

Complexation of *cis*-6,13-Dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine with the First Row Transition Metal Ions Cobalt(III), Chromium(III), and Nickel(II)

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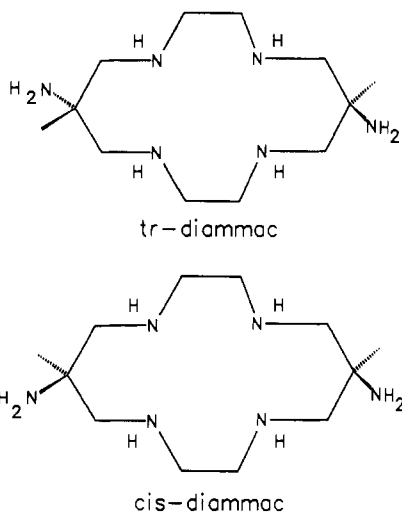
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The syntheses and characterization of the Co(III), Cr(III), and Ni(II) complexes of the pendant arm macrocyclic hexamine *cis*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine (*cis*-diammac) are reported and their spectroscopic and structural properties are compared with those of the known isomeric *trans*-diammac complexes with the aid of molecular mechanics and angular overlap model calculations. In contrast to the $[M(\textit{trans}\text{-diammac})]^{n+}$ analogues, the $[M(\textit{cis}\text{-diammac})]^{n+}$ complexes do not display short M–N bond lengths, nor are particularly high energy electronic maxima a feature. The $[M(\textit{cis}\text{-diammac})]^{n+}$ complexes exhibit trigonally twisted geometries and more positive $M^{\text{III/II}}$ redox couples than their *trans*-diammac relatives. The X-ray crystal structure of $[\text{Cr}(\textit{cis}\text{-diammac})](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ is reported: $\text{C}_{12}\text{H}_{34}\text{Cl}_3\text{CrN}_6\text{O}_{14}$, orthorhombic, space group $Pc2_1n$, $a = 10.455(4)$ Å, $b = 14.262(4)$ Å, $c = 16.905(7)$ Å, $Z = 4$.

Introduction

The coordination chemistry of the pendant arm macrocyclic hexamine *trans*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine (*trans*-diammac) has been of considerable



interest in recent years.^{3–7} When coordinated as a sexidentate, the resulting hexamine complexes of *trans*-diammac exhibit remarkable spectroscopic and structural characteristics. Specifically, each $[M(\textit{trans}\text{-diammac})]^{n+}$ complex displays an exceptionally short average M–N bond length and unusually high energy electronic maxima. The recent isolation and characterization of the *cis* isomer of this macrocycle (*cis*-diammac) and of the complex

$[\text{Cd}(\textit{cis}\text{-diammac})](\text{ClO}_4)_2$, where the ligand was coordinated as a sexidentate, revealed that the Cd–N bond lengths were not unusual and in fact were slightly longer than average for a hexaminecadmium(II) complex.⁸ However, as this d^{10} complex displays no d–d transitions, the electronic properties of complexes of *cis*-diammac could not be probed.

In this paper we report the syntheses and spectroscopic and structural characterization of the Cr(III), Co(III), and Ni(II) complexes of *cis*-diammac, all of which find the macrocycle coordinated as a sexidentate. For all three complexes, the corresponding $[M(\textit{trans}\text{-diammac})]^{n+}$ complex is known, therefore allowing a rather novel comparison between isomeric complexes of a sexidentate ligand, where the isomerism is dictated solely by the ligand rather than the metal center. The spectroscopic and structural properties of the isomeric systems have been examined with angular overlap model (AOM) and molecular mechanics (MM) calculations, and the X-ray crystal structure of $[\text{Cr}(\textit{cis}\text{-diammac})](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ is also reported.

Experimental Section

Safety Note. Perchlorate salts of complexes containing organic ligands are potentially explosive. Although we have experienced no problems with the salts reported herein, they should be handled in small quantities and never heated in the solid state.

Syntheses. The synthesis of *cis*-6,13-dimethyl-1,4,8,11-tetraazacyclotetradecane-6,13-diamine hexahydrochloride (*cis*-diammac-6HCl) has been reported.⁸ Improved separation of the mixture of *cis*- and *trans*-diammac may be achieved by removing the majority of the less soluble major isomer *trans*-diammac-6HCl, which precipitates upon concentration of the acidic ligand solution. This technique has been employed in the past to obtain *trans*-diammac-6HCl in a pure form.³ The resulting filtrate then contains an approximately 1:1 mixture of the two isomers of the macrocycle, and separation of the ligands as their Cu(II) complexes is improved. $[\text{Ni}(\textit{trans}\text{-diammac})](\text{ClO}_4)_2$ was prepared by a variation of the published synthesis;⁹ an aqueous solution of $\text{Ni}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and *trans*-diammac-6HCl (1:1) and excess NaClO_4 was neutralized and allowed to stand at room temperature, which afforded precipitation of the product as apricot crystals.

$[\text{Co}(\textit{cis}\text{-diammac})](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$. The pH of a solution of *cis*-diammac (1.33 g) in water (50 mL) was adjusted to 7 with dilute NaOH solution, $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.62 g) and activated charcoal (ca. 1 g) were added, and

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the solution was aerated for 6 h. Upon completion of the reaction, the mixture was filtered and charged onto a column (30 × 4 cm) of SP-Sephadex C-25 cation exchange resin (Na⁺ form). Three bands were eluted with 0.5 M NaClO₄ in the following order: 1 (red, $\bar{\nu}_{\max}$ 19 380, 21 010, and 27 860 cm⁻¹); 2 (orange, $\bar{\nu}_{\max}$ 20 240 and 29 410 cm⁻¹); the third band (yellow) was the desired product. Bands 1 and 2 were not crystallized. The third band was evaporated to ca. 30 mL and orange/yellow crystals deposited upon standing. Several crops were obtained, and the yield based on the electronic spectrum of the eluate was ca. 30%. Anal. Calcd for C₁₂H₃₄Cl₃CoN₆O₁₄: C, 22.1; H, 5.3; N, 12.9; Cl, 16.3. Found: C, 22.1; H, 5.2; N, 12.9; Cl, 16.3. ¹³C NMR (D₂O): δ 19.8 (methyl); 54.2, 56.0, 58.3, and 63.0 (methylenes); 68.2 (tertiary C). Electronic spectrum (water): $\bar{\nu}_{\max}$ 13 400 (0.8 M⁻¹ cm⁻¹), 21 790 (ϵ 120), 29 940 (ϵ 98).

