



One-Dimensional Azido-bridged Copper(II) Coordination Polymer with Taurine Schiff Base: Syntheses, Structure and IR Spectrum Studies

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The azido-bridged copper(II) complex with composition $[\text{Cu}(\text{pmt})(\text{N}_3)]_n$ [pmtH = *N*-(2-pyridylmethylidene)taurine] has been synthesized and characterized by elemental analysis, IR and single-crystal X-ray diffraction. The crystal of the present complex crystallizes in a monoclinic system, space group $\text{P2}_1/\text{c}$, with $a = 7.8108(10)$, $b = 18.1233(19)$, $c = 8.2006(10)$ Å, $\beta = 94.976(6)^\circ$, $V = 1156.5(2)$ Å³, $M_r = 318.80$, $D_c = 1.831$ g/cm³, $\mu = 2.077$ mm⁻¹, $F(000) = 644$, $Z = 4$, the final $R = 0.0506$ and $wR = 0.1059$ for 2147 observed reflections with $I > 2\sigma(I)$. Each Cu(II) atom is six-coordinated to two oxygen and four N atoms with a distorted 4+2 octahedral geometry. The two kinds of cycles with sharing Cu apex are alternately created and interconnected to an interesting 1-D zigzag chain propagating along the c axis. Also, the significant weak C-H...N hydrogen bond and π - π stacking interactions between the adjacent chains expanded the 1-D structure to 2-D network in the bc plane and stabilize the packing.

Key Words: Copper coordination polymer, Taurine, Schiff base, Azide-bridged, Crystal structure.

INTRODUCTION

The Schiff base complexes containing both sulfur and amino acid functionalities have aroused considerable recent interest due to their biological activities¹⁻⁴. Taurine, known as 2-aminoethanesulfonic acid, is indispensable to human life and plays a significant part in physiological functions. Recently, we reported many compounds originating from taurine salicylaldehyde Schiff base ligand, which are widely used in the assembly of one-, two- and three dimensional arrangements in view of the diverse coordination modes and bridging ability⁵⁻⁹. *N*-(2-Pyridylmethylidene)taurine (PmtH), as a multidentate ligand with five coordination sites, might be utilized as a versatile linker in the construction of interesting multi-dimensional complexes with the capability of participating in hydrogen bonding with multi-proton acceptor or donor sites, which is a candidate for construction of multi-dimensional complexes. Herein, we present a new Cu(II) 1-D coordination polymer with a Schiff base derived from the condensation of taurine and 2-pyridinecarboxaldehyde, which is synthesized in methanol-water with the physical pH value.

EXPERIMENTAL

Solvents and chemicals obtained from commercial sources were of reagent grade and used without further purification. IR spectra were taken on a Pekin-Elmer spectrum one FT-IR

spectrometer with KBr pallets in the range of 4000-400 cm⁻¹. The elemental analyses for C, H, N and S were performed on a Perkin-Elmer 2400C elemental analyzer. The crystal structure was determined by a Bruker CCD area detector.

Synthesis of the ligand pmtK: 2-Pyridinecarboxaldehyde (1.07 g, 10 mmol) in MeOH (20 mL) was added to a solution of 2-aminoethanesulfonic acid (1.25 g, 10 mmol) in MeOH (30 mL) containing KOH (0.56 g, 10 mmol). The mixture was stirred and refluxed at 323 K for 2 h and then cooled to room temperature to give a yellow precipitate, which was collected by filtration, recrystallized from anhydrous methanol, washed successively with anhydrous methanol and ether and dried *in vacuo*. Yield 2.02 g (80 %, based on 2-pyridinecarboxaldehyde). Anal. calcd. (%) for C₈H₉KN₂O₃S: C, 31.09; H, 3.27; N, 12.14; S, 12.56. Found (%): C, 30.09; H, 3.57; N, 11.11; S, 12.70. IR (KBr, ν_{max} , cm⁻¹) 1648, 1583 ($\nu_{\text{C}=\text{N}}$ + $\nu_{\text{C}=\text{C}}$); 1241, 1189, 1053 ($\nu_{\text{SO}_3^{2-}}$).

