

Synthesis and Characterization of Group 11 1,1,3,3-Tetraalkylguanidinate (TAG) Clusters: $[M_2(\mu\text{-TAG})\{\mu\text{-N}(\text{SiMe}_3)_2\}]_2$ (M = Cu, Ag, and Au)

Scott D. Bunge* and Jennifer L. Steele

Kent State University, Department of Chemistry, Kent, Ohio 44242

Received November 30, 2008

The addition of diethylcyanamide to a tetrahydrofuran solution of lithium dialkylamide $\{\text{LiN}(\text{CH}_3)_2$ or $\text{LiNCH}_2\text{CH}_2\text{CH}_2\text{CH}_2$, Li(PYR)} results in the corresponding lithium 1,1,3,3-tetraalkylguanidinate, Li(TAG). Two equivalents of Li(TAG) and 2 equiv of lithium bistrimethylsilylamide, $\text{LiN}(\text{SiMe}_3)_2$, were subsequently reacted with 4 equiv of Group 11 halide (CuCl, AgBr, and AuCl) to generate tetranuclear complexes with the general formula $[M_2(\mu\text{-TAG})\{\mu\text{-N}(\text{SiMe}_3)_2\}]_2$ where M and TAG = {Cu, DEDMG, (1)}, {Ag, DEDMG, (2)}, {Au, DEDMG, (3)}, {Cu, DEPYRG, (4)}, {Ag, DEPYRG, (5)}, and {Au, DEPYRG, (6)}. Compounds 1–6 were characterized by single-crystal X-ray diffraction. The bulk powders for all complexes were found to be in agreement with the crystal structures based on elemental analyses, FT-IR spectroscopy, ^1H and ^{13}C NMR studies.

Introduction

Over the past decade, oligonuclear copper, silver, and gold compounds have found far-reaching applications in areas such as catalysis, photonics, or as bioconjugate probes for amplification tags in gene analysis and DNA sequencing.¹ Therefore, developing methods for generating such clusters has been an active area of pursuit. Unfortunately, the development of gold(I) chemistry has been dominated by the viewpoint that gold is a prototypical soft Lewis acid, which forms its most stable complexes with soft Lewis bases.² Accordingly, the synthesis of gold(I) complexes with hard Lewis bases such as nitrogen has been limited to the use of a few specific ligand types.^{3,4} Such complexes have historically been described typically as intrinsically unstable and therefore have a pronounced tendency to decompose into

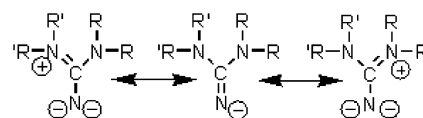


Figure 1. Zwitterionic resonance structure of the guanidinate ligand.

ill-defined aggregates.⁵ Similar problems, although to a lesser extent, have been described for copper(I) and silver(I). Accordingly, only a select group of N-donors have been utilized to isolate Group 11 complexes. For example, pyrazolate, amidinate, guanidinate, and bulky amido ligands such as $[\text{N}(\text{SiMePh}_2)_2]$ and $[\text{N}(\text{SiMe}_3)_2]$ have proven effective at isolating well-defined clusters.^{6–10} Such clusters, however, have demonstrated discrete luminescence, catalytic reactivity, and have provided ever increasing fundamental knowledge regarding the nature of closed-shell $d^{10}\text{-}d^{10}$ interactions.¹¹ Owing to the importance of Group 11 complexes and a need for additional fundamental inquiry, the following synthetic investigation was undertaken.

Our research group is currently interested in developing the coordination chemistry of the 1,1,3,3-tetraalkylguanidinate (TAG) ligand (Figure 1).¹² The use of the monoanionic TAG ligand has been sporadic in the field of inorganic chemistry.^{13,14} This deficiency is surprising since guanidine and many of its derivatives belong to one of the strongest and most versatile classes of organic bases known.^{15,16} For

* To whom correspondence should be addressed. E-mail: sbunge@kent.edu. Phone: (330) 672-9445.

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comparison, 1,1,3,3-tetramethylguanidine (H-TMG) has a basicity several orders of magnitude greater than tertiary amines.¹⁷ In addition, the zwitterionic resonance structure of the TAG anion facilitates delocalization of the negative charge on the N_{imino} atom. (Figure 1) Therefore, in principle, the TAG ligand would be expected to bind strongly to hard and soft Lewis acids.¹⁸ This degree of electronic stabilization is not obtained by utilizing "classic" amido ligands such as NPh₂, NEt₂, and NMe₂.¹⁹

In this report, the synthesis and characterization of a series of Group 11 tetranuclear complexes with the general formula [M₂(μ-TAG){μ-N(SiMe₃)₂}]₂ is described. These compounds (1–6) were characterized by single-crystal X-ray diffraction. The bulk powders for all complexes were found to be in agreement with the crystal structures based on elemental analyses, FT-IR spectroscopy, ¹H and ¹³C NMR studies.

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Experimental Section

All syntheses were handled with rigorous exclusion of air and water using standard glovebox techniques. All anhydrous solvents were stored under argon and used as received in sure seal bottles. The following chemicals were used as received from commercial suppliers: diethylcyanamide, lithium dimethylamide, pyrrolidine, *n*-BuLi (1.6 M in hexanes), LiN(SiMe₃)₂, AgBr, and AuCl. CuCl was purchased from a commercial supplier and purified using standard methods prior to use. FT-IR data were obtained on a Bruker Tensor 27 Instrument using KBr under an atmosphere of flowing nitrogen. Elemental analysis was performed on a Perkin-Elmer 2400 Series 2 CHN-S/O Elemental Analyzer. Melting points were determined on samples sealed in a glass tube under an atmosphere of argon using an Electrothermal Mel-Temp apparatus and are uncorrected. All NMR samples were prepared from dried crystalline materials that were handled and stored under an argon atmosphere and redissolved in toluene-*d*₈. All solution spectra were obtained on a Bruker DRX 400 spectrometer at 400.1 and 100.6 MHz for ¹H and ¹³C experiments.

