A Decavandate Sandwiched by Diprotonated Cryptands-222: Model for the Vanadate-Ionophore Interaction

Mahin Farahbakhsh, Hauke Schmidt, and Dieter Rehder*

Institut für Anorganische und Angewandte Chemie, Universität Hamburg,
D-20146 Hamburg, Germany
Fax: (internat.) +494041232893
E-mail: rehder@chemie.uni-hamburg.de

Received February 21, 1997

Keywords: Vanadium / Cryptands / Ionophors / Phosphatases / Decavanadate

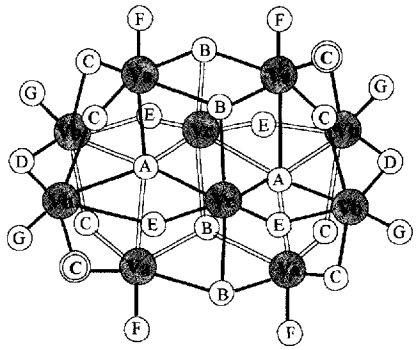
Treatment of a C222-vanadyl-AMP complex (C222 = cryptand-222, AMP = adenosine monosphosphate) with Me_2NH in the presence of air yielded centrosymmetric dihydrogendecavanadate $H_2V_{10}O_{28}^{4-}$, sandwiched by two diprotonated C222 molecules. An X-ray crystal-structure analysis was performed of this compound with the overall composition $[C222(H^+)_2]_2[H_2V_{10}O_{28}] \cdot 2^1/_2\ H_2O$. Protonation sites in the anion are μ_2-oxygen atoms linking two different vanadium centres. Protonation sites at the cryptand are the nitrogen and/or oxygen atoms of one of the $-[CH_2]_2O[CH_2]_2O[CH_2]_2-$ bridges. The relevance of the compound for the stabilisation and transport of the kinase and phosphatase inhibitor decavanadate by biogenic ionophores is addressed.

Introduction

Condensed forms of vanadate – polyoxovanadates – have recently attracted interest in the context of oxidation catalysis[1] and their potential in medical applications[2]. The role of decavanadate, particularly as an inhibitor for phosphate-metabolising enzymes, has been documented in several instances[3].

Decavanadate $V_{10}O_{28}^{6-}$ forms in mildly acidic solutions and can accept up to three protons. The unprotonated, mono-, di- and triprotonated forms have been identified and studied in solution by ^{51}V- and ^{17}O-NMR spectroscopy[4,5]. These studies, in conjunction with X-ray structure analyses of the di-[6–11] and triprotonated forms[5] with various counterions have revealed the protonation sites. In decavanadate, there are three distinguishable vanadium centres, noted as **Va**, **Vb** and **Vc** in Figure 1, all of which are in a distorted octahedral array, differentiated by the binding modes of the oxo groups: **Va** = $VO(\mu_2\text{-}O)_2(\mu_3\text{-}O)_3(\mu_6\text{-}O)$, **Vb** = $VO(\mu_2\text{-}O)_4(\mu_6\text{-}O)$, and **Vc** = $V(\mu_2\text{-}O)_2(\mu_3\text{-}O)_2(\mu_6\text{-}O)_2$. There are seven different oxo groups, denoted **A**–**G** in Figure 1, falling into four categories, namely terminal (**F** and **G**), μ_2 (**C**, **D** and **E**), μ_3 (**B**) and μ_6 (**A**). In agreement with calculations directed towards the basicity of the oxo ligands[12], the oxygen atoms **C** (μ_2, linking a **Va** and **Vb** centre) and **B** (μ_3, linking two **Va** with a **Vc** centre) have been identified as protonation sites. Diprotonation may occur at two centrosymmetrically related **C** sites[7,8,10], at two **B** sites[6] or at a **C** plus a **B** site[8]. The counterion might have a contributory effect[8]. While the protonation at **C** sites appears to be the more common case, the site **B** seems to come in where the protons are involved in dimer formation by hydrogen bonds, as in $[NH_3(C_6H_{13})]_4[H_2V_{10}O_{28}]$[6]. This is also the case for the triprotonated anion of $[PPh_4]_3[H_3V_{10}O_{28}]$, where two **C** sites and one **B** site carry protons[5].

