

Cu(II) Complexes of a Tripodal Tetraamine Incorporating a Pendant Arm and Related Schiff Base Ligand; X-ray Crystal Structure and Spectral Studies

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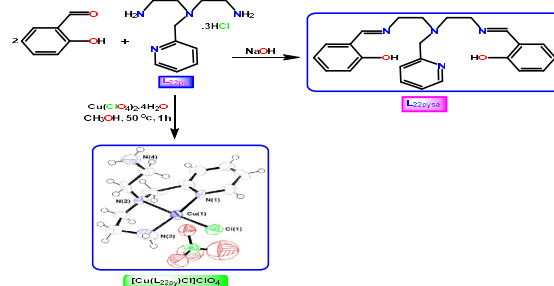
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Abstract: Two new Cu(II) complexes, [Cu(L22py)Cl]ClO₄ (**1**), Cu(L22pysa) (**2**), {L22py = N-(2-pyridylmethyl)-N-(2-aminoethyl)-1,2-diaminoethane, were prepared through the reaction of suitable metal ion salts, L22py, and salicylaldehyde in the presence of NaClO₄. The ligands were characterized by elemental analysis, IR spectroscopy, and ¹³C and ¹H NMR analysis. Additionally, X-ray crystal structure analysis was performed for complex 1. The X-ray study revealed that the Cu(II) ion exhibits a square configuration.



Keywords: Complex, Tripodal, Donor atom, Crystal structure, Schiff base

1. INTRODUCTION

Schiff base complexes are considered to be among the most important stereochemical models in main group and transition metal coordination chemistry due to their preparative accessibility and structural variety.¹⁻⁵ The stereochemical features peculiar to tripodal tetradentate amine ligands have led to their use in a wide variety of inorganic systems. Six-coordinate octahedral complexes containing such ligands invariably display cis geometries, and the inequivalence of the remaining two coordination sites in such complexes has been utilised in numerous studies aimed at monitoring the stereochemical outcome of ligand substitution reactions in Cu(III) complexes containing these ligands.⁶⁻⁹ The steric constraints imposed by such ligands often result in trigonal bipyramidal geometries for five-coordinate systems,¹⁰⁻¹² while the rare examples of four-coordinate complexes containing tripodal ligands display distorted tetrahedral geometries,^{13,14} owing to the inability of these ligands to accommodate a square planar geometry.

In addition to tren, there are several reports about synthesis and characterization of tripodal tetraamine

ligands with N₄ donor set and their related complexes.⁶⁻¹² According to literature in most of them the structure of metal complexes has been studied. In this paper, we report the synthesis and characterization of a tripodal tetraamine ligand (L_{22py}) containing a pyridine ring. Previously we have reported the synthesis and characterization of dinuclear Ni(II) complexes of above ligand.¹³ In addition to study the structure of synthesized complexes, we tried to study their magnetic properties. According to our knowledge there are some reports about the synthesis and characterization of new complexes with L_{22py}.^{6,14,15} Previously a new Cu(II) complex and its X-ray crystal structure has been reported.⁶ Recently we have been involved to synthesis and characterization of new tripodal tetraamine ligands and their complexes and in some cases we have reported the template condensation of the ligand with different aldehydes in the presence of appropriate metal ions to prepare the new Schiff base complexes.¹⁶⁻¹⁸ As it has been noted, in this work we report the synthesis and characterization of ligand L_{22py} its Schiff base with Salicylaldehyde (Figure 1) and their related Cu(II) complexes.

