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Copper Complexes of Novel Superbasic Peralkylguanidine Derivatives of Tris(2-aminoethyl)amine as Constraint Geometry Ligands

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The coordination chemistry of copper(I) and copper(II) ions with novel tripodal peralkylguanidine derivatives of the tris(2-aminoethyl)amine (tren) backbone TMG$_3$tren (tetramethylguanidino-tren) N{CH$_2$CH$_2$N=C(NMe$_2$)$_2$}$_3$ (**1**) and cyclic DMPG$_3$tren (dimethylpropyleneguanidino-tren) N[CH$_2$CH$_2$N=C{NMe(CH$_2$)$_3$NMe}]$_3$ (**2**) is reported. These sterically demanding ligands form complexes of constraint trigonal geometry. Their superbasic character with estimated pK_{BH^+} values 6 orders of magnitude higher than that of the known Me$_6$tren and their softer N-donor character compared to *tert*-amine ligands stabilize cationic mononuclear Cu(I) and Cu(II) ions by delocalization of charge into the guanidine functionalities. The crystal structures and spectroscopic features of two cationic copper(I) complexes with an uncommon trigonal-pyramidal [N$_4$Cu]$^+$ coordination sphere and a sterically protected open coordination site and of two cationic copper(II) complexes with the characteristic trigonal-bipyramidal coordination geometry [N$_4$CuCl]$^+$ and [N$_5$Cu]$^{2+}$ are reported.

Introduction

Copper complexes with multidentate tripodal alkylamine, Schiff base, or aza aromatic ligands or hybrids thereof have been extensively used to model the structure and reactivity of active sites in copper proteins that transport oxygen, transfer oxygen after O−O bond cleavage, or use oxygen as H atom acceptor, such as hemocyanine,[1] tyrosinase,[2] and galactose oxidase.[3] The ligands of the tris(2-aminoethyl)amine (tren) family shown in Figure 1 are the most prominent representatives among the tripods that force a metal cation into a trigonal-bipyramidal coordination geometry. Coordination chemistry of copper has been mainly developed with H$_6$tren (tris(2-aminoethyl)amine),[5] Me$_6$tren (tris(2-dimethylamino)amine),[5b,6] and tmpa (tris(2-pyridylmethyl)amine),[7] also with Schiff bases,[8] as well as with mixed[9] pyrazole[10] and imidazole[11] or tris(pyrazolylborate)[1h,i,12] derived tripod ligands.

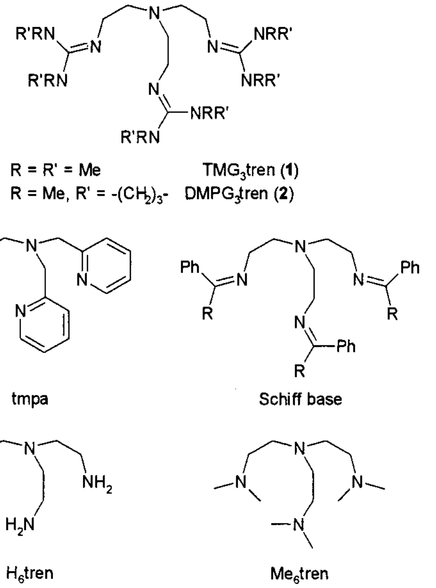

Figure 1. Structural relationship between the novel peralkylguanidino-tren ligands and the most prominent tripods of the tren ligand family.

One approach to influence the catalytic metal properties is the variation of the bite angle of these tripods and of their steric demand by introducing different arm lengths;[7a,b,10,13] another

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approach is the variation of the basicity, softness, and π-acceptor ability of the N-donor, e.g., by alkylation of the primary amine functionality of H_6tren or converting it to an sp^2 N-donor (Schiff base, tmpa).[7,8] Peralkylated guanidines belong to the strongest organic neutral bases known.[14] They are several magnitudes superior in basicity than tertiary amines due to the excellent stabilization of the positive charge in their resonance stabilized cations.[15] This trend may be demonstrated by the pK_{BH^+} (MeCN) values of the 1,2,2,6,6-pentamethylpiperidinium cation (18.62), the parent guanidinium cation (23.3), and the pentamethylguanidinium cation (25.00).[15c] However, despite their prominent proton affinity, surprisingly little is known about their capability to bind Lewis acidic metal cations. There are a few reports on coordination compounds of monoguanidines $HN{=}C(NRR')_2$.[16−20] The first complexes of chelating bisguanidines have been reported by Kuhn[21] and ourselves.[22] Coordination compounds of biologically relevant transition metals Zn, Fe, Mn, and Mo with tripodal trisguanidine TMG$_3$tren ($N\{CH_2CH_2N{=}C(NMe_2)_2\}_3$; **1**) are currently being investigated by us.[23] The pronounced tendency of biguanides to stabilize unusually high oxidation states of metals, e.g., in Ag(III)[24] and Ni(III)[25] complexes (Figure 2), attracted our attention, since highly oxidized copper(III) centers are involved in the activation and cleavage of dioxygen.[1−3,26]

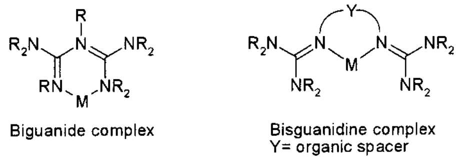

Figure 2. Guanidine-based complexes.

In proteins the H_5-guanidinium functionality of arginine serves as anion receptor.[27] The focus of this investigation is the largely unexplored capability of multidentate R_5-guanidines to serve as receptors for copper(I) and copper(II) cations. The basicity of these neutral ligands lies between that of tertiary amines and amido ligands; they are expected to be softer in character than amines. The question arises whether guanidines may be π-acidic like Schiff bases or π-basic like amido ligands. Many more aspects in guanidine coordination chemistry are unexplored such as fine-tuning of the basicity, donor strength, steric demand, and bite of chelating ligands by variation of the substituents at the guanidine function. Following our study on guanidine coordination compounds with the en and tame backbone,[22] we wish to introduce one with the tren type ligand regime and copper in oxidation states +1 and +2.

Experimental Section

Materials and Methods. All experiments were carried out in hot assembled and under vacuum cooled glassware under an inert atmosphere of argon (99.998%) dried with P_4O_{10} granulate. Solvents and

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triethylamine were purified according to literature procedures and also kept under inert atmosphere. Tris(2-aminoethyl)amine (Fluka) and *N*,*N*′-dimethylpropyleneurea (DMPU) (Aldrich) were used as purchased. Copper(II) perchlorate was dehydrated by the ortho ester method,[40] $CuCl_2$ was dehydrated by treatment with $SOCl_2$;[28] $[Cu(CH_3CN)_4]ClO_4$ was synthesized[29] and CuCl purified[30] according to literature methods. Substances sensitive to moisture and air were kept in a nitrogen-flushed glovebox (Braun, Type MB 150 BG-I).

