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Article

Solution-State and Solid-State Structural Characterization of Complexes of a New Macrocyclic Ligand Containing the 1,5-Diazacyclooctane Subunit[†]

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The synthesis and characterization of a new constrained tetraazamacrocyclic ligand, 1,4,8,11-tetraazabicyclo[9.3.3]-heptadecane (1,11-C_3-cyclam), is reported. Because of its basicity, this ligand (pK_a of the protonated form >13.5) requires aprotic solvents for its metalation reactions. Two complexes of this ligand, [Ni(1,11-C_3-cyclam](OTf)$_2$ and [Co(1,11-C_3-cyclam)(NCS)$_2$](OTf), have been characterized by single-crystal X-ray crystallography. For the Ni(II) complex, the 1,5-diazacyclooctane (daco) subunit of the ligand is in the chair–boat conformation, whereas that same subunit in the Co(III) complex is in the chair–chair conformation. For the Ni(II) complex, C(12) and H(12a) block one of the coordination sites. The ^{1}H and ^{13}C NMR spectra of the Ni(II) complex in D_2O have very sharp resonances, indicative of low-spin Ni(II). The resonance for H(12a) appears at 4.5 ppm, suggesting an interaction with Ni(II). In acetonitrile, the ^{1}H and ^{13}C spectra are broadened, indicative of a low-spin/high-spin equilibrium due to axial coordination by acetonitrile. C(12) experiences the greatest degree of broadening in the ^{13}C NMR spectrum. Variable-temperature NMR spectroscopy from –70 to +80 °C shows no significant change as a function of temperature. The electronic spectrum of the Ni(II) complex (λ_{max} = 449.9 nm) is consistent with steric and electronic factors for this complex.

Introduction

Ligands containing the 1,5-diazacyclooctane (daco) ring have been of particular interest due to the coordination constraints that they impose on metals. For example, the ligand 1,5-diazacyclooctane-*N*,*N′*-diacetate (dacoda in Figure 1) has been shown to block coordination of axial ligands in some cases.[1,2] In other cases, the daco subunit has been important in constructing some interesting models of hydrogenase enzymes.[3] Most interesting to us was the report by Legg in which the Co(dacoda) complex internally activated a C−H bond from the ligand.[2] We have been interested in the possibility of using such complexes to find other examples of intramolecular C−H bond activation so that the mechanism of this activation can be more easily studied. To this goal, our group has recently developed a program to prepare N_4 macrocyclic ligands with structural similarities to the dacoda ligand. Herein, we present the synthesis of ligands containing the daco subunit and analyze their complexation chemistry. Of particular interest are the structures of metal complexes of 1,11-C_3-cyclam. Solid-state structures with the daco subunit of this ligand in both the chair−chair and chair−boat conformations are presented and

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[†] Abbreviations: OTf = triflate = trifluoromethanesulfonate; cyclam = 1,4,8,11-tetraazacyclotetradecane; dioxocyclam = 1,4,8,11-tetraazacyclotetradecane-5,7-dione; 1,11-C_3-cyclam (1,4,8,11-tetraazabicyclo[9.3.3]heptadecane) has also been called 4,8-C_3-14-aneN_4[9] and CYC-DAC[10] in theoretical studies.

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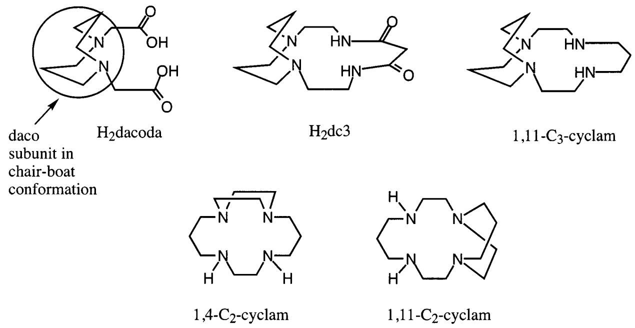

Figure 1. Structurally constrained macrocyclic ligands discussed in this paper.

discussed. Additionally, for the Ni(II) complex of 1,11-C$_3$-cyclam, evidence is presented suggesting an interaction between the Ni(II) center and a C−H bond of the daco subunit.

Experimental Section

Materials and Methods. Dioxocyclam,[4] Ni(CH$_3$CN)$_6$(BF$_4$)$_2$,[5] Ni(OTf)$_2$,[6] and Co(OTf)$_2$[6] were prepared according to the literature procedures. All other materials were purchased and used as received. All reactions were performed on the benchtop under a nitrogen atmosphere unless otherwise noted. Chromatography was performed using EM Science silica gel 60, 230−400 mesh. Electronic spectra were recorded on a Cary 50 UV−vis spectrophotometer. ^{1}H and ^{13}C NMR spectra were recorded on a Varian INOVA 400 spectrometer. Chemical shifts are reported in parts per million. ^{1}H NMR spectra are referenced using the residual protonated solvent peak [δ(CDCl$_3$) 7.27, δ(D$_2$O) 4.80, δ(CD$_3$CN) 1.94]; ^{13}C NMR spectra are referenced using the solvent signal [δ(CDCl$_3$) 77.23, δ(CD$_3$CN) 1.39] or referenced to trimethylsilylpropionate in D$_2$O. Variable-temperature NMR spectroscopy of Ni(1,11-C$_3$-cyclam)$^{2+}$ was performed using the triflate salt in CD$_3$OD from −70 to +20 °C and using the BF$_4^-$ salt in D$_2$O from 20 to 80 °C. Elemental analyses were obtained from Atlantic Microlab, Norcross, GA.

