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Six-co-ordinated vanadium-(IV) and -(V) complexes of benzimidazole and pyridyl containing ligands†

Debbie C. Crans,* Anastasios D. Keramidas, Sean S. Amin, Oren P. Anderson and Susie M. Miller

Department of Chemistry, Colorado State University, Fort Collins, CO 80523-1872, USA

A new series of vanadium-(IV) and -(V) complexes with ligands containing functionalities including hydroxyethyl, carboxylate, amine, pyridyl and benzimidazole have been prepared. The crystal structures of three complexes have been determined. All the vanadium atoms are six-co-ordinate even though previous complexes of the diethanolamine type have contained five-co-ordinate vanadium. The V–N (amine) bonds of the benzimidazole complexes are significantly longer than those of pyridyl complexes. An empirical relationship between pK_a value of the protonated ligand and the V–N (amine) bond length (*trans* to an oxo group) of the corresponding vanadium-(IV), -(V) and -(IV/V) complexes was observed. Spectroscopic studies (NMR, ESR and UV/VIS) showed that the complexes remain intact in aqueous solution. In general, the hydroxyethyl substituted vanadium complexes are less stable than corresponding acetate substituted ones and the benzimidazole complexes are less stable than corresponding pyridyl complexes. The combined knowledge concerning the properties of all these complexes provides an excellent platform to design new vanadium complexes pertinent to biological applications.

A comprehensive characterization of vanadium compounds in aqueous solution is essential for mechanistic biological studies related to the insulin-mimetic action of vanadium compounds[1] and the cofactor activity of vanadate in haloperoxidases.[2] Solid state structural information combined with characterization of solution properties are necessary to provide appropriate information for compound design, probing mechanistic and catalytic questions of relevance to the biology of vanadium compounds. In contrast to many other metals, the vanadium atom can adopt a variety of different co-ordination numbers given its small atomic radius. As a consequence it generally shows no significant preferences for five-, six- or seven-co-ordination spheres; the compound geometry is often highly ligand dependent. Even well known vanadium compounds are often poorly described with respect to their stability and structure in aqueous solution. For example, many vanadium compounds such as the oxovanadium oxalate and oxovanadium picolinate (pyridine-2-carboxylate) complexes are not stable at the physiological pH range.[1] Furthermore, the structure of the oxovanadium(V) triethanolaminate complex in aqueous solution is different to that characterized by X-ray crystallography.[3] Particularly limited information is available on the lability of most vanadium compounds and recently even the oxovanadium edta (ethylenedinitrilotetraacetate) complex was found to be labile under physiological conditions.[4,5] Thus, it becomes important to determine not only the solid state structure of vanadium complexes, but their solution structure and other properties, and such information will be particularly useful if the effects of different ligand functionalities can be identified.

The simplest tri- and tetra-dentate aminoalcohols based on diethanolamine (dea) form vanadium(V) complexes that contain a five-co-ordinate vanadium atom.[3,6–10] The complex has the amino group co-ordinated axial *trans* to an oxo group and two chelated deprotonated hydroxyethyl groups in the equatorial plane.[3] We recently found that the stability of these complexes is linked to the pK_a value of the deprotonated ligand, and that a pK_a value in the region of 8 (pK_a of $H_2VO_4^-$) leads to optimum stability.[6,10] Furthermore, substituting the hydroxyethyl arms with one to three carboxylate group(s) or a phenolate group leads to complexes that contain six-co-ordinate vanadium.[8,11] The complexes generated from ligands with co-ordinating carboxylates are typically more stable and less labile than those from ligands with co-ordinating hydroxyethyl groups although the aqueous solution properties of only a few compounds have been described in the literature.[8,12] In addition to these studies a series of compounds have been reported containing ligands with both carboxylate and pyridyl functionalities.[13,14] These complexes were characterized by X-ray crystallography and their reactivity in aqueous solution. Unfortunately, information on corresponding hydroxyethyl-containing complexes was not available. In any event the combined knowledge on the properties of complexes with hydroxyethyl, acetate and methylpyridyl functionalities provided the impetus to design new ligand systems with the additional and specific combinations of functionalities described here.

In this study we have prepared families of new ligands to define the properties of complexes containing ligands with hydroxyethyl, acetate, methylpyridyl and methylbenzimidazole type functionalities. The objective is to determine how each functionality and combination of functionalities affect co-ordination number and structure on the one hand and stability and lability on the other. We have prepared both the vanadium-(IV) and -(V) complexes and characterized some of these complexes by X-ray crystallography to be able to correlate the solution and solid state structure of these new compounds and those described previously. The solution structure and some properties of all the new complexes have been characterized by spectroscopic methods and some general patterns were identified. Specifically, it is the purpose of this paper to compare (1) the properties of vanadium complexes formed from the *N*-(2-pyridylmethyl)iminodiacetic acid/iminodiethanol ligands with (2) the properties of vanadium complexes formed from *N*-(2-benzimidazolylmethyl)iminodiacetic acid/iminodiethanol ligands. These studies will characterize the effects of a combination of four functionalities in the ligands and provide an excellent platform to design new ligands and new vanadium complexes.

Experimental

Materials

All chemicals obtained from Sigma or Aldrich were of reagent

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† *Non-SI units employed*: bar = 101 325 Pa, G = 10^{-4} T.

grade and used without further purification. (2-Pyridylmethyl)iminodiacetic acid (H_2pmida)[15] and [VO(pmida)(H_2O)]·H_2O[13] were prepared as described previously. Methanol was dried over Na and distilled. Microanalyses were performed by Desert Analytics, Tucson, AR.

Synthesis of ligands

***N*-(2-Pyridylmethyl)iminodiethanol (H_2pmide).** Diethanolamine (31.21 g, 296.8 mmol) was dissolved in Pr^{i}OH (100 cm^3), followed by addition of 2-(chloromethyl)pyridine (16.55 g, 100.9 mmol); this solution was refluxed overnight. The red solution was evaporated until dryness and the oily residue extracted with hot acetonitrile (2 × 200 cm^3). The acetonitrile was evaporated and the residue distilled under vacuum (12 mbar, 185–220 °C). The yellow oil (6.0 g, 30%) was redistilled and now passed at 195–210 °C (Found: C, 61.3; H, 8.1; N, 14.2. $C_{10}H_{16}N_2O_2$ requires C, 61.2; H, 8.2; N, 14.3%). NMR (D_2O): ^1H (300 MHz), δ 2.74 (t, 4 H, CH_2OH), 3.67 (t, 4 H, NCH_2CH$_2$), 4.82 (s, 2 H, NCH$_2$N), 7.37, 7.50, 7.85, 8.45 (t, d, t, d, 4 H, pyridine H); ^{13}C-{^1H} (75 MHz), δ 58.3, 61.5, 62.3, 125.9, 127.4, 140.8, 159.9 and 160.1.

2-(Aminomethyl)benzimidazole dihydrochloride. Glycine (10.00 g, 133.2 mmol) and 1,2-phenylenediamine (10.80 g, 99.87 mmol) were dissolved in 4 mol dm^{-3} HCl (150 cm^3). The brown solution was refluxed for 4 d. The resulting blue solution was concentrated to 50 cm^3 and kept at −20 °C overnight at which time bluish crystals had formed. The crystals (16 g, 74%) were filtered off and washed twice with acetone (50 cm^3) (Found: C, 40.3; H, 5.5; N, 17.4. $C_8H_{11}Cl_2N_3$·H_2O requires C, 40.3; H, 5.5; N, 17.65%). NMR (D_2O): ^1H (300 MHz), δ 4.85 (s, 2 H, CCH_2NH$_2$) and 7.80 (m, 4 H, aryl CH); ^{13}C-{^1H} (75 MHz), δ 36.9, 117.1, 129.9, 133.6 and 146.1. These data correspond to those reported previously.[16]

***N*-(Benzimidazol-2-ylmethyl)iminodiacetic acid (H_2bmida).** 2-(Aminomethyl)benzimidazole dihydrochloride (7.80 g, 35.5 mmol) and chloroacetic acid (6.37 g, 67.5 mmol) were dissolved in water (10 cm^3). The pH of the solution was adjusted to 8.0 by the addition of 5 mol dm^{-3} NaOH. It was refluxed and the pH checked at hourly intervals and adjusted as above. After approximately 5 h the pH no longer changed. The solution was cooled to room temperature and filtered to remove some precipitated decomposition product. The pH was adjusted to 2.5 by addition of 5 mol dm^{-3} HCl and a white precipitate began to form. The mixture was cooled to 0 °C for 6 h further to precipitate product. The precipitate (4.5 g, 25%) was filtered off and washed with cold water (10 cm^3) and twice with acetone (30 cm^3) (Found: C, 53.5; H, 4.9; N, 15.45. $C_{12}H_{13}N_3O_4$·0.5H_2O requires C, 52.9; H, 5.1; N, 15.4%). NMR (D_2O): ^1H (300 MHz), δ 3.57 (s, 4 H, NCH_2CO$_2$H), 4.34 (s, 2 H, CCH$_2$N) and 7.46 (m, 4 H, aryl CH); ^{13}C-{^1H} (75 MHz), δ 54.0, 60.3, 117.6, 126.5, 138.9, 151.7 and 177.8. The elemental analysis corresponds to those reported previously.[17]

***N*-(1-Carboxymethylbenzimidazol-2-ylmethyl)iminodiacetic acid (H_3bmidaa).** 2-(Aminomethyl)benzimidazole dihydrochloride (6.50 g, 29.6 mmol) and chloroacetic acid (16.75 g, 177.3 mmol) were dissolved in water (10 cm^3). The pH of the solution was adjusted to 8.0 by the addition of 5 mol dm^{-3} NaOH. The solution was refluxed and the pH adjusted as above at hourly intervals. After approximately 4 h the pH no longer changed. Chloroacetic acid (8.38 g, 88.7 mmol) was added and the solution refluxed overnight. The solution was cooled to room temperature and filtered to remove some precipitated decomposition product. The pH was adjusted to 2.5 by the addition of 5 mol dm^{-3} HCl and a white precipitate began to form. The mixture was cooled to 0 °C for 6 h further to precipitate product. The precipitate (6.9 g, 72%) was filtered off and washed with cold water (10 cm^3) and twice with acetone (30 cm^3) (Found: C, 45.4; H, 5.0; N, 11.3. $C_{14}H_{15}N_3O_6$·2H_2O requires C, 47.05; H, 5.3; N, 11.8%). NMR (D_2O, pD 8.5): ^1H (300 MHz), δ 3.31 (s, 4 H, NCH_2CO$_2$H), 4.04 (s, 2 H, CCH$_2$N), 5.11 (s, 2 H, aryl NCH_2CO$_2$H), 7.37 (m, 2 H, aryl CH) and 7.71 (m, 2 H, aryl CH); ^{13}C-{^1H} (75 MHz), δ 50.2, 60.4, 66.2, 68.0, 113.7, 119.7, 127.5, 127.8, 137.2, 139.6, 157.8, 175.5, 181.0 and 182.9.

***N*-(Benzimidazol-2-ylmethyl)iminodiethanol (H_2bmide).** Bicine [*N*,*N*-bis(2-hydroxyethyl)glycine] (9.00 g, 55.2 mmol) and 1,2-phenylenediamine (5.50 g, 50.9 mmol) were dissolved in 7 mol dm^{-3} HCl (60 cm^3). The brown solution was refluxed for 2 d. The resulting green solution was cooled to room temperature and the pH adjusted to 11.0 by addition of 10 mol dm^{-3} NaOH. The brown solution was concentrated *in vacuo* until a white precipitate began to form. The mixture was maintained at −10 °C overnight allowing more of the compound to precipitate. The precipitate (13 g, 93%) was filtered off and washed with cold water (10 cm^3) and twice with cold acetone (10 cm^3). The compound was recrystallized from hot acetone, initially forming an oil. After removal of the acetone the oil solidified upon standing. Owing to its hygroscopic nature the hydrochloride salt was prepared by addition of concentrated HCl to a concentrated ethanolic solution of the free ligand, and subsequent recrystallization from methanol (Found: C, 46.15; H, 6.0; N, 13.45. $C_{12}H_{17}N_3O_2$·2HCl requires C, 46.75; H, 6.2; N, 13.6%). NMR (D_2O): ^1H (300 MHz), δ 2.92 (t, 4 H, CH_2OH), 3.73 (t, 4 H, NCH_2CH$_2$), 4.17 (s, 2 H, NCH$_2$N) and 7.43 (m, 4 H, aryl CH). ^{13}C-{^1H} (75 MHz), δ 53.6, 58.5, 60.7, 117.4, 126.7, 138.4 and 152.3.

