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Coordination modes of N-(2-hydroxyphenyl)methyl-bis-(2-pyridylmethyl)amine with copper (I) and (II) halides

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Abstract

The title ligand, *N*-(2-hydroxyphenyl)methyl-bis-(2-pyridylmethyl)amine, was prepared via a condensation–reduction synthetic route. The compounds, $CuCl(C_{19}H_{19}N_3O)$ and $[CuBr(C_{19}H_{19}N_3O)]^+Br^- \cdot 3H_2O$, were readily synthesized from the reaction of CuCl or CuBr₂ and the ligand in acetonitrile. The title copper(I) compound is an O–H··· Cl hydrogen-bonded linear chain of tetrahedrally coordinated copper centers, and the title copper(II) compound exists as two strongly tetragonally distorted dibromide bridged metal cations in a dimer with the phenol hydroxyl groups weakly bound in a *trans*-fashion to one of the bridging bromides. In the copper(I) complex the phenoxy group acts only as a hydrogen bond donor, whereas in the copper(II) complex it acts both as a ligand and a hydrogen bond donor.

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1. Introduction

Copper coordination complexes have been studied as small molecule analogs of metalloproteins that mediate dioxygen activation, electron transfer, and transport processes [1]. Recently, copper complexes of various amine-based ligands have gained considerable interest as catalysts for atom transfer reactions and controlled/"living" radical polymerizations [2-4]. Tri- and tetradentate amine ligands, and in particular tripodal tetradentate amine ligands, have shown a great deal of versatility and practicality for ATRP catalysis purposes. In complexes of copper(I) and copper(II) with tripodal tetradentate amines, variations in several structural parameters, such as chelate ring size and the nature of the donor group, were found to have dramatic effects upon the structure, redox potential and spectroscopic features of the corresponding complexes [5–9].

During the course of our studies on using monoanionic tetradentate ligands to prepare copper(I)-based atom transfer radical polymerization catalysts, we investigated the complexation of a bis(picolyl)aminebased ligand [10–12] to copper(I) and copper(II) halides. Iron (III) [13,14], copper (II) [15,16], and zinc (II) [17,18] complexes of the ligand, *N*-(2-hydroxyphenyl)methylbis-(2-pyridylmethyl)amine, have been studied previously as models for the metal centers of purple acid phosphatase, galactose oxidase, and alkaline phosphatase. The ligand itself has been used as a sensitizer for esterase determination [19]. Here we report a new synthesis of the ligand, and the synthesis and structures of its complexes with copper(I) and (II) halides.

2. Experimental

2.1. Materials

CuCl (Acros) was purified until colorless by grinding into a fine powder using a mortar and pestle, stirring in

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glacial acetic acid, consecutive washes of absolute ethanol and diethyl ether, and removal of volatile materials under vacuum. Acetonitrile was dried using appropriate procedures, and standard Schlenk techniques were used to prepared the copper(I) complex. Bis(2-pyridylmethyl)ammonium tetrafluoroborate was prepared via the addition of fluorboric acid to a solution of bis(2-pyridylmethyl)amine in ethanol followed by filtration of the white precipitate product. All other chemicals were purchased from Acros and used without further purification.

2.2. Characterizations

¹³C {¹H} and ¹H NMR spectra were recorded on a Varian Mercury 300 NMR spectrometer. Chemical shifts were referenced to the proton or carbon signal of the NMR solvent. FTIR spectra were obtained with a Mattson Galaxy Series FTIR 3000. Elemental analyses were performed by Midwest Microlabs.

2.3. *N*-(2-hydroxyphenyl)methyl-bis-(2-pyridylmethyl) amine

Salicaldehyde (1.00 ml, 9.38 mmol) was added to a solution of 2.44 g of bis(2-pyridylmethyl)ammonium tetrafluoroborate in 50 ml of benzene. A Dean-Stark trap and reflux condenser were fitted to the flask and the solution was heated and stirred at reflux until no further water was collected (\sim 0.15 ml). The white precipitate was isolated by filtration and volatile materials were

removed under vacuum. The solid was then stirred in 100 ml of CH₃OH at 0 °C, and 0.349 g (9.23 mmol) of NaBH₄ was added in small portions. Once all of the NaBH₄ was added, then the solution was heated at reflux for 15 min. The solution was cooled, partitioned in equal amounts of Et₂O and H₂O, and then the aqueous layer was extracted using 3×50 ml of Et₂O. The Et₂O layers were dried over Na2SO4 and then concentrated to yield a yellow oil that crystallized over several days. Yield: 1.12 g (51%); ¹H NMR (300 MHz, CD₃CN): δ (ppm) 8.54 (m, 2H), 7.71 (m, 2H), 7.34 (m, 2H), 7.2-7.1 (m, 4H), 6.78 (m, 2H), 3.84 (s, 4H), 3.78 (s, 2H), 2.21 (br, 1H); ¹³C {¹H} NMR (75 MHz, CD₃CN): δ (ppm) 158.5, 149.0, 136.9, 130.5, 129.1, 123.5, 123.3, 122.5, 118.9, 117.5, 116.3, 58.8, 56.6; IR (thin film, NaCl plate): *v* (cm⁻¹) 3421 (br), 1591 (s).

