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Contribution from the School of Chemistry,
Georgia Institute of Technology, Atlanta, Georgia 30332

Electrochemical and Structural Studies of Nickel(II) Complexes of N-Alkylated Cyclam Ligands: X-ray Structures of *trans*-$[Ni(C_{14}H_{32}N_4)(OH_2)_2]Cl_2\cdot 2H_2O$ and $[Ni(C_{14}H_{32}N_4)](O_3SCF_3)_2$

E. Kent Barefield,* Gary M. Freeman, and Donald G. Van Derveer

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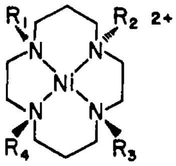
Redox potentials for oxidation and reduction of 15 nickel(II) complexes of cyclam-type ligands that contain one to four *N*-alkyl groups have been determined in acetonitrile solution. Complexes having both the *trans*-I and *trans*-III stereochemistries are included. N-Alkylation results in an anodic shift in both oxidation and reduction potentials of 0.1–0.2 V depending upon the particular complex and alkyl group introduced. Oxidation potentials span a range of 0.74 V; reduction potentials span a range of 0.67 V. Single-crystal X-ray structures of *trans*-$[Ni(C_{14}H_{32}N_4)(OH_2)_2]Cl_2\cdot 2H_2O$ (monoclinic, space group $C2/c$, $a = 9.286$ (3) Å, $b = 16.739$ (5) Å, $c = 14.336$ (4) Å, $\beta = 103.23$ (2)°, $\rho_{calcd} = 1.403$ g cm^{-3} for $Z = 4$ and $M_r = 458.12$, $R = 0.032$, $R_w = 0.039$) and $[Ni(C_{14}H_{32}N_4)](O_3SCF_3)_2$ (monoclinic, space group $P2_1/c$, $a = 8.046$ (2) Å, $b = 10.794$ (4) Å, $c = 15.075$ (4) Å, $\beta = 104.53$ (2)°, $\rho_{calcd} = 1.607$ g cm^{-3} for $Z = 2$ and $M_r = 613.28$, $R = 0.042$, $R_w = 0.042$) are also reported. Both complexes have the *trans*-III stereochemistry and a crystallographically imposed center of symmetry. The average Ni–N distance is 2.142 Å in the six-coordinate complex and 1.990 Å in the four-coordinate complex. These distances are ca. 0.1 and 0.04 Å, respectively, longer than Ni–N distances in comparable secondary amine complexes. The anodic shift in redox potentials resulting from introduction of *N*-alkyl groups is a result of the weakened Ni–N(3°) interaction.

Introduction

There has been a continued interest in the redox properties of nickel complexes of macrocyclic tetraaza ligands[1] since the first reports of the preparation of nickel(III)[2] and nickel(I)[3] complexes of saturated tetraaza macrocyclic ligands and on the electrochemical oxidation and reduction of complexes of both saturated and unsaturated tetraaza macrocyclic ligands.[3] More recently nickel(III) complexes of tetraaza macrocyclic ligands have been used as oxidants for both inorganic[4] and organic compounds[5] and nickel(I) species as reductants of alkyl halides.[6] In addition such complexes have been used as electrocatalysts for CO_2 reduction.[7]

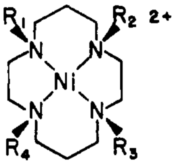
A knowledge of how structural modifications of ligands affect redox potentials of their metal complexes is of obvious importance for the design of selective reagents for oxidation or reduction. For neutral macrocyclic tetraaza ligands, a number of factors have already been identified that affect the redox potentials of their nickel complexes. These include chelate ring size,[8a,9] donor unsaturation, conjugation of donor unsaturation, and substituent pattern in the chelate rings.[8a] Relative positions of five- and six-membered chelate rings are also important.[10]

Chart I



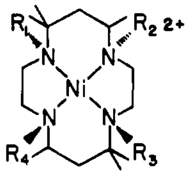
A Series

A $R_1=R_2=R_3=R_4=H$
AMe $R_1=CH_3$, $R_2=R_3=R_4=H$
AMe$_2$ $R_1=H$, $R_2=R_3=CH_3$, $R_4=H$
AMe$_3$ $R_1=R_2=R_3=CH_3$, $R_4=H$
AMe$_4$ $R_1=R_2=R_3=R_4=CH_3$
ABz $R_1=PhCH_2$, $R_2=R_3=R_4=H$
ABz$_2$ $R_1=H$, $R_2=R_3=PhCH_2$, $R_4=H$
AX$_2$ R_1&$R_2=R_3$&$R_4=$<u>o</u>-$CH_2C_6H_4CH_2$



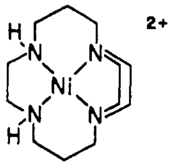
B Series

BMe$_2$ $R_1=H$, $R_2=R_3=CH_3$, $R_4=H$
BMe$_3$ $R_1=R_2=R_3=CH_3$, $R_4=H$
BMe$_4$ $R_1=R_2=R_3=R_4=CH_3$
BMe$_3$Bz $R_1=R_2=R_3=CH_3$, $R_4=PhCH_2$



C Series

C $R_1=R_2=R_3=R_4=H$
CMe$_2$ $R_1=R_3=CH_3$, $R_2=R_4=H$
CMe$_3$ $R_1=R_2=R_3=CH_3$, $R_4=H$
CMe$_4$ $R_1=R_2=R_3=R_4=CH_3$



D

A ligand modification that has not been systematically studied for its effect on redox properties is the presence of tertiary amine donors. The limited electrochemical data that are available suggest that conversion of secondary amines to tertiary amines in cyclam-like ligands (cyclam is 1,4,8,11-tetraazacyclotetradecane, the ligand for complex A in Chart I) makes oxidation more difficult and reduction easier. For example, complex A is oxidized at +0.68 V and reduced at –1.7 V,[8a] whereas AMe_4 is oxidized at +1.23 V[11] and reduced at –1.35 V.[12] Complexes C and CMe_4

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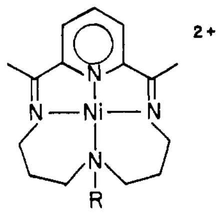
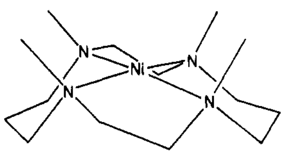
(12) Reference 6c; conditions as described in ref 8b.

are reduced at −1.42 and −0.98 V, respectively.[13] Complexes E and EMe are oxidized at +1.064 and +1.214 V, respectively.[14]