Synthesis of vanadium complexes

Na[VO$_2$(pmida)] 1. Sodium trioxovanadate NaVO$_3$ (0.400 g, 3.28 mmol) was dissolved in water (10 cm^3). Solid H_2pmida (0.800 g, 3.57 mmol) was added and the mixture stirred until dissolution was complete. The pH was adjusted to 7.5 by addition of 5 mol dm^{-3} NaOH after which point acetone (35 cm^3) was added. The resulting yellow solution was kept at −15 °C for 5 d after which time a yellow crystalline material had formed. The crystals (0.63 g, 58% with respect to NaVO$_3$) were filtered off and washed twice with ethanol (10 cm^3) and acetone (10 cm^3) (Found: C, 34.4; H, 3.5; N, 7.9. $C_{10}H_{10}N_2NaO_6V$·1.5H_2O requires C, 33.8; H, 3.7; N, 7.9%). IR (KBr, cm^{-1}): 3447s, 2365m, 2342m, 1651s, 1619s, 1398m, 1164w, 899s, 776w and 528w. NMR (D_2O): ^{51}V (79 MHz), δ −503; ^{13}C-{^1H} (75 MHz), δ 65.5, 67.7, 68.0, 127.0, 128.6, 144.5, 154.8, 159.9, 181.3 and 183.1.

[VO$_2$(Hpmide)] 2a. Vanadium(v) oxide (0.15 g, 0.80 mmol) was added to water, followed by tetraethylammonium hydroxide (0.67 g, 1.6 mmol); the solution was heated. After the V_2O_5 had dissolved H_2pmide (0.45 g, 2.3 mmol) was added, the mixture stirred and the pH adjusted to 6.6 with 6 mol dm^{-3} HCl. Acetone was added until precipitation was observed and the sample maintained at −15 °C overnight. The crystalline compound formed (0.37 g, 64% with respect to V_2O_5) was filtered off (Found: C, 34.3; H, 6.1; N, 8.0. $C_{10}H_{15}N_2O_4V$·4H_2O requires C, 34.3; H, 6.6; N, 8.0%). IR (KBr, cm^1): 3386s, 1652m, 1606m, 1477m, 1454m, 1329w, 1292w, 1076s, 1057s, 919s, 872s, 776s, 725s, 651m and 563s.

Na[VO$_2$(pmide)] 2b. The compound NaVO$_3$ (0.20 g, 1.6 mmol) was dissolved in water (10 cm^3), H_2pmide (0.45 g, 2.3 mmol) added and the mixture stirred until dissolution was complete. The pH was adjusted to 6.5 by addition of 5 mol dm^{-3} HCl. Acetone was added until the solution became cloudy. The resulting greenish solution was kept at −15 °C for 4 d at which time a yellow crystalline material had precipitated. The precipitate (0.59 g, 94% with respect to NaVO$_3$) was filtered off and washed twice with acetone (10 cm^3). NMR (D_2O): ^{51}V (79 MHz), δ −500; ^{13}C-{^{1}H} (75 MHz), δ 59.8, 60.1, 64.0, 72.8, 66.7, 125.3, 127.8, 143.8, 154.1 and 162.5. Additional characterization showed the anion to be deprotonated.

[VO(bmida)(H_2O)] 3. The complex [VO(acac)$_2$] (acac = pentane-2,4-dionate) (0.50 g, 1.9 mmol) and H_2bmida (0.53 g, 1.9 mmol) were refluxed in water (30 cm^3) for 3 h. The resulting blue solution was kept at 4 °C overnight yielding a blue precipitate. The precipitate {0.60 g, 91% with respect to [VO(acac)$_2$]} was filtered off and washed twice with acetone (10 cm^3) (Found: C, 41.2; H, 4.0; N, 11.8. $C_{12}H_{15}N_3O_6V$ requires C, 41.4; H, 4.3; N, 12.1%). IR (KBr, cm^{-1}): 2978s, 1618s, 1474m, 1455m, 1423m, 1390s, 1323m, 1278m, 1124w, 1052m, 983m, 939m, 902m, 744s and 617w.

NH_4[VO_2(bmida)] 4. The compound NH_4VO_3 (0.500 g, 4.28 mmol) and NaOH (0.190 g, 4.75 mmol) were dissolved in water (5 cm^3). Solid H_2bmida (1.266 g, 4.815 mmol) was added, the mixture stirred and the pH adjusted to 6.5 with 5 mol dm^{-3} HCl. Acetone (35 cm^3) was added and the resulting greenish solution was kept at −15 °C for 5 d at which time a yellowish solid material had formed. The precipitate (0.60 g, 35% with respect to NH_4VO_3) was filtered off and washed twice with acetone (10 cm^3) (Found: C, 36.1; H, 4.7; N, 14.0. $C_{12}H_{15}N_4O_6V\cdot 2H_2O$ requires C, 36.2; H, 4.8; N, 14.1%). IR (KBr, cm^{-1}): 2978s, 1618s, 1474m, 1455m, 1423m, 1390s, 1323m, 1278w, 1124m, 1053m, 983s, 939m, 902m, 744s, 617w and 461m. NMR (D_2O): ^{51}V (79 MHz), δ −540; ^{13}C-{^{1}H} (75 MHz), δ 61.1, 66.2, 68.0, 115.4, 119.2, 127.1, 127.5, 135.8, 140.1, 156.9, 181.0 and 183.0.

Na_2[VO_2(bmidaa)] 5a. This compound was prepared in a similar manner to **4** where the H_2bmida is replaced by H_3bmidaa. The vanadium starting material was $NaVO_3$ (0.20 g, 1.6 mmol) and the isolated yield was 0.60 g (81% with respect to $NaVO_3$) (Found: C, 34.1; H, 2.9; N, 8.5. $C_{14}H_{12}N_3Na_2O_8V\cdot 2H_2O$ requires C, 34.8; H, 3.3; N, 8.7%). IR (KBr, cm^{-1}): 3431s, 2990m, 2947m, 2137w, 1615s, 1494m, 1453m, 1390s, 1346m, 1301m, 1220w, 1166w, 1126m, 1112m, 1005m, 969m, 906s, 794m, 754m and 695m. NMR (D_2O): ^{51}V (79 MHz), δ −538; ^{13}C-{^{1}H} (75 MHz), δ 50.2, 60.4, 66.2, 68.0, 113.7, 119.7, 127.5, 127.8, 137.2, 139.6, 157.8, 175.5, 181.0 and 182.9.

[NH_4]$_2$[VO_2(bmidaa)] 5b. This compound was prepared in a similar manner to **4** where the H_2bmida is replaced by H_3bmidaa. The vanadate starting material was NH_4VO_3 (0.20 g, 1.7 mmol) and the isolated yield was 0.50 g (96% with respect to NH_4VO_3) (Found: C, 34.9; H, 4.8; N, 14.35. $C_{14}H_{21}N_5O_8V\cdot 2H_2O$ requires C, 35.4; H, 5.2; N, 14.8%). ^{51}V NMR (79 MHz, D_2O): δ −539. See later for ^{1}H and ^{13}C NMR data.

[VO(acac)(Hbmide)] 6. The compound [VO(acac)$_2$] (0.95 g, 3.6 mmol) and H_2bmide (0.89 g, 3.8 mmol) were refluxed in CH_3CN (25 cm^3) for 5 h. The solution changed from blue to green over 30 min and a green precipitate formed over the same time. The mixture was cooled to room temperature. The precipitate {0.78 g, 55% with respect to [VO(acac)$_2$]} was filtered off and washed twice with acetone (10 cm^3) (Found: C, 39.3; H, 4.4; N, 11.2. $C_{17}H_{23}N_3O_5V$ requires C, 39.0; H, 4.0; N, 11.4%). IR (KBr, cm^{-1}): 3488m, 2886m, 1578s, 1521s, 1474m, 1429m, 1374s, 1278m, 1215m, 1192m, 1082m, 1061w, 1008m, 971s, 884w, 825m, 752m, 676m, 626w, 589w, 534m and 508w.

[VO(CH_3O)(bmide)]·CH_3OH 7. The compound [VO{(CH_3)$_2$CHO}$_3$] (0.650 g, 2.66 mmol) was dissolved in CH_3OH (30 cm^3). Solid H_2bmide (0.650 g, 2.76 mmol) was added and the mixture stirred until dissolution was complete. The resulting orange solution was kept at −15 °C for 4 d after which time a yellow crystalline material had formed. The crystalline material (0.25 g, 28% with respect to [VO{(CH_3)$_2$CHO}$_3$]) was filtered off (Found: C, 45.9; H, 5.7; N, 11.9. $C_{13}H_{20}N_3O_4V$ requires C, 46.3; H, 6.06; N, 11.6%). IR (KBr, cm^{-1}): 3268s, 1627m, 1541m, 1452s, 1398m, 1323w, 1282m, 1054s, 1010w, 921s, 806w, 739s, 664s, 580s and 521m. ^{51}V NMR (79 MHz, D_2O): δ −542. See later for ^{1}H and ^{13}C NMR data.

Potentiometric measurements of pK_a values

Using standardized stock solutions of HCl (0.1373 mol dm^{-3}) and NaOH (0.1105 mol dm^{-3}), the pK_a values of the benzimidazole and pyridyl ligands were determined at ambient temperature and at a high ionic strength mainly determined by the 0.40 mol dm^{-3} KCl. Ligand concentrations titrated ranged from 8 to 12 mmol dm^{-3}. Titrant volumes were 0.2 cm^3 in the regions where the pH changed most rapidly upon addition of titrant. The titration curves from which the pK_a values were calculated were obtained from 60–90 points, depending on the specific amine titrated. The pK_a values were calculated by using an iterative error minimization of the experimental values from the calculated values using the Microsoft EXCEL version 5.0a for Power Macintosh (Soft-Art, Inc., 1985–1995) program. The theoretical values were calculated from equations applying to dibasic acids.

Preparation of NMR samples for stability measurements

Samples (1.0 cm^3) for stability measurements were prepared from a 500 mmol dm^{-3} stock solution of $NaVO_3$ at pH 7.0, a 500 mmol dm^{-3} stock solution of the ligand at pH 7.0 and a 4.00 mol dm^{-3} stock solution of KCl. All the samples contained 20% D_2O and 0.40 mol dm^{-3} KCl. The concentrations of vanadate and ligand ranged from 0.5 to 100 mmol dm^{-3}. The pH of these solutions was adjusted with NaOH or HCl (added to the ligand, prior to addition of vanadate), concentrations ranging from 0.001 to 6 mol dm^{-3}. For all other NMR measurements 500 mmol dm^{-3} stock solutions of crystalline vanadium compounds were used.

NMR spectroscopy

The NMR spectra were recorded on a Bruker ACP-300 spectrometer operating at 300 MHz for ^{1}H, 75 MHz for ^{13}C and 79 MHz for ^{51}V. The ^{51}V NMR spectra were recorded using a sweep width of about 25 000 Hz, an accumulation time of 0.1 s, a pulse angle of 90°, no relaxation delay and approximately 1000 to 5000 scans. No significant changes were observed when an increased relaxation delay was used during accumulation of the spectra. The ^{51}V spectra were referenced to external $VOCl_3$ (δ 0). An exponential line broadening of 15 Hz was imposed on the accumulated data before Fourier transformation, at which time the ^{51}V NMR spectrum was phased and manually integrated three times. Using the known total vanadium concentration (assuming all vanadium remains in oxidation state V), the individual concentrations of each vanadium species were calculated from the mole fractions of each species in the integrated spectra. The temperature for the variable-temperature experiments was calibrated using an 80% ethylene glycol sample in (CD_3)$_2$SO and the accuracy was ±1 °C.

ESR spectroscopy

The ESR spectra were recorded on a Bruker ESP 300 spectrometer in frozen solutions at −133 °C in 4 mm quartz tubes. The spectrometer was operating in the X-band (9.46 GHz) with microwave power of 200 μW. Furthermore, we used a modulation frequency of 100 kHz, a modulation amplitude of 7.95 G, a time constant of 20.48 ms and a conversion time of 81.92 ms. The spectrometer was calibrated using a powder sample of 2,2-bis(4-*tert*-octylphenyl)-1-picrylhydrazyl (dpph, $g = 2.0037$). The concentrations of the vanadium(IV) compounds were 1.00 mmol dm^{-3} in dimethylformamide (dmf)–water (1 : 1 v/v) unless

Table 1 Details of the crystallographic experiment and computations for $[VO_2(Hpmide)]\cdot 4H_2O$ **2a**, $[VO(bmida)(H_2O)]\cdot H_2O$ **3** and [VO(acac)(Hbmide)] **6**

	2a	**3**	**6**
Molecular formula	$C_{10}H_{23}N_2O_8V$	$C_{36}H_{47}N_9O_{19}V_3$	$C_{17}H_{23}N_3O_5V$
M	350.24	1056.60	400.32
Crystal system	Monoclinic	Monoclinic	Monoclinic
Space group	$P2_1/n$	$P2_1/c$	$P2_1/c$
a/Å	10.1675(7)	18.566(4)	8.743(2)
b/Å	13.3144(12)	16.035(3)	12.200(2)
c/Å	12.2148(7)	14.555(3)	17.055(3)
β/°	111.179(5)	97.64(3)	98.21(3)
U/Å^3	1541.9(2)	4294.6(15)	1800.6(6)
Z	4	4	4
D_c/g cm^{-3}	1.504	1.622	1.466
μ/mm^{-1}	0.682	0.729	0.584
2θ Range/°	4–60.0	4.0–50.0	4.0–50.0
No. unique reflections	4467	8088	3178
No. observed reflections [$F > 2.0\sigma(F)$]	3927	4832	2233
R (observed data)	0.0355	0.0624	0.0598
R'	0.1005	0.0880	0.0728

specified otherwise. The spectra were analysed to second order using the perturbation equations of Bleaney.[18,19]

