



Structural diversity, spectral characterization and computational studies of Cu(I) complexes with pyridylamide ligands



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ABSTRACT

Cu(I) complexes supported by pyridylamide ligands *N*-2-acetamidopyridine (Haap), *N*-(3-pyridyl)nicotinamide (3-pna), *N*-(2-pyridyl)isonicotinamide (2-pina) and *N*-(4-pyridyl)picolinamide (4-ppa) were synthesized and characterized. The reaction of CuCl with the deprotonated form of Haap yielded the complex [Cu₂(aap)₂]_n (**1**) with a one-dimensional polymeric structure. Complexes [Cu(3-pna)₃(NCCH₃)](HF)(SbF₆) (**2**) and [Cu(4-ppa)(NCCH₃)₂]₂BF₄ (**5**) displayed mononuclear structures with tetrahedral geometries on Cu (I) centers. Dinuclear complex [Cu₂(2-pina)₅(NCCH₃)₄](SbF₆)₂ (**3**) and tetranuclear cluster [Cu₄(2-pina)₄(NCCH₃)₄](SbF₆)₄ (**4**) were afforded from the same reaction in CH₃CN and DMF, respectively. Detailed analysis of X-ray crystal structures and Hirshfeld surface maps suggested that the weak non-covalent interactions and reaction solvents imposed a collaborative effect on the structural conformations of the Cu(I) complexes. The electrochemical properties of the complexes were investigated by cyclic voltammetry. Computational studies focusing on complex **1** revealed its unique electronic structure that corresponds to the interesting spectroscopic and electrochemical properties.

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1. Introduction

Bioinspired synthetic complexes modeling the functions of metalloproteins active sites have attracted great interest due to their novel structural features and potential catalytic activities [1]. Previous research work has demonstrated that the rational selection and design of the ligand platform played a critical role of controlling the activities and structures of these model complexes [1d,1e,2]. So far, the major ligand design strategies mainly focused on the manipulation of denticity, steric effect, coordination donors and electron properties of the ligand backbone. Recently, the effect of the secondary sphere coordination environment on the function and physical properties of the metal complexes received growing attention due to the fact that the local environment of a protein pocket often has a profound impact on the function of the active site [1a]. Therefore, in an effort to advance the modeling chemistry of metalloproteins, functional groups that can introduce weak non-covalent interactions (e.g. hydrogen bonds, $\pi \cdots \pi$ interactions) were incorporated into ligand platforms to provide an auxiliary

environment to enhance the functions. For instance, a series of pre-organized tripodal ligands with H-bond donors and acceptors have been reported to mimic the secondary coordination spheres of the catalytic sites of some iron and manganese enzymes [3]. The interesting chemistry from these studies has significantly contributed to the current understanding about the reactivity of model complexes and biological function of metalloproteins.

As part of our ongoing work on synthesizing biologically-related copper complexes with novel structures, spectroscopic properties and catalytic activities, pyridylamide ligands were employed as the supporting platforms to achieve the dual functions: (a) the pyridyl groups act as the main coordination sites to mimic the histidine donors in the active sites of copper containing proteins; (b) amide groups promote the formation of inter- or intramolecular weak interactions to simulate the outer-sphere coordination environment. Our previous research has demonstrated the versatile coordination behavior of the pyridylamide ligands with divalent transition metal ions [4]. X-ray crystallography and spectroscopic characterization showed that pyridyl nitrogens were excellent coordination donors, meanwhile the –NH–C(O)– amide groups produced diverse weak interactions in the local environment by using either H-bond donor (N–H group) or

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acceptor (C=O group). Generally, the neutral -NH-C(O)- may use the C=O oxygen as the additional coordination donor, and the N-H often forms intra- or intermolecular hydrogen bond interactions. In the deprotonated form, the amidate $\text{-N}^{\ominus}\text{-C(O)-}$ has an anionic nitrogen with better σ -donating abilities that can potentially increase the nuclearity of the metal complex and significantly change the architecture of the metal complexes [4b]. Therefore, by adjusting the functional groups of the ligands and reaction conditions, we were able to control the structures of the complexes and fine tune the geometry of the metal center(s) to obtain the desired secondary coordination sphere. This tunability makes pyridylamide ligands serve as the ideal systems for our work on examining the properties associated with the outer-sphere coordination environment in copper complexes. Herein we report the synthesis and structural characterization of new Cu(I) complexes supported by a group of pyridyl-secondary amide ligands (Scheme 1). Combined analysis based on X-ray crystal structures, Hirshfeld surface maps and theoretical studies demonstrated how weak coordination bonds, hydrogen bonds and $\pi\cdots\pi$ interactions impact the ligand binding modes, coordination environments and spectroscopic properties of the copper complexes.

