DALTON

An unusual anionic oxo–(μ-oxo)–vanadium(v) network interlinked by cationic sodium chains

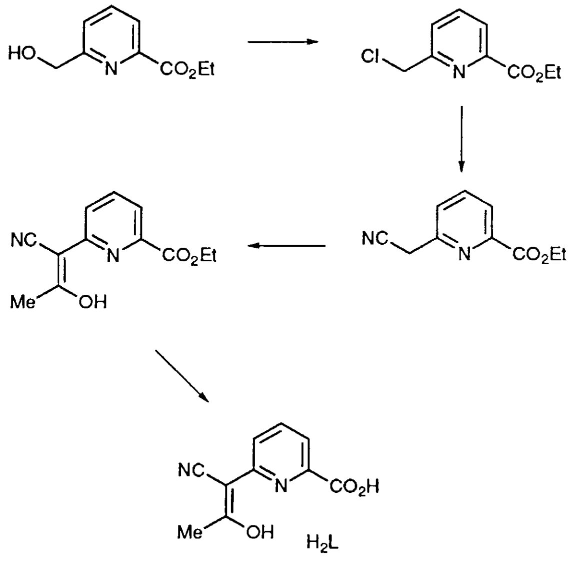
Nathalie Julien-Cailhol,[a] Eric Rose,[a] Jaqueline Vaisserman[b] and Dieter Rehder *[,c]

[a] *Laboratoire de Synthese Organique et Organometallique, Université Pierre et Marie Curie, 4, Place Jussieu, F-75252, Paris, France*
[b] *Laboratoire de Chimie des Meteaux de Transition, Université Pierre et Marie Curie, 4, Place Jussieu, F-75252, Paris, France*
[c] *Institut für Anorganische Chemie, Universität Hamburg, Martin-Luther-King-Platz 6, D-20146 Hamburg, Germany*

The new compound 6-(1-cyano-2-hydroxyprop-1-enyl)pyridine-2-carboxylic acid (H_2L) has been prepared and the structure of its ethyl ester determined. The salt NaHL reacted with VO^{2+} to form the vanadium(v) complex $[Na(MeOH)_2][VO_2L]$. Crystal-structure analysis of the complex revealed octahedral co-ordination of both the sodium and vanadium ions. Vanadium is co-ordinated to enolate oxygen, carboxylate oxygen, pyridine nitrogen, and two doubly bonded oxo groups in *cis* positions. The sixth position is occupied by the oxo group of a neighbouring vanadium centre at a rather long distance of 2.214(2) Å. Anionic, asymmetrically oxo-bridged vanadium chains are thus formed. These are interlinked by cationic sodium chains with sodium bonded to two bridging methanols, the cyano nitrogen of one of the vanadate chains and the co-ordinated carboxylate of the alternate vanadate chain. The network is further stabilized by hydrogen bonds. The relevance of the complex to biogenic vanadium compounds is discussed.

In the context of investigations into model complexes for biogenic vanadium compounds[1,2] we have developed novel ligand systems based on pyridine-2-carboxylic acid substituted by an appropriate function at the 6 position.[3] Here, we report on the synthesis of 6-(1-cyano-2-hydroxyprop-1-enyl)pyridine-2-carboxylic acid (H_2L, Scheme 1), the crystal structure of its ethyl ester, and the reaction of its sodium salt NaHL with VO^{2+}, leading to a $VO_2{}^+$ complex. The compound H_2L contains four functions which are potentially suitable for co-ordination to a metal ion, *viz.* the (enolic) OH group, the carboxylate group, the pyridine nitrogen and the nitrile group. Three of these (the hydroxide, aromatic nitrogen and carboxylate) have been discussed, based on extended X-ray absorption fine structure (EXAFS) data,[4] in the context of vanadium(v) co-ordination in the active centre of bromoperoxidase from the seaweed *Ascophyllum nodosum*. Recent X-ray diffraction results on the azide of the chloroperoxidase from the fungus *Curvularia inaequalis* have confirmed the binding of the aromatic nitrogen from histidine (His) and revealed a strong hydrogen-bonding interaction between the trigonal-bipyramidal VO_3(His)X centre and amino acid side chains, among these being serine.[5] Serine is also in the immediate vicinity of vanadium in the *A. nodosum* peroxidase.[6] Carboxylate, (phenolic) hydroxide and enamine binding has also been established for V^V and V^{IV} co-ordinated to transferrin[7] and xylose isomerase,[8] and the various inhibitory and stimulating effects of vanadate towards phosphorylation enzymes[9,10] (including the insulin mimetic effect) suggest similar binding modes, also made plausible by model studies on aqueous vanadate–dipeptide systems, where the dipeptide is, *e.g.*, alanylhistidine,[11] phenylalanylglutamate[12] or glycyltyrosine.[13]