General Synthesis of 1–6. To a lithium dialkylamide dissolved in 15 mL of tetrahydrofuran, an equivalent of dialkylcyanamide was added dropwise under an inert atmosphere of argon. The reaction mixture was then allowed to stir for 30 min completing the generation of the lithium 1,1,3,3-tetralkylguanidinate in situ. LiN(SiMe₃)₂ and MX (where MX = CuCl, AgBr, or AuCl) were then added to the reaction mixture sequentially. After stirring for 30 min, the solution was concentrated and cooled to –35 °C. X-ray-suitable, colorless crystals of 1–6 were grown in 24 h.

[Cu₂(μ-DEDMG){μ-N(SiMe₃)₂}]₂ (1). 0.25 g (2.5 mmol) diethylcyanamide; 0.13 g (2.5 mmol) lithium dimethylamide; 0.42 g (2.5 mmol) LiN(SiMe₃)₂; 0.50 g (5.0 mmol) CuCl. Yield 44% (0.47 g, 0.55 mmol). Anal. Calcd. for C₂₆H₆₈Cu₄N₈Si₄: C 36.34, H 7.98, N 13.04. Found: C 36.30, H 7.75, N 13.84. MP (dec.) 70 °C. ¹H NMR (400.1 MHz, C₇D₈): δ = 3.25 (q, J_{H–H} = 7.0 Hz, 4H, N=C(N(CH₂CH₃)₂)(N(CH₃)₂)), 2.82 (s, 4H N=C(N(CH₂CH₃)₂)(N(CH₃)₂)), 2.80 (s, 2H N=C(N(CH₂CH₃)₂)(N(CH₃)₂)), 1.02 (m, 6H N=C(N(CH₂CH₃)₂)(N(CH₃)₂)), 0.53 (s, 9H N(Si(CH₃)₃)₂), 0.47 (s, 9H N(Si(CH₃)₃)₂). ¹³C NMR (100.6 MHz, C₇D₈): δ = 162.8 (N=C(N(CH₂CH₃)₂)(N(CH₃)₂)), 45.1 (N=C(N(CH₂CH₃)₂)(N(CH₃)₂)), 40.8 (N=C(N(CH₂CH₃)₂)(N(CH₃)₂)), 13.4 (N=C(N(CH₂CH₃)₂)(N(CH₃)₂)), 7.2 (N(Si(CH₃)₃)₂). FT-IR (KBr, cm⁻¹) 2943 (s), 2826 (m), 1582 (s), 1459 (m), 1426 (w), 1360 (m), 1338 (w), 1314 (m), 1245 (s), 1200 (m), 1112 (s), 1057 (m), 1035 (m), 982 (m), 928 (s), 862 (s), 833 (s), 773 (m), 757 (m), 675 (m).

[Ag₂(μ-DEDMG){μ-N(SiMe₃)₂}]₂ (2). 0.13 g (1.3 mmol) diethylcyanamide; 0.07 g (1.3 mmol) lithium dimethylamide; 0.22 g (1.3 mmol) LiN(SiMe₃)₂; 0.50 g (2.7 mmol) AgBr. Yield 24% (0.17 g, 0.16 mmol). Anal. Calcd. for C₂₆H₆₈Ag₄N₈Si₄: C 30.12, H 6.61, N 10.81. Found: C 30.43, H 6.19, N 11.42. ¹H NMR (400.1 MHz, C₇D₈): δ = 3.20 (q, J_{H–H} = 6.7 Hz, 4H, N=C(N(CH₂CH₃)₂)(N(CH₃)₂)), 2.79 (m, 6H, N=C(N(CH₂CH₃)₂)(N(CH₃)₂)), 1.01 (m, 6H N=C(N(CH₂CH₃)₂)(N(CH₃)₂)), 0.46 (s, 9H, N(Si(CH₃)₃)₂), 0.42 (s, 9H, N(Si(CH₃)₃)₂). ¹³C NMR (100.6 MHz, C₇D₈): δ = 161.7 (N=C(N(CH₂CH₃)₂)(N(CH₃)₂)), 44.7 (N=C(N(CH₂CH₃)₂)(N(CH₃)₂)), 40.4 (N=C(N(CH₂CH₃)₂)(N(CH₃)₂)), 13.1 (N=C(N(CH₂CH₃)₂)(N(CH₃)₂)), 7.9 (N(Si(CH₃)₃)₂). FT-IR (KBr, cm⁻¹) 3160 (w), 2943 (s), 2822 (m), 1585 (s), 1458 (m), 1426 (m), 1399 (w), 1375 (m), 1353 (m), 1319 (m), 1283 (w), 1243 (s), 1195 (m), 1140 (w), 1102 (s), 1059 (m), 1031 (m), 952 (s), 831 (s), 757 (m), 671 (s), 614 (w), 599 (w), 564 (w), 493 (m).

[Au₂(μ-DEDMG){μ-N(SiMe₃)₂}]₂ (3). 0.11 g (1.1 mmol) diethylcyanamide; 0.06 g (1.1 mmol) lithium dimethylamide; 0.18 g (1.1

