(39) D. L. DuBois, W. H. Meyers, and D. W. Meek, *J. Chem. Soc., Dalton Trans.*, 1011 (1975).
(40) L. W. Gosser, *Inorg. Chem.*, **14**, 1453 (1975).
(41) J. R. Shapley and J. A. Osborn, *Acc. Chem. Res.*, **6**, 305 (1973).
(42) P. K. Maples, M. Green, and F. G. A. Stone, *J. Chem. Soc., Dalton Trans.*, 388 (1973).

Contribution of Department of Chemistry,
Bowling Green State University, Bowling Green, Ohio 43403

Cobalt(II) Complexes Containing a 12-Membered Saturated Macrocyclic Ligand[1]

C. M. SARTHER and E. L. BLINN*

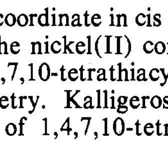
Received November 12, 1975

AIC508217

A series of high-spin five- and six-coordinate macrocyclic cobalt(II) complexes whose stoichiometry is $Co(tbcyclen)X_2 \cdot nH_2O$ (where tbcyclen is 1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane and X is NO_3, Cl, SCN, or Cl–ClO_4) have been prepared. On the basis of molecular models, conductivity, electronic spectra, and magnetic data it appears that the $Co(tbcyclen)(NO_3)_2 \cdot H_2O$ has a cis-octahedral geometry while all of the other complexes have a trigonal-bipyramidal geometry. The ligand tbcyclen stabilizes the divalent state of cobalt over the trivalent state. All attempts to oxidize $Co(tbcyclen)(NO_3)_2 \cdot H_2O$ by electrochemical means, by direct aeration, or by use of H_2O_2 have failed. (The stabilization of the divalent state by tbcyclen may be due to the weak ligand field strength of tbcyclen or to the fact that the bulky benzyl groups on the tbcyclen make it kinetically difficult to form the six-coordinate Co(III)–tbcyclen complexes.) These complexes are stable with respect to dissociation in acid–water solution but decompose rapidly in an acid solution containing both water and acetone.

Introduction

There has been considerable interest in the synthesis of macrocyclic metal compounds because of the structural similarity between these synthetic compounds and several biologically important metal complexes.[2] At present most of the published research has dealt with macrocyclic ligands containing at least 13 atoms in the ring.[2–4] Most of these relatively large macrocyclic ligands form planar or trans-octahedral complexes and are considered strong-field ligands.[2–4] It has been demonstrated that a 12-membered tetradentate macrocyclic ligand cannot form a planar complex with a divalent transition metal ion.[5] This type of ligand should coordinate around the face of either an octahedron or a trigonal bipyramid. Collman and Schneider synthesized a series of cobalt(III) complexes with 1,4,7,10-tetraazacyclododecane (cyclen, Ia).[6] On the basis of visible and infrared spectra, these cobalt(III) complexes of cyclen were assigned a cis-octahedral configuration. A crystal structure of $[Co(cyclen)(NO_2)_2]Cl$ has confirmed that the cyclen is folded and that the NO_2^- groups coordinate in cis positions.[7] Rosen and Busch[8] showed that the nickel(II) complexes of the sulfur analogue of cyclen, 1,4,7,10-tetrathiacyclododecane, also had a cis-octahedral geometry. Kalligeros and Blinn[9] prepared nickel(II) complexes of 1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane (tbcyclen, Ib) and suggested that the geometry of such compounds is either cis octahedral or trigonal bipyramidal depending on the nature of the other univalent ligand group coordinated to the metal ion.



Ia, R = H (cyclen)
b, R = $CH_2C_6H_5$ (tbcyclen)

We are interested in preparing low-symmetry complexes which are likely to have weak highly strained metal to donor bonds. The cobalt(II) complexes of tbcyclen should have these attributes. Using x-ray data Itaka, Shina, and Kimura observed greater bond angle distortions from the expected values in the cobalt(III) complex of cyclen than from the analogous cobalt(III) complexes of ethylenediamine, diethylenetriamine, and triethylenetetraamine. They attributed the additional angular distortion and strained rings in $[Co(cyclen)(NO_2)_2]Cl$ to nonbonding repulsions. Most of these nonbonded repulsions were attributed to the interaction of hydrogen on the nitrogens with other hydrogen atoms on adjacent rings.[7] Therefore it is reasonable to assume that substituting a relatively large benzyl group for the hydrogen atom on each nitrogen on cyclen should not reduce the degree of metal to nitrogen bond strain but should induce some additional steric strain. Molecular models of metal–tbcyclen complexes confirm the nonbonded interactions and suggest that these complexes should have lower symmetry than the cobalt–cyclen complexes in order to minimize the additional bond strain. Also, the use of cobalt(II), which is larger than cobalt(III) in $[Co(cyclen)(NO_2)_2]Cl$, should increase the degree of metal to nitrogen bond strain.

