

Synthesis, Structures, and DFT Study of CuBr Based Coordination Polymers via in Situ Reduction of Copper(II)

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(5) Supporting Information

ABSTRACT: This paper describes the one-pot synthesis of two CuBr based coordination polymers, {[Cu(μ_2 -L¹)Br]·1.87H₂O}_n (1) and {[Cu(μ_2 -L²)Br]·C₄H₁₀O}_n (2), where L¹ = 2,3-dihydro-5,6-bis(4-methoxyphenyl)-pyrazine and L²= 5,6-diphenyl-2,3-dihydropyrazine, upon reduction of copper(II) at ambient conditions. The structures have been confirmed by single crystal X-ray diffraction analysis. Both complexes are found to be highly inert toward oxidation. Finally, a density functional theory (DFT) study of the energetic features of several noncovalent interactions observed in the solid state has been analyzed and characterized using Bader's theory of "atoms in molecules" and the cuprophilic interactions in complex 2 using natural bond orbital methodology.



INTRODUCTION

The chemistry of the coordination polymers has advanced extensively recently, affording fascinating structures with potentials in applications.^{1–4} They are constructed from a variety of molecular building blocks with different interactions among them. High-dimensional coordination polymers often exhibit important functionalities which are absent in low-dimensional structures.⁵ Coordination polymers contain two essential components, viz., nodes and linkers.⁶ Linkers give a wide variety of linking sites with adjusted binding strength and directionality. On the other hand, transition-metal ions are frequently employed as nodes. Instead of a bare metal ion, suitable metal–ligand complexes are also used as nodes.^{7,8} In the present case, we have used CuBr clusters as the nodes and pyrazine derivatives as the linkers to form the coordination polymers.

Multinuclear d¹⁰ cuprous halide clusters are important because of their interesting photochemical and photophysical properties, with potential applications as light-emitting diodes, luminescent probes, and photovoltaics.^{9–14} They have also received considerable attention in coordination chemistry because of the exciting structural features of cuprous halide clusters acting as nodes in the construction of multidimensional coordination networks.^{15–18} Reactions involving various structural motifs of copper(I) halides and diverse multidentate N-donor ligands lead to the formation of various coordination networks with intriguing structures and functional properties.^{19–24}

Cu(I) coordination polymers are usually prepared by reaction of Cu(I) with appropriate ligands or by the reaction of copper metal with an appropriate reagent in appropriate solvents, usually in a hydrothermal condition.²⁵⁻²⁸ In our previous paper, we reported for the first time the formation of a CuSCN based coordination polymer starting from a copper(II) salt in a nonhydrothermal reaction condition at room temperature.²⁹ In the present work, we have extended the concept to form CuBr based coordination polymers starting from copper(II). Herein, we report the synthesis and characterization of these two copper(I) complexes, $\{[Cu(\mu_2-L^1)Br]\cdot 1.87H_2O\}_n$ (1) and $\{[Cu(\mu_2 L^2)Br] \cdot C_4 H_{10}O\}_n$ (2), where $L^1 = 2,3$ -dihydro-5,6bis(4-methoxyphenyl)pyrazine and L^2 = 5,6-diphenyl-2,3-dihydropyrazine. Complex 1 contains only terminal bromides and forms a one-dimensional (1D) chain, whereas complex 2 forms a three-dimensional (3D) architecture with Cu₆Br₆ cores. Both complexes show fluorescence. The presence of methoxy groups in L¹ that are crucial in the crystal growth in one direction by promoting the intermolecular interaction of the infinite 1D chains of complex 1 by establishing $CH_3 \cdots \pi$ interactions. In addition, the presence of lattice water molecules in 1 is also crucial for the final 3D architecture of this complex by connecting the infinite 1D chains by means of O-H…Br interactions. These interactions have been analyzed by means of density functional theoretical calculations.

EXPERIMENTAL SECTION

Materials. All chemicals used were purchased from Sigma-Aldrich and were of reagent grade. They were used without further purification.

Received: September 4, 2014 Revised: November 19, 2014 **Physical Measurements.** Elemental analyses (carbon, hydrogen, nitrogen, and metal) were carried out using a PerkinElmer 2400 II elemental analyzer. IR spectra in KBr (4000–400 cm⁻¹) were recorded using a PerkinElmer Spectrum Two Fourier transform infrared (FTIR) spectrophotometer. The UV–visible spectrum for complex 1 was recorded on a PerkinElmer lambda 35 spectrophotometer at 298 K in acetonitrile. The UV–visible diffuse reflectance spectrum for complex 2 was recorded on a Shimadzu UV 2401PC with an integrating sphere attachment. BaSO₄ was used as the background standard. The steady state emission spectra were recorded on a PerkinElmer LS 55 luminescence spectrometer at room temperature. The topological analysis of the complexes was produced using the TOPOS program.^{30–32}

