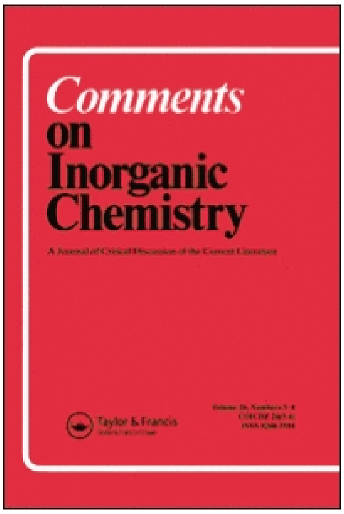

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STRUCTURE-PROPERTY RELATIONSHIPS IN POLYNUCLEAR μ-O BRIDGED AQUA CLUSTERS: EFFECT OF M-μO BOND COVALENCY

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STRUCTURE-PROPERTY RELATIONSHIPS IN POLYNUCLEAR μ-O BRIDGED AQUA CLUSTERS: EFFECT OF M-μO BOND COVALENCY

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The extent of M-μO bond covalency is the dominant factor controlling the M-μO distance, the terminal water pK_a and exchange mechanism within a range of polynuclear oxo-bridged aqueous clusters. These effects lead to limiting associative/dissociative mechanisms for water exchange on the polynuclear species.

Keywords: Oxo-bridged clusters, 170 NMR, water exchange mechanism, M-O covalency, correlation

The subject of aqua ions and their derivatives has recently received detailed attention as a self-contained subject.[1] Simple homoleptic aqua cations $[M(OH_2)_n]^{m+}$ (with $n =$ usually between 4 and 9, sometimes 10, with $m = 1–4$) are formed by most elements encompassing the s, p, d and f-blocks. However the additional and sometimes unique formation of polynuclear μ-oxo-bridged aqua derivatives is now established as central to the cationic aqueous chemistry of a large number of the heavier transition metal and main group elements. Many are formed as hydrolysis products of the homoleptic species, whilst others are driven by the tendency to form metal-metal bonds or by a stability in the higher valent states. Those polynuclear derivatives that are hydrolysis products

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frequently contain hydroxo-bridges between the metal centers whilst many others, particularly those that are formed exclusively, tend to have oxo-bridges either μ-bridging or triply μ_3-bridging and, in a few cases, μ_4- and μ_6-bridging. Detailed molecular structures of a growing number of these species have now been elucidated in recent years either by direct X-ray diffraction on crystalline derivatives or by the use of spectroscopic techniques like EXAFS. The latter, like NMR, has the added virtue of allowing measurements directly on solution species. Structural data gathered on a growing number of μ-oxo bridged dinuclear, trinuclear and tetranuclear 4d and 5d transition metal species has led to the detection of some clear structure/reactivity relationships. Those to be discussed here include electronic effects, e.g. charge distribution within M-μO bonds, thermodynamic properties such as the acidity of co-ordinated water protons (hydrolysis constants) and dynamic (kinetic) properties such as the rate and mechanism of exchange (replacement) of the co-ordinated water molecules.

(i) Trinuclear Incomplete Cuboidal μ-Oxo-Bridged Aqua Clusters

These species have the general formula $[M_3(\mu_3\text{-}X)(\mu\text{-}Y)_3(OH_2)_9]^{4+}$ and are formed by the elements niobium, molybdenum and tungsten in intermediate oxidation states having relatively low d-electron population.[2,3] They are termed *incomplete-cuboidal* since they effectively derive from a "cuboidal" $M_4(\mu_3\text{-}X,Y)_4$ structure with one corner M atom missing. Each has a triangle of M atoms with M-M distances (248–276 pm), implying a degree of M-M bonding. The μ_3-X capping atom sits above the M_3 triangle and can be O, Cl, S, Se or Te. The Y atoms, which bridge each of the M-M separations, lie below the M_3 plane, forming a kind of puckered six-atom ring with the three M atoms. Y can be O, S, Se or Te. The species of focus here has $X = Cl$, O or S with $Y = O$. Finally, each M atom is coordinated to three water molecules. The niobium cluster ($X = Cl$) is prepared either via hydrolysis of trivalent $\{NbCl_3(1,2\text{-dimethoxyethane})\}_n$ in aqueous HCl[3] or by zinc metal reduction of $\{NbCl_5\}_n$ in ethanolic HCl.[4] In each case the cluster ion is separated and purified by cation-exchange chromatography. Subsequent Nb K-edge EXAFS and $^{17}O(^{93}Nb)$ NMR studies have established that the trinuclear mixed-valence Nb(III,IV,IV) cation $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3(OH_2)_9]^{4+}$, Figure 1A, is present.[3,5] The bond distances and angles shown in Figure 1A are those established by Nb K-edge EXAFS.

