

Synthesis, Characterization, Crystal Structure and Stability of a Ternary Cu() complex with 1, 10-Phenanthroline and L-Valinate*

ZHOU Xiao-hua¹, LE Xue-yi^{1* * *}, LONG La-sheng² and CHEN Shi¹

1. Department of Applied Chemistry, College of Sciences, South-China Agricultural University, Guangzhou 510642, P. R. China;

2. Department of Chemistry, Xiamen University, Xiamen 361005, P. R. China

Received Feb. 19, 2004

Keywords Copper() complex, L-Valine, 1, 10-Phenanthroline, Crystal structure, Stability constant

Article ID 1005-9040(2005)-01-19-04

Introduction

It is important to research the mixed-ligand copper complexes containing bioligands, such as amino acids, nucleic acids and proteins, in exploring the functional mechanism of microelement copper in organism because the reaction of any micronutrient with two or more bioligands in the concentrated bioligands background gives mixed-ligand ternary complexes, which are more stable^[1] and related with storage of substance and transportation of metal ions in the life process. Furthermore, the ternary complexes can serve as useful models for gaining a better understanding of enzyme-metal ion-substrate complexes, which play an important role in metalloenzyme-catalysed biochemical reactions^[2-4]. Our research group has reported the syntheses and properties of several mixed-ligand ternary complexes of L- α -amino acid-Cu()-1, 10-phenanthroline^[5-9]. Here we report the synthesis, characterization, crystal structure and stability of a new mixed-ligand complex formed by L-valine(L-Val), copper() and 1, 10-phenanthroline(phen).

Experimental

1 Physical Measurements

The IR spectrum in KBr disc was recorded in the range of 400_ 4000 cm^{-1} on a Nicolet 170SX spectrophotometer. The elemental analyses (carbon, nitrogen and hydrogen contents) were performed on a Perkin-Elmer 240 microanalyser. The ¹H NMR spectrum was recorded on a Bruker DRX 400 instrument and the chemical shifts were given relative to TMS. The UV-Vis spectrum was mea-

sured in water on a Shimadzu UV-260 spectrophotometer at room temperature. The molar conductivity was determined in acetonitrile by using a DDS-11A conductivity gauge. The TG-DTA study was performed on a Shimadzu DTG-60 simultaneous DTA-TG apparatus. The sample was contained within alumina crucibles and heated at a rate of 7 /min from room temperature to 700 under air atmosphere. The pH potentiometric measurements were carried out by using a 702SM Titrino Lon analysis titration system with a Metrohm UX glass electrode.

2 Synthesis

The title complex was prepared by dissolving Cu(ClO₄)₂ · 6H₂O (0.5 mmol) and 1, 10-phenanthroline(0.5 mmol) in 25 mL of 50%(volume fraction) warm ethanol-water solvent with stirring, followed by the addition of the aqueous solution of L-Val(0.5 mmol). The pH of the mixture was adjusted to about 5 with a dilute HClO₄ solution and then filtered. The resulted solution was allowed to stand in a refrigerator(4). The dark blue slender crystals were collected after several days by filtration, washed with cold ethanol and air-dried (63% yield). IR, $\tilde{\nu}/\text{cm}^{-1}$: 3436(b, H₂O); 3268, 3183 (s, α -NH₂); 1630 (s, COO⁻); 1384 (s, COO⁻); 1575, 851, 724(m, Phen ring). ¹H NMR [(CD₃)₂SO], δ : 13.9(s, 4H, NH₂), 3.3(s, 4H, CH), 0.6(m, 12H, CH₃); elemental anal. (%) calcd. for C₃₄H₃₈Cl₂N₆O₁₄Cu₂: C 42.74, H 3.99, N 8.80; found: C 42.62, H 4.04, N 8.90.

* Supported by the Natural Natural Science Foundation of Guangdong Province(No.010338).