X-ray Crystallography. Single crystals of the complexes, having suitable dimensions, were used for data collection using a Bruker D8 QUEST area detector diffractometer for 1 and STOE IPDS2T diffractometer for 2, equipped with graphite-monochromated Mo K α radiation $(\lambda = 0.71073 \text{ Å})$ at 100 K. The molecular structures were solved using the SHELX-2014 package.³³ Non-hydrogen atoms were refined with anisotropic thermal parameters. Hydrogen atoms were placed in their geometrically idealized positions and constrained to ride on their parent atoms. For 1, multiscan empirical absorption corrections were applied to the data using the program SADABS.³⁴ Two of the three independent solvent water molecules showed occupation factors less than 1 (0.35 and 0.53, respectively). For 2, integration absorption corrections were applied to the data using indexed faces. Programs used were STOE X-AREA and STOE X-RED/X-SHAPE.35 For 2, the occupation factors of Cu(2) and Br(2) were less than 1 and refined to 0.42. The figures were prepared using ORTEP³⁶ and DIAMOND.³ summary of the crystallographic data is given in Table 1. Selected bond

Table 1. Crystal Data and Refinement Details of Complexes 1 and 2

| complex | 1 | 2 |
|------------------------------------|--------------------------------------|----------------------------|
| formula | $C_{36}H_{39.75}Br_2Cu_2N_4O_{5.87}$ | C52H52Br5.42Cu5.42N6O |
| formula wt | 909.33 | 1554.49 |
| cryst size (mm) | $0.11 \times 0.22 \times 0.44$ | $0.17\times0.16\times0.08$ |
| temp (K) | 100 | 100 |
| cryst syst | monoclinic | monoclinic |
| space group | $P2_{1}/c$ | $P2_1$ |
| a (Å) | 10.0229(6) | 12.9750(4) |
| b (Å) | 24.6728(14) | 16.1618(7) |
| c (Å) | 15.0813(8) | 13.1070(5) |
| α (deg) | 90 | 90 |
| β (deg) | 98.3976(19) | 94.886(3) |
| γ (deg) | 90 | 90 |
| Ζ | 4 | 2 |
| $d_{\rm calc} ({\rm g \ cm^{-3}})$ | 1.637 | 1.885 |
| $\mu \text{ (mm}^{-1})$ | 3.368 | 6.066 |
| F(000) | 1835 | 1522 |
| total reflns | 113 986 | 14 932 |
| unique reflns | 8500 | 9766 |
| obsd data $[I > 2\sigma(I)]$ | 7317 | 8483 |
| no. of params | 480 | 644 |
| R(int) | 0.049 | 0.0373 |
| R1, wR2 (all data) | 0.0338, 0.0554 | 0.0416, 0.0689 |
| R1, wR2 $[I > 2\sigma(I)]$ | 0.0242, 0.0520 | 0.0331, 0.0664 |
| | | |

lengths and bond angles are given in Table 2. Cambridge Crystallographic Data Centre (CCDC) reference numbers are 1013217 (for complex 1) and 1021117 (for complex 2).

Hirshfeld Surface Analysis. Hirshfeld surfaces^{38–40} and the associated two-dimensional (2D) fingerprint^{41–43} plots were calculated using Crystal Explorer,⁴⁴ with bond lengths to hydrogen atoms set to standard values.⁴⁵ For each point on the Hirshfeld isosurface, two distances, d_e (the distance from the point to the nearest nucleus external

to the surface) and d_i (the distance to the nearest nucleus internal to the surface), are defined. The normalized contact distance (d_{norm}) based on d_e and d_i is given by

$$d_{\text{norm}} = \frac{d_{\text{i}} - r_{\text{i}}^{\text{vdW}}}{r_{\text{i}}^{\text{vdW}}} + \frac{d_{\text{e}} - r_{\text{e}}^{\text{vdW}}}{r_{\text{e}}^{\text{vdW}}}$$

where r_i^{vdW} and r_e^{vdW} are the van der Waals radii of the atoms. The value of d_{norm} is negative or positive depending on intermolecular contacts being shorter or longer than the van der Waals separations. The parameter d_{norm} displays a surface with a red—white—blue color scheme, where bright red spots highlight shorter contacts, white areas represent contacts around the van der Waals separation, and blue regions are devoid of close contacts. For a given crystal structure and set of spherical atomic electron densities, the Hirshfeld surface is unique⁴⁶ and thus it suggests the possibility of gaining additional insight into the intermolecular interaction of molecular crystals.

Theoretical Methods. The geometries of the complexes included in this study were computed at the BP86-D3/def2-TZVP level of theory using the crystallographic coordinates within the TURBOMOLE program.⁴⁷ This level of theory that includes the latest available dispersion correction (D3) is adequate for studying noncovalent interactions dominated by dispersion effects such as π -stacking. The basis set superposition error for the calculation of interaction energies has been corrected using the counterpoise method.⁴⁸ The "atoms-in-molecules" (AIM)⁴⁹ analysis of the electron density has been performed at the same level of theory using the AIMAII program.⁵⁰

Syntheses. Synthesis of Complex { $[Cu(\mu_2 L^1)Br] \cdot 1.87H_2O]_n$ (1). The cyclic Schiff base ligand, L¹ (2,3-dihydro-5,6-bis(4-methoxyphenyl)pyrazine), was prepared by refluxing 1,2-diamino-ethane (2 mmol, 0.14 mL) with 4,4'-dimethoxybenzoin (2 mmol, 0.540 g) in methanol for ca. 1 h. The ligand was not isolated and used directly for the synthesis of the complex. A methanol solution of copper(II) perchlorate hexahydrate (2 mmol, 0.740 g) was added to the methanol solution of the ligand (1 mmol) and stirred for 30 min to develop a deep red precipitate. It was collected by filtration and dissolved in acetonitrile. A methanol/water (2:1) solution (5 mL) containing potassium bromide (2 mmol, 0.238 g) was added to it. The mixture was stirred for ca. 5 h. Diffraction quality single crystals were obtained by slow diffusion of diethyl ether into the mother liquor after a few days.