2. Experimental

2.1. Physical measurements

^1H NMR spectra were recorded on Bruker AVANCE 300 MHz spectrometer at room temperature. Chemical shifts (δ) were referenced to residual solvent signal. Elemental analyses were carried out by Atlantic Microlabs, Norcross, GA. The UV-Vis spectrum was recorded on a Cary 50 spectrometer. FT-IR spectra were collected on a Nicolet Magna 560 FT-IR spectrometer with an ATR attachment. Cyclic voltammograms were measured using EG&G Princeton Applied Research Scanning Potentiostat with a three-electrode cell (Pt disk working electrode, Pt wire auxiliary electrode and aqueous Ag/AgCl glass reference electrode). All measurements were performed in either DMF or CH_3CN degassed solution containing 1 mM analyte and 0.1 M tetrabutylammonium tetrafluoroborate at room temperature with the N_2 protection. Recrystallized ferrocene was used as the internal standard.

2.2. Chemicals

All reagents were obtained from commercial sources and used as received. Ligand *N*-2-acetamidopyridine (Haap), *N*-(4-pyridyl)picolinamide (4-ppa), *N*-(3-pyridyl)nicotinamide (3-pna) and *N*-(2-pyridyl)isonicotinamide (2-pina) were synthesized according to literature [5].

2.3. Synthesis of the metal complexes

2.3.1. $[\text{Cu}_2(\text{aap})_2]_n$ (**1**)

CuCl (0.036 g, 0.37 mmol) was added to a stirring mixture of Haap (0.050 g, 0.38 mmol) and NaH (0.011 g, 0.38 mmol) in 2 mL CH_3CN . The yellow suspension was stirred for 1 h and 20 mL of

Et_2O was added to the mixture. The solid was extracted into 2 mL DMF and the suspension was filtered. Vapor diffusion of Et_2O into the yellow filtrate at room temperature led to the formation of yellow crystals suitable for X-ray crystallographic characterization (0.051 g, 68% yield). *Anal. Calc.* for $\text{C}_{14}\text{H}_{14}\text{N}_4\text{O}_2\text{Cu}_2$: C, 42.31; H, 3.55; N, 14.10. Found: C, 42.78; H, 3.56; N, 14.24. FT-IR (cm^{-1}): 1604, 1557, 1472, 1430, 1359, 1323, 1288, 1264, 1168, 1124, 1053, 1021, 1003, 976, 872, 783, 745, 692, 619, 565, 530, 427. ^1H NMR (DMSO- d_6 , 298 K): δ = 8.38 (m, 2H), 8.03 (m, 2H), 7.60 (m, 2H), 6.86 (m, 2H), 2.22 (s, 6H) ppm. UV-Vis [DMF, λ_{max} , nm (ϵ , $\text{M}^{-1}\text{cm}^{-1}$): 323 (4800).

2.3.2. $[\text{Cu}(3\text{-pna})_3(\text{NCCH}_3)](\text{HF})(\text{SbF}_6)$ (**2**)

