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# Template Syntheses Involving Carbon Acids. Synthesis and Characterization of (3,10-Dimethyl-3,10-dinitro-1,4,8,11-tetraazacyclotetradecane)copper(II) and (1,9-Diamino-5-methyl-5-nitro-3,7-diazanonane)copper(II) Cations and Nitro Group Reduction Products

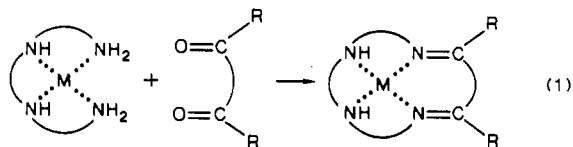Peter Comba,[1] Neil F. Curtis,*[2] Geoffrey A. Lawrance,*[3] Alan M. Sargeson,[4] Brian W. Skelton,[5] and Allan H. White*[5]

Reaction of Cu(en)$_2$$^{2+}$ (en = 1,2-diaminoethane) in methanol with formaldehyde and nitroethane in the presence of a noncoordinating base proceeds readily to produce (3,10-dimethyl-3,10-dinitro-1,4,8,11-tetraazacyclotetradecane)copper(II) and (1,9-diamino-5-methyl-5-nitro-3,7-diazanonane)copper(II) cations as the only major products. These can be readily separated chromatographically or may be prepared separately via different optimized reactions. Reduction of the nitro groups of these complexed ligands may be achieved by zinc/acid or tin/acid reduction or catalytic hydrogenation; the former lead to some fragmentation of the precursor macrocyclic ligand during reduction, while the latter yields the amine cleanly. Copper(II) complexes of the reduced forms of the ligands, namely the (3,10-diammonio-3,10-dimethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) and (5-ammonio-1,9-diamino-5-methyl-3,7-diazanonane)copper(II) cations, have been characterized. With the macrocyclic ligands, *rac* and *meso* isomers have been identified, the *meso* form being the major product. Apart from the ligands described above, other products were undetected or negligible; only the aqua(1,3-bis(2-aminoethyl)-5-ammonio-5-methyl-1,3-diazacyclohexane)copper(II) cation, present in about 3% in the reduced ligand mixture, was present in sufficient amounts to permit characterization. Complexes were characterized by electronic, infrared, and electron spin resonance spectroscopy, and two were the subject of single-crystal X-ray crystallographic analyses. (3,10-Diammonio-3,10-dimethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) perchlorate hexahydrate crystallizes in the monoclinic space group $P2_1/c$, $a$ = 8.77 (2) Å, $b$ = 14.08 (1) Å, $c$ = 13.59 (2) Å, and $\beta$ = 107.5 (1)°, with the copper atom located at a crystallographic center of symmetry so that the molecular cation is also centrosymmetric with the CuN$_4$ atoms coplanar. Copper–nitrogen distances are 2.021 (5) and 2.027 (6) Å, while inversion-related perchlorates occupy the fifth and sixth sites with Cu–O = 2.523 (7) Å. The minor species aqua(1,3-bis(2-aminoethyl)-5-ammonio-5-methyl-1,3-diazacyclohexane)copper(II) perchlorate also crystallizes in the monoclinic space group $P2_1/c$, $a$ = 12.661 (3) Å, $b$ = 13.660 (7) Å, $c$ = 16.403 (4) Å, and $\beta$ = 130.03 (2)°, with the copper ion in a pseudo-square-planar coordination environment comprising the water molecule at 1.968 (5) Å and three nitrogens at distances near 2.0 Å. Two nitrogens of the ligand are uncoordinated, the other sites about the copper being approached by perchlorate oxygen atoms (Cu–O = 2.637 (5) and 2.820 (4) Å). The copper environment deviates considerably from planarity, with atoms up to 0.15 Å from the CuN$_3$O least-squares plane, while the six-membered ring in the ligand adopts a chair conformation with all substituents except copper and one metal-bound amine being equatorial.

## Introduction

Metal template syntheses of multidentate and macromonocyclic ligands have been established over the last two decades as offering high-yielding and selective routes to new ligands and their complexes. The various synthetic routes to potentially multidentate ligands have been extensively reviewed,[6–11] and several types of template effects about transition-metal ions have been identified. A template effect may arise from the stereochemistry imposed by metal ion coordination of some of the reactants, promoting a series of controlled steps; this is the coordination or kinetic template effect and characteristically provides routes to products not formed in the absence of the metal ion.[12,13] In addition, the thermodynamic template effect refers to reactions that do proceed in the absence of the metal ion but those in which the metal ion promotes

formation of desired products by removing them from the equilibrium.[6] Lastly, an equilibrium template effect has been identified, where aspects of both effects mentioned above combine; the distinctive feature of this is the formation of different products in the absence of the metal ion.[13]

While template reactions can be compartmentalized as above, it may be more instructive to look at the specific types of reactions which have been developed in that area to date. They are quite limited in number. One of the most common methods has involved reaction of a bifunctional aldehyde or ketone with a complexed multidentate amine, e.g. eq 1, or the similar reaction of a po-



$$(1)$$

tentially multidentate aldehyde with a simple diamine.[7,8] A range of macrocycles form from reaction of acetone or similar ketone with complexes of multidentate amines, e.g. eq 2. In these



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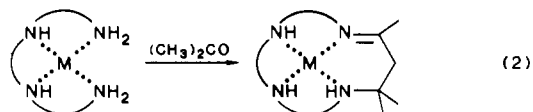
reactions, an aldol-like reaction of a ketone molecule with an initially formed coordinated imine is apparently involved.[6] With dithiolates, reaction with dibromoalkanes are possible, e.g. eq 3.[13] Less extensively studied but notable reactions are the reaction of nickel(II) dimethylglyoxime with diphenylborinic acid aminoethyl

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(5) The University of Western Australia.
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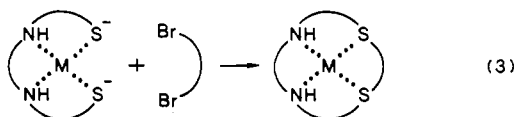
ester (DPBE) where an O–B–O linkage is introduced in the resultant macrocycle[14] (eq 4) and the reaction of a coordinated dihydrazine with formaldehyde[15] (eq 5).

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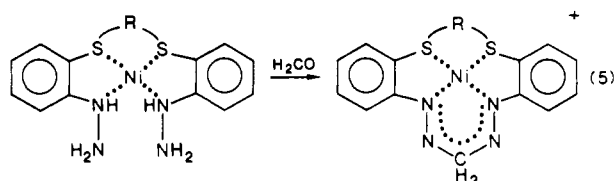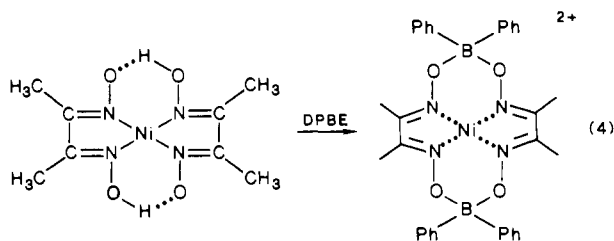
Inert metal amine complexes also undergo reactions with formaldehyde in basic solution. The $Co(en)_2gly^{2+}$ ion reacts to form the 3,10-dioxocyclam macromonocycle, characterized by a crystal structure analysis.[16] This strategy was recently extended to tris(diamine) complexes $M(en)_3^{n+}$ (M = Co(III), Rh(III), Ir(III), Pt(IV)) with formaldehyde and the carbon acid nitromethane.[17-19] This reaction probably involves formation of an imine and subsequent attack by $^-CH_2NO_2$ anion[20] (eq 6). This

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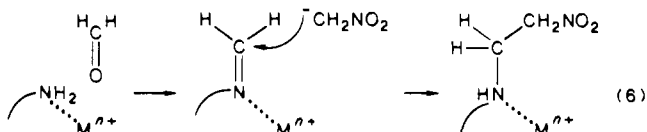
process leads in a stepwise manner to complete capping of the open faces of the octahedron to form a macrobicyclic complex in a remarkably facile and stereospecific reaction, eq 7. Where the

