Aqueous Isopolymolybdates(VI): An Oxygen-17 and Molybdenum-95 Nuclear Magnetic Resonance Study

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Aqueous molybdenum(VI) has been studied between pH 6 and 1.2 by ^{17}O and ^{95}Mo n.m.r. spectroscopy. Heptamolybdate, $[Mo_7O_{24}]^{6-}$, its monoprotonated form, and β-octamolybdate, $[Mo_8O_{26}]^4$, are clearly identified, and evidence has also been found for an intermediate species $[H_3Mo_8O_{28}]^{5-}$. The protonation site of heptamolybdate has been identified, and kinetic and structural data have been correlated to yield a scheme for the transformation of heptamolybdate to octamolybdate upon acidification.

The chemistry of aqueous molybdenum(VI) is fundamental to much heteropolyanion chemistry. Surprisingly, however, even the dominant species in the pH range 1—6 are not fully understood. It is generally agreed that the first major product to form upon acidification of aqueous $[MoO_4]^{2-}$ is heptamolybdate, $[Mo_7O_{24}]^{6-}$.[1] Even for this species the previously published ^{17}O n.m.r. spectrum[2] is incomplete. The course of further acidification depends upon the counter ion; Li^+ minimises precipitation. The most complete study of lithium isopolymolybdates is that reported by Johansson *et al.*,[3] using potentiometry, low-angle *X*-ray scattering, and Raman spectroscopy. Figure 2 of this reference illustrates both its success and its limitations, by presenting two alternative species-distribution diagrams consistent with all the data. The upper diagram proposes the following sequence of dominant species upon acidification of a 2 mol dm^{-3} solution: $[MoO_4]^{2-} \longrightarrow [Mo_7O_{24}]^{6-} \longrightarrow [HMo_7O_{24}]^{5-} \longrightarrow [H_2Mo_7O_{24}]^{4-} \longrightarrow [Mo_8O_{26}]^{4-} \longrightarrow [Mo_{16}O_{50}]^{4-} \longrightarrow MoO_3(s)$. However, the alternative scheme proposes: $[MoO_4]^{2-} \longrightarrow [Mo_7O_{24}]^{6-} \longrightarrow [H_2Mo_8O_{28}]^{6-} \longrightarrow [H_3Mo_8O_{28}]^{5-} \longrightarrow [Mo_8O_{26}]^{4-} \longrightarrow [Mo_{18}O_{56}]^{4-} \longrightarrow MoO_3(s)$. The *X*-ray and Raman evidence supports the presence of heptamolybdate and of the octamolybdate $[Mo_8O_{26}]^{4-}$, with the β structure.[3] It also probably shows the presence of other structures, but not in detail. The ion β-$[Mo_8O_{26}]^{4-}$ is also known in the solid state,[4] as is the α isomer, and also the unit 'Mo_8O_{28},' typically stabilised by pyridine[5] or by two protons.[6]

The present study uses ^{17}O and ^{95}Mo n.m.r. spectroscopy. Because the quadrupole moment of ^{95}Mo is relatively large, its spectra are only useful as complementary information. However, the quadrupole moment of ^{17}O is quite small, so that in an oxygen site with the maximum possible field gradient the natural width of the ^{17}O resonances will be less than the broadening due to, *e.g.*, exchange, provided that the anion does not contain more than about 15 MO_6 units. Thus all the ^{17}O resonances are clearly observed, and most are resolved, in typical spectra.[1,2,7]

Where such spectra may be compared with crystal structures,[1,2,4,7—9] a clear inverse correlation emerges between the ^{17}O shift and the shortest bond length to a given metal. Singly, doubly, triply, and multiply bonded oxygens may therefore be readily distinguished, especially with octahedral co-ordination,[8] even though other factors such as bond angles[9] and the lengths of other M–O bonds also affect the shifts somewhat. It supports some elements of both the above models, and disfavours others. With the addition of qualitative kinetic evidence it permits us to propose a scheme for the interconversion of the relatively different heptamolybdate and β-octamolybdate structures. Our observations are also intended to underpin a comprehensive study of molybdovanadates, currently in progress.

