

REGULAR ARTICLE

A New Copper(I) Complex Based on 4-amino-3,5-bis(3-pyridyl)-1,2,4-triazole: Synthesis, Crystal Structure, Theoretical Study, Thermal Behavior and Luminescence

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Abstract. The synthesis, characterization and structure of a 1D coordination polymer {[CuBr(3-abpt)]·2DMSO}_n (**1**) (3-abpt = 4-amino-3,5-bis(3-pyridyl)-1,2,4-triazole) is described. X-ray structural analyses reveal that **1** exhibits a 1D ladder-like chain structure and each copper(I) center in **1** displays a distorted tetrahedral coordination geometry {CuN₃Br}. Density functional theory and time-dependent density functional theory calculations at the B3LYP/LanL2DZf+6-31G* level were performed on complex **1** to rationalize its experimental absorption spectra. The luminescent property and thermal behavior of the complex were also investigated.

Keywords. Copper(I) complex; crystal structure; dft calculations; luminescence.

1. Introduction

In recent years, the design and synthesis of organic–inorganic hybrid complexes are of continuous interest not only for their various structural topologies^{1–3} but also for their potential applications in catalysis, biology and material science.^{4–8} As an important type of organic–inorganic hybrid complexes, copper(I) complexes based on copper halides and organic N-donor ligands have drawn much attention due to their intriguing photophysical properties and possible utilization in light-emitting devices, electroluminescence devices, and probes of biological systems.^{9–14} The copper(I) ion has d¹⁰ electronic configuration and can adopt diverse coordination numbers.^{15,16} Also, the associated counter anion X (X = Cl, Br, I) can be incorporated as an essential element of the framework.^{17,18} Organic N-donor ligands, particularly in the form of N-heterocycles, have been widely used in metal coordination complexes due to their rich coordination mode.^{19–21} In particular, there is a growing interest in the development of crystal materials by using triazole ligands because of their rich coordination modes and interesting

properties.^{22–24} 4-Amino-3,5-bis(3-pyridyl)-1,2,4-triazole (3-abpt) is a rigid angular multifunctional ligand containing five potential N-donors, which can serve as monodentate, bidentate and multidentate ligand.^{25–27} It has been found that many coordination complexes based on 3-abpt have novel architectures, interesting electrical and magnetic properties, and/or nonlinear optical properties.^{28–30} Accordingly, we have synthesized one new tetrahedrally coordinated copper(I) complex with 3-abpt and CuBr, which displays a 1D ladder-like chain structure. The luminescence property and thermal behavior of this copper(I) complex were also investigated. Density functional theory (DFT) and time-dependent density functional theory (TD-DFT) calculations have afforded further insight into the electronic transitions and spectral characterization of this luminous copper(I) complex.

2. Experimental

2.1 Materials and physical measurements

All chemicals and solvents used for the syntheses were reagent grade and used without further purification. The 3-abpt ligand was prepared according to literature methods.³¹

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Elemental analyses for C, H, and N were performed on a Perkin-Elmer 240C system. Infrared spectra were recorded in the region 400–4000 cm^{-1} on a Nicolet Nexus 470 spectrometer (Germany) with samples as KBr disks. The UV-Vis absorption spectra were obtained with a FLASH EA 1112 spectrophotometer. Steady-state fluorescence spectra were measured on a Fluoro-Max-P instrument; samples were dissolved in dry ethanol, filtered, transferred to a long quartz cell, and then capped and deoxygenated by bubbling with N_2 before measurement. Thermogravimetric analysis (TGA) measurements were carried out on a Perkin-Elmer Pyris 1 system under N_2 purge with a heating rate of $10^\circ\text{C}/\text{min}$.

