Applications of Vanadium-51 and Phosphorus-31 Nuclear Magnetic Resonance Spectroscopy to the Study of Iso- and Hetero-polyvanadates [1]

By **Stephen E. O'Donnell** and **Michael T. Pope,*** Department of Chemistry, Georgetown University, Washington DC 20057, U.S.A.

Vanadium-51 n.m.r. spectra of a number of iso- and hetero-polyvanadate anions are reported. Spectra of solutions containing $[V_{10}O_{28}]^{6-}$ (pH 6.5—3.5) are consistent with the known solid-state structure of this anion. The $[VO_2]^+$ cation in aqueous solution almost certainly has an octahedral *cis*-dioxo-structure as its n.m.r. linewidth is comparable with those for the *cis* compounds $[VO_2(O_4C_2)_2]^{3-}$ and $[VO_2(edta)]^{3-}$ (edta = ethylenediaminetetra-acetate), which are broader than those for pseudo-tetrahedral $[VCl_2O_2]^-$ and $[VF_2O_2]^-$. Chemical shifts of pseudo-octahedral vanadium atoms in $[V_xW_{6-x}O_{19}]^{n-}$, $[PV_xW_{12-x}O_{40}]^{n-}$, $[PMo_{12-x}V_xO_{40}]^{n-}$, and $[VV_xW_{12-x}O_{40}]^{n-}$ anions range from 506 to 545 p.p.m. (VCl_3O reference) and linewidths from 60 to 200 Hz (2.6—9 p.p.m.). Multiple lines in the specta of the 1 : 12 (Keggin) heteropolyanions confirm the existence of geometrical isomers distinguished by the relative positions of two or more vanadium atoms in the polyanion structure. Phosphorus-31 n.m.r. spectra confirm that most if not all of the possible isomers of this type are formed. The chemical shifts of ^{31}P in $[PMo_{12}O_{40}]^{3-}$ and $[PW_{12}O_{40}]^{3-}$ are *ca.* 11 and 21 p.p.m. upfield from the unprotonated $[PO_4]^{3-}$ ion (−6 with respect to 85% H_3PO_4). Introduction of V atoms in the heteropoly structures causes a progressive decrease in the chemical shift, enabling mixtures of such Keggin anions to be analyzed by n.m.r. A parallel variation in ^{51}V chemical shift is found for $[VO_4]^{3-}$ (536) and the tetrahedral vanadium in $[VV_3W_9O_{40}]^{6-}$ (553) and $[VV_2W_{10}O_{40}]^{5-}$ (556 p.p.m.).

THERE exists a considerable body of work on the numerous iso- and hetero-polyanions of vanadium, niobium, tantalum, molybdenum, and tungsten.[2-7] Although much recent attention has been directed towards the structures of such anions in crystalline salts, the synthesis and reactivity of these species in solution remains a challenging area of investigation. Experimental methods for determining the structures of solute species, particularly labile species in aqueous solution, are in short supply. The complexity of polyanion structures renders otherwise valuable techniques such as Raman spectroscopy to little more than fingerprinting procedures, and it is clearly desirable to make use of as many independent experimental methods as possible in order to construct a comprehensive picture of the solute species in polyanion solutions. Nuclear magnetic resonance spectroscopy is an obvious possible method, for most of the elements in heteropolyanions have isotopes suitable for n.m.r. detection. The use of n.m.r. spectroscopy in this area is becoming increasingly practical with the availability of pulsed Fourier-transform instrumentation.

In this paper we explore the use of ^{51}V n.m.r. for the study of heteropolyvanadates. At the time this work was undertaken, we did not have access to a pulsed Fourier-transform spectrometer, and ^{51}V was chosen because of its high natural isotopic abundance (*ca.* 100%) and n.m.r. sensitivity (0.25 relative to the proton at constant field). We were further encouraged by two earlier papers [8,9] that reported relatively narrow lines in ^{51}V n.m.r. spectra of isopolyvanadate solutions. We also report some preliminary work with ^{31}P which confirms the existence (hinted at by the ^{51}V results) of substitutional isomers of 'mixed' heteropolyanions.[10,11]

---

[1] Based on the Ph.D. Thesis of S. E. O'Donnell, Georgetown University, 1975. Presented in part at the 7th Hudson Symposium, Plattsburgh, New York, 1972.

[2] L. C. W. Baker, 'Advances in the Chemistry of Coordination Compounds,' ed. S. Kirschner, MacMillan, New York, 1971, p. 604.

[3] M. T. Pope and B. W. Dale, *Quart. Rev.*, 1968, **22**, 527.

[4] P. Souchay, 'Ions Minéraux Condensés,' Masson et Cie, Paris, 1969.

[5] H. T. Evans, jun., *Perspectives in Structural Chem.*, 1971, **4**, 1.

[6] T. J. R. Weakley, *Structure and Bonding*, 1974, **18**, 131.

[7] L. P. Kazanskii, E. A. Torchenkova, and V. I. Spitsyn, *Russ. Chem. Rev.*, 1974, **43**, 525.

[8] O. W. Howarth and R. E. Richards, *J. Chem. Soc.*, 1965, 864.

[9] J. V. Hatton, Y. Saito, and W. G. Schneider, *Canad. J. Chem.*, 1965, **43**, 47.

[10] M. T. Pope and T. F. Scully, *Inorg. Chem.*, 1975, **14**, 953.

[11] M. T. Pope, S. E. O'Donnell, and R. A. Prados, *J.C.S. Chem. Comm.*, 1975, 22.

Very recently, other n.m.r. studies of iso- and hetero-polyanions using ^{31}P, ^{17}O, and ^{51}V have been reported.[12–14]

