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Structures of Copper Complexes of the Hybrid [SNS] Ligand of Bis(2-(benzylthio)ethyl)amine and Facile Catalytic Formation of 1-Benzyl-4-phenyl-1*H*-1,2,3-triazole through Click Reaction

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A hybrid ligand, bis(2-(benzylthio)ethyl)amine (SNS), with an amine and two thioether donors reacts with Cu(II) to give mononuclear $[CuCl_2(SNS)]$ (**1**), $[CuBr_2(SNS)]$ (**2**), $[Cu(OTf)_2(SNS)(OH_2)]$ (**3**), and an one-dimensional Cu(I) coordination polymer $[Cu_2I_2(SNS)]_n$ (**4**). All complexes have been characterized by single-crystal X-ray diffraction analysis, and **1**−**3** were studied by EPR analysis at room temperature. Complexes **1** and **2** are penta-coordinated with a distorted square pyramidal metal supported by a tridentate SNS ligand on the basal plane. Complex **3** shows a tetragonally distorted octahedral sphere with two trans and weakly bonding monodentate triflates. A 12-membered ring in the solid lattice is formed by intermolecular H-bonding among the coordinated triflate and aqua ligands from four neighboring molecules. Complex **4**, the only Cu(I) in this series, shows a coordination polymer chain $[Cu_4I_4]_n$ comprising tetrahedral Cu(I) centers stitched by the SNS ligand in a unique bridge-chelate mode in the form of a helix. All four complexes are catalytically active at room temperature in a copper-catalyzed azide−alkyne cycloaddition (CuAAA) three-component click reaction of benzyl chloride, sodium azide, and phenylacetylene in an aqueous MeCN mixture to give good isolated yields of 1-benzyl-4-phenyl-1*H*-1,2,3-triazole, without the use of a base or reducing agent.

Introduction

The use of hybrid ligands,[1] especially those with labile or hemilabile[2] functions, to promote dynamic properties such as solution equilibria[3] and catalytic reversibility[4] is an area of immense significance. The classical pincer complexes[5] and many other ligand sets with a mix of hard and soft donor sites are among the myriad of examples. One of our current foci is the use of the tridentate hybrid set [SNS] with diagonally related donor atoms to support complexes that are potentially unsaturated. An application of such a design is found in the water-rich Pd(II) [SNS] complexes for aqueous Suzuki coupling.[6] Other representative developments of [SNS]-stabilized complexes include those of the fluxional Pd(II) allyl complexes,[7a] magnetically active dinuclear Ni(II) S-substituted pyrazole complexes,[7b] brain-imaging agents oxotechnetium(V) and oxorhenium(V) complexes,[7c,d] ethylene trimerization catalyst Cr(III),[7e,f] a Cu_2N_2 diamond core for electron transfer,[8a] and 1-D ribbons with Cu_6I_6 hexamers,[8b] among others.[8c,d] In this paper, we shall use such

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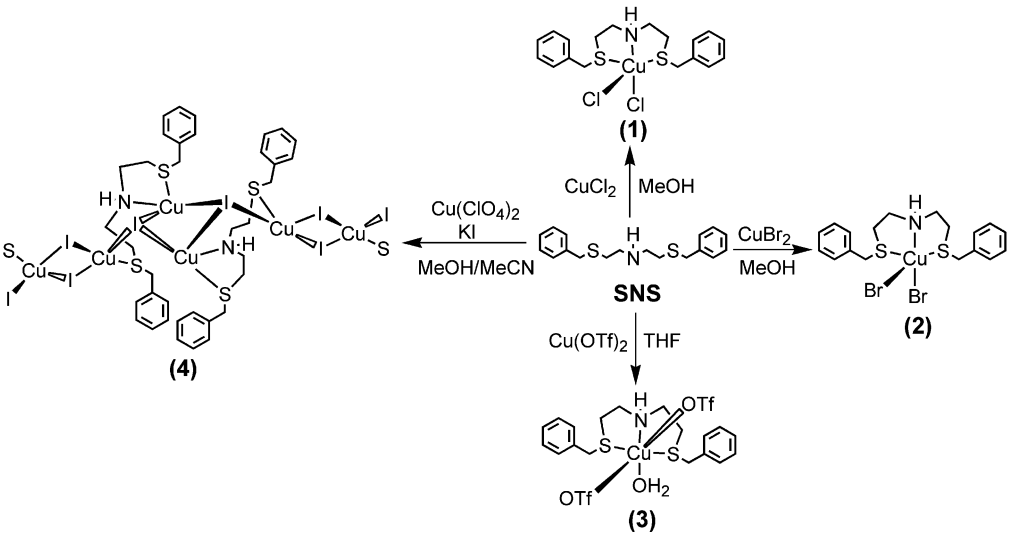
Scheme 1. Schematic Representation of the Formation of $Cu^{I/II}$ [SNS] Complexes **1**−**4**



