

Synthesis, Characterization and Crystal Structure of Bis[1-methoxy-2,2,2-tris-(pyrazol-1-yl-κN²)ethane]-copper(II) Bis-perchlorate

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Abstract: Bis[1-methoxy-2,2,2-tris-(pyrazol-1-yl-κN²)ethane]-copper(II) bis-perchlorate (2) was synthesized by reacting of pyrazole based tripodal scorpionate ligand 1-methoxy-2,2,2-tris(pyrazol-1-yl)ethane (1) with copper(II) perchlorate hexahydrate in methanol, acetonitrile and water mixture as solvent. Slow evaporation of the filtered reaction mixture in air produced blue color block crystals suitable for single crystal X-ray diffraction study of the title complex. Compound 2 crystallizes in the monoclinic space group P2₁/n with unit cell parameters, $a = 8.1269(1) \text{ \AA}$, $b = 21.8348(2) \text{ \AA}$, $c = 9.1522(1) \text{ \AA}$, $\alpha = \gamma = 90^\circ$, $\beta = 99.7611(4)^\circ$. The structure of the compound was characterized by IR Spectroscopy, elemental analysis and single crystal X-ray diffraction analysis.

Key words: Pyrazole, tripodal ligand, scorpionate ligand, single crystal X-ray diffraction.

1. Introduction

Pyrazole is a five-member heterocyclic compound with two nitrogen atoms next to each other [1]. Derivatives of pyrazole are drawing significant attention over the years because of their biological activities. Due to their topology and nature of donor atoms, pyrazole derivatives have drawn great interest in agrochemical, pharmaceutical, and chemical industries [2, 3]. Nitrogen containing five membered heterocyclic compounds could be used as antitumor, antibacterial, antifungal, antiviral, anti-parasitic, anti-tubercular and insecticidal agents [4, 5]. They have been studied extensively for useful biological effectiveness such as anti-inflammatory, anti-diabetic, anesthetic and analgesic properties [6, 7]. Pyrazole based tridentate ligands often bind metals in a scorpionate fashion and produce significant

coordination chemistry research initiatives [8-16]. In this article, the authors are reporting synthesis, characterization and crystal structure of bis[1-methoxy-2,2,2-tris-(pyrazol-1-yl-κN²)ethane]-copper(II) bis-perchlorate as part of their ongoing research efforts in this field.

2. Experimental

2.1 Materials and Method

1-Methoxy-2,2,2-tris(pyrazol-1-yl)ethane (1) ligand was synthesized according to the previously published procedure of Maria et al. [17]. Copper(II)perchlorate hexahydrate was purchased from ACROS and used as received. IR data were collected on a Nicolet IR Spectrometer 200. Elemental analyses for C, H, and N were performed by Robertson Microlit Laboratories.

Caution: Although no problem was encountered in this current work, perchlorate salts are potentially explosive. Thus, these reactions should be handled with great care.

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2.2 Synthetic Procedure for Bis[1-methoxy-2,2,2-tris-(pyrazol-1-yl-κN²)ethane]-copper(II) Bis-perchlorate

Synthetic scheme for the compound bis[1-methoxy-2,2,2-tris-(pyrazol-1-yl-κN²)ethane]-copper(II) bis-perchlorate (2) is shown in Fig. 1. Copper(II)perchlorate hexahydrate (371 mg, 1 mmol) was dissolved in 40 mL methanol. 1-Methoxy-2,2,2-tris(pyrazol-1-yl)ethane (1) (258 mg, 1 mmol) was dissolved in 25 mL methanol. The ligand solution was added drop wise to metal solution with moderate stirring. Once the addition was complete, 5 mL of acetonitrile and 5 mL of water mixture added and solution was further stirred for additional 10 mins. The resulting reaction mixture was filtered and solvent was slowly evaporated in air. Blue color block type crystals were obtained after 2 weeks (524 mg, 67.3% yield). Elemental analysis, calculated for C₂₄H₂₈N₁₂CuO₁₀Cl₂: C 37.01, H 3.62, N 21.57; found C 37.20, H 3.56, N 21.52.

