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ORIGINAL ARTICLE

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Model investigations for vanadium-protein interactions: vanadium(III) compounds with dipeptides and their oxovanadium(IV) analogues

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Abstract The reaction of VCl_3 with 1,10-phenanthroline and a series of dipeptides (H_2dip), having aliphatic as well as aromatic side chains, in methyl alcohol and in the presence of triethylamine affords vanadium(III) compounds of the general formula $[V^{III}(dip)(MeOH)(phen)]Cl$. Aerial oxidation/hydrolysis of the vanadium(III) species gives their oxovanadium(IV) analogues of the general formula $[V^{IV}O(dip)(phen)]$. X-ray crystallographic characterization of the $[V^{IV}O(dip)(phen)]$ compounds (where dip^{2-} = Gly-L-Ala, Gly-L-Val and Gly-L-Phe) revealed that the vanadium atom possesses a severely distorted octahedral coordination and is ligated to a tridentate dip^{2-} ligand at the N_{amine} atom, the deprotonated $N_{peptide}$ atom and one of the $O_{carboxylate}$ atoms, as well as an oxo group and two phenanthroline nitrogen atoms. Circular dichroism characterization of the $V^{III}/V^{IV}O^{2+}$-dipeptide compounds revealed a strong signal for the $V^{IV}O^{2+}$ species in the visible range of the spectrum, with a characteristic pattern which may be exploited to identify the N_{am}, N_{pep} and O_{car} ligation of a peptide or a protein to $V^{IV}O^{2+}$ center, and a weak Cotton effect of opposite sign to their vanadium(III) analogues. The visible spectra of the V^{III}-dipeptide compounds revealed two d-d bands with high intensity, thus indicating that the covalency of the metal-donor atoms is significant, i.e. the vanadium d orbitals are significantly mixed with the ligand orbitals, and this is confirmed by the low values of their Racah *B* parameters. The high-intensity band of the $V^{IV}O^{2+}$-dipeptide compounds at ~460 nm implies also a strong covalency of the metal with the equatorial donor atoms and this was supported by the EPR spectra of these compounds. Moreover, the $V^{III}/V^{IV}O^{2+}$-dipeptide complexes were characterized by EPR and IR spectroscopies as well as conductivity and magnetic susceptibility measurements.

Keywords Vanadium · Peptides · Circular dichroism · Electron paramagnetic resonance

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Introduction

Vanadium is a bioessential element that is found in remarkably high concentrations in marine ascidians [1], in certain mushrooms [2] and in polychaete worms [3]. In addition, two classes of vanadium enzymes, vanadium nitrogenases [4, 5] and vanadate-dependent haloperoxidases ([6] and references therein), found in Nature, as well as the vanadium's insulinomimetic action [7, 8, 9, 10, 11, 12] and anticancer activity [13, 14, 15], have spurred a considerable amount of research by bioinorganic [16, 17] and coordination chemists [16, 17], biochemists, etc. Moreover, the oxovanadium(IV) cation, $V^{IV}O^{2+}$, has been used in electron paramagnetic resonance (EPR) as a spin probe [18].

Detailed structural, physicochemical and kinetic investigations on synthetic model compounds of vanadium with peptides, that are the most closely related models to proteins, will contribute greatly to our

understanding of its biological role. Vanadium(V) is usually the stable oxidation state under aerobic conditions, while V(IV) is present in the reducing intracellular medium and may further be reduced to V(III) ([19] and references therein). To date, there are only two oxovanadium(V) compounds structurally characterized with the dipeptide glycylglycine [20, 21, 22], as well as only two oxovanadium(IV) compounds with the dipeptides glycyl-L-tyrosine [23] and glycylglycine [24]. Herein, we wish to report the synthesis and circular dichroism (CD) characterization of vanadium(III) compounds with a series of dipeptides, having aliphatic as well as aromatic side chains, and their oxovanadium(IV) analogues of the general formulae $[V^{III}(dipeptide)(MeOH)(phen)]^+$/$[V^{IV}O(dipeptide)(phen)]$ (Scheme 1). The X-ray structural characterization of the $V^{IV}O^{2+}$ species with the dipeptides glycine-L-alanine, glycine-L-phenylalanine and glycine-L-valine is also reported. In addition, the EPR, optical and infrared spectra as well as conductivity and magnetic susceptibility (room temperature) measurements are presented. This study represents the first systematic study of interaction of $V^{III}/V^{IV}O^{2+}$ species with peptides.

Materials and methods

Materials

Reagent grade chemicals were obtained from Aldrich, while the dipeptides were obtained from Neosystem and used without further purification. Dichlorobis(tetrahydrofuran)oxovanadium(IV), $[VOCl_2(THF)_2]$, was prepared by the literature procedure [25]. Reagent grade acetonitrile and triethylamine were dried and distilled over calcium hydride, while diethyl ether was dried and distilled over sodium wire. Methyl alcohol was dried by refluxing over magnesium methoxide. Synthesis, distillations, crystallization of the vanadium compounds and spectroscopic characterization were performed under high-purity argon using standard Schlenk techniques.

C, H and N analyses were conducted by the University of Ioannina's microanalytical service. Vanadium was determined gravimetrically as vanadium pentoxide or by atomic absorption, and chloride analyses were carried out by potentiometric titration.

Instrumentation

IR spectra of the various compounds dispersed in KBr pellets and in Nujol with CsI windows were recorded on a Perkin-Elmer 577 spectrometer. A polystyrene film was used to calibrate the frequency. Electronic absorption spectra were measured as solutions in septum-sealed quartz cuvettes at ~0 °C on Jasco V-570 UV/Vis/NIR and Perkin-Elmer 19 spectrophotometers. EPR spectra were recorded on a Brucker ER 200d (connected to a Brucker B-MN C5) spectrometer. Solution conductivity data were collected in methyl alcohol using a Tacussel electronique CD 6NG conductivity bridge. A temperature of 25 °C was maintained by a constant-temperature bath. The cell constant was determined to be $\kappa = 1.1025\ cm^{-1}$ by using a 0.1 M aqueous solution of potassium chloride to calibrate the conductivity cell.

The CD spectra were run on a Jasco 720 spectropolarimeter with UV-Vis (200–700 nm) and red-sensitive (400–1000 nm) photomultipliers. Unless otherwise stated, for isotropic absorption spectra in the 200–400 nm range or 400–1000 nm range we use the abbreviations UV or Vis spectra, respectively. For CD spectra we use a representation of $\Delta\epsilon$ values versus λ [$\Delta\epsilon$ = differential absorption/($b \times C_{VO}$) where b = optical path and C_{VO} = total oxovanadium(IV) concentration].

CD spectra of solid complexes

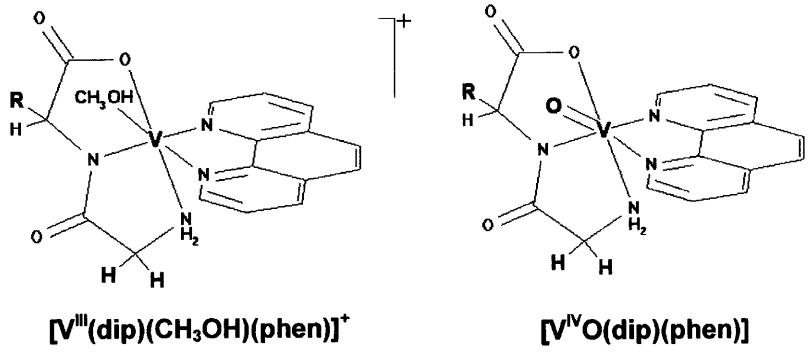
Samples of compounds were prepared as described previously [26] in KBr disks, and placed between two microscope slides. Such paired microscope slides were placed in the sample compartment, which was kept under nitrogen. Each final spectrum is the average of four spectra in all, recorded as described [26]. The position of the base line is not exactly known and the spectra obtained are a representation of ellipticity (m deg) versus λ. Owing to the high absorption for $\lambda < 500$ nm, the signal recorded is extremely noisy in this range and is not reliable.

