1996 *Inorg. Chem.* **1996,** *35,* 1996−1999

Trigonal-Bipyramidal Copper(II) Complexes with Symmetric and Unsymmetric Tripodal Tetramine Ligands

Andreas M. Dittler-Klingemann and F. Ekkehardt Hahn*

Institut für Anorganische und Analytische Chemie der Freien Universität Berlin, Fabeckstrasse 34-36, D-14195 Berlin, Germany

Received June 1, 1995⊗

The syntheses of the aliphatic tripodal tetramine ligands $N(CH_2CH_2CH_2NH_2)_3$ (**1**), $N[(CH_2CH_2CH_2NH_2)_2(CH_2CH_2NH_2)]$ (**2**), and $N[(CH_2CH_2CH_2NH_2)(CH_2CH_2NH_2)_2]$ (**3**) are reported. The tripodal N_4-ligands **1**−**3** react with $Cu(OH)_2$ in water to give blue copper(II) complexes. Addition of NH_4PF_6 to such solutions yields complexes of the type $[Cu(N_4)(NH_3)](PF_6)_2$ [**4**; N_4 = **1**, **4a**; N_4 = **2**, **4b**; N_4 = **3**, **4c**]. The molecular structures of complexes **4a**−**c** have been determined by X-ray diffraction. All three complexes can be crystallized from water. Selected crystallographic details are as follows **4a** [**4b**] {**4c**}: formula $C_9H_{27}CuF_{12}N_5P_2$ [$C_8H_{25}CuF_{12}N_5P_2$] {$C_7H_{23}CuF_{12}N_5P_2$}, M = 558.82 [544.79] {530.76} amu, monoclinic [monoclinic] {orthorhombic}, $P2_1/c$ [$C2/c$] {$P2_12_12$}, a = 8.9519(14) [30.181(6)] {15.075(5)} Å, b = 16.803(3) [8.914(3)] {12.2939(14)} Å, c = 13.834(2) [14.253(4)] {10.064(2)} Å, α = 90.0 [90.0] {90.0}°, β = 94.183(12) [93.76(2)] {90.0}°, γ = 90.0 [90.0] {90.0}°, V = 2075.3(10) [3826(3)] {1865.2(12)} Å^3, Z = 4 [8] {4}, R = 5.10 [3.42] {4.32}%, R_w = 6.67 [5.12] {5.23}% for 2480 [2137] {1533} absorption corrected structure factors $F_o^2 \geq 3\sigma(F_o^2)$ and 262 [255] {245} refined parameters. The complex dications in **4a**−**c** exhibit a trigonal-bipyramidal geometry with the tertiary nitrogen of the tripodal ligand and the ammonia nitrogen in the axial positions. Complexes with the unsymmetric ligands **2** and **3** possess both five and six membered chelate rings. Depending on the ligand, the size of the cavity for the ammonia ligand increases from **4a** to **4c**. This leads to a shortening of the Cu−NH_3 bond length with the shortest bond of this type observed for **4c**.

Introduction

Copper complexes with tripodal amine ligands have been used to model the active site in copper proteins containing type 3 dicopper centers, such as hemocyanin Hc.[1] The Cu(I) complex of the tripodal tetradentate ligand tris(2-pyridylmethyl)amine reacts at −80 °C with dioxygen to give a dinuclear Cu(II) complex with a *trans*-μ-η^1-η^1-peroxo bridge, which was the first dioxygen−dicopper complex crystallographically characterized.[2] The spectroscopic properties of this complex, however, do not match those of oxy−Hc.[3] Cu(I) complexes with isopropyl substituted tris(pyrazolyl)borate ligands react with dioxygen to give dinuclear Cu(II) complexes with a μ-η^2-η^2-peroxo bridge, which exhibit spectroscopic properties almost identical to those of oxy−Hc.[4] The ligand systems used to model Hc sites possess nitrogen donor atoms which are part of an aromatic ring systems (pyridine or pyrazolyl) for binding to copper. These groups were chosen to simulate the situation of the copper atoms in Hc which are bound by histidine nitrogen atoms. Coordination by aromatic amines is particularly suitable for the stabilization of the Cu(I) ion.

