A New Trinuclear Oxovanadium(V) Complex with DMPP Ligands – Synthesis and Structural Characterization in the Solid State and in Aqueous Solution

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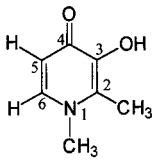
A new trinuclear oxovanadium(V) complex with the anionic dmpp ligand (Hdmpp = 3-hydroxy-1,2-dimethyl-4-pyridinone), $[V_3O_6(dmpp)_3(H_2O)](H_2O)_2$, was isolated from the reaction of Hdmpp, KOH and sodium metavanadate at pH 4.5. The solid state structure of the $[V_3O_6(H_2O)(dmpp)_3](H_2O)_2$ complex, investigated by X-ray diffraction methods, was found to contain a cyclic trinuclear metal cluster. This complex crystallises in the monoclinic system: $P2_1/n$, a = 9.5324(7) Å, b = 16.4107(11) Å and c = 18.0638(12) Å, β = 91.1010(10)°, V = 2825.3(3) Å^3, Z = 4 and $R_1(wR_2)$ = 0.0704 (0.2025). Two of the vanadium atoms (V1 and V3) are six-coordinated, with distorted octahedral geometries, and the other one (V2) is five-coordinated with a distorted square pyramidal geometry. The cyclic V_3O_4 framework has one oxygen atom bridging two vanadium atoms in two V–O–V groups, V1–O4–V2 and V2–O5–V3, and two oxygens bridging the V1–V3 atoms, V1–O6–V3 and V1–O12–V3. IR data confirm the crystallographic results, showing the characteristic V=O band in the 973–935 cm^{-1} frequency range. This compound has three bands corresponding to V=O stretching, indicative of different chemical environments around the vanadium atoms in the solid state. The ES mass spectrum in aqueous solution displays an intense peak corresponding to the $[V_3O_6(dmpp)_3(H_2O)+2H^+]^{2+}$ fragment. ^{51}V and ^1H NMR spectroscopy were used to study this complex in aqueous solution. The dissolution of the crystalline $[V_3O_6(dmpp)_3(H_2O)](H_2O)_2$ compound in water, under aerobic conditions at pH 4.2, gave one intense broad signal at δ = –490 in the ^{51}V NMR spectrum, which is attributed to a major species present in solution. The observation of only one ^{51}V NMR signal, instead of the three expected from the different chemical environments of each vanadium atom present in the solid, is consistent with a fast (in the NMR timescale) dynamic equilibrium equalising their environments. This involves a fast exchange between O8, O10 and O12 as mono- or bifunctional oxygen atoms, as well as the H_2O molecule, which acts in another fast equilibrium coordinating the vanadium atom that has a dmpp ligand with one bifunctional oxygen atom. The trinuclear oxovanadium(V) complex is relatively stable in water in the pH range 2.5–5.0. However, dissociation of the complex occurs at higher pH, leading to various hydrolysis products, which include mononuclear complex species with 1:1 and 1:2 metal-to-ligand stoichiometries, and monomeric and oligomeric species of free vanadium(V).

Introduction

Vanadium inorganic salts like sodium metavanadate and vanadyl sulfate have demonstrated insulino-mimetic effects in a variety of tissues.[1] However, due to their poor absorption, high doses of these salts are required and toxicity occurs. For this reason, they are not used in the treatment of diabetes, although some recent clinical studies were carried out with oral administration of these compounds in very low concentrations.[2–4] The insulino-mimetic properties exhibited by vanadium (V^{IV} and V^V) have led to an intensive search for a vanadium complex to be used as an effective oral substitute of insulin. The complex bis-maltolato-oxovanadium ^{IV} (BMOV)[5,6] seems to be, at present, one of the most promising compounds in this field. The ligand 3-hydroxy-1,2-dimethyl-4-pyridinone (Hdmpp) (see chemical structure in Scheme 1), currently used in the treatment of iron-overload under the name deferiprone,[7] forms a V^{IV} complex which, although not as soluble as BMOV, allows the optimization of the lipophylic-hydrophylic balance by changing the substituent group at the N atom, thus controlling its absorption into the cells.[8,9]

Oxovanadium complexes are attracting interest due to their biological relevance[10,11] as insulino-mimetics, as models of the vanadium coordination modes in biological systems (haloperoxidases, amavadine, tunichrome),[12] due



Scheme 1

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to their effects on the activity of several enzymes,[13,14] and also due to their application as catalysts.[15]

Vanadium(IV) and vanadium(V) coordinate polydentate ligands, with N and O donor atoms in most cases, resulting in complexes of different stoichiometries and structures depending on ligand design, pH, metal-to-ligand ratio and total vanadium concentration.[16–18] The vanadium(V) species present in solution have been largely identified by potentiometric[19,20] and combined potentiometric/^{51}V NMR spectroscopic[21] studies, and vanadium(IV) species have been studied by EPR spectroscopy as well.[22] The solid state structures of vanadium complexes have been determined by using X-ray crystallography[23] and EXAFS.[8] Vanadium(V), in particular, has stereochemically flexible coordination geometries ranging from tetrahedral and octahedral to trigonal pyramidal and pentagonal bipyramidal, which are thermodynamically plausible.[24] It can also form mono- and polynuclear[25] oxovanadium complexes.

