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Ligand-Controlled Syntheses of Copper(I) Complexes with Metal–Metal Interactions: Crystal Structure and Relativistic Density Functional Theory Investigation

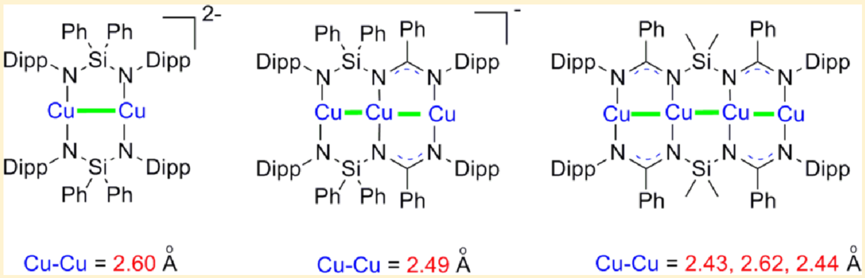
Jun-Feng Liu,[†,‡,§] Xue Min,[†,‡,§] Jin-Yu Lv,[⊥] Fu-Xing Pan,[†,‡] Qing-Jiang Pan,*[⊥] and Zhong-Ming Sun*[†]

[†]State Key Laboratory of Rare Earth Resource Utilization, Changchun Institute of Applied Chemistry, Chinese Academy of Sciences, 5625 Renmin Street, Changchun, Jilin 130022, China

[⊥]Key Laboratory of Functional Inorganic Material Chemistry of Education Ministry, School of Chemistry and Materials Science, Heilongjiang University, Harbin 150080, China

[‡]University of Chinese Academy of Sciences, Beijing 100049, P. R. China

Supporting Information



ABSTRACT: A family of di-, tri-, and tetranuclear copper(I) complexes supported by length-controlled silaamidinate ligands have been synthesized to show short $\mathrm{Cu^I}$–$\mathrm{Cu^I}$ distances (2.43–2.62 Å) and feature a linear or bent metal–metal arrangement, which is elucidated by a relativistic density functional theory calculation.

INTRODUCTION

During the past 2 decades, the synthesis and characterization of linear multinuclear metal complexes featured with metal–metal interactions have attracted much attention because of their unique structural and bonding features as well as potential applications in the field of molecular electronics.[1] After the first cases of linearly aligned trinuclear copper(II) and nickel(II) complexes supported by a di-2-pyridylamido ligand were reported by Hathaway et al.[2] and Pyrka et al.,[3] a number of extended metal atom chain (EMAC) complexes containing metal–metal interactions, including from trinuclear to nonanuclear metal atoms, have been prepared by several groups, such as Cotton et al. and Peng et al.[1,4] Yet, most successful examples of EMAC complexes are supported by a few types of multidenate organic ligands, such as oligo-α-pyridylamido, mono- and multinaphthyridylamido, multidentate phosphine, and conjugated polyene ligands.[1,4] Therefore, the rational design and synthesis of new multidentate organic ligands that are capable of accommodating multiple metal ions in a linear way remain a challenging task. On the other hand, a number of multinuclear copper(I) complexes have been extensively investigated because of their unique photoluminescent properties and potential applications in materials science.[5,6] One of the most striking features of these multinuclear copper(I) complexes is the presence of Cu–Cu bonding interactions.[6] However, studies on nearly linear three or more bonded copper(I) complexes are still rare.[7]

Our research interest focuses on the design of metal-supporting multidentate ligands and ligand-controlled synthesis of metal–metal-bonded linear low-valent multinuclear metal complexes. Recently, the sterically bulky amidinate $[(\mathrm{R^1N})_2\mathrm{CR^2}]^{2-}$ ($\mathrm{R^1}$ = ^{i}Pr, ^{s}Bu, ^{t}Bu, Cy, Ph, 4-MeC$_6$H$_4$, 2- or 4-OMeC$_6$H$_4$, 2-SMeC$_6$H$_4$, 2,6-Me$_3$C$_6$H$_3$, 2,4,6-Me$_3$C$_6$H$_2$, 2,6-Et$_2$C$_6$H$_3$, 2,6-^{i}Pr$_2$C$_6$H$_3$, C$_6$F$_5$, 3-CF$_3$C$_6$H$_4$, 3,5-Cl$_2$C$_6$H$_3$,1-naphthyl, Me$_3$Si; $\mathrm{R^2}$ = H, Me, Et, *p*-tolyl, ^{t}Bu, 4-^{t}BuC$_6$H$_4$) and silaamidinate ligands $[(\mathrm{R^3N})_2\mathrm{SiMe_2}]^{2-}$ ($\mathrm{R^3}$ = ^{t}Bu, 2,6-^{i}Pr$_2$C$_6$H$_3$) have received considerable attention as powerful ligands to construct a variety of low-valent main-group and transition-metal complexes.[8−11] In 2006, Liu and co-workers synthesized silyl-linked bis(amidinate) ligands, in which amidinate and silaamidinate functionalities have been combined into one.[12] As tetradentate ligands, the silyl-linked bis(amidinate) ligands are potential candidates to synthesize tetranuclear metal complexes. Inspired by Liu's work, we have prepared a silyl-linked monoamidinate ligand as a potential tridendate ligand to stabilize polynuclear metal complexes in a linear fashion. In this contribution, we describe the synthesis and characterization of di-, tri-, and tetranuclear copper(I)