Synthesis of H$_2$dc3. H$_2$dc3 was synthesized by a slight modification of the literature procedure.[7] The solvent volume for the reaction was doubled, and the resulting crude product was dissolved in 2 M NaOH (rather than 1 M NaOH) and then extracted with methylene chloride as stated. After removal of the solvent the crude product was dissolved in CH$_3$CN (1 g of crude product/20 mL of solvent) and filtered to remove a small amount of insoluble impurity. After solvent removal, the product was washed with acetonitrile according to the literature. Yield: 34%.

Synthesis of 1,11-C$_3$-cyclam. To a 100 mL round-bottom flask containing H$_2$dc3 (1.60 g, 6.0 mmol) was added BH$_3$·THF (1M, 40 mL) under Ar. The mixture was refluxed with stirring for 94 h. Dry methanol (9 mL) was added dropwise to the cooled mixture to quench excess borane. After bubbling ceased, HCl (3 M, 15 mL) was added dropwise, and the solution was stirred for another 15 min. The volume of solvent was reduced to about 5 mL by rotary evaporation. Methanol (30 mL) was added, and the solvent was removed again. Repetition of the addition of methanol and evaporation was performed three more times to aid in the removal of the trimethyl borate. After the fourth addition of methanol the solution was evaporated to dryness. The remaining white solid was taken up in HCl (3 M, 38 mL) and extracted with dichloromethane (38 mL). The organic layer was discarded, and aqueous KOH (15M, 30 mL) was added dropwise to the aqueous layer. The product was extracted with dichloromethane (5 × 110 mL) and dried over anhydrous K$_2$CO$_3$. Evaporation of dichloromethane yielded the crude product as a waxy white solid (1.25 g, 87%). Pure product (0.98 g, 68%) was obtained by sublimation at 40 °C (30 mtorr). ^{1}H NMR (CDCl$_3$): δ 2.74 (t, 4H), 2.63 (m, 16H), 1.87 (m, 2H), 1.71 (m, 2H), 1.51 (m, 2H). ^{13}C NMR (CDCl$_3$): δ 57.97 (s), 53.87 (s), 47.95 (s), 46.38 (s), 30.70 (s), 28.73 (s). Anal. Calcd for C$_{13}$H$_{28}$N$_4$: C, 34.01; H, 5.71; N, 14.16. Found: C, 34.09; H, 5.68; N, 14.26.

Synthesis of [Ni(1,11-C$_3$-cyclam)](BF$_4$)$_2$. In a drybox, 1,11-C$_3$-cyclam (102 mg, 0.43 mmol) and DBU (1,8-diazabicyclo[5.4.0]-undec-7-ene; 26 mg, 0.17 mmol) were stirred for 5 min in 6 mL of acetonitrile at room temperature. To this solution was added [Ni(CH$_3$CN)$_6$](BF$_4$)$_2$ (212 mg, 0.46 mmol) with stirring. The solution immediately turned orange-yellow. After being stirred for 2 h, the mixture was removed from the drybox and filtered, and the solvent was removed under reduced pressure. The resulting yellow solid was dried under vacuum, washed with dichloromethane (2 × 10 mL), and dissolved in CH$_3$CN. Diffusion of ether into the solution overnight resulted in an orange crystalline product (150 mg, 74%). ^{1}H NMR (D$_2$O): δ 4.47 (m, 1H), 3.54 (m, 2H), 3.17 (m, 2H), 2.61 (m, 17H), 2.36 (m, 1H), 2.06 (m, 1H), 1.89 (br d, 1H), 1.20 (m, 1H). ^{13}C NMR (D$_2$O): δ 65.13 (s), 60.42 (s), 57.48 (s), 53.26 (s), 51.17 (s), 31.52 (s), 28.61 (s), 26.09 (s). UV−vis in H$_2$O (λ_{max}, nm (ϵ)): 449.9 (98). Anal. Calcd for C$_{13}$H$_{28}$N$_4$B$_2$F$_8$Ni: C, 33.03; H, 5.97; N, 11.85. Found: C, 33.25; H, 5.86; N, 12.00.

Synthesis of [Ni(1,11-C$_3$-cyclam)](OTf)$_2$. 1,11-C$_3$-cyclam (145 mg, 0.60 mmol) and DBU (16 mg, 0.1 mmol) were stirred for 5 min in 5 mL of acetonitrile at room temperature. To this solution was added Ni(OTf)$_2$ (235 mg, 0.66 mmol) with stirring. The yellow solid dissolved slowly, giving a light blue solution which slowly turned orange. A small amount of gray-green precipitate formed during this time. After being stirred for 2 h, the mixture was removed from the drybox, the solvent was removed under reduced pressure, and the resulting oil was dried under vacuum for 30 min. The oil was dissolved in dichloromethane (30 mL), the solution was filtered, and the insoluble solid was discarded. The solvent was removed under reduced pressure, and the resulting oil was dried under vacuum for 1/2 h and washed with toluene (3 × 10 mL). The resulting orange solid was dissolved in 3 mL of dry ethanol, layered first with 0.5 mL of hexane and then with 8 mL of ether. Diffusion overnight resulted in an orange crystalline product (180 mg, 50%). Crystals suitable for X-ray crystallography were grown in an NMR tube by dissolving the solid in methanol and layering with hexanes and ether as above. ^{1}H NMR (D$_2$O): δ 4.48 (m, 1H), 3.54 (m, 2H), 3.17 (m, 2H), 2.61 (m, 17H), 2.36 (m, 1H), 2.06 (m, 1H), 1.89 (br d, 1H), 1.20 (m, 1H). ^{13}C NMR (D$_2$O): δ 65.16 (s), 60.47 (s), 57.51 (s), 53.27 (s), 51.19 (s), 31.59 (s), 28.65 (s), 26.11 (s). UV−vis in H$_2$O (λ_{max}, nm (ϵ)): 449.9 (99). Anal. Calcd for C$_{15}$H$_{28}$N$_4$F$_6$NiO$_6$S$_2$: C, 30.17; H, 4.73; N, 9.38. Found: C, 30.31; H, 4.69; N, 9.41.

