Phosphorus-31 and Oxygen-17 N.M.R. Evidence of Trapped Electrons in Reduced 18-Molybdodiphosphate(V), $P_2Mo_{18}O_{62}^{8-}$

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Summary Reduction of the $P_2Mo_{18}O_{62}^{6-}$ anion by two electrons results in the mixed valence form and, by using ^{31}P and ^{17}O n m.r. high resolution spectra, these electrons are deduced to be firmly trapped by two adjacent molybdenum atoms located in both half-units of the anion

Many heteropolyanions of the type $XM_{12}O_{40}^{-}$, where $M = Mo^{6+}$.or W^{6+}, may be reduced to the mixed valence forms. According to the e.s.r. work of Prados and Pope[1] the introduced electron is evenly distributed over the whole polymetallate sphere by a thermally activated hopping process. The added electrons in the two-electron reduced forms of α-$XMo_{12}O_{40}^{n-}$ were shown by ^{17}O n.m.r. spectroscopy to be very mobile, thus averaging the valence of all 12 molybdenum atoms.[2,3] In these heteropolyanions all the metal atoms occupy equivalent sites of symmetry close to C_{4v} and electrons are hopping through the bridging oxygen atoms. The structure of $P_2Mo_{18}O_{62}^{6-}$ resembles that of $PMo_{12}O_{40}^{3-}$ and may be viewed as a combination of two PMo_9O_{34} units formed from α-$PMo_{12}O_{40}^{3-}$ by the removal of one MoO_6 octahedron from each of three Mo_3O_{13} edge-sharing groups,[4] resulting in an overall anion symmetry of D_{3h} (Figure). Two non-equivalent sets of molybdenum atoms should result in a different degree of electron-trapping, though according to the e.s.r. spectrum[1] for the tungsten analogue, the added electron is evenly distributed. However, the temperature at which the electron-trapping is observable is higher than for $PW_{12}O_{40}^{4-}$.

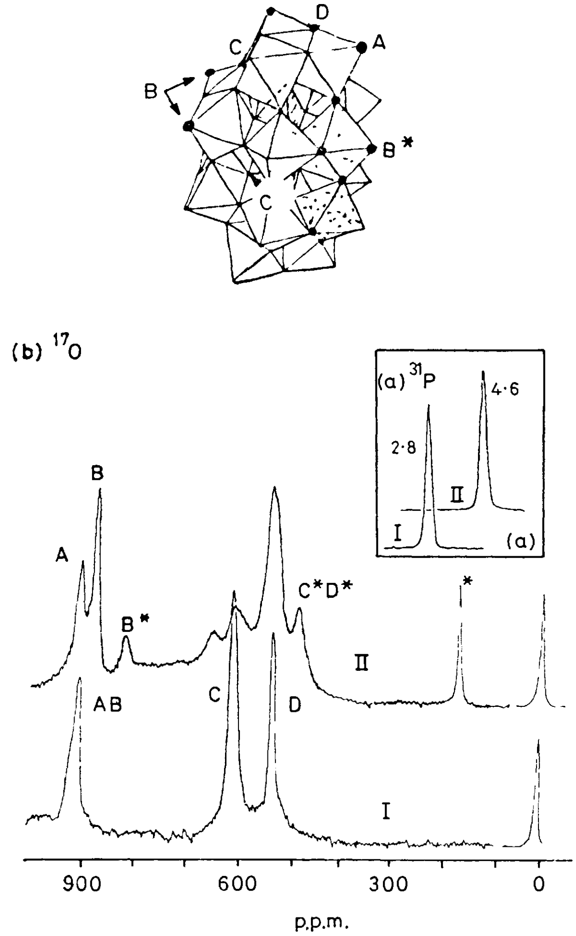

Figure. The structure of the heteropolyanion $P_2Mo_{18}O_{62}^{6-}$, and its ^{31}P (a) and ^{17}O (b) n.m.r. spectra for the initial (I) and the reduced forms (II). The line at -164 p.p.m., marked by an asterisk, is due to the SO_4^{2-} anion, transformed and enriched upon oxidation.

The tendency of molybdenum in oxidation state (VI) to form *cis*-MoO_2 bonds leads to unsymmetrical Mo–O–Mo bridges between the two half-units in $P_2Mo_{18}O_{62}^{6-}$ This results in special properties of this anion which, unlike $P_2W_{18}O_{62}^{6-}$, undergoes two-electron reduction only in the first stage,[5] and it is of interest to study the behaviour of the two electrons in this anion.

Here we have used ^{31}P and ^{17}O n.m.r. spectroscopy to elucidate the nature of the two added electrons in $P_2Mo_{18}O_{62}^{8-}$ The ^{17}O n.m.r. spectra were recorded at 12·16 MHz and the ^{31}P n.m.r. spectra at 36·433 MHz on a Bruker SXP 4-100 spectrometer at 50 °C. $Na_6P_2Mo_{18}O_{62}$ was dissolved in $H_2{}^{17}O$ (1·5% enrichment in ^{17}O). The Raman spectra of the crystalline salt and of its solution were identical, and distinguishable from the spectrum of α-$PMo_{12}O_{40}^{3-}$ by the presence of a high intensity band at 720 cm^{-1}, assigned to the unsymmetrical Mo–O–Mo bridges. This shows that the structure is retained upon dissolution. It is also confirmed by the presence of a single line in the ^{31}P n.m.r. spectrum, shifted, by $-2·8$ p.p.m., to high field relative to H_3PO_4 (Figure).