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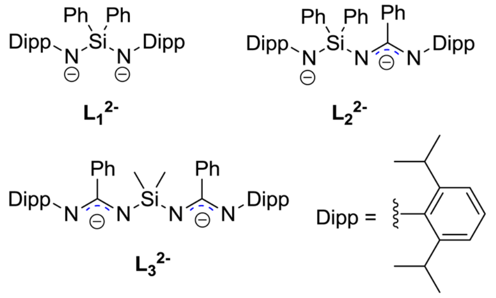
complexes with metal−metal interactions supported by a series of silaamidinate ligands (Chart 1).

Chart 1. Silaamidinate, Silyl-Linked Monoamidinate, and Silyl-Linked Bis(amidinate) Ligand Anions



■ EXPERIMENTAL SECTION

Materials, Syntheses, and Characterization. All manipulations were carried out under a purified nitrogen atmosphere using modified Schlenk techniques or in a dinitrogen-gas glovebox unless otherwise indicated. Et_2O, *n*-hexane, toluene, and tetrahydrofuran (THF) were distilled under a nitrogen atmosphere from sodium benzophenone prior to use. $H_2[L_1]$, $Li_2[L_2]$, and $Li_2[L_3]$ were prepared by literature methods.[12,13] Benzonitrile, 2,6-diisopropylaniline, dichlorodimethylsilane, and dichlorodiphenylsilane were purchased from Alfa Aesar. CuI was purchased from Sigma-Aldrich. *n*-Butyllithium (2.5 M in hexane) was purchased from J&K Scientific Ltd. KH and 18-C-6 was purchased from Aladdin Industrial Inc. Chemicals were directly used without further purification. Deuterated solvents C_6D_6 was dried over activated molecular sieves (4 Å) and vacuum-transferred before use. NMR spectra were recorded on a Bruker 400 MHz spectrometer at 298 K. UV−vis spectra were recorded in a hexane solution using a UV-3600 UV−vis−near-IR spectrometer from Shimadzu. IR spectra were obtained on a Nicolet 6700 in the range of 4000−500 cm^{-1}.

Synthesis of $Li_2[L_2]$·3THF. To a solution of $H_2[L_1]$ (5.35 g, 10 mmol) in THF (50 mL) was slowly added *n*-BuLi in hexane (2.5 M, 8 mL, 20 mmol) at 0 °C. The reaction mixture was stirred at room temperature for 4 h, and then PhCN (1.03 g, 10 mmol) in 5 mL of THF was added at 0 °C. After stirring at room temperature overnight, the reaction solution was concentrated to obtain the desired compound as a colorless solid. Yield: 5.4 g (62%). ^1H NMR (400 MHz, C_6D_6): δ 8.07 (d, J_{HH} = 6.4 Hz, 4H, Ar), 7.37−7.31 (m, 4H, Ar), 7.26−7.19 (m, 6H, Ar), 7.02−6.93 (m, 4H, Ar), 6.88 (t, J_{HH} = 7.6 Hz, 2H, Ar), 6.78 (t, J_{HH} = 7.2 Hz, 1H, Ar), 4.21−4.15 (m, 2H, C*H*), 3.43−3.36 (m, 2H, C*H*), 2.96 (t, J_{HH} = 6.4 Hz, 12H, OCH_2 of THF), 1.47 (d, J_{HH} = 6.4 Hz, 12H, 3,4-2CH_2 of THF), 1.13−1.05 (m, 24H, CH_3). Anal. Calcd for $Li_2[L_2]$·3THF: C, 76.26; H, 8.51; N, 4.85. Found: C, 76.61; H, 8.64; N, 4.53.