2.4. Chloro-{N-(2-hydroxyphenyl)methyl-bis-(2-pyridylmethyl)amino}-copper(I) (1)

The ligand (1.21 g, 3.96 mmol) was dissolved in 25 ml of dry acetonitrile, and then 0.392 g (3.96 mmol) of Cu(I)Cl was added. The solution was stirred and heated at reflux for 10 min. The solution was allowed to cool overnight, and yellow crystals formed. The supernatant was decanted and the crystals, suitable for X-ray analysis, were placed under vacuum to remove volatile materials. Yield: 1.44 g (90%); m.p. (uncorrected) = 157–159 °C; Elemental composition (C₁₉H₁₉ClCuN₃O): *Anal.* Calc. for C 56.43, H 4.79, N 10.40. Found: C 55.92, H 4.80, N 10.70%; IR (thin film, NaCl plates) *v* (cm⁻¹): 3170 (broad), 1599 (s).

Table 1

Crystal data and refinement details for complex-1 and complex-2 · 3H₂O

Formula	C ₁₉ H ₁₉ ClCuN ₃ O	$C_{38}H_{44}$ Br ₄ Cu ₂ N ₆ O ₅
Formula weight	404.36	1111.53
Crystal system	monoclinic	monoclinic
Space group	C2/c	$P2_1$
Color and habit	yellow prism	blue needle
a (Å)	15.2135(7)	10.4714(15)
b (Å)	9.2386(7)	16.251(2)
<i>c</i> (Å)	26.4877(16)	12.513(2)
β (°)	106.485(2)	102.058(7)
$V(Å^3)$	3569.9(4)	2082.4(6)
Temperature (K)	91(2)	91(2)
Wavelength (Å)	0.71073	0.71073
Ζ	8	2
Crystal dimensions (mm)	0.18 imes 0.14 imes 0.08	0.44 imes 0.16 imes 0.13
μ (Mo K α) (mm ⁻¹)	1.38	4.91
$2\theta_{\max}$ (°)	63	60
Reflections collected	24490	27201
Independent reflections	5713	11950
Reflections observed $[I > 2\sigma(I)]$	4260	11050
Parameters	228	522
R_1 (observed data)	0.0366	0.0281
wR_2 (all data)	0.0864	0.0670
Goodness-of-fit	1.01	1.04

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2.5. Dibromo-{N-(2-hydroxyphenyl)methyl-bis-(2-pyridylmethyl)amino}-copper(II) (2)

The ligand (1.44 g, 4.72 mmol) was dissolved in 20 ml of dry acetonitrile, and then 1.06 g (4.76 mmol) of anhydrous $Cu(II)Br_2$ was added. The solution was stirred and heated at reflux for 10 min. The solution was allowed to cool overnight and a green powder formed, which was recrystallized from tetrahydrofuran. Yield: 1.63 g (64%). Crystals suitable for X-ray analysis were grown from methanol by evaporation of the solvent.

2.6. X-ray structure determinations of 1 and $2 \cdot 3H_2O$

Diffraction data were collected with a Bruker SMART 1000 diffractometer, graphite-monochromated Mo K α radiation, and a nitrogen cold stream provided by a CRYO Industries apparatus. Corrections for absorption were applied using the program SADABS 2.03 [20]. The structures were solved by direct methods (SHELXS-97 [21]) and refined by full-matrix leastsquares on F^2 (SHELXL-97 [21]). All non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms on water molecules were located on a difference map and refined using distance restraints. Other hydrogen atoms were added by geometry and refined using a riding model. The maximum and minimum peaks in the final difference Fourier map corresponded to 0.53 and -0.33 eÅ⁻³ for 1 and 0.97 and -0.76 eÅ⁻³ for 2 · 3H₂O. Crystal data and refinement details for 1 and $2 \cdot 3H_2O$ are shown in Table 1. Additional experimental information, including atomic positional parameters, is supplied in CIF format as described in the supplementary material.

