IJCRT.ORG ISSN : 2320-2882

INTERNATIONAL JOURNAL OF CREATIVE RESEARCH THOUGHTS (IJCRT)

An International Open Access, Peer-reviewed, Refereed Journal

EXPLORATION OF WEAK INTERACTIONS AND CRYSTAL STRUCTURE OF NEWLY SYNTHESIZED CU(II) COMPLEX OF PYRIMIDINE DERIVED LIGAND

Saugata Konar
Assistant Professor
Department of Chemistry
The Bhawanipur Education Society College, 5, Lala Lajpat Rai Sarani, Kolkata, Kolkata 700020, India.

Abstract: One new binuclear Cu(II) coordination compound $[Cu_2(Pymox)_2](ClO_4)_2$ (**1**) of pyrimidine derived Schiff base ligand [where, PymoxH = 3-[(4,6-dimethyl-pyrimidine-2-yl)-hydrazono]-butan- 2-one oxime] has been synthesized and characterized by elemental analyses, IR and single crystal X-ray crystallography. Around the Cu(II) centre, complex **1** exhibits a distorted square planar geometry. Herein, diverse weak interactions, such as anion···π and lone pair···π interactions, have been explored in this paper, leading to various supramolecular structures. The supramolecular framework in the crystal packing of the examined molecule is responsible for these forms of weak interactions.

***Keywords*- Cu(II)/ Pyrimidine ligand/ Single crystal X-ray crystallography/ Weak interactions.**

1. INTRODUCTION

In coordination chemistry, polydentate Schiff base ligands are a well-studied topic [1, 2]. These ligands have varying preparative accessibility, structural variation, and denticity, resulting in complexes with different coordination numbers and nuclearities that have fascinating molecular and crystalline topologies. In the literature, there is a lot of work on pyridine and pyrazole derived Schiff base ligands, but there isn't much on pyrimidine derived Schiff base ligands. Pyrimidine derivatives are abundant in biological systems, with the ring system found in nucleic acids, numerous vitamins, co-enzymes, and antibiotics [3, 4].

One of the most important components in the synthesis of coordination compounds with unique structures is the careful selection of organic ligands. Because of their potential uses and interesting structures and topologies, the synthesis and research of new coordination compounds has piqued the curiosity of crystal engineers and coordination chemists. Apart from hydrogen bonding, the anion• • •π, lone pair• • • π, interactions are key molecular forces whose nature is still under debate. These interactions are unquestionably significant in shaping crystal packing, molecular assemblages, and the architecture of vast biological systems.

By considering of this, X-ray crystal structure of binuclear Cu(II) complex $[Cu_2(Pymox)_2](ClO_4)_2$ (**1**) has prepared by using pyrimidine derived ligand and this single crystal X-ray structural analysis of **1** revealed remarkable supramolecular architecture guided by various weak forces like anion• • •π, lone pair• • • π and hydrogen bonding.

2. Experimental

2.1. Materials

All chemicals were of reagent grade, purchased from commercial sources and used without further purification. Diacetylmonoxim (97%) was purchased from Aldrich Chemical Company, USA and used without further purification.

Caution! Although we have not encountered any problems, it should be kept in mind that perchlorate compounds of metal ions are potentially explosive especially in the presence of organic ligands. Only a small amount of the material should be prepared and it should be handled with care.

2.2. Physical Measurement

The infrared spectrum of the complex was recorded on a Perkin-Elmer RX I FT-IR spectrophotometer with KBr discs (4000–400 cm^{-1}). Elemental analyses (C, H, and N) were carried out using a Perkin-Elmer 2400 II elemental analyzer. UV- absorption spectra for said complex was measured with a Hitachi UV/Vis U-3501 spectrophotometer at room temperature (298 K).

2.3. Synthesis of the ligand PymoxH

The ligand PymoxH was synthesized and characterized using literature method [5].

2.4. Preparation of complexes

2.4.1. Preparation of complex **$[Cu_2(Pymox)_2](ClO_4)_2$ (1)**

The ligand PymoxH (0.442 g, 2 mmol) was added to a hot solution of $Cu(ClO_4)_2$, $6H_2O$ (0.744 g, 2 mmol) in CH_3OH (30 mL). The suspension was stirred for 2 h with constant stirring until complete dissolution of the ligand occurred. The resulting reddish brown solution was filtered to remove any undissolved ligand and left at room temperature. Reddish brown crystals suitable for X-ray diffraction were isolated after standing for several days (yield 30%). Anal. Calcd for $C_{20}H_{28}Cl_2Cu_2N_{10}O_{10}$ (**1**): C, 31.31; H, 3.65; N, 18.26%; Found: C, 31.27; H, 3.60; N, 18.29%. IR (KBr pellet/cm^{-1}): 3323 (m), 1580 (s), 1515 (s), 1420 (s), 1332 (s), 1011 (m), 909 (m).