The biological properties of vanadium complexes are strongly dependent on their solution structures. The examination of the structural and chemical selectivity of complexes with di- or polyfunctional ligands[26–34] is an important contribution to understanding the modes of action of vanadium in biological systems.[35,36] Thus, the study of their behaviour in an aqueous medium at different pH values is necessary to obtain the structures of the different species, as well as their thermodynamic and kinetic stabilities.[37] In this work, we report the synthesis and structural characterisation, both in the solid state and in aqueous solution, of a new oxovanadium(V) complex containing three anionic dmpp ligands and a cyclic trinuclear cluster.

Results and Discussion

Synthesis of the Complex $[V_3O_6(dmpp)_3(H_2O)](H_2O)_2$

3-Hydroxy-1,2-dimethyl-4-pyridinone (0.174 g, 1.25 mmol) in 5 mL of water was added to KOH (0.07 g, 1.25 mmol) in 5 mL of water and sodium metavanadate (0.169 g, 1.25 mmol)in 5 mL of water. The pH was raised to 4.5 with a solution 2 M HCl. The black crystals, which came out of solution, were isolated by filtration and dried under *vacuum*. The yield was 0.160 g (48% based on V). Anal. Calcd. (found) for $C_{21}H_{30}O_{15}N_3V_3$: calcd. C 35.2 (34.9), H 4.2 (4.1), N 5.9 (5.8). ES mass spectrum, $[V_3O_6(C_7H_9O_2N)_3(H_2O) + 2\,H^+]^{2+}$: $m/z = 342$.

IR Spectroscopic Data

The IR spectrum of the complex $[V_3O_6(dmpp)_3(H_2O)](H_2O)_2$ obtained in KBr pellets showed the characteristic V=O band in the frequency range 973–935 cm^{-1}. This compound exhibits three bands corresponding to V=O stretching, indicative of a different chemical environment around the vanadium atoms in the solid state. In addition, the V–O–V stretching modes were observed at about 640–510 cm^{-1}, in agreement with those reported in the literature.[38] The spectrum exhibits a set of four bands in the 1625–1450 cm^{-1} range, characteristic of pyridinones.[39]

IR spectroscopy provides information on the ligands chelated to the vanadium atoms but is less informative about the nuclearity of the complex.

Crystallographic Results

The X-ray crystal structure with an atomic numbering scheme for the crystalline $[V_3O_6(dmpp)_3(H_2O)](H_2O)_2$ complex is shown in Figure 1 and the bond lengths and angles are in Table 2. It contains a cyclic trinuclear oxovanadium(V) complex, $[V_3O_6(dmpp)_3(H_2O)]$, with three anionic dmpp ligands, three oxo groups, three oxygen atom bridges and one H_2O molecule. The other two H_2O molecules are included in the asymmetric unit. Oxygen atom bridges link the three vanadium atoms and each one is coordinated to one oxo group. Two vanadium atoms (V1 and V3) are six-coordinated, exhibiting a distorted octahedral geometry and one (V2) is five-coordinated with a distorted square pyramidal geometry, with the vanadium atom (V2) 0.4197 Å from the basal plane defined by O4, O5, O9 and O10 (Figure 2). In addition to the oxo group, V1 is chelated by three dmpp oxygen atoms (O7, O8 and O12, this one acting as a bridging atom between V3 and V1), V2 and V3 are chelated by two dmpp oxygen atoms (V2 by O9 and O10, V3 by O11 and O12). The V3 atom is also coordinated to one H_2O molecule.

All the vanadium atoms have a strong V=O bond, and the values for the V1–O1, V2–O2 and V3–O3 distances are compatible with those found in other similar structures.[23] This complex has a dmpp oxygen atom (O12 in V3) that is *trans* and five dmpp oxygen atoms (O7 and O8 in V1, O9 and O10 in V2, and O11 in V3) that are *cis* relative to the strong V=O bond in each vanadium atom.[25,40–42] The dmpp oxygen atoms belonging to the enolic groups are deprotonated (O7, O9 and O11). The V3–O12 bond is longer than the V–O bonds to the other

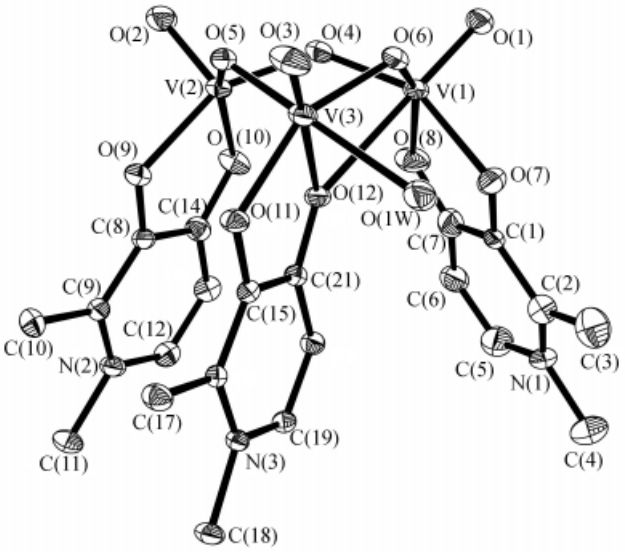

Figure 1. X-ray crystal structure of the complex $[V_3O_6(dmpp)_3(H_2O)]$ showing the atomic numbering scheme. Hydrogen atoms have been omitted for simplicity. The ORTEP plot is at the 30% probability level.