Comparatively little is known about the coordination chemistry of copper with tripodal aliphatic amines. To date, only the molecular structure of the trigonal-bipyramidal complex $[Cu(tren)(NH_3)](PF_6)_2$ [tren = tris(2-aminoethyl)amine] has been reported.[5] Aliphatic tripodal tetramines might lead to very reactive tetrahedral Cu(I) complexes which react rapidly with dioxygen. To study the coordination chemistry of copper with tripodal aliphatic tetramines, we have prepared symmetric and new unsymmetric N_4 ligands. In this contribution we present a modified synthesis of the symmetric tripodal ligand trpn **1**, the preparation of the unsymmetric ligands **2** and **3** (Figure 1), and the X-ray crystal structures of some trigonal-bipyramidal complexes $[Cu(N_4)(NH_3)](PF_6)_2$ [**4**; N_4 = **1**, **4a**; N_4 = **2**, **4b**; N_4 = **3**, **4c**]. A preliminary account of this work was presented in 1994.[6] Meanwhile a different procedure for the preparation of the hydrochloride of **2** and the crystal structure of the cobalt(III) complex $[Co(NO_3)(\mathbf{2})](ClO_4)_2$ have been published in this journal.[7]

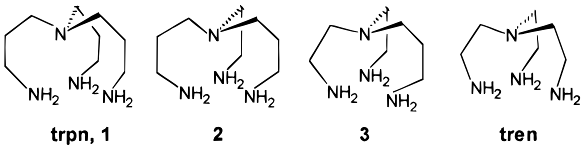


Figure 1. Topology of tripodal tetramine ligands.

Experimental Section

If not noted otherwise, all manipulations were performed in an atmosphere of dry argon using standard Schlenk techniques. Solvents were dried by standard methods and freshly distilled prior to use. ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AM 250 or WP 80 spectrometer. Infrared spectra were taken in KBr on a Perkin-Elmer 983 instrument. Elemental analyses (C,H,N) were performed at the Freie Universität Berlin on a Heraeus CHN-rapid elemental analyzer. Mass spectra (FAB) were recorded on a Varian MAT 311 A instrument.

⊗ Abstract published in *Advance ACS Abstracts,* March 1, 1996.

(1) *Bioinorganic Chemistry of Copper*; Karlin, K. D.; Tyeklar, Z., Eds.; Chapman and Hall: New York, London 1993.

(2) Jacobson, R. R.; Tyeklar, Z.; Farooq, A.; Karlin, K. D.; Liu, S.; Zubieta, J. *J. Am. Chem. Soc.* **1988**, *110*, 3690.

(3) Solomon, E. I.; Baldwin, M. J.; Lowery, M. D. *Chem. Rev.* **1992**, *92*, 541.

(4) Kitajima, N.; Fujisawa, K.; Fujimoto, C.; Moro-oka, Y.; Hashimoto, S.; Kitagawa, T.; Tatsumi, K.; Nakamura, A. *J. Am. Chem. Soc.* **1992**, *114*, 1277.

(5) Duggan, M.; Ray, N.; Hathaway, B.; Tomlinson, G.; Brint, P.; Pelin, K. *J. Chem. Soc., Dalton Trans.* **1980**, 1342.

(6) Dittler-Klingemann, A.; Hahn, F. E. *Abstracts of Papers,* The 30th International Conference on Coordination Chemistry, Kyoto, Japan, July 24−29; abstract S2-10.

(7) Fanshawe, R. L.; Blackman, A. G. *Inorg. Chem.* **1995**, *34*, 421.