a hybrid ligand to promote different structural motifs in a geometrically versatile metal such as copper[9] and to introduce labile ligands to the coordination sphere. A major impetus of the latter is to promote potentially unsaturated species for active aqueous-based catalysis. This is demonstrated by their activities in Cu(I)-catalyzed azide−alkyne cycloaddition (CuAAA) reactions in aqueous MeCN. The CuAAA reaction is one of the most popular Huisgen's dipolar cycloadditions, as it provides a facile pathway to functional 1,2,3-triazoles.[10,11] The active catalytic mixture usually contains Cu(II) with a reducing agent (usually sodium ascorbate).[10c,d] Direct entry with Cu(I) or metallic copper or its clusters is possible but met with problems such as undesirable alkyne−alkyne homocoupling.[10b] The use of nitrogen,[11a−d] phosphorus,[11e,f] and N-heterocyclic carbene ligands[11g] to protect the Cu(I) is noteworthy. Sulfur-containing ligands have also been applied in a range of catalytic systems,[12a] including the well-known aminoarenethiolato Cu(I) in asymmetric conjugate addition reactions and amination of aryl bromides.[12b,c] We herein present a structural array of Cu(I)/(II) [SNS] complexes supported by halides (Cl^-, Br^-, I^-) and a labile pseudohalide (OTf^-) (Scheme 1) as well as the crystallographic identification of $[CuCl_2(SNS)]$ (**1**), $[CuBr_2(SNS)]$ (**2**), $[Cu(OTf)_2(SNS)(OH_2)]$ (**3**), and $[Cu_2I_2(SNS)]_n$ (**4**) and their potential uses in the CuAAA click reaction.

Results and Discussion

The tridentate [SNS] ligand is represented by bis(2-(benzylthio)ethyl)amine[6,7e] with a central secondary amine flanked by two thioether functional groups. Addition reactions with $CuCl_2 \cdot 2H_2O$ or $CuBr_2$ in MeOH and $Cu(OTf)_2$ in THF result in Cu(II) five-coordinated $[CuCl_2(SNS)]$ (**1**), $[CuBr_2(SNS)]$ (**2**), and six-coordinated $[Cu(OTf)_2(SNS)(OH_2)]$ (**3**), respectively. Complexes **1** and **2** can also be obtained by adding methanolic NaCl or KBr in situ to a mixture of [SNS] and $Cu(ClO_4)_2 \cdot 6H_2O$. The use of KI under similar conditions leads to a loss of coloration and formation of the reduced $[Cu_2I_2(SNS)]_n$ (**4**), which is expected since the redox potential would favor the reduction. The IR spectra of these complexes invariably show a prominent band in the

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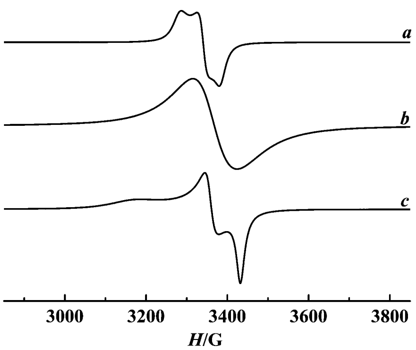

Figure 1. EPR spectra of the solid samples of complexes **1** (a), **2** (b), and **3** (c) at 298 K with frequencies at 9.7761, 9.7759, and 9.7765 GHz, respectively.

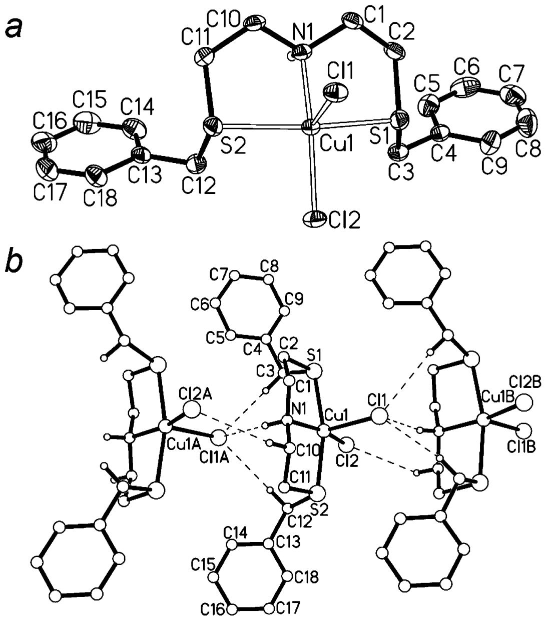

Figure 2. (a) Thermal ellipsoids at 30% probability of the molecular structure of **1**. Selected bond distances [Å] and angles [deg]: Cu1−N1 2.001(4), Cu1−S1 2.353(1), Cu1−S2 2.380(1), Cu1−Cl2 2.241(1), Cu1−Cl1 2.518(1), N1−Cu1−Cl2 162.4(1), N1−Cu1−S1 85.4(1), N1−Cu1−S2 85.3(1), N1−Cu1−Cl1 92.3(1), S1−Cu1−S2 165.44(5), S1−Cu1−Cl1 94.39(4), S2−Cu1−Cl1 97.07(4), Cl2−Cu1−Cl1 105.29(5), Cl2−Cu1−S1 92.84(5), Cl2−Cu1−S2 92.76(5). (b) A crystal structure representation showing secondary intermolecular H bonding in **1**. (Cu1···Cu1A 5.829 Å, symmetry code A: *x*, 1.5 − *y*, −0.5 + *z*.)

