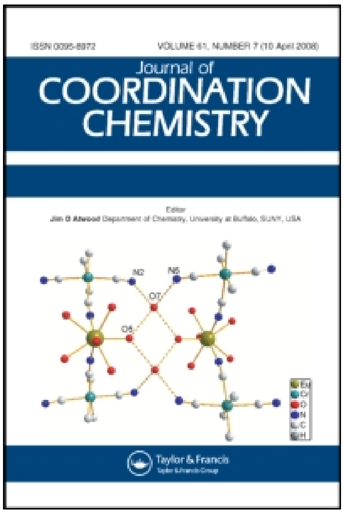

Journal of Coordination Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713455674

Crystal structure and spectroscopic properties of a new *syn-anti* carboxylate-bridged polymeric chain copper(II)-glycylglycine complex

Wen-Long Liu[a]; Yang Zou[a]; Chun-Lin Ni[a]; Zhao-Ping Ni[a]; Yi-Zhi Li[a]; Qing-Jin[a]
[a] State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute, Nanjing University, Nanjing, P.R. China

To cite this Article Liu, Wen-Long , Zou, Yang , Ni, Chun-Lin , Ni, Zhao-Ping , Li, Yi-Zhi and Qing-Jin(2004) 'Crystal structure and spectroscopic properties of a new *syn-anti* carboxylate-bridged polymeric chain copper(II)-glycylglycine complex', Journal of Coordination Chemistry, 57: 8, 657 — 664

To link to this Article: DOI: 10.1080/00958970410001704582

URL: http://dx.doi.org/10.1080/00958970410001704582

J. Coord. Chem., Vol. 57, No. 8, 20 May 2004, pp. 657–664

CRYSTAL STRUCTURE AND SPECTROSCOPIC PROPERTIES OF A NEW *SYN-ANTI* CARBOXYLATE-BRIDGED POLYMERIC CHAIN COPPER(II)–GLYCYLGLYCINE COMPLEX

WEN-LONG LIU*, YANG ZOU, CHUN-LIN NI, ZHAO-PING NI,
YI-ZHI LI and QING-JIN MENG[†]

*State Key Laboratory of Coordination Chemistry, Coordination Chemistry Institute,
Nanjing University, Nanjing, 210093, P.R. China*

(Received 04 November 2003; Revised 27 January 2004; In final form 01 April 2004)

A new polymer complex of copper(II)–glycylglycine $\{[Cu(glygly)(H_2O)][Cu(glygly)(H_2O)_2]\}_n \cdot 5nH_2O$ (**1**) is reported. It crystallizes in the $P2_1/c$ space group, with $a = 14.669(2)$, $b = 9.8480(10)$, $c = 14.053(2)$ Å, $\beta = 102.730(10)^\circ$ and $Z = 4$. Compound **1** consists of $[Cu(glygly)(H_2O)]_n$ 1D carboxylate-bridged polymeric chains, monomer $Cu(glygly)(H_2O)_2$ molecules which form hydrogen-bonded chains and uncoordinated water molecules. In all cases, the geometry around copper(II) is a slightly distorted square pyramid with the water oxygen at the apex of the pyramid. The ESR, UV-Vis and IR spectroscopy of the compound were also studied.

Keywords: Copper(II) dipeptide complex; Carboxylate bridge; Crystal structure; Spectroscopic properties

INTRODUCTION

Transition metals are involved in many biological processes which are essential to life. The metals can coordinated to O– or N– terminals from proteins in a variety of models, and play a crucial role in the conformation and function of biological macromolecules [1–7]. For mimicking the metal environment in proteins, the study of amino acid and peptide complexes containing transition metal ions are, obviously, very important [8–12]. Recently special attention has been given to Cu(II) with studies of copper small polypeptide complexes, including monohydrate, dihydrate and trihydrate complexes of Cu(II) with the simplest ‘‘poly’’ peptide [13–20].