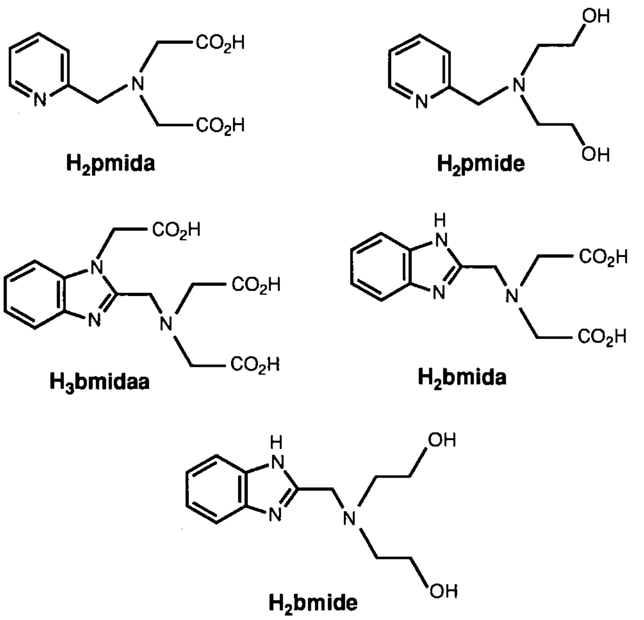
Crystallography

Intensity data were collected on a Siemens P4 diffractometer using Mo-Kα (λ = 0.7107 Å) radiation. The unit-cell constants were determined from a least-squares fit to the angles of 25 reflections. The structure was solved using the direct methods routine TREF in the Siemens SHELXTL program library.[20] Lorentz-polarization corrections were applied. The intensities of three standard reflections were examined every 97 reflections; no significant changes were noted. Neutral atom scattering factors with anomalous dispersion included were used.[21] The details of the crystallographic experiment and computations for compounds **2a**, **3** and **6** are listed in Table 1.

Compound 2a. Crystals of compound **2a** were obtained by layering acetone onto a concentrated aqueous solution of it. A clear pale yellow block (0.40 × 0.30 × 0.20 mm) was used for the X-ray experiment. Data were collected (θ–2θ scans) to $(\sin\theta)/\lambda = 0.364$ Å^{-1} ($-1 \le h \le 14$, $-1 \le k \le 18$, $-17 \le l \le 16$). A total of 4467 unique reflections were observed; all were employed during the full-matrix weighted least-squares refinement on F^2. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters; at convergence $[(\Delta/\sigma)_{max} = 0.071$ for the last cycle] $R = 0.0355$ and $wR2 = 0.1091$.

Compound 3. Crystals of compound **3** were obtained by the slow cooling of a warm (60 °C) concentrated aqueous solution of **3** to ambient temperature. A clear blue prism (0.28 × 0.20 × 0.16 mm) was used for the X-ray experiment. Data were collected (θ–2θ scans) to $(\sin\theta)/\lambda = 0.595$ Å^{-1} ($-24 \le h \le 24$, $-20 \le k \le 1$, $-1 \le l \le 17$). A total of 8088 unique reflections were observed; all were employed during the full-matrix weighted least-squares refinement on F^2. The asymmetric unit of the unit cell contains three discrete molecules of **3**. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters; at convergence $[(\Delta/\sigma)_{max} = 0.020$ for the last cycle] $R = 0.0630$ and $wR2 = 0.1486$.

Compound 6. Crystals of compound **6** were obtained by layering molar equivalents of a saturated CH_3OH solution of $[VO(acac)_2]$ with a CH_3OH solution of H_2bmide at room temperature. A clear pale green prism (0.17 × 0.32 × 0.20 mm) was used for the X-ray experiment. Data were collected (θ–2θ scans) to $(\sin\theta)/\lambda = 0.595$ Å^{-1} ($-1 \le h \le 10$, $-1 \le k \le 14$, $-20 \le l \le 20$). A total of 3178 unique reflections were observed; all were employed during the full-matrix weighted least-squares refinement on F^2. All non-hydrogen atoms were refined with anisotropic thermal displacement parameters; at convergence $[(\Delta/\sigma)_{max} = 0.001$ for the last cycle] $R = 0.0597$ and $wR2 = 0.1687$.



Scheme 1 Ligand structure and abbreviations

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1997, Issue 1. Any request to the CCDC should quote the full literature citation and the reference number 186/541.

Results and Discussion

Synthesis of the ligands and vanadium complexes

The structures and abbreviations for the ligands prepared in this work are shown in Scheme 1. Two distillations were needed to obtain pure H_2pmide which reduced the isolated yield to 30%. 2-(Aminomethyl)benzimidazole dihydrochloride was prepared in good yield by the reaction of glycine and 1,2-phenylenediamine. This compound was previously prepared,[16] but our longer refluxing time may have increased the yield from this reaction by 18%. The H_2bmida ligand was prepared by the reaction of 2-(aminomethyl)benzimidazole dihydrochloride with 1.9 equivalents of chloroacetic acid. This compound was previously prepared[17] using 3 equivalents of chloroacetic acid. Although our procedure did not give as high a yield (65%) as previously reported, it involved only a one-pot reaction and convenient isolation of the ligand.

With the exception of compound **7**, vanadium(V) complexes were synthesized using either $NaVO_3$, NH_4VO_3 or V_2O_5 in aqueous solution. Typically a 10% excess of ligand was employed to ensure complete complexation of vanadium. The pH was adjusted to near neutral or slightly acidic conditions to ensure that decavanadate did not form and interfere with complex formation. Vanadium(IV) compounds were synthesized using $[VO(acac)_2]$ in either aqueous solution or organic solvent. Direct reaction of $[VO(acac)_2]$ with H_2pmide did not generate an isolatable complex.

Characterization of solid state

Crystallography. The structure and atomic labelling scheme for compound **2a** are presented in Fig. 1. Interatomic bond

Table 2 Bond lengths (Å) for compounds [VO_2(Hpmide)]·$4H_2O$ **2a**, [VO(bmida)(H_2O)]·H_2O **3** and [VO(acac)(Hbmide)] **6**

Compound **2a**							
V−O(2)	1.6344(12)	V−O(3)	2.2975(11)	C(2)−C(3)	1.389(3)	C(6)−N(1)	1.482(2)
V−O(1)	1.6638(11)	O(3)−C(10)	1.436(2)	C(3)−C(4)	1.384(3)	C(7)−N(1)	1.483(2)
V−O(4)	1.8762(12)	O(4)−C(8)	1.419(2)	C(4)−C(5)	1.386(2)	C(7)−C(8)	1.536(3)
V−N(2)	2.1408(13)	C(1)−N(2)	1.348(2)	C(5)−N(2)	1.353(2)	C(9)−N(1)	1.496(2)
V−N(1)	2.2305(13)	C(1)−C(2)	1.388(2)	C(5)−C(6)	1.500(2)	C(9)−C(10)	1.511(2)
Compound **3**							
V(1)−O(1)	1.600(3)	C(7)−C(8)	1.380(8)	N(5)−C(24)	1.412(6)	O(16)−C(28)	1.290(6)
V(1)−O(4)	1.989(4)	C(7)−C(12)	1.392(7)	N(6)−C(18)	1.330(6)	O(17)−C(25)	1.241(6)
V(1)−O(3)	2.004(4)	C(8)−C(9)	1.366(8)	N(6)−C(19)	1.390(6)	O(18)−C(28)	1.233(6)
V(1)−O(2)	2.017(4)	C(9)−C(10)	1.410(9)	C(13)−C(14)	1.527(7)	N(7)−C(26)	1.471(6)
V(1)−N(2)	2.053(4)	C(10)−C(11)	1.375(8)	C(15)−C(16)	1.517(7)	N(7)−C(29)	1.475(6)
V(1)−N(1)	2.385(4)	C(11)−C(12)	1.398(7)	C(17)−C(18)	1.499(7)	N(7)−C(27)	1.476(7)
O(3)−C(4)	1.275(6)	V(2)−O(7)	1.600(3)	C(19)−C(20)	1.378(7)	N(8)−C(30)	1.330(6)
O(4)−C(1)	1.279(6)	V(2)−O(10)	1.995(3)	C(19)−C(24)	1.406(6)	N(8)−C(36)	1.405(7)
O(5)−C(1)	1.242(6)	V(2)−O(9)	2.004(4)	C(20)−C(21)	1.376(7)	N(9)−C(30)	1.351(6)
O(6)−C(4)	1.235(7)	V(2)−O(8)	2.014(4)	C(21)−C(22)	1.406(7)	N(9)−C(31)	1.375(7)
N(1)−C(3)	1.469(6)	V(2)−N(5)	2.056(4)	C(22)−C(23)	1.380(7)	C(25)−C(26)	1.530(7)
N(1)−C(2)	1.476(6)	V(2)−N(4)	2.351(4)	C(23)−C(24)	1.388(7)	C(27)−C(28)	1.522(7)
N(1)−C(5)	1.480(6)	O(9)−C(16)	1.283(6)	V(3)−O(13)	1.593(3)	C(29)−C(30)	1.478(7)
N(2)−C(6)	1.339(6)	O(10)−C(13)	1.294(6)	V(3)−O(15)	2.012(3)	C(31)−C(36)	1.392(8)
N(2)−C(12)	1.396(6)	O(11)−C(13)	1.214(6)	V(3)−O(16)	2.011(4)	C(31)−C(32)	1.395(8)
N(3)−C(6)	1.340(6)	O(12)−C(16)	1.232(7)	V(3)−O(14)	2.019(4)	C(32)−C(33)	1.366(10)
N(3)−C(7)	1.387(6)	N(4)−C(15)	1.477(7)	V(3)−N(8)	2.091(4)	C(33)−C(34)	1.400(10)
C(1)−C(2)	1.522(7)	N(4)−C(14)	1.481(6)	V(3)−N(7)	2.357(4)	C(34)−C(35)	1.381(9)
C(3)−C(4)	1.511(7)	N(4)−C(17)	1.483(6)	O(15)−C(25)	1.286(6)	C(35)−C(36)	1.389(8)
C(5)−C(6)	1.487(7)	N(5)−C(18)	1.331(6)				
Compound **6**							
V−O(1)	1.596(3)	V−C(9)	3.195(5)	O(2)−C(10)	1.423(5)	C(4)−C(5)	1.381(7)
V−O(2)	1.971(3)	V−C(1)	3.213(4)	O(3)−C(13)	1.279(5)	C(5)−C(6)	1.387(6)
V−O(3)	2.002(3)	N(1)−C(16)	1.473(6)	C(4)−C(11)	1.275(5)	C(7)−C(8)	1.484(6)
V−O(4)	2.011(3)	N(1)−C(8)	1.474(5)	O(5)−C(17)	1.551(9)	C(9)−C(10)	1.496(7)
V−N(2)	2.089(3)	N(1)−C(9)	1.487(6)	O(5A)−C(17)	1.589(13)	C(11)−C(12)	1.394(6)
V−N(1)	2.511(4)	N(2)−C(7)	1.342(5)	C(1)−C(2)	1.395(6)	C(11)−C(15)	1.493(6)
V−C(10)	2.911(5)	N(2)−C(1)	1.391(5)	C(1)−C(6)	1.406(6)	C(12)−C(13)	1.396(7)
V−C(11)	2.954(4)	N(3)−C(7)	1.333(5)	C(2)−C(3)	1.378(6)	C(13)−C(14)	1.493(7)
V−C(13)	2.967(5)	N(3)−C(6)	1.386(5)	C(3)−C(4)	1.402(7)	C(16)−C(17)	1.529(7)
V−C(7)	3.005(4)						

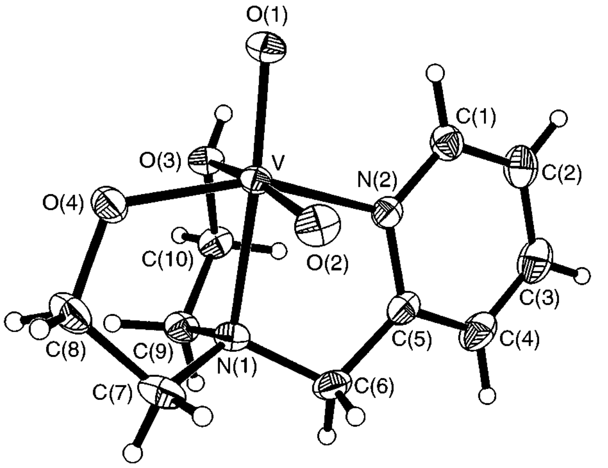


Fig. 1 Structure and atomic labelling scheme of [VO_2(Hpmide)]·$4H_2O$ **2a**

lengths and angles are provided in Tables 2 and 3. Complex **2a** has a vanadium atom in a distorted octahedral co-ordination array containing two oxo ligands and the tetradentate Hpmide$^-$ ligand. The pyridyl nitrogen atom and the two alkoxy groups of the Hpmide$^-$ ligand are co-ordinated to vanadium in the equatorial plane. The V−N (amine) bond *trans* to an oxo ligand is long [V−N(1) 2.2305(13) Å]. Most of the bond lengths for **2a** are similar to those in related vanadium complexes (see Table 4),[22–25] however one of the V=O bonds in **2a** is amongst the longest found in a vanadium(v) complex [V−O(1) 1.6638(11) Å]. This long bond is probably a result of the accumulated effects of a number of factors such as hydrogen bonding, crystal packing forces, distorted geometry, and the low charge of the complex.[26,27]

The distorted geometry of compound **2a** is supported by bond angles N(2)−V−N(1) 74.95(5), N(1)−V−O(4) 77.57(5), O(4)−V−O(1) 103.78(6) and O(1)−V−N(2) 98.18(5)°. The deviation from 90° is a result of the vanadium being out of the N(2), N(1), O(1) and O(3) plane. The V−O(3) bond is 0.4234 Å longer than the V−O(4) bond. Both hydroxyethyl groups are bound in the equatorial plane. The long V−O bond is the combined result of one of the hydroxyethyl groups being protonated and being *trans* to an oxo group. One could view the vanadium atom in a square pyramidal geometry if the long V−O bond were excluded, although in such a case a shorter V−N (aryl) bond would be expected than that observed.