Figure 1. Schematic drawing of the centrosymmetric dihydrogendecavandate(4–), showing the three vanadium sites (**Va**, **Vb**, **Vc**; shaded circles) and the seven oxo sites (**A** to **G**; open circles); the doubly circled category „**C**" oxo group is the protonation site



Results and Discussion

Vanadate forms defined complexes with nucleosides, which have been characterised in solution[13,14] as well as, more recently, in the solid state[15]. Studies with nucleotides have also been carried out sporadically[16], but detailed information on the species formed is not yet available, contrasting with the more comprehensively investigated V^{IV} (vanadyl) nucleotide system[17]. We have recently started an investigation of the vanadium/adenosine monophosphate (5′-AMP) system. To overcome solubility problems with the disodium salt $AMPNa_2$, which was used in order to open access to AMP-vanadium complexes by salt metathesis, the sodium-complexing cryptand C222 (4,7,13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane) has been em-

  0009–2940/97/0808–1123 $ 17.50+.50/0

ployed. Reaction of $AMPNa_2$, dissolved in ethanol/C222, with $[VOCl_2(thf)_2]$ led to a blue complex compound of the overall composition [(C222)VO(AMP)]. Further reaction in methylamine with exposure to air resulted in concomitant hydrolysis of the vanadyl phosphate bond(s), oxydation of V^{IV} to V^V and condensation, and led to the unprecedented formation of dihydrogendecavanadate sandwiched by two diprotonated cryptands, viz. $[C222(H^+)_2]_2[H_2V_{10}O_{28}]$.

The compound crystallises in the triclinic space group $P\bar{1}$. The structure is given in Figure 2; for selected bond lengths and bond angles see Table 1. The centrosymmetric anion exhibits the structural features commonly observed for decavanadates[5–11,18], i.e. ten distorted octahedra are edge-linked via bridging oxygen atoms (cf. Figure 1). The distortion mainly concerns the V–O bonds *trans* to the terminal, doubly bonded oxo groups. In order to detect the protonation sites, we have employed the valence bond orders $\Sigma s = (d/R_0)^{-N}$ as introduced by Brown[19] and applied previously to oxovanadates[20]. While d is the experimental V–O bond length, R_0 and N are listed constants which have values of 1.79 and −5.1, respectively, for oxygen bound to vanadium. The summation is carried out over all bonds a specific oxygen atom is involved in; ideally $\Sigma s = 2$. Bond orders, listed in Table 2, range from 1.71 to 2.03 for all but O9. Σs for O9, a doubly bridging type-C oxygen atom, is 1.19; hence O9 is obliged to carry a proton. O9 and its symmetry-related counterpart are therefore the protonation sites. The relatively low Σs of 1.71 to 1.83 for several of the other oxygen atoms might be indicative of their participation in an extended hydrogen-bonding network between the anion $[H_2V_{10}O_{28}]^{4-}$ and the two cations $[C222(H^+)_2]^{2+}$; cf., however, the dicussion below.

Two diprotonated C222 sandwich the anion. Surprisingly, examples for protonated C222 are scarce. The Cambridge file contains three entries for $[C222(H^+)_2]^{2+}$ (with an ytterbate[21] and chloride[22], respectively, as counterions). The oxygen atoms are oriented inwards towards the cryptand cavity in a symmetrical manner, the protons form an inter-cavity hydrogen-bonding network[22]. In $[C222(H^+)_2]_2[H_2V_{10}O_{28}]$, the cryptand cations interact with the anion in an asymmetric manner, using only part of the hetero atoms, which fall within three sets: Two of the oxygen atoms of each cryptand, the "outside" oxygen atoms O40 and O41, are not involved in any binding; the oxygen atoms O50 and O51 participate in hydrogen bonding; the oxygen atoms O30 and O31, and the two nitrogen atoms exhibit

Table 1. Selected bond lengths [Å] and angles [°] for the dihydrogendecavanadate anion[a]