[Cr(*cis*-diammac)](ClO₄)₃·2H₂O. A solution of *cis*-diammac (1.62 g) and triethylamine (5 mL) in absolute ethanol (200 mL) was purged with N₂ for 15 min. Anhydrous CrCl₂ (0.40 g) was added, and the mixture was stirred under N₂ and at room temperature for 2 1/2 h. The nitrogen supply was discontinued, and the mixture was refluxed for 16 h. The cooled solution was diluted to 1 L with water, acidified (pH 4), and filtered. Column chromatography as above (0.5 M NaClO₄) yielded two bands, the second of which was the desired product. The first band (red, $\bar{\nu}_{\max}$ 20 000 and 26 950 cm⁻¹) was not crystallized. The desired product was evaporated to ca. 30 mL, and yellow prisms, suitable for X-ray work, formed when the solution was allowed to stand in the dark. The solution yielded several crops, and the yield based on the electronic spectrum of the eluate was ca. 40%. The ZnCl₄²⁻ salt crystallizes more readily than the ClO₄⁻ analogue and may be prepared by diluting the yellow solution from the column 20 times and rechromatographing the complex with 1 M NaCl as the eluent. The eluate was concentrated to half-volume, and 1 g of ZnCl₂ was added to afford crystallization as the sesquiquinhydrone (tetrahydrozincate) trihydrate salt. Anal. Calcd C₁₂H₃₆Cl₆CrN₆O₃Zn_{1.5}: C, 21.4; H, 5.4; N, 12.5; Cl, 31.5. Found: C, 20.8; H, 5.4; N, 12.4; Cl, 32.2. Electronic spectrum (water): $\bar{\nu}_{\max}$ 14 620 cm⁻¹ (0.50 M⁻¹ cm⁻¹), 14 930 (ϵ 0.30), 15 110 (ϵ 0.10), 22 120 (ϵ 128), 28 570 (ϵ 68).

[Ni(*cis*-diammac)](ZnCl₄)·H₂O. A solution of *cis*-diammac (1.00 g) and NiCl₂·6H₂O (0.50 g) in water (100 mL) was made alkaline (pH 9) with dilute NaOH solution and then stirred at 80° for 4 h. The mixture was cooled and chromatographed as above with 0.5 M NaCl as the eluent. Two closely running bands eluted, the first one (yellow) did not crystallize, whereas the second band (purple) was concentrated to ca. 50 mL and 1 g of ZnCl₂ was added to afford immediate and almost complete precipitation of the desired product. The yield was ca. 60%. Anal. Calcd for C₁₂H₃₂Cl₄NiN₆OZn: C, 26.6; H, 6.0; N, 15.5; Cl, 26.2. Found: C, 26.6; H, 5.8; N, 15.7; Cl, 26.9. Electronic spectrum (water): $\bar{\nu}_{\max}$ 11 320 cm⁻¹, sh (ϵ 8.0 M⁻¹ cm⁻¹), 12 360 (ϵ 9.4), 19 370 (ϵ 5.4), 20 390 sh (ϵ 4.4), 30 960 (ϵ 6.8).

Physical Methods. Electronic spectra were recorded on a Cary 2300 UV-vis-near-IR spectrophotometer. NMR spectra were recorded with Varian GEMINI 300 and 400 spectrometers at 300 or 400 (1H) and 75 MHz (13C), with all chemical shifts being cited versus tetramethylsilane. Electrochemical measurements were performed with a Metrohm E-612 controller and an E-611 detector. Glassy-carbon working, platinum counter, and calomel reference electrodes were used in all experiments, and aqueous solutions containing ca. 10⁻³ M of each complex and 0.1 M NaClO₄ were purged with nitrogen before measurement. Molecular mechanics (MM) calculations were performed with the strain energy minimization program MOMECS7,¹⁰ using published force fields.^{11,12} Trial coordinates were produced with the graphics program SMILE.¹³ Angular overlap model calculations were performed with a modified version of the program CAMMAG.¹⁴ All 1H NMR spectra were simulated with a locally developed program.¹⁵

Structure Analysis. For the structure of [Cr(*cis*-diammac)](ClO₄)₃·2H₂O, lattice dimensions were determined by a least-squares fit to the setting parameters of 25 independent reflections, measured and refined on an Enraf-Nonius CAD4-F diffractometer, employing graphite mono-

Table I. Crystal Data

| | | | |
|--|--|---|--------------|
| space group | Pc2 ₁ n (No. 62) ^a | μ , cm ⁻¹ | 8.26 |
| a, Å | 10.455(4) | temp, K | 294 |
| b, Å | 14.262(4) | λ , Å | 0.710 69 |
| c, Å | 16.905(7) | no. of indep. reflns | 3266 |
| V, Å ³ | 2520(2) | no. of refined reflns | 2856 |
| ρ_{calcd} , g cm ⁻³ | 1.699 | Θ_{max} , deg | 27.5 |
| fw | 644.79 | R(F _o), R _w (F _o) ^b | 0.035, 0.040 |
| Z | 4 | | |

^a Variant of Pnma. ^b R(F_o) = $\sum(|F_o| - |F_c|) / \sum|F_o|$; R_w(F_o) = $\sum(\|F_o| - |F_c||) w^{1/2} / \sum|F_o|w^{1/2}$.

