a common origin for the C_7N unit of other natural products,[24] and it has been proposed that the C_7N unit in mitomycin C is also derived from glucose by a shikimate-type pathway.[25] On the other hand, the different sources of the C_2 units in geldanamycin vis-a-vis streptovaricin and rifamycin provide an interesting biosynthetic variation for molecules which appear to be otherwise biogenetically very similar.

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Charge Distribution in Large Polyoxoanions: Determination of Protonation Sites in $V_{10}O_{28}^{6-}$ by ^{17}O Nuclear Magnetic Resonance

Sir:

Several polyoxoanions of the early transition elements are known to be protonated in solution,[1-3] and/or the solid state.[3-6]

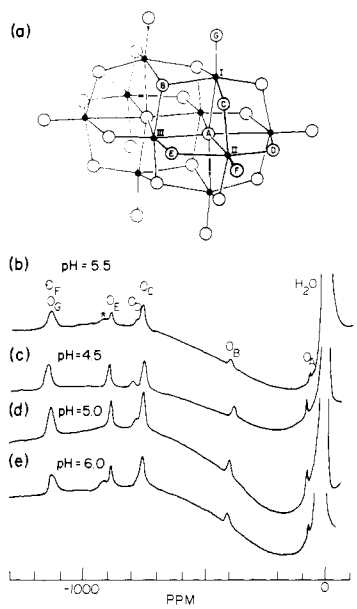

Figure 1. The D_{2h} symmetized structure of $V_{10}O_{28}^{6-}$ (see ref 13, 14) is shown in (a). Small filled circles represent vanadium atoms and large open circles represent oxygen atoms. One member of each symmetry equivalent set of atoms is labeled. ^{17}O FTNMR spectra of $V_{10}O_{28}^{6-}$ in H_2O are shown in b–e. All spectra were measured at 25 °C, with a total vanadium concentrations of 1.5–1.8 M. Chemical shift assignments are given in (b), where the asterisk labels a metavanadate resonance. For chemical shift data, see Table I.

Table I. pH Dependent ^{17}O Chemical Shifts for $Na_6V_{10}O_{28}\cdot 18H_2O$ in H_2O

	Chemical shifts[b]								
pH[a]	H_2O	Metavanadate	O_A[d]	O_B	O_C	O_D	O_E	O_F,O_G	Spectrum[c]
6.0	−1	−925	−62	−406	−766	−780	−893	−1143	e
5.5	0	−925	−63	−400	−764	−786	−895	−1146	b
5.0	−1	—	−67	−396	−764	−790	−898	−1150	d
4.5	0	—	−72	−378	−759	−803	−904	−1160	c

[a] ±0.2 pH units. [b] Negative chemical shift is in parts per million downfield from pure water at 25 °C. Accuracy is about ±2 ppm, depending on line width (see Figure 1b-e). [c] See Figure 1b-e. [d] For labeling scheme, see Figure 1a.

In no case, however, have the protonation sites been determined experimentally, and the location of protons has been surmised using bond-length-bond-strength correlations.[4-6] Since the identification of basic oxygen sites in metal-oxygen compounds has important consequences regarding the reactivity of polyoxoanions and the catalytic activity of metal oxides in general, we have investigated this problem in aqueous solution using ^{17}O NMR spectroscopy. We report here the determination of protonation sites in $V_{10}O_{28}^{6-}$.

The ^{17}O NMR spectrum shown in Figure 1b is obtained when $Na_6V_{10}O_{28}\cdot 18H_2O$[7] is dissolved in 37 atom % ^{17}O enriched water.[8] Acidification with HCl followed by stepwise addition of NaOH yields the spectra shown in Figure 1c-e.[8] Chemical shifts for all observed resonances are tabulated in Table I. The resonance at about −925 ppm which appears only at higher pH's is due to metavanadate species[9,10] which predominate in weakly basic solution.[11] The remaining resonances are assigned to oxygens in $V_{10}O_{28}^{6-}$ (see Figure 1a) utilizing the correlation between chemical shift and metal-oxygen bond order established elsewhere for polymolybdates[15] and chromates.[16] Two continuous shifts of the $V_{10}O_{28}^{6-}$ resonances occur as the solution pH is lowered (see Table I): resonances for O_B and O_C shift upfield, whereas resonances for O_A, O_D, O_E, O_F, and O_G shift downfield. When an oxygen site is protonated, the metal-oxygen bonds to that oxygen are weakened, leading to an upfield shift of its ^{17}O resonance. Thus O_B, since its resonance undergoes a pronounced upfield shift upon acidification, is the predominant protonation site. O_C, since its resonance undergoes only a small upfield shift upon acidification, is protonated to a lesser extent.[17] When V-O bonds to O_B and O_C are weakened, the remaining V-O bonds in $V_{10}O_{28}^{6-}$ are strengthened in order to maintain approximately constant total bond order at vanadium. This bond strengthening leads to the downfield shift of resonances for O_A, O_D, O_E, O_F, and O_G as the solution pH is lowered. The vibrational frequencies of $V_{10}O_{28}^{6-}$ in the terminal oxygen region also shift to higher frequency as the pH is lowered,[18-20] reflecting the increased terminal V-O bond strengths.

The protonation sites observed in $V_{10}O_{28}^{6-}$ are correctly predicted by calculating covalent bond strengths[21] using bond lengths observed in the unprotonated anion.[13,14] The sum of V-O covalent bond strengths at each oxygen site, interpreted as the relative amount negative charge removed from formally dinegative oxygen, yields the sequence of increasing negative charge $O_G \sim O_F < O_E < O_D < O_C < O_B < O_A$. Since O_A is inaccessible to protons, the sequence correctly predicts O_B and O_C to be the most basic oxygens, with O_B more basic than O_C. Note, however, that bond-length-bond-strength correlations[21] fail to give the proper basicity sequence.

We are currently measuring pH dependent ^{17}O NMR spectra of isopolymolybdates, -tungstates, -niobates, and -tantalates in order to gain further insight into the general question of charge distribution in metal-oxygen clusters and its relation to structural parameters.

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