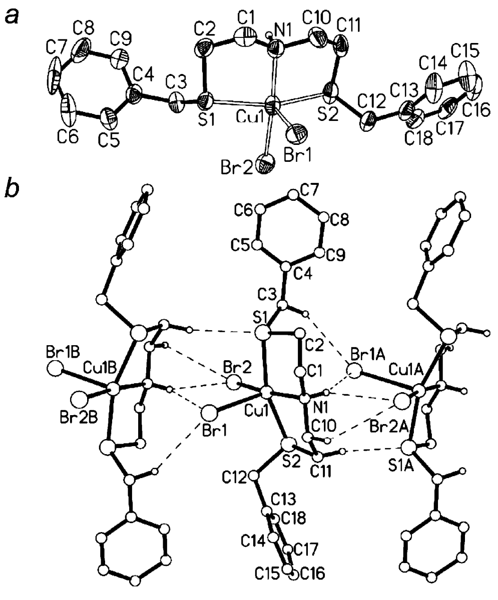

Figure 3. (a) Thermal ellipsoids at 30% probability of the molecular structure of **2**. Selected bond distances [Å] and angles [deg]: Cu1−N1 1.990(8), Cu1−S1 2.337(3), Cu1−S2 2.341(3), Cu1−Br1 2.744(2), Cu1−Br2 2.364(2), N1−Cu1−S1 85.0(2), N1−Cu1−S2 84.5(2), N1−Cu1−Br1 93.2(2), N1−Cu1−Br2 168.8(2), S1−Cu1−S2 161.8(1), S1−Cu1−Br1 91.40(8), S1−Cu1−Br2 94.65(8), S2−Cu1−Br1 103.98(8), S2−Cu1−Br2 92.75(9), Br2−Cu1−Br1 97.98(6). (b) A crystal structure representation showing secondary intermolecular H bonding in **2**. (Cu1···Cu1A 5.699 Å, symmetry code A: 1.5 − *x*, −0.5 + *y*, 0.5 − *z*)

3200−3240 cm^{-1} region attributed to the N−H group of the [SNS] ligand. Solid X-band EPR spectra were recorded for **1**−**3** at 298 K (Figure 1). Complex **1** shows a three *g*-value anisotropic EPR pattern with $g_1 = 2.13$, $g_2 = 2.09$, and $g_3 = 2.07$ (Figure 1a). Complex **2** exhibits a broad quasi-isotropic signal centered at $g_{\text{iso}} = 2.07$ (Figure 1b), corresponding to the $\Delta M_S = \pm 1$ transition. The EPR spectrum of **3** also reveals a three *g*-value anisotropic EPR spectrum with $g_1 = 2.21$, $g_2 = 2.07$, and $g_3 = 2.04$, (Figure 1c) which is consistent with the tetragonally distorted Cu(II).[13]

Single-crystal structural analysis of **1** and **2** shows that they are mononuclear and penta-coordinated Cu(II) adducts of CuX_2 with the [SNS] ligand. The tridentate hybrid ligand in the two complexes occupies the basal plane of a distorted square-pyramidal (structural indices τ[14] = 0.05 for **1** and 0.12 for **2**) metal sphere with a unique apical halide. (Max deviations of +0.0327 to −0.0368 Å in the least-squares plane {SNSCl} in **1** and +0.0651 to −0.0561 Å in the {SNSBr} plane in **2**) (Figures 2a and 3a). Its chelation results in two five-membered rings fused at the Cu−N bond. Similar coordination modes are found in some related CuX_2L (L = tridentate ligand) complexes.[15] The slightly larger chelate angle of **1** (av. 85.3°) compared to that of **2** (av. 84.8°) probably reflects the higher steric influence of bromide. In **1**, intermolecular H-bonding interactions are observed between the skeletal methylene C−H and secondary amine N−H of the ligands and the coordinated chlorides of the neighboring molecule [C10−H···Cl2 3.65, C3−H···Cl1 3.81, C12−H···Cl1 3.70, N1−H···Cl1 3.24 Å] in the *c* direction (Figure 2b and Table 1). Complex **2** is similarly

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Table 1. Hydrogen-Bond Parameters (Å) in Complexes **1**, **2**, and **3**

D−H···A[a] (Å)	D−H (Å)	D···A (Å)	H···A (Å)	∠D−H···A (deg)
		Complex **1**		
C10−H···Cl2A	0.97	3.647(5)	2.89	135
C3−H···Cl1A	0.97	3.808(5)	2.89	157
C12−H···Cl1A	0.97	3.702(5)	2.79	158
N1−H···Cl1A	0.88	3.244(4)	2.40	162
		Complex **2**		
N1−H···Br1A	0.91	3.443(8)	2.66	145
N1−H···Br2A	0.91	3.533(7)	2.91	127
C3−H···Br1A	0.97	3.80(1)	2.92	151
C10−H···Br2A	0.97	3.61(1)	3.05	119
C14−H···Br2B	0.93	3.62(1)	2.95	131
C11−H···S1A	0.97	3.75(1)	2.79	168
		Complex **3**		
N1−H···O4A	0.86	3.015(3)	2.34	136
C2−H···O3A	0.97	3.199(4)	2.33	149
O1−H···O6B	0.87	2.668(4)	2.04	128
O1−H···O5C	0.87	2.625(4)	1.76	168

[a] Symmetry codes: for **1**, A, *x*, 1.5 − *y*, −0.5 + *z*; for **2**, A, 1.5 − *x*, −0.5 + *y*, 0.5 − *z*; B, *x* − 1, *y*, *z*; for **3**, A, *x* − 1, *y*, *z*; B, 1 + *x*, *y*, *z*; C, −*x*, −*y*, −*z*.

stabilized by secondary intermolecular H-bond interactions [N1−H···Br1 3.44, N1−H···Br2 3.53, C3−H···Br1 3.80, C10−H···Br2 3.61, C11−H···S1 3.75, C14−H···Br2 3.62 Å] (Figure 3b and Table 1).

