

Supplementary Information to

Vanadate complexes in serum: a speciation modeling study[†]

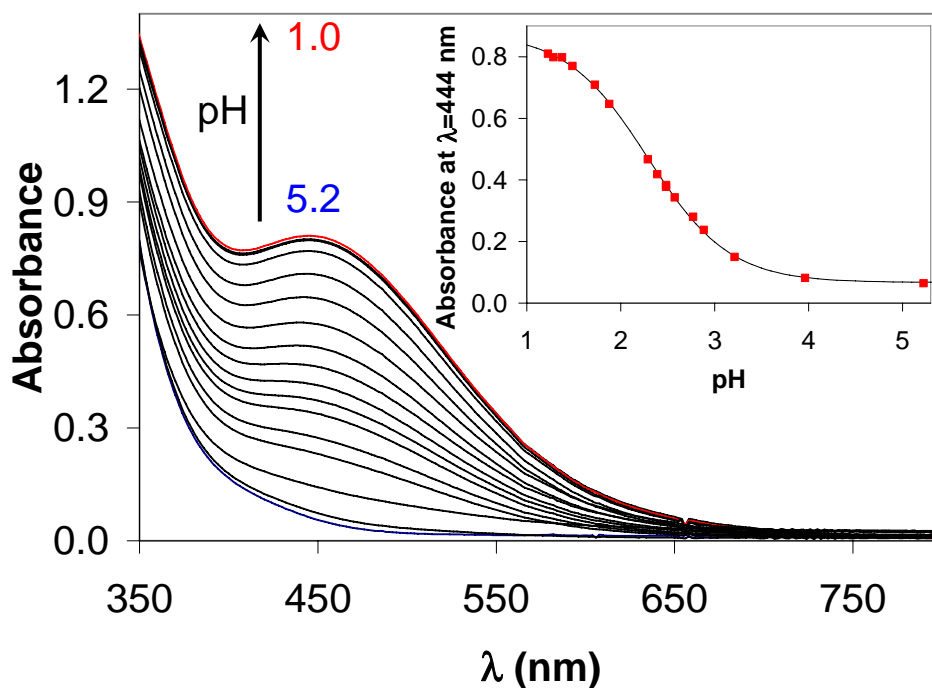
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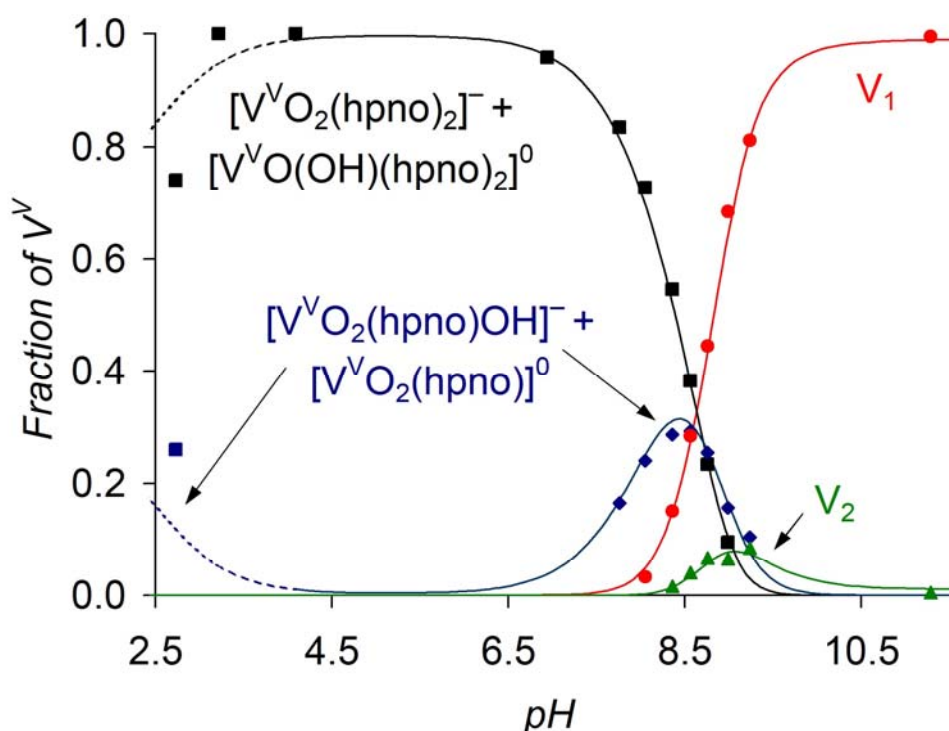
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1. UV-Vis spectra

