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A Novel Cu(II) Complex with 2,2′-Bipyridyl and *L*-Methioninate ——Synthesis, Characterization, Molecular Structure and Stability

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The ternary Cu(II) complex with 2,2′-bipyridyl (bipy) and *L*-methioninate (*L*-Met) has been synthesized and characterized by elemental analysis, molar conductivity, UV-Vis spectra, IR spectra and pH-potentiometric titration methods. The structure of the complex [Cu(*L*-Met)(bipy)(H_2O)]ClO_4·3/8H_2O was characterized by the X-ray diffraction analysis. It crystallizes in the triclinic system, space group *P*1 with four molecules in a unit cell of dimensions, $a = 0.7656(2)$ nm, $b = 1.3142(3)$ nm, $c = 2.0596(4)$ nm, $\alpha = 97.70(3)°$, $\beta = 97.96(3)°$, $\gamma = 94.33(3)°$, $V = 2.0244(8)$ nm^3, $R_1 = 0.0441$ and $wR_2 = 0.0678$. The crystal contains four crystallographically independent [Cu(*L*-Met)(bipy)(H_2O)]$^+$ complexes (Cu1—Cu4), having a distorted square-pyramidal geometry with the same coordinated atoms around each copper center. The base plane is occupied by two nitrogen atoms of one bipy, the amino nitrogen atom and one carboxylate oxygen atom from each independent *L*-Met moiety, and one water oxygen at an axial position. Cu1 and Cu3 are essentially enantiomers of Cu2 and Cu4. The four molecules are packed with each other by intermolecular hydrogen-bonding and aromatic-ring stacking interactions.

Keywords 2,2′-bipyridyl, *L*-methioninate, copper(II) complex, crystal structure

Introduction

Many enzymes require activation by metal ions and thus they often involve a ternary enzyme/substrate/metal ion complex.[1] In recent years considerable attention has been paid to the ternary metal complexes involving an aromatic amine as the primary ligand and various biomolecules (such as amino acids, nucleotides, nucleosides, nucleic acid bases, and so on) as the secondary ligands.[2-5] To date, we have studied a series of ternary metal complexes containing an aromatic amine (bipy, phen, TATP, pdphen or pyridine-like ligands) and an amino acid (Gly, *L*-Phe, *L*-His or *L*-Tyr) or a nucleotide (UTP or ATP) by UV-Vis, IR, ^1H NMR, X-ray diffraction or potentiometric pH titration methods,[5-9] and have revealed intramolecular and intermolecular noncovalent interactions in the complexes, *e.g.*, aromatic stacking, hydrogen bonding and hydrophobic interactions, and their structures dependence on ligands and central metal ions. These results have very important significance for clarification of the mechanism of metalloenzyme-catalysed biochemical reactions. As *L*-methionine is an important biological ligand, *e.g.*, in copper proteins and copper enzymes,[10] we are paying our attention to ternary metal complexes with the amino acid and aromatic amines. In the present investigation, a novel complex [Cu(*L*-Met)(bipy)(H_2O)]ClO_4·3/8H_2O (*L*-Met = *L*-methioninate group, bipy = 2,2′-bipyridyl) was synthesized and investigated by elemental analysis, molar conductivity, spectroscopic and X-ray diffraction analysis. Moreover, the stability constant of the complex was measured by potentiometric pH titration in aqueous solution.

Experimental

Materials

All starting materials were commercially available and of analytical grade quality. $Cu(ClO_4)_2 \cdot 6H_2O$ was prepared according to the reported methods.[11]

Synthesis

2,2′-Bipyridyl (1 mmol), and $Cu(ClO_4)_2 \cdot 6H_2O$ (1 mmol) were dissolved in 10 mL of water solvent with heating and stirring. To this solution was added dropwise 5 mL of aqueous solution containing *L*-Met (1 mmol). The pH of the mixture was adjusted to about 5 with dilute aqueous NaOH solution. The resulting solution was left to evaporate at room temperature. Blue crystals formed after two weeks. The crystals were filtered and air-dried. Anal. calcd for $C_{15}H_{20.75}ClCuN_3O_{7.373}S$: C 36.60, H 4.25, N 8.54; found C 36.75, H 4.30, N 8.39.