Solution CD spectra of complexes **8**·*MeOH*–**12**·*2MeOH*

The solutions were prepared using dry solvents in an inert atmosphere. Once prepared, the solution was transferred either to 1 cm or to 0.1 cm quartz cells. The cells and the sample compartment were always kept in an inert atmosphere. For each solution, three spectra were run with 10 min intervals. These spectra were always identical, so no decomposition or hydrolysis (apparently) occurred.

X-ray crystal structure characterization

Diffraction measurements for **8**·H_2O, **9** and **11**·$1.25H_2O$ were performed on a Siemens SMART diffractometer using a graphite monochromated Mo $K\alpha$ radiation. The crystals were very small and of poor quality. For structure solution and refinement, the programs SHELXS-86 [27] and SHELXS-93 [28] were used. All non-hydrogen atoms for the three structures were refined anisotropically. All hydrogen atoms were calculated by difference maps and were refined isotropically.



$[V^{III}(dip)(CH_3OH)(phen)]^+$ $[V^{IV}O(dip)(phen)]$

Scheme 1

Crystallographic data without structure factors for the three structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications CCDC 171359, CCDC 171360 and CCDC 171361 for **8**·H_2O, **9** and **11**·1.25H_2O, respectively. Copies of the data can be obtained free of charge from the CDCC, 12 Union Road, Cambridge CB2 1EZ, UK; e-mail: deposit@cdcc.cam.ac.uk; www: http://ccdc.cam.ac.uk; Tel.: +44-1223-336003.

Preparation of vanadium(III) and oxovanadium(IV) compounds

*(Glycylglycinato-O,N,N)(methyl alcohol)(1,10-phenanthroline) vanadium(III) chloride, [V^{III}(GlyGly)(MeOH)(phen)]Cl·2MeOH (**1**·2MeOH)*

Vanadium(III) chloride (0.300 g, 1.91 mmol) was dissolved in methyl alcohol (8 mL) under magnetic stirring, at ambient temperature, and the solution was cooled to ca. –15 °C. Solid 1,10-phenanthroline (0.344 g, 1.91 mmol) was added to the solution in one portion. Upon addition of the 1,10-phenanthroline the green color of the solution changed to brown. To the stirred solution, H_2GlyGly (0.25 g, 1.91 mmol) and triethylamine (0.949 g, 9.4 mmol) were added. The bath temperature was then allowed to warm to ~5 °C and over 2 h of stirring the solution cleared (the dipeptide dissolved) and its color changed to deep brown-purple. The solution was filtered off and the complex was precipitated by adding, dropwise with stirring, 30 mL of diethyl ether. The dark purple precipitate was filtered off, washed with three 15 mL portions of acetonitrile and diethyl ether (2×10 mL) and dried in vacuo. Yield: 0.38 g (40%). Anal. calcd. for $C_{17}H_{18}ClN_4O_4V{\cdot}2CH_3OH$ (M_r = 492.80): C 46.31, H 5.32, N 11.37, Cl 7.19, V 10.34; found: C 45.86, H 5.53, N 11.46, Cl 6.85, V 10.70; μ_{eff} = 2.73 μ_B at 298 K.

*(Glycylalanilato-O,N,N)(methyl alcohol)(1,10-phenanthroline) vanadium(III) chloride, [V^{III}(GlyAla)(MeOH)(phen)]Cl·2MeOH (**2**·2MeOH)*

Compound **2**·2MeOH was prepared in a fashion similar to that used for complex **1**·2MeOH. Yield: 37%. Anal. calcd. for $C_{18}H_{20}ClN_4O_4V{\cdot}2CH_3OH$ (M_r = 506.82): C 47.40, H 5.57, N 11.05, Cl 6.99, V 10.05; found: C 47.19, H 5.43, N 11.23, Cl 6.82, V 10.12; μ_{eff} = 2.65 μ_B at 298 K.

*(Glycylphenylalanilato-O,N,N)(methyl alcohol) (1,10-phenanthroline)vanadium(III) chloride, [V^{III}(GlyPhe)(MeOH)(phen)]Cl·2MeOH (**3**·2MeOH)*

The same procedure as for the above compound **1**·2MeOH was followed to prepare the complex. Yield: 50%. Anal. calcd. for $C_{24}H_{24}ClN_4O_4V$ (M_r = 582.95): C 53.57, H 5.53, N 9.61, Cl 6.08, V 8.74; found: C 53.12, H 5.38, N 9.51, Cl 5.97, V 8.81; μ_{eff} = 2.70 μ_B at 298 K.

*(Glycyltyrosinato-O,N,N)(methyl alcohol)(1,10-phenanthroline) vanadium(III) chloride, [V^{III}(GlyTyr)(MeOH)(phen)]Cl (**4**)*

The complex was prepared by the same method as used for **1**·2MeOH. Yield: 40%. Anal. calcd. for $C_{24}H_{24}ClN_4O_5V$ (M_r = 534.84): C 53.90, H 4.52, N 10.48, Cl 6.63, V 9.52; found: C 53.45, H 4.70, N 10.70, Cl 6.47, V 9.49; μ_{eff} = 2.75 μ_B at 298 K.

*(Glycylvalinato-O,N,N)(methyl alcohol)(1,10-phenanthroline) vanadium(III) chloride, [V^{III}(GlyVal)(MeOH)(phen)]Cl·2MeOH (**5**·2MeOH)*

The complex was prepared by the same method as used for **1**·2MeOH. Yield: 42%. Anal. calcd. for $C_{20}H_{24}ClN_4O_4V{\cdot}2CH_3OH$ (M_r = 534.91): C 49.40, H 6.03, N 10.47, Cl 6.62, V 9.52; found: C 49.12, H 5.95, N 10.51, Cl 6.53, V 9.53; μ_{eff} = 2.79 μ_B at 298 K.

*(Glycylleucinato-O,N,N)(methyl alcohol)(1,10-phenanthroline) vanadium(III) chloride, [V^{III}(GlyLeu)(MeOH)(phen)]Cl·2MeOH (**6**·2MeOH)*

The complex was prepared by the same method as used for **1**·2MeOH. Yield: 38%. Anal. calcd. for $C_{21}H_{26}ClN_4O_4V{\cdot}2CH_3OH$ (M_r = 548.94): C 50.32, H 6.24, N 10.21, Cl 6.46, V 9.28; found: C 49.75, H 6.11, N 9.95, Cl 6.35, V 9.25; μ_{eff} = 2.76 μ_B at 298 K.

*(Glycylglycinato-O,N,N)(1,10-phenanthroline)oxovanadium(IV), [$V^{IV}O$(GlyGly)(phen)]·2MeOH (**7**·2MeOH)*

Compound **7**·2MeOH was prepared by a similar procedure to that used for **1**·2MeOH, except that just prior to addition of diethyl ether to the methyl alcohol filtrate of the latter to precipitate it, the solution was warmed to room temperature (~30 °C), exposed to the atmosphere and stirred for an additional 2 h to obtain 0.45 g of a yellow precipitate. Yield: 48%. Anal. calcd. for $C_{16}H_{14}N_4O_4V{\cdot}2CH_3OH$ (M_r = 441.27): C 48.99, H 5.02, N 12.70, V 11.54; found: C 48.70, H 4.89, N 12.85, V 11.44; μ_{eff} = 1.65 μ_B at 298 K.

