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Vanadium(III) complexes with L-histidine in aqueous solution

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Abstract—Complex compounds of vanadium(III) with L-histidine were studied using absorption, CD and potentiometric measurements in aqueous solutions. In solutions at pH 2–4.5 consecutive mononuclear species MLH, ML_2H_2, MLH_2, ML_2H_4 and ML were observed and their stability constants were evaluated. More complex equilibria in the vanadium(III)-L-histidine system were observed at higher pH values, where mixed hydroxy- and/or oxo-species appeared in solution. At pH 6–8.5 range V_2OL_4 species predominantly exists in solution. CD spectra has confirmed the low symmetry of this species, because of the distinct splitting of $^3T_{1g} \rightarrow {}^3T_{2g}$ *d-d* transition of V^{III}. © 1997 Elsevier Science Ltd

Keywords: vanadium(III); L-histidine; complexes; stability constants; aqueous solutions.

The coordination chemistry of vanadium(III) ion has not been well recognised, so far. It was proved, however, that ascidians with a striking efficiency [1] reduced their intracellular vanadium in a two-step process to the trivalent state. As it was shown recently by Ishii *et al.* [2], also another sea animal (Pseudopotamilla occelata) contains significant amounts of vanadium(III).

Little is known concerning the interaction of vanadium(III) with amino acids. Karwecka and Pajdowski [3], Kovala-Demertzi *et al.* [4] and Magill *et al.* [5] investigated V^{III} complexes with some amino-acids in aqueous and aprotic solvents.

Recently Kanamori *et al.* [6] and Czernuszewicz *et al.* [7] synthesized the complexes of vanadium(III) with L-histidine in the solid state. Crystal structure analysis has revealed that this complex is an oxo-bridged dimer and at each vanadium(III) center one L-histidine coordinates tridentately and the second one bidentately.

In this paper we have examined the complex equilibria of V^{III} with L-histidine in aqueous solution. Inspection of these processes is rather difficult because of the strong hydrolysis of the V^{III} ion resulting in formation of various V—O oligomers at the higher pH range [1,8], accompanied by the tendency to the oxidation of vanadium(III) to vanadium(IV) and vanadium(V).

EXPERIMENTAL

Reagents

L-histidine (p.a. Aldrich), VCl_3 (p.a. Fluka), KOH, HCl, KCl, analytical grade.

Apparatus and measurements

Potentiometric measurements were carried out at 20°C with a PHM-84 Radiometer using the combined glass electrode GK 2713-Radiometer. The electrode was calibrated using HCl and KOH solutions ($I = 0.1$ M Cl^-), so that it can be assumed $c_H = [H^+]$. The straight line relation $E = f(pH)$ with Nernst slope was found. The constant ionic strength was kept as $I = 0.1$ M by KCl. All solutions were prepared by using doubly distilled water. The dissolved oxygen was removed by bubbling argon. These conditions were maintained during all the potentiometric measurements. Locally written programs were used for all calculations. Absorption spectra (UV, VIS) were measured on a Cary 5 spectrophotometer. For the measurement of CD spectra the Jasco 600 instrument was applied. The solutions with the different con-

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centrations of V^{III} (0.5–25 mM) and different ligand to metal ratios (0–6 and 15–60) were studied.

RESULTS AND DISCUSSION

Potentiometric measurements

At the beginning the protonation constants of L-histidine were re-examined at the $I = 0.1$ M Cl^-. The agreement with the literature data was very good [9]. Figure 1 summarizes the protonation equilibria for histidine. The ligand abbreviations given in the figure are those which will be used subsequently in the text.

Potentiometric titrations were performed at constant metal (C_M) and hydrogen ion concentrations (C_H), the ligand concentrations (C_{HL}, added as neutral histidine) being progressively increased. The total H^+ ion concentration in the VCl_3 solutions was examined by the Gran method [10].

