Vanadium-51 Nuclear Magnetic Resonance Study of Sulphido- and Oxosulphido-vanadate(V) Species

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The three known monomeric sulphido- and oxosulphido-vanadium(V) species $[VS_4]^{3-}$, $[VOS_3]^{3-}$, and $[VO_2S_2]^{3-}$ have been identified by high-field vanadium-51 n.m.r. spectroscopy, together with the previously unobserved ions $[VO_3S]^{3-}$, $[V_2S_7]^{4-}$, $[O_3VSVO_3]^{4-}$, $[SO_2VSVO_2S]^{4-}$, and the monoprotonated monomers. No equilibria between monomeric species are observed other than for protonation. The observed vanadium chemical shifts can be accounted for quantititatively by simple molecular-orbital theory.

Although the aqueous chemistry of oxovanadium(V) complexes has been extensively studied,[1] oxosulphidovanadium(V) chemistry has received little attention. Müller *et al.*[2] reviewed the chemistry of thiometalates of the early transition metals in their highest oxidation state, and reported that although thiomolybdates and thiotungstates have been extensively studied only three oxosulphidovanadium(V) species ($[VS_4]^{3-}$, $[VOS_3]^{3-}$, and $[VO_2S_2]^{3-}$) were known, with the data concerning them being limited to one crystal structure[3] plus u.v.–visible[4–7] and i.r.–Raman spectra.[8] Ranade *et al.*[7] describe the electronic spectrum of a species of proposed formula $[VO_3S]^{3-}$, but without further characterising it. The only polymeric sulphidovanadium(V) species to have been reported is V_2S_5, prepared by thermal decomposition of $[NH_4]_3[VS_4]$.[9]

High-field vanadium-51 n.m.r. spectroscopy has proved well suited to the study of oxovanadium(V)[1] and oxoperoxovanadium(V)[10] equilibria because it offers high dispersion and sensitivity. An isolated resonance is detectable at 10^{-4} mol dm^{-3}. It is thus an appropriate tool for the investigation of oxosulphidovanadium(V) species in solution, even though these are only reliably prepared dilute. This limitation, however, rules out ^{17}O n.m.r. spectroscopy with existing equipment.

Experimental

Preparation of Oxosulphidovanadium(V) *Species.—Aqueous reactions.* Sulphidovanadate species were prepared, usually as mixtures, by the reaction of hydrogen sulphide with vanadate solutions, under conditions based on Busine and Tridot's[11] preparation of $[VS_4]^{3-}$. An aqueous solution (10% ^2H_2O, 100 cm^3) containing ammonia (s.g. 0.880, 10 cm^3) and 0.05 mol dm^{-3} in $Na_2[HPO_4]$ was saturated at 273 K with H_2S by bubbling for *ca.* 2 h. Addition of vanadate solution (sodium metavanadate, Fisons; adjusted to pH 13 and $[V]_{total} < 0.01$ mol dm^{-3} in all cases) immediately gave the purple colour characteristic of $[VS_4]^{3-}$. No chemical interaction was observed between the thioanions and either NH_3 or phosphate, nor in the presence of 2 mol dm^{-3} $Na[ClO_4]$ to control ionic strength. The pH was adjusted using saturated aqueous sodium sulphide (Fisons) for reasons discussed below.

Solid-state reactions. The salt $Na_3[VS_4]$ was prepared from the elements (V metal, Johnson-Matthey) in stoicheiometric ratio, heated *in vacuo* to 500 °C, analogously to $K_3[VS_4]$[12] and $Tl_3[VS_4]$.[13] The salt $Na_3[VOS_3]$ was prepared by a published method.[4] Direct dissolution of the solid products in aqueous Na_2S led to spectra in which the named anion dominated the mixture of species.

pH *Measurement.*—The exposure of standard combined pH glass electrodes to solutions containing sulphide gives a black precipitate of Ag_2S; H_2S also interferes with bubbling hydrogen electrodes. The pH was therefore monitored *via* the ^{31}P n.m.r. chemical shift of the phosphate ion, calibrated by a sulphide-free titration in the same medium from pH 7 to 13.

