Preparation, Electronic Properties, and Powder-XRD Structure Analysis of 3,5-Bis(pyridin-2-yl)-H-1,2,4-triazoledichloridocopper(II)

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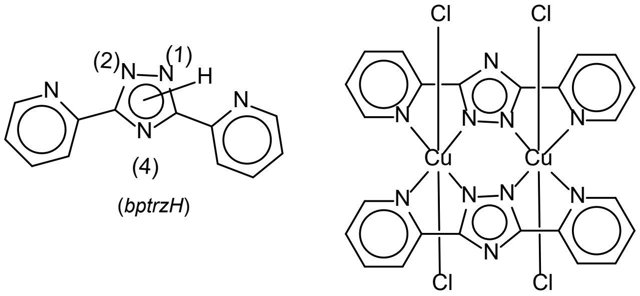
Abstract: *Salt of [Cu(*bptrzH*)Cl$_2$], (*bptrzH *= 3,5-bis(pyridin-2-yl)-H-1,2,4-triazole) has been prepared and characterized its electronic spectral and magnetic properties. This salt is paramagnetic with magnetic moment, μ_s, being 1.77–1.78 BM at 293 K, but decreased significantly with decreasing temperature to be 0.60–0.63 BM at 90 K, indicating antiferromagnetic nature. This is associated with Cu–Cu magnetic interactions at low temperatures, and suggests that the salt adopt an octahedrally polymeric structure. The electronic spectrum of this salt reveals a strong ligand field band centered at about 13,000 cm^{-1} and a very strong charge transfer absorption at about 23,000–24,000 cm^{-1}. The spectrum is better resolved at lower temperature and this is parallel to the slight change in color from yellowish-green at room temperature to bright green at low temperature (90 K). The powder XRD of this complex was refined by Le Bail method of Rietica program and found to be fit as triclinic symmetry of space group P$\bar{1}$ with the figure of merit: R_p = 5.02; R_{wp} = 7.95; R_{exp} = 5.40; Bragg R-Factor = 0.05; and GOF = 2.166.*

Keywords: *magnetic moment; copper(II);* bptrzH*; antiferromagnetic; spectrum; Rietica*

INTRODUCTION

The coordination chemistry of Cu(II) is of interest for many researchers, particularly due to the various 4-6 coordination numbers, its magnetism associated with ferro-/antiferro-magnetic property, the ability to form bi-poly nuclear compound, and strong Jahn-Teller distortion. In four coordination as in $[(C_2H_5)_2NH_2]_2[CuCl_4]$, the tetrachloridocuprate(II) was reported an interesting thermochromism from bright green at room- to low-temperatures to yellow on heating above 43 °C [1-2]. This is associated with the geometrical phase transition, square-planar (green) $\rightleftharpoons$ tetrahedral (yellow) in anionic tetrachloridocuprate(II). The phase transition is confirmed primarily due to organic counter-part change arrangement [3]. The driving force for this geometric transition is believed because of the cationic counterpart movements of particular organic species [2], while the thermochromic nature according to Bhattacharya et al., is evident due to the Jahn-Teller effects of Cu(II) and NH····Cl hydrogen bonds [4]. Since then, other studies also reported the thermochromic properties in other copper(II) compounds. Fabbrizzi et al. [5] observed continuous and discontinuous thermochromism of copper(II). The role of the organic counterpart cation to the tetrachloridocuprate(II) is then confirmed in other numerous compounds [6-11].

Another characteristic of copper(II) species is its ability to form numerous di-/poly-nuclear compounds which usually lead to typical magnetic interaction effect, that is ferro-/anti-ferromagnetic properties [12-15]. The d^9 system of Cu(II) is also well known to show structurally Jahn-Teller distortion as it has been observed in octahedral, trigonal bipyramidal, square-planar, and tetrahedral geometries, accompanying the phase transition and thus the importance in functional molecular and inorganic materials is of interest [16]. It should also be noted that the Cu(II) complexes discussed might involve bridging system Cu(II)-ligand-Cu(II) as well as interligand hydrogen bonds which might be considered to account of magnetic interactions. The organic compound, 3,5-bis(pyridine-2-yl)-1,2,4-triazole,



(a) (b)

