# Metal Complexes of N-Hydroxy-imino-di-α-propionic Acid and Related Ligands

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## Abstract

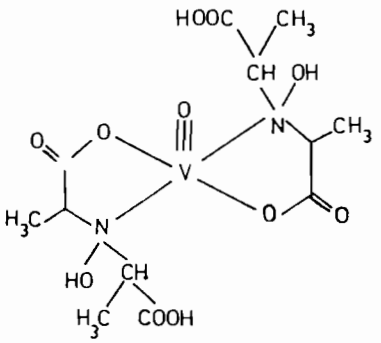
N-hydroxy-imino-di-α-propionic acid, the ligand present in the natural oxovanadium(IV) complex 'amavadin' which occurs in the toadstool *Amanita muscaria,* has been synthesised, as well as two related ligands—N-hydroxy-iminodiacetic acid and imino-di-α-propionic acid—useful for comparison purposes. The formation of complexes of these ligands with $VO^{2+}$, $Ni^{2+}$ and $Cu^{2+}$ has been studied and their stability constants have been determined.

The two N-hydroxy-substituted ligands, of low basicity, form $ML_2$ complexes with $VO^{2+}$, unlike the more basic derivatives of iminodiacetic acid. Since substitution of ligands bonded to the apical site *trans* to the oxo ligand is very fast and the formation of $ML_2$ complexes of $VO^{2+}$ exposes that apical site to the reaction media, this may be the reason why oxovanadium(IV) and the unusual derivative of iminodiacetic acid present in 'amavadin' were selected for the biological role that this complex plays in the toadstool.

## Introduction

'Amavadin', a natural compound which occurs in the toadstool *Amanita muscaria* has been reported to be a 2:1 oxovanadium(IV) complex of N-hydroxy-imino-di-α-propionic acid [1, 2], an unstudied derivative of iminodiacetic acid. The function of this compound and the reason why vanadium was selected are unknown.

To contribute to the elucidation of these problems we have undertaken a thorough study of the reactions of the $VO^{2+}$ ion with a series of polyaminocarboxylic acids in aqueous solution and found that the complexes formed are quite stable, the values of their stability constants being very close to those of the corresponding nickel complexes [3].



(I)

Another finding, with implications relative to the proposed structure of 'amavadin', was that, in the case of tridentate ligands, dimers with hydroxo bridges formed preferentially 2:1 complexes even at high ligand to metal ratios and below the range of biological pH [3].

Although of interest—both analytical and biological—these observations were made with ligands that were not as like the natural one as one might wish; a logical further step was to synthesise that same natural ligand as well as some related compounds to ascertain the effects of the substituents introduced into the molecule of the parent iminodiacetic acid to transform it into N-hydroxy-imino-di-α-propionic acid.

In the present work we report the preparation, properties and complexation reactions of three new ligands satisfying these requirements: imino-di-α-propionic acid (IDPA), N-hydroxyiminodiacetic acid (HIDA) and the required synthetic N-hydroxy-imino-di-α-propionic acid (HIDPA).

These ligands correspond to the general formula (II) where $R_1$ stands for H or OH and $R_2$ stands for H or $CH_3$. Imino-di-α-propionic acid ($R_1$ = H and $R_2$ = $CH_3$) should show the effect of replacing the two acetic acid moieties of iminodiacetic acid by two α-propionic acid moieties; N-hydroxy-iminodiacetic acid ($R_1$ = OH and $R_2$ = H) should show the effect of the hydroxyl group bonded to nitrogen; N-hydroxy-

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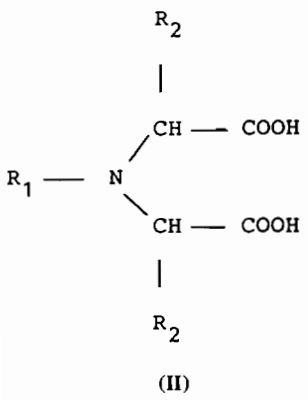


(II)

imino-di-α-propionic acid ($R_1$ = OH and $R_2$ = $CH_3$) is the ligand present in 'amavadin', combining the added effects of the hydroxyl group in $R_1$ and the methyl groups in $R_2$.

The results obtained in the study of the vanadyl complexes of these ligands lead us to think that there is a logical reason for the selection of $VO^{2+}$ and for the uncommon ligand of 'amavadin'; indeed, one wonders why a 2:1 complex, such as that represented as (I), is necessary and for what function.

A tentative (and speculative) answer is suggested, which stresses the 'uniqueness' of $VO^{2+}$, as a possible basis for the selection of this biological element [4].

## Experimental

*Reagents*

Iminodiacetic acid was a commercial product available from various sources.

The new ligands were synthesised as follows.