Table II. Positional Parameters (×10⁴) for [Cr(*cis*-diammac)]-(ClO₄)₃·2H₂O

| | x | y | z |
|-------|----------|----------|---------|
| Cr(1) | 594(1) | 0 | 2261(1) |
| N(1) | -1016(3) | 822(2) | 2320(2) |
| N(2) | -462(3) | -1194(2) | 2512(2) |
| N(3) | 467(2) | 142(2) | 3474(2) |
| N(4) | 2098(3) | -910(2) | 2148(2) |
| N(5) | 246(3) | -16(2) | 1058(2) |
| N(6) | 1966(3) | 943(2) | 1905(2) |
| C(1) | -1637(3) | 690(3) | 3105(3) |
| C(2) | -930(3) | -58(3) | 3593(2) |
| C(3) | -1157(4) | -1046(3) | 3284(3) |
| C(4) | 435(4) | -2017(3) | 2522(3) |
| C(5) | 1534(4) | -1853(2) | 1968(2) |
| C(6) | -1351(4) | -5(4) | 4454(3) |
| C(7) | 3012(3) | -527(3) | 1553(2) |
| C(8) | 2533(3) | 409(3) | 1223(2) |
| C(9) | 1425(3) | 296(3) | 635(2) |
| C(10) | -889(4) | 605(3) | 905(3) |
| C(11) | -1781(3) | 561(3) | 1604(3) |
| C(12) | 3632(5) | 936(4) | 824(3) |
| Cl(1) | 7558(1) | 2912(1) | 5567(1) |
| O(11) | 8335(4) | 3741(2) | 5476(2) |
| O(12) | 7015(3) | 2889(3) | 6348(2) |
| O(13) | 6553(5) | 2962(5) | 5017(3) |
| O(14) | 8353(8) | 2110(3) | 5485(4) |
| Cl(2) | 988(1) | 2869(1) | 3368(1) |
| O(21) | 1031(5) | 3735(4) | 3745(4) |
| O(22) | -107(4) | 2758(3) | 2881(3) |
| O(23) | 2110(5) | 2716(6) | 2913(3) |
| O(24) | 980(9) | 2161(5) | 3959(4) |
| Cl(3) | 5356(1) | 5512(1) | 6481(1) |
| O(31) | 4705(5) | 4766(3) | 6114(4) |
| O(32) | 6686(3) | 5319(4) | 6503(3) |
| O(33) | 5076(6) | 6313(3) | 6018(3) |
| O(34) | 4910(5) | 5694(4) | 7267(2) |
| OW(1) | 3961(4) | 2695(3) | 6127(2) |
| OW(2) | 3878(4) | 3164(4) | 4357(3) |

chromated Mo K α radiation. Crystallographic data are summarized in Table I. Data reduction and application of Lorentz, polarization, absorption, and decomposition corrections were carried out by using the Enraf-Nonius Structure Determination Package.

The structure was solved by Patterson techniques with SHELXS-86¹⁶ and refined by full-matrix least-squares analysis with SHELX-76.¹⁷ All non-hydrogen atoms were refined anisotropically. All H atoms were fixed at estimated positions, with the exception of those belonging to water molecules which were not modeled. Neutral atom scattering factors and anomalous dispersion coefficients for Cr were taken from the literature,¹⁸ whereas all others were supplied in SHELX-76. The atomic nomenclature is defined in Figure 3, drawn with ORTEP.¹⁹ Non-hydrogen atom coordinates are listed in Table II.

Results

The complexes [M(*cis*-diammac)]²⁺ (M = Cr(III), Co(III) and Ni(II)) were prepared in an analogous fashion to their

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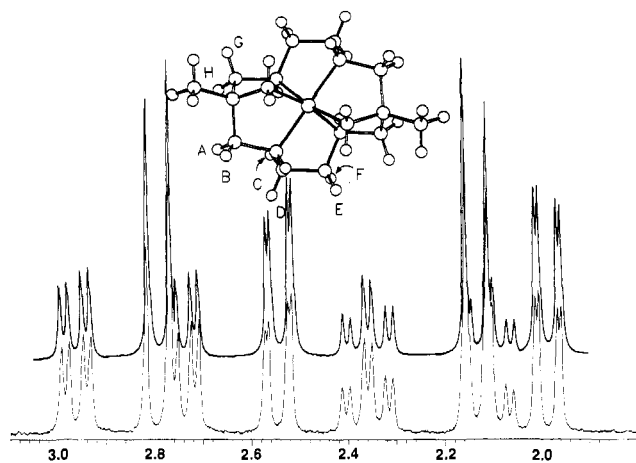


Figure 1. Simulated (top) and experimental 300-MHz ^1H NMR spectrum of $[\text{Co}(\text{cis-diammac})]^{3+}$ in D_2O .

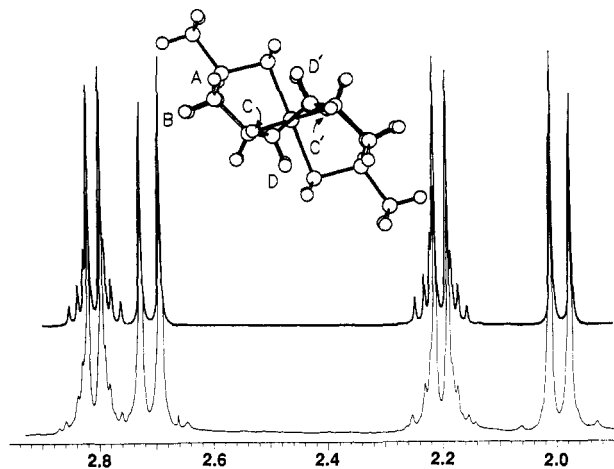


Figure 2. Simulated (top) and experimental 400-MHz ^1H NMR spectrum of $[\text{Co}(\text{trans-diammac})]^{3+}$ in D_2O .

corresponding isomeric $[\text{M}(\text{trans-diammac})]^{n+}$ complexes. Complete sixdentate coordination of *cis*-diammac was never achieved, with significant amounts of quinquedentate-coordinated complexes being found for the Co(III) and Cr(III) reactions and some quadridentate-coordinated, square-planar Ni(II) complex resulting from the reaction. Although these complexes were not isolated, their electronic spectra (Experimental Section) are consistent with $\text{Co}^{\text{III}}\text{N}_5\text{O}$, $\text{Cr}^{\text{III}}\text{N}_5\text{O}$ or low-spin $\text{Ni}^{\text{II}}\text{N}_4$ chromophores. Several quadri- and quinquedentate-coordinated complexes of *trans*-diammac have been reported;^{3-5,20-23} however they do not display particularly unusual physical properties by comparison with the sixdentate coordinated relatives. Therefore, isolation of the analogous quinque- and quadridentate-coordinated complexes of *cis*-diammac was not pursued in this work.