Complex **3** shows a tetragonally distorted octahedral Cu(II) sphere with tridentate [SNS] and monodentate aqua forming the equatorial plane (max deviations +0.1025 to −0.0973 Å in the least-squares plane of {SNSO}) and two monodentate triflates at the axial positions (Figure 4a). A combination of the Jahn−Teller effect and weak basicity of the triflate oxygen results in two very weak axial Cu−O interactions [Cu1−O2 2.415(2), Cu1−O7 2.574(3) Å], which are comparable with the axial Cu−O (triflate oxygen) bonds in complexes $[Cu(OTf)_2(bpyNO)_2]$ (2.397(2) Å;[16a] bpyNO = 2,2′-bipyridine-*N*-oxide), $[Cu(OTf)_2(2\text{-mepyz})_2(OH_2)_2]$ (2.420(4) and 2.423(6) Å;[16b] 2-mepyz = 2-methylpyrazine), $[Cu(OTf)_2(OH_2)_2(pyz)]$ (2.402(2) Å;[16b] pyz = pyrazine), and $[Cu_3(OTf)_2(\mu\text{-aapm})_2(\mu\text{-dca})_2(Haapm)_2]$ (2.534(3) Å;[16c] Haapm = *N*-(pyrimidin-2-yl)acetamide) but are shorter and presumably stronger than those in complex $[Cu(OTf)_2(ampym)_2(OH_2)_2](ampym)_2(ampym)_2$ (2.749(2) Å;[16d] ampym = 2-aminopyrimidine). The equatorial Cu−O (1.932(2) Å) is comparable with its counterpart in $[Cu(OH_2)_6]^{2+}$ (∼1.95 Å) and $[Cu(OTf)_2(ampym)_2(OH_2)_2](ampym)_2(ampym)_2$ (1.937(2) Å).[16d] The resultant [4 + 2] coordination of the metal readily provides two potential axial sites for substrate entry in the catalytic process.

The lattice structure shows significant intermolecular H-bonding between the amine, methylene, and coordinated aqua hydrogen with triflate oxygen [N1−H···O4 3.02, C2−H···O3 3.20, O1−H···O6 2.67 Å] along the *a* direction (Figure 4b and Table 1) and between the coordinated aqua hydrogen and triflate oxygen [O1−H···O5 2.63 Å] in the *b* direction (Table 1). The two ligands (triflate and water) thus play a major role in stabilizing the solid lattice. Enclaved among four molecules is a 12-membered ring formed by the association of two coordinated triflates and two coordinated aqua ligands through H-bonding (Figure 4c). Similar ring structures are found in $[Pt\{C_6H_3(CH_2NMe_2)_2\text{-}2,6\}(OH_2)](OTf)$,[16e] $[Cu(OTf)_2(2\text{-mepyz})_2(OH_2)_2]$,[16b] $[\{PtMe_3(OH_2)\}_2(1,3\text{-BAIB})](OTf)_2$[16f] (1,3-BAIB = $1,3\text{-}C_6H_4(CH{=}NCH_2CH_2NMe_2)_2$), and also in the complex $[Pd(OTf)_2(OH_2)_2(dppp)]$[16g] (dppp = *cis*-(1,3-bis(diphenylphosphino)propane)), which shows a pseudobutterfly configuration.

