doi: 10.31674/book.2025ccbsse008

Study of Synthesis, Crystal Structure, Magnetic Properties, EPR, Cyclic Voltammetric Analysis and Zigzag Chain Coordination of Polymer Prepared through Copper Catalysed Hemiacetal Synthesis

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Abstract

A 1D polymeric complex $[Cu^{II}_2(R)_2(SCN)_2]_n$ (1) has been prepared by the reaction of picolinaldehyde with NaSCN. The complex 1 has been well characterised by UV-Vis, FT-IR, and elemental analysis. Structural study of Complex 1 exhibits a unique arrangement, where copper centres in tetrahedral and pentacoordinated geometries are interconnected in a chain-like pattern. This linkage is facilitated by single thiocyanato bridges and double alkoxido bridges, resulting in the formation of dimer complexes that repeat throughout the structure. Magnetic measurements at varying temperatures reveal a strong antiferromagnetic interaction between copper centres of the dimer, facilitated by the double alkoxido bridge. The exchange coupling constant (J) is determined to be -374 cm^{-1}. This strong antiferromagnetic interaction highlights the important role of the bridging ligands in mediating magnetic exchange between the metal centres.

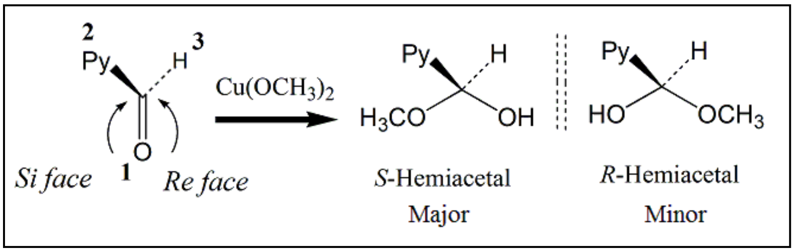
Keywords: *Alkoxo Bridges; Copper (II) Complexes; Magnetic Properties; Sinsle Step Reaction*

Introduction

Recent years have seen significant advancements in single step ligand synthesis, driven by its efficacy, ease of use, and eco-friendly nature. This approach has emerged as a potent tool in designing coordination complexes. Furthermore, decades of research have focused on one step metal/ligand reactions, aiming to uncover novel organic reactions, shed light on reaction mechanisms, and create unique compounds that cannot be synthesised directly (Chen & Tong, 2007; Zhang, 2005).

A wide range of single step ligand syntheses under hydro(solvo)thermal conditions have been documented, encompassing various reactions such as carbon-carbon bond formation (Blake *et al*., 1997; Liu, Gao & Kou, 2001), hydroxylation (Zhang, Tong & Chen, 2002; Zhang *et al*., 2002), and cycloaddition reactions (Xiong *et al*., 2002; Xue *et al*., 2002; Qu *et al*., 2003; Zhang *et al*., 2004). Other reported reactions include substitution of carboxyl with sulfonic groups (Xiong *et al*., 2001), alkylation (Cheng *et al*., 2004). Notably, the formation of polynuclear complexes often involves single step reactions between an organic ligand and a small molecule or solvent.

Here a novel synthetic route is described, wherein $Cu(ClO_4)_2 \cdot 6H_2O$ facilitates a single step reaction, enabling the addition of methanol as a nucleophile to aldehydes, resulting in the formation of hemiacetals within a methanolic medium (Scheme 1).



Scheme 1: Scheme Representation of Hemiacetal Synthesis through Single Step Reaction (Dhal et al., 2014)

Magnetic properties of interest can be achieved by employing paramagnetic metal ions as connecting points, which are bridged by ligands that enable magnetic interactions between the metal centres, ultimately giving rise to unique magnetic behaviours (Tommasino *et al*., 2012; Novitchi *et al*., 2012). The magnetic properties of these synthesised complexes, which were prepared using a building block approach, have been thoroughly investigated through various experimental methods (Gatteschi *et al*., 1991; Xue *et al*., 2002; Kahn, 1993; Sasmal *et al*., 2012; Sasmal *et al*., 2013).

This study reports the preparation, crystal structure, EPR, magnetic properties and cyclic voltammetric study of the prepared $[Cu^{II}_2(R)_2(\mu\text{-SCN})(SCN)]_n$ (1) synthesised through the reaction of picolinaldehyde with Cu^{II} and NaSCN.

Synthesis of Complex $[Cu^{II}_2(R)_2(SCN)_2]_n$ (1)

Reaction of $Cu(ClO_4)_2.6H_2O$ and Pyridine-2-carboxaldehyde was carried out in a methanolic medium with gentle heating; the reaction mixture was stirred. The mixture was then cooled, followed by the dropwise addition of an aqueous sodium thiocyanate solution, and subsequently stirred to ensure the reaction proceeded to completion. The final green solution was filtered and was set aside to undergo slow evaporation, resulting in the formation of needle-shaped green single crystals.