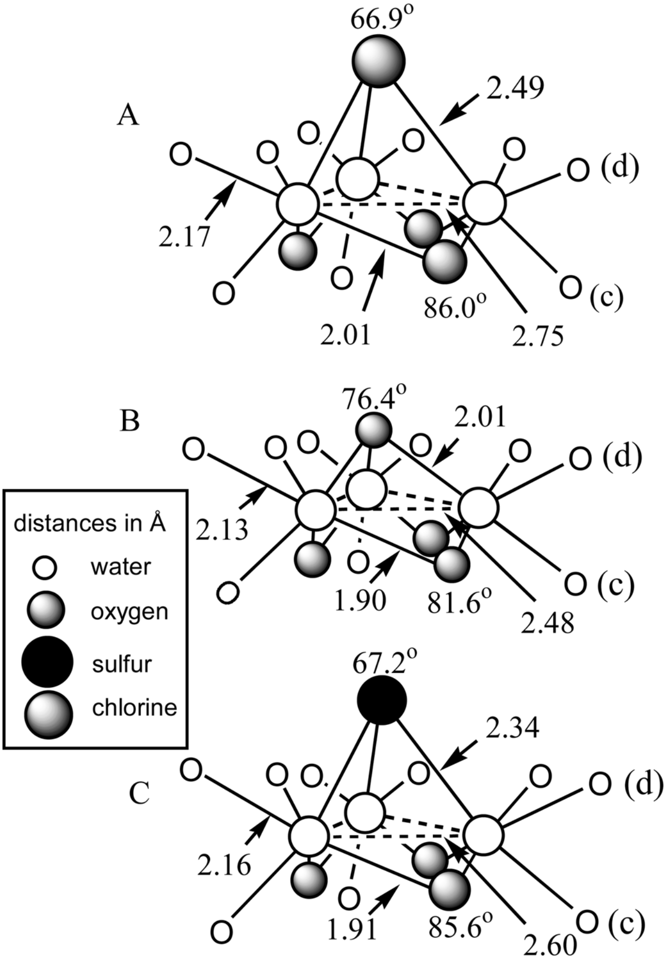

Figure 1. Structures of the incomplete cuboidal trinuclear cluster cations; **A** $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3(OH_2)_9]^{4+}$; **B** $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(OH_2)_9]^{4+}$; and **C** $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3(OH_2)_9]^{4+}$ (data from X-ray diffraction[8] or M Kedge EXAFS[5,7,9]).

For the molybdenum and tungsten clusters, details of their synthesis and characterization has been reported extensively in previous articles and reviews.[1,6] Structural data on the oxo-bridged cation, $[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(OH_2)_9]^{4+}$, Figure 1B, has been successfully elucidated by both Mo K-edge EXAFS[7] and X-ray diffraction,[8] whereas the structure of the μ_3-S bridged derivative, $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3(OH_2)_9]^{4+}$, Figure 1C, has been deduced from Mo K-edge EXAFS measurements[9] in comparison with the X-ray structures of several water ligand substituted derivatives.[10] In the two Mo species substitution of μ_3-O by μ_3-S increases the M-M separation (from 248 pm to 260 pm), which in turn opens up the M-O-M angle from 81.6° to 85.6° since the M-O(μ) distance is essentially unchanged. Both of the molybdenum clusters above are also formed by tungsten but here no structural data is directly available on the aqua ions so the cluster core parameters have been deduced solely from data on water ligand substituted derivatives. For the all oxo core $W_3(\mu_3\text{-O})(\mu\text{-O})_3{}^{4+}$,[11] both the M-M and M-O(μ) distance are somewhat longer than in the case of M = Mo (252 pm vs. 248 pm and 195 pm vs. 190 pm, respectively) leading to a slightly tighter M-O-M angle (80.5°). For the $W_3(\mu_3\text{-S})(\mu\text{-O})_3{}^{4+}$ core the longer M-M distance (262 pm) again leads to an opening up of the M-O-M angle to 83.5° since the M-O(μ) distance remains essentially unchanged (196 pm).[12] The result is that the various trinuclear clusters provide a range of M-O(μ) distances, 201 pm (Nb), 195 pm (W) and 190 pm (Mo) with which to investigate possible structure/property relationships. It is recognized that in some instances the bond distance between two atoms can provide an indication of the degree of covalency, the shorter the bond length, the greater the covalency, especially when one relates it to the sum of the ionic radii. Increasing covalency should lead to a reduction in effective positive charge at the metal atoms due to a delocalization of electron density from O to M. A powerful technique for probing local atomic electron density is NMR. Since the oxo group is the common atom for comparison between these clusters, the ^{17}O NMR chemical shift of the μ-oxo oxygen is the parameter of choice. Fortunately the ^{17}O NMR shift (vs free H_2O) for the μ-oxo oxygen on each of the above aqua clusters has been measured on enriched derivatives, 305 ppm ($Nb_3(\mu_3\text{-Cl})(\mu\text{-O})_3{}^{4+}(aq)$),[3] 797 ppm ($Mo_3(\mu_3\text{-O})(\mu\text{-O})_3{}^{4+}(aq)$)[7a] and 560 ppm ($W_3(\mu_3\text{-O})(\mu\text{-O})_3{}^{4+}(aq)$).[13] Thus a clear trend emerges with increasing covalency in M-O(μ) indicated by the increasingly less shielded oxo group Nb < W < Mo paralleling the decrease in M-O(μ) bond length. Thus the relative amount of positive charge placed on M decreases in the order Nb > W > Mo.