0020-1669/96/1335-1996$12.00/0

Modified Synthesis of $N(CH_2CH_2CH_2NH_2)_3$ (1). Tris(2-cyanoethyl)amine[8] (35 g, 0.2 mol) and NaOH (15 g, 0.375 mol) were dissolved in 350 mL of ethanol. To this was added hydrazine (50 mL of an 80% water solution). The mixture was cooled to 0 °C, and Raney nickel (8.8 g, 0.15 mol of nickel) was added in small portions. Initially a vigorous exothermic reaction was observed. The Raney nickel addition was complete after 4 h. The raction mixture was then heated to reflux for 30 min and filtered while still hot. Hydrochloric acid (50 mL of a 25% solution) was added to neutralize the sodium hydroxide. All solvents were removed, and the residue was dried by azeotropic distillation with cyclohexane. Subsequent vacuum distillation yields 18 g (48%, bp 98−104 °C, 0.04 mbar) of **1** as a colorless liquid. Anal. Calcd (found) for $C_9H_{24}N_4$ (fw = 188.32): C, 57.40 (56.14); H, 12.85 (12.23); N, 29.75 (28.34). ^1H NMR ($CDCl_3$, 80 MHz): δ 2.74 (t, 6H, H_2CNH_2), 2.49 (t, 6H, NCH_2), 1.54 (q, 6H, $CH_2CH_2CH_2$), 1.18 (s, 6H, NH_2). These values are almost identical to those reported in ref 9.

Synthesis of $N(CH_2CH_2CH_2NH_2)_2(CH_2CH_2NH_2)$ (2). For the preparation of **2**, ammonia was reacted with 2 equiv of acrylonitrile.[8] A 60.0 g (480 mmol) sample of the resulting $HN(CH_2CH_2CN)_2$ was then added at 0 °C to a solution of 55.6 g (290 mmol) of $Na_2S_2O_5$ and 47.5 g (580 mmol) formaldehyde (37% in water) in 100 mL of water. Then KCN (38.2 g, 680 mmol) was added at 0 °C, and the resulting solution was stirred at ambient temperature for 24 h. The reaction product separates as an oil. It was isolated, and the water layer was washed twice with CH_2Cl_2 (100 mL each). The combined organic phases were washed with water saturated with NaCl and dried over Na_2SO_4. After removal of the solvents an oily yellow solid was obtained. Recrystallization from methanol gave 49 g (62%) of colorless crystals of $N(CH_2CH_2CN)_2(CH_2CN)$. Anal. Calcd (found) for $C_8H_{10}N_4$ (fw = 162.17): C, 59.24 (58.92); H, 6.21 (6.59); N, 34.54 (34.06). ^1H NMR ($CDCl_3$, 250 MHz): δ 3.74 (s, 2H, NH_2CCN), 2.98 (t, 4H, NCH_2), 2.62 (t, 4H, CH_2CH_2CN). $^{13}C\{^1H\}$ NMR (DMSO-d_6, 62.90 MHz): δ 119.25 (CCCN), 116.10 (NCCN), 48.82 (NCC), 40.49 (NCCN), 15.92 (CCCN). All attempts to reduce the nitrile functions to primary amines with Raney nickel/H_2, Raney nickel/hydrazine, $LiAlH_4$, or Pd/H_2 failed. Only reduction with AlH_3 (prepared from $LiAlH_4$ and H_2SO_4) gave the unsymmetric tetramine **2**. The AlH_3 used here was prepared from 42.0 g (1.1 mol) of $LiAlH_4$ and 50.0 g (0.51 mol) of H_2SO_4 (98%) in 1 L of THF (THF = tetrahydrofuran). To the vigorously stirred suspension was added dropwise 20.0 g (123 mmol) of the trinitrile dissolved in 100 mL of THF. The mixture was stirred for 48 h at ambient temperature. Residual AlH_3 was carefulle hydrolyzed with 80 mL of water. All solids were removed by filtration and washed with MeOH (3 × 500 mL). The organic phases were combined, and all solvents were stripped *in vacuo*. The oily residue was suspended in cyclohexane and water was removed by azeotropic distillation (5 h). Distillation of the residue gave 11.0 g of **2** (51%, bp 91−95 °C, 0.01 mbar) as a slightly green liquid. Anal. Calcd (found) for $C_8H_{22}N_4$ (fw = 174.29): C, 55.13 (54.46); H, 12.72 (13.22); N, 32.15 (31.82). ^1H NMR ($CDCl_3$, 250 MHz): δ 2.76 (t, 6H, H_2CNH_2), 2.52 (t, 6H, NCH_2), 1.58 (q, 4H, $CH_2CH_2CH_2$), 1.28 (s, 6H, NH_2). $^{13}C\{^1H\}$ NMR ($CDCl_3$, 62.90 MHz): δ 56.39 ($NCCNH_2$), 51.30 (NCCC), 39.63 ($CCCNH_2$), 38.92 ($NCCNH_2$), 30.23 (CCC).

