^{17}O N.M.R. of Paramagnetic Heteropoly Blues. Discrimination between Electron Delocalisation Pathways and between Intermolecular Electron Transfer Rates

Kent Piepgrass, Julie N. Barrows, and Michael T. Pope*

Department of Chemistry, Georgetown University, Washington, DC 20057, U.S.A.

Well-resolved natural-abundance ^{17}O n.m.r. spectra of paramagnetic mixed valence heteropoly blue anions, recorded with and without the addition of Mn^{2+} to aid in assignment, reveal differences in spin densities that can be related to intramolecular electron delocalisation, and permit estimates of intermolecular electron exchange rate limits.

Among the methods that have previously been brought to bear upon the electronic structures of heteropoly blues,[1] e.s.r. spectroscopy of one-electron reduced anions,[2] and ^{183}W n.m.r. spectroscopy of diamagnetic tungstate blues[3] have proved to be particularly revealing. Both methods have their limitations however; e.s.r. is not viable for diamagnetic blues, and appears to be unobservable for blues with more than one unpaired electron,[4] whereas ^{183}W n.m.r. does not seem to be feasible for paramagnetic blues.[5] There have been some earlier reports of ^{17}O n.m.r. studies of diamagnetic (two-electron reduced) molybdate blues[6] which were interpreted to demonstrate electron localization or lack thereof, but the only successful n.m.r. investigation of paramagnetic blues has involved recent ^{31}P observations of reduced tungstophosphate[7,8] and molybdophosphate[9] anions.

The ^{17}O n.m.r. spectra of aqueous (D_2O) solutions of the oxidized Keggin-structure tungstate, $SiW_{12}O_{40}{}^{4-}$, (**0**) and its one- and two-electron reduced derivatives, $SiW_{12}O_{40}{}^{5-}$ (**I**) and $SiW_{12}O_{40}{}^{6-}$ (**II**), are shown in Figure 1. As was first reported by Klemperer *et al.*,[10] well-separated resonances for the terminal, doubly-bridging, and internal (μ_4) oxygens are observed for **0**. Since there are two kinds of μ_2 oxygens (linking corner- and edge-shared MO_6 octahedra) in the Keggin structure, two closely-spaced lines (one generally broader than the other) are observed in this region (*ca.* 400 p.p.m. for tungstates) but it has not been possible to assign them unambiguously. It is clear from the spectra of **I** and **II** that the additional electrons in these anions are 'delocalized' over the complete Keggin structure on the n.m.r. timescale. Based on e.s.r. and optical spectra such delocalization has been attributed to a combination of 'covalent' and 'hopping' mechanisms.[1—3] The modest shift of each of the lines observed in the spectrum of **II** compared with that of **0** is in qualitative agreement with analogous results reported by Kazanskii for the corresponding molybdophosphates.[6] The spectrum of **I** also shows three lines, but their greater shifts compared with those of **0** renders their assignments uncertain. However, when the spectrum of a solution spiked with Mn^{2+} (*ca.* 3 mM) is recorded, the line at 627 p.p.m. disappears while the other two are unaffected. The use of Mn^{2+} to cause relaxation of the solvent water peak in ^{17}O n.m.r. spectroscopy is well known,[11] and we have observed that when Mn^{2+} is added in increasing concentrations to aqueous solutions of oxidized Keggin polytungstates, first the solvent, then the terminal, and finally the bridging oxygen resonances are broadened, in many cases into nonobservability.[12] Consequently the line at 627 p.p.m. in

Table 1. ^{17}O N.m.r. data for heteropolyanion/heteropoly blue systems.[a]

Anion		Chemical shift/p.p.m. (linewidth/Hz)
$PW_{12}O_{40}{}^{3-}$	**0**[b]	766 (780), 428,406[c] (955)
	I	632 (200), 447 (295), 266 (540)
	II	705 (175), 401 (190), 369 (380)
$SiW_{12}O_{40}{}^{4-}$	**0**	763 (330), 417 (235), 404 (525), 25 (485)
	I	627 (270), 451 (190), 261 (460), 31 (390)
	II	727 (430), 375 (400), 388 (430), 29 (275)
$H_2W_{12}O_{40}{}^{6-}$	**0**	723 (683), 408[c] (275), 81[d] (600)
	I	581 (460), 461 (230), 273 (495)
	II	676 (485), 405 (500), 368 (575)
$PMo_{12}O_{40}{}^{3-}$ [e]	**0**	938 (70), 583 (80), 551 (165), 80 (660)
	I	784 (210), 706 (570), 567 (580), 80 (660)
	II	878 (190), 539 (235), 523 (375), 70 (1000)
$Mo_6O_{19}{}^{2-}$ [e]	**0**[f]	933 (20), 563 (10), [h]
	I[g]	770 (110), 538 (20), [h]