mmol) LiN(SiMe₃)₂; 0.50 g (2.2 mmol) AuCl. Yield 11% (0.080 g, 0.061 mmol). Anal. Calcd. for C₂₆H₆₈Au₄N₈Si₄: C 22.42, H 4.92, N 8.04. Found: C 23.27, H 4.49, N 8.79. ¹H NMR (400.1 MHz, C₇D₈): δ = 3.30 (m, 4H, N=C(N(CH₂CH₃)₂)(N(CH₃)₂)), 2.84 (s, 6H, N=C(N(CH₂CH₃)₂)(N(CH₃)₂)), 1.02 (t, *J*_{H-H} = 6.7 Hz, 6H, N=C(N(CH₂CH₃)₂)(N(CH₃)₂)), 0.59 (m, 18H, N(Si(CH₃)₃)₂). ¹³C NMR (100.6 MHz, C₇D₈): δ = 164.7 (N=C(N(CH₂CH₃)₂)(N(CH₃)₂)), 44.7 (N=C(N(CH₂CH₃)₂)(N(CH₃)₂)), 40.6 (N=C(N(CH₂CH₃)₂)(N(CH₃)₂)), 14.7 (N=C(N(CH₂CH₃)₂)(N(CH₃)₂)), 7.0 (N(Si(CH₃)₃)₂). FT-IR (KBr, cm⁻¹) 2965 (m), 2871 (m), 1570 (s), 1561 (s), 1554 (s), 1535 (m), 1510 (w), 1500 (w), 1482 (w), 1459 (m), 1449 (m), 1439 (m), 1432 (m), 1400 (w), 1377 (m), 1342 (w), 1246 (s), 1198 (w), 1127 (m), 1102 (m), 1058 (m), 1044 (m), 909 (m), 840 (s).

[Cu₂(μ-DEPYRG){μ-N(SiMe₃)₂}₂ (4). 0.18 g (2.5 mmol) pyrrolidine; 1.07 g (2.5 mmol) *n*-BuLi; 0.25 g (2.5 mmol) diethylcyanamide; 0.42 g (2.5 mmol) LiN(SiMe₃)₂; 0.50 g (5.0 mmol) CuCl. Yield 31% (0.36 g, 0.39 mmol). MP (dec.) 65 °C. Anal. Calcd. for C₃₀H₇₂Cu₄N₈Si₄: C 39.53, H 7.96, N 12.29. Found: C 39.35, H 7.42, N 13.28. ¹H NMR (400.1 MHz, C₇D₈): δ = 3.61 (t, *J*_{H-H} = 6.4 Hz, 4H, N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 3.15 (q, *J*_{H-H} = 7.0 Hz, 4H, N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 1.63 (m, 4H, N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 1.07 (m, 6H, N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 0.54 (s, 3H, N(Si(CH₃)₃)₂), 0.49 (s, 15H, N(Si(CH₃)₃)₂). ¹³C NMR (100.6 MHz, C₇D₈): δ = 160.3 (N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 68.1 (N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 49.8 (N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 46.4 (N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 26.0 (N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 7.2 (N(Si(CH₃)₃)₂). FT-IR (KBr, cm⁻¹) 3440 (w), 2974 (s), 2876 (m), 2816 (m), 1576 (s), 1460 (m), 1382 (w), 1365 (w), 1329 (m), 1288 (w), 1244 (m), 1223 (w), 1197 (w), 1112 (w), 1058 (m), 930 (s), 864 (s), 831 (s), 776 (m), 759 (m), 703 (w), 676 (m), 615 (w), 550 (m).

[Ag₂(μ-DEPYRG){μ-N(SiMe₃)₂}₂ (5). 0.090 g (1.3 mmol) pyrrolidine; 0.57 g (1.3 mmol); *n*-BuLi; 0.13 g (1.3 mmol) diethylcyanamide; 0.22 g (1.3 mmol) LiN(SiMe₃)₂; 0.50 g (2.6 mmol) AgBr. Yield 13% (0.093 g, 0.08 mmol). Anal. Calcd. for C₃₀H₇₂Ag₄N₈Si₄: C 33.09, H 6.67, N 10.29. Found: C 33.31, H 6.38, N 10.74. MP (dec.) 60 °C. ¹H NMR (400.1 MHz, C₇D₈): δ = 3.55 (m, 4H, N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 3.11 (m, 4H, N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 1.57 (m, 4H, N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 1.08 (m, 6H, N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 0.47 (s, 9H, N(Si(CH₃)₃)₂), 0.43 (s, 9H, N(Si(CH₃)₃)₂). ¹³C NMR (100.6 MHz, C₇D₈): δ = 159.3 (N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 68.2 (N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 49.1 (N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 26.0 (N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 13.4 (N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 7.9 (N(Si(CH₃)₃)₂). FT-IR (KBr, cm⁻¹) 2963 (s), 2898 (m), 2872 (m), 2805 (m), 1581 (s), 1510 (w), 1481 (m), 1460 (m), 1443 (m), 1376 (m), 1363 (m), 1337 (m), 1328 (m), 1311 (w), 1289 (m), 1253 (s), 1245 (s), 1223 (w), 1191 (m), 1165 (w), 1116 (w), 1062 (m), 1028 (w), 954 (s), 860 (s), 833 (s), 766 (m), 757 (m), 671 (m), 612 (m).

[Au₂(μ-DEPYRG){μ-N(SiMe₃)₂}₂ (6). 0.080 g (1.0 mmol) pyrrolidine; 0.42 g (1.0 mmol) *n*-BuLi; 0.10 g (1.0 mmol) diethylcyanamide; 0.17 g (1.0 mmol) LiN(SiMe₃)₂; 0.46 g (2.0 mmol) AuCl. Yield 32% (0.23 g, 0.16 mmol). Anal. Calcd. for C₃₀H₇₂Au₄N₈Si₄: C 24.93, H 5.02, N 7.75. Found: C 25.55, H 4.75, N 9.52. ¹H NMR (400.1 MHz, C₇D₈): δ = 3.64 (m, 4H, N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 3.34 (m, 4H, N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 1.54 (m, 4H, N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 1.07 (m, 6H, N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 0.56 (s, 18H, N(Si(CH₃)₃)₂). ¹³C NMR (100.6 MHz, C₇D₈): δ = 161.4 (N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 50.2 (N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 45.4 (N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 26.3 (N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 13.4 (N=C(N(CH₂CH₃)₂)(N(C₄H₈))), 6.9 (N(Si(CH₃)₃)₂). FT-IR (KBr, cm⁻¹) 2964 (s), 2870 (m), 1562 (s), 1460 (m), 1397 (m), 1343 (m), 1246 (s), 1195 (w), 1071 (m), 1028 (w), 993 (w), 908 (s), 838 (s), 774 (m), 671 (m), 617 (w), 556 (w).