Fig 1. Possible asymmetrically flanking *bptrzH* (a) and dinuclear double bridging framework with $CuCl_2$ (b)

bptrzH (Fig. 1(a)) has been known as a ligand that can provide bridging-coordination to transition metal compounds due to conformation of the ligand [17]. Thus *bptrzH* might coordinate through N^2 and N^4 donor atoms leading to dinuclear single bridging (N^2, N_{py}, N^4, N_{py}') complex. It might also be possible to coordinate through N^1 and N^2 donor atoms leading to dinuclear double bridging (N_{py}, N^1-N^2, N_{py}')$_2$ when both pyridine rings are symmetrically flanking to the triazole ring (Fig. 1(b)). However, mononuclear meridional tris-bidentate, N_{py}, N^2, is also possible to occure [18-19].

Therefore, preparation of a complex containing this organic ligand with copper(II) chloride which has not been studied, is very promising characteristics at least associated with ferro and antiferro magnetic properties for the bridging complex. Moreover, the chloride ion may also act as a bridging anionic ligand. Hence, the combination of the two species, *bptrzH* and chloride ion is expected to produce Cu(II) complex with interesting properties.

■ EXPERIMENTAL SECTION

Materials

The main chemicals of picolinic acid hydrazide, 2-cyanopyridine, methanol, and $CuCl_2{\cdot}2H_2O$, were purchased from Sigma-Aldrich. All the reagents were used without initial purification.

Procedure for Preparation of the Complex

Preparation of ligand

The compound (*bptrzH*) was synthesized according to method of Kubota et al. [20]. A mixture of picolinic acid hydrazide, 6.857 g (0.05 mol), and 2-cyanopyridine, 52.055 g (0.5 mol, in excess), were heated together at 220–225 °C for about 10 h. After cooling, the solid was filtered, washed with cold ethanol, and dried in a vacuum desiccator. Recrystallization from ethanol resulted in white solid (mp. 196 °C uncorrected, lit. 209–211 °C).

*Preparation of complex [Cu(*bptrzH*)Cl_2]*

Into a well stirred methanolic solution of $CuCl_2{\cdot}2H_2O$, 0.341 g (2 mmol), was added dropwise of a methanolic solution of *bptrzH*, 0.233 g (1 mmol), whereupon the finely greenish-yellow powders came out readily. It was carefully filtered, washed with cold methanol, and then dried in aeration. (Sample 1 and 2 were separately prepared).

Instruments and Procedure of Physical Measurements

Physical characterization

Magnetic measurements. The magnetic data for solid samples were obtained using a Newport variable temperature Gouy balance equipped with cryostat containing liquid nitrogen for low-temperature measurements and calibrated with $CoHg(NCS)_4$. All data have been corrected for diamagnetism calculated using Pascal's constants. Molar susceptibilities (χ_M) were quoted in $cm^3\ mol^{-1}$ and the magnetic moments were calculated according to the relationship $\mu_{ef} = 2.828\ \sqrt{(\chi_M.T)}$ BM.

Electronic spectral measurements. Electronic spectra were recorded on a Zeiss PMQII spectrophotometer equipped with a diffuse reflectance accessory. Solid (powder) samples were spread on white filter paper and their spectra were calibrated against magnesium oxide. For low-temperature measurement a special brass attachment with silica glass windows was used. The fitting was sealed and a stream of cold nitrogen gas was passed over the assembly to prevent condensation. The fitting was then placed in contact with the base of an insulated brass dewar filled with liquid nitrogen and low-temperature measurement was made. In the measurement of spectra of the sample at room- and low-temperatures, the sample mounting was not changed and hence any measured changes in intensities at different temperatures are significant even though the actual values for intensities are not.

Powder X-ray diffraction. The diffractogram of the complex was recorded by using a Rigaku Miniflex 600 40 kW 15 mA Benchtop Diffractometer, with CuK$_\alpha$, λ = 1.5406 Å. The powdered sample was spread on the glass plate and then was placed on the cell holder. The reflection data were recorded in a scan mode at 2–80 (degree of 2θ) with interval of 0.04 steps per 4 sec for 2 h. The recorded diffractogram was then analyzed with the Rietica program of Le Bail method (5–80 degree of 2θ) which was run within 30 cycles.

