# Oxovanadium(IV) complexes of phosphonic derivatives of iminodiacetic and nitrilotriacetic acids

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The complex formation between $V^{IV}O$ and phosphonic derivatives of iminodiacetic (Ida) and nitrilotriacetic acids (Nta) has been studied by combined application of pH-potentiometric and spectroscopic (EPR and electronic absorption) techniques. Differently from aminomonophosphonates, which are able to bind the metal ion rather weakly forming five-membered chelated rings, the mixed carboxylic–phosphonic and pure phosphonic derivatives of Ida and Nta form chelated systems resulting in very stable complexes mostly of the 1:1 type. Substitution of $CO_2^-$ by $PO_3^{2-}$ increases the stability of the complexes due to the higher basicities of the phosphonic functions. However, the higher spatial requirement of the phosphonate groups and the greater electrostatic repulsion between the dinegative phosphonate arms would mostly compensate this effect. Spectroscopic evidence has been found for a considerable distortion in the geometry of the aminophosphonate complexes. The differences in the observed stability trends between the corresponding copper(II) and $V^{IV}O$ complexes are also discussed.

Natural and synthetic aminophosphonic molecules are very effective ligands, in many cases with high specificity, for metal ions. This class of compounds includes a variety of herbicides, plant growth regulators, antibiotics and inhibitors of metallo-enzymes.[1] As potent metal binders, these molecules could be involved in interactions relevant for the fate of metal ions in the natural environment or biological systems. Therefore, numerous studies were aimed at understanding the chelating properties of this class of ligands and determining the stability of the complexes formed.[2–13] Definite conclusions have been reached for their co-ordination properties and the nature of the species formed with several metal ions. Differences in size, basicity, charge and electron-releasing ability of phosphonate and carboxylate groups have been invoked in order to explain the different complex-forming properties of aminophosphonates compared to aminocarboxylates. It has also been found that the steric demand of phosphonic groups can impose particularly distorted geometries at the metal ions and favour ligand conformations different from those of the carboxylic analogues.

Several investigations have been carried out on the interaction of iminodiacetic (Ida) and nitrilotriacetic (Nta) acids with the $V^{IV}O$ ion which is one of the most stable forms of the important biometal vanadium.[14–20] The limited flexibility of the $V^{IV}O$ geometry, which usually is tetragonal and involves four strong sites in the equatorial plane and a less effective position *trans* to the oxo group, and the relatively rigid structure of the ligands appear responsible for peculiar complex forming properties. However, no data are available for the phosphonic derivatives of Nta and Ida. Herein, we report results on the $V^{IV}O$ co-ordination ability of a number of phosphono analogues of aminopolycarboxylic ligands, as studied by spectroscopic and potentiometric techniques. Aminomethylphosphonic acid (GlyP, the phosphonic analogue of glycine),

N-(phosphonomethyl)glycine (IdaP, the mono phosphonic derivative of Ida), imino-bis(methylphosphonic acid) (Ida2P, the bis phosphonic derivative of Ida), N-(phosphonomethyl)-iminodiacetic acid (NtaP), N,N-bis(phosphonomethyl)glycine (Nta2P) and nitrilo-tris(methylphosphonic acid) (Nta3P) have been examined. Conclusions have been reached which allow a direct comparison between the tendencies of phosphonate and acetate "arms" to form chelated rings. Moreover, conclusions have been drawn about the relative stability of copper(II) and oxovanadium(IV) complexes.
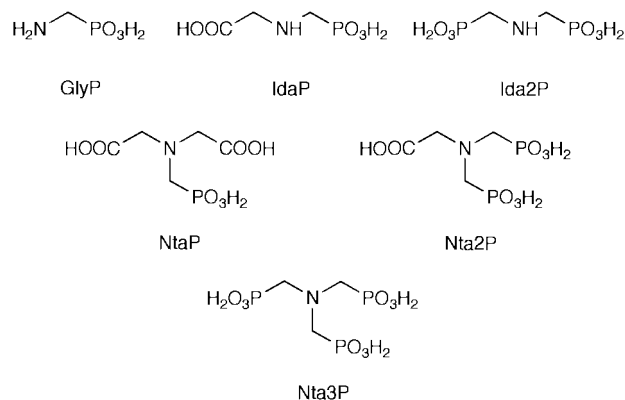


## Experimental

### Chemicals

The ligands used were Aldrich, Sigma or Fluka products of puriss. quality. The purity of the ligands was checked and the exact concentration of their solutions was determined by the

Gran method.[21] A $VO^{2+}$ stock solution, prepared as described in ref. 22, was standardised for metal concentration by permanganate titration and for hydrogen ion concentration by potentiometry using the appropriate Gran function. The ionic strength was adjusted to 0.2 mol dm$^{-3}$ KCl. In all cases, the temperature was 25.0 ± 0.1 °C.

## Potentiometric measurements

Stability constants were determined by pH-metric titration of 25.0 cm$^3$ samples. The ligand concentration was 0.004 and 0.002 mol dm$^{-3}$ and the ligand to metal ion molar ratio 4:1, 2:1 and 1:1. Titrations were performed over the pH range 1.5–11.5 with carbonate-free KOH solution (normal titration) or with HCl solution (back titration) of known concentration (ca. 0.2 mol dm$^{-3}$) under a purified argon atmosphere. In an equimolar solution of oxovanadium(IV) and the pure phosphonic derivatives of Ida and Nta, precipitation occurred in the pH range 2–5. In these cases, by back titrating the samples, pH values as low as ≈3 could be reached without precipitation probably due to the formation of oversaturated solutions. In some cases pH equilibrium could not be reached within 10 min due to either precipitation or very slow complex formation reactions. These titration points were omitted from further evaluation. The reproducibility of titration points included in the evaluation was within 0.005 pH unit in the whole pH range.

For the potentiometric titration an automatic titration set including a Dosimat 665 (Metrohm) autoburette, an Orion 710A precision digital pH-meter and an IBM compatible personal computer were used. An Orion 9103BN or a Metrohm 6.0234.1#00 type semimicro combined pH electrode was calibrated for the hydrogen ion concentration according to the method of Irving et al.[23] The difference between pH-meter readings and $-\log[H^+]$ was constant in the pH ranges 2–4 and 10–11.6. Thus the junction potential proved to be constant, although not negligible, as discussed previously.[23] Concentration stability constants $\beta_{pqr} = [M_pA_qH_r]/[M]^p[A]^q[H]^r$ were calculated with the aid of the PSEQUAD computer program.[24] The formation of hydroxo complexes of $V^{IV}O$ was taken into account in the calculations. The following species were assumed: $[VO(OH)]^+$ ($\log\beta_{1-1} = -5.94$), $[\{VO(OH)\}_2]^{2+}$ ($\log\beta_{2-2} = -6.95$), with stability constants calculated from the data of Henry et al.[25] and corrected for the different ionic strengths by use of the Davies equation, $[VO(OH)_3]^-$ ($\log\beta_{1-3} = -18.0$) and $[(VO)_2(OH)_5]^-$ ($\log\beta_{2-5} = -22.0$), taken from ref. 26.