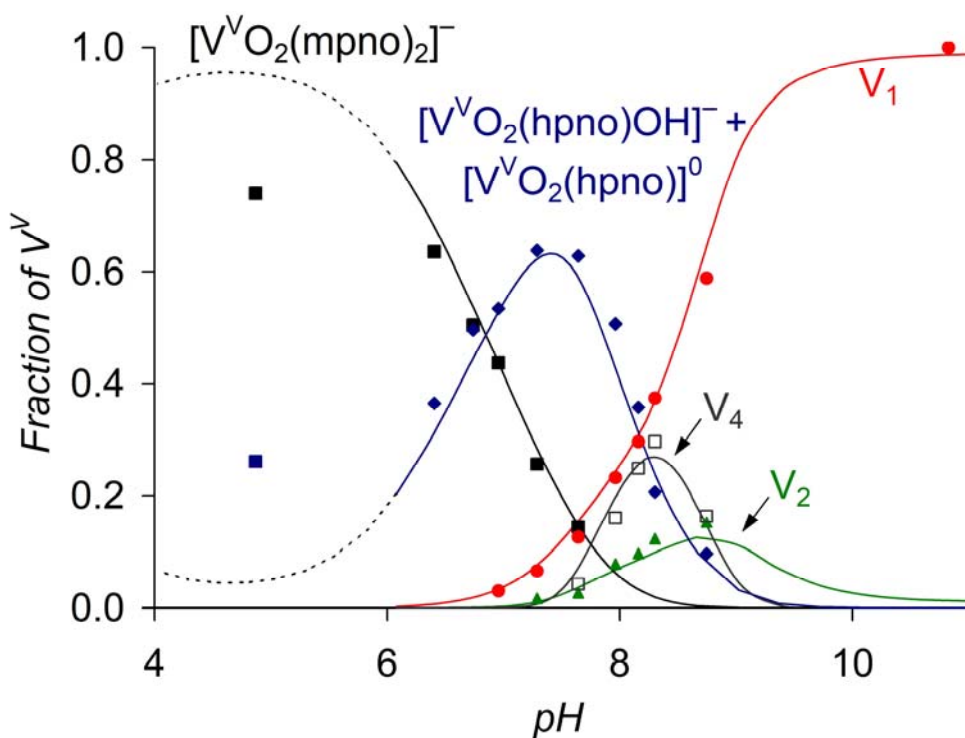


ESI Fig. S1 UV-VIS spectra over the pH range in the hpno-vanadate system at metal to ligand ratio of 1:20; $c_{\text{V}} = 5.0 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$, $I = 0.20 \text{ mol} \cdot \text{dm}^{-3}$ KCl, $T = 25 \text{ }^\circ\text{C}$, $l = 1 \text{ cm}$. Each sample prepared individually. In the inserted graph the absorbance is depicted versus pH which measured at $\lambda = 444 \text{ nm}$ (at the wavelength of the absorption maximum). The ■ represent the measured points, the full line is the fitted curve.

2. Speciations



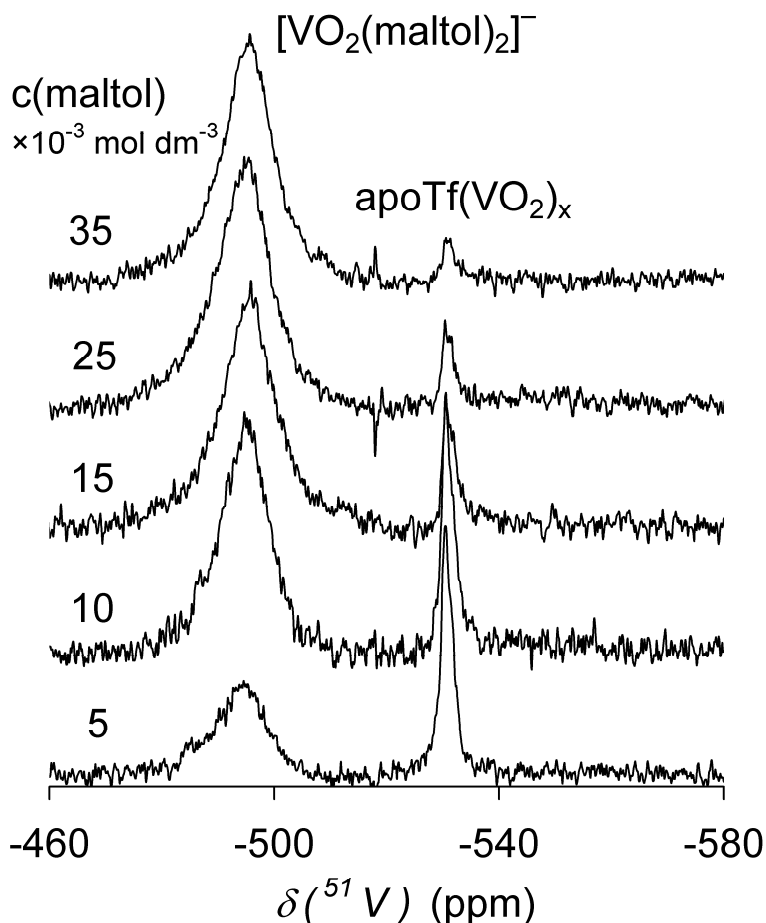
ESI Fig. S2 Speciation curves of the complexes formed in the V^V -hpno system at a metal-to-ligand ratio of 1:3. $c_{V^V} = 3.0 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$, $I = 0.20 \text{ mol} \cdot \text{dm}^{-3} \text{ KCl}$, $T = 25 \text{ }^\circ\text{C}$. Full lines are calculated curves, symbols represent experimental points based on ^{51}V -NMR spectra. ■ represents $[\text{VO}_2(\text{hpno})_2]^-$ and $[\text{VO}_2\text{H}(\text{hpno})_2]^0$ ● represents V_1 (VO^{2+} , H_2VO_4^- and HVO_4^{2-} together) ▲ represents V_2 ($\text{V}_2\text{O}_7^{4-}$, $\text{HV}_2\text{O}_7^{3-}$ and $\text{H}_2\text{V}_2\text{O}_7^{2-}$ together) ◆/■ represent $[\text{VO}_2(\text{hpno})\text{OH}]^-$ and $[\text{VO}_2(\text{hpno})]^0$ together. The most acidic sample represented by ■, contained precipitation.



