Synthesis, characterization, and X-ray crystal structures of cobalt(II) and cobalt(III) complexes of four topologically constrained tetraazamacrocycles

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Abstract

The high spin Co2+ complexes of 4,11-dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane (1), 4,10-dimethyl-1,4,7,10-tetraazabicyclo[6.5.2]pentadecane (2), 4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane (3), and racemic-4,5,7,7,11,12,14,14-octamethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane (4) have been synthesized and characterized by X-ray crystallography. The Co(III) complexes of 1–3 were also prepared by the chemical oxidation of the Co(II) complexes. The X-ray crystal structures of Co(1)Cl2, Co(3)Cl2, and [Co(3)Cl2]PF6 demonstrate that the ligands enforce a distorted octahedral geometry on Co(II) and Co(III) with two cis sites occupied by chloro ligands. In contrast, the Co(II) complex of 4 is five-coordinate with trigonal bipyramidal geometry. The methyl groups substituted on the carbon atoms of ligand 4 define a shallow cavity, allowing only one chloride ligand to bind to the chelated metal ion. This difference in coordination geometry causes Co(4)Cl+ to be much more difficult to oxidize (E1/2 = 1.176 V vs. SHE) than the octahedral Co(II) complexes of 1–3 (E1/2 from −0.157 to 0.173 V vs. SHE). The Co(III) complexes of 1–3 have three absorbances in their electronic spectra, while typical cis-Co(III)N4X2 complexes have only two. This additional splitting of energy states is attributed to the increased distortion from octahedral resulting from the short ethylene cross-bridge on the macrobicyclic ligands.

Keywords: X-ray crystal structures; Cobalt(II) complexes; Cobalt(III) complexes; Tetraazamacrocycles

1. Introduction

Co(II) and Co(III) complexes provide the historical basis for much of modern coordination chemistry [1]. When new ligands are synthesized, their complexes with these metal ions can be used to compare the properties of the new ligands with those in the vast database of known Co(II) and Co(III) complexes. In the present case, ethylene cross-bridged tetraazamacrocycles provide the relatively unusual ligand set to which the cobalt test is to be applied. These ligands (Fig. 1) are relatively simple derivatives of the ubiquitous tetraazamacrocycles but have only recently been prepared by an elegant extension of the well-known glyoxal-tetraazamacrocycle condensation reaction [2,3]. Exploitation of the folded glyoxal condensates derived from the 12-, 13-, and 14-membered macrocycles by selective alkylation of non-adjacent nitrogen atoms facilitates synthesis of the ethylene cross-bridged products in high yield [2–4]. The short cross-bridge imparts unique characteristics to these ligands. First, they are extremely basic and some of them are legitimately described as proton sponges [2,5,6]. This property, discussed in detail elsewhere [5], makes complexation with metal ions difficult under protic conditions because of the competition between protons and the metal ions for the nitrogen donors [7]. Our own studies [4,5,7,8] have shown that elimination of protons from reaction media overcomes

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2. Experimental

CoCl₂ (99.99%) and NH₄PF₆ (99%) were purchased from Aldrich Chemical Company and used as received. Cyclam, [14]aneN₄, was provided by Procter & Gamble, [13]aneN₄ was purchased from the Kansas Advanced Synthetic Laboratory of the University of Kansas, and cyclen, [12]aneN₄, was provided by Dow Chemical Co. All solvents were of reagent grade and were dried, when necessary, by accepted procedures [9].

Elemental analyzes were performed by the Analytical Service of the University of Kansas, Desert Analytics, or Quantitative Technologies, Inc. Mass spectra were measured by the Analytical Service of the University of Kansas on a VG ZAB HS spectrometer equipped with a xenon gun. The matrices used were NBA (nitrobenzyl alcohol) and TG/G (thioglycerol/glycerol).

2.1. Synthesis

4,11-Dimethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane (1), 4,10-dimethyl-1,4,7,10-tetraazabicyclo[6.5.2]-pentadecane (2), and 4,10-dimethyl-1,4,7,10-tetraazabicyclo[5.5.2]tetradecane (3), were synthesized from [14]aneN₄, [13]aneN₄, and [12]aneN₄, respectively, according to literature procedures [2,3]. A full description (including structural characterization of various precursors) of the synthesis of racemic-4,5,7,7,11,12,14,14-octamethyl-1,4,8,11-tetraazabicyclo[6.6.2]hexadecane (4) has been published [4].

2.1.1. CoLCl₂ (L = 1–3)

The ligand (1 mmol) was dissolved in 20 ml of dry MeCN in a 25 ml erlenmeyer flask in an inert atmosphere glovebox. Anhydrous CoCl₂ (130 mg, 1 mmol) was added to the stirring ligand solution, which immediately began to develop an intense purple color. The reaction mixture was stirred for 16 h at room temperature (r.t.), before being filtered to remove traces of solids. Ether diffusion into the MeCN solution in the glovebox yielded dark purple X-ray quality crystals of the pure complexes. Yields: 70–75%. Co(1)Cl₂: Anal. Calc. for C₁₄H₃₆Cl₂CoN₄: C, 43.76; H, 7.87; N, 14.58. Found: C, 43.48; H, 7.93; N, 14.24%. Co(2)Cl₂: Anal. Calc. for C₁₃H₂₃Cl₂CoN₄: C, 42.17; H, 7.62; N, 15.13. Found: C, 41.86; H, 7.58; N, 15.24%. Co(3)Cl₂: Anal. Calc. for C₁₂H₂₀Cl₂CoN₄: C, 40.46; H, 7.36, N, 15.73. Found: C, 40.36; H, 7.47; N, 15.65%. FAB⁺ mass spectra in MeCN (NBA matrix) exhibited peaks at m/z = CoL⁺ and CoLCl⁺ for all complexes.