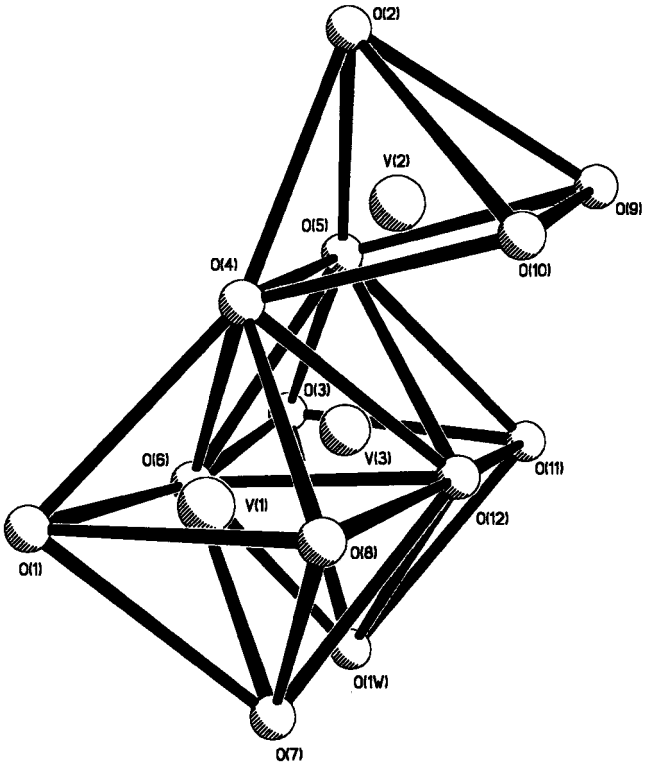

Figure 2. Coordination polyhedron in the crystal structure of the vanadium cluster in trimeric species $[V_3O_6(dmpp)_3(H_2O)]$.

ketonic groups, V1−O8 and V2−O10, (V1−O8 [2.008(4) Å], V2−O10 [2.004(4) Å] and V3−O12 [2.204(4) Å]. In addition, all these V−O bond lengths are longer than those to the enolate groups (V1−O7 [1.980(4) Å], V2−O9 [1.962(3) Å] and V3−O11 [1.909(3) Å].[43] These bond length values are all in the range of the bond lengths reported in the literature for other known polynuclear vanadium(V) complexes.[25,40−43]

The trinuclear complex contains the cyclic V_3O_4 framework.[23] This framework exhibits only one oxygen bridging two vanadium atoms in two V−O−V groups, V1−O4−V2 and V2−O5−V3, and two oxygens bridging the V1−V3 atoms, the oxo bridge V1−O6−V3 and the formal ketonic oxygen atom O12 of one dmpp. From the X-ray results one could not unambiguously distinguish between a keto-O12 and an enolate-O12 structure for this bifunctional binding group, as the C−O bond lengths to the formal keto and enolate oxygens in each C−O−V−O−C cycle are almost the same (eg. C21−O12 [1.309(5) Å], C15−O11 [1.336(5) Å], for the V3 cycle). It is possible that the π electronic cloud is delocalized among all the atoms that form each C−O−V−O−C cycle, giving an intermediate character to all the formal ketonic and enolic oxygen atoms of each dmpp. As expected, the doubly bridging dmpp oxygen atom (O12) gives V−O bond lengths [2.204(3), 2.450(3) Å] longer than the V−O distance for the bridging oxygen atoms (O6) [1.794(3), 1.857(3) Å]. The average value of the V−O−V bond lengths (V1−O4−V2, V2−O5−V3 and V3−O6−V1) is 1.82(3) Å, which is similar to that obtained for other polynuclear vanadium compounds.[44−46]

The three V−O−V bond angles, in the cyclic V_3O_4 framework, involving single bridging oxygen atoms are very similar (V1−O4−V2 = 125.61(18)°, V2−O5−V3 = 120.39(17)° and V1−O6−V3 = 119.22(17)°]. The V−O−V bond angle in the V1−O12−V3 fragment [84.98(10)°] is quite different.

Figure 3 shows an upper view of the complex along an axis perpendicular to the pseudo-plane defined by the three vanadium atoms, illustrating how the complex has lost C_{3v} symmetry. The anionic dmpp ligand bound to V3 has rotated relative to the equivalent positions of the other two ligands in the cluster, becoming almost parallel to the dmpp ligand at V2 and perpendicular to the one at V1. Its O12 oxygen binds to V1, and V3 binds a water molecule in a *cis* position relative to V3=O3, pointing outwards. V2 keeps the five coordination, as an extra water molecule *trans* to V2=O2 would be sterically hindered by the opposing dmpp ring. The methyl group at V3 points outwards, and those at V1 and V2 point t*rans* to one another.

Solution Studies

The behaviour of the crystalline compound $[V_3O_6(dmpp)_3(H_2O)](H_2O)_2$ in aqueous solution and in the presence of oxygen was investigated using ^{51}V and ^{1}H NMR and EPR spectroscopy. A freshly prepared 2 mM aqueous solution of the crystalline complex, with pH = 4.2, was grey in colour. Immediately after its preparation, this solution gave no EPR signal (data not shown), showing that all three the vanadium atoms present in the crystalline structure were in the +5 oxidation state. The ^{51}V NMR spectrum of this solution (Figure 4b) shows one single

