Chromovanadates

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Vanadium-51 and ^{17}O NMR evidence is presented for the chromovanadate species $[V_{10}O_{27}(OCrO_3)]^{6-}$, $[HV_{10}O_{27}(OCrO_3)]^{5-}$, $[VO_2(OCrO_3)_2]^{3-}$ and $[V_2O_5(OCrO_3)_2]^{4-}$. In all of these, $[CrO_4]^{2-}$ competes as a ligand with $[OH]^-$ and attaches in a similar way to vanadium.

Although it is well known that vanadium and molybdenum form both isopolyanions[1] and mixed polyanions[1,2] in their highest valence states, no chromovanadates have yet been reported. The present study describes four such Cr^{VI}–V^V species and points to the probability of further ones. It also helps to explain the two main reasons why they have not been discovered earlier. First, the species are never present in proportions significantly larger than either free vanadate or chromate, even when very high concentrations are used. This precludes the use of potentiometry. Secondly, their ^{51}V NMR resonances always lie close to those of a known protonated isopolyvanadate(V) anion, so that some care is required in order to distinguish between the two resonances. Similar difficulties are likely to hinder any future UV spectroscopic or Raman study, for the closeness of the resonances can be explained by a similarity in structure. The present study also employs ^{17}O NMR spectroscopy, which should be more sensitive to the proposed anion catenations, but even here the results are limited by the fairly rapid exchange of the oxygen atoms, which is commonly associated with chromate(VI) chemistry.[3] A further limitation of the chromovanadate system is that the species tend to dissociate reversibly into isopolyanions upon warming. This virtually precludes the use of two-dimensional ^{51}V–^{51}V NMR spectroscopy for the identification of coupled, inequivalent vanadium atoms, as this technique[2,4] only works when the resonances have been narrowed by heating the sample.

Experimental

Lithium vanadate and lithium chromate solutions were prepared from the corresponding oxides and lithium hydroxide (Aldrich). The lithium salts were chosen in order to minimise the precipitation of polyvanadates at lower pH values. Due to the high chromium concentrations necessary for forming chromovanadates, it proved impossible to maintain a satisfactorily constant ionic strength with all solutions. However, most solutions contained excess chromate, *ca.* 1 mol dm^{-3}, and in some cases this was partially replaced by an equivalent amount of sulphate in order to keep the ionic strength at least approximately constant. Vanadium concentrations were typically 0.1 mol dm^{-3}, and the concentrations of individual species were obtained from the ^{51}V NMR integrals, with a typical accuracy of $\pm 15\%$ in all but the less favourable cases.

Vanadium-51 NMR spectra were obtained at 105.2 MHz and ^{17}O spectra at 54.2 MHz, as described previously,[2] using two offset values in the latter case, for each sample, to discriminate genuine peaks from electronic artefacts. Further ^{51}V NMR spectra were obtained at 157.8 MHz in the lower pH range. Resolution enhancement was necessary in many cases, in order to reduce overlaps. Its possible effects on the integrals were minimised by the comparison of many spectra.

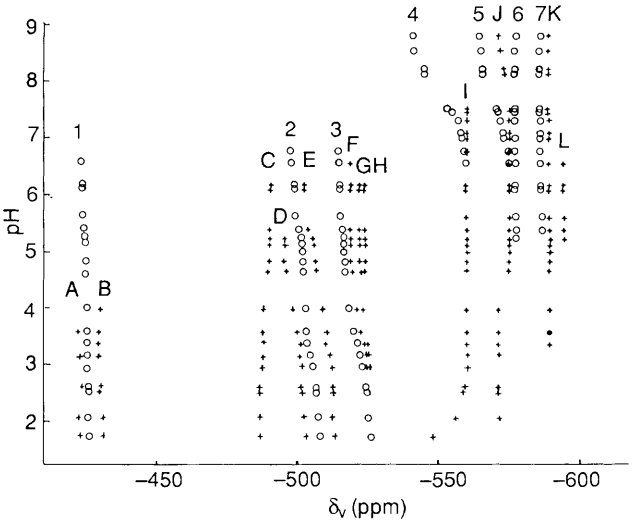

Fig. 1 Dependence of ^{51}V chemical shift (293 K) upon pH at a variety of concentrations; ○, isopolyvanadate resonances and +, chromovanadate resonances, including some peak shoulders

