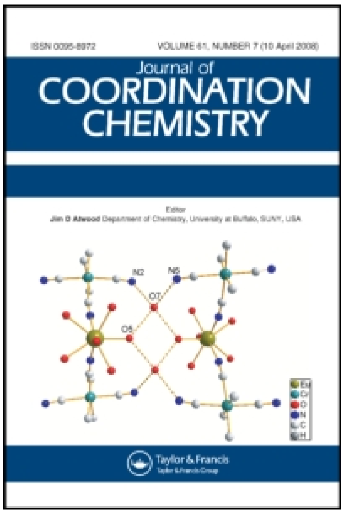

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Unusual structurally characterized pyridine carbinoxide copper(II) coordination compounds, isolated from organic solvents

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Unusual structurally characterized pyridine carbinoxide copper(II) coordination compounds, isolated from organic solvents

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The coordination behavior of pyridine carbinoxide [$NC_5H_4(CH_2O)$-2 or OPy] with copper in organic solvents was crystallographically determined. Initial attempts to generate the Cu(II) OPy derivatives from an alcoholysis exchange of $Cu(OCH_3)_2$, with H–OPy in toluene, led to the isolation of $[Cu(\mu_c\text{-}OPy)(O^cPy)]_2$ (**1**, "c" indicates chelation). The square-based pyramidal geometries noted for each Cu center resulted from one O^cPy and two μ_c-OPy ligands, generating an unusual C_i symmetry. From the reaction of H–OPy and the Cu(I) species $Cu(C_6H_2(CH_3)_3\text{-}2,4,6)$, mononuclear Cu(II) complex $Cu(O^cPy)_2(H\text{–}OPy)_2$ (**2**) was isolated. Compound **2** is unusual in that it adopts a square planar arrangement around the Cu metal center using two O^cPy ligands; however, the metal center also coordinates with two H–OPy molecules forming an octahedral geometry. Upon dissolution in water, both **1** and **2** react to form the previously reported $Cu(O^cPy)_2 \cdot 2H_2O$ (**3**). Attempts to add a Lewis base through dissolution of **1** in selected solvents (i.e., tetrahydrofuran, pyridine, 1-methylimidazole) led to $[Cu(\mu_c\text{-}OPy)(O^cPy)]_2 \cdot H_2O$ (**4**), which possesses a C_2 symmetry. The water was believed to be extracted from the "dry" solvents. A Cl derivative was also solved for the Cu(II)/Cu(I) species $[Cu(OPy)_2]_2[CuCl(H\text{–}OPy)_2]_2$ (**5**) from tetrahydrofuran dried over apparently contaminated sieves.

Keywords: Metal alkoxide; Copper; Pyridine carbinol; Water

1. Introduction

Copper alkoxides [$Cu(OR)_x$] have widespread use in a number of diverse applications, including superconductivity (YBCO) [1–3], electrochemistry [4, 5], magnetism [6–11], and biological catalysts [12–15]. These precursors are of continued interest due to their inherent physical properties (i.e., high solubility, high volatility, and low decomposition temperature), along with the ease that these characteristics can be manipulated by simple ligand substitutions. Since the structural arrangement of the

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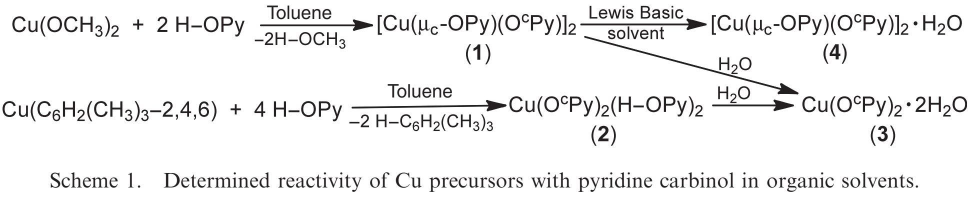
metal alkoxide ($M(OR)_x$) precursor plays a vital role in directing the final material's properties [16–20], it is critical that the connectivity of any precursor has to be clearly defined prior to initiating material investigations. *A priori* structure prediction for substituted $M(OR)_x$ is often difficult due to the large cation size to small charge ratio that favors oligomerization, along with unexpected side reactions (i.e., esterification, oxolation, etc.). Therefore, any modification to the ligand set(s) of $M(OR)_x$ requires the complex to be fully characterized prior to use; due to the number of applications that employ them, the more than 7000 reported $Cu(OR)_x$ structures do not come as a surprise [1–3, 6–8, 12, 13, 21, 22]. The nuclearities of these compounds were found to range from monomer to polymers, and seemingly every nuclearity in between.

Our efforts to generate controlled structured $M(OR)_x$ have focused on employing methanol ligands derivatized with organic, solvent-like moieties (termed H–OR*) [23, 24]. One of the OR* ligands, pyridine carbinol [$NC_5H_4(CH_2OH)$-2 or H–OPy], was found to be useful for controlled chemical manipulation of $M(OR)_x$ while maintaining structural integrity. This was clearly demonstrated for the $(OPy)_2Ti(OR)_2$ system, where >20 H–OR′ modifiers were easily substituted to form a series of $(OPy)_2Ti(OR')_2$ compounds [23, 24]. Therefore, it was of interest to determine the coordination behavior of H–OPy in the presence of Cu as a means to generate controlled structures of $Cu(OR)_x$ compounds.