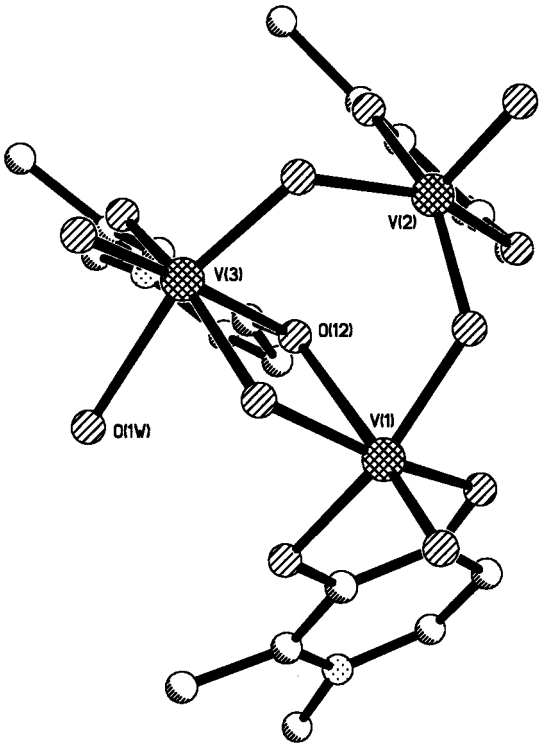

Figure 3. Upper view of the complex $[V_3O_6(dmpp)_3(H_2O)]$.

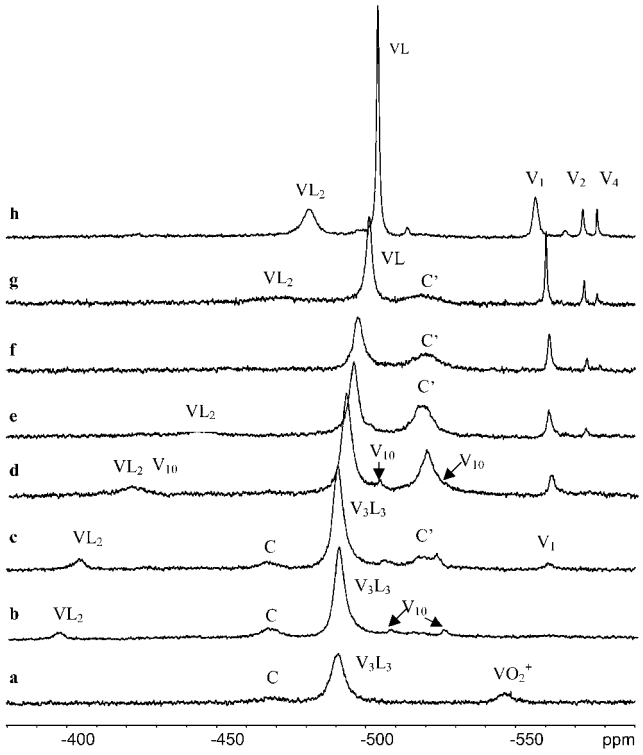

Figure 4. ^{51}V NMR spectra, at 22.0 ± 0.5 °C, of a freshly prepared 2 mM aqueous solution of the crystalline complex $[V_3O_6(dmpp)_3(H_2O)](H_2O)_2$ under aerobic conditions at a) pH = 2.8; b) pH = 4.2; c) pH = 4.7; d) pH = 5.6; e) pH = 6.1; f) pH = 6.4; g) pH = 6.9; h) pH = 7.8.

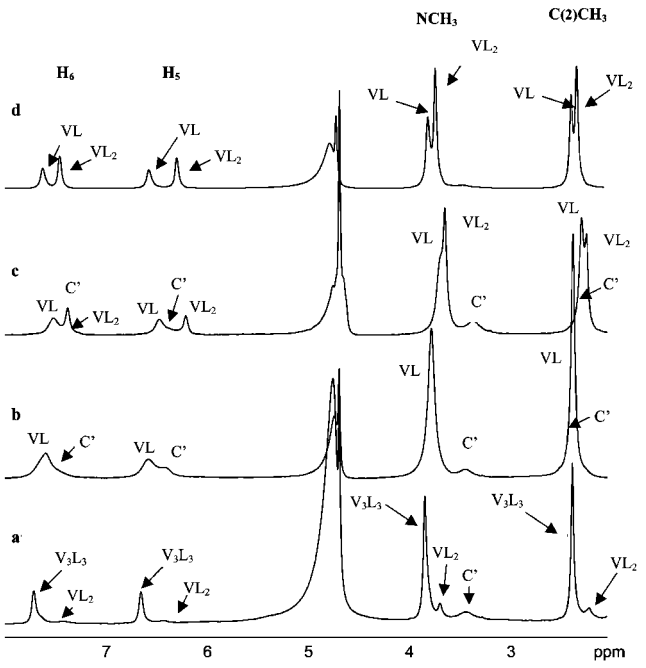

Figure 5. ^{1}H NMR spectra, at 22.0 ± 0.5 °C, of a freshly prepared 2 mM D_2O solution of the crystalline complex $[V_3O_6(dmpp)_3(H_2O)](H_2O)_2$ under aerobic conditions at a) pH = 3.6; b) pH = 5.3; c) pH = 6.8; d) pH = 8.4.

broad signal at δ = −490 (line width of 525 Hz), assigned to the cyclic trimer $[V_3O_6(dmpp)_3(H_2O)]$ (V_3L_3) as the major species present in solution. The observation of only one ^{51}V NMR signal, instead of the three expected from the different chemical environments of each V-dmpp unit present in the crystal structure, reflects the increased effective symmetry acquired by the cyclic trimer species in solution. The equivalence of its three monomer units should result from the presence of a dynamic equilibrium in solution in fast exchange conditions (in the NMR timescale). In this equilibrium, the dmpp ligand oxygen atoms bridging between two vanadium atoms of the cluster (O12 bridge between V1 and V3, O8 between V1 and V2 and O10 between V2 and V3) change their coordination between mono- and bifunctional when the compound is dissolved in water. On the other hand, the H_2O molecule acts in another fast equilibrium, coordinating the vanadium atom that has a dmpp ligand with one bifunctional oxygen atom. Thus, the presence of the polydentate oxygen donor anionic ligand (dmpp) allows the oxygen atoms to act as monofunctional or bifunctional donors.[23] The ES spectrum of the trimer in aqueous solution at pH = 4.3 exhibits an intense peak *m*/*z* = 342, corresponding to the cationic complex $[V_3O_6(dmpp)_3(H_2O)+2H^+]^{2+}$.