Synthesis of [Co(1,11-C$_3$-cyclam)(NCS)$_2$](OTf). In a drybox, 1,11-C$_3$-cyclam (204 mg, 0.86 mmol) and Co(CF$_3$SO$_3$)$_2$ (316 mg, 0.87 mmol) were stirred in acetonitrile (20 mL) for 1 h. To the cloudy orange solution was added NaSCN (140 mg, 1.74 mmol), and the solution changed immediately to green-blue. After the solution was stirred for 30 min, the flask was moved out of the drybox and opened to the air, and the solution was stirred at 60 °C

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Table 1. Crystallographic Data for [Ni(1,11-C_3-cyclam)]$(OTf)_2$ and [Co(1,11-C_3-cyclam)$(NCS)_2$]OTf

empirical formula	$C_{15}H_{28}F_6N_4O_6S_2Ni$	$C_{16}H_{28}F_3N_6O_3S_3Co$
fw	597.24	564.55
cryst syst	monoclinic	monoclinic
space group	$P2_1/c$	$P2_1/n$
a (Å)	11.060(2)	13.230(3)
b (Å)	13.818(2)	11.446(2)
c (Å)	15.638(4)	16.238(2)
β (deg)	94.48(2)	109.17(1)
V (Å^3)	2369.5(8)	2322.6(7)
Z	4	4
D_{calcd} (g/cm^3)	1.674	1.615
T (°C)	25	25
μ (mm^{-1})	1.081	1.064
R1[a] (F_o) ($I > 2\sigma(I)$)	0.0669	0.0624
wR2[b] (F_o^2) ($I > 2\sigma(I)$)	0.1817	0.1690

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum[w(F_o^2 - F_c^2)^2]/\sum[w(F_o^2)^2]]^{1/2}$, where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$. $P = (F_o^2 + 2F_c^2)/3$. For the Ni(II) complex, $a = 0.1075$ and $b = 3.8661$; for the Co(III) complex, $a = 0.1231$ and $b = 6.0776$.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for [Ni(1,11-C_3-cyclam)]$(OTf)_2$ and [Co(1,11-C_3-cyclam)$(NCS)_2$](OTf)

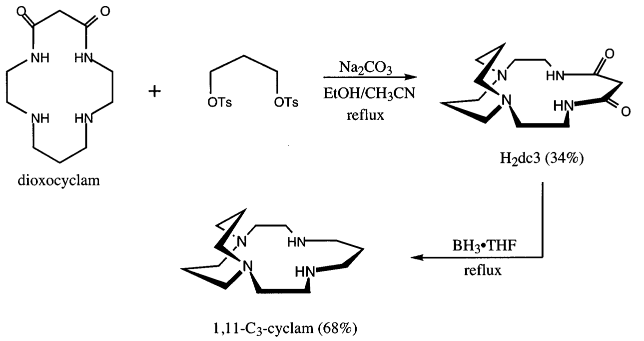
	[Ni(1,11-C_3-cyclam)]$(OTf)_2$	[Co(1,11-C_3-cyclam)$(NCS)_2$](OTf)
	Distances	
M−N(1)	1.923(6)	1.971(5)
M−N(2)	1.945(6)	1.989(6)
M−N(3)	1.918(6)	1.996(6)
M−N(4)	1.911(6)	1.978(6)
M−N(5)		1.877(6)
M−N(6)		1.893(6)
M−C(12)	2.756(7)	
M−H(12a)	2.517(7)	
deviation of metal out of N_4 plane	0.033(3)	none
	Angles	
N(1)−M−N(2)	86.9(3)	88.5(2)
N(2)−M−N(3)	89.4(3)	87.0(2)
N(3)−M−N(4)	88.1(3)	88.3(2)
N(4)−M−N(1)	95.6(4)	96.1(2)
N(5)−M−N(6)		172.6(2)

in a water bath for 2 h, during which it turned red-violet. The solution was filtered and evaporated to dryness. The solid was purified on silica gel (1.5 cm × 20 cm) using 5% methanol in CH_2Cl_2. The second component (purple) was collected and evaporated to dryness, yielding a red-violet solid (260 mg, 53%). Crystals suitable for X-ray crystallography were grown by diffusion of ether into an acetonitrile solution. ^1H NMR (CD_3CN): δ 5.55 (br s, 2H), 3.36 (m, 2H), 2.91 (m, 10H), 2.68 (m, 8H), 2.44 (m, 2H), 2.17 (m, 1H), 2.01 (m, 2H), 1.63 (m, 1H). ^{13}C NMR (CD_3CN): δ 65.21 (s), 62.03 (s), 57.41 (s), 53.33 (s), 49.53 (s), 28.63 (s), 26.18 (s), 25.12 (s). UV−vis in CH_3CN (λ_{max}, nm (ϵ)): 245.9 (1.68 × 10^4), 313.2 sh (3.47 × 10^3), 539.0 (351). Anal. Calcd for $C_{16}H_{28}N_6CoF_3O_3S$: C, 34.04: H, 5.00; N, 14.89. Found: C, 34.32; H, 5.08; N, 14.98.

pH Measurements of Solutions of the Ligands. pH measurements of solutions of the free ligands were performed using an Orion model 710A pH meter calibrated using pH 10 and pH 12 buffers. Aqueous solutions of 1,11-C_3-cyclam (0.034 M) gave pH measurements of 12.50 ± 0.03, and solutions of H_2dc3 (0.018 M due to poor solubility) gave pH measurements of 11.97 ± 0.03. Approximate pK_a values are determined from this limited data.

