^{95}Mo NMR Spectroscopy of Complexes Containing the $Mo_2O_5{}^{2+}$ Core: A Method for Identifying Single Oxo-bridged Species in Solution

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Abstract

^{95}Mo NMR spectra of several Mo(VI) complexes containing a single oxo bridge have been recorded and show a signal at approximately 120 ppm relative to sodium molybdate. It is claimed that a chemical shift of this magnitude is characteristic of the $[O_2Mo{-}O{-}MoO_2]^{2+}$ unit, where each six coordinate Mo(VI) is ligated to oxygen or nitrogen donors, and is a criterion for identifying such species in solution.

The coordination chemistry of Mo(VI) is important since it is almost certainly involved in the aqueous transport of molybdenum, as a trace element in soils, to its ultimate goal in biological systems. While the studies herein reported were performed in non-aqueous solvents the results obtained must have relevance to the aqueous phase.

All ^{95}Mo NMR spectra were recorded using a Bruker WM-250 spectrometer, ^{95}Mo resonance frequency 16.3 MHz. Aqueous sodium molybdate (2 M) was used as an external chemical shift reference. All measurements were made using a 50 KHz sweep width and 40 ms data acquisition time. All free induction decays were multiplied by an exponential window function selected to give a minimum line width of twice the digital resolution after Fourier transformation. Experimental parameters were selected to minimise the effects of acoustic ringing in the NMR probe head.

Attempted recrystallisation of $MoO_2(HPB)_2(C_2H_5OH)_2$, where HPB is the deprotonated form of 2-*o*-hydroxyphenylbenzimidazole, from dimethylformamide (DMF) yields the complex $Mo_2O_5(HPB)_2(DMF)_2(H_2O)_1$ the crystal and molecular structure of which shows it to contain the $Mo_2O_5{}^{2+}$ core [1]. The following reaction scheme is suggested:

TABLE I. ^{95}Mo NMR Spectral Data.

Complex	Solvent	Chemical shift (ppm)	Line width at half peak height (Hz)
$Mo_2O_5(HPB)_2(DMF)_2(H_2O)_1$	DMF	120	140
$Mo_2O_5(nPOBB)_2{}^a$	DCM	76	196
		47	196
$Mo_2O_5(nPOBB)_2$	DMF	122	147
		58	–
$MoO_2(nPOBB)_2{}^b$	DCM	50	170
$Mo_2O_5(AcAc)_2(DMSO)_2$	DMF	123	172
		−38	270
$Mo_2O_5(AcAc)_2(DMSO)_2$	DMSO	123	294
		−31	–
$MoO_2(AcAc)_2{}^c$	DMF	−45	225
$Mo_2O_5(PQ)_2$	DMF	123	147

[a] Ref. 4. [b] Ref. 3. [c] Ref. 2.

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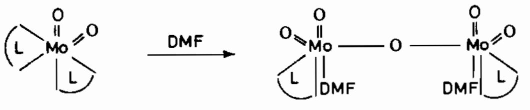
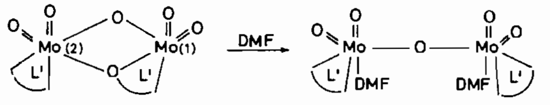


I **II**

L = HPB.

The ^{95}Mo NMR of **II** in DMF gave a signal at 120 ppm (Table I). No signal could be obtained for **I** in ethanol but is known that complexes of type **I** *i.e. cis* dioxo Mo(VI) complexes with a 2O, 2N donor set give signals in the range 50 to 60 ppm [2, 3].

The ^{95}Mo NMR of the complex $Mo_2O_5(nPOBB)_2$ in dichloromethane (DCM), where nPOBB is the deprotonated form of 1-n-propyl-2-α-hydroxybenzyl-benzimidazole, gave two signals which were assigned in the light of a subsequent X-ray crystallographic study [4]. We have now recorded the ^{95}Mo NMR spectrum of $Mo_2O_5(nPOBB)_2$ in DMF (Fig. 1). The spectrum is interpreted according to the following scheme:



III **IV**

L′ = nPOBB.

The oxygen atom of the bridging ligand is asymmetric with respect to the two Mo atoms, the Mo(2)–O bond is 2.358 Å and the Mo(1)–O bond is 2.026 Å. In a strongly coordinating solvent like DMF the longer Mo–O bond is broken to give **IV** which it is claimed is responsible for the signal at 122 ppm in the ^{95}Mo NMR spectrum. The weak signal at 58 ppm could be due to dissociation of **III** or **IV** to give the monomeric structures **V** or **VI**.

