Synthesis and Crystal Structure of the Pyridoxylidene- taurineatocopper(II) Complex

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The pyridoxylidene-aurineatocopper(II) complex $[\text{Cu}(\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}_5\text{S})_2 \cdot \text{H}_2\text{O}]$ was synthesized by the reaction of the taurine pyridoxal Schiff base and copper acetate in a water-ethanol solution, and determined by an X-ray diffraction method. The complex crystallized in a monoclinic system with space group $C2/c$, and $a = 23.908(5)\text{\AA}$, $b = 7.7562(16)\text{\AA}$, $c = 17.266(4)\text{\AA}$, $\beta = 130.45(3)^\circ$. $V = 2436.3(9)\text{\AA}^3$, $Z = 4$, $D_x = 1.712\text{ Mg/m}^3$. The neighboring molecules in the complex are connected by three types of hydrogen bonds, obtaining a three-dimensional network supramolecular architecture.

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Recently, considerable attention has been paid to the chemistry of the metal complexes of Schiff bases containing nitrogen and other donors.^{1,2} This may be attributed to their stability, biological activity and potential applications in many fields, such as oxidation catalysis and electrochemistry. Of particular interest have been those involving copper(II), since they reveal surprising molecular diversity, not only in coordination geometry, but concerning more subtle changes in the ligands.³

Although complexes of the taurine condensation salicylaldehyde Schiff base and pyridoxylidene-DL-phenylalanine have been reported,^{4,5} those of pyridoxylidene-aurine have not. In this paper, we report on the synthesis and crystal structure of the pyridoxylidene-aurineatocopper(II) complex $[\text{Cu}(\text{C}_{10}\text{H}_{13}\text{N}_2\text{O}_5\text{S})_2 \cdot \text{H}_2\text{O}]$.

The title complex was prepared by mixing an ethanol-water solution of pyridoxal (1 mmol), taurine (1 mmol) with stirring. After three hours, an aqueous solution containing 1 mmol of $\text{Cu}(\text{AcO})_2 \cdot 2\text{H}_2\text{O}$ was added dropwise under stirring. The resulting solution was left at room temperature; black crystals of the complex were obtained after 30 d.

A black crystal having dimensions of $0.20 \times 0.17 \times 0.16\text{ mm}$ was chosen for X-ray diffraction studies. The measurements were made on a Rigaku-RAXIS-IV diffractometer with graphite-monochromatized $\text{Mo } K_\alpha$ radiation ($\lambda = 0.71073\text{ \AA}$) at $291(2)\text{K}$.

Table 1 Crystal and experimental data

Formula:	$\text{C}_{20}\text{H}_{28}\text{CuN}_4\text{O}_{11}\text{S}_2$
Formula weight	628.12
Crystal system	monoclinic
Space group	$C2/c$, $Z = 4$
a	$23.908(5)\text{\AA}$
b	$7.7562(16)\text{\AA}$
c	$17.266(4)\text{\AA}$
β	$130.45(3)^\circ$
V	$2436.3(9)\text{\AA}^3$
D_x	1.712 Mg/m^3
$2\theta_{\text{max}}$	49.94° with $\text{Mo } K_\alpha$
Reflections collected/unique	3541/2012 [$R(\text{int}) = 0.0303$]
Data/restraints/parameters	2012/2/186
Goodness-of-fit on F^2	1.096
Final R indices [$I > 2\sigma(I)$]	$R1 = 0.0343$, $wR2 = 0.0889$
$(\Delta/\sigma)_{\text{max}}$	0.000
$(\Delta\rho)_{\text{max}}$	$0.492\text{ e}\text{\AA}^{-3}$
$(\Delta\rho)_{\text{min}}$	$-0.350\text{ e}\text{\AA}^{-3}$
Measurement:	Rigaku-RAXIS-IV
Program system:	raxis
Structure determination:	SHELXL-97
Refinement:	full-matrix least-squares

CCDC 281202 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif.

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Fig. 1 Structural chemical diagram.

Fig. 2 Molecular structure along with atom labeling.

