

Where Are the Protons in  $H_3V_{10}O_{28}^{3-}$ ?

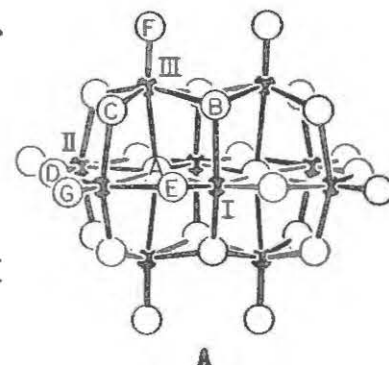
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Polyoxoanions form many interesting and unusual complexes which contain covalently bound organometallic species [1]. Unfortunately, it is very difficult to predict or control the binding sites on the polyoxoanions used by the metal centers. In order to take a more rational approach to polyoxoanion reaction chemistry, a better understanding of the charge distribution in polyoxoanions is needed. A good starting point for a study of the reactivity of a polyoxoanion is the identification of its protonation sites.

The  $V_{10}O_{28}^{6-}$  anion (see A) is a good candidate for a protonation study as its solid state structure has been determined x-ray crystallographically [2], and it can be probed in solution using  $^{17}O$  and  $^{51}V$  NMR spectroscopy.  $^{17}O$  NMR is especially useful in the identification of protonation sites as coordination of a cation to an oxygen center results in a large upfield shift of its  $^{17}O$  resonance [3]. Although several spectroscopic studies have been carried out on the  $V_{10}O_{28}^{6-}$  anion [4-8], its behavior in solution and the identity of its protonation sites are not well understood.



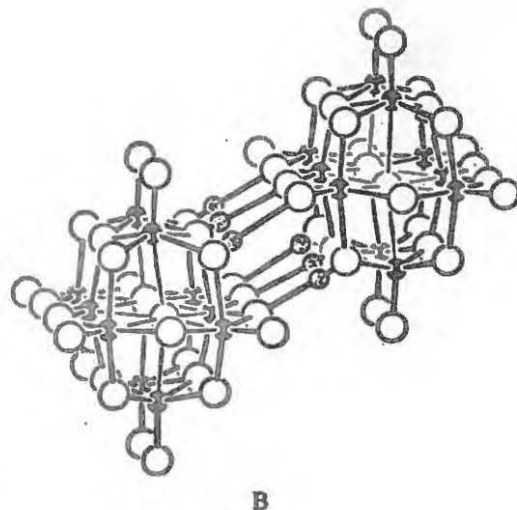
In the present investigation, the  $V_{10}O_{28}^{6-}$  anion was characterized in aqueous solution using a series of  $^{17}O$  [ $^{51}V$ ] NMR experiments. By selectively decoupling the inequivalent vanadium nuclei and observing the effect on the line widths of the oxygen resonances, unique assignments were determined for all the resonances seen in the  $^{51}V$  and  $^{17}O$  NMR spectra of the  $V_{10}O_{28}^{6-}$  anion.

Our approach to the problem of identifying the protonation sites in the  $V_{10}O_{28}^{6-}$  anion was to isolate and characterize its triprotonated analog,  $H_3V_{10}O_{28}^{3-}$  [9]. This anion was isolated as the  $CH_3CN$  soluble salts  $H_3V_{10}O_{28}^{3-}[(n-C_4H_9)_4N]_3$ , 1, and  $H_3V_{10}O_{28}^{3-}[(C_6H_5)_4P]_3$ , 2, by the acidification of an aqueous  $Na_3VO_4$  solution followed by addition of the appropriate counterion. Compound 1 was then characterized in  $CH_3CN$  solution using  $^1H$ ,  $^{51}V$ , and  $^{17}O$  NMR spectroscopy.

$^1H$  NMR spectroscopy was used to show that the anion in 1 retained its three protons in solution and did not self-condense to form water and an oxo-bridged dimer as seen for other protonated polyoxoanions [10]. The  $^{51}V$  NMR spectrum of 1 demonstrated that the two  $V_I$  centers (see A) are inequivalent in the  $H_3V_{10}O_{28}^{3-}$  anion, and that addition of water to the sample catalyzed proton exchange to give the anion effective  $D_{2h}$  symmetry. Lineshape changes were also seen in the  $^{17}O$  NMR spectrum of 1 upon water addition which were consistent with the occurrence of a water catalyzed proton exchange process. Examination of the lineshape changes showed the only resonances due to the  $O_C$  and  $O_B$  oxygens were significantly affected. These spectra indicated that two protons were associated with the  $O_C$  oxygens and one proton with the  $O_B$  oxygens. To provide additional evidence, selective enrichment experiments were carried out to help in the assignment of the resonances observed in the  $^{17}O$  NMR spectrum of 1.

An x-ray crystallographic study of **2** was performed by Professor Victor W. Day at the University of Nebraska. The protons in the  $H_3V_{10}O_{28}^{3-}$  anion in **2** were crystallographically located, and this anion was found to exist as a hydrogen bonded dimer in the solid state as shown in **B**. Two of the protons in the anion were bound to  $O_C$  oxygens and one was bound to an  $O_B$  oxygen (see **A**). These results agree with the protonation sites found in solution for the anion in **1**.

As a result of this study we have concluded that the solid state structure of the  $V_{10}O_{28}^{6-}$  anion is preserved in solution, and that the triply bridging  $O_B$  oxygens and the doubly bridging  $O_C$  oxygens are the protonation sites for the  $H_3V_{10}O_{28}^{3-}$  anion in the solid state and in solution.



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