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Structural Elucidation of Oligomeric Aqua-molybdenum Cations in Solution by ^{17}O NMR

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Abstract

^{17}O NMR spectra are reported for three diamagnetic oligomeric aquamolybdenum cations: $[Mo_2(yl\text{-}O)_2(\mu_2\text{-}O)_2(H_2O)_6]^{2+}$ (Mo(V)), $[Mo_3(\mu_3\text{-}O)(\mu_2\text{-}O)_3(H_2O)_6(H_2O)_3]^{4+}$ (Mo(IV)) and $[Mo_2(\mu_2\text{-}OH)_2(H_2O)_8]^{4+}$ (Mo(III)) enriched with ^{17}O in non-complexing aqueous solution. The chemical shifts and peak integrations provide the first direct definitive evidence for the presence of these structural units in solution.

Introduction

Molybdenum is unique for a d-block element in possessing cationic aqua ion derivatives characteristic of five oxidation states (Table I) [1]. Fueled by the further knowledge that this metal is an essential component of at least ten redox enzymes**, a considerable number of detailed studies aimed at the mechanisms governing both redox [3] and water ligand substitution [4] reactions on its fundamental aqueous solution species have been carried out within the past decade. Despite this wealth of interest, the exact solution structures of these ions have been inferred principally by indirect methods such as ion-exchange behaviour [5], comparative electronic spectral properties [6], kinetic [7] and electrochemical [8] studies, and the use of oxygen-18 isotopic labelling [9]. This latter technique requires a comparison with a rapidly formed and structurally characterized solid derivative in which the water ligands are replaced. When oxygen exchange with bulk water is slow ($t_{1/2} \sim$ hours), solution structures can be inferred by this method with reasonable certainty [10].

Oligomeric aqua ion derivatives are notoriously difficult to crystallize as covalent hydrates for X-ray diffraction analysis and the molybdenum ions are no exception. The use of EXAFS spectroscopy has succeeded in showing that oligomeric species are present [11] and in providing a measure of the number and distance of closest metal–metal and metal–oxygen contacts. The technique has however proved difficult for the exact assignment of structures in some cases [12]. One desires a more definitive solution structural probe.

The extensive work of Klemperer [13–16] has shown ^{17}O NMR spectroscopy to be a powerful tool

TABLE I. The Aqua Ions of Molybdenum

Oxidation state		Formula	Description	Colour
+2		$Mo_2(H_2O)_8{}^{4+}$	M≡M dimer	bright red
+3		$Mo(H_2O)_6{}^{3+}$	monomer	pale yellow
		$Mo_2(OH)_2(H_2O)_8{}^{4+}$	dimer	blue–green
		probably $Mo_3(OH)_4(H_2O)_{9\text{ or }10}{}^{5+}$	trimer	green
+4		$Mo_3O_4(H_2O)_9{}^{4+}$	trimer	red
+5		$Mo_2O_4(H_2O)_6{}^{2+}$	dimer	yellow–orange
+6	$pH > 7.0$	$MoO_4{}^{2-}$	monomer	colourless
	$pH < 7.0$	$Mo_7O_{28}{}^{6-}/Mo_8O_{24}{}^{4-}$	polymers	colourless
	$pH < 1.0$	$HMoO_3{}^{+}/H_2Mo_2O_6{}^{2+}$	monomer/dimer	colourless

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**See for example the series of papers under ref. 2.

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for probing both structural and dynamic aspects of oligomeric oxo-ions in solution [13]. Furthermore it was found possible to assign a chemical shift scale for the different oxygen atom environments in a given system [14] and to monitor the effects of protonation [15]. Surprisingly, there has so far been little attempt to extend the technique to the oligomeric oxo-cations of molybdenum. We report herein a structural ^{17}O NMR study of three diamagnetic oligomeric species representative of oxidation states (V), (IV) and (III) of molybdenum. We also give preliminary results of the oxygen exchange rates on these species.

