# Identification of Stereoisomers of Mixed Heteropoly Anions. Mixed Valence and Triplet State Electron Spin Resonance Spectra of Vanadium(IV)

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*Summary* The existence of several isomers of the Keggin anions $PV_xW_{12-x}O_{40}^{(3+x)-}$ and $PV_xMo_{12-x}O_{40}^{(3+x)-}$, ($x$ = 1—4), is demonstrated by $^{31}P$ n.m.r., e.s.r., and i.r. spectroscopy.

MANY heteropoly 12-metallo anions adopt the well known 'Keggin' structure found originally for $PW_{12}O_{40}^{3-}$ in 12-tungstophosphoric acid pentahydrate.[1] 'Mixed' Keggin anions such as $PV_4W_8O_{40}^{7-}$ and $SiMo_2W_{10}O_{40}^{4-}$ have been known for many years, but only recently, by means of voltammetry, has it been possible to verify that discrete complexes of this type could be isolated in pure form.[2] Such anions should be capable of existing in isomeric forms according to the different ways of arranging the two kinds of metal atom within the Keggin structure.[3] We report here the first demonstration of this type of isomerism.

We find that the n.m.r. chemical shift of a central phosphorus atom in the Keggin structure is sufficiently dependent upon the nature and disposition of the metal atoms surrounding it to permit distinction between isomers. The $^{31}P$ resonance of $PW_{12}O_{40}^{3-}$ occurs at 14·96 p.p.m. upfield from $H_3PO_4$, and, as W atoms are replaced by V or Mo, the resonance appears at lower fields. The lowest-field resonance that we have observed so far is for one of the isomers of $PV_3Mo_9O_{40}^{6-}$ at 1·68 p.p.m. Figure 1 illustrates the spectrum of 0·1 M $H_5PV_2Mo_{10}O_{40}$ in 0·25 M $H_2SO_4$ taken by Fourier transform techniques on a Bruker instrument at 36·43 MHz. The two main signals (at *ca.* 3 and 4 p.p.m.), each of which clearly has two components, have integrated intensities in the ratio 3:8. The small peak at lowest field is due to traces of $H_3PO_4$ impurity and serves as an internal reference. The $^{31}P$ n.m.r. spectrum of $H_5PV_2W_{10}O_{40}$ shows a similar pattern at 12·5—14·2 p.p.m. with the upfield line more clearly resolved into two (intensity ratio 6:2). The five possible isomers[4] of $XZ_2Z'_{10}O_{40}$ have relative statistical weights of 2(1,2), 2(1,4), 4(1,5), 2(1,6), and 1(1,11).[5] The spectrum in Figure 1 is thus consistent with the presence of all five isomers with their expected relative abundances. A more elaborate spectrum with at least 21 lines between 10·25 and 13·65 p.p.m. is given by solutions of the anion $PV_4W_8O_{40}{}^{7-}$. None of these lines overlaps with those from other heteropoly complexes. The maximum number of possible isomers for a tetrasubstituted Keggin anion is 27, but three of these are expected to have low abundances.[5]

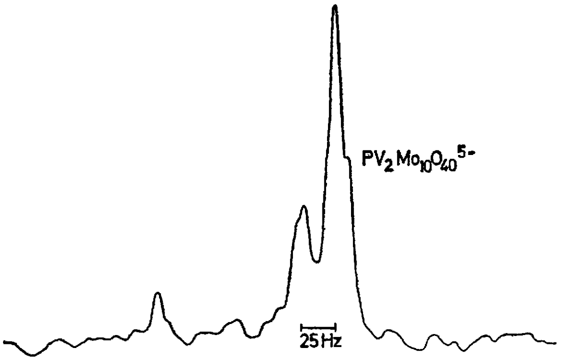

FIGURE 1. Fourier transform $^{31}P$ n.m.r. spectrum of 0·1M $H_5PV_2Mo_{10}O_{40}$ in 0·25M $H_2SO_4$.