2.1.2. [Co(4)Cl]₂[CoCl₄]

The ligand (4) (338 mg, 1 mmol) was dissolved in 20 ml of anhydrous DMF at 50–60 °C in a 25 ml erlenmeyer flask in an inert atmosphere glovebox. Anhydrous CoCl₄ (130 mg, 1 mmol) was added to the stirring ligand solution. The reaction mixture was stirred at 50–60 °C for 16 h, during which time, the solution became dark blue and all of the CoCl₂ dissolved. Filtration of the cooled solution removed traces of brown solids. Ether diffusion into the DMF solution in the glovebox resulted in dark blue X-ray quality crystals of the pure product in 48% yield (based on ligand). Anal. Calc. for C₄₀H₃₆Cl₆Co₂N₈: C, 45.04; H, 7.94; N, 10.51. Found: C, 44.73; H, 7.72; N, 10.57%. The FAB⁺ mass spectrum in DMF (NBA matrix) exhibited peaks at m/z = CoL⁺ and CoLCl⁺.
2.1.3. [Co(4)Cl]PF₆
[Co(4)Cl₂][CoCl₄] (250 mg, 0.234 mmol) was dissolved in 16 ml of dry MeOH in air. The blue solid dissolved in 16 ml of dry MeOH and chilling in a freezer, resulted in the precipitation of a pale purple solid. The powder produced was collected by filtration, washed with MeOH and ether and dried in vacuo. Yield: 55%, based on Co(4)Cl⁺. Anal. Calc. for C₂₀H₄₂ClCoF₆N₄P: C, 30.31; H, 5.48; N, 10.59. Found: C, 31.77; H, 5.71; N, 10.59. Found: C, 31.89; H, 5.41; N, 10.34%. ¹H NMR (400 MHz, CD₃CN): 1.75 (d, 1H), 1.86 (d, 1H), 2.24–2.27 (m, 1H), 2.35 (dd, 1H), 2.50 (dd, 1H), 2.60 (s, 4H), 2.66 (t, 1H), 2.75 (s, 6H), 2.84 (dd, 1H), 3.02–3.04 (m, 1H), 3.13 (td, 1H), 3.24–3.34 (m, 2H), 3.34–3.41 (m, 2H), 3.49 (q, 1H), 6.75, 70.54. FAB⁺ mass spectra in MeCN (TG/G matrix) exhibited peaks at m/z = CoCl⁺ and CoCl₂⁺ for all complexes.

2.2. Physical methods
Electrochemical experiments were performed on a Princeton Applied Research Model 175 programmer and Model 173 potentiostat in dry CH₃CN using a homemade cell in an inert atmosphere dry box under N₂. A button Pt electrode was used as the working electrode in conjunction with a Pt-wire counter electrode and a Ag-wire pseudo-reference electrode. Tetrabuty-lammonium hexafluorophosphate (0.1 M) or nBu₄NCl (0.1 M) was the supporting electrolyte in all cases. The measured potentials were referenced to SHE using ferrocene (+0.400 V vs. SHE) as the internal standard.

Magnetic studies were performed in the solid state on a Johnson Matthey MSBI magnetic susceptibility balance. The air sensitive Co(II) complexes were packed into the sample tube and sealed under nitrogen to prevent oxidation during the experiment. Diamagnetic corrections were based on literature values [10a]. Alternatively, the magnetic moment was determined by the Evans = NMR method [10b,10c] using a Bruker DRX400 spectrometer.

Conductance measurements [11] were obtained with a YSI Model 35 conductance meter at r.t. on 1 mM solutions. The air sensitive Co(II) complex solutions were prepared in an inert atmosphere glovebox, sealed, and transferred to an Ar filled glove bag where the conductances were measured.

¹H and ¹³C NMR spectra were recorded with a Bruker DRX400 spectrometer. Electronic spectra were recorded using a Cary 3 spectrophotometer controlled by a Dell Dimension XPS P133s computer.

2.3. Crystal structure analysis
X-ray data for Co(1)Cl₂, Co(3)Cl₂, and [Co(4)Cl]₃-[CoCl₄] were collected with a Siemens SMART [12] three-circle system with CCD area detector using graphite monochromated Mo Kα radiation. The crystals were held at 180 K with the Oxford Cryosystem Cooler [13]. Absorption corrections were applied by the multi-scan method, and none of the crystals showed any decay during data collection. These structures were solved by direct methods using SHELXS [14] (TREF) with additional light atoms found by Fourier methods. Hydrogen atoms were added at calculated positions and refined using a riding model. Anisotropic displacement parameters were used for all non-H atoms, while H-atoms were given isotropic displacement parameters equal to 1.2 (or 1.5 for methyl hydrogen atoms) times the equivalent isotropic displacement parameter for the atom to which the H-atom is attached. Refinement
used sHELXL-96 [15]. The final R-values for [Co(4)Cl₃]₂[CoCl₄] are affected by the presence of disordered DMF and water in the lattice, and by its weak diffraction. In [Co(4)Cl₃][CoCl₄], of the two independent cations, one is partly disordered with alternative methyl positions. The asymmetric unit contains two approximately 0.5 occupied DMF and one 0.25 water molecule. These disordered atoms were held isotropic. Despite the relatively high R-value, the overall structure is clearly defined.