It emerges from the structures of $[\text{Co}(\text{trans-diammac})]^{3+}$ and $[\text{Co}(\text{cis-diammac})]^{3+}$ shown in Figures 1 and 2 that there exists but one geometric isomer of each complex, although there are three nondegenerate conformations of each compound. An MM analysis of this system²⁴ revealed that for all $[\text{M}(\text{cis-diammac})]^{n+}$ complexes, regardless of metal ion size, the conformation designated *cis*-(*ob*)₂ is most stable.²⁵ This conformation, shown in Figure 1 for the MM-refined structure of $[\text{Co}(\text{cis-diammac})]^{3+}$, has C_2 symmetry, and this is consistent with the proton-decoupled ^{13}C NMR spectrum which displays six resonances.

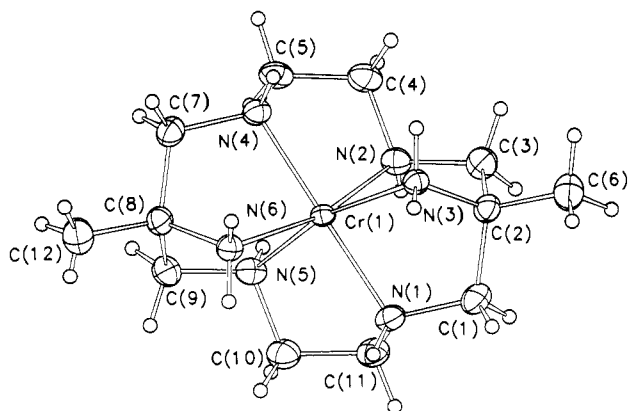
The ^1H NMR spectrum, shown in Figure 1, contains more structural information. The symmetry of the complex dictates that the eight methylene protons highlighted in Figure 1 (A–H) are all distinct from one another. Eight sets of resonances appear between 2.0 and 3.0 ppm, in addition to a single methyl resonance at 0.64 ppm, whereas all amine protons underwent deuterium exchange with the solvent. The complexity of the spectrum necessitated that simulation be carried out in order that a correct interpretation be obtained. From the simulation, it emerged that the spectrum could be separated into independent contributions from the “ethylene” protons C–F and from those of the “isolated” methylene groups A, B, G, and H. The resonances due to the

ethylene protons exhibit essentially first-order coupling, with the split triplets at 2.115 and 2.360 ppm being due to protons C and E, whereas the doublet pairs at 2.740 and 2.965 ppm are due to protons D and F. The torsion angle $\text{H}(\text{C})\text{--C--H}(\text{E})$ in the MM-refined structure is 171° , so vicinal coupling ($^3J_{\text{CE}} = 13$ Hz) is strong,²⁶ whereas coupling between protons D and F (H--C--H torsional angle 68°) is weak ($^3J_{\text{DF}} = 0.5$ Hz). Geminal coupling is the same in both methylene pairs ($^2J = -13.8$ Hz) as is vicinal coupling of the C/F and D/E pairs ($^3J = 5$ Hz), therefore two doubled doublets are found for the D/F pair and two doubled triplets are observed for the C/E pair. The isolated methylene protons exhibit AB patterns (B 2.54, A 2.135, H 2.790, G 1.985 ppm; $^2J = -13.8$ Hz) in addition to long range coupling between protons B and G ($^4J_{\text{BG}} = 2.5$ Hz), which form a “W” configuration upon examination of the MM-refined structure.

The ^1H NMR spectrum of $[\text{Co}(\text{trans-diammac})]^{3+}$ has been remeasured at higher resolution than reported in an earlier study³ (Figure 2). The C_{2h} symmetry of the *trans*- $\lambda\delta$ conformer dictates that there are but four sets of methylene protons (A, B, C, and D in Figure 2). Indeed four sets of resonances are identified in the methylene region of the spectrum. The AB quartet at 1.997 and 2.711 ppm ($^2J_{\text{AB}} = -13.3$ Hz) is due to the isolated methylene protons A and B, whereas the complicated patterns at 2.205 and 2.810 ppm are due to C and D which constitute an AA'BB' system. From the simulation, the geminal coupling constant ($^2J_{\text{CD}} = -13.8$ Hz) and the vicinal coupling constants ($^3J_{\text{CC}'} = 4.5$, $^3J_{\text{CD}'} = 5$, and $^3J_{\text{DD}'} = 9$ Hz) were obtained, which are consistent with the respective torsional angles of 68, 50, and 13° found in the MM-refined structure.

The X-ray crystal structure of $[\text{Cr}(\text{cis-diammac})](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ reveals all molecules to be on general sites, with weak hydrogen bonds (>2.0 Å) being made with the amine H atoms by perchlorate anions and water molecules. A drawing of the $[\text{Cr}(\text{cis-diammac})]^{3+}$ cation appears in Figure 3. The macrocycle has a folded configuration with the pendant primary amines occupying *cis* coordination sites. The conformations of the five-membered chelate rings including the donor atom pairs N(1)/N(2) and N(4)/N(5) are found to be oblique to the pseudo- C_2 axis (*cis*-(*ob*)₂), which is the anticipated conformation based on MM calculations²⁴ and also the conformation found in the other extant structure⁸ of a complex containing this ligand, $[\text{Cd}(\text{cis-diammac})](\text{ClO}_4)_2$. The Cr–N bond lengths (Table III) are typical of a hexaminechromium(III) complex and do not vary greatly from the mean, and the intraligand bond angles (Table IV) reveal little strain in the ligand. A significant trigonal twist distortion of the $[\text{Cr}(\text{cis-diammac})]^{3+}$ cation ($\phi \approx 52^\circ$; 60° for octahedral, 0° for trigonal prismatic) is observed, which is in contrast to the structure of $[\text{Cr}(\text{trans-diammac})](\text{ClO}_4)_3$ where a significant axial elongation (≈ 0.03 Å) and exceptionally short Cr–N bond lengths were defined (Table V).⁴