*(Glycyl-L-alaninato-O,N,N)(1,10-phenanthroline)oxovanadium (IV), [$V^{IV}O$(GlyAla)(phen)]·MeOH (**8**·MeOH)*

The same method as for **7**·2MeOH was carried out to obtain compound **8**·MeOH. Yield: 40%. Anal. calcd. for $C_{17}H_{16}N_4O_4V{\cdot}CH_3OH$ (M_r = 423.25): C 51.06, H 4.76, N 13.24, V 12.04; found: C 51.01, H 4.75, N 13.20, V 12.24; μ_{eff} = 1.62 μ_B at 298 K. Crystals of **8**·H_2O suitable for X-ray structure analysis were obtained as follows. The methyl alcohol filtrate of **2**·2MeOH (prepared by a similar method to that used for **1**·2MeOH), just prior to addition of diethyl ether to precipitate it, was warmed to room temperature and exposed to the air for about 30 min, then the solution was filtered off and vapor diffusion of diethyl ether into the filtrate resulted in the formation of yellow crystals.

*(Glycyl-L-phenylalaninato-O,N,N)(1,10-phenanthroline)oxovanadium(IV) [$V^{IV}O$(GlyPhe)(phen)] (**9**)*

Method A. Compound **9** was prepared by the same method as for **7**·2MeOH in 40% yield. Anal. calcd. for $C_{23}H_{20}N_4O_4V$ (M_r = 467.35): C 59.11, H 4.31, N 11.99, V 10.90; found: C 59.52, H 4.43, N 12.19, V 10.85; μ_{eff} = 1.70 μ_B at 298 K. Crystals of **9** suitable for X-ray structure analysis were obtained in a similar manner to that used to obtain crystals of **8**·H_2O.

Method B. [$VOCl_2(THF)_2$] (0.300 g, 1.064 mmol) was dissolved in methyl alcohol (~7 mL) at ambient temperature. Solid 1,10-phenanthroline (0.192 g, 1.064 mmol) was added to the solution in one portion and its color changed from blue to green. H_2Gly-Phe (0.236 g, 1.064 mmol) and triethylamine (0.538 g, 5.32 mmol) were added to the stirred solution. The resulting mixture was allowed to stir for 3 h, during which a sequence of color changes (from green through red brown to yellow) was accompanied by dissolution of the dipeptide and the formation of a yellow precipitate. The yellow solid was filtered off and washed with acetonitrile (2×10 mL) and diethyl ether (2×10 mL) and dried in vacuo. Yield: 0.323 g (65%).

*(Glycyl-L-tyrosinato-O,N,N)(1,10-phenanthroline)oxovanadium(IV), [$V^{IV}O$(Gly-L-Tyr)(phen)]·1.5MeOH (**10**·1.5MeOH)*

Method A. Compound **10**·1.5MeOH was prepared by the same method as for **7**·2MeOH. Yield: 40%. Anal. calcd. for $C_{23}H_{20}N_4O_5V{\cdot}1.5CH_3OH$ (M_r = 531.44): C 55.37, H 4.93, N 10.54, V 9.59; found: C 55.10, H 4.96, N 10.78, V 9.32; μ_{eff} = 1.72 μ_B at 298 K.

Method B. The complex was prepared by the same method used for **9** (method B) Yield: 80%.

*(Glycyl-L-valinato-O,N,N)(1,10-phenanthroline)oxovanadium(IV), [$V^{IV}O$(Gly-L-Val)(phen)]·H_2O (**11**·H_2O)*

The compound was prepared by the same methods A and B as for complex **9** in yields of 25% and 65%, respectively. Anal. calcd. for $C_{19}H_{20}N_4O_4V{\cdot}H_2O$ (M_r = 437.35): C 52.18, H 5.07, N 12.81, V 11.65; found: C 51.85, H 5.28, N 12.50, V 11.52. Crystals of **11**·1.25H_2O suitable for X-ray structure analysis were obtained by vapor diffusion of diethyl ether into a concentrated MeCN solution (at 4 °C) of the complex. μ_{eff} = 1.69 μ_B at 298 K.

*(Glycyl-L-leucinato-O,N,N)(1,10-phenanthroline)oxovanadium(IV), [$V^{IV}O$(Gly-L-Leu)(phen)]·2MeOH (**12**·2MeOH)*

12·2MeOH was prepared by the same methods A and B as for compound **9** in yields of 20% and 60%, respectively. Anal. calcd. for $C_{20}H_{22}N_4O_4V{\cdot}2CH_3OH$ (M_r = 497.44): C 53.12, H 6.08, N 11.26, V 10.24; found: C 53.31, H 5.95, N 11.25, V 10.08; μ_{eff} = 1.71 μ_B at 298 K.

Results and discussion

Synthesis of the compounds

The vanadium(III) compounds **1**·2MeOH–**6**·2MeOH were prepared by sequential treatment of VCl_3 (1 equiv) with 1,10-phenanthroline (1 equiv), H_2dipeptide (1 equiv) and excess triethylamine (~5 equiv) (Eqs. 1 and 2) in methyl alcohol at low temperature to avoid oxidation/hydrolysis of V^{III} to $V^{IV}O^{2+}$:

$$\left[V^{III}Cl_3(MeOH)_x\right] + \text{phen} \rightarrow \left[V^{III}Cl_3(MeOH)(\text{phen})\right] + (x-1)\text{MeOH} \quad (1)$$

$$\left[V^{III}Cl_3(MeOH)(\text{phen})\right] + H_2\text{dip} + 2Et_3N \rightarrow \left[V^{III}(\text{dip})(MeOH)(\text{phen})\right]Cl + 2Et_3NHCl \quad (2)$$

When the vanadium(III) compounds in methyl alcohol are exposed to air, they give their oxovanadium(IV) analogues, in crystalline form, which are evidently the result of hydrolysis/oxidation (Eq. 3) of the vanadium(III) species:

$$2\left[V^{III}(\text{dip})(MeOH)(\text{phen})\right]Cl + \tfrac{1}{2}O_2 + H_2O \rightarrow 2\left[V^{IV}O(\text{dip})(\text{phen})\right] + 2HCl + 2MeOH \quad (3)$$

The oxovanadium(IV) compounds **9**–**12**·2MeOH were also prepared by sequential addition of 1,10-phenanthroline (1 equiv), H_2dipeptide (1 equiv) and triethylamine (5 equiv) to a solution of [$VOCl_2(THF)_2$] (1 equiv) in methyl alcohol (Eq. 4):

$$\left[V^{IV}OCl_2(THF)_2\right] + \text{phen} + H_2\text{dip} + 2Et_3N \rightarrow \left[V^{IV}O(\text{dip})(\text{phen})\right] + 2Et_3NHCl + 2THF \quad (4)$$

When 2,2′-bipyridine is substituted for 1,10-phenanthroline, the isolated (where possible) $[V^{III}(\text{dip})(MeOH)(\text{bpy})]^+$/$[V^{IV}O(\text{dip})(\text{bpy})]$ compounds are much less stable in solution, from the hydrolytic point of view, than their 1,10-phenanthroline analogues.