Yield: 0.45 g (49%). Anal. calcd for $C_{36}H_{39.75}Br_2Cu_2N_4O_{5.87}$ (FW 909.33): C, 47.55; H, 4.41; N, 6.16; found: C, 47.5; H, 4.5; N, 6.3. IR (KBr, cm⁻¹): 1605 ($v_{C=N}$), UV–vis, λ_{max} (nm) [ε_{max} (L mol⁻¹ cm⁻¹)] (acetonitrile): 290 (14 591), 370 (770). Magnetic moment: diamagnetic.

Synthesis of Complex {[$Cu(\mu_2-L^2)Br$]· $C_4H_{10}O_{1n}$ (2). The cyclic Schiff base ligand, L² (5,6-diphenyl-2,3-dihydropyrazine), was prepared in a similar way using benzoin (2 mmol, 0.424 g) instead of 4,4'dimethoxybenzoin. The ligand was not isolated and used directly for the synthesis of the complex. A methanol solution of copper(II) perchlorate hexahydrate (2 mmol, 0.740 g) was added to the methanol solution of the ligand (1 mmol) and stirred for 15 min to develop a deep red precipitate. It was collected by filtration and dissolved in acetonitrile. A methanol/water (2:1) solution (5 mL) containing potassium bromide (2 mmol, 0.238 g) was added to it. The mixture was stirred for ca. 5 h. Diffraction quality single crystals were obtained by slow diffusion of diethyl ether into the mother liquor after a few days.

Yield: 0.60 g (39%). Anal. calcd for $C_{52}H_{52}Br_{5.4}Cu_{5.42}N_6O$ (FW 1554.49): C, 40.18; H, 3.37; N, 5.41; found: C, 40.1; H, 3.2; N, 5.5%. IR (KBr, cm⁻¹): 1605 ($v_{C=N}$). Magnetic moment: diamagnetic.

RESULTS AND DISCUSSION

Synthesis. Copper(II) is reduced to copper(I) by the benzoin (or 4,4'-dimethoxybenzoin), which is thereby oxidized to benzil (or 4,4'-dimethoxybenzil). The 1:1 condensation of benzil (or 4,4'-dimethoxybenzil) with 1,2-diaminoethane produces the six-membered cyclic Schiff bases 2,3-dihydro-5,6-bis(4-methoxybenyl)pyrazine (L^1) and 5,6-diphenyl-2,3-dihy-

| | 1 | 2 | | 1 | 2 |
|---------------------------|--------------------------------|---------------------|--|--------------------|--------------|
| Br(1)-Cu(1) | 2.3436(5) | 2.4344(12) | Br(6)–Cu(5) | _ | 2.3810(12) |
| Br(1)-Cu(2) | _ | 2.424(2) | Br(6)–Cu(6) | _ | 2.4486(11) |
| Br(1)-Cu(5) | _ | 2.3830(12) | Cu(1)-N(1) | 1.9750(15) | 1.957(6) |
| Br(2)-Cu(2) | 2.3565(5) | 2.314(3) | Cu(1) - N(19) | _ | 1.946(6) |
| Br(3)-Cu(3) | _ | 2.3620(13) | Cu(1)-N(23) | 1.9635(15) | _ |
| Br(3)-Cu(2) | _ | 2.414(3) | Cu(2) - N(4) | 2.0088(15) | _ |
| Br(4)-Cu(3) | _ | 2.3656(13) | $Cu(2) - N(26)^{a}$ | 1.9628(15) | _ |
| Br(4)-Cu(4) | _ | 2.5284(12) | Cu(4)–N(37) | - | 1.974(5) |
| Br(5)-Cu(3) | _ | 2.3802(12) | $Cu(4) - N(22)^{b}$ | - | 1.975(6) |
| Br(5)-Cu(5) | _ | 2.3499(14) | $Cu(6)-N(4)^c$ | - | 1.957(6) |
| Br(1)-Cu(1)-N(1) | 120.94(5) | 108.34(18) | $Cu(6)-N(40)^d$ | _ | 1.993(6) |
| Br(1)-Cu(1)-N(23) | 130.01(5) | _ | Br(3)-Cu(3)-Br(5) | _ | 117.00(5) |
| N(1)-Cu(1)-N(23) | 109.05(6) | _ | Br(4)-Cu(3)-Br(5) | _ | 123.45(5) |
| N(1)-Cu(1)-N(19) | _ | 131.6(2) | Br(4)-Cu(4)-N(37) | _ | 106.63(18) |
| Br(1)-Cu(1)-N(19) | _ | 119.42(17) | $Br(4)-Cu(4)-N(22)^{b}$ | _ | 109.28(16) |
| Br(1)-Cu(2)-Br(2) | _ | 115.52(11) | $N(37)^{d}-Cu(4)-N(22)^{b}$ | _ | 137.4(2) |
| Br(1)-Cu(2)-Br(3) | _ | 120.18(9) | Br(5)-Cu(5)-Br(6) | _ | 119.57(5) |
| Br(2)-Cu(2)-Br(3) | _ | 124.30(10) | Br(6)-Cu(5)-Br(1) | _ | 115.30(5) |
| Br(2)-Cu(2)-N(4) | 111.52(4) | _ | Br(5)-Cu(5)-Br(1) | _ | 125.11(5) |
| $Br(2)-Cu(2)-N(26)^{a}$ | 139.89(5) | _ | $Br(6)-Cu(6)-N(4)^{c}$ | _ | 123.03(17) |
| $N(4)-Cu(2)-N(26)^{a}$ | 108.49(6) | _ | $Br(6)-Cu(6)-N(40)^{d}$ | _ | 106.84(17) |
| Br(3)-Cu(3)-Br(4) | _ | 118.71(5) | $N(4)^{c}-Cu(6)-N(40)^{d}$ | _ | 127.3(2) |
| Summatry transformation - | 1 M AL ~ ^b Summat | my transformation - | $w + 1 w = 1/2$ $\alpha + 2$ ^C Symmetry | r transformation - | $1/2 \sim 1$ |