Three of the four functionalities in H_2L actually co-ordinate simultaneously to vanadium, providing a novel mode of co-ordination within the family of ONO donor sets. The fourth function, the nitrile nitrogen, co-ordinates to the sodium counter ion.



Scheme 1

Results and Discussion

Starting from ethyl 6-(hydroxymethyl)pyridine-2-carboxylate,[3,14a] the preparation of compound H_2L was carried out by the route depicted in Scheme 1. In order to compare the bonding parameters of co-ordinated and free H_2L, we have undertaken a crystal structure analysis of the precursor compound, the ethyl ester. Fig. 1 shows the molecular structure with selected bonding parameters. It contains a rather short enolic C–OH bond [1.27(1) Å], suggesting participation of a zwitterionic tautomeric form, in which the formally enolic proton is bound to the pyridine nitrogen. The distance between N(1) and O(1) is in fact consistent with a hydrogen bond, although the hydrogen has not been located on a Fourier-difference map. Support for this view also comes from the ^{13}C NMR chemical shift of the carbon C(5) adjacent to the pyridine N: δ 137.66 for the ester and 139.31 for H_2L, shielded with respect to ethyl 6-methylpyridine-2-carboxylate (δ 148.60). The enol proton in the ester exhibits a ^{1}H chemical shift of δ 14.04.

The monosodium salt of H_2L, NaHL, reacts with vanadyl acetylacetonate in absolute methanol under inert-gas conditions to form the complex compound $[Na(MeOH)_2][VO_2L]$. A plausible explanation for the accompanying oxidation {of V^{IV} in $[VO(acac)_2]$ to V^V in $[VO_2L]^-$} is a disproportionation reaction. Fig. 2 shows the molecular structures of the cation and the anion, and Fig. 3 a section from the crystal structure. Table 1 gives selected bonding parameters.

The ion $[VO_2L]^-$ is the first example of a vanadium complex with simultaneous co-ordination of an enolate, an aromatic amine and a carboxylate function. The co-ordination geometry of vanadium is intermediate between tetragonal pyramidal and octahedral, with the plane spanned by the three donor functions of the ligand [N(1), O(1) and O(2)] and one of the doubly bonded oxo groups [O(4)]. The second oxo group [O(5)] and a long-distance oxo ligand [O(5′) at 2.214(2) Å, corresponding to a bond order[16] of 0.342] of the adjacent vanadium unit form the axis. Atom O(5) in turn bridges to a third vanadium unit, resulting in the formation of infinite V···O=VO(L)···O chains. The bridging mode of O(5) leads to a slightly elongated V=O double bond of 1.633(2) Å. Double bonds for monomolecular oxovanadium complexes with oxo ligands not involved in contacts to additional atoms are between 1.56 and 1.60 Å.[17] The bridging mode is also reflected in a low-lying ν(V–μ-O) at 723 cm^{-1}, along with a normal VO stretch at 967 cm^{-1} for V=O(4). There is a significant deviation from linearity in the structure units O···V=O···; the angle O(5)–V–O(5′) is 166.6(2)°. The V=O(4) distance [1.631(3) Å] again slightly exceeds that expected for a V=O double bond. Here, the reason is the involvement of O(4) in hydrogen bonding to the methanol of the complex counter ion. Similar effects, *i.e.* relatively long V=O···H double bonds, have been noted previously, *e.g.* refs. 14(*b*) and 18(*a*). The pyridine nitrogen N(1) *trans* to O(4) is at the rather long distance of 2.225(3) Å as a consequence of the *trans* effect of the oxo group, while the V–O bond lengths to the enolate [O(1)] and carboxylate [O(2)] are within the range commonly observed for V–O single bonds. Comparison of the bonding parameters for the ligand in the anion $[VO_2L]^-$ with those of the unco-ordinated ester (*cf.* Fig. 1) reveals significant changes in the carboxylic acid function, *viz.* a lengthening of the C–O(co-ordinated) and a strengthening of the C–O(unco-ordinated) bonds in $[VO_2L]^-$ with respect to the ester.