Table 1. Data Collection Parameters for 1–3

| compound | 1 | 2 | 3 |
|--|--|--|--|
| chemical formula | C ₂₆ H ₆₈ Cu ₄ N ₈ Si ₄ | C ₂₆ H ₆₈ Ag ₄ N ₈ Si ₄ | C ₂₆ H ₆₈ Au ₄ N ₈ Si ₄ |
| formula weight | 859.40 | 1036.71 | 1393.11 |
| temp (K) | 100(2) | 100(2) | 100(2) |
| space group | monoclinic, <i>Pc</i> | monoclinic, <i>C2/c</i> | triclinic, <i>P1̄</i> |
| <i>a</i> (Å) | 13.7108(19) | 13.307(3) | 9.351(3) |
| <i>b</i> (Å) | 8.9694(12) | 25.557(5) | 10.226(3) |
| <i>c</i> (Å) | 20.0612(18) | 13.126(3) | 12.913(4) |
| α (deg) | | | 72.609(4) |
| β (deg) | 121.313(6) | 108.171(3) | 72.874(5) |
| γ (deg) | | | 72.622(5) |
| <i>V</i> (Å ³) | 2107.7(5) | 4241.3(15) | 1095.6(6) |
| <i>Z</i> | 2 | 4 | 1 |
| <i>D</i> _{calcd} (Mg/m ³) | 1.354 | 1.624 | 2.111 |
| μ(Mo, Kα) (mm ⁻¹) | 2.131 | 1.960 | 13.484 |
| <i>R</i> ¹ (%) (all data) | 1.78 (1.83) | 2.31 (2.78) | 3.94 (8.10) |
| w <i>R</i> ² (%) (all data) | 1.83 (4.71) | 8.14 (8.84) | 7.09 (8.19) |

$${}^a R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \times 100. {}^b wR2 = \frac{\{\sum [w(F_o^2 - F_c^2)^2]\}}{\sum w(F_o^2)^2}^{1/2} \times 100.$$

Table 2. Data Collection Parameters for 4–6

| compound | 4 | 5 | 6 |
|--|--|--|--|
| chemical formula | C ₃₀ H ₇₂ Cu ₄ N ₈ Si ₄ | C ₃₀ H ₇₂ Ag ₄ N ₈ Si ₄ | C ₃₀ H ₇₂ Au ₄ N ₈ Si ₄ |
| formula weight | 911.48 | 1088.80 | 1445.18 |
| temp (K) | 100(2) | 100(2) | 100(2) |
| space group | triclinic, <i>P1̄</i> | triclinic, <i>P1̄</i> | triclinic, <i>P1̄</i> |
| <i>a</i> (Å) | 9.5504(17) | 10.2810(13) | 9.111(5) |
| <i>b</i> (Å) | 10.6284(17) | 10.7377(14) | 10.832(6) |
| <i>c</i> (Å) | 12.746(3) | 12.8025(16) | 13.318(7) |
| α (deg) | 101.132(7) | 74.234(2) | 68.840(7) |
| β (deg) | 111.845(4) | 73.164(2) | 72.141(7) |
| γ (deg) | 104.196(5) | 67.970(2) | 73.208(8) |
| <i>V</i> (Å ³) | 1104.6(4) | 1232.6(3) | 1142.9(10) |
| <i>Z</i> | 1 | 1 | 1 |
| <i>D</i> _{calcd} (Mg/m ³) | 1.370 | 1.467 | |
| μ(Mo, Kα) (mm ⁻¹) | 2.038 | 1.690 | |
| <i>R</i> ¹ (%) (all data) | 2.22 (2.46) | 5.08 (5.61) | |
| w <i>R</i> ² (%) (all data) | 7.86 (8.97) | 15.38 (15.89) | |

$${}^a R1 = \frac{\sum ||F_o| - |F_c||}{\sum |F_o|} \times 100. {}^b wR2 = \frac{\{\sum [w(F_o^2 - F_c^2)^2]\}}{\sum w(F_o^2)^2}^{1/2} \times 100.$$

X-ray Crystal Structure Information. X-ray crystallography was performed by mounting each crystal onto a thin glass fiber from a pool of Fluorolube and immediately placing it under a liquid N₂ cooled N₂ stream, on a Bruker AXS diffractometer. The radiation used was graphite monochromatized Mo Kα radiation (λ = 0.7107 Å). The lattice parameters were optimized from a least-squares calculation on carefully centered reflections. Lattice determination, data collection, structure refinement, scaling, and data reduction were carried out using APEX2 version 1.0–27 software package.

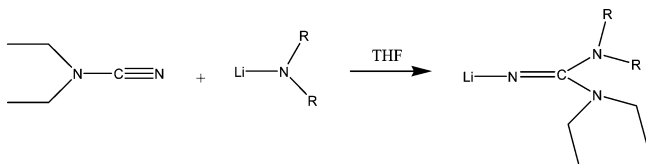
Each structure was solved using direct methods. This procedure yielded the metal atoms, along with a number of the Si, N, and C atoms. Subsequent Fourier synthesis yielded the remaining atom positions. The hydrogen atoms were fixed in positions of ideal geometry and refined within the X-SHELL software. These idealized hydrogen atoms had their isotropic temperature factors fixed at 1.2 or 1.5 times the equivalent isotropic *U* of the C atoms to which they were bonded. The final refinement of each compound included anisotropic thermal parameters on all non-hydrogen atoms. Data collection parameters are listed in Tables 1 and 2. Interatomic distances and angles are listed in Tables 3 and 4. Additional information concerning the data collection and final structural solutions of compounds 1–5 can be found in the Supporting Information. Crystals of poor quality were obtained for 6. Therefore, only the unit cell dimensions for 6 are provided in Table 1, and the molecular connectivity is provided in Supporting Information, Figure S1.

