

NMR, CD and MCD Studies of Vanadate–Nucleoside Complexes

D. C. Crans,^{*,a} S. E. Harnung,^{*,b} E. Larsen,^c P. K. Shin,^a L. A. Theisen^a and I. Trabjerg^b

^aDepartment of Chemistry, Colorado State University, Fort Collins, CO 80523, USA, ^bThe H. C. Ørsted Institute, University of Copenhagen, DK-2100 Copenhagen and ^cChemistry Department, The Royal Veterinary and Agricultural University, DK-1871 Frederiksberg, Denmark

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Complex formation between tetraoxovanadate(V) and each of the nucleosides adenosine, guanosine, cytidine and uridine has been studied in a constant salt medium at pH 7. ¹³C- and ⁵¹V NMR studies show that only complexes with the formula V₂L₂ (V = vanadate, L = nucleoside) are formed, and their formation constants have been determined. They have ⁵¹V NMR resonances around –523 ppm relative to VOCl₃, and they exhibit no CD in the spectral region of the charge-transfer transitions. MCD spectra were also measured, and all experiments are in accord with a molecular structure composed by two edge-sharing VO₆ octahedra forming an O₄V(μ-O)₂VO₄ skeleton with each of the nucleoside ligands bridging the two vanadium centres through the ribose 2',3'-oxygens, which are the oxygens outside the V₂O₆ plane.

Admixture of imidazole–HCl buffer at pH 7 gives rise to additional complexes of 1:1 stoichiometry. They have been characterized by ⁵¹V NMR and CD, and their formation constants are reported.

Vanadate(V) and the deoxynucleosides deoxyadenosine, deoxyguanosine, deoxycytidine and thymidine form very weak complexes which cannot be detected by ⁵¹V NMR or CD under conditions for which vanadate and the nucleosides form complexes.

Over the past twenty years it has been realized that vanadium is a trace element with important biological properties¹ which have been reviewed recently.² The biological activities are due to vanadium in the higher oxidation states, and an early study³ of its biochemistry included a spectrophotometric determination of the formation constant for a vanadate(V)–uridine complex formed in aqueous solution at pH 7. It was suggested that the *cis*-diol functions of uridine were used for complex formation, since methyl β-D-ribofuranoside formed a similar complex but 2'-deoxyuridine did not.

A summary of the chemistry of vanadate(V) in aqueous solution has been published.⁴ We note that only two geometries prevail: almost tetrahedral, protonated tetraoxovanadate(V) and its colourless oligomers (a dimer, a tetramer and a pentamer that all consist of corner- or edge-shared VO₄ tetrahedra) and the orange decavanadates and *cis*-dioxotetraquavanadium(V) ions with vanadium in distorted octahedral VO₆ environments.⁵¹V NMR has been a valuable tool in these studies because there is a good correlation between linewidths and chemical shifts and coordination geometry. It has been stressed¹ that no “trigonal bipyramidal” vanadium(V) species have been observed by means of NMR.

A complex formed by vanadate(V) and uridine (acetate buffer, pH 6.8) was observed⁵ to have a ⁵¹V NMR resonance at –523 ppm relative to VOCl₃. A review of the

debate on the composition of this complex and of a series of –523 ppm complexes of vanadate and the common nucleosides has been published recently, and it was shown that the stoichiometry is V₂L₂, where V = vanadate(V) and L = nucleoside.⁶

It has been proposed⁷ that the complexes V₂L₂ consist of two apex-shared VO₅ trigonal bipyramids forming a O₄V(μ-O)VO₄ species. The bidentate nucleosides are supposed to act as chelate ligands, i.e. they form cyclic esters such that each ligand binds to one vanadium atom. In view of the lack of evidence for trigonal bipyramidal structures in solutions of oxovanadates, we have turned to new types of measurements in an attempt to find experimental support for the V₂O₆ structure.

Large biomolecules may require buffers in order not to be denatured; however, the large surplus of buffers which have been used in experiments like those described here may ruin the results through undetected interference. Since vanadate is known to form complexes with organic ligands carrying hydroxy, carboxy, phosphate and amine groups, we find it appropriate to warn against the indiscriminate use of buffers. Our experiences show that vanadate–nucleoside systems are sufficiently self-buffered to maintain a constant pH.