*Imino-di-α-propionic Acid*

L-alanine (0.05 mol) in water, previously neutralised with 5 M NaOH was condensed with sodium 2-bromopropionate (0.10 mol) at room temperature and pH 8–10, with slow addition of the equivalent amount of 5 M NaOH. The product of reaction was acidified with 5 M HCl to pH ~2.5 and the solution was evaporated to dryness. The solid was treated with glacial acetic acid to separate NaCl. Addition of ethyl-acetate precipitated a white product which was re-crystallised with a mixture of ethanol, water and drops of concentrated HCl. A solid as fine colourless needles precipitated overnight in the refrigerator. Yield ~4.9 g (~60%) M.p. 234–5 °C. M.W. (titration) 161. *Anal.* Calcd. for $C_6H_{11}NO_4$: C, 44.72, H, 6.83; N, 8.70. Found: C, 44.93; H, 6.80, N, 8.60%. The NMR spectrum in $D_2O$ shows a doublet at δ = +1.543 ppm ($CH_3$) and a quartet at δ = +3.935 ppm (CH) (ref. DTSS).

*N-hydroxy-iminodiacetic Acid*

Hydroxylamine hydrochloride (0.05 mol), previously neutralised with 10 ml NaOH 5 M, was added to 0.10 mol of chloroacetic acid also previously neutralised with 20 ml 5 M NaOH. 20 ml of 5 M NaOH were added, keeping the temperature at about 10 °C in an ice-bath and the mixture was left to react for about 2 weeks.

After this period the solution was acidified to pH 2.5 with 5 M HCl and evaporated to dryness in a rotary evaporator. The residue contains the product contaminated with NaCl. Purification is achieved by repeated treatment with glacial acetic acid and re-precipitation with absolute alcohol. The product is finally washed with dry acetone and dry ether, filtered in a dry atmosphere and dried in a desiccator. Yield ~2.48 g, (40%). M.p. 137–8 °C. M.W. (titration) 149. *Anal.* Calcd. for $C_4H_7NO_5$: C, 32.21; H, 4.70, N, 9.40. Found: C, 32.40; H, 4.82; N, 9.25%. The NMR spectrum in $D_2O$ shows a singlet at δ = +3.896 ppm ($CH_2$) (ref. DTSS).

*N-Hydroxy-imino-di-α-propionic Acid*

The method of preparation is analogous to that previously described, 2-bromo-propionic acid being used instead of α-chloroacetic acid. The reaction is much faster and the reaction mixture was usually left to react for 3 days. After acidification, and since the product does not precipitate in the refrigerator, the solutions were evaporated to dryness and treated with conc. HCl (glacial acetic acid proved to be less convenient) to separate NaCl. Absolute alcohol was added followed by dry ether, which precipitated a white product. Treatment with HCl was repeated and the product was finally filtered in a dry atmosphere, washed with dry ether and kept in a desiccator since it is hygroscopic.

Even after repeated treatment with conc. HCl the product obtained corresponded to the formula $NaHL \cdot H_2L$ (a case analogous to that of potassium tetraoxalate) and all attempts to remove sodium, even with ion exchange resins, were unsuccessful. It must be said that the product is extremely soluble in water (and even in absolute alcohol) and the methods of purification used always gave sticky residues at the end. Average yield (for $NaHL \cdot H_2L$) ~15%. M.W. (titration) 376. *Anal.* Calcd. for $C_{12}H_{21}H_2O_{10}Na$: C, 38.30; H, 5.58, N, 7.45, Na, 6.11. Found: C, 38.10; H, 5.70; N, 7.30; Na, 6.00%. The NMR spectrum in $D_2O$ shows a doublet at δ = +1.518 ppm and a quartet at δ = +4.952 ppm (ref. DTSS).

*Metal Salt Solutions*

Copper nitrate and nickel nitrate solutions were prepared from analytical grade salts in deionised water and standardized by EDTA titrations. A standard 0.1 M solution of oxovanadium(IV) sulphate was prepared by dissolving the appropriate amount of

$VOSO_4 \cdot 5H_2O$ (B.D.H.) in 1 N $H_2SO_4$ and the content of $VO^{2+}$ was determined by permanganate titration. Contact with the atmosphere was reduced to a minimum and the solution kept unaltered for several months. Adequate dilutions from this standard were made when necessary and the excess of acid was determined from titrations of 1:1 mixtures of $VO^{2+}$ and EDTA with standard alkali (a well defined end point is obtained when EDTA is completely titrated and the excess acid is easily calculated).

*Carbonate-free Potassium Hydroxide*

0.100 M or 1.000 M solutions were prepared directly from Merck 'tritisol' vials, under nitrogen and using recently boiled deionised water, providing a satisfactory carbonate-free titrant.

*Potassium Nitrate*

The ionic strength of the solutions used in the titrations was adjusted to 0.10 M by adding adequate amounts of a concentrated $KNO_3$ solution prepared from a p.a. product.

*De-ionised Water*

Boiled-out distilled water passed through a mixed-bed ion-exchange resin was used throughout the present work to prepare all the solutions.