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Safty Note: The solid complex is potentially explosive and should be handled with great care.

Physical measurements

The elemental analyses (carbon, nitrogen and hydrogen contents) were performed on a Perkin-Elmer 240C microanalyser. Molar conductivity measurement was carried out in water with a DDS-11A conductivity gauge. The infrared absorption spectrum in KBr disks was collected in the range of 4000—400 cm^{-1} on a Nicolet 170SX spectrophotometer. The electronic absorption spectrum of the complex was measured in water on a pharmacia 4000 UV-Vis spectrophotometer at room temperature.

Determination of stability constants

The acidity dissociation constants $K^{H}_{H(L\text{-Met})}$ and $K^{H}_{H_2(L\text{-Met})}$ of protonated *L*-Met was determined by titrating 50 mL of 3×10^{-4} mol/L aqueous $HClO_4$ ($I = 0.1$ mol/L, $NaClO_4$; $t = 25$ ℃) in the presence and absence of *L*-Met (1.2×10^{-3} mol/L) under N_2 with 1 mL of NaOH (0.1030 mol/L). The calculation was carried out using the difference in NaOH consumption between such a pair of titrations. The values for $K^{H}_{H(L\text{-Met})}$ and $K^{H}_{H_2(L\text{-Met})}$ were calculated with a Newton-Gauss non-linear least-squares program. The pH values of the solutions were measured with an Orion SA-720 pH meter and a Russel CE 711/LF combination pH electrode.

The stability constants $K^{Cu}_{Cu(L\text{-Met})}$ and $K^{Cu(bipy)}_{Cu(bipy)(L\text{-Met})}$ of the binary $Cu(L\text{-Met})^+$ and ternary $Cu(bipy)(L\text{-Met})^+$ complexes, respectively, were measured under the same conditions as used for the acidity constants, but $NaClO_4$ was partly replaced by $Cu(ClO_4)_2$. For the binary $Cu^{2+}/(L\text{-Met})$ system, titrations were made with $[L\text{-Met}]:[Cu^{2+}] = 1:8$. For the ternary $Cu^{2+}/bipy/(L\text{-Met})$ system, the conditions were exactly the same as for the binary one except Cu^{2+} was replaced by $Cu^{2+}/bipy$ in a 1:1 ratio. Under the condition with the lower *L*-Met concentration, *i.e.* $[L\text{-Met}]:[Cu^{2+}]:[bipy] = 1:6:6$, the $Cu(bipy)^{2+}$ complex is completely formed before the coordination of the amino acid takes place. Each final result for $K^{Cu}_{Cu(L\text{-Met})}$ and $K^{Cu(bipy)}_{Cu(bipy)(L\text{-Met})}$ is the average of at least four independent pairs of titrations.

X-*Ray structural determination*

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

Table 1 Crystallographic data of the complex $[Cu(L\text{-Met})(bipy)(H_2O)]ClO_4 \cdot 3/8H_2O$

Formula	$C_{15}H_{20.75}ClCuN_3O_{7.375}S$
M_r	492.15
Crystal size (mm)	0.40 × 0.36 × 0.30
Crystal system	Triclinic
Space group	$P1$
Unit cell dimensions	$a = 0.7656(2)$ nm, $\alpha = 97.70(3)°$
	$b = 1.3142(3)$ nm, $\beta = 97.96(3)°$
	$c = 2.0596(4)$ nm, $\gamma = 94.33(3)°$
Volume (nm^3), Z	2.0244(8), 4
D_c (g/cm^3)	1.615
μ (mm^{-1})	1.358
$F(000)$	1011
Temperature (K)	293(2)
θ rang for data collection	4.40° to 30.03°
Range of h, k, l	$-10 \leqslant h \leqslant 6$, $-16 \leqslant k \leqslant 18$, $-24 \leqslant l \leqslant 28$
Reflections collected	13000
Independent reflections	11098 ($R_{int} = 0.0192$)
Max. and min transmission	1.000, 0.723
Refined parameters	1054
Goodness of fit on F^2	0.951
Final R indices $[I > 2\sigma(I)]$	$R_1 = 0.0441$, $wR_2 = 0.1071$
R indices (all data)	$R_1 = 0.0678$, $wR_2 = 0.1183$
Mar., min. height in final ΔF map (e/nm^3)	0.519, −0.425

