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Modeling the Anomalous Coordination Chemistry of Cr(III) Biscyclam

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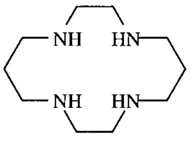
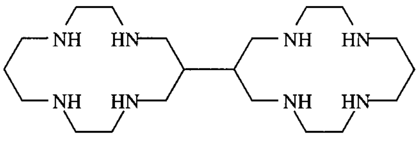
Introduction

Compounds of Cr(III) have played a pivotal role in elucidating the electronic structure, spectroscopy, and photophysics of coordination complexes.[1−3] The aza macrocycles in particular have been useful since they afford the ability to alter ligand field strength, coordination environment, and ligand geometry while maintaining a good handle on the nature of the species under investigation.[4,5] Of the myriad aza macrocycles, 1,4,7,11-cyclotetradecane, cyclam, has been studied extensively. This ligand has the flexibility to form a multidentate complex with square planar four-coordinate metals, and either cis or trans complexes with six-coordinate metals.[6] Metal−cyclam and related complexes have a rich conformational isomerism owing to the flexibility of the methylene linkages between the nitrogen donor atoms; a detailed analysis of the conformations in cobalt(III) macrocycle complexes has appeared recently.[7]

A close relative of cyclam is the potentially binucleating ligand biscyclam.[8] This ligand contains two cyclam units bridged via a saturated C−C bond. Investigations of the coordination chemistry of this and the closely related bisdioxocyclam ligand[9] have demonstrated that, like its mononucleating parent, this ligand will form square planar bimetallic complexes with metals such as Cu(II) and Ni(II).



cyclam



biscyclam

Preparation of Cr(III) cyclam complexes has typically resulted in a mixture of cis and trans isomers,[10] although the trans isomer is typically the minor product,[11] and there has been some controversy over preparation of the trans Cr(III) cyclam complexes in general.[12] Much of this early debate was put to rest by Kane-Maguire et al., with their description of a preparative route that uses cyanide as the X ligand as a synthetic intermediate which results in 97% yield of the trans product.[13]

In the course of our study of weak coupling between Cr(III) centers in bimetallic systems,[14] we have observed an anomalous behavior in the coordination chemistry of biscyclam. Whereas we were able to readily prepare cis complexes of the type $[Cr_2([14]aneN_4-)_2)X_4]X_2$ with a host of X ligands, we were unable to isolate any trans complexes. This stands in stark contrast to the behavior of monometallic cyclam where both cis and trans Cr(III) complexes are readily prepared (vide infra).

Since both cyclam and biscyclam readily form square planar four-coordinate complexes and cyclam readily forms trans six-coordinate complexes, we were curious why we were only able to obtain cis analogues in the ligation of Cr(III) with biscyclam, even when we attempted to use the cyanide intermediate method. In order to understand what processes may be involved in the determination of the coordination environment in Cr(III) biscyclam complexes, we have performed a molecular mechanics modeling study of this interesting system. We present here the results of that study.

Experimental Section

A survey of the methods attempted to prepare the trans biscyclam Cr(III) complexes include those described in the literature for the analogous cyclam compounds mentioned above, plus reaction of biscyclam with anhydrous $CrBr_3$ in DMSO, DMF, THF, and acetone and the catalytic reaction of Cr(II)/Cr(III) with zinc amalgam. A description of our synthetic methods has been presented elsewhere.[14] The preparation of cyanide and thiocyanate intermediates was attempted in many different solvent systems, with a triflate intermediate prepared from the chloride by reaction with neat triflic acid, as well as a hot melt in chloronaphthalene[15,16] No trans product was isolable. In most cases the starting cis complex was recovered in near quantitative yield.

Computational Methods

Structures of the complexes were minimized using molecular mechanics with the augmented MM2 force field[17] as implemented in the Oxford Molecular CAChe software suite (version 3.9). The calculated geometries were considered to be converged when the energy change was less than 0.004 kJ mol^{-1} per iteration. Geometries were verified to be at least local minima (and not transition states) by characterizing the stationary point via frequency analysis. The cyclam rings have a number of conformations, particularly within a cis octahedral complex.[7] These were exhaustively searched to locate the lowest-energy conformer; this was the same conformation observed in the crystal structure of $[cis\text{-}Cr([14]aneN_4)(NCS)_2]^+$.