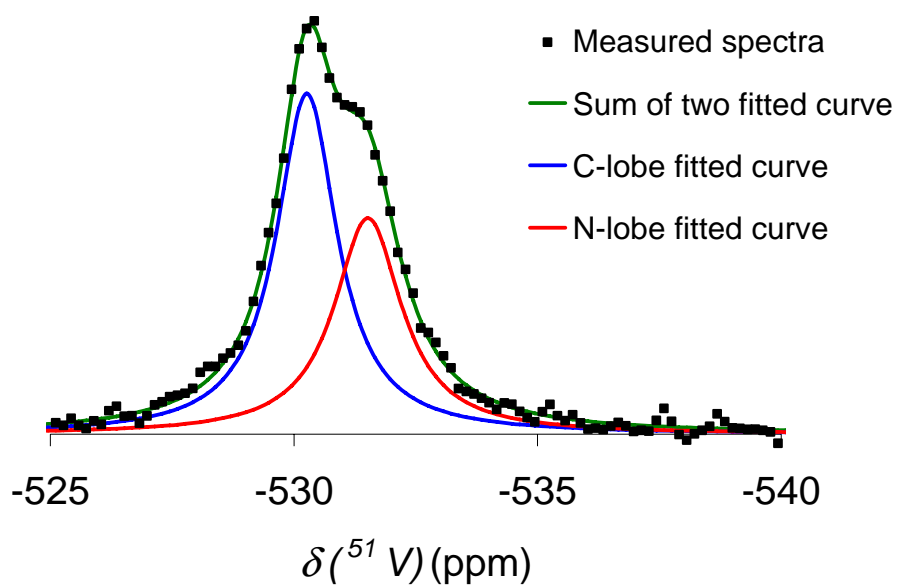
ESI Fig. S3 Speciation curves of the complexes formed in the V^V -mpno system at a metal-to-ligand ratio of 1:3. $c_{V^V} = 3.0 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$, $I = 0.20 \text{ mol} \cdot \text{dm}^{-3} \text{ KCl}$, $T = 25 \text{ }^\circ\text{C}$. Full lines are calculated curves, symbols represent experimental points based on ^{51}V -NMR spectra. ■ represents $[\text{VO}_2(\text{mpno})_2]^-$; ● represents V_1 (VO^{2+} ,

H_2VO_4^- and HVO_4^{2-} together); \blacktriangle represents V_2 ($\text{V}_2\text{O}_7^{4-}$, $\text{HV}_2\text{O}_7^{3-}$ and $\text{H}_2\text{V}_2\text{O}_7^{2-}$ together); \square represents V_4 ($\text{V}_4\text{O}_{13}^{6-}$, $\text{HV}_4\text{O}_{13}^{5-}$ and $\text{V}_4\text{O}_{12}^{4-}$ together); $\blacklozenge/\blacksquare$ represent $[\text{VO}_2(\text{mpno})\text{OH}]^-$ and $[\text{VO}_2(\text{mpno})]^0$ together. The most acidic sample represented by \blacksquare , contained precipitation.

