On the Structure, Electrochemistry, and Spectroscopy of the (*N*,*N*′-Bis(2′-(dimethylamino)ethyl)-*N*,*N*′-dimethylpropane-1,3-diamine)copper(II) Ion
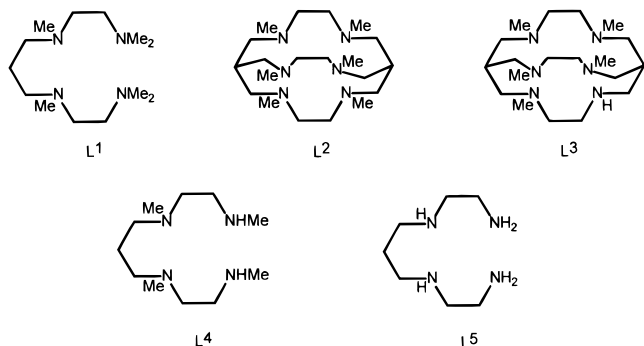
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Abstract: The synthesis, spectroscopy, and electrochemistry of the acyclic tertiary tetraamine copper(II) complex [CuL^1](ClO$_4$)$_2$ (L^1 = *N*,*N*′-bis(2′-(dimethylamino)ethyl)-*N*,*N*′-dimethylpropane-1,3-diamine) is reported. The X-ray crystal structure of [CuL^1(OClO$_3$)$_2$] reveals a tetragonally elongated CuN$_4$O$_2$ coordination sphere, exhibiting relatively long Cu−N bond lengths for a Cu^{II} tetraamine, and a small tetrahedral distortion of the CuN$_4$ plane. The [CuL^1]$^{2+}$ ion displays a single, reversible, one-electron reduction at −0.06 V *vs* Ag/AgCl. The results presented herein illustrate the inherent difficulties associated with the separation and characterization of Cu^{II} complexes of tertiary tetraamines, and some previously incorrect assertions and unexplained observations of other workers are discussed.

Introduction

A recent paper in this Journal,[1] and its preceding communication,[2] described the electrochemical and spectroscopic properties of the copper(II) complex of the hexa-N-methylated tetraamine L^1. The complex exhibited some apparently unusual electrochemical properties. In particular, it was reported that the complex exhibited two consecutive, reversible, one-electron reductions in aqueous solution, *i.e.*, Cu$^{II/I}$ then Cu$^{I/0}$, but this remarkable behavior was not substantiated by coulometry or any other quantitative electrochemical analysis. In an earlier paper,[3] we queried these results, as they were reminiscent of the electrochemical behavior that we had observed in a mixture of the related complexes [CuL^2](ClO$_4$)$_2$ and [CuL^3](ClO$_4$)$_2$, where the ligands were tetradentate coordinated. This mixture was subsequently separated and the two complexes were characterized electrochemically and structurally in the case of [CuL^3](ClO$_4$)$_2$. In this report, the X-ray crystal structure, spectroscopy, and electrochemistry of [CuL^1](ClO$_4$)$_2$ is compared with earlier results that have been reported for this complex.[1,2] In addition, the tetra-N-methylated analogue [CuL^4]$^{2+}$ has been isolated, and its relevance to earlier studies will be discussed.

Experimental Section

Safety Note. Perchlorate salts are potentially explosive. Although we have experienced no problems with the compounds reported in this work, they should only be handled in small quantities and never scraped from sintered glass frits nor heated in the solid state.

Syntheses. *N*,*N*′-**Bis(2′-(dimethylamino)ethyl)-*N*,*N*′-dimethylpropane-1,3-diamine, L^1.** The synthesis of this ligand has not been described in detail. Formic acid (50 mL) was added dropwise with stirring to an ice-chilled sample of the linear tetraamine L^5 (3.0 g, L^5 = *N*,*N*′-bis(aminoethyl)propane-1,3-diamine[4]) (**caution**: exothermic). Aqueous formaldehyde solution (40 mL, 37%) was added; the mixture was removed from the ice bath and refluxed for 24 h. The reaction mixture was taken to dryness on a rotary evaporator and the residue was taken up in NaOH solution (100 mL, 5 M), then allowed to cool to room temperature. The solution was extracted with CH$_2$Cl$_2$ (5 × 50 mL), and the extracts were dried over anhydrous Na$_2$SO$_4$. The solution was filtered and CH$_2$Cl$_2$ was removed on a rotary evaporator to leave a yellow liquid (3.7 g): ^{13}C NMR (CDCl$_3$) δ 25.0 (C−**C**H$_2$−C), 42.5 (N−**C**H$_3$), 45.8 (N(**C**H$_3$)$_2$, 55.6, 56.4, and 57.4 ppm (all N−**C**H$_2$−C).

