Asymmetric dinuclear copper(I) complexes of bis-(2-(2-pyridyl)ethyl)-2-(*N*-toluenesulfonylamino)ethylamine with short copper–copper distances†‡

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Addition of two equivalents of CuCl to deprotonated bis-(2-(2-pyridyl)ethyl)-2-(*N*-toluenesulfonylamino)ethylamine (PETAEA) and its derivatives yielded new types of dinuclear Cu(I) complexes, Cu(μ-PETAEA)CuCl, Cu(μ-PEMAEA)CuCl, and Cu(μ-PENAEA)CuCl (PEMAEA is the 4-methoxyphenyl derivative of PETAEA and PENAEA is the 4-nitrophenyl derivative), exhibiting a four coordinate N_4Cu center, a two coordinate NCuCl center, and a metal–metal distance within the range of 2.6572(8) to 2.6903(3) Å. Analysis of the covalent radii for four coordinate and two coordinate copper(I), the acute copper–nitrogen–copper angles, and density functional theory (DFT) calculations suggest a weak attraction between the two copper atoms. The complexes apparently formed in a two-step process with the formation of the tetracoordinate mononuclear complex preceding the coordination of a second equivalent of CuCl to the lone pair of the sulfonamidate ligand.

Introduction

Of the group of controlled/living radical polymerizations, atom transfer radical polymerization (ATRP)[1–5] is the subcategory that utilizes transition metal catalyzed halogen atom transfer to activate the dormant alkyl halide chain ends and to deactivate the propagating radicals. For practical applications in the laboratory, mixtures of ligand and metal salts are used to form the catalyst *in situ*. The solution chemistries of such catalyst mixtures are seldom well-understood, and it is quite possible that the compositions and structures of the complexes involved in the atom transfer chemistry may be different than assumed. A current line in ATRP research is to prepare coordination complexes whose solid state and solution structures are known and then to apply them to studying fundamental aspects of the polymerization catalysis.[6–10] While some ligand–metal combinations have yielded mononuclear complexes capable of catalyzing atom transfer, other combinations have yielded dinuclear complexes and more complicated structures.[6,10] Here, we report the unanticipated coordination of copper(I) chloride to copper(I) complexes reported in prior studies: ligand = bis-(2-(2-pyridyl)ethyl)-2-(*N*-toluenesulfonylamino)ethylamine (PETAEA).[8] The resulting new type of dinuclear Cu(I) complex exhibits linear and tetrahedral coordination environments and contains a short metal–metal distance.

Di- and polynuclear copper(I) complexes are interesting in their own right as they sometimes display remarkable structures with short metal–metal distances in the range of 2.35 Å to 2.80 Å.[11] Additionally, close copper–copper contacts have been observed in copper(I) containing metalloproteins.[12–14] There has been much debate over the existence of "cuprophilic" interactions to account for such distances or if geometric constraints of the ligand sphere dictate the copper–copper distance.[15–17] These short metal–metal distances are found in complexes derived from the clustering of monomeric species[14,18–23] or in complexes with bridging ligands that bring the metal centers in close proximity. In the latter subset, many of the complexes have symmetric structures in which each metal center has the same ligand set.[17,24–37] The remainder of the complexes contain copper centers with different coordination environments, either as a result of additional ligand coordination breaking the symmetry of a parent complex[38–40] or due to the supporting ligand enforcing different coordination environments for the metal centers.[41] There are also two examples of unsupported close copper–copper contacts between complexes in solid state structures.[42,43]

Experimental

Materials

CuCl (Acros) was purified until colorless by grinding into a fine powder using a mortar and pestle, stirring in glacial acetic acid, consecutive washes of absolute ethanol and diethyl ether, and removal of volatile materials under vacuum. All other materials were purchased from commercial sources and purified using standard techniques. All syntheses, reactions, and polymerizations were conducted under inert atmospheres using dry box or Schlenk techniques. PETAEA, Na(PETAEA) and Cu(PETAEA) were prepared according to the procedures of Goodwin *et al.*[8]

Characterizations

$^{13}C\{^1H\}$ 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

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‡ Electronic supplementary information (ESI) available: Crystallographic data for complexes **1** to **3**, and molecular orbital plots for the LUMO and top 11 HOMOs from the DFT calculations performed on complex **1**. See DOI: 10.1039/b705684b

were obtained with a Mattson Galaxy Series FTIR 3000. UV-Vis spectra were recorded on an HP 8452A spectrophotometer in THF solvent. Elemental analyses were performed by Midwest Microlabs.

Synthesis of Cu(PETAEA)/Cu(μ-PETAEA)CuCl mixture. Na(PETAEA) (1.23 g, 2.75 mmol) was dissolved in THF (75 mL). Next, CuCl (0.273 g, 2.80 mmol) was added and the solution was heated slightly to aid complexation. The orange solution was cannula filtered away from the white solid and volatile materials were removed under high vacuum leaving an orange powder. Some orange powder remained in the original flask indicating very low solubility in the solvent. The orange powder was recrystallized from acetonitrile to give an approximately 50 : 50 mixture of red–orange rhombic crystals and bright yellow needles. No mass was obtained of the mixture of products. X-Ray analysis showed that the red–orange crystals were Cu(I)PETAEA and the yellow needles were Cu(μ-PETAEA)CuCl.

