Concerning Isomerisms and Interconversions of 2:18 and 2:17 Heteropoly Complexes and Their Derivatives

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Summary Contrary to recent interpretations, it is demonstrated by ^{183}W n.m.r. and by V^{IV} e.s.r. spectroscopy that: (i) the α_2 isomer of $[(PO_4)_2W_{17}O_{53}]^{10-}$, and its α_2 $[(PO_4)_2VW_{17}O_{54}]^{8-}$ derivative, differ from α-$[(PO_4)_2W_{18}O_{54}]^{6-}$ by absence of a W atom from one of the 3-fold W_3O_{13} groups which cap the ends of the latter complex, rather than by removal or substitution of one W atom from the 12 which are around the complex's 'belt'; and (ii) β-$[(PO_4)_2W_{18}O_{54}]^{6-}$ differs from its α isomer by a 60° rotation, about its 3-fold axis, of one of the 'cap' W_3O_{13} groups rather than by a 60° rotation of one PW_9 'half-unit' relative to the other one.

THERE has been considerable recent interest[1–13] in structures, isomerisms, interconversions, and derivatives of the various 2:18 and 2:17 heteropolyanions, $[(XO_4)_2(\text{W or Mo})_{18}O_{54}]^{6-}$ and $[(XO_4)_2(\text{W or Mo})_{17}O_{53}]^{10-}$ ($X = P^V$ or As^V) (Figure 1). Recently Massart *et al.*[2] and Contant *et al.*[4] have reported ^{31}P n.m.r. results, much other data, and an overall reaction scheme of interconversions of these anions. An important aspect of their correlation, based on their ^{31}P n.m.r. results, was the conclusion that the α_2 isomer of the P_2W_{17} complex differs from the α-P_2W_{18} anion (Wells–Dawson structure[14]) by the removal of one of its 12 equivalent 'belt' W atoms. This contradicted the earlier conclusion of Kazanskii,[6] which had been based on vanadium(IV) e.s.r. measurements.

We have extended our newly developed technique[5] for direct ^{183}W n.m.r. measurements on heteropoly tungstates to a solution of the unsubstituted α_2 isomer of the P_2W_{17}

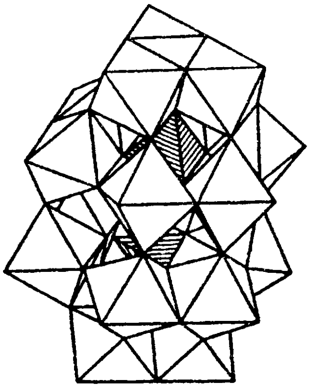

FIGURE 1. The structure of α-$[(PO_4)_2W_{18}O_{54}]^{6-}$ (Wells–Dawson structure). Each vertex of a polyhedron locates the centre of a close-packed O atom. The P atoms are at the centres of the interior (hatched) tetrahedra. Every octahedron contains a W atom. The β isomer is identical except that the W_3O_{13} cap on the top of the complex is rotated 60° about its three-fold axis. The α_2 isomer of $[(PO_4)_2W_{17}O_{53}]^{10-}$ has a structure identical to that illustrated except that one W atom and its unshared O atom have been removed from the three-fold W_3O_{13} cap on the top of the complex. In the α_1 isomer of the 17-tungsto-derivatives, it is one of the 12 equivalent W atoms (and its unshared O) from around the belt of the complex which has been removed. A vanadium(IV) atom (plus an unshared O) can be inserted in place of the missing W atom in each 17-tungsto-derivative.

complex. That method gives extremely sharp lines and very sensitive chemical shifts.[5] The spectrum unambiguously demonstrates that it is one of the W atoms (and its unshared O) from one of the W_3O_{13} end caps which gets removed from α-P_2W_{18} to form the α_2-P_2W_{17} complex.† The spectrum consists of 9 very narrow lines:[5,15] δ_W −242·27, −224·97, −222·67, −218·94, −179·62, −175·78, −159·60, −140·82, and −127·92 (each ± 0·05 p.p.m.), having respective area ratios 2:2:2:2:1:2:2:2:2 corresponding exactly to the 8 structurally distinct pairs of equivalent W atoms plus one unique W atom required by the structure described. This spectrum cannot be reconciled with removal of a 'belt' W atom. As in the case of the two-peak α-P_2W_{18} ^{183}W n.m.r. spectrum (area ratio 2:1) previously reported,[5] each peak in the new spectrum is slightly split into a very narrow doublet by ^{31}P–O–^{183}W coupling.

In our previous paper[5] we reconciled the small differences in ^2J(WOP) values for α-P_2W_{18} and for the Keggin PW_{12} complex as consistent with the small differences in P–W distances as revealed by accurate *X*-ray crystallography.[16–18] It seems likely that failure to take into account the changes which would be logically expected in the P–W distances in the PW_{17} derivatives could explain the incorrect conclusion derived earlier from ^{31}P n.m.r. chemical shifts.