IR (cm⁻¹): 3,135, 2,932, 1,635, 1,520, 1,463, 1,414, 1,384, 1,341, 1,323, 1,235, 1,197, 1,149, 1,092, 1,070, 1,012, 974, 957, 919, 853, 780, 761, 668, 648, 622, 610, 600, 412.

2.3 X-Ray Diffraction Data Collection

Compound 2 crystallizes as blue color block crystal with dimensions 0.21 mm × 0.20 mm × 0.18 mm. The crystal was mounted with polyisobutene oil on the tip of a fine glass fiber, which was fastened in a copper mounting pin with electrical solder. It was placed directly into the cold gas stream of a liquid nitrogen based cryostat, according to published methods [18]. Diffraction data were collected with the crystal at 90 K, which is standard practice in this laboratory for the majority of flash-cooled crystals. X-ray intensity data of the crystal were collected by Nonius Kappa CCD X-ray Diffractometer equipped with MoK α radiation ($\lambda = 0.71073\text{\AA}$). The intensities were measured by employing ϕ and ω scan mode for

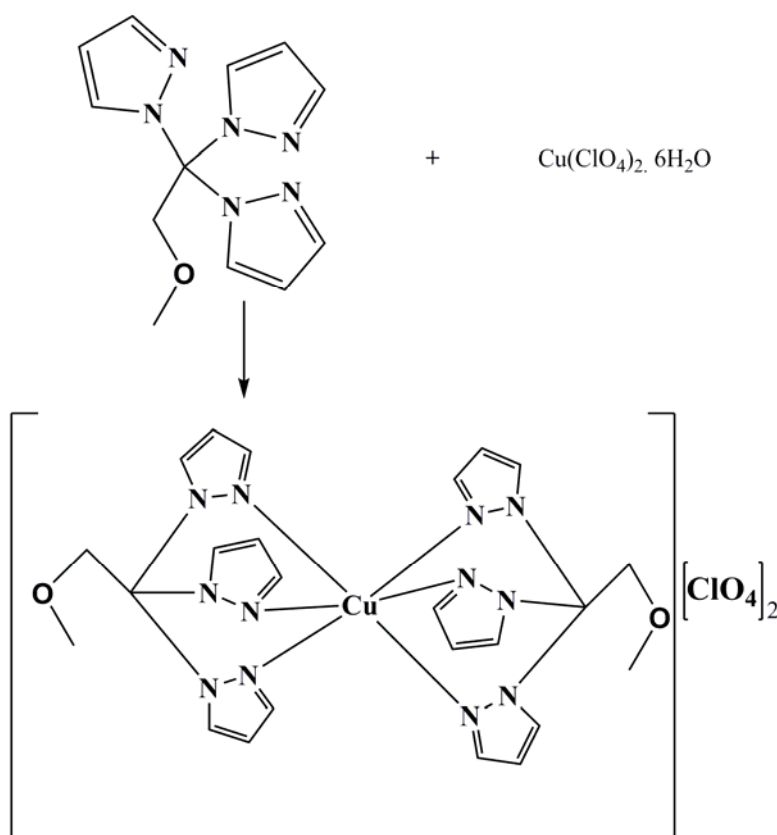


Fig. 1 Synthetic scheme for bis[1-methoxy-2,2,2-tris-(pyrazol-1-yl-κN²)ethane]-copper(II) bis-perchlorate.

Table 1 Selected bond lengths and bond angles for bis[1-methoxy-2,2,2-tris-(pyrazol-1-yl-κN²)ethane]-copper(II) bis-perchlorate.

