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Chemistry of Constrained Dioxocyclam Ligands with Co(III): Unusual Examples of C–H and C–N Bond Cleavage[†]

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The reactions between H_2dc3 and Co(acac)$_3$ have been studied in the presence and absence of base. In the presence of base, a complex with an intramolecular Co–C bond, Co(dc3-*C*-(8))(H_2O), **1**, is formed, presumably through heterolytic C–H bond activation. An X-ray crystallographic study demonstrates the presence of a Co–C bond and shows that the diazacyclooctane (daco) subunit adopts the chair–boat conformation with respect to the metal. The cobalt–carbon bond induces strain in the macrocycle as demonstrated by bond angles significantly deviating from tetrahedral. The ^{13}C NMR resonance of the carbon atom bound to cobalt (–10.5 ppm) suggests significant ionic character in the cobalt–carbon bond. However, we were unable to cleave this bond in the presence of strong acid. In the absence of base, the reaction of Co(acac)$_3$ with H_2dc3 resulted in C–N cleavage of the ligand and the formation of a complex of dioxocyclam, Co(dc)(acac), **2**. This complex has subsequently been prepared in high yield by the reaction of Co(acac)$_3$ with dioxocyclam. An X-ray crystallographic study demonstrates that dioxocyclam adopts the heretofore unreported *cis* configuration, having folded along a N–Co–N axis that is perpendicular to the Co-acac plane.

Introduction

Ligands containing the 1,5-diazacyclooctane (daco) ring have attracted interest due to the coordination constraints that they impose on metals and the potential ability of the daco subunit in the chair−boat conformation (Figure 1) to block coordination of axial ligands.[1] In one such case, a dacoda complex of Co(III) internally activated a C−H bond of the ligand toward deprotonation resulting in Co(dacoda-*C*-(2))(H_2O).[2] Recent efforts in our laboratories have been directed toward searching for examples of intramolecular C−H bond activation with other ligands containing the daco subunit. We have considered that the constraint in such

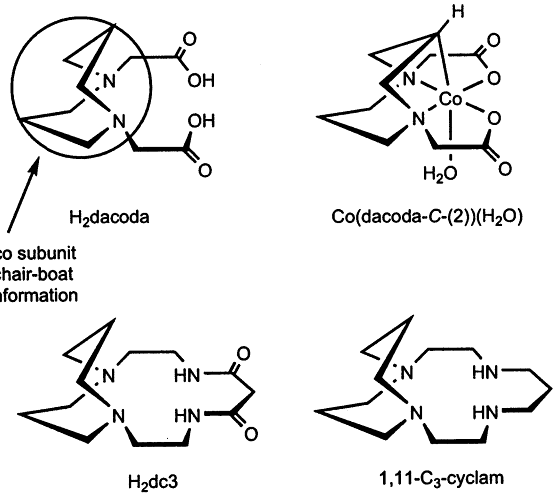

Figure 1. Ligands and complexes containing the daco subunit.

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[†] Abbreviations used in this paper: H_2dc = 1,4,8,11-tetraazacyclotetradecane-5,7-dione (dioxocyclam); H_2dc3 = 1,4,8,11-tetraazabicyclo[9.3.3]-heptadecane-5,7-dione; 1,11-C_3-cyclam = 1,4,8,11-tetraazabicyclo[9.3.3]-heptadecane.

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(1) (a) Musker, W. K.; Hussain, M. S. *Inorg. Chem.* **1966**, *5*, 1416−1419. (b) Legg, J. I.; Nielson, D. O.; Smith, D. L.; Larson, M. L. *J. Am. Chem. Soc.* **1968**, *90*, 5030−5031. (c) Nielson, D. O.; Larsen, M. L.; Willett, R. D.; Legg, J. I. *J. Am. Chem. Soc.* **1971**, *93*, 5079−5082. (d) Averill, D. F.; Legg, J. I.; Smith, D. L. *Inorg. Chem.* **1972**, *11*, 2344−2349. (e) Darensbourg, M. Y.; Font, I.; Mills, D. K.; DaPala, M.; Reibenspies, J. H. *Inorg. Chem.* **1992**, *31*, 4965−4971. (f) Goodman, D. C.; Tuntulani, T.; Farmer, P. J.; Darensbourg, M. Y.; Reibenspies, J. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 116−119.

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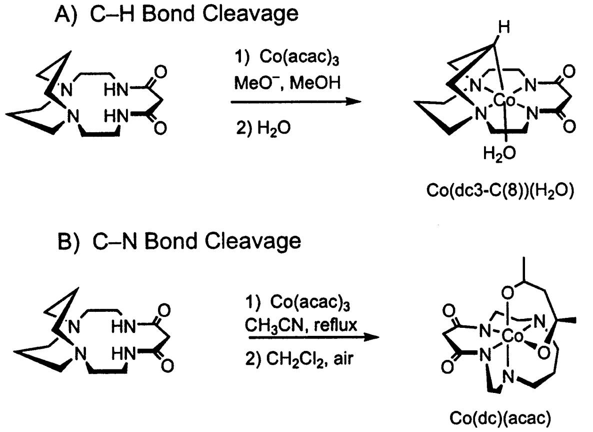
Scheme 1. C−H and C−N Bond Cleavage of H_2dc3 in the Presence of $Co(acac)_3$



systems may be conducive to observation of the intermediates in C−H bond activation so that the mechanism of such activation can be studied.