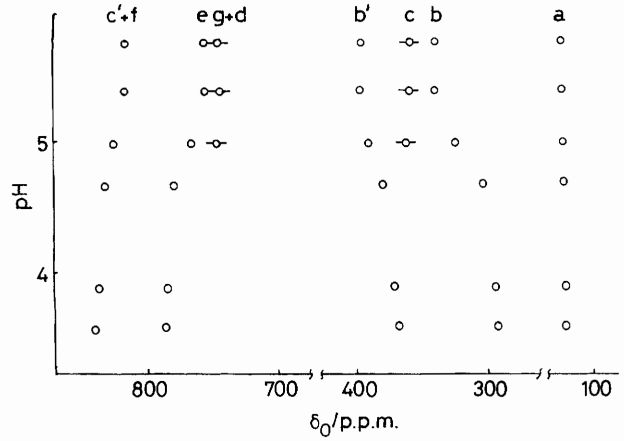

Figure 1. Dependence of ^{17}O chemical shift upon pH for heptamolybdate

Experimental

Oxygen-17 n.m.r. spectra were obtained at 54.24 MHz, and ^{95}Mo at 26.08 MHz, on a Bruker WH400 spectrometer. Solutions for ^{17}O n.m.r. spectroscopy were enriched by 2—10% in $H_2{}^{17}O$, and 30 000 transients were accumulated, typically. The resonance of solvent water was taken as $\delta_O = 0$, and alkaline $[MoO_4]^{2-}$ for $\delta_{Mo} = 0$. The polarisation-transfer method used to trace the exchange of specific oxygens has been described in a preliminary communication.[7] Other kinetic data were obtained from linewidths, determined by computer fitting. Heptamolybdate was prepared by acidification of $Li_2[MoO_4]$, itself prepared from MoO_3 (BDH Analar) and Li_2CO_3 (May & Baker). Solutions were 1—2 mol dm^{-3} in Mo. However, some measurements were performed directly on the same solutions, B—E, for which *X*-ray scattering and Raman data were reported earlier,[3] the only change being addition of small quantities of $H_2{}^{17}O$.

Results and Discussion

Oxygen-17 *N.M.R. Spectra.*—pH > 4. The observed vari-

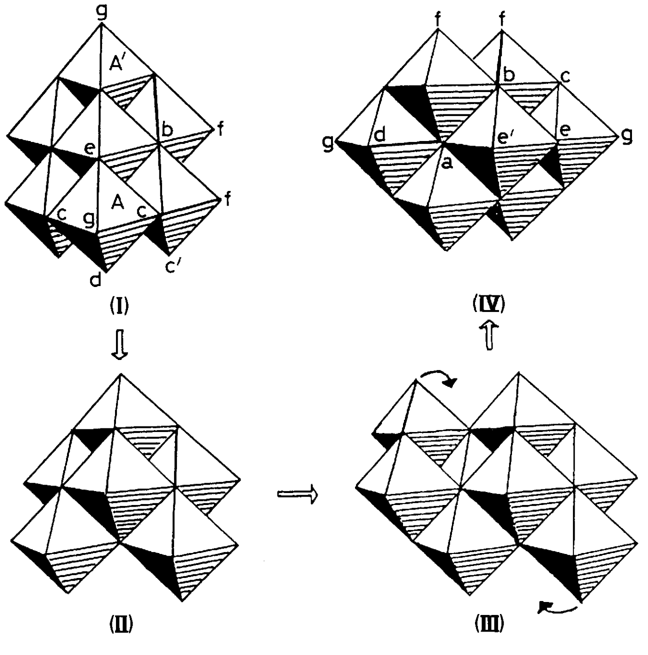

Figure 2. Structure, labelling scheme, and proposed mechanism of interchange of the species described in text. (I) $[Mo_7O_{24}]^{6-}$ and $[HMo_7O_{24}]^{5-}$; (II) hypothetical intermediate based on ref. 7; (III) $[H_3Mo_8O_{28}]^{5-}$; (IV) β-$[Mo_8O_{26}]^{4-}$

ations in isopolymolybdate species may conveniently be described by considering a progressive lowering of pH. Figure 1 shows the pH dependence of the ^{17}O shift for the resonances of the first isopolymolybdate to form, $[Mo_7O_{24}]^{6-}$. The resonances labelled c (corresponding to four oxygens per molecule) and d + g (total four oxygens) have not been reported previously, except in a preliminary communication.[7] They correspond to bridging and terminal oxygens respectively. These oxygens undergo mutual interchange not involving solvent water. The other assignments are made to accord with earlier work,[8] and fit the integrals well.

