Synthesis and Structure of the Copper Complex [Cu₂L₂^{ox}(SO₄)(H₂O)₄](H₂O)₄

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Abstract. The reaction of N-(pyridine-2-ylmethyl)pyrazine-2-carboxamide (HL) and copper(II) sulfate leads to the formation of a new copper complex, [Cu₂L₂^{ox}(SO₄)(H₂O)₄](H₂O)₄(1), in which the deprotonated amide L⁻ ligand was oxidized to a imide L^{ox-} exposed to the air in the presence of the Cu ion. The X-ray crystal analysis reveals that it consists of two mononuclear copper unit with different coordination modes, multiple O-H...O hydrogen bonding between water molecules or water and sulfate O atom to form 3D networks. CCDC: 2088935,1.

1 Introduction

Pyrazine-based amide ligands have played very important role in the copper coordination chemistry^[1-5]. These ligands exhibit different coordination modes depending on a deprotonated base used or not in the synthesis of the title complexes. The neutral form of the ligands coordinate in either a monodentate fashion via the pyrazyl N donor or in a bridging mode through the N and carbonyl O atom. When a base was used to deprotonate the NH group, which renders the ligand as an anionic moiety to coordinate with the metal ions in a bidentate fashion through the pyrazyl and amidate N donors. Bis(terdentate)pyrazine based diamide ligands and their transition metal chemistry have been well studied by Dr. Brooker's and Dr. Stoeckli Evans's group^[6]. As a homolog of the aforementioned diamide ligands, an alkylpyridine armed pyrazine-pyridine amide ligand HL^{pz} was prepared and its transition metal chemistry were also investigated by several different groups. Dr. Hubin firstly reported a trinuclear cobalt complex^[7]. Khavasi's group also reported a novel binuclear manganese(II) complex and its catalytic property^[8]. Later, they reported two temperature dependent complexes of 1D and 2D HgCl₂ coordination polymer with HL^{pz}^[9]. Recently, my previous group reported the synthesis, characterization and structures of five copper complexes with HL and its homolog ligand^[10]. As a complimentary work to my previous research, here, we report the synthesis, crystal structure of a new copper complex based on the bispyrazyl amide ligand, HL, which was reported by Dr. Brooker's group. A cobalt complex with abrupt, complete, hysteretic spin crossover properties by thermal, pressure, and electrochemical stimuli was well investigated^[11]. The most interesting part of the work is

that the HL ligand was oxidized to an imide due to the expose of the air during the reaction in the presence of the copper ions, which is consistent to the reported results^[12]. A mononuclear Cu complex with pyrazine-pyrazine imide ligand from the oxidation of an amide ligand has been reported by my group^[13]. Here, we synthesized and characterized a new mononuclear copper complex based on the same ligand.

2 Experimental

2.1 General procedures

All the chemicals commercially available were used as supplied without further purification. The HL was synthesized according to previously reported methods.^[10] Infrared spectra were recorded with a Bruker VERTEX-70 spectrometer as KBr pellets in the frequency range 4000 to 400cm⁻¹. Elemental analyses were performed with a Perkin-Elmer 2400 Series II analyzer.

2.2 Synthesis of [Cu₂L₂^{ox}(SO₄)(H₂O)₄](H₂O)₄(1)

A solution of CuSO₄·5H₂O (25.8mg,0.103mmol) in methanol was added to a solution of HL(22.3mg,0.103mmol) in CH₃OH, affording a dark green solution. Keep stirring for 6h, after the filtration, the blue filtrate was obtained. Slow evaporation of the filtrate afforded green block-shaped crystals of the title copper complex suitable for X-ray analysis. C₂₀H₂₈Cu₂N₁₀O₁₆S .Calcd.C 29.16, H 3.43, N 17.01%; found:C 29.42,H 3.28, N 16.91%. IR(KBr): 3 359(s), 2 407(w), 1 652(s), 1 356(s), 1 134(s), 1 067(s), 835(w), 673(w), 614(w), 467(w)(cm⁻¹)

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2.3 X-ray crystal structure determination

Single crystal X-ray diffraction analyses of complex **1** was carried out with a Bruker SMART APEX II CCD diffractometer equipped with a graphite monochromated Mo-K α radiation ($\lambda = 0.71073$ Å) by using a ω -scan mode. The structure of **1** was solved by direct methods and refined by full-matrix least-squares methods on F^2 using the program SHELXL 97^[14]. Using Olex2^[15]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were located by geometrically calculations, and their positions and thermal parameters were fixed during the structure refinement. The crystallographic data and experimental details of structural analyses for **1** are summarized in Table 1. Selected bond and angle parameters are listed in Table 2.