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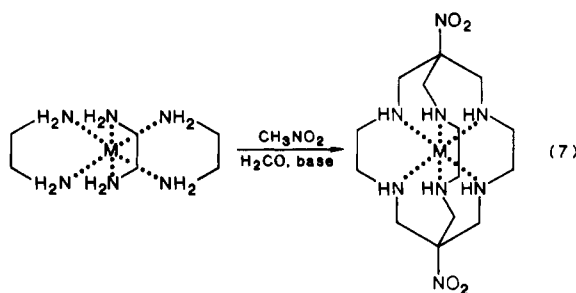
intermediate imine is exceptionally stable, as occurs with chromium(III) complexes, reaction as described in eq 6 and 7 does not proceed, however.[21] Attempts to perform the macrobicyclization in eq 7 about labile metal ions have been largely unsuccessful in protic solvents; condensation reactions that do occur

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were not elucidated. Where simple bis and tris diamine complexes are of high stability, as with copper(II) or nickel(II), reactions similar to those observed about inert metal ions might be feasible. For example, with the $Cu(en)_2^{2+}$ ion, nitroethane, and formaldehyde, the expected product is the macromonocycle **1** and other condensation products such as the intermediate multidentate **2** (eq 8). In this paper we report facile high-yielding syntheses of

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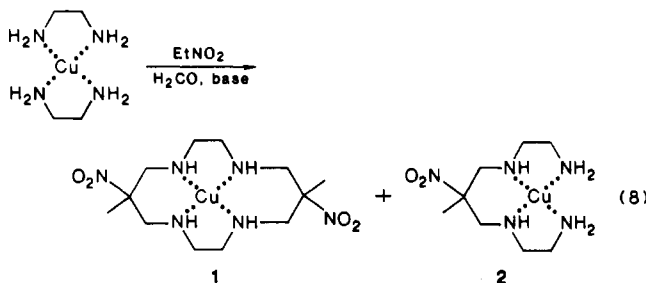
the products described in eq 8 and the corresponding amines from nitro group reduction, in addition to electrochemical and spectroscopic characterization and structural characterization of one major and a minor product of the nitro ligand reduction reactions as the copper(II) complexes.

## Experimental Section

**Syntheses.** All reactions employed usually AR grade chemicals and solvents as supplied. $[Cu(en)_2](ClO_4)_2$ was prepared by addition of excess diaminoethane to methanolic copper perchlorate, followed by cooling.

**Crude Condensation Reaction.** A solution of $Cu(ClO_4)_2\cdot6H_2O$ (7.4 g) or $Cu(NO_3)_2\cdot3H_2O$ (4.8 g) and 1,2-diaminoethane (2.4 g, 1:2 molar ratio) in methanol (200 mL) was stirred and treated with slightly more than 2 molar equiv of nitroethane (3.2 g) and 4 molar equiv of 37% aqueous formaldehyde (5 mL). Either triethanolamine or triethylamine was added as base (~2 mL). The mixture was stirred and heated at ~55 °C for 2 h and then allowed to cool to room temperature while being stirred. Saturated aqueous $NaClO_4$ solution was added with stirring until precipitation had commenced. After cooling in an ice bath the crude purple product (9.2 g) was collected, washed with ethanol and ether, and air-dried. The product proved to be overwhelmingly a mixture of two complexes, macromonocyclic $[Cu(dinemac)](ClO_4)_2$ (**1**-$(ClO_4)_2$) and multidentate $[Cu(nelin)](ClO_4)_2$ (**2**-$(ClO_4)_2$) which could be separated readily by chromatography (vide infra). The relative amounts of the two complexes varied from batch to batch, being somewhat dependent on the amounts of nitroethane and formaldehyde employed and also dependent on the choice of base. Subsequently, optimized syntheses of the two major products were developed. Since chromatographic separation proved to be facile, either a general synthesis combined with chromatographic separation or an optimized synthesis may be employed; both are described below.

**Chromatographic Separation of Condensation Reaction Products.** Crude complex mixture (1.5 g) was dissolved in distilled water (2 L) and sorbed onto a column of SP Sephadex C-25 cation-exchange resin (25 cm × 3.5 cm). After being washed with water (~$^1/_2$ L), the column was treated with 0.2 M NaCl solution, eluting only two well-separated bands.

**Band 1:** **(1,9-Diamino-5-methyl-5-nitro-3,7-diazanonane)copper(II) (2) Perchlorate, $[Cu(nelin)](ClO_4)_2$.** This purple band was collected and treated with saturated aqueous $NaClO_4$ solution until copious precipitation occurred. After cooling, the product was collected, washed with ethanol, and dried in vacuo (55%). Anal. Calcd for $C_8H_{21}Cl_2CuN_5O_{10}$: C, 19.95, H, 4.39; N, 14.54. Found: C, 19.9; H, 4.3; N, 14.2. Electronic spectrum (water): $\lambda_{max}$ 529 nm ($\epsilon$ 62.4 $M^{-1}$ $cm^{-1}$), 248 (655).

**Band 2:** **(3,10-Dimethyl-3,10-dinitro-1,4,8,11-tetraazacyclotetradecane)copper(II) Cation, $[Cu(dinemac)]^{2+}$ (1).** The purple band was collected and cooled, yielding an immediate precipitate of a chloride sesquihydrate salt. This was collected, washed with ethanol, and dried in vacuo (11%). Anal. Calcd for $C_{12}H_{29}Cl_2CuN_6O_{5.5}$: C, 30.03; H, 6.09; N, 17.51. Found: C, 30.0; H, 5.9; N, 17.4. Electronic spectrum (water): $\lambda_{max}$ 513 nm ($\epsilon$ 69.2), 254 (3650). Addition of saturated $NaClO_4$ solution and cooling the filtrate yielded a second precipitate as the perchlorate demihydrate salt. This was collected, washed with ethanol, and dried in vacuo (34%). Anal. Calcd for $C_{12}H_{27}Cl_2CuN_6O_{12.5}$: C, 24.43; H, 4.61; N, 14.25. Found, C, 24.5; H, 4.5; N, 14.2. Electronic spectrum (water): $\lambda_{max}$ 512 nm ($\epsilon$ 69.8 $M^{-1}$ $cm^{-1}$), 251 (3400).

**Optimized Synthesis of (1,9-Diamino-5-methyl-5-nitro-3,7-diazanonane)copper(II) (2) Perchlorate, $[Cu(nelin)](ClO_4)_2$.** To a solution of $[Cu(en)_2](ClO_4)_2$ (11.5 g) in methanol (200 mL) was added nitroethane

(5 mL) and triethanolamine (5 mL). While the mixture was stirred under reflux, a solution of aqueous 37% formaldehyde (5 mL) in methanol (15 mL) was added dropwise over ~1 h. The solution was then cooled in an ice bath and the product collected, washed with ethanol, and air-dried (11 g). It was recrystallized from hot water or from hot acetonitrile/propan-2-ol. Anal. Calcd for $C_8H_{23}Cl_2CuN_5O_{10}$: C, 19.95; H, 4.39; N, 14.54; Cu, 13.2. Found: C, 20.1; H, 4.4; N, 14.5; Cu, 13.2.

**Optimized Synthesis of (3,10-Dimethyl-3,10-dinitro-1,4,8,11-tetraazacyclotetradecane)copper(II) (1) Perchlorate, [Cu(dinemac)](ClO₄)₂.** To a solution of [Cu(en)₂](ClO₄)₂ (11.5 g) in methanol (200 mL) was added nitroethane (10 mL) and triethylamine (10 mL). While the mixture stirred under reflux, 37% aqueous formaldehyde solution (15 mL) was added dropwise over ~1 h. After cooling in an ice bath, the product was collected, washed with ethanol, and air-dried (11 g). It was recrystallized from hot water acidified with HClO₄ or from hot acetonitrile/propan-2-ol. Anal. Calcd for $C_{12}H_{26}Cl_2CuN_6O_{12}$: C, 24.80; H, 4.51; N, 14.47. Found: C, 24.6; H, 4.5; N, 14.4. The complex may also be obtained as a chloride dihydrate salt by dissolving the perchlorate salt in a minimum volume of boiling water and adding a few drops of concentrated HCl. The precipitate formed on cooling can be collected and recrystallized from hot water/propan-2-ol. Anal. Calcd for $C_{12}H_{30}Cl_2CuN_6O_4$: C, 29.5; H, 6.2; N, 17.2; Cu, 13.0. Found: C, 29.4; H, 6.0; N, 16.8; Cu, 12.9. Isolation as the thiocyanate salt can be achieved as above, except adding sodium thiocyanate instead of HCl. Anal. Calcd for $C_{14}H_{26}CuN_8O_4S_2$: C, 33.8; H, 5.3; N, 22.5. Found: C, 34.0; H, 5.2; N, 22.8.