Because of the above exchange process, the resonances of O_c, O_d, and O_g (see Figure 2) cannot be traced reliably below pH 4.5. However, only the resonances of O_b and $O_{b'}$ clearly decrease in frequency upon protonation. Such a decrease has now been established as a reliable marker of protonation sites.[8,9] The proton therefore presumably bridges O_b and $O_{b'}$, in $[HMo_7O_{24}]^{5-}$, or else protonates each site in turn.

Although published data clearly show that the heptamolybdate anion can undergo a single protonation, they leave open the possibility of a second protonation step. However, Figure 1 probably supports only a single protonation step, within the anion's range of stability, as may be seen by comparison with Figure 2 and 3 of ref. 9. These latter plots of pH *versus* δ_O for decavanadate clearly show inflections between the first and second protonation steps. Klemperer and co-workers[10] have explained why such inflections are to be expected. No such inflections appear for heptamolybdate in Figure 1 above. Furthermore, the arithmetical average protonation shift observed, *ca.* 20 p.p.m., compares with 23 p.p.m. for just the first protonation step of decavanadate.[9] Also, by simple inspection, pK_{a1} cannot be more than 5.0, which makes $pK_{a2} > 3$ unlikely. The existence of $[H_2Mo_7O_{24}]^{4-}$ is therefore improbable, in this medium, at least in the absence of a major change of structure, as the heptamolybdate peaks fall to zero intensity at pH *ca.* 3.5.

pH 2.9—4. Further acidification, to pH 4.7 and below, brings about changes which depend on the supporting ionic medium.

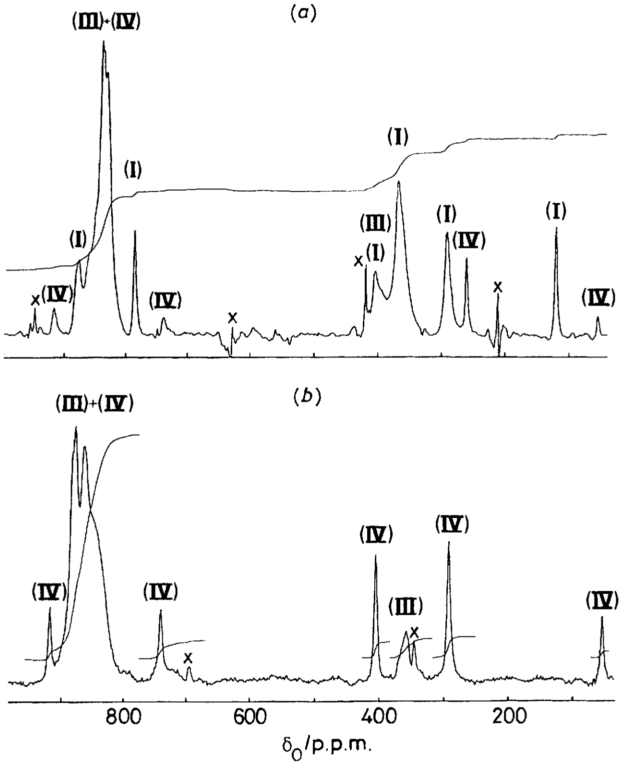

Figure 3. (*a*) Oxygen-17 n.m.r. spectrum, [Mo] = 0.4 mol dm^{-3}, 2% ^{17}O, pH 3.9, showing the presence of structures (I), (III), and (IV) in the approximate ratio 2:2:1; x indicates known spectrometer artefacts. (*b*) As above, but 1.6 mol dm^{-3}, pH 2.9, showing (IV) and (III) (or a polymerised variant) in the approximate proportion 2:3, but with the bridging resonances of (III) reduced in intensity by oxygen exchange. Labelling as in Figure 2 and Table