^{*a*}Symmetry transformation = -1 + x, *y*, *z*. ^{*b*}Symmetry transformation = -x + 1, y - 1/2, -z + 2. ^{*c*}Symmetry transformation = -x + 1, y - 1/2, -z + 1. ^{*d*}Symmetry transformation = x + 1, *y*, *z*.

Scheme 1. Syntheses of Complexes 1 and 2



dropyrazine (L^2) , following the literature method.²⁹ The extra stability of the six-membered ring may be the driving force for the

formation of the ligands. Addition of a methanol:water solution of KBr in the methanol solution of copper(I) and ligands

Table 3. All Available References of One-Dimensional Copper(I) Complexes with Pyrazines (pyz) and Substituted Pyrazines

| complex | ref |
|---|-----------|
| ${[Cu(\mu_2-L^1)Br] \cdot 1.87H_2O]_n(1)}$ | this work |
| $[Cu(\mu_2-L^1)I]_n$, $L^1 = 5,6$ -diphenyl-2,3-dihydropyrazine | 51 |
| $\{[Cu(\mu-pyz)(pyz)(PPh3)][BF_4]\cdot CH_2Cl_2\}_{\infty}$ | 56 |
| ${[Cu(\mu-pyz)(pyz)(PPh_3)][BF_4] \cdot THF}_{\infty}$ | 56 |
| $\{[Cu(\mu-pyz)(pyz)(PPh_3)][ClO_4]\cdot CH_2Cl_2\}_{\infty}$ | 56 |
| $\{[Cu(\mu-pyz)(pyz)(PPh_3)][PF_6]\cdot THF\}_{\infty}$ | 56 |
| $\{[Cu(\mu-pyz)(PPh_3)_2][BF_4]\cdot CHCl_3\}_{\infty}$ | 56 |
| $\{[Cu(\mu-pyz)_{1.5}(PPh_3)][ClO_4]\cdot THF\}_{\infty}$ | 56 |
| $\{[Cu(\mu-pyz)(pyz)(PPh_3)][PF_6]\cdot CHCl_3\}_{\infty}$ | 56 |
| $\{[Cu(\mu-pyz)(PPh_3)(OClO_3)]\cdot CHCl_3\}_{\infty}$ | 56 |
| $[(CuI)_2(2,3-dimethylpyrazine)_3]$ | 57 |
| catena[tri(μ_2 -chloro)bis(μ_2 -2,3-dimethylpyrazine- <i>N</i> , <i>N'</i>)tricopper(I)] | 54 |



Figure 1. Perspective view of one-dimensional chain of complex 1 with selective atom numbering scheme. Water molecules are not shown for clarity.

produces complexes 1 and 2 (see Scheme 1). The charge of copper(I) is balanced by bromide. The ligand coordinates copper(I) in a bidentate fashion in complex 1 and in a monodentate fashion in complex 2. The great affinity of Cu(I) to electron-deficient azines, such as pyrazine/dihydropyrazine, due to the pronounced back-bonding effects, may also contribute to stabilizing Cu(I) in the (dihydro)pyrazine environment.

