ELECTRONIC SUPPLEMENTARY INFORMATION (ESI)

On the Prediction of the ^{51}V Hyperfine Coupling Constants in V^{IV}O Complexes through DFT Methods

Giovanni Micera[a] and Eugenio Garribba*[a]

[a] *Department of Chemistry, Università of Sassari, Via Vienna 2, I-07100 Sassari, Italy. E-mail: garribba@uniss.it*

Experimental and Computational Section

Theory Background

Table S1. Ligands and V^{IV}O complexes studied.

Scheme S1. Structure of the V^{IV}O complexes studied.

Table S2. Calculated EPR parameters of **1-22** V^{IV}O complexes at the BHandHLYP/6-311g(d,p) level.

Table S3. Calculated EPR parameters of **1-22** V^{IV}O complexes at the BHandH/6-311g(d,p) level.

Table S4. Calculated EPR parameters of **1-22** V^{IV}O complexes at the B3LYP/6-311g(d,p) level.

Table S5. Calculated EPR parameters of **1-22** V^{IV}O complexes at the B3P86/6-311g(d,p) level.

Table S6. Calculated EPR parameters of **1-22** V^{IV}O complexes at the B3PW91/6-311g(d,p) level.

Table S7. Calculated EPR parameters of **1-22** V^{IV}O complexes at the BHandHLYP/6-311+g level.

Table S8. Calculated EPR parameters of **1-22** V^{IV}O complexes at the BHandHLYP/6-311g level.

Table S9. Calculated EPR parameters of **1-22** V^{IV}O complexes at the BHandHLYP/6-31g level.

References

Experimental and Computational Section

DFT calculations

All the calculations presented in this paper were performed using Gaussian 03 program (revision C.02)[1] and DFT methods.[2] The hybrid exchange-correlation functional B3P86,[3,4] B3PW91,[3,5] and B3LYP,[3,6] and half-and-half functionals BHandH and BHandHLYP were incorporated in the Gaussian 03 software.

The geometry of the **1-22** $V^{IV}O$ complexes was firstly pre-optimized at the B3LYP/sto-3g level and further optimized at the B3LYP/6-311g level of theory. For all the structures, minima were verified through frequency calculations.

The optimized structures were used to calculate the ^{51}V hyperfine coupling constants (A_{iso}, A_x, A_y and A_z) at several levels of theory: i) by fixing the basis set and changing the functional (B3LYP/6-311g(d,p), B3P86/6-311g(d,p), B3PW91/6-311g(d,p), BHandH/6-311g(d,p), BHandHLYP/6-311g(d,p)), and ii) by fixing the functional and changing the basis set (BHandHLYP/6-31g, BHandHLYP/6-311g, BHandHLYP/6-311+g, BHandHLYP/6-311g(d,p)).

A_z value (as well as A_x and A_y) is negative, but in the literature is usually reported its absolute value. In order to avoid confusion, the absolute value of A_z^{calcd} and A_z^{exptl} is indicated in the manuscript as $|A_z|^{calcd}$ and $|A_z|^{exptl}$. Therefore, the absolute percentage deviation from the experimental value is calculated as: $100 \times [(|A_z|^{calcd} - |A_z|^{exptl})/|A_z|^{exptl}]$ (Tables S2-S9 of ESI).

EPR measurements

The ^{51}V hyperfine coupling constants were taken from the data in the literature.[7-23] When this was not possible, anisotropic EPR spectra were recorded on aqueous solutions with an X-band (9.15 GHz) Varian E-9 spectrometer at 120 K. As usual for low temperature measurements, a few drops of DMSO were added to the samples to ensure good glass formation. The experimental conditions (pH and ligand to metal molar ratio) were chosen to obtain the maximum extent of formation of the $V^{IV}O$ complexes under examination. Experimental values for A_x, A_y and A_z were calculated by simulating the spectra with the computer program Bruker WinEPR SimFonia.[24]

Chemicals

All the chemicals used were products of puriss. quality. $V^{IV}O$ solutions were prepared with $VOSO_4 \cdot 5H_2O$ by following the procedure described in the literature.[25] All operations were performed under a purified argon atmosphere in order to avoid oxidation of $V^{IV}O$ ion.

Theory Background

The "additivity rule"

For an inorganic chemist it is of fundamental importance correlate EPR parameters (**g**-factor and ^{51}V hyperfine coupling constant A) with the particular electronic and geometric structure of the complex under examination. Wüthrich has firstly pointed out that hyperfine coupling constant (A value) between the unpaired electron and the nucleus of ^{51}V in tetragonal complexes of the $V^{IV}O$ ion is particularly sensitive to the donors coordinated in its equatorial plane.[26] Subsequently, Chasteen developed this idea and introduced the "additivity rule", an empirical rule affirming that the values of the ^{51}V isotropic hyperfine coupling constant measured for a $V^{IV}O$ complex in solution at room temperature (A_{iso}), and ^{51}V anisotropic hyperfine coupling constant along the z axis measured for a $V^{IV}O$ complex on a polycrystalline powder or a frozen sample can be calculated from the sum of the contributions of each equatorial donor function:[7]

$$A_{iso} = \sum_{i=1}^{4} A_{iso}(\text{donor } i) = A_{iso}(\text{donor } 1) + A_{iso}(\text{donor } 2) + A_{iso}(\text{donor } 3) + A_{iso}(\text{donor } 4) \qquad (1)$$

$$A_z = \sum_{i=1}^{4} A_z(\text{donor } i) = A_z(\text{donor } 1) + A_z(\text{donor } 2) + A_z(\text{donor } 3) + A_z(\text{donor } 4) \qquad (2)$$

Recently, the "additivity rule" has been improved by Pecoraro and co-workers.[27] Additions or corrections about the contribution of CO,[28] $N_{imidazole}$,[14,27] Cl^- and SCN^-,[29] COO^-,[30] and N_{imino}[31] appeared in these last years in the literature.

The "additivity rule" allows to correlate A_{iso} or A_z to the number and types of ligands in the equatorial plane of $V^{IV}O$ ion and has been proved and accepted in a large number of works.[27] The contribution to A_{iso} or A_z is approximately inverse to the electron donor capacity of the ligand, with the most donating ligands contributing the least to the coupling constant. Experimental A_{iso} or A_z fall in the range of ~$3x10^{-4}$ cm^{-1} with respect to the calculated value.[7,27] Actually, the analysis of the anisotropic EPR spectra is preferred to that of isotropic spectra because allows to get more detailed information on: i) the symmetry and the coordination geometry of the $V^{IV}O$ species; ii) the identity of the equatorial ligands because A_z value is more sensitive to equatorial donors than A_{iso};[7] iii) the presence of minor species in solution, which is not detectable from the examination of the isotropic spectrum.

The ^{51}V hyperfine coupling constant

$V^{IV}O$ ion has a d^1 electronic configuration with one unpaired electron. The hyperfine coupling constatn in an EPR spectrum arises from the interaction between the spin angular momentum of the electron ($S = 1/2$) with the spin angular momentum of ^{51}V nucleus ($I = 7/2$, 99.8% natural abundance).