Spectra were recorded on the following spectrometers: NMR, Bruker ARX 200; IR, Bruker IFS 88 FT; MS (EI-70 eV), Varian MAT CH-7a; MS(APCI), Hewlett-Packard HP 5989 B; elemental analysis, Heraeus CHN-Rapid; melting points, Büchi MP B-540 (uncorrected); X-ray, ENRAF-Nonius CAD4 and Stoe IPDS; ESR, Bruker ESP 300 E (X-Band); magnetic moment: Evans method.[45]

Caution! Phosgene is a severe toxic agent that can cause pulmonary embolism and in case of heavy exposure may be lethal. Use only at a well-ventilated fume hood. Perchlorate salts are potentially explosive and should be handled with care.

The preparation of *N*,*N*,*N*′,*N*′-tetramethylformamidinium chloride and 1,1,1-tris{2-[N^2-(1,1,3,3-tetramethylguanidino)]ethyl}amine (**1**) is described elsewhere.[23]

N,N′-Dimethylpropylenechlorformamidinium Chloride (2a).[31] Analogous to a literature method,[37] phosgene was passed through a solution of *N*,*N*′-dimethylpropyleneurea (DMPU) (103.8 g, 97 mL, 810 mmol) in 300 mL of toluene kept at 0 °C in a flask equipped with a reflux condenser cryostated to −30 °C for 2 h. After that time the phosgene inlet was cut off and the solution was allowed to warm to room temperature stirring for 24 h; after that period the formed suspension was warmed to 35 °C for 3 h, still maintaining the reflux condensor at −30 °C. The light yellow precipitate was filtered off, washed three times with dry ether, and dried in vacuo. Yield: 93% (138 g, 754 mmol).

^{1}H NMR (200.1 MHz, CD_3CN, 25 °C): $\delta = 3.65$ (t, $^3J_{HH} = 5.9$ Hz, 4 H, N−CH_2), 3.29 (s, 6 H, CH_3), 2.07 (quint, $^3J_{HH} = 5.8$ Hz, 2 H, ring−CH_2−) ppm. ^{13}C NMR (50.3 MHz, CD_3CN, 25 °C): $\delta = 152.8$ (CN_3), 50.7 (CH_3), 42.7 (N−CH_2), 19.0 (−CH_2−) ppm; elemental analysis calcd (%) for $C_6H_{12}N_2Cl_2$ (183.1): C 39.36, H 6.61, N 15.30; found C 39.31, H 6.53, N 14.96.

1,1,1-Tris{2-[N^2-(1,3-dimethylpropyleneguanidino)]ethyl}amine (DMPG$_3$tren = 2). To a solution of tris(2-aminoethyl)amine (4.39 g, 4.5 mL, 30 mmol) and triethylamine (9.1 g, 12.5 mL, 90 mmol) in 75 mL of acetonitrile 16.5 g (90 mmol) of $[\{NMe(CH_2)_3NMe\}C-Cl]Cl$ (**B**) dissolved in 75 mL of the same solvent was slowly added under cooling in an ice bath. After the exothermic reaction took place, the mixture was refluxed for 3 h. Afterward 3.6 g (90 mmol) of NaOH in 20 mL of water was added under vigorous stirring to deprotonate the $HNEt_3Cl$. After removal of the solvent as well as excess NEt_3 the precipitate was washed three times with dry ether to remove unreacted amine and dried in vacuo. DMPG$_3$tren (**2**) was obtained by complete deprotonation of the tris(hydrochloride) with 50 mL of 50% KOH and extraction of the aqueous phase with MeCN (3 × 50 mL). The combined filtrates were evaporated to dryness and taken up in a mixture of 50 mL of Et_2O and 10 mL of MeCN. The solution was dried over Na_2SO_4, stirred with activated charcoal to eliminate impurities, and filtered warm through Celite. After drying in vacuo, DMPG$_3$tren was obtained as a beige solid in 90% yield (12.9 g, 27.1 mmol).

mp 73 °C; ^{1}H NMR (200.1 MHz, CD_3CN, 25 °C): $\delta = 3.19-3.15$ (m, 6 H, N−CH_2), 3.03 (t, $^3J_{HH} = 6.4$ Hz, 12 H, ring−N−CH_2), 2.68 (s, 18 H, CH_3), 2.58−2.52 (m, 6 H, =N−CH_2), 1.83 (quint, $^3J_{HH} = 6.3$ Hz, 6 H, ring−CH_2) ppm; ^{13}C NMR (50.3 MHz, CD_3CN, 25 °C): $\delta = 156.9$ (CN_3), 59.1 (N−CH_2), 48.5 (ring−N−CH_2), 47.8 (=N−CH_2), 38.2 (CH_3), 20.3 (ring−CH_2−) ppm; IR (KBr): $\tilde{\nu} = 3410$ m(br), 2940 s, 1595 s, 1438 s, 1320 m, 1234 m, 1161 m, 1109 m, 1041 m, 1013 m, 875 w, 738 w cm^{-1}; MS (70 eV, EI): *m*/*z* (%) = 477 (9) $[(\mathbf{2})]^+$, 336 (24) $[(\mathbf{2})-C_7H_{14}N_3]^+$, 140 (100) $[C_7H_{14}N_3]^+$; elemental analysis calcd (%) for $C_{24}H_{48}N_{10}$ (476.7): C 60.47, H 10.15, N 29.38; found C 60.35, H 10.15, N 28.76.

General Procedure for the Synthesis of the Copper Complexes. Equimolar amounts of dehydrated metal salt and ligand were each dissolved in 5 mL of dry MeCN under argon. The solutions were combined and stirred for 30 min at 40−50 °C, filtered through Celite, and reduced in volume to approximately 2 mL. The complex was then precipitated by the addition of 10 mL of dry ether, washed with absolute ether, and dried in vacuo. Single crystals suitable for X-ray analysis can be grown by slow diffusion of ether into the acetonitrile solution.

Chloro{1,1,1-tris[N^2-(1,1,3,3-tetramethylguanidino)ethyl]amine}-copper(II) Chloride (3). General procedure with dehydrated $CuCl_2$ (134 mg, 1.0 mmol), 450 mg (1.05 mmol) **1**. Yield: 553 mg (0.96 mmol), 96%, yellow-green crystals.

mp 175 °C (dec); IR (KBr): $\tilde{\nu} = 3415$ m(br), 2883 m, 1578 s, 1556 s, 1534 s, 1479 m, 1463 m, 1424 m, 1392 s, 1344 m, 1329 m, 1232 m, 1163 m, 1148 m, 1078 m, 1066 m, 1037 m, 1007 m, 940 m, 902 m, 763 m cm^{-1}; MS (APCI, MeCN): *m*/*z* = 537 [M − Cl]$^+$, 503 $[(\mathbf{1})Cu]^+$, 441 $[(\mathbf{1})]^+$; μ_{eff} (Evans method, 5% benzene-d_6 in CD_3CN, 25 °C): μ_B/mol = 1.9 ± 0.1; elemental analysis calcd (%) for $C_{21}H_{48}N_{10}Cl_2Cu$ (575.1): C 43.86, H 8.41, N 24.35; found C 43.61, H 9.10, N 23.13.