Additional studies of the trinuclear oxovanadium(V) complex in solution were carried out in order to investigate its stability as a function of pH, using ^{51}V (Figure 4) and ^{1}H (Figure 5) NMR spectroscopy. These spectra were compared with ^{51}V and ^{1}H NMR spectra of aqueous solutions of vanadate and dmpp at different pH and metal-to-ligand ratios (see illustrative examples at Figure 6). Figure 4 shows ^{51}V NMR spectra of a 2 mM aqueous solution of the crystalline complex at different pH values. These spectra were assigned by comparison with the ^{51}V NMR spectra of the vanadate/ dmpp aqueous solutions at the same pH values, as well as on the basis of literature data.[9,21c,27] The spectral features indicate that in the pH range 2.8−5.3 the major species present in solution is the trimer $[V_3O_6(dmpp)_3(H_2O)]$, corresponding to the dominant ^{51}V NMR peak, with very small shift changes with pH, from δ = −488 (pH 2.8−3.6) to δ = −490 (pH 3.9−5.3). Some low intensity signals are also present in the ^{51}V NMR spectra in this pH range (see Figure 4a−c), which correspond to very minor species in solution. Some of these are free vanadium(V) species: dioxovanadium(V) cation (VO_2^+), δ = −543 [21c] at pH 2.8, the monovanadate (V_1), δ = −560[21c] at pH 4.7, and two of the three decavanadate (V_{10}) signals, δ = −506 and δ = −523 [27] at pH 4.2 and 4.7. At pH < 3.9, the cyclic trimer is practically the only complex present in solution (besides the species C). However, above this pH value, a small signal of the mononuclear 1:2 complex (VL_2) is also seen at high frequency (δ = −396 and δ = −405 at pH 4.2 and 4.7, respectively). According to previous studies, this complex occurs at this pH range predominantly in its monoprotonated form $[VO_2H(dmpp)_2]$.[9] At these pH values a small resonance (VL) of the mononuclear 1:1 $[VO_2(dmpp)(H_2O)_2]$ complex, if present, is hidden by the signal of the trinuclear cationic complex.[9] Its ^{51}V shift at pH 2.8−4.7 is δ = −491, and at pH 5.3 is δ = −494 (see Figure 6a). A broad signal at δ = −468 is also

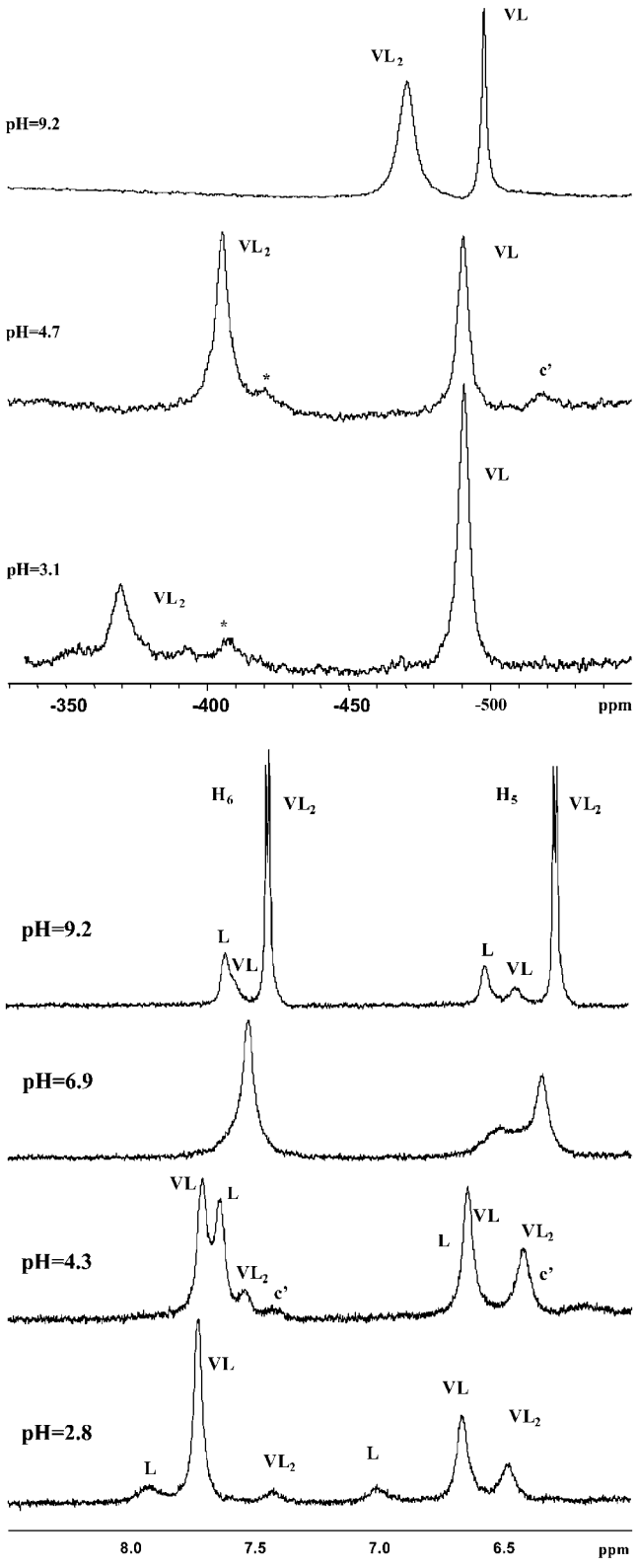

Figure 6. ^{51}V (top) and ^{1}H (bottom) NMR spectra, at 22.0 ± 0.5 °C, of a 3 mM: 6 mM vanadate-dmpp solution at different pH values.