For the determination of stability constants of V^{III} with L-histidine nine titration series were carried out. C_M was equal to 5 mM, 7.5 mM and 10 mM respectively. C_H for particular titrations were kept as 5.1 mM, 7.52 mM and 10.08 mM respectively for each C_M concentration. C_{HL} were changed in the range 1.61–25 mM. Concentration of free hydrogen ions change in the range pH 2–4.5. The total concentration of hydrogen ions (c_H) can be expressed as below:

$$C_H = [H^+] + [HL] + 2[H_2L] + 3[H_3L]$$
$$= [H^+] + \Sigma n K_n [L][H^+]^n$$

If we know succesive protonation constants of L-histidine, the concentration of free ligand ([L], [HL] or $[H_2L]$) and the average ligand number ($\bar{n}$) can be calculated.

The average ligand number ($\bar{n}$) *vs* log [HL] is presented in Fig. 2. The formation function results are independent on both C_M and C_H, meaning that neither polynuclear nor mixed (hydroxy) complexes are present in solution (in the investigated concentration range). From the formation curves of the vanadium(III) complexes it is concluded that the maximum $\bar{n}$ value attained is approximately 2 (Fig. 2). From these data it can be seen that the addition of L-histidine is responsible for the reversal of hydrolysis. The formation constants correspond to the general reaction:

$$pM + qL + rH \rightarrow M_pL_qH_r$$

$$\beta_{pqr} = \frac{[M_pL_qH_r]}{[M]^p[L]^q[H]^r}$$

The stability constants of V^{III} complexes with the L-histidine (in the pH range 2–4.5) and the protonation constants of L-histidine were calculated on the basis of the Irving-Rossotti method [11] and are reported in Table 1. The first temporary constants were obtained by Bjerrum's half $\bar{n}$ method and were further refined by the least squares method [11].

The molar ratios calculated from these constants are presented as a function of pH in Fig. 3. It is seen that in this pH range mononuclear complexes of vanadium(III) with H_2L and HL all exist. It means that an oxygen atom of the carboxyl group is involved in the complexation process.

Potentiometric measurements carried out for higher V^{III} (25 mM) and higher ligand concentrations indicate the possibility of the formation of both hydroxy (at pH > 3.5) and polynuclear complexes. This is presented in Fig. 4 where for higher $\bar{n}$ value and pH > 3.5 distinct two formation curves can be observed.

Spectroscopic measurements

Absorption and CD spectra of V^{III}-L-histidine in aqueous solutions were measured at different pH. Measurements were made for a series of solutions with constant vanadium(III) concentration and constant L/M ratio. Typical results are presented in Fig. 5(a) (b) for absorption spectra, and in Fig. 6 for CD spectra, respectively.

In the absorption spectra of all solutions investigated two bands in the visible region and a not very well shaped one in the UV were observed. The weak band at about 600 nm corresponds obviously to V^{III} ion *d-d* transition ($^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ in O_h symmetry).

As is seen in Fig. 5(a) and (b) both intensity and energy of the band at 430–480 nm region strongly depend on the pH and ligand concentration. This band can be identified as a CT transition. In the solution spectra at low pH values the energy of this transition corresponds to $\lambda = 430$ nm, which is in good agreement with recent data for the CT band found for μ-dioxobridged hydrolytic species of vanadium(III) [1,8]. Significant changes of both energy and intensity of this band with changing pH and L/M ratios clearly indicate that in V^{III}-L-histidine system in aqueous

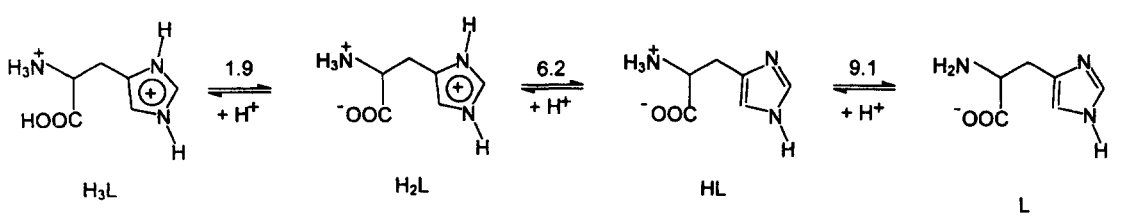

Fig. 1. Equilibrium constants and abbreviations for L-histidine.