N.M.R. Spectroscopy.—Vanadium-51 n.m.r. spectra (105.2 MHz, 1 000—10 000 transients, capillary $VOCl_3$ reference) and ^{31}P spectra (162 MHz, 32 transients) were obtained using a Bruker WH400 n.m.r. spectrometer with the sample at 273 ± 1 K in all cases. The shifts were mostly reproducible to within ±1 and ±0.01 p.p.m. respectively. Due to the large chemical shift range (+1 500 to −500 p.p.m.) the ^{51}V spectra were obtained in three separate sections and with a small flip angle.

Results and Discussion

Preparative Chemistry.—All the resonances recorded in the Table with chemical shifts above −500 p.p.m. are previously unobserved, and must arise from the presence of bonds from vanadium to sulphur. Their detailed assignments are discussed below.

The preparation of these new species revealed several important differences between sulphido- and oxo-vanadium(V) chemistry. Solutions containing one or more species, prepared by several different methods as described above, gave quite different relative peak areas under near-identical conditions of vanadium and $[HS]^-$ concentration, at pH values around 7.4, and these area ratios remained constant for several hours. At higher pH values there was also no equilibration, but a very slow relative decrease was observed with time, in the areas of peaks with higher δ values. This is consistent with slow hydrolysis of V–S bonds by $[OH]^-$, but not by water. The inertness at pH 7.4 implies that $[HS]^-$ is unable to attack V–O or V–OH bonds, and this is confirmed by the total inertness of vanadate species to added sodium sulphide at higher pH values, even when the pH is controlled by the addition of buffer. In turn, this observation must mean that the H_2S preparation method, described above, works only because H_2O is available as a leaving group at pH < 7,[1] or alternatively by concerted reactions involving the transfer of a single proton, such as in equation (1).

$$H_2S + [HVO_4]^{2-} \longrightarrow \{[HS]^- + [H_2VO_4]^-\} \longrightarrow [HVO_3S]^{2-} + H_2O \quad (1)$$

The presence of such reactions is confirmed in Figure 1 by the observation that the titration curves for $[VO_3S]^{3-}$ and $[VO_2S_2]^{3-}$ end just below their pK_a values. Attempts to extend these curves by acidification with added H_2S led to the formation of tri- and tetra-sulphido species instead. However, although attack by $[HS]^-$ is negligible, evidence is presented below for slow- to medium-rate oligomerisation equilibria of the type (2).

$$[VS_4]^{3-} + [HVS_4]^{2-} \rightleftharpoons [V_2S_7]^{4-} + [HS]^- \quad (2)$$

Thus either $[HS]^-$ or $[VO_nS_{4-n}]^{3-}$ (n = 0—4) or their protonated forms must be able to attack V–S bonds. Attack by the vanadate species would be consistent with an earlier observation[1] that $[HVO_4]^{2-}$ is the principal nucleophile in polyvanadate equilibria.

Another important difference in the presence of sulphide is that the solutions are unstable with respect to vanadium(V) reduction below pH 7. Furthermore reduction appears to be assisted by polymerisation, for it is speeded not only by acidification, but also by any raising of vanadium or lowering of $[HS]^-$ concentration. This greatly restricts the extent to which the polymerisation equilibria can be investigated. It also means that the total vanadium concentration cannot usefully exceed *ca.* 0.01 mol dm^{-3}. Nevertheless, the species $[VS_4]^{3-}$, $[VOS_3]^{3-}$, $[VO_2S_2]^{3-}$, and $[VO_3S]^{3-}$ may reasonably be identified from the available data even in the absence of equilibria. The monoprotonated forms of all four are also