A search of the literature reveals that numerous structures involving OPy bound to Cu are available [21, 22], with the favored structure type being the monomeric species $(H\text{–}OPy)_2Cu(L)_2$ (where L = carboxylates [25–32], amines [33], halides [34], or nitrates [35, 36]). Additional structures such as $[(L)Cu(\mu_c\text{-}OPy)]_4 \cdot H_2O$ (where $L = O_2C(CH_3)$ [37] or SCN [38], μ_c = bridging chelating), $[(\mu\text{-succ})Cu(\mu_c\text{-}OPy)]_n[1/2H_2O]$ [39] (succ = succinato; $[O_2C(CH_2)]_2$), and $[(Cl)Cu(\mu\text{-}Cl)(\mu\text{-}H\text{–}OPy)]_n[MeOH]$ [34] were noted as well. However, from this diverse family of compounds only one homoleptic Cu–OPy species has been isolated: $Cu(O^cPy)_2 \cdot 4H_2O$ (O^cPy = chelation) [36]. Our initial efforts for this project focused on developing the homoleptic Cu/OPy system for materials production, sans water due to the potential for uncontrolled side reactions. Subsequent hydrolysis studies were then undertaken to determine how the hydrate affected the final structures. This report details the synthesis and characterization of this unusual series of "$Cu(OPy)_2$" derivatives, which were identified as $[Cu(\mu_c\text{-}OPy)(O^cPy)]_2$ (**1**), $Cu(O^cPy)_2(H\text{-}O^cPy)_2$ (**2**), $Cu(O^cPy)_2 \cdot 2H_2O$ (**3**), and $[Cu(\mu_c\text{-}OPy)(O^cPy)]_2 \cdot H_2O$ (**4**), according to the synthesis results summarized in scheme 1.



Scheme 1. Determined reactivity of Cu precursors with pyridine carbinol in organic solvents.

2. Experimental

All compounds described below were handled with rigorous exclusion of air and water, when appropriate, using standard Schlenk line and glove box techniques. All analytical data were collected on dried crystalline samples. FT-IR data were obtained on a Bruker Vector 22 MIR spectrometer using KBr pellets under an atmosphere of flowing nitrogen. All solvents [toluene (tol), tetrahydrofuran (THF), pyridine (py), 1-methylimidazole (MeIm)] were used as received (from Aldrich, USA) in Sure/Seal^{TM} bottles and handled only under an inert atmosphere of argon. The following compounds were stored under argon upon receipt (Aldrich) and used without further purification: $Cu(OCH_3)_2$, CuCl, 1.0 M solution of BrMg(Mes) (Mes = mesityl or $C_6H_2(CH_3)_3$-2,4,6) in THF, and H–OPy. Cu(Mes) was synthesized according to literature reports using CuCl and BrMg(Mes) [40]. De-ionized (DI) water was obtained from reverse osmosis columns.

2.1. *Synthesis*

2.1.1. $[Cu(\mu_c\text{-}OPy)(O^cPy)]_2$ (1). To a stirring light blue mixture of $Cu(OCH_3)_2$ (0.500 g, 3.98 mmol) in ~10 mL of toluene, H–OPy (0.869 g, 7.96 mmol) was slowly added. The reaction mixture turned cloudy dark blue. After heating for 10 min at 100°C, the reaction mixture turned clear dark blue. After stirring for 12 h, the reaction mixture was set aside with the cap loose until X-ray quality crystals were formed. Yield: 0.863 g (77.5%). FT-IR (KBr, cm^{-1}): 3431(m), 3068(w), 3017(w), 2824(m), 2797(m), 2775(w), 2739(s), 2675(m), 1604 (s), 1569(s, sh), 1473(s, sh), 1436(s), 1350(m), 1281(m), 1146(m, sh), 1091(s), 1079(w, sh), 1045(s, sh), 1040(w, sh), 1026(w, sh), 776(w, sh), 767(s), 723(m), 655(m), 523(m), 496(s), 443(s), 423(s, sh). Anal. Calcd for $C_{12}H_{12}CuN_2O_2$ (%): C, 51.52; H, 4.32; N, 10.01. Found (%): C, 51.30; H, 4.06; N, 9.71.

2.1.2. $Cu(O^cPy)_2(H\text{-}O^cPy)_2$ (2). To a stirring light yellow mixture of Cu(Mes) (0.500 g, 2.73 mmol) in ~10 mL of toluene, H–OPy (1.19 g, 10.9 mmol) was slowly added whereupon the solution turned dark blue. After 12 h, the reaction mixture was set aside with the cap loose under an argon atmosphere until X-ray quality crystals were formed. Yield : 0.859 g (63.0%). FT-IR (KBr, cm^{-1}) : 3397(w), 3073(m), 2903(m, sh), 2858(m, sh), 2814(m), 2768(w, sh), 2680(m), 1604(m), 1569(m, sh), 1476(s, sh), 1437(m), 1356(w), 1282(w), 1214(w), 1151(s, sh), 1082(s), 1043(s, sh), 841(w), 768(s), 721(s, sh), 652(w), 604(w), 489(w), 443(w), 420 (w). Anal. Calcd for $C_{24}H_{26}CuN_4O_4$ (%): C, 57.88; H, 5.26; N, 11.25. Found (%): C, 57.60; H, 4.89; N, 10.50.