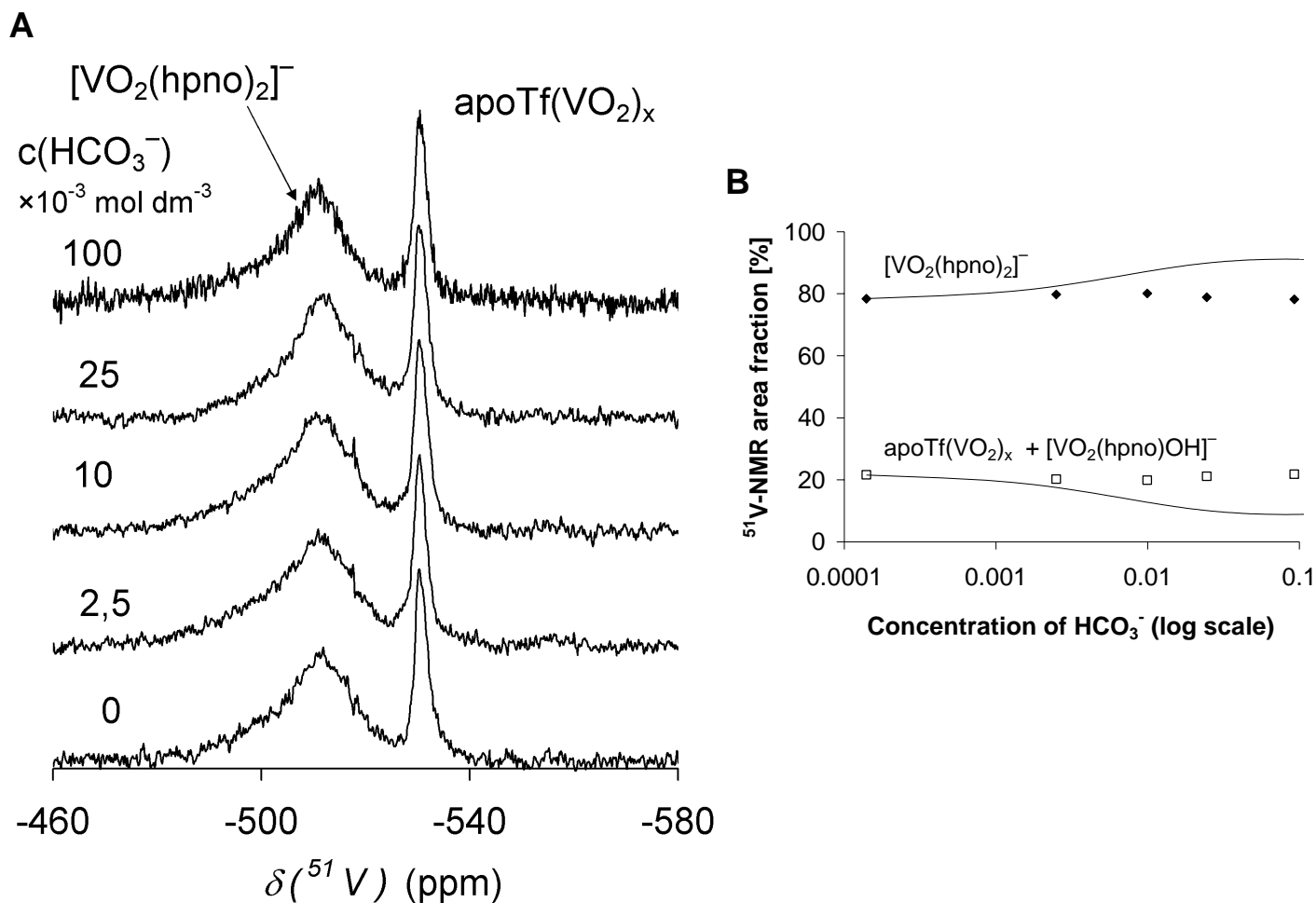
3. ^{51}V -NMR spectra



ESI Fig. S4 ^{51}V -NMR-spectra over the maltol concentration range in the vanadate-apoTf system ($c(\text{V}) = 1.2 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$, $c(\text{apoTf}) = 8.0 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$, in $0.20 \text{ mol} \cdot \text{dm}^{-3}$ HEPES buffer, $\text{pH} = 7.4$, $T = 25.0 \text{ }^\circ\text{C}$)



ESI Fig. S5 Deconvolution of the ^{51}V -NMR spectra of V^{V} -apoTf complexes using Lorentzian curves. ($c_{\text{V}^{\text{V}}} = 1.2 \cdot 10^{-3} \text{ mol} \cdot \text{dm}^{-3}$, $c_{\text{apoTf}} = 7.7 \cdot 10^{-4} \text{ mol} \cdot \text{dm}^{-3}$, in $0.20 \text{ mol} \cdot \text{dm}^{-3}$ HEPES buffer, pH = 7.4, T = 25.0 °C)



ESI Fig. S6 **A** $^{51}\text{V-NMR}$ -spectra over the HCO_3^- concentration range in vanadate-apoTf-hpno system **B** $^{51}\text{V-NMR}$ area fraction in the function of carbonate concentration. The symbols represents measured points (\blacklozenge : $[\text{VO}_2(\text{hpno})_2]^-$ \square : $\text{apoTf}(\text{VO}_2)_x + [\text{VO}_2(\text{hpno})\text{OH}]^-$), the solid lines were calculated supposing the existence of carbonate competition. ($\log K_1 = 2.66$ and $\log K_2 = 1.8$ for HCO_3^{2-} -apoTf; taken from W. R. Harris, *Biochem.*, 1985, **24**, 7412.) ($c_{\text{V}^{\circ}} = 1.0 \cdot 10^{-3} \cdot \text{mol} \cdot \text{dm}^{-3}$, $c_{\text{apoTf}} = 8.0 \cdot 10^{-4} \cdot \text{mol} \cdot \text{dm}^{-3}$, $c_{\text{hpno}} = 5.5 \cdot 10^{-3} \cdot \text{mol} \cdot \text{dm}^{-3}$ in $0.20 \text{ mol} \cdot \text{dm}^{-3}$ HEPES buffer, $\text{pH} = 7.4$, $T = 25.0 \text{ }^\circ\text{C}$)

4. Tables of stability constants

ESI Table S1 Stability constants ($\log \beta$) of vanadates (H^+/V^V); data refer to various V^V components, VO_2^+ , $H_2VO_4^-$ and HVO_4^{2-} . The data can be recalculated from each other, for calculation details see M.T. Beck and I. Nagypál, Chemistry of Complex Equilibria, Akadémiai Kiadó, Budapest, Hungary, 1990. Original data ($H_2VO_4^-$) are taken from K. Elvingson, A. González Baró, and L. Pettersson, *Inorg. Chem.* 1996, **35**, 3388.

	H^+	VO_2^+	$\log \beta$	H^+	$H_2VO_4^-$	$\log \beta$	H^+	HVO_4^{2-}	$\log \beta$
VO_2^+	0	1	0	2	1	7.00	3	1	15.17
$H_2VO_4^-$	-2	1	-7.00	0	1	0	1	1	8.17
HVO_4^{2-}	-3	1	-15.17	-1	1	-8.17	0	1	0
$V_2O_7^{4-}$	-6	2	-30.19	-2	2	-16.19	0	2	0.15
$HV_2O_7^{3-}$	-5	2	-19.85	-1	2	-5.85	1	2	10.49
$H_2V_2O_7^{2-}$	-4	2	-11.35	0	2	2.65	2	2	18.99
$V_4O_{13}^{6-}$	-10	4	-37.98	-2	4	-9.98	2	4	22.70
$HV_4O_{13}^{5-}$	-9	4	-28.63	-1	4	-0.63	3	4	32.05
$V_4O_{12}^{4-}$	-8	4	-18.76	0	4	9.24	4	4	41.92
$V_5O_{15}^{5-}$	-10	5	-23.83	0	5	11.17	5	5	52.02
$V_{10}O_{28}^{6-}$	-16	10	-19.72	4	10	50.28	14	10	131.98
$HV_{10}O_{28}^{5-}$	-15	10	-13.10	5	10	56.90	15	10	138.60
$H_2V_{10}O_{28}^{4-}$	-14	10	-8.93	6	10	61.07	16	10	142.77
$H_3V_{10}O_{28}^{3-}$	-13	10	-7.07	7	10	62.93	17	10	144.63

ESI Table S2 Stability constants ($\log \beta$) of V^V complexes [$H^+/V^V/L$; L: hpno⁻, mpno⁻, maltol⁻, dhp⁻ and pic⁻]. Data refer to different V^V component. **A:** VO_2^+ **B:** $H_2VO_4^-$ **C:** HVO_4^{2-}