Williams and Vallee have formulated a hypothesis about the nature of the environment around a metal ion in metalloenzymes to explain why the physical properties of these enzymes are different from those of synthetic coordination complexes.[10,11] They suggested that the metal ion in the metalloenzyme is contained in an irregular geometry and the metal to donor bonds are strained. The combination of strained bonds and irregular geometry (entatic state) approximate the transition state for the reaction in which that enzyme is involved. Busch[2] has suggested that the metal ion can exist in the entatic state in a metalloenzyme because of the structural constraints of the proteins which inhibit the stepwise dissociation of the donor atoms from the metal ion ("multiple juxtapositional fixedness"). A macrocyclic ligand, likewise, inhibits the stepwise dissociation of the donor atoms from the metal ion.[2,12–15] Although the Vallee and Williams hypothesis remains controversial[16,17] and the entatic state environment has been shown to be unlikely with regard to several metalloenzymes,[16] there still remains the question of whether an unusual coordination geometry accompanied by strained metal-to-donor bonds will result in complexes that will have unusual chemical and physical properties. The prime function of this research is to prepare and characterize complexes that are likely to have many of the properties of an entatic state environment. The cobalt(II) complexes of tbcyclen should contain strained metal to nitrogen bonds and should be kinetically stable because of the cyclic nature of the ligand. Therefore these complexes should show many attributes of the environment around the metal ion in a metalloenzyme. Also the benzyl groups on the nitrogens should create a hydrophobic environment around the cobalt(II). The metal ion in many metalloenzymes is believed to be in a hydrophobic environment.[18]

Experimental Section

Apparatus. All electronic spectra were recorded employing a Beckman DK-2 ratio recording spectrophotometer. The spectra of the solids were measured in a Nujol mull using the diffuse-transmittance technique.[19] Infrared spectra were taken on a Perkin-Elmer 337 instrument. The magnetic susceptibilities of all solid samples were determined by the Gouy method at room temperature. Susceptibilities of the ligand and anions were calculated from Pascal's constants.[20] Conductivity measurements were taken using an Industrial Instruments conductivity bridge. A Wenking 7131 G1RH potentiostat and a homemade ramp generator were used in the cyclic voltammetry experiment. Nitrogen analyses were taken on a Coleman Model 29 nitrogen analyzer. Carbon and hydrogen analyses were performed by Galbraith Laboratories, Inc., Knoxville, Tenn.

Synthesis of Chloro(1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane)cobalt(II) Chloride Monohydrate. To a boiling solution of 0.23 g (0.001 mol) of $CoCl_2{\cdot}6H_2O$ in 25 ml of 95% ethyl alcohol was added 0.55 g (0.0013 mol) of tbcyclen.[21] The solution was stirred until all of the tbcyclen had dissolved and a purple precipitate had formed. After evaporation of the solution to approximately 5 ml, the light purple crystals were filtered and washed with 15-ml portions of absolute ethyl alcohol; yield 0.037 g (56%). Anal. Calcd for $Co(tbcyclen)Cl_2{\cdot}H_2O$: C, 63.44; N, 8.22; H, 6.75. Found: C, 63.59; N, 8.18; H, 6.85.

Synthesis of Chloro(1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane)cobalt(II) Perchlorate Hemihydrate. An aqueous solution of 10 ml of 0.2 M (0.002 mol) $NaClO_4$ was added to a boiling solution of 0.61 g (0.001) mol) of $Co(tbcyclen)Cl_2{\cdot}H_2O$ in 50 ml of absolute ethyl alcohol. The resulting mixture was evaporated to approximately 20 ml over a water bath. The fluffy purple powder which formed was filtered and washed with water and absolute ethyl alcohol; yield 0.72 g (98%). Anal. Calcd for $Co(tbcyclen)ClClO_4{\cdot}{}^1/_2H_2O$: C, 58.78; H, 6.17; N, 7.62. Found: C, 59.36; H, 6.26; N, 7.64.