2.1.3. $Cu(OPy)_2 \cdot 2H_2O$ (3). Used **2** (0.500 g, 1.00 mmol) and ~10 mL of H_2O. Yield: 0.235 g (74.1%). FT-IR (KBr, cm^{-1}): 3330(s), 3081(w, sh), 2821(m), 1658(s, sh), 1608(m), 1570(m, sh), 1481(m), 1439(s), 1358(m), 1285(m), 1218(w), 1157(w), 1075(s), 1048(s, sh), 841(w), 775(m), 717(m), 659(m), 615(w, sh), 507(m), 414(w). Anal. Calcd for $C_{12}H_{16}CuN_2O_4$ (%) : C, 45.64; H, 5.11; N, 8.87. Found (%) : C, 46.10; H, 5.10; N, 8.64.

2.1.4. $[Cu(\mu_c\text{-}OPy)(O^cPy)]_2 \cdot H_2O$ (4). Dissolution of **1** (0.250 g, 0.447 mmol) in ~10 mL of THF yielded a dark blue reaction mixture. X-ray quality crystals were grown by slow evaporation of the volatile portion under an argon atmosphere of the reaction mixture. Yield: (THF) 0.141 g (44.8%). FT-IR (KBr, cm^{-1}): 3446(m), 3068(w), 3016(m), 2823(m), 2797(m, sh), 2775(w, sh), 2739(s), 2673(m), 1603(s), 1569(m), 1472(s, sh), 1434(s), 1350(m), 1281(s), 1146(m, sh), 1091(s), 1045(s, sh), 1026(m, sh), 767(s), 497(s). Anal. Calcd for $C_{12}H_{14}CuN_2O_3$ (%): C, 48.40; H, 4.74; N, 9.40. Found (%): C, 48.90; H, 4.39; N, 9.52.

2.2. *General X-ray crystal structure information*

Each crystal was mounted onto a thin glass fiber from a pool of Fluorolube™ and immediately placed under a liquid N_2 stream on a Bruker AXS diffractometer [26]. The radiation used was graphite monochromated Mo-Kα radiation ($\lambda = 0.7107$ Å). The lattice parameters were optimized from a least-squares calculation on carefully centered reflections. Lattice determination and data collection were carried out using SMART Version 5.054 software. Data reduction was performed using SAINT Version 6.01 software. The structure refinement was performed using XSHELL 3.0 software. The data were corrected for absorption using SADABS within the SAINT software package.

Crystal structures that contain alkoxide ligands often contain disorder within the atoms of the ligand chain, causing higher than normal final correlations [41–46]. This phenomenon subsequently leads to larger *R*-values. For this work, each structure was solved using direct methods. This procedure yielded the heavy atoms, along with a number of the C atoms. Subsequent Fourier synthesis yielded the remaining carbon positions. Hydrogens were fixed in positions of ideal geometry and refined within XSHELL software. These idealized hydrogens had their isotropic temperature factors fixed at 1.2 or 1.5 times the equivalent isotropic U of the carbons for which they were bonded. The final refinement of each compound included anisotropic thermal parameters on all non-hydrogen atoms. Due to the quality of the data collected, the crystal structure of **3** was solved in a non-centrosymmetric setting *C*2. The protons could not be located on the water and are therefore not added to the elemental weight in table 1, but are included in the elemental analyses. This is in contrast to the *C2/m* space group noted for the literature complex $Cu(O^cPy)_2 \cdot 4H_2O$ [36]. Identical unit cell parameters and structural connectivity were observed for both structural solutions; therefore, further efforts to obtain better crystals were abandoned. Additional information concerning the data collection and the final structural solutions of **1–5** can be found in the "Supplementary material". Data collection parameters for **1–5** are given in table 1 and metrical data are listed in table 2.

3. Results and discussion

There are numerous reports of structurally characterized neutral Cu species coordinated by either OPy or H–OPy [21, 22, 25–38, 47]; however, these compounds have all been isolated in the presence of potentially problematic ligands (i.e., halide, sulfate, carboxylate, or water) for materials production. In particular, these ligands lead

Table 1. Crystallographic data collection parameters for **1**–**5**.

