

研究简报

1, 10-邻菲咯啉 - 铜(II) - *L*-蛋氨酸配合物的合成、表征及其分子结构乐学义*¹ 童明良²⁽¹⁾ 华南农业大学理学院应用化学系, 广州 510642)⁽²⁾ 中山大学化学系, 广州 510275)关键词: 1, 10-邻菲咯啉 *L*-蛋氨酸 铜(II)配合物 晶体结构
分类号: 0614. 121Synthesis, Characterization and Crystal Structure of Ternary Cu (II)
Complex with 1, 10-Phenanthroline and *L*-MethioninateLE Xue-Yia*¹ TONG Ming-Liang²⁽¹⁾ Department of Applied Chemistry, College of Sciences, South-China Agricultural University, Guangzhou 510642)⁽²⁾ Department of Chemistry, Zhongshan University, Guangzhou 510275)

The complex [Cu(*L*-met) (phen) (H₂O)] NO₃ · H₂O has been synthesized and investigated by elemental analysis, molar conductivity, spectroscopic and X-ray diffraction methods, where phen = 1, 10-phenanthroline and *L*-met = *L*-methioninate group. The complex crystallized in the monoclinic space group *P*2₁ with $a = 12.053(2) \text{ \AA}$, $b = 6.886(1) \text{ \AA}$, $c = 13.385(3) \text{ \AA}$, $\beta = 113.59(3)^\circ$, $V = 1018.1(3) \text{ \AA}^3$, $Z = 2$, $D_c = 1.598 \text{ g} \cdot \text{cm}^{-3}$, $\mu = 1.223 \text{ mm}^{-1}$, $F(000) = 506$, $R_1 = 0.0306$, and $wR_2 = 0.0742$. The copper (II) atom is ligated in a distorted square-pyramidal geometry by two nitrogen atoms of one phen and the amino nitrogen atom, one carboxylate oxygen atom of *L*-met in the base plane, and an aqua at the apical position. A one-dimensional chain configuration formed by the hydrogen-bonding and weak Cu-O (the uncoordinated carboxyl oxygen atom) coordination interactions between neighboring [Cu(*L*-met) (phen) (H₂O)]⁺ cations. CCDC: 183368.

Keywords: 1, 10-phenanthroline *L*-methioninate copper (II) complex crystal structure

Considerable attention has been paid in recent years^[1-4] on the study of the ternary metal complexes involving an aromatic amine as the primary ligand, and various biomolecules, such as amino acids, peptides, nucleotides, nucleosides, and so on, as the secondary ligands, because the ternary complexes can serve as useful models for gaining a better understanding of en-

zyme-metal ion-substrate complexes, which play an important role in metalloenzyme-catalysed biochemical reactions^[5]. As related examples of such analogues and as part of our continuing interest in this study field^[4, 6, 7], in the present paper, the complex [Cu(*L*-met) (phen) (H₂O)] NO₃ · H₂O (*L*-met = *L*-methioninate group, phen = 1, 10-phenanthroline) has been

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synthesized and investigated by elemental analysis, molar conductivity, spectroscopic, and X-ray diffraction methods.

1 Experimental

1.1 Synthesis of the Complex

1, 10-phenanthroline (1mmol), and $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ (1mmol) were dissolved in 25mL of water solvent with heating and stirring, and an aqueous hot solution containing *L*-met(1mmol) was added dropwise to this solution. The pH of the mixture was adjusted to 5 with dilute aqueous NaOH solution. The resulting solution was left in a desiccator with silica gel at room temperature. Blue crystals formed after three weeks. The crystals were filtered and air-dried. Anal: $\text{C}_{17}\text{H}_{22}\text{CuN}_4\text{O}_7\text{S}$. Calcd: C, 41.67; H, 4.53; N, 11.44; Found: C, 41.78; H, 4.58; N, 11.36.

1.2 Physical Measurements

The elemental analyses (carbon, nitrogen and hydrogen contents) were performed on a Perkin-Elmer 240C microanalyser, molar conductivity was measured

in ethanol with a DDS-11A conductivity gauge. The infrared absorption spectrum in KBr disks was recorded on a Nicolet 170SX spectrophotometer. The electronic absorption spectrum of the complex was measured in ethanol on a pharmacia 4000 UV-Vis spectrophotometer at room temperature.