Results

Fig. 1 shows the chemical shifts of the ^{51}V NMR resonances observed at 105.2 MHz over the entire pH range. The numbered peaks correspond to known isopolyvanadate resonances. The lettered resonances, especially A–H, are generally much weaker, and when they are close to resonances 1–3 they become shoulders.

Resonances A–H *and* 1–3.—Fig. 2 shows a 157.8 MHz ^{51}V NMR spectrum at pH 5.25, together with an inset of the highest frequency resonances at pH 3.2. From these and other spectra, and the judicious use of resolution enhancement, it is possible to obtain approximate relative areas of resonances A–H, even though there is no single spectrum in which they can all be resolved without distortion. These areas are listed in Table 1; for resonances only visible as shoulders the areas are unavoidably more approximate. Some comparable relative areas have also been obtained from spectra in which resonances 1–3 have been subtracted by the use of isopolyvanadate spectra obtained under conditions as near identical as possible, with separate adjustment of the horizontal offset for each resonance (Fig. 3). Although resonance D is only visible as a single, fairly broad resonance at 105.2 MHz, Fig. 2 shows that it actually consists of two overlapping resonances at higher field, and this is reflected by the double entry in Table 1. There are no conditions of pH or concentration in which the relative areas of peaks A–H in Table 2 vary by an experimentally significant fraction. Fig. 1 also

shows that resonances G and H merge below pH 4.5. They broaden before merging, and subsequently remain somewhat broader, as do most of the other resonances under these conditions, which suggests exchange.

Resonances I–L *and* 4–7.—Unlike resonances A–H, the relative areas of resonances I–L and 4–7 depend strongly upon pH, and I–L also depend upon chromate concentration. This is illustrated in Fig. 4 and quantified in the first 5 columns of Table 2. Other ^{51}V NMR spectra outside this pH range confirm the same trends, although they are not included in Table 2 because of the very low concentrations of some components. The species concentrations for I, J and peak 6 ($[V_4O_{12}]^{4-}$) in Table 2 were obtained from the areas of relatively narrow resonances. In some cases these overlapped with the broader resonances 4 and 5, as is apparent from Fig. 4. It was not difficult to estimate the areas of peaks I and 6 under these conditions; if necessary the broad underlay could be removed digitally as a rolling baseline. Peak J presented more problems and the data are correspondingly less reliable.

Oxygen-17 NMR spectra were also obtained for selected solutions, with *ca.* 3 mol % isotopic enrichment. Data for two representative solutions are listed in Table 3, together with species concentrations obtained from the ^{51}V NMR spectra of the same solutions. The assignments in the final column are discussed below. Repeated measurements show that the smaller peak areas are only reliable to ±20%. Many of these resonances broaden when the sample is warmed, which implies oxygen-exchange processes.

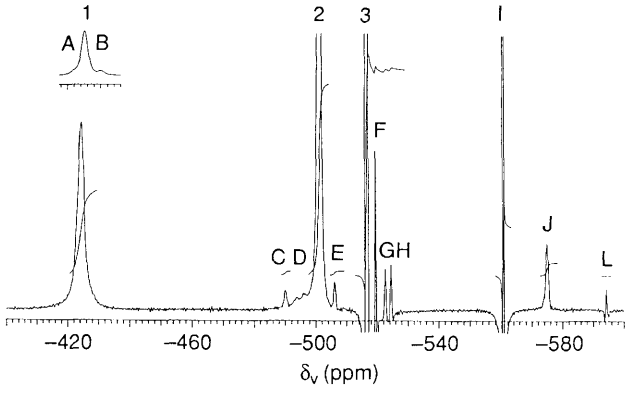

Fig. 2 157.8 MHz ^{51}V resolution-enhanced NMR spectra of solutions 0.5 mol dm^{-3} in both Cr and V. Main spectrum: pH 5.25; inset: 'central' vanadiums at pH 3.2