2.2 Synthesis of complex 1

Complex **1** was prepared by following a general synthetic procedure in which CuBr (0.014 g, 0.1 mmol) was added to 3 mL dimethyl sulfoxide (DMSO) and the resultant solution was stirred at room temperature for 0.5 h. After filtration, 1 mL DMSO as the buffer was carefully layered onto the filtrate. 4 mL CH_3OH containing 3-abpt (0.0238 g, 0.1 mmol) was then very carefully layered on the top of the buffer solution. Yellow block crystals of complex **1** (0.0352 g) were obtained after several days (yield 65.6%). Analysis calculated for $\text{C}_{16}\text{H}_{22}\text{CuBrO}_2\text{S}_2\text{N}_6$: C 35.72, H 4.12, N 15.62%; found: C 35.68, H 4.15, N 15.65%. IR for **1** (KBr pellets, cm^{-1}): 3439.2 (m), 3239.2 (s), 3088.8 (m), 1615.6 (w), 1463.3 (m), 1390.7 (m), 812.2 (w), 700.5 (m).

2.3 X-ray data collection and structure refinement

Single crystal X-ray diffraction data for complex **1** at 293 K were collected with the use of graphite-monochromated Mo- $K\alpha$ radiation ($\lambda = 0.71073 \text{ \AA}$) on a Rigaku Saturn 724+ CCD diffractometer. A well-selected $0.22 \times 0.20 \times 0.18 \text{ mm}^3$ yellow block crystal was used for the single crystal X-ray diffraction experiments. The SMART and SAINT program packages were used for data collection and integration, respectively. The collected data were also corrected for absorption using equivalent reflections and SADABS based upon Laue symmetry. The structure was solved by direct methods and refined on F^2 by the full-matrix least-squares calculations with the use of SHELX-97 program package.^{32–34} All the non-hydrogen atoms were refined with anisotropic thermal displacement coefficients. All the hydrogen atoms were placed at the calculated positions and refined following the riding model. Details of the crystal parameters, data collection and refinement of complex **1** are summarized in Table 1.

2.4 Density Functional Theoretical Study

Density functional theory (DFT) and time-dependent density functional theoretical (TD-DFT) calculations were performed to rationalize the experimental absorption spectra by using the Gaussian 09 program.³⁵ The model compound of complex **1** was selected from experimental X-ray

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

Formula	$\text{C}_{16}\text{H}_{22}\text{CuBrN}_6\text{O}_2\text{S}_2$
Formula weight	537.96
Temperature /K	293(2)
Wavelength / \AA	0.71073
Crystal system	Monoclinic
Space group	$P2_1/c$
$a/\text{\AA}$	12.444(3)
$b/\text{\AA}$	12.647(3)
$c/\text{\AA}$	16.395(6)
$\alpha/^\circ$	9.00
$\beta/^\circ$	124.47(2)
$\gamma/^\circ$	90.00
$V/\text{\AA}^3$	2127.2(11)
Z	4
$\rho_{\text{calcd.}}/\text{g}\cdot\text{cm}^{-3}$	1.661
$F(000)$	1064
Limiting indices	$-15 \leq h \leq 14, -13 \leq k \leq 15,$ $-17 \leq l \leq 20$
Reflections collected	9893
Independent reflections	4145
Independent reflections with $I > 2\sigma(I)$	3547
R_{int}	0.021
Completeness to $\Theta = 26.03$	98.7%
$\mu(\text{mm}^{-1})$	3.125
Refinement method	full-matrix least-squares on F^2
Goodness-of-fit on F^2	1.061
Final R indices [$I > 2\sigma(I)$]	$R_1 = 0.0627, wR_2 = 0.1490$
R indices (all data)	$R_1 = 0.0534, wR_2 = 0.1410$

single-crystal structure. The restricted singlet wave function for complex **1** in DMF (dielectric constant, $\epsilon = 36.71$) solution was tested to be stable with the framework of the polarized continuum model (PCM) using B3LYP functional.^{36,37} Here, the basis set 6-31G*+LanL2DZ* (using 6-31G* basis set for C, N, Br, and H atoms, adding the f-type polarization functions to Cu atom at the basis set LanL2DZ) was employed in view of the influence of d and f functions on the absorption spectra. The exponent of f orbital for Cu (3.525) atom was selected as those in previous work.³⁸ The vertical electronic excitation energies of complex **1** in DMF solution were then obtained through TD-DFT/PCM calculation at the same level.

