

**Syntheses of Macrotricyclic Polyazacryptates on Metal Ions:
X-Ray Crystal Structures of [(3,11-Dimethyl-7-nitro-1,5,9,13,16,19-
hexa-azatricyclo[9.3.3.3^{3,7}]icosane)cobalt(III)] (3+) and
[(3,11-dimethyl-7,15-dinitro-1,5,9,13,18,21-hexa-azatricyclo[9.5.3.3^{3,7}]-
docosane)cobalt(III)](3+) Ions**

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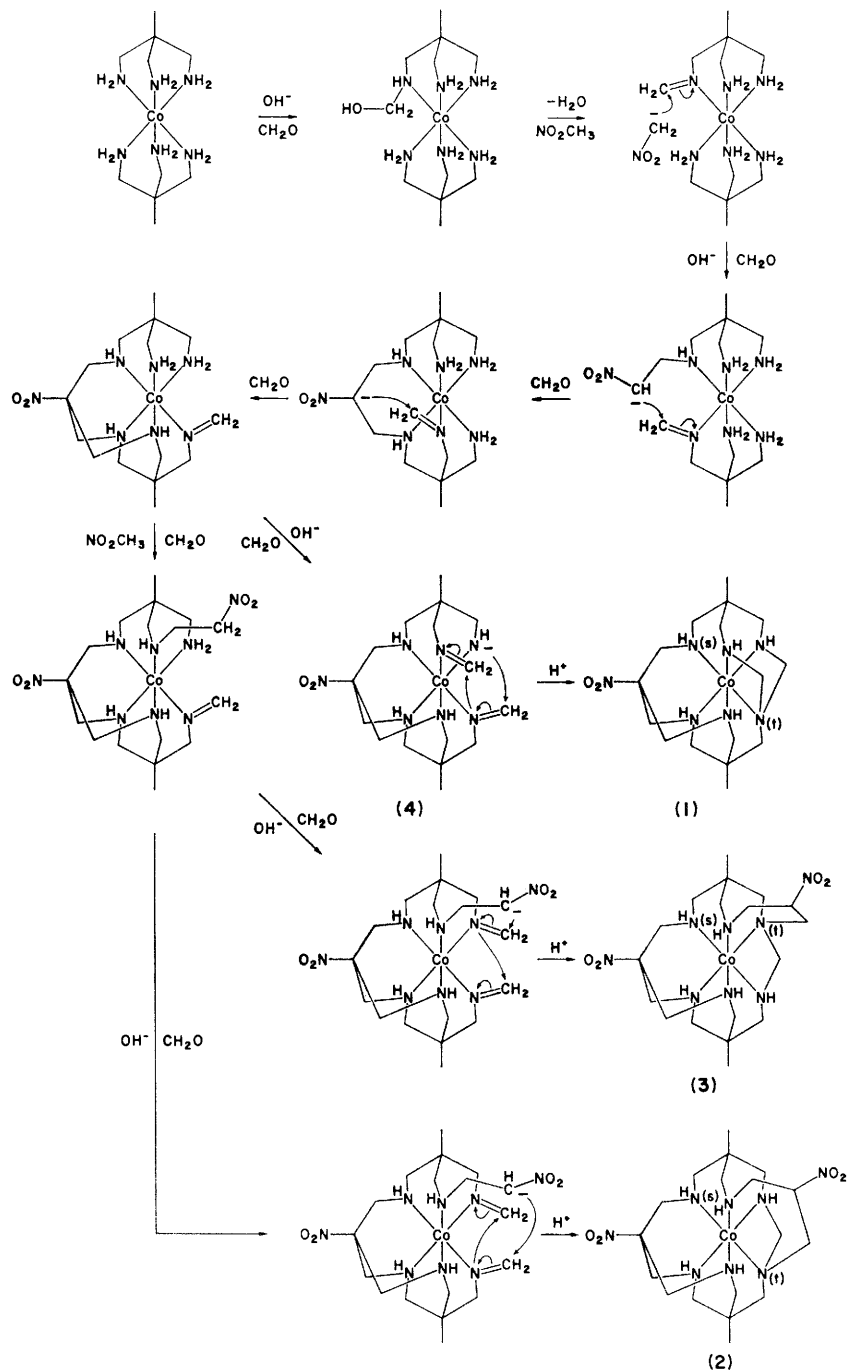
New macrotricyclic polyazacryptates with four- and six-membered chelate rings have been synthesized by the condensation of formaldehyde and nitromethane or ammonia with the bis[1,1,1-tris(aminomethyl)ethane]-cobalt(III) ion, and the structures of two of the complexes have been determined by X-ray crystallography.