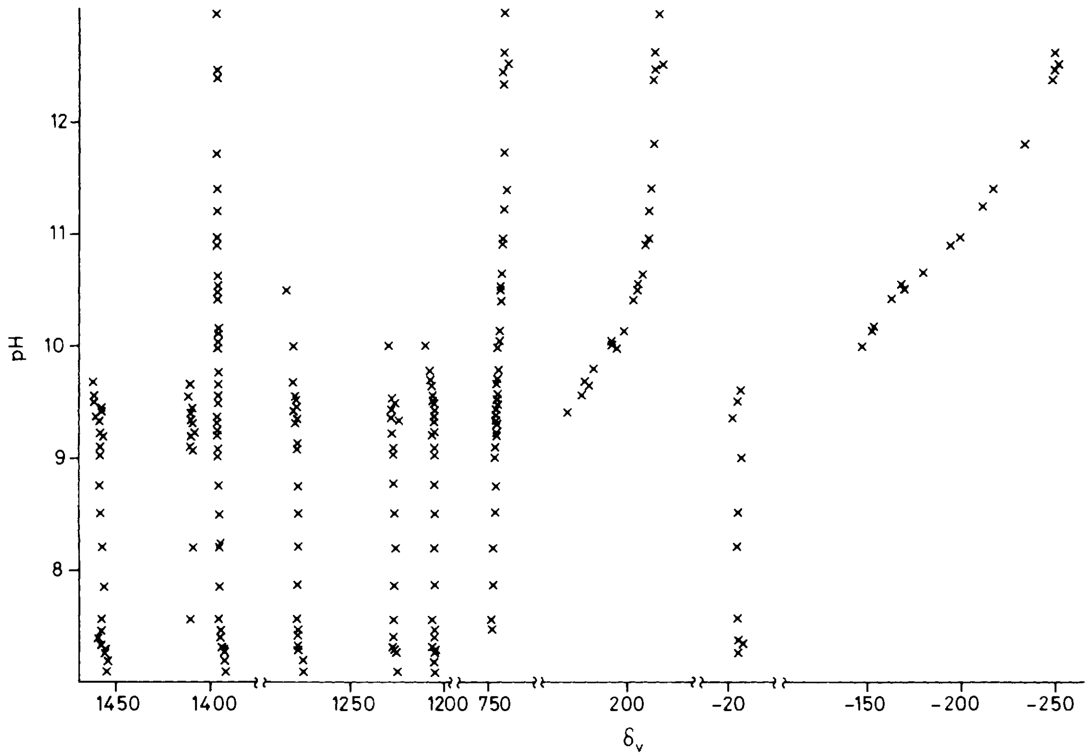

Figure 1. pH Dependence of chemical shifts of observed sulphidovanadate species. A few very minor resonances in the pH < 10 region are omitted

Table. Chemical shifts and pK_a values for oxosulphido- and sulphido-vanadate(V) species

	Number of S around one V atom				
Monomers	0[a]	1	2	3	4
Formula	$[VO_4]^{3-}$	$[VO_3S]^{3-}$	$[VO_2S_2]^{3-}$	$[VOS_3]^{3-}$	$[VS_4]^{3-}$
δ_V	−541.3	−250	184	740	1 395
Colour in solution	Colourless	Yellow	Brown	Magenta	Magenta
Formula	$[VO_3(OH)]^{2-}$	$[HVO_3S]^{2-}$	$[HVO_2S_2]^{2-}$	$[HVOS_3]^{2-}$	$[HVS_4]^{2-}$
δ_V	−538.8	−121	>230	748	1 392
pK_a[b]	12	10.5	~9.8	9.4	7.3
Formula	$[VO_2(OH)_2]^-$				
δ_V	−560.4				
pK_a[b]	7.1				
Dimers					
Formula	$[V_2O_7]^{4-}$	$[V_2O_6S]^{4-}$	$[V_2O_4S_3]^{4-}$		$[V_2S_7]^{4-}$
δ_V	−561.0	−198	*ca.* 220		1 457
pK_c	+1.39 ± 0.12				−4.8 ± 0.4[c]

[a] Vanadate data: see ref. 1. [b] For loss of one proton. [c] For $[VS_4]^{3-} + [HVS_4]^{2-} \rightleftharpoons [V_2S_7]^{4-} + [HS]^-$.

