

Synthesis and characterization of binuclear azide-bridged hydrazone Cu(II) complex



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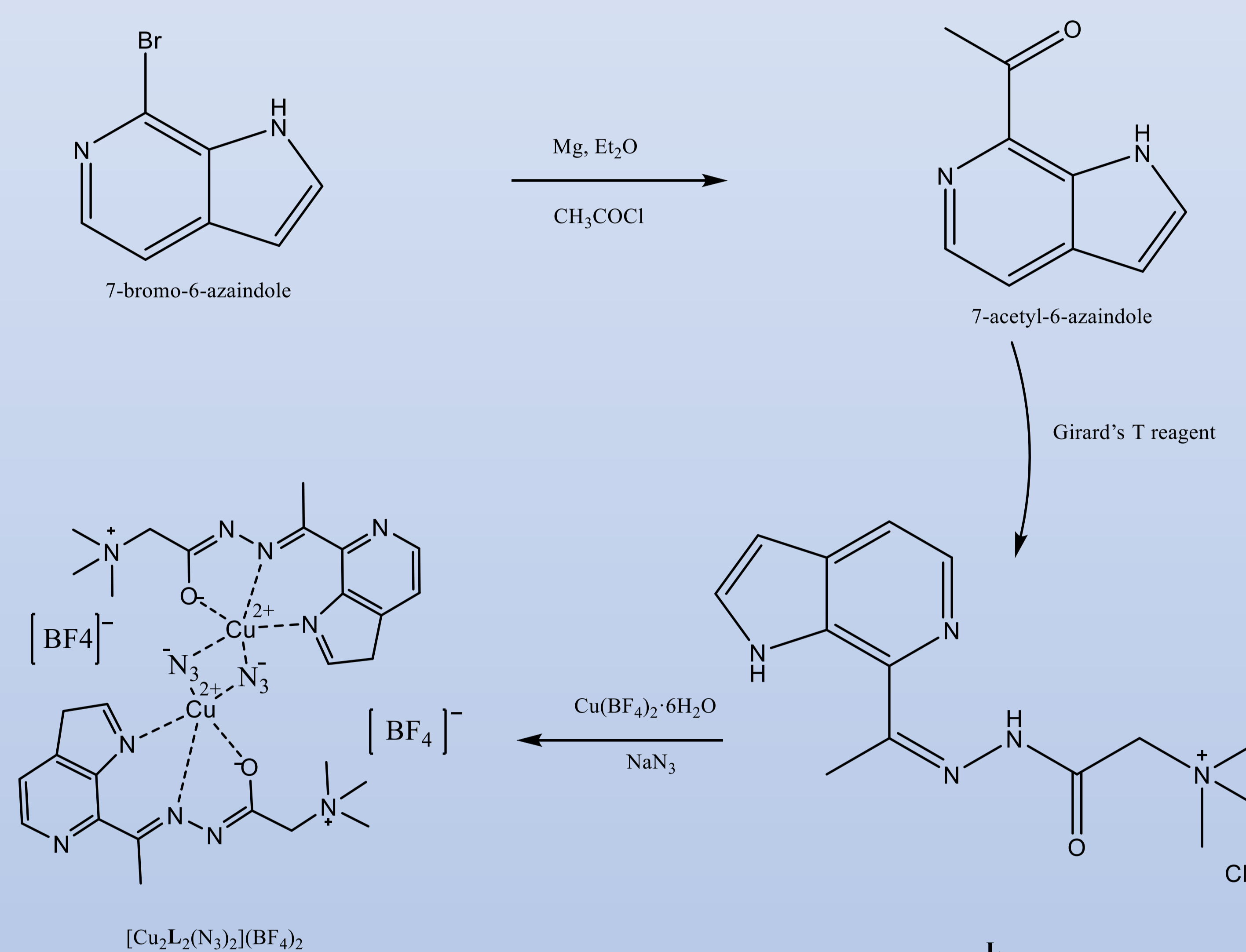
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The condensation product of 7-acetyl-6-azaindole and Girard's T reagent ((E)-2-(2-(1-(1H-pyrrolo[2,3-c]pyridin-7-yl)ethylidene)hydrazineyl)-N,N,N-trimethyl-2-oxoethan-1-aminium, HL ligand) was used as a ligand in the reaction with $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$ and NaN_3 . The reaction led to the formation of a binuclear Cu(II) complex containing two end-to-end ($\text{di-}\mu_{-1,3}\text{-N}_3$) azide bridges, as well as two NNO-donor hydrazone ligands, forming an axially elongated square pyramidal geometry around each Cu(II) center (Scheme 1). This end-to-end ($\text{di-}\mu_{-1,3}\text{-N}_3$) azide bridge binding mode has not yet been reported, in Cu(II) complexes containing the NNO-donor hydrazone ligands, which makes the structure of the complex even more interesting for further studies. The complex was characterized by elemental analysis, IR spectroscopy and X-ray crystallography, and it was found that it crystallizes in the triclinic space group P-1 with the asymmetric unit comprising one Cu(II) centre, zwitterionic ligand L, one azide (N_3^-) ligand and BF_4^- counter anion.