* * To whom correspondence should be addressed. E-mail: lexy@scau.edu.cn

3 X-ray Structural Determination of the Complex

The crystallographic data for the title complex are listed in Table 1. The data were collected by using a Bruker Smart 1K CCD diffractometer. With graphite monochromated Mo $K\alpha$ radiation ($\lambda = 0.071073$ nm), the structure was solved by using direct and Fourier methods with the SHELXS-97^[10] program and refined by full-matrix least-squares techniques. The non-hydrogen atoms were assigned with anisotropic displacement parameters in the refinement. The structure was then refined on F^2 by using the SHELXL-97 program^[11].

Table 1 Crystallographic data of the complex [Cu(L-Val)(phen)(H₂O)] · ClO₄

Formula	C ₃₄ H ₃₈ Cl ₂ Cu ₂ N ₆ O ₁₄
<i>M</i>	952.68
Colour	Dark blue
Crystal size	0.41 nm × 0.40 nm × 0.19 nm
Crystal system	Triclinic
Space group	$P\bar{1}$
Unit cell dimensions	$a = 0.8052(4)$ nm, $\alpha = 112.370(9)^\circ$ $b = 1.1590(6)$ nm, $\beta = 105.690(8)^\circ$ $c = 1.2309(6)$ nm, $\gamma = 99.094(9)^\circ$
V/nm^3	0.9778(9)
<i>Z</i>	1
$D_c/(g \cdot cm^3)$	1.618
$\mu/m\text{mm}^{-1}$	1.299
$F(000)$	488
<i>T</i> /K	293(2)
θ range for data collection	1.92 to 24.99°
Range of <i>h, k, l</i>	-9 <i>h</i> 9, -12 <i>k</i> 13, -14 <i>l</i> 14
Reflections measured	3399
Independent reflections	3074 ($R_{int} = 0.0160$)
Absorption correction	None
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	3074/0/262
Goodness of fit on F^2	1.135
Final <i>R</i> indices [$I > 2\sigma(I)$]	$R_1 = 0.0754$, $wR_2 = 0.1984$
<i>R</i> indices (all data)	$R_1 = 0.0809$, $wR_2 = 0.2017$
Max., Min. height in final ΔF map/ $(e \cdot nm^{-3})$	1190, -908

4 Determination of Stability Constants

The pH titrations were carried out according to the procedure previously reported^[8]. The stability constants $K_{Cu(L-Val)}^{Cu}$ and $K_{Cu(phen)(L-Val)}^{Cu(phen)}$ of the binary Cu(L-Val)⁺ and ternary Cu(phen)(L-Val)⁺ complexes, respectively, were measured under the same conditions as used for the acidity constants, but NaClO₄ was partly replaced by Cu(ClO₄)₂. For the binary Cu²⁺/(L-Val) system, titrations were made with $n(L-Val)/n(Cu^{2+}) = 1/5$. For the ternary Cu²⁺/phen/(L-Val) system, the conditions

were exactly the same as those of the binary one except that Cu²⁺ was replaced by Cu²⁺ in a 1/1 molar ratio of Cu²⁺ to phen. Under the condition with a lower L-Val concentration, *i.e.* $n(L-Val)/n(Cu^{2+})/n(phen) = 1/5/5$, the Cu(phen)²⁺ complex was completely formed before the coordination of the amino acid takes place. The final values of $K_{Cu(L-Val)}^{Cu}$ and $K_{Cu(phen)(L-Val)}^{Cu(phen)}$ are the averages of at least three independent titrations.

Results and Discussion

The results of elemental analyses, IR, and ¹H NMR spectra of the title complex are in agreement with the following formula: [Cu(L-Val) · (phen)(H₂O)] · ClO₄. The complex is stable in air and soluble in water, methanol and ethanol, but not in ether and other weak-polarity organic solvents. Molar conductivity measurement in acetonitrile at 10⁻³ mol/L, $\Lambda_m = 154.5$ S · cm² · mol⁻¹, would give evidence to the idea that the complex belonged to an electrolyte of 1/1 type^[12].

