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Full Length Research Article

NEW ONE-POT SYNTHETIC ROUTE AND SPECTROSCOPIC CHARACTERIZATION OF DINUCLEAR TRIPLE CARBOXYLATO-BRIDGED CU^{II} COMPLEXES OF THE POLYPYRIDYL LIGANDS

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ABSTRACT

This paper describe a new one-pot synthetic route for the preparation of dinuclear triple carboxylato-bridged copper(II) complexes incorporating polypyridyl ligands. The ligands utilized were 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), and dipyrido[3,2-a:2',3'-c]phenazine (dppz). Reaction of these ligands with copper(II) nitrate and acetylated lincomycin under mild conditions serendipitously yielded the complexes: $[Cu_2(bpy)_2(CH_3COO)(OH)(H_2O)](NO_3)_2$, $[Cu_2(phen)_2(CH_3COO)(OH)(H_2O)](NO_3)_2$ and $[Cu_2(dppz)_2(CH_3COO)(OH)(H_2O)](NO_3)_2$. The complexes were characterized by FTIR spectroscopy and elemental analysis (C, H, N), while the structure of complex 1 was confirmed via single-crystal X-ray crystallography. The X-ray analysis revealed a dinuclear core with a triple carboxylato bridge, confirming the proposed coordination geometry. The synthetic method highlights the role of acetylated lincomycin as a unique reagent in facilitating the formation of these dinuclear copper complexes. The findings underscore the potential of these complexes for further exploration in catalysis, molecular magnetism, and biomimetic chemistry.

Keywords: One-pot synthesis, Dinuclear copper complexes, Polypyridyl ligands, Triple carboxylato-bridged complexes, Spectroscopic characterization

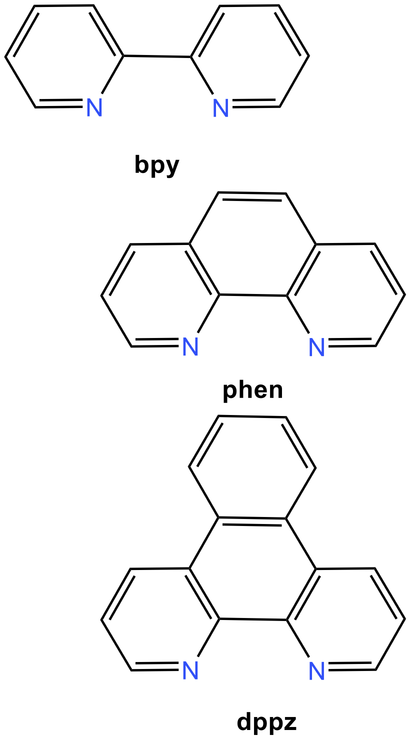
INTRODUCTION

Copper(II) complexes have garnered significant interest in coordination chemistry due to their versatile structures, unique electronic properties, and diverse applications in catalysis, biological systems, and materials science (Direm *et al.*, 2018; Ogodo and Abosede, 2018). Dinuclear copper complexes, in particular, are notable for their fascinating ability to form carboxylato-bridged motifs, which exhibit intriguing magnetic, catalytic, and biomimetic properties (Massoud *et al.*, 2015; Chailuecha *et al.*, 2006). The triple carboxylato-bridge is a distinctive structural feature in many copper complexes, stabilizing the metal centers and imparting unique reactivity profiles (Youngme *et al.*, 2008a; Youngme *et al.*, 2008b).

Polypyridyl ligands, such as 2,2'-bipyridine (bpy), 1,10-phenanthroline (phen), and dipyrido[3,2-a:2',3'-c]phenazine (dppz), are widely utilized in the design of metal complexes due to their strong chelating abilities, π-conjugated systems, and ability to modulate the electronic environment of the central metal ion (Frota *et al.*, 2024a; Frota *et al.*, 2024b; Obaleye and Abosede, 2019). These ligands also play a critical role in the stabilization of dinuclear copper(II) systems and influence their spectroscopic and catalytic properties. Despite significant advancements, the development of efficient synthetic methodologies for dinuclear copper(II) complexes and the systematic investigation of their properties have not been well documented.