Recently, we reported the Ni(II) complexes of two new N_4 macrocyclic ligands containing the daco subunit, H_2dc3,[3] and 1,11-C_3-cyclam.[4] The daco subunit in $[Ni(1,11\text{-}C_3\text{-cyclam})]^{2+}$ adopts the chair−boat conformation in which a β-methylene C−H group blocks an axial coordination site.[4] In the structure of Ni(dc3), the daco subunit is disordered; i.e., the conformation of each of the six-membered chelate rings is found in both the chair and boat conformation.[3] The shortest Ni−H distances in these two complexes are 2.52 and 2.58 Å, respectively. For the case of $[Ni(1,11\text{-}C_3\text{-cyclam})]^{2+}$, NMR studies demonstrated an interaction between Ni(II) and the C−H bond that blocks the axial coordination site. However, the occurrence of a bonding interaction between the metal and the C−H bond requires a suitably oriented *empty* metal orbital.[5,6] Because the d_{z^2} orbital of Ni(II) is filled in this case, such an interaction is unlikely. Low spin Co(III), on the other hand, has an empty d_{z^2} orbital, and we reasoned that it would be possible to observe C−H bond activation in the chair−boat conformation of Co(III) complexes of these ligands in the same way as has been observed by Legg with the dacoda complex.[2]

In the presence of base, the reaction of H_2dc3 with $Co(acac)_3$ resulted in the formation of Co(dc3-*C*-(8))(H_2O), **1**, where dc3-*C*-(8) refers to dc3 coordinated in a quinquedentate fashion with the C(8) carbon of the daco portion directly bonded to the cobalt center (Scheme 1A). In attempts to obtain an intermediate complex with an agostic Co−(C−H) interaction, H_2dc3 was treated with $Co(acac)_3$ in the absence of base. An unexpected C−N cleavage of the ligand occurred, and the dioxocyclam complex *cis*-Co(dc)(acac), **2**, was obtained, with the dioxocyclam ligand in the heretofore unreported *cis* configuration (Scheme 1B). Herein, we report these C−H and C−N bond cleavages and the structures of the resulting complexes.

Experimental Section

Materials and Methods. H_2dc3 was prepared according to the literature procedure.[4] All other materials were purchased and used as received. All reactions were performed on the benchtop under a nitrogen atmosphere unless otherwise noted. ^1H and ^{13}C NMR spectra were recorded on a Varian INOVA 400 spectrometer. Chemical shifts are reported in ppm. ^1H NMR spectra are referenced using the residual protonated solvent peak [$\delta(CD_3OD)$ 3.30, $\delta(D_2O)$ 4.80]; ^{13}C NMR spectra are referenced using the solvent signal [δ-(CD_3OD) 49.15] or DSS external reference in D_2O. Elemental analyses were obtained from Atlantic Microlab, Norcross, GA.

Synthesis of [Co(dc3-*C*-(8))(H_2O)]·4H_2O (1). In a drybox, KH (124 mg, 3.1 mmol) and H_2dc3 (243 mg, 0.91 mmol) were added to 5 mL of dry methanol. After the solution was stirred for 10 min, $Co(acac)_3$ (366 mg, 1.03 mmol) was added. The resulting solution was moved out of the drybox and stirred for 30 h at room temperature during which the color changed from green to brown to red. Subsequently, H_2O (0.5 mL) was added, and the solution was stirred for another 12 h, and then evaporated to dryness. The red solid was purified on neutral alumina, activity I (1.3 cm × 25 cm), with CH_2Cl_2/MeOH, 4:1. The pink component was collected and evaporated to dryness. The solid was washed with CH_2Cl_2 (25 mL), CH_3CN (25 mL), and ether (10 mL), yielding 180 mg of a red solid (50%). Crystals suitable for X-ray crystallography were grown from CH_3OH/H_2O by slow room temperature evaporation of the solvent. ^1H NMR data (CD_3OD) δ 3.80 (m, 2H), 3.60 (m, 2H), 3.32 (s, 2H), 3.20 (m, 4H), 2.75 (m, 4H), 2.64 (m, 3H), 2.50 (d, 2H), 2.12 (b.s, 1H), 2.02 (d, 1H). ^{13}C NMR data (CD_3OD) δ 176.69 (s), 64.79 (s), 61.07 (s), 55.67 (s), 45.92 (s), 45.67 (s), 25.13 (s), −10.53 (s). UV−Vis in H_2O (λ_{max}, nm (ϵ)): 380.9 (140.6), 500.0 (338.5). Anal. Calcd (Found) for $C_{13}H_{31}CoN_4O_7$: C, 37.68 (37.70); H, 7.54 (7.49); N, 13.52 (13.55).