		V1 (Va)	V2 (Va)	V3 (Vb)	V4 (Vc)	V5 (Vb)
O1	(F)	1.589(7)				
O2	(F)		1.611(7)			
O3	(G)			1.597(8)		
O4	(B)	1.932(7)	2.064(7)		1.896(7)	
O5	(G)					159.7(7)
O6	(B)	[2.015(7)]	[1.916(7)]		1.963(6)	
O7	(C)	1.812(7)		1.857(7)		
O8	(C)	1.890(7)				[1.772(7)]
O9[c]	(C)		1.954(7)			2.007(7)
O10	(C)		1.747(7)	[1.950(7)]		
O11	(D)			1.792(7)		[1.861(7)]
O12	(E)			2.024(7)	1.689(7)	
O13	(E)				1.687(7)	2.011(7)
O14	(A)	[2.308(6)]	2.226(6)	[2.323(6)]	2.106(6)[b]	2.305(6)

V1–O4–V2	(Va–B–Va)	97.9(3)
V1–O4–V4	(Va–B–Vc)	108.8(3)
V1–O7–V3	(Va–C–Vb)	114.7(4)
V2–O9–V5[c]	(Va–C–Vb)	112.9(3)
V3–O11–V5	(Vb–D–Vb)	115.1(4)
V3–O12–V4	(Vb–E–Vc)	111.6(4)
V1–O14–V2	(Va–A–Va)	170.0(3)
V1–O14–V3	(Va–A–Vb)	83.7(2)
V1–O14–V4	(Va–A–Vc)	89.6(2)
V2–O14–V4	(Va–A–Vc)	95.3(2)
V3–O14–V4	(Vb–A–Vc)	87.9(2)
V3–O14–V5	(Vb–A–Vb)	83.6(2)

[a] For the notations of the categories of vanadium and oxygen centres see Figure 1; distances in square brackets correspond to symmetry-generated oxygen atoms. – [b] And [2.106(6) Å]. – [c] Protonated oxygen atom.

Figure 2. SCHAKAL plot of $[C222(H^+)_2]_2[H_2V_{10}O_{28}] \cdot 2\ H_2O$

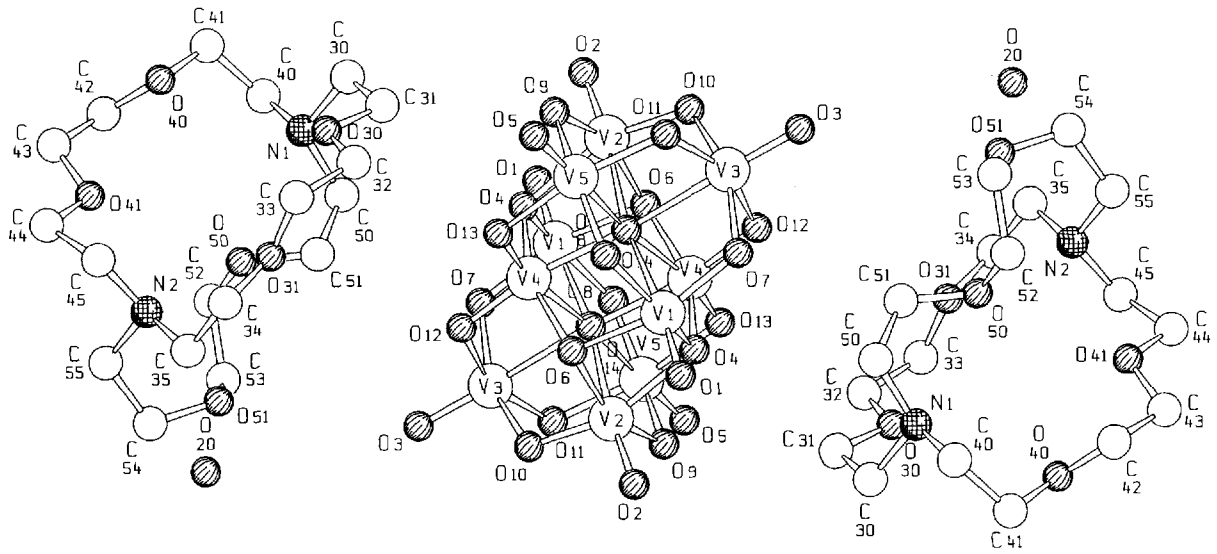


Table 2. Valence bond orders Σs of the oxo groups in dihydrogendecavanadate(4−)[a]