This study presents a new one-pot synthetic route for dinuclear triple carboxylato-bridged copper(II) complexes incorporating bpy, phen, and dppz as polypyridyl ligands. The synthesized complexes, $[Cu_2(bpy)_2(CH_3COO)(OH)(H_2O)](NO_3)_2$, $[Cu_2(phen)_2(CH_3COO)(OH)(H_2O)](NO_3)_2$ and $[Cu_2(dppz)_2(CH_3COO)(OH)(H_2O)](NO_3)_2$, were designed to evaluate the structural and spectroscopic effects of varying the polypyridyl ligand framework.

The FTIR spectroscopic characterization of these complexes sheds light on their mode of coordination of the ligands while the crystal structure of $[Cu_2(bpy)_2(CH_3COO)(OH)(H_2O)](NO_3)_2$ confirms molecular structures of the complexes. Furthermore, these complexes serve as promising candidates for exploring applications in areas such as molecular magnetism, catalysis, and potential biomimetic models of copper-containing enzymes. This work contributes to the growing body of knowledge in synthetic coordination chemistry and offers a foundation for further studies on dinuclear copper systems.



bpy

phen

dppz

Scheme 1: Ligands used

MATERIALS AND METHODS

Analytical grade reagents and solvents were purchased from VWR International and used without further purification. Elemental (C, H and N) analyses were carried out using standard methods with Elementar Analysen Systeme Vario® MICRO VI 6.2 GmbH. UV–Vis spectra were measured using a JASCO V-730 UV-Vis spectrophotometer. FTIR spectra were recorded in a range of 4,000–400 cm^{-1} on Shimadzu FTIR-8400S instrument. Melting points were taken on a Jenway analytical instrument and were uncorrected. The electrospray mass spectra were recorded on a THERMO Finnigan LCQ Advantage max ion trap mass spectrometer. The single-crystal X-ray diffraction data for 1 were collected at room temperature using Mo-Kα radiation. All measurements were taken at room temperature.

Synthesis of Dipyrido[3,2-*a*:2',3'-*c*]phenazine (dppz) ligand

The dppz ligand dipyrido[3,2-*a*:2',3'-*c*]phenazine was prepared by following the method of Dupureur and Barton, 1997. A mixture of 1,10-phenanthroline-5,6-dione (1.0 g, 4.8 mmol) and 1,2-phenylenediamine (0.6 g, 5.7 mmol) in ethanol (400 mL) was stirred for 2 hrs at 50 °C and then at room temperature overnight on a magnetic stirrer. The resulting solution was reduced in volume by rotary evaporation at 50 °C to yield a cream-coloured product. The crude product was left to stand for 8 h, methanol/water (10/90 v/v) was then added, and the product was filtered and recrystallized from methanol to give a cream solid. Yield: 0.96 g, 80%. Melting point: 250 °C. ^{1}H NMR (300 MHz, DMSO-d_6): δ (ppm) 9.7 (H4, dd, 2H), 9.3 (H2, dd, 2H), 8.35 (H6, dd, 2H), 7.95 (H7, dd, 2H) and 7.8 (H3, dd, 2H). FT-IR (KBr, ν/cm^{-1}): 3419, 1645, 1573, 1489, 1413, 1361, 1338, 1134, 1074, 1035, 815, 763, 740, 638, 563, 414.

Synthesis of complexes

CuAcLbpy: [$Cu_2(bpy)_2(CH_3COO)(OH)(H_2O)$]$(NO_3)_2$, (1)

0.121 g(0.5 mmol) of $Cu(NO_3)_2.3H_2O$ was added to 0.2908 g of acetylated lincomycin (AcL) in 10 ml methanol and the solution stirred for 1 hour. 0.0781 (0.5 mmol) of 2,2'-bipyridine was added and stirring continued for another 2 hours. The light blue precipitate was filtered washed with methanol and dried in vacuum desiccator. The remaining blue filtrate on slow evaporation gave quality single crystals suitable for X-ray analysis after a few days. Calculated: C, 40.12; H, 3.52; N, 12.76. Found: C, 37.15; H, <0.10; N, 11.33. FT-IR (KBr, ν/cm^{-1}): 3466, 3109, 3074, 3034, 2920, 2852, 2785, 2420, 2355, 2017, 1878, 1745, 1685, 1602, 1568, 1494, 1475, 1444, 1398, 1369, 1334, 1251, 1226, 1166, 1109, 1031, 1014, 977, 941, 908, 825, 775, 731, 711, 659, 634, 609, 557, 509, 459, 420.