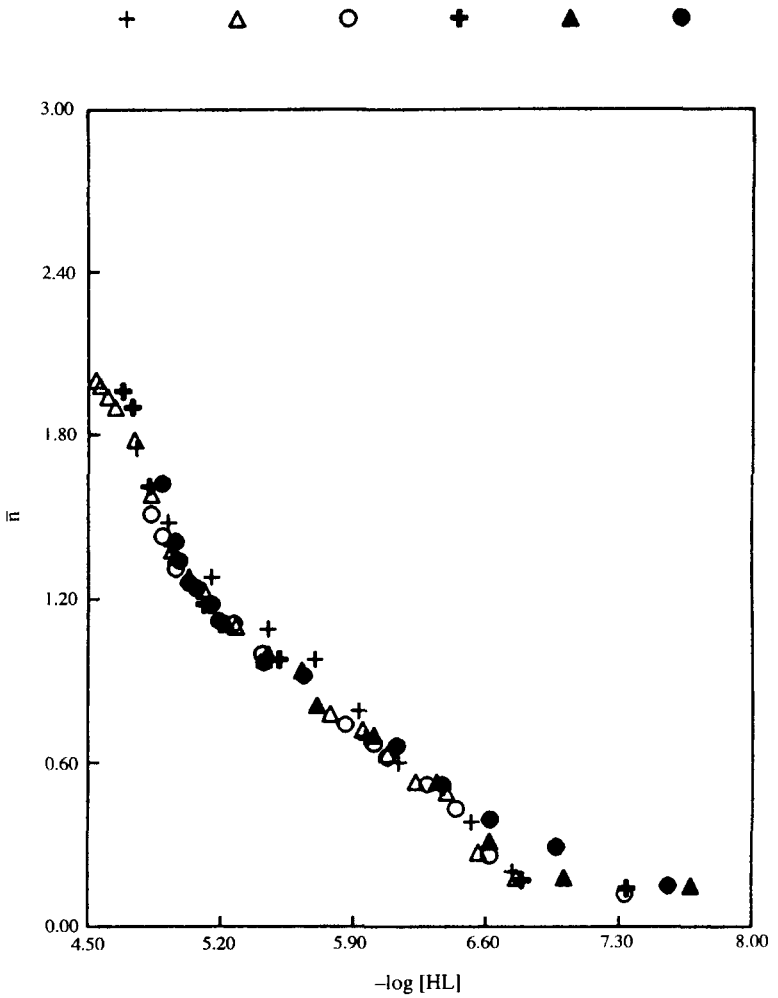

Fig. 2. Formation curve of the V^{III}-L-His system in the interval 2.0 < pH < 4.5. c_H = 5.1 mM and c_H = 10.08 mM (bold signs); c_M = 5 mM, 7.5 mM and 10 mM.

Table 1. Protonation constants of L-histidine and composition and formation constants of species in the L-his-V^{III} systems in the region 2.0 < pH < 4.5

Stoichiometry p : q : r	log β_{pqr}
0 1 1	9.1 ± 0.05
0 1 2	15.3 ± 0.05
0 1 3	17.1 ± 0.1
1 1 0	12.9 ± 0.05
1 1 1	15.3 ± 0.1
1 1 2	18.3 ± 0.2
1 2 2	29.2 ± 0.1
1 2 4	34.4 ± 0.2

solutions at higher pH values the coordination of this dimeric species with L-histidine occurs. Moreover, above pH 5.8 the energy of this band (480 nm) does not change. So, it can be expected that this band should be useful in a more detailed inspection of the complexation processes.