EXPERIMENTAL

Preparation of Compounds.—Authentic samples of the following salts were provided by Dr. C. M. Flynn, jun.: $Na_4[V_2O_7]\cdot 16H_2O$; $K_6[V_4W_9O_{40}]\cdot 24H_2O$; $[NH_4]_6[V_4W_9O_{40}]\cdot 22H_2O$; $K_5[V_3W_{10}O_{40}]\cdot 20H_2O$; $K_7[V_5W_8O_{40}]\cdot 12H_2O$; $K_7[H_2VW_{11}O_{40}]\cdot 14H_2O$; and $[NBu_4]_3[VW_5O_{19}]$. The following compounds were prepared by literature methods and had infrared spectra that agreed with those reported: $K_4[V_2W_4O_{19}]\cdot 8H_2O$;[15] $H_5[PV_2W_{10}O_{40}]\cdot 12H_2O$ [16] (Found: V, 3.75; W, 65.1; W/V, 4.85. Calc.: V, 3.60; W, 64.9%); $[NH_4]_6H[PV_4W_8O_{40}]\cdot 11H_2O$ [16] (Found: V, 7.70; W, 53.6; W/V, 1.95. Calc.: V, 7.70; W, 55.45%); $H_5[PV_2Mo_{10}O_{40}]\cdot 17H_2O$ [17] (Found: V, 4.90; Mo, 47.45; Mo/V, 5.15. Calc.: V, 5.00; Mo, 46.95%); $[AsPh_4][VCl_2O_2]$,[18] $[AsPh_4]$-$[VF_2O_2]$; [18] $[NH_4]_3[VO_2(O_4C_2)_2]$; [19] and $Na_3[VO_2(edta)]$ [20] (edta = ethylenediaminetetra-acetate). Tetraphenylarsonium pentatungstovanadate(V) was prepared by adding a solution of tetraphenylarsonium chloride (1.26 g, 3 mmol) in water (20 cm³) to a freshly prepared [15] solution of the heteropolyanion (10 cm³, 1 mmol V). The light yellow flaky precipitate that formed was recrystallized from hot acetonitrile (Found: C, 35.8; H, 2.60. Calc. for $[AsPh_4]_3$-$[VW_5O_{19}]$: C, 35.65; H, 2.45%). The i.r. spectrum of this salt was similar to that of other salts containing the pentatungstovanadate anion. Tetraphenylarsonium tetratungstovanadate(V) was precipitated similarly from a 0.2 mol dm⁻³ solution of the potassium salt in an acetate buffer (pH 4). The yellow-orange solid was recrystallized from hot acetonitrile (Found: C, 37.1; H, 3.20; V, 3.85; W, 29.6; W/V, 2.10. Calc. for $[AsPh_4]_4[V_2W_4O_{19}]$: C, 43.1; H, 3.00; V, 3.80; W, 2.75%).

Spectroscopy.—Vanadium-51 n.m.r. spectra were recorded on a Bruker HFX-90 instrument operating at 22.63 MHz with a reduced field and a homonuclear lock (' X-Lock '). Samples were contained in 10-mm non-spinning sample tubes. Vanadium trichloride oxide in a sealed coaxial tube served as the reference and provided the lock signal. Most of the spectra were enhanced using a Varian C-1024 time-averaging computer. Except where otherwise specified, all the spectra were obtained at 30 ± 1 °C. Overlapping peaks were first deconvoluted before chemical shifts were determined, and relative intensities of deconvoluted peaks were measured with a planimeter. Isopolyvanadate solutions were prepared by dissolving sodium divanadate in distilled water and adjusting the pH with HCl or Na[OH]. For equilibrium studies, solutions were prepared by dissolving sodium divanadate in 3 mol dm⁻³ lithium nitrate and the pH was then adjusted with HNO_3 or Li[OH]. There were no significant differences in chemical shifts for the solutions in water or $Li[NO_3]$ at the same pH. Solutions in which decavanadate–trioxovanadate* equilibria were involved were warmed to 60 °C for several hours and then stored for at least 4 months at room temperature before recording the spectra.

Phosphorus-31 spectra were recorded in the pulse mode on a Varian XL-100 instrument at 40.5 MHz using a deuterium lock, or on a Bruker HFX-90 instrument at 36.43 MHz using a fluorine lock. Samples were dissolved in D_2O in 5- or 10-mm tubes. A sealed coaxial tube containing 1,2-dibromo-1,1,2,2-tetrafluoroethane was used to provide the fluorine lock. Phosphorus and vanadium chemical shifts to high field are reported with δ as positive. Proton spectra (90 and 60 MHz) were recorded with Tiers salt or $SiMe_4$ as internal references.

RESULTS AND DISCUSSION

Isopolyvanadates.—Chemical-shift data for the vanadate solutions are summarized in Figure 1 and Table 1. Also plotted in Figure 1 are the data of Howarth and Richards [8] and some of the data of Hatton *et al.*[9] The overall agreement between our results and reference 8 is good when allowance is made for the temperature difference of the measurements. In reference 9 chemical shifts were reported relative to the signal of a solution of $[NH_4][VO_3]$ at pH 7. This is an unfortunate choice of reference as there are two signals (at *ca.* 575 and 582 p.p.m. relative to VCl_3O, see below) in such solutions. The data

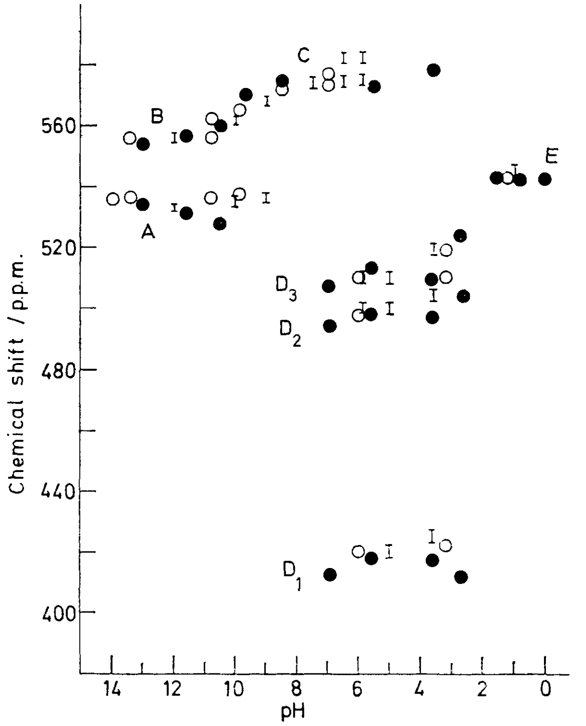


FIGURE 1 Vanadium-51 chemical shifts (p.p.m. upfield from VCl_3O) for aqueous vanadate(V) solutions. Representative data from present study (I), from ref. 8 (○), and from ref. 9 (●)

---

* Trioxovanadate = ' metavanadate.'

[12] A. D. English, J. P. Jesson, W. G. Klemperer, T. Mamouneas, L. Messerle, W. Shum, and A. Tramontano, *J. Amer. Chem. Soc.*, 1975, **97**, 4785.

[13] L. I. Lebedeva and E. V. Vanchikova, *Russ. J. Inorg. Chem.*, 1974, **19**, 1798.

[14] L. P. Kazanskii and V. I. Spitsyn, *Doklady Akad. Nauk S.S.S.R.*, 1975, **223**, 1798; L. P. Kazanskii, M. A. Fedotov, M. N. Ptushkina, and V. I. Spitsyn, *ibid.*, **224**, 866.

[15] C. M. Flynn, jun., and M. T. Pope, *Inorg. Chem.*, 1971, **10**, 2524.

[16] D. P. Smith and M. T. Pope, *Inorg. Chem.*, 1973, **12**, 331.

[17] G. A. Tisigdinos and C. J. Hallada, *Inorg. Chem.*, 1968, **7**, 437.