CuAcLphen: [$Cu_2(phen)_2(CH_3COO)(OH)(H_2O)$]$(NO_3)_2$ (2)

0.121 g (0.5 mmol) of $Cu(NO_3)_2.3H_2O$ was added to 0.2908 g of AcL in 10 ml methanol and the solution stirred for 1 hour. 0.0991 (0.5 mmol) of 1, 10-phenanthroline monohydrate was added and stirring continued for another 1 hour 15 minutes. The blue precipitate was filtered and the filtrate allowed standing till the next day. The bluer precipitate formed was washed with methanol, combined and dried in vacuum desiccator. Calculated: C, 44.20; H, 3.28; N, 11.89. Found: C, 44.10; H, 2.66; N, 12.36. FT-IR (KBr, ν/cm^{-1}): 3369, 3354, 3115, 3090, 3064, 2999, 2949, 2841, 2754, 2638, 2519, 2420, 2349, 2011, 1959, 1840, 1749, 1626, 1606, 1585, 1521, 1433, 1394, 1357, 1330, 1263, 1226, 1141, 1103, 1062, 1039, 985, 956, 914, 869, 852, 815, 790, 779, 740, 721, 696, 650, 630, 603, 561, 484, 428.

CuAcLdppz: [$Cu_2(dppz)_2(CH_3COO)(OH)(H_2O)$]$(NO_3)_2$ (3)

0.121 g (0.5 mmol) of $Cu(NO_3)_2.3H_2O$ was added to 0.2884 g (0.5 mmol) of AcL in methanol and the solution was stirred for 1 hour. 0.1400 g (0.5 mmol) of dppz and 5 ml of methanol were added and the solution further stirred for 2 hours and filtered. The blue residue was washed with methanol and dried in vacuum desiccator. Calculated: C, 50.11; H, 2.99; N, 15.38. Found: C, 48.38; H, 2.73; N, 15.08. FT-IR (KBr, ν/cm^{-1}): 3452 br, 3084, 3036, 2918, 2848, 2758, 2401, 2355, 2019, 1977, 1946, 1604, 1581, 1496, 1417, 1361, 1232, 1192, 1141, 1076, 1047, 1003, 964, 935, 902, 827, 763, 731, 669, 646, 617, 570, 497, 428, 408.

RESULTS AND DISCUSSION

Characterization of complexes 1-3

In an effort to synthesize ternary Cu(II) complexes of acetylated lincomycin with bipyridine, phenanthroline, and dipyridine phenazine, dinuclear Cu(II) complexes featuring triple carboxylato bridges and coordinated polypyridyl ligands were successfully obtained.

The crystal Structure of complex $Cu_2(bpy)_2(CH_3COO)(OH)(H_2O)_2$ **(1)** been solved **(Figure 1**). Even though the crystal structure of the complex has been previously reported, we have obtained a new preparative route for the synthesis of this ferromagnetic complex. The yield obtained following this new preparative route cannot be compared to the previously reported procedure because the yield was not reported. The infrared spectra display a broad band at about 3500 cm^{-1} which can be assigned to the bridging OH vibration of the hydroxido ligands and/or lattice water. $\nu_{as}(COO^-)$ and ν_s (COO^-) due to the two different coordination modes of carboxylate bridges in the complexes give rise to 1568 and 1398 cm^{-1} for **33,** 1521 and 1394 cm^{-1} for **34** and 1581 and 1361 cm^{-1}for **35**. ($\Delta\nu$ is 170 and 127 for complexes **33** and **34** respectively) Bands for ionic nitrate appeared at 1334-1369 cm^{-1}for **33**, 1330-1357 cm^{-1} for **34**. All these values fall within the range reported in literature (Coates, 2000).