Experimental

The ^{17}O NMR spectra were obtained at 54.2 MHz on a Bruker AM-400 spectrometer, in sealed 10 mm tubes. The number of scans was between 30 000 and 200 000 using repetition rates of 7–20 ms and pulse length of 12 μs (90° pulse $\simeq 15$ μs) in the quadratic detection mode. $1–2 \times 10^3$ data points were used over total spectral widths of 50–83 kHz without exponential filtering. A correction function was applied to eliminate the rolling of the base-line due to accoustic ringing. To suppress the large bulk water signal, Mn^{2+} was added to all solutions; this ion is acting as a very efficient relaxation agent for the bulk water oxygen because of its long electron relaxation time and its very fast coordinated/bulk water exchange rate. The chemical shifts are referenced to neat water; bulk susceptibility corrections have been taken into account. Oxygen-17 enriched water (*ca.* 10 atom %, normalised in ^1H) was from Yeda, Israel.

Results and Discussion

The yellow orange dimeric Mo(V) ion, $[Mo_2(yl\text{-}O)_2(\mu_2\text{-}O)_2(H_2O)_6]^{2+}$, was prepared by reduction of Mo(VI) in acidic solution with hydrazine as described previously [17]. Solutions were prepared by elution from a DOWEX 50W X2 column with 2 M CF_3SO_3H. A 1.0 cm^3 sample of the Mo(V) solution was then combined with 1.0 cm^3 of $H_2{}^{17}O$ (10 atom %) containing $[Mn(H_2O)_6](CF_3SO_3)_2$, and then kept at 50 °C for 12 h. This caused isotopic equilibration between the oxygen atoms in the Mo(V) dimer and bulk water. Figure 1(i) shows the ^{17}O NMR spectrum of this solution. The yl-oxygens are clearly observed at the highest downfield shift from free water, at 964 ppm (Table II). This is in the range 900–1100 ppm normally expected for an yl oxygen [13, 18]. As expected the bridging μ_2-oxygens resonate at a higher field, 582 ppm [15]. The peak integrations are in a 1:1 ratio, in agreement with the dimeric structure suggested previously [5].