3. Results and Discussion

3.1 Crystal structure description

X-ray structural analysis reveals that the new copper(I) complex $\{[\text{CuBr}(\text{3-abpt})]\cdot 2\text{DMSO}\}_n$ (**1**) crystallizes in the monoclinic system with $P21/c$ space group. The coordination environment of Cu and the line drawing of **1** are depicted in Figure 1 and Figure S1 (in Supplementary

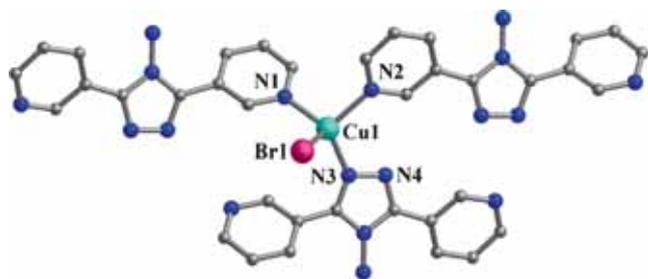


Figure 1. The coordination environment of Cu in complex **1**. (The DMSO molecule and hydrogen atoms are omitted for clarity)

Information). Selected bond lengths (Å) and angles (°) of **1** are listed in Table 2.

As shown in Figure 1, Cu atom is coordinated by one bromide ion, one triazole and two pyridyl nitrogen atoms from three different 3-abpt ligands, displaying a distorted tetrahedral coordination geometry $\{\text{CuN}_3\text{Br}\}$. The Cu–Br (2.5105(1) Å) and Cu–N bond lengths (2.010(4)–2.095(4) Å) follow in the typical ranges.^{39,40} The bond angles around the Cu atom vary from 103.33(1) to 123.12(2)°. The 3-abpt ligand exhibits a μ_3 -bridging mode, as a tridentate ligand coordinated to three copper(I) ions through triazole N3 and two pyridyl N donors. The triazole N4 and amino group are uncoordinated. The Cu1 and Cu1A are connected by two 3-abpt ligands to form a 12-membered ring (Figure 2). The 3-abpt ligand takes the *cis*-fashion to connect the two Cu atoms with a Cu...Cu distance of 5.464(1) Å. The dihedral angle between the C1–N1 and C4–N2 planes in the 3-abpt ligand is 70.95°, showing some distortion.

The 12-membered ring units in complex **1** are bridged by pyridyl of 3-abpt ligands resulting in the formation of a one-dimensional ladder-like chain structure polymer as shown in Figure 3.

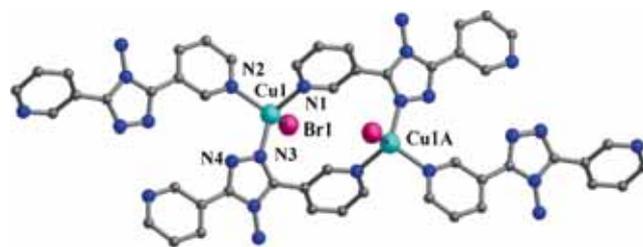


Figure 2. The ring structure in complex **1**. (The DMSO molecule and hydrogen atoms are omitted for clarity)

Table 2. Selected bond lengths (Å) and angles (°) of **1**.

Bond lengths (Å)		Bond lengths (Å)	
Cu(1)–N(1)	2.040(4)	Cu(1)–N(2)	2.095(4)
Cu(1)–N(3)	2.010(4)	Cu(1)–Br(1)	2.5105(1)
C(1)–C(7) #1	1.383(6)	C(3)–C(6) #1	1.383(7)
C(4)–C(12) #2	1.379(7)	C(5)–C(10) #2	1.388(7)
Bond angles (°)		Bond angles (°)	
N(1)–Cu(1)–N(2)	104.60(2)	N(1)–Cu(1)–N(3)	123.12(2)
N(2)–Cu(1)–N(3)	109.54(2)	N(1)–Cu(1)–Br(1)	103.33(1)
N(2)–Cu(1)–Br(1)	109.44(1)	N(3)–Cu(1)–Br(1)	106.23(1)
C(1)–N(1)–Cu(1)	122.2(3)	C(2)–N(1)–Cu(1)	121.0(3)
C(4)–N(2)–Cu(1)	121.0(3)	C(5)–N(2)–Cu(1)	122.3(3)
C(8)–N(3)–Cu(1)	131.1(3)	N(4)–N(3)–Cu(1)	120.4(3)
N(1)–C(1)–C(7) #1	123.0(4)	C(2)–C(3)–C(6) #1	119.7(4)
N(2)–C(4)–C(10) #2	123.5(4)	C(5)#2–C(10)–C(11)	118.5(4)