Experimental

Materials. All chemicals (Aldrich, Fisher, Ferak) were reagent grade and were used without further purification.

*To whom correspondence should be addressed.

⁵¹V–NMR spectroscopy. The spectra were recorded at 132 MHz on a Bruker AM-500 spectrometer (11.7 T). They were typically obtained using a 150 ppm window, a 90° pulse angle and an acquisition time of about 0.1 s with no relaxation delay. An exponential line-broadening of 10 Hz was applied to the FID prior to Fourier transformation. Chemical shifts are reported relative to the external standard reference VOCl₃ at 0 ppm. In practice we used an external reference solution containing diethanolamine and vanadate at pH 7.8, since the complex formed here has its chemical shift conveniently situated at –488 ppm.⁸ The concentrations of vanadate species were obtained through integration and were reproducible to within a few percent.

A stock solution of sodium orthovanadate (0.25 M) was prepared by dissolving vanadium pentoxide in sodium hydroxide. The samples were prepared by mixing vanadate (final concentrations from 5×10^{-4} M to 3×10^{-2} M), the nucleoside (from 0 to 2.5×10^{-2} M), imidazole (0.10 M), hydrochloric acid (to pH 7.00) and KCl (to ionic strength 0.40 M). The nucleosides studied were adenosine, guanosine, uridine and cytidine.

Samples containing the deoxynucleosides deoxyadenosine or deoxyguanosine were prepared in an analogous way to the samples described above; however, for solutions with deoxyguanidine, thymidine or deoxycytidine, acetone was added to give a mass fraction 50% in the final solutions.

¹³C NMR spectroscopy. The spectra were recorded at 132 MHz on a Bruker AM-500 spectrometer. The acquisition parameters included a spectral window of 200 ppm, a 90° pulse angle and a relaxation delay of 3.5 s. Gated decoupling was used to minimize sample heating during acquisition, and the spectra were recorded using a pulse sequence described in the automated programs in the Bruker software packet (invgate.AUR). An exponential line-broadening of 2 Hz was applied to the FID prior to Fourier transformation. The chemical shifts are reported relative to the external standard DSS at 0 ppm.

Since the spectra were recorded using decoupling, a possible ionic character of the samples interfered with the acquisition of the spectra; therefore, neither KCl nor imidazole/HCl was allowed in the solutions. A mass fraction of about 20% deuterium oxide was used as an internal lock. ⁵¹V NMR spectra were recorded to determine the concentration of free vanadate and vanadate–nucleoside complex before the ¹³C NMR spectra were recorded. The nucleosides studied were adenosine, guanosine and uridine.

CD and MCD spectroscopy. The circular dichroism was measured with an instrument based on a Cary 14 double monochromator, a MgF₂ polarizer (Karl Lambrecht), a CaF₂ modulator (Hinds International) and a lock-in amplifier (SR 510, Stanford Research Systems) used with a PC-AT microcomputer. Magnetically induced circular dichroism was measured using a superconducting magnet

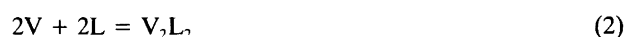
with a magnetic flux density of 4 T (Spectromag III, Oxford Instruments).

CD spectra were measured on aqueous 0.40 M KCl solutions containing 0.10 M imidazole/HCl buffer at pH 7.0 and vanadate with adenosine, guanosine, cytidine, uridine, deoxyadenosine, deoxyguanosine, deoxycytidine and thymidine, respectively. CD spectra were also measured of 0.45 M KCl solutions without imidazole at pH 7.0 of mixtures of vanadate with the nucleosides. MCD was measured on similarly composed imidazole-free solutions of vanadate with adenosine and cytidine, respectively.

Results

The stoichiometries of the vanadate–nucleoside complexes were obtained from the ⁵¹V NMR experiments. The equilibrium between monomer vanadate (V) and adenosine (L) in a constant salt medium (0.4 M KCl) buffered with imidazole/HCl at pH 7.0 was studied. The reaction gives rise to two complexes with ⁵¹V NMR resonances at –480 and –520 ppm, respectively. Further resonances are assigned⁹ to monomer vanadate (–555 ppm, V), and to dimer (–568 ppm, T₂), tetramer (–572 ppm, T₄) and pentamer vanadate (–580 ppm, T₅).