Table 1 High frequency ^{51}V NMR data

Peak	δ_V[a] (ppm)	Relative area[b]
A	−422 (sh)	≈1.5
1	−425.2	100
B	−430.0	1.5
C	−489.9	1.8
D	−494 (sh)	≈2
	−496 (sh)	≈2
2	−501.2	200
E	−506.0	1.8
3	−516.6	200
F	−519.4	3.5
G	−522.5	2.0
H	−524.4	2.0

[a] pH 5.25, excluding peaks A, 1 and B which are at pH 3.2. [b] Estimated by comparison of resolved peaks with appropriate resolution enhancement.

Discussion

Resonances A–H *and* 1–3.—Resonances 1–3 are respectively the well known 'central, corner and capping' decavanadate peaks.[5,6] Resonances A and B lie close to 1; C, D (double) and E to 2; and F (double area), G and H to 3. Figs. 2 and 3 also show that their widths have a similar, approximate relationship. Such

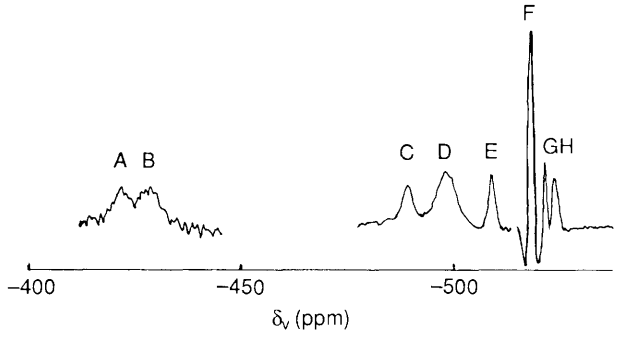

Fig. 3 Montage of ^{51}V subtraction spectra; the heights of peaks C, D and E have been doubled and those of peaks A and B quadrupled

Table 2 Dependence of ^{51}V peak areas I and J upon concentration

pH	[I][a]	[J][a]	$[V_4O_{12}]^{4-}$ [a]	$[CrO_4]^{2-}$ [a,b]	log K_I[c]	log K_J[d]
5.41	40	50.6	32.4	25	9.24	9.02
5.55	34.8	47.7	40.3	35	9.15	8.92
5.60	35.1	24.4	3.9	50	9.20	8.34
5.70	33.4	50.6	47.5	50	9.11	8.86
5.98	13.4	29.6	99.2	50	9.19	9.18
6.30	16.7	30.6	223	110	9.14	8.97
6.46	23.7	29.6	29.6	240	9.17	8.44
6.48	25.2	31.9	24.4	240	9.25	8.51
6.55	2.9	4	58.7	85	9.25	8.87
6.76	3.9	4	195	140	9.24	8.75
6.79	4.9	4	131	175	9.25	8.57
6.86	3.5	3	72.9	180	9.28	8.55
6.95	2.1	2	142	185	9.14	8.52
7.00	8.1	9.6	46.3	420	9.25	8.43
7.12	1.0	1	65.9	190	9.25	8.55
7.18	3.3	5.7	53.3	450	9.15	8.49
7.31	2.7	6	57.3	500	9.20	8.64
				Averages:	9.20 ± 0.05	8.68 ± 0.24

[a] Species concentrations in mmol dm^{-3}, assuming one V per anion in species I and two in J. [b] Calculated from the total [Cr] as described in the text. [c] $\log K_I \equiv \log [I] - 0.25 \log [V_4O_{12}^{4-}] - 2 \log [CrO_4^{2-}] + 2(pH)$. [d] $\log K_J \equiv \log [J] - 0.5 \log [V_4O_{12}^{4-}] - 2 \log [CrO_4^{2-}] + 2(pH)$.