For [Co(3)Cl₂]PF₆, X-ray data were collected with a Rigaku AFC5R diffractometer with graphite monochromated Cu Kα radiation and a rotating anode generator. An absorption correction was applied by the ψ-scan method. This structure was solved by direct methods using sHEL-92 [16] and expanded using Fourier techniques (DIRDIF-94) [17]. Refinement used sHELXL-96 [15]. The final R-values for this structure are affected by the presence of a highly mobile PF₆ group.

Crystal data appear in Table 1 and selected bond lengths and angles for all structures are in Table 2.

3. Results and discussion

3.1. Preparation of metal complexes

Due to the great proton affinity of ligands 1–4, [2,5,6] the preparation of their complexes is difficult in protic solvents [7]. However, if care is taken to eliminate protons from solution, a wide range of transition metal ions can successfully coordinate with them [4,5,7,8]. For this reason, anhydrous CoCl₂ was mixed with the ligands in aprotic solvents (MeCN or DMF) under an inert atmosphere to give the Co(II) complexes (Fig. 2). Ether diffusion into the filtered reaction mixtures yielded X-ray quality crystals of all four Co(II) complexes.

The unusual kinetic stability imparted by these cross-bridged ligands [4,7,8] is helpful in the synthesis of the Co(III) complexes of 1–3. Whereas synthesis of complexes of these ligands is prevented by the presence of protons, once the complexes are formed, even with metal ions that are usually labile, they have uncommon kinetic stabilities under harsh aqueous conditions [18]. This facilitates the air oxidation of the Co(II) complexes of 1–3 by dissolving the complexes in concentrated HCl and bubbling air through the solution. After removing the solvent and excess HCl under vacuum, the PF₆⁻ salts of the CoCl₂⁺ cations can be precipitated in pure form from MeOH solutions. The air oxidation of the complex of the highly methylated ligand, Co(4)Cl⁺, under similar conditions failed to produce the Co(III) analogue. Clearly, the five-coordinate structure (vide infra) destabilizes Co(III) to such an extent that air is not effective as the oxidizing agent. The electrochemistry of all four complexes (vide infra) is helpful in explaining this difference in behavior.

3.1.1. Crystal structures

X-ray quality crystals of all four Co(II) complexes were obtained, but the structure of Co(2)Cl₂ (not reported here) proved difficult to solve because of disorder in the macrocyclic ring. Views of the structures of Co(1)Cl₂, Co(3)Cl₂, and Co(4)Cl⁺ are shown in Fig. 3(a–c). Complex Co(3)Cl₂ contains two independent molecules in the asymmetric unit, while [Co(4)Cl₃]₂[CoCl₄] has two independent cations. For the first, the two molecules are virtually identical apart from a slight change in the bridge conformation, with maximum deviations between equivalent atoms of 0.2× (after making a best fit between them). Deviations between the independent cations of Co(4) are slightly greater but still hardly significant, reaching a maximum of 0.3× for one pair of methyl groups. As in other structures of these ligands with Mn(II), Fe(II), and Ni(II), the Co(II) complexes of 1 and 3 have six-coordinate pseudo-octahedral geometries in which the macrobicycle occupies axial and cis equatorial coordination sites. The remaining equatorial sites are occupied by two chloro ligands. The trigonal bipyramidal structure of Co(4)Cl⁺ offers a fascinating contrast. While the macrobicycle binds in the familiar fashion, two of the six C-methyl groups on the macrocyclic ring join with the two N-methyl groups to create a shallow cavity that provides space for only one chloro ligand. The result is that the Co in the complex of 4 has a five-coordinate, trigonal bipyramidal geometry (Fig. 3(c)), even though the ligand is very similar in size and shape to 1.

A more detailed inspection of the three structures shows that they follow several trends previously observed in the structures of the analogous Mn(II), Fe(II), and Ni(II) complexes [5,7,8]. First, the size of the ring system dictates the distortion of the octahedron or trigonal pyramid. The 14-membered ring in 1, engulfs the metal ion more fully than does the 12-membered ring in 3. The N⁶–M–N⁶ bond angle for Co(1)Cl₂ is 172.4(2)°, while that for Co(3)Cl₂ is only 149.81(9)°. The smaller angle for the smaller macrobicycle demonstrates a decreased complementarity of the ligand for the metal ion; this misfit leaves the metal ion protruding more extensively from the ligand cavity. For Co(4)Cl⁺, the corresponding angle is 175.0(6)° although direct comparison is less appropriate because of the unique geometry of the cobalt complex. The slightly smaller angle for 1, compared to 4, may result from the steric bulk of the two chloro ligands in Co(1)Cl₂, preventing Co(II) from going as deeply into the ligand cavity.