*Instruments*

pH measurements and titrations were made with a digital Procyon pH-meter (or a $pHM_4$ Radiometer) using a combined electrode previously calibrated in terms of $[H^+]$ at low and high pH-ranges with appropriate acid or basic solutions with 0.1 M ionic

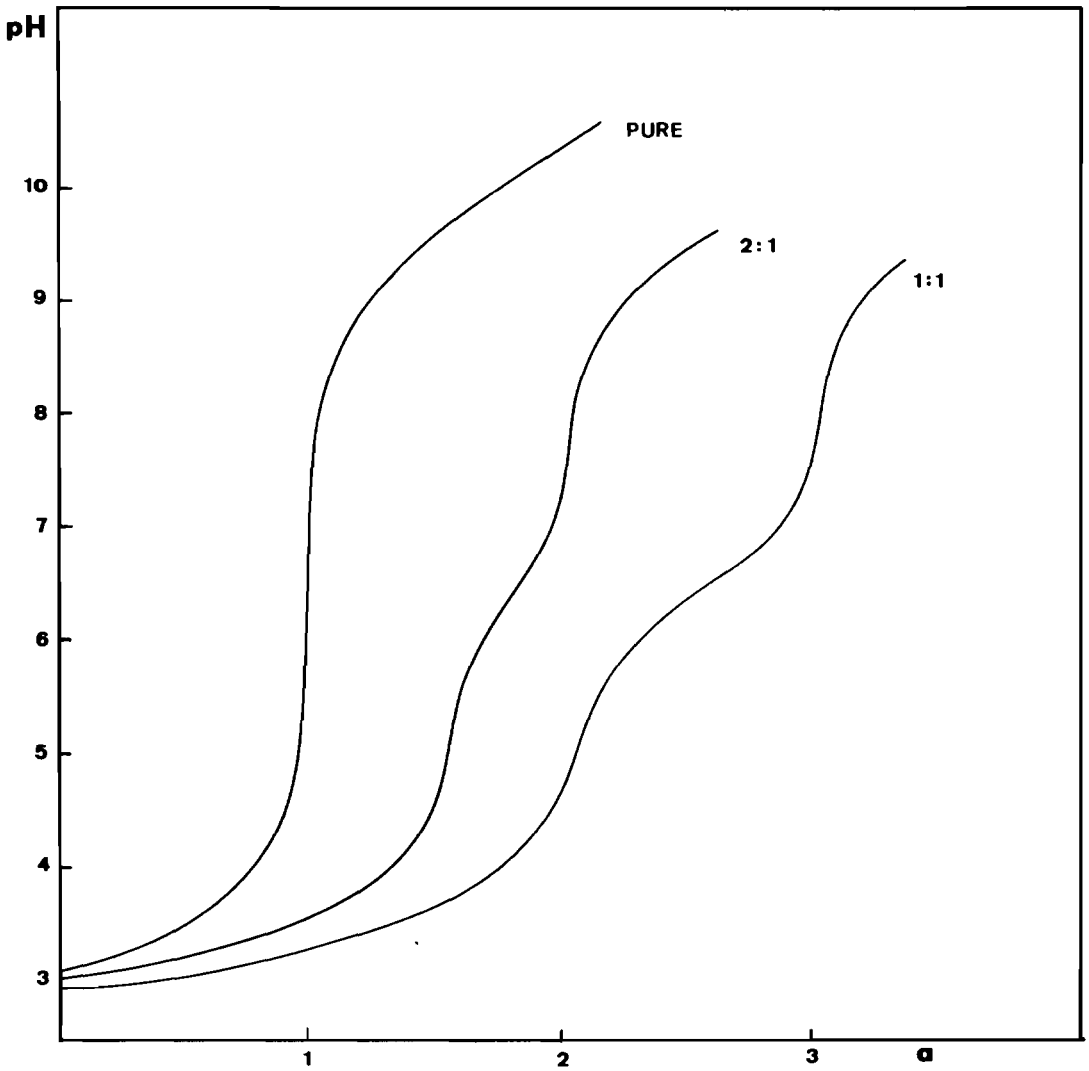



Fig. 1 Titration curve of imino-di-α-propionic acid alone and in the presence of $VO^{2+}$ in the ligand-to-metal ratios 1:1 and 2:1; T = 25.0 °C; $\mu$ = 0.10 M ($KNO_3$).

strength. Values were read to 0.001 pH units and their reproducibility was 0.003 pH units or better [5].

*Technique*

Ionisation constants of the ligands and stability constants of the copper, nickel and oxovanadium(IV) complexes of the new ligands were determined by potentiometric titrations of 1:1 or 1:2 mixtures of the ions and the ligands over a range of concentrations ($5 \times 10^{-4}$ M to $5 \times 10^{-3}$ M). Details of experimental procedures have been given in other publications from our laboratories [5].