Acetonitrile(1,1,1-tris{2-[N^2-(1,1,3,3-tetramethylguanidino)]ethyl}-amine)copper(II) Diperchlorate (4). General procedure with dehydrated $Cu(ClO_4)_2$ (262 mg, 1.0 mmol), 450 mg (1.05 mmol) **1**. Yield: 707 mg (0.95 mmol), 95%, emerald crystals.

IR (KBr): $\tilde{\nu} = 3439$ w(br), 2890 m, 1579 s, 1559 s, 1534 s, 1461 m, 1426 m, 1395 s, 1347 w, 1332 w, 1256 w, 1163 m, 1094 s, 902 m, 765 m, 623 s cm^{-1}; MS (APCI, MeCN): *m*/*z* = 642 [M − ClO_4]$^+$, 502 $[(\mathbf{1})Cu]^+$, 441 $[(\mathbf{1})]^+$; μ_{eff} (Evans method, 5% benzene-d_6 in CD_3CN, 25 °C): μ_B/mol = 1.8 ± 0.1; elemental analysis calcd (%) for $C_{21}H_{48}N_{10}O_8Cl_2Cu \times CH_3CN$ (744.2): C 37.12, H 6.91, N 20.70; found C 37.10, H 6.46, N 20.50.

{1,1,1-Tris-[N^2-(1,1,3,3-tetramethylguanidino)ethyl]amine}-copper(I) Chloride (5). General procedure with CuCl (99 mg, 1.0 mmol), 450 mg (1.05 mmol) **1**. Yield: 490 mg (0.91 mmol), 91%, pale green crystals.

mp 98 °C (dec); ^{1}H NMR (200.1 MHz, CD_3CN, 25 °C): $\delta = 3.18$ (t, $^3J_{HH} = 5.2$ Hz, 6 H, N−CH_2), 2.68 (s, 18 H, CH_3), 2.62 (s, 18 H, CH_3), 2.56 (t, $^3J_{HH} = 5.2$ Hz, 6 H, =N−CH_2) ppm; ^{13}C NMR (50.3 MHz, CD_3CN, 25 °C): $\delta = 161.8$ (CN_3), 52.5 (=N−CH_2), 48.8 (N−CH_2), 39.1 (CH_3), 39.0 (CH_3) ppm; IR (KBr): $\tilde{\nu} = 3432$ w(br), 2878 m, 1580 s, 1568 s, 1517 s, 1462 m, 1427 s, 1388 s, 1348 m, 1327 m, 1279 m, 1246 m, 1229 m, 1157 m, 1144 m, 1070 m, 1045 m, 1018 m, 999 m, 900 m, 880 m, 757 m cm^{-1}; MS (APCI, MeCN): *m*/*z* = 540 [M]$^+$, 502 $[(\mathbf{1})Cu]^+$, 441 $[(\mathbf{1})]^+$; elemental analysis calcd (%) for $C_{21}H_{48}N_{10}ClCu$ (539.7): C 46.74, H 8.96, N 25.95; found C 46.43, H 9.06, N 25.13.

{1,1,1-Tris-[N^2-(1,3-dimethylpropyleneguanidino)ethyl]amine}-copper(I) Perchlorate (6). General procedure with $[Cu(CH_3CN)_4]ClO_4$ (327 mg, 1.0 mmol), 490 mg (1.05 mmol) **2**. Yield: 555 mg (0.87 mmol), 87%, colorless crystals.

^{1}H NMR (200.1 MHz, CD_3CN, 25 °C): $\delta = 3.21$ (t, $^3J_{HH} = 5.2$ Hz, 6 H, N−CH_2), 3.05 (t, $^3J_{HH} = 6.4$ Hz, 12 H, ring−N−CH_2), 2.75 (s, 18 H, CH_3), 2.58 (t, $^3J_{HH} = 5.2$ Hz, 6 H, =N−CH_2), 1.85 (quint, $^3J_{HH} = 6.4$ Hz, 6 H, ring−CH_2) ppm; ^{13}C NMR (50.3 MHz, CD_3CN, 25 °C): $\delta = 159.3$ (CN_3), 53.1 (N−CH_2), 48.6 (=N−CH_2), 47.8 (ring−N−CH_2), 38.5 (CH_3), 21.1 (ring−CH_2−) ppm; IR (KBr): $\tilde{\nu} = 3436$ w(br), 2948 m, 2882 m, 1602 s, 1577 s, 1507 s, 1438 m, 1422 m, 1365 m, 1341 m, 1322 m, 1276 m, 1243 m, 1167 m, 1096 s(br), 1041 m, 744 m, 715 m, 622 m cm^{-1}; MS (APCI, MeCN): *m*/*z* = 639 [M]$^+$, 540 $[(\mathbf{2})Cu]^+$, 477 $[(\mathbf{2})]^+$; elemental analysis calcd (%) for $C_{24}H_{48}N_{10}O_4ClCu$ (639.7): C 45.06, H 7.56, N 21.90; found C 45.36, H 7.94, N 21.78.

{1,1,1-Tris[N^2-(1,1,3,3-tetramethylguanidino)ethyl]amine}-copper(I) Perchlorate (7). General procedure with $[Cu(CH_3CN)_4]ClO_4$ (327 mg, 1.0 mmol), 450 mg (1.05 mmol) **1**. Yield: 535 mg (0.89 mmol), 89%, colorless crystals.