Crystallography

The molecular structures of the oxovanadium(IV) compounds **8**·H_2O, **9** and **11**·1.25H_2O are illustrated in Figs. 1, 2 and 3, respectively, and their crystallographic data as well as selected bond distances and angles relevant to their coordination spheres are shown in Tables 1 and 2, respectively. The vanadium atom in these complexes is bonded to a tridentate dip^{2-} ligand at the N_{amine} atom, the deprotonated $N_{peptide}$ atom and one of the $O_{carboxylate}$ atoms, as well as an oxo group and two phenanthroline nitrogen atoms, and is 0.354(2), 0.358(3) and 0.344(3) Å above the mean equatorial plane, defined by the three ligating atoms of the dip^{2-} and a phenanthroline nitrogen, in the direction of the oxo ligand for **8**·H_2O, **9** and **11**·1.25H_2O, respectively. The dip^{2-} ligands form two five-membered fused chelate rings and are meridionally ligated to the $V^{IV}O^{2+}$ center with the amine nitrogen and the carboxylate oxygen atoms lying in a *trans* position. The V-$N_{peptide}$ bond lengths, being 1.949(6), 1.969(10) and 1.978(9) Å for **8**·H_2O, **9** and **11**·1.25H_2O, respectively (Table 2), are indicative of a very strong covalent bond of the deprotonated peptide nitrogen to vanadium. The mean d(V-N_{amide}) of ~1.97 Å for **8**·H_2O, **9** and **11**·1.25H_2O is almost identical to the average d(V-N_{amide}) of ~1.98 Å for neutral oxovanadium(IV) compounds with dianionic tetradentate ligands {e.g. *N*-[2-(4-oxopent-2-en-2-ylamino)phenyl]pyridine-2-carboxamide and *N*-[2-(4-phenyl-4-oxobut-2-en-2-ylamino)phenyl]pyridine-2-carboxamide} [29, 30]. The 1,10-phenanthroline in **8**·H_2O, **9** and **11**·1.25H_2O is unsymmetrically ligated to vanadium, with a long V-N oriented *trans* to the oxo ligand and a short V-N bond (Table 2) in the equatorial plane oriented *trans* to the deprotonated peptide nitrogen, and this unsymmetrical ligation of phen is due to the stronger *trans* influence of the oxo group than the deprotonated peptide nitrogen. Both d(V-N_{phen}) are consistent with the literature values [18, 23].

Infrared spectroscopy

Assignments of some characteristic bands are given in Table 3. The IR spectra of the V^{III}/$V^{IV}O^{2+}$ compounds exhibit weak- to medium-intensity broad bands at ca. 3400 cm^{-1}, which are assigned to ν(OH) [31] as well as a pair of bands at ~3230 and 3120 cm^{-1}; the higher frequency band is assigned to the antisymmetric stretching vibration of the -NH_2 group [31], while the lower

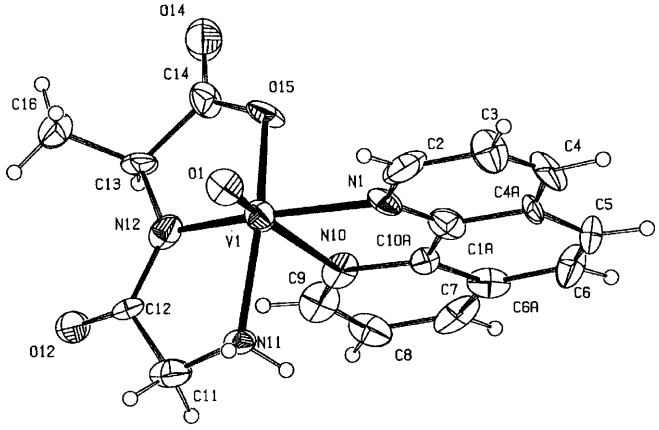


Fig. 1 X-ray crystal structure of **8**·H_2O

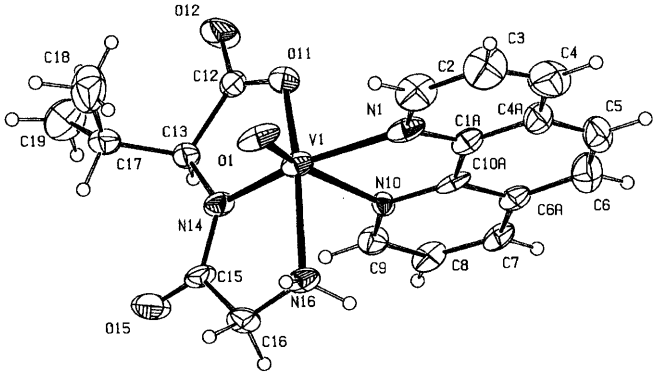


Fig. 3 X-ray crystal structure of **11**·1.25H_2O

frequency band is assigned to its symmetric stretching vibration. The ν_{as}(COO) and ν_s(COO) [31] bands of the $V^{III}/V^{IV}O^{2+}$ compounds are at ~1580 and ~1380 cm^{-1}, respectively. The relatively large value of $\Delta = [\nu_{as}(COO) - \nu_s(COO)]$ [32] is indicative of monodentate carboxylate coordination. The V=O stretching frequency for the oxovanadium(IV) compounds is at ~960 cm^{-1}. The ν(V-Cl) could not be identified in the spectra of the vanadium(III) compounds and this suggests that the chlorine atom is not coordinated to vanadium.

Conductivity

A solution of compounds **1**·2MeOH–**6**·2MeOH, i.e. the vanadium(III) compounds, in methyl alcohol (1×10^{-3} M) registered a molar conductivity of 124, 123, 122, 125, 120 and 126 $\Omega^{-1}\,cm^2\,mol^{-1}$, respectively, compared to 125 $\Omega^{-1}\,cm^2\,mol^{-1}$ for Et_4NCl at the same concentration at 25 °C. Thus, the vanadium(III) compounds in methyl alcohol behave as 1:1 electrolytes when compared to Et_4NCl. Compounds **7**·2MeOH–**12**·2MeOH, i.e. the oxovanadium(IV) compounds, are non-electrolytes in methyl alcohol.

UV-Vis spectroscopy

The isotropic UV-Vis spectral data for compounds **1**·2MeOH–**12**·2MeOH are summarized in Table 4. In the UV range the bands with λ_{max} at 195–205, 220–230, 270–275 and 290–295 nm are present in both the V(III) (**1**·2MeOH–**6**·2MeOH) and $V^{IV}O^{2+}$ (**7**·2MeOH–**12**·2MeOH) compounds. Therefore, we expect that the phenanthroline- and/or the dipeptide-related absorptions are responsible for these bands, namely: (1) the bands with λ_{max} at ~195–203 nm have n→π* and π→π* contributions from the peptide and carboxylate groups as well as from the phenanthroline π→π* bands; (2) the bands with λ_{max} at 221–227 nm may have contributions from phenanthroline π→π* bands and from the vanadium $e_\pi^b \rightarrow b_2$ [33] transition for **7**·2MeOH–**12**·2MeOH; (3) the bands at 272 and 291 nm are assigned to phenanthroline π→π* transitions. In the CD spectra (see below) of the $V^{IV}O^{2+}$ compounds **8**·MeOH–**12**·2MeOH, some additional bands and/or shoulders in the same wavelength ranges may be seen, confirming that each band of the isotropic spectra has contributions from several absorptions.

The high intensity of the bands at 450–485 and 680–690 nm in the isotropic spectra of the V(III) compounds