The structure and atomic labelling scheme of compound **3** are presented in Fig. 2. Interatomic bond lengths and angles are provided in Tables 2 and 3. The asymmetric unit of the unit cell containing three discrete [VO(bmida)(H_2O)] complexes is shown in Fig. 3. All three complexes of **3** in the asymmetric unit have vanadium atoms in distorted octahedral co-ordination spheres that contain an oxo ligand (*trans* to the amino nitrogen atom), a water molecule (*trans* to a carboxylate oxygen atom), and the co-ordinating atoms of the tetradentate bmida^{2-} ligand. The arrangement of ligand atoms in the complexes containing V(1) and V(2) is the same; however, the complex containing V(3) is enantiomerically related to those containing

Table 3 Bond angles (°) for compounds **2a**, **3** and **6**

Compound **2a**

O(2)−V−O(1)	106.09(6)
O(2)−V−O(4)	101.81(6)
O(1)−V−O(4)	103.78(6)
O(2)−V−N(2)	90.47(6)
O(1)−V−N(2)	98.18(5)
O(4)−V−N(2)	150.57(5)
O(2)−V−N(1)	94.00(6)
O(1)−V−N(1)	158.94(5)
O(4)−V−N(1)	77.57(5)
N(2)−V−N(1)	74.95(5)
O(2)−V−O(3)	163.93(5)
O(1)−V−O(3)	85.47(5)
O(4)−V−O(3)	85.77(5)
N(2)−V−O(3)	76.61(4)
N(1)−V−O(3)	73.61(4)
C(10)−O(3)−V	115.20(9)
C(8)−O(4)−V	120.30(10)
N(2)−C(1)−C(2)	122.1(2)
C(1)−C(2)−C(3)	118.7(2)
C(4)−C(3)−C(2)	119.3(2)
C(3)−C(4)−C(5)	119.3(2)
N(2)−C(5)−C(4)	121.6(2)
N(2)−C(5)−C(6)	115.19(13)
C(4)−C(5)−C(6)	123.19(15)
N(1)−C(6)−C(5)	109.42(12)
N(1)−C(7)−C(8)	107.84(13)
O(4)−C(8)−C(7)	110.39(13)
N(1)−C(9)−C(10)	111.25(12)
O(3)−C(10)−C(9)	105.32(12)
C(6)−N(1)−C(7)	112.28(13)
C(6)−N(1)−C(9)	112.63(13)
C(7)−N(1)−C(9)	109.96(13)
C(6)−N(1)−V	107.15(9)
C(7)−N(1)−V	101.42(9)
C(9)−N(1)−V	112.87(9)
C(1)−N(2)−C(5)	119.00(14)
C(1)−N(2)−V	123.80(11)
C(5)−N(2)−V	117.20(10)

Compound **3**

O(1)−V(1)−O(4)	107.4(2)
O(1)−V(1)−O(3)	94.9(2)
O(4)−V(1)−O(3)	88.2(2)
O(1)−V(1)−O(2)	100.1(2)
O(4)−V(1)−O(2)	86.4(2)
O(3)−V(1)−O(2)	164.96(14)
O(1)−V(1)−N(2)	103.3(2)
O(4)−V(1)−N(2)	149.07(15)
O(3)−V(1)−N(2)	92.3(2)
O(2)−V(1)−N(2)	85.2(2)
O(1)−V(1)−N(1)	171.3(2)
O(4)−V(1)−N(1)	75.36(14)
O(3)−V(1)−N(1)	76.80(14)
O(2)−V(1)−N(1)	88.2(2)
N(2)−V(1)−N(1)	74.68(15)
C(4)−O(3)−V(1)	123.7(3)
C(1)−O(4)−V(1)	122.4(3)
C(3)−N(1)−C(2)	112.1(4)
C(3)−N(1)−C(5)	112.2(4)
C(2)−N(1)−C(5)	114.1(4)
C(3)−N(1)−V(1)	105.9(3)
C(2)−N(1)−V(1)	104.4(3)
C(5)−N(1)−V(1)	107.4(3)
C(6)−N(2)−C(12)	106.6(4)
C(6)−N(2)−V(1)	118.9(3)
C(12)−N(2)−V(1)	133.3(3)
C(6)−N(3)−C(7)	108.2(4)
O(5)−C(1)−O(4)	122.3(5)
O(5)−C(1)−C(2)	119.1(5)
O(4)−C(1)−C(2)	118.6(4)
N(1)−C(2)−C(1)	110.6(4)
N(1)−C(3)−C(4)	114.8(4)
O(6)−C(4)−O(3)	124.7(5)
O(6)−C(4)−C(3)	117.3(4)
O(3)−C(4)−C(3)	118.0(5)
N(1)−C(5)−C(6)	108.1(4)
N(2)−C(6)−N(3)	111.0(4)
N(2)−C(6)−C(5)	121.8(4)
N(3)−C(6)−C(5)	127.0(4)
C(8)−C(7)−N(3)	131.8(5)
C(8)−C(7)−C(12)	122.1(5)
N(3)−C(7)−C(12)	106.0(4)
C(9)−C(8)−C(7)	116.9(6)
C(8)−C(9)−C(10)	121.5(6)
C(11)−C(10)−C(9)	122.0(5)
C(10)−C(11)−C(12)	116.2(5)
C(7)−C(12)−N(2)	108.1(4)
C(7)−C(12)−C(11)	121.2(5)
N(2)−C(12)−C(11)	130.7(5)
O(7)−V(2)−O(10)	108.3(2)
O(7)−V(2)−O(9)	95.2(2)
O(10)−V(2)−O(9)	87.02(15)
O(7)−V(2)−O(8)	102.8(2)
O(10)−V(2)−O(8)	84.9(2)
O(9)−V(2)−O(8)	161.8(2)
O(7)−V(2)−N(5)	101.9(2)
O(10)−V(2)−N(5)	149.75(14)
O(9)−V(2)−N(5)	92.2(2)
O(8)−V(2)−N(5)	86.6(2)
O(7)−V(2)−N(4)	171.6(2)
O(10)−V(2)−N(4)	75.61(13)
O(9)−V(2)−N(4)	77.45(14)
O(8)−V(2)−N(4)	84.8(2)
N(5)−V(2)−N(4)	74.72(15)
C(16)−O(9)−V(2)	123.7(3)
C(13)−O(10)−V(2)	123.6(3)
C(15)−N(4)−C(14)	111.5(4)
C(15)−N(4)−C(17)	112.0(4)
C(14)−N(4)−C(17)	114.3(4)
C(15)−N(4)−V(2)	106.4(3)
C(14)−N(4)−V(2)	104.6(3)
C(17)−N(4)−V(2)	107.4(3)
C(18)−N(5)−C(24)	105.5(4)
C(18)−N(5)−V(2)	119.3(3)
C(24)−N(5)−V(2)	134.8(3)
C(18)−N(6)−C(19)	107.9(4)
O(11)−C(13)−O(10)	123.5(5)
O(11)−C(13)−C(14)	120.8(4)
O(10)−C(13)−C(14)	115.7(4)
N(4)−C(14)−C(13)	111.7(4)
N(4)−C(15)−C(16)	114.8(4)
O(12)−C(16)−O(9)	125.6(5)
O(12)−C(16)−C(15)	117.0(5)
O(9)−C(16)−C(15)	117.4(5)
N(4)−C(17)−C(18)	107.7(4)
N(6)−C(18)−N(5)	112.9(4)
N(6)−C(18)−C(17)	126.7(4)
N(5)−C(18)−C(17)	120.2(4)
C(20)−C(19)−N(6)	133.1(4)
C(20)−C(19)−C(24)	121.1(5)
N(6)−C(19)−C(24)	105.8(4)
C(21)−C(20)−C(19)	117.7(5)
C(20)−C(21)−C(22)	121.0(5)
C(23)−C(22)−C(21)	122.2(5)
C(22)−C(23)−C(24)	116.3(5)
C(23)−C(24)−C(19)	121.8(5)
C(23)−C(24)−N(5)	130.4(4)
C(19)−C(24)−N(5)	107.8(4)
O(13)−V(3)−O(15)	106.3(2)
O(13)−V(3)−O(16)	94.0(2)
O(15)−V(3)−O(16)	92.6(2)
O(13)−V(3)−O(14)	100.9(2)
O(15)−V(3)−O(14)	86.0(2)
O(16)−V(3)−O(14)	164.76(14)
O(13)−V(3)−N(8)	105.1(2)
O(15)−V(3)−N(8)	148.37(15)
O(16)−V(3)−N(8)	88.8(2)
O(14)−V(3)−N(8)	84.6(2)
O(13)−V(3)−N(7)	170.6(2)
O(15)−V(3)−N(7)	74.51(14)
O(16)−V(3)−N(7)	76.61(14)
O(14)−V(3)−N(7)	88.4(2)
N(8)−V(3)−N(7)	75.1(2)
C(25)−O(15)−V(3)	121.2(3)
C(28)−O(16)−V(3)	123.6(3)
C(26)−N(7)−C(29)	112.8(4)
C(26)−N(7)−C(27)	111.5(5)
C(29)−N(7)−C(27)	112.7(4)
C(26)−N(7)−V(3)	103.3(3)
C(29)−N(7)−V(3)	109.9(3)
C(27)−N(7)−V(3)	105.9(3)
C(30)−N(8)−C(36)	106.0(4)
C(30)−N(8)−V(3)	118.2(3)
C(36)−N(8)−V(3)	135.2(3)
C(30)−N(9)−C(31)	108.3(5)
O(17)−C(25)−O(15)	124.8(5)
O(17)−C(25)−C(26)	118.5(4)
O(15)−C(25)−C(26)	116.6(4)
N(7)−C(26)−C(25)	110.0(4)
N(7)−C(27)−C(28)	112.8(4)
O(18)−C(28)−O(16)	123.4(5)
O(18)−C(28)−C(27)	121.1(5)
O(16)−C(28)−C(27)	115.4(5)
N(7)−C(29)−C(30)	109.6(4)
N(8)−C(30)−N(9)	111.4(5)
N(8)−C(30)−C(29)	122.7(5)
N(9)−C(30)−C(29)	125.9(5)
N(9)−C(31)−C(36)	106.0(5)
N(9)−C(31)−C(32)	131.7(6)
C(36)−C(31)−C(32)	122.3(6)
C(33)−C(32)−C(31)	115.5(6)
C(32)−C(33)−C(34)	123.2(7)
C(35)−C(34)−C(33)	120.8(7)
C(34)−C(35)−C(36)	116.9(6)
C(35)−C(36)−C(31)	121.2(6)
C(35)−C(36)−N(8)	130.4(5)
C(31)−C(36)−N(8)	108.4(5)