Synthesis of the title complex [Cu(pmt)(N₃)_n]: The potassium salt of Schiff base ligand *N*-(2-pyridylmethylidene)taurine, L(pmtK) (1.0 mmol) in methanol (10 mL) was added dropwise to a stirred solution of CuCl₂·2H₂O (1.0 mmol) in methanol and water (1:1 v/v, 10 mL). Then to this mixture, a solution of sodium azide (2.0 mmol) in water and methanol (1:1 v/v, 4 mL) was added slowly. The resulting blue solution was filtered and allowed to stand for 2 weeks to evaporate slowly at room temperature, giving blue prism-shaped single

crystals suitable for X-ray diffraction in yield of 60 %. Anal. calcd. (%) for $C_8H_9CuN_5O_3S$: C, 30.14; H, 2.83; N, 21.98; S, 10.05. Found (%): C, 30.97; H, 2.98; N, 21.01; S, 9.56. IR (KBr, ν_{max} , cm^{-1}) 2048 (ν_{N_3}); 1653, 1602 ($\nu_{C=N} + \nu_{C=C}$); 1208, 1179, 1150, 1055 ($\nu_{SO_3^{2-}}$).

Single crystal structure determination: A blue-prism single crystal of $[Cu(pmt)(N_3)]_n$ with dimensions of 0.30 mm \times 0.15 mm \times 0.12 mm was used for structure determination. Data were collected at 295 (2) K on a Bruker SMART CCD area detector diffractometer equipped with a graphite-monochromatic MoK_{α} ($\lambda = 0.71073 \text{ \AA}$) radiation by using a multi-scan mode. In the range of $3.36 = \theta = 27.48^\circ$, a total of 8850 reflections together with 2628 unique ones ($R_{int} = 0.0413$) were collected, of which 2147 were observed with $I > 2\sigma(I)$ and used in the succeeding structural calculations.

The structure was solved by direct methods¹⁰ and refined by full-matrix least-squares on F^2 using SHELXL-97 program package¹¹. Absorption corrections were applied using the SADABS program¹². All non-hydrogen atoms were assigned anisotropically. The hydrogen atoms were generated theoretically and treated by a mixture of independent and constrained refinement. The final cycle of refinement converged at $R = 0.0506$, $wR = 0.1059$ ($w = 1/[\sigma^2(F_o^2) + (0.0502P)^2 + 0.6394P]$, where $P = (F_o^2 + 2F_c^2)/3$), $S = 1.118$, $(\Delta/\sigma)_{max} = 0.000$, $(\Delta\rho)_{max} = 0.466$ and $(\Delta\rho)_{min} = -0.567 \text{ e \AA}^{-3}$. Crystallographic details for the structure determination are presented in Table-1. Selected bond lengths and bond angles of the title complex are listed in Table-2.

TABLE-1
CRYSTALLOGRAPHIC DATA FOR COMPOUND 1

Empirical formula	$C_8H_9CuN_5O_3S$
Formula weight	318.80
Temperature (K)	295(2)
Crystal system	Monoclinic
Space group	$P2_1/c$
Unit cell parameters	$a = 7.8108(10)$, $b = 18.1233(19)$, $c = 8.2006(10) \text{ \AA}$, $\alpha = 90$, $\beta = 94.976(6)$, $\gamma = 90^\circ$
$V (\text{\AA}^3)$	1156.5(2)
Z	4
$D_{calc} (\text{g/cm}^3)$	1.831
$\mu (\text{mm}^{-1})$	2.077
F(000)	644
Crystal size (mm)	0.30 \times 0.15 \times 0.12
θ Range ($^\circ$)	3.36–27.47
Limiting indices $h/k/l$ (max, min)	-10, 9/ -20, 23/ -10, 10
Reflections collected	8850
Independent reflections (R_{int})	2628(0.0413)
Absorption correction	SADABS
Completeness to θ	99.3 %
Max. and Min. transmission	0.779 and 0.695
Refinement method	Full-matrix least squares on F^2
Data/restraints/parameters	2628/0/ 163
Goodness-of-fit on F^2	1.118
R indices [$I > 2\sigma(I)$]	$R_1 = 0.0506$, $wR_2 = 0.1059$
R indices (all data)	$R_1 = 0.0678$, $wR_2 = 0.1164$
Largest diff. peak and hole ($e/\text{\AA}^3$)	0.466 and -0.567