One now asks if data are available on other μ-O polynuclear species to see if the correlation continues? The answer is yes. We now consider below available data in regard to several dinuclear and tetranuclear oxo-bridged clusters.

(ii) Tetranuclear $[Ru_4(\mu\text{-}O)_6(OH_2)_{12}]^{4+}$

Red-brown aqua Ru(IV) ion has been known since the 1950s but only recently has the tetranuclear cationic core structure been elucidated. Ru K-edge EXAFS measurements indicate the presence of an adamantanoidal $Ru_4(\mu\text{-}O)_6{}^{4+}$ core with a single μ-O bridge between each Ru atom.[14] The structure of the ion is shown in Figure 2. The shorter Ru-O(μ) distance (183 pm), compared with the Mo, W and Nb clusters above, suggests increased covalency and, if the correlation above continues, should be reflected in a ^{17}O NMR shift for μ-O of ~1100 ppm. The experimentally determined value is 1150 ppm.[15] Figure 3 indeed shows that for the four clusters A–D, Figures 1 and 2, an excellent linear correlation (coeff. 0.9985) is found for the M-O(μ) distance and the ^{17}O NMR shift for μ-O with a 20 pm drop in M-O(μ) distance correlating with an 800 ppm downfield NMR shift for μ-^{17}O.

Thus the trend in covalence in M-O(μ) becomes: Nb < W < Mo < Ru and it can be concluded that for similarly charged μ-oxo bridged metal clusters the extent of covalence in M-O(μ) increases from left to right across a period but decreases down a group. The higher covalence of Ru-O(μ) in $Ru_4O_6{}^{4+}$ (aq) is also reflected by a larger Ru-O(μ)-Ru

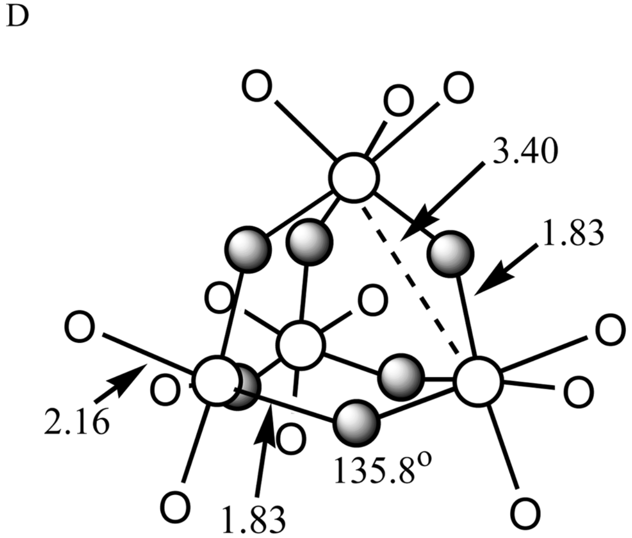

Figure 2. Structure of the Ru^{IV} cluster D $[Ru_4(\mu\text{-}O)_6(OH_2)_{12}]^{4+}$ (data from Ru Kedge EXAFS[14]).