The band in the UV region cannot be measured with the necessary accuracy. It is presumably a CT band characteristic for V^{III} tetrameric hydrolytic species [1] which, in some amount, is present also in aqueous solutions. One can expect that a more detailed inspection of *d-d* transitions will be very helpful in analysis of the complexation processes. As is seen in Fig. 5(a) and (b) only one *d-d* transition can be observed in the absorption spectra of the investigated solutions. Even this absorption band is strongly influenced by the much more intense CT band, in which both energy and intensity depend on pH and ligand concentration values. So, we measured CD spectra of V^{III}-L-histidine solutions under the same conditions as the absorption spectra. Results are presented in Fig. 6. Distinct polarisation changes in the region 550–650 nm suggests the splitting of the $^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ transition in the distinctly lower than O_h symmetry of V^{III} ion environment for higher pH values.

Now we should consider complexation processes in more detail. In Fig. 7 the typical dependence of the molar absorbance (ε) on the pH values for λ = 480

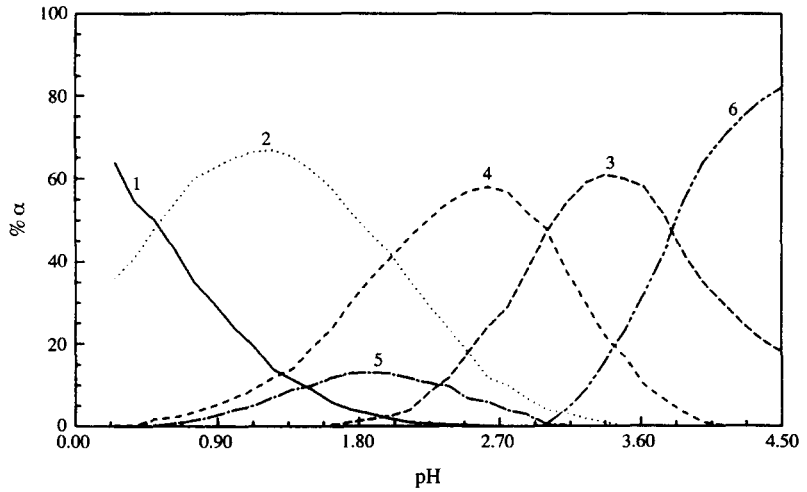

Fig. 3. Concentration distribution of the complexes formed in the V^{III}-L-His system in aqueous solutions at pH < 4.5 using β_{pqr} of the equilibrium model of Table 1. c_{his} = 10 mM, c_M = 5 mM. 1, V^{3+}/c_M; 2, MLH_2/c_M; 3, ML_2H_2/c_M; 4, MLH/c_M; 5, ML_2H_4/c_M; 6, ML/c_M.

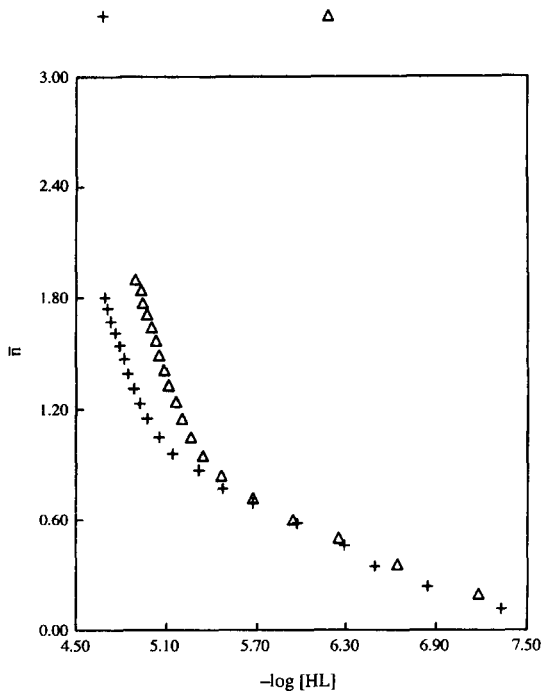

Fig. 4. Formation curve of the V^{III}-L-His system at higher metal concentration. c_M = 25 mM, c_H = 5.1 mM +, c_H = 10.08 mM △.

nm are presented respectively (for the same C_M concentrations and selected L/M ratios). Over the pH range 2–4 the concentration of any dinuclear complex species is negligible (Fig. 7). In this solution some mononuclear complex species of vanadium(III) with L-histidine exist. This is in good agreement with the potentiometric data.