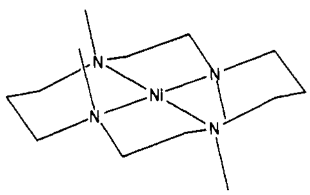


E R=H
EMe R=CH_3

We earlier prepared nickel(II) complexes of a series of N-alkylated macrocyclic ligands,[15] and the spectral properties of these complexes suggested that the ligand field strength of the macrocycle decreased with the addition of each *N*-alkyl group.[15b] A number of studies have established that a decrease in the ligand field strength of the macrocyclic ligand results in an anodic shift of both the oxidation and reduction potentials of their metal complexes.[10,16] This paper considers electrochemical results for nickel complexes (Chart I) of N-alkylated cyclam ligands that indicate that the redox potentials depend on the number and, to a lesser extent, the type of *N*-alkyl substituents. Series A and B differ in the stereochemical arrangement of the nitrogen substituents. A series complexes have the *trans*-III stereochemistry[15,17] and B series complexes have the *trans*-I stereochemistry.[15,18,19] Series C is based on the parent $Me_6[14]aneN_4$ complex, which has the *trans*-III stereochemistry.[20] A second consideration is the reason(s) for the substantial change in redox potential that is observed upon introduction of a *N*-alkyl substituent. The greater intrinsic basicity of tertiary amines compared to secondary amines[21] does not result in better donor properties toward nickel(II), at least when the tertiary donor is incorporated in a macrocyclic ligand. X-ray structural results on a six-coordinate derivative of AMe_4, $\{[Ni(C_{14}H_{32}N_4)N_3](\mu\text{-}N_3)[Ni(C_{14}H_{32}N_4)N_3]\}I$,[18] indicated that the Ni–N distances were longer than those in the unmethylated complex $[Ni(cyclam)Cl_2]$.[19b] Thus it seems likely that the major effect of the tertiary donors on the ligand field strength and the redox potential of the coordinated nickel ion probably arises from a weaker metal–nitrogen interaction. However, it has been suggested that the increase in the oxidation potential of EMe is due to weakening of one of the axial donor bonds in the six-coordinate Ni(III) product because of steric interactions with the *N*-methyl group.[14] This followed suggestions that steric interactions between *C*-methyl groups in C and axial donors was the reason that C was more difficult to oxidize than A.[8a] To further define the structural features associated with complexes of macrocyclic tertiary amine ligands, we have determined the structures of *trans*-$[Ni(C_{14}H_{32}N_4)(OH_2)_2]Cl_2 \cdot 2H_2O$ and $[Ni(C_{14}H_{32}N_4)](O_3SCF_3)_2$ (both complexes are derivatives of AMe_4) by X-ray diffraction and we include these results as a part of this paper.



trans-I



trans-III

Experimental Section

Cyclic voltammetric measurements were made with a locally constructed potentiostat and function generator (Georgia Tech Model 9-76) and a standard three-electrode cell. The working and counter electrodes were platinum; the reference electrode was 0.1 M $AgNO_3/Ag$ in acetonitrile and was separated from the cell by a salt bridge. Voltammograms were recorded with a Houston Instruments 2000 X-Y recorder or a Tektronix 5115 oscilloscope. All measurements were made on acetonitrile solutions that were 0.1 M in tetrabutylammonium tetrafluoroborate and 0.001 M in complex. Reagent grade acetonitrile (Fisher) was purified by successive distillations under nitrogen from calcium hydride and P_4O_{10} and finally by passage over a column of freshly activated alumina. In many cases a small amount of activated alumina was added to the sample cell. As previously noted, this served to improve the shapes of voltammetric waves at high potentials,[11] presumably by scavenging residual water. The supporting electrolyte (Southwestern Analytical) was dried at 0.01 torr and 100 °C for 24 h prior to use. Nitrogen used for deaeration of sample solutions was purified by passage through consecutive columns of BASF catalyst and Matheson Aquasorb. The working electrode was treated as described by Busch prior to each use.[8a]

Analytically pure samples of the perchlorate salts of all complexes shown in Chart I except BMe_3Bz and D were available from the earlier work of Wagner[15b,c] and Wagner and Hodges.[15c] These were used without further treatment. A sample of D, also as the perchlorate salt, was a gift from Wainwright;[22] the synthesis of the perchlorate salt of BMe_3Bz is given below.

NMR spectra were obtained at 300 MHz on $CDCl_3$ solutions with Me_4Si as internal standard.

5-Benzyl-8-methyl-1,5,8,12-tetraazadodecane. *N*-Benzyl-*N'*-methylethylenediamine (20 g, 0.122 mol) in 40 mL of acrylonitrile was heated at 100 °C for ca. 3 h in a sealed pressure bottle. The reaction mixture was cooled, and 0.2 g of anhydrous $ZnCl_2$ was added. The mixture was then heated with stirring at 150 °C for 24 h in the sealed pressure bottle. After the mixture was cooled to room temperature, ca. 300 mL of chloroform was added and the suspension stirred for several min. The suspension was gravity-filtered and the filtrate evaporated to a viscous, orange oil on a rotary evaporator. Yield of dinitrile: 33 g or 100%. Mass spectrum: *m/e* for parent ion 270 (calcd 270). The dinitrile was then catalytically reduced in ethanol with H_2/Raney nickel as previously described.[15a] In a typical preparation, 11.0 g (40.7 mmol) of dinitrile gave a yield of 10.0 g or 88%. ^1H NMR: δ 1.56 (q, J = 7 Hz, 2 H), 1.60 (q, J = 7, 2 H), 2.17 (s, 3 H), 2.35 (t, J = 7 Hz, 2 H), 2.4–2.6 (m, 6 H), 2.68 (t, J = 7 Hz, 2 H), 2.70 (t, J = 7 Hz, 2 H), 7.2–7.3 (m, 5 H). Mass spectrum: *m/e* for parent ion 278 (calcd 278).

1-Benzyl-4-methyl-1,4,8,11-tetraazacyclotetradecane. 5-Benzyl-8-methyl-1,5,8,12-tetraazadodecane (8.35 g, 30 mmol) in 100 mL of absolute ethanol was treated with $NiCl_2 \cdot 6H_2O$ (7.13 g, 30 mmol) over 4–5 min. After the mixture was heated at reflux for 30 min, the ethanol was removed on a rotary evaporator. The resulting green solid was dissolved in 200 mL of water and the solution gravity-filtered. The filtrate was treated with 4.5 mL of 40% glyoxal and allowed to stand for 14 h. After the reaction mixture was cooled to ca. 5 °C, $NaBH_4$ (2.27 g, 60 mmol in 20 mL of 1:1 v/v ethanol–water) was added slowly with vigorous stirring. Upon complete addition, the solution was heated to near boiling and gravity-filtered. The filtrate was cooled, $NaClO_4$ (11 g, 90 mmol) and $HClO_4$ (1 mL) were added, and the solution was extracted with three 75-mL portions of nitromethane. The nitromethane extracts were combined and evaporated to a light orange solid on a rotary evaporator. The crude complex was taken up in 150 mL of water, NaCN (7.4 g, 0.15 mol) added, and the solution heated at reflux for 7 h. Upon cooling to room temperature, the solution was extracted with three 75-mL portions of chloroform. The chloroform extracts were combined, dried over Na_2SO_4, and evaporated to dryness. The oil was stirred with 150 mL of anhydrous ether, the mixture filtered, and the ether removed on a rotary evaporator.

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Table I. Crystal Data for *trans*-$[Ni(C_{14}H_{32}N_4)(OH_2)_2]Cl_2 \cdot 2H_2O$ and $[Ni(C_{14}H_{32}N_4)](O_3SCF_3)_2$

	$[Ni(C_{14}H_{32}N_4)]$-$(O_3SCF_3)_2$	$[Ni(C_{14}H_{32}N_4)(OH_2)_2]$-$Cl_2 \cdot 2H_2O$
M_r	613.28	458.12
dimens, mm	0.56 × 0.33 × 0.22	0.37 × 0.22 × 0.22
space group	$P2_1/c$	$C2/c$
cell const		
a, Å	8.046 (2)	9.286 (3)
b, Å	10.794 (4)	16.739 (5)
c, Å	15.075 (4)	14.336 (4)
β, deg	104.53 (2)	103.23 (2)
no. of reflcns used to determine cell constants; 2θ limits, deg	15; $13.4 < 2\theta < 31.7$	15; $13.7 < 2\theta < 21.6$
Z	2	4
ρ_{calcd}, g cm^{-3}	1.607	1.403
ρ_{exptl},[a] g cm^{-3}	1.60	1.39

[a] By flotation in carbon tetrachloride/*n*-hexane.