## Spectrophotometric measurements

Electronic absorption spectra of the complexes formed in the $V^{IV}O$–ligand systems were recorded on a Hewlett-Packard 8452 diode-array spectrometer. A special titration cell was constructed for these measurements having a light tube with quartz windows on both ends (path length = 3.005 cm) built into a conventional water-jacketed potentiometric cell. Owing to the relatively high stability of the $V^{IV}O$ complexes of the Nta derivatives, the reliability of the pH-metrically determined stability constants was checked spectrophotometrically using the competition reaction with the bis complex of maltol [3-hydroxy-2-methyl-(4H)-pyran-4-one]. The fairly high differences in the electron absorption spectra of complexes [VO(malt)$_2$], malt = maltolate(1−), and VOA (where A indicates the phosphonic derivatives of Nta studied) (see Fig. 1) made possible the spectrophotometric monitoring of the ligand displacement reaction (1). Solutions of $V^{IV}O$–maltol at 1:2 metal

$$[VO(malt)_2] +$$
$$qHA^{(n-1)-} + (1-q)H_2A^{(n-2)-} + qH_2O \rightleftharpoons$$
$$VOA^{(n-2)-} + 2Hmalt + qOH^- \quad (1)$$
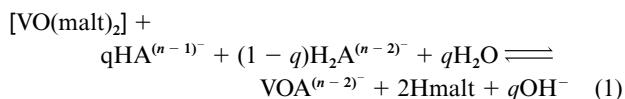
ion to ligand ratio and 0.003 and 0.006 mol dm$^{-3}$ $V^{IV}O$ concen-
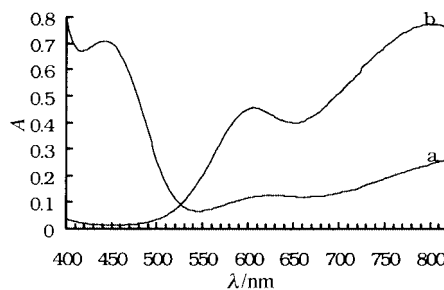
Fig. 1 Visible spectra of [VO(malt)$_2$], $c_{V^{IV}O} = 0.0028$ mol dm$^{-3}$, $c_{ligand} = 0.0057$ mol dm$^{-3}$, pH 5.50 (a), and VO(Nta), $c_{V^{IV}O} = 0.012$ mol dm$^{-3}$, $c_{ligand} = 0.012$ mol dm$^{-3}$, pH 5.55 (b).

trations were titrated in a special titration cell with a 0.02 mol dm$^{-3}$ solution of ligand A at constant pH corresponding to the optimum formation of complex VOA. After the addition of each increment of ligand solution the pH was readjusted with base to the starting value and spectra were recorded after equilibration. Absorption values at various wavelength values in the range 420–460 nm, where the spectra of the two complexes differed most significantly, were analysed and the ligand displacement constants calculated point by point. The actual protonation state of the competing phosphonate ligands was calculated using the protonation constants listed in the Tables. At least 50 data points were analysed for each system. In the knowledge of $\log\beta[VO(malt)_2] = 16.29$ (ref. 27) the $\log\beta(VOA)$ values could then be calculated.

## EPR measurements

Anisotropic X-band EPR spectra (9.15 GHz) were recorded at 120–140 K on aqueous solutions using a Varian E-9 spectrometer. As usual, the samples for low-temperature measurements were added with a few drops of DMSO to ensure good glass formation in frozen solutions.

## Results and discussion

### Aminomethylphosphonic acid (GlyP)

This ligand ($H_3A^+$) is the phosphonic analogue of glycine. According to titration data only two protons bind to it in the measurable pH range. Indeed, $\log K(HA) = 10.05$ and $\log K(H_2A) = 5.35$ values are measured for the protonation of the $NH_2$ and $PO_3^{2-}$ groups, respectively, while $PO_3H^-$ is very weakly basic and protonates with $\log K(H_3A) < 1$.[28] The corresponding values for the AlaP derivative are 10.11, 5.55 and ≈1, respectively, as reported earlier.[10] The scarce affinity of the amino group toward the 'hard' $V^{IV}O$ ion hinders the formation of very stable complexes and a conspicuous ligand excess (a molar excess greater than 10) is necessary to avoid the predominance of hydrolytic species in solution, analogously as for the aminocarboxylate analogues. As substantiated by EPR spectra, over the pH range 2.5–6 the $V^{IV}O$ complexing properties of GlyP resemble those of methylphosphonic acid (MeP).[29] The continuous decrease of the hyperfine coupling constant with increasing pH is consistent with the progressive insertion of one or two monodentate phosphonate groups in the metal co-ordination sphere. This corresponds with the formation of a protonated complex [VOAH]$^+$ [in the $V^{IV}O$–AlaP system log $\beta$(VOAH) = 14.03(9)]. The stoichiometry of the complex suggests monodentate phosphonate co-ordination of the ligand with a non-co-ordinated and protonated amino group. However, in contrast to the simple $V^{IV}O$–MeP system, two further chelated species are formed which shift the onset of hydrolysis to higher pH. A species distinguished around pH 7 by $A_\|$ $174 \times 10^{-4}$ cm$^{-1}$ is a complex with a ($NH_2$, $PO_3^{2-}$) chelated ring and, at a tenfold ligand excess, a second phosphonate arm may also be co-ordinated. On the other hand, the value of $A_\|$

$(167 \times 10^{-4}$ cm$^{-1})$ measured at pH greater than 8 indicates a bis chelated complex involving two $(NH_2, PO_3^{2-})$ rings. Stability constants log $\beta(VOA) = 10.24(4)$ and log $\beta(VOA_2) = 16.44(12)$ were determined for the chelate complexes of AlaP. Above pH 10 the decrease of intensity of the EPR signal and the appearance of broad unresolved resonances around $g = 2$ are diagnostic of the hydrolysis and formation of polynuclear hydroxo-bridged species.

On the whole, although the complexing behaviour of the ligand could appear basically similar to that of its aminocarboxylic derivative, there are some differences in their $V^{IV}O$ binding

capabilities because of the greater basicity and charge of phosphonate$(2-)$ compared to carboxylate$(1-)$: (i) the complexation equilibria shift toward more basic solution; (ii) the mono chelated complex is more stable toward the transformation into bis chelated species; and (iii) the complexes are more resistant toward hydroxo complex formation.

