

Synthesis, Characterization and Surface analysis of Copper Complex Featuring π - π Interactions and Hydrogen Bonding

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ABSTRACT

This study aimed to synthesize and characterize a copper complex using various analytical techniques. The synthesized complex was confirmed through IR spectroscopy and further characterized using X-ray diffraction, which revealed complex crystallized in the monoclinic crystal system with the P21 space group. The complex exhibited hydrogen bonding, with Hirshfeld analysis indicating a 7.1% contribution from the surfaces. The study also found that H...H interactions accounted for 59.6% of the significant amount of interaction in the surfaces. Overall, this investigation provides valuable insights into the structural properties and interactions of copper complexes. These findings provide valuable insights into the structural properties and interactions of copper complexes, which can contribute to the development of new materials with unique properties and potential applications in fields such as catalysis, electronics, and medicine. The ability to synthesize and characterize these complexes can lead to the discovery of novel copper complexes with even more remarkable properties. Further research in this area could build upon the findings of this study and advance our understanding of the structural properties and interactions of copper complexes.

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1. Introduction

Copper compounds have been widely researched because of their distinctive characteristics and possible uses in different areas, such as medicine, electronics, and catalysis¹⁻⁷. Copper complexes that feature acetate bridging have attracted significant interest because of their fascinating structural properties⁸⁻¹³. The β -dicarbonyl motif is present in a wide range of biologically and pharmaceutically active substances¹⁴⁻¹⁷, and β -diketones are especially useful in the treatment of different pathological conditions, including but not limited to cardiovascular and liver diseases, hypertension, obesity, diabetes, neurological disorders, inflammation, skin diseases, and fibrosis^{18,19}. Therefore, the formation of these structures is a topic that greatly interests chemists because of its immense importance. Copper β -diketones, among the various complexes formed by β -diketones, are of particular significance^{20,21}. In addition to their biological applications, such as their potent antibacterial properties²², these compounds are commonly utilized for extracting metals from water contaminated with metals^{23,24}, and as catalysts²⁵. Moreover, scientists have synthesized and examined Copper β -diketone complexes to explore the steric demands of β -diketone ligands. These investigations provide important information about the structural and electronic features of such complexes²⁶.

2. Experimental

2.1. Synthesis

[Cu(Hpbdo)(pbdo)(OCH₃)]. 0.06 gr (0.32 mmol) of Hpbdo and 0.01 gr (0.04 mmol) of copper chloride salt were combined in a beaker and slowly added to the bottom of a branched tube. Methanol was then slowly added to the tube until it reached a volume of one centimeter above the side branch. The tube was sealed and placed in a paraffin bath at 60 degrees Celsius for eight days. After this time, green crystals suitable for crystallization were obtained. The crystals were washed with acetone and ether and then dried. The melting point of the compound was found to be above 250 °C, and the efficiency of the synthesis was 87%. Analysis calculated for C₂₁H₂₂CuO₅ showed C 60.35%, H 5.31%, and Cu 15.20%, while the actual values found were C 60.10%, H 5.25%, and Cu 15.37%.

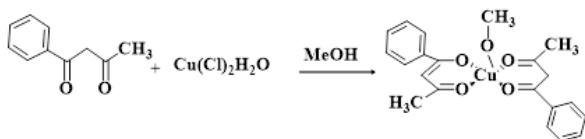


Figure 31. Preparation of the Complex

2.2. X-Ray Diffraction

Table 1 contains the crystallographic data for the complex, which were obtained by analyzing the complex using X-ray diffraction.

Table 15. The Crystallographic Data

Empirical formula	C ₄₂ H ₄₄ Cu ₂ O ₁₀
Formula weight	835.85
Temperature/K	293(2)
Crystal system	monoclinic
Space group	P2 ₁
a/Å	10.1825(8)
b/Å	8.4944(6)
c/Å	11.6227(11)
α /°	90.00
β /°	102.196(8)
γ /°	90.00
Volume/Å ³	982.61(14)
Z	1
ρ_{calc} /mg/mm ³	1.413
m/mm ⁻¹	1.139
F(000)	434.0
Crystal size/mm ³	0.65 mm × 0.4 mm × 0.32 mm
2 θ range for data collection	5.98 to 51.98°
Index ranges	-12 ≤ h ≤ 12, -10 ≤ k ≤ 10, -14 ≤ l ≤ 14
Reflections collected	8289
Independent reflections	3153[R(int) = 0.0188]
Data/restraints/parameters	3153/5/248
Goodness-of-fit on F ²	1.408
Final R indexes [I >= 2 σ (I)]	R ₁ = 0.1124, wR ₂ = 0.2951
Final R indexes [all data]	R ₁ = 0.1326, wR ₂ = 0.3255
Largest diff. peak/hole / e Å ⁻³	2.38/-0.90
Flack parameter	0.52(5)

Table 2 presents a summary of the specific bond lengths observed in both complex.