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Figure 3. ORTEP drawing of the $[\text{Cr}(\text{cis-diammac})]^{3+}$ cation.Table III. Bond Lengths (Å) for $[\text{Cr}(\text{cis-diammac})](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$

| | | | |
|-------------|----------|--------------|----------|
| N(1)–Cr(1) | 2.054(3) | N(2)–Cr(1) | 2.075(3) |
| N(3)–Cr(1) | 2.065(3) | N(4)–Cr(1) | 2.048(3) |
| N(5)–Cr(1) | 2.065(3) | N(6)–Cr(1) | 2.056(3) |
| C(1)–N(1) | 1.489(5) | C(11)–N(1) | 1.499(5) |
| C(3)–N(2) | 1.507(5) | C(4)–N(2) | 1.504(5) |
| C(2)–N(3) | 1.503(4) | C(5)–N(4) | 1.500(4) |
| C(7)–N(4) | 1.491(5) | C(9)–N(5) | 1.494(5) |
| C(10)–N(5) | 1.505(4) | C(8)–N(6) | 1.505(4) |
| C(2)–C(1) | 1.538(5) | C(3)–C(2) | 1.521(5) |
| C(6)–C(2) | 1.523(5) | C(5)–C(4) | 1.501(6) |
| C(8)–C(7) | 1.532(5) | C(9)–C(8) | 1.534(5) |
| C(12)–C(8) | 1.530(5) | C(11)–C(10) | 1.507(6) |
| O(11)–Cl(1) | 1.443(3) | O(12)–Cl(1) | 1.438(3) |
| O(13)–Cl(1) | 1.405(4) | O(14)–Cl(1) | 1.421(5) |
| O(21)–Cl(2) | 1.391(4) | OZ(22)–Cl(2) | 1.420(4) |
| O(23)–Cl(2) | 1.421(4) | O(24)–Cl(2) | 1.420(6) |
| O(31)–Cl(3) | 1.407(4) | O(32)–Cl(3) | 1.418(3) |
| O(33)–Cl(3) | 1.416(4) | O(34)–Cl(3) | 1.432(3) |

Table IV. Bond Angles (deg) for $[\text{Cr}(\text{cis-diammac})](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$

| | | | |
|-------------------|----------|-------------------|----------|
| N(2)–Cr(1)–N(1) | 91.3(1) | N(3)–Cr(1)–N(1) | 81.0(1) |
| N(3)–Cr(1)–N(2) | 81.0(1) | N(4)–Cr(1)–N(1) | 174.7(1) |
| N(4)–Cr(1)–N(2) | 84.7(1) | N(4)–Cr(1)–N(3) | 101.7(1) |
| N(5)–Cr(1)–N(1) | 84.9(1) | N(5)–Cr(1)–N(2) | 95.6(1) |
| N(5)–Cr(1)–N(3) | 165.3(1) | N(5)–Cr(1)–N(4) | 92.1(1) |
| N(6)–Cr(1)–N(1) | 102.3(1) | N(6)–Cr(1)–N(2) | 165.6(1) |
| N(6)–Cr(1)–N(3) | 105.7(1) | N(6)–Cr(1)–N(4) | 81.5(1) |
| N(6)–Cr(1)–N(5) | 81.0(1) | C(1)–N(1)–Cr(1) | 109.2(2) |
| C(11)–N(1)–Cr(1) | 104.9(2) | C(11)–N(1)–C(1) | 117.1(3) |
| C(3)–N(2)–Cr(1) | 108.6(2) | C(4)–N(2)–Cr(1) | 108.1(2) |
| C(4)–N(2)–C(3) | 113.6(3) | C(2)–N(3)–Cr(1) | 100.2(2) |
| C(5)–N(4)–Cr(1) | 106.6(2) | C(7)–N(4)–Cr(1) | 108.8(2) |
| C(7)–N(4)–C(5) | 116.3(3) | C(9)–N(5)–Cr(1) | 108.8(2) |
| C(10)–N(5)–Cr(1) | 107.6(2) | C(10)–N(5)–C(9) | 113.1(3) |
| C(8)–N(6)–Cr(1) | 99.6(2) | C(2)–C(1)–N(1) | 110.8(3) |
| C(1)–C(2)–N(3) | 105.3(3) | C(3)–C(2)–N(3) | 106.4(3) |
| C(3)–C(2)–C(1) | 112.6(3) | C(6)–C(2)–N(3) | 113.5(3) |
| C(6)–C(2)–C(1) | 109.8(3) | C(6)–C(2)–C(3) | 109.3(4) |
| C(2)–C(3)–N(2) | 110.6(3) | C(5)–C(4)–N(2) | 110.4(3) |
| C(4)–C(5)–N(4) | 108.3(3) | C(8)–C(7)–N(4) | 110.8(3) |
| C(7)–C(8)–N(6) | 106.9(3) | C(9)–C(8)–N(6) | 104.6(3) |
| C(9)–C(8)–C(7) | 113.0(3) | C(12)–C(8)–N(6) | 112.6(3) |
| C(12)–C(8)–C(7) | 110.1(3) | C(12)–C(8)–C(9) | 109.4(3) |
| C(8)–C(9)–N(5) | 110.1(2) | C(11)–C(10)–N(5) | 109.2(3) |
| C(10)–C(11)–N(1) | 107.0(3) | O(12)–Cl(1)–O(11) | 109.9(2) |
| O(13)–Cl(1)–O(11) | 108.0(3) | O(13)–Cl(1)–O(12) | 108.3(3) |
| O(14)–Cl(1)–O(11) | 108.7(3) | O(14)–Cl(1)–O(12) | 107.6(3) |
| O(14)–Cl(1)–O(13) | 114.4(5) | O(2)–Cl(2)–O(21) | 113.0(3) |
| O(23)–Cl(2)–O(21) | 110.9(4) | O(23)–Cl(2)–O(22) | 109.5(3) |
| O(24)–Cl(2)–O(21) | 108.1(4) | O(24)–Cl(2)–O(22) | 109.0(4) |
| O(24)–Cl(2)–O(23) | 106.1(5) | O(32)–Cl(3)–O(31) | 109.9(3) |
| O(33)–Cl(3)–O(31) | 105.4(3) | O(33)–Cl(3)–O(32) | 112.0(3) |
| O(34)–Cl(3)–O(31) | 112.9(4) | O(34)–Cl(3)–O(32) | 109.2(3) |
| O(34)–Cl(3)–O(33) | 107.4(3) | | |

The electronic spectra of $[\text{M}(\text{cis-diammac})]^{n+}$ (Co(III), Cr(III) and Ni(II)) are all typical of hexamine complexes, and the d–d transition energies, unlike the $[\text{M}(\text{trans-diammac})]^{n+}$ relatives, are not particularly high (Table VI). The extinction coefficient of the lower energy transition in the spectrum of $[\text{Cr}$