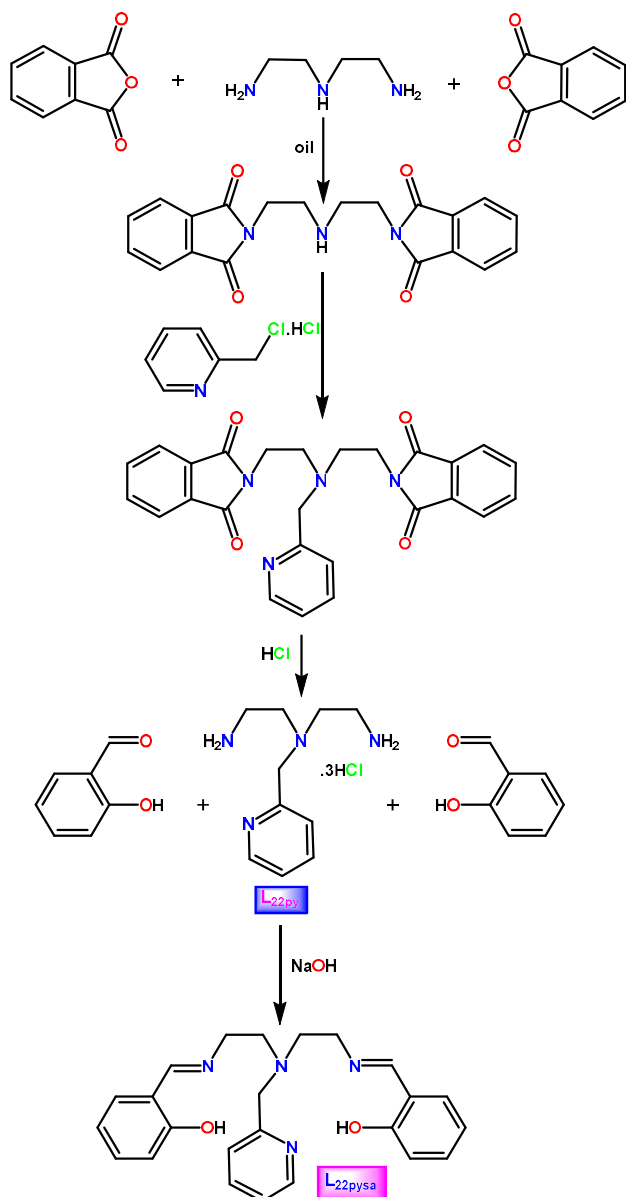


Figure 1. Synthesis route of ligands.

2. EXPERIMENTAL

General information

Metal salts were obtained from Aldrich and was used without further purification. The asymmetrical tripodal ligand was prepared as its hydrochloride salts via literature methods.^{19,20} IR spectra were measured on a Perkin Elmer FT-IRGX spectrophotometer.

X-ray crystal structure determination

A summary of the details of the crystal data, data collection and refinement details is given in Table 1. All structural determinations were carried out using a Bruker SMART-1000 CCD diffractometer equipped with Mo K α X-radiation ($\lambda = 0.71073$ Å for all compounds) at 150(2) K for **1**. Absorption corrections were applied using SADABS,²¹ and structure

solution and refinement was carried out using SHELXS-97 and SHELXL-97, respectively.²² The structure was solved by direct methods and refined by full-matrix least-squares methods on F². Hydrogen atoms were placed geometrically and refined with a riding model, with U constrained to be 1.2 (1.5 for methyl groups) times U of the carrier atom.

Table 1. Crystal data and structure refinement for complex **1**

Formula	C ₁₀ H ₂₀ Cl ₂ Cu Na ₄ O ₅
Identification code	a
Temperature	293(2) K
Wavelength	0.71073 Å
Crystal system	Monoclinic
Space group	C2/c
Unit cell dimensions	
a = 33.5400(11) Å	$\alpha = 90^\circ$
b = 13.0020(12) Å	$\beta = 103.823(11)^\circ$
c = 8.7020(9) Å	$\gamma = 90^\circ$
Volume	3684.9 Å ³
Z	8
Density (calculated)	1.610 mg m ⁻³
Absorption coefficient	1.681 mm ⁻¹
F(000)	1840
Crystal size	0.11 × 0.14 × 0.26 mm ³
Theta range for data collection	2.44 to 29.31°
Index ranges	-45 ≤ h ≤ 46, -17 ≤ k ≤ 17, -9 ≤ l ≤ 11
Reflections collected	17084
Independent reflections	4931 [R(int) = 0.1017]
Completeness to theta = 29.31°	97.9%
Refinement method	Full-matrix least-squares on F ²
Data/restraints/parameters	4931/0/175
Goodness-of-fit on F ²	3.055
Final R indices [I > 2sigma(I)]	R1 = 0.2385, wR2 = 0.5496
R indices (all data)	R1 = 0.2943, wR2 = 0.5604
Largest diff. peak and hole	5.429 and -2.540 e Å

Preparation of bis(2-aminoethyl)(pyridine-2-ylmethyl)amine (L₂₂py)

Step 1: Preparation of bis(2-phthalimidoethyl)(pyridine-2-ylmethyl)amine. Bis(2-phthalimidoethyl)amine (5 g, 13.76 mmol) was suspended in 50 cm³ of water with stirring and pH was adjusted to between 11.5 and 12 by addition of NaOH (5 M). The reaction mixture was kept at room temperature and 2-picolyl chloride (2.26 g, 13.76 mmol) was added to give a white powder. Yield: 90%. ¹H NMR δ_{H} (D₂O) 2.9 (t, 4H), 3.5 (t, 4H) 3.9 (s, 2H), 7.3 (m, 8H) 7.6 (m, 4H). ¹³C NMR δ_{C} (D₂O) 33.7, 53.2, 54.0, 122.5, 123.4, 125.4, 126, 133.7, 134.0, 147.2, 152.0, 168.0.