Table 3. Selected Inter-Atomic Distances (Å) and angles (deg) for **1–3**

| Compound 1 | | | |
|-------------------|------------|------------------|------------|
| Cu(1)–N(5) | 1.851(2) | Cu(1)–N(4) | 1.910(2) |
| Cu(2)–N(8) | 1.9086(19) | Cu(3)–N(1) | 1.858(2) |
| Cu(4)–N(1) | 1.850(2) | Cu(4)–N(4) | 1.920(2) |
| N(1)–C(1) | 1.288(3) | Cu(2)–N(5) | 1.856(2) |
| N(5)–Cu(1)–N(4) | 177.04(9) | N(5)–Cu(1)–Si(2) | 143.21(7) |
| N(5)–Cu(2)–N(8) | 176.16(10) | N(1)–Cu(3)–N(8) | 177.09(9) |
| C(1)–N(1)–Cu(4) | 132.75(18) | C(1)–N(1)–Cu(3) | 133.45(18) |
| Cu(1)–N(4)–Cu(4) | 90.58(9) | C(14)–N(5)–Cu(1) | 132.12(18) |
| Cu(1)–N(5)–Cu(2) | 93.70(9) | Si(1)–N(4)–Cu(1) | 111.32(11) |
| Cu(3)–N(8)–Cu(2) | 91.49(8) | Si(2)–N(4)–Cu(4) | 110.09(10) |
| N(1)–Cu(4)–N(4) | 177.71(10) | Cu(4)–N(1)–Cu(3) | 93.79(10) |
| Compound 2 | | | |
| Ag(1)–N(1) | 2.065(2) | Ag(1)–N(4) | 2.125(2) |
| N(1)–C(1) | 1.290(4) | Ag(2)–N(1) | 2.062(2) |
| N(2)–C(1) | 1.407(3) | N(3)–C(1) | 1.391(3) |
| N(4)–Si(1) | 1.732(2) | N(4)–Si(2) | 1.739(2) |
| Ag(1)–N(4)–Ag(2A) | 92.60(9) | C(1)–N(1)–Ag(2) | 134.9(2) |
| Ag(1)–N(1)–Ag(2) | 94.30(10) | Si(1)–N(4)–Ag(1) | 106.87(11) |
| C(1)–N(1)–Ag(1) | 130.38(19) | Si(1)–N(4)–Si(2) | 127.13(14) |
| Si(2)–N(4)–Ag(1) | 109.24(11) | Si(1)–N(4)–Ag(1) | 106.87(11) |
| Compound 3 | | | |
| Au(1)–N(2) | 2.011(9) | Au(1)–N(1) | 2.062(8) |
| N(2)–C(7) | 1.275(13) | Au(2)–N(1) | 2.073(8) |
| N(1)–Si(2) | 1.781(8) | Au(2)–N(2A) | 2.006(9) |
| N(3)–C(7) | 1.378(14) | N(3)–C(8) | 1.479(15) |
| N(2)–Au(1)–N(1) | 170.9(3) | Si(2)–N(1)–Au(1) | 108.1(4) |
| Si(1)–N(1)–Au(2) | 107.7(4) | Au(1)–N(1)–Au(2) | 94.6(3) |
| C(7)–N(2)–Au(1) | 131.5(8) | Si(1)–N(1)–Au(1) | 109.8(4) |
| Si(2)–N(1)–Au(2) | 108.4(4) | Si(1)–N(1)–Si(2) | 124.2(5) |

Table 4. Selected Inter-Atomic Distances (Å) and Angles (deg) for **4** and **5**

| Compound 4 | | | |
|------------------|------------|------------------|------------|
| Cu(1)–N(2) | 1.8544(19) | Cu(2)–N(2) | 1.8490(18) |
| N(2)–C(7) | 1.279(3) | Cu(2)–N(1) | 1.9096(18) |
| N(2)–C(7) | 1.279(3) | N(3)–C(7) | 1.427(3) |
| N(3)–C(10) | 1.455(3) | N(3)–C(8) | 1.474(3) |
| N(4)–C(12) | 1.446(3) | N(4)–C(15) | 1.478(3) |
| C(7)–N(2)–Cu(2) | 133.99(16) | N(2)–Cu(2)–N(1) | 174.10(8) |
| N(1)–Cu(2)–Cu(1) | 133.39(6) | Cu(2)–N(2)–Cu(1) | 94.76(8) |
| C(7)–N(2)–Cu(1) | 131.22(16) | Si(2)–N(1)–Si(1) | 125.09(10) |
| Compound 5 | | | |
| Ag(1)–N(2) | 2.059(6) | Ag(1)–N(1) | 2.126(6) |
| N(2)–C(1) | 1.276(10) | Ag(2)–N(1) | 2.135(6) |
| N(3)–C(1) | 1.372(10) | N(2)–Ag(2A) | 2.064(6) |
| N(4)–C(1) | 1.433(9) | N(3)–C(5) | 1.479(10) |
| N(2)–Ag(1)–N(1) | 175.3(2) | Si(1)–N(1)–Ag(1) | 109.1(3) |
| Si(1)–N(1)–Ag(2) | 110.0(3) | Si(2)–N(1)–Ag(2) | 106.7(3) |
| Ag(1)–N(1)–Ag(2) | 90.4(2) | Si(2)–N(1)–Ag(1) | 107.3(3) |

Scheme 1. General Synthesis of Li(TAG)

Results and Discussion

Synthesis. The convenient synthesis of lithium 1,1,3,3-tetramethylguanidinate via the reaction of lithium dimethylamide with dimethylcyanamide was first reported by Wade and co-workers.¹⁴ Herein, we report the generalization of this reaction (Scheme 1) to cleanly generate Li(TAG). Derivatives of Li(TAG) were subsequently used in conjunction with Li[N(SiMe₃)₂] and MX (MX = CuCl, AgBr and