Synthesis of Co(dc)(acac)·0.5H_2O (2) by C−N Bond Cleavage of H_2dc3. H_2dc3 (237 mg, 0.88 mmol) and $Co(acac)_3$ (378 mg, 1.06 mmol) were dissolved in CH_3CN (10 mL), and refluxed under Ar for 3 days. The solvent was removed, and the brown solid was dissolved in CH_2Cl_2 (60 mL) and filtered to remove trace amounts of solid. The filtrate was placed in a beaker and allowed to evaporate slowly at room temperature in the presence of air overnight. The solid was washed with CH_2Cl_2 (40 mL), and the brown-green filtrate was discarded. The red-brown residue was extracted with CH_3CN (3 × 40 mL), and the purple CH_3CN solution was evaporated to dryness yielding 128 mg of a purple solid (37%). Crystals suitable for X-ray crystallography were grown by diffusion of ether into a 4:1 solution of CH_3CN/CH_3OH and lacked the water of hydration found in the analytical sample. Anal. Calcd (Found) for $C_{15}H_{26}N_4CoO_{5.5}$: C, 45.80 (45.86); H, 6.66 (6.60); N, 14.24 (14.28). ^1H NMR data (D_2O) δ 5.90 (br s, 1H), 5.64 (s, 1H), 4.14 (br s, 1H), 3.89 (m, 1H), 3.73 (d, 2H), 3.07 (m, 3H), 2.95 (m, 1H), 2.82 (m, 3H), 2.69 (m, 1H), 2.48 (m, 1H), 2.25 (m, 1H), 2.13 (m, 4H), 1.98 (m, 5H). ^{13}C NMR data (D_2O) (DSS external reference) δ 193.14(s), 192.81 (s), 178.83 (s), 178.11 (s), 101.43 (s), 57.06 (s), 55.83 (s), 55.64 (s), 52.04 (s), 51.22 (s), 51.09 (s), 47.11 (s), 28.60 (s), 28.35 (s), 27.39 (s).

Direct Synthesis of 2 from Dioxocyclam. Dioxocyclam (194 mg, 0.85 mmol) and $Co(acac)_3$ (310 mg, 0.86 mmol) were dissolved

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(2) (a) Kanamori, K.; Broderick, W. E.; Jordan, R. F.; Willett, R. D.; Legg, J. I. *J. Am. Chem. Soc.* **1986**, *108*, 7122−7124. (b) Broderick, W. E.; Kanamori, K.; Willett, R. D.; Legg, J. I. *Inorg. Chem.* **1991**, *30*, 3875−3881.

(3) Chin, M.; Wone, D.; Nguyen, Q.; Nathan, L. C.; Wagenknecht, P. S. *Inorg. Chim. Acta* **1999**, *292*, 254−259.

(4) Hu, C.; Nguyen, T. D.; Wagenknecht, P. S.; Nathan, L. C. *Inorg. Chem.* **2003**, *42*, 742−749.

(5) (a) Brookhart, M.; Green, H. L. H. *J. Organomet. Chem.* **1983**, *250*, 395−408. (b) Timmers, F.; Brookhart, M. *Organometallics* **1985**, *4*, 1365−1371.

(6) For additional reviews on transition metal complexes of C−H σ bonds, see: (a) Hall, C.; Perutz, R. N. *Chem. Rev.* **1996**, *96*, 3125−3146. (b) Crabtree, R. H. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 789−805.

Table 1. Crystallographic Data

	1	2
formula	$C_{15}H_{31}N_4O_7Co$	$C_{15}H_{25}N_4O_4Co$
fw	414.35	384.32
cryst syst	monoclinic	triclinic
space group	$C2/m$	$P\bar{1}$
a (Å)	17.824(2)	8.007(2)
b (Å)	9.189(2)	8.424(1)
c (Å)	11.311(1)	12.751(2)
α (deg)	90	87.090(8)
β (deg)	105.115(6)	87.59(1)
γ (deg)	90	76.26(1)
V (Å^3)	1788.4(5)	834.0(2)
Z	4	2
D_{calcd} (g/cm^3)	1.539	1.530
T (°C)	25	24
μ(mm^{-1})	1.003	1.057
R1^a (F_o) ($I > 2\sigma(I)$)	0.0433	0.0416
wR2^b (F_o^2) ($I > 2\sigma(I)$)	0.1169	0.0997

^{a} $R1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. ^{b} $wR2 = [\Sigma[w(F_o^2 - F_c^2)^2]/\Sigma[w(F_o^2)^2]]^{1/2}$ where $w = 1/[\sigma^2(F_o^2) + (aP)^2 + bP]$ and $P = (F_o^2 + 2F_c^2)/3$. For **1**, a = 0.0618, b = 2.0112; for **2**, a = 0.0414, b = 1.0247.