Symmetry transformation: #1 : $-x+2, -y, -z$; #2 : $-x+1, -y, -z$

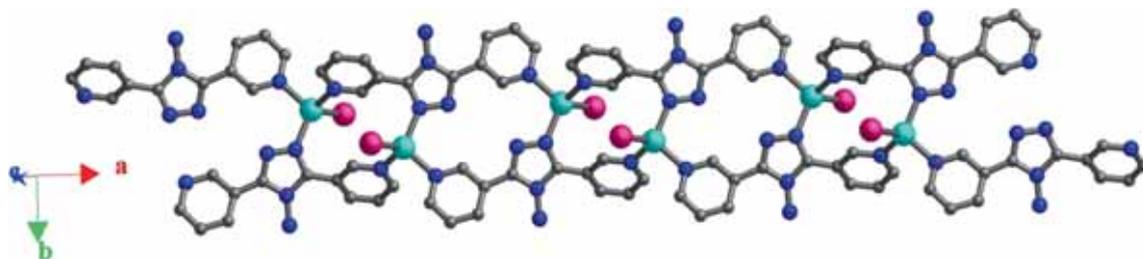


Figure 3. Packing diagram, a view down *c*-axis for complex **1**. (The DMSO molecule and hydrogen atoms are omitted for clarity)

3.2 Infrared Spectroscopy

The complex **1** was stable at room temperature and possessed good keeping qualities. IR spectrum of complex **1** is shown in Figure S2 (Supplementary Information). For complex **1**, the $\nu(\text{C-H})$ vibration of aromatic ring is observed at about 3089 cm^{-1} . The peaks at 3439 and 3239 cm^{-1} may be attributed to the vibrations of the amino group of 3-abpt. Peaks appearing at 1616 , 1463 and 1390 cm^{-1} should be assigned to stretching vibrations of the C=N/C=C bonds in **1**. The IR bands near 812 and 701 cm^{-1} belong to $\nu(\text{C-H})$ vibrations of the coordinated 3-abpt.

3.3 Experimental and Theoretical Absorption Spectra

To gain deeper insight into the electronic transitions and spectral characterization of this copper(I) complex, the TD-DFT/PCM calculations were performed for **1**. The experimental absorption spectra of **1** were

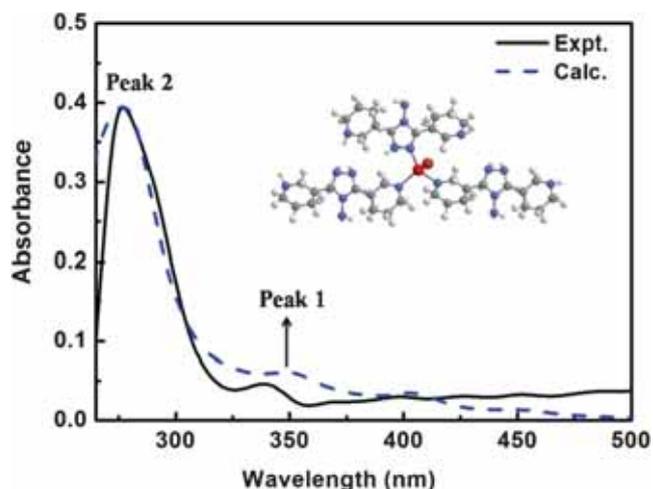


Figure 4. Absorption spectra of complex **1** obtained from experiment (black line) and TD-DFT/PCM calculations (blue dashed line) at the B3LYP/6-31G*+LanL2DZ* level. For the latter, a Lorentzian function has been adopted with the spectral linewidth set to be 70 nm. The theoretical spectrum was shifted right by 12 nm from the TD-DFT/PCM excitation energies, respectively.