3. Results and discussion

The ligand used in this study, *N*-(2-hydroxyphenyl)methyl-bis-(2-pyridylmethyl)amine, was prepared by the condensation of bis(2-pyridylmethyl)ammonium tetrafluoroborate with salicaldehyde to form the iminium salt (Scheme 1). The iminium salt precipitated from the reaction solution as it formed. The material was isolated by filtration and then reduced to the amine product by treatment with NaBH₄ in methanol. This condensation– reduction approach represents an alternative to the nucleophilic substitution routes described previously [13,15,16]. This reaction yielded satisfactory amounts of the ligand that contained no other materials as judged by its NMR spectra.

The addition of CuCl to an acetonitrile solution of the ligand followed by heating the solution at reflux formed complex-1 in good yield (Eq. (1)). An IR spectrum showed bands



corresponding to the presence of the phenolic O–H group (3170 cm^{-1}) and the aromatic rings (1599 cm^{-1}). The structure of complex-**1** is monomeric, with the coordination geometry about the metal center distorted from tetrahedral geometry due to the constraint of tethering the nitrogen donor groups (Fig. 1). Table 2 shows selected bond angle and bond length data for complex-**1**. The two N–Cu–N angles between the directly tethered nitrogen donors are less than 109.5° (81.0 and 78.1) while the other N–Cu–N angle and the three N–Cu–Cl angles are all greater than 109.5° (127.5° and



Fig. 1. Molecular structure of complex-1 showing the intermolecular $O-H\cdots$ Cl hydrogen bonding and thermal ellipsoids at the 50% probability level.



Scheme 1. Synthetic route for obtaining the ligand used in this study, N-(2-hydroxyphenyl)methyl-bis-(2-pyridylmethyl)amine.

Table 2 Selected bond lengths (Å) and angles (°) for complex-1

Sciected bolid lengths (A) and angles () for complex-1		
Cu(1)–N(1)	2.0106(16)	
Cu(1)–N(2)	2.3935(15)	
Cu(1)–N(3)	2.0053(16)	
Cu(1)–Cl(1)	2.2739(5)	
Cl(1)-Cu(1)-N(1)	116.65(5)	
Cl(1)-Cu(1)-N(2)	132.82(4)	
Cl(1)–Cu(1)–N(3)	112.91(5)	
N(1)–Cu(1)–N(2)	81.00(6)	
N(1)-Cu(1)-N(3)	127.48(6)	
N(2)–Cu(1)–N(3)	78.05(6)	

116.7, 132.8, and 112.9, respectively). The three Cu-N bond lengths (2.01, 2.01, and 2.39) and Cu-Cl bond length (2.27) all fall within the expected range for similar bis-(2-pyridylmethyl)amine complexes. Because the coordination sphere of the copper(I) center is saturated by the softer amine and chloride ligands, the pendant phenol group can only act as a hydrogen bond donor-acceptor. The phenolic hydrogen is hydrogen bonded to a chlorine atom on a neighboring complex, d(H-O) = 0.84 Å, $d(H \cdots Cl) = 2.25$ Å, $d(O \cdots Cl) = 3.08$ Å, and $\angle(OHCl) = 173.3^\circ$, to form chains of complexes throughout the crystal.

The addition of anhydrous $CuBr_2$ to an acetonitrile solution of the ligand followed by heating the solution at reflux formed complex-2 (Eq. (2)). The structure of complex-2 is



Table 3 Selected bond lengths (Å and angles (°) for complex **2**, 3H, O

dimeric with two copper complexes in the asymmetric unit (Fig. 2). Unlike the copper(I) center in complex-1, the copper(II) center can form tetragonally distorted octahedral complexes, so the phenol can potentially act both as a ligand and a hydrogen bond donor-acceptor in complex-2. The presence of both a bromide ligand and a bromide counterion to balance the 2+ charge of the copper center indicates that the coordinated phenol oxygen is protonated. Table 3 shows selected bond angle and bond length data for complex- $2 \cdot 3H_2O$. The two copper centers are 4.00 Å apart in the dimer. The $Cu \cdots Br$ distances are 3.21 and 3.32 Å and are very long, indicating only a very weak interaction between the two complexes forming the dimer. The trans Cu-O distances are quite long at 2.428(2) and 2.427(2) Å, consistent with 4+2 tetragonal distortion [22]. The copper-nitrogen distances for the amines trans to the bromide are 2.022(2) and 2.045(2) Å; and the other



Fig. 2. Molecular structure of complex-2. The bromide counterions and hydrogen-bonded water molecules have been omitted. Thermal ellipsoids are drawn at the 50% probability level.

