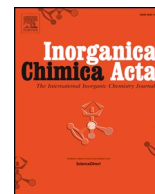




ELSEVIER

Contents lists available at ScienceDirect

Inorganica Chimica Acta

journal homepage: [www.elsevier.com/locate/ica](http://www.elsevier.com/locate/ica)

Research paper

# A new face for *bis*(pyrazol-3-yl)pyridine: Incompatible geometric preferences dictates unprecedented pincer ligand connectivity

Nicholas S. Labrum, Chun-Hsing Chen, Kenneth G. Caulton\*

Department of Chemistry, Indiana University, Bloomington, IN, United States

## ARTICLE INFO

**Keywords:**  
Copper(I) complex  
*Bis*(pyrazol-3-yl)pyridine  
Hemilabile  
Bridging pincer

## ABSTRACT

The planar pincer ligand *bis*(pyrazol-3-yl)pyridine,  $H_2L$ , binds to copper(I) iodide to give a product of formula  $(H_2L)_2(CuI)_3$  which single crystal X-ray diffraction reveals to have two unprecedented features for this ligand:  $\kappa^2$  binding of one  $H_2L$  and bridging of the second  $H_2L$  across two copper centers. The broader implications of this finding are discussed.

## 1. Introduction

The *bis*(pyrazol-3-yl)pyridine ligand [1,2] (Scheme 1) is a pincer with convergent lone pairs, and its coordination chemistry has been studied for Mn, Fe, Co, Ni and Cu, as well as Ru [3–9]. It is invariably tridentate on metals (Scheme 1) regardless of whether it is the diacid form,  $H_2L$  or singly or doubly deprotonated,  $HL^-$  or  $L^{2-}$  [1,2,10]. Many molecular parameters have been extensively varied in  $Fe(H_2L)_2^{2+}$  species in search of varied spin crossover properties [11,12], and catalysis [6–9] including for proton reduction [13] and disproportionation of hydrazines [14]. While these have involved uniformly tridentate pincer binding to metal, we report here evidence supporting a broadened view of the capabilities of this ligand class when attached to monovalent copper.

Planar multidentate ligands can be incompatible with the polyhedral preferences of certain d electron configurations. In the present case, the three convergent lone pairs of pincer ligands are then suited for metals which allow a meridional donor set. The  $d^{10}$  electron configuration (e.g.  $Ni^0$  and  $Cu^I$ ) has a strong preference for a tetrahedral four coordinate structure, and so a ligand like  $H_2L$  (Scheme 1) appears incompatible with monovalent copper [15,16]. This does not mean a reaction will not occur, but instead that unusual compromises will result. We describe here the outcome of such a conflict.

## 2. Experimental section

## 2.1. General procedures

All manipulations were carried out under an atmosphere of argon

using standard Schlenk techniques or in a glovebox under ultra-high purity nitrogen. Solvents were purchased from commercial sources, purified using Innovative Technology SPS-400 PureSolv solvent system or by distilling from conventional drying agents and degassed by the freeze–pump–thaw method thrice prior to use. Glassware was oven-dried at 150 °C overnight and flame dried prior to use. THF was stored over activated 4 Å molecular sieves and sodium metal pieces. Deuterated solvent  $CD_3CN$  was dried over  $CaH_2$ , subjected to three freeze–pump–thaw cycles, distilled and stored over 4 Å molecular sieves in the glovebox prior to use. All starting reagents were commercially available and used without further purification. All  $^1H$  NMR spectra were collected at 25 °C on a Varian Inova-400 spectrometer operating at 400.11 MHz. Spectra were referenced to the residual respective protio impurities in solvent employed.

2.2. Preparation of  $(H_2L)_2Cu_3I_3$ 

Anhydrous  $CuI$  (25 mg, 0.131 mmol) was slurried in 5 mL THF and allowed to stir for 10 min.  $H_2L$  (42.5 mg, 0.131 mmol) dissolved in 5 mL THF was added dropwise. The reaction was allowed to stir for 24 h during which time the solution became homogeneous and golden-yellow in color. A yellow-orange solid is obtained by removal of solvent under reduced pressure. Yield: quantitative.  $^1H$  NMR (400 MHz,  $CD_3CN$  298 K):  $\delta$  (ppm) 11.44 (s, 2H, pyz NH) 7.96 (t, 7.7 Hz, 1H, Ar-p), 7.82 (d, 7.7 Hz, 2H, Ar-m), 6.79 (s, 2H, pyz CH), 1.26 (s, 18H, pyz  $C(CH_3)_3$ ). MS (ESI-positive) in MeCN: observed: 513.1, calculated: 513.1,  $[M]^+$ ,  $C_{19}H_{25}CuIN_5$ ; observed: 708.4, calculated: 708.3,  $[(H_2L)(HL)Cu]^+$ ,  $C_{38}H_{49}CuN_{10}$ ; observed: 421.1, calculated: 421.1,  $[H_2LCuCl]^+$ ;  $C_{19}H_{25}CuClN_5$ , this last from chloride in the spectrometer ionization chamber.