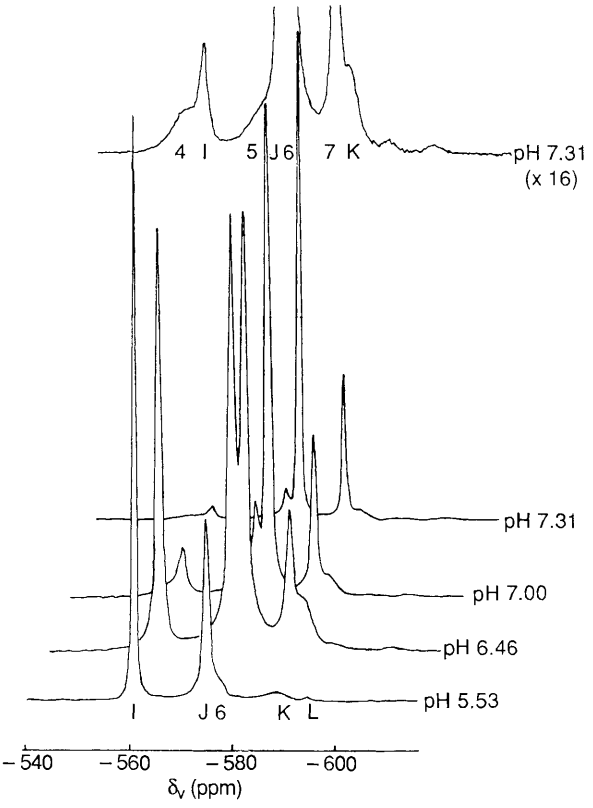

Fig. 4 Partial 105.2 MHz ^{51}V NMR spectra of solutions of 0.1 mol dm^{-3} in V and 0.5 mol dm^{-3} in Cr (293 K, pH 5.5—7.3)

Table 3 Selected ^{17}O NMR data[a]

δ_O(ppm)[b]	Linewidth/Hz	Relative area	Proposed assignment
(*a*) pH 7.1			
1115	70	6.0	$[O_3CrOCrO_3]^{2-}$
957	530	1.0	OVO_2O– in I, J
928	490	1.5	OVO_2O– in $[V_4O_{12}]^{4-}$
816	220	97	$[CrO_4]^{2-}$ + –CrO_3 in I, J
520	140	0.5	V–O–V in J
477	1000	0.8	V–O–V in $[V_4O_{12}]^{4-}$
333	90	0.9	$[O_3CrOCrO_3]^{2-}$
287	330	0.2	Not known
260	180	0.8	V–O–Cr in J
(*b*) pH 4.5			
1115	90	100	$[O_3CrOCrO_3]^{2-}$
597	470	6.4	OVO_2O– in I, J
837	310	32.2	–CrO_3 in I, J + $[HCrO_4]^-$
520	140	0.6	V–O–V in J
334	90	14.8	$[O_3CrOCrO_3]^{2-}$
289	250	1.2	Not known
260	120	0.9	V–O–Cr in J

[a] [Cr] = 600, [I] = 15.0, [J] = 8.0 and $[V_4O_{12}]^{4-}$ = 5.1 mmol dm^{-3} at pH 7.1 and [Cr] = 600, [I] = 36.0, [J] = 5.4 and $[V_4O_{12}]^{4-}$ = 0 mmol dm^{-3} at pH 4.5, assuming one V per anion in I and two V per anion in J. [b] Omits minor resonances attributable to the decavanadate.

shift and width relationships have been noted before in substituted decavanadates,[2,7] and imply a structure related to decavanadate. Also, the constant and approximately equal area ratios imply a single new species, protonating with pK_a = 4.5.

However, there is no single vanadium atom in decavanadate that can be replaced to yield more than seven vanadium resonances, whereas the present data are strongly consistent with 10 resonances, only two of which cannot be resolved. It is in any case unlikely that Cr^{VI} would be able to replace V^V in an octahedral environment. Concomitantly, there are too few resonances to allow a mixture of monosubstituted nonavanadate species, even if such were likely. A better explanation, therefore, is that chromate attaches to the exterior of the intact decavanadate anion to give monochromodecavanadate, $[V_{10}O_{27}(OCrO_3)]^{6-}$. Its point of attachment must be at O_c (Fig. 5) in order to remove all elements of symmetry.