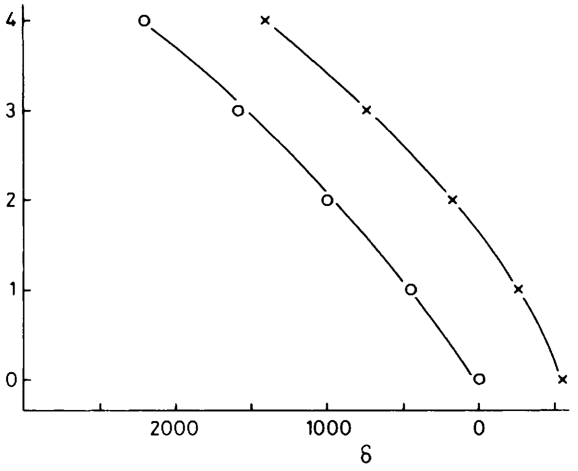

Figure 2. Comparison of chemical shifts of monomeric sulphidovanadate(V) (x) and sulphidomolybdate(VI) species (o)[14]

identified, along with their pK_a values. Also a number of polymeric species are reported, but incompletely characterised.

Chemical Shifts and Assignments.—The Table contains the chemical shift data and pK_a values for the sulphidovanadate species with some vanadate[1] species for comparison. Figure 1 is a plot of δ_V *vs.* pH for those sulphidovanadate species with > 5% of total V. At pH 13 four peaks due to sulphidovanadates are observed at δ_V = 1 395, 740, 184, and −250 p.p.m. Monomeric species are expected to predominate at this pH by analogy with the known chemistry of vanadate species.[1] Hence these resonances are assigned to $[VS_4]^{3-}$, $[VOS_3]^{3-}$, $[VO_2S_2]^{3-}$, and $[VO_3S]^{3-}$ respectively. The assumption of near-tetrahedral coordination is based on the known structure of $[VO_4]^{3-}$ and a linewidth <40 Hz for $[VS_4]^{3-}$. Somewhat increased linewidths are observed for the $[VO_2S_2]^{3-}$ and $[VO_3S]^{3-}$ species, consistently with their lower symmetry. A plot of δ against the number of sulphur atoms per vanadium (Figure 2) shows the trend expected for the replacement of an oxo ligand at a vanadium centre (vanadium-51 chemical shifts including protonation effects are discussed further below). A similar trend (also plotted in Figure 2) has recently been observed for oxosulphidomolybdenum(VI) complexes.[14]

As the pH is lowered all the monomers undergo an increase in shift due to protonation, apart from $[VS_4]^{3-}$ which decreases very slightly. This is consistent with protonation at oxygen rather than sulphur, although the latter must occur in $[VS_4]^{3-}$. The pK_a values are 7.3, 9.4, *ca.* 9.8, and 10.5 for the protonation of $[VS_4]^{3-}$, $[VOS_3]^{3-}$, $[VO_2S_2]^{3-}$, and $[VO_3S]^{3-}$ respectively in 2 mol dm^{-3} Na[ClO$_4$], obtained by computer fitting of the data to the curve predicted by the Henderson–Hasselbach equation. All these pK_a values are between 0.5 and 1.5 units lower than those measured without Na[ClO$_4$] present, as would be expected for the charges involved in the proposed equilibria. Similar differences have been measured for vanadates,[1] peroxovanadates,[10] and for the final protonation of phosphate (pK_a = 10.7 in 2 mol dm^{-3} Na[ClO$_4$] and 12.12 without Na[ClO$_4$] in this study).

Further evidence supporting these assignments can be gained from both of the solid-state reactions described above and the reaction of $Na_3[VO_4]$ with Na_2S.[7] By heating V_2O_5, Na_2CO_3, and S in the correct stoicheiometric ratio it has been claimed on the basis of u.v. spectra that $Na_3[VOS_3]$ is formed predominantly.[4] If this reaction product is extracted with a saturated aqueous solution of Na_2S, peaks at δ_V = 733 (>75%), 184, and −253 p.p.m. are observed, indicating the formation of $Na_3[VOS_3]$ (predominantly), $Na_3[VO_2S_2]$, and $Na_3[VO_3S]$ respectively.