X-ray Crystallography. X-ray data were acquired at ambient temperature using a Siemens/Bruker AXS P4 four-circle diffractometer with graphite-monochromated Mo Kα radiation (λ = 0.71073 Å) and were corrected for absorption using ψ scans. The structures were solved by the Patterson heavy atom method[8] and Fourier difference maps.[8] Refinements were performed by full-matrix least-squares on F^2.[8] One of the trifate anions in [Ni(1,11-C_3-cyclam)]$(OTf)_2$ was highly disordered, so its bond lengths and angles were restrained to match those of the normal triflate and its atoms were refined isotropically. The disorder was modeled with four orientations with site occupancies of 0.34, 0.30, 0.19, and 0.17. All other non-hydrogen atoms in both molecules were refined anisotropically. Hydrogen atoms were added in ideal positions (C−H, 0.97 Å; N−H, 0.91 Å; $U_H = 1.2U_{attached\ C\ or\ N}$) and were not refined. Crystallographic data are summarized in Tables 1 and 2, and thermal ellipsoid plots at the 30% probability level (for clarity) are shown in Figures 3 and 4. Additional details are available as Supporting Information.

Scheme 1. Synthesis of 1,11-C_3-cyclam



Results and Discussion

Synthesis of the Ligands. The yield of H_2dc3 has been significantly increased compared to that given in the literature[7] (from 21% to 34%) by a slight modification of the purification as described in the Experimental Section. The next goal was to prepare 1,11-C_3-cyclam as it has been mentioned in several papers by Hancock[9,10] and has been the subject of theoretical studies[10] but to our knowledge has not previously been synthesized. It can be obtained in high yield using a borane reduction of H_2dc3 (Scheme 1).

Like the related 1,4-C_2-cyclam first prepared by Wainwright,[11] the product can be purified by sublimation, and is hygroscopic. The ^{13}C NMR spectrum of 1,11-C_3-cyclam shows six resonances in a 4:2:2:2:2:1 ratio in two groupings. The carbons α to the amine nitrogens appear in the 46−58 ppm region and those β to the amine nitrogens in the 28−31 ppm region, consistent with those seen for other cyclic and bicyclic amines. Like the ^1H NMR of the related 1,4-C_2-cyclam, the proton NMR shows a complex splitting pattern due to the inequivalence of geminal hydrogens in the daco subunit.

Metalation of 1,11-C_3-cyclam. Initial attempts to insert metals into 1,11-C_3-cyclam involved aqueous environments analogous to typical metalations for cyclam. In these attempts the main product was the diprotonated ligand as determined by elemental analysis and ^1H NMR spectroscopy. The use of dehydrated metal salts in methanol also resulted in protonated ligand and suggested the need for aprotic solvents such as acetonitrile. Dry acetonitrile proved to be a good solvent for the reaction, and high yields of the Ni(II) complex were obtained but were typically contaminated with ap-

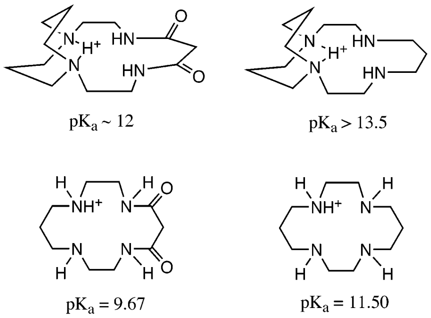


Figure 2. pK_a values for constrained ligands and their unconstrained analogues.

proximately 5% of the diprotonated ligand, which was difficult to separate from the product. Presumably the diprotonated material came from trace amounts of water left in the solvent, glassware, and hygroscopic ligand. Performing the synthesis in the presence of a small amount of DBU resulted in product with no diprotonated impurity. The use of DBU in the cobalt insertion was unnecessary, presumably because any diprotonated ligand that might form was easily separated by chromatography.

Basicity of the Ligands. These synthetic observations suggest that 1,11-C_3-cyclam is significantly more basic than unconstrained cyclic tetraamine ligands such as cyclam. The measured pH of 1,11-C_3-cyclam solutions suggests that the equilibrium in eq 1

$$H_2O + L \rightleftharpoons HL^+ + OH^- \tag{1}$$

is shifted almost completely to the right and indicates a pK_a > 13.5. The pH of solutions of the related H_2dc3 indicates an approximate pK_a value of 12. Compared to the literature values[12] for the parent cyclam and dioxocyclam macrocycles, both constrained macrocyclic ligands experience an increase in pK_a of >2.0 (Figure 2).

The exceptional basicity of these constrained macrocycles is not surprising given that a similar polyazamacrocycle with a daco-type subunit has been prepared by Bell et al. and was found to have a pK_a > 13.5.[13] The basicity is likely due to the constrained nature of the two tertiary nitrogens in the daco subunit which would be arranged with both nitrogen lone pairs capable of interacting with one proton. In contrast, the two tertiary nitrogens in 1,4-C_2-cyclam do not have the same geometry because the six-membered ring keeps the two nitrogen lone pairs from pointing in the same direction. This would suggest a lower basicity for 1,4-C_2-cyclam, and is in accordance with empirical evidence; whereas 1,11-C_3-cyclam cannot be metalated in protic solvents, 1,4-C_2-cyclam can be metalated in ethanol with no complication from ligand protonation.[11]

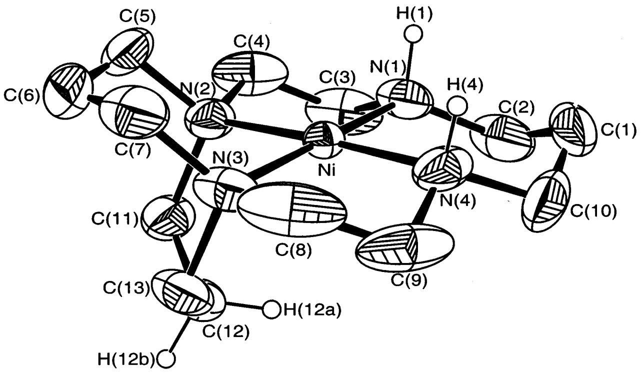


Figure 3. Thermal ellipsoid plot at the 30% (for clarity) probability level for the cation of [Ni(1,11-C_3-cyclam)](OTf)$_2$. Key hydrogen atoms are shown at ideal positions.