Yield: 7.6 g or 83%. ^{1}H NMR: δ 1.68 (q, J = 6 Hz, 2 H), 1.84 (s overlapping m, 5 H), 2.31 (t, J = 6 Hz, 2 H), 2.35 (s, 4 H), 2.57 (t, J = 6 Hz, 2 H), 2.71–2.78 (m, 4 H), 2.82 (s, 4 H), 3.50 (s, 2 H), 7.2–7.35 (m, 5 H). Mass spectrum: m/e for parent ion 304 (calcd 304).

1-Benzyl-4,8,11-trimethyl-1,4,8,11-tetraazacyclotetradecane. A mixture consisting of 6.3 g (21 mmol) of 1-benzyl-4-methyl-1,4,8,11-tetraazacyclotetradecane, 5.3 g of 90% formic acid and 5.0 g of 37% formaldehyde was heated at 95–100 °C for 14 h. Afterward the reaction mixture was evaporated to a viscous oil on a rotary evaporator. The oil was dissolved in 50 mL of water and the pH adjusted to 9–10 by adding portions of 25% w/w NaOH. This solution was extracted with three 50-mL portions of chloroform, which were combined, dried over Na_2SO_4, and evaporated to a light yellow oil. Yield: 6.9 g or 100%. ^{1}H NMR: δ 1.65 (q, J = 7, 2 H), 1.66 (q, J = 7 Hz, 2 H), 2.11 (s, 3 H), 2.19 (s, 3 H), 2.24 (s, 3 H), 2.4–2.6 (m, 16 H), 3.53 (s, 2 H), 7.2–7.35 (m, 5 H).

(1-Benzyl-4,8,11-trimethyl-1,4,8,11-tetraazacyclotetradecane)nickel(II) Perchlorate. A hot, aqueous solution of 1-benzyl-4,8,11-trimethyl-1,4,8,11-tetraazacyclotetradecane (0.50 g, 1.5 mmol in 20 mL) was treated with an aqueous solution of $Ni(ClO_4) \cdot 6H_2O$ (0.55 g, 1.5 mmol in 5 mL) over 1–2 min. The dark red solution was heated at reflux for ca. 30 min, gravity-filtered, and evaporated to dryness on a rotary evaporator. The red residue was dissolved in ca. 25 mL of dry acetonitrile and the solution gravity-filtered. The filtrate was continuously stirred while portions of anhydrous ether were slowly added to precipitate the complex. The supernatant was decanted off and the precipitate triturated with additional fresh ether. The finely divided, red solid was collected, washed with additional fresh ether, and dried in vacuo (0.01 torr, 100 °C). Yield: 0.84 g or 95%. The complex was recrystallized with nearly quantitative recovery by slow evaporation of a dilute aqueous solution over several days. Anal. Calcd for $C_{20}H_{36}Cl_2N_4NiO_8$: C, 40.71; H, 6.15; N, 9.49. Found: C, 40.59; H, 6.16; N, 9.41. The visible spectrum of this complex in nitromethane solution consists of a single absorption band at 535 nm (ϵ = 221).

***trans*-$[Ni(C_{14}H_{32}N_4)(OH_2)_2]Cl_2 \cdot 2H_2O$.** An aqueous solution of $[Ni(C_{14}H_{32}N_4)](ClO_4)_2$[15b] (0.5 g, 0.97 mmol in 25 mL) and 0.3 g (4 mmol) of KCl was evaporated to dryness on a rotary evaporator. The solid residue was extracted with two 25-mL portions of chloroform. The extracts were combined, gravity-filtered, and evaporated to a light green solid whose infrared spectrum exhibited no absorptions for perchlorate ion. This solid was dissolved in ca. 10 mL of hot water and gravity-filtered. The volume of the solution was reduced to ca. 5 mL on a steam bath and then allowed to stand at room temperature until blue crystals grew to a size that was satisfactory for X-ray diffraction measurements. The crystals were collected and air-dried. Anal. Calcd for $C_{14}H_{40}Cl_2N_4NiO_4$: C, 36.71; H, 8.80; N, 12.23. Found: C, 37.01; H, 9.29; N, 12.25. The presence of four water molecules per nickel atom (15.7% water by weight) was further substantiated by a dehydration experiment in which an air-dried sample underwent a 16% weight loss upon heating in vacuo (0.01 torr, 100 °C) over P_4O_{10} for 6 h.

Table II. Data Collection and Refinement Details for $[Ni(C_{14}H_{32}N_4)](O_3SCF_3)_2$ and $[Ni(C_{14}H_{32}N_4)(OH_2)_2]Cl_2 \cdot 2H_2O$

diffractometer	Syntex $P2_1$
monochromator (Bragg 2θ angle, deg)	graphite (12.2)
radiation; λ, Å	Mo K$\bar{\alpha}$; 0.71069
take-off angle, deg	6.75
scan method	θ–2θ
min/max scan speed, deg min^{-1}	2.0/29.3
scan width, deg	2.0
bkgd/scan time ratio (TR)[a]	1.0
no. of stds at monitoring freq/no. of reflcns	3/97
2θ limits of data, deg	$4 < 2\theta < 50$

	$[Ni(C_{14}H_{32}N_4)]$-$(O_3SCF_3)_2$	$[Ni(C_{14}H_{32}N_4)(OH_2)_2]$-$Cl_2 \cdot 2H_2O$
hkl	$-h,0,0 \rightarrow hkl$	$-h,0,0 \rightarrow hkl$
no. of data	2243	1924
no. of data used in final refinement ($F > 3\sigma(F)$)	1846	1689
no. of data/no. of variables	11.1	12.4
μ,[b] cm^{-1}	9.43	10.98
$R = [\sum \lvert\lvert F_o\rvert - \lvert F_c\rvert\rvert]/[\sum \lvert F_o\rvert]$	0.042	0.032
$R_w = [\sum(\lvert F_o\rvert - \lvert F_c\rvert w^{1/2}]/[\sum(\lvert F_o\rvert)w^{1/2}]$[c]	0.042	0.039

[a] Background counts were measured before (BG1) and at the end (BG2) of the scan. Intensities were determined from the total scan (CT) and background (BG) counts by $I = CT - TR(BG1 + BG2)$. $\sigma(I) = [CT + (TR)^2(BG1 + BG2)]^{1/2}$; $F_o = (I/Lp)^{1/2}$, where Lp is the Lorentz and polarization correction. [b] Data were not corrected for effects of absorption. [c] $w = n/(\sigma(F)^2 + mF^2)$. In the final cycle values of n and m were as follows: $[Ni(C_{14}H_{32}N_4)](O_3SCF_3)_2$, m = 1.71 and $n = 3.3 \times 10^{-4}$; $[Ni(C_{14}H_{32}N_4)(OH_2)_2]Cl_2 \cdot 2H_2O$, n = 1.00 and $m = 2.9 \times 10^{-4}$.