Table 16. Selective Bond Lengths

Cu—O11	1.899 (8)	C81—C91	1.43 (2)
Cu—O21	1.922 (9)	C91—C101	1.480 (19)
Cu—O22	1.937 (6)	O12—C72	1.272 (14)
Cu—O12	2.021 (8)	O22—C92	1.288 (16)
Cu—O	2.186 (13)	C12—C62	1.319 (19)
O11—C71	1.175 (12)	C12—C22	1.45 (2)
C51—C61	1.407 (19)	C92—C102	1.77 (2)
C71—C81	1.361 (19)	O—C	1.45 (3)

The bond angles observed in the complex are presented in Table 3.

Table 17. Bond Angles [°]

O11—Cu—O21	83.6 (6)	C71—C81—C91	126.8 (13)
O11—Cu—O22	172.0 (7)	O21—C91—C81	122.9 (13)
O21—Cu—O22	88.4 (4)	O21—C91—C101	116.8 (12)
O11—Cu—O12	89.5 (6)	C81—C91—C101	120.3 (12)
O21—Cu—O12	104.9 (4)	C72—O12—Cu	124.9 (8)
O22—Cu—O12	92.3 (4)	C92—O22—Cu	126.6 (8)
O11—Cu—O	90.4 (9)	C62—C12—C22	119.0 (14)

O21—Cu—O	156.8 (4)	C62—C12— C72	120.1 (14)
O22—Cu—O	97.1 (5)	C22—C12— C72	120.8 (12)
O11—C71— C11	126.3 (10)	C—O—Cu	118 (3)

2.3. IR Spectroscopy

The IR spectrum of the complex, which confirms their synthesis, is depicted in Figure 1. Table 4 summarizes the interpretation and peak positions of important groups within the complex structures.

Table 18. Frequencies of Important Groups of the Complexes

C-H (Aliphatic)	2922	OH(Methanol)	3418
C=C (Aromatic)	1559	C=O	1590
C-H (Stretching Aromatic)	3060	C-H (Bending Aromatic)	759

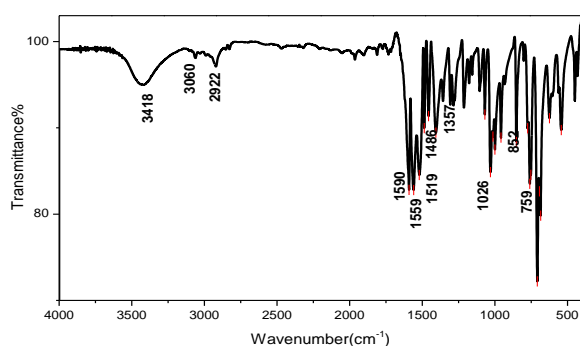


Figure 32. IR spectrum of the complex

The Crystal Explorer Ver. 3.1 program package was employed to examine the intermolecular interactions within the investigated crystals²⁷. This analysis included the utilization of Hirshfeld surface analyses, 2D fingerprint plots, and percentage contribution calculations. Specifically, Hirshfeld surfaces were utilized in this study, with no properties involved in the calculation command.

3. Result and Discussion

The Complex was prepared by reacting Hpbdo and copper chloride salt in a ratio of 1:8, also in methanol solvent. Determination of the structure by X-ray diffraction shows the complex is crystallized in the solid state in the monoclinic crystal system with space group P2₁. **Figure 2** shows each copper atom is coordinated to four oxygen atoms from two 1-phenylbutane-1,3-dione (Hpbdo) ligands, with bond lengths of 1.899 (8) Å, 2.021 (Å) 1.937 (6), and 1.922 (Å), as well as one oxygen atom from the methoxy ligand. As a result, the copper cation has an oxidation number of 2+ and a CuO₅ coordination space around it (**Figure 3**). An important feature of the structure is that one of the beta diketone ligands is coordinated to the metal as a negatively charged ligand, having lost a proton, while the other beta diketone ligand is neutrally coordinated to the metal.