1 Crystal Structure of [Cu(L-Val)(phen)(H₂O)] · ClO₄

The crystal structure and the packing of complex [Cu(L-Val)(phen)(H₂O)] · ClO₄ are shown in Figs. 1 and 2. The crystal structure consists of [Cu(L-Val)(phen)(H₂O)]⁺ cations and ClO₄⁻ anions, which are packed with each other by electro-

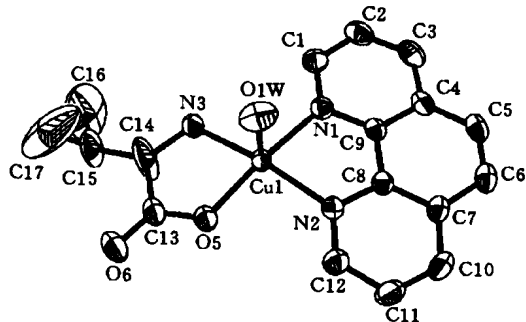


Fig. 1 ORTEP plot showing the structure of [Cu(L-Val) · (phen)(H₂O)]⁺ cation and the atom-numbering scheme.

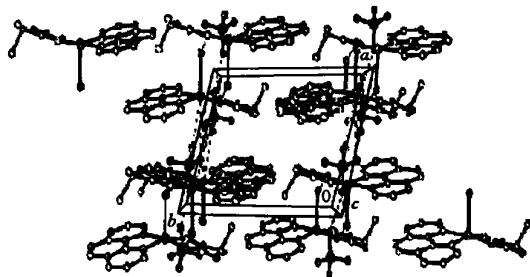


Fig. 2 Crystal packing diagram showing H-bonds of the complex.

static and hydrogen-bonding interactions [$d(O1w_O4) = 0.2951$ nm in $x - 1, y, z$, $d(O1w_O1) = 0.2860$ nm in $-x, -y + 2, -z$, $d(O1w_O2) = 0.3264$ nm in $-x, -y + 2, -z$ and $d(N3_O5) = 0.3078$ nm in $x - 1, y, z$]. As shown in Fig. 1, the structure of the [Cu(L-Val)(phen)(H₂O)]⁺ cation is similar to that of complexes [Cu(gly)(phen) · (H₂O)]⁺[6] and [Cu(L-meth)(phen)(H₂O)]⁺[7], in which each central Cu() ion is ligated in an approximately square-pyramidal geometry constructed by two nitrogen atoms of phen, the α -amino nitrogen atom, one carboxylate oxygen atom of L-Val in the equatorial plane [$d(Cu1_O5) = 0.1924(5)$ nm, $d(Cu1_N3) = 0.1990(5)$ nm, $d(Cu1_N2) = 0.2000(5)$ nm, $d(Cu1_N1) = 0.2009(5)$ nm], and one water oxygen atom at an axial position [$d(Cu_O1w) = 0.2274(6)$ nm]. The bond lengths in the complex are comparable to the corresponding values of complexes [Cu(gly)(phen) · (H₂O)]⁺ [$d(Cu_O) = 0.1956(2)$ nm, $d(Cu_N) = 0.1992(2) - 0.2023(2)$ nm, $d(Cu_Ow) = 0.2254(2)$ nm] and [Cu(L-meth)(phen)(H₂O)]⁺ [$d(Cu_O) = 0.1938(2)$ nm, $d(Cu_N) = 0.1987(2) - 0.2017(2)$ nm, $d(Cu_Ow) = 0.2352(2)$ nm]. The carboxyl group of the amino acid is coordinated to the Cu() atom *via* one oxygen atom as an unidentate, and the electron delocalization was observed in the carboxyl group. In the carboxyl group, the bond distance [0.1258(9) nm] between the coordinated oxygen atom and the carbon atom is slightly longer than that [0.1212(10) nm] between the uncoordinated oxygen atom and the carbon atom as expected. The selected bond lengths and angles are given in Table 2.

