

## Intramolecular Oxygen Exchange in the Heptamolybdate(vi) Isopolyanion

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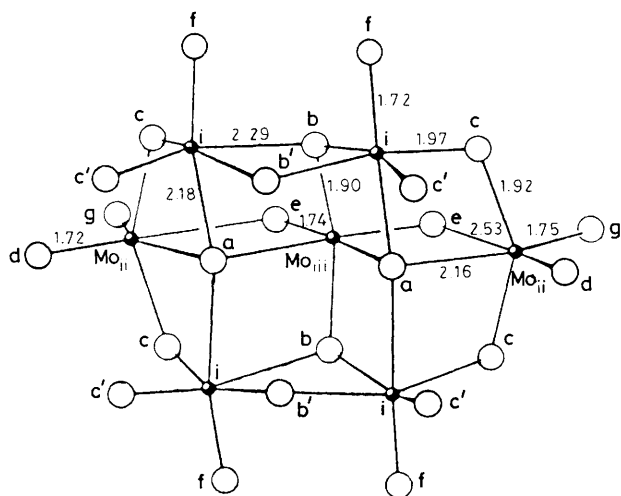
A new population-transfer technique in  $^{17}\text{O}$  n.m.r., applied to the heptamolybdate anion, reveals an interchange of specific bridging and terminal oxygens which does not involve solvent water or free molybdate ion.

The heptamolybdate(vi) anion,  $[\text{Mo}_7\text{O}_{24}]^{6-}$  with its protonated forms, is the dominant  $\text{Mo}^{\text{VI}}$  species in aqueous solution<sup>1</sup> between pH 3.5 and 5.8. Its structure in the solid state is well-established<sup>2</sup> and is shown in Figure 1, together with averaged bond lengths. There is also both diffraction<sup>3</sup> and  $^{17}\text{O}$  n.m.r.<sup>4</sup> evidence for the persistence of this structure in aqueous solution, although the n.m.r. data were obtained at relatively low frequency, where many resonances overlap.

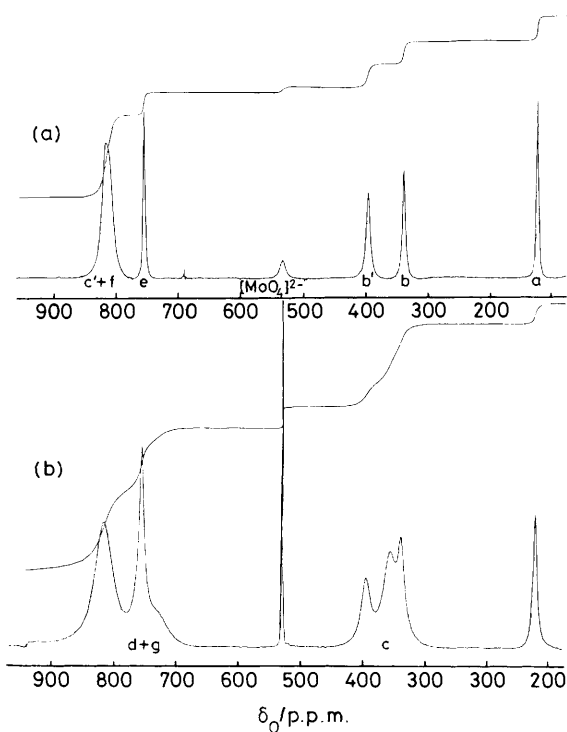
We have reinvestigated the  $^{17}\text{O}$  n.m.r. spectrum of heptamolybdate at 54.23 MHz, as part of a wider study of vanadomolybdates and related mixed-metal species. Our initial spectrum (Figure 2a, 319 K, pH 5.0, 10%  $^{17}\text{O}$ ) was inconsistent with the known structure, in that eight oxygen atoms yielded no visible resonance. However, the same anion

at 280 K and pH 5.7 (Figure 2b) showed two further broad  $^{17}\text{O}$  resonances, one in the bridging region at  $\delta_{\text{O}}$  356 p.p.m., and another, probably composite, in the (mainly) terminal region at ca. 735 p.p.m. The peak labels refer to Figure 1, and show our proposed assignment, which is based on integral values (including a 4:4 split of the highest frequency resonances at high temperature) and on the known correlation of  $^{17}\text{O}$  shift with the distance of the nearest metal atom,<sup>5</sup> and with co-ordination number.<sup>4</sup> The  $^{17}\text{O}$  shifts observed at 293 K and pH 5.4 are:  $\text{O}_a$  121.7,  $\text{O}_b$  338.6,  $\text{O}_b$  395.2,  $\text{O}_c$  358,  $\text{O}_d$  with  $\text{O}_g$  ca. 735,  $\text{O}_e$  754.4,  $\text{O}_{c'}$ , with  $\text{O}_{f'}$  815.4 p.p.m. relative to solvent water at zero.

Clearly Figure 2 reveals an exchange process involving both terminal and bridging oxygens. It also shows that this process



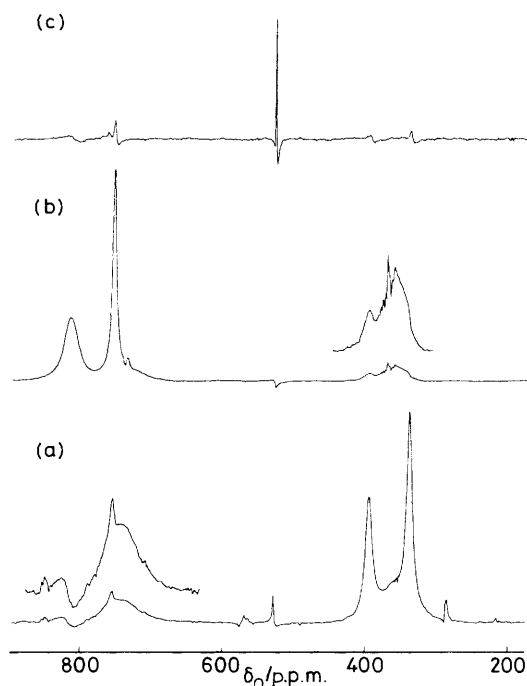
**Figure 1.** Structure and averaged bond lengths/Å in the heptamolybdate anion, redrawn from ref. 2.