In this article we present the novel structure and spectroscopic analysis of the copper(II)–glycylglycine complex $\{[Cu(glygly)(H_2O)][Cu(glygly)(H_2O)_2]\}_n \cdot 5nH_2O$ (**1**).

---

*E-mail: njulwl@vip.sina.com

[†]Corresponding author. Tel.: +86-25-3597266. Fax: +86-25-3314502. E-mail: mengqj@netra.nju.edu.cn

ISSN 0095-8972 print: ISSN 1029-0389 online
DOI: 10.1080/00958970410001704582

EXPERIMENTAL

The dipeptide, glycylglycine(glygly) was purchased from Sigma and used as received. All other reagents and solvents were analytical grade, purchased from commercial sources.

Synthesis and Crystallization

Several water solutions of glycylglycine and $Cu(ClO_4)_2 \cdot 6H_2O$ with stoichiometries ligand : metal 1 : 1 and at different pH values were prepared. Blue prismatic crystals of the compound were obtained from the pH 7.5 solution after a few weeks of slow evaporation at room temperature. The composition of the complexes was confirmed by elemental analysis. Yield: *ca.* 35%. Anal. Calcd. for $C_8H_{28}N_4O_{14}Cu_2$ (%): C, 18.08; H, 5.31; N, 10.54. Found: C, 17.88; H, 5.41; N, 10.36.

Physical Measurements

The IR spectra of KBr discs were recorded on a Bruker Vector22 spectrophotometer in the 400–4000 cm^{-1} regions. The UV-Vis spectra were performed by Shimadzu UV-3100 spectrophotometer. Elemental analyses (H, C, N) were carried out using a Perkin-Elmer 240C elemental analysis instrument. ESR spectra were obtained on a Bruker JES-FEIXG spectrometer with X-band.

X-ray Crystallography

The diffraction experiments were carried out on a Bruker AXS SMART APEX CCD diffractometer. Data were collected with graphite–monochromated Mo–K_α radiation ($\lambda = 0.71073$ Å) using SMART and SAINT programs [21]. Absorption corrections were calculated and applied for each structure by using SADABS [22]. The structures were solved by direct methods and nonhydrogen atoms were anisotropically refined by full-matrix least-squares based on F^2 using SHELXTL [23]. All hydrogen atoms were included in the refinement in calculated positions riding on their carrier atoms. The hydrogen thermal displacement parameters were fixed at 1.2 and 1.5 times the equivalent isotropic thermal displacement parameters of their internal and terminal carrier atoms, respectively. A summary of the data collection and structure refinement is listed in Table I.

RESULTS AND DISCUSSION

Description of Structure

The unit cell of Compound **1** consists of carboxylate-bridged coordination polymeric chains $[Cu(glygly)(H_2O)]_n$, monomer $Cu(glygly)(H_2O)_2$ molecules which form hydrogen-bonded chains and uncoordinated water molecules. Its ORTEP view is shown in Fig. 1. Table II summarizes the selected bond distances and angles of the complex, sequenced in order of the τ values, where $\tau = (\alpha_8 - \alpha_1)/60$ [24].

TABLE I Crystal data and structure refinement for $\{[Cu(glygly)(H_2O)][Cu(glygly)(H_2O)_2]\}_n \cdot 5nH_2O$ (**1**)

Empirical formula	$C_8H_{28}N_4O_{14}Cu_2$
Formula weight	531.44
Crystal system	Monoclinic
Space group	$P2_1/c$
a (Å)	14.669(2)
b (Å)	9.848(1)
c (Å)	14.053(2)
β (°)	102.73(1)
V (Å^3)	1980.2(4)
Z	4
D_{calc} (g cm^{-3})	1.783
μ (Mo $K\alpha$) (mm^{-1})	2.223
T (K)	293(2)
F(000)	1096.0
Crystal size (mm^3)	0.55 × 0.40 × 0.30
θ range for data collection	2.51 to 25.0
Index ranges	$-17 \le h \le 17$, $-5 \le k \le 11$, $-16 \le l \le 16$
Reflections collected	3410
Independent reflections	2538
Refinement method	Full-matrix least-squares on F^2
Data/restraints/parameters	2538/0/253
R_{int}	0.0541
R [$I > 2\sigma(I)$]	0.0421
Rw	0.1008
Goodness-of-fit on F^2	1.013
Largest difference: peak and hole (e Å^{-3})	0.919 to −0.753