**Zinc/Acid Reduction of Nitro Complexes.** Crude [Cu(dinemac)](ClO₄)₂ and [Cu(nelin)](ClO₄)₂ mixture (6 g) from the initial reaction was dissolved in ~1 M HCl (250 mL) with warming to ~50 °C. Granulated zinc (ca. 10 g) was added and the warm solution allowed to react until the color of the solution disappeared (~2 h). The mixture was filtered to remove solids, and then saturated NaOH solution was added with stirring until the pH was ~10. The mixture was filtered to remove Zn(OH)₂, the solid washed with a little warm dilute NaOH, the pH then raised to ~12, and the process repeated. The filtrate was treated with concentrated HCl to pH ~9, and excess Cu(NO₃)₂·3H₂O (4 g) was added with vigorous stirring. The resultant deep blue solution was adjusted to pH ~4 and diluted to ~20 L. This solution was sorbed onto a column (25 cm × 3.5 cm) of SP Sephadex C-25 resin and then eluted with NaCl solution (pH ~4), initially of 0.15 M and finally of 0.25 M concentration. Apart from uncomplexed copper, a number of bands were collected, in order:

**Band 1.** This was a relatively fast-moving band, highly soluble and rapidly decomposed by acid, which analyzed best for the initial reactant Cu(en)₂²⁺. This arises presumably from fragmentation during reduction and accounts for ~20% of total complexed copper. Since there was no evidence for higher multidentates, further characterization was not pursued.

**Band 2. Aqua(1,3-bis(2-aminoethyl)-5-ammonio-5-methyl-1,3-diazacyclohexane)copper(II) (5) Perchlorate, [Cu(badcH)(H₂O)](ClO₄)₃.** This minor blue band was collected and treated with saturated sodium perchlorate solution. Upon standing, blue plates of the complex deposited and were collected by filtration, washed with ethanol, and dried (3%). Anal. Calcd for $C_9H_{26}Cl_3CuN_5O_{13}$: C, 18.57; H, 4.50; N, 12.02; Cu, 11.0. Found: C, 18.9; H, 4.4; N, 11.8; Cu, 10.9. Electronic spectrum (water): pH ~1, rapid dissociation; pH ~5, $\lambda_{max}$ 620 nm ($\epsilon$ 86.6 M⁻¹ cm⁻¹), 252 (3730); pH ~10.5, $\lambda_{max}$ 608 nm ($\epsilon$ 82.0 M⁻¹ cm⁻¹), 252 (7700).

**Band 3. (1,9-Diamino-5-ammonio-5-methyl-3,7-diazanonane)copper(II) (4) Perchlorate Monohydrate, [Cu(amlinH)](ClO₄)₃·H₂O.** This major purple band was collected and treated with saturated NaClO₄ solution. Rapid crystallization ensued, and the complex was collected, washed with ethanol, and air-dried. Addition of ethanol to the filtrate and cooling produced a second crop, collected as before (31%). Anal. Calcd for $C_8H_{26}Cl_3CuN_5O_{13}$: C, 16.85; H, 4.60; N, 12.28; Cl, 18.65; Cu, 11.14. Found: C, 16.8; H, 4.9; N, 11.9; Cl, 19.1; Cu, 11.1. Electronic spectrum (water): pH ~1, rapid dissociation; pH ~5, $\lambda_{max}$ 531 nm ($\epsilon$ 56.9 M⁻¹ cm⁻¹), 247 (875); pH ~10.5, $\lambda_{max}$ 538 nm ($\epsilon$ 73.0 M⁻¹ cm⁻¹), 241 (6860).

**Band 4. *meso*-(3,10-Diammonio-3,10-dimethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) (3a) Perchlorate Dihydrate, *meso*-[Cu(diammacH₂)](ClO₄)₄·2H₂O.** The major isomer of the macrocyclic complex was collected as the first of two closely running purple bands. Addition of saturated NaClO₄ solution and cooling precipitated the complex, which was collected, washed with ethanol, and air-dried. A second crop was collected following addition of ethanol to the filtrate and further cooling and was collected as before (51%). Anal. Calcd for $C_{12}H_{36}Cl_4CuN_6O_{18}$: C, 19.02; H, 4.66; N, 11.09; Cu, 8.39. Found: C, 19.0, H, 4.7; N, 10.9; Cu, 8.4. Single crystals (for X-ray analysis) as blue prisms formed as the hexahydrate. Electronic spectrum (water): pH ~1, $\lambda_{max}$ 513 nm ($\epsilon$

72.7 M⁻¹ cm⁻¹); pH ~5, $\lambda_{max}$ 516 nm ($\epsilon$ 69.6 M⁻¹ cm⁻¹) 249 (~8050); pH ~10.5, $\lambda_{max}$ 519 nm ($\epsilon$ 88.5 M⁻¹ cm⁻¹) 254 (7970).

**Band 5: *rac*-(3,10-Diammonio-3,10-dimethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) (3b) Perchlorate Dihydrate, *rac*-[Cu(diammacH₂)](ClO₄)₄·2H₂O.** The minor isomer of the macrocyclic complex was the final band and was collected and isolated exactly as described for the major isomer (15%). Anal. Calcd for $C_{12}H_{36}Cl_4CuN_6O_{18}$: C, 19.02; H, 4.66; N, 11.09; Cu, 8.39. Found: C, 19.5; H, 4.4; N, 11.2; Cu 8.2. Electronic spectrum (water): pH ~1, $\lambda_{max}$ 511 nm ($\epsilon$ 76.2 M⁻¹ cm⁻¹); pH ~5, $\lambda_{max}$ 512 nm ($\epsilon$ 70.4 M⁻¹ cm⁻¹), 249 (7250); pH ~10.5, $\lambda_{max}$ 511 nm ($\epsilon$ 85.9 M⁻¹ cm⁻¹), 253 (8250).

**Tin/Acid Reduction of Nitro Complexes.** Crude [Cu(dinemac)](ClO₄)₂ and [Cu(nelin)](ClO₄)₂ mixture (3 g) from the initial reaction was treated exactly as described for the zinc/acid reduction, except granulated tin was employed. As for the former reaction, a fragmentation band (~20%) was observed in addition to complexed amine analogues of the dinemac and nelin ligands, but the minor cyclohexane derivative detected previously was not observed in this albeit smaller scale reaction.

**Catalytic Reduction of Nitro Compounds.** Either [Cu(dinemac)](ClO₄)₂ or [Cu(nelin)](ClO₄)₂ (~1.0 g) in water (~200 mL) was mixed with 10% Pd–C catalyst (<0.1 g) and shaken on a Paar Model 3910 hydrogenator under 50 psi of hydrogen for ~2 days. The mixture was gravity-filtered, and a slight molar excess of Cu(ClO₄)₂·6H₂O was added to the stirred, clear solution. The solution was concentrated to a small volume on a rotary evaporator and cooled, and NaClO₄ solid or saturated solution was added until precipitation had commenced. Following further cooling in an ice bath, the product was collected, washed with ethanol, and dried (yield >80%). On one occasion with each nitro complex precursor the product complex was chromatographed on SP Sephadex C-25 resin. It could be shown that the reduced amino analogues of the nitro precursors were the only products (>97%). Products were characterized by spectroscopic comparisons with authentic samples and by microanalysis (C, H, N).

**Physical Methods.** Electronic spectra were recorded on an Hitachi 220A spectrophotometer. Infrared spectra were recorded on a Perkin-Elmer 3-300 spectrometer as KBr discs. Electron spin resonance spectra were recorded on a Jeol JES-PE spectrometer fitted with an Oxford Instruments ESR9 helium flow cryostat and a Model DTC 2 temperature controller. Concentrations of the fluid or frozen solutions were in the range 10⁻⁵–10⁻³ M, while powders were undiluted. Voltammetry in aqueous 0.1 M NaClO₄ was performed with a conventional three-electrode configuration and argon purge gas using either a BAS Model CV27 or an AMEL Model 473 electrochemical controller. Working electrodes were an EG & G PAR 303 for hanging mercury drop (HMDE) or dropping mercury (DME) and glassy carbon or platinum billets.