A related phenomenon is that the Co²⁺ ion sinks more deeply into the cavities of both macrobicycles than do the larger Mn²⁺ and Fe²⁺ ions, but to a lesser extent.
than the smaller Ni\textsuperscript{2+} and Cu\textsuperscript{2+} [5,7,8]; this has been discussed in detail elsewhere [5].

X-ray quality crystals of the Co(III) complex of 3 were also obtained by diffusion of ether into an acetonitrile solution. This structure is represented in Fig. 3(d). The only overall changes from the Co(II) complex of 3 are the reduction in metal bond lengths consistent with the oxidation state changes and the movement of the smaller Co(III) ion further into the macrocyclic cavities, as evidenced by the increase in the N\textsubscript{ax}–M–N\textsubscript{ax} and N\textsubscript{eq}–M–N\textsubscript{eq} bond angles: N\textsubscript{ax}–Co(II)–N\textsubscript{ax} = 149.81(9) and N\textsubscript{ax}–Co(III)–N\textsubscript{ax} = 168.84(4), while N\textsubscript{eq}–Co(II)–N\textsubscript{eq} = 80.86(8) and N\textsubscript{eq}–Co(III)–N\textsubscript{eq} = 87.2(4). Similar size effects have been observed for the series of ions Mn(II)–Cu(II) in ligands 1 and 3 [5] and for the Mn(III) complexes with 1 and 3 [7e].

These structures represent the first cobalt complexes structurally characterized for these constrained ligands. In the complexes of the unbridged parent macrocycles, [14]aneN4 (1,4,8,11-tetraazacycletetradecane) generally binds metal ions in a square planar fashion [19,20], leaving two labile ligand binding sites at the trans, axial positions of an octahedral complex. In contrast, [12]aneN4 is too small to fit completely around the metal ion, and generally folds to occupy two cis equatorial and two axial sites of octahedral metal ions [21], paralleling the coordination mode reported here for 1 and 3. The short cross-bridge of 1, forces the [14]aneN4 ring system to behave more like [12]aneN4. The effects of the two cis labile sites have on the reactivity of the complexes are currently being explored.

3.1.2. Electronic structure

The magnetic moments of the three Co(II) complexes CoL\textsubscript{2} (L = 1–3) were obtained on the solid samples taking care to keep the complexes under an inert atmosphere. The moments fall into the normal range for high spin, octahedral d\textsuperscript{7} Co(II) complexes [10]: \( \mu_{\text{eff}} = 4.94 \) B.M. for Co(1)Cl\textsubscript{2}, \( \mu_{\text{eff}} = 4.81 \) B.M. for Co(2)Cl\textsubscript{2}, and \( \mu_{\text{eff}} = 5.08 \) B.M. for Co(3)Cl\textsubscript{2}. The magnetic moment of [Co(4)Cl]PF\textsubscript{6} was found to be \( \mu_{\text{eff}} = 4.32 \) B.M. This value is consistent with high spin five-coordinate Co(II) complexes, which typically have slightly lower moments than octahedral complexes, with observed values as low as 4.3 B.M [22–25]. This
Fig. 2. Synthesis of Co(II) complexes: (a) with ligands having unsubstituted rings, 1–3, in acetonitrile; and (b) with a hexamethylated ring, 4, in DMF.

Table 2
Selected bond lengths (Å) and angles (°)

<table>
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<tr>
<th></th>
<th>Co(1)Cl₂</th>
<th>Co(3)Cl₂</th>
<th>Co(4)Cl⁺</th>
<th>Co(3)Cl₂⁺</th>
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<tr>
<td>Bond lengths</td>
<td></td>
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<tr>
<td>Co(1)–N(1)</td>
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<td>Co(1)–N11</td>
<td>2.164(2)</td>
<td>Co(1)–N(11)</td>
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<td>Co(1)–N(8)</td>
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<td>Co(1)–N71</td>
<td>2.181(2)</td>
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<td>Co(1)–N(4)</td>
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<td>Co(1)–N41</td>
<td>2.217(2)</td>
<td>Co(1)–N(11)</td>
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<tr>
<td>Co(1)–N(11)</td>
<td>2.252(4)</td>
<td>Co(1)–N101</td>
<td>2.221(2)</td>
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<tr>
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<tr>
<td>Co(1)–Cl(2)</td>
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<td>Co(1)–Cl(2)</td>
<td>2.4121(8)</td>
<td>Co(1)–Cl(2)</td>
</tr>
</tbody>
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| Bond angles |          |          |          |           |
| N(1)–Co(1)–N(8) | 81.11(13) | N(11)–Co(1)–N(14) | 89.3(5) | Cl(1)–Co(1)–Cl(2) | 87.9(1) |
| N(1)–Co(1)–N(4) | 83.6(2) | N(11)–Co(1)–N(11) | 92.1(6) | Cl(1)–Co(1)–N(2) | 93.0(3) |
| N(8)–Co(1)–N(4) | 90.4(2) | N(14)–Co(1)–N(11) | 84.5(6) | Cl(1)–Co(1)–N(4) | 179.3(3) |
| N(1)–Co(1)–N(11) | 91.5(2) | N(11)–Co(1)–N(18) | 84.0(5) | Cl(2)–Co(1)–N(2) | 179.1(3) |
| N(8)–Co(1)–N(11) | 83.1(2) | N(14)–Co(1)–N(18) | 92.3(5) | Cl(2)–Co(1)–N(4) | 91.8(3) |
| N(4)–Co(1)–N(11) | 172.4(2) | N(11)–Co(1)–N(18) | 175.06(6) | N(1)–Co(1)–N(3) | 168.8(4) |
| N(1)–Co(1)–Cl(1) | 170.53(10) | N(11)–Co(1)–Cl(1) | 133.7(4) | N(2)–Co(1)–N(3) | 84.3(4) |
| N(8)–Co(1)–Cl(1) | 91.47(10) | N(14)–Co(1)–Cl(1) | 137.1(4) | N(3)–Co(1)–N(4) | 87.7(4) |
| N(4)–Co(1)–Cl(1) | 90.58(12) | N(11)–Co(1)–Cl(1) | 91.5(4) | Cl(1)–Co(1)–N(1) | 96.4(3) |
| N(11)–Co(1)–Cl(1) | 93.46(13) | N(101)–Co(1)–Cl(1) | 93.5(4) | Cl(1)–Co(1)–N(3) | 91.7(3) |
| N(1)–Co(1)–Cl(2) | 90.73(9) | N(11)–Co(1)–Cl(2) | 174.75(6) | Cl(2)–Co(1)–N(1) | 92.4(3) |
| N(8)–Co(1)–Cl(2) | 168.84(10) | N(14)–Co(1)–Cl(2) | 94.06(6) | Cl(2)–Co(1)–N(3) | 95.7(3) |
| N(4)–Co(1)–Cl(2) | 96.27(10) | N(101)–Co(1)–Cl(2) | 102.30(6) | N(1)–Co(1)–N(2) | 87.5(4) |
| N(11)–Co(1)–Cl(2) | 89.59(12) | N(101)–Co(1)–Cl(2) | 98.91(6) | N(1)–Co(1)–N(4) | 84.3(4) |
| Cl(1)–Co(1)–Cl(2) | 97.37(4) | Cl(11)–Co(1)–Cl(21) | 91.48(3) | N(2)–Co(1)–N(4) | 87.2(4) |