[18] E. Ahborn, E. Diemann, and A. Muller, *J.C.S. Chem. Comm.*, 1972, 378.

[19] D. N. Sathyanarayana and C. T. Patel, *Bull. Chem. Soc. Japan*, 1964, **37**, 1736.

[20] L. W. Amos and D. T. Sawyer, *Inorg. Chem.*, 1972, **11**, 2692.

points from reference 8 in Figure 1 were obtained by subtracting the chemical shifts reported in reference 9 from 575 p.p.m. The uncertainty in the reference chemical shift probably accounts for the somewhat poorer apparent agreement between references 8 and 9.

TABLE 1

Vanadium-51 n.m.r. data[a] for aqueous vanadate solutions

pH	δ [b]/p.p.m.	$\Delta\nu_{\frac{1}{2}}$ [c]/Hz	Assignment [d]
14.0	536	60	$[VO_4]^{3-}$
12.0	533, 556	60, 60	$[VO_4]^{3-}$, $[V_2O_7]^{4-}$
10.0	535, 562	80, 80	$[VO_4]^{3-}$, $[V_2O_7]^{4-}$
9.0	537, 568	100, 150	$[VO_4]^{3-}$, $[V_2O_7]^{4-}$ — $[(VO_3)_x]^{x-}$
8.5	572	180	$[(VO_3)_x]^{x-}$
7.5	574	150	$[(VO_3)_x]^{x-}$
6.5	575, 582	150, 150	$[(VO_3)_x]^{x-}$, ? [e]
5.9	575, 582	150, 150	$[(VO_3)_x]^{x-}$, ?
	500, 510	500, 200	$[V_{10}O_{28}]^{6-}$
5.0	420, 500, 510	350, 150, 150	$[V_{10}O_{28}]^{6-}$
3.6	425, 504, 519	350, 150, 150	$[V_{10}O_{28}]^{6-}$
1	545 [f]	400	$[VO_2]^+$

[a] Representative selection of data. Concentrations 0.1—0.3 mol dm^{-3} for all the samples. [b] Uncertainty ±1 p.p.m. for lines narrower than 100 Hz, ±2 p.p.m. for others. [c] Half-widths of lines, ±10%. [d] Protonated forms have been omitted. [e] Unidentified intermediate, see text. [f] Dependant on counter ion, see text.

Over the whole pH and concentration range we can identify five groups of resonances which we have labelled A (*ca.* 535), B (555), C (575, 582), D (420, 550, 510), and E (542 p.p.m.). Resonances A and B which appeared in the most alkaline solutions were relatively narrow (60—80 Hz) and they have been assigned to the $[VO_4]^{3-}$ and $[V_2O_7]^{4-}$ ions (or their protonated forms). In reference 8, A is associated with $[VO_4]^{3-}$ and B with $[V_2O_7]^{4-}$, while the opposite assignment is made in reference 9. Since we find, in agreement with reference 8, that only resonance A is present at pH 14, the first assignment appears to be correct. The narrowness of A and B is consistent with the presumed symmetrical electrical environment of the vanadium nuclei in $[VO_4]^{3-}$ and $[V_2O_7]^{4-}$ leading to inefficient quadrupole relaxation. As the pH of the solution was decreased from 13 to 10, resonances A and B broadened and shifted upfield (see Table 1 and Figure 1) and these changes are believed to result from protonation coupled with exchange between $[HVO_4]^{2-}$ and $[HV_2O_7]^{3-}$. According to a recent depolarized-light-scattering study,[21] $[HVO_4]^{2-}$ is unusually optically anisotropic and there is evidence for its association to form hydrogen-bonded dimers. Such association would facilitate exchange between $[HVO_4]^{2-}$ and $[V_2O_7]^{4-}$.

At pH 7.5 there was a single broad resonance (C, 574 p.p.m.) which has been assigned to the trioxovanadate ion $[(VO_3)_x]^{x-}$. Between pH 10 and 7.5 resonances B and C coalesced into a single peak, the chemical shift of which changed from *ca.* 562 to 574 p.p.m. This behaviour is consistent with the assumption of rapid exchange between $[H_xV_2O_7]^{(4-x)-}$ and $[(VO_3)_x]^{x-}$ anions. The structure(s) of the $[(VO_3)_x]^{x-}$ ion(s) in solution are still controversial. Most recent studies favour a tetrameric, $[V_4O_{12}]^{4-}$, over a trimeric, $[V_3O_9]^{3-}$, stoicheiometry, and the structure is presumed to be cyclic as in the corresponding phosphates. Since crystalline trioxovanadate salts contain infinite polymeric anions in which the vanadium atoms are four-,[22] five-,[22] or six-co-ordinated,[23] it has been pointed out [24] that the trioxovanadate anion in solution may not be based on linked VO_4 tetrahedra but may, with the inclusion of water molecules, incorporate VO_5 or VO_6 polyhedra. While the n.m.r. results cannot add anything definite on this question, we believe that the argument first presented by Howarth and Richards [8] is reasonably persuasive. It was pointed out that if ^{51}V chemical shifts are plotted against charge per vanadium atom the data fall on two lines, one for anions in which the vanadium is tetrahedral ($[VO_4]^{3-}$, $[V_2O_7]^{4-}$, *etc.*) and one for species in which the vanadium is octahedral ($[V_{10}O_{28}]^{6-}$, $[VO_2]^+$, *etc.*). The trioxovanadate resonance falls on the ' tetrahedral ' line.

The observation of two separate resonances, A and BC, at pH 9—10 implies, if the foregoing assignments are correct, that exchange between $[HVO_4]^{2-}$ and $[HV_2O_7]^{3-}$ is ' slow ', whereas exchange between $[HV_2O_7]^{3-}$ and trioxovanadate is ' fast '. This seems to rule out the stepwise aggregation of trioxovanadate from ' monomer ' anions and is more consistent with direct formation of a cyclic tetrameric trioxovanadate from two divanadate ions as suggested by Gaglani *et al.*[21] We attempted to measure the equilibrium constant for the divanadate–trioxovanadate system, but found, as in reference 8, that the accuracy of the results was too low to distinguish between a trimeric and tetrameric stoicheiometry for trioxovanadate.

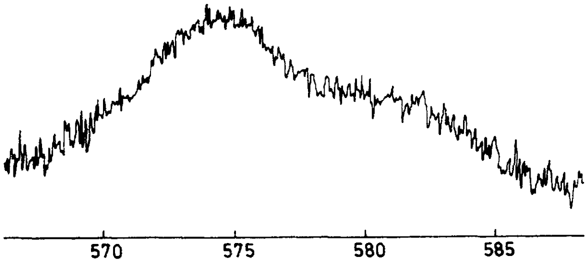


FIGURE 2 Vanadium-51 n.m.r. spectrum of 0.3 mol dm^{-3} sodium vanadate at pH 6.6

When the pH of the solution decreased to just below 7, a second peak (C_2) appeared just upfield from that of trioxovanadate (C_1). Figure 2 shows the spectrum at pH 6.6. The second resonance (C_2) at 582 p.p.m. was not observed in reference 9, whereas the C resonances at pH 7 were found to be at 573.1 and 576.8 p.p.m. with relative intensities of 1 : 9 in reference 8. The present results differ from those of reference 8 in that we find C_1 to be the more intense signal in all the solutions. The relative intensities of C_1/C_2 ranged from 2.7 to 3.2 as the total

[21] A. Gaglani, N. Asting, and W. H. Nelson, *Inorg. Chem.*, 1974, **13**, 1715.