A well-shaped crystal sample of the complex was mounted on a Bruker Smart 1 K CCD system diffractometer with graphite monochromated Mo Kα radiation at $\lambda = 0.071073$ nm. The SMART program was applied to search for diffraction peaks to determine cell parameters. The collected data were reduced using the SAINT + program[12] and the absorption corrections were allied with the Siemens Area Detector ABSorption program(SADABS).[13] The structure was solved by direct and Fourier methods. Refinements were carried by full-matrix least squares on F^2 with positional and anisotropic thermal parameters. All parameters of atomic coordinates, anisotropic thermal parameters for non-hydrogen atoms were refined to converge. Analytical expressions of neutral-atom scattering factors were employed and anomalous dispersion corrections were incorporated. All calculations were performed on a PC computer with the Siemens *SHELXS-97*[14] and *SHELXL-97*[15] program packages.

Results and discussion

The result of elemental analyses for the complex is in good agreement with the following formula: $[\mathrm{Cu}(L\text{-Met})(\mathrm{bipy})(\mathrm{H_2O})]\mathrm{ClO_4}\cdot 3/8\mathrm{H_2O}$. The complex is soluble in water, methanol or ethanol, but not in ether and other poor polar organic solvents. Molar conductivity measurement in methanol would give credence to this idea, with the complex having 1:1 electrolyte value[16] ($\Lambda = 104\ \mathrm{S\cdot cm^2/mol}$).

Infrared absorption spectrum

The infrared spectrum of the complex exhibits two strong and wide bands at 3424 and 3319 $\mathrm{cm^{-1}}$ which are most likely ascribed to the stretching vibrations of the coordinated and crystalline water molecules. The bands at 3210, 3123 and 3031 $\mathrm{cm^{-1}}$ can be attributed to the stretching vibrations of the coordinated $\mathrm{NH_2}$ group. The absence of any band in the region of 1750—1700 $\mathrm{cm^{-1}}$ in the IR spectrum of the isolated complex suggests the coordination of the $\mathrm{COO^-}$ group of L-Met to the metal ion. The bands at 1639 and 1320 $\mathrm{cm^{-1}}$ can be attributed, respectively, to the antisymmetric and symmetric stretching vibrations of the coordinated carboxylate. The separation between the bands is consistent with the monodentate coordination of the carboxylate group.[17] Thus, one can deduce that the monovalent anion of L-Met is coordinated to the metal ion as a bidentate N, O-ligand, which agrees with the result obtained by X-ray diffraction method. The band at 1607 $\mathrm{cm^{-1}}$ is most likely assigned to the stretching vibration of the $\mathrm{C=N}$ group of the bipy ligand and confirms its coordination to the metal ion.[17]

Electronic absorption spectrum

The electronic absorption spectrum of the complex in the aqueous solution presents four important absorption bands. The bands at 221 nm [$\varepsilon = 12740$ L/(mol·cm)], 244 nm [$\varepsilon = 11680$ L/(mol·cm)] and 296 nm [$\varepsilon = 11400$ L/(mol·cm)] can be attributed to the $\pi \rightarrow \pi^*$ transitions of the coordinated bipy ligand. The broad and weak absorption band is at 671 nm [$\varepsilon = 56.3$ L/(mol·cm)] to the d $\rightarrow$ d transition of the central $\mathrm{Cu^{2+}}$ ion.