(*N*,*N*′-Bis(dimethylaminoethyl)-*N*,*N*′-dimethylpropane-1,3-diamine)copper(II) perchlorate, [CuL^1](ClO$_4$)$_2$. A deep blue solution of Cu(NO$_3$)·3H$_2$O (1.5 g) and L^1 (1.5 g) in water (100 mL) was prepared, then filtered to remove any copper hydroxide that had formed. The filtrate was applied to a column (1000 × 2 cm) of Sephadex C-25 cation exchange resin (Na$^+$ form). Elution with 0.15 M NaClO$_4$ solution afforded one major blue band, which was concentrated to *ca.* 20 mL on a rotary evaporator to afford a blue precipitate. This was collected by filtration, washed with ethanol then diethyl ether, and dried in a vacuum desiccator (0.7 g). The filtrate afforded dark blue crystals of the product, suitable for X-ray work on standing. Several crops were obtained. Anal. Calcd for C$_{13}$H$_{32}$Cl$_2$CuN$_4$O$_8$·H$_2$O: C, 29.8; H, 6.5; N, 10.7. Found: C, 30.0; H, 6.4; N, 11.0. Electronic spectrum (H$_2$O) λ_{max} 628 nm (ϵ 197 M^{-1} cm^{-1}), 306 (ϵ 6500).

(*N*,*N*′-Bis(2′-(methylamino)ethyl)-*N*,*N*′-dimethylpropane-1,3-diamine)copper(II) Perchlorate, [CuL^4](ClO$_4$)$_2$. The above synthesis was repeated, except the order of addition of reagents to the precursor ligand was reversed; *i.e.*, CH$_2$O solution was added before HCOOH. The workup of the free ligand mixture was the same as described above to give an oil. Complexation to copper(II) was performed in a similar manner to that described above. Column chromatography (Sephadex C-25, Na$^+$-form, 30 × 3 cm, 0.2 M NaClO$_4$ solution) eluted a broad diffuse blue band which was evaporated to *ca.* 20 mL to afford a blue solid (0.9 g). Cyclic voltammetry (Figure 2c) and EPR spectroscopy showed this product to be a mixture of two complexes.

A solution of this mixture (0.5 g) in water (500 mL) was chromatographed (Sephadex C-25, Na$^+$-form, 100 × 2 cm, 0.2 M NaClO$_4$ solution) to give two closely running bands: the first being [CuL^1]$^{2+}$ (blue) which was isolated as above, and the second being the

[⊗] Abstract published in *Advance ACS Abstracts,* December 15, 1996.
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tetra-N-methylated analogue [CuL⁴]²⁺ (blue/indigo). Upon concentration of the eluate, a blue powder precipitated (0.2 g). Further crops were obtained from the filtrate. Anal. Calcd for $C_{11}H_{28}Cl_2CuN_4O_8$: C, 27.6; H, 5.9; N, 11.7. Found: C, 27.8; H, 6.1; N, 11.1. Electronic spectrum (H_2O) λ_{max} 588 nm (ϵ 173 M^{-1} cm^{-1}), 290 (ϵ 7300).

Physical Methods. Proton-decoupled ^{13}C nuclear magnetic resonance spectra were measured at 50.32 MHz on a Bruker AC200 spectrometer, and chemical shifts are cited *vs* tetramethylsilane. Solution UV−vis spectra were measured on a Perkin-Elmer Lambda 12 spectrophotometer. Cyclic voltammetry was performed with a BAS 100B electrochemical analyzer employing a glassy carbon working electrode, an Ag/AgCl reference electrode, and a Pt auxiliary electrode. DC polarography was performed with a Metrohm E 506 potentiostat with a E 505 model dropping Hg electrode, a calomel reference electrode, and a Pt auxiliary electrode. All solutions for electrochemistry were *ca.* 5×10^{-3} M in analyte and 0.1 M in $NaClO_4$, and were purged with N_2 before measurement. Electron paramagnetic resonance spectra were measured on a Bruker ER 200 D instrument using a Bruker ER 041 MR microwave bridge and operating at 9.278 GHz. Samples were *ca.* 10^{-3} M solutions in H_2O:DMF (2:1) and all spectra were measured at 77 K. Simulations of all EPR spectra were performed with the program EPR50F.[5]

Calculations. Molecular mechanics trial structures were built with the program HyperChem and minimized with MOMECPC[6] using a published force field.[7] Aqua ligands were modelled in all sites perpendicular to the CuN_4 plane so as to most accurately reproduce the solution structures of these species.