To validate this computational approach, the appropriateness of the CAChe parameters, and the metal-complex structures, we compared the steric energies of calculated structures of the structurally analogous ions *cis*- and $trans\text{-}[Cr([14]aneN_4)(NCS)_2]^+$, $[cis\text{-}Cr(en)_2(DMSO)Cl]^{2+}$, and $[cis\text{-}Cr(dien)(DMSO)Cl]^{2+}$ with those of the reported crystal structures.[18,19] To calculate the steric energies of the X-ray structures that do not include accurate positions of the hydrogen atoms, we fixed

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Scheme 1

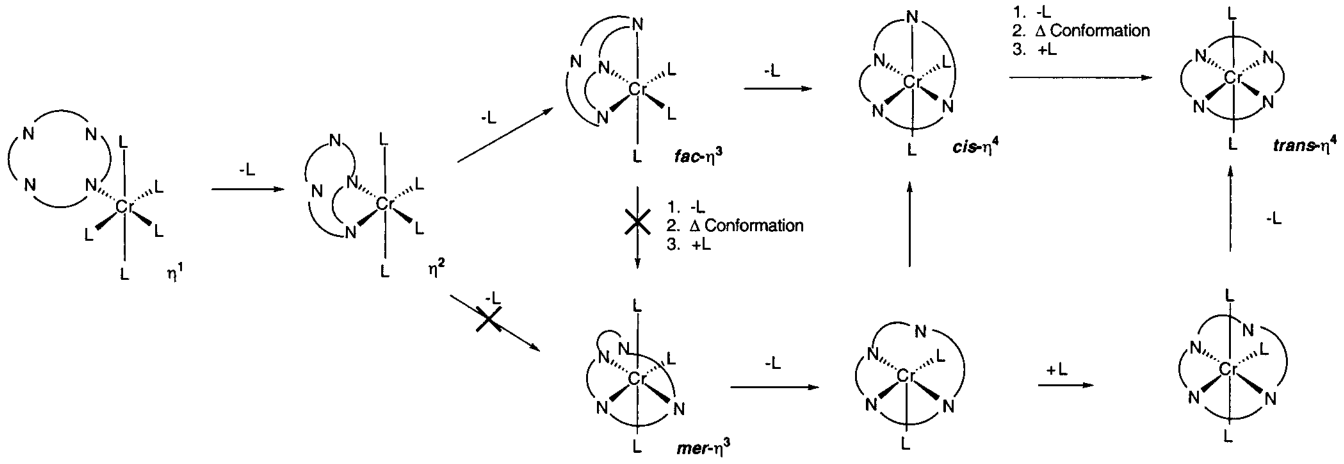

Table 1. Comparison of Steric Energies for Calculated and Observed Structures of Chromium(III) Complexes with Multidentate Amine Ligands

	calcd structure		X-ray structure	
species	calcd steric energy −(kJ mol^{-1})	av Cr−N$_{amine}$ bond length (Å)	calcd steric energy −(kJ mol^{-1})	av Cr−N$_{amine}$ bond length (Å)
[*cis*-η^4-Cr([14]aneN$_4$)(SCN)$_2$]$^+$ [a]	−452.4	2.19 ± 0.00	−320.4	2.08 ± 0.01
[*trans*-η^4-Cr([14]aneN$_4$)(SCN)$_2$]$^+$ [a]	−420.5	2.18 ± 0.00	−260.7	2.05 ± 0.01
[Cr(en)$_2$(DMSO)Cl]$^{2+}$ [b]	29.9	2.19 ± 0.01	169.1	2.07 ± 0.01
[Cr(dien)(DMSO)$_2$Cl]$^{2+}$ [b]	−166.9	2.19 ± 0.00	−34.7	2.06 ± 0.02

[a] Reference 18. [b] Reference 19.

the non-hydrogen positions, added any missing hydrogens, and minimized the resulting constrained structures. For our calculated structures, all atom positions were allowed to relax. Using the default parameters, the Cr−N bond lengths in both the cis and trans structures were 2.18 ± 0.03 Å, within ca. 0.1 Å (5%) of the experimentally determined values of 2.07 ± 0.02 Å for a range of Cr(III)−amine complexes.[20] Thus no additional parametrization was considered to be essential for the octahedral Cr(III) intermediates in our coordination model.