Step 2: Preparation of ligand L₂₂py. bis(2-phthalimidoethyl)(pyridine-2-ylmethyl)amine (5 g) was dissolved in 6 N HCl (100 cm³) and heated under reflux for 24 h to remove the protection group. The phthalic acid and inorganic salts (NaCl), which formed on cooling, were filtered off and the filtrate was evaporated to small bulk and poured into absolute EtOH. The resulting viscous precipitate was washed with absolute EtOH and dried in vacuum to give a brown powder. Yield: 46%. ¹H NMR δ_{H} (D₂O) 3.0 (t, 4H), 3.2 (t, 4H) 4.2 (s, 2H), 8.1 (m, 2H) 8.8 (m, 2H). ¹³C NMR δ_{C} (D₂O) 36.3, 50.2, 54.4, 126.2, 127.1, 141.1, 147.2.

Preparation of Schiff Base L₂₂pysa

L₂₂py.3HCl (0.1 g, 33 mmol) and NaOH (0.039 g, 0.99 mmol)

were mixed and heated under reflux for 1 hour in EtOH (15 cm³) solution. Then NaCl, which formed on cooling, was filtered off. The filtrate was added to salicylaldehyde (0.08 g, 0.66 mmol) and the solution was stirred at 30–40 °C for 1 h. The mixture was stirred at 50–60 °C for 1 h. The resulting yellow oil was washed collected. Yield: 44.1%. Anal. Calcd. (Found) for C₂₄H₂₆N₄O₂: C, 71.60 (71.47); H, 6.46 (6.42); N, 13.92 (13.83)%. IR (Nujol): 1633 (νC=N) cm⁻¹. ¹H NMR δ_H (CDCl₃) 2.8 (t, 4H), 3.6 (t, 4H) 4.0 (s, 2H), 7.3 (m, 8H) 7.6 (m, 4H) 8.2 (s, 2H). ¹³C NMR δ_c (CDCl₃) 55.3, 57.5, 60.8, 118.3, 118.6, 122.1, 122.9, 133.7, 131.2, 133.2, 136.5, 143.7, 150.4, 161.2, 165.5.

Preparation of the complex [Cu(L_{22py})Cl]ClO₄, (1)

A mixture of L_{22py}.3HCl (0.1 g, 0.33 mmol) and NaOH (0.039 g, 0.99 mmol) in EtOH (15 cm³) was heated under reflux for 1 h, allowed to cool and then filtered. A solution of Cu(ClO₄)₂.4H₂O (0.12 g, 0.37 mmol) in MeOH (5 ml) was added to the filtrate. The mixture was stirred at 50–60 °C for 1 h, during which time it turned blue in color. The solution was filtered and the filtrate reduced to ca. 10 cm³. X-ray quality crystals were obtained by slow diffusion of Et₂O vapor into the latter solution. Yield: 57%. Anal. Calcd. for C₁₀H₁₈Cl₂CuN₄O₄.H₂O: C, 31.2; H, 5.0; N, 13.9. Found. C, 31.8; H, 4.7; N, 13.4%. IR (Nujol, cm⁻¹): 3355 and 3302 (ν(N–H) stretching), 1605 and 1573 (ν(C=N and/or ν(N–H) bending), 1090 (ν(Cl–O) stretching).