Table 2 Atomic coordinates and equivalent isotropic displacement parameters

	x	y	z	U_{eq}
Cu(1)	5000	6447(1)	7500	26(1)
S(1)	3575(1)	2310(1)	6521(1)	34(1)
C(1)	5319(2)	7143(4)	10142(2)	29(1)
C(2)	4929(2)	6974(4)	9074(2)	28(1)
C(3)	4186(2)	7503(4)	8390(2)	27(1)
C(4)	3868(2)	8339(4)	8754(2)	29(1)
C(5)	4285(2)	8527(4)	9789(2)	33(1)
C(6)	3714(2)	6984(4)	7323(2)	29(1)
C(7)	3372(2)	5711(4)	5840(2)	32(1)
C(8)	3530(2)	3871(4)	5727(2)	33(1)
C(9)	6090(2)	6539(5)	10909(2)	37(1)
C(10)	3088(2)	9022(5)	8032(2)	38(1)
N(1)	4980(1)	7893(3)	10440(2)	32(1)
N(2)	3940(1)	6369(3)	6880(2)	26(1)
O(1)	5284(1)	6270(3)	8829(2)	37(1)
O(2)	2895(1)	9962(4)	8530(2)	48(1)
O(3)	3533(2)	655(3)	6103(2)	57(1)
O(4)	4282(1)	2583(4)	7539(2)	52(1)
O(5)	2959(1)	2630(3)	6487(2)	46(1)
O(6)	5000	9309(6)	7500	124(3)

U_{eq} is defined as one third of the trace of the orthogonalized U_{ij} tensor.

Table 3 Selected bond lengths [Å] and bond angles [°]

Atoms	Length	Atoms	Length
Cu(1)-O(1) ^a	1.930(2)	Cu(1)-O(1)	1.930(2)
Cu(1)-N(2) ^a	2.013(2)	Cu(1)-N(2)	2.013(2)
Cu(1)-O(6)	2.219(5)	S(1)-O(3)	1.443(3)
S(1)-O(4)	1.461(3)	S(1)-O(5)	1.457(2)
S(1)-C(8)	1.778(3)	C(1)-N(1)	1.341(4)
C(1)-C(2)	1.434(4)	C(1)-C(9)	1.484(4)
C(2)-O(1)	1.290(4)	C(2)-C(3)	1.414(4)
C(3)-C(4)	1.418(4)	C(3)-C(6)	1.460(4)
C(4)-C(5)	1.377(4)	C(4)-C(10)	1.516(4)
C(5)-N(1)	1.357(4)	C(6)-N(2)	1.281(4)
C(7)-N(2)	1.472(4)	C(7)-C(8)	1.520(5)
C(10)-O(2)	1.413(4)		
Atom	Angle	Atoms	Angle
O(1) ^a -Cu(1)-O(1)	171.84(14)	O(1) ^a -Cu(1)-N(2) ^a	88.90(10)
O(1)-Cu(1)-N(2) ^a	90.85(10)	O(1) ^a -Cu(1)-O(6)	90.85(10)
O(1)-Cu(1)-O(6)	88.90(10)	N(2) ^a -Cu(1)-O(6)	176.54(14)
O(1) ^a -Cu(1)-O(6)	94.08(7)	O(1)-Cu(1)-O(6)	94.08(7)
N(2) ^a -Cu(1)-O(6)	91.73(7)	N(2)-Cu(1)-O(6)	91.73(7)
O(3)-S(1)-O(4)	112.96(17)	O(3)-S(1)-O(4)	112.43(17)
O(5)-S(1)-O(4)	111.92(15)	O(3)-S(1)-C(8)	105.70(15)
O(5)-S(1)-C(8)	107.37(15)	O(4)-S(1)-C(8)	105.86(16)
N(1)-C(1)-C(2)	118.8(3)	N(1)-C(1)-C(9)	120.3(3)
C(2)-C(1)-C(9)	120.9(3)	O(1)-C(2)-C(3)	125.9(3)
O(1)-C(2)-C(1)	116.3(3)	C(3)-C(2)-C(1)	117.7(3)
C(2)-C(3)-C(4)	120.4(3)	C(2)-C(3)-C(6)	119.9(3)
C(4)-C(3)-C(6)	119.2(3)	C(5)-C(4)-C(3)	118.6(3)
C(5)-C(4)-C(10)	119.9(3)	C(3)-C(4)-C(10)	121.5(3)
N(1)-C(5)-C(4)	120.2(3)	N(2)-C(6)-C(3)	125.2(3)
N(2)-C(7)-C(8)	111.9(2)	C(7)-C(8)-S(1)	115.9(2)
O(2)-C(10)-C(4)	113.2(3)	C(1)-N(1)-C(5)	124.0(3)
C(6)-N(2)-C(7)	116.4(2)	C(6)-N(2)-Cu(1)	123.0(2)
C(7)-N(2)-Cu(1)	120.39(18)	C(2)-O(1)-Cu(1)	124.13(19)