For Cu(μ-PETAEA)CuCl: ^{1}H NMR (400 MHz, CD_3CN): δ 8.64 (d, 2H, $J = 5$ Hz), 7.75 (td, 2H, $J = 2$, 8 Hz), 7.66 (d, 2H, $J = 7$ Hz), 7.28 (d, 2H, $J = 8$ Hz), 7.26 (d, 2H, $J = 8$ Hz), 2.84, (t, 2H, $J = 5$ Hz), 2.78 (br s, 8H), 2.62 (br s, 2H), 2.35 (s, 3H). ^{13}C NMR (100 MHz, CD_3CN): δ 160.9, 151.3, 138.0, 129.8, 127.7, 126.0, 123.3, 57.1, 54.0, 35.3, 21.3. IR (KBr, cm^{-1}): ν 3064 (w), 2951 (m), 2899 (w), 2849 (w), 1596 (m), 1564 (w), 1478 (m), 1440 (m), 1342 (w), 1284 (m), 1282 (m). UV-Vis (THF): $\lambda_{max} = 316$ nm ($\varepsilon = 4770$ M^{-1} cm^{-1}), $\lambda_{max} = 406$ nm ($\varepsilon = 533$ M^{-1} cm^{-1}, shoulder). Elemental analysis: Calculated, C, 47.13%; H, 4.64%; N, 9.56%; Found, C, 46.57%; H, 4.67%; N, 9.62%.

Addition of CuCl to Cu(PETAEA). Cu(PETAEA) (0.139 g, 0.285 mmol) was dissolved in acetonitrile (25 mL), and then CuCl (0.0464 g, 0.469 mmol) was added. The orange solution immediately turned yellow. The yellow supernatant was isolated from excess copper(I) chloride *via* cannula filtration and solvent was removed under vacuum until significant precipitation occurred. The supernatant was removed from the solid by cannula filtration and the remaining yellow powder was dried under vacuum to yield Cu(μ-PETAEA)CuCl (0.0345 g, 21%). ^{1}H NMR, ^{13}C NMR, IR, and UV-Vis data all matched that obtained for Cu(μ-PETAEA)CuCl prepared in the preceding section; Elemental analysis: Calculated, C, 47.13%; H, 4.64%; N, 9.56%; Found, C, 46.85%; H, 4.64%; N, 9.60%.

Complexation of Na(PETAEA) with CuCl in different solvents. Na(PETAEA) was dissolved in the appropriate solvent then CuCl was added in the quantities shown in Table 1. Because of the scale of this reaction, qualitative observations were made without isolating the product. In acetone a red solution was observed; in THF a yellow solution was formed; and in toluene a very pale yellow solution formed.

Synthesis of Cu(μ-PEMAEA)CuCl. Na(PEMAEA) (0.568 g, 1.23 mmol) was dissolved in acetonitrile (50 mL). Next, CuCl (0.233 g, 2.35 mmol) was added. A yellow solution formed and was filtered away from the residual white solid. The solution was partially evaporated under vacuum and yellow crystals formed. The crystals were isolated by cannula filtration to give 0.622 g (88% yield) of yellow needles. ^{1}H NMR (300 MHz, CD_3CN): δ 8.71 (d, 2H, $J = 4$), 7.82 (d, 2H, $J = 5$ Hz), 7.76 (td, 2H, $J =$ 1, 6 Hz), 7.29 (m, 4H), 6.96 (d, 2H, $J = 7$ Hz), 2.81, (t, 2H, $J =$ 6 Hz), 2.82 (br s, 12H) ppm. ^{13}C NMR (75 MHz, CD_3CN): δ 162.4, 160.9, 154.0, 151.4, 138.1, 136.5, 129.7, 126.1, 123.4, 114.5, 56.9, 56.2, 53.876, 46.8, 35.2 ppm. UV-Vis (THF): $\lambda_{max} = 312$ nm ($\varepsilon =$ 3877 M^{-1} cm^{-1}), $\lambda_{max} = 406$ nm ($\varepsilon = 1055$ M^{-1} cm^{-1}, shoulder). Elemental analysis: Calculated, C, 45.88%; H, 4.52%; N, 9.35%; Found, C, 45.94%; H, 4.52%; N, 9.27%.

PENAEA (1.71 g, 3.77 mmol) was dissolved in acetonitrile (60 mL) then NaOH (0.307 g, 7.67 mmol) was added, and the solution was stirred for 2 h while yellow solid formed. Next, CuCl (0.357 g, 3.61 mmol) was added, and the solution was heated to help dissolve the solids. The reaction mixture was stirred overnight, but the product never fully dissolved. The solution was cannula filtered from the remaining solids, and volatile materials were removed under vacuum to give a reddish-brown sticky powder. The product was very difficult to remove from the sides of the flask, so the amount of recovered solid amounted to 0.106 g (9.5% yield). Crystals for X-ray crystallography were grown from a saturated THF solution. ^{1}H NMR (400 MHz, CD_3CN): δ 8.65 (d, 2H, $J =$ 4 Hz), 8.21 (d, 2H, $J = 9$ Hz), 7.99 (d, 2H, $J = 9$ Hz), 7.77 (td, 2H, $J = 2$, 8 Hz), 7.30 (d, 2H, $J = 8$ Hz), 7.29 (d, 2H, $J =$ 8 Hz), 2.92, (br s, 2H), 2.80 (s, 8H), 2.72 (t, 2H, $J = 6$ Hz). ^{13}C NMR (Insufficient solubility). Elemental analysis: Calculated, C, 42.82%; H, 3.92%; N, 11.35%; Found, C, 43.39%; H, 4.13%; N, 11.61%.