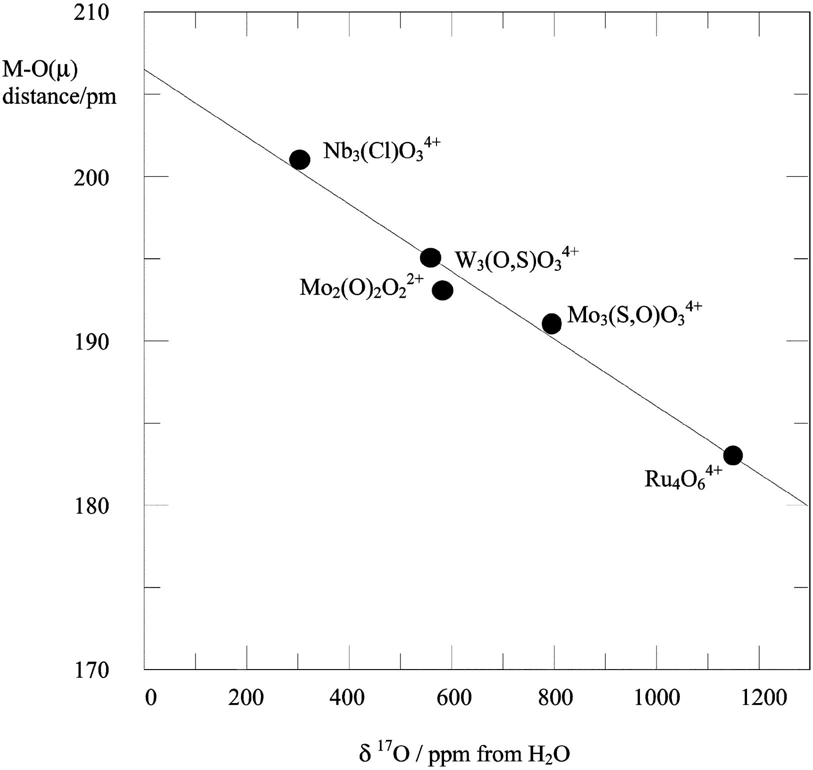

Figure 3. Plot of the M-O(μ) distances (pm) versus the μ-^{17}O chemical shift (ppm from free water) for the μ-O bridged cluster ions A–E.

angle (135.8°),[14] presumably encouraging a degree of d_π-p_π overlap. The Ru-O(μ) distance is also significantly shorter than the sum of the Shannon ionic radii for Ru^{4+} and O^{2-} (197 pm).[16]

(iii) Dinuclear Oxo-Bridged Aqua Ions

The case of three dimeric di-μ-oxo ions $[(MX_t)_2(\mu\text{-}O)_2(OH_2)_6]^{2+}$ (M = Mo^V, W^V; X_t = O and M = Tc^{VI}; X_t = N), Figure 4, is now considered. The ^{17}O NMR shift for the μ-O groups of the aqua dimer $[(MoO_t)_2(\mu\text{-}O)_2(OH_2)_6]^{2+}$ has been measured (582 ppm),[17] which predicts a value from Figure 3 for the Mo-O(μ) distance of 195 pm. The optimum distance obtained from Mo K-edge EXAFS measurements

E

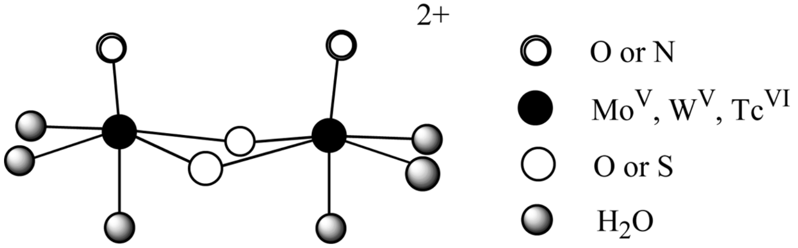

Figure 4. Structure of the dimeric μ-O ions E $[(MX)_2(\mu\text{-}O)_2(OH_2)_6]^{2+}$ ($M = Mo^V$, W^V, $X = O$; $M = Tc^{VI}$, $X = N$).

on the aqua ion and from X-ray measurements on derivatives of the $(MoO_t)_2(\mu\text{-}O)_2{}^{2+}$ core (193 pm)[18] is indeed close to this value within experimental error. Thus knowledge of the Mo-O(μ) distance does appear capable of predicting the ^{17}O NMR chemical shift of μ-O within ±30 ppm or vice versa the Mo-O(μ) distance within ±2 pm. Similar values ~600 ppm are therefore predicted for the ^{17}O NMR shift of μ-O in the case of the clusters $[(MX_t)_2(\mu\text{-}O)(\mu\text{-}Y)(OH_2)_6]^{2+}$ ($M = Mo^V$, $X_t = O$, $Y = S$;[19] $M = W^V$, $X_t = O$, $Y = O$ or S[20] and $M = Tc^{VI}$; $X_t = N$, $Y = O$[21]) on the basis of a largely similar M-O(μ) distance (in derivative complexes) to that in $[(MoO_t)_2(\mu\text{-}O)_2(OH_2)_6]^{2+}$. However, these chemical shifts have yet to be measured.