The measurements were made in media of 0.10 M ionic strength maintained with $KNO_3$. The temperature was controlled to 25.0 ± 0:1 °C by circulating water through the double-walled titration cell. The ionic product of water for this medium and temperature is $K_w = 1.68 \times 10^{-14}$ [6].

*Calculations*

The expressions used to calculate ionisation and stability constants were derived in the usual manner by considering the mass balances for the ligand and for the metal and introducing the electroneutrality conditions. When hydroxocomplexes were formed (ionisation of coordinated water in $VO(H_2O)L$ species), Napoli's calculation method [7, 8], was employed.

The results obtained were refined using the Miniquad program [9, 10].

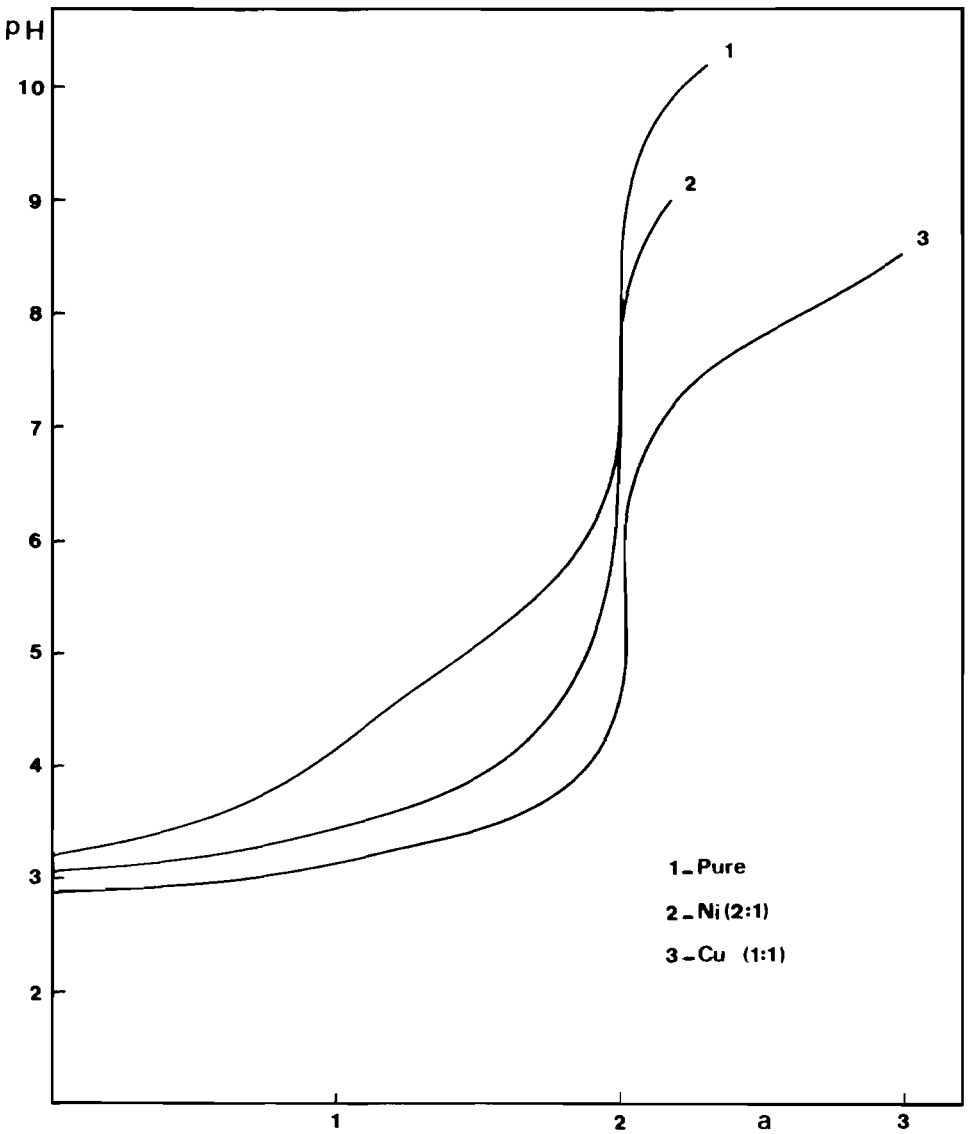



Fig 2. Titration curve of N-hydroxyiminodiacetic acid alone (*1*) and in the presence of $Ni^{2+}$ (*2*) and $Cu^{2+}$ (*3*) in the ligand-to-metal ratios 2.1 and 1; 1, respectively; T = 25 0 °C, $\mu$ = 0 10 M ($KNO_3$)

## Results and Discussion

Proton ionisation constants and stability constants of the copper, nickel and oxovanadium(IV) complexes were calculated from the results of pH titrations of the ligands alone and in the presence of the metal ions in 1:1 or 1:2 metal-to-ligand ratios.

