Inorganic Chemistry
Communication

Inorg. Chem. **2009,** *48,* 4619–4621 **4619**
DOI:10.1021/ic9003627

Synthetic, Structural, and Theoretical Investigation of Guanidinate Complexes Containing Planar Cu_6 Cores

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Received February 23, 2009

The addition of diethylcyanamide to a tetrahydrofuran solution of lithium dialkylamide $LiN(CH_3)_2$ or $\mathrm{Li\overline{NCH_2CH_2CH_2C}H_2}$, Li(PYR), results in the corresponding lithium 1,1,3,3-tetraalkylguanidinate, Li(TAG). The subsequent metathesis reaction of Li(TAG) with CuCl generates hexanuclear copper(I) complexes with the general formula $[Cu(\mu\text{-TAG})]_6$, where TAG = DEDMG (**1**) and DEPYRG (**2**).

Theoretical inquiries regarding the nature of chemical bonding present in oligonuclear copper(I) clusters have been undertaken since the inception of the first structural reports of copper complexes. Unusually short Cu−Cu interatomic distances, unique photochemistry, and interest in understanding the role of copper in biological systems have spurred a detailed investigation of closed-shell $d^{10}-d^{10}$ interactions.[1] Recently, because of the advent of unique computational approaches, the bonding in planar Cu_nH_n ($n = 3-6$) clusters has been investigated, and it was claimed that the clusters were found to possess a degree of cyclic electron conjugation.[2] Specifically, investigators have tacitly attributed the formation of stable planar copper clusters to the existence of transition-metal σ aromaticity.[3] The isolation and structural characterization of three-, four-, and five-membered copper (I) rings were singled out as a testament to this stability.

Currently, our research group has been developing the coordination chemistry of the 1,1,3,3-tetraalkylguanidinate (TAG) ligand.[4] The use of the monoanionic TAG ligand has been infrequent in the field of inorganic chemistry.[5,6] This deficiency is surprising because guanidine and many of its derivatives belong to one of the strongest and most versatile classes of organic bases known.[7] Recently, utilizing this ligand type, we isolated a set of tetranuclear (M = Cu, Ag, and Au) rings with the general formula $[M_2(\mu\text{-TAG})\{\mu\text{-N}(SiMe_3)_2\}]_2$.[8] The existence of such complexes hinted at the possibility of isolating a wider range of TAG complexes. Therefore, in this report, we describe an attempt to expand upon our previous work through the synthesis of stable homoligated Cu(TAG) clusters.

Li(TAG) is synthesized via the straightforward addition of lithium dialkylamide to a tetrahydrofuran (THF) solution of diethylcyanamide. The guanidinate is further reacted in situ with 1 equiv of CuCl to generate the corresponding $[Cu(\mu\text{-TAG})]_6$, where TAG = DEDMG (**1**) and DEPYRG (**2**). The synthesis of compounds **1** and **2** is shown in Scheme 1. Because of the photosensitivity of these complexes, the syntheses are shielded from light throughout the course of the synthesis. In each reaction, reduction to elemental metal was observed and the insoluble precipitate is removed from solution via centrifugation. The reaction mixture is then concentrated and placed in a −35 °C freezer for 24 h. For elemental analysis, recrystallization was additionally performed by redissolving the isolated solid in a THF/hexanes (1:1) mixture and then cooling the sample to −35 °C for 24 h. Colorless crystals of **1** and **2** were isolated with nonoptimized yields of 74 and 51%, respectively.

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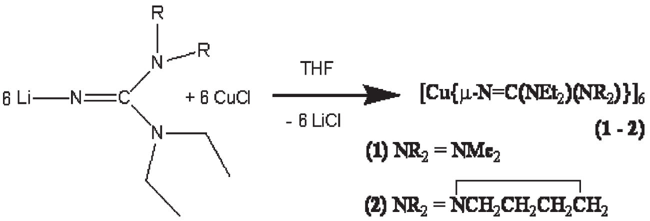
Scheme 1. Synthesis of $[Cu\{\mu\text{-}N{=}C(NEt_2)(NR_2)\}]_6$ (**1** and **2**)



An examination of the IR spectra of the resultant crystals leads to the assignment of strong bands at 1598 and 1609 cm^{-1}, for **1** and **2**, respectively, to a C═N stretching frequency of the TAG ligand coordinated to the copper metal center.[6,9] Further ^{1}H and ^{13}C NMR solution studies were performed and have resonances consistent with the proposed products being maintained in solution. The existence of multiple resonances for each alkyl substituent of the guanidinate moiety is attributed to the potential zwitterionic resonance of the TAG ligand.[8] Rotation about the C—N bond leads to the possibility of both cis and trans isomers present in solution. For the ^{13}C NMR spectra of **1** and **2**, additional characteristic low-field resonances at 160.8 and 157.8 ppm are found and can be assigned to the guanidinate's "*C*N$_3$" central carbon.[6,9]