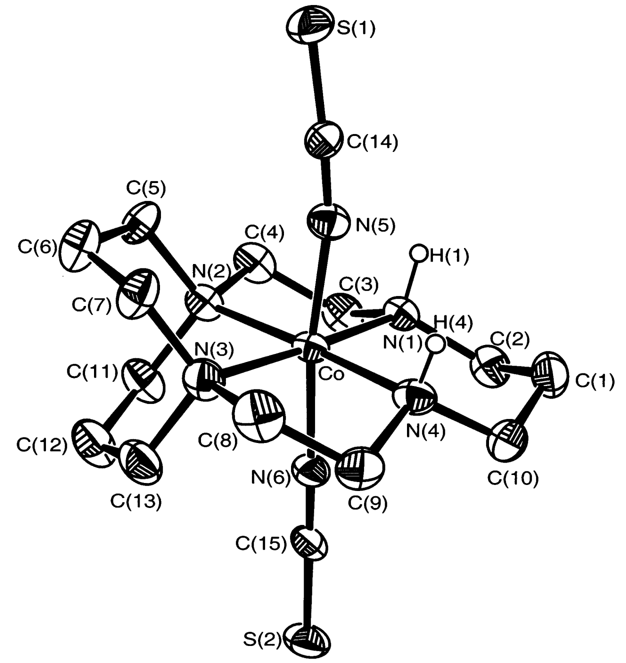


Figure 4. Thermal ellipsoid plot at the 30% (for clarity) probability level for the cation of [Co(1,11-C_3-cyclam)(NCS)$_2$](OTf). Key hydrogen atoms are shown at ideal positions.

Solid-State Structure of the Metal Complexes. For purposes of comparison, the structures of both [Ni(1,11-C_3-cyclam)](OTf)$_2$ and [Co(1,11-C_3-cyclam)(NCS)$_2$](OTf) are reported herein. The most striking difference between these two structures apart from the expected four-coordination of Ni(II) versus the six-coordination for Co(III) is the conformational difference of the 1,11-C_3-cyclam ligand (Figure 5). The conformation of the daco subunit for the Co(III) complex is the chair−chair conformation, whereas that for the Ni(II) complex is chair−boat. The energetic differences between these two conformations and the conditions that favor one conformation over the other have been significantly discussed by Darensbourg's group for tetradentate N_2S_2 ligands containing the daco subunit.[14,15] Though early papers sug-

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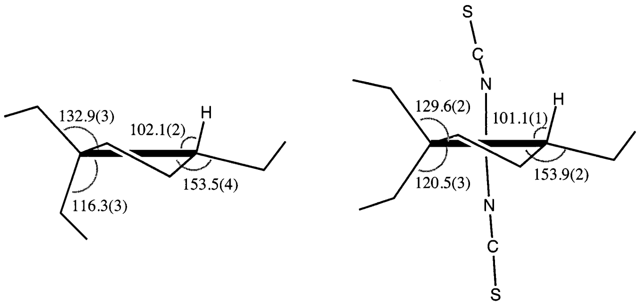

[Ni(1,11-C_3-cyclam)]$^{2+}$ [Co(1,11-C_3-cyclam)(NCS)$_2$]$^+$

Figure 5. Side view of complexes showing dihedral angles between the N_4 plane (bold line) and selected molecular planes.

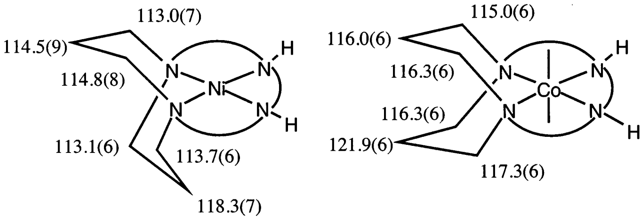

Figure 6. Comparison of the angles about carbon in the daco subunit for [Ni(1,11-C_3-cyclam)](OTf)$_2$ and [Co(1,11-C_3-cyclam)(NCS)$_2$](OTf).

gested that the chair−boat conformation would be the more stable one and would block six-coordination,[1,16] recent calculations suggested that there is little energy difference between them and that chair−chair is perhaps favored.[14,15] Certainly in the presence of good axial ligands there is no reason to expect that the chair−boat conformation would be maintained, but rather that the chair−chair conformation would be adopted so that six-coordination is allowed. Such is the case for this pair of complexes. The strong tendency toward six-coordination for Co(III) has resulted in a chair−chair conformation, whereas square-planar Ni(II) has adopted the chair−boat conformation. Though few examples of the exclusively chair−chair conformation for daco-containing tetradentate ligands are structurally characterized[14,15,17,18] they appear almost always to accompany six-coordinate complexes. Additionally, to our knowledge, this is only the second example[18] of such a ligand structurally characterized in both the chair−chair and the chair−boat conformations, providing the opportunity to further analyze factors controlling the conformation.