1.3 X-ray Structural Determination of the Complex

Details of the structure solution and refinement for the complex are shown in Table 1.

A single crystal sample with dimensions $0.42 \times 0.32 \times 0.26\text{mm}$ was used for structural determination on a Bruker Smart 1K CCD system diffractometer with graphite monochromated $\text{MoK}\alpha$ radiation at $\lambda = 0.71073\text{\AA}$. The collected data were reduced by using SAINT +^[8], and absorption correction was carried out using SADABS program^[9]. The structure was solved by direct and Fourier methods using SHELXS-97 program^[10], and refinement on F^2 was performed using SHELXL-97 program^[11] by full-matrix least squares with positional and anisotropic thermal parameters for

Table 1 Crystallographic Data of the Complex $[\text{Cu}(\text{L-met})(\text{phen})(\text{H}_2\text{O})]\text{NO}_3 \cdot \text{H}_2\text{O}$

formula	$\text{C}_{17}\text{H}_{22}\text{CuN}_4\text{O}_7\text{S}$
<i>M</i>	489.99
colour	blue
crystal size/mm	$0.42 \times 0.32 \times 0.26$
crystal system	monoclinic
space group	$P2_1$
<i>a</i> /Å	12.053(2)
<i>b</i> /Å	6.886(1)
<i>c</i> /Å	13.385(3)
β /°	113.59(3)
volume/Å ³	1018.1(3)
Z	2
D_c /(g · cm ⁻³)	1.598
μ /mm ⁻¹	1.223
<i>F</i> (000)	506
temperature/K	293(2)
θ range for data collection/°	4.17 to 30.01
range of <i>h</i> , <i>k</i> , <i>l</i>	$-16 \leq h \leq 16$, $-9 \leq k \leq 9$, $-18 \leq l \leq 9$
reflections measured	7294
independent reflections	5375 ($R_{int} = 0.0183$)
max. and min. transmission	1.000, 0.604
parameters refined	272
goodness of fit on F^2	0.971
final <i>R</i> indices($I > 2\sigma(I)$)	$R_1 = 0.0306$, $wR_2 = 0.0742$
<i>R</i> indices(all data)	$R_1 = 0.0377$, $wR_2 = 0.0774$
max. min. height in final ΔF map/(e · Å ⁻³)	0.244, -0.286

all non-hydrogen atoms. All hydrogen atoms were placed in calculated positions. Absolute structure has been determined by Flack parameter of 0.017(9)^[12]. Atomic scattering factors were taken from the international tables for X-ray crystallography^[13]. Fractional atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are listed in Table 2. The selected bond lengths and angles are collected in Table 3.

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2 Results and Discussion

The result of elemental analyses of the title com-

plex is in agreement with the following formula: [Cu(L-met)(phen)(H₂O)]NO₃·H₂O. The complex is soluble in water, methanol or ethanol, but not in ether and other weak-polarity organic solvents. Molar conductivity measurement in ethanol would give credence to this idea, with the complex approaching 1:1 electrolyte value^[14] ($\Lambda = 32.1\text{S} \cdot \text{cm}^2 \cdot \text{mol}^{-1}$).

2.1 Infrared Absorption Spectrum

The infrared spectrum of the complex shows two strong and wide bands at 3473 and 3415 cm⁻¹ which are most likely ascribed to the stretching vibrations of crystallized and coordinated water molecules. The bands at 3221 and 3122cm⁻¹ can be attributed to the