In the first-order approximation, the vanadium hyperfine coupling tensor *A* has one isotropic contribution from the Fermi contact (A_{iso}) and another from the anisotropic or dipolar hyperfine interaction, expressed by tensor **T**.[32]

$$A = A_{iso}\mathbf{1} + \mathbf{T} \tag{3}$$

Here **1** is the unit tensor; A_{iso} and the components T_{jk} of the tensor **T** are given by the following equations:

$$A_{iso} = \frac{4\pi}{3} g_e g_N \beta_e \beta_N \langle S_z \rangle^{-1} \rho^{\alpha-\beta} \tag{4}$$

$$T_{jk} = \frac{1}{2} g_e g_N \beta_e \beta_N \langle S_z \rangle^{-1} \sum_{k,l} P_{k,l}^{\alpha-\beta} \langle \Phi_k | \frac{\mathbf{r}^2 \delta_{jk} - 3\mathbf{r}_j\mathbf{r}_k}{\mathbf{r}^5} | \Phi_l \rangle \tag{5}$$

g_e is the *g*-value of the free electron (2.0023), g_N the nuclear *g*-value, β_e the Bohr magneton, β_N the nuclear magneton, $\langle S_z \rangle$ the expectation value of the electronic spin on the z axis, $\rho^{\alpha-\beta}$ the spin density at the nucleus, $P_{k,l}^{\alpha-\beta}$ the spin density matrix, and **r** the distance between the unpaired electron and the nucleus.

The tensor **T** is always traceless and may be brought to diagonal form: T_x, T_y and T_z are the elements of the diagonilized tensor:

$$T_x + T_y + T_z = 0 \tag{6}$$

The values of the ^{51}V anisotropic hyperfine coupling constants along the x, y and z axes result to be:

$$A_x = A_{iso} + T_x \tag{7}$$

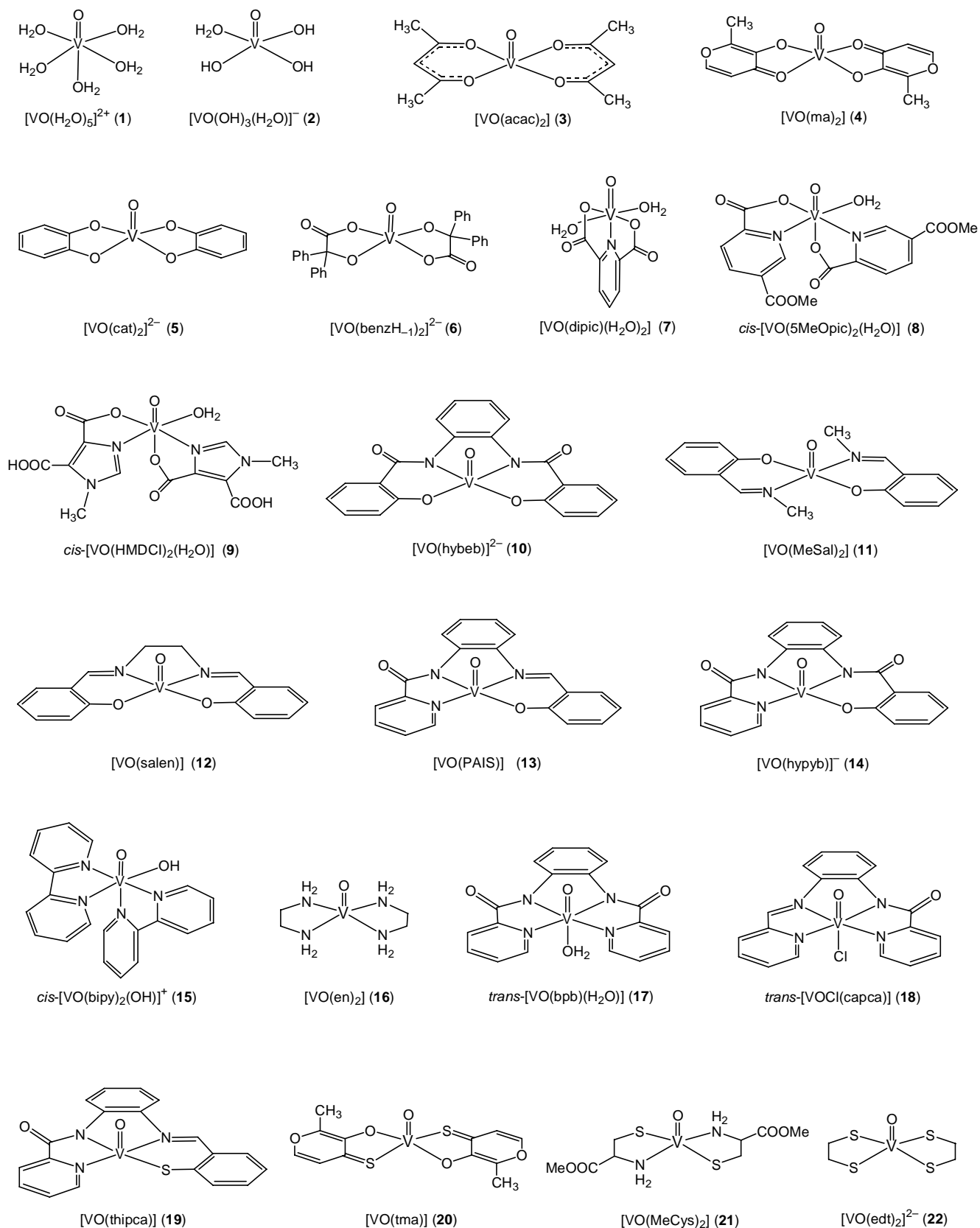$$A_y = A_{iso} + T_y \tag{8}$$

$$A_z = A_{iso} + T_z \tag{9}$$

The value of A_z in eq. 9 can be calculated empirically with the "additivity rule" by use of eq. 2. From eqs. 6-9 results that the value of A_{iso} is:

$$A_{iso} = \frac{1}{3}\left(A_x + A_y + A_z \right) \tag{10}$$

Table S1 Ligands and $V^{IV}O$ complexes studied

	Ligand	Complex	Coordination	Charge	Ref.[a]
1	H_2O	$[VO(H_2O)_5]^{2+}$	$VO(O_5)$	+2	
2	OH^-	$[VO(OH)_3(H_2O)]^-$	$VO(O_4)$	-1	
3	Acetylacetone (Hacac)	$[VO(acac)_2]$	$VO(O_4)$	0	33
4	Maltol (Hma)	$[VO(ma)_2]$	$VO(O_4)$	0	34
5	Catechol (H_2cat)	$[VO(cat)_2]^{2-}$	$VO(O_4)$	-2	35
6	Benzilic acid (Hbenz)	$[VO(benzH_{-1})_2]^{2-}$	$VO(O_4)$	-2	36
7	2,6-Pyridinedicarboxylic acid (H_2dipic)	$[VO(dipic)(H_2O)_2]$	$VO(NO_4)$	0	37
8	5-(Methoxycarbonyl)pyridine-2-carboxylic acid (5MeOpicH)	cis-$[VO(5MeOpic)_2(H_2O)]$	$VO(N_2O_3)$	0	13
9	1-Methyl-5-carboxyimidazole-4-carboxylic acid (H_2MDCI)	cis-$[VO(HMDCI)_2(H_2O)]$	$VO(N_2O_3)$	0	14
10	1,2-Bis(2-hydroxybenzamido)benzene (H_4hybeb)	$[VO(hybeb)]^{2-}$	$VO(N_2O_2)$	-2	15
11	N-methylsalicylaldimine (MeSalH)	$[VO(MeSal)_2]$	$VO(N_2O_2)$	0	16
12	N,N'-ethylenebis(salicylideneimine) (H_2salen)	$[VO(salen)]$	$VO(N_2O_2)$	0	38
13	(N-(2-salicylideneamino)phenyl)pyridine-2-carboxamide (H_2PAIS)	$[VO(PAIS)]$	$VO(N_3O)$	0	18
14	1-(2-Hydroxybenzamido)-2-(2-pyridine-carboxamido)benzene (H_3hypyb)	$[VO(hypyb)]^-$	$VO(N_3O)$	-1	15,19
15	2,2'-bipyridine (bipy)	cis-$[VO(bipy)_2(OH)]^+$	$VO(N_4O)$	+1	20
16	Ethylenediamine (en)	$[VO(en)_2]^{2+}$	$VO(N_4)$	+2	
17	1,2-Bis(2-carboxamidopyridyl)benzene (H_2bpb)	$trans$-$[VO(bpb)(H_2O)]$	$VO(N_4O)$	0	39
18	N-(2-((2-pyridylmethylene)amino)-phenyl)pyridine-2-carboxamide (Hcapca)	$trans$-$[VOCl(capca)]$	$VO(N_4Cl)$	0	21
19	N-(2-((2-thiophenylmethylene)amino)-phenyl)pyridine-2-carboxamido ($H_2thipca$)	$[VO(thipca)]$	$VO(N_3S)$	0	15
20	2-Methyl-3-oxy-4H-pyran-4-thione (Htma)	$[VO(tma)_2]$	$VO(O_2S_2)$	0	40
21	L-Methylcysteinato (MeCysH)	$[VO(MeCys)_2]$	$VO(N_2S_2)$	0	22
22	Ethane-1,2-dithiolate (H_2edt)	$[VO(edt)_2]^{2-}$	$VO(S_4)$	-2	41

[a] X-ray structures reported.

$[VO(H_2O)_5]^{2+}$ (**1**) $[VO(OH)_3(H_2O)]^-$ (**2**) $[VO(acac)_2]$ (**3**) $[VO(ma)_2]$ (**4**)

$[VO(cat)_2]^{2-}$ (**5**) $[VO(benzH_{-1})_2]^{2-}$ (**6**) $[VO(dipic)(H_2O)_2]$ (**7**)   cis-$[VO(5MeOpic)_2(H_2O)]$ (**8**)

cis-$[VO(HMDCI)_2(H_2O)]$ (**9**) $[VO(hybeb)]^{2-}$ (**10**) $[VO(MeSal)_2]$ (**11**)

$[VO(salen)]$ (**12**) $[VO(PAIS)]$ (**13**) $[VO(hypyb)]^-$ (**14**)

cis-$[VO(bipy)_2(OH)]^+$ (**15**) $[VO(en)_2]$ (**16**)   trans-$[VO(bpb)(H_2O)]$ (**17**)   trans-$[VOCl(capca)]$ (**18**)

$[VO(thipca)]$ (**19**) $[VO(tma)]$ (**20**) $[VO(MeCys)_2]$ (**21**) $[VO(edt)_2]^{2-}$ (**22**)

Scheme S1 Structure of the $V^{IV}O$ complexes studied (the abbreviations are those listed in Table S1).

6

Table S2 Calculated (at the BHandHLYP/6-311g(d,p) level) and experimental EPR parameters of **1-22** $V^{IV}O$ complexes[a,b]

	A_{iso}^{calcd}	T_x^{calcd}	T_y^{calcd}	T_z^{calcd}	A_x^{calcd}	A_y^{calcd}	A_z^{calcd}	A_x^{exptl}	A_y^{exptl}	A_z^{exptl}	Dev. (%)[c]	Ref.
1	-120.8	32.6	33.1	-65.7	-88.2	-87.7	-186.5	-68.2	-68.2	-182.6	+2.1	7
2	-91.7	35.5	36.1	-71.6	-56.2	-55.6	-163.3	-50.0	-50.0	-161.7	+1.0	7
3	-98.3	31.9	38.0	-69.9	-66.4	-60.3	-168.2	-55	-60	-166.5	+1.0	8
4	-92.7	30.2	38.8	-69.0	-62.5	-53.9	-161.7	-48.3	-57.4	-161.1	+0.4	9
5	-79.3	28.8	40.6	-69.4	-50.5	-38.7	-148.7	-45.1[d]	-45.1[d]	-154.1	-3.5	10
6	-77.2	29.0	40.4	-69.4	-48.2	-36.8	-146.6	-39.4	-51.6	-152.1	-3.6	11
7	-112.9	32.5	33.1	-65.6	-80.4	-79.8	-178.5	-68.3	-68.3	-176.3	+1.2	12
8	-98.8	32.3	34.6	-66.9	-66.5	-64.2	-165.7	e	e	-168	-1.4	13
9	-99.0	32.5	34.7	-67.2	-66.5	-64.3	-166.2	-62.1	-62.1	-171.0	-2.8	14
10	-88.2	32.2	37.1	-69.3	-56.0	-51.1	-157.5	-53.6	-53.6	-156.2	+0.8	15
11	-89.2	30.0	38.2	-68.2	-59.2	-51.0	-157.4	-53.1	-60.0	-161.0	-2.2	16
12	-90.8	30.7	37.9	-68.6	-60.1	-52.9	-159.4	-59.2	-59.2	-159.3	+0.1	17
13	-92.8	31.7	36.6	-68.3	-61.1	-56.2	-161.1	-45.0	-54.0	-154.0	+4.6	18
14	-89.3	33.7	34.8	-68.5	-55.6	-54.5	-157.8	-52.2	-52.2	-156.1	+1.1	19
15	-91.3	27.7	37.9	-65.6	-63.6	-53.4	-156.9	-53	-64	-163	-3.7	20
16	-95.1	33.4	35.5	-68.9	-61.7	-59.6	-164.0	-45.5	-45.5	-160.3	+2.3	7
17	-80.6	26.8	39.1	-65.9	-53.8	-41.5	-146.5	-51	-37	-145	+1.0	18
18	-84.6	23.1	40.6	-63.7	-61.5	-44.0	-148.3	-53.0	-49.0	-145.0	+2.3	21
19	-90.0	33.4	33.6	-67.0	-56.6	-56.4	-157.0	-52.3	-52.3	-150.6	+4.2	15
20	-89.8	29.9	37.8	-67.7	-59.9	-52.0	-157.5	-52.0	-51.5	-153.0	+5.5	22
21	-86.1	32.2	34.8	-67.0	-53.9	-51.3	-153.1	-49.3	-49.3	-145.1	+2.9	d,f
22	-82.2	32.5	34.8	-67.3	-49.7	-47.4	-149.5	-39.7	-39.7	-133.8	+11.7	23

[a] Geometry optimized at the B3LYP/6-311g level. [b] All the parameters given in 10^{-4} cm^{-1}. [c] Percentage deviation from the absolute value of A_z^{exptl}. [d] Values measured in this work. [e] Value not reported. [f] Values measured for the bis chelated complex formed by cysteamine, which binds $V^{IV}O$ ion with [2x(NH$_2$, S$^-$)] donor set.