Synthesis of Complex 1. To a solution of $H_2[L_1]$ (53.5 mg, 0.1 mmol) in THF (3 mL) was slowly added KH (32.1 mg, 0.2 mmol). The reaction mixture was stirred for 3 h and was then filtered to remove any insoluble. CuI (19.0 mg, 0.1 mmol) and 18-C-6 (52.9 mg, 0.2 mmol) were added and stirred overnight. The resulting mixture was concentrated to dryness and extracted with toluene (3 mL). After filtration, the filtrate was layered with *n*-hexane to give complex **1** as yellowish crystals. Yield: 32 mg (33%).

Synthesis of Complex 2. The mixture of $Li_2[L_2]$·3THF (86.6 mg, 0.1 mmol) and CuI (28.5 mg, 0.15 mmol) in 3 mL of THF was stirred at room temperature overnight. Volatiles were removed in vacuo, and then toluene (3 mL) was added. The resulting mixture was filtered, and the filtrate was layered with *n*-hexane to give complex **2** as yellow crystals. Yield: 43 mg (40%). IR data (cm^{-1}): 3043 (w), 2960 (s), 2868 (m), 1456 (s),1424 (s), 1380 (m), 1360 (w), 1317 (m), 1247 (m), 1202 (m), 1130 (w), 1103 (m), 1044 (m), 968 (m), 953 (m), 914 (w), 892 (w), 827 (w), 825 (w), 783 (m), 732 (m), 695 (m), 656 (w), 603 (w).

Synthesis of Complex 3. The mixture of $Li_2[L_3]$.2THF (77.3 mg, 0.1 mmol) and CuI (38.0 mg, 0.2 mmol) in 3 mL of THF was stirred at room temperature overnight. Volatiles were removed in vacuo, and then Et_2O (4 mL) was added. After filtration, the resulting solution was stored at ambient temperature for several days to give complex **3** as yellow-green crystals. Yield: 51 mg (65%). ^1H NMR (400 MHz, C_6D_6): δ 7.34 (br, 5H, Ar), 7.27−7.24 (m, 2H, Ar), 7.13−7.10 (m, 1H, Ar), 7.03 (br, 3H, Ar), 6.89 (s, 8H, Ar), 6.86−6.82 (m, 7H, Ar), 6.73 (t, J_{HH} = 7.6 Hz, 3H, Ar), 3.76−3.68 (m, 8H, C*H*), 3.29 (q, J_{HH} = 14 Hz, 4H, OCH_2CH_3), 1.36−1.22 (m, 48H, CH_3), 1.12 (t, J_{HH} = 7.2 Hz, 6H, OCH_2CH_3), 0.29 (s, 6H, $SiCH_3$), −0.12 (s, 6H, $SiCH_3$). Three protons in the aromatic ring were lost.

X-ray Crystal Structure Determination. Suitable crystals of complexes **1**−**3** were covered in mineral oil (Aldrich). Crystallographic data were collected at 296 K on a Bruker Apex II CCD diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å). Data processing was accomplished with the *SAINT* program.[14] The structures were solved by direct methods and refined on F^2 by full-matrix least squares using *SHELXTL-97*.[15] All non-hydrogen atoms were refined with anisotropic displacement parameters during the final cycles. All hydrogen atoms of the organic molecule were placed by geometrical considerations and were added to the structure factor calculations. A summary of the crystallographic data for complexes **1**−**3** is given in Table 1.

Table 1. Crystal Data and Structure Refinement Details for Complexes 1−3

	1	**2**	**3**
empirical formula	$C_{106}H_{136}Cu_2K_2N_4O_{12}Si_2$	$C_{118}H_{154}Cu_3ILi_2N_6O_7Si_2$	$C_{85}H_{110}Cu_4N_8OSi_2$
CCDC	993732	993733	993734
F_W	1919.65	2156.05	1570.15
cryst syst	monoclinic	monoclinic	orthorhombic
space group	$P2_1/c$	$C2/c$	*Pbca*
a (Å)	14.9799(7)	17.4633(13)	17.0525(12)
b (Å)	18.3062(9)	41.433(3)	21.5547(16)
c (Å)	19.7665(9)	17.0997(14)	47.094(3)
α (deg)	90	90	90
β (deg)	111.134(1)	98.686(2)	90
γ (deg)	90	90	90
V ($Å^3$)	5055.9(4)	12230.7(17)	17310(2)
Z	2	4	8
T (K)	296(2)	296(2)	296(2)
λ(Mo Kα) (Å)	0.71073	0.71073	0.71073
F(000)	2040	4536	6624
ρ_{calcd} (Mg/m^3)	1.261	1.171	1.205
μ(Mo Kα), mm^{-1}	0.588	0.840	1.043
R_1/wR_2 [$I > 2\sigma(I)$][a]	0.0543/0.1401	0.0773/0.1986	0.0741/0.1845
R_1/wR_2 (all data)	0.0902/0.1599	0.1995/0.2624	0.1883/0.2412