[22] H. T. Evans, jun., *Z. Krist.*, 1960, **114**, 257.

[23] B. D. Jordan and C. Calvo, *Canad. J. Chem.*, 1974, **52**, 2701.

[24] L. G. Sillen, *Quart. Rev.*, 1959, **13**, 146; N. Ingri and F. Brito, *Acta Chem. Scand.*, 1959, **13**, 1971.

vanadium concentration varied from 0.347 to 0.107 mol dm^{-3}. At about the same pH that the two C resonances first appear, the set of three signals, D, were observed. The latter group at *ca.* 420, 500, and 510 p.p.m. were assigned to the $[V_{10}O_{28}]^{6-}$ anion in reference 8 and we agree with this assignment. The relative intensity of $D_1 : D_2 : D_3$ was given as 1 : 3 : 1 [8] and 1 : 2 : 1.[9] Neither of these ratios accord with the subsequently determined structure of $[V_{10}O_{28}]^{6-}$ in crystalline salts.[5] In Figure 3 we illustrate a spectrum from the present work which shows the three D resonances at pH 4.5. The relative intensity of these lines, $D_1 : D_2 : D_3$, was 1 : 2 : 2 and this ratio was unaffected by changes in pH. Such a spectrum is in very satisfactory agreement with the solid-state $[V_{10}O_{28}]^{6-}$ structure illustrated in Figure 4. Lines D_2 and D_3 can be assigned to the two sets of four (C_{4v}-like) vanadium atoms with terminal unshared oxygen atoms, and the broader D_1 line to the two vanadium atoms that have no terminal oxygens. Kazanskii and Spitsyn [14] recently reported a similar spectrum and assignment. As noted by others,[3] the rate of attainment of equilibrium between trioxovanadate and decavanadate is extremely slow. This is undoubtedly a consequence of the polymeric nature of the two anions, for polyanion equilibria involving a monomeric component, *e.g.* $[MoO_4]^{2-} \rightleftharpoons [Mo_7O_{24}]^{6-}$, $[WO_4]^{2-} \rightleftharpoons [HW_6O_{21}]^{5-}$, $[VO_2]^+ \rightleftharpoons [V_{10}O_{28}]^{6-}$, are established very rapidly.[25-27] The second trioxovanadate resonance (C_2) noted above indicates the existence of an intermediate species in the trioxovanadate–decavanadate system. A plausible explanation for C_2 is the presence of an ' opened-up ' non-cyclic trioxovanadate anion, *e.g.* as in (1). The terminal vanadium atoms of such a linear anion would be expected to have chemical shifts that are different from those of the cyclic anion.

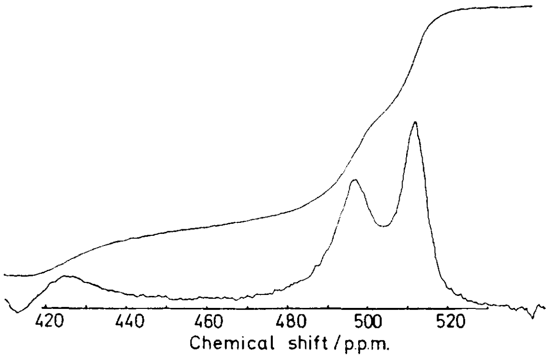


FIGURE 3 Vanadium-51 n.m.r. spectrum of sodium vanadate solution at pH 4.5 showing the three peaks assigned to the decavanadate ion. The raised baseline between the two low-field peaks is an instrumental artifact and does not indicate chemical exchange

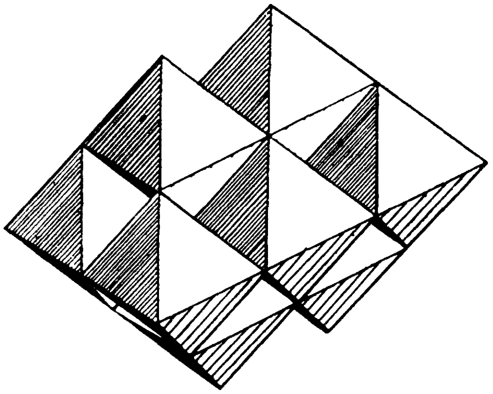
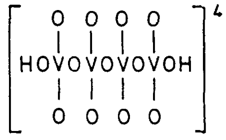


FIGURE 4 Structure of the decavanadate anion. Octahedra represent VO_6 groups (H. T. Evans, jun., *Inorg. Chem.*, 1966, **5**, 967)



$$\left[\begin{array}{c} \mathrm{O\ \ O\ \ O\ \ O} \\ |\ \ \ |\ \ \ |\ \ \ | \\ \mathrm{HOVOVOVOVOH} \\ |\ \ \ |\ \ \ |\ \ \ | \\ \mathrm{O\ \ O\ \ O\ \ O} \end{array}\right]^{4-}$$

(1)

From pH 6.5 to *ca.* 3.5 the chemical shifts of the three decavanadate resonances increased to final values of 425, 504, and 519 p.p.m. The continuous upfield shift of the spectrum is taken to indicate the protonation [27] of $[V_{10}O_{28}]^{6-}$ to $[HV_{10}O_{28}]^{5-}$ and $[H_2V_{10}O_{28}]^{4-}$. Below pH 4 precipitation of V_2O_5 began in the more concentrated solutions, and by pH 3 the decavanadate spectrum was no longer observable.