Results and Discussion

EPR study

The room-temperature EPR spectrum of compound 1, as shown in Figure 1, exhibits a tetragonal pattern characterised by two distinct g values, with the order $g_z > g_x = g_y > g_e$, indicative of its electronic structure and copper (II) ion environment.

The tetragonal EPR spectrum observed for compound 1 suggests a {*d*x2-y2}1 ground state configuration (Sasmal *et al*., 2013), consistent with the square planar and square pyramidal geometries present in compound 1, as supported by the g values obtained.

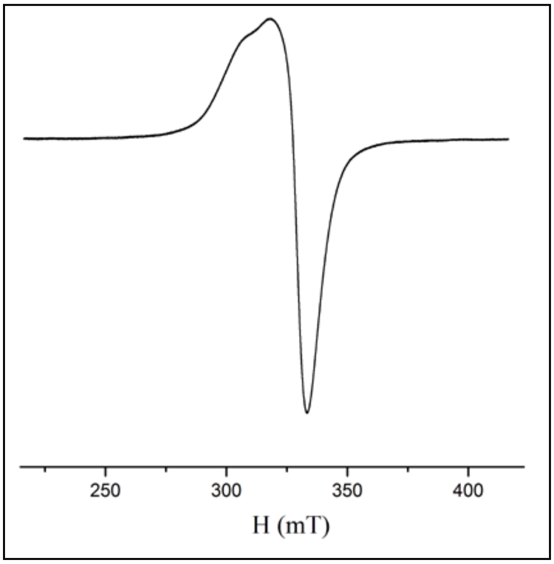


Figure 1: Room Temperature EPR Spectra of Complex 1 (Dhal et al., 2014)

Electrochemical Studies

Cyclic voltammetry measurements were performed on the complex in a solution of acetonitrile. Tetrabutylammonium perchlorate was used as a supporting electrolyte under a nitrogen atmosphere. The scan rate was 50 mV/s. Figure 2 exhibits two distinct cathodic signals in the cyclic voltammogram of the complex, appearing at potentials of -0.28 V and -0.96 V.

The first wave, which is quasi-reversible, is attributed to the reduction of $Cu^{II}Cu^{II}$ to $Cu^{II}Cu^{I}$, whereas the second wave, being fully irreversible, is assigned to the reduction of $Cu^{II}Cu^{I}$ to $Cu^{I}Cu^{I}$.

A subsequent dissolution process is observed, potentially triggered by the partial degradation of the complex liberating Cu^{I} ions following the two-step one-electron reduction. As the Cu^{I} is further reduced to Cu_0, metallic copper accumulates on the electrode surface.

A sharp anodic peak at -0.25V signifies the dissolution of the deposited Cu_0. This phenomenon implies that the Cu^{I}(μ2-O)2CuI entity is unstable and prone to rapid decomposition. Notably, this electrochemical profile is similar to that of other dimeric copper complexes (Torelli *et al*., 2002; Torelli *et al*., 2000; Basak *et al*., 2010; Banerjee *et al*., 2009), likely due to the necessary structural rearrangements accompanying reduction. Furthermore, the anodic segment of the CV curve reveals an oxidation signal at 0.41V, which is provisionally attributed to the oxidation of the metal centre-bound ligand.

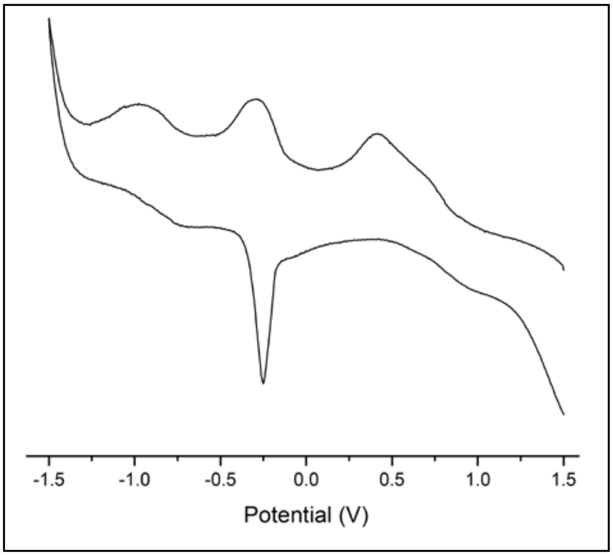


Figure 2: CV Curve of Complex 1 (Dhal et al., 2014)