Synthesis of $N(CH_2CH_2CH_2NH_2)(CH_2CH_2NH_2)_2$ (3). The unsymmetric trinitrile for the preparation of **3** was obtained as described above by Michael addition of 1 equiv of acrylonitrile to ammonia, addition of 1 equiv of cyanomethyl via the Strecker synthesis described above, and finally addition of the second C_2 fragment by addition of glyconitrile $HOCH_2CN$[10] to the central nitrogen atom. Reduction of the trinitrile was achived by use of AlH_3 as in the preparation of **2**; yield 37% (bp 93−98 °C, 0.01 mbar). Anal. Calcd (found) for $C_7H_{20}N_4$ (fw = 160.27): C, 52.46 (52.93); H, 12.58 (12.34); N, 34.96 (34.02). ^1H NMR ($CDCl_3$, 250 MHz): δ 2.50 (t, 6H, H_2CNH_2), 2.26 (t, 6H, NCH_2), 1.40 (q, 2H, $CH_2CH_2CH_2$), 1.06 (s, 6H, NH_2). ^{13}C-$\{^1H\}$ NMR ($CDCl_3$, 62.90 MHz): δ 57.95 ($NCCNH_2$), 50.87 (NCCC), 40.53 ($NCCNH_2$), 39.39 ($CCCNH_2$), 29.93 (CCC).

Table 1. Summary of Crystallographic Data for **4a**−**c**

param	**4a**	**4b**	**4c**
cryst size, mm	0.45 × 0.25 × 0.25	0.70 × 0.44 × 0.06	0.46 × 0.35 × 0.06
formula	$C_9H_{27}CuF_{12}N_5P_2$	$C_8H_{25}CuF_{12}N_5P_2$	$C_7H_{23}CuF_{12}N_5P_2$
mol wt, amu	558.82	544.79	530.76
a, Å	8.9519(14)	30.181(6)	15.075(5)
b, Å	16.803(3)	8.914(3)	12.2939(14)
c, Å	13.834(2)	14.253(4)	10.064(2)
α, deg	90.0	90.0	90.0
β, deg	94.183(12)	93.76(2)	90.0
γ, deg	90.0	90.0	90.0
V, $Å^3$	2075.3(10)	3826(3)	1865.2(12)
Z	4	8	4
space group	$P2_1/c$ (No. 14)	$C2/c$ (No. 15)	$P2_12_12$ (No. 18)
ρ_{expt}, g/cm^3	1.80	1.92	1.89
ρ_{calc}, g/cm^3	1.788	1.891	1.890
μ, cm^{-1}	13.15	14.24	14.58
radiation, λ, Å	Mo Kα, 0.710 73		
2θ range, deg	$2 \leq 2\theta \leq 50$	$2 \leq 2\theta \leq 45$	$2 \leq 2\theta \leq 50$
scan width, $\Delta\theta$, deg	0.55 + 0.35[tan(θ)]	0.55 + 0.35[tan(θ)]	0.80 + 0.35[tan(θ)]
unique data	3651	2487	2433
obsd data	2480, $F_o^2 \geq 3\sigma(F_o^2)$	2137, $F_o^2 \geq 3\sigma(F_o^2)$	1533 $F_o^2 \geq 3\sigma(F_o^2)$
R, %	5.10	3.42	4.32
R_w, %	6.67	5.12	5.23
GOF[b]	1.69	1.31	1.27
no. of var	262	255	245