A

	H^+	VO_2^+	L	hpno	mpno	maltol ^a	dhp ^b	pic ^c
$[VO_2L(OH)_2]^{2-}$	-2	1	1	-	-	-5.93	-	-
$[VO_2L(OH)]^-$	-1	1	1	4.39	3.59	4.10	6.56	2.41
$[VO_2L]^0$	0	1	1	8.93	8.52	-	12.44	7.06
$[VO_2L_2]^-$	0	1	2	15.30	12.92	16.89	19.36	12.20
$[VO_2HL_2]^0$	1	1	2	17.44	-	-	24.98	-
$[VOL_2]^+$	2	1	2	-	-	-	27.88	-

B

	H^+	$H_2VO_4^-$	L	Hpno	mpno	maltol ^a	dhp ^b	pic ^c
$[VO_2L(OH)_2]^{2-}$	0	1	1	-	-	1.07	-	-
$[VO_2L(OH)]^-$	1	1	1	11.39	10.59	11.10	13.73	9.41
$[VO_2L]^0$	2	1	1	15.93	15.52	-	19.61	14.06
$[VO_2L_2]^-$	2	1	2	22.30	19.92	23.89	26.53	19.20
$[VO_2HL_2]^0$	3	1	2	24.44	-	-	32.15	-
$[VOL_2]^+$	4	1	2	-	-	-	35.05	-

C

	H^+	HVO_4^{2-}	L	hpno	mpno	maltol ^a	dhp ^b	pic ^c
$[VO_2L(OH)_2]^{2-}$	1	1	1	-	-	9.24	-	-
$[VO_2L(OH)]^-$	2	1	1	19.56	18.76	19.27	21.96	17.58
$[VO_2L]^0$	3	1	1	24.10	23.69	-	27.84	22.23
$[VO_2L_2]^-$	3	1	2	30.47	28.09	32.06	34.76	27.37
$[VO_2HL_2]^0$	4	1	2	32.61	-	-	40.38	-
$[VOL_2]^+$	5	1	2	-	-	-	43.28	-

^a K. Elvingson, A. González Baró, and L. Pettersson, *Inorg. Chem.* 1996, **35**, 3388.

Electronic Supplementary Information for Dalton Transactions
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^b M. M. C. A. Castro, F. Avecilla, C. F. G. C. Geraldés, B. de Castro and M. Rangel, *Inorg. Chim. Acta*, 2003, **356**, 142-154

^c I. Andersson, András Gorzsás and L. Pettersson, *Dalton Trans.*, 2004, 421.

ESI Table S3 Conditional stability constants ($\log K$ and $\log \beta$) of vanadate complexes [V^V/apoTf]. Data refer to different V^V component. V₁ symbolize VO₂⁺, H₂VO₄⁻ and HVO₄²⁻ together.

	V ₁	VO ₂ ⁺	H ₂ VO ₄ ⁻	HVO ₄ ²⁻
$\log K_1$	6.03	13.90	6.10	6.87
$\log K_2$	5.46	13.33	5.53	6.30
$\log \beta_2$	11.49	27.23	11.63	13.17

ESI Table S4 Component matrix and stability constants (data refer to H_2VO_4^-) used for serum speciation calculation.

H^+	H_2VO_4^-	H_2PO_4^-	lact	cit	gly	his	apoTf	HSA	maltol	hpno	Fe(III)	Ref	$\log \beta$
-1	1	0	0	0	0	0	0	0	0	0	0	a	-8.17
-2	2	0	0	0	0	0	0	0	0	0	0	a	-16.19
-1	2	0	0	0	0	0	0	0	0	0	0	a	-5.85
0	2	0	0	0	0	0	0	0	0	0	0	a	2.65
-2	4	0	0	0	0	0	0	0	0	0	0	a	-9.98
-1	4	0	0	0	0	0	0	0	0	0	0	a	-0.63
0	4	0	0	0	0	0	0	0	0	0	0	a	9.24
0	5	0	0	0	0	0	0	0	0	0	0	a	11.17
4	10	0	0	0	0	0	0	0	0	0	0	a	50.28
5	10	0	0	0	0	0	0	0	0	0	0	a	56.9
6	10	0	0	0	0	0	0	0	0	0	0	a	61.07
7	10	0	0	0	0	0	0	0	0	0	0	a	62.93
2	1	0	0	0	0	0	0	0	0	0	0	a	7.00
-2	0	1	0	0	0	0	0	0	0	0	0	b	-18.27
-1	0	1	0	0	0	0	0	0	0	0	0	b	-6.69
1	0	1	0	0	0	0	0	0	0	0	0	b	1.85
9	14	1	0	0	0	0	0	0	0	0	0	b	89.39
10	14	1	0	0	0	0	0	0	0	0	0	b	93.93
11	14	1	0	0	0	0	0	0	0	0	0	b	96.03
-1	1	1	0	0	0	0	0	0	0	0	0	b	-5.68
0	1	1	0	0	0	0	0	0	0	0	0	b	1.51
1	1	1	0	0	0	0	0	0	0	0	0	b	5.33
2	1	1	0	0	0	0	0	0	0	0	0	b	8.37
-1	1	2	0	0	0	0	0	0	0	0	0	b	-3.9
0	1	2	0	0	0	0	0	0	0	0	0	b	2.4
1	0	0	1	0	0	0	0	0	0	0	0	c	3.65
2	2	0	2	0	0	0	0	0	0	0	0	c	19.68
3	2	0	2	0	0	0	0	0	0	0	0	c	21.61
2	3	0	2	0	0	0	0	0	0	0	0	c	22.58
2	4	0	2	0	0	0	0	0	0	0	0	c	24.59
0	1	0	1	0	0	0	0	0	0	0	0	c	0.88
1	1	0	1	0	0	0	0	0	0	0	0	c	6.92
2	1	0	1	0	0	0	0	0	0	0	0	c	10.65
1	0	0	0	1	0	0	0	0	0	0	0	d	5.61
2	0	0	0	1	0	0	0	0	0	0	0	d	9.95
3	0	0	0	1	0	0	0	0	0	0	0	d	12.89
2	1	0	0	1	0	0	0	0	0	0	0	d	14.19
3	1	0	0	1	0	0	0	0	0	0	0	d	18.25
1	2	0	0	1	0	0	0	0	0	0	0	d	12.58
2	2	0	0	1	0	0	0	0	0	0	0	d	20.06
3	2	0	0	1	0	0	0	0	0	0	0	d	25.16
6	2	0	0	2	0	0	0	0	0	0	0	d	40.69
0	1	0	0	0	1	0	0	0	0	0	0	e	1.92
0	1	0	0	0	0	1	0	0	0	0	0	f	1.72
0	1	0	0	0	0	0	1	0	0	0	0	this work.	6.1
0	2	0	0	0	0	0	1	0	0	0	0	this work.	11.63
0	1	0	0	0	0	0	0	1	0	0	0	g	1.87
1	0	0	0	0	0	0	0	0	1	0	0	a	8.44
2	1	0	0	0	0	0	0	0	2	0	0	a	23.89
1	1	0	0	0	0	0	0	0	1	0	0	a	11.10
0	1	0	0	0	0	0	0	0	1	0	0	a	1.07
1	0	0	0	0	0	0	0	0	0	1	0	this work.	5.77
1	1	0	0	0	0	0	0	0	0	1	0	this work.	11.39
2	1	0	0	0	0	0	0	0	0	1	0	this work.	15.93
2	1	0	0	0	0	0	0	0	0	2	0	this work.	22.30
3	1	0	0	0	0	0	0	0	0	2	0	this work.	24.44
0	0	0	0	0	0	0	1	0	0	0	1	h	23.54
0	0	0	0	0	0	0	1	0	0	0	2	h	46.08
0	0	0	0	0	0	0	0	0	0	1	1	i	10.53
0	0	0	0	0	0	0	0	0	0	2	1	i	19.95
0	0	0	0	0	0	0	0	0	0	3	1	i	26.97
0	0	0	0	0	0	0	0	0	1	0	1	j	11.50
0	0	0	0	0	0	0	0	0	2	0	1	j	21.40
0	0	0	0	0	0	0	0	0	3	0	1	j	29.7