X-Ray structure determinations

For complexes **1** and **3**, diffraction data were collected with a Bruker SMART 1000 diffractometer, graphite-monochromated Mo-Kα radiation, and a nitrogen cold stream provided by a CRYO Industries apparatus. Corrections for absorption were applied using the program SADABS 2.10.[44] For complex **2**, diffraction data were collected with a Siemens P4 diffractometer with the use of a copper rotating anode source and Siemens LT-2 low temperature apparatus. A correction for absorption was applied using the program XABS2.[45] The structures were solved by direct methods (SHELXS-97[46]) and refined by full-matrix least-squares on F^2 (SHELXL-97[46]). 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

Table 1

Solvent	Mass of Na(PETAEA)/mg	mmoles of Na(PETAEA)	Mass of CuCl/mg	mmoles of CuCl	Observed color
Acetone	49.8	0.102	10.9	0.110 mmol	Red–orange
THF	50.9	0.105	11.6	0.117 mmol	Yellow
Toluene	51.4	0.106	10.3	0.104 mmol	Pale yellow

Table 2 Summary of crystal structure determinations for complexes **1** to **3**

	Cu(μ-PETAEA)CuCl	Cu(μ-PEMAEA)CuCl	Cu(μ-PENAEA)CuCl
	Complex **1**	Complex **2**	Complex **3**
Formula	$C_{23}H_{27}ClCu_2N_4O_2S$	$C_{23}H_{27}ClCu_2N_4O_3S$	$C_{22}H_{24}ClCu_2N_5O_4S$
Fw	586.08	602.08	617.05
Temp./K	93(2)	133(2)	90(2)
Cryst. system	Triclinic	Triclinic	Triclinic
Space group	$P\bar{1}$	$P\bar{1}$	$P\bar{1}$
Z	2	2	4
a/Å	9.1111(6)	9.5617(12)	8.9933(9)
b/Å	10.8627(7)	9.9875(10)	10.8437(11)
c/Å	13.4127(9)	13.4720(12)	26.491(3)
α/°	68.776(3)	92.187(8)	94.085(3)
β/°	84.102(3)	91.981(9)	98.630(4)
γ/°	87.524(3)	108.049(8)	92.039(3)
V/Å^3	1230.86(14)	1220.9(2)	2544.9(4)
D_{calc}/Mg m^{-3}	1.581	1.638	1.611
μ/mm^{-1}	1.949 (Mo-Kα)	4.233 (Cu-Kα)	1.897 (Mo-Kα)
$R1$ (obs data)[a]	0.0241	0.0628	0.0270
$wR2$ (all data)[b]	0.0646	0.1700	0.0707
GOF	1.04	1.11	1.002

[a] $R1 = \Sigma \| F_o | - | F_c \| / \Sigma | F_o |$. [b] $wR2 = [\Sigma [w(F_o^2 - F_c^2)^2] / \Sigma [(wF_o^2)^2]]^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$, where $P = (F_o^2 + 2F_c^2)/3$.

peaks in the final difference Fourier map for each structure can be found in the data tables located in the ESI.‡ Crystal data and refinement details for the complexes are shown in Table 2.†

Density functional theory calculations

All the DFT calculations were performed at B3LYP/6-31g* level of theory using Gaussian 03 program.[47] The overlap populations and the Wiberg bond orders were computed and analyzed using AOMIX software.[48,49] The plots of molecular orbitals were generated with MOLEKEL graphical interface.[50]

Results and discussion

A dinuclear copper(I) complex of bis-(2-(2-pyridyl)ethyl)-2-(*N*-toluenesulfonylamino)ethylamine (PETAEA) was discovered serendipitously during an attempt to synthesize Cu(PETAEA) using THF solvent rather than CH_3CN. The sodium salt of PETAEA was prepared in THF by treatment of PETAEA with NaH, and then CuCl was added. After crystallization, a mixture of red–orange rhombic crystals and bright yellow needles was obtained. In contrast, when the synthesis was performed using CH_3CN solvent, only the red–orange rhombic crystals of Cu(PETAEA) were isolated. Despite the distinct crystal appearances, the NMR spectra of the two materials were very similar. The yellow needles, complex **1**, were suitable for X-ray analysis, so a molecular structure was obtained (Fig. 1, Table 2). X-Ray analysis also confirmed that the red–orange rhombic crystals were, in fact, Cu(PETAEA).

The structure of complex **1** was an unanticipated dinuclear copper(I) compound with the basic structure of Cu(PETAEA) and an additional equivalent of CuCl coordinated to the free lone pair of the sulfonamidate donor nitrogen. Complex **1** has one copper center with distorted tetrahedral coordination geometry, Cu1, and another with linear coordination geometry, Cu2. Table 3 compares key structural parameters of complex **1** and related

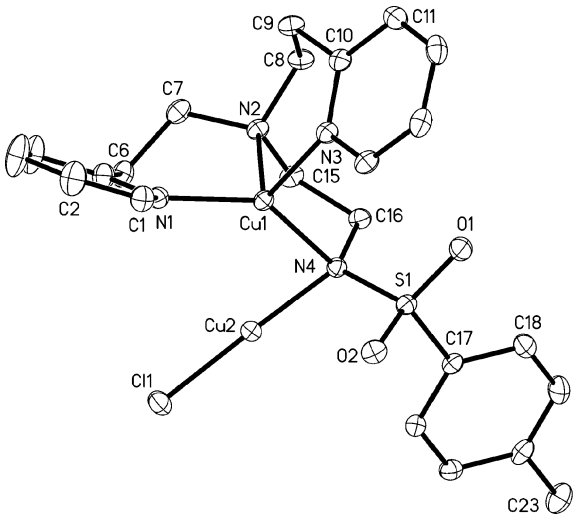


Fig. 1 Molecular structure of Cu(μ-PETAEA)CuCl, complex-**1**. Displacement ellipsoids are drawn at the 50% probability level.