A good confirmation of these processes is a lower intensity of the CT band at 430 nm for solution spectra of V^{III}-L-histidine than for pure VCl_3 aqueous solutions as seen in Table 2, which is given by reversing the hydrolysis by complexation. It means that in vanadium(III)-L-histidine solutions, in competition to hydrolysis, L-histidine complexation processes

Table 2. Influence of the L-histidine on the intensity CT band (430 nm) of the VCl_3 aqueous solution at low pH values, $C_M = 5$ mM, $C_L = 25$ mM

V^{III}[a]		V^{III} + L-histidine	
pH	Molar absorbance ($\bar{\varepsilon}$) (dm^3/mol cm)	pH	Molar absorbance ($\bar{\varepsilon}$) (dm^3/mol cm)
2.25	45	2.26	20
3.04	175	2.94	62
3.80	197	3.80	124

[a]Literature data [1].

Table 3. Dependence of the molar absorbance ($\bar{\varepsilon}$) on concentration of vanadium(III), L/M = 6, λ = 465 nm

C_M (mM)	pH	Molar absorbance ($\bar{\varepsilon}$) (dm^3/mol cm)
5	5.05	130
	5.43	200
	5.73	340
7.5	5.21	180
	5.42	233
	5.68	400

occur. Similar effects were observed recently for another simple V^{III} aminoacid system [3]. When the pH value is increased (above 4.0) as is seen in the Figs. 5(a), (b) and 7 the significant increase of the CT band intensity and its distinct bathochromic shift is observed. This intensity increase depends on the V^{III} concentration as presented in Table 3.

A good confirmation of these phenomena is given by the potentiometric results, where for solutions with higher metal ion concentrations above pH = 3.5 no one formation curve is observed (see Fig. 4). All these data indicate that at this "intermediate" pH region equilibria between mono and dinuclear complex species dominates in solution. In the solutions with higher