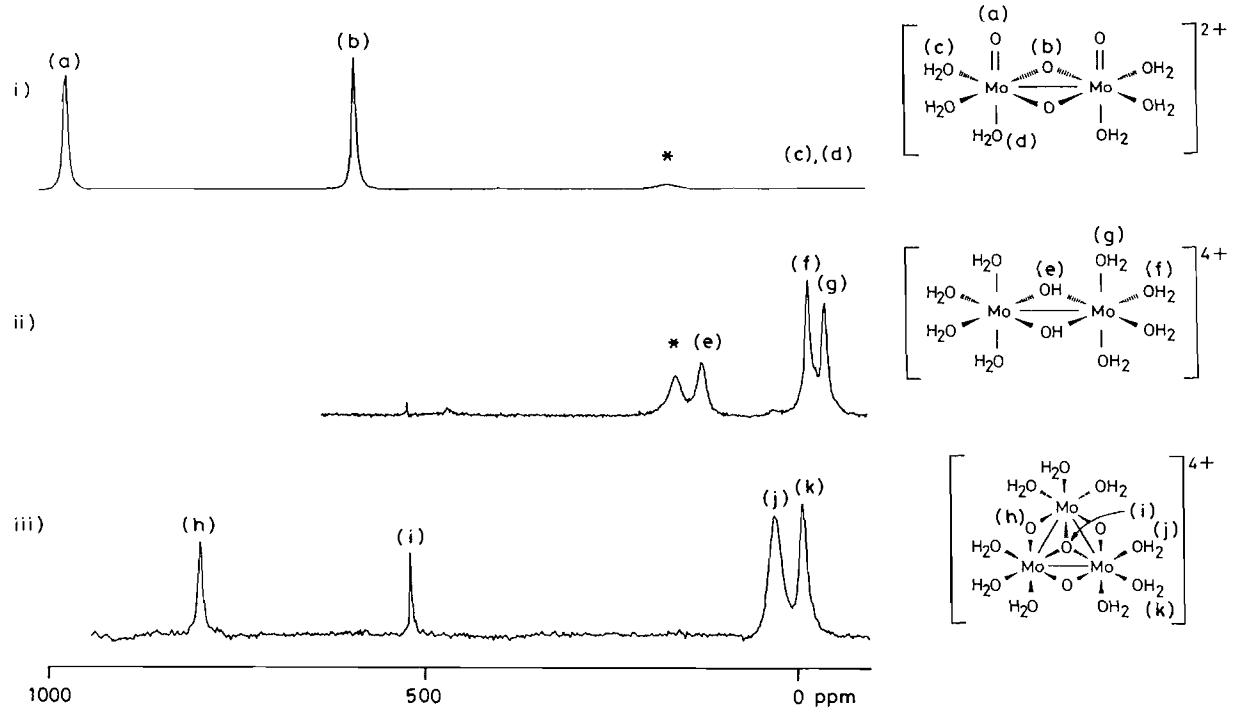

Fig. 1. 54.2 MHz ^{17}O NMR spectra at 25 °C of: (i) 0.075 M $Mo_2O_4{}^{2+}$, 0.975 M CF_3SO_3H, 0.1 M Mn^{2+}, $\mu = 1.33$ M, $H_2{}^{17}O$ (5.0 atom %); (ii) 0.05 M $Mo_2(OH)_2{}^{4+}$, 1.30 M CF_3SO_3H, 0.064 M Mn^{2+}, $\mu = 2.23$ M, $H_2{}^{17}O$ (3.3 atom %); (iii) 0.013 M $Mo_3O_4{}^{4+}$, 0.44 M $p\text{-}CH_3C_6H_4SO_3H$, 0.11 M Mn^{2+}, $\mu = 0.71$ M, μ_2- and μ_3-^{17}O (3.3 atom %) and $H_2{}^{17}O$ (4.0 atom %). * = $CF_3SO_3{}^-$.

TABLE II. Oxygen-17 Chemical Shifts and Approximate Exchange Half Lives for Oligomeric Aqua Ions of Molybdenum in Non-complexing Acidic Solution

Ion	Type of oxygen		Chemical shift[a] (ppm)	Exchange half-life (25 °C)
$[Mo_2O_4(H_2O)_6]^{2+}$	yl	(a)	964	3–4 min[b]
	μ_2-oxo	(b)	582	60 hours[b] 50 hours[c]
	H_2O *trans* to μ_2-oxo	(c)	not observed	$<10^{-3}$ s[c]
	H_2O *trans* to yl-O	(d)	not observed	$<10^{-3}$ s[c]
$[Mo_2(OH)_2(H_2O)_8]^{4+}$	μ_2-OH	(e)	124	–
	H_2O *trans* to μ_2-OH	(f)	–19	>0.1 s[d]
	H_2O *trans* to H_2O	(g)	–42	>0.1 s[d]
$[Mo_3O_4(H_2O)_9]^{4+}$	μ_2-oxo	(h)	794	immeasurably slow
	μ_3-oxo	(i)	516	immeasurably slow
	H_2O *trans* to μ_2-oxo	(j)	28	<0.1 s[e]
	H_2O *trans* to μ_3-oxo	(k)	–10	25 min[e]
Other signal	$CF_3SO_3^-$		159	

[a] Referenced to free water = 0 ppm. [b] Ref. 10, 1.0 M CH_3SO_3H. [c] 0.056 M $Mo_2O_4^{2+}$, 1.00 M CF_3SO_3H, 0.1 M Mn^{2+}, μ = 1.31 M H_2O^{17} (5.0 atom %). [d] 0.05 M $Mo_2(OH)_2^{4+}$, 1.3 M CF_3SO_3H, 0.064 M Mn^{2+}, μ = 2.23 M, H_2O^{17} (3.3 atom %). [e] 0.04 M $Mo_3O_4^{4+}$, 0.65 M p-$CH_3C_6H_4SO_3H$, 0.1 M Mn^{2+}, μ = 1.00 M (p-$CH_3C_6H_4SO_3Li$), H_2O^{17} (5.0 atom %).