complexes (**2** and **3**, Fig. 2 and 3, Table 2) with the parent complex, Cu(PETAEA). In complex **1** the Cu1–N bond distances for one pyridine nitrogen, N3, and tertiary amine nitrogen, N2, were 0.035 Å and 0.036 Å (respectively) shorter than those found for Cu(PETAEA). The other pyridine nitrogen, N1–Cu1 distance was 0.019 Å longer than that found in the parent complex. The Cu1–N distance for the sulfonamidate nitrogen donor was significantly longer (by 0.137 Å) than that found in Cu(PETAEA). The bond angles between the neutral amine donors N3–Cu1–N2, N2–Cu1–N1, and N3–Cu1–N1 were 3.1°, 0.4°, and 3.2° (respectively) larger than those found in the parent complex. These bond distance and bond angle data were consistent with Cu1 being located closer to the N1–N2–N3 face of the tetrahedral coordination sphere in complex **1** *versus* the parent complex. This repositioning of the copper center would open up extra space to accommodate the additional steric demands imposed by the CuCl unit.

Table 3 A comparison of key bond lengths (Å) and bond angles (°) between the parent complex, Cu(PETAEA), and complexes **1** through **3**

	Cu(PETAEA)	Complex **1**	Complex **2**	Complex **3**
N1–Cu1	1.957(4)	1.9755(15)	1.990(4)	1.9797(17)
N3–Cu1	2.087(4)	2.0517(15)	2.050(4)	2.0264(17)
N2–Cu1	2.203(4)	2.1671(15)	2.154(3)	2.1456(16)
N4–Cu1	1.979(4)	2.1158(14)	2.126(3)	2.1980(16)
N4–Cu2	N/A	1.9054(15)	1.900(3)	1.8988(17)
Cl1–Cu2	N/A	2.1060(5)	2.0960(12)	2.1068(6)
Cu1–Cu2	N/A	2.6903(3)	2.6572(8)	2.6730(4)
Cu1–N4–Cu2	N/A	83.81(5)	82.39(13)	81.10(6)
N3–Cu1–N2	96.43(16)	99.48(6)	99.39(15)	102.61(7)
N2–Cu1–N1	100.35(17)	100.75(6)	100.50(14)	101.77(7)
N3–Cu1–N1	106.11(17)	109.29(6)	109.96(14)	116.30(7)
N4–Cu2–Cl1	N/A	174.18(5)	174.12(11)	176.67(5)
N3–Cu1–N4	107.93(17)	108.60(6)	109.94(14)	107.91(6)
N2–Cu1–N4	84.69(16)	85.04(5)	85.75(13)	82.60(6)
N1–Cu1–N4	144.77(17)	140.05(6)	137.90(14)	133.03(6)

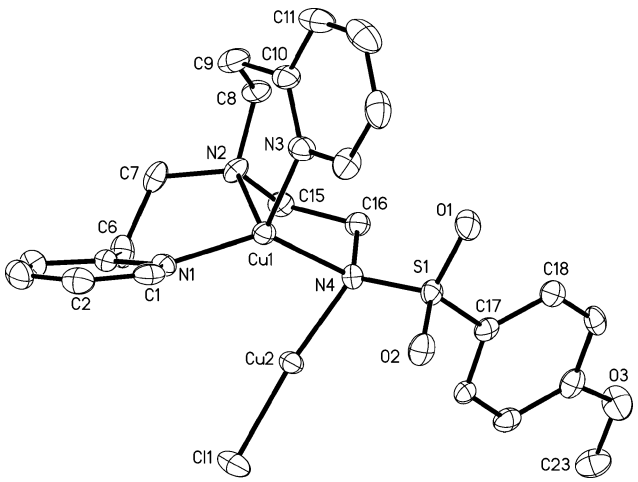


Fig. 2 Molecular structure of Cu(μ-PEMAEA)CuCl, complex **2**. Displacement ellipsoids are drawn at the 50% probability level.

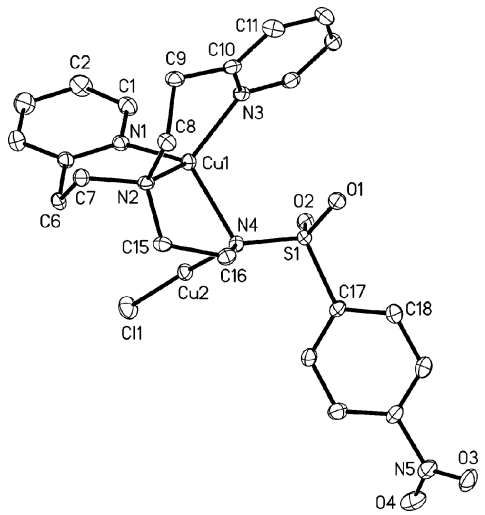


Fig. 3 Molecular structure of Cu(μ-PENAEA)CuCl, complex **3**. Displacement ellipsoids are drawn at the 50% probability level.