Preparation of Copper Complexes. The preparation of **4a** is described as an example. Freshly precipitated $Cu(OH)_2$ (1.2 g, 12.3 mmol) was suspended in water (50 mL), and 2.43 g (12.9 mmol) of ligand **1** were added dropwise with a syringe. The blue suspension was stirred at room temperature until the hydroxide had dissolved (2 h), and then 4.9 g (30.0 mmol) of NH_4PF_6 was added. After being stirred for 30 min, the solution was filtered and cooled to 5 °C. After 24 h deep blue crystals had formed. The crystals were collected by filtration and washed with cold methanol.

For 4a. Yield 3.6 g [52% relative to $Cu(OH)_2$]. Anal. Calcd (found) for $[Cu(\mathbf{1})(NH_3)](PF_6)_2$, $C_9H_{27}N_5CuF_{12}P_2$ (fw = 558.82): C, 19.34 (19.17); H, 4.87 (4.93); N, 12.53 (12.18). MS (+FAB, 3-nitrobenzyl alcohol/DMSO, *m/z*): 517 (4), 384 (16), 251 (100, $[Cu(\mathbf{1})]^+$), 192 (63).

For 4b. Yield 22.4%. Anal. Calcd (found) for $[Cu(\mathbf{2})(NH_3)](PF_6)_2$, $C_8H_{25}N_5CuF_{12}P_2$ (fw = 544.79): C, 17.64 (17.29); H, 4.63 (4.31); N, 12.86 (12.52). MS (+FAB, 3-nitrobenzyl alcohol/DMSO, *m/z*): 370 (15), 237 (100, $[Cu(\mathbf{2})]^+$), 216 (13), 178 (60).

For 4c. Yield 20%. Anal. Calcd (found) for $[Cu(\mathbf{3})(NH_3)](PF_6)_2$, $C_7H_{23}N_5CuF_{12}P_2$ (fw = 530.76): C, 15.84 (15.74); H, 4.37 (4.21); N, 13.19 (12.83). MS (+FAB, 3-nitrobenzyl alcohol/DMSO, *m/z*): 223 (100, $[Cu(\mathbf{3})]^+$), 193 (17).

Crystal Structure Analyses. Crystals of **4a**−**c** are air-stable. Suitable specimens were mounted on an Enraf-Nonius CAD-4 diffractometer. Important crystal and data collection details are listed in Table 1. Data for all three compounds were collected at 20(3) °C using $\omega-2\theta$ scans. Raw data were reduced to structure factors[11] (and their estimated standard deviations) by correcting for scan speed, Lorentz, and polarization effects. Empirical absorption corrections based on 3 ψ-scans were applied to each data set. The space group was uniquely defined by systematic absences for **4a** and **4b**. Systematic absences and density measurements indicated the space group $P2_12_12$ for **4c**. This choice was confirmed by the successful solution and refinement of the structure. All three structures were solved by standard Patterson methods. The positional parameters for all non-hydrogen atoms were refined by using first isotropic and later anisotropic thermal parameters. Difference Fourier maps calculated at this stage showed for all three

---

[8] Buc, S. R.; Ford, J. H.; Wise, E. C. *J. Am. Chem. Soc.* **1945**, *67*, 92.

[9] Chin, J.; Banaszczyk, M.; Jubian, V.; Zou, X. *J. Am. Chem. Soc.* **1989**, *111*, 186.