measured in a $2.25 \times 10^{-5}\text{ mol dm}^{-3}$ DMF solution. Figure 4 makes a comparison between the scaled absorption spectra of complex **1** with the Lorentzian function⁴¹ and the experimental results, displaying a qualitative agreement in the shape of the absorption spectra. The lowest dipole-allowed absorption bands (peak 1) and the relatively stronger absorption bands (peak 2) of complex **1** are mainly assigned to the $\pi \rightarrow \pi^*$ transitions. As schematically illustrated in Figure 5, the lowest dipole-allowed absorption band of complex **1** is mainly ascribed to metal to ligand charge transfer. And the strongest absorption band of complex **1** involves ligand-ligand charge transfer.

3.4 Thermogravimetric Analysis (TGA)

To examine thermal stabilities of the complex **1**, thermogravimetric analyses (TGA) were carried out between 20 and 800°C in flowing nitrogen at $10^\circ\text{C}\cdot\text{min}^{-1}$. As depicted in Figure 6, complex **1** shows a weight loss of $\sim 28.54\%$ from 250 to 400°C , corresponding to the loss of DMSO molecules (expected = 29.04%). The second weight loss of $\sim 44.25\%$ occurs in the range 430 – 740°C , which can be attributed to the release of 3-abpt ligand (calcd 44.28%). In summary, the thermogravimetric analyses show that the complex **1** has reasonable thermal stability.

3.5 Luminescence Behavior

It is well-known that metal-organic coordination complexes constructed from central d^{10} metal atoms and organic ligands possess varied luminescent properties.^{42,43} Organic ligands and their coordinate modes obviously affect their emission wavelengths and luminescent mechanisms.^{44,45} In order to examine the fluorescent property of this d^{10} transition metal complex, the fluorescence spectra of complex **1** in ethanol solution was measured. As shown in Figure 7, the complex **1** shows a broad emission band in the blue region (maximal emission peak at 550 nm) for excitation at $\lambda_{\text{ex}} = 370\text{ nm}$. To understand more thoroughly the

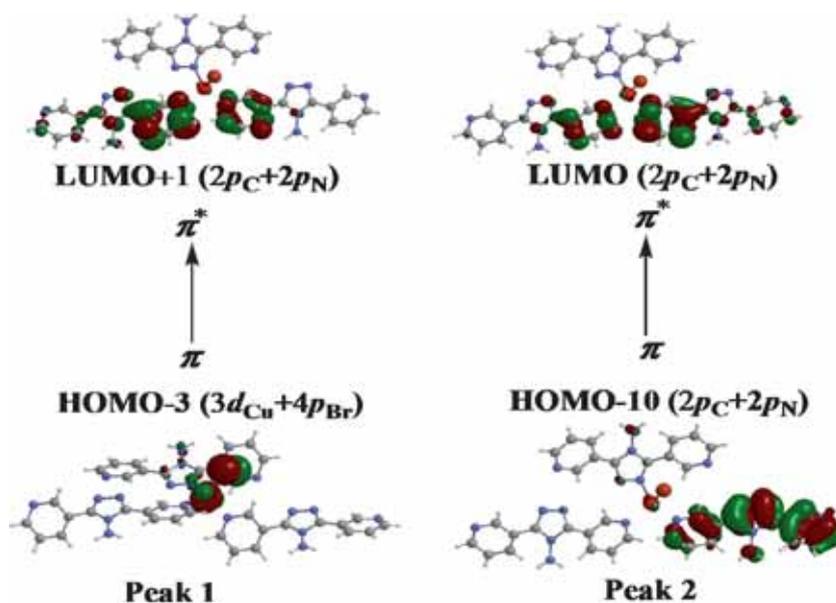


Figure 5. Assignment to absorption peaks of complex **1**. The molecular orbitals were obtained through DFT/PCM calculations at the B3LYP/6-31G*+LanL2DZ* level.