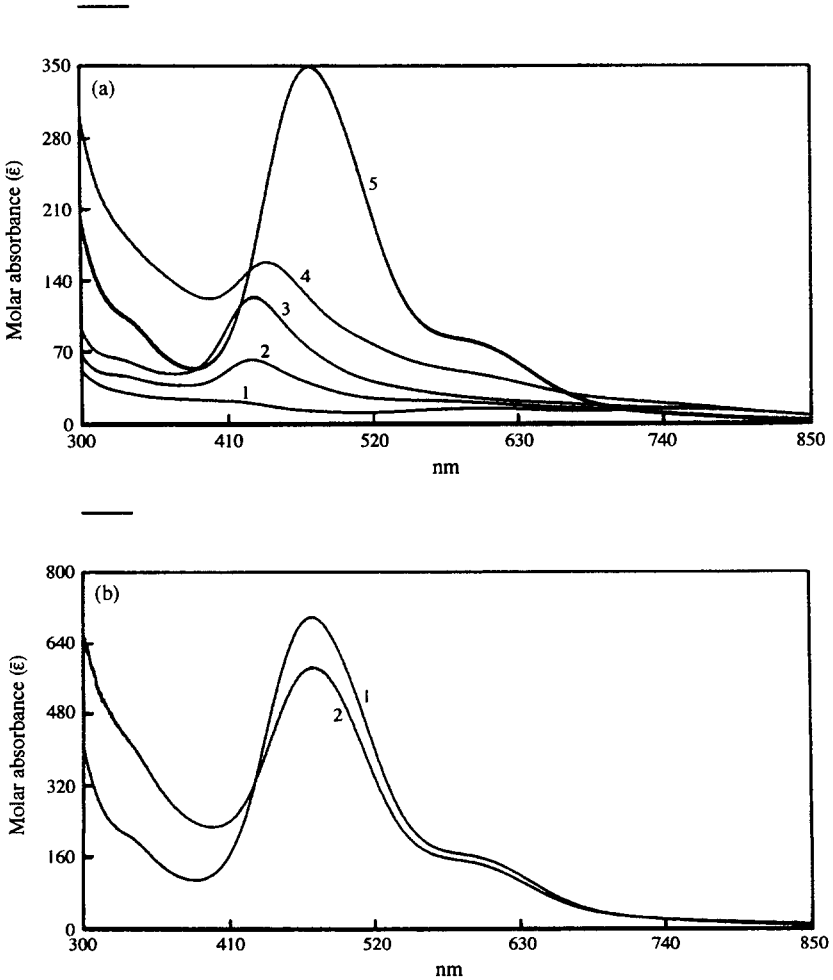

Fig. 5. Absorption spectra of V^{III}-L-histidine system. $c_M = 5$ mM, L/M = 5. (a) 1, pH = 2.26; 2, pH = 2.94; 3, pH = 3.76; 4, pH = 5; 5, pH = 6.2. (b) 1, pH = 6.79; 2, pH = 9.52.

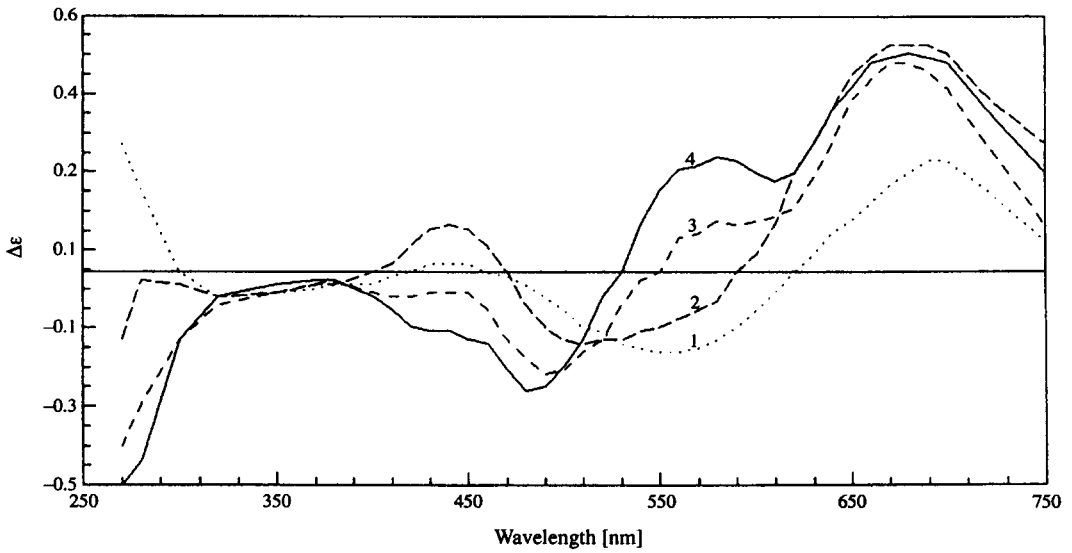

Fig. 6. CD spectra of V^{III}-L-histidine system. c_M = 5 mM, L/M = 5. 1, pH = 4.7; 2, pH = 6.3; 3, pH = 6.8; 4, pH = 8.6.