\* Corresponding author.

E-mail address: [caulton@indiana.edu](mailto:caulton@indiana.edu) (K.G. Caulton).



Scheme 1.

### 2.3. X-ray diffraction study

A yellow crystal (approximate dimensions  $0.300 \times 0.250 \times 0.100 \text{ mm}^3$ ) was placed onto the tip of MiTeGen and mounted on an Apex Kappa Duo diffractometer and measured at 150 K. A preliminary set of cell constants was calculated from reflections harvested from three sets of 12 frames. These initial sets of frames were oriented such that orthogonal wedges of reciprocal space were surveyed. This produced initial orientation matrices determined from 442 reflections. The data collection was carried out using Mo  $K\alpha$  radiation (graphite monochromator) with a frame time of 5 s and a detector distance of 5.0 cm. A randomly oriented region of reciprocal space was surveyed to achieve complete data with a redundancy of 4. Sections of frames were collected with  $0.50^\circ$  steps in  $\omega$  and  $\phi$  scans. Data to a resolution of  $0.84 \text{ \AA}$  were considered in the reduction. Final cell constants were calculated from the xyz centroids of 9850 strong reflections from the actual data collection after integration (SAINT). The intensity data were corrected for absorption (SADABS) [17]. The space group  $P-1$  was determined based on intensity statistics and systematic absences. The structure was solved using SIR-92 and refined (full-matrix-least squares) using the Oxford University Crystals for Windows system [18,19]. A direct-methods solution was calculated, which provided most non-hydrogen atoms from the E-map. Full-matrix least squares/difference Fourier cycles were performed, which located the remaining non-hydrogen atoms.

$(\text{H}_2\text{L})_2\text{Cu}_3\text{I}_3$  contains disordered solvent THFs. Attempts in modeling all solvent THF were made but were unsuccessful, and Platon SQUEEZE was then implemented (void volume  $842.7 \text{ \AA}^3$ ,  $236 e^-$ ). All non-hydrogen atoms were refined with anisotropic displacement parameters. The hydrogen atoms were placed in ideal positions and refined as riding atoms except for those of parent N atoms. Crystal data, data collection, and refinement parameters are summarized in Table 1.

### 3. Results and discussion

Reaction of equimolar  $\text{H}_2\text{L}$  and  $\text{CuI}$  in THF occurs within 24 h, as is

Table 1

Crystal data and structure parameters for  $(\text{H}_2\text{L})_2\text{Cu}_3\text{I}_3$ .

Empirical formula	$\text{C}_{44}\text{H}_{62}\text{Cu}_3\text{N}_{10}\text{O}_{1.50}$	
Formula weight	1326.39	
Crystal size (mm)	$0.300 \times 0.250 \times 0.100$	
Wavelength	0.71073 $\text{ \AA}$	
Crystal system, space group	Triclinic, $P-1$	
Unit cell dimensions ( $\text{ \AA}$ , $^\circ$ )	$a = 14.2411(4)$	$\alpha = 68.7232(16)$
	$b = 15.5003(5)$	$\beta = 72.9370(16)$
	$c = 17.7193(5)$	$\gamma = 69.1016(16)$
Volume ( $\text{ \AA}^3$ )	3344.05(9)	
Z	2	
Density ( $\text{mg/M}^3$ )	1.317	
$F(000)$	1308.00	
Theta range for data collection ( $^\circ$ )	1.469–25.080	
Index ranges	$-15 \leq h \leq 16$ , $-16 \leq k \leq 18$ , $0 \leq l \leq 21$	
Reflections collected	11,821	
Independent reflections	11,821 [ $R_{\text{int}} = 0.033$ ]	
Completeness to theta = $25.080^\circ$	99.5%	
Data/restraints/parameters	11,768/351/666	
Goodness-of-fit on $F^2$	1.0016	
Final R indices [ $I > 2\sigma(I)$ ]	$R_1 = 0.0443$ , $R_{2w} = 0.0997$	
R indices (all data)	$R_1 = 0.0582$ , $R_{2w} = 0.1077$	
Largest diff. peak/hole ( $e \text{ \AA}^{-3}$ )	1.12/−1.01	