Table S3 Calculated (at the BHandH/6-311g(d,p) level) and experimental EPR parameters of **1-22** $V^{IV}O$ complexes[a,b]

	A_{iso}^{calcd}	T_x^{calcd}	T_y^{calcd}	T_z^{calcd}	A_x^{calcd}	A_y^{calcd}	A_z^{calcd}	A_x^{exptl}	A_y^{exptl}	A_z^{exptl}	Dev. (%)[c]	Ref.
1	-127.3	30.9	31.9	-62.8	-96.4	-95.4	-190.1	-68.2	-68.2	-182.6	+4.1	7
2	-90.8	35.1	35.9	-71.0	-55.7	-54.9	-161.8	-50.0	-50.0	-161.7	+0.1	7
3	-98.0	31.4	38.1	-69.5	-66.6	-59.9	-167.5	-55	-60	-166.5	+0.6	8
4	-92.4	29.6	38.9	-68.5	-62.8	-53.5	-160.9	-48.3	-57.4	-161.1	-0.1	9
5	-76.8	27.7	40.7	-68.4	-49.1	-36.1	-145.2	-45.1[d]	-45.1[d]	-154.1	-5.8	10
6	-75.5	28.3	40.4	-68.7	-47.2	-35.1	-144.2	-39.4	-51.6	-152.1	-5.2	11
7	-111.5	32.3	32.6	-64.9	-79.2	-78.9	-176.4	-68.3	-68.3	-176.3	+0.1	12
8	-97.7	32.0	34.2	-66.2	-65.7	-63.5	-163.9	*e*	*e*	-168	-2.4	13
9	-98.1	32.2	34.3	-66.5	-65.9	-63.8	-164.6	-62.1	-62.1	-171.0	-3.7	14
10	-87.3	31.7	36.9	-68.6	-55.6	-50.4	-155.9	-53.6	-53.6	-156.2	-0.2	15
11	-87.8	29.4	38.1	-67.5	-58.4	-49.7	-155.3	-53.1	-60.0	-161.0	-3.5	16
12	-89.6	30.1	37.8	-67.9	-59.5	-51.8	-157.5	-59.2	-59.2	-159.3	-1.1	17
13	-91.7	31.3	36.3	-67.6	-60.4	-55.4	-159.3	-45.0	-54.0	-154.0	+3.4	18
14	-88.5	33.4	34.4	-67.8	-55.1	-54.1	-156.3	-52.2	-52.2	-156.1	+0.1	19
15	-89.9	26.8	37.6	-64.4	-63.1	-52.3	-154.3	-53	-64	-163	-5.3	20
16	-94.2	33.0	35.4	-68.4	-61.2	-58.8	-162.6	-45.5	-45.5	-160.3	+1.4	7
17	-79.7	26.0	39.1	-65.1	-53.7	-40.6	-144.8	-51	-37	-145	-0.1	18
18	-83.6	22.1	40.6	-62.7	-61.5	-43.0	-146.3	-53.0	-49.0	-145.0	+0.9	21
19	-89.9	33.1	33.3	-66.4	-56.8	-56.6	-156.3	-52.3	-52.3	-150.6	+3.8	15
20	-88.5	29.4	37.7	-67.1	-59.1	-50.8	-155.6	-52.0	-51.5	-153.0	+1.7	22
21	-86.5	31.9	34.7	-66.6	-54.6	-51.8	-153.1	-49.3	-49.3	-145.1	+5.5	*d,f*
22	-83.5	32.2	34.7	-66.9	-51.3	-48.8	-150.4	-39.7	-39.7	-133.8	+12.4	23

[a] Geometry optimised at the B3LYP/6-311g level. [b] All the parameters given in 10^{-4} cm^{-1}. [c] Percentage deviation from the absolute value of A_z^{exptl}. [d] Values measured in this work. [e] Value not reported. [f] Values measured for the bis chelated complex formed by cysteamine, which binds $V^{IV}O$ ion with [2x(NH$_2$, S$^-$)] donor set.

Table S4 Calculated (at the B3LYP/6-311g(d,p) level) and experimental EPR parameters of **1-22** $V^{IV}O$ complexes[a,b]

	A_{iso}^{calcd}	T_x^{calcd}	T_y^{calcd}	T_z^{calcd}	A_x^{calcd}	A_y^{calcd}	A_z^{calcd}	A_x^{exptl}	A_y^{exptl}	A_z^{exptl}	Dev. (%)[c]	Ref.
1	-97.6	31.9	32.1	-64.0	-65.7	-65.5	-161.6	-68.2	-68.2	-182.6	-11.5	7
2	-74.0	33.7	34.3	-68.0	-40.3	-39.7	-142.0	-50.0	-50.0	-161.7	-12.2	7
3	-77.3	29.5	37.1	-66.6	-47.8	-40.2	-143.9	-55	-60	-166.5	-13.6	8
4	-69.3	27.4	38.2	-65.6	-41.9	-31.1	-134.9	-48.3	-57.4	-161.1	-16.3	9
5	-59.2	25.8	39.9	-65.7	-33.4	-19.3	-124.9	-45.1[d]	-45.1[d]	-154.1	-18.9	10
6	-57.3	26.0	39.5	-65.5	-31.3	-17.8	-122.8	-39.4	-51.6	-152.1	-19.3	11
7	-89.7	30.9	32.0	-62.9	-58.8	-57.7	-152.6	-68.3	-68.3	-176.3	-13.4	12
8	-79.1	30.6	32.7	-63.3	-48.5	-46.4	-142.4	e	e	-168	-15.2	13
9	-79.0	31.1	32.9	-64.0	-47.9	-46.1	-143.0	-62.1	-62.1	-171.0	-16.4	14
10	-70.7	30.0	35.6	-65.6	-40.7	-35.1	-136.3	-53.6	-53.6	-156.2	-12.7	15
11	-69.3	27.6	36.8	-64.4	-41.7	-32.5	-133.7	-53.1	-60.0	-161.0	-17.0	16
12	-70.9	28.0	36.6	-64.6	-42.9	-34.3	-135.5	-59.2	-59.2	-159.3	-14.9	17
13	-73.9	29.7	35.0	-64.7	-44.2	-38.9	-138.6	-45.0	-54.0	-154.0	-10.0	18
14	-72.0	32.0	32.8	-64.8	-40.0	-39.2	-136.8	-52.2	-52.2	-156.1	-12.4	19
15	-69.7	24.4	35.7	-60.1	-45.3	-34.0	-129.8	-53	-64	-163	-20.4	20
16	-74.1	31.5	34.3	-65.8	-42.6	-39.8	-139.9	-45.5	-45.5	-160.3	-12.7	7
17	-60.3	24.2	38.5	-62.7	-36.1	-21.8	-123.0	-51	-37	-145	-15.2	18
18	-63.0	20.4	39.9	-60.3	-42.6	-23.1	-123.3	-53.0	-49.0	-145.0	-15.0	21
19	-71.7	31.5	31.6	-63.1	-40.2	-40.1	-134.8	-52.3	-52.3	-150.6	-10.5	15
20	-67.6	27.7	36.5	-64.2	-39.9	-31.1	-131.8	-52.0	-51.5	-153.0	-10.2	22
21	-67.2	30.1	33.0	-63.1	-37.1	-34.2	-130.3	-49.3	-49.3	-145.1	-13.9	d,f
22	-61.2	29.7	32.6	-62.3	-31.5	-28.6	-123.5	-39.7	-39.7	-133.8	-7.7	23

[a] Geometry optimised at the B3LYP/6-311g level. [b] All the parameters given in 10^{-4} cm^{-1}. [c] Percentage deviation from the absolute value of A_z^{exptl}. [d] Values measured in this work. [e] Value not reported. [f] Values measured for the bis chelated complex formed by cysteamine, which binds $V^{IV}O$ ion with [2x(NH$_2$, S$^-$)] donor set.