Table III. Final Positional Parameters (with Esd's) for Non-Hydrogen Atoms of *trans*-$[Ni(C_{14}H_{32}N_4)(OH_2)_2]Cl_2 \cdot 2H_2O$

atom	x	y	z
Ni	−0.25000	−0.25000	−0.50000
Cl	−0.20071 (7)	−0.36535 (4)	−0.18511 (4)
O1	−0.1155 (2)	−0.2923 (1)	−0.3975 (1)
O2	−0.50000	−0.4854 (2)	−0.25000
O3	0.00000	−0.5040 (3)	−0.25000
N1	−0.0783 (2)	−0.1682 (1)	−0.5115 (1)
N2	−0.3527 (2)	−0.1680 (1)	−0.4198 (1)
C1	−0.1416 (3)	−0.0879 (2)	−0.5428 (2)
C2	−0.2255 (3)	−0.0489 (2)	−0.4738 (2)
C3	−0.3691 (3)	−0.0873 (2)	−0.4657 (2)
C4	−0.5000 (3)	−0.2052 (2)	−0.4267 (2)
C5	−0.4841 (3)	−0.2950 (2)	−0.4114 (2)
CN1	0.0448 (3)	−0.1567 (2)	−0.4253 (2)
CN2	−0.2812 (3)	−0.1570 (2)	−0.3158 (2)

$[Ni(C_{14}H_{32}N_4)](O_3SCF_3)_2$. The crude iodide salt of the tetramethylcyclam complex, prepared as previously described,[15b] was dissolved in water along with 5 equiv of sodium trifluoromethanesulfonate and the solution extracted with several small portions of nitromethane. The nitromethane extracts were combined and dried over sodium sulfate for ca. 1 h after which the sodium sulfate was removed by gravity filtration and the nitromethane removed with a rotary evaporator. The solid residue was dissolved in a minimum amount of hot water and the solution treated with a small amount of trifluoromethanesulfonic acid to induce crystallization. The pinkish orange solid was dried under vacuum at room temperature. Crystals for X-ray diffraction measurements were grown by ether diffusion into a nitromethane solution of the complex at room temperature. The red crystals were collected and air-dried.

Crystallographic Studies on *trans*-$[Ni(C_{14}H_{32}N_4)(OH_2)_2]Cl_2 \cdot 2H_2O$ and $[Ni(C_{14}H_{32}N_4)](O_3SCF_3)_2$. Crystal data are contained in Table I; diffractometer settings and certain details of data collection and refinement are given in Table II. Scattering factors were taken from the usual source;[23a] those for all atoms except hydrogen were corrected for real and imaginary anomalous dispersion components with use of the dispersion factors given by Cromer.[23b] Structures were solved by standard heavy-atom methods. All computations were carried out on a CDC Cyber 730 computer using Sheldrick's SHELX-76 program package with minor local modifications. All non-hydrogen atoms were located and subjected to

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(23) (a) Cromer, D. T.; Waber, J. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.2A. (b) Cromer, D. T. "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV, Table 2.3.1.

Table IV. Final Positional Parameters (with Esd's) for Non-Hydrogen Atoms of $[\mathrm{Ni(C_{14}H_{32}N_4)}](\mathrm{O_3SCF_3})_2$

atom	*x*	*y*	*z*
Ni	0.00000	0.50000	0.50000
N1	0.0385 (3)	0.4333 (3)	0.3838 (2)
N2	−0.1553 (3)	0.3607 (3)	0.5117 (2)
C1	0.0819 (4)	0.2984 (3)	0.3875 (2)
C2	−0.0585 (5)	0.2144 (3)	0.4033 (3)
C3	−0.0922 (4)	0.2338 (3)	0.4967 (3)
C4	−0.1682 (5)	0.3654 (4)	0.6095 (2)
C5	−0.1907 (5)	0.4989 (4)	0.6311 (2)
CN1	−0.1094 (5)	0.4597 (4)	0.3029 (2)
CN2	−0.3340 (4)	0.3795 (3)	0.4501 (3)
S	0.3933 (1)	0.26822 (9)	0.16879 (6)
O1	0.5529 (4)	0.2537 (3)	0.2347 (2)
O2	0.3671 (4)	0.1838 (3)	0.0949 (2)
O3	0.2439 (4)	0.2861 (4)	0.2011 (2)
C	0.4186 (6)	0.4133 (4)	0.1145 (4)
F1	0.5552 (4)	0.4136 (3)	0.0830 (3)
F2	0.4400 (6)	0.5057 (3)	0.1729 (3)
F3	0.2844 (4)	0.4413 (3)	0.0475 (3)

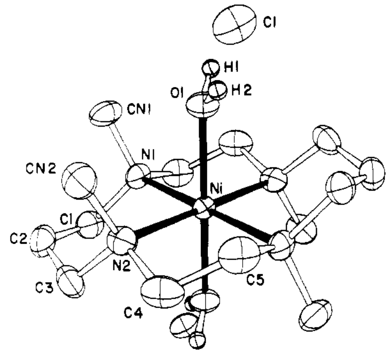

Figure 1. ORTEP drawing of *trans*-$[\mathrm{Ni(C_{14}H_{32}N_4)(OH_2)_2}]\mathrm{Cl_2}\cdot 2\mathrm{H_2O}$. Thermal ellipsoids for non-hydrogen atoms are at the 50% level; those for hydrogen have been reduced for clarity of presentation. Hydrogen atoms attached to carbon atoms and lattice water molecules have been omitted.

Table V. Selected Interatomic Distances (Å) and Angles (deg) in *trans*-$[\mathrm{Ni(C_{14}H_{32}N_4)(OH_2)_2}]^{2+}$

	Distances		
Ni-N1	2.136 (2)	N1-C1	1.495 (3)
Ni-N2	2.148 (2)	C1-C2	1.537 (4)
Ni-O1	2.141 (2)	C2-C3	1.508 (4)
		C3-N2	1.496 (3)
		N2-C4	1.485 (4)
N1-CN1	1.491 (3)	C4-C5	1.522 (5)
N2-CN2	1.499 (3)	C5-N1′	1.493 (4)
	Angles		
N1-Ni-N2	93.6 (1)	Ni-N1-C1	110.5 (1)
N1-Ni-O1	89.2 (1)	Ni-N1-C5′	102.5 (2)
N2-Ni-O1	88.7 (1)	Ni-N1-CN1	117.6 (2)
		Ni-N2-C3	110.8 (1)
N1-C1-C2	114.3 (2)	Ni-N2-C4	102.2 (2)
C1-C2-C3	117.1 (2)	Ni-N2-CN2	117.4 (2)
C2-C3-N2	114.6 (2)		
C3-N2-C4	110.4 (2)	CN1-N1-C5′	108.3 (2)
N2-C4-C5	110.3 (2)	CN1-N1-C1	107.8 (2)
C4-C5-N1′	110.0 (2)	CN2-N2-C4	108.0 (2)
C5-N1′-C1′	109.9 (2)	CN2-N2-C3	107.7 (2)

Table VI. Selected Interatomic Distances (Å) and Angles (deg) in $[\mathrm{Ni(C_{14}H_{32}N_4)}]^{2+}$

	Distances		
Ni-N1	1.989 (3)	N1-C1	1.496 (5)
Ni-N2	1.991 (3)	C1-C2	1.513 (5)
		C2-C3	1.513 (5)
N1-CN1	1.503 (4)	C3-N2	1.498 (4)
N2-CN2	1.517 (4)	N2-C4	1.505 (4)
		C4-C5	1.498 (5)
		C5-N1′	1.491 (5)
	Angles		
N1-Ni-N2	92.6 (1)	Ni-N1-C1	114.0 (2)
		Ni-N1-C5′	105.7 (2)
N1-C1-C2	114.4 (3)	Ni-N1-CN1	112.3 (2)
C1-C2-C3	112.3 (3)	Ni-N2-C3	115.7 (2)
C2-C3-N2	114.4 (3)	Ni-N2-C4	105.1 (2)
C3-N2-C4	106.7 (3)	Ni-N2-CN2	111.4 (2)
N2-C4-C5	106.6 (3)		
C4-C5-N1′	106.9 (3)	CN1-N1-C5′	107.3 (3)
C5-N1′-C1′	106.9 (3)	CN1-N1-C1	110.2 (3)
		CN2-N2-C4	107.9 (3)
		CN2-N2-C3	109.6 (2)

anisotropic refinement after which a difference Fourier map revealed the positions of all carbon-bound hydrogen atoms in both structures. All oxygen-bound hydrogen atoms in the aquo complex were also located from the difference Fourier map. In subsequent cycles of least-squares refinement, hydrogen atom positional parameters were held constant and the isotropic thermal parameter for each group of hydrogen atoms was allowed to vary. Final positional parameters for non-hydrogen atoms are given in Tables III and IV. Hydrogen atom positional and thermal parameters, anisotropic thermal parameters for non-hydrogen atoms, and structure factor tables are available as supplementary material.