Table 2 Atomic Coordinates ($\times 10^4 \text{\AA}$) and Equivalent Isotropic Displacement Parameters $U(\text{eq})$ ($\times 10^3 \text{\AA}^2$) for the Complex

atom	x	y	z	$U(\text{eq})$	atom	x	y	z	$U(\text{eq})$
Cu(1)	5894(1)	9081(1)	8617(1)	38(1)	S(1)	9180(1)	9556(2)	13890(1)	82(1)
O(1w)	6050(2)	5843(2)	8129(1)	47(1)	O(2w)	2164(2)	8064(4)	9140(2)	75(1)
O(1)	4769(1)	8494(2)	9281(1)	45(1)	O(2)	4630(1)	7839(3)	10838(1)	49(1)
N(1)	7167(1)	8772(3)	10112(1)	37(1)	N(2)	6963(2)	9863(3)	7848(2)	43(1)
N(3)	4579(2)	9519(2)	7137(2)	42(1)	C(1)	5235(2)	8116(3)	10292(2)	36(1)
C(2)	6616(2)	7947(3)	10841(2)	34(1)	C(3)	7144(2)	8864(4)	11972(2)	43(1)
C(4)	8462(2)	8258(5)	12603(2)	55(1)	C(5)	9688(3)	11659(6)	13441(3)	80(1)
C(6)	8162(2)	10044(4)	8243(2)	54(1)	C(7)	8774(3)	10319(5)	7548(3)	68(1)
C(8)	8134(3)	10352(4)	6454(3)	70(1)	C(9)	6870(3)	10164(4)	6007(2)	59(1)
C(10)	6327(2)	9945(3)	6752(2)	45(1)	C(11)	5038(2)	9814(3)	6372(2)	47(1)
C(12)	4301(3)	9956(4)	5248(2)	59(1)	C(13)	3044(3)	9877(4)	4948(2)	75(1)
C(14)	2591(3)	9591(4)	5718(3)	69(1)	C(15)	3384(2)	9387(4)	6820(2)	56(1)
C(16)	4887(4)	10115(4)	4506(2)	75(1)	C(17)	6086(4)	10201(4)	4860(2)	74(1)
N(4)	9106(2)	5189(4)	8918(2)	62(1)	O(3)	8276(2)	5167(5)	8003(2)	91(1)
O(4)	10145(2)	4921(6)	9039(2)	113(1)	O(5)	8881(2)	5540(4)	9743(2)	89(1)

Table 3 Selected Bond Lengths (\AA) and Angles ($^\circ$)

Cu(1)-O(1)	1.938(2)	Cu(1)-N(1)	1.987(2)	Cu(1)-N(3)	2.003(2)
Cu(1)-N(2)	2.017(2)	Cu(1)-O(1W)	2.352(2)	Cu(1)-O(2a)	2.828(2)
S(1)-C(5)	1.769(4)	S(1)-C(4)	1.822(3)	O(1)-C(1)	1.268(3)
O(2)-C(1)	1.236(3)	N(1)-C(2)	1.494(3)	N(2)-C(6)	1.332(3)
N(2)-C(10)	1.357(3)	N(3)-C(15)	1.332(3)	N(3)-C(11)	1.360(3)
O(1W)···O(2b)	2.788(2)	O(1W)···O(3)	2.795(3)	O(2W)···O(5a)	2.870(3)
O(2W)···O(2)	2.935(3)	O(2W)···O(1)	3.084(2)	N(1)···O(2Wa)	3.121(3)
N(1)···O(4c)	3.077(3)				
O(1)-Cu(1)-N(1)	85.13(7)	O(1)-Cu(1)-N(3)	93.60(8)	N(1)-Cu(1)-N(3)	176.90(8)
O(1)-Cu(1)-N(2)	175.10(8)	N(1)-Cu(1)-N(2)	98.61(7)	N(3)-Cu(1)-N(2)	82.51(8)
O(1)-Cu(1)-O(1W)	94.48(6)	N(1)-Cu(1)-O(1W)	93.62(8)	N(3)-Cu(1)-O(1W)	89.29(7)
N(2)-Cu(1)-O(1W)	88.47(7)	O(1)-Cu(1)-O(2a)	78.62(6)	N(1)-Cu(1)-O(2a)	90.00(7)
N(3)-Cu(1)-O(2a)	86.98(6)	N(2)-Cu(1)-O(2a)	98.14(7)	O(1W)-Cu(1)-O(2a)	171.92(5)
C(1)-O(1)-Cu(1)	116.17(14)	C(2)-N(1)-Cu(1)	109.45(11)	C(6)-N(2)-Cu(1)	129.45(17)
C(10)-N(2)-Cu(1)	111.27(16)	C(15)-N(3)-Cu(1)	129.19(18)	C(11)-N(3)-Cu(1)	111.54(15)
O(2)-C(1)-O(1)	123.32(19)	O(2)-C(1)-C(2)	119.36(19)	O(1)-C(1)-C(2)	117.30(18)