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

■ RESULTS AND DISCUSSION

Synthesis, Characterization, and Structure of Complexes 1−3. Di-, tri-, and tetranuclear copper(I) complexes, labeled as **1**−**3**, respectively, were afforded by the reaction of A_2L (A = K or Li) with CuI in a molar ratio of 1:1, 1:1.5, and 1:2 (Scheme 1). The molecular structures of complexes **1**−**3** were characterized by single-crystal X-ray diffraction. The

Scheme 1. Synthesis of Complexes 1−3

$$2\,K_2[L_1] + 2\,CuI \xrightarrow{18\text{-}C\text{-}6} (K\text{-}18\text{-}C\text{-}6)_2\,[Cu_2(L_1)_2] + 2\,KI$$

1

$$2\,Li_2[L_2] + 3\,CuI \longrightarrow (Li_2I)\,[Cu_3(L_2)_2] + 2\,LiI$$

2

$$2\,Li_2[L_3] + 4\,CuI \longrightarrow [Cu_4(L_3)_2] + 4\,LiI$$

3

crystallographic data and selected bond distances and angles for complexes **1**−**3** are given in Tables 1 and 2, respectively.

As shown in Figure 1, the complex anion in **1** consists of two copper centers and silaamidinate ligands. Each copper atom is coordinated by two nitrogen atoms from two silaamidinate ligands with a Cu−N mean distance of 1.887 Å. The distance of Cu−Cu in complex **1** is 2.5998(7) Å, which is shorter than the sum of the van der Waals radii of two copper atoms (2.8 Å).[16]

The complex anion of **2**, shown in Figure 2, contains a Cu_3 unit surrounded by two silyl-linked monoamidinate ligands that adopt trans structure. The Cu_3 unit is close to a collinear structure [Cu2−Cu1−Cu2 = 173.62(6)°] and can be divided into two outer and one central copper(I) ions, in which each outer copper(I) ion is bonded to an amidinato nitrogen atom and a silaamidinato nitrogen atom from different silyl-linked monoamidinate ligands; the central copper(I) ion is coordinated by two nitrogen atoms from two silyl-linked monoamidinate ligands. The mean distance of Cu2−N is 1.850 Å, shorter than that of Cu1−N (1.938 Å). The two Cu−Cu distances in complex **2** are equal (2.490 Å), markedly shorter than the Cu−Cu bond length in complex **1**, but slightly longer than those of the linear trinuclear copper(I) anion in $(HNEt_3)[Cu_3(btspda)_2]$ [btspda = *N*,*N*′-bis(*p*-tolysulfonyl)-pyridine-2,6-diaminato; 2.466(1) and 2.468(1) Å].[7b]

Similar to the case for complex **2**, complex **3** is featured with four bonded copper atoms that are coordinated by two silyl-linked bis(amidinate) ligands (Figure 3). The bond angle of Cu2−Cu3−Cu4 [154.95(5)°] is larger than that of Cu1−Cu2−Cu3 [149.04(5)°]. The average bond length of Cu1−N and Cu4−N is 1.871 Å, slightly shorter than that of Cu2−N and Cu3−N (1.896 Å). The distance of Cu2−Cu3 is 2.6232(12) Å, longer than those in complexes **1** and **2**. The Cu1−Cu2 and Cu3−Cu4 mean distance of 2.436 Å in complex **3** is the shortest among the three complexes but slightly greater than the shortest Cu−Cu bond length, 2.348(2) Å, found in linear trinuclear copper(I) complex $[Cu_3(tolN_5tol)_3]$.[7a]