The exchange half life of yl-oxygens is around 3–4 min at 25 °C [10], whereas that for the μ_2-oxygens is between 2–3 days. Resonances due to the coordinated water ligands are not resolvable from the base-line implying that, at 25 °C, exchange is occurring with a half life of $<10^{-3}$ s. This is in agreement with the known rapid equilibration of anionic ligands, e.g. NCS^-, with these water ligands [19]. The high lability is thought to be due to the strong *trans* effect resulting from both the yl- and μ_2-oxygen atoms. The diamagnetism of this dimeric ion is believed to arise from a strong metal–metal interaction leading to d-electron coupling. The Mo–Mo distance from EXAFS [12] is 2.56 Å, within the range for a single Mo–Mo bond. Superexchange through the μ_2-oxygens however can also not be ruled out.

The blue–green dimeric Mo(III) ion $[Mo_2(\mu_2\text{-}OH)_2(H_2O)_8]^{4+}$, was prepared directly in the NMR tube by reduction of the above oxygen-17 enriched $Mo_2O_4^{2+}$ solutions with either amalgamated zinc shot or with a slight excess of $Eu(CF_3SO_3)_2$* in 2 M CF_3SO_3H. The resulting ^{17}O NMR spectrum, Fig. 1(ii), is identical in each case. Concentrations of Mo(III) in the solutions were standardized at the 360 nm peak (ϵ = 910 per dimer). Previously, this ion had been formulated as either containing a mono-μ_2-oxo or a di-μ_2-hydroxo group on the basis of its charge per molybdenum value of 2.0 and elution behaviour of a 4+ cation [5]. The Mo–Mo separation from EXAFS [12] is 2.45 Å which would in principle be accomodated by a bent structure involving either type of bridging group. The di-μ_2-hydroxo formulation has been favoured on the basis of a close similarity of the electronic spectrum of the ion with that of structurally characterized dimeric Mo(III) complexes known to have the di-μ_2-hydroxo bridging group [6]. Figure 1(i) shows unequivocally that this latter formulation is correct. The resonance of the bridging oxygen occurs at 124 ppm (Table II) at a much higher field than would be expected for a μ_2-oxo group [13, 15], and is consistent with the presence of a protonated μ_2-hydroxo group. The coordinated water ligands now exchange slowly with bulk water ($t_{1/2} > 0.1$ s) consistent with the presence of a substitution inert Mo(III) centre. The two types of water occur in a 1:1 ratio as separate resonances and can be readily assigned, those *trans* to the μ_2-hydroxo groups resonating at the lower field (–19 ppm). Furthermore , the peak integration of the μ_2-hydroxo group is one half that for each of the coordinated waters which can only be supportive of the di-μ_2-hydroxo structure for the Mo(III) ion. As in the case of the Mo(V) dimer, the diamagnetism of this ion probably arises from a strong Mo–Mo interaction or through superexchange through the μ_2-hydroxo groups or a combination of both.

Finally, Fig. 1(iii) illustrates the ^{17}O NMR spectrum obtained from an oxygen-17 enriched solution of the Mo(IV) ion in enriched acidic water. The enrichment was achieved by a slight modification of a previously described synthetic procedure [20]. Solutions of dimeric Mo(V) and monomeric Mo(III),

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*Solutions of $Eu(CF_3SO_3)_2$ were prepared by amalgamated zinc reduction of $Eu(CF_3SO_3)_3$ in 2 M CF_3SO_3H.