Reduction of the anion $PV_2W_{10}O_{40}{}^{5-}$ by controlled potential electrolysis at a graphite electrode yields the complexes $PV^{IV}V^{V}W_{10}O_{40}{}^{6-}$ (I) and $PV^{IV}{}_2W_{10}O_{40}{}^{7-}$ (II) which have been isolated as potassium salts. The experimental and computer-simulated e.s.r. spectra of a solution of anion (I) are shown in Figure 2. The simulation was achieved by combining 8- and 15-line spectra with the same $g$ (1·952) and with $a = 104{\cdot}5$ and 53 G respectively. The relative intensities of the 8- and 15-line spectra were 7 : 4, a choice based on the hypothesis that those two isomers (1,2 and 1,6) in which vanadium atoms are separated by a single oxygen atom would give a 15-line spectrum due to rapid electron exchange, whereas the other three isomers, containing vanadium atoms separated by at least an –O–W–O– sequence, would give an 8-line spectrum. The successful simulation, particularly with respect to the relative line intensities, is further proof of the presence of the five possible isomers in their expected relative abundances. We may also infer that the rapid electron-hopping observed in mixed valence heteropoly anions[6] takes place between neighbouring metal atoms.

Upon further reduction of anion (I) to anion (II) the e.s.r. spectrum collapses to a 15-line pattern with the expected intensity variation, for which $g = 1{\cdot}95$ and $a = 53$ G. This spectrum is less intense than that shown in Figure 2 presumably owing to partial spin coupling. It may well be that those isomers contributing to the 15-line triplet spectrum are those which gave the 8-line spectrum in Figure 2; it seems likely that the 'vicinal' (1,2 and 1,4) isomers containing the $V^{IV}$–O–$V^{IV}$ arrangement would be diamagnetic. Magnetic susceptibility measurements and rigid-matrix e.s.r. spectra of salts of anion (II) are planned. The e.s.r. spectrum of a neat powdered sample of the potassium salt shows the expected half-field ($\Delta m_s = 2$) absorption.

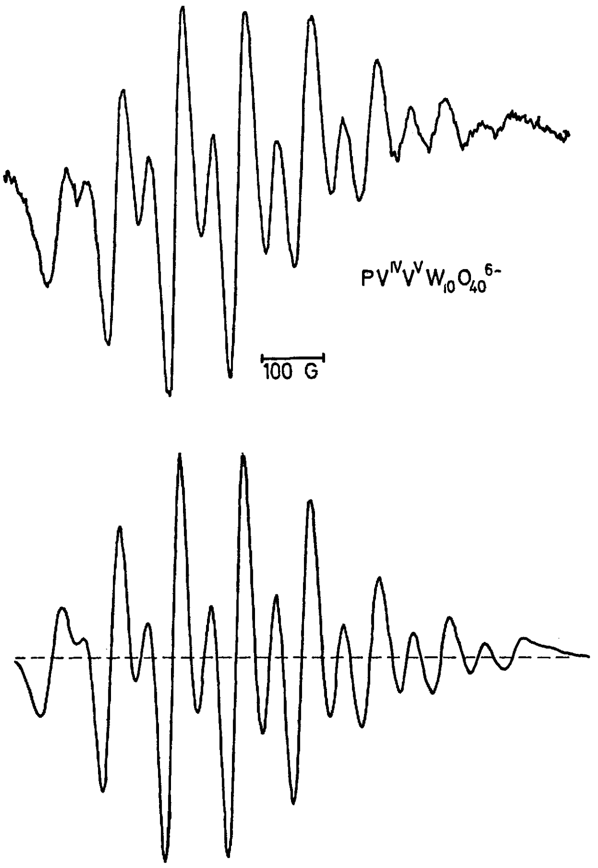

FIGURE 2. Experimental (upper) and simulated (lower) e.s.r. spectrum of an aqueous solution of $PV^{IV}V^{V}W_{10}O_{40}{}^{6-}$ at pH 5.

Qualitative evidence for the presence of more than one isomer in salts of anion (I) is given by i.r. spectroscopy. The i.r. spectrum of $PW_{12}O_{40}{}^{3-}$ shows a sharp intense absorption at *ca.* 1080 cm$^{-1}$ ascribed to the phosphate $T_2$ mode.[7] The band is shifted to 1065 cm$^{-1}$ and broadened somewhat in the spectrum of $PV_2W_{10}O_{40}{}^{5-}$, but is clearly split into four components (1048, 1065, 1082, and 1100 cm$^{-1}$) in spectra of $PV^{IV}V^{V}W_{10}O_{40}{}^{6-}$. Since reduction in symmetry of a $T$ mode can generate a maximum of three components, this result indicates the presence of at least two isomers.

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