seen between pH 2.8 and 5.3, corresponding to another complex labelled as C, and a new signal at δ = −519 appears at pH > 3.9, corresponding to another complex, labelled as C′. Both complexes C and C′ were not characterised.

Above pH 5.3 (Figure 4d−h), decomposition of the trinuclear oxovanadium(V) complex takes place, which is replaced by the two mononuclear complexes VL and VL_2, whose ^{51}V NMR resonances are shifted to lower frequency when the pH increases, as they become deprotonated.[9] From pH 5.6 to 7.8, the ^{51}V shifts of VL and VL_2 change from δ = −493 and δ = −424 to δ = −504 and δ = −480, respectively. The signal of complex C disappears at pH 5.6 and the signal at δ = −519, corresponding to complex C′, reaches a maximum intensity at pH ≈ 6 and disappears at pH 7.8. The signals of decavanadate stay very small (Figure 4d,e) and new resonances corresponding to other free vanadium(V) oligomeric species also appear: the divanadate V_2 (δ = −572) and tetravanadate V_4 (δ = −578) (Figure 4f−h). Above pH 7 the colour of the solution changes to yellow and at pH 7.8 only the signals corresponding to the mono- (δ = −556), di- (δ = −572) and tetravanadate (δ = −577) species, and those assigned to the two mononuclear complexes VL (δ = −504) and VL_2 (δ = −480) are observed. According to previous studies, these complexes occur at this pH in their deprotonated forms $[VO_2(dmpp)(H_2O)(OH)]^-$ and $[VO_2(dmpp)_2]^-$, respectively.[9]

^{51}V NMR spectra of aqueous solutions of vanadate and dmpp were obtained as a function of pH in the 2.3 to 9.2 range, at 3 mM vanadate concentrations and at 1:1, 1:2 and 1:5 metal-to-ligand ratios. Figure 6 (top) shows a few illustrative examples at the 1:2 ratio. VL and VL_2 predominate over the entire pH and metal-to-ligand ranges studied, and their shifts change with pH in accordance with what was found in the trimer solution. In the pH range 2.3−6.9, their intensities are much higher in the spectra of the vanadate-dmpp mixtures than in those of the trimer. Complex C′ (at δ = −519) is also present between pH 4.0 and 6.4, but complex C (at δ = −468) is not, as it is only present in vanadate/dmpp mixtures with excess vanadate (data not shown). Although this observation points to the possibility that C may be a dimeric complex, the characterisation of complexes C and C′, as well as of the signals at δ = −420 to −405 and at δ = −350, observed at acid pH [see Figure 6 (top)], and the detailed interpretation of the pH dependence of the ^{51}V shifts of the VL and VL_2 complexes in terms of the species previously observed by potentiometry[9] will be the subject of a future publication.

^{1}H NMR spectra were also obtained from a 2 mM D_2O solution of the crystalline complex at different pH values (Figure 5). These spectra were assigned by comparison with those of solutions of vanadate and dmpp, at 3 mM vanadate concentrations and at 1:1 and 1:2 metal-to-ligand ratios, obtained as a function of pH [see Figure 6 (bottom), for some representative spectra] and by comparison of the intensities of the ^{51}V and ^{1}H signals of the different complexes. The spectrum at pH 3.6 (Figure 5a) shows four intense signals (H_6 at δ = 7.72, H_5 at δ = 6.66, N−CH_3 at δ = 3.86 and C(2)−CH_3 at δ = 2.40, data not shown) from the trinuclear complex V_3L_3, the major species in solution. The symmetry

of the spectrum again reflects the equivalence of the three monomer units in solution. These signals are in slow exchange on the NMR timescale with the very weak signals from the complexes VL_2 and C. The signals of the V_3L_3 complex are shifted to higher frequencies relative to the respective signals of the free Hdmpp ligand at pH 7 (H_6 at $\delta = 7.53$, H_5 at $\delta = 6.41$, $N-CH_3$ at $\delta = 3.68$ and $C(2)-CH_3$ at $\delta = 2.30$, data not shown), due to complexation. However, the trimer has very similar shifts to the 1:1 monomer VL [see Figure 6 (bottom)], possibly because the coordination of the V^V ion is similar in both compounds and the relative orientations of the pyridinone rings in the trimer, near the edge of their respective dipolar shift cones, lead to negligible intramolecular ring current effects. At pH 5.3, the signals broaden and the spectrum (Figure 5b) is quite similar to that of a 1:1 vanadate/ dmpp solution, except for the relative intensities of the complexes present, in agreement with dissociation of the complex and the presence of the mononuclear complexes resulting from its hydrolysis, with relative intensities $VL > C' >> VL_2$. At pH 6.8 (Figure 5c) the signals of the complexes present, $VL > VL_2 >> C'$, start to sharpen and at pH 8.4 (Figure 5d) only the VL and VL_2 complexes are present. The protons of the VL_2 complex are shifted to lower frequency relative to those of the VL complex, due to the mutual effect of the pyridinone ring currents in an octahedral complex. Comparison with the ^1H NMR spectra of free Hdmpp solutions at the same pH values showed that no free ligand could be detected at any pH studied. The results from ^1H NMR spectroscopy are, therefore, in good agreement with those obtained by ^{51}V NMR spectroscopy.