^{1}H NMR (200.1 MHz, CD_3CN, 25 °C): $\delta = 3.19$ (t, $^3J_{HH} = 5.4$ Hz, 6 H, N−CH_2), 2.70 (s, 18 H, CH_3), 2.64 (s, 18 H, CH_3), 2.58 (t, $^3J_{HH} = 5.2$ Hz, 6 H, =N−CH_2) ppm; ^{13}C NMR (50.3 MHz, CD_3CN, 25

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Table 1. Selected Bond Lengths [pm] and Bond Angles [deg] for Complexes **3**−**6**, Crystallographic Standard Deviations in Parentheses[a]

	[(**1**)Cu^{II}Cl]Cl (**3**)	[(**1**)Cu^{II}(NCMe)]$(ClO_4)_2$ (**4**)	[(**1**)Cu^{I}]Cl (**5**)	[(**2**)Cu^{I}]ClO_4 (**6**)
Cu(1)−N(2)	210.4(3)	205.4(4)	205.2(2)	205.1(3)
Cu(1)−N(5)	209.1(3)	205.7(4)	205.2(2)	203.6(3)
Cu(1)−N(8)	210.9(3)	208.2(4)	205.2(2)	205.1(3)
Cu(1)−N(1)	211.1(3)	207.8(5)	219.0(3)	217.4(3)
Cu(1)−L_{ax}	228.5(1)	200.2(5)		
ϕ C−N_{eq}	131.4 ± 0.3	130.8 ± 0.7	129.4 ± 0.0	130.3 ± 0.5
ϕ C−NR_2	136.4 ± 0.5	136.3 ± 0.8	137.6 ± 0.6	137.8 ± 1.6
N(1)−Cu(1)−N(11)	178.40(9)	177.62(17)		
ϕ N_{eq}–CuN_{eq}	118.1 ± 2.6	118.6 ± 1.4	119.0 ± 0.0	119.2 ± 1.6
ϕ N_{ax}–CuN_{eq}	81.9 ± 0.3	83.2 ± 0.4	84.3 ± 0.0	84.8 ± 0.1
ϕ $\Sigma°CN_3$	360.0 ± 0.0	360.0 ± 0.0	360.0 ± 0.0	359.8 ± 0.0
ϕ $\Sigma°N_{eq}$	358.5 ± 0.4	359.8 ± 0.1	357.5 ± 0.0	357.8 ± 0.3
ϕ $\Sigma°NR_2$	358.6 ± 0.5	359.8 ± 0.3	356.6 ± 1.5	352.4 ± 5.9

[a] Calculated average values (ϕ) are denoted with standard deviation (±).

°C): δ = 161.8 (CN_3), 52.5 (=N−CH_2), 48.8 (N−CH_2), 39.1 (CH_3), 39.0 (CH_3) ppm; IR (KBr): $\tilde{\nu}$ = 3437 w(br), 2876 m, 1588 s, 1570 s, 1518 m, 1456 m, 1428 m, 1389 s, 1343 w, 1326 w, 1248 w, 1229 w, 1158 m, 1142 m, 1092 s, 883 w, 757 w, 621 w cm^{-1}; MS (APCI, MeCN): m/z = 602 $[M]^+$, 502 $[(\mathbf{1})Cu]^+$, 441 $[(\mathbf{1})]^+$; elemental analysis calcd (%) for $C_{21}H_{48}N_{10}O_4ClCu$ (603.7): C 41.78, H 8.01, N 23.20; found C 42.48, H 7.60, N 22.80.

X-ray Structure Analysis. Crystal data and experimental conditions are listed in Table 3. The molecular structures are illustrated as ORTEP[32] plots in Figures 7−10

Selected bond lengths and angles with standard deviations in parentheses are presented in Table 1. Intensity data were collected with graphite monochromated Mo Kα radiation (λ = 71.073 pm). The collected reflections were corrected for Lorentz and polarization effects. Structures **4**, **5**, and **6** were solved by direct methods and refined by full-matrix least-squares methods on F^2 while **3** was solved with SIR92.[33] Hydrogen atoms were calculated and isotropically refined.[34]

Results and Discussion

Synthetic Studies. Multidentate alkyltetramethylguanidines are synthesized by treating primary polyamines with Vilsmeyer salts, a method described earlier by Eilingsfeld and Seefelder[35] and improved by Kantlehner et al.[36] for monoguanidines. Because of difficulties in purification of bis- and trisguanidines, there is a need for selective reactions in this synthesis. A close to quantitative transformation of a primary amine functionality into the guanidine is accomplished by the reaction with the Vilsmeyer salt $[(Me_2N)_2C{-}Cl]Cl$ obtained by reaction of tetramethylurea with phosgene,[37] trichloromethylchloroformate (diphosgene),[38a] or oxalyl chloride in toluene.[39] Cyclic guanidines may be prepared by a similar strategy.[38] The corresponding guanidinium salt is then deprotonated in THF/NaH or in a two-phase system of 50% NaOH(aq)/MeCN to yield the free base. By using this protocol 1,1,1-tris{2-[N^2-(1,1,3,3-tetramethylguanidino)]ethyl}amine (**1**) (TMG_3tren) has been obtained in a yield of 86%.[23] We were interested to create a ligand with cyclic guanidine functionalities, as in five- and six-membered cyclic guanidines the lone pairs at the nitrogen atoms are forced into better conjugation; thus an enhanced N-basicity and a better donor strength than that of non cyclic counterparts may be anticipated. Treatment of commercially available *N,N′*-dimethylpropyleneurea (DMPU) with phosgene leads to the corresponding chloroamidinium salt which is condensed with H_6tren to finally yield the new ligand 1,1,1-tris{2-[N^2-(1,3-dimethylpropyleneguanidino)]ethyl}amine (**2**) ($DMPG_3$tren).

Both ligands **1** and **2** have been used in the synthesis of stable and highly crystalline copper complexes **3**−**6**. It is remarkable that guanidines as very strong but polarizable bases stabilize both copper(I) and copper(II) centers in the same N_4-donor regime. This is in contrast to the known instability for some copper(I) complexes of H_6tren ligands, which are harder in character and sterically less shielded: their complexes tend to disproportionate to copper(0/II).[6c] Due to the high proton affinity of our guanidines, the dominant species in aqueous solution are hydrated guanidinium hydroxides. Therefore, these ligands tend to form basic copper(II) salts from aqua complexes. To overcome the tendency of protolysis, the Cu(II) salts were dehydrated by the ortho ester method[40] prior to their use as starting material. The complexes are synthesized in good yields by combining the dehydrated metal salts with 1.05 equiv of **1** and **2** in dry acetonitrile. Surprisingly, all complexes **3**−**6** are ionic, even those of copper(I) such as **5** that contains a nonsolvated chloride ion in the solid state structure (vide infra). Consequently, **3**−**6** are soluble in polar aprotic media such as MeCN and acetone or CH_2Cl_2 but insoluble in diethyl ether and hydrocarbons.

Due to the high proton affinity of the ligand, all complexes **3**−**6** are sensitive to moisture. The hydrolytic sensitivity of their M−N bond is between amine and amido complexes. We proved that only the M−N and not the C═N bonds are hydrolytically cleaved by water.[23]

The copper(I) complexes are highly sensitive to oxygen. We are currently investigating this reaction by means of UV−vis

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(34) Crystallographic data (excluding structure factors) for the structures reported in this paper have been deposited with the Cambridge Crystallographic Data Centre as Supplementary Publication No. CCDC-161187 (**3**), CCDC-161186 (**4**), CCDC-161184 (**5**), and CCDC-161185 (**6**). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+ 44) 1223 336−033; e-mail: deposit@ccdc.cam.ac.uk).

