Solution Structures and Spectra of VO(II)-Serine-Phenanthroline Ternary System

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ESR spectra of VO(II)-serine(Ser)-phen system in binary solvent glycol/water ($V/V = 1:1$) solution at various acidities (pH = 1—14) have been observed at low temperature. It was found that in different pH ranges different structural complexes were formed. According to Johnson's rule and IR, their possible structures were suggested. The bonding parameters of complexes were calculated from ESR parameters. It can be seen that the α^2 values of complexes decrease following the increasing of an N donor replacing theO donor of water on the equatorial plane in the complexes. This means that the covalent bonding between vanadium and ligands increases as amino and phen ligands replace water ligands. The crystal field parameters were calculated by using electronic spectral data. The coordination law was discussed. It was obtained that the coordination reactivity of phen is much stronger than that of Ser.

Keywords VO(II) complex, serine, phenanthroline, ESR spectra, crystal field parameter

Introduction

VO(II) is a useful paramagnetic probe of protein structure. Vanadyl amino acid complexes play an important role in biochemistry.[1] ESR spectra of both VO(II)-amino acid and VO(II)-phen binary complexes have been investigated.[2-4] However, ESR spectra of VO(II)-amino acid-phen ternary complexes were rarely reported. In order to explore the ligand competitive reactivity of ser and phen, the ESR spectra of VO(II)-ser-phen ternary systems in mixed solvent glycol/water ($V/V = 1:1$) at various acidities have been studied at 173 K in present paper. A detailed information about different compositions and structures of the complexes at different pH ranges were obtained.

Experimental

Materials and physical measurements

All reagents and solvents are of AR grade. All ESR spectra were recorded on a Bruker ER200D-SRC spectrometer with X-band at field modulation frequency 100 kHz, microwave power 20 mW, amplitude modulation of 5×10^{-4} T and measurement temperature 173 K. IR spectrum was measured on a Perkin Elmer 577 spectrometer with KBr pressing pills. Electronic spectrum was determined by Specord 200 spectrophotometer.

Preparation of the samples

(1) Solution samples: $VOSO_4 \cdot 2H_2O$, serine and phen with the equivalent molar amount were dissolved in a mixed solvent glycol/water ($V/V = 1:1$) at room temperature. The solution concentration was controlled at about 10^{-2} mol/L. The pH value was adjusted between 1—14 by using solution of KOH or H_2SO_4 (1 mol/L) in glycol/water binary solvent. The pH value was measured by a pH meter.

(2) Powder sample: The sample solution with pH

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= 8.2 was added to dioxane-methanol mixture, thus the brown precipitate appeared. The precipitate was separated from the solution by filtration, washed with ether and dried overnight in a vacuum drier for IR measurement.

Results and discussion

Electron spin resonance

The ESR spectra of VO(II)-Ser-phen ternary systems measured in glycol/water binary solvent at 173 K exhibit anisotropic axisymmetric feature. Their typical spectra and its computer simulation are presented in Fig. 1. The simulated spectrum is coincided with the experimental spectrum. The ESR spectral parameters are listed in Table 1. The plot of hyperfine splitting constants as a function of pH value is shown in Fig. 2.

It is well-recongnized that the electronic spectra, the vanadium hyperfine splitting constant, and the V—O stretching frequency are all sensitive to the remaining ligand environment of vanadyl complexes. According to Johnson's isotropic ligand donor additivity rules[5] (H_2O : 30.0×10^{-4} T; COO^- : 26.5×10^{-4} T; aromatic N: 23.8×10^{-4} T; aliphatic N: 22.5×10^{-4} T), the possible structures of various components in the solution were suggested and given in Table 2. From Table 2, we see that the calculated values are rather accordant with the measured ones.