Spectra of two series of buffered solutions were measured: series (a), with 10^{-3} M vanadate and adenosine varying from 0 to 6×10^{-3} M, and series (b), with 10^{-2} M vanadate and adenosine varying from 0 to 6×10^{-2} M. The data obtained are consistent with the simple model of reactions (1) and (2) of only two complexes being formed. The formation constants are given by eqns. (3) and (4), where [V] is given by eqn. (5).



$$K_1 = [VL]/[V][L] \quad (3)$$

$$K_2 = [V_2L_2]/[V]^2[L]^2 \quad (4)$$

$$[V] = [HVO_4^{2-}] + [H_2VO_4^-] \quad (5)$$

Fig. 1 shows for series (a) plots of the concentrations of both the –480 and –520 ppm complexes as functions of the product $[V]^2[L]^2$. Only the –520 ppm complex shows a linear correlation; therefore, this complex is a dimer with respect to both vanadate and adenosine. The constant K_2 was determined from the slope.

Fig. 2 shows for series (a) plots of the concentrations of both the –480 and 520 ppm complexes as functions of the product $[V][L]$. Only the –480 ppm complex shows a linear correlation; therefore, this complex has the composition VL. The constant K_1 was determined from the slope.

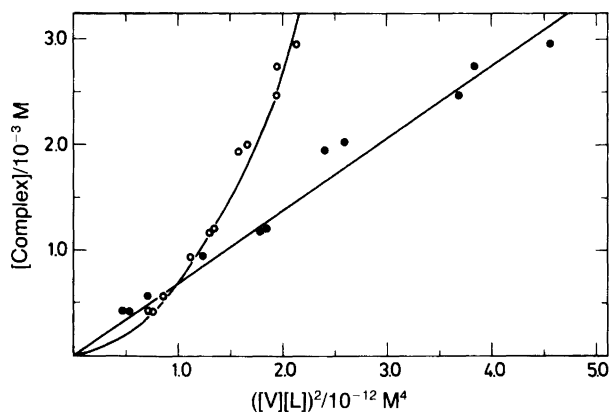


Fig. 1. The measured concentrations of the species having ^{51}V resonance at -523 ppm (●) and -480 ppm (○) are related to the product $[\text{V}]^2[\text{L}]^2/10^{-12} \text{ M}^4$. Only the -523 ppm species shows a linear relationship.

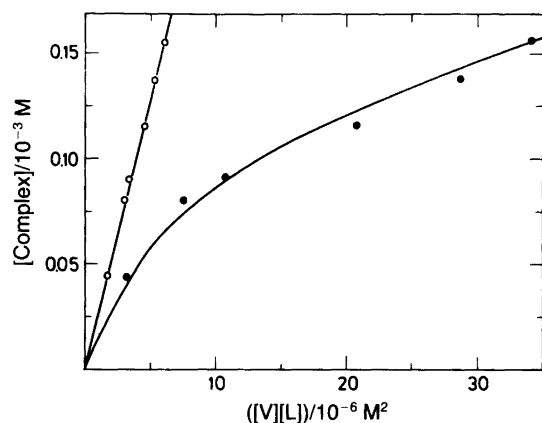


Fig. 2. The measured concentrations of the species having ^{51}V resonance at -523 ppm (●) and -480 ppm (○) are related to the product $[\text{V}][\text{L}]/10^{-6} \text{ M}^2$. Only the -480 ppm species shows a linear relationship.