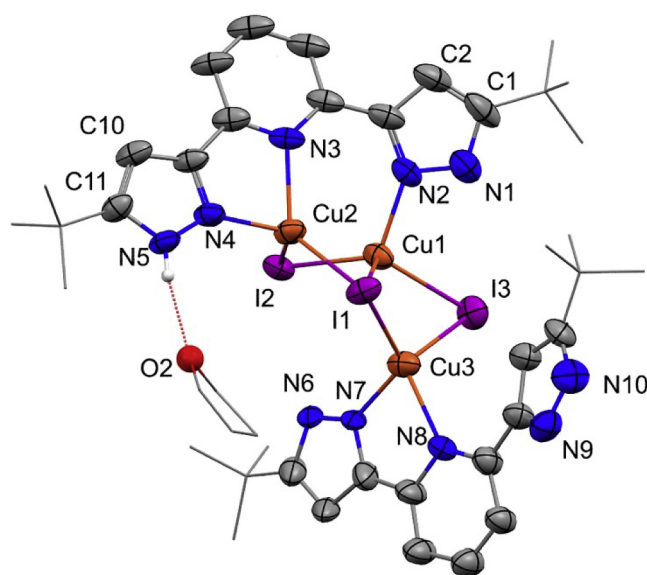


Fig. 1. Mercury drawing (50% probabilities) of the nonhydrogen atoms of  $(\text{H}_2\text{L})_2\text{Cu}_3\text{I}_3$  showing selected atom labels; unlabeled atoms are carbons. Selected structural parameters ( $\text{ \AA}$ ): I1–Cu1, 2.8383(8); I1–Cu2, 2.5446(8); I1–Cu3, 2.5998(8); I2–Cu1, 2.6037(9); I2–Cu2, 2.7208(9); I3–Cu1, 2.6323(8); I3–Cu3, 2.6221(8); Cu1–N2, 2.047(5); Cu2–N3, 2.177(4); Cu2–N4, 2.007(5); Cu3–N7, 1.929(6); Cu3–N8, 2.251(5).

evident by full dissolution of the  $\text{CuI}$ . The  $^1\text{H}$  NMR spectrum (see ESI) of the isolated product, in  $\text{CD}_3\text{CN}$ , shows twofold symmetry of the  $\text{H}_2\text{L}$  ligand as judged by both pyridyl and pyrazole hydrogens, including detection of the NH protons at 11.4 ppm. The ESI mass spectrum shows not only the ion  $(\text{H}_2\text{L})\text{Cu}^+$ , but also  $(\text{H}_2\text{L})(\text{HL})\text{Cu}^+$ , which will be seen to result from pincer ligand redistribution in a multimetal aggregate more complicated than simply monomeric  $(\text{H}_2\text{L})\text{Cu}$ .

Single crystal X-ray diffraction revealed (Fig. 1) the compound to have the unusual formula  $(\text{H}_2\text{L})_2\text{Cu}_3\text{I}_3$ . This reveals how the geometrical constraints of this pincer ligand are accommodated by the geometric demands of  $\text{Cu}^{\text{I}}$ . The molecule has no symmetry, although all coppers in a nonlinear  $\text{Cu}_3$  array achieve coordination number four. Both pincer ligands carry protons on both  $\beta\text{N}$ , as judged by  $> 110^\circ$   $\alpha\text{N}\beta\text{NC}$  angles; when deprotonated, the lone pair compresses this angle to  $\sim 107^\circ$  [20]. One  $\text{H}_2\text{L}$  is  $\kappa^3$  and the other is  $\kappa^2$  (to  $\text{Cu3}$ ), the latter with its NNH functionality directed outwards from the molecule, away from any metal, apparently to avoid a filled/filled interaction with  $\text{Cu3}$ . The distance  $\text{Cu3-N7}$  is short, at 1.929(6)  $\text{ \AA}$  while  $\text{Cu3-N8}$  of pyridine is very long, at 2.251(5)  $\text{ \AA}$ , apparently a response to orienting its attached  $\text{N9/N10}$  pyrazole lone pairs away from  $\text{Cu3}$ ; this is a remarkable example where the pyrazole of this bridging pincer rotates its donor nitrogens towards the exterior of the molecule. All Cu have approximately tetrahedral surroundings, and the rejected pyrazole occurs to avoid higher coordination number for  $d^{10} \text{Cu}^{\text{I}}$ .

The structure shows a second noteworthy feature: the  $\kappa^3 \text{H}_2\text{L}$  is only bidentate to one copper,  $\text{Cu2}$ , but then links over to the central copper,  $\text{Cu1}$ , via a second pyrazole  $\alpha\text{N}$ . This is an unprecedented bridging mode for this pincer ligand class. The distortion of the  $\kappa^2$  ( $\text{N8}$ ) pincer from planarity is also evident in the  $\kappa^3$  pincer, where the bridging pyrazole is rotated  $26^\circ$  away from its attached pyridine plane. Two iodides are doubly bridging and one (I1) is triply bridging. The central copper,  $\text{Cu1}$ , carries three iodides and one nitrogen ligand. This unsymmetrical pincer linkage enables each copper to have an approximately tetrahedral ligand environment, and is surely driven by the fact that a monomer  $(\text{H}_2\text{L})\text{CuI}$  would have a bad geometry due to the obligatory planar donor set in the pincer ligand.

As is typical for iodide, angles  $\text{Cu-I-Cu}$  are very acute, at  $55\text{--}62^\circ$ . This brings the metals into short  $\text{Cu/Cu}$  contacts,  $\text{Cu1/Cu2}$  at

Download English Version:

<https://daneshyari.com/en/article/11009834>

Download Persian Version:

<https://daneshyari.com/article/11009834>

[Daneshyari.com](https://daneshyari.com)