Table S5 Calculated (at the B3P86/6-311g(d,p) level) and experimental EPR parameters of **1-22** $V^{IV}O$ complexes[a,b]

	A_{iso}^{calcd}	T_x^{calcd}	T_y^{calcd}	T_z^{calcd}	A_x^{calcd}	A_y^{calcd}	A_z^{calcd}	A_x^{exptl}	A_y^{exptl}	A_z^{exptl}	Dev. (%)[c]	Ref.
1	-103.9	31.4	31.5	-62.9	-72.5	-72.4	-166.8	-68.2	-68.2	-182.6	-8.7	7
2	-78.9	32.9	33.8	-66.7	-46.0	-45.1	-145.6	-50.0	-50.0	-161.7	-10.0	7
3	-82.0	28.9	36.4	-65.3	-53.1	-45.6	-147.3	-55	-60	-166.5	-11.5	8
4	-74.9	26.9	37.3	-64.2	-48.0	-37.6	-139.1	-48.3	-57.4	-161.1	-13.7	9
5	-63.2	25.2	39.0	-64.2	-38.0	-24.2	-127.4	-45.1[d]	-45.1[d]	-154.1	-17.3	10
6	-61.5	25.4	38.7	-64.1	-36.1	-22.8	-125.6	-39.4	-51.6	-152.1	-17.4	11
7	-93.1	30.9	31.1	-62.0	-62.2	-62.0	-155.1	-68.3	-68.3	-176.3	-12.0	12
8	-83.6	30.0	31.8	-61.8	-53.6	-51.8	-145.4	*e*	*e*	-168	-13.5	13
9	-84.8	30.4	32.2	-62.6	-54.4	-52.6	-147.4	-62.1	-62.1	-171.0	-13.8	14
10	-76.1	29.4	34.8	-64.2	-46.7	-41.3	-140.3	-53.6	-53.6	-156.2	-10.2	15
11	-74.0	27.0	36.0	-63.0	-47.0	-38.0	-137.0	-53.1	-60.0	-161.0	-14.9	16
12	-76.3	27.4	35.8	-63.2	-48.9	-40.5	-139.5	-59.2	-59.2	-159.3	-12.4	17
13	-78.2	29.1	34.2	-63.3	-49.1	-44.0	-141.5	-45.0	-54.0	-154.0	-8.1	18
14	-76.3	31.3	32.0	-63.3	-45.0	-44.3	-139.6	-52.2	-52.2	-156.1	-10.6	19
15	-74.9	23.8	34.9	-58.7	-51.1	-40.0	-133.6	-53	-64	-163	-18.0	20
16	-77.2	30.9	33.7	-64.6	-46.3	-43.5	-141.8	-45.5	-45.5	-160.3	-11.5	7
17	-64.9	23.7	37.5	-61.2	-41.2	-27.4	-126.1	-51	-37	-145	-13.0	18
18	-67.6	20.0	38.9	-58.9	-47.6	-28.7	-126.5	-53.0	-49.0	-145.0	-12.8	21
19	-74.8	30.7	31.0	-61.7	-44.1	-43.8	-136.5	-52.3	-52.3	-150.6	-9.4	15
20	-70.8	27.1	35.6	-62.7	-43.7	-35.2	-133.5	-52.0	-51.5	-153.0	-8.7	22
21	-70.6	29.5	32.4	-61.9	-41.1	-38.2	-132.5	-49.3	-49.3	-145.1	-12.7	*d,f*
22	-64.0	28.9	31.9	-60.8	-35.1	-32.1	-124.8	-39.7	-39.7	-133.8	-6.7	23

[a] Geometry optimised at the B3LYP/6-311g level. [b] All the parameters given in 10^{-4} cm^{-1}. [c] Percentage deviation from the absolute value of A_z^{exptl}. [d] Values measured in this work. [e] Value not reported. [f] Values measured for the bis chelated complex formed by cysteamine, which binds $V^{IV}O$ ion with [2x(NH$_2$, S$^-$)] donor set.

Table S6 Calculated (at the B3PW91/6-311g(d,p) level) and experimental EPR parameters of **1-22** $V^{IV}O$ complexes[a,b]

	A_{iso}^{calcd}	T_x^{calcd}	T_y^{calcd}	T_z^{calcd}	A_x^{calcd}	A_y^{calcd}	A_z^{calcd}	A_x^{exptl}	A_y^{exptl}	A_z^{exptl}	Dev. (%)[c]	Ref.
1	-106.2	31.4	31.5	-62.9	-74.8	-74.7	-169.1	-68.2	-68.2	-182.6	-7.4	7
2	-81.4	32.9	33.7	-66.6	-48.5	-47.7	-148.0	-50.0	-50.0	-161.7	-8.5	7
3	-84.7	28.9	36.3	-65.2	-55.8	-48.4	-149.9	-55	-60	-166.5	-10.0	8
4	-76.0	26.9	37.2	-64.1	-49.1	-38.8	-140.1	-48.3	-57.4	-161.1	-13.0	9
5	-65.8	25.2	38.9	-64.1	-40.6	-26.9	-129.9	-45.1[d]	-45.1[d]	-154.1	-15.7	10
6	-64.3	25.5	38.5	-64.0	-38.8	-25.8	-128.3	-39.4	-51.6	-152.1	-15.6	11
7	-95.7	30.8	31.1	-61.9	-64.9	-64.6	-157.6	-68.3	-68.3	-176.3	-10.6	12
8	-85.8	30.0	31.8	-61.8	-55.8	-54.0	-147.6	*e*	*e*	-168	-12.1	13
9	-87.1	30.3	32.1	-62.4	-56.8	-55.0	-149.5	-62.1	-62.1	-171.0	-12.6	14
10	-78.7	29.4	34.8	-64.2	-49.3	-43.9	-142.9	-53.6	-53.6	-156.2	-8.5	15
11	-75.8	27.0	36.0	-63.0	-48.8	-39.8	-138.8	-53.1	-60.0	-161.0	-13.8	16
12	-78.9	27.5	35.7	-63.2	-51.4	-43.2	-142.1	-59.2	-59.2	-159.3	-10.8	17
13	-79.9	29.1	34.2	-63.3	-50.8	-45.7	-143.2	-45.0	-54.0	-154.0	-7.0	18
14	-78.7	31.3	32.0	-63.3	-47.4	-46.7	-142.0	-52.2	-52.2	-156.1	-9.0	19
15	-77.4	23.9	34.8	-58.7	-53.5	-42.6	-136.1	-53	-64	-163	-16.5	20
16	-79.6	30.9	33.5	-64.4	-48.7	-46.1	-144.0	-45.5	-45.5	-160.3	-10.2	7
17	-67.2	23.8	37.3	-61.1	-43.4	-29.9	-128.3	-51	-37	-145	-11.5	18
18	-69.9	20.0	38.8	-58.8	-49.9	-31.1	-128.7	-53.0	-49.0	-145.0	-11.2	21
19	-77.1	30.7	30.9	-61.6	-46.4	-46.2	-138.7	-52.3	-52.3	-150.6	-7.9	15
20	-73.2	27.1	35.5	-62.6	-46.1	-37.7	-135.8	-52.0	-51.5	-153.0	-7.3	22
21	-72.8	29.4	32.3	-61.7	-43.4	-40.5	-134.5	-49.3	-49.3	-145.1	-11.2	*d,f*
22	-66.1	29.0	31.9	-60.9	-37.1	-34.2	-127.0	-39.7	-39.7	-133.8	-5.1	23