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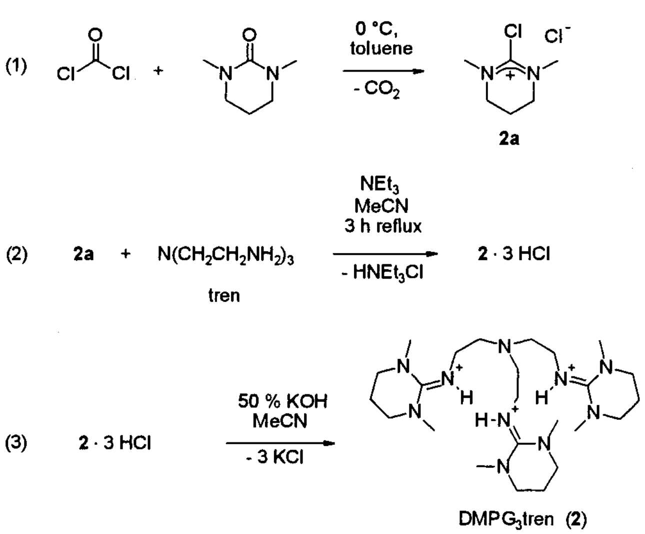


Figure 3. Preparation of peralkylated oligoguanidines, e.g., DMPG$_3$-tren (**2**).

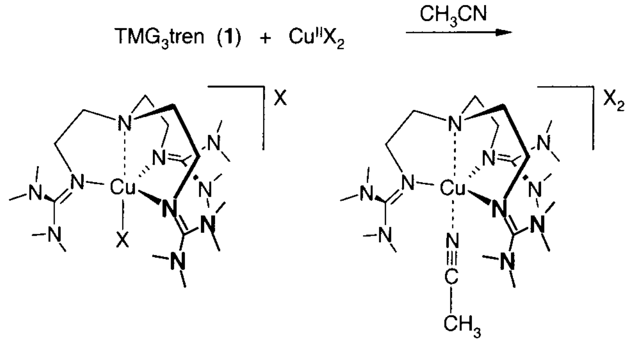
and Raman spectroscopies[41] as well as other oxidative addition reactions.

Spectroscopic Studies. All complexes show the parent molecular ions in the APCI mass spectra obtained from MeCN solutions. Their composition is confirmed by the characteristic isotopic patterns which are in accord with simulated ones.

A difference between the free guanidine base and its coordinated or protonated forms can be recognized in the infrared spectra where the free ligands show a single absorption ν(C═N) at wavenumbers of 1620 (TMG$_3$tren) and 1595 (DMPG$_3$tren) cm^{-1} (KBr pellet). In complexes with Lewis acids this absorption shows fine structure which is a typical feature due to lowering of the molecular symmetry in guanidinium cations. It is also found in the hexamethylguanidinium cation.[42] As a consequence to weakening of the double bond, the absorption for the C═N stretching frequency is shifted to lower wavenumbers by 60 cm^{-1} in Cu(II) and 50 cm^{-1} in Cu(I) complexes.

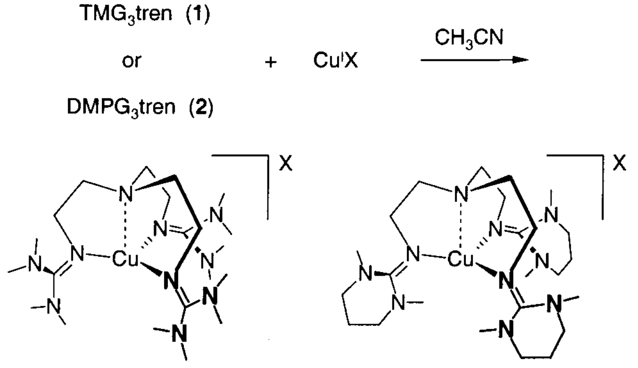
As expected, the Cu(I) complexes **5**, **6**, and **7** are diamagnetic and colorless. Their 200 MHz room-temperature ^{1}H and ^{13}C NMR spectra in CD$_3$CN reveal two sets of chemically inequivalent *N*-methyl protons. This behavior is explained by a rigid >C═N− bonding axis on the NMR time scale rendering one NMe$_2$ group cis and the other one trans with respect to the Cu substituent. By raising the temperature, coalescence of the proton signals cannot be observed up to temperatures of 336 K for **7** at 500 MHz in CD$_3$CN,[43] which is probably due to the sterically congested situation of the coordinated tren ligand. The barrier to rotation about the C═N bond should be higher than the estimated 71 kJ/mol.[44]

The magnetic susceptibilities of the paramagnetic Cu(II) complexes were determined by the Evans method[45] for [(TMG$_3$tren)Cu^{II}Cl]Cl (**3**), $\mu_{eff} = 1.9 \pm 0.1\ \mu_B$, and [(TMG$_3$-tren)Cu^{II}(NCMe)](ClO$_4$)$_2$ (**4**), $\mu_{eff} = 1.8 \pm 0.1\ \mu_B$. The values are well in accordance with literature values[46] of known tren complexes: μ_{eff}[(Me$_6$tren)Cu^{II}X]X (X = Br, ClO$_4$), 1.86 μ_B;[4] μ_{eff}[(H$_6$tren)Cu^{II}Cl]$_2$(BPh$_4$)$_2$, 2.01 μ_B; μ_{eff}[(H$_6$tren)Cu^{II}Br]$_2$-(BPh$_4$)$_2$, 1.94 μ_B.[5f]



X = Cl (**3**) X = ClO$_4$ (**4**)

Figure 4. Complex formation of copper(II) perchlorate and chloride with TMG$_3$tren (**1**).



X = Cl (**5**), ClO$_4$ (**7**) X = ClO$_4$ (**6**)

Figure 5. Complex formation of Cu(I) salts with TMG$_3$tren (**1**) and DMPG$_3$tren (**2**).

EPR spectra of the two copper(II) complexes **3** and **4** were recorded in frozen solution of acetonitrile (120 K) at 9.2608 GHz (X-Band) and values for *g* and *A* were estimated from simulated spectra.[47]

Complex **3** shows a single unresolved line at g_{iso}= 2.141(5) with 13.68 mT peak-to-peak distance. The absence of any resolution by substituting one nitrogen with a chlorine atom in the first ligand sphere is mainly caused by the two magnetic isotopes (^{35}Cl 75.8%, ^{37}Cl 24.2%) with spin 3/2 (2 × 4 = 8 instead of 3 lines), the 4.0 (^{35}Cl) and 4.9 (^{37}Cl) times higher quadrupole moments, the slightly higher gyromagnetic moments (1.35 and 1.13 times greater than for ^{14}N), and the 8 times higher spin−orbit constants.[48] The latter causes a faster spin relaxation via the spin−orbit coupling and therefore broadens the lines more at the same temperature. The higher spin−orbit constants are probably also responsible for reduction of the *g*-anisotropy of complex **3** compared to complex **4**, visible by comparing the spectral width of both spectra (13.68 mT for **3**$_{exp}$, 18.57

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(43) Maximum ^{1}H NMR recording temperature in CD$_3$CN (bp 81 °C) due to field inhomogeneity.