measurement, taken on a CD₃CN solution of the complex, indicates that the Co(4)Cl⁺ cation retains its five-coordinate geometry in solution.

The electronic spectra of the Co(II) complexes (L = 1–3) in acetonitrile are similar to those of other high spin octahedral Co(II) complexes, having a single major absorption band centered between 500 and 600 nm (in the present cases, split into two overlapping maxima), as exemplified by the Co(2)Cl₂ spectrum, Fig. 4(a); this is due to the ⁴T₁₈g(P) → ⁴T₁₈g(D) transition [26]. The weak shoulder at 672 nm is probably due to the transition to [4]A₂g and is only clearly observed for this complex. The absorption maxima and extinction coefficients are as follows: for Co(1)Cl₂ λ_max = 540 (24 M⁻¹ cm⁻¹) and 558 nm (21 M⁻¹ cm⁻¹), for Co(2)Cl₂ λ_max = 544 (23 M⁻¹ cm⁻¹) and 568 nm (22 M⁻¹ cm⁻¹), and for
Fig. 3. Representations from crystal structures of: (a) Co(1)Cl$_2$; (b) Co(3)Cl$_2$; (c) Co(4)Cl$^-$; and (d) Co(3)Cl$_2^+$. Crystal data are given in Table 1. Selected bond lengths and angles may be found in Table 2, and atomic coordinates are collected in Tables 3–5, and in the supplementary material.
Co(3)Cl2 ϵmax = 546 (34 M⁻¹ cm⁻¹) and 568 nm (35 M⁻¹ cm⁻¹). The somewhat higher extinction coefficients for Co(3)Cl2 may result from the more distorted geometry caused by the smaller ligand.

As expected, the spectrum of [Co(4)Cl]⁺ (Fig. 4(b)) is quite different from that of the three octahedral complexes, exhibiting at least four major bands in the region 300–1100 nm: ϵmax = 474 (30 M⁻¹ cm⁻¹), 556 (41 M⁻¹ cm⁻¹) and 583 nm (40 M⁻¹ cm⁻¹) for this split band, ϵmax = 728 (9.3 M⁻¹ cm⁻¹), and 989 nm (8.7 M⁻¹ cm⁻¹). Comparison with other high spin, five-coordinate Co(II) spectra reveals a similarity to known trigonal bipyramidal complexes, as expected on the basis of the the crystal structure and magnetic moment (vide supra) [22–26].

The Co(III) complexes of 1–3 are low spin d⁶ and diamagnetic, as evidenced by sharp proton and carbon nmr spectra, indicating electronic structures typical of octahedral Co(III) amine complexes [1]. Their electronic spectra, however, are not quite so commonplace as those of well known cis diacidotetramine complexes (see Section 3.1.1 discussions, vide supra). Typically, trans CoN2X2⁺ octahedral complexes are green and have three absorption bands in their electronic spectra, while the cis isomers of the same donor set are generally purple with only two absorption bands in their electronic spectra.

The difference in the number of absorption bands between these classical cis and trans isomers is due to a larger splitting of the lowest energy excited 1T1g state by the stronger distortion upon descent in symmetry from the octahedral field to the trans geometry; this gives rise to well separated transitions to the E(1T1g) and A(1T1g) excited states and, consequently, two absorptions are observed. The splitting of the 1T1g state is generally less in the cis complexes (in the simplest model, half as much), giving only a single broad absorption [1,26].

