Polyhedron 80 (2014) 157–165

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly

Syntheses and characterization of five-coordinate copper(II) complexes based on tridentate SNS pincer ligand precursors

John R. Miecznikowski [a,*], Matthew A. Lynn [b], Jerry P. Jasinski [c], Wayne Lo [d], Daniel W. Bak [e], Mekhala Pati [e], Elizabeth E. Butrick [a], Anne Elise R. Drozdoski [a], Kerry A. Archer [a], Christine E. Villa [a], Elise G. Lemons [a], Erin Powers [a], Margaret Siu [a], Camile D. Gomes [a], Nicholas A. Bernier [a], Kaitlyn N. Morio [a]

[a] Department of Chemistry and Biochemistry, Fairfield University, 1073 North Benson Road, Fairfield, CT 06824, USA
[b] Department of Science and Mathematics, National Technical Institute for the Deaf, Rochester Institute of Technology, 52 Lomb Memorial Dr., Rochester, NY 14623, USA
[c] Department of Chemistry, Keene State College, 229 Main Street, Keene, NH 03435-2001, USA
[d] Department of Chemistry, Boston College, 140 Commonwealth Avenue, Chestnut Hill, MA 02467, USA
[e] Department of Chemistry and Molecular Biology, Cell Biology, and Biochemistry, Boston University, 24 Cummington Street, Boston, MA 02215, USA

ARTICLE INFO

Article history:
Received 23 December 2013
Accepted 11 March 2014
Available online 1 April 2014

Honoring the 70th birthday of Professor Vukadin Leovac.

Keywords:
SNS pincer ligand
Mononuclear Cu complexes
X-ray crystallography
Cyclic voltammetry
EPR spectroscopy

ABSTRACT

A series of tridentate pincer ligands, each possessing two sulfur- and one nitrogen-donor functionalities (SNS), based on a bis-imidazolyl precursor were metallated with $CuCl_2$ to give new tridentate SNS pincer copper(II) complexes [(SNS)$CuCl_2$]. These purple complexes exhibit a five-coordinate pseudo-square pyramidal geometry at the copper center. The [(SNS)$CuCl_2$] complexes were characterized with single crystal X-ray diffraction, electrospray mass spectrometry, EPR spectroscopy, attenuated total reflectance infrared spectroscopy, UV–Vis spectroscopy, cyclic voltammetry, and elemental analysis. The EPR spectra are consistent with typical anisotropic Cu(II) signals with four hyperfine splittings in the lower-field region ($g_{||}$). Various electronic transitions are apparent in the UV–Vis spectra of the complexes and originate from d-to-d transitions or various charge transfer transitions. We preformed computational studies to understand the influence that structural constraints internal to our tridentate SNS ligand precursors have on the oxidation state of the resulting bound copper complex. We have determined that a d^9 copper(II) metal center is better situated than a d^{10} copper(I) center to bind our tridentate SNS ligand set when it does not contain an internal CH_2 group. Without this methylene linker, the SNS ligand forces the N and S atoms into a T-shaped arrangement about the metal center.

1. Introduction

Recently, we have prepared and reported a series of tridentate pincer ligand precursors, each of which possesses SNS donor atoms [1,2]. In our previous studies, we have used a variety of these ligand sets to prepare tetradentate zinc(II) and tridentate Cu(I) SNS pincer complexes. The SNS ligand framework can be constructed through the linking of two thioimidazolyl and thiotriazolyl heterocycles with one pyridinyl unit, resulting in an organic framework that is capable of tridentate chelation of a metal ion. Using 2,6-dibromopyridine as a starting material results in the binding of the thioimidazolyl groups directly to the pyridine moiety (**1a–c**), thereby generating a stiff ligand system in which rotation about the C–N bond that links the pyridinyl and imidazolyl moieties is the only way in which these rings can move relative to each other. We have also prepared SNS ligands with a greater degree of flexibility (**2a–c** and **3a–c**) by employing 2,6-(dibromomethyl)pyridine, thereby introducing a methylene linker into the ligand set. We were able to fine-tune further the electronic environment within the framework of these systems by using imidazolyl- (**2a–c**) and triazolyl- (**3a–c**) based precursors in the preparation of the pincer ligands.