O1	(**F**) tl	1.83	O8	(**C**) μ_2	1.83
O2	(**F**) tl	1.71	O9	(**C**) μ_2	1.19
O3	(**G**) tl	1.79	O10	(**C**) μ_2	1.78
O4	(**B**) μ_3	1.91	O11	(**D**) μ_2	1.81
O5	(**G**) tl	1.80	O12	(**E**) μ_2	1.87
O6	(**B**) μ_3	1.88	O13	(**E**) μ_2	1.91
O7	(**C**) μ_2	1.77	O14	(**A**) μ_6	2.03

[a] The numbering of the oxygen atoms corresponds to that given in Figure 2, categories (capital letters in parentheses) to Figure 1; the bonding mode is also indicated: tl = terminal; the standard deviation for Σs amounts to of 0.05.

Table 3. Interatomic distances [Å] in $[C222(H^+)_2]$[a] and between H_2O (O20) and $[H_2V_{10}O_{28}]^{4-}$

N1-O30	2.90	N2-O31	2.85	O30-O31	2.87
N1-O40	2.87	N2-O41	2.82	O40-O41	2.79
N1-O50	2.80	N2-O51	2.87	O41-O50	3.24
N1-O50*	3.09	N2-O30	4.84	O50-O51	2.72
N1-O31	4.72	N2-O40	5.08	O20-O1	3.00
N1-O41	4.43	N2-O50	3.00	O20-O2	3.15
N1-O51	5.46	N2-O50*	4.32	O20-O11	2.83

[a] An asterisk relates to 25% of an alternate conformation of the cryptand.

bond orders less than those one would expect from involvement in simple hydrogen bonding. Rather, these atoms are the cation protonation sites. Since we could not locate these protons from the Fourier difference map, we suggest that the two protons are delocalised over O30, O31, N1 and N2, giving rise, together with the hydrogen-bonding net within the cryptand, to the conformation of the cryptand as depicted in Figure 2, somewhat distorted (see below for a more detailed discussion) from the ideal *endo-endo* conformation that prevails in the free cryptand-222[23], its compounds with alkaline[24a] and alkaline earth cations[24b], or in $[C222(H^+)_2]Cl_2$[22]. In $[C222(H^+)_2]_2[H_2V_{10}O_{28}]$, the interatomic N•••N distance amounts to 5.32 Å, which is definitely less than in the empty C222 (6.87 Å)[23] and in $[C222(H^+)_2]Cl_2$ associated with $[(H_2O)_3ScCl_3]$ (6.34 Å)[22a], but compares with $[C222(H^+)_2]Cl_2$ associated with $[H_3O^+]_2Cl_2$ (5.71 Å)[22b]. A similar distance, 5.75 Å, has also been noted for $[C222(K^+)]$[24a].

The "asymmetric" association of the cryptands to decavanadate is reflected in conformational deviations from those that are normally found: While in $[C222(H^+)_2]Cl_2$ the six oxygen atoms directed towards the cavity give rise to torsion angles between 54 and 58° (N−C−C−O)[22b] and from 56 to 64° (O−C−C−O[22a]; compare the average value of 177° for the empty C222[23]), torsion angles in $[C222(H^+)_2]_2[H_2V_{10}O_{28}]$ vary from 41 to 79° (N−C−C−O) and 38 to 66° (O−C−C−O). The conformational asymmetry is also reflected in the non-bonding N•••O distances (Table 3).

Hydrogen-bonding interaction between dihydrogendecavanadate and $C222(H^+)_2$, if any, is very weak, as documented by the interatomic cation-anion distances. The closest contacts, 3.8 Å, are those between O50/O3(**G**),O7(**C**), O12(**E**) and O30/O13(**E**). $[C222(H^+)_2]_2[H_2V_{10}O_{28}]$ further contains two water molecules (O20) of crystallisation associated with the anion, linked by a hydrogen bond to doubly bridging O11(**D**) and, to a lesser extent, to the terminal **F**-type oxygen atoms O1 and O2 (Table 3). A further water of crystallisation, hydrogen-bonded to O50, has been localized in 25% of the compound represented by a 25% disorder of O50, C51 and C52 (not shown in Figure 2).