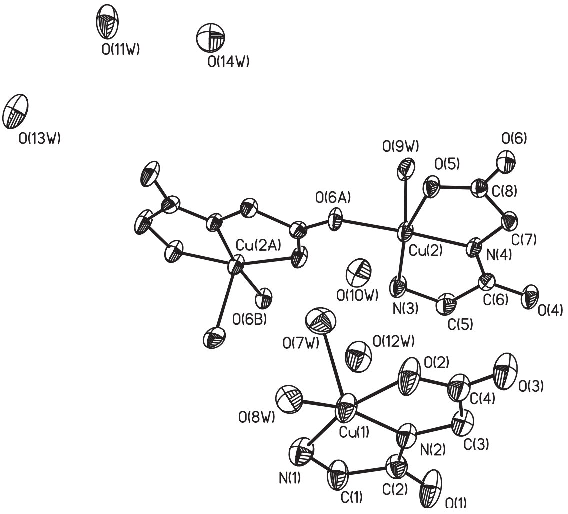

FIGURE 1 ORTEP view of Compound **1**, with hydrogen atoms omitted for clarity, showing the labeling and the 50% probability thermal ellipsoids.

In the $[Cu(glygly)(OH_2)]_n$ coordination polymeric chains, Cu(II) is at the center of a square base center of an elongated square–pyramid. Three of the basal coordination sites of Cu(II) are occupied by the terminal amino nitrogen (Cu(2)–N(3), 1.90 Å), the deprotonated peptide nitrogen (Cu(2)–N(4), 2.00 Å) and one of the carboxylate oxygens

TABLE II Selected bond lengths (Å) and angles (°) for **1**

Bond lengths				
Cu(1)–N(1)	2.012(4)	Cu(2)–N(3)	1.996(3)	
Cu(1)–N(2)	1.899(3)	Cu(2)–N(4)	1.900(3)	
Cu(1)–O(2)	1.980(3)	Cu(2)–O(5)	2.040(3)	
Cu(1)–O(7W)	2.315(3)	Cu(2)–O(9W)	2.379(3)	
Cu(1)–O(8W)	1.986(3)	Cu(2)–O(6a)	1.947(3)	
Bond angles				
α_1	O(8W)–Cu(1)–N(2)	159.79(12)	O(5)–Cu(2)–N(3)	161.89(12)
α_2	O(7W)–Cu(1)–N(2)	110.42(12)	O(9W)–Cu(2)–N(3)	96.92(14)
α_3	O(7W)–Cu(1)–O(8W)	88.87(11)	O(5)–Cu(2)–O(9W)	94.74(11)
α_4	O(2)–Cu(1)–N(2)	82.55(12)	N(3)–Cu(2)–N(4)	83.54(12)
α_5	N(1)–Cu(1)–N(2)	83.23(13)	O(6a)–Cu(2)–N(3)	99.45(12)
α_6	O(8W)–Cu(1)–N(1)	100.83(14)	O(5)–Cu(2)–N(4)	81.44(12)
α_7	O(2)–Cu(1)–O(7W)	92.52(11)	O(6a)–Cu(2)–O(9W)	91.19(11)
α_8	O(2)–Cu(1)–N(1)	164.95(12)	O(6a)–Cu(2)–N(4)	171.47(13)
α_9	O(2)–Cu(1)–O(8W)	90.93(12)	O(5)–Cu(2)–O(6a)	94.09(11)
α_{10}	O(7W)–Cu(1)–N(1)	97.03(13)	O(9W)–Cu(2)–N(4)	96.39(11)
	$\tau = (\alpha_8 - \alpha_1)/60$	0.086		0.160

Symmetry transformations used to generate equivalent atoms: (a) $-x+1, y+1/2, -z+1/2$; (b) $-x+1, y-1/2, -z+1/2$.