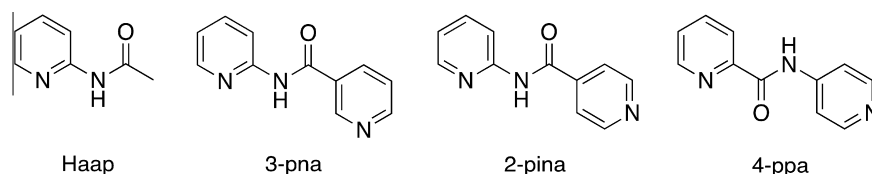
A solution of $[\text{Cu}(\text{NCCH}_3)_4]\text{SbF}_6$ (0.039 g, 0.084 mmol) in 1 mL CH_2Cl_2 was added to a stirred solution of 3-pna (0.050 g, 0.25 mmol) in 1 mL CH_2Cl_2 . The yellow suspension was stirred for 6 h and 15 mL of Et_2O was added to the mixture. The resulting orange powder was collected and washed with Et_2O (5 mL \times 3). The powder was extracted into 2 mL CH_3CN and the turbid solution was filtered. Vapor diffusion of Et_2O into the light yellow filtrate at room temperature led to the formation of yellow crystals suitable for X-ray crystallographic characterization (0.048 g, 60% yield). *Anal. Calc.* for $\text{C}_{35}\text{H}_{31}\text{N}_{10}\text{O}_3\text{F}_7\text{SbCu}$: C, 43.88; H, 3.26; N, 14.62. Found: C, 43.62; H, 3.59; N, 14.71. FT-IR (cm^{-1}): 2366, 1678, 1628, 1598, 1584, 1544, 1484, 1468, 1437, 1367, 1350, 1310, 1240, 1177, 1157, 1050, 912, 888, 782, 727, 696, 635, 629, 552, 537, 523, 465, 433, 416. ^1H NMR (DMSO- d_6 , 298 K): δ = 11.05 (s, 3H), 8.41 (m, 4H), 8.22 (m, 5H), 7.84 (m, 5H), 7.65 (m, 5H), 7.22 (m, 5H), 2.04 (s, 3H) ppm.

2.3.3. $[\text{Cu}_2(2\text{-pina})_3(\text{NCCH}_3)_4](\text{SbF}_6)_2$ (**3**)

A solution of $[\text{Cu}(\text{NCCH}_3)_4]\text{SbF}_6$ (0.079 g, 0.17 mmol) in 1 mL CH_2Cl_2 was added to a stirring solution of 2-pina (0.050 g, 0.25 mmol) in 1 mL CH_2Cl_2 . The solvent was removed under reduced pressure after 1 h and the resulting orange solid was washed with Et_2O (5 mL \times 3). The solid was extracted into 2 mL CH_3CN and the turbid solution was filtered. Vapor diffusion of Et_2O into the light yellow filtrate at room temperature led to the formation of yellow crystals suitable for X-ray crystallographic characterization (0.059 g, 52% yield). *Anal. Calc.* for $\text{C}_{41}\text{H}_{39}\text{N}_{13}\text{O}_3\text{F}_{12}\text{Sb}_2\text{Cu}_2$: C, 36.20; H, 2.89; N, 13.38. Found: C, 36.44; H, 2.50; N, 13.26. FT-IR (cm^{-1}): 2357, 1686, 1600, 1576, 1523, 1496, 1464, 1433, 1417, 1369, 1305, 1262, 1240, 1155, 1124, 1097, 1062, 1003, 898, 856, 777, 757, 693, 657, 623, 545, 519, 453. ^1H NMR (DMSO- d_6 , 298 K): δ = 11.14 (s, 3H), 8.20 (m, 12H), 7.88 (m, 5H), 7.20 (m, 7H), 2.03 (s, 12H) ppm.

2.3.4. $[\text{Cu}_4(2\text{-pina})_4](\text{SbF}_6)_4$ (**4**)

A solution of $[\text{Cu}(\text{NCCH}_3)_4]\text{SbF}_6$ (0.116 g, 0.25 mmol) in 1 mL DMF was added to a stirred solution of 2-pina (0.050 g, 0.25 mmol) in 1 mL DMF. The red orange solution was stirred for 4.0 h and 20 mL of Et_2O was added to the mixture. The resulting orange solid was washed with Et_2O (5 mL \times 3). Dissolving the product in DMF and vapor diffusion of Et_2O into the clear red orange solution at room temperature led to the formation of red orange crystals suitable for X-ray crystallographic characterization (0.106 g, 72%



Scheme 1. Pyridylamide ligands Haap, 3-pna, 2-pina and 4-ppa applied in this work.

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