Table 2 Selected bond lengths(nm) and bond angles(°)

Cu1_N1	0.2009(5)	Cu1_N3	0.1990(5)
Cu1_N2	0.2000(5)	Cu1_O1W	0.2274(6)
Cu1_O5	0.1924(5)		
O5_Cu1_N3	84.0(2)	O5_Cu1_N2	93.3(2)
N1_Cu1_N3	98.4(2)	N3_Cu1_O1W	99.0(3)
N1_Cu1_O1W	92.0(2)	O5_C13_O6	123.6(8)
C16_C15_C14	125.6(13)	C17_C15_C14	103.0(2)

2 Electronic Absorption Spectrum

The electronic absorption spectrum of the complex in the aqueous solution presents four important absorption bands, in which the bands at 206.5 nm ($\epsilon = 20680$ L · mol⁻¹ · cm⁻¹), 224.0 nm ($\epsilon = 31030$ L · mol⁻¹ · cm⁻¹) and 271.5 nm ($\epsilon = 29830$ L · mol⁻¹ · cm⁻¹) can be attributed to the $\pi \rightarrow \pi^*$ transitions of the coordinated phen ligand,

and the broad and weak absorption band at 624 nm ($\epsilon = 1023$ L · mol⁻¹ · cm⁻¹) to the $d \rightarrow d$ transition of the central Cu²⁺ ion, which is similar to the related aromatic amine-Cu²⁺-amino acid complex-^[5-9,13,14].

3 Thermal Analysis

The TGA-DTA study of the title complex showed four mass loss stages. The first mass loss (3.16%) occurs between 102.7 - 131.6 (endothermic peak observed at 123.9 in DTA), corresponding to the loss of the coordinated water molecule; the second and the third mass losses (25.14%) occur between 131.7 - 319.4 (three strong exothermic peaks observed at 208.6, 215.3 and 285.7, respectively, in DTA), corresponding to the loss of the L-Val ligand and the combustion of the organic groups; the fourth mass loss (55.14%) occurs from 319.5 to the temperature of constant weight (broad exothermic peak observed at 497.2 in DTA), corresponding to the decomposition of ClO₄⁻ and the destruction of the bone structure.

4 Stability of the Complex in Aqueous Solution

The acidity dissociation constants $K_{H_2(L-Val)}^H$ and $K_{H(L-Val)}^H$ of L-Val were calculated by using eqs. (1) and (2), respectively. The stability constants $K_{Cu(L-Val)}^{Cu}$ and $K_{Cu(phen)(L-Val)}^{Cu(phen)}$ of the binary Cu(L-Val)⁺ and ternary Cu(Phen)(L-Val)⁺ complexes are defined by eqs. (3) and (4), respectively.

$$H_2(L-Val)^+ = H^+ + H(L-Val),$$

$$K_{H_2(L-Val)}^H = \frac{[H^+][H(L-Val)]}{[H_2(L-Val)^+]} \quad (1)$$

$$H(L-Val) = H^+ + (L-Val)^-,$$

$$K_{H(L-Val)}^H = \frac{[H^+][(L-Val)^-]}{[H(L-Val)]} \quad (2)$$

$$Cu^{2+} + (L-Val)^- = Cu(L-Val)^+,$$

$$K_{Cu(L-Val)}^{Cu} = \frac{[Cu(L-Val)^+]}{[Cu^{2+}][(L-Val)^-]} \quad (3)$$

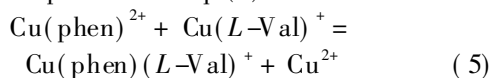
$$Cu(phen)^{2+} + (L-Val)^- = Cu(phen)(L-Val)^+,$$

$$K_{Cu(phen)(L-Val)}^{Cu(phen)} = \frac{[Cu(phen)(L-Val)^+]}{[Cu(phen)^{2+}][(L-Val)^-]} \quad (4)$$

The acidity dissociation constants ($\lg K_{H_2(L-Val)}^H$ and $\lg K_{H(L-Val)}^H$) of ligand L-Val are 2.411 and 9.344, respectively, and the stability constants ($\lg K_{Cu(L-Val)}^{Cu}$ and $\lg K_{Cu(phen)(L-Val)}^{Cu(phen)}$) for the binary Cu(L-Val)⁺ and ternary Cu(phen)(L-Val)⁺ complexes are 7.90 and 7.68, respectively.