Table V. Average M–N Bond Lengths (Å) and $\text{M}^{\text{III/II}} E_{1/2}$ values (V vs SHE) (Values in Brackets Predicted by Molecular Mechanics)

| | $[\text{M}(\text{trans-diammac})]^{n+}$ | | $[\text{M}(\text{cis-diammac})]^{n+}$ | |
|---------|---|--------------------|---------------------------------------|--------------------|
| | M–N _{sec,prim} | $E_{1/2}$ | M–N _{sec,prim} | $E_{1/2}$ |
| Co(III) | 1.937, 1.946 ^a | –0.57 ^a | [1.954, 1.945] | –0.44 ^b |
| Cr(III) | 2.040, 2.067 ^c | –1.26 ^c | 2.061, 2.061 ^b | –1.11 ^b |
| Ni(II) | 2.071, 2.126 ^d | +0.67 ^b | [2.101, 2.083] | +0.74 ^b |

^a Reference 3. ^b This work. ^c Reference 4. ^d Reference 9.

$[\text{cis-diammac}]^{3+}$ is twice that of the higher energy maximum; a phenomenon also noted in the spectrum of the macrobicyclic cage complex $[\text{Cr}(\text{diamsar})]^{3+}$, which was also trigonally twisted.²⁷ The electronic spectrum of each $[\text{M}(\text{cis-diammac})]^{n+}$ and $[\text{M}(\text{trans-diammac})]^{n+}$ complex have been fitted with angular overlap model (AOM) calculations, based on the MM-refined structures of each complex. The results of the fit are given in Table VI, and the electronic parameters that were used are listed in Table VII. Assignment of the transitions was based on the C_2 symmetry of all complexes except $[\text{Co}(\text{trans-diammac})]^{3+}$, which possesses C_{2h} symmetry.²⁸ The absence of π -bonding in the M–N bonds of amine complexes eliminates the e_π parameter, and spin-orbit coupling, which is a minor perturbation on the electronic spectra of first-row transition metal ions, was neglected in all cases. In order that a meaningful fit was obtained, certain constraints had to be placed on the e_σ values. The four M–N_{sec} bonds in the $[\text{M}(\text{trans-diammac})]^{n+}$ complexes were considered to be equivalent, which is indeed so if the *trans*- $\lambda\delta$ conformer is present, but only approximately true for the lower symmetry *trans*- $\delta\delta$ isomer. Inspection of the MM-refined structures of the C_2 symmetrical *cis*-(*ob*)₂ conformers reveals that the pairs of symmetry related M–N_{sec} bond lengths are significantly different; therefore the use of a single e_σ parameter for these four bonds would be clearly inappropriate. Instead, the M–N_{prim} bond lengths and the long pair of M–N_{sec} bonds have been modeled with the same e_σ parameter. It has been shown that, for hexamine complexes of Co(III), Cr(III), and Ni(II), the e_σ values for secondary amines are greater than those of primary amines for bond lengths of equal dimension.¹² In the case of the $[\text{M}(\text{cis-diammac})]^{n+}$ complexes, although the M–N_{prim} bond lengths are shorter than the M–N_{sec} bonds, the stronger ligand field exhibited by the secondary amines compensates for this, resulting in similar e_σ values.

Aqueous differential pulse polarography (scan rate 2 mV/s) identified $\text{M}^{\text{III/II}}$ couples for all complexes (Table V). The $[\text{Co}(\text{cis-diammac})]^{3+}$ and $[\text{Ni}(\text{cis-diammac})]^{2+}$ complexes yielded quasi-reversible cyclic voltammograms (Co(III/II), $\Delta E_p = 140$ mV, $i_{pa}/i_{pc} = 1.0$ at 100 mV/s scan rate; Ni(III/II), $\Delta E_p = 150$ mV, $i_{pa}/i_{pc} = 1.0$ at 100 mV/s scan rate), whereas the Cr^{III/II} couple was totally irreversible, with no anodic wave being observed at a scan rate of 100 mV/s. The half-wave potentials for the three $[\text{M}(\text{cis-diammac})]^{n+}$ complexes were all more positive than those of the corresponding $[\text{M}(\text{trans-diammac})]^{n+}$ isomer (Table V). The stability of the Ni(III) and Co(II) complexes, on the voltammetric time scale, is consistent with expectations, as other hexamine complexes of these metal ions have been well characterized, both spectroscopically and structurally.^{29,30} The irreversible Cr^{III/II} cyclic voltammogram is typical of hexaminechromium(III) complexes, where dissociation of the complex

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(28) Given the NMR results, one should model the electronic spectrum of $[\text{Co}(\text{trans-diammac})]^{3+}$ as a mixture of the *trans*- $\lambda\delta$ and *trans*- $\delta\delta$ conformers; however, there are too few observables to make such a fit meaningful. Moreover, the two conformers exhibit quite similar geometries, therefore modeling the *trans*- $\lambda\delta$ conformer alone should not introduce any significant errors.

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Table VI. Experimental and Calculated Electronic Transitions (cm^{-1})