[a] Geometry optimised at the B3LYP/6-311g level. [b] All the parameters given in 10^{-4} cm^{-1}. [c] Percentage deviation from the absolute value of A_z^{exptl}. [d] Values measured in this work. [e] Value not reported. [f] Values measured for the bis chelated complex formed by cysteamine, which binds $V^{IV}O$ ion with $[2\times(NH_2, S^-)]$ donor set.

Table S7 Calculated (at the BHandHLYP/6-311+g level) and experimental EPR parameters of **1-22** $V^{IV}O$ complexes[a,b]

	A_{iso}^{calcd}	T_x^{calcd}	T_y^{calcd}	T_z^{calcd}	A_x^{calcd}	A_y^{calcd}	A_z^{calcd}	A_x^{exptl}	A_y^{exptl}	A_z^{exptl}	Dev. (%)[c]	Ref.
1	-124.8	31.3	32.4	-63.7	-93.5	-92.4	-188.5	-68.2	-68.2	-182.6	+3.2	7
2	-87.1	35.3	36.2	-71.5	-51.8	-50.9	-158.6	-50.0	-50.0	-161.7	-1.9	7
3	-97.1	32.3	38.3	-70.6	-64.8	-58.8	-167.7	-55	-60	-166.5	+0.7	8
4	-92.4	30.4	39.0	-69.4	-62.0	-53.4	-161.8	-48.3	-57.4	-161.1	+0.4	9
5	-77.2	28.8	40.8	-69.6	-48.4	-36.4	-146.8	-45.1[d]	-45.1[d]	-154.1	-4.7	10
6	-75.3	29.1	40.4	-69.5	-46.2	-34.9	-144.8	-39.4	-51.6	-152.1	-4.8	11
7	-106.0	33.2	33.5	-66.7	-72.8	-72.5	-172.7	-68.3	-68.3	-176.3	-2.0	12
8	-99.0	31.9	34.7	-66.6	-67.1	-64.3	-165.6	e	e	-168	-1.4	13
9	-95.4	32.7	34.7	-67.4	-62.7	-60.7	-162.8	-62.1	-62.1	-171.0	-4.8	14
10	-83.9	32.5	37.4	-69.9	-51.4	-46.5	-153.8	-53.6	-53.6	-156.2	-1.5	15
11	-85.5	30.0	38.7	-68.7	-55.5	-46.8	-154.2	-53.1	-60.0	-161.0	-4.2	16
12	-87.9	31.1	38.2	-69.3	-56.8	-49.7	-157.2	-59.2	-59.2	-159.3	-1.3	17
13	-88.3	32.0	36.9	-68.9	-56.3	-51.4	-157.2	-45.0	-54.0	-154.0	+2.1	18
14	-84.3	34.1	35.1	-69.2	-50.2	-49.2	-153.5	-52.2	-52.2	-156.1	-1.7	19
15	-89.5	28.1	38.0	-66.1	-61.4	-51.5	-155.6	-53	-64	-163	-4.5	20
16	-90.1	33.4	36.1	-69.5	-56.7	-54.0	-159.6	-45.5	-45.5	-160.3	-0.4	7
17	-76.7	26.6	39.9	-66.5	-50.1	-36.8	-143.2	-51	-37	-145	-1.2	18
18	-83.9	22.9	40.8	-63.7	-61.0	-43.1	-147.6	-53.0	-49.0	-145.0	+1.8	21
19	-84.9	33.8	34.1	-67.9	-51.1	-50.8	-152.8	-52.3	-52.3	-150.6	+1.5	15
20	-88.8	29.7	38.5	-68.2	-59.1	-50.3	-157.0	-52.0	-51.5	-153.0	+1.8	22
21	-80.1	32.2	35.4	-67.6	-47.9	-44.7	-147.7	-49.3	-49.3	-145.1	+2.6	d,f
22	-75.8	32.9	35.5	-68.4	-42.9	-40.3	-144.2	-39.7	-39.7	-133.8	+7.8	23

[a] Geometry optimised at the B3LYP/6-311g level. [b] All the parameters given in 10^{-4} cm^{-1}. [c] Percentage deviation from the absolute value of A_z^{exptl}. [d] Values measured in this work. [e] Value not reported. [f] Values measured for the bis chelated complex formed by cysteamine, which binds $V^{IV}O$ ion with [2x(NH_2, S^-)] donor set.

Table S8 Calculated (at the BHandHLYP/6-311g level) and experimental EPR parameters of **1-22** $V^{IV}O$ complexes[a,b]

	A_{iso}^{calcd}	T_x^{calcd}	T_y^{calcd}	T_z^{calcd}	A_x^{calcd}	A_y^{calcd}	A_z^{calcd}	A_x^{exptl}	A_y^{exptl}	A_z^{exptl}	Dev. (%)[c]	Ref.
1	-127.4	31.2	32.4	-63.6	-96.2	-95.0	-191.0	-68.2	-68.2	-182.6	+4.6	7
2	-90.3	35.5	36.2	-71.7	-54.8	-54.1	-162.0	-50.0	-50.0	-161.7	+0.2	7
3	-100.5	32.2	38.1	-70.3	-68.3	-62.4	-170.8	-55	-60	-166.5	+2.6	8
4	-95.6	30.4	38.8	-69.2	-65.2	-56.8	-164.8	-48.3	-57.4	-161.1	+2.3	9
5	-79.6	29.0	40.6	-69.6	-50.6	-39.0	-149.2	-45.1[d]	-45.1[d]	-154.1	-3.2	10
6	-77.2	29.1	40.2	-69.3	-48.1	-37.0	-146.5	-39.4	-51.6	-152.1	-3.7	11
7	-109.2	32.6	33.5	-66.1	-76.6	-75.7	-175.3	-68.3	-68.3	-176.3	-0.6	12
8	-98.1	32.3	34.6	-66.9	-65.8	-63.5	-165,0	e	e	-168	-1.8	13
9	-97.6	32.7	34.6	-67.3	-64.9	-63.0	-164.9	-62.1	-62.1	-171.0	-3.6	14
10	-87.1	32.4	37.2	-69.6	-54.7	-49.9	-156.7	-53.6	-53.6	-156.2	+0.3	15
11	-87.6	29.9	38.5	-68.4	-57.7	-49.1	-156.0	-53.1	-60.0	-161.0	-3.1	16
12	-89.4	30.7	38.0	-68.7	-58.7	-51.4	-158.1	-59.2	-59.2	-159.3	-0.8	17
13	-90.9	31.9	36.6	-68.5	-59.0	-54.3	-159.4	-45.0	-54.0	-154.0	+3.5	18
14	-87.4	33.9	34.9	-68.8	-53.5	-52.5	-156.2	-52.2	-52.2	-156.1	+0.1	19
15	-90.8	28.0	38.0	-66.0	-62.8	-52.8	-156.8	-53	-64	-163	-3.8	20
16	-94.2	33.5	36.1	-69.6	-60.7	-58.1	-163.8	-45.5	-45.5	-160.3	+2.2	7
17	-79.4	26.7	39.5	-66.2	-52.7	-39.9	-145.6	-51	-37	-145	+0.4	18
18	-82.4	22.6	41.1	-63.7	-59.8	-41.3	-146.1	-53.0	-49.0	-145.0	+0.8	21
19	-88.3	33.6	33.8	-67.4	-54.7	-54.5	-155.7	-52.3	-52.3	-150.6	+3.4	15
20	-92.4	29.6	38.2	-67.8	-62.8	-54.2	-160.2	-52.0	-51.5	-153.0	+4.7	22
21	-84.9	32.3	35.3	-67.6	-52.6	-49.6	-152.5	-49.3	-49.3	-145.1	+5.1	d,f
22	-82.8	33.6	34.7	-68.3	-49.2	-48.1	-151.1	-39.7	-39.7	-133.8	+12.9	23