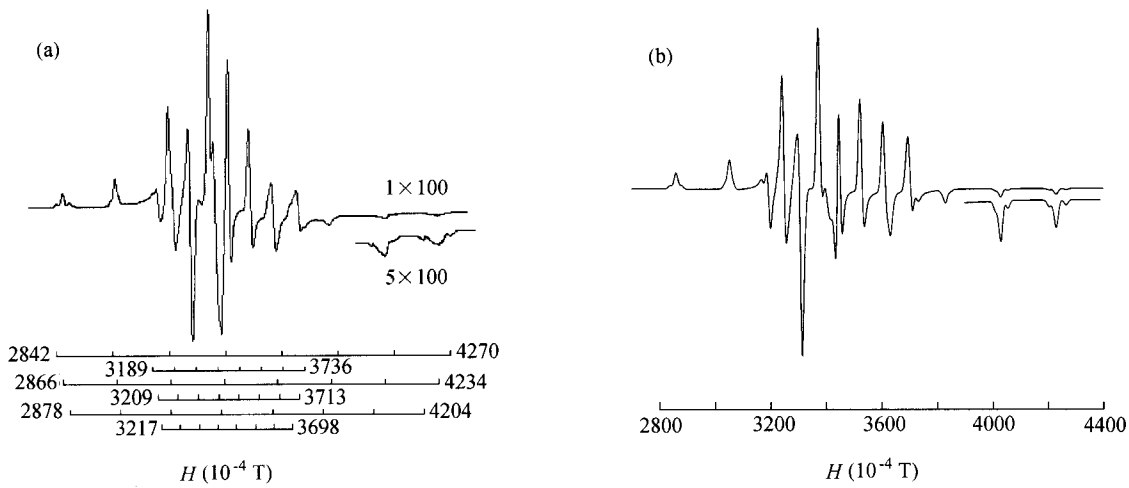


Fig. 1 ESR spectra of VO(II)-Ser-phen system in pH = 2.45 solution at 173 K: (a) experimental spectrum; (b) simulated spectrum.

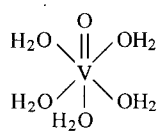
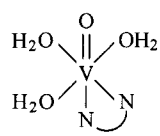
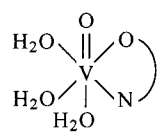
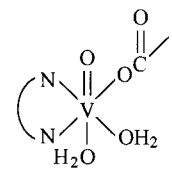
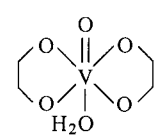
Table 1 ESR spectral and bonding parameters of the complexes

Components	$g_\perp$	$g_{\parallel}$	$\bar{g}$	$10^4 A_{\parallel}$ (T)	$10^4 A_\perp$ (T)	$10^4 \bar{A}$ (T)	α^2	κ (cm^{-1})	κ_0
1	1.986	1.933	1.968	204.0	78.0	120.0	0.981	0.0102	0.85
2	1.987	1.937	1.970	195.2	72.1	113.1	0.964	0.0099	0.80
3	1.989	1.942	1.973	189.4	68.7	108.9	0.953	0.0096	0.78
4	1.990	1.946	1.975	179.0	64.4	102.6	0.909	0.0091	0.73
5	1.990	1.961	1.980	169.2	50.0	89.7	0.980	0.0080	0.65

As shown in Fig. 2, there are different complexes in the solution over different pH ranges, for example, there is only component **5** at pH > 10.5 range, its spectral parameter $\bar{A} = 89.7 \times 10^{-4}$ T is the same as that of $[VO(OCH_2CH_2O)_2]^{2-,2}$ which indicates that Ser and phen are not coordinated to VO(II). At $2.3 \leq pH \leq 4.0$ and $4.0 \leq pH \leq 5.6$, there are three kinds of complexes (**1**, **2**, **3**) and complexes (**2**, **3**, **4**) in the solution, respectively. Therefore, the ESR spectrum is the overlapped result of the three kinds of complexes as shown in Fig. 1. At $7.4 < pH < 9.0$, there is only complex **4**. In the other pH ranges, two kinds of complexes coexist in

the solution. The relative content of the various components in the solution at various pH ranges can be evaluated by using the computer simulation, and shown in Fig. 3, which indicates that the cordination reactivity of phen to VO(II) is stronger than that of Ser.