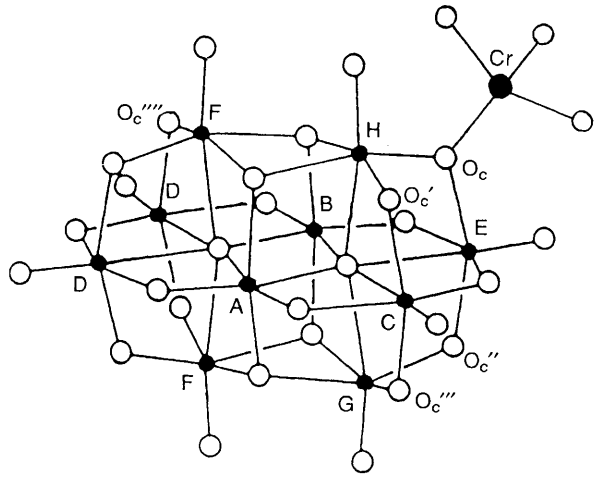

Fig. 5 Proposed structure for a monochromodecavanadate

It is significant that decavanadate also protonates most strongly at O_c.[8] The addition of a CrO_3 unit is evidently comparable to that of a proton, and indeed occurs at a similar pH, for pK_{a_1} of decavanadate is 6.0 under similar conditions.[6,9] Similarly pK_{a_2} for decavanadate is 3.7, and pK_{a_1} for monochromodecavanadate is 4.5. The notional binding of a CrO_3 unit is however much less complete than that of a proton. This unfortunately precludes any ^{17}O NMR study.

Fig. 5 also offers a tentative proposal for the assignment of resonances A–H, based on the above mentioned shift relationships, and the assumption that the greatest perturbations of shift arise from the vanadium atoms closest to chromium. The assignments are also consistent with the processes of incipient exchange described above. In particular, resonances G and H will merge if the chromate unit moves to O_c''. The same process will merge the two putative F resonances even more readily, provided that their shift separation is very small, but will only broaden the other more separated resonances. By the same token, any exchange of chromate between O_c and O_c' cannot be fast, even though it may also be present.

Resonances I–L *and* 4–7.—Resonances 4–7 are essentially identical to four known[5] isopolyvanadate resonances, which arise respectively from tetrahedrally co-ordinated vanadium in the species $[H_2VO_4]^-$ (4; −560.4 ppm), $[H_2V_2O_7]^{2-}$ (5; −572.7 ppm), $[V_4O_{12}]^{4-}$ (6; −577.6 ppm) and $[V_5O_{15}]^{5-}$ (7; −586.0 ppm). The first two species are also known to deprotonate, with corresponding increases in shift, above pH 7. This is reflected in Fig. 1. Under these conditions they also broaden due to exchange reactions.[5]

In contrast, resonances I–L are constant in shift above pH 5, to the upper pH limit of their range of existence. This probably implies that they do not bear exchangeable protons. The only exception to this is resonance J, which shifts slightly above pH 7.5. This slight apparent shift may in fact arise from overlap with an increasing amount of a similar species (perhaps bearing only one chromate – see below) rather than from deprotonation.

Below pH 4.5, resonance J dwindles to zero, but a new, weak and broad resonance is detectable at a slightly higher shift. We are not able to identify this at present, nor the similarly weak resonances K and L, although K may arise from the attachment of chromate to tetravanadate. Below pH 3, resonance I shifts strongly in a way suggestive of rapid exchange with $[VO_2]^+$.