Symmetry transformations used to generate equivalent atoms:

a: $-x + 1, y, -z + 3/2$

Table 4 Hydrogen-bonds [Å, °]

D-H...A	D-H	H...A	D...A	D-H...A
O(2)-H(2E)...O(5) ^b	0.83(4)	1.91(4)	2.714(4)	164(4)
O(4)-H(4E)...N(1) ^c	1.02(2)	1.71(3)	2.727(3)	174(13)
O(6)-H(6E)...O(3) ^d	0.86(2)	2.06(3)	2.869(3)	157(5)

Symmetry transformations used to generate equivalent atoms:

b: $-x + 1/2, y + 1/2, -z + 3/2$ c: $-x + 1, -y + 1, -z + 2$ d: $x, y + 1, z$

The structure was solved by direct methods and refined by full-matrix least squares techniques anisotropically for all non-H atoms. All H atoms were added according to theoretical modes. The crystal data and experimental parameters are listed in Table 1. A chemical diagram of the title complex is shown in Fig. 1, and the crystal structure is shown in Fig. 2. The final positional parameters for all non-hydrogen atoms are given in Table 2, and selected bond lengths and bond angles are summarized in Table 3. The hydrogen-bonding distances and angles are presented in Table 4.

The complex has a distorted square-pyramidal coordination geometry with each copper atom bond to two pyridoximine ligands through the phenolic oxygen and the imine nitrogen atoms. The apical position is occupied by an oxygen (O(6)) of the water molecule [N(2)-Cu(1)-O(6) = 91.73(7)° and N(2)-Cu(1)-N(2A) = 176.54(14)°]. The distance of Cu(1)-O(6) is 2.219(5) Å, which is longer than that of Cu(1)-O(1) (1.930(2) Å). Additionally, the O atoms of the sulfo group have not been coordinated. These characteristics are different from those of aqua(5-phosphopyridoxylidene-DL-phenylalanineato)-copper(II)⁴ and [Cu(TCSSB)₂(H₂O)₂]₂·[Cu(TCSSB)₂]₂·6H₂O.⁵

Of particular interest, the neighboring molecules in the complex are connected by three types of hydrogen bonds, (O(2)-H(2E)...O(5) (2.714 Å), O(4)-H(4E)...N(1) (2.727 Å), O(6)-H(6E)...O(3) (2.869 Å)), obtaining a three-dimensional network supramolecular architecture, which contributes to the stability of the structure.

References

1. S. S. Djebbar, B. O. Benali, and J. P. Deloume, *Transit. Metal. Chem.*, **1998**, 23, 443.
2. S. S. Djebbar, B. O. Benali, and J. P. Deloume, *Polyhedron*, **1997**, 16, 2175.
3. X. Z. Sun, Y. F. Sun, B. H. Ye, and X. M. Chen, *Inorg. Chem. Commun.*, **2003**, 6, 1412.
4. A. F. Marinovich, R. S. Omahony, J. M. Waters, and T. N. M. Waters, *Croatia Chem. Acta*, **1999**, 2-3, 685.
5. S. H. Zhang, Y. M. Jiang, and Z. Y. Zhou, *Chin. J. Chem.*, **2004**, 22, 1303.