In the ^{17}O n.m.r. spectrum three lines are observed, shifted to low field relative to H_2O (Figure), whose intensities are compatible with the presence of the 18 terminal (911 p.p.m.), 24 corner-sharing (615 p.p.m.), and 12 edge-sharing oxygen atoms (534 p.p.m.) found in the *X*-ray structure determination.[4] The internal oxygen atoms of the two PO_4 groups are not observed owing to the lack of enrichment at these sites, which is due to a slower oxygen exchange. Assignment of the lines is based on the common correlation between the downfield chemical shift and the increase of p_π–p_π interaction in Mo–O bonds. The observed ^{17}O n.m.r. spectrum is different from that of $P_2W_{18}O_{62}^{6-}$, [6,7] revealing the slight differences in the symmetry of the anion structures noted by Pope.[8]

Addition of 1M Na_2SO_3 to 1M $Na_6P_2Mo_{18}O_{62}$ gives the two-electron reduced form which has only one line in the ^{31}P n.m.r. spectrum at $-4·6$ p.p.m. This indicates the presence of only one reduced form and implies that one electron is located in each PMo_9O_{34} half-unit. If this were not the case, two lines should be observed in the ^{31}P n.m.r. spectrum owing to the non-equivalence of the two phosphorus atoms.

It should also be noted that the two-electron reduced form of $P_2Mo_{18}O_{62}^{8-}$ gives no e.s.r. signal, thus showing complete pairing of the two electrons, most probably by super-exchange (unlike for α-$PMo_{12}O_{40}^{5-}$, where an incompletely paired state is observed, and for $Mo_6O_{19}^{4-}$, where the two electrons are only weakly coupled).

On the other hand, the ^{17}O n.m.r. spectrum of the reduced form is rather complicated, showing splitting of the lines. For the two-electron reduced form of α-$PMo_{12}O_{40}^{5-}$, the ^{17}O n.m.r. spectrum is the same as for the non-reduced form, but all the lines are shifted to higher field by *ca.* 40 p.p.m.,[3] indicating the screening of the oxygen atoms by rapid intra-ionic electron delocalization. The ^{31}P n.m.r. line is also shifted to high field for this system upon reduction.

The splitting of the ^{17}O lines in the reduced $P_2Mo_{18}O_{62}^{8-}$ may be caused by the trapping of two electrons. The integrated intensities of the three lines assigned to the terminal oxygen atoms are in the ratio 6 : 10 : 2. Line (A), with the highest chemical shift, coincides with that for the non-reduced form and is attributed to the oxygen atoms in Mo_3O_{13} groups. Line B*, of lowest intensity (821 p.p.m.), should be assigned to the terminal oxygen atoms bound to the reduced molybdenum atoms The anion diamagnetism implies that the only possibility is that of trapping electrons by two adjacent molybdenum atoms Line B, of highest intensity, is due to the remaining terminal oxygen atoms of the non-reduced ring-forming octahedra

The splitting of the remaining lines in the middle part of the spectrum may also be explained by the trapping of two electrons and it may be argued that the closer these electrons are to the bridging oxygen atoms, the higher is the upfield shift that is observed The line C*D*, with a relative intensity of 7, at 482 p p m is assigned to the bridging oxygen atoms of two adjacent MoO_6 octahedra

The presence of the corner-sharing oxygen atoms in the almost linear bridge Mo–O–Mo results in a complete paired state in the two-electron form The introduction of one electron results in the symmetry of a 'reduced' octahedron, close to C_{4v}, and this octahedron induces distortion of the neighbouring one, making conditions more favourable for the introduction of a second electron, so that the second half-wave potential, $E_{1/2}$, becomes indiscernable from the first Therefore the one-electron state for $P_2Mo_{18}O_{62}{}^{6-}$ might be impossible, especially when the protonation of the reduced anion is due to an increasing negative charge However, under deprotonated conditions it is possible to produce the one-electron form for α-$PMo_{12}O_{40}{}^{3-}$ [1]

For the one-electron reduced anion, $P_2W_{18}O_{62}{}^{7-}$, the e s r spectrum reveals the delocalization of an electron over the whole or part of the structure but the introduction of the second electron would probably result in the complete localization of the electron pair in two adjacent tungsten atoms in both half-units, as in the reduced $P_2Mo_{18}O_{62}{}^{8-}$ Indirectly, this is confirmed by observation of the shift of the ^{31}P n m r line from -13 to $-1{\cdot}3$ p p m in the two-electron form of $P_2W_{18}O_{62}{}^{8-}$

From the results obtained it may be argued that the degree of the interaction of two electrons within a polymolybdate structure depends on the angle of the Mo–O–Mo bridges which plays a major role in delocalization processes In the two-electron form of $Mo_6O_{19}{}^{4-}$ the electrons are firmly trapped and are weakly coupled because of the orthogonality of the d_{xy} orbitals of two adjacent Mo atoms, and because the small Mo–O–Mo angle results in a smaller degree of p_π—d_π interaction In the two-electron form of $P_2Mo_{18}O_{62}{}^{8-}$ two electrons are strongly coupled and firmly trapped because of the almost linear bridging The reduced α-$PMo_{12}O_{40}{}^{5-}$ is an intermediate case, revealing complete delocalization with residual paramagnetism, as was shown by an isotropic line in the e s r Mo^{5+} spectrum and by ^{17}O n m r spectroscopy [2] This is due to the intermediate values of the angles of the Mo–O–Mo bridges, showing a higher degree of covalency than in $Mo_6O_{19}{}^{4-}$

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