Most media cause substantial precipitation and afford very limited evidence for other isopolymolybdates. However, careful dissolution of MoO_3 with Li_2CO_3 avoids these problems and gives solutions up to 2 mol dm^{-3} whose n.m.r. spectra and pH depend on the stoicheiometry. The first new peaks to appear upon further acidification are broad, particularly at higher temperatures and concentrations. At 0.4 mol dm^{-3} and 294 K [Figure 3(*a*)], however, they may be at least partially distinguished from the heptamolybdate peaks. Resonances are observed at *ca.* 860, 850, and 840 p.p.m., presumably arising from terminal oxygens, also at *ca.* 395 and 370 p.p.m., presumably from singly bridging oxygens, and at 261 p.p.m. We believe that this latter resonance arises from quadruply bridging oxygens. The peak areas cannot be determined accurately because of overlaps, but are consistent with those anticipated from structure (III) in Figure 2, *i.e.* $[H_3Mo_8O_{28}]^{5-}$. This species is present as *ca.* 40% of the total [Mo], at both 0.4 and 1.6 mol dm^{-3}, which supports the above proposal and argues against any more highly polymerised species at this pH. It also fits the formula proposed in Johansson's second scheme (see above). As the pH is lowered further, the heptamolybdate peaks decrease and new peaks appear as listed in the Table, whilst the peaks attributed to $[H_3Mo_8O_{28}]^{5-}$ remain unaffected. The oxygen shifts of the new peaks correspond closely with those observed for octamolybdate, β-$[Mo_8O_{26}]^{4-}$, in acetonitrile solution.[8] This confirms earlier proposals, based on equilibrium data, for the presence of octamolybdate in aqueous solution. For ease of comparison, the Table also includes the ^{17}O shifts of $[Mo_7O_{24}]^{6-}$.

When the pH is lowered further to 2.9 [Figure 3(*b*), solution E of ref. 3] there is no change in the oxygen shifts; it follows that octamolybdate does not protonate at this pH. However,

Table. Oxygen chemical shifts and assignments

$[Mo_7O_{24}]^{6-}$ (I)		$[H_3Mo_8O_{28}]^{5-}$ (III)		$[Mo_8O_{26}]^{4-}$(aq) (IV)		$[Mo_8O_{26}]^{4-}$(CD_3CN)	
δ_O [a]	Assignment [b]	δ_O	Assignment	δ_O	Assignment	δ_O	Assignment
121.7	a	261	a	53.5	a	56	a
338.6	b	370, 395	b, c, e	290.7	b	296	b
356.5	c			404.3	c	425	c
395.2	b′			738.2	e	743	e
745	d, g	840, 850, 860	d′, e′, f, g, *etc.*	861.6, 876, 878	d′, f, g	866	d′, f, g
754.4	e			917.3	e′	900	e′
815	f, c′						

[a] At 294 K, solvent water ($\delta_O = 0$). [b] Letters are based on an established[8] labelling scheme for decavanadate, with primes added to indicate nearness to 'missing' octahedra (see Figure 2, and Figure 1 of ref. 7). Assignments are proposed on the basis of peak areas and the correlation of δ_O with bond length.

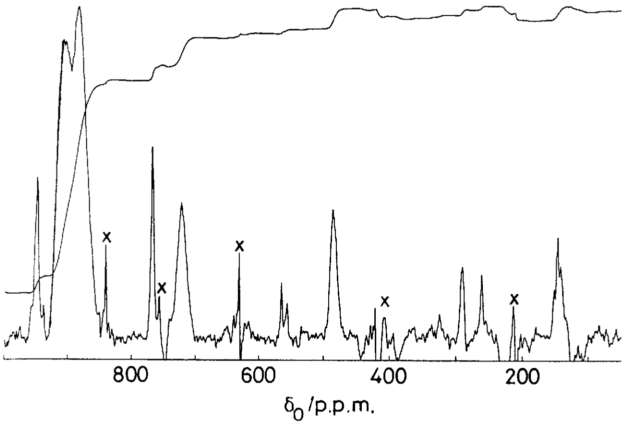

Figure 4. Oxygen-17 n.m.r. spectrum of pH 1.2, 0.4 mol dm^{-3}, 55 °C, 2% ^{17}O-enriched solution, showing unknown species; x indicates known spectrometer artefacts