### *N*-(Phosphonomethyl)glycine (IdaP)

In the measurable pH range the ligand $(H_4A^+)$ exhibits only three protonation processes with log $K(H_nA)$ values of 10.02 $(>NH)$, 5.39 $(PO_3^{2-})$, and 2.20 $(CO_2^-)$ (see Table 1). The values are in fairly good agreement with those measured previously.[3,6,7,13,30] The log $K(H_4A)$ value of $PO_3H^-$ is less than 1 and cannot be determined by pH potentiometry (a value of 1.23 has been reported in ref. 6). The ligand is the monophosphonic derivative of iminodiacetic acid and can yield two joined five-membered chelated rings, one of the glycinate and another of the aminomethylphosphonate type. An analysis of the anisotropic EPR spectra (Table 2) collected on frozen $V^{IV}O$–IdaP solutions gives a clear indication for the tridentate coordinating mode of the ligand and the formation of stable complexes. Indeed, a limited ligand excess is enough to prevent hydrolysis below pH 7. At pH values as low as 2 a slight decrease of the parallel $^{51}V$ coupling constant from that of the aqua ion reveals complexed species in which one or more water molecules in the metal environment are replaced by oxygen donors of phosphonate and/or carboxylate groups. The fitting of potentiometric data assumes a protonated complex [VOAH]. Therefore, it may be assumed that the ligand is bound through the oxygen atoms of both monodentate $CO_2^-$ and $PO_3^{2-}$ groups and keeps the imino nitrogen protonated. The derived equilibrium constant for the reaction $VO^{2+} + HA^{2-} \rightleftharpoons$ [VOAH] is log $K = 4.35$. With glycine, the formation of the analogous $[VOAH]^{2+}$ species occurs with log $K = 1.17$, while with AlaP the corresponding log $K$ is 3.92, consistent with the involvement of both the carboxylate and the phosphonate groups of IdaP in the metal binding. At pH 3 a precipitate starts to form with IdaP (most likely the neutral complex with the ligand in the

**Table 1** Proton (log $K$) and oxovanadium(IV) complex formation constants of iminodiacetic acid (Ida) and its phosphonic derivatives at $I = 0.20$ mol dm$^{-3}$ KCl and 25 °C

|  | Ida | IdaP | Ida2P |
|---|---|---|---|
| log $K(NH)$ | 9.29(3) | 10.02(3) | 10.77(2) |
| log $K(PO_3^{2-})$ | — | 5.39(2) | 6.30(2) |
| log $K(PO_3^{2-})$ | — | — | 4.86(2) |
| log $K(PO_3H^-)$ | — | — | ≈1.5(4) |
| log $K(CO_2^-)$ | 2.54(4) | 2.20(5) | — |
| log $K(CO_2^-)$ | ≈1.7(3) | — | — |
| VOAH | — | 14.37(5) | 17.55(10) |
| VOA | 8.84(2) | 10.69(3) | 12.22(8) |
| $(VOAH_{-1})_2$ | 9.56(4) | 10.74(6) | 12.67(13) |
| VOA$_2$H | 20.08(9) | 23.35(3) | 26.29(9) |
| VOA$_2$ | 15.32(6) | 15.89(11) | — |
| Number of points | 399 | 556 | 940 |
| Fitting parameter[a] | 0.0064 | 0.0088 | 0.0124 |
| VO + AH $\rightleftharpoons$ VOAH | — | 4.35 | 6.78 |
| log $K_{VOA} - \Sigma$log $K_{HA}$ | −4.67 | −6.92 | −11.20 |
| VOA + A $\rightleftharpoons$ VOA$_2$ | 6.48 | 5.20 | — |
| log $[K(VOA)/K(VOA_2)]$ | 2.36 | 5.49 | — |
| VOA + AH $\rightleftharpoons$ VOA$_2$H | 1.95 | 2.64 | 3.30 |
| p$K(VOAH)$ | — | 3.68 | 5.33 |
| p$K(VOA_2H)$ | 4.76 | 7.46 | — |

[a] Goodness of fit between the experimental and the calculated titration curves expressed in cm$^3$ of titrant.

**Table 2** Spectral data for the complexes

| Ligand | Complex | $g_\parallel$ | $10^4 A_\parallel(^{51}V)$/cm$^{-1}$ | Donor set | $\lambda_{max}$ [a]/nm |
|---|---|---|---|---|---|
| GlyP | [VOA] or [VOA$_2$H]$^-$ | 1.939 | 174 | $(NH_2, PO_3^{2-})$ $(NH_2, PO_3^{2-})$, PO$_3^{2-}$ | [b] |
|  | [VOA$_2$]$^{2-}$ | 1.945 | 167 | 2 $(NH_2, PO_3^{2-})$ |  |
| Ida | [VOA] | 1.942 | 170 | $(NH_2, 2 CO_2^-)$ | 605(9), 870(17) |
|  | [VOA$_2$]$^{2-}$ | 1.944 | 169 | $(NH, 2 CO_2^-)(NH, CO_2^-)$ | 590(9), 800(15)[c] |
| IdaP | [VOAH] | 1.930 | 181 | $PO_3^{2-}$ and/or $CO_2^-$ |  |
|  | [VOA]$^-$ | 1.941 | 171 | $(NH, PO_3^{2-}, CO_2^-)$ | 610(17), 830(18) |
|  | [VOA$_2$]$^{4-}$ | 1.947 | 163 | $(NH, PO_3^{2-}, CO_2^-)$ $(NH, PO_3^{2-})$ | 560(14), 810(18) |
| Ida2P | [VOAH]$^-$ | 1.930 | 180 | $2PO_3^{2-}$ or $PO_3^{2-}$ | 645(9), 870(17) |
|  | [VOA]$^{2-}$ | 1.942 | 171 | $(NH, 2 PO_3^{2-})$ | 590(18), 830(16) |
|  | [VOA$_2$H]$^{5-}$ | 1.942 | 161 | $(NH, 2 PO_3^{2-})$ $(NH, PO_3^{2-})$ |  |
| Nta | [VOAH] |  |  | $(3 CO_2^-)$ | 340(10), 610(12), 795(21) |
|  | [VOA]$^-$ | 1.937 | 176 | $(N, 3 CO_2^-)$ | 330(21), 605(11), 800(19) |
|  | [VOAH$_{-1}$]$^{2-}$ | 1.939 | 172 | $(N, 3 CO_2^-, OH^-)$ | 355(12) (sh), 590(9), 845(20) |
| NtaP | [VOAH$_2$] | 1.933 | 182 | $(2 CO_2^-, PO_3H^-)$ | 340(6) (sh), 630(8), 805(16) |
|  | [VOAH]$^-$ | 1.934 | 178 | $(N, 2 CO_2^-, PO_3H^-)$ | 340(6) (sh), 625(8), 845(16) |
|  | [VOA]$^{2-}$ | 1.935 | 176 | $(N, CO_2^-, PO_3^{2-})$ | 345(13) (sh), 630(7), 860(17) |
|  | [VOAH$_{-1}$]$^{3-}$ | 1.937 | 173 | $(N, 2 CO_2^-, PO_3^{2-}, OH^-)$ | 360(12) (sh), 595(6), 870(14) |
| Nta2P | [VOAH$_2$]$^-$ | 1.933 | 181 | $(PO_3H^-, PO_3^{2-}, CO_2^-)$ | 345(9) (sh), 650(11), 820(19) |
|  | [VOAH]$^{2-}$ | 1.932 | 180 | $(N, PO_3H^-, PO_3^{2-}, CO_2^-)$ | 345(9) (sh), 650(6), 850(16) |
|  | [VOA]$^{3-}$ | 1.934 | 178 | $(N, 2 PO_3^{2-}, CO_2^-)$ | 345(8) (sh), 650(6), 870(13) |
|  | [VOAH$_{-1}$]$^{4-}$ | 1.935 | 174 | $(N, 2 PO_3^{2-}, CO_2^-, OH^-)$ | 345(19) (sh), 600(6), 875(10) |
| Nta3P | [VOAH$_2$]$^{2-}$ | 1.931 | 181 | $(PO_3H^-, 2 PO_3^{2-})$ | 670(10), 795(16) |
|  | [VOAH]$^{3-}$ | 1.930 | 180 | $(N, PO_3H^-, 2 PO_3^{2-})$ | 675(7), 870(14) |
|  | [VOA]$^{4-}$ | 1.929 | 179 | $(N, 3 PO_3^{2-})$ | 350(7), 675(7), 875(13) |
|  | [VOAH$_{-1}$]$^{5-}$ | 1.935 | 173 | $(N, 3 PO_3^{2-}, OH^-)$ | 395 (sh), 455 (sh), 570(15), 665(11), 870(16) |