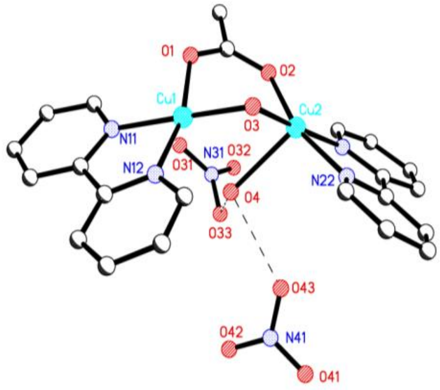
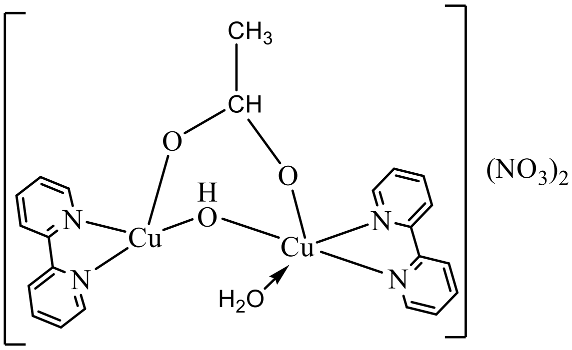
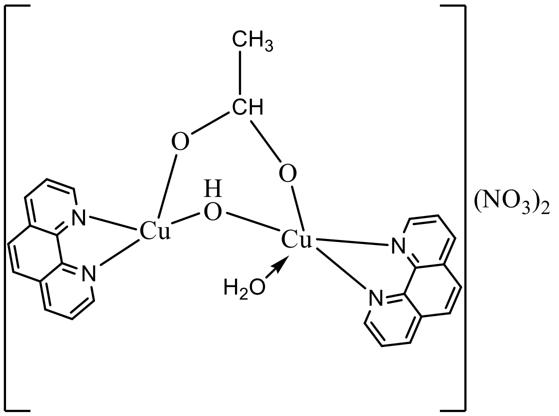


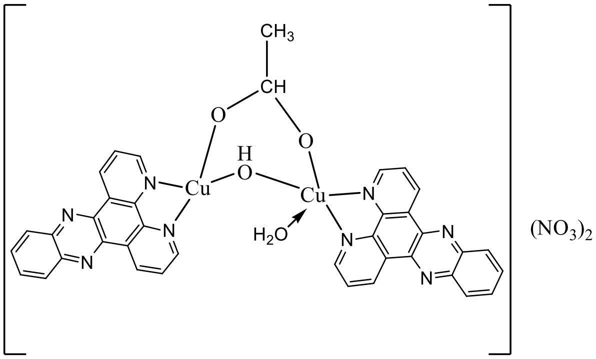
Figure 1: Crystal structure of complex [$Cu_2(bpy)_2(CH_3COO)(OH)(H_2O)$]$(NO_3)_2$



[Cu₂(bpy)₂(CH₃COO)(OH)(H₂O)](NO₃)₂ (1)



{Cu₂(phen)₂(CH₃COO)(OH)(H₂O)}.2NO₃ (2)



{Cu₂(dppz)₂(CH₃COO)(OH)(H₂O)](NO₃)₂ (3)
Figure 2: Structures of complexes **1-3**

The ferromagnetic dinuclear triply-bridged copper(II) complexes containing carboxylato bridges, $\{Cu_2(bpy)_2(CH_3COO)(OH)(H_2O)\}.2NO_3$ (**1**), $\{Cu_2(phen)_2(CH_3COO)(OH)(H_2O)\}.2NO_3$ (**2**) and $\{Cu_2(dppz)_2(CH_3COO)(OH)(H_2O)\}.2NO_3$ (**3**) have been serendipitously discovered by a route that is more reproducible and that has higher yields than the previously reported procedures. Though the 2,2'-bipyriddine and 1,10-phenanthroline analogues of these complexes have been reported earlier the dppz analogue (complex **3**) of the dinuclear carboxylato-bridged copper(II) complexes have not been reported.

Conclusion

In this study, a novel one-pot synthetic strategy for the preparation of dinuclear triple carboxylato-bridged copper(II) complexes incorporating bpy, phen, and dppz as polypyridyl ligands has been developed. The serendipitous use of acetylated lincomycin played a pivotal role in the formation of these complexes, illustrating its potential utility as a reagent in coordination chemistry. The characterization techniques employed, including FTIR spectroscopy, elemental analysis, and single-crystal X-ray diffraction for complex 1, confirmed the structures and coordination geometries of the synthesized complexes. The triple carboxylato-bridged motif in these dinuclear systems provides a stable platform for exploring their electronic, magnetic, and catalytic properties. The first report of the dppz analogue (complex **3**) of the dinuclear carboxylato-bridged copper(II) complexes of this work contributes to the growing field of polypyridyl copper chemistry and opens pathways for the rational design of related systems with potential applications in diverse areas, including catalysis and bioinorganic modeling. Future work will focus on detailed investigation of the properties and applications of these complexes in molecular catalysis and biological systems.

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