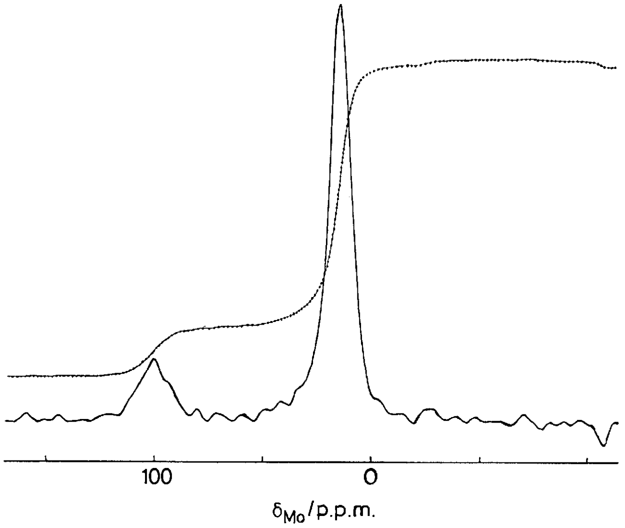

Figure 5. Molybdenum-95 n.m.r. spectrum of $[Mo_8O_{26}]^{4-}$ at 99 °C and pH 2.9

the intensity of the two broad peaks falls somewhat, particularly that at *ca.* δ 400 p.p.m. It falls further, reversibly, upon warming the solution, but the ^{95}Mo n.m.r. and kinetic evidence given below suggest that this is due to lability rather than loss of $[H_3Mo_8O_{28}]^{5-}$. In fact, this species, possibly protonated or further polymerised, is the dominant species in terms of molybdenum content at pH < 3.

pH < 2.8. Acidification of solution E (2 mol dm^{-3}, pH 2.9) with $HClO_4$ leads to the immediate formation of a white precipitate, presumably of MoO_3, which does not redissolve upon warming. However, acidification of the same solution can be achieved without precipitation if it is first diluted to 0.4 mol dm^{-3}. Figure 4 shows the ^{17}O n.m.r. spectrum obtained at pH 1.2. Although the spectrum is not of high quality, because of the dilution, it clearly shows a set of peaks distinct from any discussed above, as anticipated by Johansson *et al.*[3] The combined area of the peaks in the terminal Mo–O region, 700—960 p.p.m., is too large relative to the other, bridging oxygens for any conceivable structure based simply on these resonances. However, some of the bridging-oxygen resonances may well be rendered unobservable by exchange. For this reason, we are unable to propose a structure or structures based on this spectrum, beyond noting that it is roughly consistent with the $[Mo_{36}O_{112}(OH_2)_{16}]^{8-}$ anion reported by Paulat-Böschen[11] and also with one half of this virtually dimeric structure. Essentially the same spectrum persists, with minor shift changes, at pH 0.6.

Molybdenum-95 *N.M.R. Spectra.*—The low-field ^{95}Mo n.m.r. spectrum of heptamolybdate has been reported by Vold and Vold[12] and by Reilley and co-workers.[13] It reveals that this anion is in exchange with free $[MoO_4]^{2-}$. The half-life of each species may be loosely estimated from the excess linewidths in their spectra, and is typically 0.17 s at 301 K. The corresponding oxygen half-life, obtained from our ^{17}O n.m.r. spectra under comparable conditions (pH 5.1, 293 K), is 0.005 s. Both half-lives presumably arise from the same multistage exchange process, namely acid-catalysed attack of (probably) $[HMoO_4]^-$ on heptamolybdate. Both rates are an order of magnitude less than that of the internal oxygen exchange in heptamolybdate under the same conditions,[7] although the rates converge at lower pH.

Maksimovskaya and Chumachenko,[14] working at 19.6 MHz, report a second ^{95}Mo resonance for heptamolybdate at δ_{Mo} = 200—210 p.p.m. We have not observed this, and have also been unable to resolve separate ^{95}Mo resonances in heptamolybdate, perhaps because of internal exchange processes. Instead, we see a single, very broad peak at δ_{Mo} = +26.8 p.p.m., as previously reported.

In comparison, we observe a broad single resonance at δ_{Mo} = +14.3 p.p.m. for dodecamolybdophosphate, but find two resonances, even at 99 °C, for octamolybdate (solution E, above). One peak is at 100 p.p.m. and the other, × 5.3 in area, is at +13 p.p.m. (Figure 5). We have also observed 14 resonances between +92 and +127 p.p.m. for molybdenum octahedra in 'capping' positions in the decavanadate structure (corresponding to Mo_I of Figure 1, ref. 7)[15] and therefore tentatively propose that the smaller resonance at 100 p.p.m. in Figure 5 arises from the four Mo_I resonances in octamolybdate. This implies that octamolybdate is present as *ca.* 32% of solution E (as [Mo]), which is consistent with the lower-temperature ^{17}O n.m.r. spectra. However, it also implies that the ^{95}Mo shifts in octamolybdate do not bear direct comparison with the ^{51}V shifts in decavanadate, where the resonances of 'capping' V_I are those at the lowest frequency.