The use of zinc(II) chloride to prepare zinc(II) compounds that contain these ligand precursors (Fig. 1**1a–c**, **2a–c**, and **3a–c**) has proven to be straightforward and demonstrates the influence that various modifications within the ligand set can have on the

* Corresponding author. Tel.: +1 203 254 4000x2125; fax: +1 203 254 4034.
E-mail addresses: jmiecznikowski@fairfield.edu (J.R. Miecznikowski), malntm@rit.edu (M.A. Lynn), jjasinsk@keene.edu (J.P. Jasinski), wayne1728@gmail.com (W. Lo), dbaknd06@gmail.com (D.W. Bak), mekhalap@bu.edu (M. Pati), elizabeth.butrick@student.fairfield.edu (E.E. Butrick), adrozdoski206@yahoo.com (A.E.R. Drozdoski), karcher19@gmail.com (K.A. Archer), Christine.villa@student.fairfield.edu (C.E. Villa), elise.lemons@student.fairfield.edu (E.G. Lemons), erinapow12@gmail.com (E. Powers), margaret.siu@student.fairfield.edu (M. Siu), Camile.gomes@student.fairfield.edu (C.D. Gomes), nicholas.bernier@student.fairfield.edu (N.A. Bernier), knm28@georgetown.edu (K.N. Morio).

http://dx.doi.org/10.1016/j.poly.2014.03.020
0277-5387/

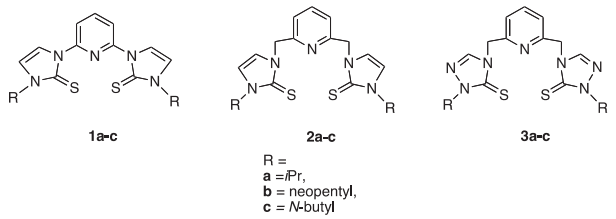

Fig. 1. SNS ligand precursors previously prepared by Miecznikowski et al. [1,2] and Jin and co-workers [3].

coordination of the metal center. By and large, these syntheses result in the formation of four-coordinate pseudo-tetrahedral zinc(II) complexes in which a chloride and the SNS tridentate ligand are bound to the metal center. The specific SNS ligands that gave rise to these systems were of two types: they either (1) possessed methylene linkers between the pyridinyl and the imidazolyl or triazolyl groups or (2) they did not have such a linker and contained only imidazolyl (not triazolyl) groups. The counterion for such systems was found to be a trichloro- or a tetrachlorozincate anion. In one instance, however, a five-coordinate pseudo-trigonal–bipyramidal zinc(II) complex resulted when the ligand contained thiotriazolyl functionalities and no methylene linkers between the triazolyl and pyridinyl groups. In this complex, the tridentate ligand bonded to the zinc(II) center via the pyridinyl N atom and the available triazolyl N atoms. This NNN binding of the ligand placed these three atoms in a meridional arrangement about the metal center with the pyridinyl N atom occupying an equatorial position and the two triazolyl N atoms in axial positions.

Given that copper metalloproteins contain nitrogen (N-His) and sulfur (cysteine) donor atoms to the metal center, we have chosen to investigate the synthesis of copper-containing systems that contain our SNS ligand sets. The preparation of copper complexes that contain nitrogen and sulfur donor atoms is certainly of interest in bioinorganic chemistry. For example, in electron-transfer proteins, cysteine–thiolate copper ion interactions are important [4,5]. Sulfide–Cu interactions are found in the Cu_4–S cluster in the enzyme nitrous oxide reductase [6–8]. In addition, thioether methionecopper ion interactions occur in type 1 "blue" electron transfer proteins and in the active site of certain monooxygenases [9,10]. Recently, Hor and co-workers reported a five-coordinate mononuclear Cu(II) complex that contained a tridentate ligand with SNS donor atoms [11]. Three- [12–16], four- [17–20], and five-coordinate [11,18,19,21–34] mononuclear copper(II) complexes have been reported previously. For the five-coordinate copper(II) complexes, both pseudo-trigonal bipyramidal and pseudo-square pyramidal coordination environments at the copper(II) center have been reported.