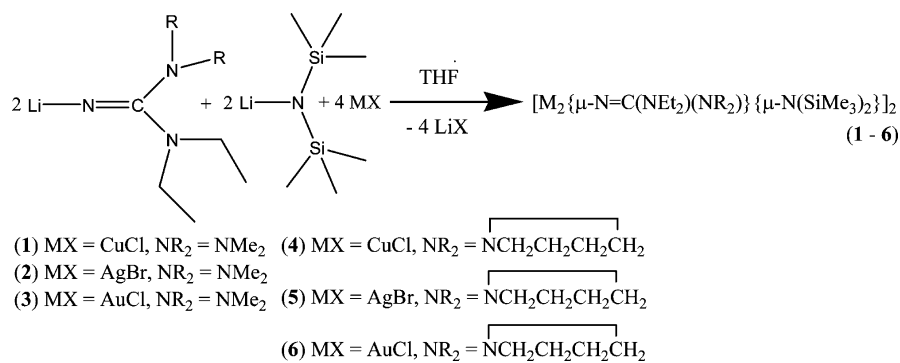
AuCl) to form the corresponding heteroligated M(TAG) complex [M₂(μ-TAG){μ-N(SiMe₃)₂}]₂. The synthesis of compounds **1–6** is shown in Scheme 2. Because of the photosensitivity of these complexes, the syntheses are shielded from light throughout the course of the synthesis. In each reaction, reduction to elemental metal is observed, and the insoluble precipitate is removed from solution via centrifugation prior to concentration. The reaction mixture is concentrated and cooled to –35 °C to facilitate isolation of **1–6** as colorless crystals. All six complexes were isolated in non-optimized yields from 11 to 44%. 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. Dried crystals of **1–6** are stable under argon at –35 °C in the absence of light for several months.

Spectroscopic Studies. Colorless crystals of **1–6** were dried in vacuo to yield the bulk powder and used subsequently in the following analyses. All complexes are moderately soluble in toluene and readily soluble in THF and CHCl₃ and exhibited expected ¹H and ¹³C resonances in solution NMR spectra. In the ¹H NMR spectra, the N(SiMe₃)₂ ligand for **1–6** is implied by the observation of a singlet falling between δ = 0.62 and δ = 0.47. Multiple resonances between δ = 3.7 and δ = 1.0 are assigned to the alkyl substituents of the guanidinate ligands. The existence of multiple resonances for each alkyl substituent of the guanidinate moiety has been tentatively attributed to the potential zwitterionic resonance of the ligand (Figure 1). Rotation about the C–N bond results in the possibility of both *cis* and *trans* isomers present in solution. In the ¹³C NMR spectra, the low field resonance (~161 ppm) for the central carbon atom “CN₃” of the TAG ligand is an additional distinguishing feature. FT-IR spectroscopy was utilized to confirm the ν(C=N) of the absorption bands around 1550 cm^{–1} corresponding to the N_{imino} donor coordinated to Cu, Ag, and Au.

Structural Descriptions. Compounds **1–6** were further examined by X-ray crystallography. Thermal ellipsoid plots of **1–5** are presented in Figures 2–6. The quality of data obtained for **6** was not suitable for discussion of interatomic distances and angles. Additional crystals of **6** were examined, but satisfactory diffraction was not obtainable. The plot for **6** is shown in Supporting Information, Figure S1. The data collection parameters for all six complexes are presented in Tables 1 and 2, and selected interatomic distances and angles are provided in Tables 3 and 4. The general [M₂(μ-TAG)-{μ-N(SiMe₃)₂}]₂ structure exhibits only minor variation with alteration of the TAG ligand or the Group 11 metal. Because of this similarity, when appropriate, a general description for complexes **1–5** is provided.

Complexes **1–5** were found to exist in the solid-state as a planar M₄N₄ ring with the metal ions bridged by alternating TAG and N(SiMe₃)₂ ligands. Notably, the bridging nitrogen atoms for each ligand were found to exist in the plane of the M₄ unit. The N–M–N angle ranged from 174° to 177°. Significant deviations from the plane of the M₄ unit have been found in previously reported tetranuclear copper and silver clusters.^{9,20} The C=N_{imino} donor of the TAG ligand

Scheme 2. Synthesis of Compounds 1–6



ranges from 1.28 Å to 1.29 Å and are typical for a carbon–nitrogen double bond. The other two C–N distances range from 1.37 Å to 1.43 Å, and the interactions of these N atoms with metals are negligible (the shortest M···N distance is 3.34 Å). There is a small angle ranging from 16°

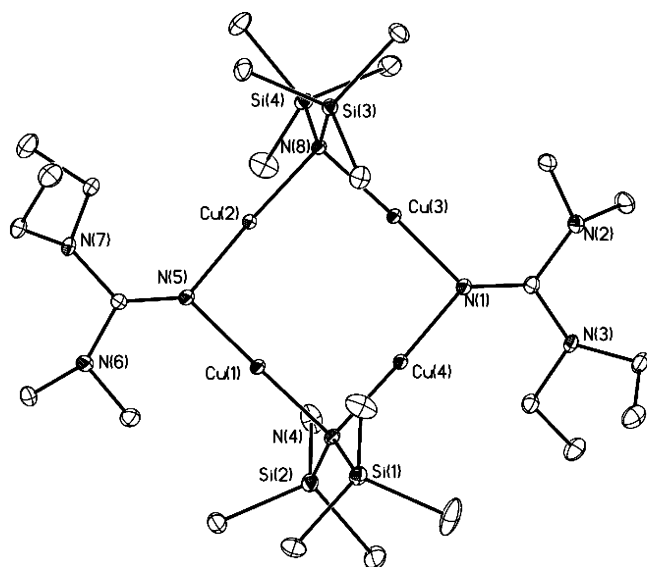


Figure 2. Thermal ellipsoid plot of 1. Ellipsoids are drawn at the 30% level. H atoms have been omitted for clarity.