RESULTS AND DISCUSSION

Elemental Analysis of *bptrzH* and the Complex

BptrzH was isolated as white solid having melting point (196 °C) close to the literature (209–211 °C). The elemental analysis was found to be C = 64.79 (64.56), H = 3.84 (4.06), and N = 31.05 (31.37)%, with calculated figures in the bracket for $C_{12}H_9N_5$. ^{1}H-NMR spectrum of this compound confirms the corresponding formula, showing four strong resonances at 7.3, 7.8, 8.4, and 8.8 ppm by integration ratio of 1:1:0.9:1 respectively. Thus, this corresponds to the four different positions of hydrogen atoms in pyridine rings. The weak and broad resonance at 13.6 ppm is believed to be due to the only one H(N) in the triazole ring [20].

Direct interaction of copper(II) chloride with *bptrzH* ($C_{12}H_9N_5$) in methanol resulted in greenish-yellow finely powder. The C–H–N elemental analysis, C = 38.90 (39.19), H = 1.97 (2.46), N = 18.71 (19.28)%, with calculated figures in the bracket for $[Cu(C_{12}H_9N_5)Cl_2]$, signify this complex formula.

Magnetic Moment

The effective magnetic moment for the complex at room temperature, μ_{293K}, is 1.77–1.78 BM. This is remarkably close to the spin-only value for one unpaired electron (μ_s = 1.73 BM) in d^9-octahedral configuration. The effective magnetic moment, however, is significantly temperature dependent, being gradually decreased with decreasing temperature to about 0.61–0.63 BM at 89–99 K, and increased with increasing temperature to about 1.85–1.92 BM at 353–373 K. The change in moment was found to be reversible as shown by the magnetic data listed in Table 1 which were recorded according to the order of measurements. The trend of decrease in the moment as displayed in Fig. 2 suggests the possibility of further decreases at very low temperatures.

The decreasing magnetic moment within the experimental temperatures in this compound is associated with the antiferromagnetic behavior due to the interaction of metal atoms, Cu-Cu. No effect of externally magnetic field is observed as shown by the moment values recorded with 15 A at 176–90 K (sample 1) and at 156–89 K (sample 2). As temperature is gradually lowered the Cu(II)-Cu(II) distance in the molecule becomes gradually shorter, and the interaction of the one unpaired electron in Cu(II)-Cu(II) becomes stronger. The magnetic interaction should be then an anti-parallel couple spin of electron, and as a result the magnetic moment is lowered. The reproducibility of this behavior in this complex is confirmed by magnetic data from the two samples (sample 1-2) which were separately prepared in different batch. This antiferromagnetic behavior is much the same as the plot of magnetic susceptibility with temperature in another octahedral dimer, $[Cu(bptrzH)(CF_3SO_3)H_2O]_2$ [18]. Such typical behavior

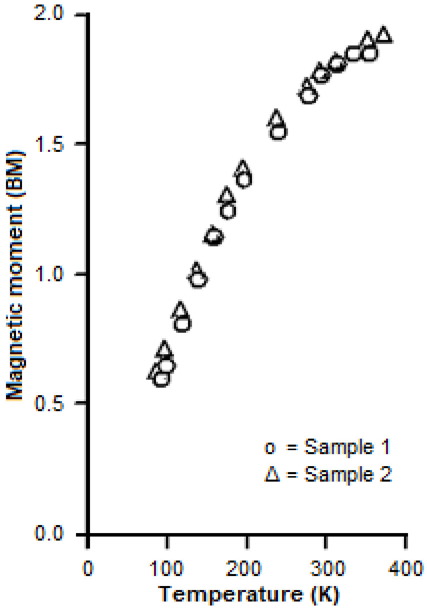


Fig 2. Magnetic moment of [Cu(*bptrzH*)Cl$_2$]