3 Results and discussion

3.1 Crystal structure of complex **1**

Single crystal X-ray analysis reveals that complex **1** crystallizes in the tetragonal, $I41/a$ space group. In the title compound, it consists of two monocopper units and four free water molecules as shown in Fig1. The Cu1 is five-coordinated by three N atoms from the oxidized imide ligand and two O atoms from water and sulfide anion with a square pyramidal geometry. The coordination mode of Cu2 is six-coordinated by three N atoms from the oxidized imide ligand and three O atoms from water molecules with an octahedral geometry. The bond distance of Cu2-O10 is 0.2696 nm, which is longer than other Cu-O bond distances assigned as a weaker bond interactions. There are multiple O-H...O hydrogen bonding between water molecules or water and sulfide O atom to form 3D networks as shown in Fig2. The carbonyl groups in the title complex are available for the coordination with secondary metal ions to construct heteronuclear metal complexes.

Fig.1 Molecular structure of the complex **1** shown with 30% probability displacement ellipsoids. Hydrogen atoms and the uncoordinated water molecule are deleted for clarity.

Fig. 2 Intermolecular hydrogen bonding diagram of complex **1**

Table 1 Crystal data and structure refinement for **1**

Complex	1
Empirical formula	$C_{20}H_{28}Cu_2N_{10}O_{16}S$
Formula weight	586.44
T/K	296(15)
Crystal system	Tetragonal
Space group	$I41/a$
a/nm	8.271 2(5)
b/nm	13.603 3(8)
c/nm	14.743(9)
$\alpha/^\circ$	110.958 (7)
$\beta/^\circ$	102.332 (7)
$\gamma/^\circ$	93.857 (7)
V/nm^3	1494.4(16)
Z	2
$D_c/(g \cdot cm^{-3})$	1.831
μ/mm^{-1}	1.587
$F(000)$	840
θ range/ $^\circ$	2.553 ~ 26.021
Reflections collected/unique	5 814/442
Data / restraints / parameters	5 814/0/442
Final R indices ($I > 2\sigma(I)$)	$R_1=0.0721$, $wR_2=0.1623$
R indices (all data)	$R_1=0.1308$, $wR_2=0.1915$

Table 2 Selected bond distances (nm) and angles ($^\circ$) for **1**

Cu1-N1	0.1937(4)	Cu2-N6	0.1944(5)
Cu1-N2	0.2009(5)	Cu2-N7	0.2005(5)
Cu1-N4	0.2006(4)	Cu2-N9	0.2009(5)
Cu1-O1	0.1936(4)	Cu2-O8	0.2374(5)
Cu1-O5	0.2438(4)	Cu2-O9	0.1953(4)

		Cu2-O10	0.2696(5)
O1-Cu1-O5	88.56(17)	O8-Cu2-O10	174.81(15)
O1-Cu1-N2	99.17(18)	O9-Cu2-O8	93.14(19)
O1-Cu1-N1	178.82(19)	O9-Cu2-O10	84.03(17)
O1-Cu1-N4	96.81(18)	O9-Cu2-N7	98.1(2)
N2-Cu1-O5	91.31(17)	O9-Cu2-N9	97.4(2)
N1-Cu1-O5	90.76(17)	N7-Cu2-O8	88.95(18)
N1-Cu1-N2	81.81(18)	N7-Cu2-O10	87.15(17)
N1-Cu1-N4	82.29(18)	N7-Cu2-N9	163.9(2)
N4-Cu1-O5	94.95(17)	N6-Cu2-O8	96.69(18)
N4-Cu1-N2	162.98(18)	N6-Cu2-O9	170.2(2)
N6-Cu2-O10	86.14(17)	N6-Cu2-N7	81.78(19)
N6-Cu2-N9	82.19(19)	N9-Cu2-O8	94.47(18)
N9-Cu2-O10	90.21(17)		

4 Conclusions

In summary, we successfully synthesized a new copper(II) complex derived from N-(pyridine-2-ylmethyl)pyrazine-2-carboxamide(HL), in which the deprotonated amide was oxidized to imide ligand. The X-ray analysis reveals that the coordination modes and geometries of the copper center change with the choice of the anion in the synthesis of the title complexes.

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