Physiological Aspects and Conclusion

$[C222(H^+)_2]_2[H_2V_{10}O_{28}]$ represents an ion triplet consisting of two essentially isolated cations and an anion, held together mainly by ionic Coulomb forces. Hydrogen bonds do not play a significant role. The diprotonated cryptand attains a distorted *endo-endo* conformation, which, to our knowledge, has so far not been observed in any cryptand complex. The distortion comes about by an asymmetric interaction with the anion: The cryptand uses only four of its oxygen atoms, two of which form a protonation face together with the two nitrogen atoms. This kind of interaction may be of some relevance for the encapsulation of decavanadate by biogenic ionophores.

Among the various biological functions of vanadium[25], a general role has been noted which is correlated to the similarities between vanadates and phosphates[3,26]: Mono-, di- tetra- and decavanadates have been reported to mesh in with phosphate-metabolising enzymes. Functions noted for decavanadate are the activation of a 5′-nucleotidase from rat kidney[27], and the inhibition of several kinases[3,28], Ca^{2+}-ATPase[29] and muscle phosphorylase[30]. Further, the inositol triphosphate induced Ca^{2+} release is inhibited by decavanadate[31]. Decavanadate is in equilibrium with mono- and various oligovanadates. At the physiological level of overall vanadium concentrations (about 0.5 μM), appreciable amounts of decavanadate will not be present. Special cell compartments may, however, accumulate vanadium and hence enhance the equilibrium amount of decavanadate. The availability of decavanadate also depends on the pH range at which it exists: Decavandate forms under moderately acidic conditions, beginning at pH ≈ 6.5[32]. The protonated forms ($HV_{10}O_{28}^{5-}$, $H_2V_{10}O_{28}^{4-}$, $H_3V_{10}O_{28}^{3-}$) need more acidic media. The kinetics of the degradation of decavanadate, once formed in acidic media, are slow enough, however, to provide physiologically active decavanadate at pH ≈ 7[29a,33]. Apart from removal of decavanadate by degradation to vanadates of lower nuclearity, intracellular reduction to VO^{2+} (and perhaps further to V^{III}) by various intracellular reducing agents is a factor to be considered. The half-life of vanadium(V) in the intracellular medium has been estimated to approximately half an hour[34]. Alternatively, appropriate "shielding" of decavanadate(V) prior to, or simultaneously with, reduction may result in the preservation of the decavanadate core, as has been shown by the existence of fully reduced decavanadates(IV) derivatised by surrounding the cluster shell with tripodal alkoxides[35].

In any case, there are limiting conditions for the existence of decavanadate and the question arises, whether decavana-

date(V), once formed, can be stabilised by interaction with biogenic molecules. These molecules may be proteins such as the substrate kinases and phosphorylases mentioned above. The quality of binding may be a combination of ion-pair interaction and hydrogen bonds as in pyridinium[8] and guanidinium decavanadates[18a]. The kinetic of this kind of binding have been investigated for, e.g., tetravandate[36], and the binding itself documented by an X-ray diffraction study of the complex formed between monovanadate and ribonuclease T_1[37] from a mould. A number of model studies, using small peptides, has also revealed several features of vanadate binding to peptides (and proteins)[32c,38], among these the formation of glycylglycine decavanadate $(NH_4)_6(Gly\text{-}Gly)_2V_{10}O_{28}$, with a non-covalent interaction between decavanadate and glycyclglycine[18b] – as in $[C222(H^+)_2]_2[H_2V_{10}O_{28}]$.

Alternatively to binding to proteins, which will essentially immobilise the decavanadate anion, the interaction with ionophores might be considered. In the context of the cryptands as model systems, K^+- or Na^+-carrying ionophores such as valinomycin, antamanide and enniatin may be quoted[39], all of which contain, in addition to an oxygen coordination set, nitrogen functions as potential protonation sites. These ionophores may sandwich decavanadate – and compensate for its high anion charge – in a similar way to that demonstrated here for $[C222(H^+)_2]_2[H_2V_{10}O_{28}]$, namely by ion-pair (salt-bridge) interactions, using a minimum of two sets of oxygen functions per macrocycle for direct contacts to the cluster anion. Decavanadate is thus removed from equilibria where it decomposes to tetra-, di- and monovanadate. At the same time, a protective transport system for decavanadate is provided, effective possibly also for the trans-membrane transport.