Table 2. Selected Bond Lengths (Å) and Angles (deg) for Complex [Co(dc3-*C*-(8))(H_2O)]·$4H_2O$ (**1**)

Co−N(1)	1.916(2)	Co−N(2)	1.946(2)
Co−C(8)	1.970(4)	Co−O(2)	2.143(3)
O(1)−C(2)	1.279(3)	N(1)−C(2)	1.309(3)
O(2)−Co−N(1)	92.8(1)	O(2)−Co−N(2)	93.85(9)
O(2)−Co−C(8)	160.0(2)	N(1)−Co−C(8)	100.6(1)
N(2)−Co−C(8)	72.8(1)	Co−N(2)−C(7)	92.7(2)
N(2)−C(7)−C(8)	100.9(2)	C(7)−C(8)−H(8)	116.6
Co−C(8)−C(7)	91.7(2)	Co−C(8)−H(8)	116.6

in absolute ethanol (20 mL), and refluxed overnight. The red-purple solution was evaporated to dryness, and the solid was washed with CH_2Cl_2 (80 mL), and acetone (10 mL). The solid was redissolved in a minimum of methanol, precipitated by addition of ether, collected by filtration, and washed with ethanol (2 mL) resulting in 270 mg of a purple solid (81%). The ^1H and ^{13}C NMR spectra matched those of **2** prepared from H_2dc3.

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 the semiempirical method XABS2.[7] The structures were solved by the Patterson heavy atom method and Fourier difference maps.[8] Refinements were performed by full-matrix least-squares on F^2.[8] All non-hydrogen atoms in both molecules were refined anisotropically. Hydrogen atoms were added in ideal positions as appropriate on carbon, nitrogen, and oxygen, and were not refined. Crystallographic data are summarized in Tables 1−3, and thermal ellipsoid plots[8] at the 50% probability level are shown in Figures 2 and 3. Additional details are available via Supporting Information.

Results and Discussion

Synthesis of Co(dc3-*C*-(8))(H_2O) through C−H Bond Activation. Binding of macrocyclic diamide ligands such as dioxocyclam and H_2dc3 to metals typically requires deprotonation of the amide nitrogens resulting in a dianionic tetraazamacrocycle.[3] Accounting for this, initial attempts to insert Co(III) into H_2dc3 involved first deprotonating H_2dc3 using KH in DMF. After addition of $Co(acac)_3$ and workup, the neutral complex Co(dc3-*C*-(8))(H_2O) was obtained by chromatography on alumina, albeit in low yield. X-ray crystallography confirmed the presence of a Co−C bond, conductivity confirmed that the complex is neutral, and NMR spectroscopy confirmed the diamagnetic nature of the complex. These data support the assignment of the product as a Co(III) complex of a quinquedentate trianionic ligand formed from the deprotonation of the C−H bond. Subsequently, the reaction was performed in basic methanol, and the same product was obtained in much higher yields.

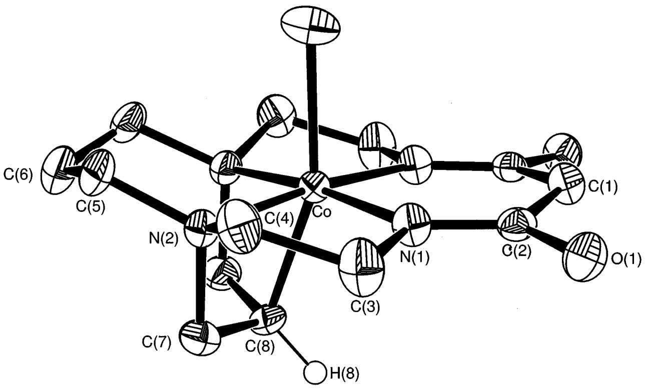

Figure 2. Thermal ellipsoid plot for [Co(dc3-*C*-(8))(H_2O)]·$4H_2O$, **1**, at the 50% probability level. The hydrogen atoms, except for H(8), and water molecules of crystallization have been omitted for clarity.

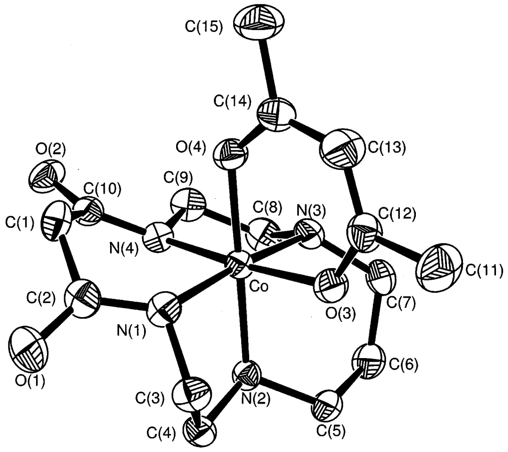

Figure 3. Thermal ellipsoid plot for Co(dc)(acac), **2**, at the 50% probability level. The hydrogen atoms have been omitted for clarity.