[a] Values of $\varepsilon$/dm$^3$ mol$^{-1}$ cm$^{-1}$ shown in parentheses are referred to the total metal concentration and to the maximum extent of formation of the species. [b] Not measurable because of the extensive formation of hydrolytic species. [c] Previously attributed as a hydrolytic species (ref. 20); the most likely structure involves three carboxylates and one nitrogen in the equatorial plane and a nitrogen in the axial position.
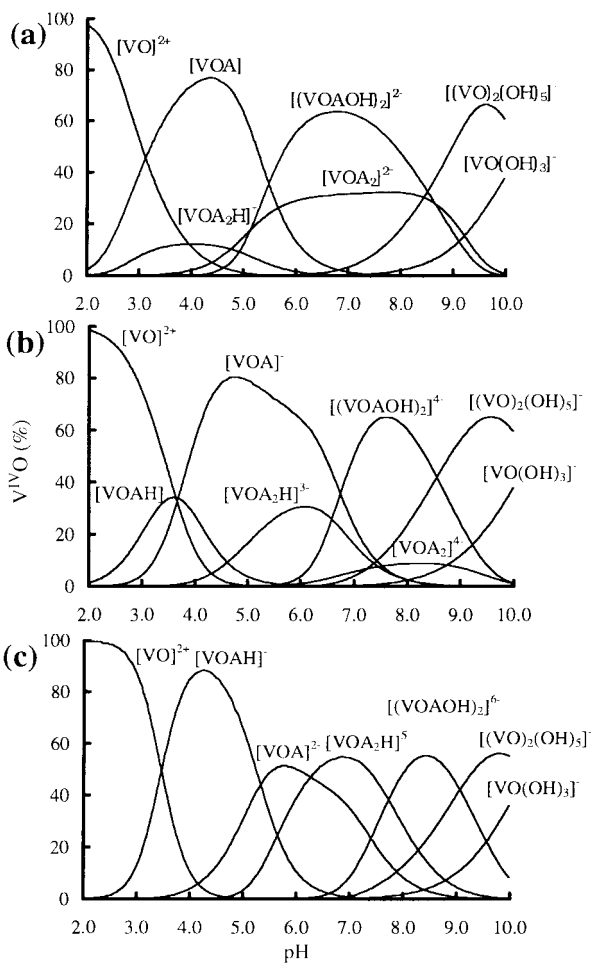
**Fig. 2** Species distribution diagram for (a) $V^{IV}O$–Ida, (b) $V^{IV}O$–IdaP and (c) $V^{IV}O$–Ida2P systems; $c_{V^{IV}O} = 0.002$ mol dm$^{-3}$, $c_{ligand} = 0.004$ mol dm$^{-3}$.

$^-O_2CCH_2NH_2^+CH_2PO_3^{2-}$ or $^-O_2CCH_2NHCH_2PO_3H^-$ form), which, however, could be avoided during pH-metric titrations due to the lower metal ion concentrations applied. The redissolution of the solid takes place with increase of pH, namely upon full deprotonation of the ligand. A 1:1 [VOA]$^-$ complex is formed to increasing extent from pH 4 to 7.5 by the co-ordination of a tridentate ligand molecule (see Fig. 2). The complex [VOA]$^-$ exhibits $A_\parallel = 171 \times 10^{-4}$ cm$^{-1}$ and $g_\parallel = 1.941$, which indicate the presence of the imino nitrogen atom co-ordinated in the equatorial plane. Complexes with exclusive (NH, CO$_2^-$) or (NH, PO$_3^{2-}$) donor sets would not be stable in the presence of a limited ligand excess, as demonstrated by the $V^{IV}O$–Gly and –GlyP systems. Therefore, the ligand is tridentate in [VOA]$^-$, as supported by the fairly high value of the formation constant (log $K = 10.69$, *cf.* 6.51 for the 1:1 complex of glycine[31]). Ida-type ligands strongly prefer facial tridentate co-ordination because of the strain in the C–N–C angle in the meridional isomer. Although it is expected that the longer C–P and P–O bonds in phosphonic derivatives should decrease the strain, the *fac* co-ordination is common for IdaP. For instance, the ligand has been found co-ordinated facially to Pt$^{IV}$.[12] Notably, the analogous $V^{IV}O$ complex of Ida yields two isomeric forms in solution, which were assumed as the species in which the nitrogen donor is in the axial or equatorial position.[20] In the case of IdaP, the electrostatic repulsion disfavours the co-ordination of two charged groups in the equatorial plane and a single isomer is observed for the monochelated species in solution. Therefore, a *fac* type arrangement is likely in [VOA]$^-$. The nitrogen atom is located in the equatorial plane, one of the carboxylate or phosphonato (preferably the latter) donors is in an adjacent equatorial site and the other behaves as an axial

donor. This co-ordination mode of IdaP is confirmed by the absence of monomeric monohydroxo species. In fact, since the ligand occupies only two sites of the equatorial plane, the species [VOAH$_{-1}$]$^{2-}$, or [VOA(OH)]$^{2-}$, which predominates above pH 8, can undergo dimerisation and yield complexes with two μ-hydroxo bridges in the equatorial plane. In contrast, in the *mer* type arrangement only one free site should be available for hydroxo binding and monomeric hydrolytic species would be expected.[17]