**Crystallography. Crystal Data for *meso*-[Cu(diammacH₂)](ClO₄)₄· 6H₂O (3a-(ClO₄)₄·6H₂O; $C_{12}H_{44}Cl_4CuN_6O_{22}$):** $M_r = 829.9$; monoclinic, space group $P2_1/c$; $a = 8.77$ (2) $b = 14.08$ (1) $c = 13.59$ (2) Å, $\beta = 107.5$ (1)°, $U = 1600$ (2) Å³; $D_m = 1.72$ (1) g cm⁻³, $D_c$ ($Z = 2$) = 1.72 g cm⁻³; $F(000) = 862$; $\mu_{Mo} = 10.9$ cm⁻¹; specimen 0.34 × 0.26 × 0.26 mm; $A^*_{min} = 1.24$, $A^*_{max} = 1.31$; $2\theta_{max} = 50°$; $N = 1936$, $N_o = 1393$; $R = 0.054$, $R' = 0.061$; $T \sim 295$ K.

**Crystal Data for [Cu(badcH)(H₂O)](ClO₄)₃ (5-(ClO₄)₃; $C_9H_{26}Cl_3CuN_5O_{12}$):** $M_r = 582.2$; monoclinic, space group $P2_1/c$ ($C^5_{2h}$, No. 14); $a = 12.661$ (3), $b = 13.660$ (7), $c = 16.403$ (4) Å, $\beta = 130.03$ (2)°, $U = 2172$ (1) Å³; $D_m = 1.78$ (1) g cm⁻³, $D_c$ ($Z = 4$) = 1.78 g cm⁻³; $F(000) = 1196$; $\mu_{Mo} = 14.1$ cm⁻¹; specimen 0.32 × 0.28 × 0.35 mm; $A^*_{min} = 1.37$, $A^*_{max} = 1.48$. $2\theta_{max} = 50°$; $N = 3516$, $N_o = 2765$; $R = 0.041$, $R' = 0.046$; $T \sim 295$ K.

**Structure Determination.** Unique data sets were measured within the specified $2\theta_{max}$ limit on a Syntex P2₁ four-circle diffractometer in conventional $2\theta/\theta$ scan mode and with a monochromatic Mo Kα radiation source. $N$ independent reflections were obtained, $N_o$ with $I > 3\sigma(I)$ being considered "observed" and used in the full-matrix least-squares refinement after analytical absorption correction and solution of the structures by the heavy-atom method. Anisotropic thermal parameters were refined for the non-hydrogen atoms; $(x, y, z)_H$ were located and refined for all ligand H atoms, $(U_{iso})_H$ being estimated. Residuals quoted on $|F|$ at convergence are conventional $R$ and $R'$. Neutral-complex scattering factors were used;[22] computation used the X-RAY 76 program system[23] implemented on a Perkin-Elmer 3240 computer by S. R. Hall. Important results are given in Figures 1 and 2 and Tables I–IV; non-hydrogen atom labeling is shown in the figures. Interatomic (non-hydrogen) distances,

(22) Ibers, J. A., Hamilton, W. C., Eds. *International Table for X-ray Crystallography*; Kynoch: Birmingham, England, 1974; Vol. IV.

(23) Stewart, J. M., Ed. *The X-ray System-Version of March 1976*; Technical Report TR-446, Computer Science Center, University of Maryland: College Park, MD, 1976.

**Table I.** Non-Hydrogen Atom Coordinates for
[Cu(diammacH$_2$)](ClO$_4$)$_4$·6H$_2$O

| atom | $x$ | $y$ | $z$ |
|---|---|---|---|
| | | Cation | |
| Cu | 0 | 0 | 0 |
| N(1) | 0.1803 (8) | −0.0745 (4) | 0.0972 (3) |
| C(2) | 0.2743 (11) | −0.0281 (5) | 0.1943 (4) |
| C(3) | 0.1678 (10) | 0.0067 (4) | 0.2580 (4) |
| C(31) | 0.0701 (11) | −0.0717 (5) | 0.2891 (5) |
| N(31) | 0.2826 (8) | 0.0462 (4) | 0.3569 (4) |
| C(4) | 0.0633 (10) | 0.0926 (4) | 0.2086 (4) |
| N(5) | −0.0670 (7) | 0.0629 (3) | 0.1147 (3) |
| C(6) | −0.1704 (10) | 0.1449 (5) | 0.0664 (5) |
| C(7) | −0.2813 (10) | 0.1103 (5) | −0.0366 (4) |
| | | Anion | |
| Cl(1) | 0.2885 (3) | 0.1684 (1) | −0.0461 (1) |
| O(11) | 0.1654 (8) | 0.1458 (4) | −0.0040 (4) |
| O(12) | 0.3157 (8) | 0.0894 (4) | −0.1071 (4) |
| O(13) | 0.2470 (11) | 0.2482 (4) | −0.1100 (5) |
| O(14) | 0.4340 (9) | 0.1893 (5) | 0.0337 (5) |
| Cl(2) | −0.3189 (3) | 0.1506 (1) | 0.3242 (1) |
| O(21) | −0.2880 (10) | 0.0668 (4) | 0.2753 (5) |
| O(22) | −0.2442 (10) | 0.2281 (4) | 0.2912 (5) |
| O(23) | −0.2583 (11) | 0.1419 (5) | 0.4335 (5) |
| O(24) | −0.4851 (9) | 0.1681 (5) | 0.2986 (5) |
| | | Solvent Molecules | |
| O(1) | 0.5131 (8) | 0.3969 (4) | 0.0583 (4) |
| O(2) | 0.8999 (9) | 0.5854 (4) | 0.0087 (4) |
| O(3) | 0.3243 (10) | 0.3370 (5) | 0.1822 (4) |

**Table II.** Non-Hydrogen Atom Coordinates for
[Cu(badcH)(OH$_2$)](ClO$_4$)$_3$

| atom[a] | $x$ | $y$ | $z$ |
|---|---|---|---|
| Cu | 0.08702 (5) | 0.23648 (4) | 0.24145 (4) |
| O | 0.0576 (3) | 0.2857 (3) | 0.3383 (3) |
| N(1) | 0.1241 (3) | 0.1919 (2) | 0.1453 (3) |
| C(11) | −0.0107 (5) | 0.1574 (4) | 0.0446 (4) |
| C(12) | −0.1215 (5) | 0.2266 (4) | 0.0169 (3) |
| N(12) | −0.1120 (4) | 0.2389 (3) | 0.1106 (3) |
| C(2) | 0.1844 (4) | 0.2697 (3) | 0.1235 (3) |
| N(3) | 0.2997 (3) | 0.3158 (3) | 0.2235 (3) |
| C(31) | 0.3564 (5) | 0.3946 (4) | 0.2010 (4) |
| C(32) | 0.2809 (5) | 0.4889 (4) | 0.1758 (4) |
| N(32) | 0.2984 (4) | 0.5230 (3) | 0.2696 (3) |
| C(4) | 0.4056 (4) | 0.2425 (3) | 0.2953 (3) |
| N(5) | 0.2829 (4) | 0.1974 (3) | 0.3597 (3) |
| C(5) | 0.3462 (5) | 0.1580 (3) | 0.3146 (4) |
| C(51) | 0.4571 (5) | 0.0817 (4) | 0.3883 (4) |
| C(6) | 0.2263 (5) | 0.1127 (3) | 0.2075 (3) |
| Cl(1) | 0.0563 (1) | 0.0186 (1) | 0.3614 (1) |
| O(11) | 0.0158 (4) | 0.0658 (3) | 0.2684 (3) |
| O(12) | −0.0219 (4) | −0.0684 (3) | 0.3316 (4) |
| O(13) | 0.0190 (5) | 0.0810 (3) | 0.4098 (4) |
| O(14) | 0.1968 (5) | 0.0017 (5) | 0.4322 (4) |
| Cl(2) | 0.3098 (1) | 0.0307 (1) | −0.0008 (1) |
| O(21) | 0.1753 (3) | 0.0459 (3) | −0.0313 (3) |
| O(22) | 0.3202 (4) | 0.0910 (3) | −0.0659 (3) |
| O(23) | 0.4113 (4) | 0.0591 (4) | 0.1078 (3) |
| O(24) | 0.3267 (5) | −0.0675 (3) | −0.0152 (3) |
| Cl(3) | 0.6848 (1) | 0.2926 (1) | 0.2103 (1) |
| O(31)* | 0.8015 (7) | 0.2276 (5) | 0.2782 (6) |
| O(32)* | 0.6521 (13) | 0.3445 (11) | 0.2572 (10) |
| O(33)* | 0.7444 (10) | 0.3630 (7) | 0.1816 (10) |
| O(34)* | 0.5729 (15) | 0.2587 (10) | 0.1231 (11) |
| O(35)* | 0.6359 (11) | 0.2300 (7) | 0.2542 (8) |
| O(36)* | 0.5871 (19) | 0.3177 (10) | 0.1148 (8) |
| O(37)* | 0.7401 (12) | 0.3719 (6) | 0.2728 (7) |
| O(38)* | 0.7302 (26) | 0.2279 (10) | 0.1829 (22) |