^a K. Elvingson, A. González Baró, and L. Pettersson, *Inorg. Chem.* 1996, **35**, 3388. ^b I. Andersson, A. Gorzsás, C. Kerezi, I. Tóth and L. Pettersson, *Dalton Trans.*, 2005, 3658. ^c A. Gorzsás, I. Andersson and L. Pettersson *Dalton Trans.*, 2003, 2503. ^d A. Gorzsás, K. Getty, I. Andersson and L. Pettersson *Dalton Trans.*, 2004, 2873. ^e D. C. Crans, R. L. Bunch and L. A. Theisen, *J. Am. Chem. Soc.* 1989, **111**, 7597. ^f M. Fritzsche, V. Vergopoulos, D. Rehder, *Inorg. Chim. Acta* 1993, **211**, 11. ^g Calculated based on G. Heinemann, B. Fichtl, M. Mentler, W. Vogt, *J. Inorg. Biochem.* 2002, **90**, 38. ^h Calculated based on H. Sun, M. C. Cox, H. Li and P. J. Sadler, *Struct. Bonding*, 1997, **88**, 71. ⁱ Y. Li, A. Martell, *Inorg. Chim. Acta*, 1993, **214**, 103. ^j A. Stefanovic, J. Havel, L. Sommer, *Collec. Czech. Chem. Commun.*, 1968, **33**, 4198.

5. Crystallographic data

Computing details

Data collection: MACH3/PC (Enraf Nonius, 1996); cell refinement: MACH3/PC (Enraf Nonius, 1996); data reduction: PROFIT (Streltsov & Zavodnik, 1989); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX publication routines (Farrugia, 1999).

(VO₂(hpno)₂·NH₄·3H₂O)

Crystal data

C₁₀H₁₈N₃O₉V₁

M_r = 375.21

Monoclinic, C2/c

Hall symbol: -C 2yc

a = 16.1650 (19) Å

b = 9.6283 (9) Å

c = 11.8184 (17) Å

β = 121.333 (9)°

V = 1571.2 (3) Å³

Z = 4

*F*₀₀₀ = 776

D_x = 1.586 Mg m⁻³

Mo *K*α radiation, λ = 0.71073 Å

Cell parameters from 25 reflections

θ = 9.1–15.5°

μ = 0.68 mm⁻¹

T = 293 K

Prism, orange

0.35 × 0.3 × 0.25 mm

Data collection

Enraf Nonius MACH3 diffractometer

Monochromator: graphite

T = 293 K

profiled ω/2θ scans

Absorption correction: ψ scan

North A.C.T., Phillips D.C. & Mathews F.S. (1968) Acta.