Results and Discussion

The sequence of modeled steps in the ligation is shown in Scheme 1. The steric energies of the starting species and the intermediates encountered during ligation of the cyclam or biscyclam macrocycles are collected in Table 1.

In our analysis of the formation mechanism, there were several underlying assumptions: (1) the starting metal species was taken to be Cr(DMSO)$_6^{3+}$; (2) addition of the cyclam ligand to the metal was modeled as a sequential process, with coordination to a single nitrogen, then to the second, etc., and addition of the biscyclam to the metal involved individual stepwise addition of each macrocyclic moiety; (3) each step was preceded by loss of a DMSO in the metal inner coordination sphere, i.e., we modeled a dissociative interchange mechanism. For biscyclam, this may tend to underestimate the effect of charge accumulation as the second metal is coordinated; however, we proceeded on the assumption that the observed effect was ligand based rather than the effect of localized dipoles. Considering the observed chemistry of copper and nickel complexes, and the ability of Cr(III) to readily form cis bimetallic complexes, this seemed reasonable.

The ground state of the cyclam ligand is an all-chair configuration. In this structure, the nitrogen lone pairs are generally directed toward the center of the ring, albeit somewhat above or below the mean ligand plane. There are several energetically equivalent conformations of this ligand, differing only in the orientations of the amine hydrogens and lone pairs, that are interconverted by amine inversion.

In coordinating the first nitrogen to the chromium ion, the cyclam macrocycle becomes slightly distorted. One of the amine groups must swing out of the center of the cyclam to attack the metal, while the rest of the macrocycle adjusts to accommodate the steric bulk of the solvated metal. Much of the induced strain is spread out over the macrocycle, primarily in the angle strain, which increases nearly 11-fold and dwarfs any other steric component of the energy. What little bond-stretching does occur is localized in the ring near the coordinating nitrogen.

There are three choices for coordinating the second macrocycle nitrogen to the metal center to form a five-membered, six-membered, or nine-membered ring. Predictably, the steric energy difference between the five- and six-membered bidentate ligations is small, with the five-membered-ring system ca. 5 kJ mol^{-1} higher in energy. This energy difference appears as minor bond-stretch and bond-angle distortions for the five-membered system. We assumed that the six-membered ring would be preferentially formed. The putative nine-membered bidentate ligation is a much higher energy species, greater by over 100 kJ mol^{-1}, largely manifested as distortions of the DMSO ligands out of their ideal octahedral positions and strain of the Cr−O−S angles. Curiously, addition of the second nitrogen to the metal coordination sphere is quite endothermic. This is the result of the strain induced in the cyclam ligand and many small but significant distortions of the ligands out of the metal's octahedral field.

In coordinating the third nitrogen there is a significant geometric choice to be made. The third nitrogen could attach

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Table 2. Calculated Energies for Cyclam or Biscyclam Macrocycle Ligands and Model Complexes