Kinetics of Oxygen Exchange.—Our preliminary communication[7] described a new method of saturation transfer which revealed a specific internal exchange process in heptamolybdate. The same method has now been applied to several of the solutions described above, with selective inversion carried out at many different resonance positions. However, in contrast to previously, all the oxygen exchange in these solutions is dominated by exchange with solvent. Heptamolybdate itself undergoes such exchange at pH < 4, and indeed at 328 K its resonances become very broad indeed. The ^{17}O resonances of octamolybdate do not broaden noticeably even at 333 K, but even so the saturation-transfer method reveals exchange with solvent water. This contrasts with most octahedrally coordinated vanadates and molybdovanadates, which do not undergo oxygen exchange with solvent under these conditions.[15]

Under all conditions the species attributed to $[H_3Mo_8O_{28}]^{5-}$ is the most ready to undergo oxygen exchange. Indeed, one can also observe exchange between this species and either Mo_7 or β-Mo_8, under appropriate conditions, although such exchange may take place at least partially *via* solvent water, whose ^{17}O relaxation time is relatively long. The same explanation is probable for oxygen exchange observed between different octamolybdate resonances, in an almost non-specific pattern. The time-scale of these exchange processes, 0.001 s at 308—328 K, is comparable to the ^{17}O relaxation rates in the isopolyanions, which makes their observation less easy. Little exchange is observed at room temperature, where relaxation competes even more effectively.

One possible explanation for the relative lability of the isopolymolybdates, particularly around pH 3—4, is that the $[H_3Mo_8O_{28}]^{5-}$ species, which is present over this pH range, acts as a kinetic intermediate for oxygen exchange. Its structure is likely to be that of the $[H_2Mo_8O_{28}]^{6-}$ anion reported by Isobe *et al.*[6] and as discrete anions incorporating two pyridine ligands.[5] This is structure **(III)** of Figure 2; the pyridine ligands in this structure each displace one oxygen in the octahedra marked by curved arrows. Clearly this octahedron, with its three non-bridging ligands, is a likely site for protonation and for oxygen exchange with solvent. This may explain the contribution of structure **(III)** to oxygen lability, noted above.

McCarron *et al.*[5] have proposed a partial mechanism for the formation and interrelation of octamolybdates. We present a related but different proposal in Figure 2, which also includes heptamolybdate. This has structure **(I)**, here presented in an unusual orientation. Our recent communication[7] shows that one of the seven octahedra in **(I)**, namely A or A′, becomes labile on acidification. Three long Mo–O bonds are broken and the resulting MoO_4 tetrahedron remains attached only at one O_c oxygen. Because of this, and also the known acid-catalysed exchange process between molybdate and heptamolybdate, it is reasonable to guess that further acidification will detach this tetrahedron, giving structure **(II)**, in an unknown state of protonation. This structure is not known in the solid state, and it may exist only as a putative intermediate on the way to structure **(III)**, in which a 'Mo_2O_5' unit has been added so as to create a S_2 symmetry. The marked dependence of the linewidths of **(III)** upon concentration suggest that this addition actually involves the reaction of at least two condensed species, such as **(I)** or **(II)**. The same process may account for the apparent scrambling of ^{95}Mo resonances in heptamolybdate.

Finally, structure **(III)** can become **(IV)** by a simple folding-in of the two 'labile' octahedra, as indicated by arrows. A related transition could also yield the α-octamolybdate structure,[16,17] although we have no evidence for this being present in aqueous solution.

Our conclusions differ substantially from the recalculation by Tytko *et al.*,[18] who postulate a very wide range of species including a diprotonated heptamolybdate. We believe that our simpler results arise in part from the use of a 2 mol dm^{-3} Li^+ medium, which favours octamolybdate, and in part from the inability of our method to detect minor or labile species.

Acknowledgements

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