It is interesting to note here that we have previously used these two ligands to prepare copper(I) complexes in the presence of iodide.⁵¹ It was observed that L¹ formed a dinuclear copper(I) complex with I⁻. Similar dinuclear copper(I) iodide complexes with pyrazine based ligands structures are huge in the literature. $^{51-55}$ On the other hand, L² formed a one-dimensional copper(I) complex with iodide, where halides behaved as terminal ligands and L² behaved as a bridging bidentate ligand to connect copper(I) centers. The structure of this complex is very similar to that of complex 1. Similar one-dimensional copper(I) complexes with pyrazine based ligands are also reported by several groups.^{56,57} Table 3 gathers all available references of such one-dimensional copper(I) complexes with substituted pyrazines. It is of immense importance that similar copper(I) complexes with several pseudohalides are also reported in the literature.^{29,51}

By contrast, the formation of complex **2** is unique in the sense that no such complexes with pyrazine based ligands are reported

in the literature, although complexes having Cu_3Br_3 cores with other coligands could be found in the literature (Cambridge Structural Database (CSD) Search, version 5.35 updates (November 2013)).^{58,59}

Description of the Structures. $\{[Cu(\mu_2-L^1)Br] \cdot 1.87H_2O\}_n$ (1). Complex 1 crystallizes in the monoclinic space group $P2_1/c$. Two crystallographically independent trigonal planar copper(I) sites, Cu(1) and Cu(2), are present in the asymmetric unit. A perspective view of the one-dimensional chain of complex 1 is shown in Figure 1. Each copper(I) center is bonded to two donor nitrogen atoms from two different Schiff base molecules $\{N(1)\}$ and N(23) for Cu(1); N(4) and N(26)^a for Cu(2) $\{a = -1 + x, a = -1 + x\}$ y, z) and one bromide {Br(1) for Cu(1); Br(2) for Cu(2)}. The cyclic Schiff base L^1 is acting as a bridging ligand to form a zigzag chain (Figure 1). Sum of the different angles around each copper(I) center is very close to 360° { 360° for Cu(1) and 359.9° for Cu(2)}, indicating trigonal planar geometry. The deviation of Cu(1) from the mean plane passing through the coordinating atoms Br(1), N(1), and N(23) is 0.0045(5) Å. Similarly, the deviation of Cu(2) from the mean plane passing through the coordinating atoms N(4), Br(2), and $N(26)^a$ is -0.0996(5) Å. Selected bond lengths and bond angles are given in Table 2.

The hydrogen atoms H(1SA) and H(1SB) attached to O(1S) are involved in hydrogen bonding interactions with bromide ion



Figure 2. Two-dimensional architecture of complex 1 via hydrogen bonding interactions (hybrid water bromide tetramer is highlighted). Hydrogen bonds are shown by dotted lines.

Br(1) and the symmetry related bromide ion, Br(2)^b (b = x, 1/2 - y, 1/2 + z), respectively (Figure 2). Similarly, hydrogen atoms H(1S) and H(2S) attached to O(2S) are involved in hydrogen bonding interactions with bromide ion Br(1) and the symmetry related bromide ion, Br(2)^b (b = x, 1/2 - y, 1/2 + z), respectively, to form a bromide–water hybrid tetramer. This type of bromide–water hybrid tetramer can be found in the literature.⁶⁰ These bromide–water hybrid tetramers are connected via the copper(I) complex to form a 2D layer (Figure 2). Details of the hydrogen bonding interaction are given in Table 4. Topological analysis of the hydrogen-bonded structure of the complex reveals a 3-connected uninodal net with 6^3 -hcb topology (Figure 3).

Table 4. Hydrogen Bond Distances (Å) and Angles (deg) of Complex 2

| D–H…A | D–H | Н…А | D····A | ∠D−H…A |
|----------------------------|------|---------|----------|--------|
| $O(1S)-H(1SA)\cdots Br(1)$ | 0.87 | 2.6500 | 3.484(3) | 160.00 |
| $O(1S)-H(1SB)\cdots Br(2)$ | 0.87 | 2.8300 | 3.689(3) | 171.00 |
| $O(2S)-H(2S)\cdots Br(1)$ | 0.84 | 2.55(4) | 3.394(2) | 177(3) |
| $O(2S)-H(1S)\cdots Br(2)$ | 0.84 | 2.63(3) | 3.461(2) | 176(3) |
| | | | | |

Two methylene hydrogen atoms, H(3B), attached to C(3) and H(27B) attached to C(27), are involved in intermolecular C– H… π interactions with the symmetry related (-1 + *x*, *y*, *z*) phenyl ring C(37)–C(38)–C(39)–C(40)–C(41)–C(42) and (1 + *x*, *y*, *z*) phenyl ring C(7)–C(8)–C(9)–C(10)–C(11)–C(12). One methyl hydrogen atom, H(36C), attached to C(36) is also involved in C–H/ π interaction with the symmetry related (2 – *x*, -*y*, 1 – *z*) phenyl ring C(37)–C(38)–C(39)–C(40)–C(40)–C(41)–C(42) to form a two-dimensional sheet, as shown in Figure 4. Geometric features of the C–H/ π interactions are given in Table 5. Combinations of C–H/ π and hydrogen bonding interactions form a three-dimensional network structure.