[a] Geometry optimised at the B3LYP/6-311g level. [b] All the parameters given in 10^{-4} cm^{-1}. [c] Percentage deviation from the absolute value of A_z^{exptl}. [d] Values measured in this work. [e] Value not reported. [f] Values measured for the bis chelated complex formed by cysteamine, which binds $V^{IV}O$ ion with $[2 \times (NH_2, S^-)]$ donor set.

Table S9 Calculated (at the BHandHLYP/6-31g level) and experimental EPR parameters of **1-24** $V^{IV}O$ complexes[a,b]

	A_{iso}^{calcd}	T_x^{calcd}	T_y^{calcd}	T_z^{calcd}	A_x^{calcd}	A_y^{calcd}	A_z^{calcd}	A_x^{exptl}	A_y^{exptl}	A_z^{exptl}	Dev. (%)[c]	Ref.
1	-0.4	30.0	31.8	-61.8	29.6	31.4	-62.2	-68.2	-68.2	-182.6	-65.9	7
2	9.2	35.1	36.0	-71.1	44.3	45.2	-61.9	-50.0	-50.0	-161.7	-61.7	7
3	3.6	30.9	38.6	-69.5	34.5	42.2	-65.9	-55	-60	-166.5	-60.4	8
4	6.9	28.7	39.9	-68.6	35.6	46.8	-61.7	-48.3	-57.4	-161.1	-61.7	9
5	15.5	27.5	42.1	-69.6	43.0	57.6	-54.1	-45.1[d]	-45.1[d]	-154.1	-64.9	10
6	16.0	27.7	41.9	-69.6	43.7	57.9	-53.6	-39.4	-51.6	-152.1	-64.8	11
7	2.2	32.0	33.6	-65.6	34.2	35.8	-63.4	-68.3	-68.3	-176.3	-64.0	12
8	7.5	31.7	35.0	-66.7	39.2	42.5	-59.2	e	e	-168	-64.8	13
9	7.6	32.7	34.6	-67.3	40.3	42.2	-59.7	-62.1	-62.1	-171.0	-65.1	14
10	11.8	32.1	37.8	-69.9	43.9	49.6	-58.1	-53.6	-53.6	-156.2	-62.8	15
11	11.4	29.1	39.5	-68.6	40.5	50.9	-57.2	-53.1	-60.0	-161.0	-64.5	16
12	8.3	30.0	38.8	-68.8	38.3	47.1	-60.5	-59.2	-59.2	-159.3	-62.0	17
13	8.8	31.5	37.5	-69.0	40.3	46.3	-60.2	-45.0	-54.0	-154.0	-60.9	18
14	11.3	34.0	35.4	-69.4	45.3	46.7	-58.1	-52.2	-52.2	-156.1	-62.8	19
15	9.2	27.6	38.2	-65.8	36.8	47.4	-56.6	-53	-64	-163	-65.3	20
16	10.1	32.6	35.7	-68.3	42.7	45.8	-58.2	-45.5	-45.5	-160.3	-63.7	7
17	18.1	26.1	40.8	-66.9	44.2	58.9	-48.8	-51	-37	-145	-66.3	18
18	16.2	22.2	42.3	-64.5	38.4	58.5	-48.3	-53.0	-49.0	-145.0	-66.7	21
19	12.8	33.7	34.3	-68.0	46.5	47.1	-55.2	-52.3	-52.3	-150.6	-63.3	15
20	13.4	28.4	39.1	-67.5	41.8	52.5	-54.1	-52.0	-51.5	-153.0	-64.6	22
21	16.6	31.9	36.0	-67.9	48.5	52.6	-51.3	-49.3	-49.3	-145.1	-64.6	d,f
22	24.6	33.5	35.3	-68.8	58.1	59.9	-44.2	-39.7	-39.7	-133.8	-67.0	23

[a] Geometry optimised at the B3LYP/6-311g level. [b] All the parameters given in 10^{-4} cm^{-1}. [c] Percentage deviation from the absolute value of A_z^{exptl}. [d] Values measured in this work. [e] Value not reported. [f] Values measured for the bis chelated complex formed by cysteamine, which binds $V^{IV}O$ ion with [2x(NH_2, S^-)] donor set.

References

1   M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, Gaussian 03, Revision C.02, Gaussian, Inc., Wallingford CT, 2004.

2   R. G. Parr and W. Yang, *Density-Functional Theory of Atoms and Molecule*s, Oxford University Press, Oxford, United Kingdom, 1989.

3   A. D. Becke, *J. Chem. Phys.*, 1993, **98**, 5648.

4   (*a*) J. P. Perdew, *Phys. Rev. B*, 1986, **33**, 8822; (*b*) J. P. Perdew, *Phys. Rev. B*, 1986, **34**, 7406.

5   (*a*) J. P. Perdew, in *Electronic Structure of Solids*, ed. P. Ziesche and H. Eischrig, Akademie Verlag, Berlin, Germany, 1991, p. 11; (*b*) J. P. Perdew and Y. Wang, *Phys. Rev. B*, 1992, **45**, 13244.

6   C. Lee, W. Yang and R. G. Parr, *Phys. Rev. B*, 1988, **37**, 785.

7   N. D. Chasteen, in *Biological Magnetic Resonance*, ed. L. J. Berliner and J. Reuben, Plenum Press, New York, USA, vol. 3, 1981, p. 53.

8   E. Garribba, G. Micera and D. Sanna, *Inorg. Chim. Acta*, 2006, **359**, 4470.

9   G. R. Hanson, Y. Sun and C. Orvig, *Inorg. Chem.*, 1996, **35**, 6507.

10 M. Branca, G. Micera, A. Dessì, D. Sanna and K. N. Raymond, *Inorg. Chem.*, 1990, **29**, 1586.

11 E. Garribba, G. Micera, A. Panzanelli and D. Sanna, *Inorg. Chem.*, 2003, **42**, 3981.

12 T. Jakusch, W. Jin, L. Yang, T. Kiss and D. C. Crans, *J. Inorg. Biochem.*, 2003, **95**, 1.

13 J. Gätjens, B. Maier, T. Kiss, E. M. Nagy, P, Buglyó, H. Sakurai, K. Kawabe and D. Rehder, *Chem. Eur. J.*, 2003, **9**, 4924.