Compound **6**

O(1)−V−O(2)	102.4(2)
O(1)−V−O(3)	102.6(2)
O(2)−V−O(3)	154.99(13)
O(1)−V−O(4)	100.77(15)
O(2)−V−O(4)	86.86(12)
O(3)−V−O(4)	87.76(13)
O(1)−V−N(2)	97.56(15)
O(2)−V−N(2)	89.93(13)
O(3)−V−N(2)	87.56(13)
O(4)−V−N(2)	161.65(13)
O(1)−V−N(1)	169.99(15)
O(2)−V−N(1)	75.01(12)
O(3)−V−N(1)	80.48(12)
O(4)−V−N(1)	88.82(12)
N(2)−V−N(1)	72.91(12)
O(1)−V−C(10)	126.9(2)
O(2)−V−C(10)	25.78(13)
O(3)−V−C(10)	129.69(14)
O(4)−V−C(10)	75.59(14)
N(2)−V−C(10)	93.96(14)
N(1)−V−C(10)	52.60(12)
O(1)−V−C(11)	97.00(15)
O(2)−V−C(11)	107.11(13)
O(3)−V−C(11)	68.96(13)
O(4)−V−C(11)	20.27(12)
N(2)−V−C(11)	154.57(13)
N(1)−V−C(11)	92.99(12)
C(10)−V−C(11)	93.83(14)
O(1)−V−C(13)	99.9(2)
O(2)−V−C(13)	149.57(13)
O(3)−V−C(13)	19.81(12)
O(4)−V−C(13)	68.77(13)
N(2)−V−C(13)	107.36(14)
N(1)−V−C(13)	86.16(12)
C(10)−V−C(13)	125.42(14)
C(11)−V−C(13)	49.40(13)
O(1)−V−C(7)	119.91(14)
O(2)−V−C(7)	87.93(12)
O(3)−V−C(7)	80.31(12)
O(4)−V−C(7)	139.14(12)
N(2)−V−C(7)	22.55(12)
N(1)−V−C(7)	50.81(11)
C(10)−V−C(7)	82.43(13)
C(11)−V−C(7)	136.42(12)
C(13)−V−C(7)	98.58(12)
O(1)−V−C(9)	148.7(2)
O(2)−V−C(9)	48.11(12)
O(3)−V−C(9)	107.44(13)
O(4)−V−C(9)	89.25(13)
N(2)−V−C(9)	75.29(14)
N(1)−V−C(9)	26.97(12)
C(10)−V−C(9)	27.88(13)
C(11)−V−C(9)	101.84(13)
C(13)−V−C(9)	111.35(13)
C(7)−V−C(9)	58.31(13)
O(1)−V−C(1)	79.96(14)
O(2)−V−C(1)	89.21(11)
O(3)−V−C(1)	95.86(11)
O(4)−V−C(1)	176.07(11)
N(2)−V−C(1)	18.20(12)
N(1)−V−C(1)	90.28(11)
C(10)−V−C(1)	100.85(13)
C(11)−V−C(1)	163.65(11)
C(13)−V−C(1)	114.98(12)
C(7)−V−C(1)	40.66(11)
C(9)−V−C(1)	88.21(12)
C(16)−N(1)−C(8)	111.1(4)
C(16)−N(1)−C(9)	113.5(4)
C(8)−N(1)−C(9)	110.5(4)
C(16)−N(1)−V	112.9(3)
C(8)−N(1)−V	105.2(2)
C(9)−N(1)−V	103.1(3)
C(7)−N(2)−C(1)	105.1(3)
C(7)−N(2)−V	120.8(3)
C(1)−N(2)−V	133.8(3)
C(7)−N(3)−C(6)	106.9(3)
C(10)−O(2)−V	117.2(3)
C(13)−O(3)−V	128.1(3)
C(11)−O(4)−V	126.6(3)
N(2)−C(1)−C(2)	131.0(4)
N(2)−C(1)−C(6)	108.5(4)
C(2)−C(1)−C(6)	120.5(4)
N(2)−C(1)−V	28.0(2)
C(2)−C(1)−V	103.1(3)
C(6)−C(1)−V	136.2(3)
C(3)−C(2)−C(1)	117.2(4)
C(2)−C(3)−C(4)	121.5(4)
C(5)−C(4)−C(3)	122.4(4)
C(4)−C(5)−C(6)	115.9(4)
N(3)−C(6)−C(5)	131.1(4)
N(3)−C(6)−C(1)	106.2(3)
C(5)−C(6)−C(1)	122.6(4)
N(3)−C(7)−N(2)	113.3(4)
N(3)−C(7)−C(8)	125.5(4)
N(2)−C(7)−C(8)	121.2(4)
N(3)−C(7)−V	149.7(3)
N(2)−C(7)−V	36.7(2)
C(8)−C(7)−V	84.7(2)
N(1)−C(8)−C(7)	109.0(4)
N(1)−C(8)−V	48.7(2)
C(7)−C(8)−V	68.0(2)
N(1)−C(9)−C(10)	109.0(4)
N(1)−C(9)−V	50.0(2)
C(10)−C(9)−V	65.5(2)
O(2)−C(10)−C(9)	109.5(4)
O(2)−C(10)−V	37.0(2)
C(9)−C(10)−V	86.7(3)
O(4)−C(11)−C(12)	124.6(4)
O(4)−C(11)−C(15)	115.8(4)
C(12)−C(11)−C(15)	119.5(4)
O(4)−C(11)−V	33.1(2)
C(12)−C(11)−V	92.9(3)
C(15)−C(11)−V	146.1(3)
C(11)−C(12)−C(13)	124.9(4)
O(3)−C(13)−C(12)	124.1(4)
O(3)−C(13)−C(14)	116.0(4)
C(12)−C(13)−C(14)	120.0(4)
O(3)−C(13)−V	32.1(2)
C(12)−C(13)−V	92.3(3)
C(14)−C(13)−V	147.7(3)
N(1)−C(16)−C(17)	118.4(4)
C(16)−C(17)−O(5)	107.0(5)
C(16)−C(17)−O(5A)	99.0(6)
O(5)−C(17)−O(5A)	154.1(6)

Table 4 Compilation of important bond lengths (Å) for new and previously reported oxovanadium-(IV) and -(V) complexes containing nitrogen and oxygen donating ligands

Complex[a]	V=O	V–N (aryl)	V–N (amine)	V–N[b]	V–O[c]	V–O[d]	Oxidation state	Ref.
[VO(pmida)(H_2O)]	1.60(1)	2.11(1)[e]		2.30(1)	1.98(1) 2.02(1)		IV	13
[VO(*S*-peida)(H_2O)]	1.602(3)	2.108(3)[e]		2.292(3)	1.977(3) 2.010(2)		IV	14
[VO_2(*S*-peida)]$^-$	1.649(2)	2.106(3)[e]		2.263(3)	1.990(3) 2.177(2)		V	14
[V_2O_3(*S*-peida)$_2$]$^-$	1.622(4) A 1.613(4) B	2.100(5) A 2.099(5) B		2.293(4) A 2.278(4) B	2.000(4) A 1.983(4) B 2.019(4) A 2.013(4) B		IV, V	14
[VO_2(Hpmide)]	1.6343(12) 1.6640(12)	2.1408(14)		2.2304(14)		1.8761(12) 2.2995(12)	V	This work
[VO(bmida)(H_2O)]	1.600(3)	2.053(4)[f]		2.385(4)	2.004(4) 1.989(4)		IV	This work
[VO(acac)(bmide)]	1.596(3)	2.089(3)[f]		2.511(4)		1.971(3)	IV	This work
[VO(hebab)]	1.595(3)		2.147(3)	2.309(3)		1.822(3) 1.885(3)	V	11
[VO(Hhida)(H_2O)]	1.596(5)			2.307(6)	1.983(5) 1.994(5)	2.070(5)	IV	12
[VO_2(Hhida)]$^-$	1.663(3) 1.624(3)			2.251(3)	1.969(3) 1.988(3)	2.287(3)	V	12
[V_2O_2(μ-O)(Hhida)$_2$]$^-$	1.6071(3)			2.277(2)	1.9851(15) 1.9807(15)	2.1109(15)	IV, V	12
[V_2O_3(nta)$_2$]$^-$	1.607(6)			2.297(6)	2.041(5) 1.982(5)		IV, V	22
[VO_2(tea)]	1.633(6)			2.276(7)		1.797(4) 1.793(4) 1.792(4)	V	3
[VO_2(tpa)]	1.617(13)			2.279(15)		1.794(4) 1.794(5) 1.793(2)	V	3
β-*cis*-[VO_2(edda)]$^-$	1.6324(13) 1.6549(13)		2.120(2)	2.245(2)	2.1815(12) 1.9611(3)		V	9
[VO_2(edta)]$^{3-}$	1.639(2) 1.657(1)		2.359(2)	2.366(2)	2.001(2) 1.999(2)		V	23
[VO(Hedta)]$^-$	1.588(4)		2.154(5)	2.301(5)	2.007(4) 1.987(4) 1.976(4)		IV	24
[VO(NH_2O)$_2$(im)$_2$]$^-$	1.605(3)	2.079(4)[g,h] 2.336(4)[g,i]					V	25
[VO(tcda)]	1.608(1)		2.114(2) 2.134(2)	2.310(2)	1.994(1) 1.983(1)		IV	26
[VO_2(Htcda)]	1.641(2) 1.628(2)		2.094(2)	2.255(3) 2.403(2)	1.964(2)		V	26
[VO_2L^1]	1.647(2) 1.649(1)		2.115(2)	2.303(2) 2.285(2)	1.989(2)		V	27

[a] hebab = 1,1-Bis(2-hydroxyethyl)-4-(2-hydroxybenzyl)-1,4-diazabutane; H_2hida = *N*-(2-hydroxyethyl)iminodiacetic acid; im = imidazolate; H_2tcda = 1,4,7-triazacyclononane-1,4-diacetic acid; HL^1 = 1,4,7-triazacyclononane-1-acetic acid. [b] Amine nitrogen *trans* to oxo group. [c] Carboxylate oxygen. [d] Hydroxyethyl oxygen. [e] Pyridine nitrogen. [f] Benzimidazole nitrogen. [g] Imidazole nitrogen. [h] *cis* to oxo group. [i] *trans* to oxo group.

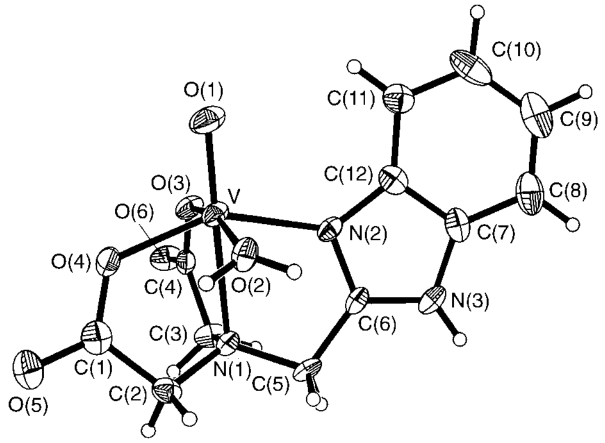


Fig. 2 Structure and atomic labelling scheme of [VO(bmida)(H_2O)] **3**

V(1) and V(2). The crystal is not chiral, given that the space group contains both an inversion centre and a glide plane.

Bond lengths and angles in the primary co-ordination sphere are similar to those in related vanadium(IV) complexes (see compilation in Table 4).[22] In each of the three complexes, the V–N (amine) bond *trans* to the V=O bond is distinctly elongated. Pairwise comparison of V–X bond lengths in the three independent complexes reveals no significant differences, with the exception of the V(1)–N(1) (amine) bond [longer than either V(2)–N(4) or V(3)–N(7)] and the V(3)–N(9) (benzimidazole) bond [longer than either V(1)–N(3) or V(2)–N(6)]. Presumably differential packing forces account for these small distortions. All the V–N (amine) bond lengths are long and will be discussed below.

The structure and atomic labelling scheme of compound **6** are presented in Fig. 4; interatomic bond lengths and angles are provided in Tables 2 and 3. Complex **6** also has a vanadium atom in a distorted octahedral co-ordination array containing the bidentate acac and the tridentate Hbmide$^-$ ligand. The benzimidazole nitrogen atom and the deprotonated alkoxo group of the Hbmide$^-$ ligand are co-ordinated in the equatorial plane, as are the two oxygen atoms of the acac$^-$ ligand. The second

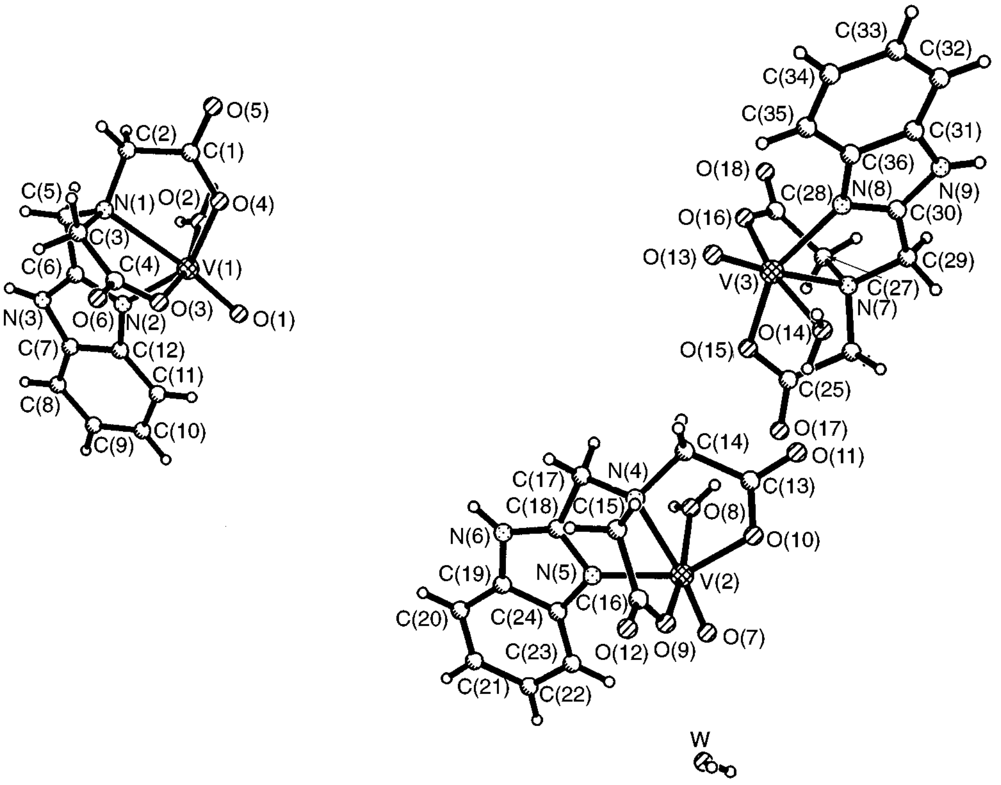


Fig. 3 The unit cell and atomic labelling scheme of the three [VO(bmida)(H_2O)]·H_2O