Results

Description of the Structure of *trans*-$[\mathrm{Ni(C_{14}H_{32}N_4)(OH_2)_2}]\mathrm{Cl_2}\cdot 2\mathrm{H_2O}$. The crystal structure consists of monomeric *trans*-$[\mathrm{Ni(C_{14}H_{32}N_4)(OH_2)_2}]^{2+}$ cations, in which the nickel atom is six-coordinate, chloride anions, and two water molecules of crystallization. The Cl-O1 distance of 3.15 Å suggests that the chloride ions are hydrogen-bonded to the coordinated water molecules since this distance is within the normal range of values observed for such interactions.[24] The cation has a crystallographically imposed center of symmetry. A perspective drawing of the complex is shown in Figure 1. A listing of selected interatomic distances and angles is given in Table V.

The ligand stereochemistry is the expected *trans*-III structure that was previously shown to result from alkylation of $[\mathrm{Ni(cyclam)}]^{2+}$,[15b,17] as opposed to the *trans*-I stereochemistry that results when preformed tetramethylcyclam is used to form the complex.[15c,18] The Ni-O1 distance of 2.141 (2) Å is the same as the average of the Ni-N distances.

Description of the Structure of $[\mathrm{Ni(C_{14}H_{32}N_4)}](\mathrm{O_3SCF_3})_2$. The crystal structure consists of monomeric cations of the indicated formula, in which the nickel atom is planar and four-coordinate, and noninteracting trifluoromethanesulfonate anions. The cation has a crystallographically imposed center of symmetry. The stereochemistry of the macrocycle and its interaction with the metal are the same as that in *trans*-$[\mathrm{Ni(C_{14}H_{32}N_4)(OH_2)_2}]\mathrm{Cl_2}\cdot 2\mathrm{H_2O}$ (Figure 1). Selected interatomic distances and angles are given in Table VI.

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(24) Hamilton, W. C.; Ibers, J. A. "Hydrogen Bonding in Solids"; W. A. Benjamin: New York, 1968; pp 209–211, 262.

(25) Peak currents at equivalent concentrations and scan conditions were essentially the same for all complexes. Coulometry was used earlier to establish that oxidation and reduction of C were one-electron processes.[8a]

(26) ESR spectra obtained on oxidized forms of A,[8a] $\mathrm{AMe_4}$,[27] and C[8a] are entirely consistent with a Ni(III) formulation. Similarly, ESR spectra on reduced forms of A,[8a] C,[8a] and $\mathrm{CMe_4}$[14] are consistent with a Ni(I) formulation. Since the ligands for all complexes except $\mathrm{AX_2}$ are fully saturated both oxidation and reduction should be metal-centered in these cases as well.

(27) Mocella, M. T. Ph.D. Thesis, University of Illinois, 1974.

(28) Failure to achieve oxidation of $\mathrm{CMe_4}$ has also been noted by others.[14]

(29) Barefield, E. K.; Mocella, M. T. *J. Am. Chem. Soc.* **1975**, *97*, 4238.

(30) $[\mathrm{Ni(TMEDA)(NO_2)_2}]$, Ni-N = 2.086 (9) Å: Drew, M. G. B.; Rogers, D. *J. Chem. Soc., Chem. Commun.* **1965**, 476. $[\mathrm{Ni(en)_3}]\mathrm{SO_4}$, Ni-N = 2.124 (6) Å: Hague, M. U.; Caughlan, C. N.; Emerson, K. *Inorg. Chem.* **1970**, *9*, 2421. *trans*-$[\mathrm{Ni}(N,N'\text{-DMEDA})_2\mathrm{Br_2}]$, Ni-N = 2.125 (7) Å: Pajunen, A.; Luukkonen, E. *Suom. Kemistil. B* **1969**, *42*, 172. It is recognized that these complexes do not constitute a rigorous comparison of the intrinsic differences in nickel-nitrogen distances for primary, secondary, and tertiary amines because of differences in nonbonding interactions within each complex. However, the very short bond distance observed in the TMEDA complex is certainly suggestive.

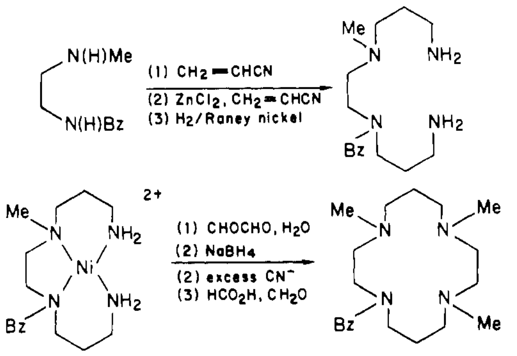
Table VII. Redox Potentials (V) for Nickel(II) Complexes of N-Alkylated Cyclam-Type Ligands

	oxidation			reduction		
complex	E_a	E_c	$E_{1/2}$	E_a	E_c	$E_{1/2}$
A[a]			+0.68			-1.70
AMe	+0.797	+0.727	+0.76	-1.710	-1.623	-1.67
AMe_2	+0.962	+0.882	+0.92	-1.537	-1.457	-1.50
AMe_3	+1.065	+1.002	+1.03	-1.458	-1.382	-1.42
AMe_4	+1.258	+1.180	+1.22[b]	-1.357	-1.280	-1.32[c]
ABz	+0.835	+0.766	+0.80	-1.651	-1.557	-1.60
ABz_2	+1.021	+0.954	+0.99	-1.415	-1.347	-1.38
AX_2	+1.535	+1.467	+1.50	-1.420	-1.355	-1.39
BMe_2	+0.967	+0.889	+0.93	-1.533	-1.445	-1.49
BMe_3	+1.157	+1.078	+1.12	-1.380	-1.302	-1.34
BMe_4	+1.320	+1.227	+1.27	-1.225	-1.152	-1.19
BMe_3Bz	+1.362	+1.267	+1.31	-1.095	-1.025	-1.06
C[a]			+0.87			-1.57
CMe_2				-1.377	-1.310	-1.34
CMe_3				-1.242	-1.180	-1.21
CMe_4				-1.037	-0.965	-1.00
D	+1.027	+0.878	+0.95	-1.648	-1.573	-1.61

[a] Date reported in ref 8a; identical values were obtained in this work. [b] Similar value reported in ref 11. [c] Similar value reported in ref 12.

Synthesis of BMe_3Bz. This complex, which has not been previously described, was prepared by combination of the free ligand and nickel perchlorate in aqueous solution. Assignment of the stereochemistry of the complex as *trans*-I is by analogy with earlier studies that indicate that this stereoisomer is the predominant form obtained from reactions of tetra-N-alkylated cyclam ligands with aquated nickel ion.[15a,c,31,32] The observation of a single absorption band in the visible spectrum at 535 nm is consistent with the proposed *trans*-I stereochemistry.[15c]

The benzyltrimethylcyclam ligand was synthesized by the reaction sequence



The nickel(II) templated cyclization of 5,8-disubstituted 1,5,8,12-tetraazadodecanes has been previously described by one of us.[15a] However, in the earlier work we were unable to cyanoethylate *N*-benzylethylenediamines with acrylonitrile. This has now been accomplished by use of $ZnCl_2$ as a catalyst. The best results were obtained by a stepwise alkylation sequence in which the methylamino group was alkylated prior to addition of the $ZnCl_2$. No attempt has been made to characterize the benzylmethylcyclam complex that is formed after the BH_4^- reduction of the glyoxal cyclization product.