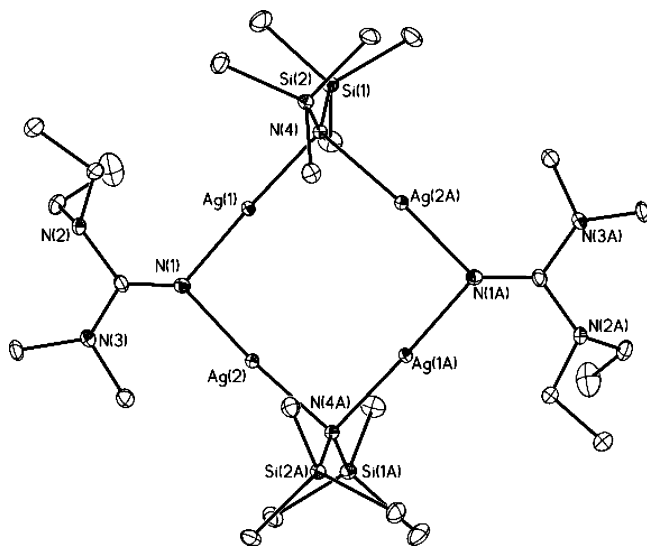


Figure 3. Thermal ellipsoid plot of 2. Ellipsoids are drawn at the 30% level. H atoms have been omitted for clarity.

to 31° between the plane of the “CN₃” framework of the TAG group and the plane of the M₄ unit. The two silicon atoms on each N(SiMe₃)₂ ligand reside on opposite sides of the M₄N₄ plane.

Because of both experimental and theoretical interest in closed-shell d¹⁰-d¹⁰ interactions between Group 11 metals, a discussion involving the M···M distances of 1–5 is warranted. To place the family of TAG complexes into proper context, Table 5 lists the interatomic M···M distances and M–N distances for previously reported tetranuclear Group 11 amides and imides. Complexes 1–5 perhaps best resemble the bis(trimethylsilyl)amides, [M[μ-N(SiMe₃)₂]₄], where M = Cu, Ag, and Au.^{8–10,21} The replacement of two disilylamides by two TAG ligands results in a slight increase in the average M–N distance and a corresponding increase in the M···M distance (2.72 Å, Cu; 3.06 Å, Ag; 3.06 Å, Au). These distances are slightly long in comparison to other Group 11 clusters and are clearly enforced by the ligand geometries, but at the same time they also demonstrate potentially weak M···M interactions stabilizing the complex. Similar reasoning applies to the previously reported cyclic Group 11 mesityl complexes and the gold amide [Au{μ-N(SiMe₃)₂}(PEt₃)₂](BF₄).^{4,22} Also, upon further inspection of 1–5, each tetranuclear cluster is void of intermolecular M···M interaction between the M₄ units; the closest distance is greater than 6 Å. Trinuclear Group 11 pyrazolate com-

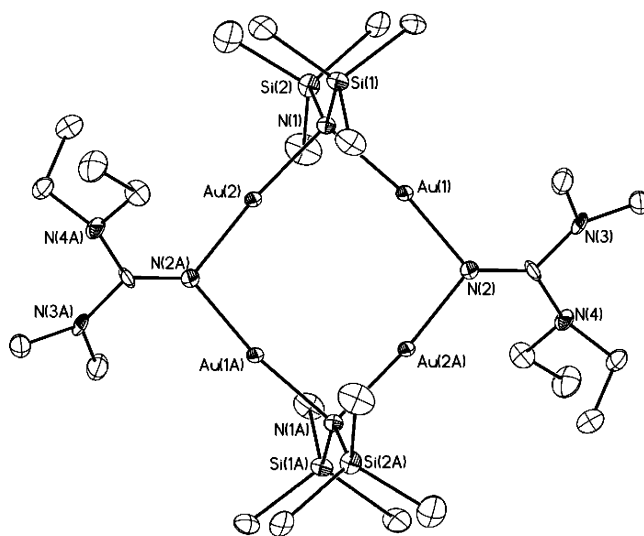


Figure 4. Thermal ellipsoid plot of 3. Ellipsoids are drawn at the 30% level. H atoms have been omitted for clarity.

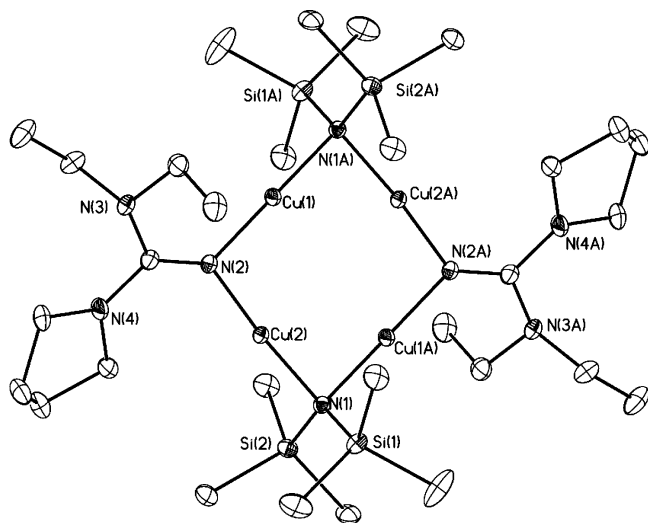


Figure 5. Thermal ellipsoid plot of **4**. Ellipsoids are drawn at the 30% level. H atoms have been omitted for clarity.

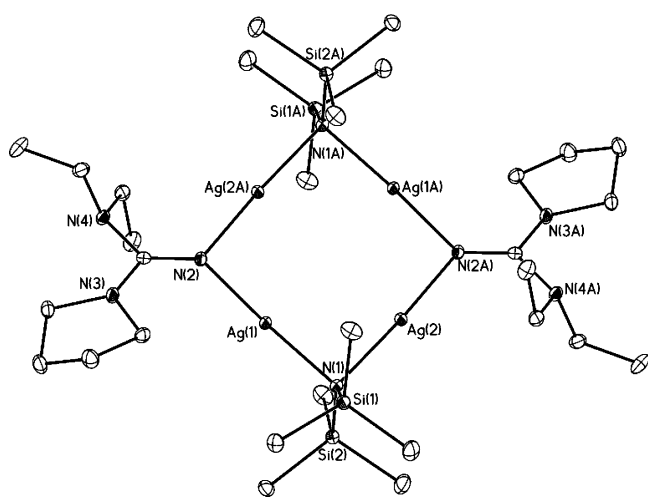


Figure 6. Thermal ellipsoid plot of **5**. Ellipsoids are drawn at the 30% level. H atoms have been omitted for clarity.