What factors favor the chair−boat conformation in the Ni(1,11-C_3-cyclam)$^{2+}$ complex? Darensbourg's group has mentioned that there is angular strain evident in the β-CH_2 groups of the daco bridge for a complex in the chair−chair conformation.[14] This becomes very clear when a comparison is made of the bond angles about the carbon atoms in the daco subunit for the structures reported herein (Figure 6). Note that every bond in the Co(III) complex is distorted further away from the ideal tetrahedral angle of 109.5° than the corresponding angle in the Ni(II) complex. On average, this distortion is 2.5°, providing evidence that, in the absence of axial ligation, the chair−boat conformation may be more stable due to a lack of steric repulsion between the β-CH_2 groups.

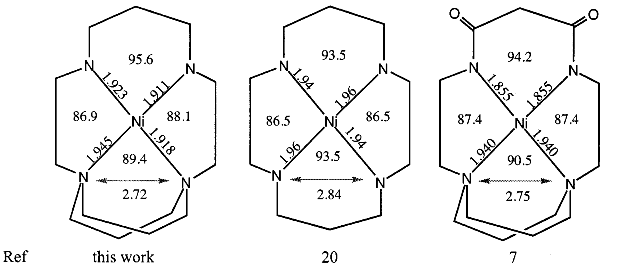

Figure 7. Comparison of the coordination spheres of Ni(1,11-C_3-cyclam)$^{2+}$, Ni(cyclam)$^{2+}$, and Ni(dc3). All bond lengths are given in angstroms.

Another effect of the conformational difference is that the chair−boat conformation of the Ni(II) complex displays a significantly larger tilt of the daco subunit with respect to the N_4 plane than the Co(III) complex (Figure 5). This places a C−H bond of the proximal β-CH_2 group close to the Ni(II) [Ni−H(12a) = 2.52 Å, Ni−C(12) = 2.76 Å], which is also evident from the NMR spectra (vide infra). Similar Ni−C and Ni−H distances have been observed before.[1,17] Interestingly, the slight out of plane distortion of the Ni(II) center (0.03 Å) is away from C(12).

A final structural aspect worthy of consideration is the degree of distortion about the metal imposed by the constrained ligand. Comparisons can be made between the 1,11-C_3-cyclam complexes and the corresponding cyclam complexes in the trans III[19] configuration (Figure 7). Trans III was chosen due to its stereochemical similarity to the 1,11-C_3-cyclam complexes. Comparison is also made with Ni(dc3).

The most notable feature is the angular distortion between the 1,11-C_3-cyclam complex and the cyclam complex. For the cyclam complex, the coordination environment is more symmetric; i.e., the angles subtended by Ni and the nitrogens connected by the three-carbon linkages are identical (93.5°). For the 1,11-C_3-cyclam complex, on the other hand, the angle spanned by the nitrogens in the daco subunit is compressed to 89.4° (with an accompanying compression of the corresponding N····N distance), opening up the other N−Ni−N angles relative to those of the cyclam structure. Note that the angles for the 1,11-C_3-cyclam complex are very similar to that for the dc3 complex, indicating that this angular distortion is largely imposed by the ligand architecture, rather than electronic considerations. A similar comparison can be made between [Co(1,11-C_3-cyclam)(NCS)$_2$]$^+$ and [Co(cyclam)(NCS)$_2$]$^+$. The structure of [Co(cyclam)(NCS)$_2$]$^+$ demonstrates (amine-N)−Co−(amine-N) bond angles of 93.7° and 86.3° for the angles spanned by the three-carbon linkages and the two-carbon linkages, respectively.[21] The additional three-carbon strap in [Co(1,11-C_3-cyclam)(NCS)$_2$]$^+$ compresses the bond angle spanned by the nitrogens in the daco

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subunit to below 90° (Table 2). This lends further evidence that this pattern of bond angles is due to the ligand architecture.

Prior Calculations on Ni(II) Complexes of Tetraamine Ligands. To place these results in context and compare the Ni(II) complex of 1,11-C_3-cyclam with those of the ligands cyclam and 1,4-C_2-cyclam, it is important to know that the strain-free Ni−N bond length for low-spin Ni(II) in polyamine ligands is 1.91 Å[9] and that the same value for high-spin Ni(II) is 2.10 Å.[22] In addition, Hancock et al. have calculated hole sizes in the form of best fit metal−nitrogen bond distances for cyclam and 1,11-C_3-cyclam and found them to be 2.07 and 2.05 Å, respectively.[10] These are the average M−N bond distances that would minimize ligand strain. Moreover, the sharpness of size selectivity has been calculated for these two ligands, and it is found that cyclam has a greater tolerance toward variation of metal size.[10] Thus, the additional bridge has a small effect on hole size but also an effect on selectivity. Unfortunately, the same calculations for 1,4-C_2-cyclam have not been performed, but the piperazine ring in 1,4-C_2-cyclam would appear to impart more structural rigidity than the daco ring in 1,11-C_3-cyclam. Also, calculations on another pair of tetraamine ligands, with one containing the daco subunit and another containing the piperazine subunit, demonstrate that the one with the piperazine subunit displays a sharper size selectivity,[10] in agreement with expectations. Several authors have discussed that ligand size selectivity may be a major factor affecting the high-spin/low-spin equilibrium for Ni(II) complexes.[23−26] Thus, for this set of ligands, one would predict cyclam to be the most likely ligand to allow high-spin Ni(II) and for 1,4-C_2-cyclam to be the least likely, with 1,11-C_3-cyclam falling in between.