Surprisingly, the electronic spectra of the CoLCl2⁺ complexes (L = 1–3) in acetonitrile (Fig. 5, Table 3) all have three absorptions and the complexes range in color from the expected purple (L = 3) to blue–green (L = 2) to green (L = 1). The latter two colors and the third absorption band were unexpected, because all previous characterization of the metal complexes with these ligands indicate that the short ethylene cross-bridge limits them to cis binding only—and the crystal structure of Co(3)Cl2⁺ confirms this geometry. The conflict between the crystal structure and what these electronic spectra suggest must indicate that the ethylene cross-bridge of these ligands distorts the octahedral geometry more than is typical of cis complexes, resulting in sufficient splitting of the 1T1g energy level to give rise to two absorption bands and the unexpected green color.

Several trends in the electronic spectra appear to follow ring size for these Co(III) complexes. First, the wavelengths of all three absorptions increase smoothly...

![Fig. 4](image-url) The electronic spectra in acetonitrile of: (a) Co(2)Cl2 is representative of the three six-coordinate complexes, and is common to octahedral Co(II) complexes, while that of (b) [Co(4)Cl]PF6 are more similar to known five-coordinate, trigonal bipyramidal complexes [22–26].

![Fig. 5](image-url) The electronic spectrum in acetonitrile of Co(2)Cl2⁺ is representative of the three six-coordinate complexes. The presence of three absorption bands is uncommon to cis octahedral CoN2X2⁺ complexes. The large distortion from octahedral caused by the ethylene cross-bridge of ligands 1–3 is the probable cause of the similarity to classic trans-CoN2X2⁺ spectra [1,26].
with increasing ligand ring size. Second, the extinction coefficients of the smallest ligand (3) complex are consistently higher than those of the two larger complexes, which are very similar to each other. A likely explanation is that the smaller ring distorts the basic octahedral geometry even more than do the other two ligands, which could result in an axial field and higher extinction coefficients. Finally, the colors of the complexes range from purple for the smallest ring to green for the largest ring, with the intermediate ring size having an intermediate blue–green color.

The electronic spectra of octahedral Co(III) complexes have often been used to estimate the ligand field strengths of the ligands, expressed with the parameter $\Delta_o$ [27]. The value of $\Delta_o$ can be taken as the energy of the lowest absorption band $(^1A_1g(^3A_2g))$ plus the Racah parameter C (3800 cm$^{-1}$ for Co$^{3+}$) [27,28]. For the three octahedral dichloro complexes, this calculation gives: Co(1)Cl$_2^+$: $\Delta_o = 19,430$ cm$^{-1}$; Co(2)Cl$_2^+$: $\Delta_o = 20,470$ cm$^{-1}$; Co(3)Cl$_2^+$: $\Delta_o = 21,130$ cm$^{-1}$.

Thus, as the macrocycle becomes smaller, it exerts a greater ligand field strength on Co(III). This trend is also observed for unbridged cis-tetraazamacrocycles Co(III) complexes [28]. It is interesting that the most distorted (higher extinction coefficient) ligand 3 also has the highest ligand field strength. Comparisons of these values with those of Co(III) complexes of some unbridged tetraazamacrocycles is informative. The values for cis-Co([14]aneN$_4$)Co$_2^+$, cis-Co([13]aneN$_4$)Co$_3^+$, and cis-Co([12]aneN$_4$)Co$_4^+$ are $\Delta_o = 23,030$, 23,760, and 22,670 cm$^{-1}$, respectively [28]. Thus, the ligand field strengths of the ethylene cross-bridged tetraazamacrocycles are smaller than those of unbridged analogues binding in a similar cis fashion (enforced in these analogues by the bidentate carbonate ligand).

Two explanations can be proposed for the lower ligand field strengths of the current ligands. First, for the unbridged macrocycle complexes, $\Delta_o$ is calculated from the lowest energy absorption (only two major absorptions are seen) in the electronic spectra of the complexes. This energy is actually an average of the unresolved $E^1(T_{1g})$ and $A^1(T_{1g})$ state energies, although for cis complexes $\Delta_o$ should be obtained from the $A^1(T_{1g})$ (lowest) energy band only. Thus, the reported energies will be a bit larger than the true values. In our cross-bridged complexes, the calculation of $\Delta_o$ is more precise because the absorptions due to transitions to the $E^1(T_{1g})$ and $A^1(T_{1g})$ states are resolved, indicating a larger difference between the unique N–N axis field strength and that of the two degenerate N–Cl axes. A second explanation for the lower ligand field strengths is a lower equatorial field due to the presence of N–Cl donors rather than the N–O donors in the unbridged ligand complexes. Further, because the equatorial nitrogen donors in the cross-bridged ligands are constrained by the ethylene bridging group, the N–N distance is less flexible than in the unbridged macrocycles. This constraint may reduce the overlap between the nitrogen donor orbitals and the metal ion bonding orbitals, resulting in lower equatorial field strengths. In contrast, the axial direction still contains two nitrogens. The result is a sufficient difference between the axial and equatorial ligand field strengths to split the T-state. The axial N–N set is also somewhat weakened in field strength by distortion from the ideal linear array, possibly leading to a decrease in ligand field strength compared to an unbridged macrocycle chelated in the same fashion.