Compound	**1**	**2**	**3**	**4**	**5**
Empirical formula	$C_{24}H_{24}Cu_2N_4O_4$	$C_{24}H_{26}CuN_4O_4$	$C_{12}H_{12}CuN_2O_4$	$C_{24}H_{28}Cu_2N_4O_6$	$C_{48}H_{52}Cl_2Cu_4N_8O_8$
Formula weight	559.55	498.03	311.78	595.58	1194.04
Temperature (K)	173(2)	203(2)	173(2)	152(2)	161(2)
Crystal system	Orthorhombic	Monoclinic	Monoclinic	Monoclinic	Triclinic
Space group	*Pbca*	*P2(1)/n*	*C2*	*C2*/c	*P*-1
Unit cell dimensions (Å, °)					
a	11.6631(11)	8.619(6)	13.440(2)	19.016(2)	12.8587(15)
b	13.1930(12)	9.827(7)	7.1060(9)	13.2165(15)	14.3987(17)
c	14.9030(14)	13.531(10)°	8.2535(11)°	13.2713(15)	15.6225(18)
α					73.622(2)
β		101.244(10)	110.516(3)	133.8930(10)	89.854(2)
γ					63.834(2)
Volume (Å^3), *Z*	2293.1(4), 4	1124.0(14), 2	738.25(18), 2	2403.6(5), 4	2465.7(5), 2
Calculated density (mg m^{-3})	1.621	1.472	1.403	1.646	1.608
Absorption coefficient μ (Mo-Kα) (mm^{-1})	1.894	1.011	1.489	1.818	1.872
R_1^a (%) (all data)	3.41 (4.45)	2.62 (2.74)	3.29 (3.29)	2.35 (2.60)	8.91 (9.61)
wR_2^b (%) (all data)	8.33 (8.88)	7.40 (7.50)	9.77 (9.78)	6.54 (6.73)	19.42 (19.71)

[a] $R_1 = \Sigma\|F_o|-|F_c\|/\Sigma|F_o| \times 100$; [b] $wR_2 = [\Sigma w(F_o^2 - F_c^2)^2/\Sigma(w|\ F_o|^2)^2]^{1/2} \times 100$.

Table 2. Metrical parameters for **1**–**5**.

	1	**2**	**3**	**4**	**5**
Distances (Å)					
Cu–O	1.9039(19)	1.9274(18)	1.896(2)	1.9138(14)	av. 1.905(6)
Cu–N	1.990(2) 1.999(2)	OPy 1.9888(17) HOPy 2.769(2)	1.981(3)	(μ-OPy) 1.9934(16) 1.9957(17)	Cu(II) 1.963(7) 1.975(7) Cu(I) 2.008(7) 2.016(7)
av. Cu–(μ-O)	1.937(2)	–	–	1.9306(13)	–
$Cu \cdots OH_2$	–	–	3.870(2)	7.402	–
av. Cu–Cl	–	–	–	–	2.4645(2)
Angles (°)					
O–Cu–O	–	180.0	178.0(9)	–	177.8(3)
O–Cu–(μ-O)	170.98(8)	–	–	178.16(5)	–
(μ-O)–Cu–(μ-O)	87.76(8)	–	–	87.74(5)	–
O–Cu–N	84.41(9) (μ) 83.42(9)	OPy 96.04(5) O_{OPy}–N_{HOPy} 85.83(5)	84.32(12)	84.08(6) (μ) 83.81(6)	Cu(II) 84.0(3)
N–Cu–N	164.35(9)	180.0	176.5(9)	166.77(6)	Cu(II)172.5(3) Cu(I) 136.1(3)
Cu–(μ-O)–Cu	92.25(8)	–	–	92.16(5)	–
av. N–Cu–Cl	–	–	–	–	103.95(2)

Not present in molecule.

to higher processing temperatures, uncontrolled reactivity, or incomplete decomposition/removal during processing, often causing significant deleterious properties [1–3, 6–8, 12, 13, 16–20, 41, 44–46, 48, 49]. The lone homoleptic species reported, $Cu(O^cPy)_2 \cdot 4H_2O$ [36], was synthesized through the derivatization of CuL_2 ($L = Cl$, NO_3 or SO_4) with H–OPy in an ethanol aqueous mixture held at pH 10 by tetraethylammonium hydroxide. The simple alkoxide ligand set of this precursor was of interest for ceramic materials production, if it could be produced without water present.

3.1. *H–OPy derivatization*

The synthesis of the hydrate free homoleptic Cu–OPy species was undertaken following the alcoholysis exchange of the commercially available $Cu(OCH_3)_2$ with two equivalents of H–OPy in toluene. After stirring for 12 h, the initial light blue solution turned cloudy dark blue, then turned into a clear dark blue solution upon heating for 10 min at 100°C. After stirring for 12 h, the volatile portion of the reaction was allowed to slowly evaporate until X-ray quality crystals were formed. Since NMR data for the paramagnetic Cu(II) species were not informative, FT-IR data were used to assist in the characterization of the reaction products. As per the literature reports, Cu–O bond stretches are known to fall between 545–520 and 450–410 cm^{-1} [41], whereas the Cu–pyridine dicarboxylic acid complex reportedly has bond stretches for the in-plane and out-of-plane deformation of the pyridine ring that fall around 680 and 433 cm^{-1} [48, 50]. IR stretches present in the spectrum of **1** (523, 496, 443, and 423 $cm-^{1}$) indicate that OPy is chelated to Cu. Since it was not readily apparent if OCH_3 were fully replaced by the OPy ligands due to similar stretching and bending peaks expected for these two alkoxides, single crystals were grown and used for single crystal X-ray diffraction experiments.