NMR Spectroscopy of the Ni(II) Complex. Because NMR spectroscopy is sensitive to the presence of paramagnetic species, it is here worth comparing NMR spectra of the Ni(II) complexes of cyclam, 1,11-C_3-cyclam, and 1,4-C_2-cyclam in both D_2O and CD_3CN. According to Vigee et al.,[27] the thermodynamic binding strength of acetonitrile is greater than that for water with Ni(cyclam)$^{2+}$. Solvent binding to Ni(II) would be accompanied by a conversion to the larger high-spin electronic configuration. Interestingly, the cyclam complex shows paramagnetism in the weakest donor solvent, water,[26] the 1,11-C_3-cyclam complex shows no evidence of paramagnetism in D_2O (Figure 8), but paramagnetic broadening in CD_3CN (Supporting Information), and the 1,4-C_2-cyclam complex prepared by Wainwright[11] shows no broadening in either D_2O[23] or acetonitrile.[28] Wainwright has ascribed the lack of axial ligand binding in that complex to the inability of 1,4-C_2-cyclam to accommodate the larger high-spin Ni(II).[11] This empirical evidence is in agreement with the predicted ability (vide supra) of these ligands to accommodate the larger high-spin Ni(II).

The ^{1}H and ^{13}C resonances of the spectra of diamagnetic [Ni(1,11-C_3-cyclam)]$(BF_4)_2$ in D_2O were assigned using COSY, HETCOR, and similarities with the corresponding cyclam complex assigned by Billo et al.[23] Noteworthy concerning the ^{1}H NMR is the position of the proton resonance we have assigned to H(12a), located at 4.5 ppm, significantly downfield from what would be expected for the central methylene hydrogens of a three-carbon linkage in cyclam-type complexes. This shift is likely due to the electron-withdrawing effect of Ni(II) and was used to corroborate the assignment of this proton.[29] The ^{13}C NMR spectrum in CD_3CN looks very similar to that in D_2O, with the exception of the aforementioned broadening. Notably, the C12 peak has broadened to the point of being barely observable over the noise. Because there are three carbon resonances in that region of the spectrum assigned to carbons β to the amine nitrogens, it is most likely that the broadened resonance is due to the carbon closest to the paramagnetic Ni(II). This supports the assignment of that resonance to C12.

This evidence suggests that C12 and H12 are in close proximity to Ni(II) and is indicative that the solid-state structure is retained in solution. We were curious as to whether the position of this resonance was due to C12 undergoing rapid conversion between the chair and boat conformations, with the position of the resonance being due to an average of the two positions, or whether it was static. Variable-temperature NMR spectroscopy showed no significant changes between −70 and +80 °C. Though we cannot rule out rapid inversion of boat to chair with a low barrier,[34] we believe that these results suggest a static structure in solution similar to the solid-state structure and as evidenced by the spectra that there is a notable interaction between Ni(II) and the C(12)−H(12a) bond.

Electronic Structure of Ni(II) Complexes. Complexes of constrained macrocycles have been of particular interest with respect to the effects of the constraint on electronic spectra.[9−11,30−32] Shown in Figure 9 are the structures of several Ni(II) complexes of structurally constrained cyclam

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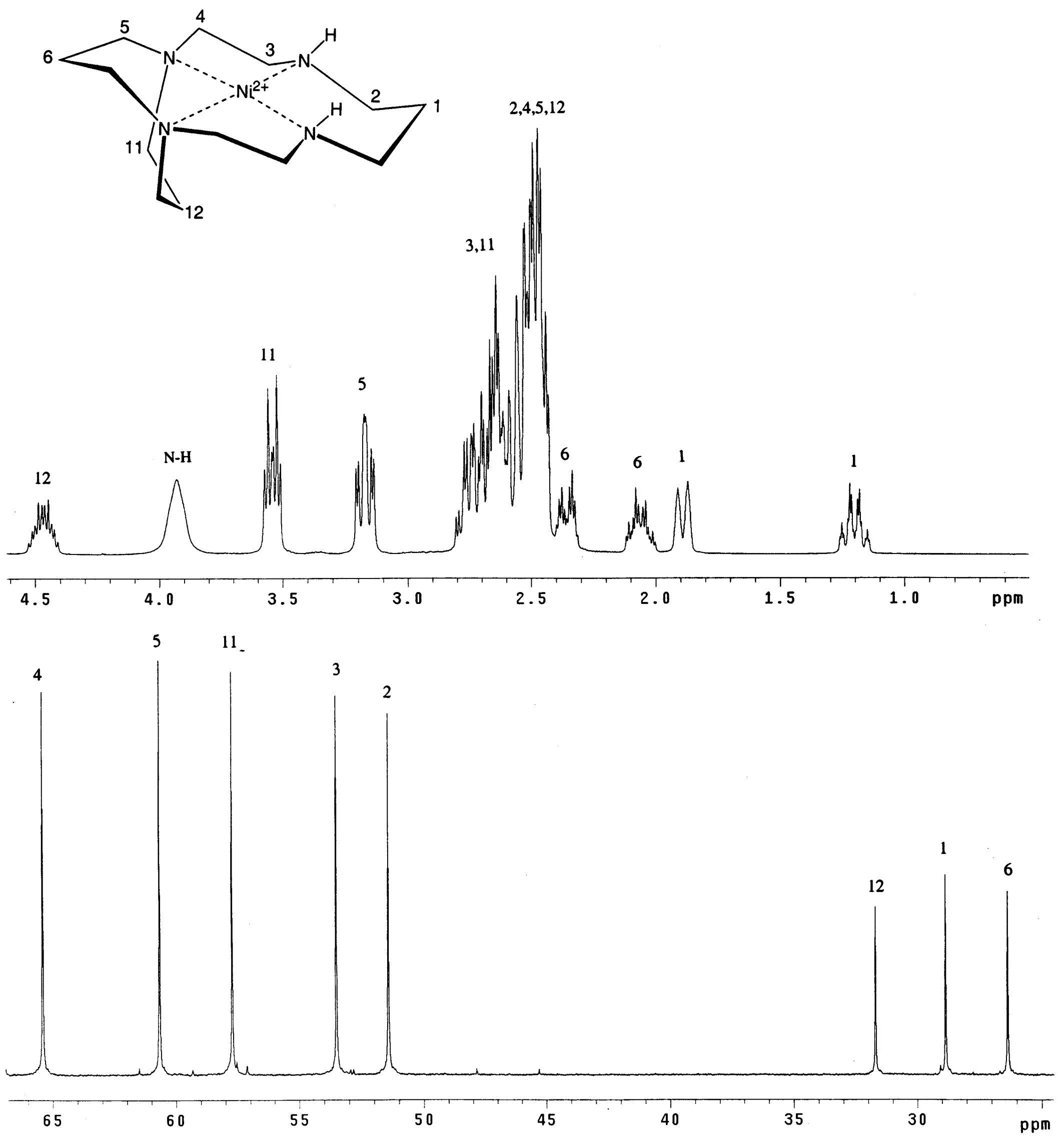
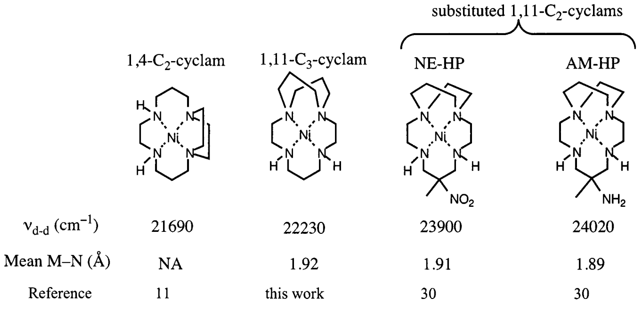