The second copper(I) center, Cu2, exhibited a linear coordination geometry with a Cu2–N4 bond distance of 1.9054(15) Å and a Cu2–Cl1 bond distance of 2.1060(5) Å. The Cu–Cl bond distance is very similar to that found for the dichlorocuprate anion, 2.107(1) Å,[51] and the Cu–N bond distance is similar to the amidate nitrogen–copper bond distance of 1.875(2) Å found in another heterocuprate anion containing complex.[10] The N4–Cu2–Cl1 bond angle of 174.18(5)° falls short of 180° for linear geometry but is well within the range of bond angles found for dihalocuprate anions, as these anions are known to distort slightly from linear geometry in order to accommodate crystal packing forces.[51]

The bond distances and angles about the copper centers in complex **1** are most consistent with a structure comprised of a tetrahedrally coordinated copper(I) cation bridged by a dative interaction with the sulfonamidate nitrogen lone pair to a two coordinate heterocuprate anion (Fig. 4). This conclusion is also supported by the significantly longer N4–Cu1 distance in complex **1** *versus* Cu(PETAEA), which is most likely due to both the delocalization of the sulfonamidate negative charge onto the chloride ligand in the heterocuprate section and the greater steric bulk of the three-coordinate *versus* two-coordinate sulfonamidate nitrogen donor. Two derivatives of complex **1** were prepared: Cu(μ-PEMAEA)CuCl (PEMAEA is the 4-methoxyphenyl derivative of PETAEA), complex **2**, and Cu(μ-PENAEA)CuCl (PENAEA is the 4-nitrophenyl derivative of PETAEA), complex **3**. The acidity of the ligand's sulfonamide group varied with substitution as follows: $-CH_3$, $pK_a = 10.17$; $-OCH_3$, $pK_a = 10.22$; $-NO_2$, $pK_a = 9.14$.[52] Assuming that the pK_a difference between PETAEA and PEMAEA is too small to have a significant impact on the complex's structure and considering only differences between PETAEA and PENAEA, the N4–Cu1 distance correlated inversely with the sulfonamide acidity, but there was little difference in N4–Cu2 distances between the three complexes. The data were consistent with an increase in electron withdrawing ability of the ligand weakening the dative interaction between the sulfonamide nitrogen and the tetrahedrally coordinated copper center but not affecting the covalent bonding between the sulfonamide nitrogen and the linearly coordinated copper center to a significant degree. The Cu1–Cu2 distance also did not appear to correlate with the pK_a of the ligand's sulfonamide group.

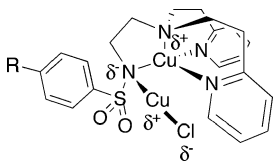


Fig. 4 Drawing of complex **1** showing a probable distribution of partial charges within the complex.

The Cu1–Cu2 distance in complex **1** was 2.6903(3) Å. A Cambridge Crystallographic Database search for dinuclear copper(I) complexes indicated that this distance was well within the range of Cu–Cu distances for which ligand-supported "cuprophilic" interactions have been proposed. This distance was also less than the interatomic distances for unsupported short copper–copper distances observed in solid state structures (2.905(3) Å[43] and 2.8924(3) Å[42]). Thus, a question raised by the novel structure of

complex **1** was what kind of interaction exists between the two copper centers?

The covalent radius of linear copper(I) has been measured at 1.13 Å.[53] This value (1.13 Å) added to the covalent radius of chlorine (0.995 Å) yields a calculated copper(I) chlorine bond distance of 2.125 Å, which is slightly longer than the experimentally determined distance of 2.1060(5) Å in complex **1** and another reported (NCuCl) heterocuprate Cu(I)–Cl distance of 2.103(1) Å.[10] A reasonable model compound to estimate a radius for tetracoordinate Cu(1) in complex **1** would be a homoleptic, tetrahedral copper(I) ion with amine/pyridyl ligands: $Cu(pyridine)_4^+$.[54] The copper–nitrogen bond distance in this complex is 2.046(4) Å, and subtraction of the covalent radius of nitrogen (0.75 Å) yields a radius of 1.296 Å for the copper(I) ion. The sum of the radii for Cu(1) and Cu(2), as estimated, is 2.426 Å which is less than the experimental separation of 2.6903(3) Å.

While this estimate for the sum of the radii of Cu(1) and Cu(2) would suggest that a bonding interaction between Cu(1) and Cu(2) is not necessary to account for the structure of complex **1**, the acute Cu1–N4–Cu2 angle of 83.81(5)° is substantially less than would be expected for pyramidal geometry about N4. The acute angle would support the existence of an attractive interaction between the metal centers. Such acute copper–ligand–copper angles have also been observed in V-geometry ligand bridged dicopper(I) complexes such as $Cu_2(Si(SiMe_3)_3)_2BrLi(thf)_3$ (60.6°, $d_{Cu\text{–}Cu}$ = 2.369(1) Å)[22] and calculated for $Se(CuPH_3)_2$ (75.4°, $d_{Cu\text{–}Cu}$ = 2.695 Å) and $Se(CuPMe_3)_2$ (74.9°, $d_{Cu\text{–}Cu}$ = 2.690 Å).[55]

In order to assess the degree of the bonding interaction between the two copper centers, we performed density functional theory (DFT) calculations on complex **1**, as well as on two other molecular systems exhibiting very short Cu(I)–Cu(I) distances. The details of the quantum mechanical calculations are reported in the Experimental section. Complexes with Cu(I)–Cu(I) distances as short as 2.412 Å are well known;[56] however, the existence of weak bonding between the formally closed shell d^{10} centers is still subject to debate. Despite several theoretical studies that addressed these so called "cuprophilic" interactions, no clear picture of this unusual metal–metal bonding is yet available. Early extended Hückel calculations by Mehrotra and Hoffmann[15] showed the importance of the copper $(n-1)d-ns/np$ atomic orbital mixing in stabilizing the Cu–Cu interaction. The electron correlation effects that contribute to this type of weak bonding were also pointed out by Pyykkö[11] as a possible contributing factor to the ability of Cu(I) centers to cluster. The DFT study by Hermann, Boche and Schwerdtfeger[57] showed that the strength of cuprophilic interactions depends on the nature of the other ligands and that the strength of the Cu–Cu interaction increases with increasing σ-donor and π-acceptor capability of the ligands. Vega and Saillard[58] have studied Cu(I)–Cu(I) interactions in a series of Cu(I) clusters by means of DFT and concluded that the extent of the metal–metal interaction mainly depended on the electron donor ability of the attached ligand. It has also been shown that intermolecular forces can enhance the metal–metal interaction.[37]

The DFT calculations performed on complex **1** using the geometry extracted from the X-ray crystal structure showed non-negligible molecular orbital (MO) overlap between the hybrid d_{z^2} and $d_{x^2-y^2}$ orbitals of the two copper centers. Analysis of the wave function coefficients for HOMO-4 and HOMO-5 (Fig. 5) showed that these hybrid MO's are mainly composed of the Cu d_{z^2} and $d_{x^2-y^2}$ orbitals but also exhibited some additional s character. The calculated Wiberg bond order (BO) for this Cu(I)–Cu(I) interaction is relatively small (0.18) but not negligible.