Table 3. Selected Bond Lengths (Å) and Angles (deg) for Complex Co(dc)(acac) (**2**)

Co−N(1)	1.929(3)	Co−N(2)	1.998(3)
Co−N(3)	1.996(3)	Co−N(4)	1.913(3)
Co−O(3)	1.928(2)	Co−O(4)	1.907(2)
C(2)−O(1)	1.248(4)	C(10)−O(2)	1.254(4)
N(1)−C(3)	1.465(4)	N(4)−C(9)	1.468(4)
N(1)−C(2)	1.326(5)	N(4)−C(10)	1.326(4)
O(4)−Co−O(3)	92.9(1)	O(4)−Co−N(1)	96.7(1)
O(4)−Co−N(3)	89.8(1)	O(4)−Co−N(2)	178.4(1)
N(4)−Co−O(3)	175.6(1)	N(4)−Co−N(1)	92.8(1)
N(4)−Co−N(3)	85.8(1)	N(4)−Co−N(2)	94.8(1)
O(3)−Co−N(1)	90.2(1)	O(3)−Co−N(3)	91.6(1)
O(3)−Co−N(2)	88.6(1)	N(1)−Co−N(3)	173.2(1)
N(1)−Co−N(2)	83.7(1)	N(3)−Co−N(2)	89.8(1)

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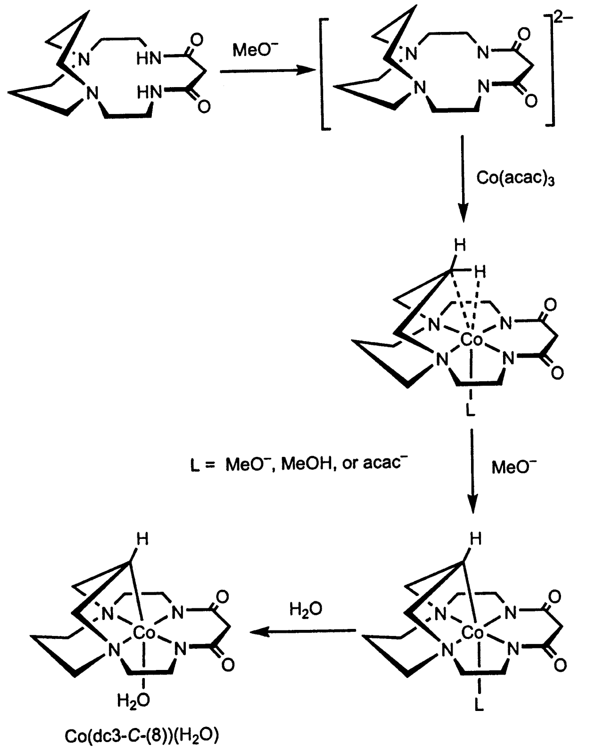
(7) Parkin, S.; Moezzi, B.; Hope, H. *J. Appl. Crystallog.* **1995**, *28*, 53−56.

(8) *SHELXTL Software*, Version 5.03; (Siemens) Bruker Analytical X-ray Systems, Inc.: Madison, WI, 1994.

Scheme 2. Mechanism for the Formation of Co(dc3-*C*-(8))(H_2O)



The fact that methoxide can deprotonate a C−H bond of the ligand indicates that the presence of Co(III) significantly enhances the acidity of this bond. We propose the intermediacy of a complex with an agostic Co−(C−H) interaction (Scheme 2) as first proposed for the internal activation of a C−H bond in the Co(III) complex of dacoda.[2]

As previously discussed,[2] the described mechanism requires an empty d_{z^2} orbital to accept electron density from the C−H bond. For the Co(III) complex of dacoda, it was shown that C−H activation occurred in the presence of strong axial ligands (CN^-, NO_2^-, SO_3^{2-}, or NH_3) but not with weaker axial ligands (Cl^-, SCN^-, or H_2O).[2b] This result was explained in terms of the $d_{xy} - d_{z^2}$ energy gap. In order for C−H activation to occur, the agostic intermediate needs to be low spin, ensuring an empty d_{z^2} orbital. This required strong axial ligands.[2] For the Co(III) complex of dc3 reported herein, the only axial ligands present were MeO^-, MeOH, and $acac^-$, certainly weaker ligands than those necessary for the dacoda case, yet activation still occurred. A likely explanation is that $dc3^{2-}$ is a stronger σ-donor than $dacoda^{2-}$, increasing the energy of the d_{z^2} orbital because of its *x*- and *y*-axis orbital components, without affecting the energy of the d_{xy} orbital. The relative ligand field strength of these equatorial ligands is apparent from a comparison of the UV−vis spectra of Co(dc3-*C*-(8))(H_2O), and Co(dacoda-*C*-(2))(H_2O), the axial ligands being identical in both cases. The lowest energy absorptions for these complexes are 500 and 510 nm, respectively, indicating a stronger ligand field strength for $dc3^{2-}$ versus $dacoda^{2-}$.