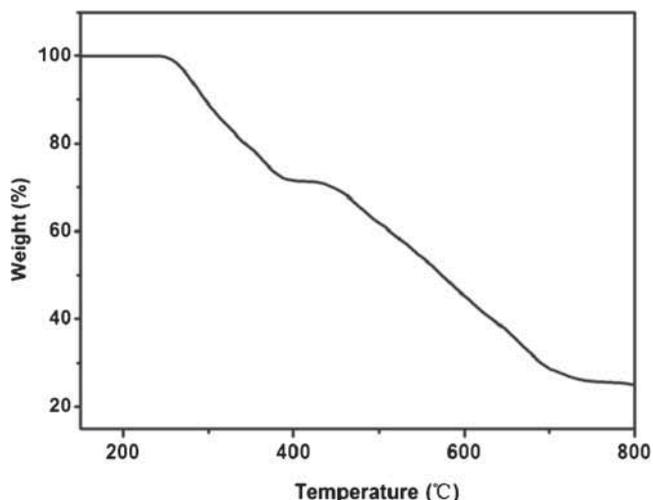


Figure 6. TGA curve of complex **1**.

nature of this emission band, the luminescence of 3-abpt ligand was also investigated in EtOH solution at room temperature. The free 3-abpt ligand exhibits maximum emission at 418 nm upon excitation at 330 nm, which may be attributed to the $\pi-\pi^*$ transition. By comparing the profiles and locations of the emission peaks of complex **1** with the corresponding free 3-abpt ligand, we can see a significant shift in the emission wavelength for the bound ligand, which probably comes from intra-ligand $\pi-\pi^*$ transitions and metal-to-ligand charge transfer (MLCT) transitions.^{46,47} The red-shift of the peak in **1** is presumably a result of coordination of the relevant ligand to the metal atom.⁴⁸ These

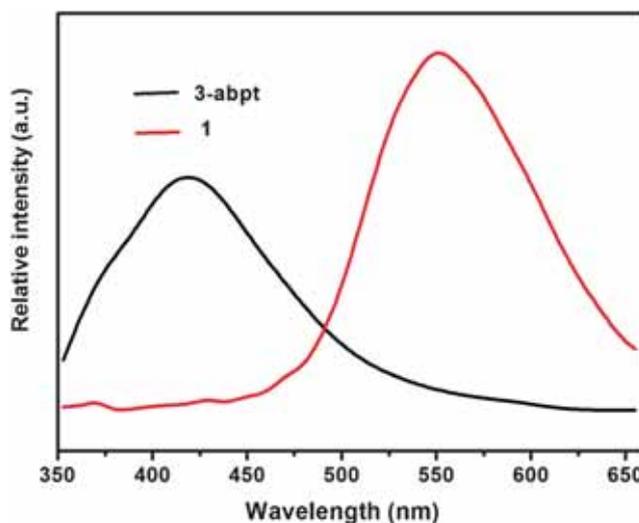


Figure 7. Fluorescence spectra of 3.0×10^{-5} M solutions of **1** and 3-abpt in ethanol at room temperature. Excitation wavelengths (nm): 370 (**1**), 330 (3-abpt).

results indicate that such metal complexes could be good candidates for photoactive materials.

4. Conclusions

In summary, a luminous copper(I) complex based on 4-amino-3,5-bis(3-pyridyl)-1,2,4-triazole (3-abpt) has been successfully prepared by slow diffusion method. X-ray single crystal analysis reveals that the central portion of complex **1** consists of a 12-membered ring core and displays an infinite ladder-like chain structure. The

theoretical absorption spectra of complex **1** obtained from DFT and TD-DFT calculations are in good agreement with the experimental spectrum. The intense fluorescent property of the title complex suggests that it may be used in the field of photoluminescent materials.

Supplementary Information (SI)

Crystallographic data (excluding structure factors) for the structure in this paper have been deposited with the Cambridge Crystallographic Data Centre, CCDC, 12 Union Road, Cambridge CB21EZ, UK. Copies of the data can be obtained free of charge on quoting the depository number CCDC-1506863 (Fax: +44-1223-336-033; E-Mail: deposit@ccdc.cam.ac.uk, <http://www.ccdc.cam.ac.uk>). The line drawing of complex **1** (Figure S1), FT-IR spectrum of complex **1** (Figure S2) and check cif file are given in Supplementary Information, which are available at www.ias.ac.in/chemsci.

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