1. The ligand synthesis was carried out in two steps – the first step was obtaining 7-acetyl-6-azaindole using 7-bromo-6-azaindole as a starting compound. The reaction was performed by adding 0.75 mmol (18.2 mg) of Mg to 0.75 mmol (147 mg) of 7-bromo-6-azaindole in anhydrous diethyl ether and making a Grignard's reagent, which then reacted with equimolar amount (0.75 mmol, 58.9 mg) of acetyl chloride and a small amount (2 mol %) of FeCl_3 as a catalyst. This reaction was carried out at -60°C using dry ice as a cooling bath.



2. The next step was to synthesize the condensation product of 7-acetyl-6-azaindole and Girard's T reagent. The reaction was carried out by dissolving 0.5 mmol (80 mg) of 7-acetyl-6-azaindole in methanol and adding 0.5 mmol (83.8 mg) of Girard's T reagent to the reaction mixture, which was then refluxed for 3 h. After cooling down to room temperature, the bright yellow precipitate was filtered and rinsed with ethanol. The reaction yield was 81 % and the ligand was then characterized by elemental analysis, IR and NMR spectroscopy.

Scheme 1. Synthesis of complex

3. The synthesis of the complex was performed by dissolving 0.25 mmol (77.3 mg) of ligand in 20 mL of methanol and then adding 0.25 mmol (86.3 mg) of $\text{Cu}(\text{BF}_4)_2 \cdot 6\text{H}_2\text{O}$, previously dissolved in 5 mL of H_2O , and 1 mmol (65 mg) of NaN_3 directly into the reaction mixture. The mixture was refluxed for 2 h, and after 10 days dark green monocrystals of complex were obtained and filtered from the solution.

The crystal structure of compound $[\text{Cu}_2\text{L}_2(\mu_{1,3}\text{-N}_3)_2](\text{BF}_4)_2$ was determined by single crystal X-ray diffraction methods. Crystallographic data and refinement details are given in Table I.