Cryst. A24, 351 Number of ψ scan sets used was 5 Theta

correction was applied. Averaged transmission function

was used. Fourier smoothing - Window value 5

*T*_{min} = 0.786, *T*_{max} = 0.842

4140 measured reflections

1607 independent reflections

1582 reflections with *I* > 2σ(*I*)

*R*_{int} = 0.036

θ_{max} = 26.5°

θ_{min} = 3.6°

h = -20→19

k = -10→12

l = -14→10

3 standard reflections

every 99 reflections

intensity decay: 2%

Refinement

Refinement on *F*²

Least-squares matrix: full

R[*F*² > 2σ(*F*²)] = 0.041

wR(*F*²) = 0.117

S = 1.20

1607 reflections

141 parameters

8 restraints

Primary atom site location: structure-invariant direct

Secondary atom site location: difference Fourier map

Hydrogen site location: inferred from neighbouring sites

H atoms treated by a mixture of independent and constrained refinement

w = 1/[σ²(*F*_o²) + (0.0438*P*)² + 4.0866*P*] where *P* = (*F*_o² + 2*F*_c²)/3

(Δ/σ)_{max} = 0.009

Δρ_{max} = 0.45 e Å⁻³

Δρ_{min} = -0.37 e Å⁻³

Extinction correction: none

methods

Special details

Geometry. All e.s.d.'s (except the e.s.d. in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell e.s.d.'s are taken into account individually in the estimation of e.s.d.'s in distances, angles and torsion angles; correlations between e.s.d.'s in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell e.s.d.'s is used for estimating e.s.d.'s involving l.s. planes.

Refinement. Refinement of F^2 against ALL reflections. The weighted R -factor wR and goodness of fit S are based on F^2 , conventional R -factors R are based on F , with F set to zero for negative F^2 . The threshold expression of $F^2 > \sigma(F^2)$ is used only for calculating R -factors(gt) etc. and is not relevant to the choice of reflections for refinement. R -factors based on F^2 are statistically about twice as large as those based on F , and R -factors based on ALL data will be even larger.

Table S5 Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (\AA^2)

	x	y	z	$U_{\text{iso}}^*/U_{\text{eq}}$	Occ.(<1)
C2	0.37150 (17)	0.0135 (3)	0.7816 (2)	0.0274 (5)	
C3	0.3238 (2)	-0.0644 (3)	0.8303 (3)	0.0409 (7)	
H3	0.3594	-0.1156	0.9078	0.049*	
C4	0.2247 (2)	-0.0652 (3)	0.7640 (3)	0.0432 (7)	
H4	0.1933	-0.117	0.7972	0.052*	
C5	0.17008 (19)	0.0106 (3)	0.6472 (3)	0.0385 (6)	
H5	0.1028	0.0092	0.6024	0.046*	
C6	0.21662 (18)	0.0863 (3)	0.5999 (3)	0.0307 (5)	
H6	0.1814	0.1375	0.5223	0.037*	
N1	0.31476 (14)	0.0867 (2)	0.6668 (2)	0.0252 (4)	
N2	0.5515 (14)	-0.212 (2)	0.965 (2)	0.093 (6)	0.5
O1	0.49436 (14)	0.3049 (2)	0.8555 (2)	0.0360 (5)	
O2	0.36162 (12)	0.16278 (19)	0.62129 (16)	0.0274 (4)	
O1W	0.5	-0.4072 (4)	0.75	0.105 (2)	
O3	0.46346 (13)	0.0261 (2)	0.83392 (18)	0.0338 (4)	
O2W	0.2684 (5)	-0.2811 (9)	0.5549 (8)	0.081 (2)	0.5
O3W	0.5640 (5)	-0.2263 (7)	0.9561 (7)	0.0239 (10)	0.5
V1	0.5	0.20040 (6)	0.75	0.0227 (2)	
H11	0.5	-0.499 (2)	0.75	0.027*	
H12	0.544 (3)	-0.343 (5)	0.773 (6)	0.027*	0.5
H13	0.310 (4)	-0.353 (4)	0.593 (6)	0.027*	0.5
H14	0.225 (5)	-0.226 (7)	0.489 (6)	0.027*	0.5
H21	0.532 (5)	-0.137 (5)	0.918 (6)	0.027*	0.5
H22	0.552 (5)	-0.239 (7)	1.035 (4)	0.027*	0.5
H23	0.547 (3)	-0.275 (3)	0.916 (3)	0.027*	
H24	0.6040 (19)	-0.219 (4)	0.969 (4)	0.027*	

Table S6 Atomic displacement parameters (Å^2)

	U^{11}	U^{22}	U^{33}	U^{12}	U^{13}	U^{23}
C2	0.0246(11)	0.0306(12)	0.0246(12)	-0.0020(9)	0.0111(10)	0.0036(9)
C3	0.0381(15)	0.0456(16)	0.0383(15)	-0.0049(13)	0.0195(13)	0.0123(13)
C4	0.0369(15)	0.0482(17)	0.0520(17)	-0.0096(13)	0.0283(14)	0.0063(14)
C5	0.0252(13)	0.0423(15)	0.0484(16)	-0.0053(11)	0.0195(12)	-0.0008(13)
C6	0.0214(11)	0.0340(13)	0.0308(13)	-0.0006(10)	0.0094(10)	0.0008(10)
N1	0.0213(9)	0.0291(10)	0.0247(10)	-0.0028(8)	0.0116(8)	0.0010(8)
N2	0.100(10)	0.107(11)	0.102(10)	0.038(7)	0.074(8)	-0.005(7)
O1	0.0294(9)	0.0426(11)	0.0372(10)	0.0027(8)	0.0182(8)	-0.0085(8)
O2	0.0215(8)	0.0369(10)	0.0240(8)	-0.0016(7)	0.0119(7)	0.0078(7)
O1W	0.204(7)	0.033(2)	0.089(3)	0	0.084(4)	0
O3	0.0231(9)	0.0421(11)	0.0312(9)	0.0001(8)	0.0106(7)	0.0114(8)
O2W	0.066(4)	0.099(6)	0.096(5)	0.007(3)	0.057(4)	0.006(4)
O3W	0.029(2)	0.026(2)	0.023(2)	0.016(2)	0.017(2)	0.0018(17)
V1	0.0188(3)	0.0256(3)	0.0250(3)	0	0.0122(2)	0

Table S7 Geometric parameters (\AA , $^\circ$)