(44) Value calculated by $\Delta G^{\ddagger} = (19.1 \times 10^{-3})T_c(9.97 + \log T_c - \log |\nu_A - \nu_B|)$, $\Delta\nu$ obtained from experimental 300 K spectrum. Hesse, M.; Meier, H.; Zeeh, B. In *Spektoskopische Methoden in der organischen Chemie*, 4. Aufl.; Thieme Verlag: Stuttgart, New York, 1991.

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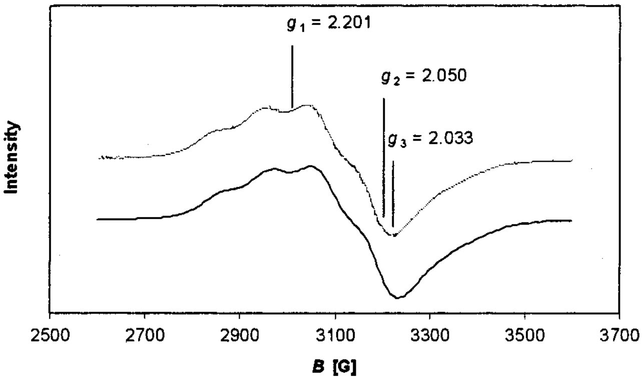

Figure 6. Experimentally determined (bottom, —) and simulated (top, ···) EPR spectra (X-band) of complex $[(TMG_3tren)Cu^{II}(NCMe)](ClO_4)_2$ (**4**) in frozen solution of acetonitrile (120 K), microwave frequency = 9.2608 GHz (A_1 = 98; A_2 = 32; A_3 = 58 × 10^{-4} cm^{-1}).

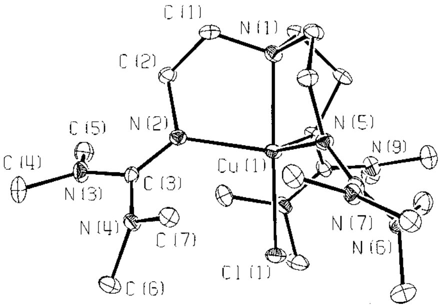

Figure 7. ORTEP view of $[(TMG_3tren)Cu^{II}Cl]Cl$ (**3**). Thermal ellipsoids are at 30% probability level; second peripheral chloride anion and hydrogen atoms omitted for clarity.

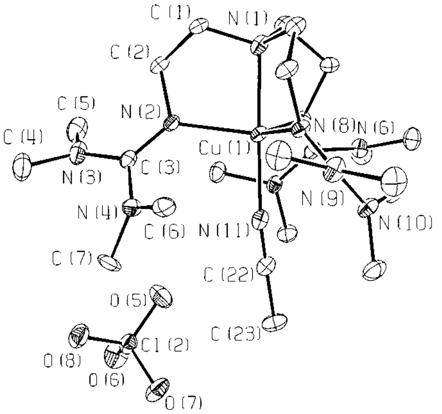

Figure 8. ORTEP view of $[(TMG_3tren)Cu^{II}(NCMe)](ClO_4)_2$ (**4**). Thermal ellipsoids are at 30% probability level; second peripheral perchlorate anion and hydrogen atoms omitted for clarity.

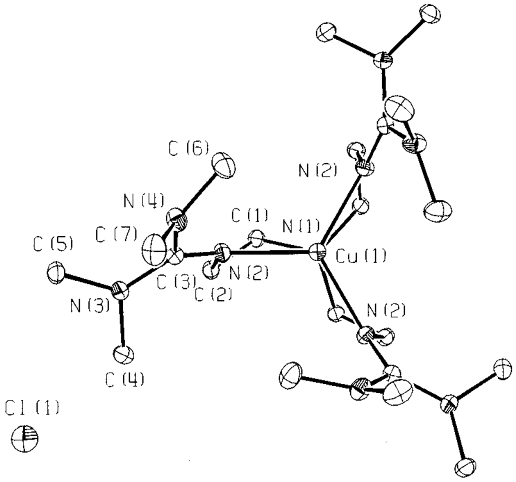

Figure 9. ORTEP view of $[(TMG_3tren)Cu^{I}]Cl$ (**5**) with crystallographically imposed C_3 symmetry, projection along the C_3 axis. Thermal ellipsoids are at 30% probability level; hydrogen atoms omitted for clarity.

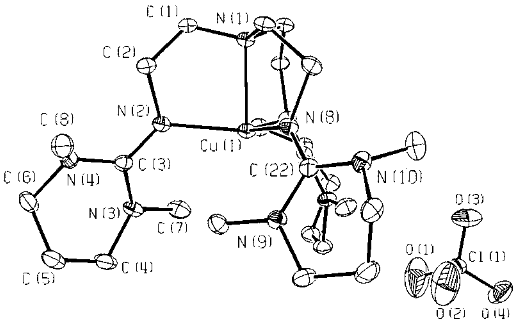

Figure 10. ORTEP view of $[(DMPG_3tren)Cu^{I}]ClO_4$ (**6**). Thermal ellipsoids are at 30% probability level; hydrogen atoms omitted for clarity.

mT for $\mathbf{4}_{exp}$).[49] The latter is speculative because it is not possible to exclude a reduction of $^{63,65}Cu$ hyperfine interaction as a reason for the more narrow overall spectral width.

The EPR spectrum of complex **4** (Figure 6) has been analyzed by least-squares fits to an orthorhombic spin Hamiltonian. The g-tensor with $g_1 = 2.201(5)$, $g_2 = 2.050(5)$, and $g_3 = 2.033(5)$ obtained by best fit is in the expected range for Cu(II) complexes.[1c,5a,c,f,50,51] The small but detectable deviation from axial symmetry ($g_2 - g_3 = 0.02$) is in agreement with the crystallographic data (vide infra). Overall, the spectrum is consistent with trigonal-bipyramidal geometry for d^9 configurations[1c,5a] with elongated axial ligands due to Jahn–Teller distortion ($g_{\|}$ (g_1) > $g_{\perp}$ (g_2,g_3) ≈ 2.04).[52] The poor resolution is caused by inhomogeneous broadening due to hyperfine interaction with the nitrogen atoms in the first ligand sphere. The individual hyperfine tensors are most likely magnetically inequivalent with respect to the g-tensor axes because of symmetry reasons.

