

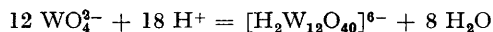
Proton Magnetic Resonance of Aqueous Metatungstate Ion: Evidence for Two Central Hydrogen Atoms

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THE isomorphism of metatungstic acid with heteropolytungstates possessing the Keggin structure¹ requires that the metatungstate ion contains twelve tungsten and forty oxygen atoms. Most investigations of isopolytungstates^{2,3} have concluded that the metatungstate ion has a charge of -6 , so that the formula of this anion must be written with two non-replaceable hydrogen atoms, $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$. It has generally been assumed that these hydrogen atoms occupy the central tetrahedral cavity in the Keggin structure, but no direct evidence for this has been forthcoming. We have examined the ^1H magnetic resonance of solutions of sodium metatungstate, $\text{Na}_6[\text{H}_2\text{W}_{12}\text{O}_{40}] \cdot 22\text{H}_2\text{O}$, in several aqueous solvents and in

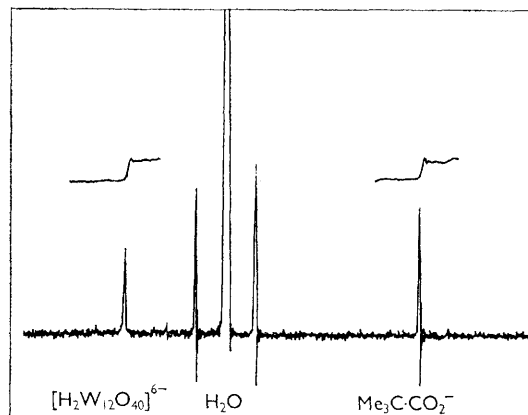
deuterium oxide. In all cases a narrow resonance line appeared downfield from water. The resonance also occurred in solutions of sodium orthotungstate acidified according to the stoichiometry of the equation



The chemical shift of this absorption with reference to Tiers' salt, sodium 3-(trimethylsilyl)-1-propanesulphonate, varied from 6.2 p.p.m. in neutral solutions (water, D_2O , phosphate buffer of pH 6.75) to 6.0 p.p.m. in 1.0 M-sulphuric acid.⁴ The integrated intensity of the absorption line compared with that of an internal standard of potassium pivalate,⁵ $\text{Me}_3\text{C}\cdot\text{CO}_2\text{K}$, showed that it was due

to two hydrogen atoms per twelve tungsten atoms (see Figure). Solutions of the isostructural heteropoly-anions, $[\text{SiW}_{12}\text{O}_{40}]^{4-}$ and $[\text{CoW}_{12}\text{O}_{40}]^{6-}$ in 1.0M-sulphuric acid showed only a resonance due to water. Since these anions are protonated to varying degrees in acidic solutions, such results demonstrate that protons attached to the outside of a Keggin structure exchange rapidly with those of the solvent water. Protons occupying the central tetrahedral cavity of the Keggin structure would not be expected to interact or exchange with the solvent molecules to any significant extent. These internal protons would be attached to oxygen atoms which are in turn each bound to three tungsten atoms of a trigonal W_3O_{13} unit formed by edge-sharing of WO_6 octahedra.⁶ Four of these W_3O_{13} units, by appropriate sharing of oxygen atoms, constitute the complete polytungstate structure. Since each of the four oxygen atoms forming the central tetrahedral cavity will be considerably polarised by its three neighbouring tungsten(VI) atoms, protons attached to such oxygens will be deshielded with respect to normal hydroxide protons, as observed here. Another effect which could influence the shielding of the central protons is the possibility of field-induced interatomic ring currents either in the W_3O_{13} units or throughout the whole anion. The reduction behaviour of anions with the Keggin structure³ demonstrates the existence of low-lying delocalized orbitals through which such an

effect could be realized.⁷ We are further investigating this aspect, and are also using the resonance to trace the formation of metatungstate ion in acidified tungstate solutions.



FIGURE

60 Mc./sec. proton magnetic resonance spectrum of $\text{Na}_6[\text{H}_2\text{W}_{12}\text{O}_{40}] \cdot 22\text{H}_2\text{O}$ and $\text{Me}_3\text{C}\cdot\text{CO}_2\text{K}$ in D_2O at 40°C (spinning side-bands of water peak shown). Ratio of concentrations of $[\text{H}_2\text{W}_{12}\text{O}_{40}]^{6-}$ to $\text{Me}_3\text{C}\cdot\text{CO}_2^- = 9.2$.

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¹ R. Signer and H. Gross, *Helv. Chim. Acta*, 1934, **17**, 1076.

² J. Aveston, *Inorg. Chem.*, 1964, **3**, 981 and references therein.

³ M. T. Pope and G. M. Varga, Jr., *Inorg. Chem.*, 1966, **5**, 1249.

⁴ This corresponds to a shift of 1.4 to 1.0 p.p.m. downfield from the water signal in these solutions.

⁵ G. D. Haines and C. F. Hammer, private communication.

⁶ The two hydrogen atoms are presumably randomly attached to two of the four equivalent oxygen atoms forming the central cavity.

⁷ F. A. Cotton (*Inorg. Chem.*, 1964, **3**, 1217) has made some LCAO-MO calculations for an M_3O_{13} cluster assuming metal-metal bonding. Tungsten-tungsten distances in heteropolytungstates rule out direct metal-metal bonding, but extended molecular orbitals are possible involving the close-packed oxygen atoms as well as the tungsten atoms. The limiting case of this is reached with WO_3 and the formation of tungsten bronzes.