(Cu(2)–O(5), 2.04 Å) of the ligand and the fourth by the second carboxylate oxygen atom (Cu(2)–O(6A), 1.95 Å) of an adjacent glygly dianion. In the axial coordination position lies the oxygen O(9W) of water (Cu(2)–O(9W), 2.38 Å). Closer inspection of the data in Table II, shows the penta-coordinate Cu in the coordination polymeric chains a trigonal bipyramidally distorted, square-based pyramidal (TBDSBP) stereochemistry ($\tau = 0.160$), where $\tau = (\alpha_8 - \alpha_1)/60$, $\tau = 1.0$ for the regular trigonal bipyramidal (RTB) and $\tau = 0.0$ for a regular square-based pyramid (RSBP). Bond angles in the square plane vary from 81.44(12) to 99.45(12)°. The metal lies 0.13 Å out of the least-squares basal plane, towards O(9W). The axial Cu–O(9W) bond is longer by 0.34–0.43 Å than the Cu–O bond lengths in the basal plane. The two individually almost planar chelating rings Cu(2)N(3)C(5)C(6)N(4) and Cu(2)N(4)C(7)C(8)O(5) are slightly twisted out of coplanarity; the dihedral angle between their least-squares planes is 5.2°. The molecular geometry is close to that predicted for $\mathrm{M(tridentate)(unidentate)_2}$ systems by simple donor atom repulsion theory [25], and is similar to that of $\mathrm{Cu(glygly)(OH_2)_2 \cdot H_2O}$ with the same coordinated glygly ligand [20].

Neighboring copper ions in the polymer are linked through terminal carboxylate oxygen atoms of glygly ligand and form a $\cdots$Cu$\cdots$O–Cu–O$\cdots$Cu$\cdots$ zigzag *syn-anti* conformational chain (Fig. 2(a)). The closest Cu$\cdots$Cu distances in this polymeric chain are 5.310 Å. The polymeric chain is additionally stabilized by the presence of hydrogen bonds involving the amino group and carboxylate oxygen O(6A) and lattice water molecule O(10W) [N(3)–H(3B)$\cdots$O(10W) = 3.037 Å; O(10W)–H(10B)$\cdots$O(6A) = 2.887 Å] (see Table III).

The coordination environment of Cu(II) in the monomer $\mathrm{Cu(glygly)(H_2O)_2}$ is similar to that of the polymeric chain. The copper ions are five-coordinate with three donor atoms of the deprotonated tridentate glygly (N(1), N(2) and O(2)) and two oxygens (O(7W) and O(8W)) of aqua ligands (Fig. 1). Water molecule O(7W) has a much larger Cu–O distance than O(8W) (Cu(1)–O(7W) 2.32 Å and Cu(1)–O(8W) 1.99 Å). The Cu(1)–O(8W) is much closer to the glygly donor oxygen value (Cu(1)–O(2), 1.98 Å). Roughly, O(8W) and the three donor atoms (N(1), N(2) and O(2)) of the