[a] Atoms marked with an asterisk were refined with a population of 0.5.

interatomic angles, ligand hydrogen geometries, structure factor amplitudes tables, thermal parameters and hydrogen atom parameters are deposited as supplementary material. Extinction was not a significant problem in either structure.
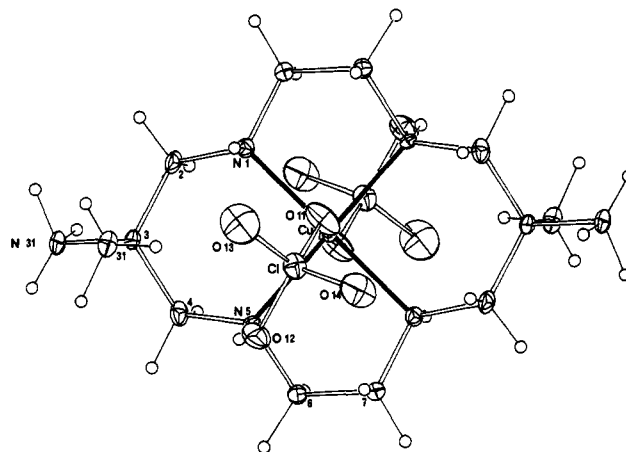


**Figure 1.** The cation *meso*-(3,10-diammonio-3,10-dimethyl-1,4,8,11-tetraazacyclotetradecane)copper(II). 20% thermal ellipsoids are shown for the non-hydrogen atoms; hydrogen atoms have arbitrary radii of 0.1 Å.
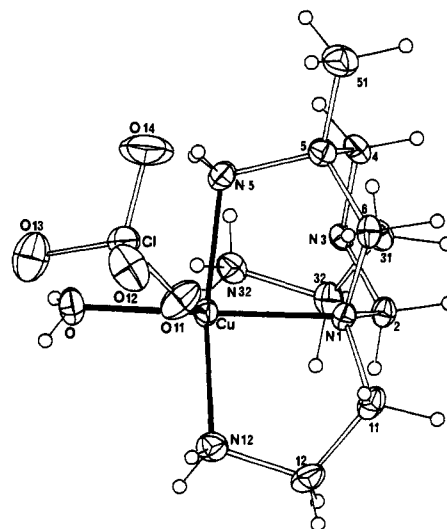


**Figure 2.** The cation aqua(1,3-bis(2-aminoethyl)-5-ammonio-5-methyl-1,3-diazacyclohexane)copper(II).

**Table III.** Copper Atom Environments[a]

| [Cu(diammacH$_2$)](ClO$_4$)$_4$·6H$_2$O | | | |
|---|---|---|---|
| | $r$ | N(5) | O(11) |
| N(1) | 2.021 (5) | 94.3 (2) | 95.4 (2) |
| N(5) | 2.027 (6) | | 87.9 (2) |
| O(11) | 2.523 (7) | | |

| [Cu(badcH)(OH$_2$)](ClO$_4$)$_3$ | | | | | |
|---|---|---|---|---|---|
| | $r$ | N(5) | N(12) | O | O(11) | O(12)[b] |
| N(1) | 2.007 (5) | 84.9 (2) | 86.1 (2) | 177.0 (2) | 98.1 (2) | 96.0 (2) |
| N(5) | 2.002 (3) | | 164.7 (2) | 93.9 (2) | 86.9 (1) | 120.3 (1) |
| N(12) | 2.000 (3) | | | 95.7 (2) | 82.2 (1) | 72.9 (1) |
| O | 1.968 (5) | | | | 84.5 (2) | 82.2 (2) |
| O(11) | 2.637 (5) | | | | | 150.3 (2) |
| O(12)[b] | 2.820 (4) | | | | | |

[a] $r$ is the copper–ligand distance (Å); other entries are the angles (deg) subtended by the relevant atoms of the head of the row and column. Independent geometries only are given. [b] $(\bar{x}, {}^1/_2 + y, {}^1/_2 - z)$.

**Table IV.** Macrocyclic Torsion Angles (deg) for
[Cu(diammacH$_2$)](ClO$_4$)$_4$·6H$_2$O (Atoms Denoted by Number;
Nitrogen Atoms Italicized)

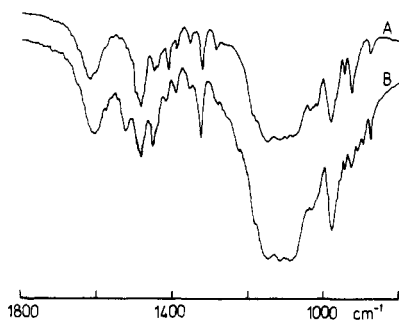| atoms | angle | atoms | angle |
|---|---|---|---|
| 7–1–2–3 | −1.4 | 4–5–6–7 | 8.7 |
| 1–2–3–4 | −109.5 | 5–6–7–1′ | −122.9 |
| 2–3–4–5 | 108.2 | 6–7–1′–2′ | 6.9 |
| 3–4–5–6 | 0.6 | | |

**Figure 3.** Infrared spectra of the *meso* (A) and *rac* (B) isomers of (3,10-diammonio-3,10-dimethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) as KBr disks (**3a** and **3b**, respectively).

**Table V.** Ring Torsion Angles (deg) for [Cu(badcH)(OH₂)](ClO₄)₃ (Atoms Denoted by Number; Nitrogen Atoms Italicized)

| atoms | angle | atoms | angle |
|-------|-------|-------|-------|
| 6–1–2–3 | −65.4 | · 3–4–5–6 | 56.6 |
| 1–2–3–4 | 59.3 | 4–5–6–1 | −59.7 |
| 2–3–4–5 | −55.9 | 5–6–1–2 | 64.6 |

**Variations and Abnormal Features.** For aqua(1,3-bis(2-amino-ethyl)-5-ammonio-5-methyl-1,3-diazacyclohexane)copper(II) (**5**) perchlorate, the third perchlorate ion is disordered over two locations; two sets of oxygen atoms were successfully refined with anisotropic thermal parameters and populations constrained at 0.5 in the final model. For *meso*-(3,10-diammonio-3,10-dimethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) (**3a**) perchlorate, measurement of data was hampered by wide line widths and decomposition (compensated for by scaling) in the X-ray beam. Anion thermal motion is very high; $U_{ij}$ for C(6) was not positive definite and was refined as the isotropic form. (This however, did not inhibit successful definition of the hydrogen atom disposition for the ligand.) Solvent hydrogen coordinates were estimated from difference maps but would not refine meaningfully.

**Results**

Condensation about Cu(en)₂²⁺ in methanol with formaldehyde and the carbon acid nitroethane proceeds readily and is quite specific, with the macromonocyclic tetraamine complex [Cu(dinemac)]²⁺ (**1**) and the related multidentate [Cu(nelin)]²⁺ (**2**) as the only major products. Sensitivity of the reaction to choice of noncoordinating base and relative amounts of reactants, presumably related to the markedly different stabilities of the cyclic and noncyclic products in acid, allowed optimized routes for the synthesis and recrystallization of each product to be developed. In common with copper(II) complexes of most saturated macromonocyclic tetraamines, the dinemac complex is stable for long periods in quite strong acid, while the nelin complex is rapidly dissociated. Analogous syntheses can be performed with nitropropane as the carbon acid.

Nitro group reduction proceeds cleanly by using hydrogen and Pd–C catalyst to generate the reduced amine form of the ligand. However, reduction with zinc or tin in acid occurs with some fragmentation of the precursor molecules, although it still offers a facile and relatively high-yielding route. The pendant amines on both the reduced macrocycle (diammac) and linear multidentate (amlin), although potentially able to coordinate to axial sites above and below the copper(II)–tetraamine plane, show no evidence of doing so, since electronic and electron spin resonance spectroscopy in basic aqueous or aprotic solutions are not consistent with CuN₆ chromophores, as described in the Discussion.