species[a]	MM2 steric energy (kJ mol^{-1})	comments
DMSO	1.2	ligand
cyclam (all-chair)	38.3	ligand
biscyclam (all-chair)	146.9	ligand
$Cr(DMSO)_6^{3+}$	203.8	solvated metal
$Cr(DMSO)_5^{3+}$	180.7	solvated metal
$[N1\text{-}\eta^1\text{-}Cr(DMSO)_5\text{-cyclam}]^{3+}$	262.1	initial macrocycle coordination
$[N1,N2\text{-}\eta^2\text{-}Cr(DMSO)_4\text{-cyclam}]^{3+}$	298.0	bidentate macrocycle coordination, forming six-membered ring
$[N1,N4\text{-}\eta^2\text{-}Cr(DMSO)_4\text{-cyclam}]^{3+}$	298.0	bidentate macrocycle coordination, forming five-membered ring
$[N1,N3\text{-}\eta^2\text{-}Cr(DMSO)_4\text{-cyclam}]^{3+}$	363.8	bidentate macrocycle coordination, forming nine-membered ring
proto-*fac* $[N1,N2\text{-}\eta^2\text{-}Cr(DMSO)_3\text{-cyclam}]^{3+}$	246.6	bidentate with loss of solvent from incipient *fac* position
proto-*mer* $[N1,N2\text{-}\eta^2\text{-}Cr(DMSO)_3\text{-cyclam}]^{3+}$	264.7	bidentate with loss of solvent from incipient *mer* position
$[\textit{fac}\text{-}N1,N2,N3\text{-}\eta^3\text{-}Cr(DMSO)_3\text{-cyclam}]^{3+}$	269.2	tridentate macrocycle coordination
$[\textit{mer}\text{-}N1,N2,N3\text{-}\eta^3\text{-}Cr(DMSO)_3\text{-cyclam}]^{3+}$	617.5	tridentate macrocycle coordination
$[\textit{cis}\text{-}\eta^4\text{-}Cr(DMSO)_2\text{-cyclam}]^{3+}$	158.0	tetradentate macrocycle coordination
$[\textit{trans}\text{-}\eta^4\text{-}Cr(DMSO)_2\text{-cyclam}]^{3+}$	153.6	tetradentate macrocycle coordination
$[(\textit{cis}\text{-}\eta^4\text{-}Cr(DMSO)_2)\text{-biscyclam}]^{3+}$	208.0	metal coordinated to only one of the cyclam moieties
$[(\textit{cis}\text{-}\eta^4\text{-}Cr(DMSO)_2)\text{-}(\eta^1\text{-}Cr(DMSO)_5)'\text{-biscyclam}]^{6+}$	430.2	initial macrocycle coordination
$[(\textit{cis}\text{-}\eta^4\text{-}Cr(DMSO)_2)\text{-}(N1,N2\text{-}\eta^2\text{-}Cr(DMSO)_4)'\text{-biscyclam}]^{6+}$	558.3	bidentate macrocycle coordination, forming six-membered ring
$[(\textit{cis}\text{-}\eta^4\text{-}Cr(DMSO)_2)\text{-}(\textit{fac}\text{-}N1,N2,N3\text{-}\eta^3\text{-}Cr(DMSO)_3)'\text{-biscyclam}]^{6+}$	494.4	tridentate macrocycle coordination
$[(\textit{cis}\text{-}\eta^4\text{-}Cr(DMSO)_2)\text{-}(\textit{cis}\text{-}\eta^4\text{-}Cr(DMSO)_2)'\text{-biscyclam}]^{6+}$	425.2	tetradentate macrocycle coordination
$[(\textit{cis}\text{-}\eta^4\text{-}Cr(DMSO)_2)\text{-}(\textit{trans}\text{-}\eta^4\text{-}Cr(DMSO)_2)'\text{-biscyclam}]^{6+}$	378.7	
$[(\textit{trans}\text{-}\eta^4\text{-}Cr(DMSO)_2)\text{-}(\textit{trans}\text{-}\eta^4\text{-}Cr(DMSO)_2)'\text{-biscyclam}]^{6+}$	367.9	

[a] N1, N2, etc. refers to the numbering of the macrocycle N atoms coordinated to Cr(III) in the calculation.

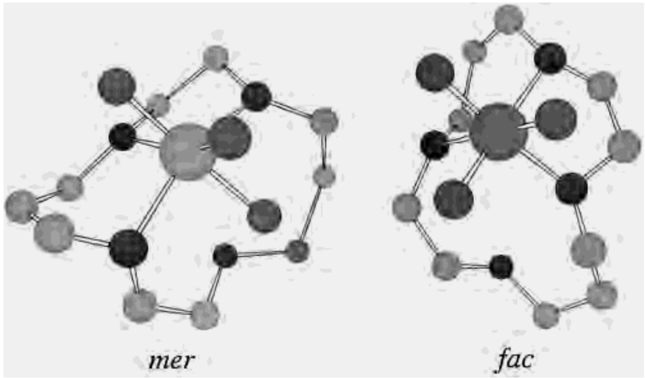

Figure 1. A ball and stick representation of the two possible formation intermediates of the η^3 form of cyclam. The hydrogens have been removed for clarity as have all but the O atoms of DMSO.

with a *mer* or *fac* geometry (Figure 1). The energy of the bidentate intermediate that loses a DMSO from the incipient *mer* position (for the macrocycle) is inherently somewhat higher than the one that loses DMSO from the incipient *fac* position (Table 2). In fact, loss of this ligand results in significant stabilization of the whole complex, by reducing the unfavorable steric interactions with the unligated portion of the macrocycle and the DMSO. Macrocyclic ligand attachment in the *fac* geometry is nearly isoenergetic with the proto-*fac* lacunary complex and is much lower in energy than attachment in the *mer* geometry. Thus it is likely that the tridentate intermediate will be coordinated as *fac*.