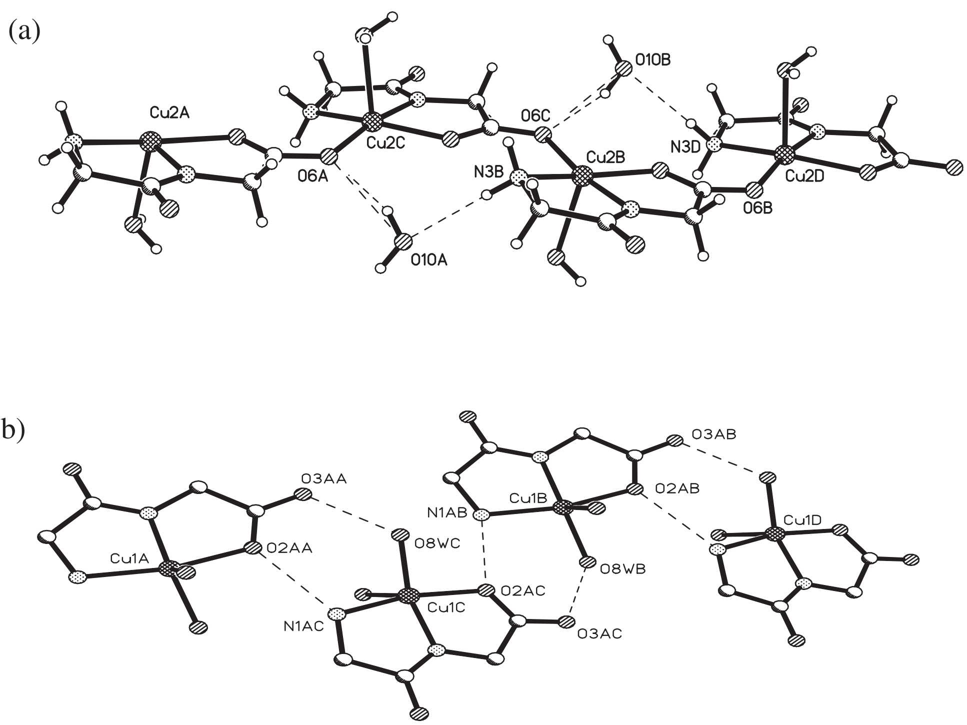

FIGURE 2 A portion of the crystal packing: (a) showing a carboxylate-bridged polymeric chain along the *b*-axis; (b) showing a hydrogen-bonded chain along the *b*-axis (without hydrogen atoms).

TABLE III Selected H-bond distances (Å) and angles (°) for **1**

D–$H\cdots A$	$d(D–H)$ (Å)	$d(H\cdots A)$ (Å)	$\alpha(D–H\cdots A)$ (°)	$d(D\cdots A)$ (Å)	*Symmetry operation*
N(1)–H(1A)···O(13W)	0.900	2.159	166.91	3.043	$-x+2,\ -y+1,\ -z+1$
N(1)–H(1B)···O(2)	0.900	2.356	124.37	2.959	$-x+2,\ y-1/2,\ -z+1/2$
N(1)–H(1B)···O(8W)	0.900	2.390	142.47	3.152	$-x+2,\ y-1/2,\ -z+1/2$
N(3)–H(3A)···O(12W)	0.900	2.169	151.41	2.990	
N(3)–H(3B)···O(10W)	0.900	2.182	158.36	3.037	
O(7W)–H(7C)···O(1)	0.850	2.171	125.95	2.758	$x,\ -y+3/2,\ z+1/2$
O(7W)–H(7D)···O(13W)	0.850	2.269	116.15	2.751	$x,\ -y+3/2,\ z-1/2$
O(8W)–H(8A)···O(14W)	0.850	1.864	163.04	2.689	$-x+2,\ -y+2,\ -z+1$
O(8W)–H(8B)···O(3)	0.850	1.864	151.81	2.644	$-x+2,\ y-1/2,\ -z+1/2$
O(8W)–H(8B)···O(2)	0.850	2.571	150.78	3.339	$-x+2,\ y-1/2,\ -z+1/2$
O(9W)–H(9B)···O(4)	0.850	2.028	133.64	2.686	$x,\ -y+3/2,\ z+1/2$
O(9W)–H(9A)···O(14W)	0.853	2.115	139.14	2.816	$-x+1,\ -y+2,\ -z+1$
O(10W)–H(10A)···O(1)	0.850	2.223	169.54	3.063	$-x+1,\ -y+1,\ -z$
O(10W)–H(10B)···O(6)	0.850	2.071	160.58	2.887	$x,\ y-1,\ z$
O(11W)–H(11B)···O(7W)	0.850	2.082	149.48	2.847	$-x+1,\ -y+1,\ -z+1$
O(11W)–H(11A)···O(4)	0.850	1.909	148.13	2.669	$x,\ y-1,\ z+1$
O(12W)–H(12B)···O(11W)	0.850	2.124	117.92	2.631	$-x+1,\ -y+1,\ -z+1$
O(12W)–H(12A)···O(11W)	1.004	1.692	153.76	2.631	$-x+1,\ -y+1,\ -z+1$
O(13W)–H(13B)···O(9W)	0.850	2.344	112.77	2.785	$-x+1,\ -y+1,\ -z+1$
O(13W)–H(13A)···O(3)	0.850	2.182	120.76	2.717	$x,\ y-1,\ z+1$
O(14W)–H(14A)···O(1)	0.850	2.063	134.84	2.730	$x,\ y,\ z+1$
O(14W)–H(14B)···O(12W)	0.850	2.049	140.12	2.756	$x,\ -y+3/2,\ z+1/2$