The dinemac macrocycle can in principle exist in either *meso* (*anti*) or *rac* (*syn*) form, depending on whether nitro groups are on opposite sides or the same side of the macrocyclic plane, respectively; the same applies to the reduced diammac macrocycle. With the copper(II) diammac complex, chromatographic separation of the protonated pendant amine diastereoisomers was achieved on Sephadex C-25 resin with the complexes being isolated in a *meso:rac* ratio of ~3:1. The two isomers show characteristically different electronic spectra and infrared spectra. In aqueous base (pH ~10.5) the electronic spectrum of the *meso* isomer has a maximum at 519 nm, but this is shifted to 511 nm for the *rac* isomer; differences in acid are less marked but obvious (see Experimental Section). The infrared spectrum of each isomer is reproduced in part in Figure 3, and the differences are pronounced. The spin resonance spectra also differ slightly. Although chromatographic separation of the Cu(dinemac) isomers was not achieved, preferential crystallization of the *rac* isomer from chloride ion solution appears to have occurred and again assigned

*meso:rac* forms were isolated in an approximately 3:1 ratio, consistent with the result for the diammac macrocycle. Minor spectroscopic differences between the isolated forms support their assignment as the proposed and expected geometrical isomers.

Assignment of the major diammac isomer as the *meso* form was confirmed by the crystallography. Single-crystal X-ray structure determination establishes the structure of the perchlorate salt of **3a** to be [Cu(diammacH₂)](ClO₄)₄·6H₂O, with the diprotonated diammac macrocycle in the *meso* configuration. Location and meaningful refinement of hydrogen atom positional parameters for the ligand suggests affiliations of 1, 3, and 1 hydrogens, respectively, with N(1), N(31), and N(5), although the hydrogen affiliation of the solvent molecule is crystallographically undetermined. Half of the formula unit comprises the asymmetric unit of the structure; the copper atom is located at a crystallographic center of symmetry, so that the cation is also centrosymmetric. Copper–nitrogen distances are 2.021 (5) and 2.027 (6) Å, in a pseudo-square-planar disposition about the copper. CuN₄ is necessarily planar because of the center of symmetry; other ligand atom deviations from this plane, δ(C(2)), δ(C(3)), δ(C(31)), δ(C(4)), δ(C(6)), δ(C(7)), and δ(N(31)), are 0.79, 0.39, −1.08, 0.83, 0.40, −0.35, and 1.23 Å, respectively. The fifth and sixth coordination sites of the copper are approached by inversion-related perchlorate O(11) at 2.523 (7) Å. Non-hydrogen atom coordinates, distances and angles in the copper atom environment, and macrocyclic torsion angles are collected in Tables I, III, and IV. An ORTEP drawing of the cation appears in Figure 1. The coordination geometry is very similar to that observed for [Cu(cyclam)](ClO₄)₂, also centrosymmetric with Cu–N = 2.02 (4) and 2.02 (3) Å and Cu–O 2.57 (4) Å,²⁴ and a hexamethyl derivative of cyclam which has Cu–N = 2.018 (4), 2.028 (4), 2.028 (4), and 2.045 (4) Å and Cu–O = 2.67 (4) and 2.70 (4) Å.²⁵

Apart from the expected products Cu(nelin)²⁺ and Cu(dinemac)²⁺, no other species were detected chromatographically, but they may have been present as minor components of the observed bands. Likewise, chromatographic separation on SP Sephadex C-25 resin of the copper(II) complexes of the reduced (pendant amine) ligands identified the expected Cu(diammac)²⁺ (**3**) and Cu(amlin)²⁺ (**4**) complexes (or their protonated forms) as the major multidentate products. Only one other band was detected from a relatively large scale Zn/HCl reduction and was present to ≤3% only. Crystallization of this complex was achieved from aqueous perchlorate solution, and microanalysis fitted a structure incorporating the potentially five-coordinate ligand 1,3-bis(2-aminoethyl)-5-amino-5-methyl-1,3-diazacyclohexane (badc, V). A single-crystal X-ray structure determination established the structure of the perchlorate salt of **5** as [Cu(badcH)(OH₂)](ClO₄)₃, with the monoprotonated base badc described above coordinated as a tridentate ligand, as shown in Figure 2. Location and meaningful refinement of all hydrogens atoms of the structure suggest affiliation of 2, 0, 3, and 2 hydrogens, respectively, with N(12), N(3), N(32), and N(5) and a normal H₂O water molecule. One formula unit comprises the asymmetric unit of the structure. Non-hydrogen atom coordinates, distances and angles in the copper atom environments, and ring torsion angles are collected in Tables II, III, and V.

The copper atom in Cu(badcH)(OH₂)³⁺ has the common pseudo-square-planar coordination environment comprised of the water molecule (pyramidal at O with Cu–O–H(a,b) = 112 (6) and 120 (5)° and H–O–H = 111 (7)°), N(1), N(12), and N(5), the distances to the latter all lying between 2.00 and 2.01 Å. N(3)

(24) Tasker, P. A.; Sklar, L. *J. Cryst. Mol. Struct.* **1975**, *5*, 239.
(25) Ochiai, E. I.; Rettig, S. J.; Trotter, J. *Can. J. Chem.* **1978**, *56*, 267.

**Table VI.** Redox Couples for Copper(II) Amine Complexes in Aqueous 0.1 M NaClO$_4$ Solution[a]

| complex[f] | pH | dc | | cyclic voltammetry[b] | | | |
| | | $E_{1/2}(Cu^{II/I})$, V | $E_{1/2}(NO_2 \rightarrow NHOH)$, V | $E_{1/2}(Cu^{II/I})$,[c] V | $\Delta E$, mV | $i_{pc}/i_{pa}$ | $E_p(NO_2 \rightarrow NHOH)$, V |
|---|---|---|---|---|---|---|---|
| Cu(Ia) | ~6 | -0.68 | -0.95 | -0.71 | irrev | | -0.99 |
| Cu(Ib) | ~6 | -0.72 | -0.96 | -0.74 | irrev | | -1.00 |
| Cu(II) | ~6 | -0.61 | -1.01 | -0.59 | 77 | 0.95 | -1.06 |
| Cu(IIIa) | ~1 | -0.78 | | -0.81 | irrev | | |
| | ~5 | -0.71 | | -0.73 | irrev | | |
| | ~10 | -0.86 | | -0.89 | irrev[d] | | |
| Cu(IIIb) | ~1 | -0.71 | | -0.76 | irrev | | |
| | ~5 | -0.65 | | -0.70 | irrev | | |
| | ~10 | -0.84 | | -0.87 | irrev | | |
| Cu(IV) | ~5 | -0.66 | | -0.65 | 105 | 0.95 | |
| | ~10 | -0.69 | | -0.68 | 60 | 0.96 | |
| Cu(V)(OH$_2$) | ~5 | -0.38 | | -0.37 | 70 | ~1[e] | |
| | ~10 | -0.50 | | -0.49 | 59 | 0.92 | |

[a] Measured at DME or HMDE vs. Ag/Ag$^+$ at ambient temperature; reference electrode calibrated as -0.12 V vs. saturated calomel electrode. [b] Behavior at solid billet electrodes qualitatively similar. [c] $E_p$ reported for irreversible couples. [d] Ill-defined anodic wave ~190 mV more positive than the cathodic wave. [e] Complicated by adsorption effects. [f] Perchlorate salts.
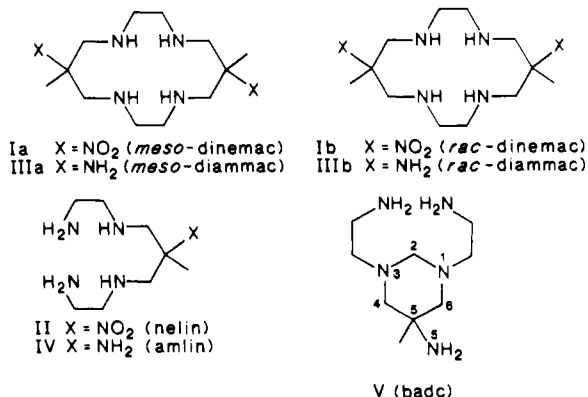
**Table VII.** Electronic Transitions and Spin Hamiltonian Parameters for Copper(II) Complexes of Pendant Amine Multidentates

| complex[c] | electronic transition[a] $\bar{\nu}$, cm$^{-1}$ ($\epsilon$, M$^{-1}$ cm$^{-1}$) | spin Hamiltonian params[b] | | | | | |
| | | $g_{iso}$ | $g_\perp$ | $g_\parallel$ | $A_{iso}$ | $A_\perp$ | $A_\parallel$ |
|---|---|---|---|---|---|---|---|
| Cu(IV) | 18 590 (73) | 2.104 | 2.055 | 2.202 | 85 | 32 | 200 |
| Cu(IIIa) | 19 270 (88) | 2.102 | 2.054 | 2.198 | 88 | 34 | 205 |
| Cu(IIIb) | 19 570 (86) | 2.099 | 2.053 | 2.191 | 88 | 31 | 210 |
| Cu(V)(OH$_2$) | 16 450 (82) | 2.121 | 2.064 | 2.235 | 71 | 18 | 186 |