Stability of the complex in aqueous solution

The acidity dissociation constants $K^{\mathrm{H}}_{\mathrm{H_2}(L\text{-Met})}$ and $K^{\mathrm{H}}_{\mathrm{H}(L\text{-Met})}$ of L-Met were calculated using Eqs. (1) and (2), respectively. The stability constants $K^{\mathrm{Cu}}_{\mathrm{Cu}(L\text{-Met})}$ and $K^{\mathrm{Cu(bipy)}}_{\mathrm{Cu(bipy)}(L\text{-Met})}$ of the binary $\mathrm{Cu}(L\text{-Met})^+$ and ternary $\mathrm{Cu(bipy)}(L\text{-Met})^+$ complexes are defined by Eqs. (3) and (4), respectively.

$$\mathrm{H_2}(L\text{-Met})^+ = \mathrm{H^+} + \mathrm{H}(L\text{-Met})$$

$$K^{\mathrm{H}}_{\mathrm{H_2}(L\text{-Met})} = \frac{[\mathrm{H^+}][\mathrm{H}(L\text{-Met})]}{[\mathrm{H_2}(L\text{-Met})^+]} \tag{1}$$

$$\mathrm{H}(L\text{-Met}) = \mathrm{H^+} + (L\text{-Met})^-$$

$$K^{\mathrm{H}}_{\mathrm{H}(L\text{-Met})} = \frac{[\mathrm{H^+}][(L\text{-Met})^-]}{[\mathrm{H}(L\text{-Met})]} \tag{2}$$

$$\mathrm{Cu^{2+}} + (L\text{-Met})^- = \mathrm{Cu}(L\text{-Met})^+$$

$$K^{\mathrm{Cu}}_{\mathrm{Cu}(L\text{-Met})} = \frac{[\mathrm{Cu}(L\text{-Met})^+]}{[\mathrm{Cu}][(L\text{-Met})^-]} \tag{3}$$

$$\mathrm{Cu(bipy)^{2+}} + (L\text{-Met})^- = \mathrm{Cu(bipy)}(L\text{-Met})^+$$

$$K^{\mathrm{Cu(bipy)}}_{\mathrm{Cu(bipy)}(L\text{-Met})} = \frac{[\mathrm{Cu(bipy)}(L\text{-Met})^+]}{[\mathrm{Cu(bipy)^{2+}}][(L\text{-Met})^-]} \tag{4}$$

The acidity dissociation constants ($K^{\mathrm{H}}_{\mathrm{H_2}(L\text{-Met})}$, $K^{\mathrm{H}}_{\mathrm{H}(L\text{-Met})}$) of the ligand L-Met are 2.28 and 9.21 respectively, and the stability constants ($K^{\mathrm{Cu}}_{\mathrm{Cu}(L\text{-Met})}$, $K^{\mathrm{Cu(bipy)}}_{\mathrm{Cu(bipy)}(L\text{-Met})}$) for the binary $\mathrm{Cu}(L\text{-Met})^+$ and ternary $\mathrm{Cu(bipy)}(L\text{-Met})^+$ complexes are 7.98 and 7.66 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 determining the position of Eq. (5):[18]

$$\mathrm{Cu(bipy)^{2+}} + \mathrm{Cu}(L\text{-Met})^+ = \mathrm{Cu(bipy)}(L\text{-Met})^+ + \mathrm{Cu^{2+}} \tag{5}$$

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

$$10^{\Delta\log K_{\mathrm{Cu}}} = \frac{[\mathrm{Cu(bipy)}(L\text{-Met})^+][\mathrm{Cu^{2+}}]}{[\mathrm{Cu(bipy)^{2+}}][\mathrm{Cu}(L\text{-Met})^+]} \tag{6}$$

where $\Delta\log K_{\mathrm{Cu}} = K^{\mathrm{Cu(bipy)}}_{\mathrm{Cu(bipy)}(L\text{-Met})} - K^{\mathrm{Cu}}_{\mathrm{Cu}(L\text{-Met})}$ (7)