Preparation of complex [Cu(L_{22pysa})] (C₂₄H₂₄N₄O₂Cu), (2)

This complex was prepared by a template condensation method. L_{22py}.3HCl (0.1 g, 33 mmol) and NaOH (0.039 g, 0.99 mmol) were mixed and heated under reflux for 1 h in EtOH (15 cm³) solution. Then NaCl, which formed on cooling, was filtered off. The filtrate was added to salicylaldehyde (0.08 g, 0.66 mmol) and the solution was stirred at 30–40 °C for 1 h. Et₃N (0.17 g, 1.68 mmol) was added to the solution, then Cu(ClO₄)₂.4H₂O (0.114 g, 0.37 mmol) dissolved in MeOH (5 cm³) was added. The mixture was stirred at 50–60 °C for 1 h. The resulting blue powder was washed with Et₂O. Yield: 24.1%. Anal. Calcd. (Found) for C₂₄H₂₄N₄O₂Cu: C, 62.20 (62.08); H, 5.18 (5.12); N, 12.09 (12.01)%. IR (Nujol): 1628, 1601, 1536 (νC=N and νC=C) cm⁻¹ and 1096 (νClO₄).

3. RESULTS AND DISCUSSION

Synthesis and characterization

The amine L_{22py}, was first described by Fenton and coworkers who used it as a building block for the preparation of macrocyclic ligands.²³ However, the synthesis was problematic and yields were low. More recently alternative synthetic routes were provided by Skinner and coworkers^{24,25} and by Cheng et al.²⁶ We used a new method here¹⁹ however we used a different second synthetic reaction step that provided L_{22py} in good yields. After preparation of ligand L_{22py} the complexes **1** and **2** were synthesized by neutralization of the hydrochloric salts of the L_{22py} tripodal ligand with sodium hydroxide, and its Schiff base with salicylaldehyde, L_{22pysa} respectively with Cu(II) perchlorate. The IR spectra (Figure 2) and analytical data are consistent with their structure and formulation. In the IR spectrum of complex

1 a pair of sharp ν(N–H) bands at about 3150–3300 cm⁻¹ correspond to the coordinated primary amine groups.²⁷ In the case of Schiff base ligand L_{22pysa} and complex **2**, the condensation of all primary amino group is confirmed by the lack of N–H stretching band in the IR region (3150–3450 cm⁻¹) and the presence of strong C=N stretching at 1633 and 1628 cm⁻¹ band respectively (Figure 2). The stretching bands of the pyridine C=N groups and bending bands of primary amine groups appear, as expected, at about 1578–1610 cm⁻¹.

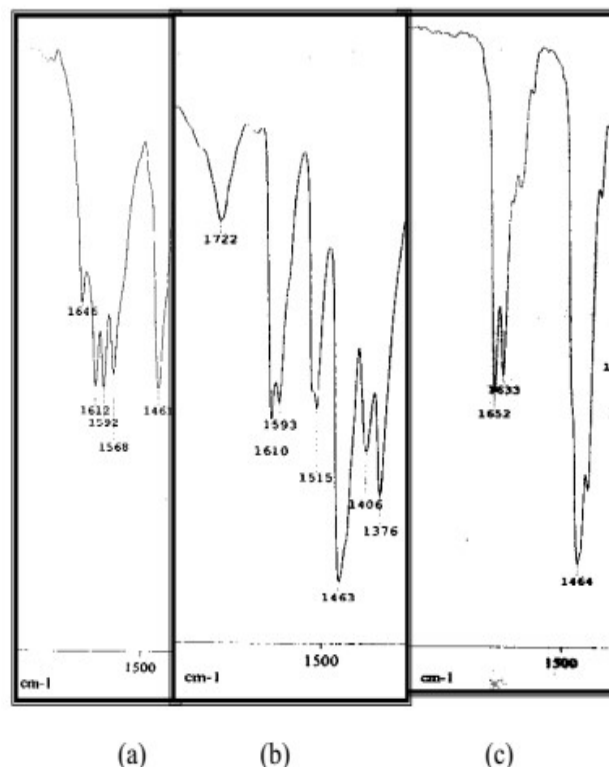


Figure 2. The comparison of the important section of IR spectra of ligand protected amine, (a), ligand L_{22py}, (b), and Schiff base L_{22pysa}, (c).

X-ray crystal structure analysis

The stability of five- and six-membered chelate rings in coordination complexes is usually explained in terms of the chelate effect, in which a positive entropy term renders chelation thermodynamically favorable.²⁸ However, the process of chelation becomes less entropically favourable for systems in which chelate rings containing more than six atoms can be formed, and such rings are also inherently strained. In agreement with this, a search of the Cambridge Structural Database²⁹ revealed 9891 metal complexes containing the chelated –N(CH₂)₂N– fragment and 2762 containing the chelated –N(CH₂)₃N– fragment, but only 140, 59 and 6 containing the chelated –N(CH₂)₄N–, –N(CH₂)₅N– and –N(CH₂)₆N– fragments, respectively. In the majority of these latter complexes, the large chelate rings are incorporated in macrocyclic or cryptand ligands, and this preorganisation