[VOA]$^-$
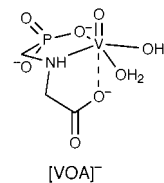
The co-ordination of a second ligand molecule to the metal ion gives rise to [VOA$_2$H]$^{3-}$. The process is not accompanied by a significant change in the EPR parameters, which indicate that the second ligand binds vanadium through one or two oxygens and the nitrogen atom is not available for metal co-ordination because it is in a protonated form. Also the value of the equilibrium constant for the process [VOA]$^-$ + HA$^{2-}$ ⇌ [VOA$_2$H]$^{3-}$ (log $K = 2.64$) suggests a weak binding mode of the second ligand. The proton release from the ammonium group of this ligand occurs with a p$K$ value of 7.46 (10.02 in free IdaP) and corresponds to distinct changes of the spectral features. The EPR parameters of [VOA$_2$]$^{4-}$ are $g_\parallel = 1.947$ and $A_\parallel = 163 \times 10^{-4}$ cm$^{-1}$, which are close to those of the bis chelated complex of glycinate(1$-$). Therefore, it may be assumed that, upon proton dissociation of the ammonium group, the co-ordination mode of the second ligand switches to (NH, PO$_3^{2-}$) and yields a N$_2$O$_2$ donor set in the equatorial plane. The relatively high value of log($K_{VOA}/K_{VOA_2}$) = 5.49 compared to 2.36 measured for Ida, 1.20 for glycine[31] and 4.04 for AlaP indicates that charge and steric effects disfavour the accommodation of a second ligand molecule in the metal co-ordination sphere. Electron absorption data too (see Table 2) are supportive of the donor set assumed for [VOA$_2$]$^{4-}$. On the whole, it may be concluded that the $V^{IV}O$–IdaP system apparently behaves similarly as the analogous system GlyP or AlaP. In fact, the tridentate character makes IdaP complexes more stable, even if only two in-plane sites of $V^{IV}O$ are occupied by the ligand. A comparison with the complexes of Ida indicates that the replacement of carboxylate by phosphonate arms produces an increase in log $\beta$ values for both VOA and VOA$_2$ complexes (in the latter to a lower extent). However, if the constants are corrected for the basicity of the co-ordinating donor groups, see the values of [log $K_{VOA}$ − Σlog $K_{HA}$] listed in Table 1, it may be seen that steric and electrostatic effects disfavour the binding of phosphonate ligand to a higher extent the greater the charge is. Similar conclusions were drawn for the aminophosphonato complexes of Cu$^{II}$.[13]

**Imino-bis(methylphosphonic acid) (Ida2P)**

This ligand (H$_5$A$^+$) is provided with two phosphonic groups. Four of the five protonation processes can be measured by pH potentiometry and log $K$(H$_n$A) values of 10.77 (NH), 6.30 (PO$_3^{2-}$), 4.86 (PO$_3H^-$) and 1.5 (PO$_3H_2$), are calculated (see Table 1). Comparable values (10.79, 6.08, 5.04 and 0.86) have been reported,[7] while values of 11.6, 5.5, 5.5 and 1.4 have been determined by another study.[32] In this case too, one of the PO$_3$H$_2$ groups appears very acidic and has a p$K$ value less than 1. The complexing behaviour of the ligand is analogous to that for IdaP. The EPR data indicate that at acidic pH values (up to pH ≈ 6) the co-ordination of the phosphonato groups predominates to yield a species with [VOAH]$^-$ composition. The

**Table 3** Proton (log $K$) and oxovanadium(IV) complex formation constants (log $\beta$) of nitrilotriacetic acid (Nta) and its phosphonic derivatives at $I = 0.20$ mol dm$^{-3}$ KCl and 25 °C

|  | Nta | NtaP | Nta2P | Nta3P |
|---|---|---|---|---|
| log $K$(N) | 9.56(2) | 10.52(2) | 11.44(4) | 12.27(6) |
| log $K$(PO$_3^{2-}$) | — | 5.52(3) | 6.38(3) | 7.18(6) |
| log $K$(PO$_3^{2-}$) | — | — | 4.96(2) | 5.74(6) |
| log $K$(PO$_3^{2-}$) | — | — | — | 4.53(6) |
| log $K$(PO$_3$H$^-$) | — | — | — | ≈1 |
| log $K$(CO$_2^-$) | 2.40(4) | 2.33(3) | 2.09(6) | — |
| log $K$(CO$_2^-$) | ≈1.6(3) | ≈1.4(4) | ≈1 | — |
| log $K$(CO$_2^-$) | ≈1.4(4) | — | — | — |
| VOAH$_4$ | — | — | — | 33.3(2) |
| VOAH$_3$ | — | — | — | 31.39(9) |
| VOAH$_2$ | — | 20.4(3) | 24.5(1) | 28.94(5) |
| VOAH | 15.69(6) | 18.76(5) | 21.26(9) | 24.84(5) |
| VOA | 13.18(4) | 15.14(5) | 16.78(9) | 17.66(4) |
| VOA (spectrophot.) | 12.6(4) | 14.9(5) | 16.0(5) | 18.0(4) |
| VOAH$_{-1}$ | 6.07(3) | 7.06(5) | 7.87(9) | 8.33(5) |
| Number of points | 750 | 846 | 546 | 1317 |
| Fitting parameter[a] | 0.0102 | 0.00991 | 0.0104 | 0.00723 |
| log $K_{VOA}$ − Σlog $K_{HA}$ | −1.78 | −4.63 | −9.09 | −13.26 |
| p$K$(VOAH$_4$) | — | — | — | 1.9 |
| p$K$(VOAH$_3$) | — | — | — | 2.45 |
| p$K$(VOAH$_2$) | — | 1.6 | 3.25 | 4.10 |
| p$K$(VOAH) | 2.51 | 3.62 | 4.48 | 7.18 |
| p$K$(VOA) | 7.11 | 8.08 | 8.91 | 9.33 |

[a] Goodness of the fit between the experimental and the calculated titration curves, expressed in cm$^3$ of titrant.

log $K$ value for the reaction VO$^{2+}$ + HA$^{3-}$ ⇌ [VOAH]$^-$ is 6.78, higher than with IdaP, consistent with the greater basicity of PO$_3^{2-}$ compared to CO$_2^-$. The release of the proton from the protonated amino group of [VOAH]$^-$ occurs with a p$K$ value of 5.33. In the 1:1 complex [VOA]$^{2-}$ the ligand is tridentate with the nitrogen atom and a phosphonate group bound in two equatorial positions, while the other phosphonate moiety acts as an axial donor. The assignment is supported by stability data. Indeed, the formation constant of the Ida2P species is several orders of magnitude larger than for IdaP and Ida complexes. However, in this case too, the increase of stability vanishes as the basicity of all the donor groups is taken into account, further supporting the negative effects of steric and electrostatic factors. The bis complex [VOA$_2$H]$^{5-}$ is analogous to the [VOA$_2$]$^{4-}$ species of IdaP, except for the presence of a hydrogenphosphonate group in the non-co-ordinating arm of the second ligand. The equilibrium constant for the process [VOA]$^{2-}$ + HA$^{3-}$ ⇌ [VOA$_2$H]$^{5-}$ (log $K$ = 3.30) supports that, in spite of the (NH, PO$_3^{2-}$) chelating mode, the co-ordination of the second ligand is hindered. The unavailability of a sixth co-ordination position and charge effects do not promote the full deprotonation of the second ligand, therefore a [VOA$_2$]$^{6-}$ species is lacking in this system. Above pH 8 a mixed ligand hydroxo species [VOAH$_{-1}$]$_2^{6-}$, with polynuclear structure, prevails in solution.