glygly form a slightly distorted square plane in which the bond angles vary from 82.55(12) to 100.83(14)°, the Cu atom lies 0.18 Å above the plane, with the O(7W) water molecule approximately in the apical position of a square pyramid ($\tau = 0.089$). Two carboxylate oxygen atoms O(2) and O(3) of monomer are connected to the amino nitrogen N*(1) and the aqua oxygen O*(8W) of an adjacent molecule via hydrogen bonds (N(1)–H(1B) $\cdots$ O(2), 2.959 Å; O(8W)–H(8B) $\cdots$ O(3), 2.644 Å), as shown in Fig. 2(b), and form a zigzag *syn-anti* hydrogen-bonded chain along the *b*-axis. The distance between two closest Cu(II) ions in this chain is 5.418 Å.

The hydrogen-bonding interactions (Table III) involving the water molecules, the carboxylate oxygen atoms and the carbonyl oxygen atoms play an important role in stabilization of the whole crystal structure by holding together the polymeric chains, hydrogen-bonded chains and water molecules together forming a three-dimensional network structure (Fig. 3).

Infrared Spectra

In the IR spectra, the compound has a broad absorption at 3330 cm^{-1}, corresponding to the presence of water ν(OH) and the antisymmetric and symmetric –NH_2 stretching modes. The $\nu(NH_2)$ bands are in agreement with the terminal amino group of glycylglycine dianion occupying one coordination site of the metal ion [26]. The strong typical band at 1611 cm^{-1}, so-called amide band which is essentially related to the C=O stretching of the carbonyl group of the amide linkage, is clearly displaced to lower energy after coordination, in agreement with its participation in N-bonding [26]. The strong bands at 1573 and 1407 cm^{-1} are assigned as the ν_{as}(COO) and ν_s(COO), respectively, for the bridging mode of carboxylate ligation [27].

Electronic Spectra

The *d–d* transition spectra in MeOH of the complex have a broad band centered at about 633 nm, suggestive of approximately square–pyramidal geometry with mixed O, N-ligation at Cu(II) as observed in other Cu(II) peptides complexes [17,18,26]. The intense absorption at 231 nm can be assigned to a $N^- \rightarrow$ Cu(II) ligand-to-metal

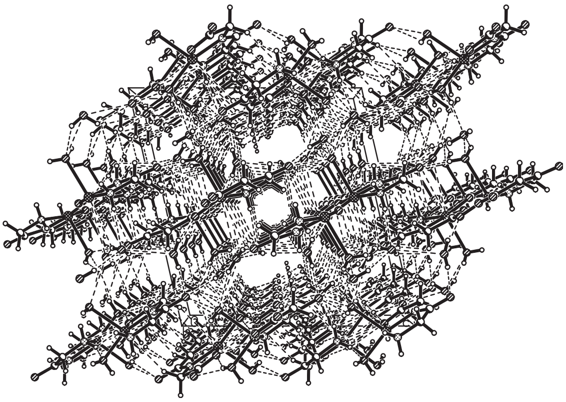

FIGURE 3 A view of the packing of $\{[Cu(glygly)(H_2O)][Cu(glygly)(H_2O)_2]\}_n \cdot 5nH_2O$ along the *b*-axis, showing a three-dimensional network structure.