[10] American Cyanamide Co. (A. Cresswell, Inv.) U. S. Patent 2,517,-544 (Aug 8, 1950) [*Chem. Abstr.* **1950**, *44*, 11181e].

[11] Neutral scattering factors were used: *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2B. Terms of anomalous dispersion from: *International Tables for X-Ray Crystallography*; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for **4a**−**c**

Lengths

	4a	**4b**	**4c**
Cu−N1	2.060(4)	2.078(3)	2.064(7)
Cu−N2	2.074(5)	2.047(3)	2.037(7)
Cu−N3	2.117(5)	2.191(3)	2.153(7)
Cu−N4	2.108(5)	2.045(3)	2.069(8)
Cu−N5	2.066(5)	2.022(3)	1.993(7)

Angles

	4a	**4b**	**4c**
N1−Cu−N2	90.7(2)	84.6(1)	84.7(3)
N1−Cu−N3	92.7(2)	93.1(1)	83.9(3)
N1−Cu−N4	90.1(2)	90.5(1)	92.8(3)
N1−Cu−N5	176.6(2)	171.4(1)	175.3(3)
N2−Cu−N3	122.2(2)	101.3(1)	117.2(3)
N2−Cu−N4	127.9(2)	150.5(1)	140.4(4)
N2−Cu−N5	87.2(2)	90.9(1)	90.7(3)
N3−Cu−N4	109.8(2)	108.0(1)	101.7(4)
N3−Cu−N5	90.6(2)	95.0(1)	97.3(3)
N4−Cu−N5	89.2(2)	89.9(1)	91.5(3)

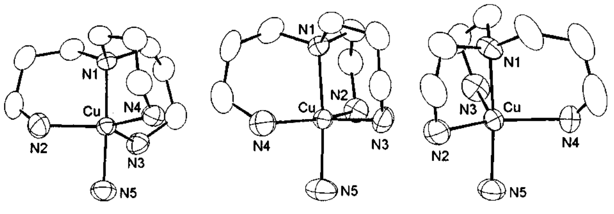
compounds the positional parameters of the hydrogen atoms. However, all hydrogen atoms were added to the structure models on calculated positions [d(C−H) = 0.95 Å, d(N−H) = 0.87 Å][12] and are unrefined. The isotropic temperature factors for hydrogens were fixed to be 1.3 times the B_{eq} of the parent atom. The correct crystallographic enatiomer for **4c** was identified by refinement of both possible sets of coordinates. All calculations were carried out with the MolEN package.[13] ORTEP[14] was used for all molecular drawings. Table 2 lists selected bond distances and angles in the cations of **4a**−**c**.

Results and Discussion

A series of trigonal-bipyramidal Cu^{II} complexes with symmetric and unsymmetric tripodal tetramine ligands has been synthesized and structurally characterized. The preparation of the ligands and the structural trends observed in the Cu^{II} complexes of these ligands are discussed below.

Ligand Syntheses. Previous preparations of **1** by Michael addition of acrylamide to ammonia and reduction of the triamide with $LiAlH_4$ lead to N−CH_2 bond cleavage and low yields of **1**.[15] The synthesis of **1** by Michael addition of acrylonitrile to ammonia and reduction of the resulting tris(2-cyanoethyl)amine with Raney nickel/hydrogen at 40 psi has been reported to proceed with high yield.[9] We have modified this procedure by substitution of hydrogen with hydrazine (5 equiv of hydrazine per molecule trinitrile, 80% in water). The reaction with Raney nickel/hydrazine proceeds below 50 °C at ambient pressure.[16] Ligand **1** was obtained, after purification by distillation, in about 50% yield, eliminating the reduction step under high hydrogen pressure.