undoubtedly aids chelation. Usually coordination chemistry of Cu(II) complexes show the structure around the metal ion are distorted octahedral, square pyramidal, trigonal bipyramidal or tetrahedral geometry but in this work it has been square.³⁰ Suitable crystals of **1** were obtained by slow diffusion of diethyl ether vapor into methanol-ethanol solutions. The structure of this compound with the atomic numbering schemes is shown in Figure 3. Single crystal X-ray structure analysis shows that three of nitrogens and one chloride ion have been coordinated to Cu(II) metal central ion. One molecule of perchlorate ion is as counter ion. The molecular structure of complex **1** has been determined by single crystal X-ray diffraction studies and has been shown to exhibit square-coordinated Cu ion by one pyridine donor, one tertiary amine, one chloride ion and one primary amine functions. As can be seen in Figure 3 one of the primary amine groups hasn't been coordinated to the metal ion. The refinement data are listed in Table 1. Selected bond lengths and bond angles are given in Table 2. The Cu–N bond lengths are in the expected range from 1.94(2) to 2.25(6) Å.

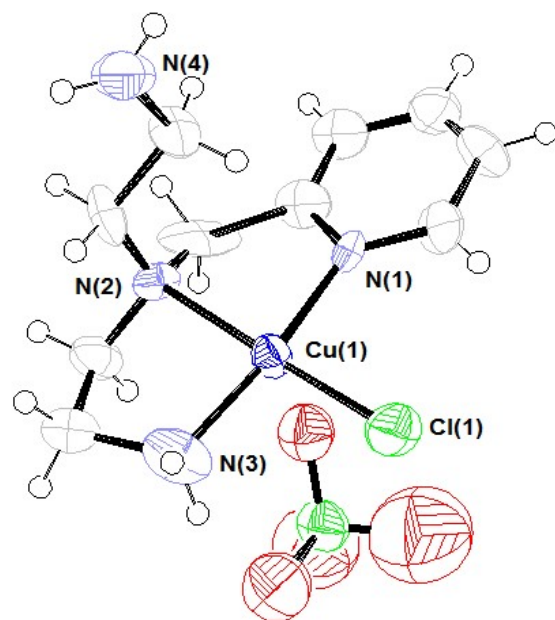


Figure 3. X-ray crystal structure of complex **1**.

Table 2. Selected bond length (Å) and bond angles (°) for complex **1**

Bond lengths (Å)	
Cu(1)–N(1)	1.97(18)
Cu(1)–N(2)	2.08 (15)
Cu(1)–N(3)	1.94(2)
Cu(1)–Cl(1)	2.25(6)
Bond angles (°)	
N(3)–Cu(1)–N(1)	170.2(8)
N(3)–Cu(1)–N(2)	86.8(8)
N(1)–Cu(1)–N(2)	84.2(7)
N(3)–Cu(1)–Cl(1)	91.8(7)
N(1)–Cu(1)–Cl(1)	97.7(6)
N(2)–Cu(1)–Cl(1)	170.9(5)

As can be seen in the X-ray, the chloride ion is located *trans* position to the N-tert. The longest bond distance is related to the Cu–Cl (2.25 Å) and the shortest bond length is related to the Cu–N_{amine} (1.94 Å). But about the structure of complex **2**, unfortunately we couldn't get fine crystals for X-ray crystallography analysis, but according to results of IR spectrum and microanalysis and in the compare of our previous works we predict the structure should be distorted octahedral, due to the fact that the Schiff base ligand is eight coordinated with the N₄O₂ donor sets. Since both oxygens of hydroxyl group have been deprotonated so, both oxygen atoms of Schiff base are coordinated to the metal ion.

4. CONCLUSIONS

In this report we tried to report the synthesis and characterization of a new Schiff base ligand and related complex with the Cu(II) metal ion. For this mean, firstly we prepared a tripodal amine with the N₄ donor atoms, and then by the reaction of the synthesized tripodal amine with the salicylaldehyde, the Schiff base was prepared. In the end, the X-ray of the complex of Cu(II) with the tripodal amine was reported and also we studied the IR and ¹H, ¹³C NMR of Schiff base and related complex with the Cu(II).

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Appendix A. Supplementary material

CCDC 1434325 contains the supplementary crystallographic data for complex **1**. These 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.

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