| | Co(III) | | exptl | Cr(III) | | exptl | Ni(II) | |
|----------------------------------|---------------------|----------------------|--------------------------|----------------------|--------|---------------------|----------------------|-------|
| | exptl | AOM | | exptl | AOM | | exptl | AOM |
| $[M(\text{trans-diammac})]^{n+}$ | | | | 31 350 | 4B | 31 940 ^c | 32 930 | 3B |
| | 30 490 ^a | 30 720 | 1A_g | 30 250 | 4A | 31 940 ^c | 32 460 | 3B |
| | | 30 690 | 1B_g | | | | | |
| | | 30 140 | 1A_g | 24 640 | 4A | | 21 690 | 3B |
| | 22 370 | 22 410 | 1B_g | 22 970 | 4A | 20 520 | 20 250 | 3B |
| | | 22 070 | $^1A_g, ^1B_g$ | 22 610 | 4B | | 19 370 | 3A |
| | | 13 660 | 3B_g | 15 450 | 2B | 12 960 | 13 930 | 3A |
| | 13 420 | 13 320 | 3A_g | 15 380 | 2A | 12 520 | 12 790 | 3B |
| | | 13 310 | $^3B_g \leftarrow ^1A_g$ | 14 970 | 2B | | 12 620 | 3B |
| | | | | 14 680 | 2B | 11 280 | 11 360 | 1A |
| | | | | $^2A \leftarrow ^4B$ | | 11 180 | $^1A \leftarrow ^3A$ | |
| $[M(\text{cis-diammac})]^{n+}$ | | | | 30 770 | 4B | | 31 980 | 3B |
| | 29 940 ^c | 30 660 | 1A | 30 380 | 4B | 30 960 ^c | 30 460 | 3A |
| | | 30 380 | 1A | 28 680 | 4A | | 29 760 | 3B |
| | | 29 270 | 1B | | | | | |
| | | | | 22 350 | 4B | 20 390 | 20 050 | 3B |
| | | | | 21 960 | 4A | 19 370 | 19 680 | 3A |
| | 21 790 | 21 930 | 1B | 21 370 | 4A | | 18 390 | 3B |
| | | 21 890 | 1A | | | | | |
| | | 21 530 | 1B | 15 110 | 2A | | 12 550 | 3B |
| | | | | 14 930 | 2B | 12 360 | 12 390 | 3B |
| | 13 120 | $^3A, ^3B$ | 15 080 | 2B | | 12 040 | 3A | |
| 13 400 | 12 770 | $^3B \leftarrow ^1A$ | | | | | | |
| | | | 14 570 | 2A | 11 320 | 11 350 | 1A | |
| | | | 14 510 | $^2B \leftarrow ^4B$ | | 11 290 | $^1A \leftarrow ^3A$ | |

^a Reference 3. ^b Reference 4. ^c This work.

Table VII. Electronic Parameters (cm^{-1})

| | $[M(\text{trans-diammac})]^{n+}$ | | | $[M(\text{cis-diammac})]^{n+}$ | | |
|---------|----------------------------------|-------|-------|--------------------------------|-------|-------|
| | e_σ | F_2 | F_4 | e_σ | F_2 | F_4 |
| Co(III) | 8400 | 1220 | 12 | 8700 | 1220 | 120 |
| | 8200 ^a | | | 8450 | | |
| | | | | 8450 ^a | | |
| Cr(III) | 8300 | 1100 | 95 | 8300 | 1200 | 85 |
| | 7600 ^a | | | 800 | | |
| | | | | 8000 ^a | | |
| Ni(III) | 4700 | 1210 | 68 | 4650 | 1210 | 68 |
| | 4150 ^a | | | 4450 | | |
| | | | | 4450 ^a | | |

^a Primary amine.

upon reduction is generally rapid unless the metal is encapsulated by the ligand.²⁷

Discussion

This study has presented a rare opportunity for comparisons of geometrically isomeric systems where the isomerism is inherent to and directed by the ligand. MM calculations predicted that the $[M(\text{cis-diammac})]^{n+}$ complexes would not display the unusually short M–N bond lengths typical of $[M(\text{trans-diammac})]^{n+}$ relatives,²⁴ and this has been borne out in the two extant crystal structures of sixdentate-coordinated complexes of *cis*-diammac, Cd(II) and Cr(III).

The electronic spectra of the three $[M(\text{cis-diammac})]^{n+}$ complexes display electronic maxima at lower energy than their respective *trans* isomers, and these spectra have been modeled with AOM calculations (Table VI). Interestingly, the mean e_σ values of the $[M(\text{cis-diammac})]^{n+}$ complexes (Table VII), which are representative of the donor strength, do not differ markedly from those of their respective *trans* isomers, despite the average M–N bond lengths being considerably shorter in the latter complexes (Table V). This highlights the effect of the symmetry of the chromophore on the observed ligand field strength. In this case, the $[M(\text{trans-diammac})]^{n+}$ complexes exhibit approximate

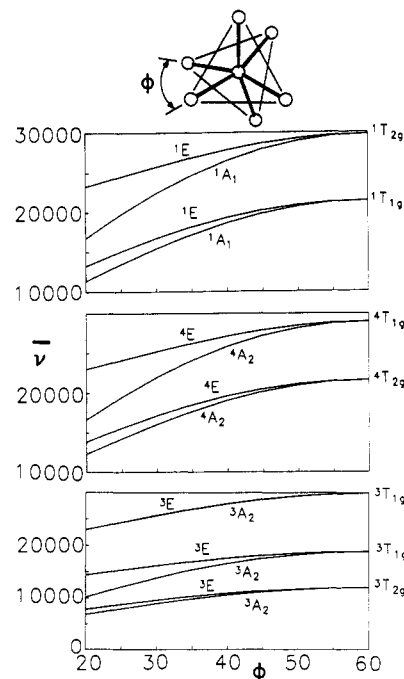


Figure 4. Energies of the spin allowed d–d transitions (cm^{-1}) as a function of the trigonal twist angle ϕ (deg). All electronic parameters were held constant. Key: top, Co(III); center, Cr(III); bottom, Ni(II).

axial symmetry, whereas the $[M(\text{cis-diammac})]^{n+}$ isomers show a significant trigonal twist distortion. The energies of the relevant electronic states of hexaammine complexes of Co(III), Cr(III), and Ni(II) as a function of the trigonal twist angle ϕ alone are shown in Figure 4. It is apparent that the energies of all spin-allowed transitions decrease with the trigonal angle ϕ , and a pronounced splitting of the second spin allowed transition is predicted to occur when ϕ falls below $\approx 45^\circ$. MM calculations predict that the twist angles for the $[M(\text{cis-diammac})]^{n+}$

complexes will be 52, 48, and 48° for Co(III), Cr(III), and Ni(II) respectively. The observation of lower energy electronic maxima for the $[M(\textit{cis}\text{-diammac})]^{n+}$ complexes relative to the $[M(\textit{trans}\text{-diammac})]^{n+}$ isomers, despite the similar mean e_{σ} values, is consistent with this.