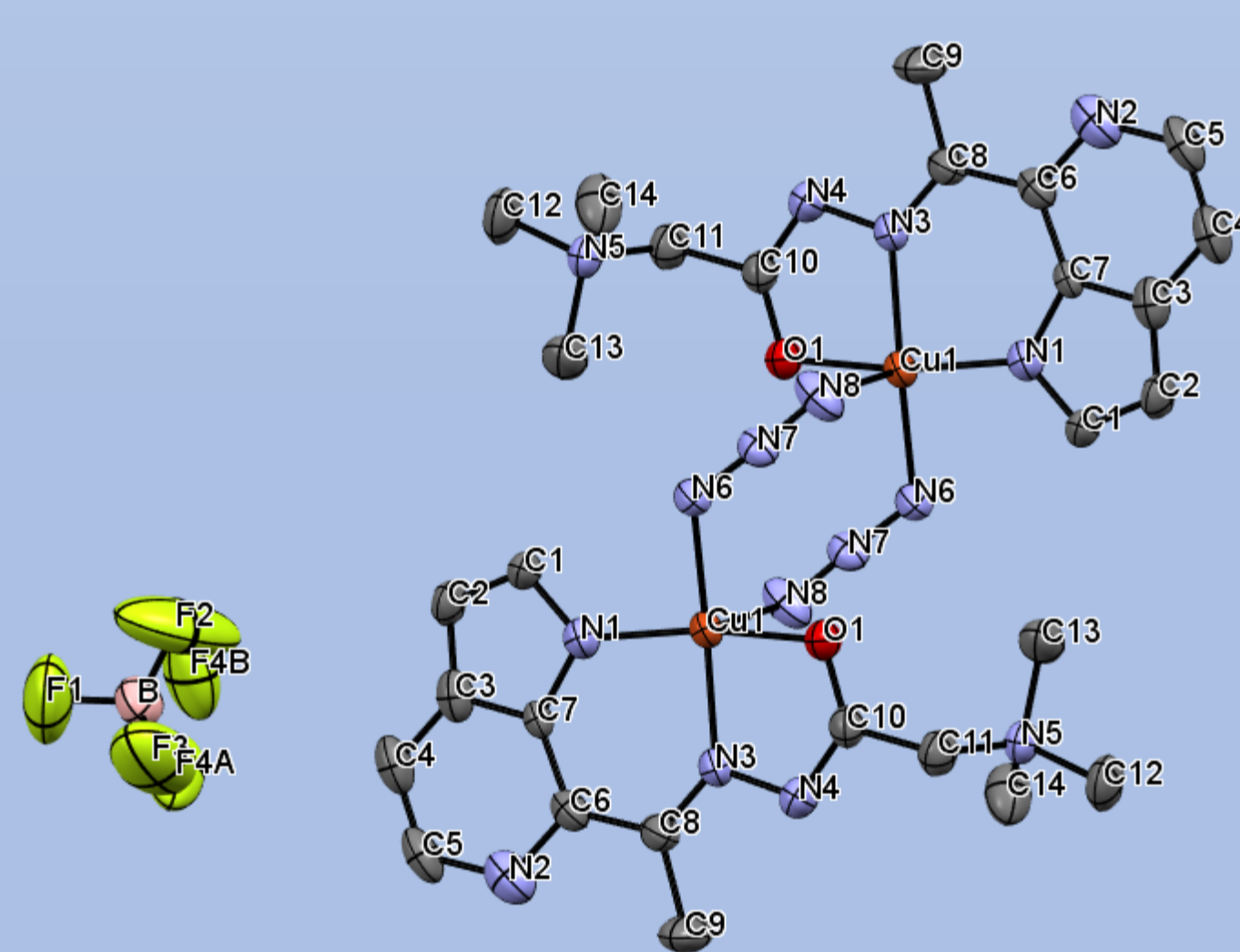


Figure 1. ORTEP representation of the complex. Thermal ellipsoids are drawn at the 50% probability level.

Table I. Crystal data and structure refinement details for complex

Formula	$\text{C}_{28}\text{H}_{38}\text{B}_2\text{Cu}_2\text{F}_8\text{N}_{16}\text{O}_2$
Fw / g mol ⁻¹	931.44
Crystal size, mm	0.50×0.40×0.10
Crystal color	green
Crystal system	triclinic
Space group	P-1
<i>a</i> / Å	7.8476
<i>b</i> / Å	9.8765
<i>c</i> / Å	13.299
<i>α</i> / °	110.341
<i>β</i> / °	103.742
<i>γ</i> / °	92.524
<i>V</i> / Å ³	929.7
<i>Z</i>	1

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