The V=O···V chains, carrying one negative charge per vanadium centre, are interlinked by sodium chains (Fig. 3). The sodium ions are octahedrally co-ordinated by four oxygens of bridging methanol molecules (in the tetragonal plane) and,

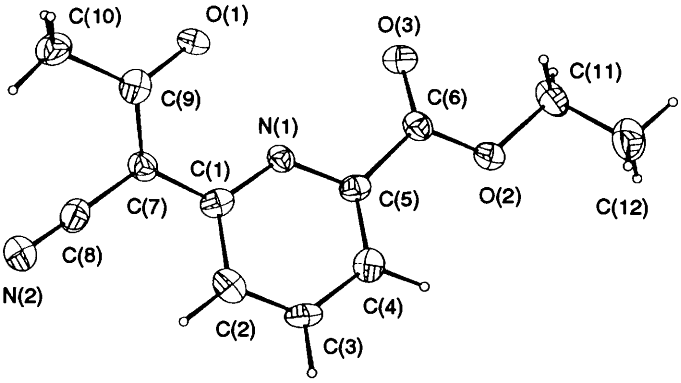


Fig. 1 A CAMERON[15] drawing (50% probability ellipsoids) of the ethyl ester of H_2L. Selected bond lengths (Å) and bond angles (°): O(1)–C(9) 1.27(1), O(2)–C(6) 1.319(9), O(3)–C(6) 1.20(1), C(7)–C(9) 1.40(1) and N(2)–C(8) 1.14(1); N(1)–C(1)–C(7) 119.0(7), C(7)–C(9)–O(1) 122.6(7), C(5)–C(6)–O(3) 121.0(7) and O(2)–C(6)–O(3) 126.7(8)

Table 1 Selected bond lengths (Å) and angles (°) for $[Na(MeOH)_2][VO_2L]$

Anion, vanadium centre			
V(1)–O(1)	1.928(2)	V(1)–O(5)	1.633(2)
V(1)–O(2)	2.002(3)	V(1)···O(5′)	2.214(2)
V(1)–O(4)	1.631(3)	V(1)–N(1)	2.225(3)
O(1)–V(1)–O(2)	154.4(1)	O(2)–V(1)–N(1)	75.4(1)
O(5)–V(1)–O(5′)	166.6(2)	O(5)–V(1)–O(1)	82.7(1)
O(4)–V(1)–N(1)	161.8(1)	O(5)–V(1)–O(2)	97.5(1)
O(1)–V(1)–O(4)	101.9(1)	O(5)–V(1)–O(4)	87.5(1)
O(1)–V(1)–N(1)	83.3(1)	O(5)–V(1)–N(1)	90.8(1)
O(2)–V(1)–O(4)	94.4(1)		
Anion, ligand system			
O(2)–C(6)	1.284(4)	C(7)–C(8)	1.431(5)
O(3)–C(6)	1.232(4)	N(2)–C(8)	1.139(5)
O(1)–C(9)	1.282(4)	O(3)···O(12)	2.646(4)
C(7)–C(9)	1.397(4)	O(4)···O(11)	2.917(4)
C(1)–C(7)	1.451(5)		
V(1)–O(1)–C(9)	130.9(2)	N(2)–C(8)–C(7)	178.3(5)
O(1)–C(9)–C(7)	123.9(3)	V(1)–O(2)–C(6)	120.9(2)
C(1)–C(7)–C(9)	126.3(3)	O(2)–C(6)–O(3)	123.7(3)
Cation			
Na(1)–O(2)	2.421(3)	O(2)–Na(1)–N(2)	174.7(1)
Na(1)–N(2)	2.440(4)	O(11)–Na(1)–O(12′)	174.1(1)
Na(1)–O(11)	2.449(4)	O(2)–Na(1)–O(11)	82.7(1)
Na(1)–O(12)	2.387(4)	O(2)–Na(1)–O(12)	91.9(1)
Na(1)–O(11′)	2.449(4)	O(11)–Na(1)–O(12)	79.7(1)
Na(1)–O(12′)	2.564(4)	N(2)–Na(1)–O(11)	94.8(1)
		N(2)–Na(1)–O(12)	89.6(1)

