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STRUCTURE OF A RIGID HEXAAXIA CAGE COBALT(III) DICHLORIDE PERCHLORATE

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Introduction

Sarcophagine complexes are of interest because the cage ligands encapsulate the metal making it substitutionally inert and the complex resistant to demetallation, allowing preparation of less stable oxidation states in conditions that would normally be inaccessible. Such complexes have displayed interesting photophysical, redox, and stereochemical properties¹ as well. The complex cations often have high internal symmetry and relatively weak intermolecular interactions which can lead to challenges with single crystal structure determination². Herein we report the structure of 1,2-dimethyl-3,10,14,21,24,31-hexaazapentacyclo-[10.10.10.0^{4,9}.0^{15,20}.0^{25,30}]dotriacontane cobalt(III), also called Δ -*lel*₃-[Co((CH₂)₇-char)]³⁺, crystallized as the anhydrous dichloride-perchlorate salt.

Synthesis

The complex was prepared by the base catalyzed co-condensation of propanal and formaldehyde on tris-1,2-diaminocyclohexane cobalt(III) as shown¹ in Scheme 1. A solution of **1** as the Δ -*lel*₃-[Co(*R,R*)-chxn]₃ (CF₃SO₃)₂·2H₂O³ (8.88 g, 10 mmol) in acetonitrile (160 mL) was treated with paraformaldehyde (3.0 g, 100 mmol), propanal (5.76 g, 100 mmol), and triethylamine (2.0 g, 20 mmol) for 3 hours at 20 °C. The crude products were concentrated to dryness and reduced with NaBH₄ (0.76 g, 20 mmol) in an aqueous buffer solution (NaHCO₃, 8.4 g in 400 mL H₂O), then separated by cation-exchange chromatography (Sephadex, Na⁺ form, 0.1 M trisodium citrate) into an orange lead fraction containing the cage complex, **2**, and a trailing orange-pink byproduct, **3**. Complex **2** was crystallized from concentrated aqueous HCl solution as the trichloride salt, which was itself recrystallized from HClO₄ solution to give the dichloride perchlorate salt studied herein.

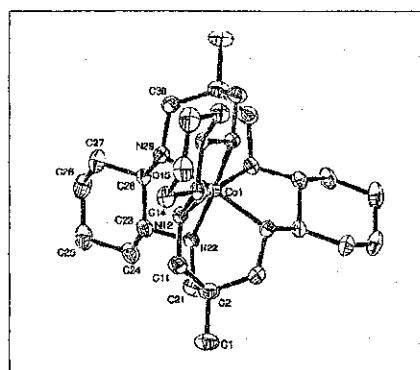


Figure 1. ORTEP perspective drawing of the Δ (*R,R*)-*lel*₃-[Co((CH₂)₇-char)]³⁺ cation.

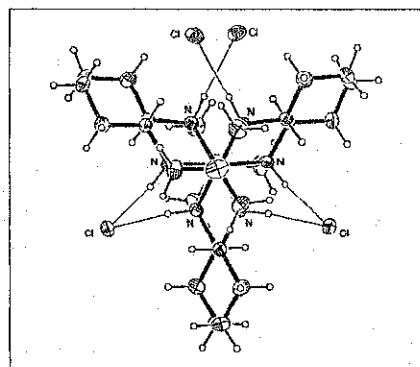


Figure 2. ORTEP perspective drawing of the Δ (*R,R*)-*lel*₃-[Co((CH₂)₇-char)]³⁺ cation viewed down the pseudo 3-fold axis showing the positions of the hydrogen bonded chloride ions.

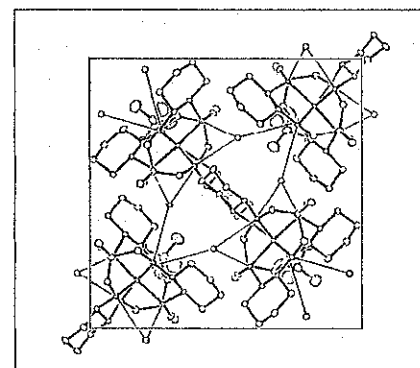


Figure 3. Projection down the *c* axis of the structure of Δ (*R,R*)-*lel*₃-[Co((CH₂)₇-char)](Cl)₂(ClO₄).