For a distorted octahedral (do) coordination sphere of

Cu^{2+}, the statistical value $\Delta\log K_{st/do} = -0.9$,[19] however, the $\Delta\log K_{Cu}$ value $(7.66 - 7.98 = -0.32)$ of the ternary complex is larger than the statistical value. The increased stability may be mainly attributed to (1) the π_A—π_B cooperative effect between the heteroaromatic *N*-base (bipy) π_A and the O donor ligand (*L*-Met) π_B, which depends on the coexistence of the π back-bond from Cu^{2+} to the heteroaromatic *N*-base ligand and pπ → dπ bond between the π-donating oxygen and Cu^{2+}; and (2) the hydrophobic interaction between the side chain of *L*-Met and one of the pyridine rings of bipy (Fig. 1),[20] which has been further confirmed by the fact that $\Delta\log K_{Cu}$ value (−0.32) of the ternary bipy-Cu(II)-*L*-Met complex is larger than that $(8.01 - 8.44 = -0.43)$ of ternary bipy-Cu(II)-*L*-alanine complex with the similar coordination geometry.

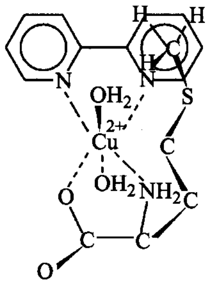

Fig. 1 A tentative structure of the ternary bipy-Cu(II)-*L*-Met complex in aqueous solution, showing the hydrophobic interaction between bipy and the side chain of *L*-Met.

Crystal structure

The selected bond lengths and angles of the complex are given in Table 2. The structure analysis indicates that the complex crystallizes in the triclinic space group *P*1 with four molecules in the unit cell, and consists of the discrete $[Cu(L\text{-Met})(bipy)(H_2O)]^+$ cations, slightly distorted perchlorate anions, and crystallization water molecules which are packed with each other by electrostatic-bonding, and hydrogen-bonding interactions (Table 3). Interestingly, the crystal of the complex contains four crystallo-graphically independent $[Cu(L\text{-Met})(bipy)(H_2O)]^+$ complexes **Cu1**, **Cu2**, **Cu3** and **Cu4** in the unit cell. Each Cu(II) ion coordinates two nitrogen atoms of bipy and the amino nitrogen and one carboxylate oxygen atoms of *L*-Met in the equatorial positions [Cu(1)—O(1) 0.1933(5), Cu(1)—N(1) 0.1988(5), Cu(1)—N(2) 0.1998(5) and Cu(1)—N(3) 0.2013(5) nm for complex **Cu1**; Cu(2)—O(3) 0.1924(4), Cu(2)—N(4) 0.1990(5), Cu(2)—N(5) 0.1999(5) and Cu(2)—N(6) 0.1993(5) nm for complex **Cu2**; Cu(3)—O(5) 0.1945(4), Cu(3)—N(7) 0.2011(5), Cu(3)—N(8) 0.1965(5) and Cu(3)—N(9) 0.1982(5) nm for complex **Cu3**; Cu(4)—O(7) 0.1938(5), Cu(4)—N(10) 0.1987(5), Cu(4)—N(11) 0.1994(5) and Cu(4)—N(12) 0.2011(5) nm for complex **Cu4**]. One water oxygen atom at an axial position [Cu(1)—O(1w) 0.2330(5) nm for complex **Cu1**, Cu(2)—O(2W) 0.2326(5) nm for complex **Cu2**, Cu(3)—O(3w) 0.2404(5) nm for complex **Cu3** and Cu(4)—O(4w) 0.2375(5) nm for complex **Cu4**]. The resulting coordination geometries are described as a distorted square-pyramidal geometry (Fig. 2). The bond angles observed around the central Cu atoms range from 81.3(2)°—100.5(2)° in the equatorial positions and from 87.54(19)°—106.81(19)° (apical positions), showing the angle variability in the geometry adopted by the five-coordinate Cu(II) complexes. The carboxyl group of the amino acid coordinates to the Cu(II) atom via one oxygen atom as an unidentate; electron delocalization was observed in the carboxyl group. In the carboxyl groups, the bond distances [0.1260(7)—0.1279(8) nm] between the coordinated oxygen atoms and the carbon atoms are slightly longer than those [0.1217(7)—0.1236(8) nm] between the uncoordinated oxygen atoms and the carbon atoms as expected. The molecular structures exhibit significant asymmetry. The aforementioned bond lengths and angles are comparable to those observed for the complex $[Cu(L\text{-Phe})(bipy)(H_2O)]ClO_4$.[4(a)]