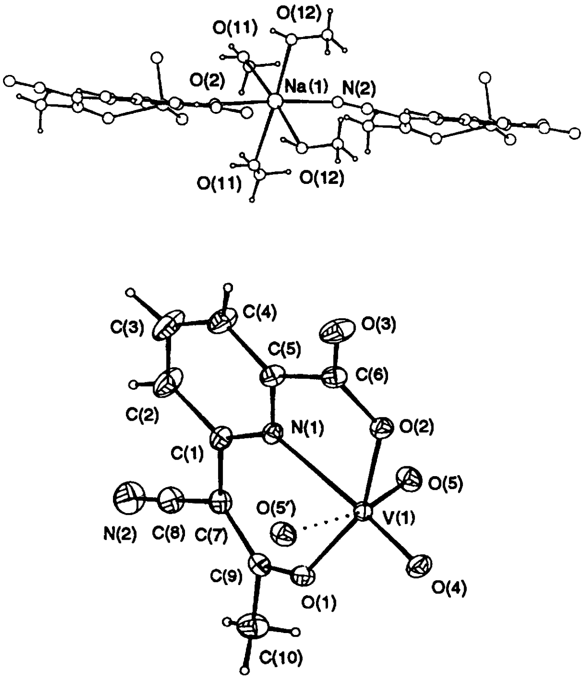


Fig. 2 Molecular structures for the cation and anion of $[Na(MeOH)_2][VO_2L]$. The numbering scheme for the ligand is the same as that used in Fig. 1

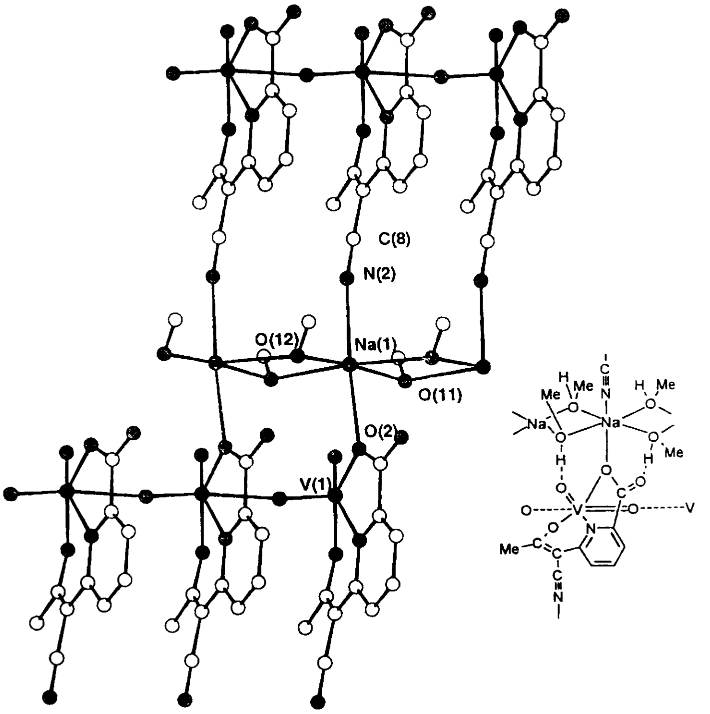


Fig. 3 Part of the crystal structure of $[Na(MeOH)_2][VO_2L]$, with the cationic chain in the centre. The inset shows a schematic drawing of a section from the two-dimensional layer

axially, by direct links to $[VO_2L]^-$ through the nitrile nitrogen [N(2)] of one of the oxovanadium chains and the carboxylate oxygen O(2) of the other oxovanadium chain. Atom O(2) hence co-ordinates both the vanadium(V) and the sodium centres. A comparable case has been reported for $[Na_2(MeOH)(H_2O)][V^{IV}O(L')]_2 \cdot H_2O$,[18b] ($H_3L'$ = 3-hydroxy-3-methylglutaric acid) where the bond lengths to the O,O'-bonded carboxylate are Na–O 2.482(9) and Na–(μ-O) 2.604(9) Å. Additional linkages between the cationic and the anionic chains are achieved by a hydrogen-bonding network between the methanolic hydrogens and the unco-ordinated carboxylate oxygen O(3) [2.646(4) Å] on the one hand, and the oxo ligand O(4) [2.917(4) Å] on the other hand. The C≡N bond length [1.139(5) Å] is not affected by the sodium co-ordination. The bond lengths between the sodium ion and the ligand functions (Table 1) are comparable with those of related complexes. Examples are Na–N 2.460(7) Å in 15-crown-5·Na(NCMe)Cl (15-crown-5 = 1,4,7,10,13-pentaoxacyclopentadecane),[19] Na–N 2.364–2.395(5) Å in 15-crown-5·Na[(NC)$_2$CH],[20] Na–O (carboxylate) 2.395(5) and Na–O (phenolate) 2.383(4) Å in sodium (*p*-aminosalicylate)[21] and Na–O 2.451(3) Å in [Na(EtOH)]Br.[22]