Bond lengths (Å)		Bond angles (°)	
Cu1-N2	1.9865 (16)	N2-Cu1-N4 ⁱ	93.89 (7)
Cu1-N2 ⁱ	1.9866 (16)	N2 ⁱ -Cu1-N4 ⁱ	86.11 (7)
Cu1-N4 ⁱ	2.0056 (16)	N2 ⁱ -Cu1-N4	93.89 (7)
Cu1-N4	2.0057 (16)	N2-Cu1-N6	80.52 (6)
Cu1-N6	2.3750 (18)	N2 ⁱ -Cu1-N6	99.48 (6)
Cu1-N6 ⁱ	2.3750 (18)	N4 ⁱ -Cu1-N6 ⁱ	84.47 (6)

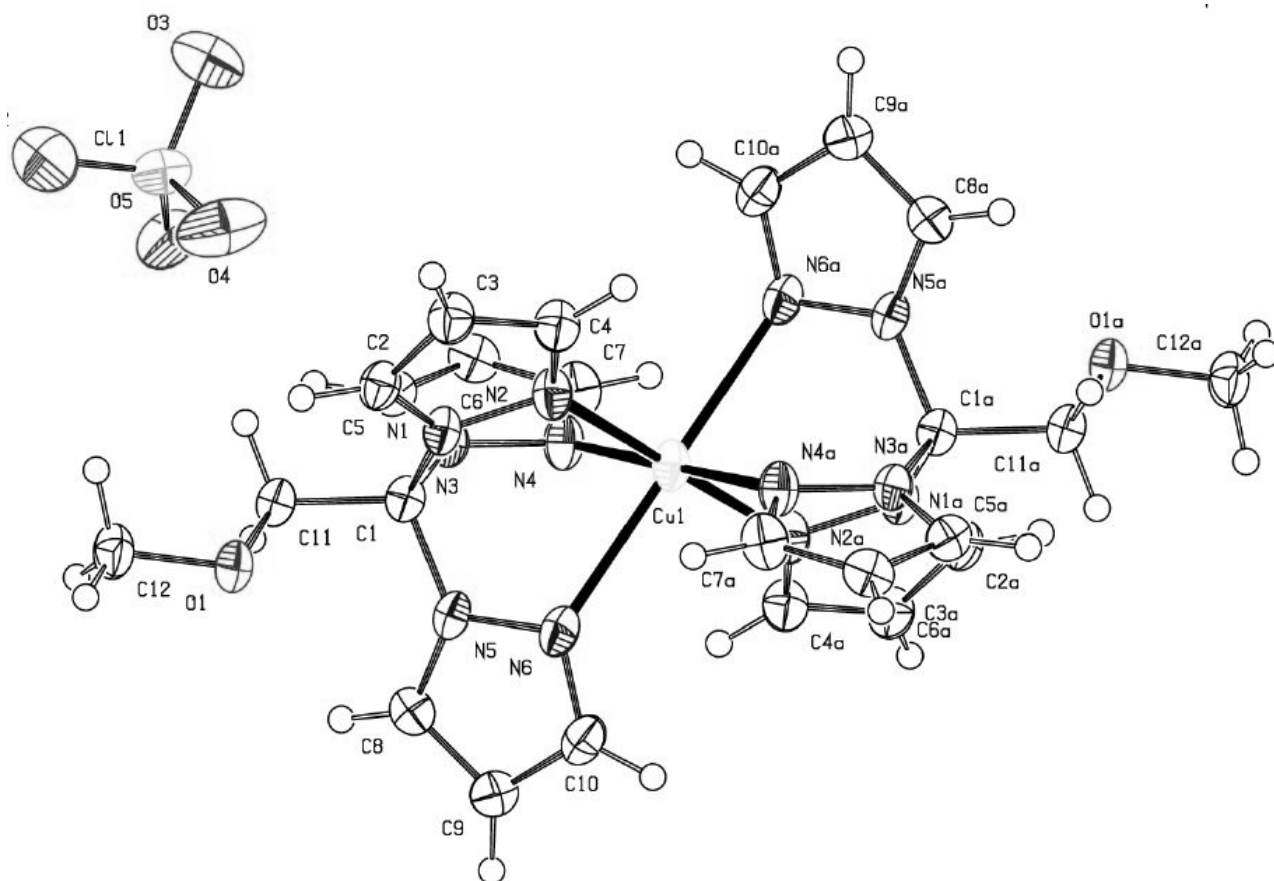


Fig. 2 View of molecular structure of bis[1-methoxy-2,2,2-tris-(pyrazol-1-yl-κN²)ethane]-copper(II) bis-perchlorate, with atom labeling. Displacement ellipsoids are drawn at the 50% probability level.