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

Cu(1)—O(1)	0.1933(5)	Cu(3) - O(5)	0.1945(4)
Cu(1)—N(1)	0.1988(5)	Cu(3)—N(7)	0.2011(5)
Cu(1)—N(2)	0.1998(5)	Cu(3)—N(8)	0.1965(5)
Cu(1)—N(3)	0.2013(5)	Cu(3)—N(9)	0.1982(5)
Cu(1)—O(1w)	0.2330(5)	Cu(3)—O(3w)	0.2404(5)
Cu(2)—O(3)	0.1924(4)	Cu(4)—O(7)	0.1938(5)
Cu(2)—N(4)	0.1990(5)	Cu(4)—N(10)	0.1987(5)
Cu(2)—N(5)	0.1999(5)	Cu(4)—N(11)	0.1994(5)
Cu(2)—N(6)	0.1993(5)	Cu(4)—N(12)	0.2011(5)
Cu(2)—O(2w)	0.2326(5)	Cu(4)—O(4w)	0.2375(5)
O(1)-Cu(1)-N(1)	174.4(2)	O(5)-Cu(3)-N(8)	93.8(2)
O(1)-Cu(1)-N(2)	93.2(2)	O(5)-Cu(3)-N(9)	83.5(2)
N(1)-Cu(1)-N(2)	81.3(2)	N(8)-Cu(3)-N(9)	177.0(2)

Continued

O(1)-Cu(1)-N(3)	84.1(2)	O(5)-Cu(3)-N(7)	164.1(2)
N(1)-Cu(1)-N(3)	100.5(2)	N(8)-Cu(3)-N(7)	82.3(2)
N(2)-Cu(1)-N(3)	159.1(2)	N(9)-Cu(3)-N(7)	100.0(2)
O(1)-Cu(1)-O(1w)	94.16(19)	O(5)-Cu(3)-O(3w)	95.3(2)
N(1)-Cu(1)-O(1w)	87.54(19)	N (8)-Cu(3)-O(3w)	91.03(19)
N(2)-Cu(1)-O(1w)	94.08(19)	N(9)-Cu(3)-O(3w)	90.5(2)
N(3)-Cu(1)-O(1w)	106.81(19)	N(7)-Cu(3)-O(3w)	100.1(2)
O(3)-Cu(2)-N(4)	92.5(2)	O(7)-Cu(4)-N(12)	84.9(2)
O(3)-Cu(2)-N(6)	84.00(19)	O(7)-Cu(4)-N(10)	93.78(19)
N(4)-Cu(2)-N(6)	167.0(2)	N(12)-Cu(4)-N(10)	176.7(2)
O(3)-Cu(2)-N(5)	170.4(2)	O(7)-Cu(4)-N(11)	168.6(2)
N(4)-Cu(2)-N(5)	82.0(2)	N(12)-Cu(4)-N(11)	99.7(2)
N(6)-Cu(2)-N(5)	99.6(2)	N(10)-Cu(4)-N(11)	81.0(2)
O(3)-Cu(2)-O(2w)	97.2(2)	O(7)-Cu(4)-O(4w)	92.9(2)
N(4)-Cu(2)-O(2w)	92.6(2)	N(12)-Cu(4)-O(4w)	92.4(2)
N(6)-Cu(2)-O(2w)	100.2(2)	N(10)-Cu(4)-O(4w)	90.7(2)
N(5)-Cu(2)-O(2w)	91.0(2)	N(11)-Cu(4)-O(4w)	97.3(2)