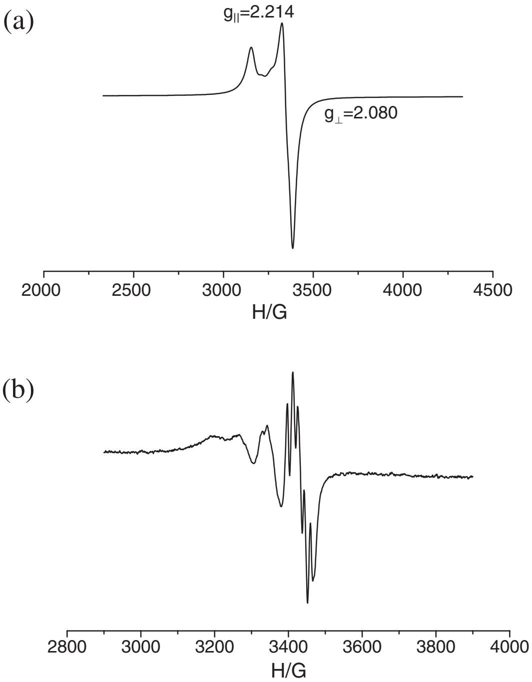

FIGURE 4 (a) X-band ESR spectra for Compound **1** polycrystalline powder at 298 K; (b) experimental ESR spectra for Compound **1** in MeOH at room temperature.

charge transfer (LMCT) transition [26,28]. A band at 278 nm is tentatively assigned to a $COO^- \rightarrow Cu(II)$ charge-transfer transition [26].

ESR Spectra

The X-band ESR spectra of a polycrystalline powder of the complex recorded at room temperature (frequency = 9.7750 GHz, power = 19.920 mW, modulation amplitude = 4.00 G) shows no hyperfine splitting with the values: $g_{\parallel} = 2.214$, and $g_{\perp} = 2.080$ (Fig. 4(a)). These spectra are consistent with a square pyramidal stereochemistry. The values of $g_{\parallel} > g_{\perp} > g_e$ imply that the 3*d* unpaired electron of the copper(II) ion occupy the d_{x2-y2} orbital. The $g_{\parallel} < 2.3$ of the complex indicates a fair degree of covalent character in the Cu–L bonding. ESR experimental spectra at room temperature in MeOH exhibit a line-shape with five nitrogen superhyperfine (shf) structure indicating ligation of two nitrogen atoms to the metal ion (Fig. 4(b)). These results are in agreement with the symmetry around copper derived from the X-ray structure determination.

Acknowledgments

This work was supported financially by the National Natural Science Foundation of China (No. 20171022), the Science & Technology Department of Jiangsu Province and the Center of Materials Analysis of Nanjing University.

Supplementary Materials

Crystallographic data for the structure reported in this article has been deposited at the Cambridge Crystallographic Data Center as supplementary publication; CCDC reference number 218113 for Compound **1**. Copies of this information can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge, CB2 1EZ, UK (Fax: +44-1223-336-033; E-mail: deposit@ccdc.cam.ac.uk or www: http://www.ccdc.cam.ac.uk).