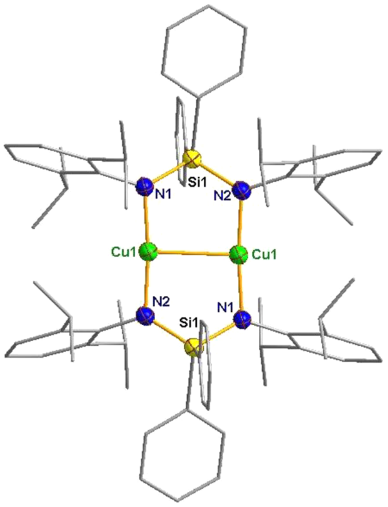


Figure 1. Perspective drawing for the complex anion of **1** with atom labeling. The copper (green), nitrogen (blue), and silicon (yellow) atoms are drawn with 50% probability thermal ellipsoids. The carbon (gray) atoms are drawn as wireframe style, and the hydrogen atoms and disorder are omitted for clarity. Symmetry code: $-x + 1, -y + 1, -z + 1$.

Photophysical Properties. In a previous experimental study,[6a] complexes $[Cu_2(dcpm)_2]\cdot Y_2$ [Y = ClO_4^- and PF_6^-; dcpm = bis(dicyclohexylphosphanyl)methane] display intense absorption at 311 and 307 nm in a CH_2Cl_2 solution. A metal−metal 3d → 4p transition was assigned to these bands, similar to the $\sigma^*(d_{z^2}) \rightarrow \sigma(p_z)$ transition of their analogues $[Au_2(dcpm)_2]^{2+}$ and $[Au_2(dmpm)_3]^{2+}$ [dmpm = bis(dimethylphosphanyl)methane].[17] Detailed assignment was discussed in our previous theoretical study.[18] We applied $[M_2(dpm)_2]^{2+}\cdot 2MeCN$ [M = Cu, Ag, and Au; dpm = bis(diphosphanyl)methane] to model experimental complexes in an acetonitrile solution. $[Cu_2(dpm)_2]^{2+}\cdot 2MeCN$ was calculated to show the lowest-energy absorption at 283 nm, corresponding to experimental 307 and 311 nm of

Table 2. Comparison of Selected Bond Distances (Å) and Angles(deg) for Complexes 1−3[a]

complex	Cu−Cu		Cu−N		Cu−Cu−Cu	
1	Cu1−Cu1#1	2.5998(7)	Cu1−N1	1.892(2)		
			Cu1−N2#1	1.881(2)		
2	Cu1−Cu2	2.4904(9)	Cu1−N2	1.938(5)	Cu2#2−Cu1−Cu2	173.62(6)
	Cu1−Cu2#2	2.4904(9)	Cu1−N2#2	1.938(5)		
			Cu2−N1	1.839(5)		
			Cu2−N3#2	1.861(5)		
3	Cu1−Cu2	2.4325(12)	Cu1−N1	1.880(5)	Cu1−Cu2−Cu3	154.95(5)
	Cu2−Cu3	2.6232(12)	Cu1−N5	1.862(5)	Cu4−Cu3−Cu2	149.04(5)
	Cu3−Cu4	2.4393(12)	Cu2−N2	1.891(5)		
			Cu2−N6	1.897(6)		
			Cu3−N3	1.902(6)		
			Cu3−N7	1.892(6)		
			Cu4−N8	1.860(5)		
			Cu4−N4	1.883(5)		

[a] Symmetry code: #1, $-x + 1, -y + 1, -z + 1$; #2, $-x, y, -z + {}^1/_2$.

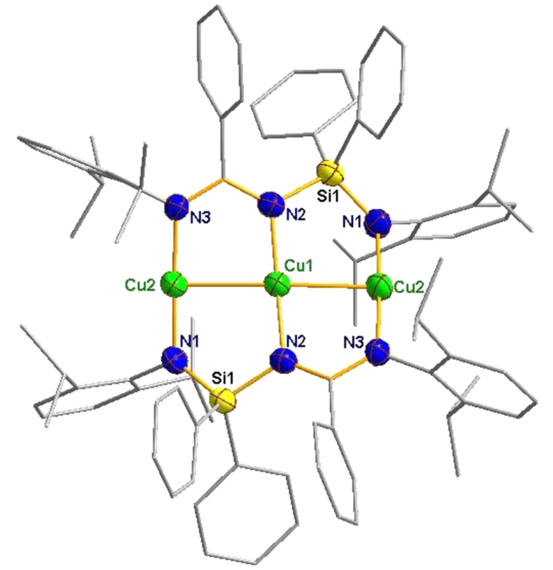


Figure 2. Perspective drawing for the complex anion of **2** with atom labeling. The copper (green), nitrogen (blue), and silicon (yellow) atoms are drawn with 50% probability thermal ellipsoids. The carbon (gray) atoms are drawn as wireframe style, and the hydrogen atoms, solvent molecules, and disorder are omitted for clarity. Symmetry code: $-x$, y, $-z + {}^{1}/_{2}$.