Crystal Structure Description

Crystal Structure Analysis of $[Cu^{II}_2(R)_2(SCN)_2]_n$ (1)

Structural analysis of complex 1 reveals that the complex crystallises in the monoclinic P21/*c* space group. The crystal structure of the synthesised complex reveals a dinuclear entity, comprising two Cu atoms, two ligands (R), and two SCN moieties, which are linked by a double-alkoxido bridge, forming a $[Cu^{II}_2(R)(SCN)]_2$ core within the asymmetric unit (Figure 3). The chelating ligand R, identified as *S*-methoxy(pyridine-2) methanol, is generated in a single step through a copper-facilitated reaction, which is a crucial intermediate in the process.

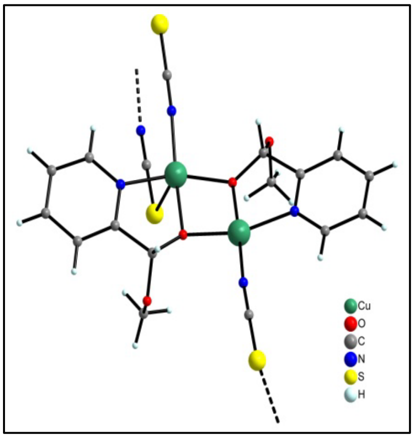


Figure 3: Perspective View of Asymmetric Unit of the Complex $[Cu^{II}_2(R)_2(SCN)_2]_n$ (Dhal et al., 2014)

The coordination environments around the two Cu^{II} ions within the dinuclear unit exhibit subtle differences. Specifically, the Cu2 centre adopts a distorted square-pyramidal geometry, characterised by an Addison parameter (Addison *et al*., 1984) (τ) of 0.2158. It features an elongated axial Cu2-S23 bond (2.8286(8) Å) that semi-coordinates each Cu2 atom to the Cu1 atom of an adjacent dimer (Figure 4).

Cu1 adopts a more precise square planar coordination. As the axial Cu1-S28 distance of 3.243(8) Å exceeds the typical range for a covalent Cu-S bond with a notable interaction between copper and the sulphur centre. The basal plane of each copper atom is formed by one nitrogen atom from the pyridine ring and another from the thiocyanate moiety and two bridging □-alkoxido oxygen atoms from the methoxy(pyridine-2) methanol ligand.

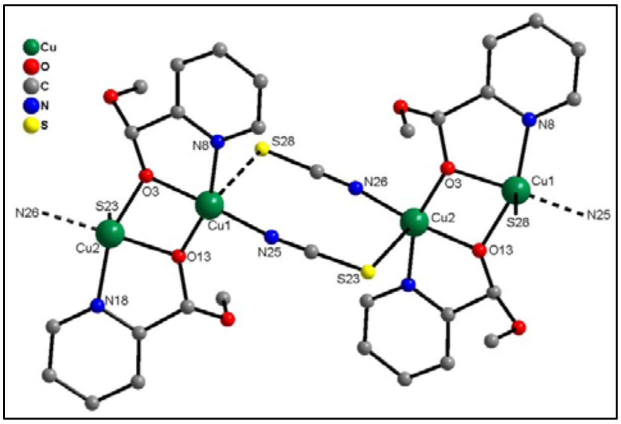


Figure 4: Representation of the Weak Cu···S Bonds in Compound 1 (Dhal et al., 2014)

Each Cu2 atom is linked to the Cu1 atom of an adjacent dimer through the Cu2-S23 bond, resulting in a zigzag chain that propagates through the c-axis as shown in Figure 5. This one-dimensional polymer features an alternating arrangement of double methoxido and single thiocyanato bridges between Cu1 which is square planar, and Cu2 ions, which are square pyramidal in nature. The zigzag chains are spatially separated due to the significant steric hindrance imposed by the methoxy substituents.

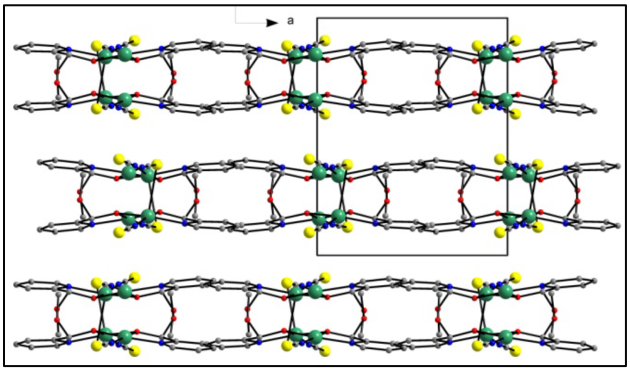


Figure 5: View of Complex 1 Along the ab Plane (Dhal et al., 2014)