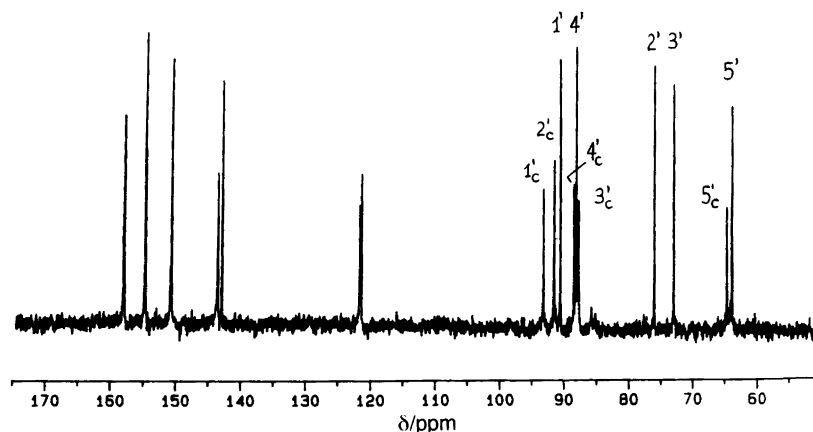


Fig. 3. The ^{13}C NMR spectrum at 126 MHz of 25 mM adenosine, 15 mM vanadate, 20 wt % D_2O at pH 7.0. The signals from the carbons of the ribose ring are indicated, those with an index c are due to the V_2L_2 complex.

Table 1. Formation constants of coordination compounds formed from mononuclear vanadate at pH 7.0 using imidazole as buffer and maintaining a constant ionic strength of 0.4 M with KCl.

Nucleoside	$K_2/10^6 \text{ M}^{-3}$	K_1/M^{-1}
Adenosine	66	26
Guanosine	23	12
Uridine	52	26
Cytidine	15	18

The same results have been obtained for series (b) above.

Similar analyses were performed with the vanadate complexes formed with guanosine, uridine and cytidine. In all cases two resonances were found, and the stoichiometry was determined to be 2:2 and 1:1 for complexes with resonance around -520 and -480 ppm, respectively.

The formation constants are recorded in Table 1. We estimate that the constants for the V_2L_2 complexes are accurate within 30% and those for VL within 50%.

It is noted that in all cases the resonance at -480 ppm was absent when imidazole was not used as a buffer.

In the case of vanadate–deoxynucleoside complexes, ^{51}V NMR spectra of solutions of $5.0 \times 10^{-3} \text{ M}$ deoxyadenosine or $1.0 \times 10^{-3} \text{ M}$ vanadate and $5.0 \times 10^{-3} \text{ M}$ deoxyguanosine showed only resonances corresponding to V, T_2 , T_4 and T_5 . However, by addition of acetone it was possible to increase the solubility of the deoxynucleosides and obtain solutions of 0.010 M vanadate and 0.160 M deoxyuridine, 0.005 M vanadate and 0.310 M thymidine or 0.080 M deoxycytidine. Under such conditions weak resonances at -563 ppm appeared. Assuming the formation of an ester VL, a formation constant of about 0.4 M^{-1} was estimated for each of the three esters.

^{13}C NMR spectra were recorded under conditions (absence of buffer) where only the 2:2 vanadate–nucleoside complexes are formed. Solutions of the nucleosides with

Table 2. ^{13}C NMR resonances for ribose carbons in free adenosine and for the ligand in the V_2L_2 (see also Fig. 3 and Experimental section for details).

Atom	Adenosine, L	V_2L_2
C1'	91.0	93.7
C2'	76.4	92.0
C3'	73.4	88.2
C4'	88.5	88.9
C5'	64.3	65.1

and without vanadate were measured. It is convenient that solutions containing known concentrations of both the 2:2 vanadate–nucleoside complex and the free nucleoside al-

low a direct comparison of the resonances of the two species. A spectrum of adenosine and vanadate is given in Fig. 3 and the chemical shifts of the carbons in the ribose moiety are given in Table 2. Similar results were obtained with the nucleosides uridine and guanosine.

All mixtures of vanadate and the nucleosides in 0.40 M KCl solutions with 0.10 M imidazole/HCl buffer at pH 7.0 showed circular dichroism in the region 300–400 nm. Representative spectra are given in Figs. 4 (adenosine) and 5 (uridine). The composition of the solutions as calculated from the added amounts of vanadate and nucleoside and the equilibrium constants from Table 1 are shown in Tables 3 and 4. The spectra in Fig. 5 show points with $\Delta A = 0$ for all observed mixtures of vanadate and uridine.