Conclusion

The compound [Na(MeOH)$_2$][VO$_2$L] is interesting in several aspects. (*i*) Sodium attains the rare co-ordination sphere of five oxygen functions plus one nitrile nitrogen. (*ii*) The anion [VO$_2$L]$^-$ is the first example of simultaneous co-ordination of vanadium to an aromatic nitrogen, enolate oxygen and carboxylate oxygen, a mode with some relevance to the vanadate–protein interaction and biogenic vanadium compounds, including the active centres in vanadate(v)-dependent haloperoxidases. This model character is further stressed by the hydrogen-bonding interaction between the anion [VO$_2$L]$^-$ and the methanol groups in the co-ordination sphere of the sodium counter ion, mimicking a corresponding interaction between the co-ordinated vanadate centre and serine in *C. inaequalis* chloroperoxidase. (*iii*) Considering the polymeric ··· V(O)(μ-O) ··· V(O)(μ-O) ··· chains, [VO$_2$L]$^-$ features an unusual one-dimensional structural motif in polyoxometalate chemistry.[23]

Experimental

General and spectroscopic measurements

All operations concerning the vanadium complex were carried out under nitrogen and in absolute, oxygen-free solvents. Starting compounds were obtained from commercial sources. Ethyl 6-(hydroxymethyl)pyridine-2-carboxylate was prepared, starting from pyridine-2,6-dicarboxylic acid, according to our published procedure.[14a] Infrared spectra were obtained on a Perkin-Elmer 1700 XFT spectrometer as KBr mulls; ^{1}H, ^{13}C and ^{51}V NMR spectra on a Bruker AM 360 spectrometer with the common parameter fittings and mass spectra on a Nermag R 30–40 spectrometer, employing chemical ionization in the presence of NH$_3$.

Preparations and characterizations

Ethyl 6-(1-cyano-2-hydroxyprop-1-enyl)pyridine-2-carboxylate and 6-(1-cyano-2-hydroxyprop-1-enyl)pyridine-2-carboxylic acid (H$_2$L). Ethyl 6-(hydroxymethyl)pyridine-2-carboxylate (5 g, 28 mmol)[14a] was converted into the 6-chloromethyl derivative by treatment with a three-fold excess of SOCl$_2$ in the cold, subsequent addition of water and sodium carbonate to adjust to pH 7, extraction with diethyl ether, evaporation and crystallization at −18 °C. Yield: 91%. Pale, yellow oil, m.p. *ca.* 10 °C (from ether), *m*/*z* 200 (M + H$^+$). It was converted into the corresponding 6-cyanomethyl derivative by treatment of 5 g (25 mmol) with K[18-crown-6]CN (1.8 g, 28 mmol) in acetonitrile underargon(18-crown-6 = 1,4,7,10,13,16-hexaoxacyclooctadecane). The reaction mixture was treated with water, extracted with CH$_2$Cl$_2$, the organic layer washed with saturated aqueous sodium carbonate, evaporated and chromatographed on silica gel. The eluate was distilled *in vacuo* [130 °C, 0.01 mmHg (*ca.* 1.33 Pa)] to yield 3.44 g (72% yield) of the desired product. M.p. 48 °C, *m*/*z* 191 (M + H$^+$).