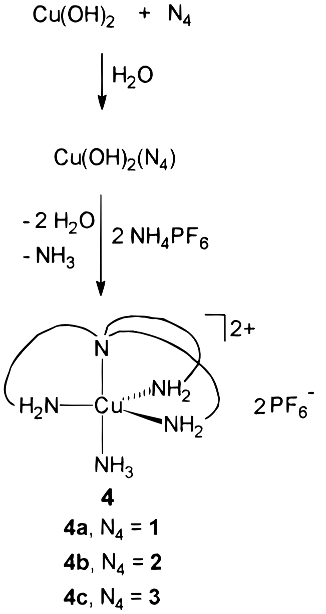
The hydrochloride of the unsymmetric ligand **2** was obtained previously by addition of (2-bromoethyl)phthalimide to diphthaloyldipropylenetriamine followed by acidic removal of phthalic acid in 34% yield.[7] Our strategy for the preparation of **2** and of the previously unknown unsymmetric ligand **3** involves the synthesis of unsymmetric trinitriles by cyanomethylation[17] of β-aminonitriles and subseqent reduction of the nitrile functions with AlH_3.[18] This leads directly to the free tetramine ligands.



4a **4b** **4c**

Figure 2. ORTEP plots of the trigonal-bipyramidal dications in complexes **4a**−**c**.

Scheme 1. Preparation of Cu^{II} Complexes of Ligands **1**−**3**



Copper Complexes. Freshly prepared $Cu(OH)_2$ suspended in water reacts with stoichiometric amounts of the tripodal ligands **1**−**3** to give blue solutions which contain unidentified copper complexes (probably hydroxides). Addition of 2 equiv of NH_4PF_6 to such solutions yields the deep blue complexes **4a**−**c**, which contain an ammonia coligand, as depicted in Scheme 1.

Complexes of type **4** are air-stable and water-soluble. They can be crystallized from this solvent as deep blue plates.

Molecular Structures. The molecular structures of complexes **4a**−**c** were established by X-ray diffraction methods. In all three cases ionic compounds, composed of a trigonal-bipyramidal $[Cu(N_4)(NH_3)]^{2+}$ dication and two PF_6^- anions had formed. The three dications of **4a**−**c** are depicted in Figure 2.

In the dications, the central nitrogen atom of the tetramine and the ammonia nitrogen atom occupy the axial positions. This geometry was previously observed for the complex $[Cu(tren)(NH_3)](ClO_4)_2$.[5] The $[Cu(\mathbf{1})]^{2+}$ dication in **4a** exhibits more or less exact C_3 symmetry, while the $[Cu(tren)(NH_3)]^{2+}$ dication resides on a 3-fold axis and shows crystallographically imposed C_3 symmetry.[5] The major difference between these two dications of symmetrical tripodal tetramines is found for the N_{tert}−Cu−NH_2 angles. These are all smaller than 90° for the $[Cu(tren)(NH_3)]^{2+}$ dication,[5] and they are larger than 90° in $[Cu(\mathbf{1})]^{2+}$(Table 2).

---

(12) Churchill, M. R. *Inorg. Chem.* **1972**, *12*, 1213.

(13) MolEN: Molecular Structure Solution Procedures. Program Descriptions, Enraf-Nonius: Delft, The Netherlands, 1990. Definition of residuals: $R = \sum||F_o| - |F_c||/\sum|F_o|$, $R_w = [\sum w||F_o| - |F_c||^2/\sum w|F_o|^2]^{1/2}$, GOF $= [\sum w||F_o| - |F_c||^2/(n_o - n_p)]^{1/2}$ with n_o = number of structure factors and n_p = number of parameters, $w = 1/[\sigma(F)]^2$.

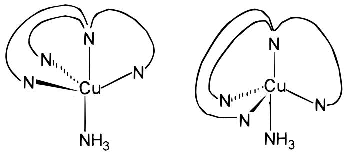
(14) Johnson, C. K. *ORTEP II*; Report ORNL-5138; Oak Ridge National Laboratory: Oak Ridge, TN, 1971.

(15) Hahn, F. E.; Tamm, M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 203.