' Cationic ' Vanadium(V).—Below pH 1 vanadium(V) exists in solution as the vanadyl cation, $[VO_2]^+$, which, according to Raman studies,[28] has a *cis*-dioxo-structure and is presumably a pseudo-octahedral species, $[VO_2(OH_2)_4]^+$. In perchloric and nitric acid solutions the ^{51}V n.m.r. spectrum consisted of a single broad (400 Hz) line at 545 ± 2 p.p.m. In hydrochloric, sulphuric, and phosphoric acid solutions the line was considerably broader (600—1 500 Hz) with a chemical shift ranging from 520 to 587 p.p.m. In Table 2 are presented ^{51}V n.m.r. data for some mononuclear oxovanadates. The chemical shifts and linewidths of the *cis*-dioxo-octahedral [20,29,30] compounds $[VO_2(O_4C_2)_2]^{3-}$ and $[VO_2(edta)]^{3-}$ are comparable to those observed for solutions

TABLE 2

N.m.r. data for some oxovanadates [a]

Compound	Solvent	δ/p.p.m.	$\Delta\nu_{\frac{1}{2}}$/Hz
$[NH_4]_3[VO_2(O_4C_2)_2]$	Water	533 [b]	*ca.* 250
$Na_3[VO_2(edta)]$	Water	513 [b]	*ca.* 800
$[AsPh_4][VCl_2O_2]$	MeCN	301 [c]	*ca.* 60
$[AsPh_4][VF_2O_2]$	Dimethyl sulphoxide	64 [c]	*ca.* 60
' NH_4VO_3 '	$HSClO_3$	4 [c]	*ca.* 60
' NH_4VO_3 '	$HSFO_3$	66 [c]	*ca.* 60

[a] Concentration 0.1 mol dm^{-3}. [b] ±1.5 p.p.m. [c] ±1.0 p.p.m.

---

[25] G. Schwarzenbach and J. Meier, *J. Inorg. Nuclear Chem.*, 1958, **8**, 302.

[26] O. Glemser and K.-H. Tytko, *Z. Naturforsch.*, 1969, **B24**, 648; K.-H. Tytko and O. Glemser, *ibid.*, 1971, **B26**, 659.

[27] F. J. C. Rosotti and H. S. Rosotti, *J. Inorg. Nuclear Chem.*, 1956, **2**, 201.

[28] W. P. Griffith and T. D. Wickens, *J. Chem. Soc.* (*A*), 1968, 1087; W. P. Griffith and P. J. B. Lesniak, *ibid.*, 1969, 1066.

[29] J. L. Hoard, W. R. Scheidt, and R. Countryman, *J. Amer. Chem. Soc.*, 1971, **93**, 3878.

[30] J. L. Hoard, W. R. Scheidt, and C. C. Tsai, *J. Amer. Chem. Soc.*, 1971, **93**, 3867.

of V^V in weakly complexing acids and provide further evidence for the *cis*-dioxo $[VO_2(OH_2)_4]^+$ structure of the vanadyl cation. The broader lines and slight differences in chemical shift observed for solutions of vanadium in HCl, H_2SO_4, and H_3PO_4 suggest the formation of chloro-, sulphato-, and phosphato-compounds that still contain the 'octahedral' *cis*-VO_2 group. As shown by the data in Table 2, the pseudo-tetrahedral compounds $[VCl_2O_2]^-$ and $[VF_2O_2]^-$ have much narrower lines and very different chemical shifts. The linewidths for the last two ions are comparable with those for VCl_3O and $[VO_4]^{3-}$ and with those for the species formed when ammonium trioxovanadate is dissolved in neat chlorosulphonic and fluorosulphonic acids, see Table 2. We conclude on the basis of the linewidths that the solute species in $HSClO_3$ and $HSFO_3$ have a pseudo-tetrahedral structure. A compound $[VO(SFO_3)_3]$ has been reported by Kleinkopf and Shreeve [31] and it is possible that this and a chlorosulphonate analogue have been formed in the present case. However, in view of the similarity of the chemical shifts, the possibility cannot be excluded that $[VF_2O_2]^-$ has been formed in the $HSFO_3$ solution. No ^{51}V–^{19}F coupling was observable in any of the spectra of the fluoro-compounds, due presumably to rapid exchange with free fluoride ions.

Heteropolyvanadates.—We examined a number of heteropolyanions that contain V^V. These compounds have two general stoicheiometries and structures: (*a*) hexametallates, $[M_6O_{19}]^{n-}$ (M = V or W); (*b*) dodecametallates (Keggin anions), $[XM_{12}O_{40}]^{n-}$ (M = V, W, or Mo). In both structures the metal atoms, M, are octahedrally co-ordinated by five bridging and one terminal oxygen atoms (Type I polyanion structures [32]). Although the environment of the metal atoms is strongly axial (C_{4v}-like), the ^{51}V n.m.r. linewidths are remarkably narrow (typically 50—90 Hz), particularly when the metal atoms in neighbouring (edge- or corner-shared) octahedra are not vanadiums. Thus a linewidth of *ca.* 60 Hz observed for $[VW_5O_{19}]^{3-}$ at pH 2 may be contrasted with those (*ca.* 150 Hz) for the two high-field lines of $[V_{10}O_{28}]^{6-}$ (Table 1). Kazanskii and Spitsyn [14] reported linewidth differences between $[VW_5O_{19}]^{3-}$ (0.03 G) and $[V_2W_4O_{19}]^{4-}$ (0.06 G) * anions in aqueous solution and argued on this basis that the two VO_6 groups in $[V_2W_4O_{19}]^{4-}$ occupy mutually *cis* positions in the octahedral M_6O_{19} structure. Although these arguments are plausible, we have not observed consistently significant differences of linewidths in our spectra. Chemical shifts for some heteropolyvanadates are given in Table 3. These are in good agreement with those reported by Kazanskii and Spitsyn, except for $[V_2W_4O_{19}]^{4-}$.

As noted for the isopolyvanadates, the chemical shifts for the heteropolyvanadates in aqueous solutions were pH dependent; the lines moved to higher field as the pH of the solution was decreased and this presumably signifies protonation of the anions. Drastic pH changes cause the slower hydrolytic conversions [equations (1)—(4)] that we have described elsewhere.[15,33,34] Changes in

$$[HV_2W_4O_{19}]^{3-} \xrightarrow{\text{pH } ca. \text{ 2}} [VW_5O_{19}]^{3-}, \textit{etc.} \qquad (1)$$

$$[VW_5O_{19}]^{3-} \xrightarrow{\text{pH } ca. \text{ 4}} [V_2W_4O_{19}]^{4-}, \textit{etc.} \qquad (2)$$

$$[HV_2W_4O_{19}]^{3-} \xrightarrow{\text{pH } ca. \text{ 2}} [V_4W_9O_{40}]^{6-}, \textit{etc.} \qquad (3)$$

$$[H_2VW_{11}O_{40}]^{7-} \xrightarrow{\text{pH } ca. \text{ 2}} [H_2W_{12}O_{40}]^{6-}, [VO_2]^+, \textit{etc.} \qquad (4)$$