TABLE-2
SELECTED BOND LENGTHS (\AA) AND ANGLES ($^\circ$) FOR 1

Cu(1)–N(3)	1.961(3)	S(1)–O(1)	1.427(3)
Cu(1)–O(3)	1.967(2)	S(1)–O(2)	1.444(3)
Cu(1)–N(2)	1.992(3)	S(1)–O(3)	1.493(3)
Cu(1)–N(1)	2.014(3)	N(3)–N(4)	1.194(4)
C(1)–N(1)	1.326(4)	N(4)–N(5)	1.151(4)
N(3)–Cu(1)–O(3)	92.27(11)	N(5)–N(4)–N(3)	176.3(4)
N(3)–Cu(1)–N(2)	169.39(12)	O(1)–S(1)–O(2)	114.57(18)
O(3)–Cu(1)–N(2)	94.88(11)	O(1)–S(1)–O(3)	111.47(16)
N(3)–Cu(1)–N(1)	92.94(12)	O(2)–S(1)–O(3)	109.99(17)
O(3)–Cu(1)–N(1)	171.95(11)	N(4)–N(3)–Cu(1)	125.5(2)
N(2)–Cu(1)–N(1)	80.84(12)	S(1)–O(3)–Cu(1)	132.50(15)

RESULTS AND DISCUSSION

IR spectra: The bands at 1648 cm^{-1} and $1241, 1189, 1053 \text{ cm}^{-1}$ in the IR spectrum of free Schiff-base ligand are assigned to $\nu(C=N)$ and $\nu(SO_3^{2-})$ absorption, respectively. However, in the complex they correspondingly shift to 1653 cm^{-1} and $1208, 1179, 1055 \text{ cm}^{-1}$, indicating the coordination of N atom in the Schiff-base and the sulfonate group to the metal ion. In addition, the strong and broad absorption at 2048 cm^{-1} corresponds to the peaks of asymmetric azide.

Crystal structure description of the title complex: X-ray analysis reveals that compound **1** crystallizes in the space group $P2_1/c$ with a coordination polymer which is connect with alternate $[Cu(pmt)]$ block through a pair of $\mu_{1,1}-N_3$ and μ_2-SO_3 . As shown in Figs. 1 and 2, the Cu(II) atom is six-coordinated with two oxygen and four N atoms, exhibiting a distorted 4+2 octahedral geometry (Table-2). The equatorial positions are occupied by the three donor atoms [N(1), N(2), O(3)] of the pmt ligand and the fourth atom belonging to $\mu_{1,1}$ -azide [N(3)] at distances close to 2 \AA , whereas the oxygen [O(2B)] from μ_2 -bridging sulfonate of neighboring $[Cu(pmt)]$ unit and the N-atom [N(3A)] of another bridging $\mu_{1,1}$ -azide occupy the axial sites at separations longer than 2.5 \AA . The relatively large Cu–O_{axial} and Cu–N_{axial} bond lengths may be accounted for the Jahn-Teller distortion effect of the Cu(II) ion, which avoids the formation of the typical binuclear complex.