Electrochemical Studies. Cyclic voltammetry data for 17 1,4,8,11-tetraazacyclotetradecane complexes shown in Chart I are given in Table VII. All complexes except the CMe_n complexes exhibit two one-electron waves[25] corresponding to Ni(III)/Ni(II) and Ni(II)/Ni(I) processes.[26] Complexes CMe_2, CMe_3, and CMe_4 exhibit only waves corresponding to the Ni(II)/Ni(I) process.[28] Both oxidations and reductions exhibit quasi-reversibility at scan rates of 200 mV/s for all complexes except BMe_4 where $I^{a}_{p}/I^{c}_{p} = 1$ for oxidation only at scan rates >500 mV/s.

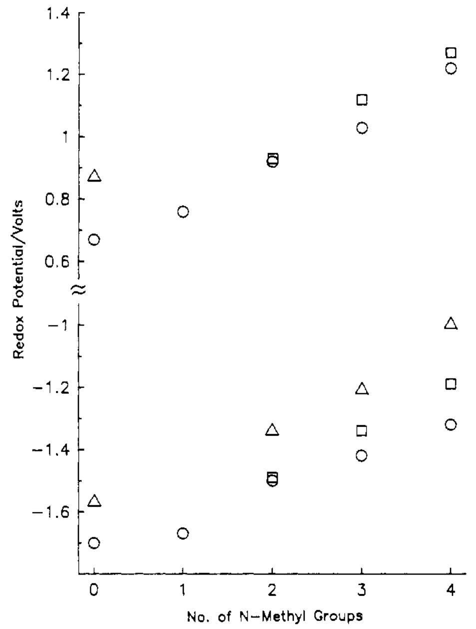


Figure 2. Variation of redox potentials for AMe_n (○), BMe_n (□), and CMe_n (△) complexes with the number of *N*-methyl groups.

Both the Ni(III)/Ni(II) and Ni(II)/Ni(I) redox processes become more anodic as the number of *N*-alkyl groups increases. This is illustrated graphically for the A, B, and C series in Figure 2. The difference in $E_{1/2}$ values for the oxidation and reduction processes for all complexes in the A and B series, except AX_2 ($\Delta = 2.89$ V), is close to 2.42 V, which Fabbrizzi has noted is characteristic of nickel complexes of both saturated and unsaturated neutral tetraaza macrocyclic ligands.[10] Complex D has a difference in $E_{1/2}$ values of 2.56 V. The average change in $E_{1/2}$ for the oxidation and reduction processes per methyl group is 0.14 and 0.1 V, respectively for the AMe_n series and 0.17 and 0.15 V, respectively for the BMe_n series. The change in $E_{1/2}$ for reduction per methyl group in the C series is 0.14 V. A benzyl group has a slightly greater effect on redox potentials than a methyl group (compare ABz and ABz_2 with the corresponding methylated compounds and BMe_3Bz with BMe_4). Complex AX_2 has the most anodic Ni(III)/Ni(II) process observed at +1.50 V, whereas CMe_4 has the most anodic Ni(II)/Ni(I) process at -1.0 V.

Comparison of the redox potentials for the AMe_n and BMe_n series indicates that there is relatively little difference in the *trans*-I and *trans*-III stereochemistries. Both oxidation and reduction potentials for AMe_2 and BMe_2 are nearly the same. The small anodic shifts observed for BMe_3 and BMe_4 complexes compared to their AMe_n counterparts are only about 0.1 V.

Discussion

The synthesis of tetramethylcyclam was originally conceived as a way to obtain a stable Ni(III) complex that could not undergo oxidative dehydrogenation reactions.[29] It had also been expected that the potential for oxidation of the Ni(II) species would be about the same, and possibly less, than that of the cyclam complex. This expectation was based on the fact that tertiary amines are intrinsically more basic than secondary amines[21] and on structural data that suggested Ni-N(3°) distances could be less than either Ni-N(2°) or Ni-N(1°) distances.[30] However, both electrochemical and structural data on complexes of N-alkylated cyclam and related ligands indicate that the interactions of the tertiary nitrogens with the metal are weaker than those of the secondary amine nitrogens. Information concerning the reason for the longer Ni-N(3°) distances can be obtained from the comparison of the structural features of the four- and six-coordinate *trans*-III tetramethylcyclam complexes with those of four- and six-coordinate complexes of macrocyclic secondary amine ligands that is given in the following sections.

Comparison of the Structures of *trans*-$[Ni(C_{14}H_{32}N_4)(OH_2)_2]Cl_2 \cdot 2H_2O$ and $[Ni(C_{14}H_{32}N_4)](O_3SCF_3)_2$. The Ni-N

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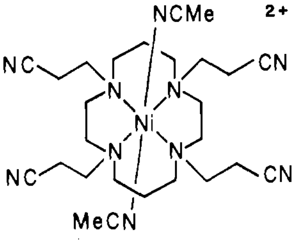
(31) Freeman, G. M.; Barefield, E. K.; Van Derveer, D. G. *Inorg. Chem.* **1984**, *23*, 3092.

(32) Lincoln, S. F.; Coates, J. H.; Hadi, D. A. *Inorg. Chim. Acta* **1984**, *81*, L9.

distance of 1.990 Å in $[Ni(C_{14}H_{32}N_4)]^{2+}$ is 0.15 Å less than the distance observed in the six-coordinate diaqua complex. The C1–C2–C3 angle is 4.8° less than the angle observed in the diaqua complex. It should be noted that the structural parameters for $[Ni(C_{14}H_{32}N_4)(OH_2)_2]^{2+}$ are, within experimental error, the same as the corresponding parameters for $\{[Ni(C_{14}H_{32}N_4)N_3](\mu\text{-}N_3)[Ni(C_{14}H_{32}N_4)N_3]\}^{1+}$,[18] which is the only other *trans*-III complex of tetramethylcyclam that has been structurally characterized. The structural features of *trans*-$[Ni(C_{14}H_{32}N_4)(OH_2)_2]^{2+}$ are also essentially the same as those determined for *trans*-III, six-coordinate complexes of two other tetra-N-alkylated cyclam ligands.[31] The increase in the C1–C2–C3 angle for the six-coordinate complex is consistent with the expansion of the ring that is required to accommodate the larger nickel ion that is present in the high-spin form. This effective increase in size is a result of the σ-antibonding character of the d_{z^2} and $d_{x^2-y^2}$ orbitals, with respect to the nickel–nitrogen interactions, that results from ligation by the two water molecules. The CN1–N1–Ni and CN2–N2–Ni angles are 5.3 and 6.0° larger, respectively, in *trans*-$[Ni(C_{14}H_{32}N_4)(OH_2)_2]^{2+}$ than the corresponding values observed in the four-coordinate complex. The increase in these angles in the six-coordinate complex may be a result of steric interactions between the *N*-methyl groups and the axial water molecules although the possibility that they result as a consequence of the lengthening of the Ni–N distance along cannot be eliminated. Presumably this point could be resolved by molecular mechanics calculations.