14 T. S. Smith II, C. A. Roof, J. W. Kampf, P. G. Rasmussen and V. L. Pecoraro, *J. Am. Chem. Soc.*, 2000, **122**, 767.

15 A. D. Keramidas, A. P. Papaioannou, A. Vlahos, T. A. Kabanos, G. Bonas, A. Makriyannis, C. P. Raptopoulou and A. Terzis, *Inorg. Chem.*, 1996, **35**, 357.

16 C. R. Cornman, K. M. Geisre-Bush, S. R. Rowley and P. D. Boyle, *Inorg. Chem.*, 1997, **36**, 6401.

17 J. A. Bonadies and C. J. Carrano, *J. Am. Chem. Soc.*, 1986, **108**, 4088.

18 C. R. Cornman, E. P. Zovinka, Y. D. Boyajina, K. M. Geisre-Bush, P. D. Boyle and P. Singh, *Inorg. Chem.*, 1995, **34**, 4213.

19 T. A. Kabanos, A. D. Keramidas, A. B. Papaioannou and A. Terzis, *Chem. Comm.*, 1993, 643.

20 E. J. Tolis, M. J. Manos, A. J. Tasiopoulos, C. P. Raptopoulou, A. Terzis, M. P. Sigalas, Y. Deligiannakis and T. A. Kabanos, *Angew. Chem.*, 2002, **41**, 2797.

21 E. J. Tolis, K. D. Soulti, C. P. Raptopoulou, A. Terzis, Y. Deligiannakis and T. A. Kabanos, *Chem. Comm.*, 2000, 601.

22 V. Monga, K. H. Thompson, V. G. Yuen, V. Sharma, B. O. Patrick, J. H. McNeill and C. Orvig, *Inorg. Chem.*, 2005, **44**, 2678.

23 J. K. Money, K. Folting, J. C. Huffman, D. Collison, J. Temperley, F. E. Mabbs and G. Christou, *Inorg. Chem.*, 1986, **25**, 4583.

24 WINEPR SimFonia, version 1.25, Bruker Analytische Messtechnik GmbH, Karlsruhe, Germany, 1996.

25 I. Nagypál and I. Fábián, *Inorg. Chim. Acta*, 1982, **61**, 109.

26 K. Wütrich, *Helv. Chim. Acta*, 1965, **48**, 1012.

27 T. S. Smith II, R. LoBrutto and V. L. Pecoraro, *Coord. Chem. Rev.*, 2002, **228**, 1.

28 B. J. Hamstra, A. P. L. Houseman, G. J. Colpas, J. W. Kampf, R. LoBrutto, W. D. Frasch and V. L. Pecoraro, *Inorg. Chem.*, 1997, **36**, 4866.

29 E. J. Tolis, V. I. Teberekidis, C. P. Raptopoulou, A. Terzis, M. Sigalas, Y. Deligiannakis and T. A. Kabanos, *Chem. Eur. J.*, 2001, **7**, 2698.

30 T. Jakusch, P. Buglyó, A. I. Tomaz, J. Costa Pessoa and T. Kiss, *Inorg. Chim. Acta*, 2002, **339**, 119.

31 E. Garribba, E. Lodyga-Chruscinska, G. Micera, A. Panzanelli and D. Sanna, *Eur. J. Inorg. Chem.*, 2005, 1369 and references therein.

32 (*a*) R. S. Drago, *Physical Methods in Chemistry*, Saunders, Philadelphia, USA, 1977; (*b*) J. E. Wertz, J. R. Bolton, *Electron Spin Resonance: Elementary Theory and Practical Applications*, Chapman and Hall, New York, USA, 1986; (*c*) F. E.; Mabbs, D. Collison, *Electron Paramagnetic Resonance of d-Transition Metal Compounds*, Elsevier, Amsterdam, The Netherlands, 1992.

33 (*a*) P. Hon, R. L. Belford and C. E. Pfluger, *J. Chem. Phys*., 1965, **43**, 3111; (*b*) E. Shuter, S. J. Rettig and C. Orvig, *Acta Crystallogr. C*, 1995, **51**, 12; (*c*) A. H. Mahmoudkhani, B. Casari and V. Langer, *Z. Kristallogr.-New Cryst. Struct*., 2001, **216**, 205; (*d*) M. A. K. Ahmed, H. Fjellvag, A. Kjekshus and B. Klewe, *Z. Anorg. Allg. Chem*., 2004, **630**, 2311; (*e*) E. V. Fedorova, V. B. Rybakov, V. M. Senyavin, A. V. Anisimov and L. A. Aslanov, *Kristallografiya*, 2005, **50**, 256; (*f*) M. Hoshino, A. Sekine, H. Uekusa and Y. Ohashi, *Chem. Lett*., 2005, **34**, 1228.

34 P. Caravan, L. Gelmini, N. Glover, F. G. Herring, H. Li, J. H. McNeill, S. J.Rettig, I. A. Setyawati, E. Shuter, Y. Sun, A. S. Tracey, V. G. Yuen and C. Orvig, *J. Am. Chem. Soc*., 1995, **117**, 12759.

35 S. R. Cooper, Y. B. Koh and K. N. Raymond, *J. Am. Chem. Soc*., 1982, **104**, 5092.

36 N. D. Chasteen, R. L. Belford and I. C. Paul, *Inorg. Chem*., 1969, **8**, 408.

37 (*a*) B. H. Bersted, R. L. Belford and I. C. Paul, *Inorg. Chem*., 1968, **7**, 1557; (*b*) A. Sundheim and R. Mattes, *Z. Naturforsch. B*, 1993, **48**, 125; (*c*) M. Chatterjee, S. Ghosh and A. K. Nandi, *Transition Met. Chem*., 1999, **24**, 183; (*d*) Y. Heng Xing, K. Aoki and F. Ying Bai, *J. Coord. Chem*., 2004, **57**, 157.

38 P. E. Riley, V. L. Pecoraro, C. J. Carrano, J. A. Bonadies and K. N. Raymond, *Inorg. Chem*., 1986, **25**, 154.

39 A. T. Vlahos, E. I. Tolis, C. P. Raptopoulou, A. Tsohos, M. P. Sigalas, A. Terzis and T. A. Kabanos, *Inorg. Chem*., 2000, **39**, 2977.

40 H. Sakurai, Z. Taira and N. Sakai, *Inorg. Chim. Acta*, 1988, **151**, 85.

41 (*a*) R. W. Wiggins, J. C. Huffman and G. Christou, *Chem. Comm*., 1983, 1313; (*b*) J. K. Money, J. C. Huffman and G. Christou, *Inorg. Chem*., 1985, **24**, 3297.

42 I. Correia, J. Costa Pessoa, M. T. Duarte, R. T. Henriques, M. F. M. Piedade, L. F. Veiros, T. Jakusch, T. Kiss, Á. Dörnyei, M. M. C. A. Castro, C. F. G. C. Geraldes and F. Avecilla, *Chem. Eur. J.*, 2004, **10**, 2301.