^{51}V spectra corresponding to reactions (1)—(3) were observed, but the reactions are complex and no attempts were made to identify intermediates and establish mechanisms. In the case of reaction (4) changes in both ^1H and ^{51}V n.m.r. spectra were recorded. At pH 4 the ^1H spectrum of $[H_2VW_{11}O_{40}]^{7-}$ had a line at 6.08 p.p.m. due to the non-labile protons in the central tetrahedral cavity of the Keggin structure. The corresponding line for $[H_2W_{12}O_{40}]^{6-}$ occurred at 6.09 p.p.m. and both lines could be distinguished in the spectrum of a mixture of the two polyanions. When an equimolar amount of DCl was added to an unbuffered solution of of $[H_2VW_{11}O_{40}]^{7-}$ at pH 4 the proton n.m.r. signal disappeared within the time of mixing and recording the spectrum (<5 min). Under the same conditions the ^{51}V spectrum showed two lines, one at 539 p.p.m. corresponding to the original anion, but now twice as broad (*ca.* 100 Hz) than at pH 4, and the other at *ca.* 550 p.p.m. Further acidification caused the line at 550 p.p.m. to grow in relation to the other, and by pH 1 the line at 539 p.p.m. had completely disappeared. This process was reversible, for by careful addition of 1 mol dm^{-3} Li[OH] the line at 539 p.p.m. could be restored at the expense of that at 550 p.p.m. Only on prolonged standing (several days at room temperature) and with excess of acid (>10 mol per mol of heteropolyanion) could spectra be obtained showing the very broad peak at 545 p.p.m. corresponding to $[VO_2]^+$. We interpret the above observations as follows. Addition of acid to $[H_2VW_{11}O_{40}]^{7-}$ results in protonation of the anion, presumably at one of the bridging oxygens adjacent to the vanadium atom. Such

TABLE 3

Vanadium-51 chemical shifts for some heteropolyanions [a]

Compound	Solvent	δ/p.p.m.
$K_4[V_2W_4O_{19}]$	Buffer (pH 4)	506 [b]
$[AsPh_4]_4[V_2W_4O_{19}]$	MeCN	507
$K_3[VW_5O_{19}]$	pH 2	522
$K_7[H_2VW_{11}O_{40}]$	pH 4	539
$[NBu_4]_4[PVW_{11}O_{40}]$	dmf [c]	545
$H_4[PMo_{11}VO_{40}]$	0.25 mol dm^{-3} H_2SO_4	530

[a] Concentration 0.1 mol dm^{-3}. [b] At 513 p.p.m. according to ref. 14. [c] *NN*-Dimethylformamide.

---

* 1 G = 10^{-4} T.

[31] G. C. Kleinkopf and J. M. Shreeve, *Inorg. Chem.*, 1964, **3**, 607.

[32] M. T. Pope, *Inorg. Chem.*, 1972, **11**, 1973.

[33] C. M. Flynn, jun., and M. T. Pope, *Inorg. Chem.*, 1971, **10**, 2745.

[34] C. M. Flynn, jun., M. T. Pope, and S. E. O'Donnell, *Inorg. Chem.*, 1974, **13**, 831.

a protonation would be expected to alter the electric-field gradient surrounding the vanadium nucleus and would contribute to the observed increase in linewidth. Exchange between ' internal ' and ' external ' protons is rapid (complete within 5 min for *ca.* 0.05 mol dm^{-3} solution at room temperature) and this suggests that a rapid partial hydrolysis of the anion occurs. The partially hydrolyzed anion, which would account for the n.m.r. line at 550 p.p.m., may have the vanadium atom attached to the polytungstate structure by only one or two bridging oxygens and as a result would leave the central oxygens of the Keggin structure exposed to the solvent, facilitating exchange of the central protons. The possibility of direct exchange between internal and external protons by a ' tunneling ' process cannot be completely ruled out, but seems unlikely. Launay[35] showed that the Keggin anion with a single proton in the central cavity, $[HW_{12}O_{40}]^{7-}$, is converted into normal $[H_2W_{12}O_{40}]^{6-}$, by a first-order process which has a half-life of *ca.* 50 min at pH $\leqslant 2$. However, exchange rates involving the central protons in both of these anions are very slow.[35,36]

Heteropolyanions with two or more Vanadium Atoms: Geometrical Isomers.—Numerous possibilities for isomerism arise when heteropolyanions contain mixtures of addenda atoms (V, Mo, or W). A simple example is the anion $[V_2W_4O_{19}]^{4-}$ which in principle could exist as two isomers, whereas the Keggin anion $[PV_6W_6O_{40}]^{9-}$ could have as many as 48.[10] The ^{51}V n.m.r. spectrum of $[V_2W_4O_{19}]^{4-}$ had a single line and this suggests, but does not prove, that only a single isomer is present.* On the other hand both ^{31}P and ^{51}V spectra of solutions of $[PV_xW_{12-x}O_{40}]^{n-}$ and $[PMo_{12-x}V_xO_{40}]^{n-}$ anions had several lines which we attribute to the presence of isomers. The n.m.r. data for these anions are reported in Table 4. Spectra were recorded for several different preparations of each anion, and lines which varied considerably in intensity from spectrum to spectrum, and which are believed to be due to impurities, are not listed in the Table. The spectra of the tungstates showed essentially no ' impurity ' lines with the exception of some samples of $[PV_2W_{10}O_{40}]^{5-}$, the ^{51}V spectra of which showed a narrow line of variable intensity at 530 p.p.m. ($[VW_5O_{19}]^{3-}$?). The ^{31}P spectra of $[PV_2W_{10}O_{40}]^{5-}$ and $[PV_2Mo_{10}O_{40}]^{5-}$ have been discussed elsewhere,[11,37] and the number and relative intensities of the lines have been related to the statistical abundances of the five possible isomers. The quality of the ^{51}V spectra of these two ions, while sufficient to confirm the presence of isomers, does not permit more quantitative conclusions to be drawn.†

For more highly vanadium-substituted Keggin anions the number of possible isomers increases considerably.[10] In the molybdate series $[PMo_{12-x}V_xO_{40}]^{n-}$ it is difficult to obtain a pure sample for the anion with $x = 3$ using literature methods.[17] The ^{31}P spectrum of a sample of $H_6PMo_9V_3O_{40}$, for which the analytical quotient Mo/V was determined to be 4.19, is given in Supplementary Publication No. SUP 21852 (6 pp.).‡ The spectrum clearly shows lines due to H_3PO_4, $[PMo_{11}VO_{40}]$,$^{4-}$ and isomers of $[PMo_{10}V_2O_{40}]^{5-}$. On the other hand the anion $[HPV_4W_8O_{40}]^{6-}$ is well characterized and can be prepared in an analytically pure form.[16] The spectrum of this anion (SUP 21852) certainly has no lines due to $[PV_2W_{10}O_{40}]^{5-}$, $[PVW_{11}O_{40}]^{4-}$, or $[PW_{12}O_{40}]^{3-}$. Whether the more than 20 lines observed are due solely to some or all of the 27 possible isomers of $[PV_4W_8O_{40}]^{7-}$ (which have varying statistical abundances[10]) or are due partly to the isomers expected to be present in an equimolar mixture of $[PV_3W_9O_{40}]^{6-}$ and $[PV_5W_7O_{40}]^{8-}$ cannot of course be established since the last two ions have never been well characterized.[16]