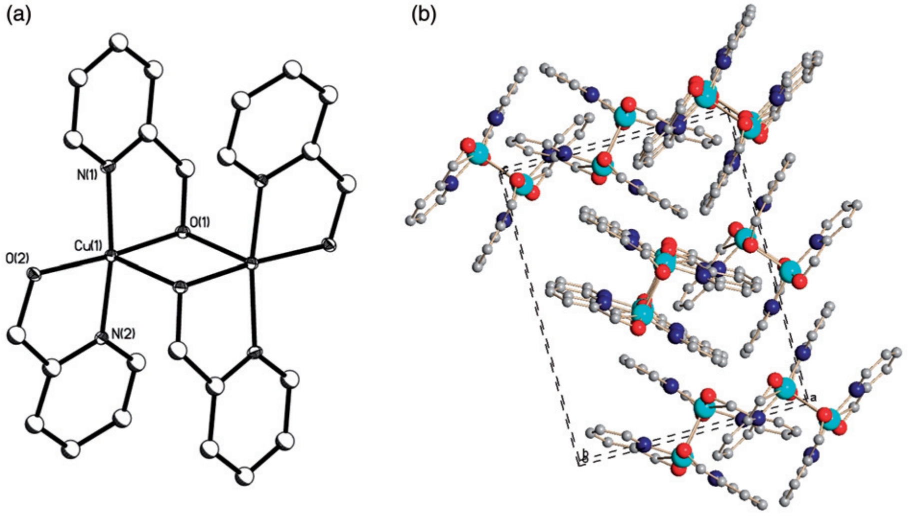


Figure 1. (a) Structure plot of **1**. Thermal ellipsoids of heavy atoms are drawn at the 30% level and carbon atoms are shown as ball and stick for clarity. (b) Packing diagram of **1** along the *a*-axis.

The structure proved to be **1** (figure 1), the first homoleptic, solvent-free OPy/Cu complex reported [21, 22, 25–38]. In **1**, each Cu is chelated by two OPy ligands in a *trans* arrangement forming two “$(O^{c}Py)_2Cu$” moieties linked by a μ-O of the adjacent OPy ligand. This results in a slightly distorted square-base pyramidal geometry (trigonal index $(\tau) = 0.11$) [51] around each Cu, where μ-O is located in the apex position due to the chelation effect of the OPy ligand, not as a result of a lone pair associated with the metal. The arrangement of the OPy ligands forces **1** into a C_i symmetry. The Cu–O distance (av. 1.90 Å) of **1** is in agreement with literature compounds: $Cu(O^{c}Py)_2 \cdot 4H_2O$ (1.89 Å) [36] and $[(NO_3)_3(H_2O)_2Ln(\mu_c\text{-}OPy)_2Cu]$ [47] (Ln = La, Gd, Tb) (av. 1.90 Å). As expected, the Cu–(OPy) distances were substantially shorter than the Cu–(H–OPy) distances (av. 2.29 Å) [25, 28–30, 32, 33, 35, 36]. There appears to be little change in the Cu–N distances of the OPy (av. 1.99 Å for **1**; 1.97 Å [36, 47]) *versus* the H–OPy (1.97 Å) [25, 28–30, 32, 33, 35, 36] derivatives. There are no π–π intermolecular interaction of the py rings of OPy. As per the literature the Cu/OPy compounds are all monomers, hence it is difficult to find a suitable model to compare the remaining metrical data. The $[(NO_3)_3(H_2O)_2Ln(\mu_c\text{-}OPy)_2Cu]$ [47] (Ln = La, Gd, Tb) derivatives were the best alternative with Cu–(μ-O) distances ranging from 2.298 to 2.444 Å (the Ln cation employed appears to dictate the distance). For **1**, the shorter 1.937(2) distance of Cu(II) (0.71 Å) [52] is not comparable to the smallest Ln(III) (La = 1.063 Å) [52] and direct comparisons are not meaningful. For the majority of $(OPy)_2Cu(L)_2$ compounds, a rigorous 180° angle exists for the O–Cu–O and N–Cu–N angles [21, 22, 25–38]. For **1**, these angles were significantly distorted from the ideal angle with the variation attributed to the bridging μ_c-OPy ligand. The same bridge-induced distortion was also noted for $[(NO_3)_3(H_2O)_2Ln(\mu_c\text{-}OPy)_2Cu]$ [47]. An examination of the packing diagram (figure 1b) demonstrates the tight packing arrangement of these dimers in comparison to the monomer in literature and hydrated species [21, 22, 25–38]. There is a lack of π-interaction between the py moieties, which