the diffraction angle ranging from 1.0 to 27.5°. A total number of 7,240 reflections were measured of which 3,671 were found to be independent. The criterion ($I > 2\sigma(I)$) was employed to the independent data set and 3,099 reflections were treated as observed. The structure was solved by direct methods using SHELXS-97 [19]. The final refinement cycles converged to $R = 0.033$ and $wR(F^2) = 0.089$ for 3,671 observed reflections. Some of the key bond lengths and bond angles which play an important role in

determining the structural properties of this molecule are presented in Table 1. The view of the molecular structure of the title compound 2, with atom labeling is shown in Fig. 2.

3. Results and Discussion

Treatment of the tripodal scorpionate ligand 1-methoxy-2,2,2-tris(pyrazol-1-yl)ethane (1) with commercially available copper(II)perchlorate hexahydrate in methanol, acetonitrile and water

mixture afforded block shaped crystal of bis[1-methoxy-2,2,2-tris-(pyrazol-1-yl-κN²)ethane]-copper(II) bis-perchlorate (2), suitable for X-ray diffraction study. Compound 2 crystallizes in the form of blue crystals in the monoclinic space group P2₁/n with unit cell parameters, $a = 8.1269$ (1) Å, $b = 21.8348$ (2) Å, $c = 9.1522$ (1) Å, $\alpha = \gamma = 90^\circ$, $\beta = 99.7611$ (4)°. In the crystal, the copper(II) ion is coordinated by six nitrogen atoms from two tridentate ligand molecules of 1 with an average copper(II)-nitrogen distance of 2.1224 Å, which is longer than corresponding nickel(II) complexes which the authors characterized previously [9, 10]. Copper ion with two ligand molecules forms a complex with distorted octahedral geometry. The copper ion is situated in the inversion center. The average nitrogen—copper(II)-nitrogen angle between adjacent pyrazole-ring-coordinated nitrogen atoms is 83.7° for the six acute angles and 96.3° for the six obtuse angles, very similar to parameters, which the authors observed in case of nickel(II) complexes [9, 10]. Intramolecular hydrogen bonds of the nature carbon-hydrogen-oxygen are present between methyl group of 1 and oxygen atoms from perchlorate anions. Hydrogen atoms were found in difference Fourier maps, but subsequently included in the refinement using riding models, with constrained distances set to 0.95 Å (C_{sp2}H), 0.98 Å (RCH₃) and 0.99 Å (R₂CH₂). U_{iso}(H) parameters were set to values of either 1.2U_{eq} or 1.5U_{eq} (RCH₃ only) of the attached atom. All esds (except the esd in the dihedral angle between two l.s. planes) are estimated using the full covariance matrix. The cell esds are taken into account individually in the estimation of esds in distances, angles and torsion angles; correlations between esds in cell parameters are only used when they are defined by crystal symmetry. An approximate (isotropic) treatment of cell esds is used for estimating esds involving l.s. planes. Refinement progress was checked using Platon [20] and by an R-tensor [21]. The final model was further checked with the International Union of Crystallography utility *checkCIF*.

5. Conclusion

In summary, the authors have successfully synthesized and characterized the coordination complex between copper(II) metal ion and pyrazole based tridentate ligand 1-methoxy-2,2,2-tris(pyrazol-1-yl)ethane. The authors are hopeful that the methodology employed here could further be extended to other transition metals as well. Given the fact that the pyrazole derivatives are gaining increasing attention due to their potential applications, the authors hope to work with other research group(s) mainly interested in property studies and hence carry out further research in a complementary and fruitful way.

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