X-ray Crystal Structure. Cell constants were determined by a least-squares fit to the setting parameters of 25 independent reflections measured on an Enraf-Nonius CAD4 four circle diffractometer employing graphite monochromated Mo $K\alpha$ radiation and operating in the $\omega-2\theta$ scan mode. Data reduction and empirical absorption corrections (ψ-scans) were applied with the XTAL package.[8]

The structure was solved by heavy atom methods with SHELXS-86[9] and refined by full-matrix least-squares analysis with SHELXL-93.[10] Only the atoms Cu, N(1), N(2), Cl, C(2), and C(6) were refined with anisotropic thermal parameters. Unresolved disorder in the complex resulted in unacceptably large anisotropic thermal parameters for the remaining non-H atoms, so they were refined isotropically. All H atoms were included at estimated positions. Crystal data are assembled in Table 1 and the atomic nomenclature is defined in Figure 1 drawn with the program PLATON.[11]

The complex is located on a *222* site (D_2) which results in disorder of all atoms except Cu, Cl, O(1), and C(3), each of which lie on at least one 2-fold axis. The severe disorder in the structure necessitated the use of "soft" restraints on some bond lengths; specifically the N(1)−C(4), N(2)−C(3'), C(3)−C(4), C(5)−C(6), and C(6)−C(7) bond lengths were restrained to be equal with an effective standard deviation of 0.03 Å, and the perchlorato ligand (disordered about a 2-fold axis) was modelled as an ideal tetrahedron (all O···O distances approximately equal).

Results and Discussion

Chromatographic separation of the two N-methylated complexes [CuL¹]²⁺ and [CuL⁴]²⁺ from their co-crystallized mixture required long columns and light loading to achieve the separations described. A similar difficulty was found[3] in separating the hexa- and penta-N-methylated hexaamine complexes [CuL²]²⁺ and [CuL³]²⁺ which also co-crystallize. If the correct reaction conditions are chosen (see Experimental Section), then the hexa-

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Table 1. Crystal Data

specimen	blue prism, 0.30 × 0.30 × 0.20 mm
crystal system	tetragonal
space group	$P\,\bar{4}n2$ (No. 118)
formula	$C_{13}H_{32}Cl_2CuN_4O_8$
a, Å	9.1203(6)
c, Å	13.0859(9)
V, Å³	1088.5(1)
ρ_{calcd}, g cm⁻³	1.547
fw	506.87
Z	2
μ, cm⁻¹	12.94
temp, K	296
λ, Å	0.71073
N	3697
N_o ($Fo > 2\sigma$)	2126
goodness of fit	1.072
$2\theta_{max}$, deg	50
$R(F_o)^a$, $wR_2(F_o^2)^b$	0.0632, 0.1735

^{a} $R(F_o) = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR_2(F_o^2) = (\Sigma w(F_o^2 - F_c^2)/\Sigma wF_o^2)^{1/2}$, $w = (\sigma^2(F_o^2) + (0.1331P)^2 + 0.04P)^{-1}$, where $P = {}^1/_3 \max(F_o^2, 0) + {}^2/_3 F_c^2$.
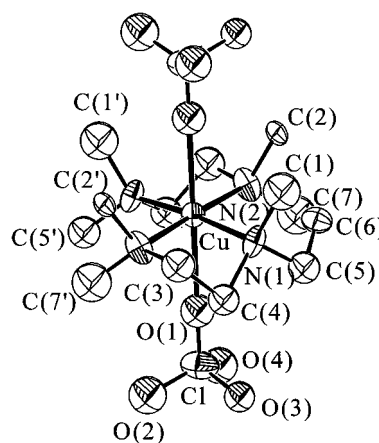
Figure 1. View of the [CuL¹(OClO₃)₂] molecule showing 20% probability ellipsoids, H atoms omitted for clarity. Primes denote symmetry equivalent atom (symmetry operator: $-y + {}^1/_2$, $-x + {}^1/_2$, $-z + {}^1/_2$). Selected bond lengths and angles: Cu−N(1) 2.050(7), Cu−N(2) 2.129(8), Cu−O(1) 2.562(7) Å; N(1)−Cu−N(2) 96.7(5), N(1)−Cu−N(1') 174(1), N(2)−Cu−N(2') 177.7(9), N(1)−Cu−N(2') 83.2(5)°.