This work was supported by the *Deutsche Forschungsgemeinschaft* and the *Fonds der Chemischen Industrie.*

Experimental Section

Starting materials were obtained from commercial sources [cryptand-222 (C222): Merck-Schuchardt, disodium 5′-adenosine monophosphate ($AMPNa_2$): Serva] or prepared according to a literature procedure $[VOCl_2(thf)_2]$[40]. – IR: Perkin Elmer FT-IR 1720. – NMR: Bruker AM 360 with the common instrument settings.

Bis{cryptand-222(H_2^+)}dihydrogendecavanadate $[(C222)H_2^+]_2[H_2V_{10}O_{28}]$: $AMPNa_2$ (783 mg, 2 mmol) was dissolved at 40°C and under N_2 in 120 ml of dry ethanol containing 4 mmol of C222. This solution was treated with $VOCl_2(thf)_2$ (565 mg, 2 mmol). A blue solid formed immediately. After 4 d of stirring at 65°C, the precipitate was filtered off, washed with ethanol and dried under vacuum to yield a blue powder of composition (C222)VO(AMP). – IR (KBr): ν = 3338, 3186 and 2938 cm^{-1} (NH_2, NH, OH of water of crystallisation), 1605 (C=N), 1108 (P=O), 996 (V=O and phosphate), 819 (COP); δ = 1688 and 1644 (NH_2). – UV (DMSO): λ_{max} (lg ε) = 261 nm (4.3), 583 (2.2), 687 (2.2), 869 (2.2). – ^{31}P NMR (DMSO): δ = −2.4. – The blue product was treated with 30 ml of Me_2NH to yield a blue-green solution which turned yellow when exposed to air after a couple of days. Orange crystals of $[(C222)H_2^+]_2[H_2V_{10}O_{28}] \cdot 2^1/_2\ H_2O$, suitable for the X-ray structure analysis grew within 45 d. The absence of sodium was verified by photometry.

Table 4. Crystal structure and refinement data for $[C222(H^+)_2][H_2V_{10}O_{28}] \cdot 2\frac{1}{2}H_2O$

empirical formula	$C_{36}H_{76}N_4O_{42.5}V_{10}$
molecular mass [g mol^{-1}]	754.41
cystal system	triclinic
space group	$P\bar{1}$
a [Å]	9.920(2)
b [Å]	12.925(4)
c [Å]	13.630(3)
α [°]	117.15(2)
β [°]	91.91(2)
γ [°]	101.54(2)
Z	1
V [$Å^3$]	1507.9(6)
$\rho_{calcd.}$ [g cm^{-3}]	1.932
μ [mm^{-1}]	13.4
$F(000)$	890
crystal dimensions [mm]	0.3×0.2×0.1
θ range [°]	3.68 to 76.38
hkl range	$-12<h<12$, $-16<k<14$, $0<l<17$
measured reflections	6696
independent reflections	6352
R_{int}	0.0760
refined parameters	431
goodness of fit	1.124
final R (R_w) for reflections with $I>2\sigma(I_0)$	0.0885 (0.2209)
$\rho_{fin.}$ max/min [e $Å^{-3}$]	1.34/–1.73

Crystal-Structure Determination: The data were collected with a CAD 4 diffractometer in the θ-2θ scan mode using a graphite monochromator and Cu-K_α radiation (λ = 154.178 pm) at 153 K. Crystal data and details of the refinement are summarised in Table 4. The programme systems SHELXS 86 and SHELXL 93 were employed throughout. Hydrogen atoms were placed into calculated positions (in the case of the protons at O9, N1/O30 and N2/O31) and included with common isotropic thermal parameters in the last cycle of refinement based on F^2. The disordered cryptand atoms O50, C51 and C52 were treated with a 25:75 model and refined isotropically and without hydrogen atoms. All other non-hydrogen atoms were refined anisotropically. The less populated (25%) cryptand conformation contained a water molecule hydrogen-bonded to O50. Absorption corrections have been carried out with DIFABS. 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-100259. Copies of the data can be obtained free of charge on application to The Director, CCDC, 12 Union Road, Cambridge CB2 1EZ, UK [fax: int. code +44(1223)336-033, e-mail: deposit@chemcrys.cam.ac.uk].