TABLE 4

Phosphorus-31 and ^{51}V chemical shifts for some dodecametallophosphates[a]

Ion	^{31}P, $\delta \pm 0.05$	^{51}V, $\delta \pm 2$	^{51}V, $\Delta\nu_{\frac{1}{2}}$/Hz
$[PW_{12}O_{40}]^{3-}$	14.96[b]		
$[PVW_{11}O_{40}]^{4-}$	14.80	545[c]	60
$[PV_2W_{10}O_{40}]^{5-}$	13.90(1)[d]	547(1)	100
	14.20(3)	553 } (2.6)	100—150
	14.27(1)	557 }	
$[HPV_4W_8O_{40}]^{6-}$	10.25—13.65 (>20 lines)	561	400
$[PMo_{12}O_{40}]^{3-}$	5,[e] 4.3[f]		
$[PMo_{11}VO_{40}]^{4-}$	4.05	530	60
$[PMo_{10}V_2O_{40}]^{5-}$	3.09(3)	529(1)	100
	3.79(8)	535(3.2)	100
		543(1.1)	200
$[PMo_9V_3O_{40}]^{6-}$	1.68—3.35	535[g]	150
	(>6 lines)	545	250

[a] 0.1 mol dm^{-3} in 0.25 mol dm^{-3} H_2SO_4 except where otherwise specified; chemical shifts in p.p.m. upfield from H_3PO_4 or VCl_3O. [b] Lit.: 17.7 ± 0.5,[13] 15.[14] [c] Tetrabutylammonium salt in dmf. [d] Figures in parentheses indicate relative areas of lines. [e] Ref. 40. [f] Ref. 13. [g] May represent $[PMo_{10}V_2O_{40}]^{5-}$ impurity.

A few years ago we established[33,38] the existence of a series of anions $[V_xW_{13-x}O_{40}]^{n-}$ (x = 3—5; n = 5—7) which, we argued, were derived from the unknown Keggin anion, $[VW_{12}O_{40}]$.$^{3-}$. The most stable of these, $[V_4W_9O_{40}]^{6-}$, is identical to the ion formulated as $[V_3W_7O_{31}]^{5-}$ by earlier workers. The ^{51}V spectra of $[V_4W_9O_{40}]^{6-}$ and $[V_3W_{10}O_{40}]^{5-}$ each consisted of three lines (see Table 5 and SUP 21852). Solutions of $[V_5W_8O_{40}]^{7-}$ were too unstable to permit recording of a reliable spectrum. The lines at 553 p.p.m. for $[V_4W_9O_{40}]^{6-}$ and 558 p.p.m. for $[V_3W_{10}O_{40}]^{5-}$ are assigned to the central tetrahedral vanadium on the basis of the following arguments. (*i*) The intensity ratios of the high-field lines to the rest of the

---

* We have argued elsewhere that the *cis* isomer is the most likely species (C. M. Flynn, jun., and M. T. Pope, *Inorg. Chem.*, 1973, **12**, 1626).

† It should of course be realized that there does not have to be a one-to-one correspondence of relative intensities of the lines in the V and P spectra, since both may have accidentally identical chemical shifts for different groups of isomers.

‡ For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1975, Index issue (items less than 10 pp. are supplied as full-size copies).

[35] J.-P. Launay, Thesis, University of Paris VI, 1974; J.-P. Launay, M. Boyer, and F. Chauveau, *J. Inorg. Nuclear Chem.*, 1976, **38**, 243.

[36] M. T. Pope and G. M. Varga, jun., *Chem. Comm.*, 1966, 653.

[37] M. T. Pope, S. E. O'Donnell, and R. A. Prados, *Adv. Chem. Ser.*, 1976, **150**, 85.

[38] C. M. Flynn, jun., and M. T. Pope, *Inorg. Chem.*, 1972, **11**, 1950.

TABLE 5

Vanadium-51 n.m.r. data for $[V_4W_9O_{40}]^{6-}$ and $[V_3W_{10}O_{40}]^{5-}$ [a]

Anion	Solvent	δ/p.p.m.	Area		$\Delta\nu_{\frac{1}{2}}$ [b]/Hz
$[V_4W_9O_{40}]^{6-}$	pH 4 [c]	506	38.5 [d]	3.10 [e]	200
		530	82.2		200
		553	38.9	1.00	100
	0.1 mol dm^{-3} HCl	522 535	74.7	2.94	
		553	25.4	1.00	100
	0.25 mol dm^{-3} H_2SO_4	525 536 544	233.0	3.06	
		554	76.2	1.00	100
$[V_3W_{10}O_{40}]^{5-}$	pH 2 [f]	506	50.0	2.08	150
		530 535	23.80		
		558	138.2	1.00	100

[a] Concentration 0.1 mol dm^{-3}. [b] Estimated (±10%) for non-overlapping lines only. [c] Acetate buffer. [d] Arbitrary units. [e] Ratio of line intensities. [f] Hydrogensulphate buffer.

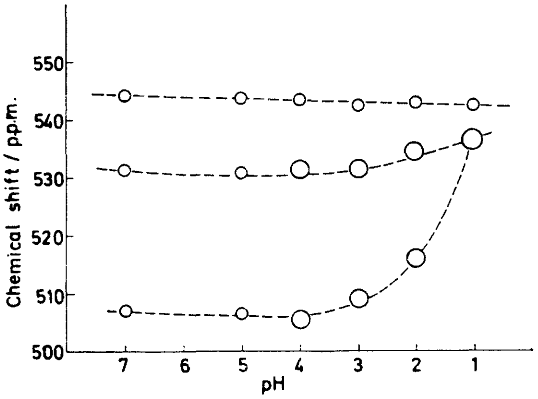


FIGURE 5 Variation of ^{51}V chemical shifts of $[V_4W_9O_{40}]^{6-}$ ion as a function of pH

spectrum are close to 1 : 3 and 1 : 2. (*ii*) The lines are relatively narrow. (*iii*) The virtual pH independence of the chemical shift of the line at 553 p.p.m., in contrast to the others (Figure 5), suggests that it is due to a vanadium atom well shielded from effects of protonation. The presence of two lines (or presumably envelopes of lines) at *ca.* 506 and 530 p.p.m., which must be due to the external octahedral vanadium atoms, is tentatively rationalized as follows. The low-field line is assigned to vanadium atoms in those VO_6 octahedra which share an edge with another VO_6 octahedron. In support of such an assignment we note that the chemical shifts of anions in which there are pairs of edge-shared VO_6 octahedra ($[V_{10}O_{28}]^{6-}$, $[V_2W_4O_{19}]^{4-}$) range from 490 to 520 p.p.m. Secondly, protonation of the anion is most likely to occur on oxygen atoms that bridge two vanadiums and this would account for the sensitivity of the line at 506 p.p.m. to pH changes (Figure 5). Finally, if we make the reasonable assumption that all possible isomers of $[V_4W_9O_{40}]^{6-}$ and $[V_3W_{10}O_{40}]^{5-}$ are present in their statistical abundances,[10] the relative intensities of the resonances at 506 and 530 p.p.m. are approximately rationalized. For $[V_4W_9O_{40}]^{6-}$ with 13 isomers the ratio of ' edge-shared ' octahedral vanadium atoms to all the other octahedral vanadium atoms is 228 : 432 or 1 : 1.89. The corresponding ratio for the five possible isomers of $[V_3W_{10}O_{40}]^{5-}$ is 12 : 54 or 1 : 4.5. The experimental ratios of intensities of the lines at 506 and 530 p.p.m. are 1 : 2.1 and 1 : 4.8 respectively.