Several macrobicyclic octa-, hepta-, and hexa-aza metal ion cages^{1,2} have been synthesized *via* template condensations based on $[M(en)_3]^{n+}$ complexes (en = ethylenediamine) and related substrates (M = Pt^{IV}, Rh^{III}, Co^{III}). This work has arisen from a growing understanding of the formation, stability, and reactivity of co-ordinated imines such as Co^{III}-N=CHR, derived from Co^{III} amines and aldehydes.^{3,4} The interesting properties observed for the macrobicyclic systems include unusual stability, chiroptical phenomena, and fast electron transfer reactions.

Condensation of formaldehyde and nitromethane with the $[Co(tame)_2]^{3+}$ [tame = 1,1,1-tris(aminomethyl)ethane] ion in aqueous solution at pH *ca.* 10.5 for 5 h results in a modest yield (*ca.* 50%) of the highly constrained macrotricyclic caged ion [(3,11-dimethyl-7-nitro-1,5,9,13,16,19-hexa-azatricyclo-

[9.3.3.3^{3,7}]icosane)cobalt(III)] (3+) [(1) in Scheme 1]. The structure of the (ZnCl₄)Cl salt, isolated after quenching of the reaction mixture to pH *ca.* 3 and chromatography on SP-Sephadex C-25, has been established by single crystal X-ray analysis. The structure (Figure 1) shows that three formaldehyde and one nitromethane molecules have condensed to form a trigonal cap on one side of the complex, and two formaldehyde molecules have condensed on the other side to form two four-membered chelate rings fused at a tertiary nitrogen donor [N(4)].

Several minor products were also isolated ($\leq 10\%$) and two of these [(2), (3) in Scheme 1] have chromatographic properties very similar to those of (1). The structure of (2) [(3,11-dimethyl-7,15-dinitro-1,5,9,13,18,21-hexa-azatricyclo[9.5.3.3^{3,7}]docosane)cobalt(III)]Cl₃, was also determined by an



Scheme 1

X-ray study (Figure 2). This shows a similar chelate ring arrangement to that of (1) but with a six-membered ring replacing one of the fused four-membered rings. A trigonal cap has again resulted on one side of the molecule through the condensation of three formaldehyde and one nitromethane molecules. The six-membered ring on the other side results from the condensation of two formaldehydes and one nitromethane, and this is fused at a tertiary nitrogen donor [N(4)] with a four-membered ring analogous to those found in the structure of (1).

The proposed mechanism for these condensations (Scheme

1) is based partly on evidence from previous Co^{III}-imine chemistry, and partly on the nature of several Co^{III}-N=CH₂ intermediates isolated during the condensation of [Co(tame)]³⁺ with formaldehyde.⁵ The exact order of Co^{III}-N=CH₂ formation and ring closure may not be that depicted but in the synthesis of (2) and (3), either the condensation of nitromethane and one formaldehyde occurs first at the tertiary nitrogen [N(t) in Scheme 1] or the six-membered ring closure precedes that of the fused four-membered ring.

The complex (1) has several unique structural and chemical features not previously encountered in Co^{III}-amine chemistry.