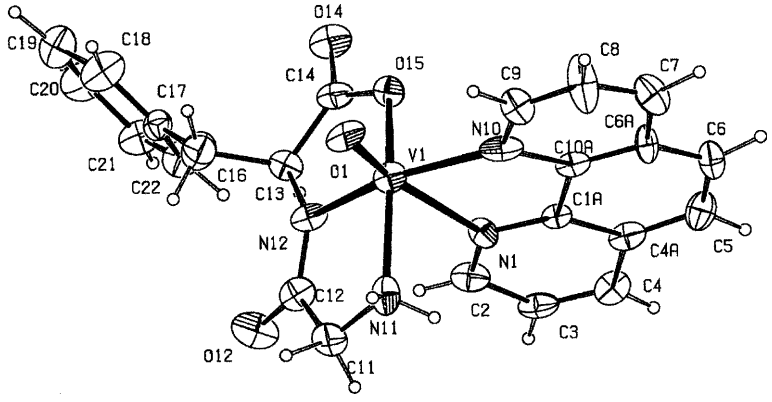


Fig. 2 X-ray crystal structure of **9**

Table 1 Crystallographic data for **8**·H_2O, **9** and **11**·1.25H_2O

	8·H_2O	**9**	**11**·1.25H_2O
Empirical formula	$C_{17}H_{18}N_4O_5V$	$C_{23}H_{20}N_4O_4V$	$C_{19}H_{22.50}N_4O_{5.25}V$
Formula weight	409.29	467.37	441.85
Temperature (K)	293(2)	293(2)	293(2)
Wavelength (Å)	0.71073	0.71073	0.71073
Crystal system	Orthorhombic	Orthorhombic	Orthorhombic
Space group	$C222_1$	$P2_12_12$	$C222_1$
Unit cell dimensions (Å)	$a = 13.847(3)$	$a = 11.8889(8)$	$a = 13.436(2)$
	$b = 23.243(4)$	$b = 12.5916(10)$	$b = 23.996(4)$
	$c = 11.987(2)$	$c = 13.6745(11)$	$c = 12.802(2)$
Volume ($Å^3$)	3858.1(13)	2047.1(3)	4127.4(11)
Z	8	4	8
Density (calculated) (Mg/m^3)	1.409	1.516	1.422
Absorption coefficient (mm^{-1})	0.549	0.525	0.520
$F(000)$	1836	964	1688
Crystal size (mm)	0.15×0.1×0.03	0.25×0.1×0.05	0.15×0.1×0.04
θ range for data collection (°)	1.71–28.82	1.62–28.94	1.70–23.33
Limiting indices	$-18 = h = 18$, $-29 = k = 28$, $-15 = l = 13$	$-15 = h = 12$, $-14 = k = 28$, $-15 = l = 13$	$-14 = h = 13$, $-26 = k = 26$, $-14 = l = 14$
Reflections collected	9071	12,176	11,664
Independent reflections	4447 ($R_{int} = 0.6040$)	4722 ($R_{int} = 0.2653$)	2977 ($R_{int} = 0.3601$)
Absorption correction	SADABS	SADABS	SADABS
Max. and min. transmission	1.000000 and 0.412198	1.000000 and 0.192529	1.000000 and 0.46518
Refinement method	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2	Full-matrix least-squares on F^2
Data/restraints/parameters	4378/0/245	4672/0/290	2927/2/276
Goodness-of-fit on F^2	0.865	0.789	0.972
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.1214$, $wR2 = 0.1797$	$R1 = 0.1082$, $wR2 = 0.2330$	$R1 = 0.0847$, $wR2 = 0.1888$
R indices (all data)	$R1 = 0.4756$, $wR2 = 0.3827$	$R1 = 0.3152$, $wR2 = 0.3605$	$R1 = 0.1536$, $wR2 = 0.3651$
Absolute structure parameter	–0.09(12)	–0.21(9)	0.04(8)
Largest diff. peak and hole	–	0.798 and –1.082 e $Å^{-3}$	0.626 and –0.497 e $Å^{-3}$

1·2MeOH–**6**·2MeOH and of the band at 450–465 nm of the $V^{IV}O^{2+}$ compounds **7**·2MeOH–**12**·2MeOH indicates that the covalency of the metal-donor atoms is significant, i.e. the vanadium "d orbitals" are significantly mixed with the ligand orbitals. Thus, the d-d transitions have an appreciable charge-transfer character. For the V(III) complexes this is reflected in the Racah (B) and nephelauxetic (β) parameters (see below). The absence of bands in the near-IR for the V(III) species **1**·2MeOH–**6**·MeOH indicates that these compounds are six coordinate [36].

The d-d bands in the electronic spectra of the V(III) compounds, in combination with the Tanabe-Sugano diagrams for the d^2 configuration assuming an octahedral ligand field, are used to calculate the Δ_O values (ligand field splitting) and the Racah parameter B (a measure of the electronic repulsion between terms of the same multiplicity) [34]. In six-coordinate vanadium(III) compounds the ground state is $^3T_{1g}(F)$ (assuming an octahedral coordination and using the corresponding symmetry notation) and three spin-allowed transitions are expected: I: $^3T_{1g}(F) \rightarrow {}^3T_{2g}$; II: $^3T_{1g}(F) \rightarrow {}^3T_{1g}(P)$; and III: $^3T_{1g}(F) \rightarrow {}^3A_{2g}$. Band III is normally weak; if it appears at all, it would be observed at relatively high energies, where it is usually obscured by charge-transfer bands. Assuming that bands I and II are the first two absorptions included in Table 4 for compounds **1**·2MeOH–**6**·2MeOH, the values of Δ_O, B and β [35] may be calculated and are included in Table 5. From Table 5 it is evident that the Racah parameter B is reduced to ca. 55–65% of the free ion value, which is 860 cm^{-1}. The B and β values of compounds **1**·2MeOH–**6**·2MeOH are comparable to those of $[V^{III}(CN)_6]^{3-}$ (550 cm^{-1}, 0.640) [36] and $[VCl_6]^{3-}$ (536 cm^{-1}, 0.623) [36], but higher than those for $[V^{III}(S_2PPh_2)_3]$ and $[V^{III}(S_2AsPh_2)_3]$, being (395 cm^{-1}, 0.459) and (397 cm^{-1}, 0.462) [36] respectively. The covalency of the metal-donor atom bonds in the latter two compounds is expected to be more important.

CD spectroscopy

The circular dichroism data for compounds **2**·2MeOH–**6**·2MeOH (solid state)[1] and **8**·MeOH–**12**·2MeOH (solution and solid states) are listed in Table 6. The CD spectra of **8**·MeOH–**12**·2MeOH in methyl alcohol or in acetonitrile in the 200–400 nm range are similar (Table 6). These spectra are complex, as might be expected for compounds where the metal and two different ligands display electronic transitions. For example, Gly-L-Val itself displays two bands at 202 and 206 nm with $\Delta\epsilon = +4.2$ and -2.2 $dm^3\,mol^{-1}\,cm^{-1}$,

[1]The vanadium(III) compounds are sensitive to hydrolysis/oxidation in solution. Their lifetime in solution is sufficient to run their UV-Vis spectra but not their CD spectra, which take several minutes. Thus, only solid state (KBr disks) CD spectra of **2**·2H_2O and **4**·2H_2O–**6**·2H_2O are included in Table 6. Compound **3**·2H_2O did not give any signal

Table 2 Selected bond lengths (Å) and angles (°) for **8**·H_2O, **9** and **11**·1.25H_2O

Compound **8**·H_2O			
V(1)-O(1)	1.625(4)	O(1)-V(1)-N(12)	107.7(2)
V(1)-O(15)	2.004(4)	N(12)-V(1)-O(15)	79.0.(2)
V(1)-N(1)	2.125(5)	N(12)-V(1)-N(11)	80.4(2)
V(1)-N(12)	1.949(6)	O(1)-V(1)-N(1)	92.9(2)
V(1)-N(11)	2.092(5)	O(15)-V(1)-N(1)	91.5(2)
V(1)-N(10)	2.323(5)	O(1)-V(1)-N(10)	164.0(2)
		O(15)-V(1)-N(10)	82.6(2)
		N(1)-V(1)-N(10)	73.5(2)
		O(1)-V(1)-O(15)	106.7(2)
		O(1)-V(1)-N(11)	95.3(2)
		O(15)-V(1)-N(11)	153.5(2)
		N(12)-V(1)-N(1)	159.0(2)
		N(11)-V(1)-N(1)	102.2(2)
		N(12)-V(1)-N(10)	86.7(2)
		N(11)-V(1)-N(10)	79.8(2)
Compound **9**			
V(1)-O(1)	1.614(7)	O(1)-V(1)-O(17)	102.0(4)
V(1)-N(14)	1.969(10)	O(17)-V(1)-N(14)	79.4(4)
V(1)-N(11)	2.079(10)	O(17)-V(1)-N(10)	93.7(4)
V(1)-O(17)	1.969(8)	O(1)-V(1)-N(11)	99.7(4)
V(1)-N(10)	2.075(11)	N(14)-V(1)-N(11)	80.6(4)
V(1)-N(1)	2.331(10)	O(1)-V(1)-N(1)	164.5(4)
		N(14)-V(1)-N(1)	86.8(4)
		N(11)-V(1)-N(1)	79.2(3)
		O(1)-V(1)-N(14)	108.3(4)
		O(1)-V(10-N(10)	92.9(4)
		N(14)-V(1)-N(10)	158.5(4)
		O(17)-V(1)-N(11)	154.1(4)
		N(10)-V(1)-N(11)	99.0(4)
		O(17)-V(1)-N(1)	83.4(3)
		N(10)-V(1)-N(1)	72.1(4)
Compound **11**·1.25H_2O			
V(1)-O(1)	1.585(7)	O(1)-V(1)-N(14)	107.9(4)
V(1)-O(11)	1.976(6)	N(14)-V(1)-O(11)	79.6(3)
V(1)-N(1)	2.155(11)	N(14)-V(1)-N(16)	80.5(4)
V(1)-N(14)	1.978(9)	O(1)-V(1)-N(1)	92.9(4)
V(1)-N(16)	2.158(8)	O(11)-V(1)-N(1)	94.2(3)
V(1)-N(10)	2.349(8)	O(1)-V(1)-N(10)	164.4(4)
		O(11)-V(1)-N(10)	83.2(3)
		O(1)-V(1)-O(11)	103.9(3)
		O(1)-V(1)-N(16)	95.7(3)
		O(11)-V(1)-N(16)	155.5(3)
		N(14)-V(1)-N(1)	159.1(3)
		N(16)-V(1)-N(1)	99.4(4)
		N(14)-V(1)-N(10)	86.9(3)
		N(16)-V(1)-N(10)	81.6(3)