(16) Furst, A.; Berlo, R. C.; Hooton, S. *Chem. Rev.* **1965**, *65*, 51.

(17) Kaderabeck, V.; Denkstein, J. *Collect. Czech. Chem. Commun.* **1966**, *31*, 2915.

(18) Yoon, N. M.; Brown, H. C. *J. Am. Chem. Soc.* **1968**, *90*, 2927.



$[Cu(tren)]^{2+}$ $[Cu(\mathbf{1})]^{2+}$

Figure 3. Comparison of the molecular structures of complex dications $[Cu(tren)]^{2+}$ and $[Cu(\mathbf{1})]^{2+}$.

The situation changes again for the dications of **4b** and **4c**. First of all the ligand is now capable of forming both five and six membered chelate rings incorporating the copper ion. This leads to a severe distortion of the trigonal-bipyramidal coordination environment around the copper atom. The $N_{eq}-Cu-N_{eq}$ angles vary from 101.3(1) to 150.5(1)° for **4b** and from 101.7(4) to 140.4(4)° for **4c**, while the $N_{ax}-Cu-N_{ax}$ bond angles remain almost linear in **4a**−**c** (Table 2). Apart from the changes in the $N_{eq}-Cu-N_{eq}$ angles for the unsymmetrical ligands, another trend is visible for the angles involving the central ligand nitrogen atom N_{tert}, copper, and the equatorial nitrogen atoms. These $N_{tert}-Cu-N_{eq}$ angles are always larger than 90° for six membered chelate rings and smaller than 90° for five membered rings. Thus, all three $N_{tert}-Cu-N_{eq}$ angles are larger than 90° in **4a**. In **4b** one of these angles, involving the ethylamine chain [$N1-Cu-N2 = 84.6(1)°$] is smaller than 90°, while in **4c** both $N_{tert}-Cu-N_{eq}$ angles involving nitrogens in five membered rings are smaller than 90°. The series is completed by the known complex $[Cu(tren)(NH_3)](ClO_4)_2$, which contains only five membered chelate rings with all $N_{tert}-Cu-N_{eq}$ angles smaller than 90°.

The difference in the coordination environment between the dications $[Cu(\mathbf{1})(NH_3)]^{2+}$ and $[Cu(tren)(NH_3)]^{2+}$ is illustrated in Figure 3. Exemplified on the two extremes it can be seen that the size of the cavity for the ammonia coligand expands from **4a** over **4b** and **4c** to the largest value in $[Cu(tren)(NH_3)]^{2+}$. This change is also reflected in the $Cu-NH_3$ bond distances.

As the space for binding expands from **4a** to **4c** the length of the Cu−N5 bond decreases from 2.066(5) to 1.993(7) Å. On the other hand, the length of the bonds between copper and the central nitrogen atoms of the ligand remains essentially unchanged from **4a** to **4c** (Table 1).

With complexes **4a**−**4c** we present three new complexes forming, together with the known complex $[Cu(tren)(NH_3)]$-(ClO_4), a complete series of trigonal-bipyramidal Cu^{II} complexes with aliphatic tripodal tetramine ligands. Variation of the length of the ligand arms leads to different size chelate rings, distortion of the trigonal-bipyramidal coordination environment, and a variation in the room available for binding of the fifth monodentate ligand. Related oberservations have been made with octahedral cobalt(III) complexes of the type $[Co(N_4)(H_2O)_2]^{3+}$ (L = **1**, **2**, tren), which have have been found to be effective reagents for the hydrolysis of phosphate esters, with the rate of the reaction dependent on the type of ligand used.[7,9]

Acknowledgment. We thank the Deutsche Forschungsgemeinschaft and the Fonds der Chemischen Industrie for finacial support.

Supporting Information Available: Tables of crystal and data collection details, atomic coordinates, bond distances and angles, and thermal parameters and figures molecular plots of cations and anions for **4a**−**c** (20 pages). Ordering information is given on any current masthead page.

IC9506670