Synthesis of Nitrato(1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane)cobalt(II) Nitrate Monohydrate. In a boiling solution of 1 g (0.003 mol) of $Co(NO_3)_2{\cdot}6H_2O$ in 75 ml of 95% ethyl alcohol, 1 g (0.0018 mol) of tbcyclen[21] was dissolved with stirring. Initially a light blue powder appears in the solution. This powder dissolved and pink crystals formed. The solution was evaporated over a water bath to approximately 25 ml and then filtered. The precipitate was washed with absolute ethyl alcohol; yield 1.22 g (92%). Anal. Calcd for $Co(tbcyclen)(NO_3)_2{\cdot}H_2O$: C, 59.99; H, 6.27; N, 11.44. Found: C, 59.35; H, 6.62; N, 11.10.

Synthesis of Isothiocyanato(1,4,7,10-tetrabenzyl-1,4,7,10-tetraazacyclododecane)cobalt(II) Thiocyanate Dihydrate. Ten milliliters of an aqueous 0.03 M solution (0.003 mol) of NaSCN was added to a boiling solution of 0.515 g (0.007 mol) of $Co(tbcyclen)(NO_3)_2{\cdot}H_2O$ in 25 ml of 95% ethyl alcohol. A light purple powder formed. The solution was heated over a water bath to evaporate the ethyl alcohol to approximately 15 ml. The remaining solution was filtered and the powder was washed with water and absolute ethyl alcohol; yield 0.469 g (88.7%). Anal. Calcd for $Co(tbcyclen)(SCN)_2{\cdot}2H_2O$: C, 61.35; H, 6.48; N, 11.30. Found: C, 61.37; H, 6.26; N, 10.99.

Results and Discussion

The elemental analyses of the compounds prepared in this study are consistent with the stoichiometry of $Co(tbcyclen)X_2$ (where X = NO_3, Cl, SCN, or Cl–ClO_4). All the complexes are varying shades of purple except $Co(tbcyclen)(NO_3)_2{\cdot}H_2O$ which is pink. These colors persisted when the compounds were dissolved in various nonaqueous solvents.

All of the compounds prepared in this study are one to one electrolytes in organic solvents (Table I). These data indicate that one anion is in the coordination sphere while the other anion is functioning as a noncoordinating counteranion. Further evidence that both anions are not in the coordination sphere around the cobalt(II) comes from the fact that the perchlorate anion replaced only one chloride in the complex $Co(tbcyclen)Cl_2{\cdot}H_2O$. Such evidence suggests that only one chloride is coordinated to the cobalt while the other chloride is functioning as a noncoordinating anion. Also only minor splittings were observed for Cl–O stretches in the complex $Co(tbcyclen)Cl{\cdot}ClO_4{\cdot}H_2O$ at 1100 and 1060 cm^{-1}. The splitting was not extensive enough to suggest coordination of the perchlorate anion.[22] Therefore the evidence indicates that the chloride is coordinated to the cobalt(II) and the perchlorate functions as an anion.

Table I. Conductivity Data for Co–tbcyclen Compounds

Compd	Conductance, Λ, Ω^{-1} cm^2 mol^{-1}		
	CH_3NO_2	CH_3CN	CH_3OH
$Co(tbcyclen)(NO_3)_2{\cdot}H_2O$	82.3	137	107
$Co(tbcyclen)Cl_2{\cdot}H_2O$	66.8		
$Co(tbcyclen)ClClO_4{\cdot}{}^1/_2H_2O$	64.2		
$Co(tbcyclen)(SCN)_2{\cdot}2H_2O$		129	

On the basis of the above data these complexes can have a coordination number of either 5 or 6. The five-coordinated cobalt complexes would have four nitrogens from the tbcyclen and a halide, a nitrate, or a thiocyanate bonded to the cobalt. If these complexes were six-coordinate, they would have four nitrogens from the tbcyclen bonded to the cobalt(II) and a monodentate anion and coordinated water in the coordination sphere. Also the nitrate can take up two positions in the coordination sphere if the nitrate functions as a bidentate ligand. It is possible to distinguish high-spin six-coordinate cobalt(II) complexes from high-spin five-coordinate cobalt(II) complexes. High-spin six-coordinate cobalt(II) complexes have magnetic moments between the ranges of 4.7 and 5.2 μ_B while the magnetic moments of high-spin five-coordinate cobalt(II) complexes are somewhat lower.[23-26] Also the electronic spectra of five- and six-coordinate cobalt(II) complexes are different enough to be diagnostic of the coordination number.[23-26]