[a] Aqueous solution, ambient temperature (297 K) except where noted. [b] Denotes number of additional electrons. [c] Overlapping lines. [d] Internal oxygen atoms; not observed in reduced anions. [e] Tetra-n-butylammonium salt, enriched in ^{17}O, in acetonitrile. [f] 353 K; Data of Klemperer *et al.*, ref. 10. [g] 338 K. [h] Resonances for the central oxygen atoms were not observed in acetonitrile solution.

the spectrum of **I** can be confidently attributed to the terminal oxygens. Thus, upon reduction to **I**, the terminal and one of the bridging oxygen resonances† of **0** are shifted upfield and the other bridging oxygen resonance is shifted downfield. An almost identical pattern of shifts was observed for two other polytungstate blue systems and is summarized in Table 1. Also shown in Table 1 are data for two molybdate systems, $PMo_{12}O_{40}{}^{3/4-}$ and $Mo_6O_{19}{}^{2/3-}$. The paramagnetic molybdates are accessible only in aprotic solvents and spectra were recorded on samples enriched in ^{17}O. For each of the four Keggin anions examined it is noteworthy that, upon reduction to **I**, the lines for the two kinds of bridging oxygens undergo shifts of very different magnitudes, and in the case of the tungstates at least, the shifts are of different signs. In order to seek a possible explanation for this difference, we note first that since, on the n.m.r. timescale, the unpaired electrons are delocalized over all the metal atoms in each anion, the reduced species, **I**, have effective cubic symmetry. The observed isotropic shifts are therefore considered to be scalar in origin and may be factored into contributions from unpaired electron delocalization and indirect spin delocalization.[13] We consider next the effect of an unpaired electron temporarily resident on one of the metal atoms of each polyanion. The site symmetry of each metal is approximately C_{4v} and the unpaired electron occupies a d_{xy}-like orbital[1,2] that is orthogonal to the bonds to the terminal and internal oxygens. The isotropic shift of the terminal oxygens (*ca.* 140 p.p.m. upfield for each anion‡) must therefore be the result of indirect spin delocalization through σ and π bonds. The virtual absence of any shift for the internal oxygens, when these were observable, is