Conclusions.—Chemical shifts so far observed for vanadium span almost 600 p.p.m., but for oxo-compounds fall within the range 420—560 p.p.m. Shifts for central phosphorus and vanadium atoms in Keggin anions are all positive with respect to the uncomplexed $[XO_4]^{3-}$ ions, and there is a progressive shift to higher fields as the proportion of tungsten atoms increases. This is seen most clearly in the sequence of increasing ^{31}P shifts for $[PMo_9V_3O_{40}]^{6-}$, $[PMo_{10}V_2O_{40}]^{5-}$, $[PMo_{11}VO_{40}]^{4-}$, $[PMo_{12}O_{40}]^{3-}$, $[HPV_4W_8O_{40}]^{6-}$, $[PV_2W_{10}O_{40}]^{5-}$, and $[PW_{12}O_{40}]^{3-}$. A similar trend is observed for ^{51}V in $[VV_3W_9O_{40}]^{6-}$ (553) and $[VV_2W_{10}O_{40}]^{5-}$ (556 p.p.m.). The resonance of the central vanadium in the last anion is thus 20 p.p.m. with respect to free $[VO_4]^{3-}$ and this is virtually identical to the corresponding ^{31}P Δ shift for the analogous anions $[PV_2W_{10}O_{40}]^{5-}$ (14) and $[PO_4]^{3-}$ (−6).[39] Since in all the Keggin anions the central atoms are constrained to occupy regular tetrahedral sites, the variations in P and V chemical shifts just described can, according to the theory of Letcher and Van Wazer,[40] be rationalized by assuming small reductions in the π character of the P–O (and presumably V–O) bonds that occur as a consequence of heteropolyanion formation.

The close parallel of chemical shifts for ^{31}P and ^{51}V as central atoms in Keggin anions is quite unexpected* in view of the various factors that can contribute to the chemical shift. For example, the relative energies and sizes of the 3*d* orbitals are quite different for the two elements, and one might expect a much larger paramagnetic term, $\sigma^{(2)}$, in the chemical shifts of vanadium.[41] Kazanskii and Spitsyn [14] suggested that there is a linear correlation between vanadium chemical shifts in $[VW_5O_{19}]^{3-}$, $[PMo_{11}VO_{40}]^{4-}$, $[H_2VW_{11}O_{40}]^{7-}$, and $[PVW_{11}O_{40}]^{4-}$, and the isotropic *g* values for the corresponding reduced [vanadium(IV)] anions, and that such a correlation is not unexpected according to the theory developed for $\sigma^{(2)}$ by Jameson and Gutowsky.[41] It is not immediately obvious why there should be a linear correlation between $\langle g \rangle$ and σ, and the experimental evidence is not convincing when one considers that the *g* values for the four ions fall in the narrow range 1.952—1.964. Our e.s.r. [42] and n.m.r. data for these anions do not fit a

---

* The parallel does not extend to other compounds; contrast $\Delta(PCl_3O - PO_4^{3-})$ = 4 p.p.m. with $\Delta(VCl_3O - VO_4^{3-})$ = 536 p.p.m.

[39] R. A. Y. Jones and A. R. Katritzky, *J. Inorg. Nuclear Chem.*, 1960, **15**, 193.

[40] J. H. Letcher and J. R. Van Wazer, *Topics Phosphorus Chem.*, 1967, **5**, 75.

[41] C. J. Jameson and H. S. Gutowsky, *J. Chem. Phys.*, 1964, **40**, 1715.

[42] H. So, C. M. Flynn, jun., and M. T. Pope, *J. Inorg. Nuclear Chem.*, 1974, **36**, 329; J. J. Altenau, M. T. Pope, R. A. Prados, and H. So, *Inorg. Chem.*, 1975, **14**, 417.

straight line, although there appears to be a general trend of increasing $\langle g \rangle$ with decreasing σ.

For quadrupolar nuclei such as ^{51}V, n.m.r. linewidths may provide some information about the symmetry of the electric field surrounding the nucleus. In iso- and hetero-polyanions, vanadium atoms can have approximately tetrahedral, tetragonal (octahedral, one terminal oxygen), or rhombic (octahedral *cis*-dioxo) site symmetries. The range of linewidths observed for each type of vanadium (Table 6) shows the anticipated trend.

TABLE 6

Vanadium-51 n.m.r. linewidths in polyvanadates

Site symmetry of V	Range of linewidths (Hz)
Tetrahedral	60—100
Tetragonal (no neighbouring V [a])	60—80
Tetragonal (with neighbouring V [b])	100—200
Rhombic	200—800

[a] As in $[VW_5O_{19}]^{3-}$. [b] As in $[V_{10}O_{28}]^{6-}$.

The present work indicates some of the kinds of information concerning heteropolyanions in solution that can be obtained from n.m.r. measurements. Much of this information, *e.g.* the discovery and analysis of geometrical isomers, is inaccessible by other experimental methods and it opens up new areas of study. As instrumentation and more sophisticated pulse techniques become generally available we can expect to see an increasing number of papers in this field, making use of a broader range of nuclei.[43] Such work can have as profound an effect on the extensive and complex chemistry of iso- and hetero-polyanions as did proton n.m.r. spectroscopy on organic chemistry.

We thank the U.S. Air Force Office of Scientific Research and the National Science Foundation for support, and Dr. E. Sokolowski of the National Institutes of Health and Drs. A. D. English and J. P. Jesson, Central Research Department, E. I. duPont de Nemours and Co., for assistance in obtaining the ^{31}P n.m.r. spectra.

[6/455 *Received, 8th March,* 1976]

[43] See, for example, J. Banck and A. Schwenk, *Z. Physik*, 1975, **B20**, 75 (^{183}W); R. R. Vold and R. L. Vold, *J. Mag. Res.*, 1975, **19**, 365 (^{95}Mo and ^{7}Mo).