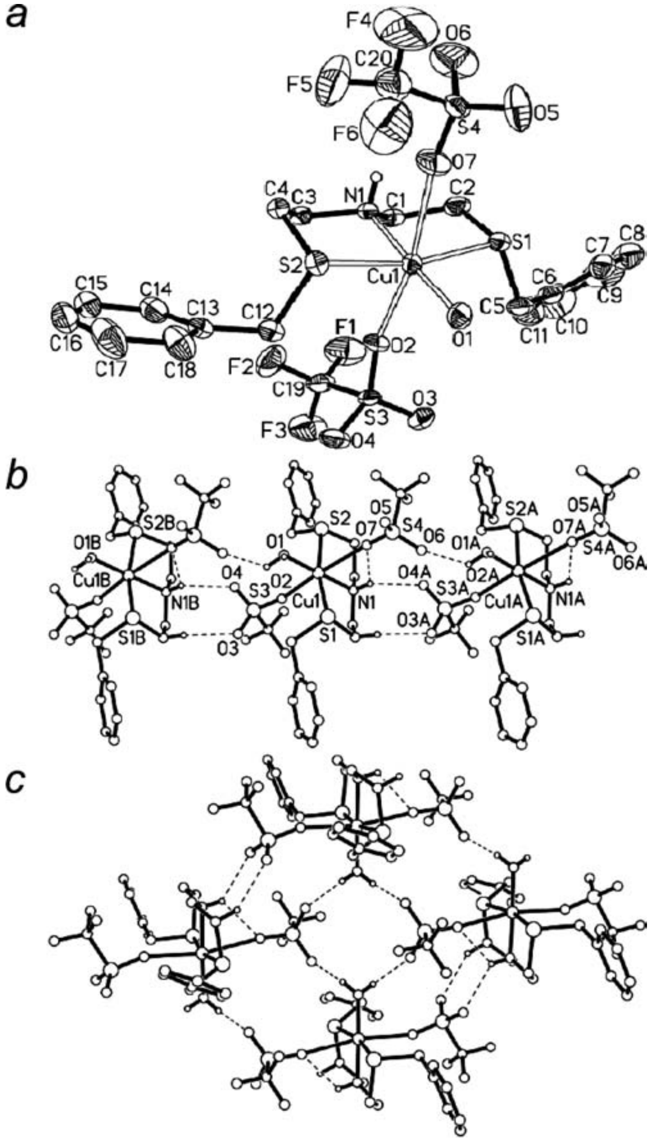

Figure 4. (a) Thermal ellipsoids at 30% probability of the molecular structure of **3**. Selected bond distances [Å] and angles [deg]: Cu1−N1 1.976(2), Cu1−S1 2.3573(8), Cu1−S2 2.3738(8), Cu1−O1 1.932(2), Cu1−O2 2.415(2), Cu1−O7 2.574(3), N1−Cu1−S1 85.64(7), N1−Cu1−S2 87.28(7), N1−Cu1−O1 178.2(1), N1−Cu1−O2 89.72(8), N1−Cu1−O7 80.4(1), S1−Cu1−O1 93.67(8), S1−Cu1−O2 97.33(5), S1−Cu1−O7 86.48(8), S1−Cu1−S2 167.16(3), S2−Cu1−O1 93.09(8), S2−Cu1−O2 93.33(5), S2−Cu1−O7 81.79(7), O1−Cu1−O2 92.01(9), O1−Cu1−O7 97.9(1), O2−Cu1−O7 169.16(9). (b) H-bonding supramolecular structure in **3**. (c) O−H···O H−bonding cyclic structure in **3**.

X-ray structural analysis of **4** shows an asymmetric unit with two independent copper atoms. The structure reveals a novel one-dimensional coordination polymer formed by a chain of two types of $[Cu_2I_2]$ parallelograms (Cu1−Cu1A−I1−I1A and Cu2−Cu2B−I2−I2A) interconnected orthogonally by triply bridging iodides and chelate-bridging SNS (Figure 5a). The latter coordination mode, which is not found in the earlier Cu(II) complexes, shows a N,S chelated to one Cu and S-bonded to its Cu neighbor in the next Cu_2 sphere. The

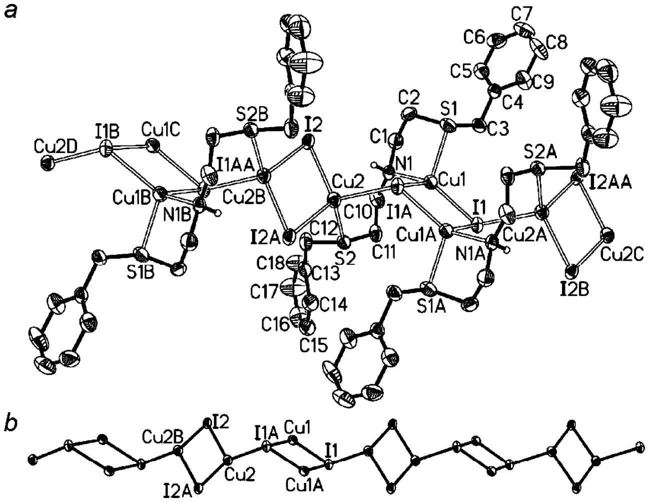

Figure 5. (a) Thermal ellipsoids at 30% probability of the molecular structure of **4**. Selected bond distances [Å] and angles [deg]: Cu1−N1 2.085(5), Cu1−S1 2.307(2), Cu1−I1 2.5831(9), Cu1−I1A 2.7463(9), Cu1−Cu1A 2.525(2), Cu2−S2 2.332(2), Cu2−I1A 2.6816(8), Cu2−I2 2.6329(9), Cu2−I2B 2.6509(8), Cu2−Cu2B 2.844(2), N1−Cu1−S1 91.2(2), N1−Cu1−I1 119.4(1), N1−Cu1−I1A 100.4(1), N1−Cu1−Cu1A 134.4(1), S1−Cu1−I1 112.96(5), S1−Cu1−Cu1A 131.02(7), S1−Cu1−I1A 103.68(5), I1−Cu1−I1A 123.53(3), Cu1A−Cu1−I1A 58.50(3), Cu1A−Cu1−I1 65.03(3), Cu1−I1−Cu2A 113.02(3), Cu1−I1−Cu1A 56.47(3), S2−Cu2−I1A 107.51(5), S2−Cu2−I2 113.94(5), S2−Cu2−I2B 99.10(5), S2−Cu2−Cu2B 121.55(6), I2−Cu2−I2B 114.88(3), I2−Cu2−I1A 109.54(3), I2B−Cu2−I1A 111.33(3), I2−Cu2−Cu2B 57.75(3), I2B−Cu2−Cu2B 57.14(3), I1A−Cu2−Cu2B 130.45(4), Cu2A−I1−Cu1A 93.79(2), Cu2−I2−Cu2B 65.12(3). (symmetry codes: A, 1 − *x*, −*y*, 1 − *z*; B, 1 − *x*, 1 − *y*, 1 − *z*; C, *x*, *y* − 1, *z*; D, *x*, 1 + *y*, *z*). (b) [Cu$_4$I$_4$]$_n$ coordination polymer chain along the *b* direction.

overall polymer chain thus shows intercalation of doubly bridging μ_2- and singly bridging μ_3-iodides with Cu$_4$ as the repeating unit, namely, [Cu$_4$I$_4$]$_n$. The triply bridging iodide also brings a set of copper atoms to within bonding distance (Cu1−Cu1A 2.525 Å), which is significantly shorter than the other pair (Cu2−Cu2A 2.844 Å). The SNS ligand crosses between two Cu$_2$ moieties with longer separations (Cu1···Cu2 3.963 Å), whereas the remaining metal separation is even longer (Cu1···Cu2A 4.391 Å). There are no apparent interchain interactions, either via H-bonding or Cu···Cu interactions (Cu1···Cu1E 7.211 Å, symmetry code E: 2 − *x*, −*y*, 1 − *z*).