Cu···Cu intrachain separation is 2.968(4) Å, consistent with known dialkoxido-bridged copper complexes (Seppälä *et al*., 2012). The Cu1(μ-O)$_2$Cu2 bridging unit exhibits a slight fold, with a dihedral angle of 15.11(8)° between Cu1-O3-O13-Cu2. Within the equatorial planes, Cu-N bond lengths (1.916-1.996 Å) are comparable to Cu-O bond lengths, which are around 1.919-1.935 Å and significantly shorter than the axial Cu-S distance of 2.8286(8) Å. The basal planes of Cu1 and Cu2 are oriented at an angle of 26.40° relative to each other.

Magnetic Studies

The room-temperature χmT value of compound **1** exhibits a value of approximately 0.40 cm^3 K mol^{-1}, significantly lower than the expected value. As the temperature decreases, $_mT$ steadily declines, eventually reaching a plateau at 0.03 cm^3 K mol^{-1} below around 80 K (Figure 6).

The structure of complex **1** feature alternating zigzag chains so the magnetic interaction along the lengthy axial Copper Sulphur bond is likely insignificant. Consequently, complex 1 can be magnetically treated as a Cu^{II} dimer connected by double methoxido bridges, disregarding the chain-like arrangement.

The magnetic properties were successfully modelled using the classical Bleaney-Bowers S = 1/2 dimer approach (Bleaney & Bowers, 2012). This approach accurately describes the magnetic behaviour of the complex across the entire temperature range, yielding best-fit parameters of g = 2.150, J = -374 cm^{-1} and a 3.3 % paramagnetic impurity (with the Hamiltonian defined as H = -JS$_1$S$_2$, represented by the solid line in Figure 6). In the inset of Figure 6 the presence of this paramagnetic impurity is accounted for in the observed low-temperature divergence in the χ_m plot and the residual low-temperature $\chi_m T$ value is approximately 0.03 cm^3 K mol^{-1}.

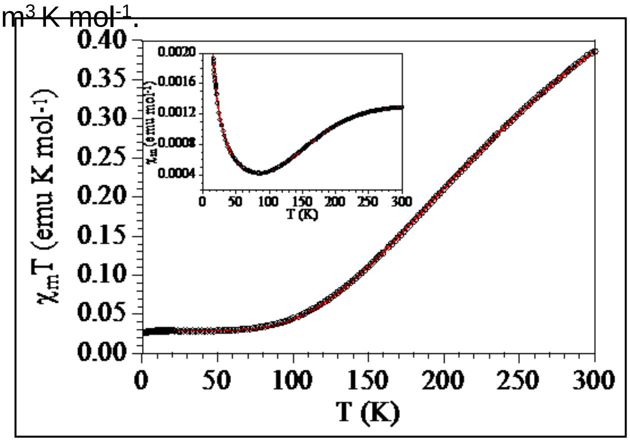


Figure 6: Temperature Dependence of the χmT Product Per Cu^{II} Dimer of Compound 1, Thermal Variation of □$_m$ is Shown in the Inset (Dhal et al., 2014)

The strong antiferromagnetic coupling can be readily rationalised based on established magneto-structural relationships for double alkoxido bridges occupying equatorial sites. These studies have identified the bond angles (α) between copper and oxygen as the key factors influencing magnetic coupling, along with the angle between the Cu_2O_2 plane (τ) and the C-O bond of the alkoxido ligand. The slightly lower observed coupling of -374 cm-1 in **1** may be attributed to the non-planarity of the Cu_2O_2 unit, as evidenced by a dihedral angle of 15.11(8)°.

Conclusion

Here a polymeric copper (II) complex, $[Cu^{II}_2(R)_2(SCN)_2]_n$ has been reported. It is prepared via a single step reaction of picolinaldehyde in methanolic medium. The formation of this complex proceeds through the in-situ generation of the (S)-methoxy(pyridine-2) methanol ligand, which is produced via copper-catalysed hemiacetal formation resulting from the nucleophilic attack of methoxide on picolinaldehyde. The planar $[Cu^{II}_2(R)_2(SCN)_2]$ dimers exhibit strong antiferromagnetic coupling, consistent with established magneto-structural relationships observed in $Cu(\mu\text{-}O)_2Cu$ dimers that have been structurally and magnetically characterised.

Acknowledgement

The author extends her sincere gratitude to Prof. Samiran Mitra for his mentorship and to Dr. Arup Mandal of Rammohan College for his valuable support and constant encouragement.

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