Massart *et al.*[2] also suggested that the origin of the α–β isomerism in the P_2W_{18} anion was more likely to be a 60° rotation of one of the three-fold W_3O_{13} caps[8] on the ends of the complex, than the 60° rotation of a whole PW_9 'half-unit' relative to the other 'half-unit' as had been concluded from the *X*-ray crystallographic study of Matsumoto and Sasaki.[3] The crystallographic decision on this point is a difficult one. The matter is resolved, in favour of the 60° rotation of just one W_3O_{13} cap, by the ^{183}W n.m.r. spectrum of the β-P_2W_{18} complex. If the isomerism results from the rotation of a whole PW_9 'half-unit,' there would be just two lines in the spectrum, having area ratio 2:1. Actually, the spectrum (Figure 2) consists of four very sharp doublets having the total area ratios 2:2:1:1. This corresponds exactly to rotation of one W_3O_{13} cap by 60°. Each doublet is baseline-resolved, average width at half-height is *ca.* 0·2 Hz, and results from the ^{31}P–O–^{183}W coupling splitting each peak.

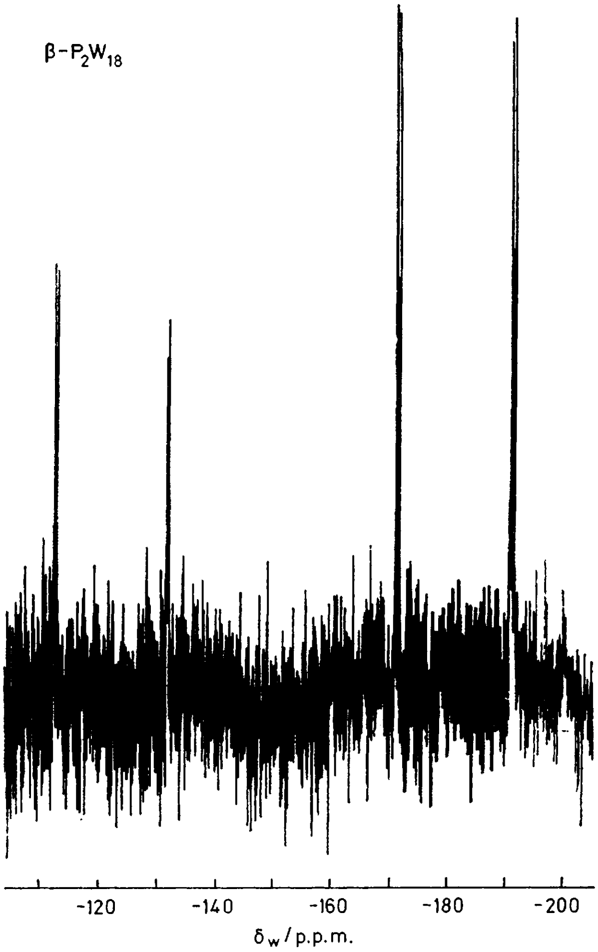

FIGURE 2. The ^{183}W n.m.r. spectrum of β-$[(PO_4)_2W_{18}O_{54}]^{6-}$. δ_W values are: −191·12, −171·08, −131·05, and −111·58 (each ±0·05 p.p.m.) (refs. 5 and 15).

With respect to substituted P_2W_{17} products, we have reinforced and extended Kazanskii's[6] e.s.r. data and conclusion by measurement of the complexes derived by treating vanadium(IV) with both the α_1 and α_2 P_2W_{17} species, yielding α_1 and α_2 derivatives of formula $[(PO_4)_2VW_{17}O_{54}]^{8-}$. The e.s.r. spectra of these complexes are significantly

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† *Added in proof*: Following submission of this communication, an i.r. spectroscopic study of solids has been reported which supports our conclusion: C. Rocchiccioli-Deltcheff and R. Thouvenet, *Spectroscopy Letters*, 1979, **12**, 127.

different. The g-values obtained from frozen glass spectra at 77 K (confirmed by simulation) were: $g_{\parallel}$ = 1·885 (α_1) and 1·917 (α_2); $g_{\perp}$ = 1·964 (α_1) and 1·970 (α_2). The values for the α_2 isomer are strikingly similar to those of substituted Keggin anions, $[XO_4VW_{11}O_{36}]^{n-}$, the ranges observed[19] for six complexes being $g_{\parallel}$ = 1·915—1·922; $g_{\perp}$ = 1·966—1·970. The conclusion is that the α_2 isomer contains the V atom in one of the three-fold cap groups.

The vanadium(IV—V) redox potentials for the 2 isomers, determined from cyclic voltammograms, are: 0·54 (α_1) and 0·45 (α_2) V *vs.* S.C.E. (pH 4·7). The indicated relative stability of V^{IV} in the equatorial site is consistent with the proposal that $[P_2W_{18}O_{62}]^{6-}$ is reduced initially at one of the twelve equivalent equatorial W atoms.[20]

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