Figure 6 (bottom) shows the aromatic region of the ^1H NMR spectra of a 3 mM:6 mM vanadate-dmpp solution at some of the pH values between 2.8 and 9.2. At this metal-to-ligand ratio of 1:2, it was found that, while at pH 2 to 2.8 the relative concentrations of the species are $VL >> VL_2 \approx L$, at pH 4 to 5 VL decreases and L increases, so that $VL \approx L > VL_2 >> C'$. Above pH 5, L and VL decrease and VL_2 becomes the dominant species. The complex C′ is only present in the range of pH 4.0 to 5.6, and complex C is not detected at low pH. For a 1:1 metal-to-ligand ratio (3 mM: 3 mM vanadate-dmpp, data not shown), VL is the dominant species at pH 2 (92%), with $VL >> VL_2$, and VL slowly decreases its percentage up to pH 5 (80% VL), with $VL >> VL_2 > C'$. Above pH 5, VL continues to decrease, VL_2 increases more sharply and C′ disappears. The detailed interpretation of the pH dependence of the distribution of the VL and VL_2 species by NMR spectroscopy and potentiometry[9] will be presented in a future publication.

Thus, the differences observed in the ^{51}V and ^1H NMR spectra of a V_3L_3 solution and a vanadate-dmpp 1:1 solution in the pH range of 2.5−5.0, where the trimer is stable in solution, can be summarised as follows: slightly different ^{51}V shifts of V_3L_3 and VL, sharper proton resonances of VL at the same pH values, smaller relative intensity of VL_2 and larger relative intensity of C′ in the trimer solution, and presence of species C at low pH in the trimer solution, which is not present in the vanadate-dmpp 1:1 solution.

The stability of the solution structure of the trinuclear complex at pH 4.2 with time was also studied by ^{51}V NMR spectroscopy. The spectra obtained (see Supporting Information, Figure 1S) show that there are no changes in the signal corresponding to the $[V_3O_6(dmpp)_3(H_2O)]$ complex (see Figure 4b), even 5 days after the dissolution of the crystalline compound in water and in the presence of oxygen, which indicates that the structure of the trinuclear oxovanadium(V) complex is stable in solution at this pH. The low intensity signals also present decrease their intensity somewhat.

Thus, we can conclude that the major species resulting from the dissolution of the crystalline compound in water, under aerobic conditions and at pH 2.5−5.0, is a trinuclear oxovanadium(V) cationic complex, which is relatively stable in this pH range. However, when the pH increases above 5.0, dissociation of the complex takes place with the appearance in solution of various hydrolysis products, including free V^V oligomeric species and the mononuclear V^V species with metal to ligand ratios of 1:1 and 1:2.

Experimental Section

Reagents: Sodium metavanadate, $NaVO_3$, and the ligand 3-hydroxy-1,2-dimethyl-4-pyridinone (Hdmpp) were purchased from Sigma and ACROS Organics, respectively, and used without further purification. D_2O (99.9 atom% D), DCl and NaOD were obtained from Cambridge Isotope Laboratories. All the experiments were carried out in aqueous solution and under aerobic conditions.

Methods: IR Spectroscopy: Vibrational spectra were obtained in potassium bromide pellets on a Bruker Vector 22 MIR spectrometer. − Elemental Analysis: Analyses for C, H and N were performed using a Carlo Erba EA 1108 elemental analyser. − Mass Spectrometry: A mass spectrum was obtained in aqueous solution on a LC/NS Mass Spectrometer Finnigan Navigator with ES(+) ion mode and direct injection. − NMR Spectroscopy: ^{51}V and ^1H NMR spectra were recorded on a Varian Unity-500 Spectrometer operating at 131.404 MHz and 499.824 MHz, respectively, using a 5 mm broad band probe, at 22.0±0.5 °C. The pH of the D_2O solutions was adjusted with DCl and CO_2-free NaOD using a Crison MicropH 2002 pH-meter with an Ingold 405-M5 combined electrode. ^{51}V NMR chemical shifts were externally referenced to a $VOCl_3$ solution at $\delta = 0$. The ^{51}V NMR acquisition parameters were: 33 KHz spectral width, 25 μs pulse width, 0.5 s acquisition time and 10 Hz line broadening. A pre-saturation pulse sequence was used for ^1H NMR spectra to eliminate the residual water signal. − EPR Spectroscopy: The EPR spectrum of the freshly prepared aqueous solution of the crystalline compound $[V_3O_6(dmpp)_3(H_2O)](H_2O)_2$ was obtained at room temperature on a Bruker ESP300E spectrometer, operating at 9.77 GHz. The frequency was calibrated with diphenylpycryl-hydrazyl (dpph) and the magnetic field using Mn^{2+} in MgO.