(iv) Structure-Reactivity Correlations

(a) Water Ligand Acidity. The degree of covalency in the M-O(μ) reflects the extent of local positive charge on the M atom in the cluster. This should manifest itself in other properties, for example, the observed acidity of the co-ordinated water protons (pK_a value). For the tetrapositive clusters the trend above predicts that the Nb cluster $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3(OH_2)_9]^{4+}$ should have the most acidic water protons with $[Ru_4(\mu\text{-}O)_6(OH_2)_{12}]^{4+}$ having the least acidic with the trinuclear Mo and W clusters somewhat intermediate. This is exactly what is observed experimentally. $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3(OH_2)_9]^{4+}$ hydrolyses even in solutions where $[H^+] = 1.0\,mol\ dm^{-3}$ indicating a $pK_a < 0$[3] whereas $[Ru_4(\mu\text{-}O)_6(OH_2)_{12}]^{4+}$ shows no tendency to hydrolyze below pH 2 ($pK_a > 2$).[15] Finally, the experimentally determined pK_a values for the

$[M_3(\mu_3\text{-}X)(\mu\text{-}O)_3(OH_2)_9]^{4+}$ clusters (M = Mo, W; X = S or O) have the expected intermediate values of between 0.2–0.7.[9,22,23] In all cases measured the M-OH_2 distance shows little or no variation.

Thus the first main conclusion from these findings for the polynuclear species is:

> For a given overall charge, the degree of covalence in the bonds to the μ-oxo groups in polynuclear μ-oxo-bridged aqua metal cations affects the local positive charge on the metal center to the extent of governing the acidity of coordinated water protons: the more covalent the M-O(μ) bond the lower the effective local positive charge on M and the less acidic are the water protons (higher pK_a) and vice-versa.

Table 1 summarizes the important parameters under discussion for the various clusters considered here.

(b) Terminal Water Ligand Exchange. The effective local positive charge on M should influence the mechanism of exchange (replacement) of the coordinated terminal water ligands. One could make a simple rationale that the higher the local positive charge on M the greater will be the attraction to the entering water and the more associative should be the mechanism of exchange (replacement) with a significant incoming ligand participation towards the formation of the transition state. Conversely the lower the charge on M the more dissociative the mechanism should be with little incoming ligand participation. Here the bond energy to the leaving water makes up the bulk of the observed activation energy. Is this the case? The answer is again yes based on findings from variable temperature ^{17}O NMR studies. The water exchange process on $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3(OH_2)_9]^{4+}$ is characterized by a very low $\Delta H^{\neq}$ value (37 kJ mol^{-1}) and a significantly negative $\Delta S^{\neq}$ value (–72 J K^{-1} mol^{-1}).[3] Furthermore hydroxo forms are not kinetically significant as evident from no significant rate acceleration on lowering the $[H^+]$. Similar parameters/behavior characterize water ligand substitution on low d-electron hexaaqua ions such as $[Ti(OH_2)_6]^{3+}$, $[V(OH_2)_6]^{3+}$ and $[Mo(OH_2)_6]^{3+}$, for which there is considerable evidence supporting an associative mechanism.[1,2,24] Activation parameters for water exchange on $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3(OH_2)_9]^{4+}$ ($\Delta H^{\neq}$ 81 kJ mol^{-1}, $\Delta S^{\neq}$ +59 J K^{-1} mol^{-1}), and $[Ru_4(\mu\text{-}O)_6(OH_2)_{12}]^{4+}$ ($\Delta H^{\neq}$ 85 kJ mol^{-1}, $\Delta S^{\neq}$ +65 J K^{-1} mol^{-1}), on

Table 1. Selected parameters for various m-oxo-bridged metal clusters

Cluster	d-elect/M	M-μ ^{17}O/ppm	M-M/pm	M-μ-O/pm	M-O-M	M-OH_2/pm	pK_a (H_2O)	Ref.
Dinuclear								
$[(MoO)_2(\mu\text{-}O)_2(OH_2)_6]^{2+}$	1.00	582	256	193	83.1	?	>2	[17,18]
$[(MoO)_2(\mu\text{-}O)(\mu\text{-}S)(OH_2)_6]^{2+}$	1.00	?	269	195	87.5	?	>2	
$[(WO)_2(\mu\text{-}O)_2(OH_2)_6]^{2+}$	1.00	?	255	191	83.6	?	>2	
$[(TcN)_2(\mu\text{-}O)_2(OH_2)_6]^{2+}$	1.00	?	254	194	84.0	?	>2	[21]
Trinuclear								
$[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3(OH_2)_9]^{4+}$	1.33	305	275	201	86.0	217	<0	[3,5]
$[Mo_3(\mu_3\text{-}O)(\mu\text{-}O)_3(OH_2)_9]^{4+}$	2.00	797	248	190	81.6	213	<1	[8,17,22]
$[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3(OH_2)_9]^{4+}$	2.00	?	260	191	85.6	216	<1	[9,10]
$[W_3(\mu_3\text{-}O)(\mu\text{-}O)_3(OH_2)_9]^{4+}$	2.00	560	$252^{a,b}$	$195^{a,b}$	$80.5^{a,b}$	?	<1	[11,13]
$[W_3(\mu_3\text{-}S)(\mu\text{-}O)_3(OH_2)_9]^{4+}$	2.00	?	$261^{c,d}$	$196^{c,d}$	$83.5^{c,d}$	?	<1	[12]
Tetranuclear								
$[Ru_4(\mu\text{-}O)_6(OH_2)_{12}]^{4+}$	4.00	1150	340	183	135.8	216	~2?	[14,15]