Compounds **1** and **2** were further examined by X-ray crystallography and found to be similar in structure and are represented by the thermal ellipsoid plot of **1** shown in Figure 1.[10] For each compound, the TAG ligand symmetrically bridges two Cu atoms with Cu—N bond lengths ranging from 1.850(3) to 1.857(3) Å in **1** and from 1.848(3) to 1.863(3) Å in **2**. These values are similar to the average Cu—N distance of 1.857 Å found in the tetranuclear copper imide $[Cu\{\mu\text{-}N{=}C(t\text{-}Bu)(Ph)\}]_4$ and slightly shorter than Cu—N distances found in cyclic amides.[11] The TAG ligands alternate above and below the plane of the Cu$_6$ ring [Cu—N—Cu (av.) 94.6° for **1** and 92.6° for **2**, with an angle ranging from 54° to 64° between the plane of the "CN$_3$" framework and that of the Cu$_6$ core. The N—Cu—N angles are nearly linear, ranging from 172.30(13) to 176.07(13)°. The C═N imino donor distances in **1** and **2** range from 1.268(4) to 1.278(4) Å and are typical for a C═N bond. The other two C—N distances range from 1.409(4) to 1.413(4) Å, and the interactions of these N atoms with Cu atoms are negligible (the shortest Cu···N distance is 3.339 Å).

The degree of aggregation exhibited by **1** and **2** is unusual when compared to other guanidinate and amidocopper(I) clusters.[12] In **1** and **2**, the hexagonal Cu$_6$ core contains Cu—Cu—Cu angles ranging from 118.74(2) to 120.978(19)° for **1** and from 117.28(2) to 121.79(2)° for **2**. The six Cu atoms lie within ±0.036 Å for **1** and ±0.045 Å for **2** of a common plane. Because of interest in examining closed-shell d^{10}—d^{10} interactions between group 11 metals, a discussion involving the Cu···Cu distances of **1** and **2** is warranted. Unlike previously reported trinuclear pyrazolate systems, each hexanuclear cluster is void of extended intermolecular Cu···Cu interactions; the closest distance is greater than 7 Å.[13] The only potential interaction occurs within the Cu$_6$ core. The Cu···Cu distances for **1** [2.7147(6), 2.7257(6), and 2.7370(6) Å] and for **2** [2.6756(7) and 2.6965(7) Å] are similar to those reported for amidocopper clusters and are longer than those reported in cyclic organocopper systems.[14]

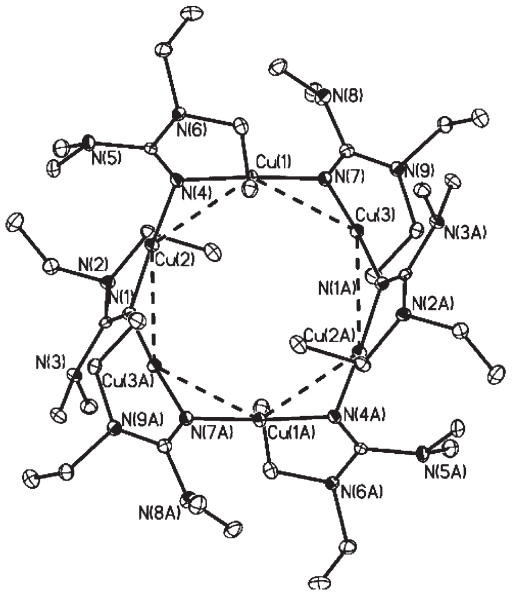


Figure 1. Thermal ellipsoid plot of **1**. Ellipsoids are drawn at the 30% level. H atoms have been omitted for clarity. The additional "A" letters in the atom labels indicate that these atoms are at $(-x, 2 - y, 2 - z)$.

Notably, neutral hexanuclear copper(I) complexes have typically been found in the solid state with distorted octahedral structures.[15] Nearly planar Cu$_6$ rings are quite rare.[16] However, hexanuclear coinage metal clusters singly bridged by monoanionic ligands are known for gold(I), including the X-ray-characterized $[Au(\mu\text{-}PR_2)]_6$ (R = *t*-Bu and

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(10) Crystal data for **1**: $C_{42}H_{96}Cu_6N_{18}$, M_w = 1234.61 g·mol^{-1}, monoclinic, space group C2/c, a = 21.9704(19) Å, b = 13.0146(12) Å, c = 20.8282(19) Å, β = 106.834(2)°; V = 5700.3(9) Å^3, Z = 4, ρ_{calcd} = 1.439 g·cm^{-3}, 1.84 < λ < 25.50, of 23 605 measured reflections, 5327 were independent and 4822 observed with I > 2σ(I), −26 < h < 26, −15 < k < 15, −25 < l < 25; R1 = 0.0337, wR2 = 0.0981, GOF = 0.813 for 310 parameters, $\Delta\rho_{max}$ = 0.742 e·Å^{-3}. Crystal data for 2: $C_{54}H_{108}Cu_6N_{18}$, M_w = 1390.82 g·mol^{-1}, triclinic, space group P, a = 10.9625 (17) Å, b = 12.575(2) Å, c = 13.1497(18) Å, α = 117.965(5)°, β = 91.535(4)°, γ = 96.698(3); V = 1583.2(4) Å^3, Z = 1, ρ_{calcd} = 1.459 g·cm^{-3}, 1.76 < λ < 28.00, of 16 154 measured reflections, 7600 were independent and 3681 observed with I > 2σ(I), −14 < h < 14, −16 < k < 16, −17 < l < 17; R1 = 0.0413, wR2 = 0.1123, GOF = 0.841 for 358 parameters, $\Delta\rho_{max}$ = 0.647 e·Å^{-3}. CCDC 648742 for 1 and 648743 for 2.