Table 3 Characteristic IR bands of the vanadium(III) compounds and their oxovanadium(IV) analogues

Compound	IR bands						
	ν(OH)	$\nu_{as}(NH_2)$	$\nu_s(NH_2)$	$\nu(C=O)_{peptide}$	ν_{as}(COO)	ν_s(COO)	ν(V=O)
1·2MeOH	3400wb	3276m	3200w(sh)	1625s	1571vs	1392s	–
2·2MeOH	3400wb	3230wb	3060wb	1625s(sh)	1580vsb	1390wb	–
3·2MeOH	3400wb	3240wb	3080wb	1630sb	1575vsb	1385m(sh)	–
4	3366mb	3231mb	3100wb	1610vs(sh)	1580vsb	1380mb	–
5·2MeOH	3400mb	3230mb	3090wb	1620vsb	1580vsb	1380mb(sh)	–
6·2MeOH	3400mb	3220mb	3130wb	1620vs	1590vsb	1375w	–
7·2MeOH	3423mb	3239mb	3124w	1616vs	1593vs(sh)	1405m	963
8·MeOH	3420mb	3240m	3125w	1616vs	1578	1380	950
9	–	3250m	3149m	1651vs	1595s(sh)	1370s	957
10·1.5MeOH	3396mb	3299wb	3106m	1629vs	1590vs	1406s	968
11·H_2O	3400mb	3239m	3145w	1647s	1587vs	1397m	963
12·2MeOH	3423mb	3235m	3144w	1646s	1598vs	1402m	961

Table 4 UV-visible spectral data for the vanadium(III) and oxovanadium(IV) compounds

Compound	λ_{max} (nm) (ϵ, M^{-1} cm^{-1})
1·2MeOH[a]	689 (470), 483 (800), 292(sh) (9000), 272 (22,500), 224 (28,500), 203 (32,500)
2·2MeOH[a]	685 (450), 477 (720), 291(sh) (9500), 272 (27,000), 225 (31,000), 202 (40,000)
3·2MeOH[a]	685 (340), 468 (520), 291(sh) (8900), 272 (21,200), 223(sh) (29,000), 203 (41,500)
4[a]	687 (400), 470 (550), 291(sh) (9000), 272 (22,000), 223(sh) (30,000), 203 (42,500)
5·2MeOH[a]	683 (190), 451 (430), 291(sh) (7300), 272 (18,900), 221(sh) (25,200), 197 (40,500)
6·2MeOH[a]	684 (170), 452 (390), 290(sh) (5900), 2712 (15,200), 222 (20,500), 196 (33,600)
7·2MeOH[a]	712 (52), 446 (530), 356 (1020), 291(sh) (8700), 271 (24,000), 226 (34,700), 202 (34,200)
8·MeOH[a]	707 (47), 447 (610), 357 (1200), 291(sh) (9600), 271 (25,600), 227 (36,600), 202 (35,000)
9[a]	703 (57), 449 (590), 357 (1220), 291(sh) (10,100), 271 (25,100), 225 (37,500), 201 (43,600)
9[b]	699 (57), 453 (690), 359 (1040), 291(sh) (9800), 272 (25,200), 226 (35,600), 199 (44,000)
9[c]	710 (70), 465 (800), 361 (950), 290(sh) (9800), 271 (26,000), 295 (37,000), 196 (51,000)
10·1.5MeOH[a]	702 (52), 449 (570), 357 (1140), 292(sh) (8500), 272 (21,000), 226 (35,000), 200 (44,000)
11·H_2O[a]	700 (79), 450 (654), 356 (1700), 291(sh) (11,200), 272 (28,600), 226 (38,900), 201 (40,200)
12·2MeOH[a]	709 (55), 449 (594), 357 (1440), 291(sh) (10,200), 271 (26,400), 226 (36,700), 201 (37,000)

[a]In methyl alcohol
[b]In ethyl alcohol
[c]In acetonitrile

Table 5 Values for Δ_0, B and β parameters[a] of the octahedral V^{III} compounds **1**·2MeOH–**6**·2MeOH

Compound	Δ_0 (cm^{-1})	B (cm^{-1})[b]	β
1·2MeOH	15,540	481	0.559
2·2MeOH	15,640	495	0.576
3·2MeOH	15,700	525	0.610
4	15,640	521	0.606
5·2MeOH	15,810	581	0.675
6·2MeOH	15,810	581	0.675

[a]These three parameters were calculated using the procedure described in [35]
[b]The free-ion value of the Racah parameter B for V(III) is 860 cm^{-1}

respectively. A red shift for these two bands is expected upon complexation. These bands in **11**·H_2O may superimposed with the vanadium $e_\pi{}^b \rightarrow e_\pi{}^*$ [33] transition (C_{4v} symmetry notation is used in this work), which may also exhibit optical activity induced by the coordination of the optically active ligand. The CD band with λ_{max} at 242–248 nm is assigned to the vanadium $e_\pi{}^b \rightarrow b_2$ transition. Phenanthroline $\pi \rightarrow \pi^*$ bands, which in the free ligand appear at 263, 275 and 290 nm (isotropic absorption) [37], may be responsible for the CD bands at ~265, ~280 and ~295 nm. The anisotropy factors g_{an} ($g_{an} = \Delta\epsilon/\epsilon$ at the wavelength of the CD λ_{max}) are in the range 10^{-5}–10^{-4} for **8**·MeOH–**12**·2MeOH. The bands with λ_{max} at 344–348 nm in methyl alcohol are assigned to CT bands and also have a g_{an} value of about 10^{-4}. These low values of g_{an} are in agreement with bands arising from groups with no intrinsic optical activity [38].