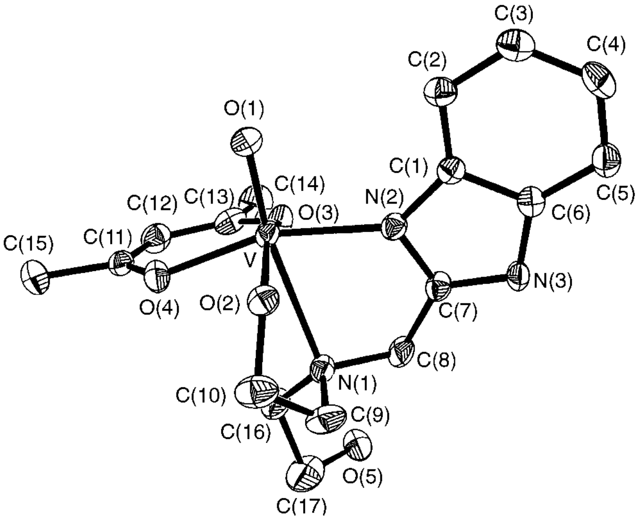


Fig. 4 Structure and atomic labelling scheme of [VO(acac)(Hbmide)] **6**

alkoxy oxygen atom of the Hbmide$^-$ ligand is pendant. If we exclude the V–N (amine) bond, a distorted eight-membered ring emerges. This ring consists of the following series of atoms V–O(2)–C(10)–C(9)–N(1)–C(8)–C(7)–N(2). Once again, most bond lengths are similar to those in related vanadium(IV) complexes (see Table 4) with the exception of a long V–N bond of 2.511(4) Å which extends from the vanadium(IV) atom to the amine nitrogen *trans* to the oxo group.

The V–N (aryl) bond distances of our benzimidazole complexes are almost the same as those observed in [VO(bbimae)(NCS)$_2$] [2.079(4) and 2.082(5) Å] {bbimae = 2-[bis(benzimidazol-2-ylmethyl)amino]ethanol}.[28] The V–N (amine) bond lengths in the benzimidazole complexes **3** and **6** are amongst the longest V–N bond distances reported for oxovanadium(IV) complexes. Only one complex with a longer V–N bond distance exists, [VO(bbimae)(NCS)$_2$],[28] 2.525(4) Å. The fact that **6** has a longer V–N bond than **3** suggests that compounds containing the hydroxyethyl functionality have longer V–N bonds than those with the acetate functionality. The pyridyl complexes in general have shorter V–N (aryl) bonds than their benzimidazole analogues.

A second comparison between complexes containing hydroxyethyl and acetate groups involves the bond lengths between vanadium and the oxygen atoms. Complex **6** has a long V–O (alkoxide) bond length of 1.971(3) Å, although this bond is shorter bond than the V–O (acetate) bonds in **3** [2.004(4) Å and 1.989(4) Å]. Complex **2a** has a V–O (alkoxide) bond length of 1.8762(12) Å which is typical for such a bond [an additional V–O (alkoxide) group is protonated and *trans* to an oxo ligand, 2.2975(11)]. Both the V–O (alkoxide) bonds in **2a** and **2b** are shorter than the V–O (acetate) bonds in [VO(pmida)(H_2O)] [1.98(1) and 2.02(1) Å].[13] First, both types of compounds clearly show that the protonated V–O (alkoxide) bond lengths are longer than V–O (carboxylate), which again are longer than V–O (alkoxide). Furthermore, the V–O (acetate) bond lengths of bmida, pmida and *S*-peida complexes of vanadium(IV/V) are longer than the V–O bond lengths in their hydroxyethyl analogues [*S*-H_2peida = (*S*)-1-(2-pyridyl)ethyliminodiacetic acid].[13,14] Since V–O (alkoxide) bond lengths of 1.95–2.00 Å typically are observed when oxygen atoms are bridging, the possibility for hydrogen bonding in the crystal of **6** was explored. Indeed, hydrogen bonding between the O(2) atom and the N(3)–H (benzimidazole hydrogen atom) was observed, with a bond distance of 1.65 Å.

Does ligand basicity correlate with V–N bond length? In Fig. 5 we have plotted the V–N (amine) bond length (*trans* to an oxo group) of our complexes and previously characterized complexes in the literature as a function of the pK_a of the protonated ligand (protonation of central amine). Fig. 5 contains vanadium-(IV), -(V) and mixed-valence-(IV/V) complexes, with vanadium in co-ordination spheres ranging from five to seven. Several general patterns are observable. First, the oxidation state of the metal ion affects the V–N bond length; for example the vanadium(IV) complexes typically have longer V–N bond lengths compared to the vanadium(V) and mixed-valence-(IV/V)

Table 5 Experimental ESR parameters[a]

Complex	$g_{\perp}$	$g_{\parallel}$	$10^4\,A_{\perp}/\mathrm{cm}^{-1}$	$10^4\,A_{\parallel}/\mathrm{cm}^{-1}$	g_0	$10^4\,A_0/\mathrm{cm}^{-1}$
[VO(pmida)(H_2O)]	1.983	1.945	−63.4	−170.1	1.971	−99.0
3	1.981	1.943	−62.3	−170.8	1.968	−99.8
6	1.966	1.945	−60.4	−166.2	1.959	−95.4
V–BrPO,[b] high pH	1.979	1.948	−50.0	−160.0	1.969	−87.0
low pH	1.980	1.950	−55.0	−168.0	1.970	−93.0

[a] Model calculations were performed using the following equations: $g_{\parallel,\mathrm{calc}} = \Sigma n_i g_{\parallel,i}/4$; $A_{\parallel,\mathrm{calc}} = \Sigma n_i A_{\parallel,i}/4$; $g_{0,\mathrm{calc}} = \Sigma n_i g_{0,i}/4$; $A_{0,\mathrm{calc}} = \Sigma n_i A_{0,i}/4$. [b] Ref. 32; V–BrPO = vanadium bromoperoxidase.

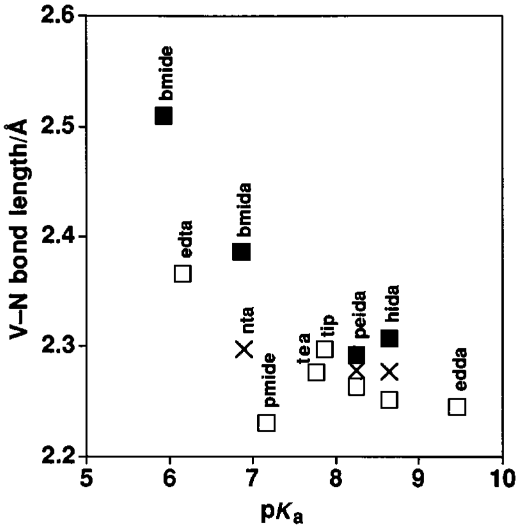


Fig. 5 Plot of the V–N (amine) bond length [vanadium-(IV) (■), -(V) (□) and -(IV, V) (×)] as a function of the pK_a of amine based ligands

complexes. Secondly, the V–N bond lengths are longer in complexes with the benzimidazole ligand compared to those with the pyridyl ligands. Thirdly, the V–N bond length in **2a** which is six-co-ordinate is shorter than that in the five-co-ordinate V–tea and V–tpa complexes (tea = triethanolamine, tpa = triisopropanolamine). However, despite these variations, the general pattern is emerging with respect to V–N bond length and the protonated pK_a value of the ligand in all the vanadium complexes examined. The only major deviants in Fig. 5 are **2a** and **6**. The distorted vanadium atoms in **2a** and **6** may account for the unusually short and long V–N bond length in these complexes and attest to the variations that can be expected in these systems.

Infrared spectroscopy. The solid state properties of compounds **1**, **2a**, **3**, **4**, **5a**, **6** and **7** were examined using infrared spectroscopy. The vanadium(IV) compounds **3** and **6** have single V=O stretches, at 983 and 971 cm^{-1} respectively, values similar to those observed for other six-co-ordinate vanadium(IV) compounds such as [VO(pmida)(H_2O)] (985 cm^{-1})[13] and $[NH_4]_2[VO(C_2O_4)_2(H_2O)]\cdot H_2O$ (976 cm^{-1}).[29] The observation of single V=O bond stretches for these compounds is consistent with their crystal structures. The dioxovanadium(V) compounds **1**, **2a**, **4**, **5a** and **7** have two V=O stretches, one symmetric and one asymmetric,[30] in the range 955 to 899 cm^{-1}. As a comparison the vanadium(V) complex K[VO_2(dmedda)]·H_2O (dmedda = dimethylethylenediiminodiacetate) has V=O stretches at 935 and 900 cm^{-1}.[31] These observations are consistent with the X-ray structural data for compound **2a**.

Solution chemistry

The stability, structure and lability of these compounds in solution is essential to their possible biological action. The structures of the three complexes characterized above by X-ray crystallography provides a firm background upon which their solution structure and of others in this series can be related. Accordingly, we characterized the vanadium(IV) complexes in frozen solution by ESR spectroscopy, the vanadium(V) complexes by NMR spectroscopy in aqueous solution at ambient temperature and both the vanadium-(IV) and -(V) complexes by UV/VIS spectroscopy in aqueous solution at ambient temperature. A vanadium(IV) compound (**6**) that was sparingly soluble in aqueous solution was dissolved in dmf–water (1:1 v/v).

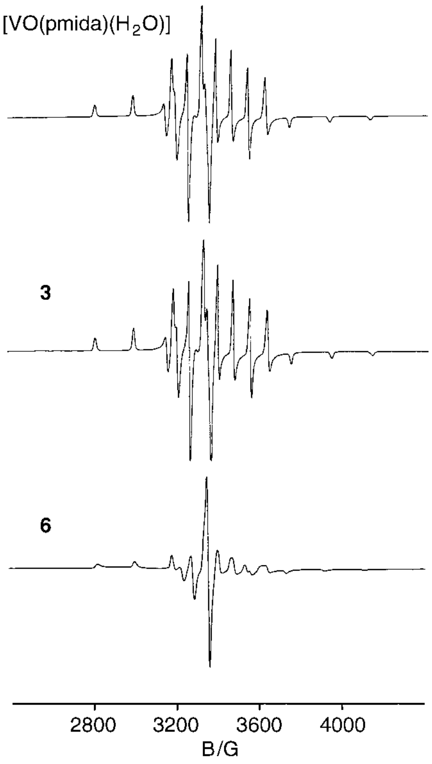


Fig. 6 The ESR spectra of [VO(pmida)(H_2O)], [VO(bmida)(H_2O)] **3** and [VO(acac)(Hbmide)] **6** recorded at −133 °C in dmf–water (1:1 v/v) at 1.0 mmol dm^{-3} concentration

Vanadium(IV) complexes: ESR spectroscopy. The typical anisotropic ESR spectra of [VO(pmida)(H_2O)], **3** and **6** in dmf–water (1:1 v/v) solutions are shown in Fig. 6. The parameters of these spectra are listed in Table 5. Using model compounds of similar strength field groups the equatorial environments for both [VO(pmida)(H_2O)] and **3** in dmf–water solutions[19] are calculated to give $g_{\parallel} = 1.941$ and $A_{\parallel} = 171.8 \times 10^{-4}$ cm^{-1}. These values compare favourably with the experimental values listed in Table 5. Although the environments of vanadium in [VO(pmida)(H_2O)] and **3** are different the substitution of a pyridine nitrogen with a benzimidazole nitrogen generates only a minor perturbation as monitored by ESR spectroscopy. For **6**, model compounds in dmf led to the estimate of parameters of $g_{\parallel} = 1.957$ and $A_{\parallel} = 153.8 \times 10^{-4}$ cm^{-1}.[19] We attribute the difference in $A_{\parallel}$ between the value estimated for the model compound and the observed parameters for **6** to the distorted geometry in the compound.

Table 6 Summary of equilibrium constants for formation of vanadium(V) complexes in aqueous solution[a]

	pK_a				
Ligand	Protonated ligand	Aromatic nitrogen[b]	K_{com}[c]/dm^3 mol^{-1}	pH[d]	K_{eq}[e]/dm^3 mol^{-1}
pmide	7.16	1.39	5600 ± 310	7.0	3.9×10^3
pmida	8.25[f]	2.85[f]	4600 ± 300	7.5	7.8×10^3
bmide	5.93	2.15	470 ± 13	6.9	6.7×10
			60 ± 0.80	8.4	
bmida	6.87	3.95	3100 ± 260	7.5	9.9×10^2
tea	7.76[g]	—	206	8.0	2.0×10^3
dea	8.88[g]	—	58	8.5	5.1×10^2

[a] The reactions were studied at 0.5 to 100 mmol dm^{-3} concentrations of vanadate and ligand; KCl was added to give a total ionic strength of 0.40 mol dm^{-3}. [b] Values are accurate to ±0.05 units. [c] [complex]/[V][L]. [d] The H$^+$-dependent formation constant was measured at the indicated pH. [e] [complex]/[H$_2$VO$_4$$^-$][L]. [f] Ref. 15. [g] Ref. 33.