[1] C. L. Hill, C. M. Prosser-McCartha, *Coord. Chem. Rev.* **1995**, *32*, 407.
[2] *Polyoxometalates: From Platonic Solids to Anti-Retroviral Activity* (Eds.: M. T. Pope, A. Müller), Kluwer, Dordrecht, **1994**.
[3] P. J. Stankiewicz, A. S. Tracey, D. C. Crans in *Vanadium and Its Role in Life*, vol. 31 of *Metal Ions in Biological Systems* (Eds.: H. Sigel, A. Sigel), Marcel Dekker, New York **1995**, ch. 9.
[4] O. W. Howarth, *Progr. Nucl. Magn. Reson. Spectrosc.* **1991**, *22*, 453.
[5] V. W. Day, W. G. Klemperer, D. J. Maltbie, *J. Am. Chem. Soc.* **1987**, *109*, 2991.
[6] P. Roman, A. Aranzabe, A. Luque, J.M. Gutiérrez-Zorilla, M. Martínez-Ripoll, *J. Chem. Soc., Dalton Trans.* **1995**, 2225.

[7] A. S. J. Wery, J. M. Gutiérrez-Zorilla, A. Luque, P. Roman, *Polyhedron* **1996**, *24*, 4555.
[8] J. M. Arrieta, *Polyhedron* **1992**, *23*, 3045.
[9] T. Debaerdemaker, J. M. Arrieta, J. M. Amigo, *Acty Crystallogr. B* **1982**, *38*, 2465.
[10] N. V. Caparelli, D. M. L. Goodgame, P. B. Hayman, A. C. Skapski, *J. Chem. Soc., Dalton Trans.* **1986**, 776.
[11] J. M. Arrieta, A. Arnaiz, L. Lorente, C. Santiago, G. Germain, *Acta Crystallogr. C* **1988**, *44*, 1004.
[12] J.-Y. Kempf, M.-M. Rohmer, J.-M. Poblet, C. Bo, M. Beńard, *J. Am. Chem. Soc.* **1992**, *114*, 1136.
[13] A. S. Tracey, J. S. Jaswal, M. J. Gresser, D. Rehder, *Inorg. Chem.* **1990**, *29*, 4283.
[14] J. Richter, D. Rehder, L. Wyns, A. Haikal, *Inorg. Chim. Acta* **1995**, *238*, 155.
[15] S. J. Angus-Dunne, R. J. Batchelor, A. S. Tracey, F. W. B. Einstein, *J. Am. Chem. Soc.* **1995**, *117*, 5292.
[16] A. S. Tracey, M. J. Gresser, *Inorg. Chem.* **1988**, *27*, 1269.
[17] [17a] D. Mustafi, J. Telser, M. W. Makinen, *J. Am. Chem. Soc.* **1992**, *114*, 6219. – [17b] G. Micera, A. Dessi, D. Sanna, *Inorg. Chem.* **1996**, *35*, 6349. – [17c] S. F. Jiang, M. W. Makinen, *Inorg. Chem.* **1995**, *34*, 1736.
[18] [18a] X. Wang, H.-X. Liu, X.-X. Xu, X.-Z. You, *Polyhedron* **1993**, *12*, 77. – [18b] D. C. Crans, M. Mahroof-Tahir, O. P. Anderson, M. M. Miller, *Inorg. Chem.* **1994**, *33*, 5586.
[19] I. D. Brown in: *Structure and Bonding in Crystals* (Eds.: M. O'Keefe, M. Navrotzky), Academic Press, New York, **1981**, vol. II, ch. 14. An alternative value of R_0 for V–O, viz. 1.774, has recently been proposed (G. J. Palenik, *Inorg. Chem.* **1997**, *36*, 122). In order to provide consistency with other bond-order calculations on decavanadates, we have employed the original R_0 = 1.79 listed by Brown.
[20] [20a] H. T. Evans, Jr., M. T. Pope, *Inorg. Chem.* **1984**, *23*, 501. – [20b] Q. Chen, D. P. Goshorn, C. P. Scholes, X. Tan, J. Zubieta, *J. Am. Chem. Soc.* **1992**, *114*, 4667.