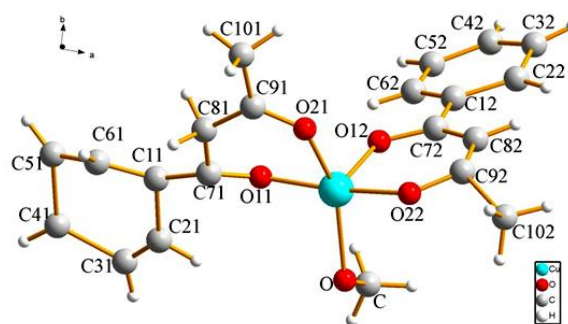


Figure 33. The Crystal Structure of the complex

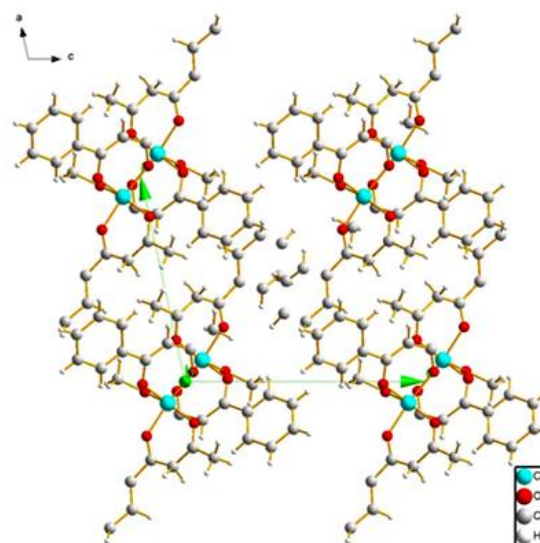


Figure 34. Crystal Network of the complex

The important point about the structure is that one of the beta diketone ligands is coordinated to the metal by losing a proton as a negatively charged ligand, and the other beta diketone ligand is neutrally coordinated to the metal. In the crystal structure of complex, the coordination sphere around each copper is in the form of a pyramid with a square base. Two oxygens of one Hpbdo ligand are placed at the base, and one oxygen of the pbdo-ligand is placed at the top of the pyramid, while an oxygen atom of methanol solvent occupies the fourth position in the square base (Figure 4).

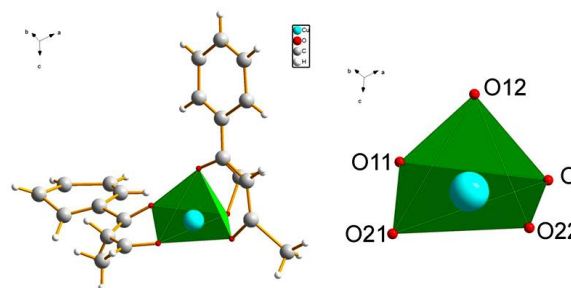


Figure 35. Coordination Sphere of Copper in Complex

This complex also showed a hydrogen bond that its details are presented in Table 5.

Table 19. Hydrogen Bond Information

D-H...A	D-H	H...A	D-A	D-H...A
O-H...O22	0.87	2.147	2.889	134.40

In order to have more intense view about these interactions we will present Hirshfeld Analysis. The results of the Hirshfeld Surfaces Analysis for the complexes are showcased in **Figure 5**. This analysis utilized the d_{norm} property to highlight specific areas. Blue regions on the surfaces indicate that the contact distance between atoms inside and outside the surface is greater than the sum of their respective van der Waals radii. White areas represent a contact distance equal to the sum of the van der Waals radii. Additionally, small amounts of red areas indicate a contact distance between atoms inside and outside the surface that is less than the sum of their respective van der Waals radii²⁸.

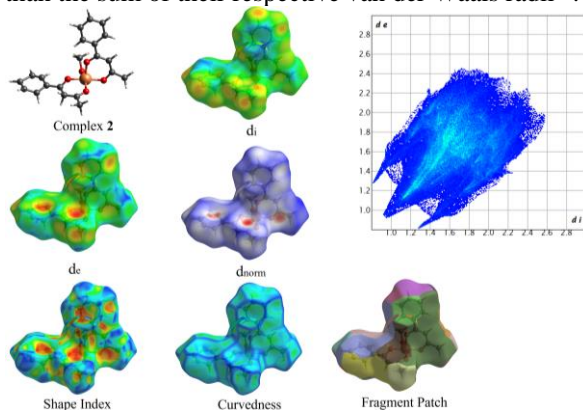


Figure 36. Hirshfeld surfaces analysis of complex

Figure 6 provide a comprehensive breakdown of the percentage contributions by atoms in the surface area to offer a more detailed understanding of the various interaction contributions in these complexes. It is important to note that the figures are calculated with reciprocal contacts, so internal and external terms are not mentioned. H...H interactions make a significant contribution to the surface, accounting for 59.6% in complex. The sum of the hydrogen bond contribution is 7.1%.

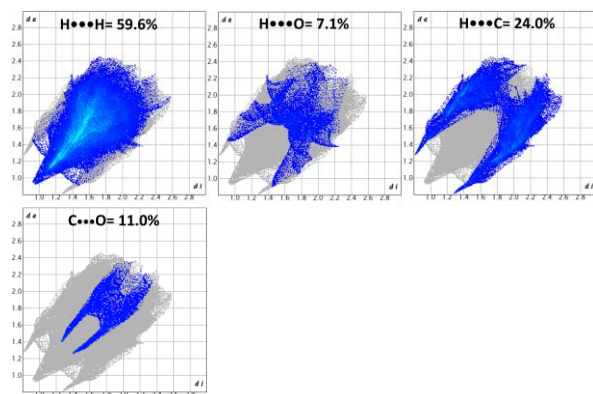


Figure 37. Surface contributions percentage of complex

Conclusion

In conclusion, this research effectively produced a copper complex and verified its structures through IR spectroscopy. The complexes were further examined using X-ray diffraction, which disclosed that the [Cu(Hpbdo)(pbdo)(OCH₃)] complex crystallized in the monoclinic crystal system with the P2₁ space group. The complexes exhibited Hydrogen bond, and Hirshfeld analysis indicated that the surfaces hydrogen bond contribution was 7.1%. Moreover, the study discovered that the significant amount of interaction in the surfaces was associated with H...H interactions, which accounted for 59.6% in the complex. In general, this investigation offers valuable insights into the structural properties and interactions of these copper complexes.

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