Haloperoxidases have an imidazole functionality co-ordinated to a vanadium(V) centre as recently demonstrated by X-ray crystallography.[2] A crystal structure of a chloroperoxidase from the fungus *Curvularia inaequalis* reveals the catalytic vanadium(V) centre to be five-co-ordinate[2] and trigonal bipyramidal in geometry (2.1 Å resolution). Upon reduction to cofactor bound vanadium(IV) there is probably a change in ligating groups and/or co-ordination sphere to a square pyramidal five-co-ordinate geometry that is favoured by vanadium(IV) complexes or to a six-co-ordinate octahedral geometry. The ESR parameters of our complexes compare favourably with those for vanadium bromoperoxidase at low pH (Table 5).[32] Thus, the vanadium(IV) in these enzymes may be co-ordinated with similar strength field groups. It is likely that the vanadium(V) co-ordination sphere is different from that of the vanadium(IV) in the enzyme, a fact that must be accommodated as the enzyme is passing through the various intermediates in the catalytic cycle.

Vanadium(V) complex stability: ^{51}V NMR spectroscopic studies. The solution properties of the vanadium(V) complexes of pmide, bmida and bmide were compared to those of that of pmida. The latter is very closely related to the peida complex, which is known and has previously been characterized in great detail.[14] Initially, the stability of the complexes of pmida, pmide, bmida and bmide was determined as a function of pH by ^{51}V NMR spectroscopy. Both pmida and pmide form complexes at $\delta \approx -500$; pmide and bmide both form more than one complex. The pmide ligand forms one major complex at neutral pH (δ −500) and a second minor complex that has no observable pH dependence (δ −505). The bmide ligand forms one complex that is most stable at low pH (δ −540), a second complex which is more stable at alkaline pH (δ −488) and a minor complex which has no observable pH dependence (δ −505). With the exception of bmide, the chemical shifts and linewidths all fall within the region expected (δ −480 to −520) for this type of five- and six-co-ordinate complexes.[8]

The formation constants were determined within 0.5 pH units of the pH where most complex was observed. Measurements were made at a series of vanadate and ligand concentrations, and the data analysed as described previously for the determination of stoichiometry and calculation of formation constants.[3] As expected all the major complexes were found to have a 1 : 1 stoichiometry and their pH-dependent and -independent formation constants are listed in Table 6.[33] As seen from Table 6, the pH-dependent composite formation constants (K_{com} values) for the pmida, pmide and bmida complexes are significantly larger than those of dea and tea. The size of K_{com} reflects the true value of the amount of complex present in solution at the pH of the measurements. The relative and comparable stability of complexes at neutral pH is not immediately obvious from the pH-independent constants (K_{eq} values, Table 6) because the H$^+$ and/or OH$^-$ concentrations contribute to these constants. The bmide ligand forms two complexes with vanadate, one with a similar formation constant to that with dea and the second which is 10-fold larger. The tea complex has a formation constant that is *ca.* three-fold larger than that of the bmide complex at pH 8.4, whilst it is half the value of the bmide complex formed at pH 6.9. The degree of substitution has been shown to play a measurable effect on the stability of the corresponding vanadium complexes and is described in detail elsewhere.[10] A better comparison for the ligands prepared in this work is with tea since it is a tertiary amine. From Table 6 we can see that the complexes formed by the pyridyl ligands are more stable than those of corresponding benzimidazole ligands. Specifically, the formation constant of the pmida complex is 1.5-fold higher than that for bmida, and that pmide is at least 10-fold larger than those for all the bmide complexes. These stability differences can be rationalized by the electron donating properties of the heteroaromatic nitrogen in both the pyridyl and benzimidazole complexes. The availability of the nitrogen lone pair can increase the stability of dea-type complexes by up to two orders of magnitude.[6] Since the pK_a of the central protonated amine in the pyridyl ligands is 7.16 and 8.25 compared to 5.93 and 6.87 for the benzimidazole ligands, the electron donating properties of the central amine in the pyridyl compounds are greater than those in the benzimidazole compound. Accordingly one would expect the better bases, the pyridyl ligands, to form more stable complexes. Indeed, the pyridyl complexes are found to be more stable than the benzimidazole complexes.

In Fig. 5 we illustrated the fact that the V−N bond lengths of the pyridyl complexes are shorter than those in the benzimidazole complexes. Comparing the four vanadium(V) complexes of pmida, pmide, bmida and bmide, the shorter V−N bond length does correlate with the more stable complex. The stability order of these complexes in aqueous solution directly follows the V−N bond length! However, this pattern does not apply when extending such a comparison to vanadium complexes with ligand structure slightly different from that of secondary or tertiary diethanolamine derivatives.

If only electronic properties affected the stability of these complexes one would expect a similar ratio in stability between the pmide/bmide and pmida/bmida compounds. The 1.5-fold increased stability of the pmida over the bmida complex is significantly less than the 12-fold increased stability of the pmide over the bmide complex. This observation is consistent with the possibility that other factors such as solubility play a role in complex stability; that is the bmide complex is of lower stability than expected when compared to the pmide complex. The reduced solubility upon substitution with the benzimidazole functionality is apparent for both bmide and bmida and corresponding vanadium complexes. The significantly lower solubility of two hydroxyethyl groups over the acetate groups may explain the greater complex stability observed with bmida than bmide.

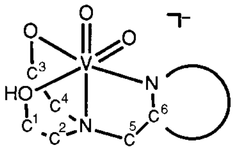
The formation constant for the pmide complex is 100-fold greater than the dea and 25-fold greater than tea complexes.[8] Identification of sources for this enhanced stability will aid in further ligand and vanadium complex design. In contrast to previous solid state and solution characterizations of this type of vanadium(v) complexes, the crystal structure of the pmide complex demonstrates that it contains six-co-ordinate vanadium(v). It is possible that the increased stability of this complex is due to a change in co-ordination number around the vanadium atom. However, if the six-co-ordination was the only factor responsible for the compound stability, one would also expect the bmide complexes to be very stable. This is not observed. We identify the limited solubility of bmide and its vanadium(v) complexes as a key factor in the decrease in stability of these complexes. We also identify the pK_a value close to that of $H_2VO_4^-$ as an important factor to maximize solution stability of the complex.[10] Since the complexes of pmide, pmida and bmida are all generated from ligands with pK_a values for the protonated amine around 8 (pK_a, $H_2VO_4^-$) it is not unprecedented that these complexes are very stable compared to, for example, that of bmide. When combined, these considerations suggest that vanadium complexes of soluble ligands generating six-co-ordinate complexes will have the greatest stability in aqueous solution.

Several minor complexes form with the hydroxyethyl ligands. The second pmide complex at δ −505 is observed from pH 7 to 9. Owing to the signal overlap at neutral pH the δ −505 resonance is best observed at high pH. At all pH values this is a weak complex. The bmide ligand forms two additional complexes with vanadate, a 1:1 complex at δ −488 and a complex with a 2:2 stoichiometry at δ −505. The latter complex is particularly weak and observable only at very high vanadate and ligand concentrations. Furthermore, upon acidification (to pH 7–7.5) of solutions containing high concentrations of 1:1 or 1:2 ratios of vanadate and bmide a yellow precipitate forms. This precipitate was not readily soluble in aqueous solution; it contains some oligomeric form of vanadium (as suggested by elemental analysis), however dissolution in methanol forms the bmide complex and $[VO(OCH_3)_3]$. These minor complexes (at δ −488 and −505) will not be discussed further in this paper.

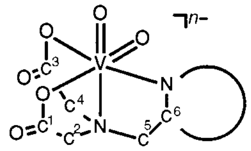
Interestingly, a comparison of ^{51}V NMR shifts for complexes **2a** and **7** gives values of δ −500 and −542, respectively. The analogous carboxylate compounds **1** (δ −503) and **4** (−540) show a similar difference in chemical shifts. Thus the ≈40 ppm difference could be interpreted as a difference in electron density at the vanadium atom. Comparison of these four complexes shows that carboxylate or hydroxyethyl groups have minimum influence on the ^{51}V NMR shifts suggesting that the co-ordination of the aromatic nitrogen is responsible for the observed ≈40 ppm difference. The benzimidazole nitrogen is more basic than the pyridyl nitrogen in the respective aromatic frameworks. Thus the greater shielding effect of the benzimidazole group leads to resonance at higher field. The increased electron density at the vanadium nucleus for the benzimidazole compounds also can be observed by X-ray crystallography. The V–N (aryl) bond lengths of the benzimidazole compounds are found to be shorter than those of the pyridyl compounds (see Table 4) consistent with the σ-donating character being greater in the benzimidazole compounds.[34a] Perhaps it is worth noting that this trend is opposite to that observed with the basicity of the central nitrogen amine atom. Interestingly, the V–N bond lengths follow the trend (amine *vs.* aryl, see Table 4) dictated by basicity: the more basic the nitrogen atom, the shorter is the V–N bond.

Vanadium(v) complex solution structure: ^1H and ^{13}C NMR spectroscopic studies. Proton and ^{13}C NMR spectroscopy is a powerful tool in deciphering the solution structure of vanadium(v) complexes.[8,34b] The ^1H NMR spectra of the complexes described here were obtained. However, most had overlapping and broad resonances making the interpretations less definitive and more difficult to describe. The ^{13}C NMR spectra on the other hand provide one signal for each carbon environment making interpretation clear. Table 7 lists selected ^{13}C CIS values for **1**, **2b**, **4** and **5b** and also gives illustrations of the solution structures consistent with the data.

Table 7 Carbon-13 NMR CIS values for a series of vanadium(v) pyridyl and benzimidazole compounds in aqueous solution[a]



$[VO_2(pmide)]^-$



$[VO_2(pmida)]^-$
$[VO_2(bmida)]^-$
$[VO_2(bmidaa)]^{2-}$

	CIS						
Complex	C^1	C^2	C^3	C^4	C^5	C^6	pH[b]
1	5.5	6.3	7.4	8.9	7.9	5.7	6.5
2b	2.5	1.5	11.4	1.8	4.3	2.4	6.0
4	3.2	5.9	5.2	7.6	7.1	5.1	4.7
5b	3.2	5.0	5.1	6.8	7.1	2.7	4.0

[a] The ^{13}C NMR spectra were obtained at ambient temperature with 0.1 mol dm^{-3} concentration of ligand or complex. [b] Of 0.1 mol dm^{-3} solutions

Complex **1.** The solution structure and assignments of resonances in the ^1H NMR spectra for $[VO_2(S\text{-peida})]^-$ (a complex closely related to **1**) have previously been reported.[14] Ten ^{13}C resonances were observed in a spectrum recorded at 10 °C and the CIS values were determined. The C^1 and C^3 carbonyl CIS values of 5.5 and 7.4 ppm are similar to those of the β-*cis*-$[VO_2(edda)]^-$ complex suggesting co-ordination of the carboxylate groups *cis* and *trans* to an oxo group.[8] The C^6 pyridyl carbon has a CIS value of 5.7 ppm showing the effects of a pyridyl nitrogen co-ordinated to the vanadium atom. Thus, we conclude in agreement with previous workers that the solution structure of $[VO_2(pmida)]^-$ corresponds to the structure characterized by X-ray crystallography for $[VO_2(S\text{-peida})]^-$.

Complex **2b.** The solution structure of compound **2b** and those of other complexes reported in this paper are not known and have been characterized in this work. The assignments were based on literature precedent, correlation spectroscopy (COSY) and two-dimensional heteronuclear correlation (HETCOR) experiments. The ^1H NMR spectrum observed at 0 °C gives several resonances in the methylene region, some of which are assigned to the protons in the hydroxyethyl arms (six resonances) and others to the protons in the pyridyl methylene (two doublets). The signals at δ 2.58 and 3.33 are assigned to the β-CH_2 group in the hydroxyethyl arms. The resonances at δ 3.84 and 4.25 are due to α-CH_2 protons in a hydroxyethyl arm and that at δ 3.30 is a composite due to α- and β-CH_2 protons in one hydroxyethyl arm. The resonance at δ 4.35 is assigned to a β-CH_2 and a CH_2 of the pyridyl methylene group. The remaining pyridyl methylene proton is assigned to the resonance at δ 4.05. This spectrum is consistent with a complex containing two co-ordinated hydroxyethyl groups (bound *cis* and *trans* to the oxo group), a pyridyl nitrogen, an amine nitrogen and two oxo groups, totalling six substituents.