Table 1. Magnetic moment of [Cu(*bptrzH*)Cl_2] at various temperatures

Sample 1			Sample 2		
T/K	$\chi_M/10^{-6}$	μ_{ef}/BM	T/K	$\chi_M/10^{-6}$	χ_M/BM
293.2	1336	1.77	293.2	1359	1.78
176.3	1115	1.25	237.2	1346	1.60
176.3 (**15A**)*	1175	1.28	156.5	1072	1.16
90	500	0.60	156.5 (**15A**)*	1081	1.16
90 (**15A**)*	518	0.61	89	551	0.63
99	531	0.65	89 (**15A**)*	550	0.63
118.1	689	0.81	99	632	0.71
137.2	878	0.98	118.1	785	0.86
156.5	1052	1.15	137.2	952	1.02
195.8	1194	1.37	176.3	1219	1.31
237.2	1273	1.55	195.8	1272	1.41
275	1304	1.69	275	1352	1.72
313.2	1304	1.81	313.2	1326	1.82
333.2	1288	1.85	353.2	1286	1.90
353.2	1209	1.85	373.2	1245	1.92

* The moment was measured in different (electro)magnetic fields, by applying electric current 15 A vs 10 A, and it turned out to give relatively the same results, indicating that the magnetic properties do not depend on external magnetic field strength

in magnetism is very common for poly- or di-nuclear copper(II) with ligand other than *bptrzH* due to Cu-Cu interaction and the role of counterion [12-14,21], ferromagnetic-antiferromagnetic coupling [15-16] and ferromagnetic domain [22]. Thus, this complex is proposed to be dimer [Cu(*btrzH*)Cl_2]$_2$ (as in Fig. 1(b)) following Prins et al. [18].

Electronic Spectrum

The electronic spectrum of this complex, [Cu(*bptrzH*)Cl_2], as shown in Fig. 3, reveals two well resolved of absorption bands. The peak at lower energy which is relatively asymmetrical band centered at around 13,000 cm^{-1} should be the octahedral ligand-field band attributed as $^2E_g \rightarrow {}^2T_{2g}$ while the one centered at much higher energy, around 23,000–24,000 cm^{-1} might be associated with the "charge-transfer" band of metal-ligand, π-π*, and this is what dominates the greenish yellow color of this species. A very clear shoulder band at around 16000 cm^{-1} might be associated with Jahn-Teller distortion [16,23-24] due to primarily asymmetrical electronic configuration in e_g^3 orbitals.

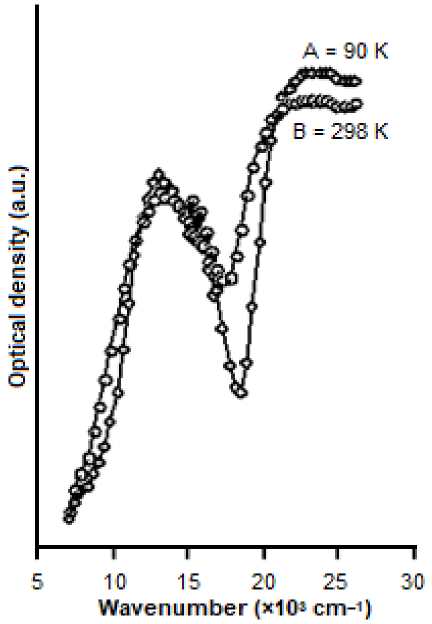


Fig 3. Electronic spectra of [Cu(*bptrzH*)Cl_2]

Structural Analysis

The complex compound resulted from interaction of copper(II) chloride and *bptrzH* apparently does not dissolve in a various commonly known solvents, water,