N-methylated tetraamine L¹ can be made in almost quantitative yield. However, if the order of addition of reagents is reversed, then an almost equal amount of the tetra-N-methylated ligand L⁴ is produced. The exact isomeric form of this ligand is not known. In all probability, the ligand has one methyl group per N-atom, but efforts to obtain X-ray quality crystals of complexes of this ligand have been unsuccessful. The solution electronic spectra of [CuL¹]²⁺ and [CuL⁴]²⁺ exhibit visible maxima at much lower energy compared with their parent complex [CuL⁵]²⁺ (λ_{max} 522 nm, ϵ 78 M^{-1} cm^{-1}).[12] This is consistent with the weaker overall ligand fields that typically arise from N-methylation of coordinated amines through elongation of the Cu−N bond lengths (see below). The higher extinction coefficients of the methylated complexes relative to [CuL⁵]²⁺ reflect somewhat distorted chromophores compared with the virtually planar CuN_4 group of the precursor complex [CuL⁵]²⁺.

The X-ray crystal structural analysis of [CuL¹(OClO₃)₂] reveals a tetragonally elongated *trans*-CuN_4O_2 coordination sphere as shown in Figure 1. This geometry is common to most six-coordinate Cu(II) complexes, and is a consequence of the pseudo Jahn−Teller effect.[13] The averaged Cu−N bond lengths are *ca.* 0.1 Å longer than those generally found in primary and

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secondary amine relatives,[14,15] but similar to those reported for other tertiary amine Cu^{II} complexes.[3,16,17] A slight tetrahedral distortion of the CuN_4 group is also observed (± 0.04 Å deviation of pairs of *trans* N-donors from the least-squares plane). Nonbonded repulsions between the *N*-methyl groups are the primary cause of the observed elongation of the Cu–N bonds and for the distortion of the nominally planar CuN_4 unit. This was confirmed by molecular mechanics modelling of the crystallographically observed conformation ($\delta\delta$) which gave similar calculated Cu–N bond lengths and N–Cu–N bond angles to those observed in the crystal structural analysis. This was useful in establishing that the structure used to model the crystallographic disorder was plausible.

Electron paramagnetic resonance spectra of the two purified Cu^{II} complexes each exhibit features characteristic of a d^9 ion in a pseudo-axial ligand field: $[CuL^1]^{2+}$ $g_{\parallel}$ 2.231 ($A_{\parallel}$ 172 G), $g_{\perp}$ 2.054 ($A_{\perp}$ ~30 G); $[CuL^4]^{2+}$ $g_{\parallel}$ 2.205 ($A_{\parallel}$ 184 G) and $g_{\perp}$ 2.045 ($A_{\perp}$ ~30 G). The spectrum of the co-crystallized mixture of $[CuL^1](ClO_4)_2$ and $[CuL^4](ClO_4)_2$ shows features due to both complexes around 3050 and 3080 G, as well as broadening of lines around 2890 and 3300 G, showing that $[CuL^1]^{2+}$ and $[CuL^4]^{2+}$ are indeed the two components of the co-crystallized mixture obtained in the Experimental Section.

Electrochemistry of $[CuL^1]^{2+}$ and $[CuL^4]^{2+}$ was conducted in aqueous solution. Cyclic voltammetry identified reversible waves at E° −0.060 V *vs* Ag/AgCl for $[CuL^1]^{2+}$ and E° −0.308 V *vs* Ag/AgCl for $[CuL^4]^{2+}$ (Figure 2, a and b). In both cases, the anodic/cathodic current ratios (i_a/i_c) were unity in the scan rate range 10−200 mV s^{-1}, indicating that the putative $[CuL^1]^+$ and $[CuL^4]^+$ ions are stable on the voltammetric timescale. A relatively weak wave is seen in the cyclic voltammogram of $[CuL^1]^{2+}$ at *ca.* −0.3 V (Figure 2b). Importantly, the peak heights for this wave were found to be independent of the concentration of $[CuL^1]^{2+}$ (whereas the cathodic and anodic current maxima for the wave at −0.06 V were directly proportional to concentration, as expected). This behavior is consistent with strong adsorption of $[CuL^1]^{2+}$ to the carbon working electrode.[18] The cyclic voltammogram of the co-crystallized mixture of $[CuL^1](ClO_4)_2$ and $[CuL^4](ClO_4)_2$ is also shown in Figure 2c. The two reversible waves clearly coincide with those of their component molecules. This cyclic voltammogram is identical with that reportedly[2] due solely to the $[CuL^1]^{2+}$ ion.

Quantitative DC polarography (on an Hg electrode) indicated that the reversible waves shown as a and b in Figure 2 are each due to single electron transfer processes by wave height comparisons with the $Co^{III/II}$ couple of a known hexaamine complex.[19] At more negative potentials (*ca.* −0.37 V *vs* SCE), less intense waves (less than one electron) were identified in the polarograms of both complexes. This behavior is indicative of a slow chemical reaction following an initial single electron transfer step to generate an electroactive species which is reduced in a second single electron transfer process.