[a] based on the X-ray structure of $(NH_4)_5[W_3O_4F_9]$.[11c]

[b] based on the X-ray structure of $Na_2Ga_2[W_3O_4(O_2CEt)_8]_2$.[11a]

[c] based on the X-ray structure of $[W_3O_3S(Hnta)_3]^{2-}$.[12b]

[d] based on the X-ray structure of $[W_3O_3S(NCS)_9]^{5-}$.[12a]

the other hand, are consistent with a mechanism more dissociative in character.[9,15] Indeed for the incomplete cuboidal Mo and W clusters the kinetic studies reveal evidence of dominant participation from labilizing hydroxo-aqua ions reminiscent of the water ligand replacement behavior on the more electron-rich aqua ions of trivalent Fe, Ru, Rh, Ir and Ga.[1,2,24]

Thus, the second conclusion from these findings is that:

> the degree of covalence in the bonds to the μ-oxo groups in polynuclear μ-oxo-bridged aqua metal cations affects the local positive charge on the metal center to the extent of governing the mechanism of coordinated water ligand replacement: the more covalent the M−O(μ) bond the lower the effective local positive charge on M and the more dissociative the mechanism and vice-versa.

As a consequence, despite the higher pK_a, the dominant participation of hydroxo ions in water exchange is predicted for $[Ru_4(\mu\text{-}O)_6(OH_2)_{12}]^{4+}$, but so far the process has only been measured at a single $[H^+]$ value ($0.02\,mol\,dm^{-3}$) so this has yet to be confirmed. These results, however, show there is no link between the pK_a value and participation from hydroxo ions in the mechanisms of water ligand replacement. The water ligands of $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3(OH_2)_9]^{4+}$ are the most acidic yet hydroxo species play no role in the kinetics of water ligand replacement because of the associative nature of the mechanism.

(iv) Mononuclear Aqua Ions

Water exchange kinetic data (k_{H_2O}, $\Delta H^{\neq}$, $\Delta S^{\neq}$, $\Delta V^{\neq}$) is now available for ~30 homoleptic aqua and aquapentammine ions across the periodic table representing the s, p, d and f-blocks.[1,2,24] For 22 of the aqua and aquapentammine ions, a plot of log k_{H_2O} versus $\Delta H^{\neq}$ for the process is a straight line with an excellent correlation coefficient of 0.9953, Figure 5. This indicates that the rate of water exchange for these ions is largely controlled by the activation enthalpy, which in turn correlates with the energy involved in breaking the bond to one of the resident water ligands. Thus the fastest rates of exchange are found where the bond to the resident waters is especially weak, as in the case of low charged group 1 metals such as Cs^+, Jahn-Teller distorted centers such as Cr^{2+} and Cu^{2+} and poorly coordinated large metals such as Hg^{2+} and the Ln^{3+} ions.

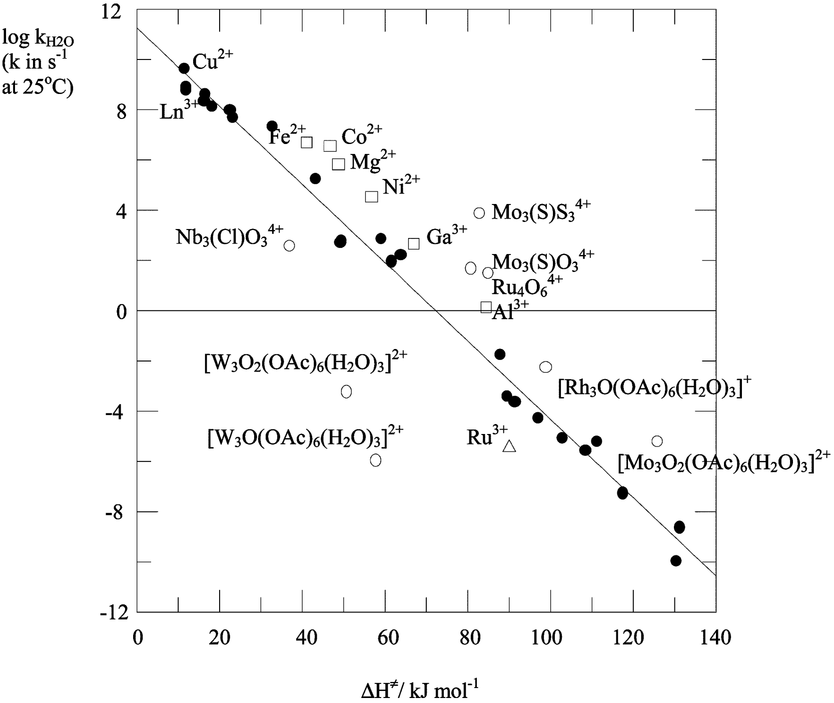

Figure 5. Plot of log k_{H_2O} (k_{H_2O} at 25°C in s^{-1}) versus $\Delta H^{\neq}{}_{H_2O}$ (kJ mol^{-1}) for water exchange on 30 homoleptic aqua and aquapentammine ions (filled circles, open squares and open triangles) along with cluster aqua ions A–G (open circles).