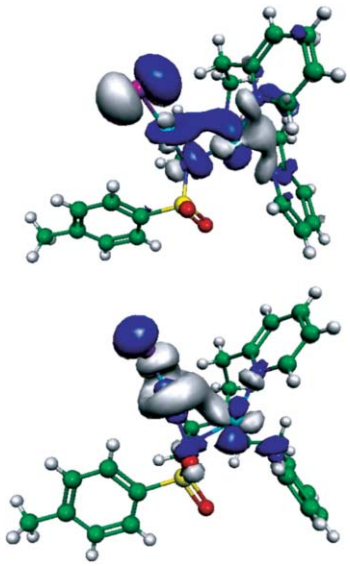
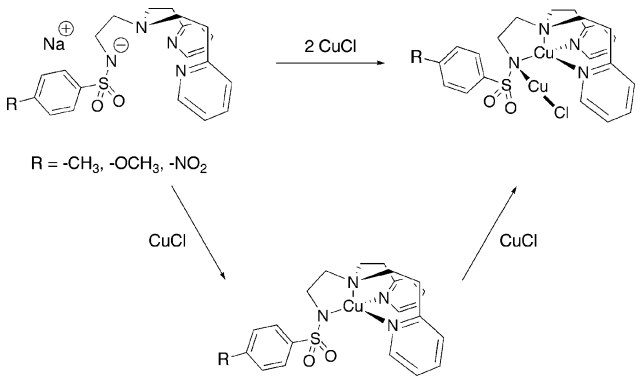


Fig. 5 Molecular orbital plots for HOMO-4 (top) and HOMO-5 (bottom) for DFT calculations performed on complex **1**.

In order to compare this interaction to similar Cu–Cu bonding in other known compounds exhibiting short Cu(I)–Cu(I) distances, we performed analogous DFT calculations on X-ray extracted coordinates of Cu_2R_2 (R = 2-$C(SiMe_3)_2C_5H_4N$)[56] and $[Cu_2(dcpm)_2](ClO_4)_2$ (dcpm = bis(dicyclohexylphosphanyl)-methane).[59] For the calculation involving the latter compound, the bulky cyclohexyl groups were replaced by methyl groups (dmpm). The metal–metal separations in these species are 2.412 and 2.639 Å, respectively. The calculated BO for $[Cu_2(dmpm)_2]^{2+}$ (which exhibits Cu–Cu distance similar to complex **1**) is 0.49, while for Cu_2R_2 the calculated Cu–Cu BO is 0.79. In general, although the Cu–Cu interaction between two d^{10} closed shell ions possesses a formal bond order of 0, the non-negligible extent of the overlap between the hybrid metal 3d/4s orbitals results in weak bonding with apparent bond orders[60] between 0 and 1. Such bonding should be therefore characterized as being a relatively weak interaction, somewhere between van der Waals forces and a real atomic bond in a purely chemical sense.

This structure of complex **1** suggested a synthetic pathway in which Cu(PETAEA) was formed first, and then an additional equivalent of CuCl was incorporated from the reaction mixture (Scheme 1). The starting material, Na(PETAEA), is less soluble in THF than CH_3CN, so the rate of formation of Cu(PETAEA) should be slower in the former solvent. Thus, in THF the Cu(PETAEA) formed early in the reaction remained in contact with CuCl for a significant amount of time. Under these conditions, the kinetics of CuCl complexation with Cu(PETAEA) could be competitive with its reaction with Na(PETAEA). The incorporation of additional equivalents of copper(I) halides into a complex has also been observed for organocopper(I) compounds.[21,22]

The formation of the CuCl adducts was investigated using several deliberate routes. First, the role of deprotonated ligand solubility was investigated. Solvents of several different dielectric constants were selected (acetonitrile, acetone, THF and toluene),



Scheme 1 Synthetic transformation pathways for obtaining complex **1** and related complexes.

and one equivalent of CuCl was added to Na(PETAEA) in each. The solubility of Na(PETAEA) in these solvents decreased in the order: acetonitrile, acetone, THF and toluene. In acetonitrile and acetone red–orange Cu(PETAEA) formed, and in THF a mixture of Cu(PETAEA) and complex **1** formed as described above. In toluene very little product formed, but what did form was the yellow complex **1**. These observations were consistent with the dinuclear complex formation hypothesis described above. Similarly, complex **3** was formed as the only product in the attempted synthesis of Cu(PENAEA) in acetonitrile because Na(PENAEA) was sparingly soluble in this solvent.

Secondly, CuCl was added to previously formed Cu(PETAEA). Cu(PETAEA) was dissolved in acetonitrile and mixed with an additional equivalent of CuCl. The solution changed from red–orange to yellow as all of the Cu(PETAEA) was converted into complex **1**. Thirdly, it was demonstrated through the synthesis of complex **2** that addition of more than one equivalent of CuCl during complexation will form the dinuclear complex exclusively. All of these results indicated that the ligand-bridged dinuclear copper(I) complex is quite stable and will form under conditions in which CuCl is present along with the monometallic complex, as a result of either the reaction stoichiometry or the insolubility of the sodium salt of the ligand.