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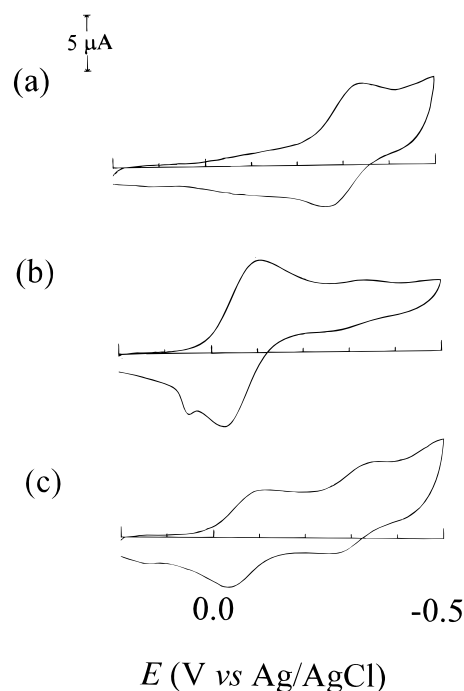
Figure 2. Cyclic volammograms of *ca.* 5 mM solutions of (a) $[CuL^4](ClO_4)_2$, (b) $[CuL^1](ClO_4)_2$, and (c) the co-crystallized mixture of $[CuL^4](ClO_4)_2$ and $[CuL^1](ClO_4)_2$. Scan rate 20 mV s^{-1} (see Physical Methods section for other experimental conditions). Minor anodic wave in (b) (*ca.* +0.06 V) absent when switching potential set to −0.30 V.

Bulk electrolysis performed on the two Cu^{II} complexes (over an Hg pool working electrode, E = −0.40 V *vs* Ag/AgCl) resulted in the passage of two electrons per complex ion, *i.e.*, complete reduction to copper metal with dissociation of the complex. Importantly, a residual blue color (Cu^{II}) was observed in each solution after the passage of one electron per complex ion; *i.e.*, not all of the Cu^{II} complex had been reduced at this time. Polarography experiments (also with an Hg working electrode) showed that $[CuL^1]^{2+}$ and $[CuL^4]^{2+}$ are reduced in this potential range but their Cu^{I} analogues are not. Therefore, the second equivalent of electrons in the bulk electrolysis experiments of $[CuL^1]^{2+}$ and $[CuL^4]^{2+}$ must arise from partial or complete dissociation of $[CuL^1]^+$ and $[CuL^4]^+$ to generate other Cu^{I} species which are electroactive at this potential. This behavior is consistent with the polarographic results, which also were suggestive of partial dissociation of the putative tetradentate coordinated Cu^{I} complexes of L^1 and L^4 at the Hg electrode. In conclusion, the cyclic voltammetry, polarography, and bulk electrolysis experiments all indicate that reversible consecutive one electron transfer reductions of tetradentate coordinated $[CuL^1]^{2+}$ to $[CuL^1]^+$ then $[CuL^1]^+$ to $[CuL^1]^0$ do not occur within this potential range, on either a glassy carbon or an Hg electrode. Instead, a reversible single electron reduction of the Cu^{II} complex occurs to form a Cu^{I} species which ultimately dissociates in aqueous solution, although this dissociation is slow on the voltammetric timescale. These results cast doubt on the validity of the stability constant data reported[1] for the complex $[CuL^1]^+$, calculated from questionable electrochemical data.

Conclusions

The double wave voltammetric behavior found, to various degrees, in all of the tertiary amine complexes discussed in this work and elsewhere,[1,2,20] has its origins in two effects. Strong adsorption of the hydrophobic Cu^{II} complexes to electrode

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surfaces is to be expected in aqueous solution giving rise to two waves instead of the anticipated single response. Secondly, this report and an earlier paper[3] illustrate the inherent difficulties associated with the purification and characterization of the Cu^{II} complexes of tertiary amines. It is easy to believe that seemingly crystalline samples of complexes of this type are pure, when, in fact, a number of components, with quite distinct electrochemical and spectroscopic properties, may co-crystallize. We believe that these phenomena may have misled other workers in their interpretation of the electrochemical behavior of complexes of this type.[1,2] We are currently pursuing further studies aimed at clarifying further the electrochemical properties of these complicated systems.

Supporting Information Available: Tables of full crystal data, non-H positional and thermal parameters, bond lengths and angles, H-atom positional parameters, experimental and simulated EPR spectra, and molecular mechanics refined structures (12 pages). See any any current masthead page for ordering and Internet access instructions.

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