3. Single crystal X-ray crystallography

Selected crystal data for **1** is given in Table 1 and selected metrical parameters of the complex **1** are given in Table 2. For complex **1** data collections were made using Bruker SMART APEX II CCD area detector equipped with graphite monochromated Mo Kα radiation (λ = 0.71073 Å) source in ω scan mode at 150(2) K. Cell parameters refinement and data reduction were carried out using Bruker SMART [6] and Bruker SAINT softwares for all the complexes. The structures were solved by direct and refined by full-matrix least-squares based on F^2 using the SHELXS-97 and SHELXL-97 programs [7].

4. Results and discussion

4. 1. Description of structure of complex ***1***

The perspective view of molecular structure of complex **1** with atom numbering scheme is shown in Fig. 1. Crystallographic and bond metrical parameters are listed in Table 1 and 2 respectively. Complex **1** crystallizes in space group C 2/c and the unit cell of **1** comprises of four molecules. The geometry at the metal center is distorted square planar. Each anionic ligand chelates to the one metal through its pyrimidine nitrogen N1, hydrazine nitrogen N4, oximate nitrogen atom N5 and to another metal through its oximate oxygen atom O1. So, from structural analysis it is evident that each ligand was serving as a tridentate one to each Cu(II) center and the residual coordination sphere is satisfied by the oximate oxygen (O1) attached with oximate nitrogen (N5) in anti-fashion. The oximate oxygen (O1) is not available at all to coordinate to the same Cu(II) atom because if it happens then the complex suffers a lot of steric strain due to three membered chelate rings. Hence it affords such kind of dimerization. Both unit of the complex are identical and the central Cu(II) atom is shifted by a distance 0.191Å from the mean plane constituted by N4N5N5O1. The angle between these two mean square planes is 49.52˚. Two perchlorate geganions are there to satisfy the charge of the complex. With respect to the mean six membered Cu(II)–bridge segment [Cu1O1N5Cu1O1N5Cu1] two sets of ligands are spanning themselves in trans or anti orientation. The adjacent *cis* angles are shifted roughly ±10° from the ideal 90° due to some steric requirements mainly from seven peripheral methyl groups. The H–bonding interactions are obtained between oxygen atoms of perchlorate anion and the hydragenyl hydrogen atom (NH31).

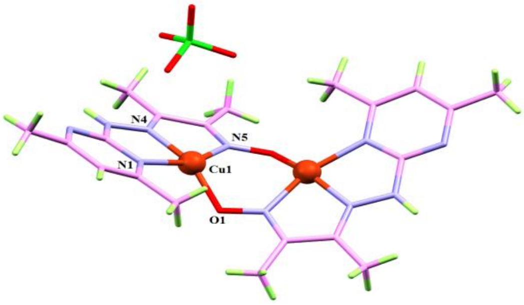

Fig. 1 Molecular structure of **1** with partially labeled atoms (Color code: Cu, orange; O, red; N, blue; C, light purple; H, aquamarine.).

Table 1: Experimental data for crystallographic analysis of complex **1**

Compound	**1**
Empirical formula	$C_{20}H_{28}Cl_2Cu_2N_{10}O_{10}$
Formula weight	766.52
Temperature (K)	150(2)
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	
a (Å)	19.7677(4)
b (Å)	8.5485(2)
c (Å)	18.6223(4)
α (˚)	90
β (˚)	106.699(1)
γ (˚)	90
Volume (Å^3)	3014.16(11)
Z	4
Density$_{cal}$ (Mg m^{-3})	1.689
Absorption coefficient (mm^{-1})	1.657
F(000)	1560
Independent reflections [R$_{int}$]	7802[R(int)= 0.035]
Data/restraints/parameters	7802,0,207
Reflections collected	27480
Final R indices [I > 2σ (I)]	R1=0.0402, WR2=0.1360
Largest difference peak and hole (eÅ^{-3})	-0.36, 0.76

Table: 2: Selected bond distances (Å) and angles (°) data for **1**

Selected Bonds	(Å)	Selected Angles	(^{O})
Complex 1			
Cu1-O1	1.8885(12)	O1-Cu1-N1	101.45(5)
Cu1-N1	2.0522(11)	O1-Cu1-N4	154.84(5)
Cu1-N4	1.9337(14)	O1-Cu1-N5	100.76(5)
Cu1-N5	1.9949(13)	N1-Cu1-N4	79.66(5)
		N1-Cu1-N5	157.67(5)
		N4-Cu1-N5	79.25(5)

4.2. Weak interactions

Perchlorate anion establishes strong anion–π contacts with Pymox ligand through O2 and O5. The shortest separation distances reflecting these interactions are O2⋯C8 = 3.219(3) Å and O5⋯C6 = 3.038(3) Å, which are below the sum of the corresponding van der Waals radii (the sum of van der Waals radii of O and C is 3.22 Å). The coordinating O1 atom is orientated toward the *π*-face of nearest pyrimidine moiety of a discrete $[Cu_2(Pymox)_2]^{2+}$ unit (Fig. 1). The distance between O1 and the centroid of the pyrimidine moiety is 3.824 Å. This O1 atom establishes lone pair–π interaction with the nearest pyrimidine ring. The shortest separation distance reflecting this interaction is O1⋯C4 = 3.212(2) Å and O1⋯C5 = 3.177(2) Å, which is below the sum of the corresponding van der Waals radii (the sum of van der Waals radii of O and C is 3.22 Å). This lone pair–π interaction is responsible for holding discrete $[Cu_2(Pymox)_2]^{2+}$ units along the *c* axis, thus generating a infinite 1D zig zag chain (Fig. 2). Dimethyl-pyrimidine part of the Pymox ligand plays very crucial role in the 2D packing of complex **1** by establishing unique lone pair–π–anion type interaction involving both the π faces. Overall 3D packing of the complex is achieved by various hydrogen bonds.