[a] Measured in water at pH ~10. [b] $A$ values in 10$^{-4}$ cm$^{-1}$. [c] Perchlorate salts.

and N(32) (the latter coordinately saturated by hydrogen atoms anyway) are uncoordinated, the fifth and sixth sites of the copper being approached by O(11) (2.637 (5) Å) and O(12) ($\bar{x}$, $^1/_2$ + $y$, $^1/_2 - z$) (2.820 (4) Å) of one of the perchlorate ions. The copper environment deviates considerably from planarity; for a least-squares plane calculated through O, N(1), N(12), and N(5) ($\chi^2$, 1919), atom deviations respectively are 0.10, 0.12, -0.15, and -0.14 Å with $\delta$(Cu) = 0.07 Å (i.e. away from O(11)). In the five-membered chelate rings, $\delta$(C(11)) and $\delta$(C(12)) are -0.43 and 0.10 and $\delta$(C(5)) and $\delta$(C(6)) are -0.10 and -0.74 Å; i.e., both rings are envelopes with the deviant atom that which is attached to the common tetrahedral N(1) (C(11) and C(6)). The six-membered ring N(1), C(2), N(3), C(4), C(5), C(6) is a chair, with torsion angles in the bonds successively from N(1) being -65.4, 59.3, -55.9, 56.6, and -59.6° and all substituents except Cu and N(5) being equatorial.

The incorporation of the carbon acid nitroethane into the nelin(II) and dinemac (I) ligands is supported by microanalysis and indirectly by the crystal structure of the reduced diammac complex (3a). The six-membered chelate ring with nitro and methyl



Ia  X = NO$_2$ (*meso*-dinemac)
IIIa  X = NH$_2$ (*meso*-diammac)

Ib  X = NO$_2$ (*rac*-dinemac)
IIIb  X = NH$_2$ (*rac*-diammac)

II  X = NO$_2$ (nelin)
IV  X = NH$_2$ (amlin)

V (badc)

substituents has been characterized structurally in a related copper(II) complex.[26] Further, characteristic infrared bands

assignable to the nitro group occur at ~1555 cm$^{-1}$ (s, $\nu_{as}$) and ~1355 cm$^{-1}$ (m, $\nu_s$), while irreversible reduction of the nitro groups occurs in the voltammetry. All nitro-substituted complexes exhibit a one-electron Cu(II)/Cu(I) couple and a multielectron irreversible wave assigned to -NO$_2 \rightarrow$ -NHOH by comparison with similar studies of nitro ligands on cobalt(III) complexes.[27] In the pendant amine complexes the nitro reduction wave is absent, and the Cu(II)/Cu(I) couple is shifted to a different potential. The $E_{1/2}$ values for the complexes are collected in Table VI. The copper couple is at best quasi-reversible, and the copper(I) compounds are not stable on the coulometric time scale.

Amine ligands III and IV, apart from the four nitrogens about the copper square plane, have the capacity to coordinate the pendant amine groups in axial sites when these are not protonated. At least in aqueous solution, there is no evidence for this from electronic spectroscopy since spectra in acidic, neutral, and basic solution are very similar. While the crystal structure of complexed IIIa is of the diprotonated ligand, a crystal structure of the copper(II)-complexed neutral ligand prepared by another route shows $^-$OClO$_3$ occupying the axial sites and not -NH$_2$ groups.[28] Evidently, there is a preference for four-coordination about copper(II), and this was also probed in solution by electron spin resonance and electronic spectroscopy.

Spin Hamiltonian parameters calculated from the ESR spectra of the complexed pendant amine ligands are collected in Table VII. The $g$ values are indicative of a d$_{x^2-y^2}$$^1$ ground state, while the $A$ parameters support a square-planar CuN$_4$ geometry in solution. Typical spectra are shown in Figure 4. Minor differences in the ESR spectra of complexed IIIa and IIIb support their assignment as geometric isomers. Solvent effects on the spectra are small or absent, and the complexes of III and IV are spectroscopically very similar to Cu(cyclam)$^{2+}$ (cyclam = 1,4,8,11-tetraazacyclotetradecane),[29] supporting no appreciable axial interaction by the pendant amines. Electronic spectra (Table VII) also do not support a CuN$_6$ geometry in solution. Detailed analysis of spectra is deferred to the Discussion.

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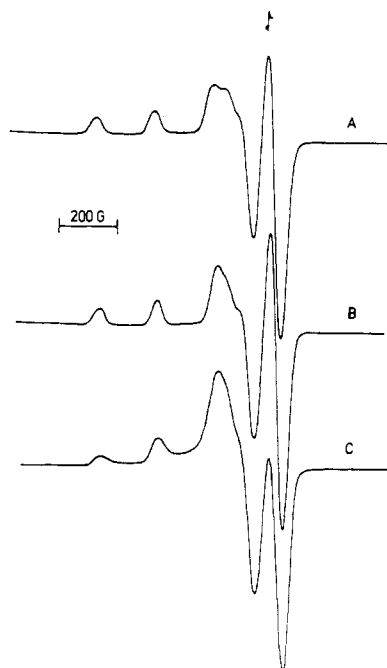(29) Addison, A. W.; Sinn, K. *Inorg. Chem.* **1983**, *22*, 1225.

**Figure 4.** ESR spectra in dimethyl sulfoxide at 4 K of (A) (1,9-diammonio-5-methyl-5-nitro-3,7-diazanonane)copper(II) and the (B) *meso* and (C) *rac* isomers of (3,10-diammonio-3,10-dimethyl-1,4,8,11-tetraazacyclotetradecane)copper(II) cations (**4**, **3a**, and **3b**, respectively). The marker of the reference material dpph is shown at the top of the spectra.

## Discussion

The facility of template syntheses involving formaldehyde and carbon acids clearly demonstrated about inert metal ions[17-20] extends to reactions about the relatively labile copper(II) ion. Further work in progress has established that reactions like those described here about copper(II) also occur about nickel(II).[30] The $d^9$ copper(II) ion displays Jahn–Teller effects, which usually distort an octahedral structure at least tetragonally.[31] Stepwise enthalpies of formation of $M(en)^{2+}$ and $M(en)_2^{2+}$ are lower for $d^8$ nickel(II) than for copper(II), but the order is markedly reversed for the tris complexes as a consequence of Jahn–Teller destabilization with $Cu(en)_3^{2+}$.[32] Consequently, while macrobicyclization is inherently possible about $Ni(en)_3^{2+}$, the preference with copper(II) for square-planar or elongated octahedral geometries will probably direct carbon acid syntheses toward tetradentate and macromonocyclic ligand formation. This propensity toward planar four-coordinate ligands about copper(II) has been applied here to the preferential synthesis of such species.

Even about nickel(II), however, there is apparently a preference for the formation of such products. Recently, reaction of formaldehyde and ammonia with $Ni(en)_3^{2+}$ has been shown to form the macrobicycle 1,3,6,8,10,13,16,19-octaaza[6.6.6]eicosane, but in very low yield ($\sim 1\%$).[33] The major product of the reaction of formaldehyde and ammonia with $Ni(en)_3^{2+}$ is the tripodal hexadentate complex **VI**, with some formation of square-planar complex **VII** rather than the hexadentate macrobicycle **VIII**.[30,33] The cavity in the 20-membered [6.6.6]macrobicycles **VIII** and **IX** is clearly appropriate for many M(II), M(III), and M(IV) ions, since very stable complexes of **IX** with all of the first-row metal ions in one or more of these oxidation states have been prepared by insertion of the metal ion into the free macrobicyclic ligand isolated from the cobalt complex.[34-36] Possibly reaction



VI

VII

VIII

IX
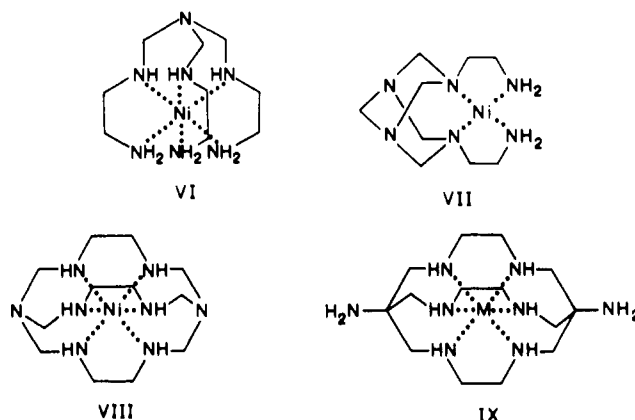
in aprotic solvents may improve yields of macrobicycles from complexes such as $Ni(en)_3^{2+}$,[21] but our results indicate that at least in protic solvents diamines of $Ni^{2+}$ and $Cu^{2+}$ generate multidentate or macromonocyclic ligands from reaction with formaldehyde and carbon acids.