Typical titration curves are shown in Figs. 1, 2, 3.

In the cases of $Ni^{2+}$ and $Cu^{2+}$ the two protons of the ligands (abbreviated $LH_2$) were displaced when either 1:1 or 1:2 metal-to-ligand ratios were used; the corresponding titration curves have well defined equivalence points at $a = 2$ (two equivalents of titrant added per mol of ligand) showing that ML and $ML_2$ complexes are formed, for which stability constants have been determined. The formation of hydroxocomplexes of the ML species at high pH was disregarded.

The values of log $K_{ML}$ correspond to what one might expect for complexes of nickel and copper with tridentate N-substituted iminodiacetates taking into account the value of $pk_2$ of these ligands.

The case of the vanadyl complexes, being of particular interest in the present work, was more extensively studied. As can be seen in the titration curves (Figs. 1 and 3), a third proton is titrated when the standard alkali titrant solution is added to 1:1 mixtures of $VO^{2+}$ and each ligand. This proton can only ionise from a coordinated water molecule, thereby forming a hydroxo species (which has been shown to dimerise to a certain extent) [7, 8].

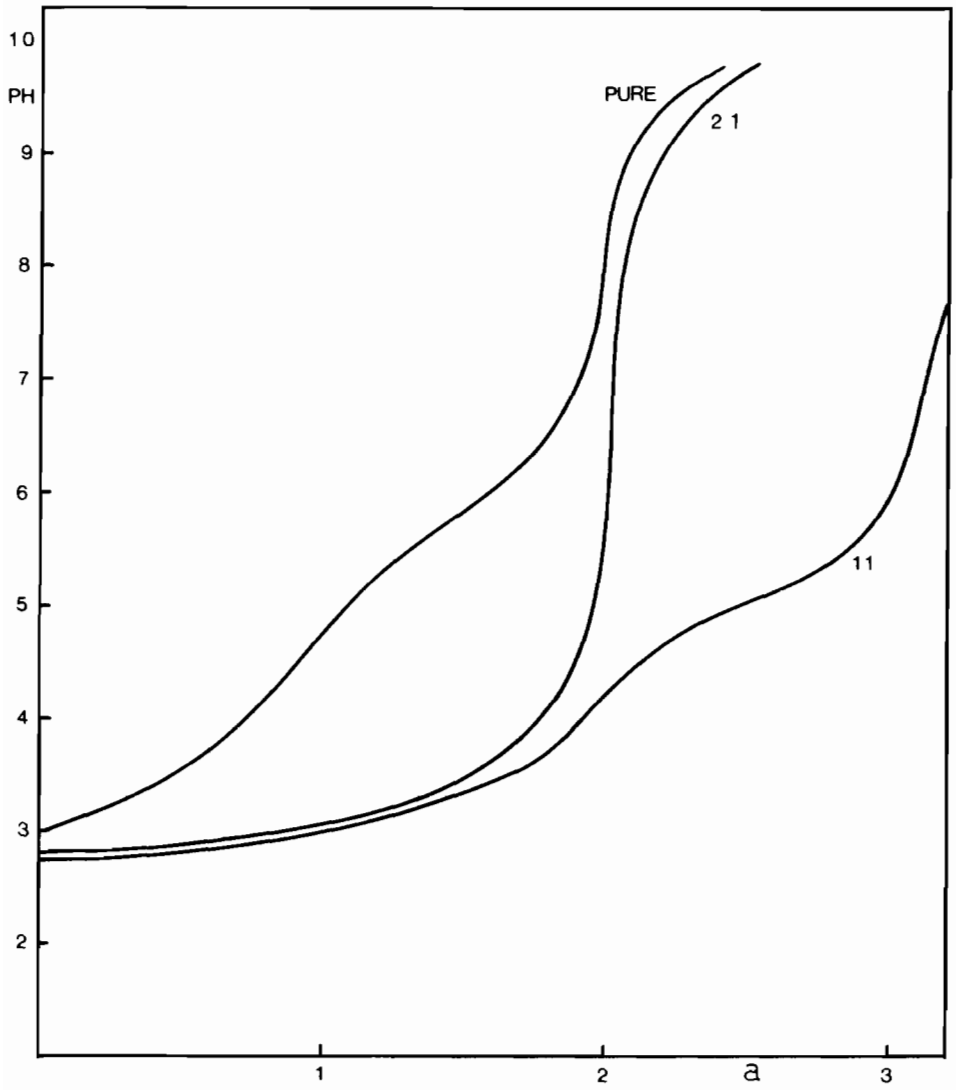



Fig. 3 Titration curve of N-hydroxyimino-di-α-propionic acid alone and in the presence of $VO^{2+}$ in the ligand-to-metal ratios 1:1 and 2:1; T = 25.0 °C; $\mu$ = 0.10 M ($KNO_3$).