### 3.1.3. Solution properties

Conductance experiments were performed on the Co(II) complexes in the absence of air in order to determine the extent of chloride ligand displacement by solvent. The 1 mM complex solutions were prepared in an inert atmosphere glovebox, sealed, and transferred to an argon filled glovebag, where the measurements were taken. The results (Table 4) show that the ionization (displacement of chloride by solvent) of these complexes in solution correlates with the solvent dielectric constant and solvent coordinating ability. In the low dielectric non-coordinating solvent, nitromethane, the six-coordinate complexes behave as non-electrolytes revealing that the chlorides remain bound and indicating that the structure of the complex in solution is six-coordinate pseudo-octahedral as in the solid state. In contrast, the five-coordinate complex [Co(4)Cl]PF$_6$ behaves in nitromethane as expected, with a molar conductance consistent with a 1:1 electrolyte, indicating the presence of the unbound anion, but no dissociation of the single bound chloride ligand. In a coordinating solvent with a slightly higher dielectric constant, acetonitrile, all four complexes have conductances somewhat less than is expected for 1:1 electrolytes which implies that solvent has partially displaced one chloride ligand from the coordination spheres of the six-coordinate complexes. However, in methanol, this first chloride ligand is fully replaced by solvent and all complexes exceed typical 1:1 electrolyte behavior. In water, the conductance values are consistent with 2:1 electrolyte behavior for the three six-coordinate complexes, indicating that all chloride ligands have been replaced by water molecules. Surprisingly, the conductance of the five-coordinate complex,

---

**Table 3**

Electronic spectra of Co(III) complexes

<table>
<thead>
<tr>
<th>Complex</th>
<th>Absorption in nm (extinction coefficient M$^{-1}$ cm$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[Co(1)Cl]PF$_6$</td>
<td>640 (140) 447 (130) 371 (860)</td>
</tr>
<tr>
<td>[Co(2)Cl]PF$_6$</td>
<td>600 (150) 434 (140) 356 (660)</td>
</tr>
<tr>
<td>[Co(3)Cl]PF$_6$</td>
<td>577 (250) 415 (210) 349 (950)</td>
</tr>
</tbody>
</table>

---

**Notes:**

- The values are taken as the energy of the lowest absorption band $(^1A_1g(^3A_2g))$ plus the Racah parameter C (3800 cm$^{-1}$ for Co$^{3+}$).
- The values for the three octahedral dichloro complexes are calculated as follows:
  - Co(1)Cl$_2^+$: $\Delta_o = 19,430$ cm$^{-1}$
  - Co(2)Cl$_2^+$: $\Delta_o = 20,470$ cm$^{-1}$
  - Co(3)Cl$_2^+$: $\Delta_o = 21,130$ cm$^{-1}$

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**Further Reading:**

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Table 4
Molar conductance of Co(II) complexes in various solvents

<table>
<thead>
<tr>
<th>Complex</th>
<th>Molar conductance</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Water</td>
</tr>
<tr>
<td>Co(II)Cl₂</td>
<td>270</td>
</tr>
<tr>
<td>Co(II)Cl₃</td>
<td>254</td>
</tr>
<tr>
<td>Co(II)Cl₄</td>
<td>242</td>
</tr>
<tr>
<td>[Co(III)Cl]PF₆</td>
<td>200</td>
</tr>
<tr>
<td>1:1</td>
<td>118–131</td>
</tr>
</tbody>
</table>

Theoretical electrolyte type ranges from Ref. [11].

[Co(4)Cl]PF₆, is intermediate between those for 1:1 and 2:1 electrolytes. This suggests that the single chloro ligand is only partially displaced, even in water.

3.1.4. Electrochemical studies

The cyclic voltammograms of: (a) [Co(4)Cl]PF₆, and (b) Co(2)Cl₂ (the latter is representative of all three six-coordinate Co(II) complexes) are shown in Fig. 6. The redox potentials and peak separations of all four complexes are given in Table 5. Electrochemical studies of all complexes were performed in acetonitrile and were obtained separately on solutions using both TBA(PF₆) and TBACL as supporting electrolytes; Fig. 6(a) is a scan for [Co(4)Cl]PF₆ with PF₆⁻ as the electrolyte while Fig. 6(b) is a scan for Co(2)Cl₂ with Cl⁻ as the electrolyte. The voltammograms of the three Co(III) complexes with ligands 1–3 were also obtained and display essentially identical potentials and reversibility to those of the corresponding divalent species. The PF₆⁻ electrolyte allowed scanning to higher potentials but gave multiple peaks at potentials identified as belonging to Co³⁺/²⁺ couples for the six-coordinate complexes. This behavior can be explained by the conductance measurements (vide supra); in acetonitrile at least two Co(II) species exist in equilibrium for each compound, the dichloro and the chloroacetonicotritilre adducts. In TBACL, this area of the voltammograms simplifies to a single couple, because the excess Cl⁻ forces the equilibrium towards the dichloro species. Unfortunately, the TBACL electrolyte affords a smaller voltage window for the voltammogram, since Cl⁻ begins to oxidize at around 1 V under our conditions. This irreversible oxidation was observed for all three six-coordinate complexes. Fig. 6 and Table 5 present the clearest data, with electrolyte type identified.