Solid State Structure of [Co(dc3-*C*-(8))(H_2O)]·$4H_2O$. There are striking similarities between the structure reported herein and that of Co(dacoda-*C*-(2))(H_2O).[2a] There exists a short Co−C bond (1.97 Å for the dc3 complex vs 1.94 Å for the dacoda complex) when compared with typical Co−alkyl bonds with *trans* N-donors or water (1.98−2.01 Å).[9] Interestingly, Co(III) is displaced from the coordination plane *away* from the alkyl carbon in both structures (0.113(2) Å for the dc3 complex). The sixth coordination site in both cases is occupied by water with a relatively long Co−OH_2 bond (2.14 Å for the dc3 complex vs 2.15 Å for the dacoda complex), indicative of the strong *trans* influence of alkyl ligands. Finally, the Co−N_{daco} bond lengths are quite similar in both complexes (1.95 Å for the dc3 complex vs 1.93 Å for the dacoda complex). A feature not present in the dacoda complex is the Co−N_{amido} bond length. These bond lengths (1.92 Å) are shorter than the Co−N_{daco} bond lengths (1.95 Å), which is consistent with the stronger donor ability of deprotonated amide nitrogens compared to amine nitrogens.[10]

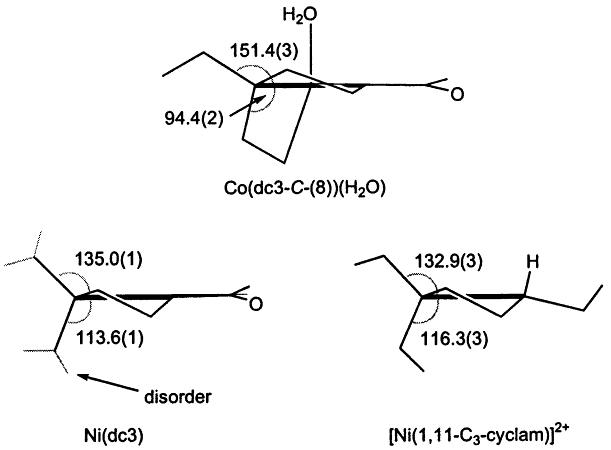


Figure 4. Side view of complexes showing dihedral angles between the N_4 plane (bold line) and selected molecular planes.

The conformation of the daco subunit for the Co(III) complex is chair−boat. The cobalt−carbon bond is part of a strained four-membered metallacycle. The strain induced by the Co−C(8) bond is manifested in bond angles severely distorted from tetrahedral. The Co−N(2)−C(7) and N(2)−C(7)−C(8) angles are 92.7° and 100.9°, respectively, whereas the C(7)−C(8)−C(7a) angle is 117.7°. These are all within 2° of the corresponding angles in Co(dacoda-*C*-(2))(H_2O).

The Co−C bond also has a significant effect on the dihedral angles between the daco subunit and the coordination plane (Figure 4). Compared with daco subunits in other complexes, the Co−C bond has pulled one trimethylene group into a more perpendicular orientation with respect to the N_4 plane, opening up the angle between the N_4 plane and the other trimethylene group.

NMR Spectroscopy of Co(dc3-*C*-(8))(H_2O). The cobalt center in Co(dc3-*C*-(8))(H_2O) was confirmed to be low spin d^6 by observation of a high-resolution ^1H NMR spectrum. The ^1H and ^{13}C NMR resonances of the spectra were assigned using COSY and HETCOR spectra (Supporting Information). Noteworthy concerning the ^1H NMR is the position of the proton resonance assigned to H(8), located at 2.1 ppm, which is similar to those values typically found

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(9) Toscano, P. J.; Marzilli, L. G. *Prog. Inorg. Chem.* **1984**, *31*, 105−205.

(10) Billo, E. *Inorg. Nucl. Chem. Lett.* **1974**, *10*, 613−617.

for Co−alkyls.[11] The ^{13}C NMR resonance of C(8) at −10.5 ppm is similar to the value of −9.2 ppm in Co(dacoda-C(2))-(H_2O) and is weak, presumably for the same reasons (smaller nuclear Overhauser enhancement and coordination to Co) discussed therein.[2b] These ^{13}C resonances are found at significantly higher fields than corresponding carbons in organocobalt(III) complexes with unsaturated equatorial ligands,[12] which indicates greater ionic character in these Co−C bonds.[2b]

Because the Co−C bond in **1** has significant ionic character, we reasoned that it could be broken by the addition of strong acid to form the agostic compound already discussed . However, attempts to break it using triflic acid failed, indicating either a very strong bond or a lack of significant polarization. Attempts to prepare the agostic complex through the intermediacy of a Co(II) complex using the precedence of Legg's group[2] have also failed. Subsequently, we attempted to obtain the agostic intermediate by metalation of H_2dc3 with Co(acac)$_3$ in the absence of base, reasoning that without base the agostic intermediate would not be deprotonated. However, the only product isolated from this reaction was not a dc3 complex, but rather a complex of dioxocyclam resulting from C−N bond cleavage of the original dc3 ligand.