Selected bond lengths (A and angl	les ($^{-1}$) for complex-2 \cdot 3H ₂ O		
Cu(1)–O(1)	2.428(2)	Cu(2)–O(2)	2.427(2)
Cu(1)–N(1)	2.003(3)	Cu(2)–N(4)	1.997(2)
Cu(1)–N(2)	2.022(2)	Cu(2)–N(5)	2.045(2)
Cu(1)–N(3)	2.007(2)	Cu(2)–N(6)	1.990(2)
Cu(1)–Br(1)	2.3981(5)	Cu(2)–Br(2)	2.4125(5)
Cu(1)–Br(2)	3.3190(6)	Cu(2)–Br(1)	3.2137(6)
Br(1)-Cu(1)-O(1)	93.65(5)	Br(2)–Cu(2)–O(2)	94.18(5)
Br(1)-Cu(1)-N(1)	95.74(7)	Br(2)–Cu(2)–N(4)	96.62(7)
Br(1)-Cu(1)-N(2)	176.58(7)	Br(2)–Cu(2)–N(5)	176.82(7)
Br(1)-Cu(1)-N(3)	97.94(7)	Br(2)–Cu(2)–N(6)	98.05(7)
O(1)–Cu(1)–N(1)	97.86(8)	O(2)–Cu(2)–N(4)	98.40(9)
O(1)–Cu(1)–N(2)	89.59(8)	O(2)–Cu(2)–N(5)	88.77(8)
O(1)–Cu(1)–N(3)	88.73(8)	O(2)–Cu(2)–N(6)	87.37(9)
N(1)-Cu(1)-N(2)	82.71(10)	N(4)-Cu(2)–N(5)	81.74(10)
N(1)-Cu(1)-N(3)	164.40(10)	N(4)-Cu(2)–N(6)	163.79(10)
N(2)-Cu(1)-N(3)	83.22(10)	N(5)-Cu(2)–N(6)	83.26(9)
$Cu(1) \cdots Cu(2)$	4.0029(8)		

copper-nitrogen distances are 2.003(3), 2.007(2), 1.997(2), and 1.990(2) A. The Cu-Br distances are 2.4125(5) and 2.3981(5) A. The N-Cu-N and N-Cu-Br bond angles within the square plane total 360° within experimental error (359.6° and 359.8°). The N-Cu-N bond angles are less than 90° due to the geometrical constraints of the bis-(2-pyridylmethyl)amine fragment of the ligand (ranging from 81.8° to 83.3°), while the N-Cu-Br bond angles are greater than 90° for the same reason (ranging from 95.8° to 98.1°). The chloride counterpart of complex-2 has been reported [16], and the structure is largely similar to complex-2. As for complex-2, there are two crystallographically independent molecules within the unit cell. The copper-oxygen distances are 2.570(4) and 2.457(5) Å which are trans to the long $Cu \cdots Cl$ bridge bonds of 3.104 and 3.039 Å. The copper-nitrogen distances for the amines trans to the chloride are 2.041(4) and 2.059(4) Å; and the other copper-nitrogen distances are 1.987(5), 1.978(5), 1.980(5), and 1.978(5) A.

During recrystallization from methanol, water was incorporated into the crystal, and formed a hydrogenbonded network with the complex and the bromide counterions. A stereoview of the unit cell is shown in Fig. 3. The phenolic hydrogen of one-half of the dimer is hydrogen bonded to a bromide anion, d(H-O) =0.94 Å, $d(H \cdots Br) = 2.25$ Å, $d(O \cdots Br) = 3.16$ Å, and \angle (OHBr) = 159(6)°, while the phenolic hydrogen of the other half is hydrogen bonded to a molecule of water, d(H-O) = 0.94Å, $d(H \cdots O') = 1.71$ Å, $d(O \cdots O') = 2.63$ Å, and \angle (OHO') = 167(3)°. Of the three waters of crystallization there are five $H \cdots Br$ contacts ranging from 2.31 to 2.50 Å and one long contact (3.07 Å) to a bromide coordinating to a copper center. There is one $H \cdots O$ contact (1.75 Å) between two water molecules. The network criss-crosses the crystal lattice, with one portion of the network being the water-Br-Cu-Br series of hydrogen bond connections and the "perpendicular" portion of the network being the water-Br-phenol-tophenol-water-Br series of connections.



Fig. 3. A stereoview of the unit cell of complex-2 showing the water/ bromide anion hydrogen bonding network.

4. Supplementary material

Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-218053 (complex-1) and CCDC-218054 (complex- $2 \cdot 3H_2O$). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: +44-1223-336-033; email: deposit@ccdc.cam.ac.uk or www: http://www. ccdc.cam.ac.uk).

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