The visible CD spectra of complexes **8**·MeOH–**12**·2MeOH display similar band patterns and comparable $\Delta\epsilon$ values in both solution (Fig. 4) and solid states. This means that the main features of the molecular structures of the $V^{IV}O^{2+}$ compounds are maintained in solution. The main features of these CD spectra are the following: (1) a positive band with λ_{max} at 400–410 nm, possibly due to the transition $b_2(d_{xy}) \rightarrow a_1(d_{z^2})$, which will be designated as band III ([39, 40] and references therein), (2) a negative band with λ_{max} at 470–480 nm assigned to $b_2(d_{xy}) \rightarrow b_1(d_{x^2-y^2})$ (band II) and (3) a positive band with λ_{max} at 720–735 due to $b_2(d_{xy}) \rightarrow e(d_{xz,yz})$ (band I). In the Vis spectra, band I appears as a broad absorption with λ_{max} at 700–710 nm, bands II and III being under a relatively intense band at 445–450 nm. CD solution (water, pH 7.5–9.5) studies concerning the reaction of $V^{IV}O^{2+}$ species with small peptides, where is reported the equatorial ligation of carboxylate oxygen, deprotonated peptide nitrogen and amine nitrogen atoms, reveal an almost similar pattern with the CD spectra of compounds **8**·MeOH–**12**·2MeOH [40]. The g_{an} values are ~10^{-2} for band I (and ~10^{-3} for band II), indicating that this band corresponds to a magnetic dipole-allowed transition [38].

The solid state (KBr disk) CD spectra recorded for **2**·2MeOH–**6**·2MeOH show relatively weak signals, especially in the range 400–550 nm where two bands are present, but with opposite signs to those of their oxovanadium(IV) analogues.

Chirality in transition metal compounds, and particularly in amino acid and dipeptide complexes, is generally attributed to one or more of the following structural features: (1) chiral distortions within the metal ion-donor group cluster (inherent dissymmetry); (2) chiral distributions of chelate rings (configurational dissymmetry); (3) chiral conformations of chelate rings (conformational dissymmetry); (4) asymmetric centers within the ligand (vicinal dissymmetry) [41, 42]. As emphasized previously [39, 43], in oxovanadium(IV) complexes, apart from the chirality of the amino acid moiety, two enantiomers **Ia**

Table 6 CD spectral data for the optically active vanadium(III) (solid state) and oxovanadium(IV) (solution and solid states) compounds

Compound	λ_{max} (nm) ($\Delta\epsilon$, M^{-1} cm^{-1})
CD (solution)	
8·MeOH[a]	726 (1.12), ~590sh (0.062), ~475 (–0.85), 406 (0.15), 348 (0.2), 293 (2.48), 278 (2.83), 242 (–6.61), 234sh (–5.4), 200 (9.63)
8·MeOH[b]	732 (0.55), 546 (0.0075), 472 (–0.56), 405 (0.1), 294 (2.35), 282 (2.08), 268sh (0.22), 245 (–4.19), 234sh (–2.13), 220 (0.82), 206 (3.53)
9[a]	723 (0.52), ~587sh (0.003), 478 (–0.59), 342 (0.05), 405 (0.15), 294 (1.50), 278 (2.32), 264sh (–0.87), 244 (–6.60), 234 (–3.62), 217sh (7.55)
9[b]	727 (0.58), 542 (0.27), 475 (–0.46), 395 (1.0), 345 (0.3), 294 (7.56), 279 (7.16), 269sh (0.44), 247 (–18.48), 235sh (–9.50)
10·1.5MeOH[a]	722 (0.48), ~600 (0.099), 477 (–0.38), 398 (0.08), 345 (0.1), 293 (1.55), 283 (1.91), 267sh (–0.10), 245 (–2.59), 225 (6.78)
11·H_2O[a]	725 (1.20), ~580sh (0.1), 480 (–1.02), 407 (0.13), 345 (0.3), 294 (3.82), 280 (4.32), ~265sh (–0.45), 243 (–14.1), 226 (0.44), 209 (0.3)
11·H_2O[b]	736 (1.46), ~535 (0.18), 472 (–1.54), 410 (0.12), 349 (0.2), 295 (5.0), 280 (3.9), ~270sh, 248 (–15.4), ~230sh, 204
12·2MeOH[a]	726 (0.98), ~593sh (0.05), 480 (–0.78), 407 (0.15), 345 (0.3), 294 (3.1), 280 (3.55), ~265sh (0.36), 242 (–9.91), 222 (1.65), 210 (1.80)
12·2MeOH[b]	345 (0.3), 295 (3.36), 280 (3.84), ~265sh (0.61), 243 (–9.05), ~232sh (–6.72), ~216sh (2.31)
CD (solid)[c]	
2·2MeOH	780 (+ +), 510 (–), 450 (+)
4	740 (+ + +), 500 (–), 430 (+)
5·2MeOH	758 (+ +), 553 (–), 490 (+)
6·2MeOH	765 (+ +), 480 (–), 420 (+)
8·MeOH	799 (+ + +), 565 (+), 480 (– –)
9	783 (+ +), 545 (+), 465 (– –)
10·1.5MeOH	780 (+ + +), 547 (+), 480 (– –)
11·H_2O	793 (+ + +), 570 (+), ~480 (– –)
12·2MeOH	771 (+ + +), ~570 (+), 485 (– –)

[a]In methyl alcohol
[b]In acetonitrile
[c](+ + +): positive and intense signal; (+ +): positive medium signal; (+): positive weak signal; (– –): negative medium signal; (–): negative weak signal

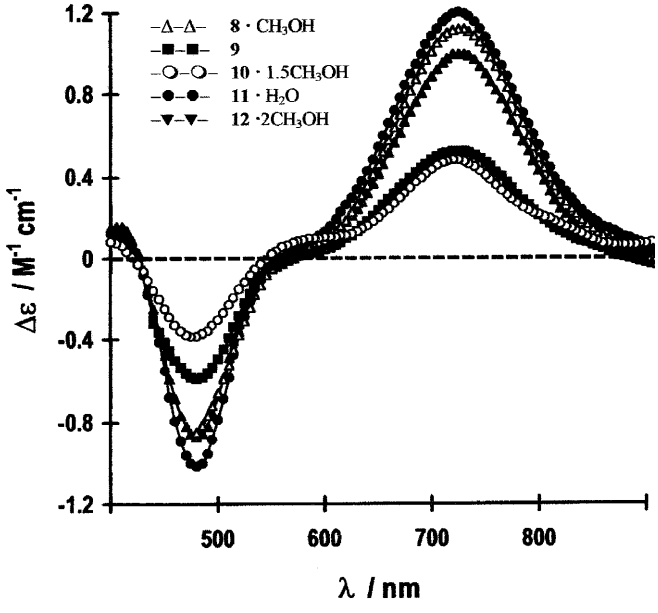
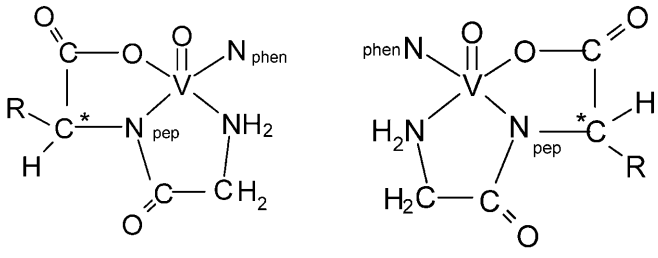


Fig. 4 CD spectra of the complexes **8**·MeOH–**12**·MeOH in dry methyl alcohol in the visible range: **8**·MeOH (*open triangles*); **9** (*filled squares*); **10**·1.5MeOH (*open circles*); **11**·H_2O (*filled circles*); **12**·2MeOH (*filled inverted triangles*)

and **Ib** (Scheme 2) may be considered for each complex (where the asymmetric carbons have the L configuration in both enantiomers). This is a general characteristic of oxovanadium(IV) compounds containing at least one equatorial chelate ring with two different donor atoms.