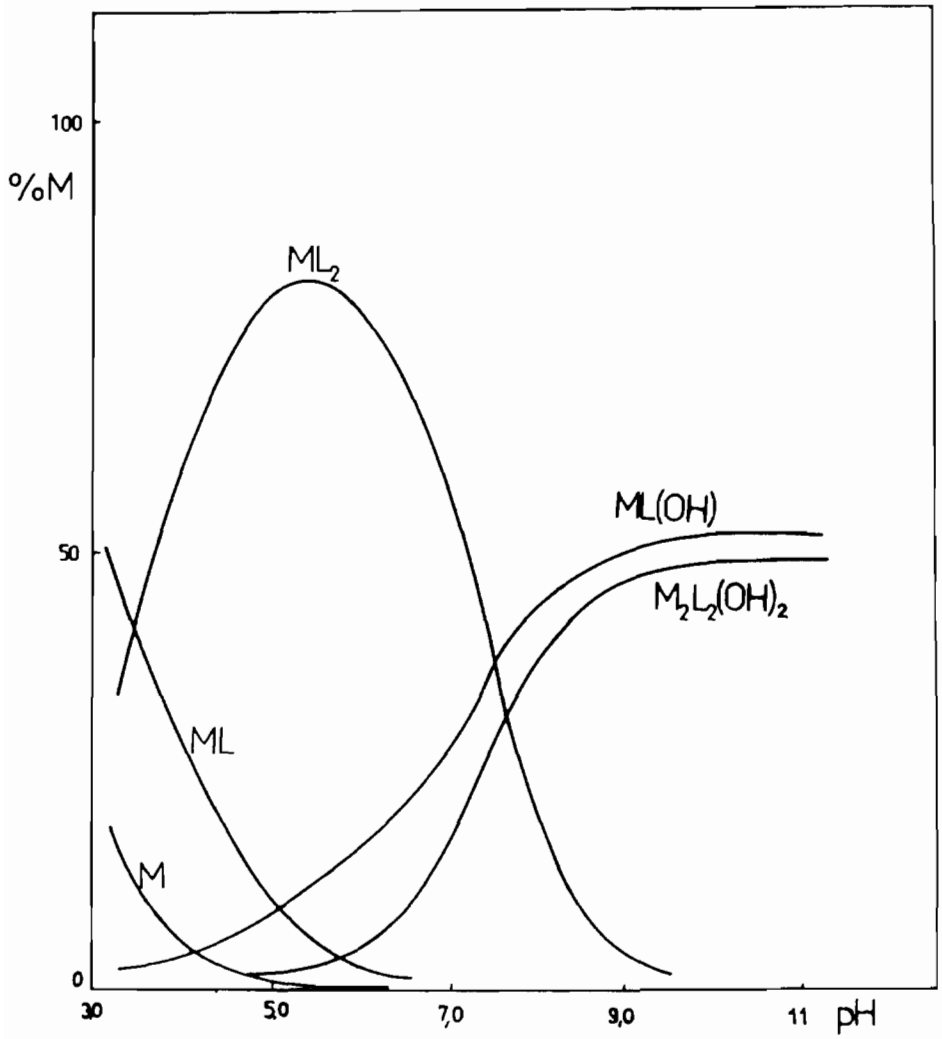



Fig. 4. Distribution of the species as function of pH for $VO^{2+}$ complexes with HIDPA in the ligand-to-metal ratio 2 1. T = 25.0 °C; $\mu$ = 0 10 M ($KNO_3$).

In the case of imino-di-α-propionic acid the same effect is observed when $VO^{2+}$-to-ligand ratios of 1:2 (or more) are used; hence, only the $VO(H_2O)L$ complex forms and this ionises to give VO(OH)L (and $(VO)_2(OH)_2L_2$ species), but there is no evidence for the formation of $VOL_2$ complexes. This is the behaviour already observed for N-substituted iminodiacetic acids [7, 8], but quite different from what happens in the case of N-hydroxyiminodiacetic acid and N-hydroxy-imino-di-α-propionic acid, when $VOL_2$ complexes are formed preferentially in identical conditions in the pH range 3–7, the hydrocomplexes and polynuclear species derived from $VO(H_2O)L$ being predominant only for pH > 7.5 (Fig. 4).

All the results obtained are summarised in Table I together with the corresponding values already known for iminodiacetic acid.

As can be seen from the values presented in this Table, the introduction of methyl groups as $R_2$ in the molecule of iminodiacetic acid, leading to imino-di-α-propionic acid, causes only a slight increase in the basicity of the nitrogen atom of the ligands. The stability of its metal complexes also increases showing that the presence of the methyl groups does not cause appreciable steric hindrance.