The magnetic moments for $Co(tbcyclen)Cl_2{\cdot}H_2O$, $Co(tbcyclen)Cl{\cdot}ClO_4{\cdot}{}^1/_2H_2O$, and $Co(tbcyclen)(SCN)_2{\cdot}2H_2O$ (4.6, 4.6, and 4.8 μ_B, respectively) and their electronic spectra (Table II, Figure 1) are consistent with the other five-coordinate cobalt (II) complexes. Also, the infrared spectra showed a broad band around 3400 cm^{-1} which is indicative of lattice water, not coordinated water.[27] Therefore on the basis of the above data we conclude that all of the cobalt(II) complexes of tbcyclen except $Co(tbcyclen)(NO_3)_2{\cdot}H_2O$ have a coordination number of 5. Drieding models of the above complexes indicate that a trigonal-bipyramidal configuration around the cobalt(II) is less strained than a square-pyramidal configuration around the cobalt(II). These are believed to be the first trigonal-bipyramidal cobalt(II) complexes containing a macrocyclic ligand reported in the literature.

Although the spectra of $Co(tbcyclen)Cl_2{\cdot}H_2O$, $Co(tbcyclen)Cl{\cdot}ClO_4{\cdot}{}^1/_2H_2O$, and $Co(tbcyclen)(SCN)_2{\cdot}2H_2O$ in the solid phase and in nonaqueous solution reveal similarities which could be attributed to similar structures, there are differences in the number of bands, the position of the absorption maxima, and the extinction coefficients as a function of solvent for each of these compounds. The reason that bands in the infrared region were observed in the diffuse-transmittance spectra but not in solution was that these compounds have low solubilities in most solvents and the bands in the infrared region are likely to have relatively small extinction coefficients. A reason for the differences observed in the electronic spectra as a function of solvent and complex may be the fact that the coordinated anion can be partially displaced by a polar solvent. A plot of the equivalent conductance of $Co(tbcyclen)Cl_2{\cdot}H_2O$ in nitromethane vs. the square root of the equivalent concentration resulted in a curve. Such a deviation from linearity usually indicates that the coordinated

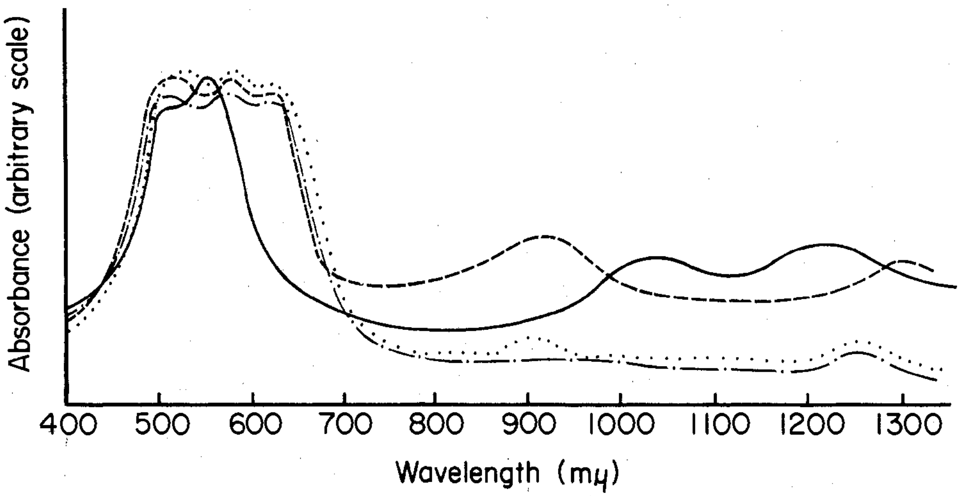


Figure 1. Electronic spectra of cobalt(II)–tbcyclen compounds in the solid state: —, $[Co(tbcyclen)NO_3]NO_3\cdot H_2O$; - - -, $[Co(tbcyclen)Cl]Cl\cdot H_2O$; · · ·, $[Co(tbcyclen)Cl]ClO_4\cdot {}^1/_2H_2O$; —·—, $[Co(tbcyclen)SCN]SCN\cdot 2H_2O$.