Figure 8. ^{1}H (top) and ^{13}C (bottom) NMR spectra for $[Ni(1,11\text{-}C_3\text{-cyclam})](BF_4)_2$ in D_2O.



	1,4-C_2-cyclam	1,11-C_3-cyclam	NE-HP	AM-HP
$\nu_{d\text{-}d}$ (cm^{-1})	21690	22230	23900	24020
Mean M–N (Å)	NA	1.92	1.91	1.89
Reference	11	this work	30	30

Figure 9. Comparison of structural and electronic properties of Ni(II) complexes of constrained cyclam ligands.

ligands along with the energy of their d−d transitions and average experimental Ni−N bond lengths for each complex. Hancock has published several papers discussing factors that affect the transition energy of tetraamine−Ni(II) complexes, namely, (1) the donor strengths of the nitrogens, i.e., tertiary > secondary > primary, and (2) steric effects.[10,30,31] Steric effects include those factors which affect the degree of overlap in the Ni−N bond such as a deformation in the bond length away from the strain-free Ni−N bond length of 1.91 Å for low-spin Ni(II) and distortions in bond angles. Note that all of the ligands in the diagram above have the same total donor strengths in that they each have two tertiary and two secondary amines. Thus, the significant differences in transition energies (21690−24020 cm^{-1}) for this series must have to do with steric constraints.

Note that the energy of the transition for the 1,11-C_3-cyclam complex is greater than that of the 1,4-C_2-cyclam complex. This can be explained by the earlier inference that the piperazine ring in 1,4-C_2-cyclam imparts more structural rigidity than the daco ring in 1,11-C_3-cyclam and thus may not allow the ligand to maximize its overlap with Ni(II). Additionally, the six-membered piperazine ring has poorer coordinating abilities than either the seven-membered homopiperizine or eight-membered daco ring due to a best fit M−N bond length for piperazine of 3.8 Å vs 2.1 Å for homopiperazine and daco.[10,31]

Explanation of why the 1,11-C_3-cyclam complex has a lower transition energy than the complexes of either of the substituted 1,11-C_2-cyclams can be based on MM calculations of the best fit length of the M−N bond required to coordinate the metal with minimum strain energy to the ligand. Hancock has calculated the best fit value of AM-HP to be 1.90 Å, whereas he has calculated a value for 1,11-C_3-cyclam of 2.05 Å.[10,33] Thus, there is little strain in the AM-HP complex relative to the 1,11-C_3-cyclam complex.

Conclusions

A new class of ligands based on the cyclam and dioxocyclam frameworks but with a 1,5-diazacyclooctane group has been prepared and characterized. These ligands are strongly basic, and thus metalations must be carried out in aprotic solvents. The electronic spectroscopy of Ni(1,11-C_3-cyclam)$^{2+}$ is consistent with the interplay between the donor strength of the ligand and its steric properties as has been discussed by Hancock. Complexes of the 1,11-C_3-cyclam ligand have been characterized in both the chair−chair and chair−boat conformations, and the structures demonstrate less steric strain in the chair−boat conformation, bolstering early claims that this conformation might be favored for steric reasons.[1,16] Most noteworthy here is the solution-state characterization of Ni(1,11-C_3-cyclam)$^{2+}$ by NMR spectroscopy, which indicates that the chair−boat structure is maintained in solution and that there is a noticeable interaction of the Ni(II) center with C12 and H12a. We plan to exploit this interaction using metals with empty d_{z^2} orbitals to possibly achieve new examples of intramolecular C−H bond activation.

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Supporting Information Available: 2D NMR spectra (COSY, HETCOR) for [Ni(1,11-C_3-cyclam)]$(BF_4)_2$ in D_2O, ^1H and ^{13}C NMR spectra of [Ni(1,11-C_3-cyclam)]$(BF_4)_2$ in CD_3CN, and X-ray crystallographic files in CIF format for the structure determinations of [Ni(1,11-C_3-cyclam)](OTf)$_2$ and [Co(1,11-C_3-cyclam)(NCS)$_2$]-(OTf). This material is available free of charge via the Internet at http://pubs.acs.org.

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(33) In ref 10, the author has renamed AM-HP[30] as HSAR-HP.

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