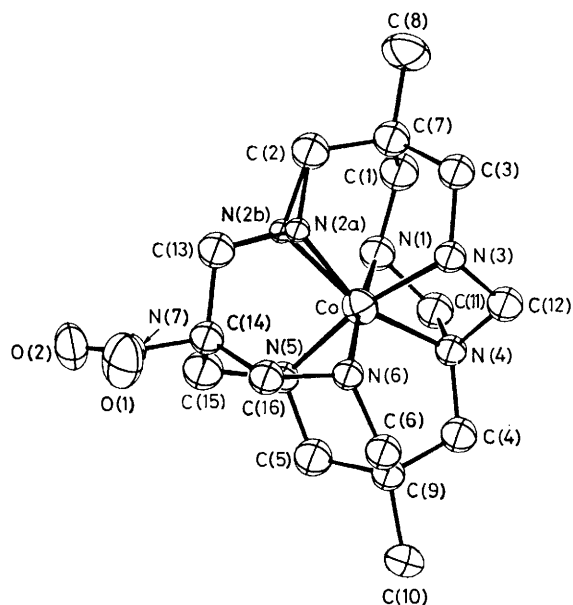


Figure 1. The [(3,11-dimethyl-7-nitro-1,5,9,13,16,19-hexa-azatricyclo[9.3.3.3^{3,7}]icosane)cobalt(III)](3+) cation, complex (1).

Crystal data: $\text{CoC}_{16}\text{H}_{33}\text{N}_7\text{O}_2\text{ZnCl}_4\text{Cl}\cdot 0.5\text{H}_2\text{O}$; monoclinic, $a = 30.482(2)$, $b = 9.007(1)$, $c = 20.428(1)$ Å, $\beta = 111.28(1)^\circ$, space group $C2/c$; $D_m = 1.69(2)$, $D_c = 1.67$ g cm⁻³ for $Z = 8$. Intensity data were collected on a Hilger and Watts Y290 diffractometer using Cu- K_α radiation. The structure was solved by Patterson and difference Fourier techniques and refined by full-matrix least-squares on 2678 reflections with $I > 4\sigma(I)$ (corrected for absorption, $\mu = 112.3$ cm⁻¹) to a final R factor of 0.046. Hydrogen atoms were included in refined or calculated positions and N(2) was disordered over sites N(2a) and N(2b) corresponding to enantiomeric forms of the complex ion.† Relevant bond lengths: Co-N(2) (av.), 1.93(1); Co-N(1), N(3) (av.), 1.95(1); Co-N(4), 1.93(1); Co-N(5), N(6) (av.), 1.97(1); N-C (av.), 1.48(1); C-C (av.), 1.53(1) Å. Distorted angles: N(1)-Co-N(4), 71.7(2); N(3)-Co-N(4), 73.5(2); Co-N(3)-C(12), 92.3(3); Co-N(4)-C(12), 92.0(3); N(3)-C(12)-N(4), 102.0(5)°.

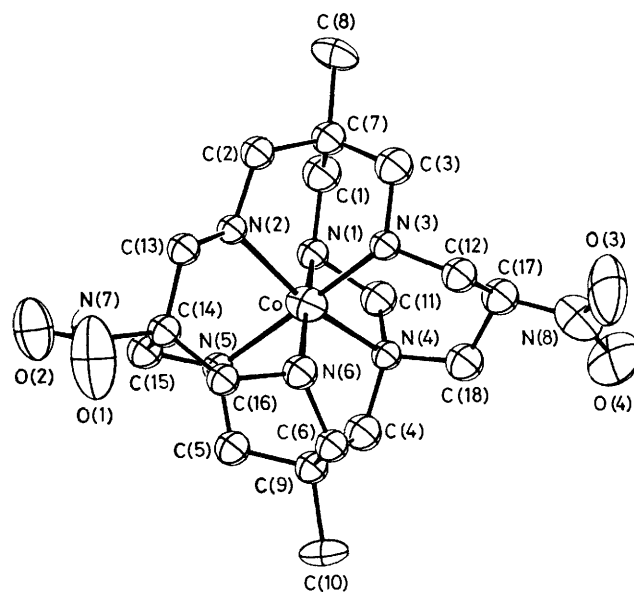


Figure 2. The [(3,11-dimethyl-7,15-dinitro-1,5,9,13,18,21-hexa-azatricyclo[9.5.3.3^{3,7}]dicosane)cobalt(III)](3+) cation, complex (2).