**Figure 2.** 54.23 MHz  $^{17}\text{O}$  N.m.r. spectra of aqueous  $[\text{Mo}_7\text{O}_{24}]^{6-}$ , 10%  $^{17}\text{O}$ : (a) pH 5.0, 319 K; (b) pH 5.7, 280 K.

does not cause any other oxygens in the anion to exchange, for their resonances all narrow upon increasing the temperature. Thus, unlike decavanadate,<sup>6</sup> the heptamolybdate anion can undergo oxygen exchange without overall breaking of its structure. Furthermore, the narrow  $[\text{MoO}_4]^{2-}$  resonance at 529 p.p.m. in Figure 2b demonstrates that the monomeric molybdate anion does not take part in the present exchange process (although it does react with heptamolybdate at higher temperatures.)

But is the lower-temperature exchange process purely internal, or does it involve solvent water? Population-transfer



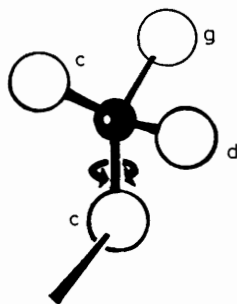
**Figure 3.**  $^{17}\text{O}$  N.m.r. subtraction spectra of  $[\text{Mo}_7\text{O}_{24}]^{6-}$ , pH 5.7, 293 K, made as described in text, and showing population transfer solely between the broad terminal and bridging oxygen resonances: (a) irradiation at  $\delta_{\text{O}}$  358 p.p.m., (b) at 735 p.p.m., (c) at 0 p.p.m. (water resonance).

methods offer almost the only clear cut way of answering such questions. However, neither selective irradiation by DANTE<sup>7</sup> nor 2D NOESY<sup>8</sup> methods are practicable when both  $T_1$  and  $T_2$  are very short.

Instead, it is possible to take advantage of an apparent weakness of the n.m.r. method as applied to strongly ionic solutions. The  $\pi$ -pulse width of the spectrometer (Bruker WH400, 10 mm sample diameter) is *ca.* 100  $\mu\text{s}$  with these solutions and therefore affects only a limited spectral range, *ca.* 100 p.p.m. either side of the spectrum centre in quadrature mode. Hence one can achieve selective irradiation by placing the spectrum centre at (*e.g.*) the broad bridging  $^{17}\text{O}$  resonance position, and performing two interleaved  $(\pi-\tau-\pi/8-0.1\text{ s})_n$  experiments, one with  $\tau = 3\text{ ms}$  (typically) and a dummy with  $\tau = 100\text{ ms}$ . The 3 ms delay permits significant exchange but is sufficiently short to prevent complete relaxation. Subtraction of these spectra yields Figure 3a. Figure 3b shows the result of the reverse experiment, with inversion at the terminal oxygens. Figure 3c shows the null result, excepting a possible slight transfer to  $[\text{MoO}_4]^{2-}$ , when the water peak at  $\delta = 0$  is inverted.

This selective-inversion method is not as precisely quantitative as selective irradiation, nor is it suited to less well-separated resonances. However, in the present case it clearly shows that the bridging-terminal oxygen exchange does not involve solvent. In contrast, we have used the same method, with more complex anion mixtures and suitably weighted subtractions, in order to edit the  $^{17}\text{O}$  spectra into those of the species which either do or do not exchange with solvent water.

Figure 4 suggests a possible mechanism for the internal process. The proposed intermediate is not altogether without structural precedent<sup>9</sup>. Its formation would only involve the breakage of three already long bonds, namely  $\text{O}_c\text{-Mo}_i$ , 1.97;  $\text{O}_e\text{-Mo}_{ii}$ , 2.53;  $\text{O}_a\text{-Mo}_{ii}$ , 2.16 Å, where  $\text{Mo}_{ii}$  is the part-detached molybdenum.



**Figure 4.** Possible mechanism for interchange of  $O_c$ ,  $O_d$ , and  $O_g$ , showing an intermediate formed from the right hand  $Mo_{ii}$  in Figure 1.

In the intermediate, the  $Mo_{ii}$  atom is only attached to the remainder of the polyanion by one bond,  $Mo_i$  to  $O_c$ , so that  $O_c$ ,  $O_g$ , and  $O_d$  can interchange by rotation.

The exchange rate is only weakly increased by lowering pH. We also observe a change of chemical shift with pH which implies<sup>4</sup> protonation at  $b'$  and, especially,  $b$ . This probably rules out protonation of  $O_c$  as an explanation of the required rupture of one  $Mo_i-O_c$  bond. Furthermore, exchange is still substantial at pH values as high as 5.5. It appears that even the unprotonated heptamolybdate anion is internally labile. The partial detachment of one  $MoO_3$  unit may be an essential component of the process known at higher temperature and lower pH in which molybdate adds to heptamolybdate to give

octamolybdate,  $[Mo_8O_{26}]^{4-}$ . The transition from heptamolybdate to octamolybdate<sup>10</sup> can be effected by adding a  $Mo^{VI}$  atom with two oxygens to create an octahedron with the four  $O_a$  and  $O_b$  oxygens, and then swinging the  $Mo_iO_3$  unit to join with this new octahedron.

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