Ranade *et al.*[7] suggested on the basis of u.v. spectra that the $[VO_3S]^{3-}$ anion may be prepared by the reaction of $Na_3[VO_4]$ and Na_2S in methanol. The ^{51}V n.m.r. spectrum of $Na_3[VO_4]$ in methanol showed three resonances, at −531.2, −546.4, and −566.5 p.p.m. These are assigned to the species $[VO_3(OMe)]^{2-}$, $[HVO_4]^{2-}$, and $[V_2O_7]^{4-}$ respectively, on the basis of previous and closely analogous data.[1] On reaction of $Na_3[VO_4]$ with Na_2S in methanol a yellow colour appeared in parallel with a new resonance at δ_V = −120.0 p.p.m., assigned to $[VO_2S(OMe)]^{2-}$, or $[HVO_3S]^{2-}$ as observed above. Thus the shifts of the monomers prepared as above are consistent with the data gained from the original aqueous preparation.

In further support of the above assignments, alkaline $[HS]^-$ ('sodium sulphide solution') was added to a solution initially containing almost solely $[VS_4]^{3-}$ and its oligomers, at pH 7. It was noted that each successive substitution of O for S occurred only as the pH approached the pK_a for deprotonation of the species to be attacked. This is consistent with hydrolysis reactions of type $[VS_nO_{4-n}]^{3-} + [OH]^- \longrightarrow [VS_{n-1}O_{5-n}]^{3-} + [HS]^-$, whereas the corresponding reaction of $[VS_nO_{3-n}(OH)]^{2-}$ leads only to deprotonation.

Dimerisation Equilibria.—An attempt was made to observe possible equilibria between species in the 1 200—1 500 p.p.m. region, using the DANTE[15] experiment in the hope of seeing the transfer of excitation from a single resonance to other frequencies. However, no transfers were detected, indicating relatively slow equilibria between mono- and polymeric tri- or tetra-sulphido species. The resonance at 1 457 p.p.m. does, however, show a consistent intensity relationship with that of $[VS_4]^{3-}$ at 1 395 p.p.m., such that it may be assigned to the species $[V_2S_7]^{4-}$. Equation (2) (pK_c = −4.80 ± 0.4) gives a better fit to an equilibrium constant than any other reasonable reaction. The other peaks in this region may be due to symmetrical higher polymers of V^V and S^{2-}, such as $[V_4S_{12}]^{4-}$, or to species with persulphide and further catenated sulphides, as have been found in thiomolybdate complexes,[16] *e.g.* $[MoS(S_4)_2]^{2-}$,[17] $[Mo_2S_2(\mu\text{-}S)_2(S_2)(S_4)]^{2-}$,[16] $[Mo_2(S_2)_6]^{2-}$,[16] and $[Mo_3S_{13}]^{2-}$.[18] It is possible that such catenated S ligands could also complex to vanadium. As none of the pairs of peaks in the spectral range 1 200—1 500 p.p.m. has constant integral ratios, unsymmetrical polymers can be eliminated, apart from the possibilities presented by accidental shift coincidence. There is also more specific evidence for the dimeric species $[O_3VSVO_3]^{4-}$ and $[SO_2VSVO_2S]^{4-}$. As the peaks corresponding to $[VO_3S]^{3-}/[HVO_3S]^{2-}$ and to $[VO_2S_2]^{3-}/[HVO_2S_2]^{2-}$ pass through their titration inflections they broaden and in the former case split with one component fixed in shift at *ca.* −198 p.p.m. (Figure 3) over a narrow pH range close to 11.0. This fixed component increases in area when the concentration of $[VO_3S]^{3-}/[HVO_3S]^{2-}$ is raised, in a manner at least qualitatively consistent with the equilibrium (3). Unfortunately the

$$[VO_3S]^{3-} + [HVO_3S]^{2-} \rightleftharpoons [O_3VSVO_3]^{4-} + [HS]^- \quad (3)$$

data do not permit an equilibrium constant to be obtained reliably, although in qualitative terms it is slightly lower than that for equilibrium (2) above. No splittings are observed in the corresponding disulphido equilibrium, but the broadenings imply a similar formation of $[SO_2VSVO_2S]^{4-}$ at pH ≈ 9.6.