 $\{[Cu(\mu_2-L^2)Br] \cdot C_4H_{10}O\}_n$ (2). Complex 2 crystallizes in the monoclinic space group $P2_1$. It features a three-dimensional CuBr based coordination polymer with Cu₆Br₆ core. Six crystallographically independent Cu(I) centers {Cu(1), Cu(2)with site occupation factor 0.42, Cu(3), Cu(4), Cu(5), and Cu(6) and six bromide centers {Br(1), Br(2) with site occupation factor 0.42, Br(3), Br(4), Br(5), and Br(6)} are present in the asymmetric unit (see Figure 5). Among them, three copper centers $\{Cu(2), Cu(3), and Cu(5)\}$ and three bromide centers $\{Br(1), Br(3), and Br(5)\}\$ form a six-membered ring, which assumes a screw-boat conformation with puckering parameters q(2) = 0.9901(12)Å and $\phi(2) = 198.86(8)^{\circ.61}$ Cu(3) and Cu(5) are bonded to Br(4) and Br(6), respectively, which are in turn bonded respectively with Cu(4) and Cu(6) to form a Cu_6Br_6 core. Three Cu(I) centers, Cu(1), Cu(4), and Cu(6), are bonded to two donor nitrogen atoms of the Schiff base ligand {N(1) and N(19) for Cu(1); N(22)^b and N(37) for Cu(4); $N(4)^{c}$ and $N(40)^{d}$ for Cu(6) { (c = 1 - x, 1/2 + y, 2 - z; d = 1 + x, 1/2 + y, 1/ y_{1} z). This pattern continues to form a 3D infinite structure (Figure 6). The Cu(I)–Cu(I) distances present in the complex are within the range 2.80–2.89 Å, which is very close to the sum of their van der Waals radii (2.80 Å). The attractive interactions between these types of closed-shell d¹⁰ metal ions are receiving great attention nowadays because of their interesting structural, optical, and electronic properties.⁶²⁻⁶⁴ This behavior has been frequently observed in gold, with the term "aurophilicity" being coined to describe Au(I)-Au(I) interactions. 65-67 A better insight into the nature of the 3D framework of the complex can be achieved by the application of a topological approach. The 3D skeleton can be symbolized as a 3,3,3,3,4,4-connected six-nodal net with a point symbol $(10.12^2)(10^3)(3.10^3.11^2)(3.12^2)(3^2.4)$ 10.11.12 (3².4) (Figure 6). There are no hydrogen bonding



Figure 3. The 6³-hcb topology of complex 1 via hydrogen bonding interactions.



Figure 4. Two-dimensional architecture of complex 1 via $C-H\cdots\pi$ interactions.

interactions present in the complex. The hydrogen atom H(16) attached to C(16) is involved in C–H/ π interaction with the symmetry related (-1 + *x*, *y*, *z*) phenyl ring C(25)–C(26)–C(27)–C(28)–C(29)–C(30), as shown in Figure S1 (Supporting Information). Geometric features of the C–H/ π interactions are given in Table 4.

IR Spectra, Electronic Spectra, and Fluorescence Spectra. In the IR spectra of both complexes, distinct bands due to the azomethine (C=N) groups were observed around $1600 \text{ cm}^{-1.68}$ Complex 1 shows a broad band at 3478 cm⁻¹ due to O-H stretching vibration. The UV-vis spectrum of complex 1 was recorded in acetonitrile. It shows absorption bands in the UV region due to charge transfer transitions (Figure S2, Supporting

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Table 5. Geometric Features of the C–H/ π Interactions of Complexes 1 and 2^{*a*}

| complex | C-H…Cg(ring) | H…Cg (Å) | C–H…Cg (deg) | C…Cg (Å) | sym transformation |
|---------|-------------------------------|----------|--------------|------------|--------------------|
| 1 | $C(3)-H(3B)\cdots Cg(6)$ | 2.63 | 145 | 3.484(2) | -1 + x, y, z |
| | $C(27) - H(27B) \cdots Cg(3)$ | 2.70 | 144 | 3.5475(19) | 1 + x, y, z |
| | C(36) - H(36C) - Cg(6) | 2.80 | 148 | 3.671(2) | 2 - x, -y, 1 - z |
| 2 | C(16) - H(16) - Cg(8) | 2.59 | 162 | 3.504(8) | -1 + x, y, z |

^{*a*}For complex 1, Cg(3) = center of gravity of six-membered ring C(7)–C(8)–C(9)–C(10)–C(11)–C(12) and Cg(6) = center of gravity of six-membered ring C(37)–C(38)–C(39)–C(40)–C(41)–C(42). For complex 2, Cg(8) = center of gravity of six-membered ring C(25)–C(26)–C(27)–C(28)–C(29)–C(30).



Figure 5. Perspective view of Cu_6Br_6 core of complex 2.



Figure 6. The 3,3,3,3,4,4-connected six-nodal net of complex 2.

Information). The UV-vis spectrum of complex **2** was recorded in the solid state, as it is insoluble in acetonitrile and in other solvents as well. The solid state diffuse reflectance UV-vis spectrum of complex **2** shows a broad absorption band between 300 and 800 nm, which may be assigned as copper(I) to ligand charge transfer transitions (Figure S3, Supporting Information). Complex **1** shows a fluorescence emission band at 396 nm upon excitation at 290 nm in acetonitrile solution (Figure S2,

a

de d e 2.4 2.4 2.2 2.2 2.0 2.0 1.8 1.8 1.6 1.6 1.4 1.4 1.2 1.2 1.0 1.0 0.8 0.8 0.6 0.6 di di 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4 0.6 0.8 1.0 1.2 1.4 1.6 1.8 2.0 2.2 2.4 (Å) (Å)

Figure 7. (a) Hirshfeld surface mapped over d_{norm} ; (b) 2D fingerprint plots; (c) 2D fingerprint plots with Br···H/H···Br interactions highlighted in color for complex 1.