Confirmation of the structural interpretation based on ^1H NMR spectroscopy was made using ^{13}C NMR spectroscopy (Table 7). The C^3 CIS value of 11.4 ppm is indicative of a deprotonated hydroxyethyl group co-ordinated *cis* to an oxo group as observed in the tea complex.[8] The C^1 CIS value of 2.5 ppm is indicative of very weak co-ordination to a vanadium atom consistent with a protonated hydroxyethyl group *trans* to an oxo group. The C^2 and C^4 CIS values listed in Table 7 are consistent with the chelation of the amine nitrogen to the vanadium atom. Thus, the ^{13}C NMR data confirm the ^{1}H NMR data, supporting the interpretation that **2b** maintains the molecular structure of **2a** in solution. Given the greater simplicity in structural interpretation of the ^{13}C NMR spectra of these types of complexes, in the following we will only describe the ^{13}C NMR results for the new complexes reported in this paper.

Complex **4.** The key resonances in the ^{13}C NMR spectrum indicative of an asymmetric solution structure for complex **4** are C^1 and C^3; their chemical shifts require that these two carbon atoms are in different environments. The C^1 and C^3 carbonyl CIS values of 3.2 and 5.2 ppm are smaller than the values for corresponding carbons in the pyridyl analogue complex **1**, presumably reflecting the weaker co-ordination of the benzimidazole moiety. We conclude that complex **4** contains two co-ordinated carboxylate groups, a benzimidazole nitrogen, an amine nitrogen and two oxo groups, totalling six substituents. The solution structure for **4** is consistent with the crystal structures for $[VO_2(S\text{-peida})]^-$ [14] and **3**.

Complex **5b.** The C^1 and C^3 carbonyl CIS values are within 0.1 ppm of the values observed for complex **4**. The third carboxylate (C^{12}) has a CIS value of −6.2 ppm, consistent with this group being pendant. The C^2 and C^4 on the acetate arms and the C^5 on the benzimidazole arm have values within 0.9 ppm of those observed for **4**. This documents the similarity of these two complexes. We conclude that the solution structure of **5b** contains a vanadium co-ordinated through two *cis* carboxylates, one benzimidazole nitrogen, one amine nitrogen and two oxo groups. The third carboxylate in the bmidaa ligand is pendant.

Complex **7.** The limited solubility of this complex and free ligand coupled with dynamic processes in aqueous solution made a detailed characterization of this complex difficult.

In summary, the vanadium(V) pyridyl and benzimidazole complexes maintain the same structure in aqueous solution as in the solid state. All complexes have six-co-ordinate vanadium centres and show structural similarities with the corresponding vanadium(IV) complexes.

Vanadium(V) complex lability: ^{1}H and ^{13}C NMR spectroscopic studies. The structural studies showed that the pyridyl and benzimidazole complexes deviated significantly from previously characterized vanadium(V) triethanolamine[3] and iminodiacetate complexes.[8,12] Since the complexes are all labile and undergo dynamic processes in aqueous solution,[34b] the following studies were carried out to examine the lability of the pyridyl and benzimidazole complexes in the neutral pH range.

Complex **1.** If complex **1** was rigid on the NMR time-scale we would expect to observe six unique environments for the acetate arms and pyridyl methylene protons. The ^{1}H NMR spectrum at 10 °C contains one multiplet and two quartets (centred at δ 4.33, 4.21 and 3.53). The protons from the methylene of one of the acetate groups have a J_{AB} value of 16 Hz and a large difference in chemical shift ($\delta_A - \delta_B$ 1.02 ppm). The second acetate group has an AB splitting pattern with a J_{AB} of 19 Hz. The pyridyl protons have an AB multiplet splitting pattern making the accurate determination of a coupling constant more difficult (J_{AB} 10–16 Hz). This spectrum is consistent with the unsymmetrical nature of a *cis* carboxylate complex. Increasing the temperature results in resonance broadening, until coalescence at 50 °C. A similar exchange process is observed with ^{13}C NMR spectroscopy, here the carbonyl carbon resonances are no longer observed at 35 °C, although it is still possible to observe the methylene carbon resonances of the acetate groups. From both the ^{1}H and ^{13}C NMR data it is clear that at higher temperatures the two different acetate groups become identical and thus indistinguishable.

Complex **2b.** If complex **2b** was rigid on the NMR time-scale we would expect to observe ten unique environments for the hydroxyethyl arm and pyridyl methylene protons. At 0 °C seven resonances are observed in the methylene region of the ^{1}H NMR spectrum thus supporting the possibility that dynamic processes of an intramolecular nature are occurring at this temperature. As described above the ^{1}H NMR spectrum of **2b** is consistent with a complex containing six-co-ordinate vanadium, a protonated hydroxyethyl group (presumably undergoing intramolecular dynamic processes), and a co-ordinated deprotonated hydroxyethyl arm *trans* to a co-ordinated pyridyl group. The ^{13}C NMR spectrum shows four unique carbon environments for the hydroxyethyl group carbons at 0 °C consistent with the CH_2OH group being co-ordinated to the vanadium atom in a *cis* manner. However, at 35 °C these resonances coalesce indicative of a rapid intramolecular exchange process. From these observations it is clear that **2b** undergoes dynamic processes at a lower temperature than that of **1**.

Complexes **4** and **5a.** The ambient temperature ^{1}H and ^{13}C NMR spectra of complexes **4** and **5a** are very similar to those of **1**. A detailed study was carried out for **5a** and the following observations were made. At 10 °C the protons from the methylene of one of the acetate groups, has a J_{AB} value of 16 Hz and a large difference in chemical shift ($\delta_A - \delta_B$ 0.65 ppm). The second acetate group has almost coalesced to give a single resonance and an additional resonance for the third N-benzimidazole acetate group is also observed. The AB splitting pattern for the benzimidazole methylene protons has $J_{AB} = 16$ Hz. Increasing the temperature above 10 °C shows signal broadening in both ^{1}H and ^{13}C NMR spectra as observed with **1**. The ^{1}H and ^{13}C NMR spectra of **4** were indistinguishable with those of **5a**. We conclude that both **4** and **5a** have unsymmetrical *cis* carboxylate solution structures undergoing similar dynamic processes as those of **1** albeit at lower temperatures.

Complex **7.** Proton NMR spectra at ambient temperature show broad lines for complex **7**. Although the signals did sharpen at 0 °C the spectrum still showed insufficient detail for the structural analysis described above. Owing to insolubility of both the ligand and complex even in solvents such as MeOH a corresponding ^{13}C NMR analysis was not carried out.

Comparing the variable-temperature studies of the diethanolamine complexes[8,34b] with the ^{1}H and ^{13}C NMR studies of the pyridyl and benzimidazole complexes described above the following lability order is apparent: $V^V(\text{mdea}) \approx V^V(\text{tea}) > V^V(\text{dea}) >$ **7** $>$ **2b** $>$ V(nta) $>$ **4** $>$ **1**, (mdea = methyl diethanolamine, nta = nitrilotriacetate). Several features in this order of complex lability are important. First of all these complexes show dynamic processes on the same time-scale and all complexes are labile at ambient temperature. As pointed out previously, this observation is not limited to vanadium(V) complexes with diethanolamine type ligands but was also observed for complexes with edta,[5] alizarin (1,2-dihydroxyanthraquinone),[4] tricine[7] {*N*-[tris(hydroxymethyl)methyl]glycine} and several catechols.[35,36] However, within the small differences in the lability of these complexes, we were able to identify the effects of various functionalities. The replacement of a hydroxyethyl or acetate group with a benzimidazole or pyridyl functionality diminishes the lability of the vanadium complex. This pattern would suggest that the V−N (aryl) bond is shorter than the V−O bond, however the opposite is observed in our crystal structures (Table 4). Recognizing that one of the hydroxyl groups is protonated easily reconciles the fact that the V−O bond is more labile than the V−N (aryl) bond. We conclude that the acetate groups in these pyridyl and benzimidazole complexes impart a greater degree of inertness than do hydroxyethyl groups, in agreement with the trend observed for the related diethanolamine and iminodiacetate complexes.[8] Unfortunately, the magnitude of these effects are small.

UV/VIS Spectroscopy. The UV/VIS spectra of vanadium-(IV) and -(V) complexes with pmida, pmide, bmida and bmide were recorded and the absorption maxima and absorption co-

Table 8 The UV/VIS absorption data for complexes **1**, **2a**, **3**, **4**, **6** and **7** and other known compounds in water or dmf–water

Compound	pH	λ/nm (ε/dm³ mol⁻¹ cm⁻¹)							
H_2pmida	3.9							259 (3400)	201 (5700)
[VO(pmida)(H_2O)][a]	5.5	770 (27)	550 (15)	350 (sh) (310)					
1	7.0				293 (sh) (1350)			260 (4500)	192 (22000)
[VO(*S*-peida)(H_2O)][b]	4	758 (27.4)	565 (16.4)	355 (357)	294 (sh) (642)			258 (4970)	
[VO_2(*S*-peida)]$^-$ [b]	4				300 (sh) (1070)			265 (4640)	
H_2pmide	7.8							259 (4100)	197 (8300)
2a	6.5				286 (sh) (2000)			259 (5200)	194 (13 000)
H_2bmida	8.8					280 (6800)	273 (7200)	244 (6200)	204 (29 000)
3	6.9	783 (36)	582 (19)	360 (sh) (46)	320 (212)	278 (4600)	271 (5300)	225 (4200)	196 (25 000)
4	6.8				295 (sh) (1800)	275 (7900)	270 (8400)	225 (7900)	195 (42 000)
H_2bmide	5.2					275 (8000)	269 (7600)	247 (5200)	199 (27 000)
6	5.8	898[c] (140)		345[c] (sh) (880)	304[c] (5400)	279 (9800)	272 (1100)	243 (8800)	199 (48 000)
7	6.3				295 (sh) (1580)	279 (7300)	272 (8200)	243 (7700)	199 (44 000)

[a] Ref. 37. [b] Ref. 14. [c] Crystalline compound dissolved in dmf–water (1 : 1 v/v).

efficients are listed in Table 8. The visible region shows three weak absorptions for vanadium(IV) compounds, similar to those for other monomeric six-co-ordinate vanadium(IV) compounds such as [VO(pmida)(H_2O)][37] and [VO(*S*-peida)(H_2O)][14] (Table 8). As expected the absorption bands of **1** are almost identical to those of [VO_2(*S*-peida)]$^-$ (Table 8) and similar to those of compound **2a**. Thus it is reasonable to assume that the assignments made for the *S*-peida complexes[14] are valid for the pmida complexes. The limited solubility of **6** required that this compound be examined in dmf–water.

The UV spectra of the vanadium-(IV) and -(V) complexes are similar to those of the free ligands. In addition to these bands, shoulders are observed ≈300 nm. These are assigned to the charge transfer from the pyridyl or the benzimidazole to the vanadium atom.[14] The remaining bands (below 280 nm) are assigned predominantly to the π–π* ligand based transitions and other ligand to metal charge transfer transitions.

Comparing the two absorbances in the visible spectra of [VO(pmida)(H_2O)], [VO(*S*-peida)(H_2O)] and **3** no major differences are observed. This is in agreement with the similarities in the parameters ($g_\perp$, $g_\parallel$) observed in the ESR spectra for these compounds.[19] The differences in the absorbances and the ESR parameters for **6** compared to those of [VO(pmida)(H_2O)], [VO(*S*-peida)(H_2O)] and **3** are probably related to the asymmetry and the different ligand field of the donating ligand moieties in **6**.

Conclusion

A series of new vanadium-(IV) and -(V) compounds have been prepared with pyridyl and benzimidazole ligands. The crystal structures of [VO_2(Hpmide)]·4H_2O, [VO(bmida)(H_2O)]·H_2O and [VO(acac)(Hbmide)] have been solved, revealing the vanadium centre to be six-co-ordinate. Complex **2** was prepared for comparison with **1** and showed that substitution of carboxylate with hydroxyethyl groups makes the complex more stable and more labile. Substitution of carboxylate with hydroxyethyl groups has previously resulted in less stable complexes. The reverse pattern reported previously is also observed for the benzimidazole containing ligands. The previous observation correlating the stability of related complexes to the pK_a value of protonated amine ligands is interestingly also followed for these complexes and may explain these apparent contradictory stability patterns observed with the pyridyl and benzimidazole complexes. Based on our solid state and solution structural characterization of **2a**, the stability of the six-co-ordinate vanadium complexes tends to be higher than that of five-co-ordinate complexes, although it is very difficult to make such quantitative comparisons among complexes containing ligands with different functionalities, pK_a values and co-ordination numbers to the vanadium atom. The solution and solid state characterization showed that the benzimidazole complexes of bmida and bmide shared structural properties with their pyridyl analogues. However, despite structural similarities, distinct differences in both stability and lability were observed in solution among these complexes. In the course of this work an empirical relationship between the pK_a value of the protonated ligand and the V−N bond length (*trans* to an oxo group) of the corresponding complex was observed. Although some variation is found depending on the oxidation state of the vanadium, generally lower pK_a values translate into longer V−N bonds. Whether these differences will have any bearing on the biological properties of these compounds remains to be determined. In short, vanadium-(IV) and -(V) complexes with ligands containing functionalities including hydroxyethyl, carboxylate, amine, pyridyl and benzimidazole are now added to our library of compounds facilitating further rational design of complexes with specific properties.

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