X-ray Crystallography: Selected crystallographic data are shown in Table 1. Three dimensional X-ray data were collected at low temperature (173 K) in the range $1.68 < 2\theta < 28.32°$ on a Siemens SMART 1000 CCD diffractometer by the Ω-scan method. Complex scattering factors were taken from the program package

Table 1. Crystallographic data for the complex $[V_3O_6(Hdmpp)_3(H_2O)](H_2O)_2$

Empirical formula	$C_{21}H_{30}N_3O_{15}V_3$
Formula mass	717.30
Crystal system	monoclinic
Space group	$P2_1/n$
a (Å)	9.5324(7)
b (Å)	16.4107(11)
c (Å)	18.0638(12)
α (deg)	90
β (deg)	91.1010(10)
γ (deg)	90
V (Å^3)	2825.3(3)
Z	4
T (K)	193
λ (Å)	0.71073
$D_{calcd.}$ (gcm^{-3})	1.686
$F(000)$	1464
No. of reflns collected	19434
No. of indep reflns.	6989
R_1 [a]	0.0704
wR_2(all data)	0.2025
Largest diff peak and hole (e·Å^{-3})	2.04, −0.887

[a] $R_1 = \Sigma||F_0| - |F_c||/\Sigma[|F_0|$, $wR_2 = \{\Sigma[w(||F_0|^2 - |F_c|^2|)^2]/\Sigma[w(F_0^4)]\}^{1/2}$.

SHELXTL.[48] The structure was solved by direct methods and refined by using full-matrix least-squares methods on F^2. The data were processed and corrected for Lorentz and polarisation effects and for absorption (semi-empirical method). The non-hydrogen atoms were refined with anisotropic thermal parameters in all cases. The hydrogen atoms of the H_2O molecules were refined with isotropic thermal parameters. The other hydrogen atoms were refined to carbon, which were placed in idealised positions and refined by using a riding mode. A final difference Fourier map showed no residual density outside −0.887 to +2.041; the highest peaks in this case suggested the presence of a residual density in the middle of one pyridinone group but its assignment was not possible. Selected bond lengths and bond angles appear in Table 2.

Crystallographic data (excluding structure factors) for the structure reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication no. CCDC-160778. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [Fax: (internat.) +44−1223/336−033; E-mail: deposit@ccdc.cam.ac.uk].

Supporting Information: ^{51}V NMR spectra (131.404 MHz, 22.0 ± 0.5 °C) of $[V_3O_6(dmpp)_3(H_2O)](H_2O)_2$ in aqueous solution (2 mM, pH = 4.2) in the presence of oxygen, as a function of time (10 minutes to 5 days) (Figure 1S).

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Table 2. Selected bond lengths (Å) and angles (deg) in $[V_3O_6(Hdmpp)_3(H_2O)](H_2O)_2$ with estimated standard deviation in parentheses

Bond lengths			
V(1)−O(1)	1.599(3)	V(3)−O(3)	1.609(4)
V(1)−O(6)	1.794(3)	V(3)−O(5)	1.813(3)
V(1)−O(4)	1.817(3)	V(3)−O(6)	1.857(3)
V(1)−O(7)	1.980(4)	V(3)−O(11)	1.909(3)
V(1)−O(8)	2.008(4)	V(3)−O(12)	2.204(3)
V(1)−O(12)	2.450(3)	V(3)−O(1 W)	2.180(4)
V(2)−O(2)	1.613(4)	O(7)−C(1)	1.433(7)
V(2)−O(4)	1.795(3)	O(8)−C(7)	1.259(7)
V(2)−O(5)	1.824(4)	O(9)−C(8)	1.325(5)
V(2)−O(9)	1.962(3)	O(10)−C(14)	1.310(6)
V(2)−O(10)	2.004(4)	O(11)−C(15)	1.336(5)
		O(12)−C(21)	1.309(5)
Bond angles			
O(1)−V(1)−O(6)	103.03(17)	O(4)−V(2)−O(9)	153.53(15)
O(1)−V(1)−O(4)	103.18(17)	O(5)−V(2)−O(9)	88.57(14)
O(6)−V(1)−O(4)	93.88(15)	O(2)−V(2)−O(10)	102.7(2)
O(1)−V(1)−O(7)	102.01(17)	O(4)−V(2)−O(10)	86.67(15)
O(6)−V(1)−O(7)	90.56(17)	O(5)−V(2)−O(10)	152.79(15)
O(4)−V(1)−O(7)	152.69(16)	O(9)−V(2)−O(10)	79.36(14)
O(1)−V(1)−O(8)	100.36(18)	O(3)−V(3)−O(5)	102.16(19)
O(6)−V(1)−O(8)	156.20(15)	O(3)−V(3)−O(6)	105.34(17)
O(4)−V(1)−O(8)	84.93(17)	O(5)−V(3)−O(6)	92.03(14)
O(7)−V(1)−O(8)	80.33(19)	O(3)−V(3)−O(11)	95.80(16)
O(1)−V(1)−O(12)	1767.19(17)	O(5)−V(3)−O(11)	100.14(14)
O(6)−V(1)−O(12)	74.47(12)	O(6)−V(3)−O(11)	152.82(14)
O(4)−V(1)−O(12)	78.40(12)	O(3)−V(3)−O(12)	172.09(16)
O(7)−V(1)−O(12)	76.89(13)	O(5)−V(3)−O(12)	83.65(14)
O(8)−V(1)−O(12)	82.04(13)	O(6)−V(3)−O(12)	79.86(13)
O(2)−V(2)−O(4)	103.26(18)	O(11)−V(3)−O(12)	77.54(12)
O(2)−V(2)−O(5)	103.6(2)	V(2)−O(4)−V(1)	125.61(18)
O(4)−V(2)−O(5)	94.01(15)	V(3)−O(5)−V(2)	120.39(17)
O(2)−V(2)−O(9)	101.69(17)	V(1)−O(6)−V(3)	119.22(17)
		V(3)−O(12)−V(1)	84.98(10)

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