Table 2 Possible structures of the various component complexes in the VO(II)-Ser-phen system

Components	1	2	3	4	5
10^4A_{meas} (T)	120.0	113.1	108.9	102.6	89.7
possible structure					
$10^4\overline{A}_{calcd}$ (T)	30.0×4 = 120.0	30.0×3 + 23.8 = 113.8	30.0×2 + 26.5 + 22.5 = 109.0	30.0 + 23.8×2 + 26.5 = 104.1	—
composition	$[VO(H_2O)_5]^{2+}$	$[VO(H_2O)_3(phen)]^{2+}$	$[VO(H_2O)_3(Ser)]^{+}$	$[VO(H_2O)_2(phen)(Ser)]^{+}$	$[VO(OCH_2CH_2O)_2]^{2-}$

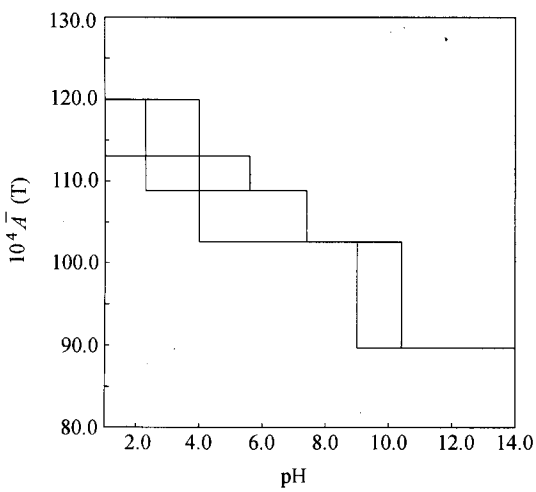


Fig. 2 Relationship between hyperfine splitting constant $\overline{A}$ and pH of solution.

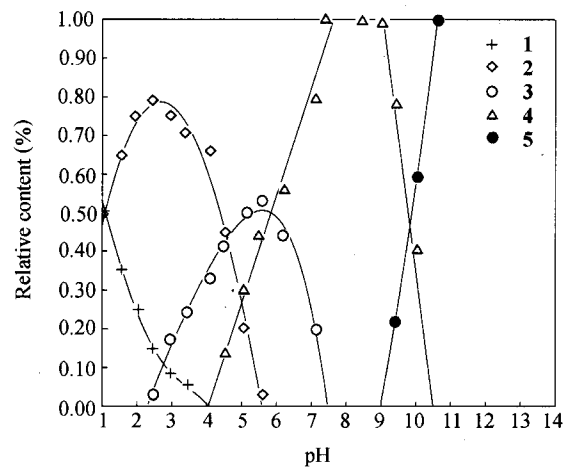


Fig. 3 Relationship of the relative content of the various components and pH value of the solution.

Infrared spectra

The IR spectrum of complex **4** shows that the absence of a peak around 1700 cm^{-1} due to $\nu_{C=O}$ of free carboxylic group indicates that the serine is bound to vanadyl ion through carboxyl. Two bands (ν^{as}_{coo-} and ν^{s}_{coo-}) of asymmetric and symmetric stretching vibrations of COO^- group in the complex shift to 1654 cm^{-1} and 1419 cm^{-1} respectively, and $\Delta\nu^{as-s}$ = 245 cm^{-1}. This means that the carboxyl group is coordinated to vanadyl ion as monodentate form.[6] The stretching vibration band of free NH_2 at 3430 cm^{-1} has been observed. It shows that the amino group of Ser does not coordinate with oxovanadium ion. However, the stretching vibration band of V = O measured at 980 cm^{-1} clearly suggests that the *trans*-position of V = O is coordinated with H_2O molecule. Besides, the bands at ca. 1561 cm^{-1} (ring stretching vibration), 855 cm^{-1} and 740 cm^{-1} (C—H out-of-plane deformation) in the IR spectra of the phen ligand are observed to shift to 1539 cm^{-1}, 847 cm^{-1} and 720 cm^{-1} in the IR spectra of complex **4**. From here we see that phen is coordinated to vanadium ion as bidentale ligand.[7] The formation of V—N bond is further confirmed by the appearance of additional peak at about 433 cm^{-1}.[8] The IR spectral data strongly support the ESR spectral result.