Molecular Structures. The crystal structures of complexes **3**–**6** were established by X-ray crystallography. Single crystals were grown by slow diffusion of ether into saturated acetonitrile solutions. The results are displayed in Figures 7–10, selected bonding distances and angles are collected in Table 1, and parameters of the data collection and refinement are shown in Table 3. All complexes possess a close to trigonal molecular geometry with the tertiary amine nitrogen atom located in the apical and three guanidine nitrogens in the equatorial positions. **5** has crystallographically imposed C_3 symmetry. The copper(II) complexes **3** and **4** have a trigonal-bipyramidal core with a chloro ligand for monocationic **3** or an acetonitrile ligand for dicationic **4** occupying the axial position trans to the *tert*-amine

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Table 2. Structural Features of Complexes **3**−**6** and Literature Counterparts[a]

complex	axial distortion[b] [pm]	$d(M-N_{eq})$[c] [pm]	$d(M-N_{ax})$ [pm]	$d(M-L_{ax})$ [pm]	τ[d]
$[(\mathbf{1})Cu^{II}Cl]^+$ (**3**)	29.5	210.1 ± 0.8	211.1(3)	228.5(1)	0.96
$[L^2Cu^{II}Cl]^+$[6b] (**A**)	20.8	218.6 ± 0.0	204.0(6)	223.4(2)	1.01
$[L^3Cu^{II}Cl]^+$[7a,d] (**A′**)	31.8	206.5 ± 0.5	205.0(6)	223.3(2)	1.00
$[(\mathbf{1})Cu^{II}(NCMe)]^{2+}$ (**4**)	24.5	206.4 ± 1.3	207.8(5)	200.2(5)	0.95
$[L^1Cu^{II}(NCMe)]^{2+}$[5b] (**B**)	16.2	207.0 ± 0.0	198(1)	200(2)	1.01
$[L^2Cu^{II}(NCMe)]^{2+}$[5b] (**B′**)	16.3	214.2 ± 1.1	200.4(6)	196.5(7)	0.97
$[(\mathbf{1})Cu^{I}]^+$ (**5**)	20.5	205.2 ± 0.0	219.0(3)		
$[(\mathbf{2})Cu^{I}]^+$ (**6**)	18.6	204.6 ± 0.7	217.4(3)		
$[L^2Cu^{I}(ClO_4)]^+$[6c] (**C**)	19.1(8)	212.2 ± 0.0	220.0(7)	353(1)	
$[L^3Cu^{I}(NCMe)]$[7c] (**C′**)	56.8	211.0 ± 1.5	243.9(8)	199.9(9)	0.99
$[L^4Cu^{I}]$[8a] (**C″**)	20.8(1)	201.0 ± 0.7	223.2(2)		

[a] $L^1 = H_6$tren, $L^2 = Me_6$tren, L^3 = tmpa, $L^4 = S_3$tren, Schiff base $N(CH_2CH_2N{=}CH{-}Ph)_3$. Standard deviations in parentheses. [b] Distance of M to equatorial plane defined by the three equatorial nitrogen atoms. [c] Average bond distance of three equatorial nitrogen atoms to metal center. [d] $\tau = 1$ for ideal trigonal bipyramidal geometry; $\tau = 0$ for ideal square pyramidal structure.

Table 3. Crystal Data and Structure Refinement for **3**−**6**

	$[(TMG_3tren)$-$Cu^{II}Cl]Cl$ (**3**)	$[(TMG_3tren)$-$Cu^{II}(NCMe)](ClO_4)_2$ (**4**)	$[(TMG_3tren)$-$Cu^{I}]Cl$ (**5**)	$[(DMPG_3tren)$-$Cu^{I}]ClO_4$ (**6**)
empirical formula	$C_{21}H_{48}N_{10}Cl_2Cu$	$C_{23}H_{51}N_{11}O_8Cl_2Cu$	$C_{21}H_{48}N_{10}ClCu \times O$	$C_{24}H_{48}N_{10}O_4ClCu$
formula weight [g mol^{-1}]	575.1	744.2	539.7 × 16.0	639.7
temperature [K]	203(2)	193(2)	203(2)	193(2)
crystal system	triclinic	monoclinic	hexagonal	monoclinic
space group	$P\bar{1}$	$P2_1/c$	$R\bar{3}$	$P2_1/n$
a [pm]	1310.4(1)	1137.2(2)	1181.3(2)	1512.2(2)
b [pm]	1310.7(1)	1491.2(1)	1181.3(2)	1179.0(1)
c [pm]	2921.0(2)	1154.5(3)	3505.6(2)	1742.3(2)
α [deg]	89.985(8)	90	90	90
β [deg]	89.599(11)	94.194(19)	90	104.458(12)
γ [deg]	60.428(7)	90	120	90
volume [Å^3]	4363.2(6)	1819.5(7)	4236.6(11)	3007.9(6)
Z	2	4	3	4
ρ [mg m^{-3}]	1.321	1.422	1.307	1.413
μ [mm^{-1}]	0.935	0.841	0.900	0.863
F(000)	1860	1572	1787	1360
crystal size [mm^3]	0.70 × 0.70 × 0.20	1.20 × 0.30 × 0.15	0.72 × 0.51 × 0.06	0.54 × 0.45 × 0.15
diffractometer	Stoe IPDS	Enraf Nonius CAD4	Enraf Nonius CAD4	Enraf Nonius CAD4
scan technique	*ω*-scan	*ω*-scan	*ω*-scan	*ω*-scan
θ-range for data collection [deg]	1.91−25.95	2.40−24.97	2.31−25.00	2.22−24.96
index ranges				
h	$-16 \le h \le 16$	$-19 \le h \le 19$	$-12 \le h \le 0$	$0 \le h \le 17$
k	$-16 \le k \le 16$	$-15 \le k \le 0$	$-12 \le k \le 0$	$0 \le k \le 13$
l	$-35 \le l \le 35$	$0 \le l \le 19$	$-41 \le l \le 41$	$-20 \le l \le 20$
reflections collected	50906	6641	1916	5477
independent reflections	15843	6091	1649	5265
R_{int}	0.0570	0.0298	0.0491	0.0303
observed reflections [$F \ge 4\sigma(F)$]	9893	5019	1544	4368
data/restraints/parameters	15843/0/965	6091/0/418	1649/0/167	5265/0/361
goodness of fit on F^2	0.805	1.198	1.055	1.052
R_1 [$F_0 \ge 4\sigma(F)$][a]	0.0434	0.0618	0.0432	0.0518
wR_2 (all data)[a]	0.1198	0.2073	0.1206	0.1489
transmission (max/min)	0.8351/0.5607	0.8842/0.4319	0.9480/0.5633	0.8814/0.6529
largest diff peak and hole [e Å^{-3}]	1.056/−1.692	0.626/−1.349	0.894/−0.788	1.217/−0.548