This Cu(I) coordination polymer is assembled by bridging iodides and the [SNS] hybrid ligand. The latter effectively stitches the two rhombic Cu$_2$I$_2$ entities by traversing across two metal centers, thereby fixing two Cu$_2$I$_2$'s into a Cu$_4$I$_4$ core (Figure 5b). This results in an unusual form of helical arrangement of the SNS hybrid ligand wrapping around the tetrahedral copper atoms along the metal chain. A myriad of CuI discrete molecular entities, as well as 1-D and 2-D structures, have been reported in recent years.[8b,9b,c,17] The known 1-D polymer system contains the likes of a zigzag [CuI]$_n$ chain,[17a,b] [CuI]$_n$ columnar chain,[17e] staircase [CuI]$_n$ chain,[17f−k] [Cu$_8$I$_7$]$_n^{n+}$ cluster-based stair-like double chain,[17l] double six-membered rings [Cu$_6$I$_6$]$_n$ core-based chains,[17m] [Cu$_{14}$I$_{18}$]$^{4-}$ anion,[17n] [Cu$_6$I$_5$]$_n^{n+}$ and [Cu$_2$I]$_n^{n+}$ chains, and so forth.[17o] The connected rhombic [Cu$_4$I$_4$]$_n$ motif of **4** is a new addition to this range of 1-D polyiodocuprates.

CuAAA Click Reaction Catalyzed by 1−4. A typical Cu-catalyzed Huisgen reaction couples organoazide with a terminal alkyne. We are seeking higher click efficiency by carrying out a room temperature three-component reaction using phenylacetylene, benzyl chloride, and an inorganic azide (NaN$_3$) as a one-pot mixture in MeCN/H$_2$O (v/v 2:1, 6 mL) in the air. Similar success was reported in an aqueous ionic liquid medium but under a fairly high level (15%) of Cu(I) catalysts and in the presence of a base (Na$_2$CO$_3$).[11h] The reaction readily proceeds to give 1-benzyl-4-phenyl-1*H*-1,2,3-triazole without the need to introduce either a base or reducing agent. The presence of MeCN, which is usually not a desirable solvent, as it could saturate the active Cu(I) catalyst, presumably promotes the reduction of Cu(II) to Cu(I) (for **1**−**3**).[10f,18] The product, 1-benzyl-4-phenyl-1*H*-1,2,3-triazole,[11g,19] was purified (by column chromatography), isolated, and confirmed by ^{1}H and ^{13}C NMR[20] and X-ray crystallographic analyses.[19] Some representative catalytic data are summarized in Table 2. All four complexes give good isolated yields, with up to 98% for catalyst **3** (5% loading; entry 16) or 87% for **4** (2% loading; entry 19). The yields drop to 49−75% when the catalyst loading is reduced to the lower limit of 0.5 mol % (entries 3, 9, 15, 21). All catalysts are still active in pure water, even at 0.5 mol % loading (entries 6, 12, 18, 24), but the yields are generally lower. Good activities of [CuX(NHC)] (NHC = N-heterocyclic carbene) on similar click chemistry but using organic azide have been reported.[11g] Within this system, **3** generally shows the highest activities, possibly attributed to the ready formation of catalytically active unsaturated species through facile dissociation of triflate and water, as well as its higher solubility and stability in the aqueous-based media.

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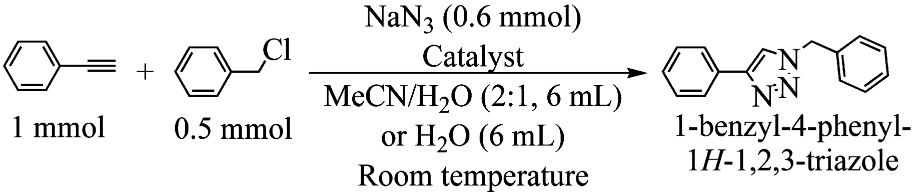
(20) NMR data for catalytic product of 1-benzyl-4-phenyl-1*H*-1,2,3-triazole: ^{1}H NMR (500 MHz, CDCl$_3$, 25°C): δ 5.57 (s, 2H, CH$_2$), 7.26−7.41 (m, 8H), 7.66 (s, 1H), 7.79 and 7.80 (d, 2H). ^{13}C NMR (125.77 MHz, CDCl$_3$, 25°C): δ 54.2, 119.4, 125.7, 128.0, 128.1, 128.8, 129.1, 130.5, 134.6, 148.2.