Fig. 4 shows that the major new resonances are I and J. We have attempted to assign these by both equilibrium measurements and ^{17}O NMR, despite the problems outlined in the Introduction. Both methods require the formulation of proposed structures, followed by the demonstration that these fit the data better than other proposals. Our formulation of the structures was guided initially by the argument given above for the absence of protonation, together with the similarity of the shifts of I and J to those of $[H_2VO_4]^-$ and $[H_2V_2O_7]^{2-}$ respectively, and the analogy with monochromodecavanadate (above). We propose simply that each $[OH]^-$ ligand is replaced by $[OCrO_3]^{2-}$, giving the new species $[VO_2(OCrO_3)_2]^{3-}$ and $[(O_3CrO)VO_2(O)VO_2(OCrO_3)]^{4-}$. The V_2Cr_2 species must be symmetrical to account for there being only a single resonance J. Somewhat similar phosphovanadate species have been proposed by Gresser *et al.*[10]

Equilibrium data. If these formulae are correct, then equilibrium constants should be obtainable for the overall reactions (1) and (2). Unfortunately, however, the concentration

$$[H_2VO_4]^- + 2[CrO_4]^{2-} + 2H^+ \rightleftharpoons [VCr_2O_{10}]^{3-} + H_2O \quad (1)$$
(Species I)

$$2[H_2VO_4]^- + 2[CrO_4]^{2-} + 2H^+ \rightleftharpoons [V_2Cr_2O_{13}]^{4-} + H_2O \quad (2)$$
(Species J)

of $[H_2VO_4]^-$ cannot be measured conveniently because of the smallness of peak 4 and its overlapping with other peaks. Instead, it is necessary to note that the concentration must be in constant ratio with the fourth root of the $[V_4O_{12}]^{4-}$ concentration (resonance 6), whose area can be measured much more accurately. (This does not imply any direct reaction of chromate with tetravanadate.) The log ratios (3) and (4) should

$$\log K_I \equiv \log [I] - 0.25 \log [V_4O_{12}]^{4-} - 2 \log [CrO_4]^{2-} + 2(pH) \quad (3)$$

$$\log K_J \equiv \log [J] - 0.5 \log [V_4O_{12}]^{4-} - 2 \log [CrO_4]^{2-} + 2(pH) \quad (4)$$

then be constant also. These relationships are tested in the final two columns of Table 2. The fit is quite good for I, and all other proposals are far worse. The fit for J is less convincing, but is still appreciably better than any alternative. In particular, polymeric structures and structures with only one chromate unit can be ruled out.

Oxygen-17 NMR data. Several of the oxygen resonances listed in Table 3 can be assigned from previous studies on isopolyvanadates[5] and chromates.[3] The new resonances may also be readily assigned by type from their region of shift.[8] However, their detailed assignment depends upon a knowledge of their areas, and measured areas can be diminished by rapid chemical exchange when the linewidths become large, as a result of spectrometer dead-time and the problems of correcting a noisy baseline. The new assignments proposed in Table 3 are all consistent with our proposals that species I and J are, respectively, VCr_2 and (symmetric) V_2Cr_2 species, if the following propositions are accepted.

(*i*) The mutual exchange of all $-OCrO_3$ oxygens is rapid, except for those of dichromate. The expected resonances are thus subsumed into the $[CrO_4]^{2-}$ resonance and contribute to its significantly increased linewidth. This exchange should also affect the pH dependence of the chromate resonance, although protonation should be a contributing factor.

(*ii*) Similarly, rapid exchange occurs for the $-OCrO_3$ bridging oxygens in I. The slower exchange in J gives the resonance at δ_O 260 ppm, and may be attributable to the greater anionic charge of J.[5]

(*iii*) At higher pH values, the exchange also removes the terminal $-VO_2-$ resonance of I, although not the coincident resonance of J. Phosphate is also known to labilise some vanadate resonances.[10,11]

All the chromovanadate species which we have identified are closely analogous to known vanadate species in which the ligand $[OH]^-$ has been replaced by $[OCrO_3]^{2-}$. The partial charge on the ligating oxygen is probably similar in the two cases, although both steric hindrance and the added, more remote negative charge must render $[OCrO_3]^{2-}$ the poorer ligand, particularly with decavanadate. Although the chromovanadates are novel, some solid-state examples exist of molybdate tetrahedra similarly bound to isopolymolybdate anions by a single oxygen.[12]

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