Single Crystal X-ray Crystallography

Crystal Data: Co(C₂₇H₄₄N₆)³⁺(Cl⁻)₂(ClO₄⁻); transparent orange tetragonal bipyramidal crystal bounded by the {1 0 1}, {0 1 1} and {4 1 0} planes; 0.16 × 0.20 × 0.22 mm; *M*_r = 704.07 Daltons; tetragonal, *P*4₁2₁2, No. 92; Rigaku AFC6R diffractometer; *a* = 15.315(2), *c* = 13.764(3) Å, *V* = 3228.5(9) Å³, *T* = 296 K; *Z* = 4; *d*_{calc} = 1.45 Mg/m³; *μ* = 70.6 cm⁻¹; CuKα, λ = 1.54184 Å; 2θ_{max} = 120°; 10,049 data; *T*_{min} = 0.367, *T*_{max} = 0.495 analytical correction; 2414 unique data, *R*_{int} = 0.062. Final model: anisotropic nonhydrogen atoms, idealized riding hydrogen atoms; final *R*₁ = 0.039, *R*₂ = 0.053 for 1752 data with *I*(*h*) > 3σ(*I*(*h*)) from RAELS00⁴. Details of the data collection, structure solution, and refinement may be found in the extended abstract.

Refinement of the other enantiomorph converged with *R*₁ = 0.1264, *R*₂ = 0.1779, and goodness of fit = 4.658 indicating the veracity of the enantiomorph chosen and thus of the space group choice.

Results and Discussion

The x-ray structure of the anhydrous mixed chloride-perchlorate salt (Figure 1) reveals an encapsulated cobalt(III) ion coordinated to the six secondary amine nitrogen donors of the hexadentate ligand in a near octahedral configuration. The analysis also shows that the cage complex retains the Δ -absolute configuration of the template ion and that the configuration about each coordinated secondary nitrogen atom is the same (*S*). The conformations of the C-C bonds in the equatorial five-membered chelate rings are fixed parallel (*lel*) to the C₃ axis of the cage complex by the rigid (*R,R*)-*trans*-1,2-cyclohexanediamine units in this Δ configurational stereoisomer (Figure 2). The cyclohexane rings fused to these equatorial chelate rings each assume the same chair conformation. The fused six-membered chelate rings of the cage bridgeheads appear conformationally somewhat more flexible and could adopt a right or left handed helical arrangement with respect to the molecular three-fold axis. In the structure, however, both trigonal caps adopt slight right-handed conformations that are nearly eclipsed. The cage cation is therefore assigned the Δ -D₃-*lel*₃ configuration.

The unit cell contains four cations, four perchlorate anions, and eight chloride ions thus requiring the cations and perchlorate anions to be located in two fold sites about the tertiary two fold axes. The structure consists of a network of cations linked together by hydrogen bonds between the chloride ions and the amine protons. Each chloride ion has two short hydrogen bonds, 3.17 Å and 3.20 Å, to one cation and one longer interaction, 3.40 Å, to another, thus utilizing all the potential hydrogen bonding sites of the cation. These interactions propagate to form a three dimensional network of hydrogen bonded cations and chloride anions propagating along the *c* axis as illustrated in Figure 3. The perchlorate anions are left simply to fill in the vacant spaces remaining in the network. The perchlorate anions are somewhat smaller than the available holes leading to their disorder about the two fold sites.

The visible absorption spectrum has two d-d bands at λ_{max} (ϵ /dm³ mol⁻¹ cm⁻¹) of 476 (131) and 348 nm (121) that have their respective origins in the ¹A_{1g} to ¹T_{1g} and ¹A_{1g} to ¹T_{2g} electronic transitions of a Co(III)N₆ chromophore with O_h symmetry. The optical rotatory dispersion (ORD) spectrum features two wings of opposite sign with maxima at λ_{max} ([M]/deg M⁻¹ m²) of 503 (6535) and 437 nm (-5812). The wings are inverted in sign and blue-shifted relative to the ORD of the template ion **1**³, pinpointing the hazards in making absolute configuration assignments solely from ORD or CD spectra in solution. The sign of the A or E symmetry component needs to be established from a single crystal study.

References

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