Interpretation of the shift in the $M^{III/II}$ redox couples (Table IV) from $[M(\textit{trans}\text{-diammac})]^{n+}$ to $[M(\textit{cis}\text{-diammac})]^{n+}$ is somewhat more problematical. It has been shown that steric relaxation upon reduction is correlated with the half-wave potentials of a range of hexaamminecobalt(III) complexes,³¹ although other effects such as solvation and ion pairing are of some importance. MM calculations predict that $[M(\textit{cis}\text{-diammac})]^{n+}$ complexes should prefer extended M–N bond lengths and reduction will assist this, whereas the $[M(\textit{trans}\text{-diammac})]^{n+}$ analogues oppose an extension of the M–N bonds and reduction to the divalent state should be generally more difficult than for other hexamine complexes. This is qualitatively in agreement with the results presented herein.

The ¹H NMR spectrum of $[\text{Co}(\textit{cis}\text{-diammac})]^{3+}$ (Figure 1) was indicative of the complex existing primarily in the *cis*-(*ob*)₂ conformation in solution. Although the *cis*-(*lel*)₂ conformation possesses the same symmetry, and might be expected to give rise to a similar spectrum, it has been calculated to be ≈ 33 kJ/mol less stable than the *cis*-(*ob*)₂ conformer,²⁴ therefore, its presence in solution can be effectively ruled out. The presence of the asymmetric *cis*-(*lel*),(*ob*) conformer, which is predicted to be ≈ 6.5 kJ/mol less stable than the *cis*-(*ob*)₂ conformer, would result in a more complicated spectrum than that found, where all 16 methylene protons would be inequivalent. The relative concentrations of each conformer may be calculated based on their strain minimized energies.³² At room temperature, the concentration ratio of the *cis*-(*ob*)₂ conformer to the *cis*-(*lel*),(*ob*) conformer (which is degenerate with *cis*-(*ob*),(*lel*)) is calculated to be ≈ 9:1.

By contrast, MM calculations predict that the *trans*-λδ conformer is only 2.6 kJ/mol more stable than the *trans*-δδ conformer (which is degenerate with *trans*-λλ), whereas the *trans*-δλ conformer is ≈ 30 kJ/mol less stable than the *trans*-λδ conformer. On the basis of these strain energies, the ratio of the *trans*-λδ and *trans*-δδ (*trans*-λλ) conformers in solution should be ≈ 3:2. However, whether both species can be identified simultaneously in the NMR spectrum depends on the rate of interconversion between the conformers. An MM reaction profile³³ of the interconversion between the *trans*-δδ and *trans*-λδ conformers, where the total strain energy has been plotted as a function of the N–C–C–N torsional angle is shown in Figure 5. The transition state geometry is also shown, where the five-membered chelate ring is perfectly flat. The barrier to inversion is ≈ 20 kJ/mol which is comparable with similar calculations on other amine complexes bearing five-membered chelate rings.^{34,35} Moreover, this barrier is sufficiently small that exchange between the two conformations is rapid at room temperature on the NMR time scale; therefore, the observed spectrum is necessarily an average of the spectra due to these two conformers. Nevertheless, the observed spectrum is very well resolved, which indicates that both the *trans*-λδ and *trans*-δδ conformers exhibit similar spectra.

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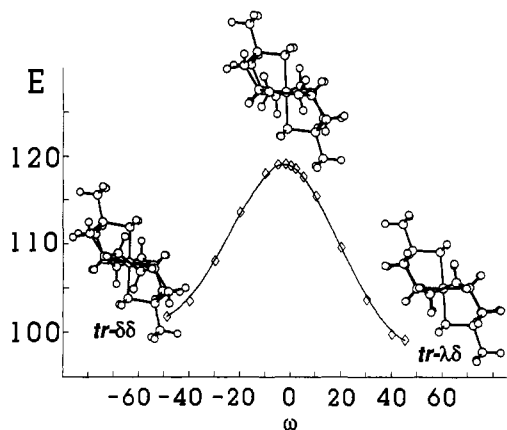


Figure 5. Total strain energy (kJ/mol) of $[\text{Co}(\textit{trans}\text{-diammac})]^{3+}$ as a function of the N–C–C–N torsional angle ω (deg).

Inspection of the MM refined structures of the *trans*-λδ and *trans*-δδ conformers reveals that the *trans* torsional angles are essentially reversed upon inversion of the five-membered chelate ring, i.e. H(C)–C–C–H(C') changes from 68° (*trans*-λδ) to 11° (*trans*-δδ) and H(D)–C–C–H(D') changes from 13° (*trans*-λδ) to 67° (*trans*-δδ) whereas the magnitudes of the *cis* torsional angles are essentially the same (although the signs are reversed). Although this conversion should result in a reversal of the ${}^3J_{CC'}$ and ${}^3J_{DD'}$ coupling constants, the observed resonances due to these protons should be essentially the same if the chemical shifts can be assumed to be unaffected. This was borne out of the simulated spectrum by reversing the ${}^3J_{CC'}$ and ${}^3J_{DD'}$ coupling constants, which had no effect on the calculated spectrum. Although the solution structures of the paramagnetic Cr(III) and Ni(II) complexes of *cis*- and *trans*-diammac could not be probed by NMR, MM calculations predict the *trans*-δδ and *cis*-(*ob*)₂ conformers to be at least 6 kJ/mol more stable than any other respective conformation, and therefore these conformers should be dominant in solution.

Conclusions

The results presented herein demonstrate that complexes of the two isomeric, sexidentate macrocyclic ligands display quite different physical and structural properties as a result of the mode of coordination dictated by the ligand. Specifically, the $[M(\textit{trans}\text{-diammac})]^{n+}$ complexes display exceptionally short M–N bond lengths, very high energy electronic maxima, and particularly negative $M^{III/II}$ redox couples, whereas the $[M(\textit{cis}\text{-diammac})]^{n+}$ isomers do not. A notable feature of the $[M(\textit{cis}\text{-diammac})]^{n+}$ complexes is the trigonal twist distortion that is affected by the ligand. It must be said that variations in the physical properties of geometrical isomers of coordination compounds are, of course, commonplace. The present study is novel in that the isomerism is prearranged by each macrocyclic ligand, with there being but one possible mode of sexidentate coordination in each case.

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Supplementary Material Available: Complete crystal data, H atom coordinates, thermal parameters, torsional angles and hydrogen bonds (<2.5 Å) for $[\text{Cr}(\textit{cis}\text{-diammac})](\text{ClO}_4)_3 \cdot 2\text{H}_2\text{O}$ (6 pages). Ordering information is given on any current masthead page.