Bonding characteristic of the complexes

From Table 2, it can be seen that all complexes possess C_{4v} symmetry. At C_{4v} symmetry the relationship between the spectral and the bonding parameters can be represented as follows:[9]

$$A_{\parallel} = -\kappa + p[-\frac{4}{7}\alpha^2 + (g_{\parallel} - g_e) + \frac{3}{7}(g_{\perp} - g_e)] \quad (1)$$

$$A_{\perp} = -\kappa + p[\frac{2}{7}\alpha^2 + \frac{11}{14}(g_{\perp} - g_e)] \quad (2)$$

$$p = g_e\beta_e g_N\beta_N < \gamma^{-3} > \quad (3)$$

where $g_e = 2.0023$, $\kappa = \kappa_0 p$, κ_0 is isotropic Fermi contact term. Taking $p = 0.0124$ cm^{-1}, introducing the spectral parameters from Table 1 and p value into Eqs. (1) and (2), we obtained the values α^2, κ and κ_0 which are also listed in Table 1. From Table 1, we can see that the α^2 values of complexes decrease as the number of ligands bound to vanadium increases. This means that the covalent bonding between vanadium and ligands increases when water molecules are replaced by Ser and phen. The change of κ value also confirms that κ decreases as the electronegativity of ligands decreases. From Table 1, we can also see that α^2 values 0.98 of components **1** and **5** indicate that the in-plane π bonding almost is ionic, and the $3d_{xy}$ vanadium orbital is relatively non-bonding. The α^2 value 0.90 of complex **4** indicates that the in-plane π bonding is somewhat covalent, so that the unpaired electron is not entirely localized on the vanadium ion in this case.

Electronic spectra

Energy level diagram in crystalline fields of O_h and compressed C_{4v} symmetry is given in literature.[10] For the ground state configuration the one d electron in VO(II) is placed in the b_2 orbital. Thus the predicted transition is

$$^2B_2 \longrightarrow {}^2E \qquad \Delta E^2_{B_2-{}^2E} = -3D_s + 5D_t \quad (4)$$

$$^2B_2 \longrightarrow {}^2B_1 \qquad \Delta E^2_{B_2-{}^2B_1} = -10D_q \quad (5)$$

$$^2B_2 \longrightarrow {}^2A_1 \qquad \Delta E^2_{B_2-{}^2A_1} = -10D_q - 4D_s - 5D_t \quad (6)$$

where D_q is the spectral parameter in O_h feild. The parameters D_s and D_t specify the degree of tetragonality present in the field. D_s is a second order radial integral, while D_t is a fourth order radial integral.[11]

Three absorption bands at 12195 cm^{-1}, 14388 cm^{-1}, 21978 cm^{-1} in the electronic spectrum of the complex **4** measured at pH = 8.2 are attributed to, $^2B_2 \longrightarrow {}^2E$, $^2B_2 \longrightarrow {}^2B_1$ and $^2B_2 \longrightarrow {}^2A_1$ transitions of oxovanadium respectively. On this basis, the D_q = 1439 cm^{-1}, D_s = −2826 cm^{-1} and D_t = 743 cm^{-1} were calculated from Eqs. (4)—(6). From this result it is clear that a rather exaggerated tetragonal distortion is present in the complex **4** $[VO(H_2O)_2(phen)(Ser)]^+$, and that a model which only considers σ-bonding to be present, cannot provide an adequate description of the electronic structure of the complex. It is thus evident that an accurate description of the electronic structure of the complex must include provisions for π-bonding.

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