[a] $R_1 = \Sigma||F_0| - |F_c||/\Sigma|F_0|$; $wR_2 = \{\Sigma[w(F_0^2 - F_c^2)^2]/\Sigma[w(F_0^2)^2]\}^{1/2}$.

functionality. This is the expected coordination geometry also known from Cu(II)−tren complexes even with rather weakly coordinating anions such as triflate[5b] or perchlorate.[4b] In the copper(I) complexes **5** and **6**, however, the axial position trans to the amine functionality remains unoccupied regardless of the coordinative ability of an anion such as chloride or acetonitrile as solvent. The incapacity of our Cu(I) complexes to take up a second axial ligand is attributed to their 18 valence electron count. In contrast, Karlin's 18 valence electron [(tmpa)Cu(NCMe)]$^+$ complex coordinates an additional axial nitrile ligand.[7c] As a consequence, the axial amine ligand is released into a weaker bonding interaction (Table 2). Tetracoordination was also observed for $[L^4Cu]^+[BPh_4]^-$,[8a] a Schiff base derivative of tren, if noncoordinating anions and noncoordinating solvent such as acetone were applied.

The copper atom in **3**−**6** is slightly axially distorted, being localized below the equatorial plane defined by the guanidine nitrogen atoms. Consequently, the $N_{ax}-Cu-N_{eq}$ angles are smaller than 90°. In complexes involving longer arm lengths of the tripod,[7a,b,10,13] copper can also be localized above the plane of the three equatorial nitrogen atoms, leading to average $N_{ax}-Cu-N_{eq}$ angles that are larger than 90°. As a measure for the degree of trigonality, the structural index parameter $\tau = (\beta - \alpha)/60°$ [53] was established by Addison and Reedijk.[54] Table 2 compares the distortions from trigonality of our complexes with counterparts from literature of the tren family. The comparison reveals that our guanidine tripods **1** and **2** induce larger axial displacement of the copper atom from the equatorial plane than the purely amine based tren ligands H_6tren (L^1) and Me_6tren (L^2), although not as large as pyridine based tmpa (L^3).

Shorter Cu−N bonds and an increase in the contraction of the TMG_3tren ligand is observed for dicationic **4** when compared to monocationic **3**. This trend can be assigned to the higher effective charge at the metal center.[55] The axial distortion of Cu from the equatorial plane is dependent on ionic radii, electronic configuration, and the coordination number of the metal ions: it is larger for pentacoordinate d^9 Cu(II) (ionic radius 79 pm)[56] than for tetracoordinate d^{10} Cu(I) (74 pm).[56] Interestingly, d^9 Cu(II) ions show shorter bonds to the equatorial guanidine nitrogen atoms than to the axial amine nitrogen atom. The opposite trend—longer equatorial than axial Cu−N distances—has been found for other Cu(II) complexes of the tren ligand family with H_6tren, Me_6tren, and even tmpa with sp^2 N-donor atoms (Table 2, first and second sections). Surprisingly, differences between long axial amine and short equatorial guanidine bonding distances become even more evident for diamagnetic tetracoordinate d^{10} Cu(I) complexes (Table 2, third section), and they are most prominent for isoelectronic pentacoordinate d^{10} Zn(II) ions (ionic radius 82 pm)[56] ($Zn-N_{ax}$ 226.9(2) and $Zn-N_{eq}$ 204.0 ± 0.8 pm).[23] With respect to the general trend of shorter M−N bonds, guanidine-based tren ligands have stronger metal ligand interactions than their amine or pyridine-based counterparts (L^1, L^2, L^3, Table 2). Their excellent donor quality can be attributed in part to their superbasic character 6 orders of magnitude higher than that of *tert*-amines and to their smaller steric hindrance at the sp^2 donor atom compared to tertiary amine tripods. In their donor quality, in their hydrolytic lability of the M−N bond, in their bite indicated by the axial Cu displacement, and in their ability to stabilize some coordination compounds with unusual trigonal-monopyramidal geometry, our neutral guanidine ligands should in fact be placed between the prominent ligand classes H_6tren, Me_6tren, and tmpa introduced by Karlin et al.[7a−c] and the tripodal secondary tren-amido(3−) ligands introduced by Schrock et al.[57]

Besides electronic effects, the steric congestion in the periphery of our multidentate guanidines is an important feature of all structures. Table 1 reveals average values for the sum of angles very close to 360° at the three coordinating guanidine nitrogen atoms $\Sigma°N_{eq}$, at all the other 3 × 2 guanidine nitrogen atoms $\Sigma°NR_2$, and finally at the central guanidine carbon atom $\Sigma°CN_3$. These planar building blocks are, however, twisted by approximately 40° into a propeller-like conformation in order to reduce steric repulsions. As a consequence, the methyl groups of the NMe_2 substituents are staggered and the torsion angles Cu−N−C−N and N−C−N−C are in the range 20−45°, predominantly 35−45° out of plane (Figure 9). Similar dihedral angles out of ideal π-conjugation have been found for the ground state of the hexamethylguanidinium cation[58] and in complexes of **1** with Mn^{2+}, Fe^{2+}, and Zn^{2+} ions.[23] There is a trend that lone pairs at peripheral nitrogen atoms in the more rigid cyclic guanidine system $DMPG_3$tren (**2**) are forced into better conjugation within the CN_3 guanidine unit. In a close to planar arrangement, delocalization of the positive charge is improved, and differences in the three guanidine CN_3 bond lengths are diminished. Thus, ligand **2** should provide enhanced basicity compared to **1**. The equatorial and axial Cu−N bond distances of **2** are in fact smaller compared to **1**; however, they are not significantly smaller as the donor character includes both steric (rigidity) and electronic (basicity) effects.

Conclusion

A novel tripod ligand with three superbasic pentaalkylguanidine donor functions and a constraint geometry to stabilize cationic metal ions in a trigonal-bipyramidal coordination has been introduced. Peralkyloligoguanidines such as **1** and **2** are in fact a new class of N-donor ligands within the large family of multidentate N-donors that typically contain multidentate amines, imines (Schiff bases), and azaaromatic building blocks. Due to their ability to delocalize positive charge into the three guanidinium moieties, TMG_3tren (**1**) and $DMPG_3$tren (**2**) stabilize cationic and dicationic complexes. Our current interest is focused on the activation of small molecules such as dioxygen and their transformations in the molecular pocket imposed by the guanidine ligand regime.

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Supporting Information Available: Figure showing experimentally determined and simulated EPR spectra of **3** in frozen acetonitrile solution (1 page). This material is available free of charge via the Internet at http://pubs.acs.org.

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(53) β and α are defined as the largest and second largest metal centered angleS between two donors A and B in a pentacoordinated molecule ($\beta \geq \alpha$).

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