The slowest rates are where the bond to the leaving water is especially strong, such as in the case of high charged d-metals such as Cr^{3+} and the low spin ions of Ru^{3+}, Rh^{3+}, and Ir^{3+}, each with high degrees of associated LFSE.

The situation regarding Figure 5 becomes more interesting, however, when the oxo-bridged aqua clusters are considered. In addition to the clusters mentioned above, we include parameters here for water exchange on several μ_3-oxo-capped μ-acetato trimetal aqua species, $[M_3(\mu_3\text{-}O)_x(\mu\text{-}O_2CCH_3)_6(OH_2)_3]^{2+}$ (M = Mo or W, x = 1 or 2),[25] Figure 6.

The parameters ($\log k_{H_2O}$ and $\Delta H^{\neq}$) for water exchange on $[Nb_3(\mu_3\text{-}Cl)(\mu\text{-}O)_3(OH_2)_9]^{4+}$[3] and on the two tritungsten complexes; $[W_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_6(OH_2)_3]^{2+}$[26] and $[W_3(\mu_3\text{-}O)_2(\mu\text{-}O_2CCH_3)_6(OH_2)_3]^{2+}$[26] each lie significantly off the correlation line of Figure 5 to the LHS, indicating the presence of a relatively low value for the

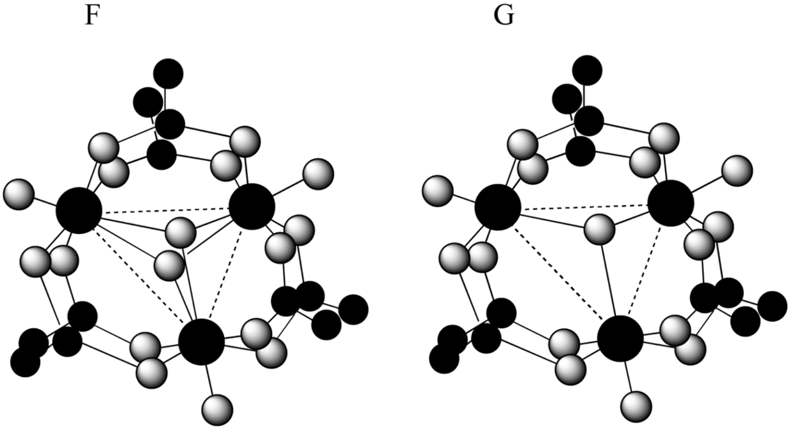

Figure 6. Structure of the μ-acetato-oxo-bridged trinuclear clusters: F$[M_3(\mu_3\text{-}O)_2(\mu\text{-}O_2CCH_3)_6(OH_2)_3]^{2+}$ (M = Mo, W) and G $[W_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_6(OH_2)_3]^{2+}$.

activation enthalpy compared to the observed exchange rate constant. Water exchange on each of these complexes has a significantly large negative activation entropy (range –72 to $-164\,J\ K^{-1}\ mol^{-1}$) and so one concludes that water exchange here operates with significant incoming water ligand participation in a contracted transition state highly associative in character. On the other hand parameters for the clusters, $[Mo_3(\mu_3\text{-}S)(\mu\text{-}O)_3(OH_2)_9]^{4+}$,[9] $[Mo_3(\mu_3\text{-}S)(\mu\text{-}S)_3(OH_2)_9]^{4+}$[27] and $[Ru_4(\mu\text{-}O)_6(OH_2)_{12}]^{4+}$[15] along with the μ-acetato clusters $[Mo_3(\mu_3\text{-}O)_2(\mu\text{-}O_2CCH_3)_6(OH_2)_3]^{2+}$[26] and $[Rh_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_6(OH_2)_3]^{+}$[28] lead to points lying well to the RHS of the correlation line with a relatively high activation enthalpy for their rates of exchange. Moreover each is characterized by a significantly positive activation entropy (range $+43$ to $+77\,J\ K^{-1}\ mol^{-1}$). Here one concludes that a limiting or close to limiting dissociative mechanism is relevant with little incoming ligand participation.