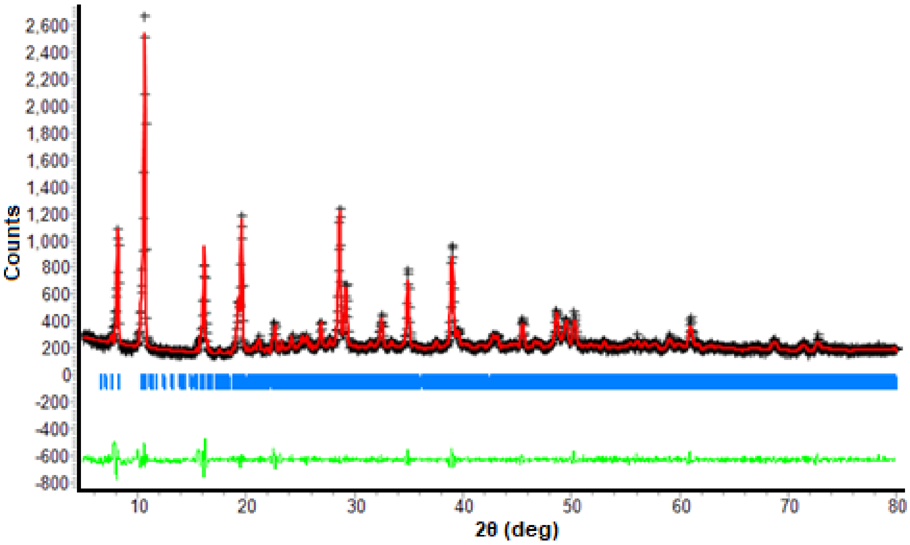


Fig 4. Diffractogram of [Cu(*bptrzH*)Cl$_2$]. The black signs (+) represent the observed-experimental data, the red full line is the calculated refinement at 5–80° of 2θ for the expected model of triclinic symmetry of space group P$\bar{1}$ which are the blue bar-lines, and the green curve-line indicates the differences between the observed diffractogram and the refinement

nitromethane, ethanol, methanol, acetone, acetonitrile, and so far attempt to grow a single crystal was unsuccessful. Structural analysis was then performed from its powder XRD. This is quite common for the oxides compounds following Rietveld method [e.g. 25-27]. However, it has been applied to that of iron(II) complex [28] quite recently and found to be a significant result. Since then, referring to the suggestion by Toby as well [29], application of this method has been extensively performed to some powdered complexes [30-38] and the results were found to be reasonably acceptable.

For these reasons, the powder X-ray diffraction of this complex was then recorded and the diffractogram together with its refinement following Le Bail method of Rietica program is shown in Fig. 4. It is obvious that the calculated red full line does almost pass through the black experimentally observed data, and this is confirmed by the almost linear green-curve line which reflects the tiny difference between both data. This suggests that the refinement is considerably fit for triclinic symmetry of space group P$\bar{1}$ with Goodness of Fitting (GOF) 2.166, derived Bragg R-Factor 0.05, and low figures of merit: R_p = 5.02, R_{wp} = 7.95, and R_{exp} = 5.40. The detailed cell parameters are: a = 10.83314 Å; b = 13.5746 Å; c = 14.5156 Å; α = 112.3884°; β = 86.0523°; γ = 94.8069°; V = 1965.1938 Å^3; and Z = 2 (Table 2).

Table 2. Detailed cell parameters of (a), [Cu(*bptrzH*)$_2$Cl$_2$], and (b)

Compound	(a)	(b) [18]
Symmetry	Triclinic	Triclinic
Space Group	P$\bar{1}$	P$\bar{1}$
a (Å)	10.8331	8.841(3)
b (Å)	13.5746	14.132(6)
c (Å)	14.5156	14.382(6)
V (Å^3)	1965.1938	1606(1)
α (°)	112.3884	112.58(3)
β (°)	86.0523	92.23(3)
γ (°)	94.8069	102.45(3)
R_p	5.02	
R_{wp}	7.95	
R_{exp}	5.40	
Z	2	2 (dimer)
GOF: χ^2	2.166	
R_{Bragg}	0.05	

(b) [Cu(*bptrzH*)(CF$_3$SO$_3$)(H$_2$O)]$_2$

The antiferromagnetic interaction of Cu(II) at lower temperatures suggests that this complex is likely to adopt a dimer of [Cu(*bptrzH*)Cl$_2$]$_2$ (Fig. 1(b)) following the structure of [Cu(*bptrzH*)(CF$_3$SO$_3$)(H$_2$O)]$_2$ [18]

which is known as dinuclear double bridging as also observed in spin crossover system of [Fe_2(*bptrz*)$_2$$Cl_4$] [19].

■ CONCLUSION

The complex of [Cu (*bptrzH*)Cl_2] has been successfully isolated as greenish-yellow finely powder from the reaction of copper(II) chloride with the *bptrzH* ligand which is insoluble in some common solvents. The complex shows antiferromagnetic Cu-Cu interactions with magnetic moment of 1.78 BM at 293 K and gradually down with temperatures to 0.63 BM at 90 K. It is believed to have a geometrical structure of dinuclear double bridging octahedral coordination.

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