Symmetry operations: a: $-x+1, y+1/2, -z+2$; b: $-x+1, y-1/2, -z+2$; c: $-x+2, y+1/2, -z+2$

stretching vibrations of the coordinated NH_2 group. The absence of any bands in the region $1750 \sim 1700\text{cm}^{-1}$ in the IR spectrum of the isolated complex suggests the coordination of the COO^- group of the *L*-methioninate to the metal ion. The bands at 1643 and 1325cm^{-1} can be attributed, respectively, to the antisymmetric and symmetric stretching vibrations of the coordinated carboxylate. The $\Delta\nu_{\text{CO}}$ ($\nu_{\text{CO}}^{\text{as}} - \nu_{\text{CO}}^{\text{s}} = 318\text{cm}^{-1}$) between the two bands shows that the carboxylate is monodentate^[15]. Thus, one can deduce that the monovalent anions of *L*-met are coordinated to the metal ion as a bidentate N, O-ligand. The band at 1601cm^{-1} is most likely assigned to the stretching vibration of the $\text{C}=\text{N}$ group of the phen ligand and confirms its coordination to the metal ion. Furthermore, this band could also be ascribed to the deformation mode δ_{NH} of the N-H group belonging to the amino acid moiety^[15].

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 222 ($\varepsilon = 29200\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$), 274 ($\varepsilon = 25300\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) and 295nm ($\varepsilon = 10060\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) can be attributed to the $\pi \rightarrow \pi^*$ transitions of the coordinated phen ligand, and the broad absorption band at 623nm ($\varepsilon = 80\text{L} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$) to the $d \rightarrow d$ transition of the central Cu^{2+} ion.

2.3 Crystal Structure

The complex consists of a discrete $[\text{Cu}(\text{L-met})(\text{phen})(\text{H}_2\text{O})]^+$ cation, a nitrate anion, and a crystalline water molecule, which are packed with each other by electrostatic and hydrogen bonding interactions ($\text{O}(1\text{W}) \cdots \text{O}(3) = 2.795(3) \text{ \AA}$, $\text{O}(2\text{W}) \cdots \text{O}(5\text{a}) = 2.870(3) \text{ \AA}$, $\text{O}(2\text{W}) \cdots \text{O}(2) = 2.935(3) \text{ \AA}$, $\text{O}(2\text{W}) \cdots \text{O}(1) = 3.084(2) \text{ \AA}$, $\text{N}(1) \cdots \text{O}(2\text{W}\text{a}) = 3.121(3) \text{ \AA}$, $\text{N}(1) \cdots \text{O}(4\text{c}) = 3.077(3) \text{ \AA}$) ($a: -x+1, y+1/2, -z+2$; $b: -x+2, y+1/2, -z+2$). As shown in Fig. 1, the structure of $[\text{Cu}(\text{L-met})(\text{phen})(\text{H}_2\text{O})]^+$ cation is similar to that of the complex reported recently $[\text{Cu}(\text{L-phe})(\text{phen})(\text{H}_2\text{O})]^+$ ^[16], in which the central Cu(II) ion coordinates the two nitrogen atoms of phen and the amino nitrogen and carboxylate oxygen