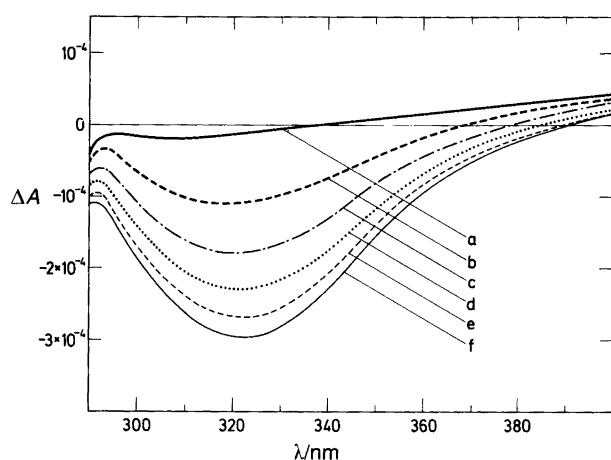


Fig. 4. Circular dichroism of adenosine–vanadate solutions. The composition of solutions (a)–(f) is given in Table 2. Light path 1.00 cm.

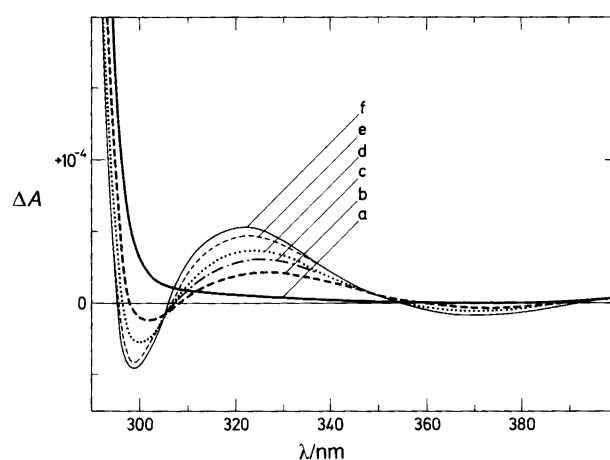


Fig. 5. Circular dichroism of uridine–vanadate solutions. The composition of solutions (a)–(f) is given in Table 3. Light path 1.00 cm.

Table 3. Composition of adenosine–vanadate solutions (L–V) (cf. Fig. 4).^a

	$c(\text{L})/\text{mM}$	$c(\text{V})/\text{mM}$	$[\text{L}]/10^{-5} \text{ M}$	$[\text{V}]/10^{-5} \text{ M}$	$[\text{VL}]/10^{-5} \text{ M}$	$[\text{V}_2\text{L}_2]/10^{-5} \text{ M}$
a	10.04	0	1004	0	0	0
b	9.80	0.201	969	8.7	2.2	4.6
c	9.56	0.393	931	13.9	3.4	11.0
d	9.34	0.576	895	18.2	4.2	17.5
e	9.13	0.750	860	22.2	5.0	24.0
f	8.92	0.917	826	25.9	5.6	30.1

^aAll solutions had $c(\text{KCl}) = 0.40 \text{ M}$, $c(\text{imidazole}) = 0.10 \text{ M}$ and pH adjusted to 7.0 with hydrochloric acid.

Table 4. Composition of uridine–vanadate solutions (L–V) (cf. Fig. 5).^a

	$c(\text{L})/\text{mM}$	$c(\text{V})/\text{mM}$	$[\text{L}]/10^{-5} \text{ M}$	$[\text{V}]/10^{-5} \text{ M}$	$[\text{VL}]/10^{-5} \text{ M}$	$[\text{V}_2\text{L}_2]/10^{-5} \text{ M}$	$[\text{V}_2\text{L}_2]/[\text{VL}]$
a	10.04	0	1004	0	0	0	
b	9.78	0.203	967	9.4	2.4	4.3	1.8
c	9.55	0.396	931	15.2	3.7	10.4	2.8
d	9.32	0.580	894	20.0	4.7	16.7	3.6
e	9.11	0.756	860	24.4	5.5	22.9	4.2
f	8.91	0.924	827	29.0	6.1	28.9	4.7

^aAll solutions had $c(\text{KCl}) = 0.40 \text{ M}$, $c(\text{imidazole}) = 0.10 \text{ M}$ and pH adjusted 7.0 with hydrochloric acid.

Solutions of vanadate and the nucleosides in 0.45 M KCl at pH 7.0 but without imidazole showed no CD in the spectral region 300–400 nm.