[21] [21a] Y.-J. Li, Q.-X. Zhu, Z.-H. Xu, G.-X. Xu, Y.-Z. Han, J.-S. Ma, *Huaxue Xuebao (Acta Chim. Sin.)* **1992**, *50*, 746. – [21b] Z.-H. Xu, Y.-J. Li, Q.-X. Zhu, Y.-Z. Han, G.-X. Zu, I. S. Butler, *J. Chem. Crystallogr.* **1994**, *24*, 577. The same compound – $[C222(H^+)_2][(NO_3)_2Y(NSC)_3(H_2O)]$ – is described.
[22] [22a] G. R. Willey, P. R. Meehan, M. D. Rudd, M. C. B. Drew, *J. Chem. Soc., Dalton Trans.* **1995**, 3173. – [22b] L. R. MacGillivray, J. L. Atwood, *J. Org. Chem.* **1995**, *60*, 4972.
[23] B. Metz, D. Moras, R. Weiss, *J. Chem. Soc., Perkin Trans. 2* **1976**, 423.
[24] [24a] D. Moras, B. Metz, R. Weiss, *Acta Crystallogr. B* **1973**, *29*, 383. – [24b] D. Moras, R. Weiss, *Acta Crystallogr. B* **1973**, *29*, 396.
[24] B. Metz, D. Moras, R. Weiss, *Acta Crystallogr. B* **1973**, *29*, 1377.
[25] [25a] D. Rehder, *Angew. Chem.* **1991**, *103*, 152; *Angew. Chem. Int. Ed. Engl.* **1991**, *30*, 148. – [25b] D. Rehder, *BioMetals* **1992**, *5*, 3. – [25c] *Vanadium in Biological Systems* (Ed.: N. D. Chasteen), Kluwer, Dordrecht, **1990**.
[26] P. J. Stankiewicz, A. S. Tracey in *Vanadium and Its Role in Life*, vol. 31 of *Metal Ions in Biological Systems* (Eds.: H. Sigel, A. Sigel), Marcel Dekker, New York **1995**, ch. 8.
[27] M. Le Hir, *Biochem. J.* **1991**, *273*, 795.
[28] D. W. Boyd, K. Kustin, M. Niwa, *Biochim. Biophys. Acta* **1985**, *827*, 472.
[29] [29a] P. Csermely, A. Martonosi, G. C. Levy, A. J. Ejchart, *Biochem. J.* **1985**, *230*, 807. – [29b] D. C. Crans, C. M. Simone, R. C. Holz, L. Que, Jr., *Biochemistry* **1992**, *31*, 11731.
[30] G. Soman, Y. C. Chang, D. J. Graves, *Biochemistry* **1983**, *22*, 4994.
[31] K. J. Föhr, Y. Wahl, R. Engling, T. P. Kemmer, M. Gratzl, *Cell Calcium* **1991**, *12*, 735.
[32] [32a] L. Pettersson, B. Hedman, A.-M. Nenner, I. Andersson, *Acta Chem. Scand. A* **1985**, *39*, 499. – [32b] A. S. Tracey, M. J. Gresser, S. Liu, *J. Am. Chem. Soc.* **1988**, *110*, 5869. – [32c] K. Elvingson, M. Fritzsche, D. Rehder, L. Pettersson, *Acta Chem. Scand.* **1994**, *48*, 878.
[33] R. K. Murmann, K. C. Giese, *Inorg. Chem.* **1978**, *17*, 1160.
[34] N. D. Chasteen, J. K. Grady, C. E. Hoolway, *Inorg. Chem.* **1986**, *25*, 2754.
[35] M. I. Khan, Q. Chen, D. P. Goshorn, J. Zubicta, *Inorg. Chem.* **1993**, *32*, 672.
[36] D. C. Crans, C. M. Simone, *Biochemistry* **1991**, *30*, 6734.
[37] D. Kostrewa, H.-W. Choe, U. Heinemann, W. Saenger, *Biochemistry* **1989**, *28*, 7592.
[38] D. C. Crans, H. Holst, A. D. Keramidas, D. Rehder, *Inorg. Chem.* **1995**, *34*, 2524.
[39] B. C. Pressman in *Inorganic Biochemistry* (Ed.: G. L. Eichhorn), Elsevier, Amsterdam **1973**, ch. 6.
[40] H. Tietz, K. Schmetlick, G. Kreisel, *Z. Chem.* **1985**, *25*, 290.

[97040]