After loss of a ligand from the *fac* tridentate complex two things may occur: either an unlikely, highly endergonic transformation to the proto-*mer* isomer or, more likely, the slightly endergonic addition of the fourth macrocycle nitrogen generating the cis isomer. However, even if the energetically unfavorable *mer*-η^3 isomer were to form, the portion of the macrocycle containing the free, fourth nitrogen is still on the same side of the complex as the three bound nitrogens. The DMSO ligand must dissociate from the metal, opening up the coordination site that would lead to the cis-η^4 complex. Thus, by our model, the cis isomer is the kinetic product. This sequence is consistent with the observed production of predominantly cis complex that then requires isomerization to the somewhat thermodynamically more stable trans isomer.

Formation of the biscyclam complex follows a similar sequence. The energetic changes during coordination of the first metal ion to one of the biscyclam macrocycles are nearly indistinguishable from coordination to cyclam. The cis isomer in the first macrocycle is kinetically favored. The trends during coordination of the metal to the second macrocycle of the biscyclam are similar as well, kinetically generating the cis,cis′ isomer of the bimetallic complex. One significant difference that appears in the biscyclam complex is bond-stretch and bond-angle strain localized in and near the C−C bridge between the macrocycles, but this contribution is nearly identical for each of the cis,cis′, cis,trans′, and trans,trans′ isomers.

Isomerization from the cis to trans isomer is a key issue in understanding the observed biscyclam product. Isomerization requires three steps: (1) loss of a solvent in the metal coordination sphere; (2) a conformational change of the macrocycle; and (3) recoordination of the solvent. The DMSO ligand-binding energies are small (5−6 kJ mol^{-1}), so they should be readily reversible. The conformational isomerism of the cyclam or biscyclam ligand about the metal center is thus the important step. That conformational change is most likely to occur either by a pseudorotation of the coordinated ligand nitrogens within the metal coordination sphere or by reversible decoordination of one of the macrocycle nitrogens, with concomitant inversion of that amine while free from the metal center.

The cis−trans isomerization proceeds readily under relatively mild conditions for $[(\textit{cis}\text{-}\eta^4\text{-}Cr(DMSO)_2)\text{-cyclam}]^{3+}$. We have attempted the cis−trans isomerization of the [(cis-η^4-Cr-

$(DMSO)_2)-(cis-\eta^4-Cr(DMSO)_2)'$-biscyclam$]^{6+}$ complex at temperatures as high as 350 °C in a chloronaphthalene heterogeneous melt, yet observed no isomerization.[21] Even though the trans,trans′ complex is the lowest energy conformation, we are unable to corroborate this calculated result experimentally. It would appear that the kinetic barrier to cis → trans isomerization is greater for the biscyclam ligand than for the cyclam ligand.

Conclusions

We began this investigation working on the hypothesis that the major impediment to cis → trans isomerization was the strain contained in the C−C tether between the two macrocyclic moieties. Although our calculations show that the bridge does contribute to the total strain energy as manifested in the calculated steric energies, we find no significant difference between the contributions of the bridge carbon atoms of either isomer. It would appear that addition of a large constituent (such as a second macrocycle) to the cyclam macrocycle conformationally restricts its ability to undergo cis → trans isomerization. This suggests that pseudorotation may not be a significant pathway for cis → trans isomerization in cyclam and biscyclam chromium complexes; instead, amine dissociation and inversion may be more likely. We are currently examining the effect that coordinated cyanide has on the cis → trans isomerization of the monometallic Cr(III) biscyclam complex to better understand why this isomerization method, which produces nearly quantitative cis → trans conversion for cyclam, fails for biscyclam.

The calculated structures of all complexes reported here are available as a ZIP archive of Brookhaven Protein Databank (.pdb) files at http://www.wmich.edu/chemistry/archive/cyclam.zip.

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(21) We use the eta (η) notation to indicate the number of donor nitrogens coordinated by the macrocycle.