References

[1] G.A. Jeffrey and W. Saenger, Hydrongen Bonding in Biological Structures (Springer, Berlin, 1991).
[2] G.A. Jeffery, An Introduction to Hydrogen Bonding (Oxford University Press, New York, 1997).
[3] E. Colacio, M. Ghazi, R. Kivekäs and J.M. Moreno, *Inorg. Chem.* **39**, 2882 (2000).
[4] A.C. Rizzi, O.E. Piro, E.E. Castellano, O.R. Nascimento and C.D. Brondino, *Inorg. Chim. Acta* **305**, 19 (2000).
[5] W.D. Morgan, B. Birdsall, P.M. Nieto, A.R. Gargaro and J. Feeney, *Biochemistry* **38**, 2127 (1999).
[6] K. Pervushin, M. Billeter, G. Siegal and K. Wüthrich, *J. Mol. Biol.* **264**, 1002 (1996).
[7] A. Karaliota, O. Kretsi and C. Tzougraki, *J. Inorg. Biochem.* **84**, 33 (2001).
[8] H.C. Freeman, In: G.L. Eichhorn (Ed.), Inorganic Biochemistry (Elsevier, Amsterdam, 1975), pp. 121–166.
[9] A.S. Brill, Transition Metals in Biochemistry (Springer Verlag, Berlin, 1977).
[10] R. Österberg, *Coord. Chem. Rev.* **12**, 309 (1974).
[11] N.V. Nagy, T. Szabo-Planka, A. Rockenbauer, G. Peintler, I. Nagypal and L. Korecz, *J. Am. Chem. Soc.* **125**, 5227 (2003).
[12] A.J. Tasiopoulos, E.J. Tolis, J.M. Tsangaris, A. Evangelou, J.D. Woollins, A.M.Z. Slawin, J.C. Pessoa, I. Correia and T.A. Kabanos, *J. Biol. Inorg. Chem.* **7**, 363 (2002).
[13] B. Radomska, T. Głowiak and M. Kubiak, *J. Mol. Struct.* **323**, 169 (1994).
[14] W.J. Puspita, A. Odani and O. Yamauchi, *J. Inorg. Biochem.* **73**, 203 (1999).
[15] O.R. Nascimento, A.J. Costa-Filho, D.I. De Morais, J. Ellena and L.F. Delboni, *Inorg. Chim. Acta* **312**, 133 (2000).
[16] M. Tiliakos, D. Raptis, A. Terzis, C.P. Raptopoulou, P. Cordopatis and E. Manessi-Zoupa, *Polyhedron* **21**, 229 (2002).
[17] G. Facchin, M.H. Torre, E. Kremer, O.E. Piro, E.E. Castellano and E.J. Baran, *J. Inorg. Biochem.* **89**, 174 (2002)
[18] M. Tiliakos, E. Katsoulakou, V. Nastopoulos, A. Terzis, C. Raptopoulou, P. Cordopatis and E. Manessi-Zoupa, *J. Inorg. Biochem.* **93**, 109 (2003).
[19] G. Facchin, M.H. Torre, E. Kremer, O.E. Piro and E.E. Castellano and E.J. Baran, *Z. Naturforsch.* **55b**, 1157 (2000).
[20] I. Bytheway, B.N. Figgis and A.N. Sobolev, *J. Chem. Soc., Dalton Trans.* 3285 (2001).
[21] SMART & SAINT Software Reference manuals, Version 6.22 (Bruker AXS Inc., Madision, WI, 2000).
[22] G.M. Sheldrick, SADABS software for empirical absorption correction (University of Gottingen, Germary, 1996).
[23] SHELXTL Reference manuals, Version 6.10 (Bruker AXS Inc., Madision, WI, 2000).
[24] A.W. Addison, T.N. Rao, J. Reedijk, J. van Rijn and G.C. Verschoor, *J. Chem. Soc., Dalton Trans.* 1349 (1984).
[25] D.L. Kepert, Inorganic Stereochemistry (Springer-Verlag, Berlin, 1982), pp. 65–69.
[26] J. Dehand, J. Jordanov, F. Keck, A. Mosset, J.J. Bonnet and J. Galy, *Inorg. Chem.* **18**, 1543 (1979).
[27] G.B. Deacon and R.J. Phillips, *Coord. Chem. Rev.* **33**, 227 (1980).
[28] H. Sigel and R.B. Martin, *Chem. Rev.* **82**, 385 (1982).