This compound (2.5 g, 13.15 mmol) was treated with a mixture of glacial acetic acid (6 ml) and acetic acid anhydride (10 ml). The ethyl ester of H$_2$L was extracted with CH$_2$Cl$_2$, the CH$_2$Cl$_2$ solution washed with aqueous sodium carbonate, and concentrated *in vacuo* to yield a yellow oil. Dilution with ether led to a pale yellow precipitate, which was filtered off and recrystallized several times from ether and finally from ether–light petroleum (b.p. 80–110 °C). The crystals (2.68 g, 88% yield) thus obtained were suitable for structure analysis, m.p. 130 °C (Found: C, 61.95; H, 5.15; N, 12.00. C$_{12}$H$_{12}$N$_2$O$_3$ requires C, 62.05; H, 5.15; N, 12.05%); δ_H(CDCl$_3$) 1.44 (3 H, t, *J* 7.1, CH$_2$C*H*$_3$), 4.48 (2 H, q, *J* 7.1, CH$_2$), 2.42 [3 H, s, =C(OH)C*H*$_3$], 7.55 (1 H, d, *J* 7.3, H^2), 7.69 (1 H, d, *J* 7.3, H^3), 7.85 (1 H, dd, *J* 7.3 Hz, H^4) and 14.04 (1 H, br s, OH); δ_C(CDCl$_3$), 15.11 (C^{12}), 25.23 (C^{10}), 64.01 (C^{11}), 79.45 (C^7), 118.80 (C^4), 119.55 (C^8), 123.57 (C^2), 137.66 (C^5), 139.58 (C^3), 155.06 (C^1) and 190.14 (C^9); *m*/*z* 233 (M + H), 216 (M + H − OH), 188 (M + H − OEt), and 160 (M + H − CO$_2$Et).

For saponification, the ester (2 g, 8.62 mmol) was suspended in 1 mol dm^{-3} sodium hydroxide (8.6 cm^3) and stirred for 15 h. The solution thus obtained was acidified with HCl to pH 6, and evaporated to dryness. A yellow powder was obtained, which was recrystallized by dissolution in acetone and reprecipitation with water several times to yield 1.67 g (95%) of H$_2$L (Found: C, 58.45; H, 4.00; N, 13.70. C$_{10}$H$_8$N$_2$O$_3$ requires C, 58.80; H, 3.95; N, 13.70%); δ_H(D$_2$O) 2.03 (3 H, s, CH$_3$), 6.74 (1 H, d, *J* 8.6, H^2), 7.22 (1 H, d, *J* 8.6, H^3) and 7.65 (1 H, dd, *J* 8.6 Hz, H^4); δ_C(D$_2$O) 27.61 (C^{10}), 75.87 (C^7), 117.91 (C^4), 122.09 (C^2), 123.48 (C^8), 139.31 (C^5), 143.48 (C^3), 152.83 (C^1), 165.51 (C^6) and 195.37 (C^9); $\tilde{\nu}_{max}$/cm^{-1} 1613 (C=N), 1648 (CO$_2{}^-{}_{asym}$), 2206 (C≡N) and 3436 (OH); *m*/*z* 205 (M + H), 180 (M + H − CN), 161 (M + H − OH) and 174 (M + H − OH − CH$_3$). Conversion of the acid H$_2$L into the sodium salt NaHL was carried out by adding an equimolar amount of methanolic NaOH.

[Na(MeOH)$_2$][VO$_2$L]. The salt NaHL (226 mg, 1 mmol) was dissolved in methanol (15 cm^3) and treated dropwise with a solution of [VO(acac)$_2$] (239 mg, 1 mmol) in methanol (15 cm^3). The green solution obtained was refluxed for 1 h, cooled to room temperature, and concentrated to half its original volume. The bordeau red solution was layered with pentane (10 cm^3) and placed in the dark at room temperature. Red-brown crystals suitable for X-ray analysis separated out in several days. These were filtered off and dried in a N$_2$ stream. Yield 95 mg (28%) (Found: C, 38.45; H, 3.50; N, 7.65. C$_{12}$H$_{14}$N$_2$NaO$_7$V requires C, 38.70; H, 3.75; N, 7.50%); δ_H(CD$_3$OD) 2.35 (3 H, s, CH$_3$), 7.82 (1 H, d, H^2), 7.88 (1 H, d, H^3) and 8.15 (1 H, t, H^4); δ_C(CD$_3$OD) 27.56 (C^{10}), 82.81 (C^7), 117.84 (C^4), 118.53 (C^8), 121.70 (C^2), 138.96 (C^3), 146.59 (C^5), 150.09 (C^1), 168.58 (C^6) and 207.04 (C^9); δ_V(CD$_3$OD) −551.9; $\tilde{\nu}_{max}$/cm^{-1} 723 [V–(μ-O)], 967 (V=O) and 2211 (C≡N).