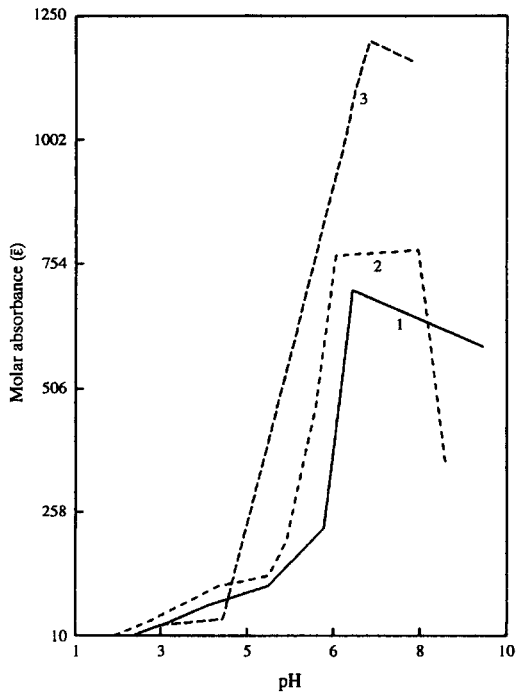

Fig. 7. The change with pH of the ε values. c_M = 5 mM, λ = 480 nm. 1, L/M = 5; 2, L/M = 6; 3, L/M = 15.6.

(6–8) pH values the dinuclear species of vanadium-(III) with L-histidine are the most stable. In this pH region no further strong intensity changes are observed. Moreover no further bathochromic shift of the CT band can be stated. The absorption spectrum of this complex species is characterised by a very intense charge-transfer band at λ = 480 nm. The more accurate pH region of the dominating existence of this species depends obviously on the L/M ratio and metal ion concentration.

We found further confirmation of the dimeric species stoichiometry and its relative stability by using the modified "straight line" method [12]. We have measured absorption of solutions with C_M = const

and different C_L concentrations (with such an excess of ligand for which C_L = [L]) at pH 7.2. If we assume that: $pM + npL = M_pL_{np}$, and:

$$K' = K^{1/p} = \frac{[M][L]^n}{[M_pL_{np}]^{1/p}}$$

The stoichiometry and the conditional stability constant of this species can be calculated from the relation:

$$\frac{A^{1/p}}{v^n} = \frac{m_0 l_0^n v_0}{V^{n+1}} \varepsilon^{1/p} \frac{1}{K'} - \frac{(l_0)^n}{(V)^n} p\varepsilon^{1/p-1} \frac{1}{K'} A$$

where: A = absorbance at λ = 480 nm, v = varying volumes of ligand, m_0 = initial metal concentration, l_0 = initial ligand concentration, v_0 = constant volume of metal, V = total volume, ε = molar coefficient extinction of complex.

The straight line relation was obtained for $n = 2$ and $p = 2$ (Fig. 8). These data indicated that in aqueous solution at pH = 7.2 the dinuclear complex V_2OL_4 exists. The conditional stability constant at pH = 7.2 is log K = 7.83 (Fig. 8).

Taking into account this very simplified procedure we do not consider this K value as physically significant. It is however a good confirmation of the stoichiometry of the dinuclear complex in aqueous solutions.

At pH above 8.5–9 the intensity of the CT band decreases presumably because of the oxidation process of V^{III} to V^{IV} in strongly basic solutions.

It is note worthy that the compound $[V_2O(L\text{-}his)_4] \cdot 2H_2O$ was isolated recently in the solid phase by Kanamori *et al.* [6] and Czernuszewicz *et al.* [7]. These authors determined the X-ray structure of this compound. In this coordination polyhedron each V^{III} ion has a strongly distorted octahedral environment comprising a tridentately coordinated L-histidine ligand, a bidentately coordinated L-histidine and a bridging oxoligand. The bidentate ligand coordinates to the V^{III} ion *via* the amino- and imidazolyl nitrogen atoms, whereas the tridentate one additionally *via* oxygen of the carboxylic group. The V—N distance in the *trans* position with respect to the bridging oxo-group is elongated due to the *trans* influence of the bridging ligand. It is very reasonable, taking into account the spectral behaviour of our V_2OL_4 species in solution to assume for them, the same coordination mode with L-histidine molecules.