Comparison of the Structures of Nickel(II) Complexes of Secondary Amine and Tertiary Amine Macrocyclic Ligands. The most obvious difference in the structures of complexes of macrocyclic secondary and tertiary amine ligands is the longer nickel–nitrogen distances that are present in both four- and six-coordinate complexes of the latter ligands. The Ni–N distance in $[Ni(C_{14}H_{32}N_4)]^{2+}$ (1.990 Å) is 0.04 Å longer than the Ni–N distances in $[Ni(cyclam)]I_2{\cdot}H_2O$[33] and $[Ni_2(dicyclam)](ClO_4)_4$.[34] Nickel–nitrogen atom distances in $[Ni(C_{14}H_{32}N_4)(OH_2)_2]^{2+}$ and in each of the other structurally characterized, six-coordinate complexes of tertiary amine ligands having the *trans*-III stereochemistry[16,31] are 0.08–0.11 Å longer than the Ni–N distance in $[Ni(cyclam)Cl_2]$.[21] In every case the Ni–N–C and C–N–C angles in the tertiary amine complexes are smaller than the corresponding angles in the secondary amine complexes. Both the longer Ni–N bond distances and the smaller Ni–N–C and C–N–C angles in the tertiary amine complexes must be a result of nonbonding repulsive interactions between *N*-methyl groups (a 1,3 interaction) and between the *N*-alkyl groups and methylene groups in the di- and trimethylene chains. Note that the longest Ni–N distances (2.174 Å) occurs in F,[31] which has the largest nitrogen substituents of the structurally characterized complexes with *trans*-III stereochemistry. The greater difference in the Ni–N(3°) and Ni–N(2°) distances for the six-coordinate complexes relative to that in the four-coordinate forms probably reflects the effect of interactions between the *N*-alkyl groups and the axial ligands.



F

Electrochemistry. As described above the introduction of *N*-alkyl substituents results in anodic shifts for both the oxidation and reduction potentials. The effect of N-methylation on oxidation potentials has been previously noted for E and EMe.[14] This anodic shift was attributed primarily to a steric interaction between the *N*-methyl group and one of the axial ligands (acetonitrile) in the six-coordinate Ni(III) product. Our data do not rule this out as a contributing factor but the most important difference must be the longer Ni–N distances for the tertiary amine donor. The weaker Ni–N interaction for the tertiary amine results in stabilization of antibonding σ orbitals in the nickel(II) complex and makes removal of an electron a more unfavorable process. Exactly the same effect is observed for an increase in the macrocycle ring size.[8a,9] A exists as a 78:22 mixture of six- and four-coordinate species in acetonitrile solution[10] whereas AMe_4 is fully six-coordinate.[35] Steric interactions between nitrogen substituents and axial ligands will increase in the trivalent complex as a result of the (anticipated) decrease in the nickel–nitrogen bond distances, but it does not seem likely that such steric interactions can affect the oxidation potential nearly as much as the increase in Ni–N(3°) distances. The absence of an oxidation wave for any of the CMe_n complexes was unexpected. Oxidations would be predicted at about +1.06, +1.2, and +1.4 V for CMe_2, CMe_3, and CMe_4, respectively, on the basis of the 2.4-V difference expected in oxidation and reduction processes; vide supra. This suggests that there may be a severe steric interaction of some type that interferes with coordination of axial ligands in the oxidation product although poor electron-transfer kinetics cannot be eliminated as a possibility.

The anodic shift of the Ni(II)/Ni(I) process that occurs upon N-alkylation is the result expected for an increase in nickel donor distance since reduction involves addition of an electron to a σ-antibonding orbital. An anodic shift of the Ni(II)/Ni(I) process also accompanies an increase in macrocycle ring size.[8a,9]

The slightly greater effect of a *N*-benzyl group compared to a *N*-methyl group on the redox potentials is most likely a result of a slightly longer Ni–N distance resulting from increased nonbonding interactions between the larger benzyl group and methylene groups in the macrocyclic ring. In the case of AX_2, the Ni(II)/Ni(I) process is quite similar to that of AMe_4 (−1.39 vs. −1.32 V) whereas the Ni(III)/Ni(II) process is considerably more anodic (+1.5 vs. +1.22 V). The very large effect on the oxidation process probably results from inhibition of axial ligation and perhaps some resistance to shortening of the Ni–N distances in the trivalent complex. In contrast to other members of the A series of complexes, it was not possible to prepare a bis(cyanide) complex of AX_2.[15b] This suggested that the *o*-phenylene groups might lie over the metal. That something other than a bis(acetonitrile) complex is being formed as the oxidation product must also be considered as a possibility. The large difference in $E_{1/2}$ values for the oxidation and reduction processes compared to that for the other complexes in the A and B series also suggests that the oxidation product may be unique.

The oxidation potential of D is comparable to that for AMe_2 or BMe_2; however, the reduction potential is a bit more negative than that of either of these complexes. This accounts for the fact that the difference in the oxidation and reduction potentials is greater than 2.42 V. The more difficult reduction for D suggests that the 1,4-bridge restricts the expansion of the macrocycle that is required to accommodate the larger nickel(I) ion.

Summary. The data presented indicate that the redox potentials of cyclam-like complexes can be "tuned" over a considerable range by the introduction of nitrogen substituents. The primary reason for the systematic anodic shift for the oxidation and reduction potentials is most likely the increase in the nickel–nitrogen bond distance of the tertiary donor. These complexes constitute a structurally well-defined series of one-electron-oxidizing agents and reducing agents of varying strength.

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Registry No. A, 52610-79-4; AMe, 57379-00-7; AMe_2, 57379-02-9; AMe_3, 57379-06-3; AMe_4, 52610-80-7; ABz, 58802-45-2; ABz_2, 57378-98-0; AX_2, 57378-96-8; BMe_2, 57427-02-8; BMe_3, 57427-04-0; BMe_4,

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48175-68-4; BMe$_3$Bz, 99922-38-0; BMe$_3$Bz(ClO$_4$)$_2$, 99922-39-1; C, 18444-42-3; CMe$_2$, 100017-84-3; CMe$_3$, 99922-40-4; CMe$_4$, 57427-08-4; D, 72984-97-5; *trans*-[Ni(C$_{14}$H$_{32}$N$_4$)(OH$_2$)$_2$]Cl$_2$·2H$_2$O, 100017-83-2; *trans*-[Ni(C$_{14}$H$_{32}$N$_4$)(OH$_2$)$_2$]Cl$_2$, 100017-81-0; [Ni(C$_{14}$H$_{32}$N$_4$)](O$_3$SCF$_3$)$_2$, 59461-42-6; [Ni(C$_{14}$H$_{32}$N$_4$)]I$_2$, 100017-82-1; [Ni(C$_{14}$H$_{32}$N$_4$)](ClO$_4$)$_2$, 41296-56-4; 1-benzyl-4,8,11-trimethyl-1,4,8,11-tetraazacyclotetradecane, 99922-43-7; 1-benzyl-4-methyl-1,4,8,11-tetraazacyclotetradecane, 99922-42-6; 5-benzyl-8-methyl-1,5,8,12-tetraazadodecane, 99922-41-5; *N*-benzyl-*N'*-methylethylenediamine, 56904-09-7; acrylonitrile, 107-13-1; trifluoromethanesulfonate, 37181-39-8.

Supplementary Material Available: Tables of anisotropic thermal parameters for non-hydrogen atoms, positional and isotropic thermal parameters for hydrogen atoms, and structure factors for *trans*-[Ni(C$_{14}$H$_{32}$N$_4$)(OH$_2$)$_2$]Cl$_2$·2H$_2$O and [Ni(C$_{14}$H$_{32}$N$_4$)](O$_3$SCF$_3$)$_2$ (20 pages). Ordering information is given on any current masthead page.