Table 5. Structurally Characterized Cyclic $M_4(NR)_4$ Complexes ($M = \text{Cu, Ag, or Au}$)

| complex | M–M Å (avg.) | M–N Å (avg.) | ref |
|--|-----------------|-----------------|----------|
| $[\text{Cu}\{\mu\text{-N}(\text{CH}_3)(\text{CH}_2)_2\text{N}(\text{CH}_3)_2\}_4]$ | 2.62 | 1.91 | 20 |
| $[\text{Cu}\{\mu\text{-N}(\text{CH}_2\text{CH}_3)_2\}_4]$ | 2.67 | 1.90 | 23 |
| $[\text{Cu}\{\mu\text{-N}\{\text{Si}(\text{CH}_3)_3\}_2\}_4]$ | 2.68 | 1.92 | 8, 21 |
| $[\text{Cu}\{\mu\text{-N}\{\text{Si}(\text{CH}_3)_2(\text{Ph})_2\}_2\}_4]$ | 2.68 | 1.92 | 24 |
| $[\text{Cu}\{\mu\text{-N}(\text{CH}_3)_2\}_4]$ | 2.70 | 1.89 | 20 |
| $[\text{Cu}_4\{\mu\text{-1,2-bis}(t\text{-Bu})_2\text{amido}(\text{dimethyl})\text{siloxylbenzene}\}_2]$ | 2.71 | 1.88 | 25 |
| $[\text{Cu}\{\mu\text{-N}\{\text{Sn}(\text{CH}_3)_3\}_2\}_4]$ | 2.71 | 1.89 | 26 |
| $[\text{Cu}\{\mu\text{-pyrrolidiny}\}_4]$ | 2.72 | 1.89 | 20 |
| 1 | 2.72 | 1.88 | <i>a</i> |
| 4 | 2.72 | 1.88 | <i>a</i> |
| $[\text{Cu}\{\mu\text{-N}=\text{C}(t\text{Bu})(\text{Ph})\}_4]$ | 2.77 | 1.86 | 27 |
| $[\text{Ag}\{\mu\text{-2,2,6,6-Tetramethylpiperidino}\}_4]$ | 2.99 | 2.13 | 9 |
| $[\text{Ag}\{\mu\text{-N}\{\text{Si}(\text{CH}_3)_3\}_2\}_4]$ | 3.00 | 2.12 | 9 |
| 2 | 3.05 | 2.10 | <i>a</i> |
| 5 | 3.07 | 2.09 | <i>a</i> |
| $[\text{Au}\{\mu\text{-N}\{\text{Si}(\text{CH}_3)_3\}_2\}_4]$ | 3.02 | 2.08 | 10 |
| 3 | 3.06 | 2.04 | <i>a</i> |

^a This work.

plexes typically exhibit extended $M\cdots M$ intermolecular interaction between clusters.⁷

(20) Gambarotta, S.; Bracci, M.; Floriani, C.; Chiesivilla, A.; Guastini, C. *J. Chem. Soc., Dalton Trans.* **1987**, 1883.

Zwitterionic Resonance. As shown in Figure 1, the zwitterionic resonance structure of the TAG anion facilitates delocalization of the negative charge on the N_{imino} atom. A convenient method to assess the extent of delocalization within the “ $-\text{N}=\text{C}-\text{N}-$ ” component of the TAG ligand is the Δ_{CN} parameter; $\Delta_{\text{CN}} = d(\text{C}-\text{N}) - d(\text{C}=\text{N})$.¹⁶ Δ_{CN} values range from 0 Å in a fully delocalized system and up to ~ 0.10 Å in a fully localized system. For complexes **1–5**, the value of Δ_{CN} can be calculated from the crystallographic data and are found to be both dependent on the nature of TAG and also the metal. The Cu(DEDMG) complex had the largest Δ_{CN} (0.122 Å) versus the Ag(DEDMG) (0.102 Å) and Au(DEDMG) complex (0.103 Å). While the Cu(DEPYRG) and Ag(DEPYRG) complexes (**4** and **5**) had a slightly lower value ($\Delta_{\text{CN}} = 0.096$ Å). Although care must be taken in over interpreting the crystallographic data, it is clear that the Δ_{CN} for complexes **1–5** (~ 0.10 Å) indicates a fully localized system with each TAG retaining C–N and C=N groups. This is consistent with the soft Lewis acidic character of Cu, Ag, and Au requiring the minimum amount of electron density donated from the N_{imino} group.

Concluding Remarks

In this work we have demonstrated that 1,1,3,3-tetraalkylguanidinate ligands are a versatile ligand set for isolating Cu(I), Ag(I), and Au(I) clusters in modest yield. Six tetranuclear complexes have been synthesized and characterized. Analogous to Group 11 chalcogenides and acetylides, it is likely that these six guanidinate clusters represent a subset of a much larger family of complexes. The luminescent properties of the TAG complexes and the synthesis of additional 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: A ball-and-stick plot for **6** is found in Figure S1 and crystallographic data in CIF file format. This material is available free of charge via the Internet at <http://pubs.acs.org>. Crystallographic data (excluding structure factors) for the structures in this paper have been deposited with the Cambridge Crystallographic Data Centre as supplementary publication nos. CCDC 649451 for **1**, CCDC 649452 for **2**, CCDC 649453 for **3**, CCDC 649454 for **4**, and CCDC 649455 for **5**. Copies of the data can be obtained on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, U.K. (fax: +44-(0)1223-336033 or e-mail: deposit@ccdc.cam.ac.uk).

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