A common way to quantify the stability of a ternary complex is based on a comparison with the corresponding binary parent complex, *i.e.*, by de-

termining the position of eq. (5)^[15]:



The corresponding equilibrium constant $10^{\Delta \lg K_{\text{Cu}}}$ [eq. (6)] may be calculated with eq. (7)

$$10^{\Delta \lg K_{\text{Cu}}} = \frac{[\text{Cu(phen)(L-Val)}^+][\text{Cu}^{2+}]}{[\text{Cu(phen)}^{2+}][\text{Cu(L-Val)}^+]} \quad (6)$$

where $\Delta \lg K_{\text{Cu}} = K_{\text{Cu(phen)(L-Val)}^+}^{\text{Cu(phen)}} - K_{\text{Cu(L-Val)}^+}^{\text{Cu}}$

For a distorted octahedral (do) coordination sphere of Cu^{2+} , the statistical value $\Delta \lg K_{\text{st/do}} = -0.9$ ^[16]. However, the $\Delta \lg K_{\text{Cu}}$ value (7.68 - 7.90 = -0.31) of the ternary complex is larger than the statistical value. The increased stability may be mainly attributed to the $\pi\text{-}\pi^*$ cooperative effect between the heteroaromatic N -base(phen) π and the O donor ligand(L-val) π^* , which depends on the coexistence of the π back-bond from Cu^{2+} to the heteroaromatic N -base ligand and $p\pi$ - $d\pi$ bond between the π -donating oxygen and Cu^{2+} .

References

- [1] Cleare M. J., Hydes P. C., *Metal Ions in Biological Systems*, Dekker, New York, **1980**, 1
 [2] Ji L. N., Le X. Y., *Chin. Sci. Bull.*, **2001**, 47, 1

- [3] Freedmann T. B., Loehr J. S., Loehr T. M., *J. Am. Chem. Soc.*, **1976**, 98, 2809
 [4] Xu H., Deng H., Hu H. Y., *Chem. J. Chinese Universities*, **2003**, 24(1), 25
 [5] Zhou X. H., Le X. Y., Li M. H., *Chem. J. Chinese Universities*, **2000**, 21(5), 681
 [6] Zhou X. H., Le X. Y., Li M. H., *Chin. Chem. Bull.*, **2001**, 64, 48
 [7] Le X. Y., Tong M. L., *Chin. J. Inorg. Chem.*, **2002**, 18, 1023
 [8] Le X. Y., Tong M. L., Fu Y. L., *et al.*, *Chin. J. Chem.*, **2003**, 21, 44
 [9] Le X. Y., Zhou X. H., Huang C. J., *et al.*, *J. Coord. Chem.*, **2003**, 56(10), 861
 [10] Sheldrick G. M., *SHELXS-97, Program for X-ray Crystal Structure Determination*, Göttingen University, Göttingen, **1997**
 [11] Sheldrick G. M., *SHELXL-97, Program for X-ray Crystal Structure Refinement*, Göttingen University, Göttingen, **1997**
 [12] Gear W. J., *Coord. Chem. Rev.*, **1971**, 7, 81
 [13] Sugimori T., Mosuda H., Ohata N., *et al.*, *Inorg. Chem.*, **1997**, 36, 576
 [14] Antolini L., Marcotrigiano G., Menabue L., *et al.*, *Inorg. Chem.*, **1983**, 22, 141
 [15] Sigel H., McCormick D. B., *Acc. Chem. Res.*, **1970**, 3, 102
 [16] Sigel H., *Angew. Chem. Int. Ed. Engl.*, **1975**, 14, 394