Table II. Electronic Spectra of Co(II)–tbcyclen Compounds

Compd	Medium	Max., mμ (ε)
$[Co(tbcyclen)Cl]Cl\cdot H_2O$	Solid	535, 610, 670, 900 1250
	CH_3CN	536 (62), 580 (53.5), 612 (58)
	CH_3OH	530 (58), 585 (44), 610 (59)
	C_2H_5OH	530 (57.5), 575 (49), 605 (53), 900 (12), 1280 (19.4)
	CH_3NO_2	530 (145), 605 (167.5), 640 (157.5), 700 (130)
$[Co(tbcyclen)Cl]ClO_4\cdot {}^1/_2H_2O$	Solid	530, 610, 680, 1250
	CH_3NO_2	530 (81), 570 (69), 610 (73)
	CH_3OH	530 (70.5), 580 (63), 610 (65.5)
$[Co(tbcyclen)NCS]SCN\cdot 2H_2O$	Solid	515, 600, 660, 1175
	CH_3CN	520 (225), 590 (150), 850 (70), 975 (45), 1170 (80)
$[Co(tbcyclen)NO_3]NO_3\cdot H_2O$	Solid	500, 540, 1000, 1175
	CH_3NO_2	510 (32), 540 (40), 630 sh, 1000 (6.2), 1210 (8.2)
	CH_3CN	500 (42), 540 (50), 630 sh, 1000 (6.0), 1200 (7.5)
	H_2O	496 (80), 575 (56.7)

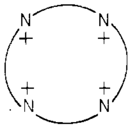
chloride is being partially displaced by the solvent.[28] Therefore, a mixture of solvated and unsolvated species exists in solution. It is for this reason that some of the spectra vary as a function of solvent. Adding NH_4Cl to a solution of $[Co(tbcyclen)Cl]Cl\cdot H_2O$ in C_2H_5OH resulted in shifting most of the bands to lower energies. The added chloride ions shift the equilibrium to less $[Co(tbcyclen)C_2H_5OH]^{2+}$ and more $[Co(tbcyclen)Cl]^+$.

The magnetic moment for $Co(tbcyclen)(NO_3)_2\cdot H_2O$ is considerably higher than those of all other complexes prepared in this study. A magnetic moment of 5.01 μ_B is within the range expected for high-spin six-coordinated cobalt(II) compounds. Also the electronic spectrum for $Co(tbcyclen)(NO_3)_2\cdot H_2O$ is consistent with those of the other published six-coordinated cobalt(II) complexes (Table II).[23] Since the electronic spectra in solution and in the solid state are similar, we conclude that the geometries of $Co(tbcyclen)(NO_3)_2\cdot H_2O$ are also similar in both states. The broad peak around 3400 cm^{-1} suggests that the H_2O in $Co(tbcyclen)(NO_3)_2\cdot H_2O$ is not coordinated to the cobalt(II). Also, the conductivity of $Co(tbcyclen)(NO_3)_2\cdot H_2O$ in organic solvents (Table I) indicates that this complex is a one to one electrolyte. Therefore we conclude that one of the nitrates is probably coordinated to the cobalt(II) as a bidentate ligand while the other nitrate functions as a counteranion. By comparing the infrared spectra of solid $Co(tbcyclen)(NO_3)_2\cdot H_2O$ and $Co(tbcyclen)Cl_2\cdot H_2O$ and by eliminating peaks associated with the ligand tbcyclen it was possible to tentatively assign the frequencies 1530 and 1185 cm^{-1} to the bidentate nitrate.[29–31] The absorptions at 1355 and 830 cm^{-1} could be due to the counteranion NO_3^-.[32] On the basis of models and the above data we conclude that $Co(tbcyclen)(NO_3)_2\cdot H_2O$ has a cis-octahedral configuration in the solid state and in organic solvents. A similar cis-octahedral geometry was observed for $Ni(tbcyclen)(NO_3)_2\cdot {}^1/_2H_2O$.[9]