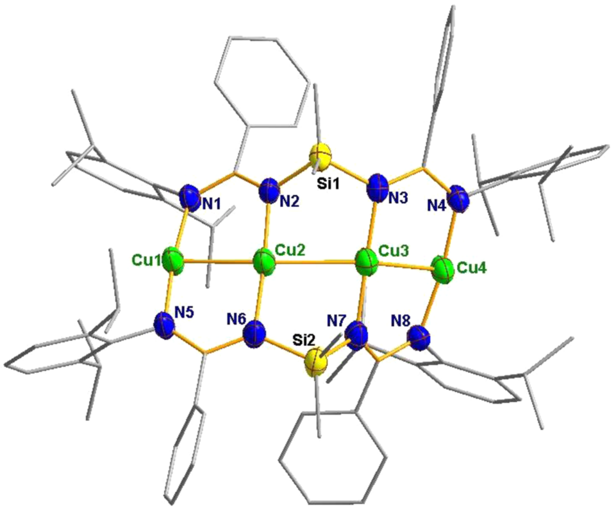


Figure 3. Perspective drawing for the complex **3** with atom labeling. The copper (green), nitrogen (blue), and silicon (yellow) atoms are drawn with 50% probability thermal ellipsoids. The carbon (gray) atoms are drawn as wireframe style, and the hydrogen atoms and solvent molecule are omitted for clarity.

$[Cu_2(dcpm)_2]\cdot Y_2$ (Y = ClO_4^- and PF_6), respectively. A mixed character of $\sigma^*(s,d_{z^2}) \rightarrow \sigma(sp_z)$ and $\sigma(Cu-P) \rightarrow \sigma(sp_z)$ was assigned to these low-energy absorptions, in contrast to the pure metal-centered $\sigma^*(s,d_{z^2}) \rightarrow \sigma(sp_z)$ transition of analogous $[M_2(dpm)_2]^{2+}\cdot 2MeCN$ (M = Au and Ag).

In the present study, complexes **1**−**3** were measured to exhibit lowest-energy absorption at 280, 281, and 296 nm, respectively (Figure S1 in the Supporting Information, SI). A pronounced red shift of the absorption wavelength is found from bi- and trinuclear to tetranuclear copper complexes. Considering previous experimental and theoretical studies, we assigned these absorptions to $\sigma^*(s,d_{z^2}) \rightarrow \sigma(sp_z)$ and $\sigma(Cu-N) \rightarrow \sigma(sp_z)$ character. Because the Cu−N bond has more covalency than Cu−P, the σ(Cu−N) bond shall have more participation in its low-energy absorption. This more participation may cause a shorter absorption band in our complex **1** (280 nm) than in $[Cu_2(dcpm)_2]\cdot Y_2$ [Y = ClO_4^- (311 nm) and PF_6^- (307 nm)].

Density Functional Theory (DFT) Calculations. In this work, we have fully optimized tri- and tetranulcear copper complexes. The GGA-PBE functional[19] was applied in these calculations. All-electron correlation-consistent Gaussian basis sets of double-ζ-polarized quality[20] (labeled as DZP) were used. We applied a scalar relativistic four-component all-electron approach[21,22] to describe relativistic effects. In the calculations, a little structural simplification by replacing Dipp (Chart 1) with a phenyl group was applied to save computational cost. So, **2a** and **3a** represent real complexes **2** and **3**, respectively. Computational details are given in the SI. The binuclear complex **1** was not considered because the GGA-PBE functional used underestimates the Cu−Cu bonding.