The chemical shift of −198 p.p.m. for $[O_3VSVO_3]^{4-}$ is consistent (see below) with a slight lengthening of the V–S bond upon formation of the V–S–V bridge. A V–O–V bridge is considered unlikely in view of the stoicheiometry observed.

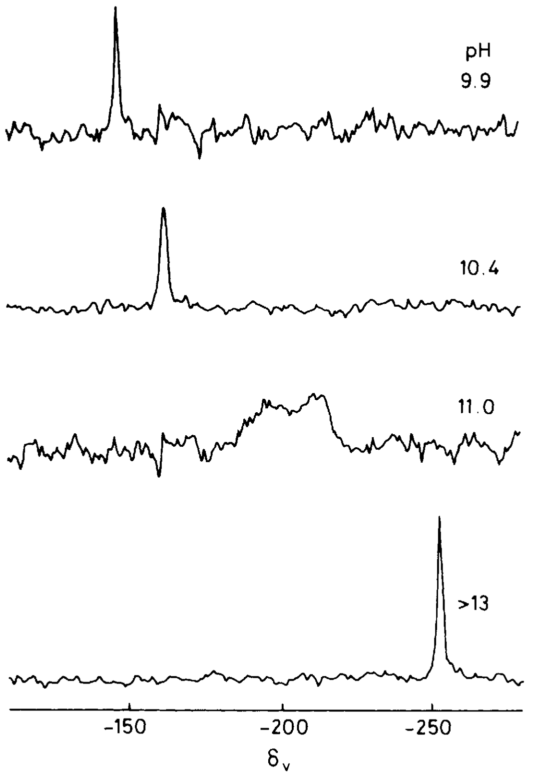

Figure 3. ^{51}V N.m.r. spectra showing the equilibrium between $[VO_3S]^{3-}$, $[HVO_3S]^{2-}$ and $[O_3VSVO_3]^{4-}$

Interpretation of Chemical Shifts.—The chemical shifts of the sulphidovanadate ions, together with other related near-tetrahedral species such as $VOCl_3$, VOF_3, $[VO_2Cl_2]^-$,[19] $VOBr_3$,[20] and $[VSe_4]^{3-}$ (in $Tl_3[VSe_4]$)[13] may be readily interpreted using the calculation method of Becker and Berlage,[13] which is in turn based on work by Harrison[21–23] and Jameson and Gutowsky.[24] The calculations are relatively crude, being essentially of Hückel type, with core and resonance integrals explicitly related to SCF atomic orbital energies and metal to ligand bond lengths. Thus σ^P, the paramagnetic contribution to the shielding at vanadium, is given by equation (4) where μ_B is the

$$\sigma^P = 4\mu_0\mu_B^2\gamma\langle r_d^{-3}\rangle c^2(3 - c^2)/\pi\Delta E \qquad (4)$$

Bohr magneton, γ is a scaling factor, and c^2 a measure of the d character at vanadium. The simpler of Becker and Berlage's alternatives is used, which assumes constant $\langle r_d^{-3}\rangle$, and a further simplification is made, in line with ref. 24, by assuming that the ligand orbitals are of purely p character. With these assumptions, we use a scaling factor (γ) of 0.5 and a chemical shift base (on the simplest theory this is the shift of V^{5+}) of −1 200 on the $\delta(VOCl_3) = 0$ scale. Because Becker and Berlage only discuss S and Se complexes, we have for consistency used the very similar SCF atomic orbital data of Clementi and Roetti[25] for all ligands. Species with more than one ligand are treated by assuming cumulative ligand contributions to the d-electron density on V, and a geometrically averaged mean excitation energy.