$[Mo(H_2O)_6]^{3+}$*, were first separately enriched. The two solutions were then combined in the normal 1:1 ratio and heated at 80 °C for 1–2 h to allow synthesis of the enriched Mo(IV) ion. Purified solutions of the Mo(IV) ion (0.1 M per Mo) were subsequently obtained following displacement elution from a short (5 cm × 1 cm) column of DOWEX 50W X2 resin with a solution of 0.25 M La^{3+} in 1.00 M p-$CH_3C_6H_4SO_3H$. The final inert core oxygen enrichment was 3.3 atom %. Solutions were then combined with further volumes of the $H_2{}^{17}O$ (10 atom %), containing Mn^{2+}, to re-enrich all of the coordinated waters (4% in this case).

Two types of bridging oxygen atoms are observed in the region 400–800 ppm characteristic of μ_2- and μ_3-oxo groups [13]. The peak integration ratio of 3:1 immediately assigns the triangular Mo_3O_4 unit unequivocally. The three μ_2-oxo groups resonate at a lower field (794 ppm) than the μ_3-capping oxo group (516 ppm). The two types of coordinated water show slow exchange on the NMR time scale. They can be assigned from their 2:1 peak integration ratio. The six waters *trans* to the μ_2-oxo groups resonate at a lower field (28 ppm) than the three waters *trans* to the μ_3-oxo group (−10 ppm). Total integration over the entire spectrum, normalised with respect to the oxygen-17 enrichment, is only supportive of one structure, the triangular $[Mo_3(\mu_3\text{-}O)(\mu_2\text{-}O)_3(H_2O)_6(H_2O)_3]^{4+}$ formulation.

Oxygen exchange on both the μ_2- and μ_3-oxo groups is immeasurably slow at 25 °C with no detectable exchange occurring after 13 months in our NMR work**. Exchange on the two types of water ligands is however readily observed, but with markedly differing rates. The half life for the three waters *trans* to the capping μ_3-oxo group is 25 min at 25 °C (0.65 M H^+, μ = 1.0 M, p-$CH_3C_6H_4SO_3Li$). However, the half life for the six waters *trans* to the μ_2-oxo group under the same conditions is much shorter, and, at temperatures above 40 °C, short enough to cause broadening of the oxygen-17 resonance. The half life at 25 °C is therefore estimated to be <0.1 s implying a factor of >10^3 difference in rate between the two types of water. This is presumed to be due to the much greater *trans* effect of μ_2- *versus* μ_3-oxo groups.

Previously there had been much conflict regarding the detailed structure of the Mo(IV) ion arising from ion-exchange [5], kinetic [7] and EXAFS [11, 12] studies. The NMR spectrum of this ion clearly allows a direct definitive assignment of the trimeric structure for this ion in solution.

Conclusion

This work has demonstrated the use of ^{17}O NMR as a powerful probe, under favourable conditions of slow exchange and diamagnetism, for the direct assignment of oligomeric oxo-aqua ions structures in solution. Excellent spectra can be obtained with relatively dilute (<0.1 M) solutions at enrichments of <5 atom%. Methods of enriching the oligomeric ions require a knowledge of the synthetic chemistry and a feel for the magnitude of the oxygen exchange rates on both precursor and final species. ^{17}O NMR can provide a uniquely selective and quantitative measure of the exchange rates at the different oxygen atoms in these oligomeric ions.

Work in progress has shown that the analogous oligomeric aqua ions of tungsten(V)* and (IV) [22] have the same dimeric and trimeric structures respectively in solution as those observed for molybdenum. The rates for exchange on the two types of water ligand on $[W_3(\mu_3\text{-}O)(\mu_2\text{-}O)_3(H_2O)_6(H_2O)_3]^{4+}$ [22] have a similar factor of 10^3 difference in rate. However, exchange on the tungsten ion occurs approximatively 100 times slower than on molybdenum.

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*Separate experiments on $Mo(H_2O)_6{}^{3+}$ have estimated a lower limit for the water exchange half life at 25 °C of 1.0 s.

**A half life of *ca.* 4 days at 25 °C for the capping μ_3-oxo group has been reported from an oxygen-18 study in 1.00 M CH_3SO_3H solution [21].

*Obtained as a bi-product in the preparation of the tungsten(IV) aqua ion.

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