_2O. c) Relative to 1.0 M Na_2MoO_4 in D_2O.
d) Under nitrogen atmosphere. e) Ref.10. f) Containing 6.25% CD_3CN and 0.58 M $[(C_2H_5)_4N]NCS$. g) Ref.4. h) Ref.5. i) Both for Mo-W and W-W. Ref.6.
j) Ref.7. k) Ref.8. l) $\delta(^{95}\mathrm{Mo})$ = 609 ppm has been reported (Ref.11).
m) Data on the corresponding complex, $[Mo_2(\mu\text{-}O)_2(O)_2(\mu\text{-}R\text{-}pdta)]^{2-}$ (R-$pdta^{4-}$= (R)-propylenediaminetetraacetate(4-)). Ref.12.

to molybdenum along the metal-metal bond. In actual fact, an XPS study on the series of compounds provides a consistent evidence for this explanation.20)

Enhanced deshielding is observed for $[W_3(O)_4(NCS)_9]^{5-}$ as compared with a similar trinuclear W^{IV} complex, $[W_3(O)_2(CH_3COO)_6(H_2O)_3]^{2+}$. The shorter and therefore stronger W-W bonds may be responsible for the significantly larger chemical shift for the former than for the latter, although the influence of charge of the complex, stress of the skeletal structure, and ligand properties could not be ignored.

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Note added in proof: Recent relevant data (C.G.Young, E.M.Kober, and J.H.Enemark, Polyhedron, 6, 255 (1987); K.Piepgrass and M.T.Pope, J.Am.Chem.Soc., 109, 1586 (1987)) are consistent with our results and discussion.

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