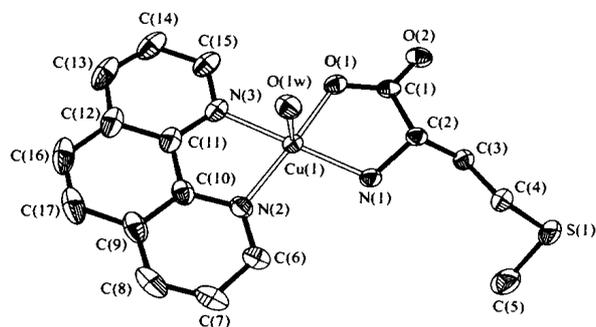


Fig. 1 ORTEP plot showing the structure of $[\text{Cu}(\text{L-met})(\text{phen})(\text{H}_2\text{O})]^+$ cation and the atom-numbering scheme

atoms of *L*-met in the equatorial positions ($\text{Cu}(1) - \text{O}(1) = 1.938(2) \text{ \AA}$, $\text{Cu}(1) - \text{N}(1) = 1.987(2) \text{ \AA}$, $\text{Cu}(1) - \text{N}(3) = 2.003(2) \text{ \AA}$, $\text{Cu}(1) - \text{N}(2) = 2.017(2) \text{ \AA}$), and one water oxygen atom at an axial position ($\text{Cu}(1) - \text{O}(1\text{W}) = 2.352(2) \text{ \AA}$), the resulting coordination geometry being described as a distorted five-coordinate square-pyramidal geometry (Fig. 1). The square-pyramidal geometry around copper is not severely distorted, the X-Cu-Z angles being $175.10(8)$ to $176.90(8)^\circ$ where X and Z are any two atoms which lie trans to each other and the X-Cu-Y angles ranging from $85.13(7)$ to $98.61(7)^\circ$ where X and Y are any atoms which lie cis to each other. In addition, O(1), N(1), N(2), N(3), and Cu atoms deviate by $0.0028, -0.0026, -0.0028, 0.0026,$ and -0.0512 \AA , respectively, from the least-squares plane ($1.9640x + 6.6482y - 3.3682z = 0.4465$) defined by the four ligating atoms O(1), N(1), N(2), and N(3), indicating the five atoms is approximately coplanar. The bond lengths in the complex are similar to the corresponding values found for the complex $[\text{Cu}(\text{L-phe})(\text{phen})(\text{H}_2\text{O})]^+$ ($\text{Cu}-\text{O} = 1.927(6) \text{ \AA}$, $\text{Cu}-\text{N} = 1.968(9) \sim 2.077(6) \text{ \AA}$, $\text{Cu}-\text{O}(\text{W}) = 2.213(10) \text{ \AA}$).

The most interesting finding is that, in the crystal of the complex, the neighboring $[\text{Cu}(\text{L-met})(\text{phen})(\text{H}_2\text{O})]^+$ cations are linked with each other by intermolecular hydrogen bonding and weak long-rang Cu-O (the uncoordinated carboxyl oxygen atom) coordination ($2.828(2) \text{ \AA}$) interactions in the direction of the *a* axis, forming a one-dimensional chain configuration (Fig. 2) in which the carbon chains of *L*-met stack

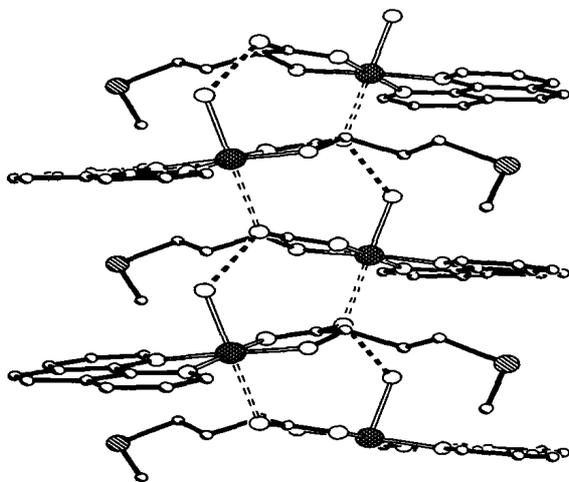


Fig. 2 Perspective view showing the one-dimensional chain in the complex

with the aromatic-rings of phen in the form of ... ABAB..., and leading to the central Cu (II) ion having a distorted and longed octahedral coordination geometry, and thereby prohibiting the coordination of the sulphur atom of the amino acid to the central Cu (II) ion.

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