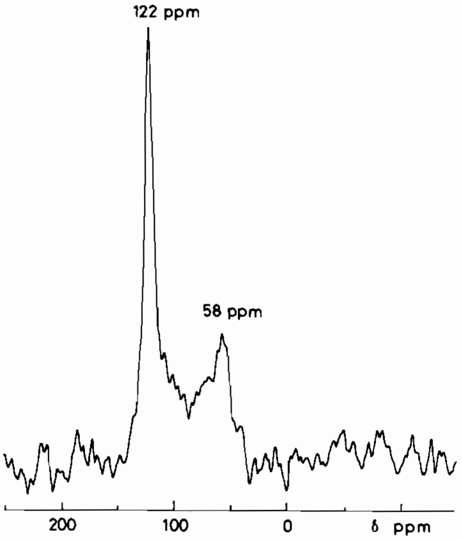
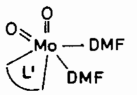
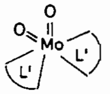


Fig. 1. ^{95}Mo NMR spectrum of $Mo_2O_5(nPOBB)_2$ in DMF.



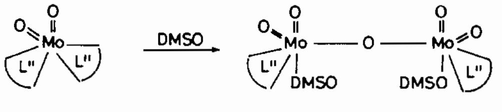
V



VI

$MoO_2(nPOBB)_2$ *i.e.* **VI** in DCM is known to give a chemical shift of 50 ppm [3].

In a recent paper Hider and Wilkins reported the reaction of $MoO_2(AcAc)_2$, where AcAc is acetyl-acetonate, with dimethylsulphoxide (DMSO) to give $Mo_2O_5(AcAc)_2(DMSO)_2$ which gives an infrared band at approximately 780 cm^{-1}, characteristic of the $Mo_2O_5^{2+}$ core [5]. The reaction scheme suggested is:



VII **VIII**

L″ = AcAc

We have recorded the ^{95}Mo NMR spectrum of $Mo_2O_5(AcAc)_2(DMSO)_2$ in DMF (Fig. 2) and DMSO. The signals at 123 ppm we assign to structure **VIII** (with coordinated DMSO or DMF) and the signal at −38 ppm (in DMF) and −31 ppm (in DMSO) to a

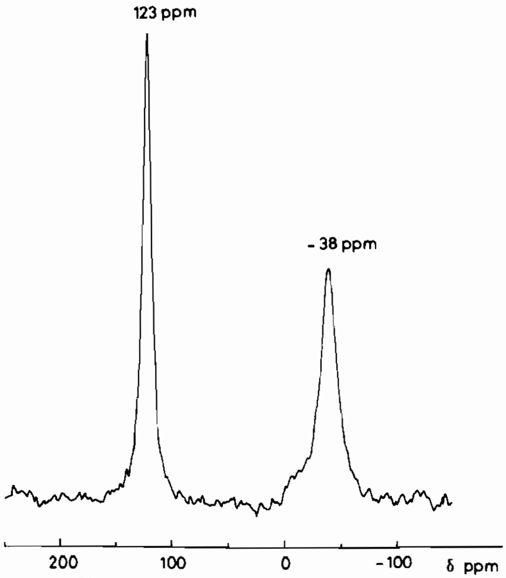
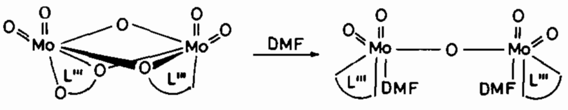


Fig. 2. ^{95}Mo NMR spectrum of $Mo_2O_5(AcAc)_2(DMSO)_2$ in DMF.

monomeric species. Monomeric $MoO_2(AcAc)_2$ is known to give a chemical shift of −45 ppm in DMF [2].

The complex $Mo_2O_5(PQ)_2$, where PQ is 9, 10-phenanthrenesemiquinone, has the triply bridged structure **IX** [6]. The ^{95}Mo NMR spectrum of this complex in DMF shows a single relatively sharp peak at 123 ppm which we interpret as being due to the single oxo bridged species **X** formed by cleavage of the long Mo to ligand oxygen bridge bonds.



IX **X**

L''' = PQ.

Attempts to record ^{95}Mo NMR data for $Mo_2O_5(PQ)_2$ in DCM were unsuccessful, no signals were detected after 60 h. This failure is presumably a consequence of extreme line broadening in this system.

On the basis of the above results we claim that a ^{95}Mo NMR signal at about 120 ppm is indicative of a single oxo bridged species of the type exemplified by **II**, **IV**, **VIII** and **X**.

References

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