Synthesis of Co(dc)(acac) through C−N Bond Cleavage of H_2dc3. Treatment of H_2dc3 with Co(acac)$_3$ in methanol in the absence of base under an inert atmosphere resulted in no chromatographically isolable products. However, it was discovered that exposure of the final solution to air resulted in an isolable complex with analytical data inconsistent with any complexes of dc3. Structural determination demonstrated that the additional C_3 strap of H_2dc3 had been lost so that a complex of dioxocyclam, Co(dc)(acac), was isolated (Scheme 1, Figure 3).[13] (We have also been able to prepare this complex directly from Co(acac)$_3$ and dioxocyclam.) Apparently, Co(III) catalyzes N-dealkylation of the H_2dc3 ligand, and exposure to air is required for this step. This suggests oxidative N-dealkylation. Such reactions are of interest due to the importance of selective catalysts for the oxidative dealkylation of tertiary amines to secondary amines.[14]

Oxidative dealkylation of coordinated polyamine ligands is rare but has been precedented.[15] For example, Co(III) complexes of tris(3-aminopropyl)amine[15a] and spermine[15b] (spermine = 4,9-diaza-1,12-diaminododecane) have both been shown to undergo oxidative N-dealkylation of the coordinated polyamine ligand. In the case of the spermine complex, the cleavage was attributed to the energetically unfavorable seven-membered chelate ring. It is possible in the case reported herein that the steric constraint of the dc3 ligand contributes to the instability of the coordinated ligand with respect to oxidative C−N cleavage.

Solid State Structure of *cis*-Co(dc)(acac). As demonstrated in the structure of *cis*-Co(dc)(acac) (Figure 3) the dioxocyclam ligand has adopted the *cis* configuration. To our knowledge, this is the first observation of the dioxocyclam ligand in the *cis* configuration, although for complexes of cyclam, both the *trans* and *cis* configurations are common[16] and the analogous complex of cyclam, *cis*-[Co-(cyclam)(acac)]$^{2+}$ has been reported.[17] ^{13}C NMR spectroscopy (Supporting Information) confirms an asymmetric structure in solution as the acac$^-$ ligand accounts for five resonances (in similar position to other acac complexes of Co(III)[17]) and the dioxocyclam ligand accounts for 10 resonances, indicating no two carbons are related by symmetry.

The geometry about cobalt is a slightly distorted octahedron with the Co(III) coordinated by the four nitrogen atoms of the tetraazamacrocycle and the two oxygen atoms from acac$^-$. Co(III) and the bidentate acac$^-$ ligand form a planar ring, and the dioxocyclam ligand is folded along a N−Co−N axis perpendicular to this Co[acac] plane. The mean Co−N_{amido} bond length of 1.92 Å is comparable with those in **1**, whereas the mean Co−N_{amine} bond length of 2.00 Å is slightly longer than those in **1** and comparable with those in [Co(cyclam)(acac)]$^{2+}$. The mean Co−O bond length (1.92 Å) is comparable with those of cobalt(III) complexes with acac chelates.[17,18] As expected, the N−Co−N angles of the five-membered rings (83.7° and 85.8°) are smaller than those of six-membered rings (89.8°and 92.8°). The saturated six-membered chelate ring adopts the chair conformation, consistent with the analogous cyclam complex.[17]

Of particular interest is the six-membered chelate ring containing the two amide functional groups and the effect of the *cis* configuration on its geometry. In the case of a known structure of a dioxocyclam complex, Ni(dc),[3] with the macrocyclic ligand in the *trans* configuration, this six-membered chelate ring is nearly planar, and the plane defined by C(2), N(1), C(10), N(4) is nearly coplanar with the coordination plane (dihedral angle estimated at 171°). For the *cis* complex reported herein, however, this coplanarity is noticeably absent, with the dihedral angle between these planes being 160.0(2)°. The *cis* configuration appears to have caused a distortion of this six-membered ring relative to the

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[11] Gianotti, C.; Gaudemer, A.; Fontaine, C. *Tetrahedron Lett*. **1970**, *11* (37), 3209−3212.