Contribution from the Departments of Chemistry, The University of North Carolina at Chapel Hill,
Chapel Hill, North Carolina 27514, and University of California at Davis, Davis, California 95616

Magnetic Properties and Structural Characterizations of Dichloro(2,5-dithiahexane)copper(II) and Dichloro(4,7-dithiadecane)copper(II): Observation of Heisenberg Alternating-Chain Magnetism

William E. Hatfield,* Leonard W. ter Haar, Marilyn M. Olmstead, and W. Kenneth Musker

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The syntheses, crystal and molecular structure determinations, and magnetic properties of the compounds dichloro(2,5-dithiahexane)copper(II), [Cu(C$_4$H$_{10}$S$_2$)Cl$_2$], and dichloro(4,7-dithiadecane)copper(II), [Cu(C$_8$H$_{14}$S$_2$)Cl$_2$], are reported. [Cu(C$_4$H$_{10}$S$_2$)Cl$_2$] crystallizes in the monoclinic space group $P2_1/n$ with two molecules in a unit cell of dimensions a = 6.875 (2) Å, b = 8.963 (2) Å, c = 14.513 (4) Å, and β = 90.48 (2)° at 293 K. [Cu(C$_8$H$_{14}$S$_2$)Cl$_2$] crystallizes in the monoclinic space group $P2_1/c$ with two molecules in a unit cell of dimensions a = 9.592 (2) Å, b = 17.193 (4) Å, c = 7.813 (2) Å, and β = 101.03 (2)° at 140 K. The structures were solved by direct methods to final R_w = 0.038 based on 1075 independent data with $I > 3\sigma(I)$ for [Cu(C$_4$H$_{10}$S$_2$)Cl$_2$] and R_w = 0.035 based on 1604 independent data with $I > 3\sigma(I)$ for [Cu(C$_8$H$_{14}$S$_2$)Cl$_2$]. The structures of both compounds consist of parallel-planar dimers of [Cu(RSC$_2$H$_4$SR)Cl$_2$] units, which are arranged in alternatingly bridged chains by long copper(II)–sulfur contacts of greater than 5 Å. The centrosymmetric chloro-bridged dimers are formed by axial coordination to a given copper(II) ion by a chloride ligand in the plane of the adjacent copper(II) ion. The axial bond distances are 3.075 (1) Å for [Cu(C$_4$H$_{10}$S$_2$)Cl$_2$] and 2.663 (1) Å for [Cu(C$_8$H$_{14}$S$_2$)Cl$_2$], and the Cu–Cl···Cu' angles are 94.3 (1) and 93.8 (1)°, respectively. Magnetic susceptibility data reveal antiferromagnetic interactions that may be described by Heisenberg alternating-chain theory with exchange coupling constants and alternation parameters (J, α) being −10 cm^{-1}, 0.87 and −20.6 cm^{-1}, 0.35 for [Cu(C$_4$H$_{10}$S$_2$)Cl$_2$] and [Cu(C$_8$H$_{14}$S$_2$)Cl$_2$], respectively.

Introduction

We have previously reported that *catena*-dichloro(3,6-dithiaoctane)copper(II), Cu(4,6-DTO)Cl$_2$, has an alternatingly spaced structure at 140 K and exhibits magnetic properties that may be explained by Heisenberg alternating-chain exchange theory.[1] This was an unexpected result in view of the known structure of bis(μ-chloro)bis[chloro(5,8-dithiadodecane)copper(II)],[2] which has been described as being a bis(μ-chloro)-bridged dimer. With an aim toward increasing the number of alternatingly bridged, alternatingly spaced copper(II) chain compounds, we have prepared and characterized two additional compounds with dithiaalkane bidentate ligands, those being Cu(2,5-DTH)Cl$_2$ (where DTH is 2,5-dithiahexane) and Cu(4,7-DTD)Cl$_2$ (where DTD is 4,7-dithiadecane). The syntheses, crystal and molecular structures, and results of magnetic studies are discussed in this article.

Experimental Section

Syntheses. All materials were reagent grade. The ligand 2,5-dithiahexane was obtained from Aldrich Chemical Co., Milwaukee, WI.

The ligand 4,7-dithiadecane was prepared by adding 38.27 g (0.50 mol) of CH$_3$CH$_2$CH$_2$SH to 1 L of absolute methanol. Freshly cut sodium (12 g, 0.52 mol) was added with stirring. ClCH$_2$CH$_2$Cl (24.74 g, 0.25 mol) was added dropwise to the reaction mixture over 30 min. After the mixture was stirred overnight, the methanol was removed by use of a rotary evaporator. The residue was treated with water and extracted with ether. The combined ether extracts were dried over anhydrous Na$_2$SO$_4$ and reduced in volume by use of a rotary evaporator. Distillation yielded 14.97 g (0.0837 mol, 34% yield) of a clear oil, bp 70–72 °C (0.15 torr). ^{1}H NMR (CDCl$_3$, ppm): 1.28 (t, 3, CCH$_3$), 1.82 (m, 2, CCH$_2$C), 2.52 (m, 4, –CH$_2$SCH$_2$–).

[Cu(2,5-DTH)Cl$_2$]. A solution of 2,5-DTH (0.122 g, 1.00 mmol) in 1.00 mL of anhydrous methanol was added to a solution of CuCl$_2$ (0.134 g, 1.00 mmol) in 10.0 mL of anhydrous methanol. The mixture turned dark olive green immediately, and small dark crystals formed after a few moments. The reaction flask was capped and stored overnight at −5 °C. The product was collected by filtration and air-dried; yield 64.8% (0.166 g) of dark green microcrystals. UV–vis (Nujol mull, nm): 825 (w), 465, 395, 290.

Table I. Crystal Data

	[Cu(2,5-DTH)Cl$_2$]$_2$	[Cu(4,7-DTD)Cl$_2$]$_2$
formula	Cu$_2$Cl$_4$S$_4$C$_8$H$_{20}$	Cu$_2$Cl$_4$S$_4$C$_{16}$H$_{36}$
fw	513.40	625.61
a, Å	6.875 (2)	9.592 (3)
b, Å	8.963 (2)	17.193 (4)
c, Å	14.513 (4)	7.813 (2)
β, deg	90.48 (2)	101.03 (2)
μ(Mo K$\bar{\alpha}$), cm^{-1}	34.5	24.2
Z	2	2
D_{obsd}(298 K), g cm^{-3}	1.89	1.60
D_{calcd}, g cm^{-3}	1.91 (298 K)	1.64 (140 K)

[Cu(4,7-DTD)Cl$_2$]. Dark green needles of this compound were obtained by following a procedure identical with that above; yield 58.6% (0.184 g). UV–vis (Nujol mull, nm): 815 (2), 452, 385, 290, 210 (sh).

Spectra. Visible spectra were recorded on a Varian Instruments Cary 17 spectrophotometer, NMR spectra were recorded on a Varian Instruments EM360 spectrometer, and EPR spectra were recorded on a Varian Instruments E109 spectrometer.

Magnetic Susceptibility Measurements. Magnetic susceptibility data were collected with the use of a Princeton Applied Research Model 155 vibrating-sample magnetometer (VSM) operating at an applied field strength of 10 kOe. Temperatures at the sample were measured with a calibrated GaAs diode by observing the voltage on a Fluke 8502A 6.5 place digital multimeter; further details of the apparatus and measure-

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* To whom correspondence should be addressed at The University of North Carolina.

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