### Phosphonic derivatives of Nta

The NtaP (H$_5$A$^+$), Nta2P (H$_6$A$^+$) and Nta3P (H$_7$A$^+$) ligands differ from nitrilotriacetic acid in the stepwise replacement of carboxylic by phosphonic groups. Four protons are titrable for NtaP and five for Nta2P and Nta3P. The most basic donor for all ligands is the tertiary amino group and the basicity increases with increasing number of phosphonic functions due to the electron repelling effect of their dinegative charge. The next most basic groups are the phosphonates which protonate in the pH range 4.5–7.2. The remaining CO$_2^-$ and PO$_3$H$^-$ groups are very weakly basic (log $K$ values are around or less than 1), which can be determined pH-metrically only with rather high uncertainties. The protonation constants listed in Table 3 are in reasonably good agreement with earlier reports.[6,7,11,13]

The Nta-like ligands are potentially tetradentate metal binders. It is worth noting that only species with 1:1 ligand-to-metal ratio are formed with V$^{IV}$O. The speciation curves of the complexes formed in the V$^{IV}$O–Nta and phosphonic derivatives systems are displayed in Fig. 3. Owing to the 'hard' character of V$^{IV}$O, donor arrangements are strongly favoured in which oxygen atoms are in the equatorial plane and the nitrogen, if co-ordinated, occupies the weaker axial position *trans* to the oxo group. Therefore, three strong donors, taking part in chelated rings, are in the equatorial plane and their replacement by N or O atoms from a second ligand is strongly hindered.

The formation of protonated complexes VOAH$_n$ can be deduced from pH-metry and electron absorption spectra (see later). The more carboxylate groups are replaced by phosphonates, the more protonated complexes are formed: $n = 2$ or 1 for NtaP and Nta2P, while $n = 4, 3, 2$ or 1 for Nta3P.

Protonated species are substantiated by the fitting of potentiometric data in the acidic pH range. An examination of the stepwise deprotonation constants p$K$(VOAH$_n$) suggests that all VOAH$_n$ complexes are chelated. In fact, partial formation constants (log $K$ values) calculated for processes VO$^{2+}$ + H$_n$A ⇌ [VO(H$_n$A)] are generally greater than 3.5 indicating chelated ligands. However, the undissociated protons could be bound either to the phosphonate or the amino moieties. The preponderant species above pH 5 have composition VOA. With Nta3P a very stable [VOAH]$^{3-}$ complex is also formed.

The exclusive presence of oxygen donors in the equatorial plane of V$^{IV}$O makes the equilibria difficult to follow by EPR spectroscopy, at least in the acidic pH range, inasmuch as only minor changes, with respect to the aqua ion, are observed in the spectra (Table 2). Nevertheless, a significant and continuous decrease of the $^{51}$V coupling constant with increasing pH is a good spectral indication for stepwise deprotonation of the phosphonic groups and their co-ordination in the equatorial plane to form VOA species. Much more indicative are electronic absorption spectra which exhibit significant shifts (see Fig. 4). In particular, the absorption which falls at *ca.* 770 nm for the aqua ion undergoes a red shift at pH values as low as 1.5–2. Such a shift is a spectroscopic feature indicative of the onset of V$^{IV}$O complex formation by phosphonate ligands.[29]

Owing to the very high stability of the Nta-like complexes, the proton displacement reactions are almost complete at acidic
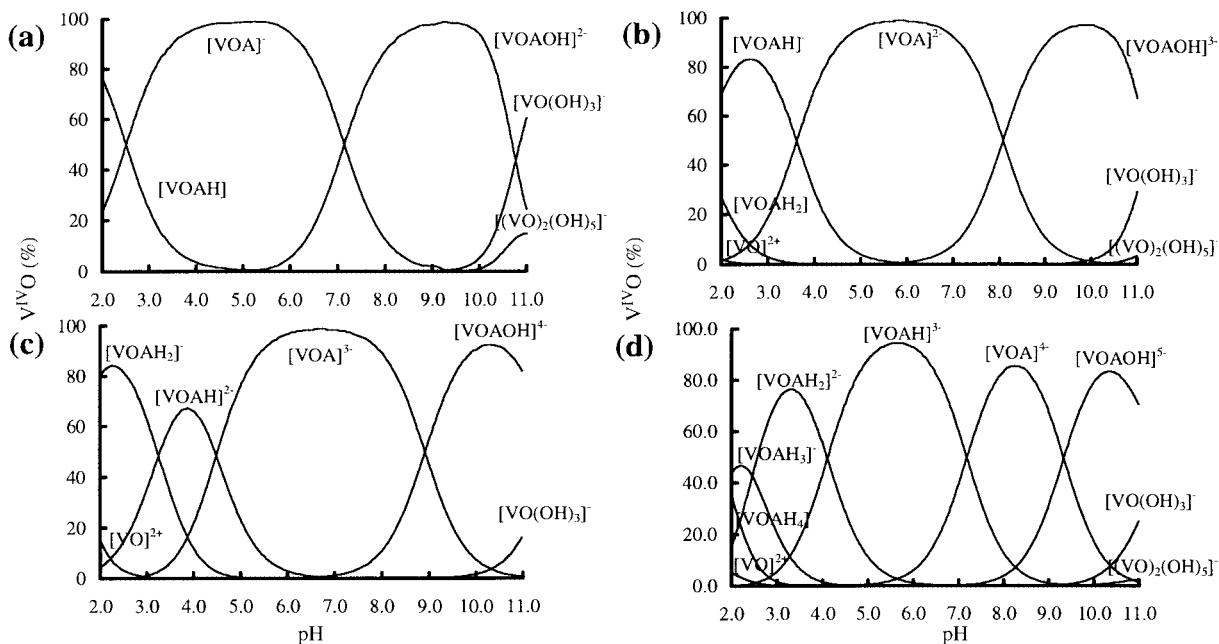
**Fig. 3** Species distribution diagram for (a) $V^{IV}O$–Nta, (b) $V^{IV}O$–NtaP, (c) $V^{IV}O$–Nta2P and (d) $V^{IV}O$–Nta3P systems; $c_{V^{IV}O} = 0.002$ mol dm$^{-3}$, $c_{ligand} = 0.004$ mol dm$^{-3}$.
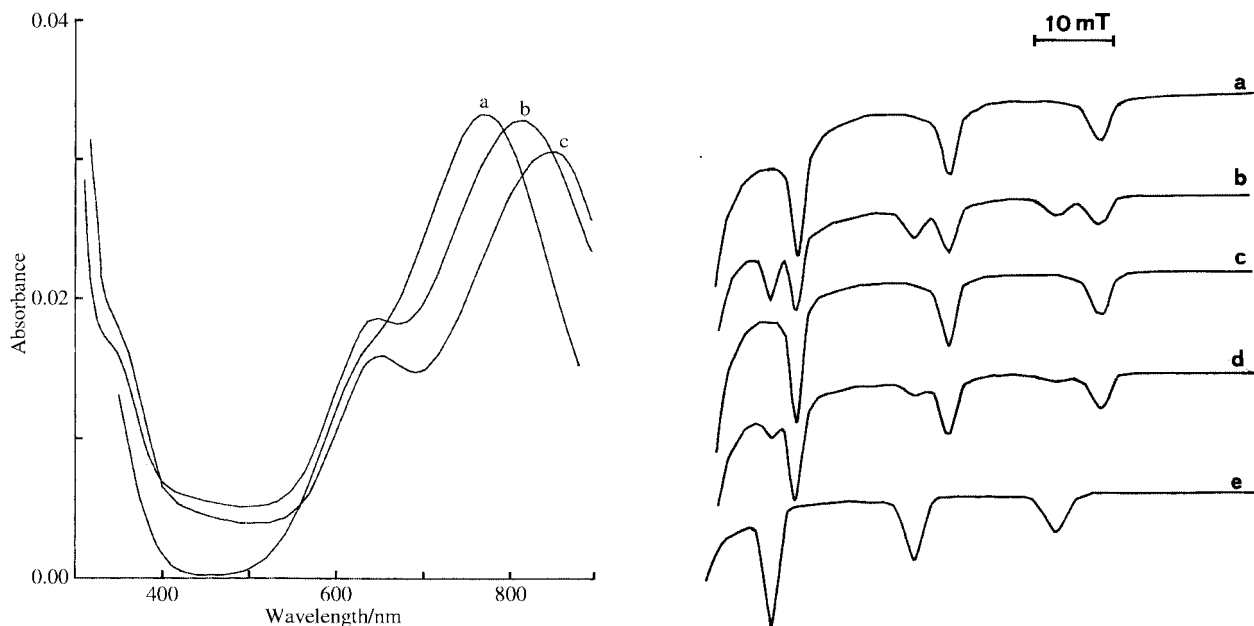