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cyclo-hexyl) and $[Au\{\mu\text{-}S(C_6H_2(^iPr)_3\text{-}2,4,6)\}]_6$.[17] Because of a deficiency in planar Cu_6 complexes, a density functional theory (DFT) investigation was undertaken to provide insight into the bonding and potential cyclic conjugation responsible for the formation of **1** and **2**.

A theoretical inquiry of $[Cu\{\mu\text{-}N{=}C(NH_2)_2\}]_6$ (**3**) (Figure S2 in the Supporting Information) was performed to model the bonding in **1** and **2**. When the interatomic distances and angles of **2** are used as the framework, a natural bond orbital (NBO) analysis of **3** at the B3LYP/6-311+G(d,p) level of theory was performed.[18,19] According to the analysis, the Cu atoms have $4s^{0.55}3d^{9.76}$ valence atomic occupations (AOs) and an effective atomic charge of +0.68 e, while the N_{imino} atoms have $2s^{1.47}2p^{4.58}$ atomic occupation and an effective atomic charge of −1.08 e. Examination of the atomic occupation of Cu indicates that the 3d atomic orbitals (AOs) are almost completely occupied, and thus the net bonding effect from molecular orbitals (MOs) composed of 3d AOs is not significant. Instead, there are Cu−N 2c−2e σ bonds (occupation number 1.93 e) formed from a $sp^{1.76}$ hybrid (64% p character) on the N interacting with a $sp^{0.01}d^{0.13}$ hybrid (88% s character) on Cu. In further support of the NBO analysis, the MOs of **3** were calculated at the B3LYP/LACVP level of theory.[20] An examination of the MOs (Figures S3−S5 in the Supporting Information) indicates that there are localized 3d AOs instead of delocalized electron density in the Cu_6 ring itself. σ-Bond delocalization has recently been reported in a theoretical investigation of a planar Cu_6H_6 system.[2,3]

It was of interest to quantify the difference in electron cyclic conjugation in **3** versus the Cu_6H_6 system. Therefore, the nucleus-independent chemical shift (NICS) and the ^{65}Cu isotropic shielding tensor elements were additionally computed at the B3LYP/6-311+G(d,p) level of theory.[19] The NICS(0) values were generated according to the procedure described by Schleyer et al. through calculation of the magnetic shielding tensor element located at the center of the Cu_6 ring.[21] The NICS(0) values for **3** and Cu_6H_6 were found to be +0.02 and −0.47, respectively. Aromatic systems typically have significantly negative values (e.g., −9.7 for benzene), whereas antiaromatic systems have large positive values.[3] Both **3** and Cu_6H_6 have values close to zero, and thus this metric indicates little cyclic conjugation in both systems.

The absolute ^{65}Cu isotropic shielding tensor elements for **3** and Cu_6H_6 were also generated in the process of calculating NICS(0) (Table S1 in the Supporting Information). For **3**, σ^{iso} was found to be at 620 ppm, while in Cu_6H_6, the $^{63}Cu\ \sigma^{iso}$ value is found to be shifted significantly downfield to 1539 ppm. This shift is attributable to an increase in the electron cyclic conjugation present in Cu_6H_6 versus that found in **3**. Overall, DFT calculations have demonstrated that the extent of Cu···Cu interaction in **3** is modest (if present at all) and less than that found in the theoretical Cu_6H_6 system.

In conclusion, it is likely that complexes **1** and **2** will be the forerunners of a broader class of clusters. On the basis of the theoretical calculation, Cu···Cu interactions are fairly weak and the factors controlling the stability of $[Cu(\mu\text{-}TAG)]_6$ systems are attributable to the strong Cu−N interactions and not the presence of transition-metal aromaticity. The photochemistry of the current compounds and the synthesis of additional group 11 TAG clusters are currently under investigation.

Acknowledgment. The authors acknowledge Kent State University and the National Science Foundation (NSF-REU) for support of this work.

Supporting Information Available: Experimental procedures and characterization data for **1** and **2**, thermal ellipsoid plot for **2** (Figure S1), ball-and-stick plot and a list of molecular orbitals (Figures S2− S5), and Cartesian coordinates and shielding tensors for **3** and $[Cu_6H_6]$ (Tables S1−S3). This material is available free of charge via the Internet at http://pubs.acs.org.

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