The Co³⁺/²⁺ wave is typical of octahedral Co(II) complexes and becomes more positive and more reversible as the ring size of the macrobicyclo increases from 3 to 1. The data shows that the largest ligand (1) better accommodates the interchange of large high spin Co(II) and small low spin Co(III) than does the smallest ligand (3), with 2 being intermediate in behavior. The larger ligands seem to stabilize the larger Co(II) ion better, and the smallest ligand stabilizes Co(III) better, as seen in the range of potentials for this couple, which becomes more positive (i.e. harder to oxidize) as the ring size increases. The values for this couple are: \( E_{1/2} = -0.157 \text{ V (Co(3)Cl)} \), \( E_{1/2} = -0.009 \text{ V (Co(2)Cl)} \), and \( E_{1/2} = +0.173 \text{ V (Co(I)Cl)} \). An irreversible reduction to Co(I) is observed for all four complexes. The lack of reversibility is probably due to loss of chloro ligands upon reduction. The size trend seen for the 2+/3⁺ couple is not as evident for the reduction process; the medium sized ligand 2 has the lowest reduction potential.

For Co(4)Cl⁺, the supporting electrolyte makes a large difference in the voltammogram. In Cl⁻, only a single, reversible reduction from Co(II) to Co(I) is observed. However, in PF₆⁻, where a wider potential window is available, an additional reversible oxidation is observed. In addition, the reduction that was reversible in Cl⁻ becomes irreversible and a second irreversible reduction is seen at an even lower potential. The striking features of the voltammogram for [Co(4)Cl]PF₆ are its much higher potential (approximately 1 V) for the Co³⁺/²⁺ wave, while its irreversible reduction to Co⁺ is several hundred mV less cathodic than those for the three six-coordinate complexes. The milder reduction of [Co(4)Cl]PF₆ probably arises from the greater stabilization of Co⁺, a d⁶ ion, in the five-coordinate geometry. We surmise that loss of Cl⁻ by the reduced Co⁺ accounts for the lack of reversibility here and in the other complexes; as with the oxidation of six-coordinate complexes, this reduction becomes more reversible in a chloride medium. [Co(4)Cl]PF₆ is much more difficult to oxidize than the six-coordinate complexes as a result of its unique geometry, but this oxidation is not highly irreversible at its high potential \( E_{1/2} = 1.151 \text{ V, } \Delta E = 134 \text{ mV} \). Co(III) is destabilized by the five-coordinate trigonal bipyramidal geometry while it is stabilized greatly by the pseudo-octahedral geometries allowed by the other ligands (1–3). Finally, unique to this

Fig. 6. Cyclic voltammograms in acetonitrile of: (a) [Co(4)Cl]PF₆ in TBA(PF₆) supporting electrolyte; and (b) Co(2)Cl₂ in TBACL supporting electrolyte.
complex is the absence of the second oxidation seen in the octahedral complexes, and the appearance of a second reduction, not observed for in the octahedral complexes.

4. Conclusions

Using the simple, but topologically constrained cross-bridged macrobicyclic ligands, 1–4, we have produced high spin cis complexes where unbridged tetraazamacrocycles generally produce trans isomers. Magnetic and spectroscopic measurements on the chloro complexes of the Co(II) ions reveal that the coordination spheres of the divalent metal complexes 1–3 are all quite similar six-coordinate pseudo-octahedra, but the complex of 4 is five-coordinate with only one bound chloride, as a result of ligand steric effects. X-ray crystal structures of Co(1)Cl2, Co(3)Cl2, and Co(4)Cl+ confirm these geometries and provide data for comparison to the complexes of these ligands with other metal ions. The pseudo-octahedral complex of the smallest ring 3 is more distorted than the others because the Co2+ ion is larger than ideal, whereas the complex, Co(1)Cl2, is less distorted from octahedral due to the better fit of the ligand with Co2+. The chemical oxidation of the Co(II) complexes by air in acidic aqueous media results in the dichloro Co(III) complexes of 1–3, while the Co(II) complex of 4 is unchanged by this treatment. Unusual colors and electronic spectra for these Co(III) complexes indicate large distortions from idealized pseudo-octahedra, an effect traceable to the short ethylene cross-bridge. The electronic spectra also allow calculation of the ligand field strengths for 1–3, which are slightly lower than those for corresponding unbridged tetraazamacrocycles (when bound in the same way), possibly due to reduced orbital overlap caused by the short ethylene cross-bridge. The X-ray crystal structure of Co(3)Cl2+ exhibits the bond length and angle changes expected for metal ion oxidation. In acetonitrile, the +3 and +1 oxidation states are readily detectable. The derivatives of the larger rings are harder to oxidize, which can be attributed to the match of larger rings to the larger divalent ions, as opposed to that of smaller rings with smaller trivalent ions. The distinctive coordination geometry of the complex with 4 is readily apparent in its electrochemistry as well as its chemical, magnetic, and spectroscopic properties.

5. Supporting information available

Tables of coordinates, bond distances and angles, anisotropic displacement parameters, and hydrogen coordinates and isotropic displacement parameters for Co(1)Cl2, Co(3)Cl2, [Co(4)Cl]2[CoCl4] * DMF ≈ 0.25H2O, and [Co(3)Cl2]PF6 are available from the authors on request.

6. Supplementary material

The material is available from the authors on request.

Acknowledgements

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References