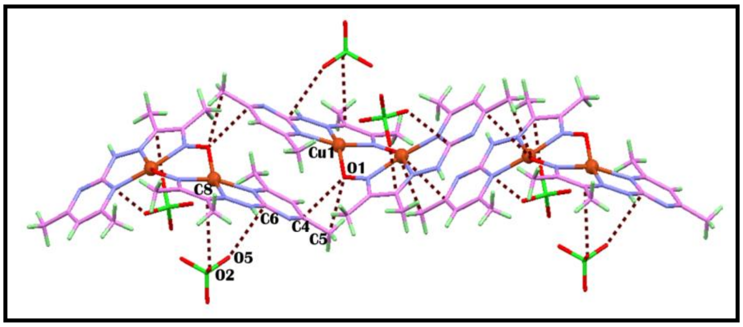

Fig. 2 Dimeric $[Cu_2(Pymox)_2]^{2+}$ units form a 1D infinite zig-zag chain along crystallographic *c* axis. This assembly is viewed along *a* axis. Dangling perchlorate anions form anion-π contacts with coordinated Pymox ligand. The coordinating O1 atom of Pymox ligand is involved in lone pair-π interaction. Other perchlorate anions are omitted for clarity. Color code: Cu, orange; O, red; N, blue; C, light purple; H, aquamarine.

4.3. Electronic spectra

The electronic absorption spectrum of the complex **1** was measured in DMF solvent. The electronic spectrum of the Cu(II) complex exhibits bands at 322 nm and 405 nm which could be attributed to the pyrimidine to Cu(II) charge transfer (LMCT) transition. The d-d transition has been detected as a relatively broad band with low intensity in the 533 nm range (Fig. 3).

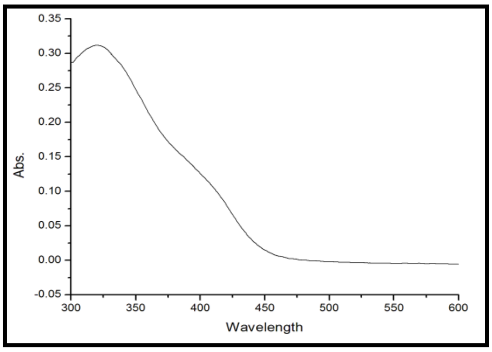

Fig.3 Electronic spectra of Complex **1**

5. Conclusion

PymoxH, a Schiff base ligand derived from pyrimidine, generates a coordination compound of Cu(II) complex **1** during research. Cu(II) complex features a distorted square planar environment around the metal centre of said complex. Understanding how diverse supramolecular interactions like anion···π and lone pair···π cooperate and direct the supramolecular assembly of the molecular building blocks within the ligand moiety appears to be fascinating.

Acknowledgements

S. K. is thankful to The Bhawanipur Education Society College, Kolkata 700020 for providing research grant (Project No. BESC/RPC/2019–2020/SC1/02).

Appendix A. Supplementary data:

CCDC 913122 contains the supplementary crystallographic data for **1**. 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; fax: (+44) 1223-336-033; or e-mail: deposit@ccdc. cam.ac.uk.

References

[1] Davis, M.B. 1997. Coordination Chemistry Reviews, 164: 27-160.
[2] Smith, D.R. 1998. Coordination Chemistry Reviews, 172 : 457-573.
[3] Rice, W.G., Turpin, J.A., Schaeffer, C.A., Graham, L., Clanton, D., Buckheit Jr., R.W., Zaharevitz, D., Summers, M.F., Wallqvist, A. and Covell, D.G. 1996. Journal of Medicinal Chemistry, 39 : 3606-3616.
[4] Otsuka, M., Fujita, M. and Sugiura, Y. J. 1994. Journal of Medicinal Chemistry, 37 : 4267-4269.
[5] Konar, S., Dey, A., Choudhury, S. R., Das, K., Chatterjee, S., Ray, P. P., Castro, J. O., Frontera, A. and Mukhopadhyay, S. 2018. The Journal of Physical Chemistry C, 122: 8724−8734.
[6] Bruker. 2001. SMART v5.631, Bruker AXS Inc., Madison, WI, USA.
[7] Sheldrick, G.M. 1997. SHELXS-97 and SHELXL-97, University of Göttingen, Göttingen, Germany.