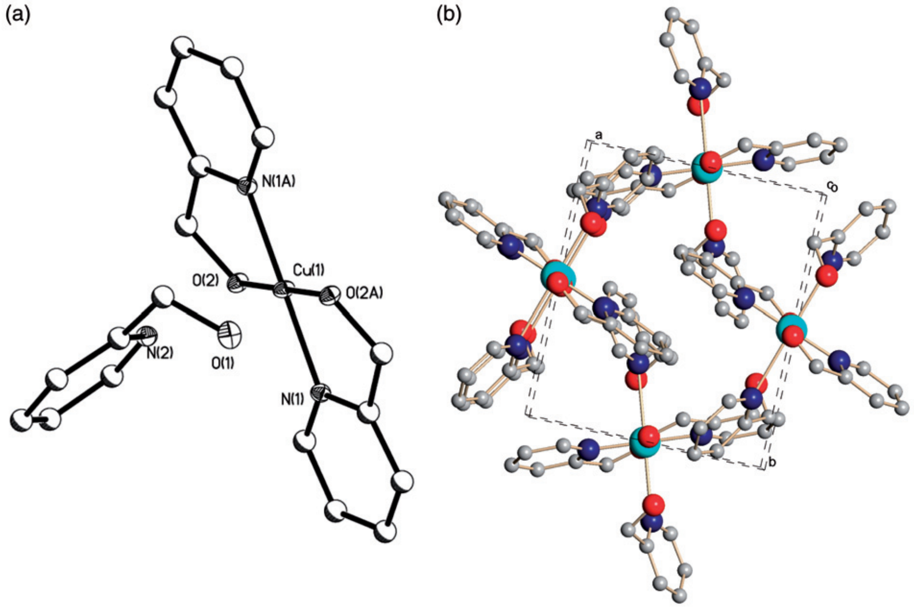


Figure 2. (a) Structure plot of **2**. Thermal ellipsoids of heavy atoms are drawn at the 30% level and carbon atoms are shown as ball and stick for clarity. (b) Packing diagram of **2** along the *c*-axis.

stack perpendicular to each other. The elemental analysis of the bulk powder of **1** was consistent with the single crystal structure.

In an attempt to generate the Cu(I) OPy analog, an alkyl/alcoholysis exchange reaction was undertaken using Cu(Mes) (scheme 1). The initial pale yellow solution again turned dark blue upon the addition of H–OPy, which suggests that the Cu(I) metal center had been oxidized to Cu(II). After stirring for 12 h, the reaction mixture was vacuum distilled to a blue powder. The FT-IR spectrum had the appropriate C–H, Cu–N, and Cu–O stretches (*vide infra*) associated with O^cPy ligands but there was also a broad stretch at 3397 cm^{-1} present, tentatively assigned as an OH stretch [41, 48, 50]. A crystal structure analysis was initiated to fully explain this curious stretch. The structure was successfully solved as monomeric **2** (figure 2) where the starting Cu(I) metal center has been oxidized to Cu(II), binding two O^cPy ligands. The oxidation is believed to be a result of the reduction of the acidic methylene protons of the OPy ligand and not any adventitious water that may be present in the THF as noted for **4** (*vide supra*). However, further work is necessary to verify the source of the Cu oxidation that occurs. Two additional H–OPy ligands bind to the metal center through the O of methanol moiety forming an octahedral (O_h) geometry (figure 2b). The presence of the H–OPy ligands explains the OH stretch observed in the FT-IR spectrum. The construction of **2** is similar to $CuL_2(HOPy)_2$ species [21, 22, 25–38] except $L = O^cPy$ for the first time. The packing diagram (figure 2b) shows a less densely packed species in comparison to **1** due to the axial H–OPy ligands. A comparison of the metrical data of **2** (table 2) and $Cu(O^cPy)_2 \cdot 4H_2O$ [36] indicates that there is little variation in angles and distances between the two compounds. The H–OPy ligands are significantly removed from the Cu center [2.769(2) Å] and appear to have little influence on the square-planar

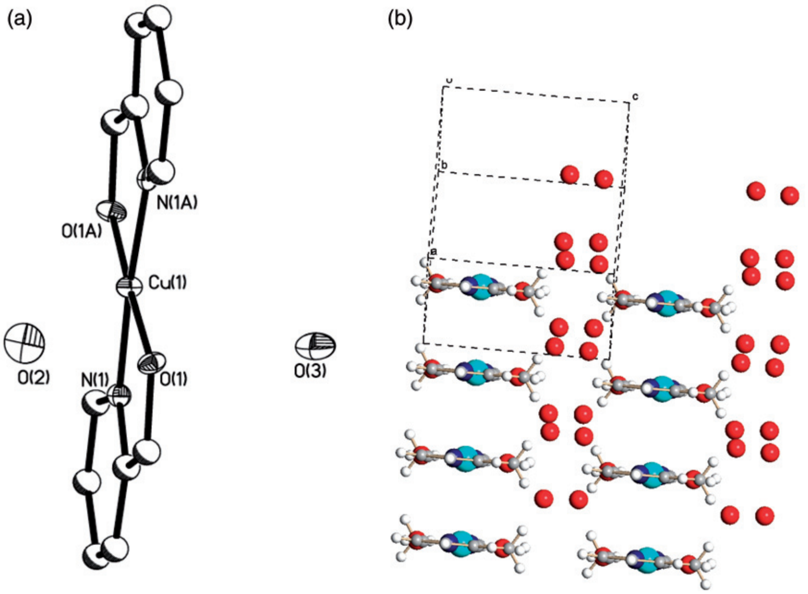


Figure 3. (a) Structure plot of **3**. Thermal ellipsoids of heavy atoms are drawn at the 30% level and carbon atoms are shown as ball and stick for clarity. (b) Packing diagram of **3** along the *c*-axis.

arrangement of the $Cu(OPy)_2$ moiety. Again, elemental analyses of the bulk powders of **2** were consistent with the single crystal structure.