(b)



Figure 8. (a) Hirshfeld surface mapped over d_{norm} ; (b) 2D fingerprint plots; (c) 2D fingerprint plots with Br···H/H···Br interactions highlighted in color for complex 2.



Figure 9. Theoretical models used to analyze the noncovalent interactions in complex 1.

Supporting Information). Complex 2 shows a broad emission band at 443 nm upon excitation at 340 nm in the solid state at room temperature (Figure S3, Supporting Information).

Hirshfeld Surface Analysis. The Hirshfeld surfaces mapped with d_{norm} for complexes 1 and 2 are illustrated in Figures 7 and 8, respectively. The dominant interactions between O…H, Br…H, and N…H atoms in both complexes can be seen in the Hirshfeld surface as the bright red areas. Other visible spots in the Hirshfeld

surfaces correspond to H…H contacts. The small extent of area and light color on the surface indicates weaker and longer contact other than hydrogen bonds.

Two-dimensional fingerprint plots complement these surfaces, quantitatively summarizing the nature and type of intermolecular contacts experienced by the molecules in the crystal. The Br \cdots H/H \cdots Br intermolecular interactions appear as distinct spikes in the 2D fingerprint plots of both complexes. The

Article

(c)



Figure 10. Distribution of bond paths and critical points. The bond and ring critical points are shown in red and yellow, respectively. The bond paths are represented by solid lines apart from those characterizing noncovalent interactions that are represented by dashed lines.

fingerprint plots can be decomposed to highlight particular atom pair close contacts.⁶⁹ This decomposition enables separation of contributions from different interaction types, which overlap in the full fingerprint. The amount of Br…H/H…Br interactions comprises 13.8 and 21.3% of the Hirshfeld surfaces for each molecule of complex 1 and complex 2, respectively.

Theoretical Study. We have divided the theoretical study into two parts. In the first part we have analyzed the interesting $C-H/\pi$ interactions observed in complex 1 that are crucial for understanding the final 3D architecture of this complex (see Figure 4), connecting the infinite polymeric 1D chains. In the second part we have analyzed the cuprophilic Cu…Cu interactions observed in complex 2 using the natural bond orbital scheme and examining the Cu donor-acceptor orbitals involved. As previously mentioned, the *p*-methoxy groups of the ligand in complex 1 establish a variety of self-complementary C- H/π interactions in the solid state interconnecting the polymeric chains. We have studied this interaction using a monomeric model (see Figure 9A) to keep the size of the system computationally approachable. We have computed the interaction energy of the self-complementary dimer, and the resulting interaction energy is $\Delta E_1 = -10.0$ kcal/mol, which is large because it accounts for four weak C–H/ π interactions. In order to examine whether the coordinated Cu atoms have a long-range effect on the strength of the interaction, we have also computed a theoretical model (see Figure 9B) where the coordinated Cu(I)atoms have been eliminated. The resulting interaction energy is almost unchanged ($\Delta E_2 = -9.9$ kcal/mol), indicating that the effect of Cu is negligible. In addition to the C-H/ π bonding network observed in the dimer, a weak C-H···H-C interaction is also observed (see red dashed lines in Figure 9). Recently, a combined computational and CSD study has demonstrated the importance of these weak interactions in the solid state.⁷⁰ In fact, the binding energy of the dimer of dodecahedrane,⁷¹ which is stabilized only by C-H···H-C interactions, is approximately 3 kcal/mol. This interaction is governed by dispersion and orbital effects, since the electrostatic contribution is repulsive. A delicate balance between these terms can result in a very weak stabilizing

or destabilizing interaction. To further analyze the importance on this interaction (de)stabilizing the dimer, we have computed the binding energy of the dimer in a new theoretical model where one methyl group has been replaced by a hydrogen atom (see Figure 9C) and consequently the C-H···H-C interaction is not established. As a result, the interaction energy is significantly reduced to $\Delta E_3 = -5.4$ kcal/mol because only one bifurcated $CH_3 \cdots \pi_2$ interaction is evaluated. The contribution of the C–H··· H–C interaction can be evaluated as $\Delta E_{C-H\cdots H-C} = \Delta E_2/2$ – $\Delta E_3 = +0.5$ kcal/mol. Therefore, in the dimer of complex 2 this contribution is slightly repulsive. A likely explanation is that the repulsive electrostatic term (dipole-dipole interaction) is higher in absolute value than the sum of the other favorable contributions to the interaction. This is due to the inductive effect of the oxygen atom of the methoxy group that increases the positive charge of the interacting hydrogen atoms (in comparison to alkanes). Since the C-H…H-C interaction energy is very small (within the accuracy of the density functional theory (DFT) method), we have computed the $\Delta E_{C-H\cdots H-C}$ using a higher level of theory (RI-MP2/def2-TZVP) and the resulting value is also repulsive (1 kcal/mol), giving reliability to the DFT method.