Table 2. Catalytic Formation of 1-Benzyl-4-phenyl-1*H*-1,2,3-triazole from a CuAAA Click Reaction Promoted by Copper Complexes with [SNS] Hybrid Ligand



entry	catalyst	solvent	reaction time, h	catalyst loading, mol %	isolated yield, %
1	**1**	$MeCN/H_2O$	24	2	82
2	**1**	$MeCN/H_2O$	24	1	74
3	**1**	$MeCN/H_2O$	24	0.5	49
4	**1**	$MeCN/H_2O$	1	5	91
5	**1**	H_2O	15	5	54
6	**1**	H_2O	24	0.5	37
7	**2**	$MeCN/H_2O$	24	2	86
8	**2**	$MeCN/H_2O$	24	1	84
9	**2**	$MeCN/H_2O$	24	0.5	75
10	**2**	$MeCN/H_2O$	1	5	92
11	**2**	H_2O	15	5	87
12	**2**	H_2O	24	0.5	57
13	**3**	$MeCN/H_2O$	24	2	92
14	**3**	$MeCN/H_2O$	24	1	89
15	**3**	$MeCN/H_2O$	24	0.5	72
16	**3**	$MeCN/H_2O$	1	5	98
17	**3**	H_2O	15	5	75
18	**3**	H_2O	24	0.5	36
19	**4**	$MeCN/H_2O$	24	2	87
20	**4**	$MeCN/H_2O$	24	1	85
21	**4**	$MeCN/H_2O$	24	0.5	72
22	**4**	$MeCN/H_2O$	1	5	83
23	**4**	H_2O	15	5	77
24	**4**	H_2O	24	0.5	54

The ability of the hybrid ligand [SNS] to stabilize complex formation in both Cu(II) and Cu(I) is an advantage of the current system. It offers practical convenience to the preparation of a catalyst precursor and a ready stabilizing source for the metal in both oxidation states. The high air and water stability and the avoidance of potentially hazardous organic azides are additional advantages.

Isolation of these complexes under similar conditions suggests that the hybrid ligand uses its mix of soft−hard functions to support different redox states of the metal (Cu(I)/(II)) and ligand demands (denticity and lability). Not only can it adapt to different metal geometries (square-pyramidal, octahedral, and tetrahedral) but it also adjusts its coordination modes to adapt to the metal nuclear and topological assemblies (mono- and polymeric). These electronic, geometrical, steric, and conformational adaptations of the SNS ligand help it support complexes with dynamic behaviors. Ligands of this nature are probably best used in a complex environment when the metal needs to consistently switch between saturation and unsaturated states and among different redox states, nuclearities, and even topologies. This ability to support dynamic changes within a self-contained system is probably the single most important feature of a hybrid ligand. Ongoing efforts in our laboratory are directed at the exploitation of such potential.

Experimental Section

Materials and Physical Measurements. All of the starting chemicals were used as purchased. The SNS ligand of bis(2-(benzylthio)ethyl)amine was prepared according to the literature procedures.[7e,6] Elemental analyses for C, H, and N were performed on a Perkin-Elmer PE 2400 CHNS elemental analyzer. Infrared spectra were obtained on the Shimadzu IR-470 spectrometer from samples in KBr discs. The NMR spectra were measured at 25 °C using a Bruker ACF 500 NMR spectrometer. EPR spectra were measured at Nanjing University using a Bruker ER 200-D-SRC spectrometer for solid samples at 298 K. The general procedure for a CuAAA catalytic preparation is given:

In a vial fitted with a screw cap, benzyl chloride (0.5 mmol), sodium azide (0.6 mmol), phenylacetylene (1.0 mmol), and Cu(II)/(I) [SNS] complexes (**1**−**4**) were added to a solvent [$MeCN/H_2O$ (v/v 2:1, 6 mL) mixture or pure water (6 mL)]. The reaction mixture was stirred at room temperature in the air. The product was obtained by extraction with Et_2O and purified by column chromatography and confirmed by ^1H and ^{13}C NMR and X-ray structural analyses.

Caution! *Sodium azide is potentially explosive and hence must be handled with great caution.*

Syntheses. [$CuCl_2$(SNS)] (1). A MeOH solution (5 mL) of $CuCl_2 \cdot 2H_2O$ (0.1 mmol, 0.017 g) was added to a MeOH solution (5 mL) of the SNS ligand (0.1 mmol, 0.032 g), and the mixture was stirred at room temperature. Slow evaporation of the resulting solution afforded blue crystals of **1** after ~2 weeks. Yield: 0.019 g (42%). Anal. calcd for $C_{18}H_{23}Cl_2CuNS_2$ (451.93): C, 47.84; H, 5.13; N, 3.10. Found: C, 47.94; H, 4.98; N, 3.17%. IR bands (cm^{-1}): 3210m, 3084m, 2928m, 1601m, 1490m, 1454m, 1417m, 1078m, 969m, 762m, 701vs.

$CuBr_2$(SNS)] (2). Complex **2** (green crystals) was prepared similarly to **1**, using $CuBr_2$ as the substrate. Yield: 0.042 g (78%). Anal. calcd for $C_{18}H_{23}Br_2CuNS_2$ (540.85): C, 39.97; H, 4.29; N, 2.59. Found: C, 40.13; H, 4.14; N, 2.81%. IR bands (cm^{-1}): 3207m, 3052m, 2968m, 2932m, 1598m, 1492m, 1454m, 1413m, 1071m, 1001m, 963m, 761m, 696vs.

[Cu(OTf)$_2$(SNS)(OH$_2$)] (3). The THF solution (3 mL) of Cu(OTf)$_2$ (0.1 mmol, 0.036 g) was added to a THF (5 mL) solution of SNS (0.1 mmol, 0.032 g), and the mixture was stirred. Slow evaporation of the resulting solution afforded green crystals of **3** after ~4 weeks. Yield: 0.036 g (52%). Anal. calcd for $C_{20}H_{25}CuF_6NO_7S_4$ (697.19): C, 34.45; H, 3.61; N, 2.01. Found: C, 34.65; H, 3.46; N, 2.05%. IR bands (cm^{-1}): 3212m, 1656m, 1604m, 1494m, 1457m, 1424m, 1286b, 1262b, 1243b, 1172s, 1079m, 1032m, 771m, 706m, 635m, 572m, 516m.