3.2. *Hydration*

Due to the unusual structures reported for **1** and **2**, it was of interest to determine how water would affect these structures in comparison to the previously reported monohydrate $Cu(O^cPy)_2 \cdot 4H_2O$ [36] (*C2*/*m*, monoclinic). For each reaction the appropriate precursor (**1** or **2**) was readily dissolved in DI water and the reaction mixture was stirred for 12 h, whereupon the dark blue solution turned light blue. After this time, the volatile component was allowed to slowly evaporate until X-ray quality crystals were isolated. FT-IR data of these crystals indicated that the O^cPy moieties were present along with an OH stretch. Single crystal X-ray structures were undertaken for each product and compound **3** was solved as the di-hydrated monomeric species (figure 3), which was further substantiated by an acceptable elemental analysis. Due to the quality of the crystal data, the non-centrosymmetric setting (*C2*, monoclinic) was the highest possible space group that would yield a structural solution. The final structure is in agreement (i.e., a, b, c, α, β, γ, V, and connectivity) with the reported $Cu(O^cPy)_2 \cdot 4H_2O$ [36]. While the structures are identical, the number of waters reported for **3** and $Cu(O^cPy)_2 \cdot 4H_2O$ [36] are different. This is mainly due to the elemental analysis determinations of water content, the symmetry of the space group of the final structural solution, and the previous authors' [36] choice to discuss the four bridging waters that occur upon unit cell expansion. Figure 3(b) shows the four water molecules that act as bridges upon expansion to obtain

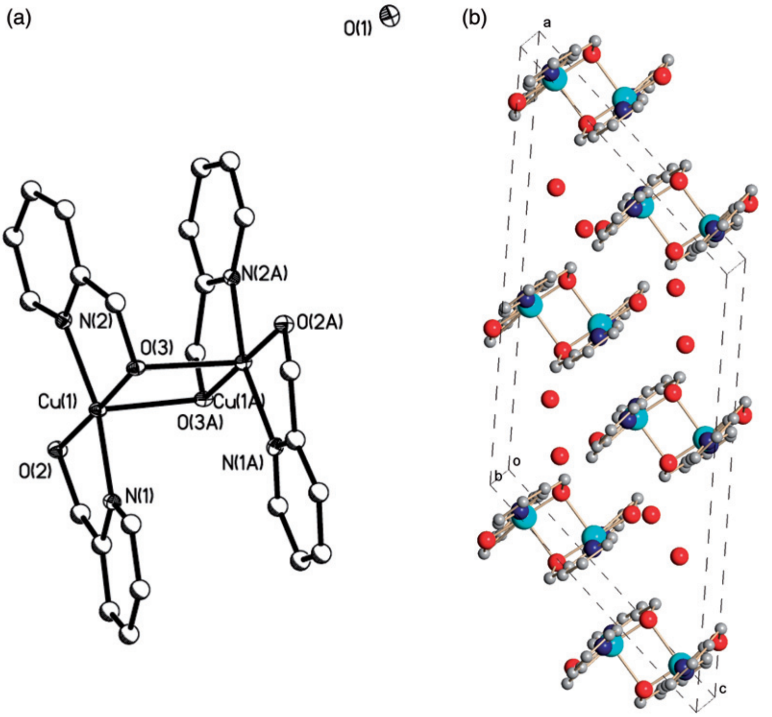


Figure 4. (a) Structure plot of **4**. Thermal ellipsoids of heavy atoms are drawn at the 30% level and carbon atoms are shown as ball and stick for clarity. (b) Packing diagram of **4** along the *b*-axis.

the packing diagram. The metrical data of both structures are, in general, agreement but the square-planar arrangement of copper of **3** [N–Cu–N (178.0 Å) and O–Cu–O (176.5 Å)] are more distorted (table 2) in comparison to 180.0° noted for Cu(O^{c}Py)$_2 \cdot 4H_2O$ [36].

Attempts to disrupt the structure of **1** through the introduction of a Lewis base (as noted for the structure of **2** by the bound H–OPy ligands) was undertaken through the simple dissolution of **1** in a series of coordinating solvents, with the first efforts focused on THF. Unexpectedly, the *hydrated* compound **4** (figure 4) was isolated, which was surprising due to the "anhydrous conditions" employed for all aspects of this reaction. Other "anhydrous" Lewis basic solvents (i.e., py, MeIm) were also investigated with similar results. The most likely source of the H_2O is adventitious water that must be present in the Sure/Seal^{TM} (99.99%) solvent used. Apparently, the hydrate is a very stable species that is readily formed by **1** using any water molecules available. Initially, the structure of **4** appears to be the simple hydrate derivative of **1**; however, closer inspection of the arrangement of the O^{c}Py and μ$_c$-OPy ligands around the distorted square-base pyramidal Cu centers ($\tau = 0.19$) indicates that a simple C_2 rotation is present, not the C_i observed for **1**. Therefore, a rearrangement of the "Cu(OPy)$_2$" moieties occurred by either a dissociation of the dimer or a break in the Cu–N interaction that reforms upon crystallization. The latter is most likely since **3** would be formed if the dimer dissociates in the presence of water. In comparison to **1**, the packing diagram of **4** (figure 4b) is clearly less dense based on the inclusion of the single water molecule. There is no apparent π–π interaction between the py rings