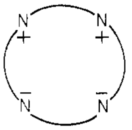
The electronic spectrum of $Co(tbcyclen)(NO_3)_2\cdot H_2O$ in aqueous solution is different from that observed in organic solvents (Table II). The spectrum in water resembles the spectra for all of the other five-coordinated Co–tbcyclen complexes. Therefore, either one of the coordinated oxygens on the bidentate nitrate dissociated from the cobalt(II) and reduced the coordination number from 6 to 5 or water displaced the coordinated nitrate ion. The chemistry of $Ni(tbcyclen)(NO_3)_2\cdot {}^1/_2H_2O$ is similar to that of $Co(tbcyclen)(NO_3)_2\cdot H_2O$. The bidentate nitrate in $Ni(tbcyclen)(NO_3)_2\cdot {}^1{}_2H_2O$ is displaced by water to form in solution $Ni(tbcyclen)H_2O^{2+}$. Partial proof that water displaces the coordinated nitrate from the nickel(II) is that $Ni(tbcyclen)(NO_3)_2\cdot {}^1/_2H_2O$ is a two to one electrolyte in water.[9] Therefore neither of the nitrates is coordinated to the nickel(II) in aqueous solution. Unfortunately the low solubility of $Co(tbcyclen)(NO_3)_2\cdot H_2O$ prevents the obtaining of conductivity data to confirm that this compound is also a two to one electrolyte in aqueous solution.

The extinction coefficients observed for all solution spectra are unusually high, but similar high extinction coefficients were observed by Collman and Schneider[6] for the cobalt(III) complexes of cyclen and by Kalligeros and Blinn[9] for the $Ni(tbcyclen)X_2$ complexes. These high extinction coefficients were attributed to the low symmetry of the complex and strained metal to nitrogen bonds. Collman and Schneider's explanation for the high extinction coefficients of their compounds is consistent with the crystallographic data observed on [Co(cyclen)(NO$_2$)$_2$]Cl.[7]

The configuration of the ligand tbcyclen around the cobalt(II) can be speculated from models. The benzyl groups could be positioned on the same side of the metal ion (II). A similar configuration was observed by Barefield and Wagner[33] for the square-pyramidal complex [Zn(*N*-Me$_4$cyclam)Cl]Cl.[34] Another possibility is that the two adjacent benzyl groups could be positioned on one side of the metal ion while the other two benzyl groups can be positioned on the opposite side. The product of N-alkylation of Ni(cyclam)$^{2+}$ [34] has such a configuration (III).[34] Other configurations are possible but have not been observed for planar complexes. However, unlike the 14-membered ring *N*-Me$_4$cyclam, the smaller 12-membered ring tbcyclen must fold around the faces of either an octahedron or a trigonal bipyramid. On the basis of models, the least sterically strained configuration of the tbcyclen around cobalt(II) appears to be one in which the two trans benzyl groups are on one side of the metal ion while the other two trans benzyl groups are on the opposite side of the metal ion (IV and V). Such a geometry will minimize the front- and back-strain imposed by the benzyl groups. Even in this configuration the two benzyl groups on the back side of the molecule (pointing away from the monodentate ligands) are so close together that there is still considerable intramolecular crowding between benzyl groups. The back-strain in these complexes is much greater than the front-strain. A reduction of the steric interaction of the benzyl groups in the back of these complexes can be attained by increasing the N–Co–N bond anle in the equatorial plane from 90° (the octahedral geometry), IV, to 120° (the trigonal-bipyramidal geometry), V. Most nickel(II) and cobalt(II) complexes of the tbcyclen were found to have a coordination number of 5 instead of 6. Despite the reduced nonbonding interactions in the trigonal-bipyramidal configuration the steric constraints imposed by the bulky ligand should result in a distorted coordination polyhedron.

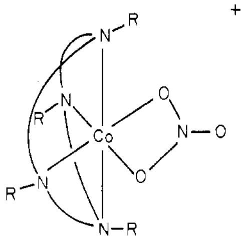


II

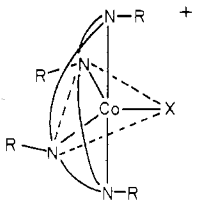


III

+ and – represent the R groups above or below the plane of the paper



IV



V

A unique property of the ligand tbcyclen is that it stabilizes the divalent state of cobalt instead of the trivalent state. We know of no published report of a saturated nitrogen-containing polydentate ligand that stabilized the divalent state for cobalt. All attempts to oxidize Co(tbcyclen)(NO$_3$)$_2$·H$_2$O by direct aeration or by the addition of a 100-fold molar excess of H$_2$O$_2$ have failed. The cyclic voltammogram of Co(tbcyclen)(NO$_3$)$_2$·H$_2$O in a methanol–water mixture (85% CH$_3$OH), using a 0.5 M NaCF$_3$CO$_2$ electrolyte, showed only the oxidation of the solvent.