These mechanistic conclusions correlate with the predictions based upon the magnitude of the local positive charge on M as defined by the degree of covalency in the bonds to the $\mu\text{-}O^{2-}$ (or $^{-}O_2CCH_3$) ligands. Thus, unlike simple mononuclear aqua ions, these parameters in cluster aqua ions affect the local charge on M to the extent of affecting the acidity of the terminal water ligand protons and the mechanism of terminal water ligand exchange, which is associative for O-bridged clusters with more ionic $M\text{-}\mu O^{2-}$ $(\mu\text{-}O_2CCH_3^-)$ bonds (higher charge on M)

(M = Nb, W) but dissociative for O-bridged clusters with more covalent M-μO^{2-} (μ-$O_2CCH_3^-$) bonds (lower charge on M) (M = Mo, Ru, Rh). The inclusion of data for $[Rh_3(\mu_3\text{-}O)(\mu\text{-}O_2CCH_3)_6(OH_2)_3]^+$ (planar μ3-O and absence of M-M bonding)[28] emphasizes the dominant effect from the μ-ligands.

Finally, one now asks whether similar conclusions can be drawn from Figure 5 regarding the mechanistic behavior of simple mononuclear aqua ions? The hexaaqua ions of Mg^{2+}, Fe^{2+}, Co^{2+}, Ni^{2+}, Ga^{3+} and Al^{3+} (Figure 5 open squares) each lie distinctly to the RHS of the correlation line. Furthermore each is characterized by a significantly positive value for the water exchange activation volume (+4 to +7 cm^3 mol^{-1}) and, for Co^{2+}, Ni^{2+} and Al^{3+}, the largest positive activation entropy (+37 J K^{-1} mol^{-1} (Co^{2+}), +32 (Ni^{2+}) and +42 (Al^{3+})). While it is tempting to conclude that metal aqua ions lying significantly to the RHS of the line follow dissociative water exchange paths, the situation is not so clear cut for mononuclear homoleptic aqua ions wherein an associative pathway is indicated from activation volume measurements and supported by theoretical studies.[24] Thus the points for Be^{2+} ($\Delta V^{\neq}_{ex}$ –13.6 cm^3 mol^{-1}), Ti^{3+} ($\Delta V^{\neq}_{ex}$ –12.1 cm^3 mol^{-1}), V^{3+} ($\Delta V^{\neq}_{ex}$ −8.9 cm^3 mol^{-1}) and Cr^{3+} ($\Delta V^{\neq}_{e}$ −9.6 cm^3 mol^{-1}), along with Pd^{2+} ($\Delta V^{\neq}_{ex}$ −2.2 cm^3 mol^{-1}), Pt^{2+} ($\Delta V^{\neq}_{ex}$ −4.6 cm^3 mol^{-1}), Rh^{3+}, ($\Delta V^{\neq}_{ex}$ −4.2 cm^3 mol^{-1}), Ir^{3+} ($\Delta V^{\neq}_{ex}$ −5.7 cm^3 mol^{-1}) and the heavier lanthanide 3+ ions ($\Delta V^{\neq}_{ex} \sim -6$ cm^3 mol^{-1}), all lie pretty well on the line of correlation with values for the activation entropy lying either side of zero (range –26 to +29 J K^{-1} mol^{-1}). The one exception seems to be $[Ru(OH_2)_6]^{3+}$ ($\Delta V^{\neq}_{ex}$ −8.3 cm^3 mol^{-1}), whose point lies distinctly to the LHS of the correlation line (open triangle). Interestingly this ion has the most negative activation entropy (–48 J K^{-1} mol^{-1}) of all the measured homoleptic hexaaqua species. In the absence of water exchange data for $[Co(OH_2)_6]^{3+}$ and $[Mo(OH_2)_6]^{3+}$, we speculate as to whether water exchange on $[Ru(OH_2)_6]^{3+}$ is the best established example to date of the process taking place at, or close to, the associative limit?

Thus the final conclusion stemming from these observations is as follows:

> The line of least squares representing a plot of log k_{H_2O} for water exchange on 22 homoleptic aqua and aquapentammine ions across the s, p, d and f-blocks versus the activation enthalpy $\Delta H^{\ddagger}$ for

> exchange divides a region of limiting dissociative behavior to the RHS of the line from a region of limiting associative behavior to the LHS.

Given the behavior of the μ-oxo-bridged cluster aqua ions of Nb, Mo, W, and Ru in regard to Figure 5, measurement of the water exchange activation volumes on these and on the μ-acetato clusters $[M_3(\mu_3\text{-}O)_x(\mu\text{-}O_2CCH_3)_6(OH_2)_3]^{2+}$ (M = Mo or W, x = 1 or 2) is now of much interest as reflecting possible examples of aqua complexes each following limiting associative (or dissociative) water exchange mechanisms.

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