Solutions of vanadate and the deoxynucleosides in 0.40 M KCl with 0.10 M imidazole/HCl at pH 7.0 showed no CD in the 300–400 nm region.

Magnetically induced circular dichroism was measured for the 2:2 complexes with vanadate and adenosine as a purine nucleoside and with cytidine as an example of a pyrimidine nucleoside. In both spectra ΔA decreased monotonically from 300 to 400 nm. This signal is dominated by the MCD of the tail from the MCD of the uncoordinated vanadate ($V + T_2 + T_4 + T_5$) of tetrahedral symmetry.^{10,11} However, using the formation constants (Table 1) and assuming that $\Delta\epsilon/B$ has the same value for both the 2:2 complexes, we reach approximate MCD curves for these complexes with a maximum near 320 nm and with the ratio $\Delta\epsilon/\epsilon B = (6 \times 10^4 \text{ T})^{-1}$.

Discussion

The V_2O_{10} structure. It will be shown firstly, that all available experiments indicate that complexes with the composition V_2L_2 are formed spontaneously in aqueous solutions (pH ca. 7) from protonated forms of tetraoxovanadate(V), V, and the nucleosides, L; secondly, the complexes consist of two edge-shared VO_6 octahedra forming a $O_4V(\mu-O)_2VO_4$ skeleton with the nucleosides bridging the two vanadium centres through the 2' and 3' oxygens on the ribose ring, such that the four oxygen atoms outside the V_2O_6 plane are connected pairwise by the nucleosides so that the nucleosides are bidentate ligands but are not chelate, i.e. not bound to the same metal ion; and thirdly that there is some evidence in the literature that this kind of complexation is found for other vicinal diols.

^{51}V NMR spectra. These have been published for vanadate and uridine in an acetate buffer at pH 6.8,⁵ for vanadate and uridine in the buffer HEPES [*N*-(2-hydroxyethyl)piperazine-*N'*-ethanesulphonic acid] at pH 7.5,⁷ for vanadate and inosine in the buffer tris [tris(hydroxymethyl)methaneamine] at pH 7.22 and without any buffer at pH 7.15,¹² and for vanadate and inosine in HEPES as well as in tris at pH 7.00.⁶ Together with the results of this work, the general pattern⁹ of resonances at pH 7 is as follows. Firstly, for tetraoxovanadates, there is a monomer at -555 ppm (pH-dependent), and the following oligomers (corner- or edge-shared VO_4 -tetrahedra): a dimer from -568 to -570 ppm, a tetramer from -572 to -575 ppm and a pentamer at -580 ppm. Secondly, there is a rather broad resonance from -520 to -523 ppm; quite frequently this band has a shoulder on the up-field side, and in the case of vanadate and uridine monophosphate it has been resolved into a sum of lorentzian lines.¹³ Thirdly, further resonances have been observed only with the buffers tris⁶ (-510 and -542 ppm) or imidazole (-480 ppm). In the case of vanadate and tris it has been shown that with tris in high concen-

trations the signals¹⁴ are found at different positions, and in low concentrations no signals⁸ have been observed. We conclude that the buffers tris and imidazole form complexes with vanadate and the nucleosides, whereas acetate and HEPES apparently are inactive (innocent) in this respect. (*Vide infra* on the composition of VL-complexes.)

The stoichiometry of the complexes at -523 ppm has been subject to some debate^{6,9} but it was shown⁷ as being V_2L_2 for V = vanadate and L = uridine. This composition has now been established (Ref. 6 and this paper) for the -523 ppm complexes of all the common nucleosides, and the values of the formation constants K_2 (Table 1) agree well with those of Ref. 6.

With regard to the geometry of the V_2L_2 complexes, we shall see in the remainder of this section that the available ^{51}V NMR information fits in with the proposed V_2O_{10} structure.