**Fig. 4** Electronic absorption spectra of $[VO(H_2O)_5]^{2+}$ (a) and of the $V^{IV}O$–Nta2P system ($c_{V^{IV}O} = 0.01$ mol dm$^{-3}$, $c_{ligand} = 0.02$ mol dm$^{-3}$) at pH 1.5 (b) and 3. 5 (c).



**Fig. 5** High field parallel region of frozen solution EPR spectra recorded at 140 K on the following systems: $V^{IV}O$–Nta3P 1:1, pH 5.50 (a); –maltol–Nta3P 1:2:1, pH 5.50 (b); –Nta3P 1:2, pH 5.45 (c); –maltol–Nta3P 1:2:2, pH 5.45 (d); and –maltol 1:2, pH 6.15 (e). In all systems $c_{V^{IV}O}$ is 0.002 mol dm$^{-3}$.

pH and the free $VO^{2+}$ ion is present in rather low concentrations at the starting pH values. In spite of this pH-metry can be applied for the determination of stability constants as the equilibrium system is better "fixed" in the high pH range to the uncomplexed $V^{IV}O$ hydroxo species.[33] In these systems proton displacement reactions between $[(VO)_2(OH)_5]^-$ and $[VO(OH)_3]^-$ and protonated form(s) of the ligands were followed. In order to confirm the reliability of the stability constants listed in Table 3, ligand displacement spectrophotometric measurements were also carried out (see Experimental section). Unfortunately, other polydentate ligands which form only 1:1 complexes with $V^{IV}O$ were not suitable for the ligand displacement study, as the differences of the spectral behaviour of the complexes of the two competing ligands were negligible. Significant differences were found, however, between the visible spectra of $[VO(malt)_2]$ formed exclusively in the pH range 5–7[27] and the corresponding VOA complexes of the Nta-type ligands. In order to use reac-

tion (1) for the determination of the stability constant log $K$(VOA) we had to prove that the two maltolate molecules are displaced in a single step without the formation of a ternary complex $[VO(malt)A]^{(n-1)-}$. EPR Measurements in the $V^{IV}O$–maltol–A systems indicated only binary complexes in the optimaum pH range of the formation of VOA. As an illustration, the EPR spectra obtained in the $V^{IV}O$–maltol, –Nta3P and –maltol–Nta3P ternary systems are illustrated in Fig. 5. The log K(VOA) values obtained by spectrophotometry are also included in Table 3. Although the uncertainties in these constants are generally higher than those determined by pH-metry, the agreement between the two sets of data is beyond the

experimental error. Accordingly, we consider our stability data accurate enough to give a reliable description of the $V^{IV}O$–A systems.

The EPR parameters of complex VOA (see Table 3) substantiate that the amino nitrogen occupies an axial position *trans* to the oxo group, whereas oxygens from the phosphonate and carboxylate groups are in the equatorial plane, similarly as found with Nta.[19,20] The fourth equatorial binding site is occupied by a water molecule. A comparison of the basicity-adjusted stability constants listed in Table 3 gives a reliable indication about this tetradentate binding mode of the ligands. The participation of all the donor groups of the ligands in the species VOA is clearly reflected in the basicity-adjusted stability constants which are more than two orders of magnitude larger for the Nta than for the Ida derivatives with the same number of phosphonic groups, *i.e.* NtaP *vs.* IdaP and Ida2P *vs.* Nta2P. As observed with Ida-type systems, as the number of the phosphonic groups increases, the overall stability gain vanishes.



[VOA]$^{4-}$          [VOAH$_{-1}$]$^{5-}$
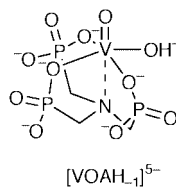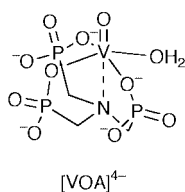
At higher pH values the water molecule bound to vanadium loses a proton and monohydroxo complexes VOAH$_{-1}$ are formed. Owing to the tetradentate co-ordination mode of the Nta derivatives, the hydrolytic behaviour is different from that of the Ida-like ligands. Indeed, only one co-ordination site is accessible to hydroxo ions in the equatorial plane and this hinders the formation of di-μ-hydroxo bridged species. Therefore, in contrast to Ida-like ligands, Nta derivatives yield mononuclear VOAH$_{-1}$ complexes. Distinct changes of the spectral parameters accompany the change in the co-ordination sphere of the metal ion in the monomeric species. The p$K$ values for the process depend on the ligand and increase with increasing charge, namely in the order NtaP (8.08) < Nta2P (8.91) < mNta3P (9.33). This indicates that the strong electron-releasing effect of charged phosphonate groups hinders hydroxo binding. The corresponding value of 7.11 measured for Nta is in accordance with this trend.

In solutions as concentrated as 0.1 mol dm$^{-3}$, the [VOA]$^{4-}$ species of Nta3P undergoes an oligomerisation process. This can readily be followed by EPR spectroscopy which shows a strong decrease in intensity of the monomeric signals and the appearance of dimeric features consisting of a broad resonance with $\Delta H_{pp}$ = 117.6 mT centered at $g$ $ca.$ 2.02, accompanied by a $\Delta M_S$ = ±2 half-field transition. These spectral features are analogous to those reported for complexes formed by Ida and ethylene glycol bis(2-aminoethyl ether)-$N,N,N',N'$-tetraacetic acid.[20,34] The EPR spectrum of the complex could be interpreted as due to a dimeric species in which the magnetic interaction between the metal ions has predominantly dipolar origin. Under the assumption that the angle formed by the V–V and V=O directions is $ca.$ 35 ± 10°, as is suggested by an examination of molecular models, the measured zero-field splitting parameter permits one to calculate a distance of $ca.$ 3.0–3.5 Å between the two metal ions.[35] A plausible structure for the dimer [(VOA)$_2$]$^{8-}$ is shown.