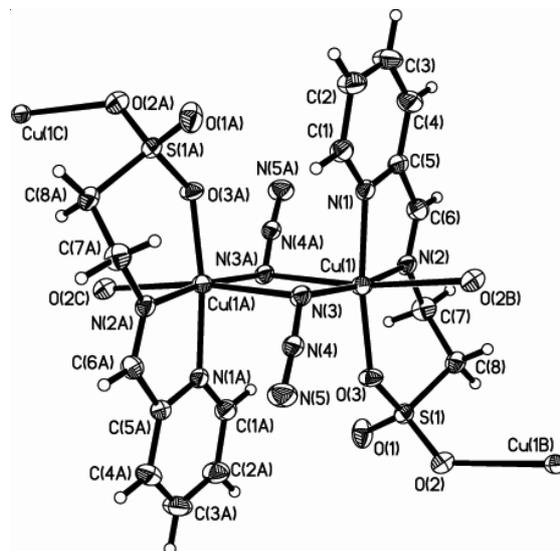


Fig. 1. Coordination environment of Cu(II) ion in **1** drawn at 30 % probability thermal ellipsoids. [symmetry codes: A: -x, 1-y, -z; B: -x, 1-y, 1-z; C: x, y, -1+z]

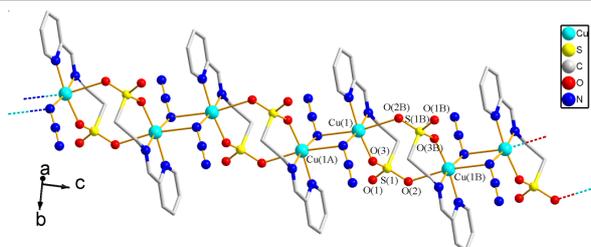


Fig. 2. A segment of the one dimensional zigzag chain structure of **1** along *c* axis. (C atoms have been drawn with wires and H atoms omitted for clarity)

This original sulfonate μ_2 -bridging coordination mode in **1** leads to forming eight-membered $(-\text{Cu}-\text{O}_{\text{chelate}}-\text{S}-\text{O}_{\text{bridging}}-)_2$ rings between neighboring Cu(II) atoms with a Cu...Cu distance of 5.43(3) Å. The structure of **1** also clearly illustrates that two azide ions, trans to each other, bridge copper(II) centers by adopting the end-on (μ -1,1- N_3) coordination mode. The central $\text{Cu}(\text{N}_3)_2\text{Cu}$ ring is coplanar and forms a parallelogram [$\angle\text{Cu}(1)-\text{N}(3)-\text{Cu}(1\text{A}) = 92.76(6)^\circ$, $\angle\text{N}(3)-\text{Cu}(1)-\text{N}(3\text{A}) = 87.24(6)^\circ$], which characterized by a two-fold axis perpendicular to the $\text{Cu}(1)/\text{N}(3\text{A})/\text{Cu}(1\text{A})/\text{N}(3\text{A})$ plane and the distance of $\text{Cu}(1)\cdots\text{Cu}(1\text{A})$ is 3.34(7) Å, a little longer than that reported other comparable structures^{13,14}. The two azide ligands are perfectly parallel to each other with the identical angles [$\angle\text{N}(3)-\text{N}(3\text{A})-\text{N}(4\text{A}) = \angle\text{N}(3\text{A})-\text{N}(3)-\text{N}(4) = 127.68(7)^\circ$] and nearly linear with $\angle\text{N}(3)-\text{N}(4)-\text{N}(5) = \angle\text{N}(3\text{A})-\text{N}(4\text{A})-\text{N}(5\text{A})$ angles of $176.3(4)^\circ$. Table-2 indicate that the $\mu(1,1)$ bridging azide is almost asymmetric of the difference between two *N-N* distances at 0.04 Å. These interconnected rings create a one-dimensional zigzag chain propagating along the *c* axis in the monoclinic unit cell (Fig. 2).

A notable feature of the complex lies in the 2D network built through hydrogen bonds given in Fig. 3, showing the neighboring molecules are connected each other by intermolecular hydrogen bonds of $\text{C}(6)-\text{H}(6)\cdots\text{N}(5)$ with the separate $\text{C}\cdots\text{N}$ distances of 3.272(5) Å. The weak π - π stacking interactions can also be observed between the parallel pyridine rings of adjacent chains (Fig. 3). The interplanar perpendicular distance and ring-centroid separation distance are 3.43(4) Å and 4.43(8) Å, respectively. The 1D chain structure is expanded into two-dimensional network in the *bc* plane by hydrogen bonds and together with π - π stacking interactions and help to stabilize the coordination complex.