Octahedral VO_6 as found in the ion $VO_2(ox)_2^{3-}$ has a chemical shift of -529 ppm;¹⁵ we note that no examples of genuine VO_5 -structures in solution are mentioned in Ref. 15. The ion $H_3V_{10}O_{28}^{3-}$ has recently been investigated.¹⁶ Raman spectroscopy and vapour-pressure osmometry have shown that the ion does not dissociate in aqueous solution. The structure can be thought of as composed of three types of V_2O_{10} structures, and the two outside the V_6 plane have a chemical shift at -524 ppm. In the ion dihydrogen phosphotetradecavanadate, $H_2PV_{14}O_{42}^{7-}$, the 12 vanadium atoms with octahedral coordination have a chemical shift at -523 ppm, whereas the two vanadium atoms in trigonal bipyramidal environments have -575 ppm.²⁴

Various vicinal diols have been studied.¹⁷ The spectra of vanadate with ethylene glycol was measured in tris-HCl buffer at pH 7.5. A strong signal at -522 ppm was assigned to a V_2L_2 species, and no interference from the buffer was observed. Similarly, 2,3-butanediol (probably a mixture of the racemate and the meso form) gave rise to one signal at -525 ppm due to species of composition V_2L_2 . Finally, *rac*-1,2-propanediol under similar conditions gave at least two signals centred around -526 ppm. These NMR data were shown¹⁷ to be consistent with the V_2L_2 complexes having the bipyramidal V_2O_9 structure, with bidentate and chelate diols. However, the data are also consistent with the proposed V_2O_{10} structure with bidentate, bridging ligands. Indeed, with this model the main difference between the six different isomeric V_2L_2 species (including two pairs of enantiomers) is the methyl groups being adjacent to the same vanadium atom or to different vanadium atoms.

^{51}V NMR spectra¹⁴ of vanadate in the presence of *cis*-1,2-cyclohexanediol with HEPES or tris at pH 7.5 showed that tris is not innocent here. Therefore HEPES was used in a study¹⁸ of vanadate with *cis*-1,2-cyclohexanediol and (racemic) *trans*-1,2-cyclohexanediol at pH 7.5. The spectra were very similar, particularly in the region near -520 ppm, where two peaks were observed, one being a shoulder on the up-field side of the other. The signals are due to V_2L_2

isomers, and were explained in terms of the V_2O_9 structure with chelate diols. However, the occurrence of two isomers is equally well explained in terms of the V_2O_{10} skeleton with non-chelate, bridging ligands, since in the case of the *cis*-diol the cyclohexane parts are *cis/trans* with respect to the V_2O_6 plane, and the complexes of the *trans*-diol are racemic/meso isomers.

There is no indication from ^{51}V NMR spectra that the deoxynucleosides form complexes of the type V_2L_2 .

^{13}C NMR spectra. The examples given in Fig. 3 and Table 2 show that the 2',3'-diols in the ribose moiety are engaged in the bonding between vanadate and nucleoside, and only one complex species is formed. A similar result has been obtained¹³ for vanadate and uridine monophosphate at pH 6.8. However, if the concentrations of vanadate and nucleoside are increased 100-fold, then the resonances from the ribose carbons are doubled;⁹ this indicates that under such conditions, two complexes are formed. We note that with the proposed V_2O_{10} structure two stereoisomers are predicted, whereas the V_2O_9 structure predicts three isomers.

Circular dichroism. In the spectral range 300–400 nm CD is associated with charge-transfer transitions from the HOMO's of the ligator atoms to the empty *d*-orbitals of vanadium.¹⁹ In this connection it may be noted that at wavelengths below 300 nm very intense absorptions and CD spectra due to the internal nucleoside transitions are observed; however, we shall only be concerned here with the electronic transitions at wavelengths longer than 300 nm. The fact that CD is observed only for solutions containing vanadate, nucleoside and imidazole shows that complexes VL are optically active, but complexes V_2L_2 are not. This conclusion is substantially supported by the fact that in some spectra points with $\Delta A = 0$ can be found which are independent of the ratio $[V_2L_2]/[VL]$ (Fig. 5 and Table 4).

These complexes have the CD of transitions involving the metal orbitals induced by inherently chiral ligands. A condition for this to happen is that the ligand is bidentate and chelate²⁰ (*in casu* that the ligand forms a cyclic ester to one metal centre).