Crystal data: $\text{CoC}_{18}\text{H}_{36}\text{N}_8\text{O}_4\text{Cl}_2\cdot 2\text{H}_2\text{O}$; monoclinic, $a = 19.476(3)$, $b = 8.919(3)$, $c = 29.936(6)$ Å, $\beta = 93.97(1)^\circ$, space group $C2/c$; $D_m = 1.60(2)$, $D_c = 1.61$ g cm⁻³ for $Z = 8$. Intensity data were collected on a Hilger and Watts Y290 diffractometer using Cu- K_α radiation. The structure was solved by Patterson and difference Fourier techniques and refined by full-matrix least-squares on 1657 reflections with $I > 3\sigma(I)$ (corrected for absorption, $\mu = 86.3$ cm⁻¹) to a final R factor of 0.089. Hydrogen atoms were included in refined or calculated positions.† Relevant bond lengths: Co-N(1), 1.93(1); Co-N(4), 2.00(1); Co-N, 1.97(1)-2.07(1); N-C (av.), 1.49(1); C-C (av.), 1.53(1) Å. Distorted angles: N(1)-Co-N(4), 73.3(4); Co-N(3)-C(12), 122.4(8); Co-N(4)-C(18), 125.8(8); Co-N(1)-C(11), 91.9(7); Co-N(4)-C(11), 89.4(7); N(1)-C(11)-N(4), 105(1)°.

One side of the $\text{Co}^{\text{III}}\text{N}_6$ chromophore is severely distorted from octahedral geometry. This results from the constraints imposed on the closely octahedral $[\text{Co}(\text{tame})_2]^{3+}$ ion⁶ by the trigonal nitromethane-formaldehyde cap on one side and the fused four-membered rings on the opposite side. The contribution to the distortion effect by the nitromethane-formaldehyde cap is seen from an examination of a flexible scale model. Models of the distorted intermediates (4) also indicate favourable stereochemistry for the four-membered ring closure and this factor may be important in their formation.

The reduction potential for (1) ($E = -0.62$ V vs. standard hydrogen electrode in 0.1 M NaClO_4) is the lowest we have observed for Co^{III} -amine complexes. It can be argued that a reason for the low potential is the strained macrotricyclic cage which would inhibit the generation of the larger Co^{2+} ion.

Reduction of (1) with Zn in acid conditions converted the nitro group into the amine, cleaved the four-membered rings, and removed the Co^{II} ion. The resulting tripodal sexidentate amine ligand is currently being used in attempts to encapsulate labile divalent metal ions.

† The atomic co-ordinates for this work are available on request from the Director of the Cambridge Crystallographic Data Centre, University Chemical Laboratory, Lensfield Rd., Cambridge CB2 1EW. Any request should be accompanied by the full literature citation for this communication.

The macrotricyclic hepta-aza cryptate [(3,11-dimethyl-1,5,7,9,13,16,19-hepta-azatricyclo[9.3.3.3^{3,7}]icosane)cobalt(III)](3+) (6) has also been synthesized in reasonable yield (ca. 30%) using a strategy similar to that for (1) but replacing the NO_2CH_2^- nucleophile with NH_3 . This replaces the C- NO_2 moiety of (1) with an N atom. The extraordinary kinetic stability of the four-membered ring structures in the Co^{III} complexes (1) and (6) is emphasized by the lack of observable decomposition or dissociation of the complexes in 6 M HCl over several hours at 50–60 °C. Furthermore, treatment of (6) with aqueous $\text{CF}_3\text{SO}_3\text{H}$ over several days at room temperature yields a tri-imine complex (80%) in which the aza cap has been ruptured, the methene groups retained, and the four-membered rings left intact.

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