Interesting spectral trends can be derived by comparison of the electronic absorption data collected on $V^{IV}O$–Nta, –NtaP, –Nta2P, and –Nta3P systems. All the VOA and VOAH$_{-1}$ complexes exhibit at least three absorption bands (Table 2). According to the well known scheme proposed by Ballhausen and Gray[36] for the $V^{IV}O$ aqua ion, the band at $ca.$ 800 nm may be attributed to the d$_{xy}$ ⟶ d$_{xz}$, d$_{yz}$ transition, whereas that at $ca.$ 600 nm is d$_{xy}$ ⟶ d$_{x^2-y^2}$. For the VOA complexes a red shift



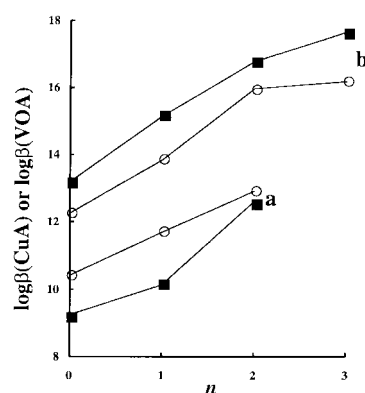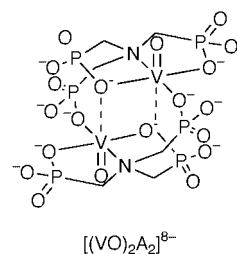**Fig. 6** Comparison of log $\beta$(CuA) (○) and log $\beta$(VOA) (■) values for Ida-like HN(CH$_2$PO$_3$H$_2$)$_n$(CH$_2$CO$_2$H)$_{2-n}$ (a) and Nta-like N(CH$_2$PO$_3$H$_2$)$_n$(CH$_2$CO$_2$H)$_{3-n}$ (b) ligands.



[(VO)$_2$A$_2$]$^{8-}$

is exhibited by both these absorptions upon replacement of carboxylates by phosphonates, which could reflect the extent of distortion in the metal geometry due to the repulsion of the phosphonate groups. The energy of the 600 nm band is a measure of the σ in-plane bond strength and its decrease conforms to a less effective orbital overlap due to the distortion. The absorption at 800 nm measures the energy difference between d$_{xz}$, d$_{yz}$ and the ground level d$_{xy}$. Since the d$_{xz}$ and d$_{yz}$ orbitals are involved in π bonds with the oxo ligand, the bathochromic shift of the band indicates a less effective donation by the oxo ligand. Therefore, structural and electronic rearrangements following the co-ordination of phosphonate arms lead to a weakening also of the axial V=O bond. As expected, on passing from VOA to VOAH$_{-1}$, a blue shift takes place for the band at $ca.$ 600 nm because of the greater ligand strength of the hydroxo ion compared to water. The [VOAH$_{-1}$]$^{5-}$ species of Nta3P exhibits a set of multiple absorptions which could indicate that a significant change in geometry (distortion toward a trigonal bipyramid) occurs upon co-ordination of OH$^-$.[37]

## Conclusion

The phosphonic derivatives of Ida and Nta act as very effective ligands towards $V^{IV}O$. The assistance of at least two carboxylic and/or phosphonic arms in amino-phosphonic or -carboxylic ligands is necessary to avoid the predominance of hydroxo binding. Therefore, the Ida and Nta derivatives examined herein form complexes much more stable than those of simple aminocarboxylic or aminophosphonic acids. The data listed in Tables 1 and 3 and also in Fig. 6, in which the log $\beta$(VOA) values are reported as a function of the number of phosphonate groups in the ligands, indicate that the stability of the complexes increases with increasing number of the more basic phosphonates. However, the opposite trend in the basicity-adjusted stability constants listed in Tables 1 and 3 shows that this stability increase is overcompensated by the higher spatial requirement and electrostatic repulsion between the dinegatively charged phosphonato arms. More reliable measurements for the metal binding ability of the ligands are either conditional stability constants or free (uncomplexed) metal ion concentrations (pM = −log[M$^{n+}$]) under given conditions. For example, the pVO values for the conditions $c_{V^{IV}O}$ = 0.002 mol

**Table 4** Copper(II) complex formation constants (log $\beta$) of imino-diacetic acid (Ida) and nitrilotriacetic acid (Nta) at $I = 0.20$ mol dm$^{-3}$ KCl and 25 °C

|  | Ida | Nta |
|---|---|---|
| CuAH | — | 13.72(2) |
| CuA | 10.41(1) | 12.25(1) |
| CuAH$_{-1}$ | 1.59(1) | 3.04(1) |
| CuA$_2$H | 21.62(5) | — |
| CuA$_2$ | 16.24(1) | 16.35(1) |
| Number of points | 442 | 521 |
| Fitting parameter $^a$ | 0.0103 | 0.01152 |

$^a$ Goodness of the fit between the experimental and the calculated titration curves, expressed in cm$^3$ of titrant.

dm$^{-3}$, $c_{ligand} = 0.004$ mol dm$^{-3}$, pH 7.0 are as follows: VO–Ida, 5.54; VO–IdaP, 5.50; VO–Ida2P, 5.80; VO–Nta, 8.17; VO–NtaP, 8.94; VO–Nta2P, 9.55, VO–Nta3P, 9.68. On the whole, the trend indicates at neutral pH only a slight increase in VO binding capability with increasing number of phosphonates involved in co-ordination.

Also the comparison between copper(II) and oxo-vanadium(IV) complexes permits one to derive significant conclusions. While the V$^{IV}$O–Ida derivatives are somewhat weaker than the corresponding copper(II) complexes, the stability sequence is just the opposite with the Nta derivatives (Fig. 6). In order to have fully comparable data, the stability constants of the complexes formed in the Cu$^{II}$–Ida and –Nta systems were redetermined under our experimental conditions (see Table 4). The data show reasonably good agreement with those reported earlier.[38] Copper(II) has a high affinity for the *N*-donor ligands, whereas V$^{IV}$O has a scarce affinity. The ligand Ida has a tridentate character and prefers the *fac* rather than *mer* co-ordination type. Two isomeric complexes could be formed: the nitrogen atom occupies the equatorial plane in one of them and the axial position in the other. Owing to the electrostatic repulsion between the negatively charged groups of the phosphonate and carboxylate arms, the isomer with the N atom in the equatorial plane is preferred, because it has one of these groups in a distant apical position. Therefore, this ligand conformation favours the copper(II) ion which binds stronger to nitrogen donors and disfavours V$^{IV}$O. On the other hand, Nta-like ligands act in a tetradentate manner by inserting three oxygens in the equatorial plane and the N atom in the axial position of the metal ions. Owing to higher affinity for the oxygen donors, V$^{IV}$O takes strong advantage of the tetradentate character of Nta-like ligands. Instead, CuA complexes of Nta-like ligands are less stable than expected for nitrogen-containing ligands. It is worth mentioning that, consistent with the above assumption, the equatorial co-ordination of the N atom was demonstrated by the crystal structure determination of sodium aqua(nitrilotriacetato)cuprate(II).[39]

## Acknowledgements

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