Crystallography

Crystal structure determinations were carried out at room temperature on a CAD4 Enraf-Nonius {[Na(MeOH)$_2$]-[VO$_2$L]} or Philips PW 1100 diffractometer (ester) in the ω–2θ scan mode, with Mo-Kα irradiation (λ = 0.710 69 Å) and a graphite monochromator. The structures were solved with the SHELXS program system.[24] Computations were performed by using the personal computer version of CRYSTALS.[25] Hydrogen atoms were placed in calculated positions and included in the last cycles of the refinement. Refinements were carried out on *F*, weighting schemes employed: $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$, $R' = \Sigma w(|F_o| - |F_c|)^2/\Sigma w F_o{}^2$.

Crystal data. C$_{12}$H$_{12}$N$_2$O$_3$, M = 232, orthorhombic, space group *Pna*2 (no. 33), a = 6.409(1), b = 7.596(3), c = 23.959(5) Å, U = 1166.4 Å^3, Z = 4, μ = 0.9 cm^{-1}, D_c = 1.32 g cm^{-3}, crystal dimensions 0.2 × 0.4 × 0.6 mm, *F*(000) = 380.7, θ range 1.5–25°, 1250 reflections, 1095 unique, 727 with $F_o > 1.5\sigma F_o{}^2$, allowance for absorption effects with DIFABS[26] (minimum 0.86, maximum 1.09), 154 variables, R = 0.0567, R' = 0.0515, goodness of fit = 0.56, $\Delta\rho_{min}$ = −0.19, $\Delta\rho_{max}$ = 0.19 e Å^{-3}.

C$_{12}$H$_{14}$N$_2$NaO$_7$V, M = 372, monoclinic, space group *P*2$_1$, a = 3.8297(9), b = 16.550(14), c = 11.971 Å, β = 93.46(4)°, U = 755(2) Å, Z = 2, μ = 7.0 cm^{-1}, D_c = 1.64 g cm^{-3}, crystal dimensions 0.2 × 0.2 × 0.4 mm, *F*(000) = 381, θ range 1–30°, 2384 reflections, 2281 unique, 2126 with $F_o{}^2 > 3\sigma F_o{}^2$,

R_{int} 0.0114, 252 variables, allowance for absorption effects with DIFABS (minimum 0.86, maximum 1.14), $R = 0.0310$, $R' = 0.0335$, $\Delta\rho_{min} = -0.43$, $\Delta\rho_{max} = 0.56$ e Å^{-3}.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1996, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 186/3.