C2—O3	1.285 (3)	O1—V1	1.6412 (19)
C2—N1	1.373 (3)	O2—V1	1.9773 (17)
C2—C3	1.397 (4)	O1W—H11	0.881 (19)
C3—C4	1.370 (4)	O1W—H12	0.87 (2)
C3—H3	0.93	O3—V1	2.1817 (19)
C4—C5	1.397 (4)	O2W—O2W ⁱ	1.262 (16)
C4—H4	0.93	O2W—H13	0.91 (2)
C5—C6	1.359 (4)	O2W—H14	0.90 (2)
C5—H5	0.93	O3W—H21	0.98 (4)
C6—N1	1.356 (3)	O3W—H22	1.06 (4)
C6—H6	0.93	O3W—H23	0.62 (3)
N1—O2	1.350 (3)	O3W—H24	0.59 (2)
N2—H21	0.86 (2)	V1—O1 ⁱⁱ	1.6411 (19)
N2—H22	0.86 (2)	V1—O2 ⁱⁱ	1.9773 (17)
N2—H23	0.816 (19)	V1—O3 ⁱⁱ	2.1817 (19)
N2—H24	0.833 (19)		
O3—C2—N1	116.0 (2)	C2—O3—V1	111.86 (15)
O3—C2—C3	126.9 (2)	O2W ⁱ —O2W—H13	135 (4)
N1—C2—C3	117.1 (2)	O2W ⁱ —O2W—H14	25 (5)
C4—C3—C2	120.0 (3)	H13—O2W—H14	158 (7)
C4—C3—H3	120	H21—O3W—H22	102 (5)
C2—C3—H3	120	H21—O3W—H23	113 (5)
C3—C4—C5	120.8 (3)	H22—O3W—H23	112 (5)
C3—C4—H4	119.6	H21—O3W—H24	106 (5)
C5—C4—H4	119.6	H22—O3W—H24	118 (5)
C6—C5—C4	119.1 (2)	H23—O3W—H24	106 (5)
C6—C5—H5	120.4	O1 ⁱⁱ —V1—O1	104.42 (15)
C4—C5—H5	120.4	O1 ⁱⁱ —V1—O2 ⁱⁱ	102.08 (9)
N1—C6—C5	119.5 (2)	O1—V1—O2 ⁱⁱ	90.88 (8)
N1—C6—H6	120.3	O1 ⁱⁱ —V1—O2	90.88 (8)
C5—C6—H6	120.3	O1—V1—O2	102.08 (9)
O2—N1—C6	119.9 (2)	O2 ⁱⁱ —V1—O2	158.89 (11)
O2—N1—C2	116.56 (19)	O1 ⁱⁱ —V1—O3	162.20 (9)
C6—N1—C2	123.5 (2)	O1—V1—O3	89.48 (9)
H21—N2—H22	134 (7)	O2 ⁱⁱ —V1—O3	88.55 (7)
H21—N2—H23	107 (6)	O2—V1—O3	75.13 (7)
H22—N2—H23	114 (7)	O1 ⁱⁱ —V1—O3 ⁱⁱ	89.48 (9)
H21—N2—H24	97 (6)	O1—V1—O3 ⁱⁱ	162.20 (9)
H22—N2—H24	115 (6)	O2 ⁱⁱ —V1—O3 ⁱⁱ	75.13 (7)
H23—N2—H24	72 (4)	O2—V1—O3 ⁱⁱ	88.55 (7)
N1—O2—V1	115.95 (13)	O3—V1—O3 ⁱⁱ	79.40 (11)
H11—O1W—H12	135 (4)		

Symmetry codes: (i) $-x+1/2, -y-1/2, -z+1$; (ii) $-x+1, y, -z+3/2$.

Table S8 *Hydrogen-bond geometry* (Å, °)

D—H···A	D—H	H···A	D···A	D—H···A
O1W—H11···O1 ⁱ	0.881 (19)	2.293 (17)	3.061 (4)	145.6 (3)
O1W—H11···O1 ⁱⁱ	0.881 (19)	2.293 (17)	3.061 (4)	145.6 (3)
O1W—H12···N2	0.87 (2)	2.54 (6)	2.917 (19)	107 (5)
O1W—H12···O3W	0.87 (2)	2.30 (6)	2.723 (8)	110 (5)
N2—H21···O3	0.86 (2)	1.88 (4)	2.72 (2)	163 (7)
N2—H22···O1 ⁱⁱⁱ	0.86 (2)	1.91 (4)	2.73 (2)	160 (6)
N2—H23···O1W	0.816 (19)	2.12 (2)	2.917 (19)	164 (4)
N2—H24···O2W ^{iv}	0.833 (19)	2.30 (3)	3.09 (2)	159 (4)
N2—H24···O2W ^v	0.833 (19)	2.30 (2)	3.115 (17)	167 (4)
O2W—H13···N2 ^v	0.91 (2)	3.00 (6)	3.115 (17)	89 (4)
O2W—H14···N2 ^{vi}	0.90 (2)	2.74 (8)	3.09 (2)	105 (6)
O2W—H14···O3W ^{vi}	0.90 (2)	2.47 (8)	2.877 (10)	108 (6)
O2W—H13···O3W ^v	0.91 (2)	2.69 (6)	2.829 (11)	89 (4)
O3W—H23···O1W	0.62 (3)	2.12 (2)	2.723 (8)	164 (4)
O3W—H24···O2W ^v	0.59 (2)	2.30 (2)	2.829 (11)	151 (5)

Symmetry codes: (i) $-x+1, y-1, -z+3/2$; (ii) $x, y-1, z$; (iii) $-x+1, -y, -z+2$; (iv) $x+1/2, -y-1/2, z+1/2$; (v) $-x+1, y, -z+3/2$; (vi) $x-1/2, -y-1/2, z-1/2$.

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