Table 3 Hydrogen bonding and aromatic-ring stacking interaction (nm)

O(1w)···O(10)	0.3045(10)	N(6)···O(13)	0.2987(8)
O(2w)···O(16)	0.2941(10)	O(2)···O(2w)	0.2827(7)
O(3w)···O(8b)	0.2787(7)	N(12)···O(5w)	0.3065(9)
O(3w)···O(24b)	0.2970(2)	O(4)···O(1w)	0.2706(7)
O(3w)···O(22'b)	0.3020(2)	N(9)···O(6wb)	0.2856(12)
O(4w)···O(6c)	0.2803(7)	N(3)···O(9)	0.3024(7)
O(4w)···O(5w)	0.3054(11)	bipy···bipy	0.351
N(6)···O(14a)	0.2957(11)		

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

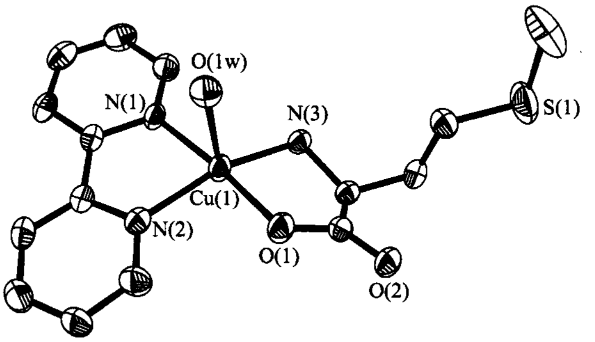

Fig. 2 Structure of one of four crystallographically independent molecules of [Cu(*L*-Met)(bipy)(H_2O)]$^+$. The perchlorate ion, crystallization water molecule and hydrogen atoms were omitted for clarity.

Although the four complex units are similar, a number of differences can be found on closer inspection. The notable one is that, if the difference of bond lengths and angles is omitted, complexes **Cu1** and **Cu3** are essentially enantiomers of complexes **Cu2** and **Cu4**. Furthermore, the complexes are packed with each other by intermolecular hydrogen bonding [O(2)···O(2w) 0.2827(7) nm, O(3w)···O(8b) 0.2787(7) nm, O(4w)···O(6c) 0.2803(7) nm, O(4)···O(1w) 0.2706(7) nm, N(9)···O(6wb) 0.2856(12) nm] and aromatic-ring stacking interaction (the average distance between two neighboring bipyridyl rings 0.351 nm), forming a superamolecular configuration (Fig. 3). It may be concluded that no intramolecular hydrophobic interaction between the aromatic-ring of bipy and the side chain of *L*-Met in the crystal existed as in the aqueous solutioin.

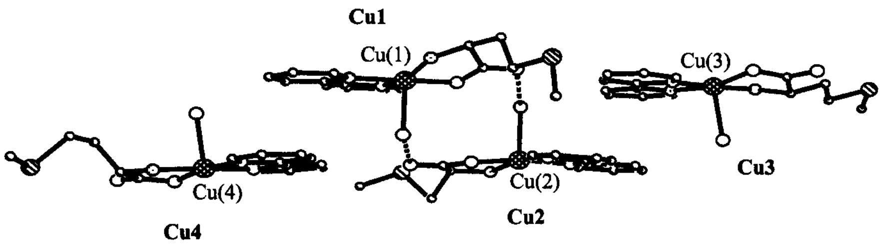

Fig. 3 Stereoscopic packing between four crystallographically independent molecules of [Cu(*L*-Met)(bipy)(H_2O)]$^+$ with **Cu1**, **Cu2**, **Cu3** and **Cu4** forms.

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