We have recently published a synthetic, spectroscopic, and computational study of several copper(I) systems that we have prepared using our SNS ligands **2a**, **3a**, and **3c** [35]. Of particular note is that when the ligand set possesses a methylene linker between the pyridinyl and the thioimidazolyl or thiotriazolyl groups, the resulting metal-bound systems exhibit pseudo-trigonal-planar binding of the tridentate ligand set in an SNS fashion. Also of interest was our finding that when copper(II) chloride is used as the source of the metal ion, a disproportionation reaction occurs in which copper(I) ions are produced and bound by the SNS ligand to give a monocationic copper(I)-bound complex with the general formula $[(SNS)Cu]^+$. Two of these cations are balanced by one copper(II)-containing $CuCl_4^{2-}$ anion.

For our current work, our focus is on the synthesis and characterization of novel copper–SNS complexes with the ligand precursors that were not used in our previous study. Reaction of copper(II) chloride with ligand sets **1a**–**c**, which have thioimidazolyl groups and no internal methylene linkers, gives rise to five-coordinate copper(II) complexes in which the SNS ligand set and two chlorides are bound to the metal center. Disproportionation of the metal was not observed during these syntheses.

Therefore, we present here the syntheses, X-ray crystallographic, spectroscopic and electrochemical characterizations of copper(II) complexes that contain ligand precursors **1a**–**c**. As with our previous work with zinc(II), we find that fine-tuning of the SNS ligand set allows for the preparation of copper complexes with various coordination environments about the metal center. The availability of the copper(I) and copper(II) oxidation states allows an extra area of study in which the charge on the metal center can be controlled through modification of the ligand set. Our computational study of these systems provides insight into the influence of the ligand sets on the oxidation state and the coordination environment of our Cu–SNS systems.

2. Experimental

2.1. General procedures

All reagents used are commercially available and were used as received. All of the reagents and solvents were purchased from Acros Organics except for diethyl ether, and sodium acetate, which were purchased from Fisher. 2,6-bis{[*N*-butyl] imidazole-1-ylidene-2-thione} pyridine, and 2,6-bis{[*N*-isopropyl] imidazole-1-ylidene-2-thione}pyridine, 2,6-bis{[*N*-neopentyl]imidazole-1-ylidene-2-thione} pyridine were reported previously [1,3].

Each sample was analyzed by direct flow injection (injection volume = 3 or 10 μL) ElectroSpray Ionization (ESI) on a Waters Qtof API US instrument in the positive mode. The optimized conditions were found as follows: capillary = 3000 kV, cone = 10 or 35 V, source temperature = 120 °C and desolvation temperature = 120 or 350 °C.

Cyclic voltammetry experiments were performed using a Cypress Electroanalytical System with a silver wire reference electrode, a glassy carbon working electrode, and a platinum counter electrode. The supporting electrolyte for the cyclic voltammetry experiments was tetra-*N*-butylammonium tetrafluoroborate. The solvent for the cyclic voltammetry experiments was dimethyl sulfoxide. The ferrocenium/ferrocene couple was used as an internal reference; reduction potential values were corrected by assigning the ferrocenium/ferrocene couple to 0.40 V versus SCE.

IR spectra were collected using a Thermo Nicolet AVATAR 380-FT-IR with a SMART SPECULATR reflectance adaptor. C, H, N elemental analyses were performed by Atlantic Microlab Inc. (Norcross, GA).

Low temperature (10 K) EPR measurements were made using a Bruker X-band ESEXSYS E 500 spectrometer equipped with an ESR900 continuous flow liquid helium cryostat. EPR spectra were collected at (9.24 GHz), (2 mW) microwave power, and with a (1G) modulation amplitude. The EPR sample of a copper complex was prepared by dissolving 3 mg of the copper complex in 0.8 mL of methanol. Spectra were collected of oxidized samples and required no reduction prior to data collection.

2.2. Density functional calculations

GAUSSIAN 03 was used to perform single-point calculations and geometry optimizations using the B3LYP hybrid functional. The 6-311g(d) basis set as provided with the software was employed for H, C, N, and S and 6-311g(d,p) was used for Cu. Calculations were performed using *N*-methyl pendant groups and C_2 symmetry in all cases. Frequency analyses were performed on the optimized