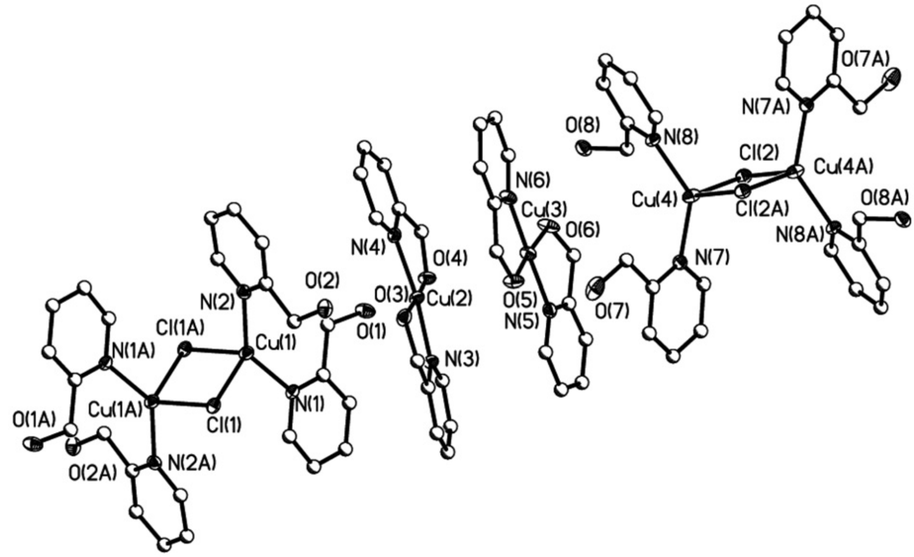


Figure 5. Structure plot of **5**. Thermal ellipsoids of heavy atoms are drawn at the 30% level and carbon atoms are shown as ball and stick for clarity.

of adjacent compounds; however, there is a weak interaction between the py ring of one molecule and the Cu metal center of the next compound ($\text{Cu–OPy}_{\text{centroid}} = 3.985\,\text{Å}$). While the distances of **4** are similar to those observed for **1**, the angles around the Cu metal center show significant variations (table 2). This is most likely a reflection of the different ligand arrangements noted previously. The elemental analysis of the bulk powder was consistent with the single hydrate.

Further attempts to use THF that had been stored over sieves and were dried at elevated temperature under vacuum (10^{-3} Torr) yielded the unusual mixed-valent-layered structure $[\text{Cu(OPy)}_2]_2[\text{CuCl((H–OPy)}_2]_2$ (**5**). The Cl^- is believed to be from the contaminated sieves. While several attempts were undertaken to generate **5** from a rational route, none were proven successful. However, we present the structural details of **5** (figure 5) due to its unusual characteristics. The salt of **5** consists of a layer of trigonal CuCl anions solvated by two H–OPy ligands bound through N of pyridine. This is proposed to be Cu(I) due to the length of the Cu–Cl bond (table 2) and charge balance due to the isolation of the two protons on the H–OPy ligands. The next two layers consist of two $[\text{Cu(OPy)}_2]$ moieties followed by CuCl(H–OPy)_2 again forming an a–b–b–a arrangement. Only two other Cu–OPy–Cl containing structures have been reported [21, 22]. The first is polymeric $[\text{(Cl)Cu}(\mu\text{-Cl})(\mu\text{-HOPy}) \cdot \text{CH}_3\text{OH}]_n$ [34] synthesized from the reaction of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ with HOPy in methanol. The Cu maintains its +2 oxidation state and hence the Cu(II)–N, 1.9957(17) Å and Cu–O, 1.9959(16) Å bond distances are in agreement with those of **5**; however, the Cu(II)–Cl distances (2.242 Å) are substantially shorter than those noted for **5**, presumably due to the Cu(I)–Cl distance. As per the literature, Cu(I)–Cl distances are consistent with this moiety of **5** [21, 22]. The other literature complex is the Cu(II) mononuclear salt [(Cl)Cu(HOPy)][Cl] [36]. The Cu–N (1.982 Å) of this compound and **5** are in agreement; however, the Cu–OH (2.140 Å) distance is slightly elongated due to the protonation of the H–OPy *versus* the deprotonated **5**. All other attempts using scrupulously dried solvents (i.e., THF, py, MeIm) led to insoluble materials that could not be crystallized.

4. Conclusion

Using organic solvents, OPy derivatized Cu(OR)$_x$ coordination compounds were isolated as either the homoleptic dinuclear species **1** with C_i symmetry or the *bis*-H–OPy solvated monomer **2**. Upon dissolution in water, both **1** and **2** were readily converted to the same O^{c}Py monomeric, monohydrate, which was found to be in agreement with the literature complex [36]. Crystallization of **1** from "dry" Lewis basic solvents (i.e., THF, py, MeIm) also led to a hydrated compound dinuclear **4**, which had C_2 symmetry. The scrupulously dry solvents did not lead to dissolution of either **1** or **2**. The unusual salt Cu(I)/Cu(II) Cl compound **5** was isolated from a THF solution stored over sieves. Combined, these structures demonstrate the strong hydrophilicity of the Cu–OPy system and the preference for monomers in the presence of solvent molecules. However, dinuclear, homoleptic species are available under the proper conditions. An exploration of these novel Cu–OPy precursors for nanomaterial applications is underway.

Supplementary material

Complete Crystallographic Information Files (CIF) for **1–5** have been deposited with the Cambridge Crystallographic Data Centre (www.ccdc.cam.ac.uk; deposit@ccdc.cam.ac.uk) and allocated the deposition numbers CCDC 739754–739758.

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