[Cu$_2$I$_2$(SNS)]$_n$ (4). A MeOH solution (5 mL) of Cu(ClO$_4$)$_2$·6H$_2$O (0.1 mmol, 0.037 g) was added to the MeOH solution (5 mL) of the SNS ligand (0.1 mmol, 0.032 g), and the mixture was stirred for about 5 min. A methanol solution (5 mL) of KI (0.2 mmol, 0.033 g) was added. The solution readily changed from green to brown with some white precipitates. MeCN was then added to dissolve the precipitate completely. Slow evaporation of the resulting weak brown solution afforded colorless crystals of **4** after ~4 weeks. Yield: 0.031 g (45%). Anal. calcd for $C_{18}H_{23}Cu_2I_2NS_2$ (698.37): C, 30.96; H, 3.32; N, 2.01. Found: C, 31.43; H, 2.90; N, 2.14%. IR bands (cm^{-1}): 3239m, 3026m, 2928m, 2912m, 2851m, 1601m, 1493m, 1450m, 1409m, 1083m, 950m, 849m, 810m, 770m, 698vs.

X-Ray Crystallography. All measurements were conducted at room temperature on a Bruker AXS SMART APEX diffractometer, equipped with a CCD area detector using Mo Kα radiation (λ = 0.71073 Å). The collecting of frames of date, indexing reflection, and determination of lattice parameters and polarization effects were performed with the SMART suite of programs.[21] The integration of intensity of reflections and scaling was carried out by SAINT.[21] The empirical absorption correction was performed by SADABS.[22] The space group determination, structure solution and least-squares refinements on $|F|^2$ were carried out with SHELXS-97 and SHELXL-97.[23] The structures were solved by direct methods to locate the heavy atoms, followed by difference maps for the light non-hydrogen atoms. Anisotropic thermal parameters were refined for the rest of the non-hydrogen atoms. Hydrogen atoms were placed geometrically and refined isotropically. CCDC reference numbers: 692260 (**1**), 692261 (**2**), 692262 (**3**), and 692263 (**4**).

Crystal Refinement Data. [CuCl$_2$(SNS)] (1). Formula: $C_{18}H_{23}Cl_2CuNS_2$, blue rod crystal, monoclinic space group $P2_1/c$; a = 13.957(2), b = 13.636(2), c = 11.479(2) Å; β = 112.206(3)°; V = 2022.6(6) Å^3; Z = 4. Crystal size: 0.40 × 0.14 × 0.08 mm^3; GOF = 1.064. Reflections collected: 13 716. Independent reflections: 4639 [R_{int} = 0.0547]; R_1 = 0.0661; wR_2 = 0.1599.

[CuBr$_2$(SNS)] (2). Formula: $C_{18}H_{23}Br_2CuNS_2$, green thin plate crystal, monoclinic space group $P2_1/n$; a = 8.957(2), b = 11.332(2), c = 21.243(4) Å; β = 90.554(4)°; V = 2155.9(7) Å^3; Z = 4. Crystal size: 0.20 × 0.10 × 0.02 mm^3; GOF = 1.034. Reflections collected: 11 725. Independent reflections: 3806 [R_{int} = 0.0738]; R_1 = 0.0724; wR_2 = 0.1890.

[Cu(OTf)$_2$(SNS)(OH$_2$)] (3). Formula: $C_{20}H_{25}CuF_6NO_7S_4$, green plate crystal, triclinic space group $P\bar{1}$; a = 8.3046(8), b = 11.467(1), c = 16.216(2) Å; α = 104.804(2), β = 91.809(2), γ = 105.428(2)°; V = 1430.9(2) Å^3; Z = 2. Crystal size: 0.60 × 0.40 × 0.10 mm^3; GOF = 1.027. Reflections collected: 18 481. Independent reflections: 6559 [R_{int} = 0.0331]; R_1 = 0.0477; wR_2 = 0.1378.

[Cu$_2$I$_2$(SNS)]$_n$ (4). Formula: $C_{18}H_{23}Cu_2I_2NS_2$, colorless plate crystal, triclinic space group $P\bar{1}$; a = 9.1552(6), b = 10.7244(7), c = 12.2586(8) Å; α = 93.343(1), β = 100.822(1), γ = 105.480(1)°; V = 1131.8(1) Å^3; Z = 2. Crystal size: 0.36 × 0.20 × 0.04 mm^3; GOF = 1.099. Reflections collected: 14 980. Independent reflections: 5182 [R_{int} = 0.0344]; R_1 = 0.0478; wR_2 = 0.1182.

Acknowledgment. We thank Professor Jing-Lin Zuo (Nanjing University, China) for EPR measurements and helpful discussions. We are also grateful to G. K. Tan for crystallographic assistance. This work was supported by the Agency for Science, Technology & Research (R143-000-277-305), Ministry of Education (R-143-000-361-112), and the National University of Singapore.

Supporting Information Available: X-ray crystallographic file in CIF format for the four molecules (**1**−**4**). This material is available free of charge via the Internet at http://pubs.acs.org.

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