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References

1 *Vanadium in Biological* Systems, ed. N. D. Chasteen, Kluwer, Dordrecht, 1990; *Metal Ions in Biological Systems*, eds. H. Sigel and A. Sigel, Marcel Dekker, New York, 1995, vol. 31.
2 R. Wever and K. Kustin, *Adv. Inorg. Chem.*, 1990, **35**, 81; D. Rehder, *Angew. Chem., Int. Ed. Engl.*, 1991, **30**, 148; A. Butler and C. Carrano, *Coord. Chem. Rev.*, 1991, **109**, 61; D. Rehder, *BioMetals*, 1992, **5**, 3.
3 N. Julien-Cailhol, Thèse de Doctorat de L'Université Paris 6, 1995.
4 J. M. Arber, E. de Boer, C. D. Garner, S. S. Hasnain and R. Wever, *Biochemistry*, 1989, **28**, 7968; see also, J. Hormes, U. Kuetgens, R. Chauvistre, W. Schreiber, N. Anders, H. Vilter, D. Rehder and C. Weidemann, *Biochim. Biophys. Acta*, 1988, **956**, 293.
5 A. Messerschmidt and R. Wever, presented at the 7th International Conference on Bioinorganic Chemistry, Lübeck, 1995; *J. Inorg. Biochem.*, 1995, **59**, 580, 584.
6 H. Vilter, personal communication.
7 N. D. Chasteen, E. M. Lord, H. J. Thompson and J. K. Grady, *Biochim. Biophys. Acta*, 1986, **64**, 884; A. Butler and H. Eckert, *J. Am. Chem. Soc.*, 1989, **111**, 2802.
8 R. Bogumil, J. Hüttermann, R. Kappl, R. Stabler, C. Sudfeld and H. Witzel, *Eur. J. Biochem.*, 1991, **196**, 305.
9 G. L. Mendz, *Arch. Biochem. Biophys.*, 1991, **291**, 201.
10 P. J. Stankiewicz and A. S. Tracey, *Metal Ions in Biological Systems*, eds. H. Sigel and A. Sigel, Marcel Dekker, New York, 1995, vol. 31, ch. 8; P. J. Stankiewicz, A. S. Tracey and D. C. Crans, *Metal Ions in Biological Systems*, eds. H. Sigel and A. Sigel, Marcel Dekker, New York, 1995, vol. 31, ch. 9.
11 K. Elvingson, M. Fritzsche, D. Rehder and L. Pettersson, *Acta Chem. Scand.*, 1994, **48**, 878.
12 D. Rehder, H. Holst, R. Quaas, W. Hinrichs, U. Hahn and W. Saenger, *J. Inorg. Biochem.*, 1989, **37**, 141.
13 D. C. Crans, H. Holst, D. Keramidas and D. Rehder, *Inorg. Chem.*, 1995, **34**, 2524.
14 (*a*) V. Vergopoulos, S. Jantzen, N. Julien, E. Rosc and D. Rehder, *Z. Naturforsch., Teil B*, 1994, **49**, 1127; (*b*) V. Vergopoulos, W. Priebsch, M. Fritzsche and D. Rehder, *Inorg. Chem.*, 1993, **32**, 1844.
15 L. J. Pearce and D. J. Watkin, CAMERON, Chemical Crystallographic Laboratory, Oxford, 1994.
16 I. D. Brown and K. K. Wu, *Acta Crystallogr., Sect. B*, 1976, **52**, 1957; I. D. Brown and R. D. Shannon, *Acta Crystallogr., Sect. A*, 1973, **29**, 266.
17 See, for example, C. J. Carrano, C. M. Nunn, R. Quan, J. A. Bonadies and V. L. Pecoraro, *Inorg. Chem.*, 1990, **29**, 944; J. B. Pessoa, J. A. L. Silva, A. L. Vieira, L. Vilas-Boas, P. O'Brien and P. Thornton, *J. Chem. Soc., Dalton Trans.*, 1992, 1745; C. R. Cornman, J. Kampf and V. L. Pecoraro, *Inorg. Chem.*, 1992, **31**, 1981; S. A. Fairhurst, D. L. Hughes, G. J. Leigh, J. R. Sanders and J. Weisner, *J. Chem. Soc., Dalton Trans.*, 1994, 2591; D. C. Crans, R. A. Felty, H. Chen, H. Eckert and N. Das, *Inorg. Chem.*, 1994, **33**, 2427 and refs. therein.
18 (*a*) T. M. Dewey, J. du Bois and K. N. Raymond, *Inorg. Chem.*, 1993, **32**, 1729; (*b*) S. L. Castro, M. E. Cass, F. J. Hollander and S. L. Bartley, *Inorg. Chem.*, 1995, **34**, 466.
19 E. Rentschler, W. Massa, S. Vogler, K. Dehnicke, D. Fenske and G. Baum, *Z. Anorg. Allg. Chem.*, 1991, **59**, 592.
20 W. Hiller, S. Frey, J. Strähle, G. Boche, W. Zarges, K. Harms, M. Marsch, R. Wollert and K. Dehnicke, *Chem. Ber.*, 1992, **87**, 125.
21 L. B. Cole and E. M. Holt, *Inorg. Chim. Acta*, 1989, **160**, 195.
22 F. R. Fronczek, V. J. Gatto, C. Minganti, R. A. Schultz, R. D. Gandour and G. W. Gokel, *J. Am. Chem. Soc.*, 1984, **106**, 7244.
23 *Polyoxometalates*, eds. M. T. Pope and A. Müller, Kluwer, Dordrecht, 1994.
24 G. M. Sheldrick, SHELXS 86, Program for crystal structure solution, University of Göttingen, 1986.
25 D. J. Watkins, J. R. Carruthers and P. W. Bettridge, *Crystals User Guide*, Chemical Crystallography Laboratory, University of Oxford, 1988.
26 DIFABS, N. G. Walker and D. Stuart, *Acta Crystallogr., Sect. A*, 1983, **39**, 158.

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