Conclusions

In summary, dinuclear copper(I) complexes were prepared using PETAEA and its derivatives, and these compounds featured a four coordinate N_4Cu center, a two coordinate NCuCl center, and a metal–metal distance within the range of 2.6572(8) to 2.6903(3) Å. The copper–copper distance and the structural features of the complex were consistent with a weak attraction between the two closed shell metal centers, and DFT calculations support this idea. The complexes apparently formed in a two-step process with the formation of the tetracoordinate mononuclear complex preceding the coordination of a second equivalent of CuCl to the lone pair of the sulfonamidate ligand.

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References

1 M. Sawamoto and M. Kamigaito, *Kobunshi Ronbunshu*, 1997, **54**, 875–885.
2 T. E. Patten and K. Matyjaszewski, *Adv. Mater.*, 1998, **10**, 1–15.
3 T. E. Patten and K. Matyjaszewski, *Acc. Chem. Res.*, 1999, **32**, 895–903.
4 M. Kamigaito, T. Ando and M. Sawamoto, *Chem. Rev.*, 2001, **101**, 3689–3745.
5 K. Matyjaszewski and J. Xia, *Chem. Rev.*, 2001, **101**, 2921–2990.
6 A. T. Levy, M. M. Olmstead and T. E. Patten, *Inorg. Chem.*, 2000, **39**, 1628–1634.
7 Y. Inoue and K. Matyjaszewski, *Macromolecules*, 2003, **36**, 7432–7438.
8 J. M. Goodwin, M. M. Olmstead and T. E. Patten, *J. Am. Chem. Soc.*, 2004, **126**, 14352–14353.
9 Y. Inoue and K. Matyjaszewski, *Macromolecules*, 2004, **37**, 4014–4021.
10 T. E. Patten, C. Troeltzsch and M. M. Olmstead, *Inorg. Chem.*, 2005, **44**, 9197–9206.
11 P. Pyykkö, *Chem. Rev.*, 1997, **97**, 597–636.
12 K. H. Nakagawa, C. Inouye, B. Hedman, M. Karin, T. D. Tullius and K. O. Hodgson, *J. Am. Chem. Soc.*, 1991, **113**, 3621–3623.
13 H. Bertagnolli and W. Kaim, *Angew. Chem., Int. Ed. Engl.*, 1995, **34**, 771–773.
14 I. J. Pickering, G. N. George, C. T. Dameron, B. Kurz, D. R. Winge and I. G. Dance, *J. Am. Chem. Soc.*, 1993, **115**, 9498–9505.
15 P. K. Mehrotra and R. Hoffmann, *Inorg. Chem.*, 1978, **17**, 2187–2189.
16 K. M. Merz, Jr. and R. Hoffmann, *Inorg. Chem.*, 1988, **27**, 2120–2127.
17 F. A. Cotton, X. Feng, M. Matusz and R. Poli, *J. Am. Chem. Soc.*, 1988, **110**, 7077–7083.
18 C. S. Arcus, J. L. Wilkinson, C. Mealli, T. J. Marks and J. A. Ibers, *J. Am. Chem. Soc.*, 1974, **96**, 7564–7565.
19 C. Mealli, C. S. Arcus, J. L. Wilkinson, T. J. Marks and J. A. Ibers, *J. Am. Chem. Soc.*, 1976, **98**, 711–718.
20 S. Seth, A. K. Das and T. C. W. Mak, *Acta Crystallogr., Sect. C*, 1995, **C51**, 2529–2532.
21 C.-S. Hwang, M. M. Olmstead, X. He and P. P. Power, *J. Chem. Soc., Dalton Trans.*, 1998, 2599–2600.
22 A. Heine, R. Herbst-Irmer and D. Stalke, *J. Chem. Soc., Chem. Commun.*, 1993, 1729–1731.
23 M. Krieger, S. Schlecht, K. Harms and K. Dehnicke, *Z. Anorg. Allg. Chem.*, 1998, **624**, 1565–1567.
24 D. W. Widlicka, E. H. Wong, G. R. Weisman, K.-C. Lam, R. D. Sommer, C. D. Incarvito and A. L. Rheingold, *Inorg. Chem. Commun.*, 2000, **3**, 648–652.
25 A. A. D. Tulloch, A. A. Danapoulos, S. Kleinhenz, M. E. Light, M. B. Hursthouse and G. Eastham, *Organometallics*, 2001, **20**, 2027–2031.
26 C. He, J. L. DuBois, B. Hedman, K. O. Hodgson and S. J. Lippard, *Angew. Chem., Int. Ed.*, 2001, **40**, 1484–1487.
27 C. Harding, V. McKee and J. Nelson, *J. Am. Chem. Soc.*, 1991, **113**, 9684–9685.
28 Z. Li, S. T. Barry and R. G. Gordon, *Inorg. Chem.*, 2005, 1728–1735.
29 W.-H. Chan, S.-M. Peng and C.-M. Che, *J. Chem. Soc., Dalton Trans.*, 1998, 2867–2871.
30 J. S. Bradley, R. L. Pruett, E. Hill, G. B. Ansell, M. E. Leonowicz and M. A. Modrick, *Organometallics*, 1982, **1**, 748–752.
31 Z. Mao, H.-Y. Chao, Z. Hui, C.-M. Che, W.-F. Fu, K.-K. Cheung and N. Zhu, *Chem.–Eur. J.*, 2003, **9**, 2885–2897.
32 E. C. Constable, T. Kulke, M. Neuburger and M. Zehnder, *Chem. Commun.*, 1997, 489–490.
33 E. C. Constable, A. J. Edwards, M. J. Hannon and P. R. Raithby, *J. Chem. Soc., Chem. Commun.*, 1994, 1991–1992.
34 C. He and S. J. Lippard, *Inorg. Chem.*, 2000, **39**, 5225–5231.
35 R. R. Gagne, R. P. Kreh, J. A. Dodge, R. E. Marsh and M. McCool, *Inorg. Chem.*, 1982, **21**, 254–261.
36 K. T. Potts, M. Keshavarz-K, F. S. Tham, H. D. Abruna and C. Arana, *Inorg. Chem.*, 1993, **32**, 4450–4456.
37 K. Johnson and J. W. Steed, *J. Chem. Soc., Dalton Trans.*, 1998, 2601–2602.
38 M. Maekawa, M. Munakata, S. Kitagawa, T. Kuroda-Sowa, Y. Suenaga and M. Yamamoto, *Inorg. Chim. Acta*, 1998, **271**, 129–136.