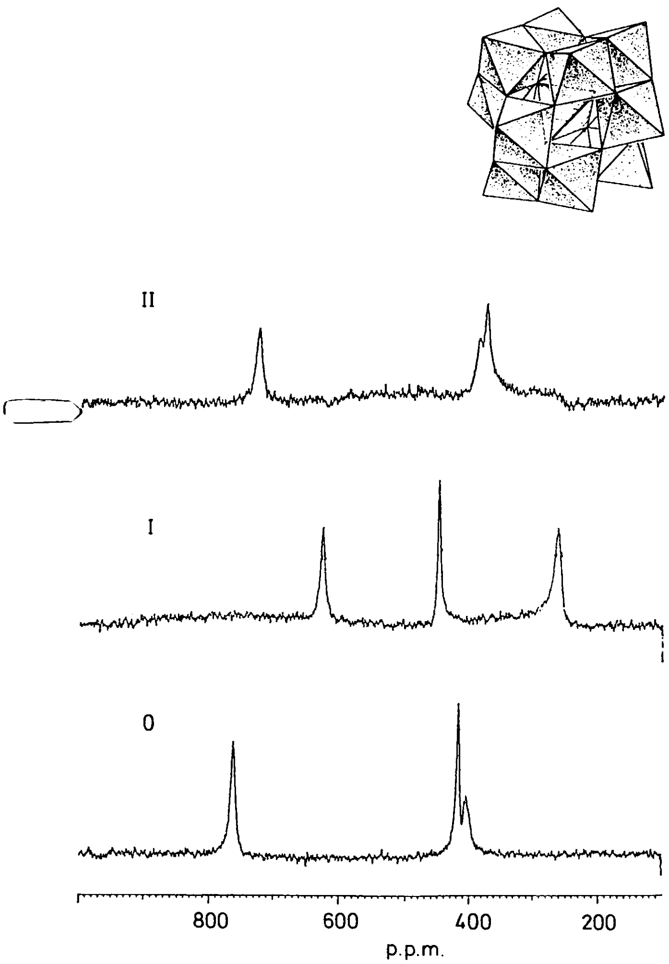

Figure 1. ^{17}O N.m.r. spectra (14.688 MHz, sweep width 60 000 Hz, 60 000 transients) of aqueous solutions (0.31 M) of $H_4SiW_{12}O_{40}$ (**0**), $H_5SiW_{12}O_{40}$ (**I**), and $H_6SiW_{12}O_{40}$ (**II**). Each anion has the Keggin structure shown in polyhedral form in the inset. Chemical shifts relative to external H_2O. The resonance for the internal oxygen (25—31 p.p.m.) is not shown.

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† Although we cannot track unambiguously which of the two closely spaced (in **0**) bridging resonances is shifted downfield, we note that one of the two lines is broader than the other in each tungstate spectrum. In the case of 12-molybdophosphate, the two 'bridging' lines of **I** have similar widths, and the shifts of each have been taken from the average of the two chemical shifts of the oxidized anion, from which $\Delta\delta = 0$ and 139 p.p.m.

‡ The shifts for the terminal and doubly bridging oxygens shown by the data in Table 1 are 'exchange-averaged' over the twelve equivalent sets of the Keggin structure. Shifts for oxygen atoms adjacent to the reduced metal ion are, to first order, twelve times as large.

consistent with the very low bond order for M–O_{int}.[1]§ The four equatorial oxygens of the MO_6 octahedron are all approximately equidistant from the metal ion but experience very different shifts depending upon whether they link octahedral corners or edges. This suggests that the observed shifts are the sum of two opposing contributions, upfield and downfield, that are of different magnitudes for the two kinds of oxygen. The sign of the shift induced by indirect spin delocalization depends upon the sequence of orbitals involved and should be similar for both types of bridging oxygens. We suggest that the different net spin densities on these oxygens are the result of differences in direct unpaired electron delocalization. Approximate bond angles in Keggin anions are M–O_{cor}–M, 150° and M–O_{edge}–M, 125° and these imply that d–p–d π-bonding is more extensive across the corner-shared junctions.¶ We therefore propose that the line shifted downfield (for $PMo_{12}O_{40}^{4-}$ the line shifted to 706 p.p.m.) represents the corner-shared oxygen. The $Mo_6O_{19}^{2-}$ anion has a structure with edge-shared octahedra only (Mo–O–Mo, 115°), and it is consistent with the above assignment that no line is shifted downfield upon reduction of this anion.

With the observation of well-resolved spectra for the paramagnetic heteropolyanions, measurement of intermolecular electron transfer rates can be contemplated, although lineshape analysis is complicated by the quadrupolar nature of ^{17}O. Kozik *et al.*,[7,8] from a careful analysis of ^{31}P n.m.r. spectra of tungstophosphate heteropoly blues, have verified that intermolecular electron transfer approaches diffusion-controlled limits for these species in aqueous solution. Barrows[9] has shown similarly that the rate of exchange for $PMo_{12}O_{40}^{3/4-}$ is *ca.* 5×10^3 dm^3 mol^{-1} s^{-1} in acetonitrile at 24 °C. In preliminary experiments, spectra of equimolar mixtures of **0** and **I** species were measured. For $PW_{12}O_{40}^{3/4-}$ and $SiW_{12}O_{40}^{4/5-}$ at 24 °C, and for $H_2W_{12}O_{40}^{6/7-}$ at 65 °C, the spectra were fully coalesced, signifying that $k_{ET} > 4 \times 10^4$ dm^3 mol^{-1} s^{-1}. Corresponding experiments with $H_2W_{12}O_{40}^{6/7-}$ at 24 °C and with $PMo_{12}O_{40}^{3/4-}$ and $Mo_6O_{19}^{2/3-}$ in acetonitrile at 24 °C indicated slower rates of exchange, but further analysis has not yet been possible.

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§ The internal oxygen atoms lie within 2.4 Å of the unpaired electrons, and their insensitivity confirms the absence of a significant dipolar contribution to the observed shifts.

¶ ^{183}W N.m.r. spin–spin coupling constants are also dependent upon W–O–W bond angle and are greatest for corner-shared contacts (see P. J. Domaille, *J. Am. Chem. Soc.*, 1984, **106**, 7677, and references therein). See also the discussion of e.s.r. data by S. P. Harmalker, M. A. Leparulo, and M. T. Pope, *ibid.*, 1983, **105**, 4286.

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