Cobalt(II) complexes coordinated to relatively strong-field ligands in aqueous solution are unstable in the presence of oxygen and will oxidize to cobalt(III).[36] In general cobalt(II) coordinated to a nitrogen polydentate ligand in aqueous solution can usually be easily oxidized to the trivalent state using O$_2$ or H$_2$O$_2$. Also the standard reduction potentials of most cobalt(III) complexes are more negative than the reduction potential for oxygen–water, 1.185 V.[37] For example the reduction potential of Co(NH$_3$)$_6^{3+}$ in water is +0.1 V[38] and the half-wave potential of [Co(cyclam)(NO$_2$)$_2$]$^+$ in methanol is −0.459 V.[38,39] In contrast, cobalt(II) complexes coordinated to weak-field ligands such as H$_2$O are stable in aqueous solution with respect to oxidation.[36] The reduction potential for Co(H$_2$O)$_6^{3+}$ is +1.84 V.[37] Also, it has been observed that the more saturated the coordinated macrocyclic ligand, the easier it is to oxidize the Co(II) macrocyclic complex to the Co(III) macrocyclic complex.[39] Since the ligand tbcyclen is totally saturated, it would be expected to stabilize the cobalt(III) relative to the cobalt(II) state. Since this is not the case, the ligand tbcyclen must be an unusually weak polyamine ligand. Support for the contention that tbcyclen is a weak-field ligand can be made by comparing the *Dq* for Ni(tbcyclen)(NO$_3$)$_2$·$^1/_2$H$_2$O with that for the isostructural Co(tbcyclen)(NO$_3$)$_2$·H$_2$O. The *Dq* value observed for Ni(tbcyclen)(NO$_3$)$_2$·$^1/_2$H$_2$O (975 cm^{-1}) is between the values observed for water and ammonia.[9] The *Dq* value for tbcyclen bonded to cobalt(II) may also be between the *Dq* values observed for the NH$_3$ and the H$_2$O since it was observed that Co(II)–tbcyclen complexes are stable in the presence of water but in an aqueous ammonia solution the ligand is displaced by ammonia and tbcyclen precipitates out of solution.

The difficulty in oxidizing the Co(II)–tbcyclen compounds to the cobalt(III) compounds may also be due to the steric hindrance imposed by the benzyl groups. The cobalt(III) ion is usually observed to have a coordination number of 6. Since the benzyl groups on the nitrogen atoms inhibit the formation of a six-coordinate octahedral geometry for both Co(II)– and Ni(II)–tbcyclen complexes (except in the cases where the anion is a small sized weak field bidentate ligand), then it should be even more difficult to attain a coordination number of 6 around the smaller cobalt(III) ion. Therefore the oxidation of Co(tbcyclen)(NO$_3$)$_2$·H$_2$O might be difficult because the resulting six-coordinate Co(III)–tbcyclen complex is not kinetically attainable. The steric constraints of the bulky cyclic ligand inhibited the compression of the cobalt–nitrogen bonds. In contrast, the less bulky ligand cyclen should have fewer nonbonding steric interactions than tbcyclen and therefore cyclen complexes of cobalt(III) can be easily prepared by the oxidation of Co(II)–cyclen complexes.[6]

Co(tbcyclen)(NO$_3$)$_2$·H$_2$O is kinetically stable in water for 24 h at pH 3. At lower pH values the complex precipitates. Generally, compounds which contain a macrocyclic ligand that coordinates coplanar to a metal ion resist stepwise dissociation in acid while compounds containing linear ligands undergo rapid dissociation in acid.[11,12] However, the decomposition of Co(tbcyclen)(NO$_3$)$_2$·H$_2$O in an acetone–water mixture at approximately pH 3 is too fast to measure by conventional techniques. One explanation for the faster rate of decomposition of Co(tbcyclen)(NO$_3$)$_2$·H$_2$O in acetone–water compared to that in pure water may be due to the acetone better solvating the tbcyclen than water as the tbcyclen is dissociating from the metal ion. A quantitative study of the rates of decomposition of a variety of metal–tbcyclen complexes is currently in process.

Acknowledgment. Acknowledgment is made to the donors of the Petroleum Research Fund, administered by the American Chemical Society, for partial support of this research; acknowledgment is also made for partial support from the