39 M. G. B. Drew, A. Lavery, V. McKee and S. M. Nelson, *J. Chem. Soc., Dalton Trans.*, 1985, 1771–1774.
40 J. Diez, M. P. Gamasa, J. Gimeno, A. Aguirre and S. Garcia-Granda, *Organometallics*, 1997, **16**, 3684–3689.
41 R. Clerac, F. A. Cotton, L. M. Daniels, J. Gu, C. A. Murillo and H.-C. Zhou, *Inorg. Chem.*, 2000, **39**, 4488–4493.
42 A. Sundararaman, L. N. Zakharov, A. L. Rheingold and F. Jäkle, *Chem. Commun.*, 2005, 1708–1710.
43 K. Singh, J. R. Long and P. Stavropoulos, *J. Am. Chem. Soc.*, 1997, **119**, 2942–2943.
44 G. M. Sheldrick, *SADABS*, University of Göttingen, Göttingen, Germany, 2000.
45 S. R. Parkin, B. Moezzi and H. Hope, *J. Appl. Crystallogr.*, 1995, **28**, 53–56.
46 G. M. Sheldrick, *SHELXTL*, Bruker Analytical X-ray Instruments, Inc., Madison, WI, 2004.
47 M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, J. A. Montgomery, Jr., T. Vreven, K. N. Kudin, J. C. Burant, J. M. Millam, S. S. Iyengar, J. Tomasi, V. Barone, B. Mennucci, M. Cossi, G. Scalmani, N. Rega, G. A. Petersson, H. Nakatsuji, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, M. Klene, X. Li, J. E. Knox, H. P. Hratchian, J. B. Cross, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, P. Y. Ayala, K. Morokuma, G. A. Voth, P. Salvador, J. J. Dannenberg, V. G. Zakrzewski, S. Dapprich, A. D. Daniels, M. C. Strain, O. Farkas, D. K. Malick, A. D. Rabuck, K. Raghavachari, J. B. Foresman, J. V. Ortiz, Q. Cui, A. G. Baboul, S. Clifford, J. Cioslowski, B. B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. L. Martin, D. J. Fox, T. Keith, M. A. Al-Laham, C. Y. Peng, A. Nanayakkara, M. Challacombe, P. M. W. Gill, B. Johnson, W. Chen, M. W. Wong, C. Gonzalez and J. A. Pople, *Gaussian 03, Revision A.1*, Gaussian, Inc., Pittsburgh, PA, 2003.
48 S. I. Gorelsky, *AOMix: Program for Molecular Orbital Analysis, http://www.sg-chem.net/*, York University, Toronto, Canada, 1997.
49 S. I. Gorelsky and A. B. P. Lever, *J. Organomet. Chem.*, 2001, **635**, 187–196.
50 P. Flukiger, H. P. Luthi, S. Prtmann and J. Weber, *MOLEKEL 4.3*, Swiss Center for Scientific Computing, Manno, Switzerland, 2000–2002.
51 M. Asplund, S. Jagner and M. Nilsson, *Acta Chem. Scand. Ser. A*, 1983, **37**, 57–62.
52 A. V. Willi, *Helv. Chim. Acta*, 1956, **39**, 46–53.
53 A. Bayler, A. Schier, G. A. Bowmaker and H. Schmidbaur, *J. Am. Chem. Soc.*, 1996, **118**, 7006–7007.
54 K. Nilsson and Å. Oskarsson, *Acta Chem. Scand. Ser. A*, 1982, **36**, 605–610.
55 A. Schäfer and R. Ahlrichs, *J. Am. Chem. Soc.*, 1994, **116**, 10686–10692.
56 R. I. Papasergio, C. L. Raston and A. H. White, *J. Chem. Soc., Dalton Trans.*, 1987, 3085–3091.
57 H. L. Hermann, G. Boche and P. Schwerdtfeger, *Chem.–Eur. J.*, 2001, **7**, 5333–5342.
58 A. Vega and J.-Y. Saillard, *Inorg. Chem.*, 2004, **43**, 4012–4018.
59 C.-M. Che, Z. Mao, V. M. Miskowski, M.-C. Tse, C.-K. Chan, K.-K. Cheung, D. L. Phillips and K.-H. Leung, *Angew. Chem., Int. Ed.*, 2000, **46**, 4084–4088.
60 B. O. Roos, A. C. Borin and L. Gagliardi, *Angew. Chem., Int. Ed.*, 2007, **46**, 1469–1472.