Further confirmation is found in the CD spectra of the vanadium(III)-L-histidine system in aqueous solution. The distinct splitting of the $^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ transition which is observed is undoubtedly related to the significant symmetry lowering of this dinuclear species (Fig. 6). The more detailed data are collected in Table 4 where energies of the particular sublevels are collected. Besides the splitting, the change of $\Delta\varepsilon$ (− to +) is observed for the pH region above 6. These data indicate both strong distortion of O_h symmetry of vanadium(III) ion environment, as well as a different conformation mode of optically active ligand in the higher pH region. We expect that CD spectra should be very informative of the ligand coordination mode. It is necessary however to collect more extensive

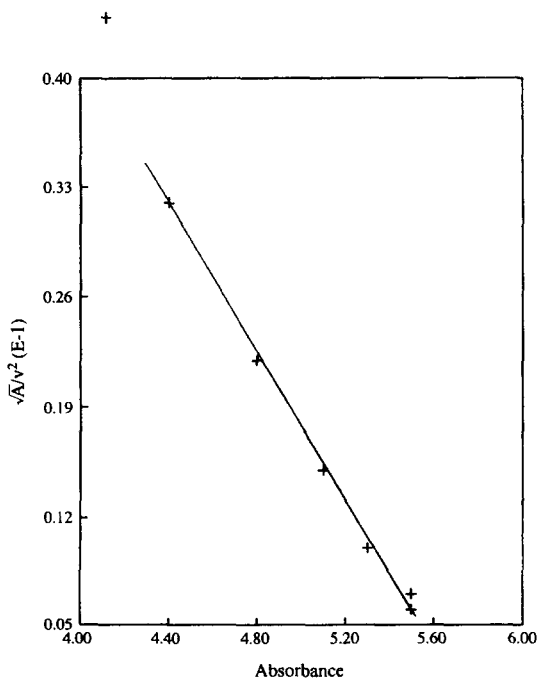

Fig. 8. Modified "straight line" for vanadium(III) complex with L-histidine. Dependence of $A^{1/p}/v^n$ on absorbance at λ = 480 nm. c_M = 5 mM = const., pH = 7.2 = const. $p = 2$, $n = 2$, $\varepsilon = 2.35\ 10^3$ dm^3/mol cm, log K = 7.83.

Table 4. The splitting of $^3T_{1g} \rightarrow {}^3T_{2g}$ transition for different pH values in the CD spectra of vanadium(III)-L-histidine system $c_M = 5$ mM, L/M = 5

V^{III} + Hist. pH	$\nu_1(cm^{-1})$	$\nu_2(cm^{-1})$	$\Delta\nu(cm^{-1})$
2.61	13495(+)	—	—
4.17	13531(+)	18148(−)	4617
4.7	14430(+)	17985(−)	3555
6.0	14688(+)	17543(−)	2859
6.8	14815(+)	17094(+)	2279
7.9	14492(+)	16920(+)	2428
8.75	14535(+)	17065(+)	2530
8.88	14684(+)	17271(+)	2587

experimental data. It should be pointed out for instance that splitting of the considered $^3T_{1g}(F) \rightarrow {}^3T_{2g}(F)$ transition will be related not only to the symmetry of coordination polyhedron but also to the π-donor and π-acceptor properties of the ligand. It can be extremely difficult for complexes of V^{III} with histidine, for which both π-donor and π-acceptor ligand subunits are involved in the complexation process with vanadium(III). These results ensured us that at least with such an aminoacid as L-histidine vanadium(III) is able to form strong, thermodynamically stable complexes with L-histidine at the physiological pH range (6–8). This means that its role in the different biochemical precesses *in vivo* cannot be neglected.

In further work, which is in progress, we will determine more precisely the role of the imidazole ring in the stabilisation of V^{III} complexes.

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