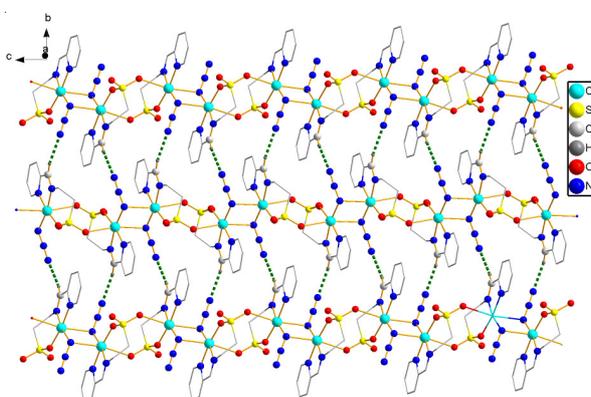


Fig. 3. 2-D crystal packing for **1**, showing hydrogen bonds as dashed lines. (H atoms bonded to C atoms have been omitted, except for including hydrogen bonds)

Conclusion

In this paper, we reported the synthesis and crystal structure with a new Cu(II) coordination polymer $[\text{Cu}(\text{pmt})(\text{N}_3)]_n$ containing taurine Schiff base. Its structure is elucidated by elemental analysis, IR and X-ray diffraction measurements. The two kinds of cycles with sharing Cu apexes are alternately created and interconnected to an interesting 1-D zigzag chain Cu(II) coordination polymer along the *c* axis and further expanded to 2D network in the *bc* plane via the significant weak $\text{C}-\text{H}\cdots\text{N}$ hydrogen bond and π - π stacking interactions between the adjacent 1D chains.

Supplementary data: CCDC-745395 contains the supplementary crystallographic data for this article. This data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html> [or from the Cambridge Crystallographic Data Centre, 12, Union Road, Cambridge, CB2 1EZ, UK; Telephone: (44) 01223 762910; Facsimile: (44) 01223 336033; E-mail: deposit@ccdc.cam.ac.uk].

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REFERENCES

1. S. Hiroyasu, *Eur. J. Pharmacol.*, **424**, 19 (2001).
2. C.O. Eimear, F. Etelka, R. Antal and B.N. Kevin, *J. Inorg. Biochem.*, **77**, 135 (1999).
3. B.S. Georgia and P. Eunhyue, *FEMS Microbiol. Lett.*, **226**, 195 (2003).
4. D.M. Julius and B.L. John, *Biochem. Pharmacol.*, **55**, 557 (1998).
5. B. Sreenivasulu, M. Vetrichelvan, F. Zhao, S. Gao and J.J. Vittal, *Eur. J. Inorg. Chem.*, **22**, 4635 (2005).
6. S.H. Zhang, G.Z. Li, F. Zhong and X.Z. Feng, *Chin. J. Struct. Chem.*, **26**, 1491 (2007).
7. X.M. Chen, S.H. Zhang and Y. Yang, *Acta Crystallogr.*, **E63**, 1317 (2007).
8. S.H. Zhang, Y.M. Jiang and Z.M. Liu, *J. Coord. Chem.*, **61**, 1927 (2008).
9. M. Xing, S.H. Zhang, R.B. Du, Y.M. Jiang, W.N. Sun and S.M. Liao, *Chin. J. Inorg. Chem.*, **22**, 179 (2006).
10. J.M. Li, Y.M. Jiang, Y.F. Wang and D.W. Liang, *Acta Crystallogr.*, **E61**, 2160 (2005).
11. Y.M. Jiang, J.M. Li and F.Q. Xie, *Chin. J. Struct. Chem.*, **25**, 767 (2006).
12. G.M. Sheldrick, Sadabs, Program for Absorption Correction of the Area Detector Data, Göttingen University, Germany (1996).
13. G.M. Sheldrick, SHELXS-97, Program for X-ray Crystal Structure Solution. Göttingen University, Germany, (1997).
14. G.M. Sheldrick, SHELXL-97, Program for X-ray Crystal Structure Refinement, Göttingen University, Germany (1997).