The introduction of a hydroxyl group bonded to nitrogen, *e.g.* the replacement of H by OH as $R_1$ in general formula (**II**), has, on the contrary, a dramatic effect; indeed, in both N-hydroxy-iminodiacetic acid and N-hydroxy-imino-di-α-propionic acid, the basicity of the nitrogen atom, as reflected in the values of $pk_2$, drops ten thousand times, *i.e.*, $pk_2$ values are about 4 log units lower.

The effect on the stability constants of the metal complexes is not so pronounced. There is a general decrease relative to the corresponding values found for the complexes of iminodiacetic and imino-di-α-

TABLE I. Proton Ionisation Constants ($pk_1$ and $pk_2$), Stability Constants of Metal Complexes ($\log K_{ML}$, $\log K_{ML_2}$) and Proton Ionisation Constants of Aquo-aminopolycarboxylate Complexes of Oxovanadium(IV). $T = 25.0 \pm 0.1$ °C, $\mu = 0.10$ *M* ($KNO_3$).[a,b]

| Ligand | $H^+$ | | $Ni^{2+}$ | | $Cu^{2+}$ | | $VO^{2+}$ | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| | $pk_1$ | $pk_2$ | $\log K_{ML}$ | $\log K_{ML_2}$ | $\log K_{ML}$ | $\log K_{ML_2}$ | $\log K_{ML}$ | $\log K_{ML_2}$ | $-\log K_1$[c] | $-\log \beta_{22}$[c] |
| Iminodiacetic acid | 2.61 | 9.34 | 8.13 | 6.0 | 10.57 | 5 97 | 9.00 ±0.02 | | 5.8 ± 0.1 | 9.1 ± 0.1 |
| Imino-di-α-propionic acid | 2.43 ±0.01 | 9.38 ±0.01 | 8.24 ±0.05 | 6.1 ±0.1 | 10.68 ±0.02 | 4.5 ±0.1 | 9.54 ±0.01 | | 6 1 ± 0.1 | 9.2 ± 0.1 |
| N-hydroxyimino-diacetic acid | 2.82 ±0.01 | 5.48 ±0.03 | 6.43 ±0.05 | 4.54 ±0.03 | 8.33 ±0.05 | 3 8 ±0.1 | 7.16 ±0.03 | 6.10 ±0.05 | 5 0 ± 0.1 | 6.4 ± 0.1 |
| N-hydroxyimino-di-α-propionic acid | 2.74 ±0.02 | 5.77 ±0.02 | 6.07 ±0.02 | 5.06 ±0.02 | 8.15 ±0.02 | 4.3 ±0.1 | 7.34 ±0.02 | 5.51 ±0.05 | 5.0 ± 0.1 | 6.6 ± 0.1 |

[a] All values quoted with standard deviations are from the present work. Values for iminodiacetic acid (except for $VO^{2+}$) are from A. Martell and R. Smith. Critical stability constants: Plenum Press, N.Y. 1974. [b] $K_{ML} = [ML]/[M][L]$; $K_{ML_2} = [ML_2]/[ML][L]$. [c] $K_1 = [VO(OH)L][H^+]/[VO(H_2O)L]$; $\beta_{22} = [(VO)_2(OH)_2L_2][H^+]^2/[VO(H_2O)L]^2$

propionic acids, but this decrease is less than that found for the proton–ligand complex $HL^-$. On the other hand it is curious to note that whereas the introduction of two methyl groups in iminodiacetic acid did not result in a sufficiently high steric hindrance to decrease the stability constants of the metal complexes, the opposite effect is observed for the $Cu^{2+}$ and $Ni^{2+}$ (but not for the $VO^{2+}$) complexes when the two methyl groups are introduced in the less basic N-hydroxy-iminodiacetic acid, even if the value of $pk_2$ for N-hydroxy-imino-di-α-propionic acid has increased more significantly than in the previous case.

The most important difference is however, as commented before, the possibility of formation of 1:2 oxovanadium(IV) complexes. Indeed, the low basicity of the nitrogen atom of these ligands allows a much higher concentration of their deprotonated forms at low pH, and the replacement of coordinated water by a second molecule of the ligand is favoured relative to the ionisation of those water molecules to form the hydroxo complexes and their dimers. This situation is the opposite of that found for more basic ligands, such as iminodiacetic or imino-di-α-propionic acids and indicates that the 'conditional' constants of the vanadyl complexes of the less basic ligands at low pH are higher than those of the complexes of the more basic ligands.

Figure 4 illustrates the resulting distribution of the species in the case of the N-hydroxy-imino-di-α-propionic acid–$VO^{2+}$ system for a 2:1 ligand-to-metal ratio.

Hence, the reason for the selection of N-hydroxy-imino-di-α-propionic acid to complex $VO^{2+}$ may well be the need to ensure the formation of $VOL_2$ complexes corresponding to formula (I). Since the replacement of the two acetic acid by two α-propionic acid moieties is not required for this purpose and the stability of the complexes formed in both cases is not very different, this aspect is probably related to the biological process of synthesis of the ligands, subject to stereochemical conditions (note that the natural ligand is optically active [1, 2]). It may be said, however, that the presence of the $-CH_3$ groups confers increased solubility of the ligand in polar solvents, particularly in water, and this may be of some importance.