In the solid state, **8**·MeOH, **10**·1.5MeOH and **11**·H_2O all would be described by the *A*,L notation [44] (L for the dipeptide ligands and *A* for the vanadium center, taking as the main axis the V=O bond). In solution, both isomers *A*,L and *C*,L certainly exist; their relative ratio is not known but should be near 1:1. For this reason, in solution the inherent and configurational dissymmetries are not expected to have significant contributions here. The two fused chelate rings in **8**·MeOH–**10**·1.5MeOH and **11**·H_2O are nearly planar in the solid state. The small deviations of the four carbon atoms (Fig. 5) in the backbone of the two chelate rings [e.g. C(11), C(12), C(13) and C(14) for **8**·H_2O], from the mean planes defined by the vanadium atom and the two donor atoms of each chelate ring, mean that in the present $V^{IV}O^{2+}$ compounds the puckering of the dipeptide ligands is not very significant. In Cu^{II}-dipeptide complexes [45] where the chelate rings are also nearly planar, the conformational effect due to chelate ring puckering also makes a negligible contribution to optical activity, this being confirmed by theoretical calculations [41, 46]. Thus, it is concluded that even in the solid state the chelate ring conformation should have only a minor effect, and that the vicinal effect due to the side groups dominates the signal and magnitude of the rotatory strengths.

At this point it is worth noting that the CD signals of **8**·MeOH–**12**·2MeOH are quite strong and this is due



Ia **Ib**

A,L *C*,L

Scheme 2

to the substitution on the COO^- terminal chelate rings of the dipeptides. This fact has been verified experimentally [45] and theoretically [46] in Cu^{II}-dipeptide complexes.

Magnetic susceptibility studies

The magnetic moments of the V^{III} compounds (**1**·2MeOH–**6**·2MeOH) are in the range 2.65–2.76 μ_B at 298 K, while those of their oxovanadium(IV) analogues (**7**·2MeOH–**12**·2MeOH) are in the range 1.62–1.72 μ_B at 298 K, in agreement with the spin-only values expected for d^2, $S=1$ and d^1, $S=1/2$ systems for the V^{III} and $V^{IV}O^{2+}$ species, respectively.

EPR spectra

The EPR parameters (A and g tensors) of the distorted octahedral $V^{IV}O^{2+}$-dipeptide compounds **11**·H_2O and **12**·2MeOH, with a weak sixth ligand *trans* to the oxo group, were determined by computer simulation of the experimental EPR spectra and are given in Table 7. The EPR spectra of the oxovanadium(IV) compounds **11**·H_2O and **12**·2MeOH are typical of monomeric $V^{IV}O^{2+}$ ($S=1/2$, $I=7/2$) species with no evidence for magnetic coupling between electron spins, that is, line broadening or splitting in the spectral features. The EPR data of these two complexes are almost identical with those of **7**·2MeOH–**10**·1.5MeOH reported in the literature and are included in Table 7 as well for comparison. The $A_{z,\text{peptide}}$ values for **7**·2MeOH–**12**·2MeOH were derived from the so-called additivity relationship [47] (Eq. 5):

$$A_{z,\text{calcd}} = \sum \eta_i A_{zi}/4 \qquad (5)$$

where i denotes the different types of ligation to $V^{IV}O^{2+}$ equatorial donor atoms, η_i (= 1–4) is the number of donor atoms of type i, and $A_{z,i}$ is the measured coupling constant (from model studies) when all four equatorial donor atoms are of type i. The mean $A_{z,\text{peptide}}{}^2$ is 34.7×10^{-4} cm^{-1} and it is the lowest A_z value reported so far [47] for various types of equatorial nitrogen donor atoms. Such low $A_{z,i}$ values reflect relatively strong σ and some π bonding of the deprotonated peptide nitrogen atom to the vanadium atom.

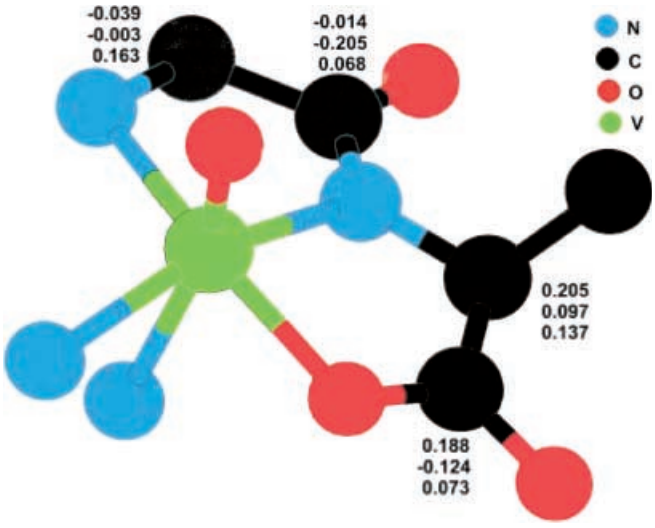


Fig. 5 Plot of the $[V^{IV}O(dip)(phen)]$ compounds showing the deviations of the four carbons of the chelate rings from the mean planes defined by vanadium-N_{amine}-$N_{peptide}$ and vanadium-$N_{peptide}$-$O_{carboxylate}$ atoms

Conclusions

In conclusion, vanadium(III) compounds and their oxovanadium(IV) analogues of the general formulae $[V^{III}(dip)(MeOH](phen)]^+$/$[V^{IV}O(dip)(phen)]$ with a series of dipeptides, having aliphatic as well as aromatic side chains, were synthesized and structurally (for the $V^{IV}O^{2+}$ complexes) and physicochemically characterized.

The vanadium(III) species are susceptible to hydrolysis/oxidation to their $V^{IV}O^{2+}$ compounds, which are also susceptible to hydrolysis but to a much lesser extent. When phen is replaced by bpy (T.A. Kabanos et al., unpublished results), which is a more flexible ligand, the hydrolytic stability of the $V^{III}/V^{IV}O^{2+}$-dipeptide fragments is substantially reduced and this presumably means that the degree of hydrolytic stability varies significantly, depending on the nature of the ligands co-coordinated to the vanadium center.

The oxovanadium(IV) compounds gave quite strong CD signals in the visible range of the spectrum with a characteristic pattern which may be used as a fingermark

[2]The $A_{z,i}$ values for $i = RCO_2^-$, RNH_2 and =N= (aromatic imine, i.e. the phenanthroline nitrogen) were derived from oxovanadium(IV) compounds reported in [47] and [18] are 42.70, 40.1 and 41.80×10^{-4} cm^{-1}, respectively

Table 7 Spin-Hamiltonian parameters for the [$V^{IV}O$(dipeptide)(phen)] complexes

Compound	g_z	g_x	g_y	A_z	A_x	A_y	$A_{z,\text{peptide}}$	Ref
7·2MeOH	1.952	1.980	1.984	160.0	53.0	58.1	35.4	[18]
8·MeOH	1.952	1.984	1.980	158.6	54.5	55.0	34.0	[18]
9	1.951	1.981	1.983	159.0	54.0	58.0	34.4	[23]
10·1.5MeOH	1.952	1.982	1.984	160.0	53.0	58.0	35.4	[23]
11·H_2O	1.951	1.984	1.984	159.1	54.5	54.5	34.5	This work
12·2MeOH	1.952	1.984	1.984	159.2	54.3	54.3	34.6	This work

for N_{amine}-$N_{peptide}$-$O_{carboxylate}$ ligation of a peptide or a protein to $V^{IV}O^{2+}$ center. In contrast, their vanadium(III) analogues gave rather weak Cotton effects of opposite sign.

Efforts to prepare $V^{III}/V^{IV}O^{2+}/V^{V}$ complexes with sulfur, basic and acidic side chains are under way, as well as efforts to replace the phen ligand in the V^{III}-dipeptide compounds with a more suitable bidentate ligand to make them less susceptible to hydrolysis/oxidation and thus enabling us to better characterize these compounds.

The EPR spectra of $V^{IV}O^{2+}$-dipeptide compounds, **7**·2MeOH–**12**·2MeOH, and in particular the $A_{z,\text{amide}}$ contribution to their experimental A_z values, indicate that the V-$N_{peptide}$ bond is quite strong.

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