We have further analyzed the dimer shown in Figure 9 using Bader's theory of atoms in molecules. The distribution of critical points and bond paths is shown in Figure 10. The intermolecular $C-H/\pi$ interactions are characterized by the presence of a bond critical point that connects one hydrogen atom of the methyl group with the closest carbon atom of the ring. The C-H···H-C interaction is confirmed by the AIM analysis, and it is also characterized by the presence of a bond critical point that connects both hydrogen atoms. It should be mentioned that the existence of a bond critical point is a confirmation of interaction; however, it does not imply that the interaction is energetically favorable. The distribution of critical points shown in Figure 10 also shows the existence of an interesting C-H…Cu agostic interaction⁷² that is characterized by a bond critical point that connects the Cu atom with the C-H bond critical point. The value of the Laplacian of the electron density computed at the

aforementioned bond critical points is positive, as is common in closed-shell interactions.

The second part of the theoretical study is devoted to the analysis of the Cu···Cu interactions observed in the intricate Cu– Br polymeric skeleton of complex **2**. Interestingly, several Cu(I)–Cu(I) distances present in **2** are within the range 2.80– 2.89 Å (close to the sum of their van der Waals radii, 2.80 Å). We have analyzed the interaction between these closed-shell d¹⁰ metal ions from an orbital point of view. We have performed natural bond orbital (NBO) calculations in the theoretical model complex shown in Figure 11, where the N-donor ligand has been



Figure 11. Theoretical model used for the NBO analysis of complex 2. Distances in Å.

substituted by HCN, focusing our attention on the second order perturbation analysis that is very useful to study donor–acceptor interactions.⁷³ This analysis of the Fock matrix in NBO basis reveals that the strongest contributions to the Cu(I)-Cu(I) interactions derive from donation of electron orbital occupancy from valence Lewis-type lone pairs (LP) of one Cu into an unfilled valence non-Lewis-type lone pair (LP*) of the other Cu ion and vice versa (see Table 6). In the Cu(1)-Cu(2) interaction

Table 6. Second Order NBO Analysis of the Model Complex Shown in Figure 11^a

| donor NBO (i) | acceptor NBO (j) | E ⁽²⁾ (kcal/mol) | $\begin{array}{c}E_{(j)}-E_{(i)}\\(\mathrm{au})\end{array}$ | F(<i>i,j</i>) (au) | |
|--|--------------------|--------------------------------|---|-------------------------|--|
| CR(3)Cu1 | LP*(7)Cu2 | 0.68 | 5.62 | 0.056 | |
| CR(3)Cu2 | LP*(6)Cu1 | 0.63 | 6.01 | 0.056 | |
| LP(5)Cu1 | LP*(7)Cu2 | 3.62 | 0.33 | 0.031 | |
| LP(5)Cu2 | LP*(6)Cu1 | 6.92 | 0.02 | 0.023 | |
| LP(3)Cu3 | LP*(6)Cu4 | 1.22 | 0.42 | 0.020 | |
| LP(5)Cu4 | LP*(6)Cu3 | 1.79 | 0.32 | 0.021 | |
| LP(3)Cu5 | LP*(6)Cu6 | 0.51 | 0.42 | 0.013 | |
| LP(5)Cu6 | LP*(6)Cu5 | 2.07 | 0.34 | 0.024 | |
| ^{<i>a</i>} Abbreviations: CR = core; LP = Lewis-type lone pair; LP* = unfilled lone pair. | | | | | |

(shortest contact) the concomitant second order stabilization energy for both LP \rightarrow LP* electron donations is $E^{(2)} = 10.54$ kcal/mol; that is considerably higher than the stabilization energies computed for the Cu(3)–Cu(4) ($E^{(2)} = 3.01$ kcal/mol) and Cu(3)–Cu(4) ($E^{(2)} = 2.58$ kcal/mol) interactions. This result clearly demonstrates that the stabilization energy depends on the Cu…Cu distance, which strongly affects orbital overlap. For the Cu(1)…Cu(2) interaction the NBO analysis also reveals weak CR \rightarrow LP* electron donations with modest concomitant second order stabilization energies of 0.68 and 0.63 kcal/mol. This donation of electron orbital occupancy from a core orbital of one Cu into an unfilled valence non-Lewis-type lone pair (LP*) of the other Cu and vice versa is not observed for the other two interactions due to their longer Cu–Cu distances (see Figure 11).

SUMMARY

This paper describes the synthesis of two CuBr based coordination polymers containing cyclic Schiff bases upon reduction of copper(II) at ambient condition. Complex 1 forms an 1D chain with 6³-hcb topology, whereas complex 2 forms a 3D architecture. We have analyzed the interesting C-H/ π and C–H···H–C noncovalent interactions in complex 1 both energetically and using Bader's theory of atoms in molecules. While the C-H···H-C interaction is very weak and repulsive, the C-H/ π interactions play an important role in the crystal packing and they are responsible for the different solid state architecture of complex 1 compared to 2. In the latter complex, we have analyzed the closed-shell d¹⁰ Cu…Cu interaction from an orbital point of view. We have performed natural bond orbital (NBO) analysis, and we have found a favorable orbital contribution that is rationalized by means of donor-acceptor orbital interactions (LP \rightarrow LP* electron donation).

ASSOCIATED CONTENT

Supporting Information

Figures S1–S3 showing highlighted C–H/ π interactions in complex 2 and UV–vis fluorescence spectra of complexes 1 and 2. X-ray crystallographic information files (CIF) are available for both complexes. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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