Optimized geometry parameters (Table S4 in the SI) are in good agreement with those found by X-ray crystallography: for **2a**, $Cu_{out}-Cu_{cent}$ = 2.443 Å, $Cu_{out}-N$ (av) = 1.879 Å, $Cu_{cent}-N$ = 1.913 Å, and $Cu_{out}-Cu_{cent}-Cu_{out}$ = 173.7° (Cu_{cent} = Cu1; Cu_{out} = Cu2); for **3a**, $Cu_{out}-Cu_{inn}$ = 2.432 Å, $Cu_{inn}-Cu_{inn}$ = 2.553 Å, $Cu_{out}-N$ (av) = 1.887 Å, $Cu_{inn}-N$ = 1.902 Å, and $Cu_{inn}-Cu_{inn}-Cu_{out}$ = 146.7° (Cu_{inn} = Cu2, Cu3; Cu_{out} = Cu1, Cu4). It is shown that the calculated Cu−Cu distances are close to the experimental values. Moreover, both experimental results and theoretical calculations indicate strong metal−metal attractive interaction, which is supposed to be repulsive between positive copper(I) ions.

To provide insight into the Cu^I-Cu^I attraction, we calculated electronic structures of polynuclear **2a** and **3a**. Considering that complexes **2** and **3** were experimentally synthesized in the solid state, the environmental effect appears to affect their electronic properties. Thus, we used the conductor-like screening model (COSMO) to simulate the environmental effects. Close inspection of the electronic orbitals finds several strong σ- and π-bonding orbitals present in a much lower energy area. For example, three two-electron three-center σ bonds of **2a** are localized on orbitals H-33, H-35, and H-36. They are greatly stable because they are 2.75−2.90 eV energetically lower than the HOMO (see Table S5 in the SI). Two-electron three-center π bonds come from H-18 and H-19 orbitals. Similar cases are found for **3a.** Partial bonding orbitals of the two complexes are presented in Figure 4. Therefore, these strong and stable σ- and π-bonding orbitals have contributed to the Cu−Cu attractive interaction and short distances.

The X-ray structures show a Cu−Cu−Cu colinear structural feature in the trinuclear complex **2** (173.6°) but bent ones in the tetranuclear complex **3** (152.0°, mean value). This feature has been well reproduced by optimizations of **2a** (173.7°) and **3a** (146.7°). From a structural point of view, we would question the ligand effects first. One can see that two L_2^{2-} ligands of **2** are trans each other. If two L_2^{2-} ligands adopt a cis arrangement, the obtained complex resembles parts of the tetranuclear **3**. Thus, we theoretically design a complex **2b**, featured with the *cis*-L_2^{2-} structure. Isomer **2b** was optimized to be 3.01 kJ/mol higher in energy than isomer **2a.** A bent Cu−Cu−Cu angle at 155.2° was calculated for **2b** (Figure S9 and Table S4 in the SI), which directly evidence that the ligand arrangement is one of the key factors affecting the complex structure.

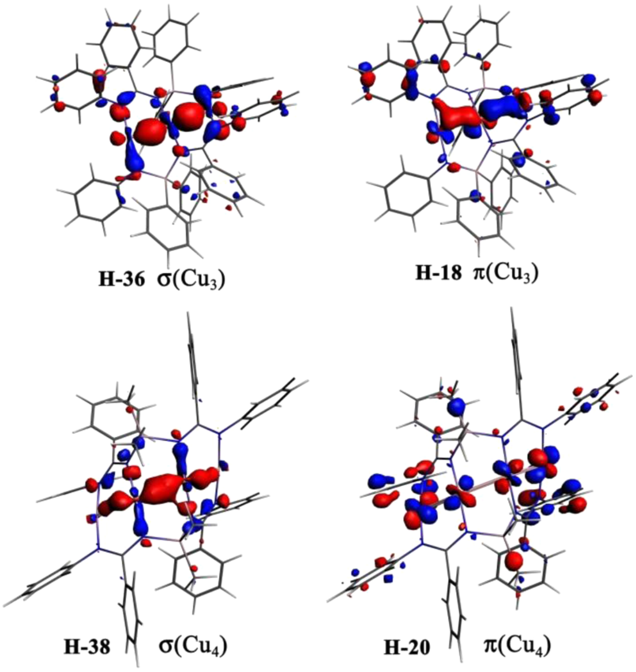


Figure 4. Diagrams of σ- and π-bonding orbitals of **2a** and **3a**.