The obvious question is why is a $VOL_2$ complex necessary and for which function.

A tentative (and speculative) suggestion is offered, taking into account the characteristics that make $VO^{2+}$ 'unique' among the common metal ions and that may be the reason for the selection of this oxocation for biological purposes.

Firstly, $VO^{2+}$ behaves as a transition metal ion forming complexes as stable as those of nickel(II) with the donor atoms occupying the remaining octahedral sites around the V(IV) ion, *i.e.*, complexes

with a square pyramidal structure relative to $VO^{2+}$. However, unlike all common metal ions, these coordination sites are not all equivalent: the apical site *trans* to the oxo ligand on vanadium(IV) is far more labile towards substitution reactions than the *cis* equatorial sites [11]—typical rate constants are $k > 10^7$ $s^{-1}$ for the first case and $k \approx 10^{-1}$ $s^{-1}$ for the second. Furthermore, oxovanadium(IV) complexes are oxidised by outer sphere oxidants provided that an aquo-ligand is present in an equatorial site, but the conjugate base, the hydroxo complex is oxidised much more rapidly to give *cis*-oxo species [11]. Other metal ions of sub-groups IV, V and VI of the Periodic Table also form oxocations, *e.g.* Ti, Cr and Mo, but solubility reasons exclude titanium complexes, redox properties and inertness of Cr(III) exclude chromium, and molybdenum(V) complexes with common ligands are frequently binuclear with $Mo_2O_4^{2+}$ cores.

Hence a $VO^{2+}$ complex is particularly advantageous if a reaction center ensuring high substitution rates is necessary, provided that the equatorial coordination positions are blocked to avoid the formation of hydroxocomplexes or their dimers and to prevent oxidation; such a complex must expose the apical site *trans* to the oxo ligand to the reaction medium. The selection of a ligand such as N-hydroxy-imino-di-α-propionic acid satisfies the required conditions: a 2:1 sphere pyramidal complex of $VO^{2+}$ can be formed, avoiding the formation of hydroxocomplexes and their folded dimers, which might prevent coordination to the apical sites besides being more easily oxidisable. The choice of a tridentate ligand may also be of some significance, note that in the $VO^{2+}$ complexes of tetradentate nitrilotriacetic acid or pyridine-methylimino-diacetic acid the apical site *trans* to oxygen is blocked by the nitrogen atom of the iminodiacetic moiety and substitution rates of reaction are much smaller [11]. The fact that we are referring to simple ligands does not rule out the possibility that in the actual fungus *Amanita muscaria* the vanadyl complex 'amavadin' may be loosely bonded to a macromolecular component, this bond being destroyed in the process of the isolation procedure.

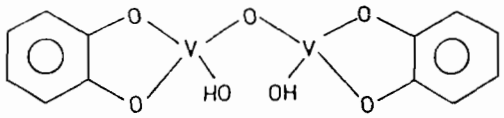
A final point of interest is the possibility that other types of more common biological ligands could satisfy the same requirements, *e.g.* porphyrins or catechol derivatives which also form 2:1 $VO^{2+}$ complexes of high stability instead of N-hydroxyimino-di-α-propionic acid.

Again this is a matter for speculation, but it is a fact that vanadyl complexes of these ligands behave differently from that of HIDPA.

For example, monoelectronic oxidation of *e.g.* vanadyl octaethylporphyrin gives a species with two unpaired electrons, *i.e.*, a π radical cation and not a V(V) octaethylporphyrin complex [12]. Whether or not this is of importance for the role that 'amavadin' is called to play is unknown, but if redox reactions are involved in the catalytic cycle, this is certainly an aspect to be taken into consideration.

On the other hand the catechol type of ligands form V(III) complexes that are stronger than the corresponding $VO^{2+}$ ones. This increases considerably the redox potential of the $VO^{2+}/V^{3+}$ system and may invalidate for this reason the choice of vanadium. The complexes formed by the aminopolycarboxylates with $V^{3+}$ and $VO^{2+}$ are closer in stability, at least in the very few cases studied (one example is that of nitrilotriacetic acid for which $\log K_{V(III)L} = 13.41$ [13] and $\log K_{VOL} = 11.47$).

It has also been reported that at pH above 6, the blue vanadyl pyrocatecholates change to a yellow compound without the oxoligand, which corresponds to the formula **III** [14]:




**(III)**

This compound seems to be formed even at high ligand-to-metal ratios. Again in this case the vanadyl complexes differ from the complexes of $VO^{2+}$ with N-hydroxyimino-di-α-propionic acid.

In these conditions it is likely that 'amavadin' is indeed 'unique' for its function, but it is still not clear what kind of function it performs.

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