Observed condensations about $Cu(en)_2^{2+}$ are remarkably clean, with the only significant reaction being the six-membered ring formation based on condensation of two formaldehyde molecules and one nitroethane molecule with two cis primary amine sites. The only other complexed ligand identified was **V**, present to more than 3%, the nitro precursor of which might arise where a single formaldehyde has bridged the internal cis amines of **II** to form a six-membered diazacyclohexane ring with two pendant ethyl amines, presumably by reaction between an intermediate aminol and the adjacent deprotonated amine. Both types of condensation reaction occurring here have been observed about inert metal ion complexes.[17-20,37]

The ligands prepared following nitro group reduction have pendant amines that in principle can coordinate axially (X). Such



X

XI
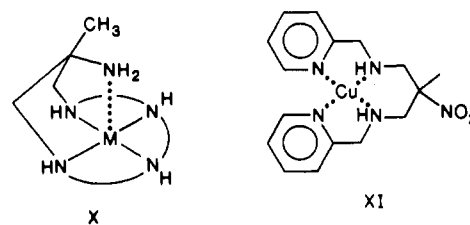
axial interaction may be precluded by protonation, as in the product **3a**, analyzed by X-ray crystallography in this study. However, an independent structure of the unprotonated form of *meso*-diammac (**3a**), prepared by another route, shows that perchlorate oxygens occupy the axial sites in the solid state in preference to the pendant amines.[28] Inspection of models reveals that approach of the amine in X would have to be fairly close for it to occupy a position directly above the metal ion; longer metal–amine bonds lead to a lateral displacement. Given the propensity of Cu(II) for elongated axial bonding, it is perhaps not surprising that coordination of the pendant amines is not observed. However, with nickel(II), *meso*-diammac (**IIIa**) coordinates as a hexadentate ligand or as a tetradentate ligand, and when coordinated to cobalt(III), **IIIa** acts as a hexadentate; characterization of these complexes is being pursued.[30,38]

The spin Hamiltonian parameters observed for the copper(II) amine complexes indicate a $d_{x^2-y^2}^1$ ground state, and they are compatible with square-planar structure with little axial interaction.[39,40] Typically, $CuN_4$ chromophores exhibit $g_{\parallel}$ values in

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the range 2.17–2.23 and $g_\perp$ values around 2.05. However, we should realize that differences in $g$ values are usually very subtle; they may be the result of such different effects as tetrahedral distortion of square-planar species and changes in covalency, and they may be irrelevant for quantitative analysis.[41] The $A$ parameters are usually much more indicative of the local geometry. Here, observed $A_\parallel \sim 190$ G and $A_\perp \sim 20$ G are quite consistent with a square-planar geometry. Solvent effects (in water, dimethyl sulfoxide, or pyridine) on the observed spectra were small or not observed, implying that any interactions in the axial positions are weak even in basic solution. It has been found in general that 14-membered tetraza macrocyclic rings are well suited for square-planar coordination of copper, developing strong in-plane interactions, a high-energy d–d transition, large $A_\parallel$ values, and small $g_\parallel$ values.[42] The complexed 14-membered macrocycles **3a** and **3b** fit this pattern.

While electronic spectroscopy is at best a modest guide to structure, Hathaway has found a correlation between the energies of the d–d transitions of CuN$_x$ ($x$ = 4–6) species and their structure.[43] Complexes with tetragonal–octahedral CuN$_6$ chromophores have transitions in the region 15 500–18 500 cm$^{-1}$, and those with square planar CuN$_4$ chromophores have transitions in the region 18 000–20 000 cm$^{-1}$. The copper(II) complex of IX has a defined CuN$_6$ chromophore and transitions in the region of 15 000 cm$^{-1}$ but is nearly trigonal prismatic.[36] Absorbance maxima for the copper(II) complexes of IIIa, IIIb, and IV have maxima in solution above 18 500 cm$^{-1}$, which is consistent with the essentially CuN$_4$ environment implied by electron spin resonance studies.

The crystal structure analysis of the Cu(II) complex of IIIa indicated planarity of the copper and four nitrogen donors. This is likely to be the preferred arrangement with the four-coordinate ligands. Only in complexes such as XI[26] are deviations from planarity clearly observed. This is largely a consequence of the enforced planarity of the pyridine rings, which might have an influence on the disposition of the tetrahedral carbon atoms in the ligand and hence the donor set. Unlike the case of copper(II), copper(I) amine complexes are commonly tetrahedral, and comparative crystal structures with tetradentate ligands coordinated to copper in both oxidation states exist.[44]

The voltammetric reductions of the copper(II) complexes, defined as one electron by wave height comparisons with known one-electron couples, fall clearly into two groups. The macrocyclic ligand complexes undergo irreversible reductions, while the open-chain tetraamine complexes exhibit quasi-reversible behavior. The distinction may relate to the greater ability of the open-chain tetraamines to change geometry and adopt a tetrahedral coordination about the copper(I) ion. Not only may the cavity in the 14-membered macrocycles be inappropriate for the larger copper(I) ion, but the ability of these ligands to distort to a tetrahedral geometry is probably reduced, so that the copper(I) ion may dissociate and disproportionate rapidly. The copper(II) complex of V, which exhibits tetrahedral distortion from a perfect square plane in the solid state, also produces quasi-reversible behavior in the voltammetry, as does the already tetragonally distorted

complex XI.[26] With none of these saturated multidentate amine ligands is the lifetime of the copper(I) complex substantial. The redox potentials for compounds **1a** and **1b** and also for **3a** and **3b** are not equivalent. Since electron spin resonance spectra and infrared spectra also differ, the definition of these species as *meso* and *rac* isomers seems adequately established. To date, structural characterization of only the *meso* isomer has been achieved with any metal ion, so final confirmation of the racemic forms has not been forthcoming.

Determined $E_{1/2}$ values for the copper(II)/copper(I) couple in the CuN$_4$ complexes vary between about –0.6 and –0.8 V (vs. Ag/Ag$^+$) in water; the variation is presumably largely a consequence of the different substituent groups –NO$_2$, –NH$_3^+$ (in acid), or –NH$_2$ (in base). Inductive effects of such substituents are not identical and have been defined previously on cobalt(III) macrobicyclic complexes.[27,45] The irreversible multielectron reduction (–NO$_2 \rightarrow$ –NHOH, 4e, neutral solution) in compounds **1** and **2** occurs at a somewhat more negative potential ($\sim$–150 mV) than the like reduction in cobalt(III) macrobicycles.[27] In the latter compounds the nitro group is attached to an apical carbon (XII)
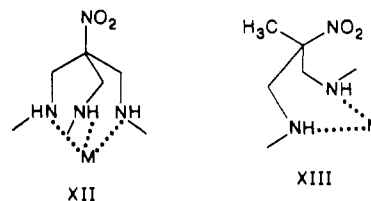


remote from the metal center while in the present complexes the nitro group may in certain conformations experience a closer approach to the metal ion and interact more directly with $d_{z^2}$, $d_{yz}$, and $d_{xz}$ orbitals (XIII). The copper complex of V, which exhibits a CuN$_3$O chromophore in the solid state, is reduced at a potential $\sim$200 mV more positive than that observed for the CuN$_4$ complexes.

The syntheses established here for reaction with Cu(en)$_2^{2+}$ are being extended to allow investigation of the facility of these reactions with other multidentate amine precursor complexes and with other carbon acids apart from nitroalkanes. Comparison of the outcome of such condensation reactions around various metal ions is also being probed. Evidently, at least around copper(II), facile routes to new multidentate and macromonocyclic ligands can be developed from template reactions of multidentate amines with formaldehyde and carbon acids.

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