In addition, the metal−metal bonding properties may affect the structural feature of the complex. **2a** was calculated to show two-electron three-center σ- and π-bonding orbitals, as can be seen in Figure 4. This electron-delocalizing feature favors a linear Cu−Cu−Cu structure. However, we found that two-center bonds localized on two *adjacent* copper(I) atoms are dominant in the occupied orbitals of **3a** such as H-3, H-16, H-23, and H-27 (Table S5 in the SI). For example, the H-27 orbital is featured with two σ bonds, each of which is localized between *adjacent* Cu_{out} and Cu_{inn} (Figure 5). Moreover, the two $\sigma(Cu_{out}-Cu_{inn})$ orbitals are overall antibonding, $[\sigma(Cu_{out}-Cu_{inn}) + \sigma(Cu_{out}-Cu_{inn})]^*$. Therefore, **3a** prefers a bent Cu−Cu−Cu feature because of dominant two-center-localized bonds between two *adjacent* copper(I) atoms in occupied orbitals.

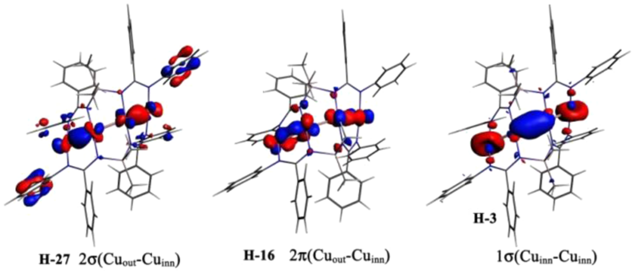


Figure 5. Diagrams of two-center σ- and π-bonding orbitals of **3a**. Cu_{out} = Cu1, Cu4; Cu_{inn}= Cu2, Cu3.

As stated in the literature,[23] the long intramolecular closed-shell interactions in $[Ag_4Y_2]^{2+}$ and $[Au_4Y_2]^{2+}$ [Y = 3,5-bis[(*N*-methylimidazolyl)methyl]pyrazole] were attributed to the population of the bonding, nonbonding, and antibonding combinations of the *ns* atomic shells in the $[M_4]^{4+}$ core. Herein, we also calculated the Mulliken population of copper atoms in complexes **2a** and **3a**. As seen in Table S6 in the SI, electronic configurations $3d^{9.714}s^{0.574}p^{0.51}$ and $3d^{9.694}s^{0.684}p^{0.34}$ were calculated for the inner and outer copper(I) atoms of **2a**, respectively. Quite similar electronic configurations, $3d^{9.704}s^{0.554}p^{0.46}$ and $3d^{9.714}s^{0.664}p^{0.30}$, have been obtained for copper(I) atoms of **3a**. This rationalizes that tri- and tetranuclear copper complexes possess close Cu−Cu distances between 2.44 and 2.62 Å (see Table S4 in the SI). The addition of one more copper atom from **2a** to **3a** slightly shortens the $Cu_{out}-Cu_{inn}$ distance but results in the elongation of the $Cu_{inn}-Cu_{inn}$ distance simultaneously. About 2.21 and 2.73 electron transfers were found in these two complexes, reflecting the covalent character between their metal centers and ligands.

Complex **2a′** was also taken into account to investigate the role of the bridging silicon atoms in the ligands. **2a′** is analogous to **2a**, but they differ in their bridging ligands. The former has a carbon bridging atom (N−C−N), while the latter possesses a silicon one (N−Si−N). The Cu^I-Cu^I distance was calculated to be 2.342 Å for **2a′**, about 0.10 Å shorter than the one for **2a**. This reveals that the inclusion of the silicon atom in the **2a** ligands plays a role in decreasing the electronic delocalization properties.

■ CONCLUSION

In summary, di-, tri-, and tetranuclear copper(I) complexes with metal−metal interactions have been prepared by rational length control of silaamidinate ligands. The bond lengths of Cu−Cu decrease with increasing metal atom chain from complexes **1** to **3**. The spectroscopic properties of complexes **1**−**3** have also been studied. The relativistic DFT calculations have rationalized the short Cu−Cu distances by the metal−metal attractive interaction that comes from the strong and stable σ- and π-bonding orbitals. Both ligand and electronic effects result in a linear Cu−Cu−Cu arrangement in complex **2** and a bent one in complex **3**.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

X-ray crystallographic data in CIF format, selected bond lengths and angles, UV−vis absorption spectra, luminescence measurement, computational details, and Cartesian coordinates. This material is available free of charge via the Internet at http://pubs.acs.org.

■ AUTHOR INFORMATION

Corresponding Authors

*E-mail: panqjitc@163.com.
*E-mail: szm@ciac.ac.cn. Web page: http://zhongmingsun.weebly.com/.

Author Contributions

[§]J.-F.L. and X.M. contributed equally.

Notes

The authors declare no competing financial interest.

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