Figure 4 shows that the calculated and observed chemical shifts correlate well, and hence that the observed chemical shifts are consistent with the proposed formulations of the sulphidovanadate species. The same calculations also reveal a weakening of the V–S bond relative to V–O, despite an increase in covalency. They also afford a qualitative insight into the consequences for chemical shift of protonating the ligands. Protonation at oxygen is here simply treated as a lengthening of the V–O distance to 1.9 Å. Little change is then predicted for $[VO_4]^{3-}$ (observed, +2.4 p.p.m.) but larger changes (typically +40 p.p.m.) are predicted for oxygen protonation of all three oxosulphido species. These agree at least qualitatively with the data of Figure 1, except for $[VOS_3]^{3-}$, where the observed shift on protonation is very small. This may imply that the oxygen atom in $[VOS_3]^{3-}$ is not available for protonation. The effects of S-protonation are harder to judge in the present theory, because they are highly sensitive to any assumptions made about changes in V–S bond length. However, a null protonation shift is a reasonable possibility, and hence the small observed protonation shift of $[VS_4]^{3-}$ is not unexpected. In general, the vanadium shift is expected to increase as the V–S bond lengthens, if any other bonds to V remain unaffected.

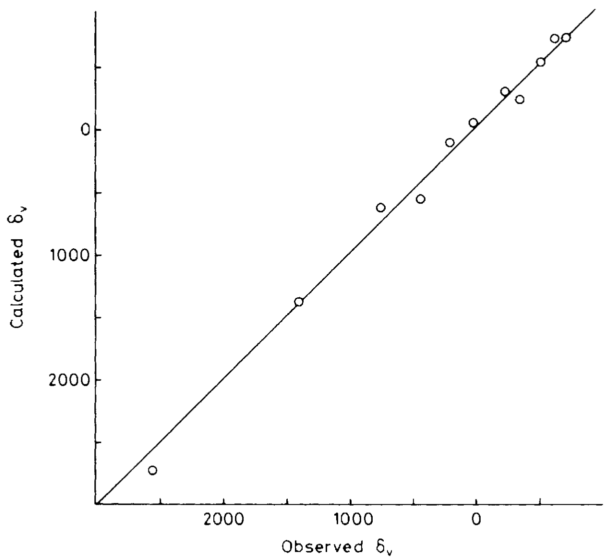

Figure 4. Calculated *vs.* observed chemical shifts of vanadium(v) species. In ascending order of observed shifts: VOF_3 (in tetrahydrofuran and $CHCl_3$), $[VO_4]^{3-}$, $[VO_2Cl_2]^-$,[19] $[VO_3S]^{3-}$, $VOCl_3$, $[VO_2S_2]^{3-}$, $VOBr_3$,[20] $[VOS_3]^{3-}$, $[VS_4]^{3-}$, and $Tl_3[VSe_4]$(solid state)[13]

Conclusions

Although the chemistry and properties of sulphidovanadate species differ substantially from those of oxovanadates, the differences may all be related to the known energies and radii of sulphur orbitals. Thus we have shown that both the weakness of the V–S bond and the very large chemical shifts {that for $[V_2S_7]^{4-}$ sets the current high-frequency record for vanadium(v) species in diamagnetic solution} are readily explained by simple calculation. The observed colours are similarly explained.

A more elaborate argument is necessary to understand why the pK_a decreases in the monomers with increased replacement of O by S. The short V–O bond, unlike that to S, gains strength by secondary $p \longrightarrow d$ π bonding, and this π bonding is enhanced within any one bond when the number of oxygen atoms surrounding the vanadium is reduced. Thus in the analogous molybdenum(vi) complexes[14] the ^{17}O n.m.r. shift increases monotonically from 544 to 759 p.p.m. between $[MoO_4]^{2-}$ and $[MoOS_3]^{2-}$. As oxygen becomes bound more tightly to vanadium, it will necessarily be harder to protonate; hence the observed trend.

The weakness of the V–S bond must also contribute to the surprising nucleophilic inefficacy of $[HS]^-$ towards vanadates. It only seems able to attack the V–OH_2 bond. However, in view of this inefficacy, one is surprised to observe relatively rapid monomer–dimer equilibria. A possible explanation may be reactions of type (5) similar to those proposed previously for vanadates.[1]

$$[V^*O_3S]^{3-} + [O_3VSVO_3]^{4-} \rightleftharpoons [O_3V^*SVO_3]^{4-} + [VO_3S]^{3-} \quad (5)$$

Finally, one notes the more marked tendency of the sulphidovanadates to dimerise, with S-bridging. This bonding arrangement reduces steric and electrostatic repulsions, and leaves the strong V–O bonds unaffected.

Acknowledgements

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