[12] (a) Bied-Charreton, C.; Septe, B.; Gaaudemer, A. *Org. Magn. Reson.* **1975**, *7*, 116−124. (b) Needham, T. E.; Matwiyoff, N. A.; Walker, T. E.; Hogenkamp, H. P. C. *J. Am. Chem.* Soc. **1973**, *95*, 5019−5024. (c) Hogenkamp, H. P. C.; Tkachuck, R. D.; Grant, M. E. *Biochemistry* **1975**, *14*, 3707−3714.

[13] Dioxocyclam is a starting material for H_2dc3, but the synthesis and purification of H_2dc3 yields ligand uncontaminated with dioxocyclam, precluding the possibility that Co(dc)(acac) formed from fortuitous dioxocyclam in the starting material.

[14] (a) Riley, D. P.; *J. Chem. Soc., Chem. Commun.* **1983**, 1530−1532. (b) Riley, D. P.; Fields, D. L.; Rivers, W. *J. Am. Chem. Soc.* **1991**, *113*, 3371−3378.

[15] (a) Calafat, A. M.; Marzilli, L. G. *Inorg. Chem*. **1993**, *32*, 2906−2911. (b) Yashiro, M.; Mori, T.; Sekigushi, M.; Yoshikawa, S.; Shiraishi, S. *J. Chem. Soc., Chem. Commun.* **1992**, 1167−1168. (c) Sonnberger, B.; Hühn, P.; Wasserburger, A.; Wasgestian, F. *Inorg. Chim. Acta* **1992**, *196*, 65−71.

[16] (a) Bosnich, B.; Poon, C. K.; Tobe, M. L. *Inorg. Chem.* **1965**, *4*, 1102−1108. (b) Donnelly, M. A.; Zimmer, M. *Inorg. Chem*. **1999**, *38*, 1650−1658.

[17] Simon, E.; L'Haridon, P.; Pichon, R.; L'Her, M. *Inorg. Chim. Acta* **1998**, *282*, 173−179.

[18] (a) Chiang, C.; Leon, A.; Marzilli, L. G. *Inorg. Chem*. **1979**, *18*, 791−795. (b) Kruger, G. J.; Reynardt, E. C. *Acta Crystallogr., Sect. B* **1974**, *30*, 822−824. (c) Suzuki, T.; Kashiwabara, K.; Kita, M.; Fujita, J.; Kaizaki, S. *Inorg. Chim. Acta,* **1998**, *281*, 77−84.

more common *trans* configuration of the dioxocyclam macrocycle. However, the dihedral angle reported here is significantly lower than that for the fully saturated six-membered rings in *cis*-[Co(cyclam)(acac)]$^{2+}$. From the data on that cyclam complex,[17] the dihedral angle can be estimated at 143°. The smaller deviation from planarity for the *cis*-dioxocyclam complex compared to the *cis*-cyclam complex is likely due to the substantial sp^2 character of the deprotonated amido nitrogens resulting from conjugation. This sp^2 character is evidenced by the rather short C−N bond distance (average $C-N_{amide} = 1.33$Å) here compared with the normal C−N single-bond distance of 1.47 Å.[19] The distortion of this portion of the dioxocyclam ligand away from the planarity consistent with sp^2 hybridization would appear to be energetically unfavorable, and thus, it is not surprising that the *cis* configuration of dioxocyclam has not been previously observed. Nor is it surprising that ^{1}H NMR demonstrates that this complex decomposed significantly when left in D_2O at room temperature overnight. (The complex appears substantially more stable in methanol.)

Conclusions

The chemistry of the constrained dioxocyclam ligand, H_2-dc3, with Co(acac)$_3$ demonstrates that the dc3 ligand is noninnocent. Activation of the C(8)−H bond to deprotonation by methoxide is compelling evidence for an agostic intermediate. Additionally, the fact that this occurs in the absence of strong axial ligands demonstrates the effect of the equatorial ligand strength on this process. The structure closely parallels that of Co(dacoda-*C*-(2))(H_2O). We have not been able to prepare the analogous complex of 1,11-C_3-cyclam, nor have we attained one of our original goals, the isolation of the proposed agostic intermediate to Co(dc3-*C*-(8))(H_2O). Attempts to prepare the intermediate in the absence of a base resulted in unexpected C−N cleavage of the ligand and the discovery of a new coordination mode for dioxocyclam. The likelihood that this occurs through oxidative cleavage tempers our earlier excitement that the strong donor characteristics of this ligand might be effective at stabilizing high metal oxidation states,[3] raising questions about the practical conditions under which ligand degradation might predominate.

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Supporting Information Available: ^{1}H, ^{13}C, 2D NMR spectra (COSY, HETCOR) and X-ray crystallographic files in CIF format for the structure determinations. This material is available free of charge via the Internet at http://pubs.acs.org.

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(19) Bu, X. H.; Cao, X. C.; An, D. L.; Zhang, R. H.; Thomas, C.; Kimura, E. *J. Chem. Soc., Dalton Trans.* **1998**, 433−438.