We can now draw the following three conclusions. (i) Complexes of type VL formed in imidazole buffer with a ^{51}V NMR resonance around -480 ppm show optical activity in the charge-transfer transitions and have the nucleoside bound as a chelate. (ii) Complexes of vanadate and the deoxynucleosides (where the ligand cannot be chelate) are indeed optically inactive in the charge-transfer region. (iii) Complexes of the type V_2L_2 , which are formed independently of the buffer, have nucleosides bound as bidentate ligands through the 2',3'-oxygens of the ribose moieties; however, the ligands are *not* chelate, meaning that each ligand must be bound to two vanadium atoms.

Magnetic circular dichroism. MCD of the first spin-allowed electronic transition in tetrahedrally coordinated com-

plexes of transition-metals with a d^0 electron configuration is a negative *A*-term.¹¹ For the colourless VO_4^{3-} ion the characteristic ratio of extremal spectral values^{10,11} is $\Delta\epsilon(282\text{ nm})/\epsilon(270\text{ nm})B = +(7500\text{ T})^{-1}$, and the MCD decreases monotonical towards longer wavelengths. Similar values are found for colourless oligomer vanadates with tetrahedral coordination.¹⁰

Absorption and MCD spectra of $[(C_4H_9)_4N]_3H_3[V_{10}O_{28}]$ are well known.²¹ In this orange compound all vanadium atoms are to a good approximation octahedrally surrounded by oxygen, and the MCD (B-type) is characterized by the value $\Delta\epsilon(315\text{ nm})/\epsilon(350\text{ nm})B = +(2 \times 10^4\text{ T})^{-1}$. A similar value²¹ has been observed for $[(C_4H_9)_4N]_4H_5[PV_{14}O_{42}]$. In this brown compound 12 vanadium atoms are octahedrally coordinated and two are five-coordinate with trigonal bipyramidal geometry. The intensity (per vanadium atom) of the absorption is increased (by a factor of ca. 1.3 relative to the decavanadate) but the position is unchanged.

In general^{10,22} the change in coordination from VO_4 to VO_6 is accompanied by a red shift of the first (low-energy) absorption band. Despite the opinion expressed in a recent paper,²³ we know of no examples of transition-metal complexes with no *d*-electrons where a red shift is associated with a decrease in coordination number.¹⁹

The absorption (low intensity, ca. 350 nm; not reported here) and the MCD of vanadate and the common nucleosides in aqueous solution at pH 7 show that the coordination number of oxygen around vanadate in the compounds of composition V_2L_2 is higher than four. Our analysis of the MCD does not rule out the possibility that vanadium is five-coordinate. On the other hand, the low value of $\Delta\epsilon/\epsilon B$ may indicate that an approximate centre of inversion (O_h symmetry) is the cause of this low MCD intensity.

Complexes of composition VL. These have not been observed unless a buffer was used. In particular, we note that the ^{13}C NMR of aqueous solutions of vanadate and the nucleosides at pH 7 but without buffer did not show any evidence of more than one complex, which through ^{51}V NMR was identified as the V_2L_2 species.

In a recent study⁶ of complex formation between vanadate and the common nucleosides in aqueous KCl (1 M) at pH 7, HEPES was used as buffer. In one experiment (with inosine) KCl was omitted but the buffer was not. The formation of V_2L_2 complexes was observed, with formation constants as found in the present paper. However, complexes with the stoichiometry VL were also observed having a ^{51}V NMR resonance identical to that of monomer vanadate(V). As an explanation of this discrepancy, we suggest that HEPES is not an innocent buffer and that complexes of vanadate, nucleoside and HEPES have been formed.

Conclusions

In aqueous KCl solutions at pH 7 tetraoxovanadate(V) forms complexes of 2:2 stoichiometry with each of the common nucleosides. Such complexes do not exhibit circular dichroism associated with absorption in the spectral region of the charge-transfer transitions. The explanation of this observation combined with the ^{13}C NMR data is that each of the two nucleoside ligands connects different vanadium atoms through the 2',3'-oxygens on the ribose ring. The data in their entirety are in accord with a molecular structure composed of two edge-sharing VO_6 octahedra forming a $\text{O}_4\text{V}(\mu\text{-O})_2\text{VO}_4$ skeleton, with the nucleosides connecting the oxygens outside the V_2O_6 plane. Such species have not yet been isolated in the solid state, but the experimental evidence found in the literature for vanadate complexes with other vicinal diols adapts well to this structure.

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