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Communications

Stereospecific Template Synthesis of a Macrotetracyclic Hexaazacryptate: X-ray Crystal Structure of (9,17-Dimethyl-13-nitro-1,3,5,7,11,15-hexaazatetracyclo-[11.5.1.1^{3,9}.1^{5,1}]henicosane)cobalt(III) Chloride

Sir:

The reactivity of the coordinated imines Co^{III}—N=CH_2 toward nucleophilic reagents was recently exploited in the synthesis of several macrotricyclic polyazacryptates[1,2] with fused four- and six-membered chelate rings. The grossly distorted nature of these encapsulated metal ions coupled with their remarkable stability brings about new prospects for modulating the chemical, electrochemical, and spectroscopic properties of Co^{III} amines and in particular the Co^{III} polyazacryptates.[3,4] This note reports the synthesis, structure, and properties of a macrotetracyclic polyazacryptate with three fused four-membered chelate rings and describes some synthetic derivatives of the complex.

Results and Discussion. Treatment of $[Co(tame)_2]Cl_3$ [tame = 1,1,1-tris(aminomethyl)ethane] in water at pH ca. 10.5 (Na_2CO_3) with formaldehyde and nitromethane (60 equiv) over 10 h gave a deep orange-brown solution. Four major products were isolated after quenching to pH ca. 3 and ion-exchange chromatography on SP-Sephadex C-25 (Na^+ form) using 0.05 M trisodium citrate and 0.01 M disodium (+)-tartrate eluants. Three of these were obtained in greater yields under alternative reaction conditions and were shown by ^1H and ^{13}C NMR spectroscopy to be identical with the macrotricyclic Co^{III} polyazacryptates reported recently[1] with similar reagents. The fourth major product (ca. 10%) was identified as the macrotetracyclic metal ion cage [(9,17-dimethyl-13-nitro-1,3,5,7,11,15-hexaazatetracyclo[11.5.1.1^{3,9}.1^{5,17}]henicosane)cobalt(III)](3+) (**5** in Scheme I) by a single-crystal X-ray study of the hydrated yellow trichloride salt.[5]

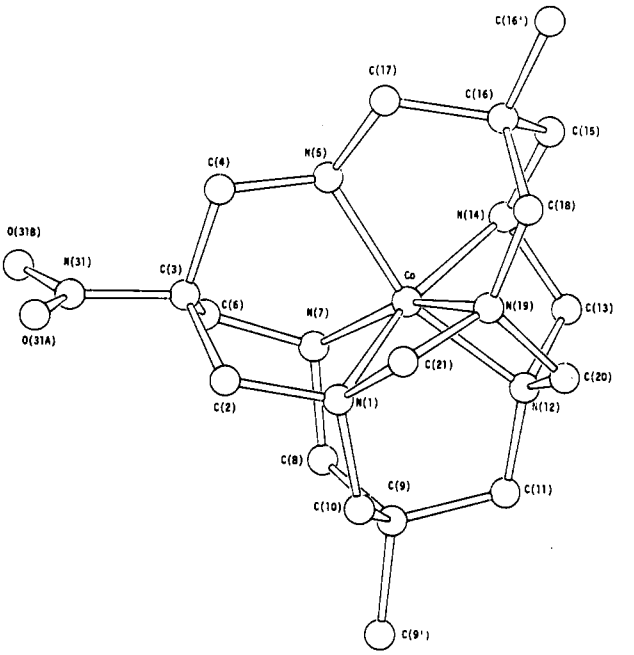

Figure 1. Molecular structure of the macrotetracyclic cation **5** as the trichloride salt. Bond lengths (Å): Co–N(1,14)$_{av}$ = 1.942 (4); Co–N(12,19)$_{av}$ = 1.922 (4); Co–N(5,7)$_{av}$ = 1.956 (4); N–C$_{av}$ = 1.487 (2); C–C$_{av}$ = 1.534 (2). Distorted angles (deg): N(1,12)–Co–N(19,14)$_{av}$ = 73.7 (2); N(1,14)–Co–N(12,19)$_{av}$ = 95.7 (2); N(12)–Co–N(19) = 73.5 (2); N(5,7)–Co–N(12,19)$_{av}$ = 159.1 (2); Co–N(1)–C(21) = 88.7 (4); Co–N(14)–C(13) = 90.6 (4); Co–N(12,19)–C(13,21)$_{av}$ = 90.9 (3); Co–N(12,19)–C(20,20)$_{av}$ = 92.3 (3); N(1,12,12)–C(21,20,13)–N(19,19,14)$_{av}$ = 102.4 (3).

The results indicate two independent molecules in the asymmetric unit, and the structure (Figure 1) shows that a trigonal cap has formed through the condensation of one nitromethane and three formaldehyde molecules. The chemistry to this point is analogous to that in the syntheses of the macrotricyclic complexes,[1] but in the present case, a further three formaldehydes have condensed in sequence to form three fused four-membered rings, one of which is fused to the six-membered rings imposed by the cap. The resulting macrotetracyclic cage has three chiral tertiary and three chiral secondary nitrogen donors and was further characterized by its ^1H and ^{13}C NMR spectra [^1H signals at δ 5.6–6.0 (complex AB patterns, 6 protons), δ 2.6–4.6 (broad complex pattern, 18 protons), δ 1.0 (singlet, 6 protons) relative to internal sodium 3-(trimethylsilyl)propanesulfonate; $^{13}C\{^1H\}$

(1) Gainsford, G. J.; Geue, R. J.; Sargeson, A. M. *J. Chem. Soc., Chem. Commun.* **1982**, 233.
(2) Gainsford, G. J.; Geue, R. J.; Sargeson, A M. I.U.Cr. Conference, Ottawa, Canada, 1981, Poster 08.2-44.
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(5) Crystal data: $CoC_{17}H_{33}N_7O_2Cl_3 \cdot 3H_2O$; monoclinic, space group $P2_1/n$; a = 23.03 (1), b = 10.519 (5), c = 22.26 (1) Å; β = 106.77 (5)°; D_{measd} = 1.52 (1), D_{calcd} = 1.51 g cm^{-3} for Z = 8, T = 295 K. A unique data set was measured to $2\theta_{max}$ = 45° with a Syntex $P2_1$ four-circle diffractometer in conventional $2\theta/\theta$ scan mode and fitted with a monochromatic Mo Kα radiation source (λ = 0.7106$_9$ Å). A total of 6776 independent reflections were obtained, 3710 with $I > 3\sigma(I)$ being considered "observed" and used in the basically 9 × 9 block-diagonal least-squares refinement after analytical absorption correction (μ_{Mo} = 9.9 cm^{-1}; specimen 0.45 × 0.26 × 0.12 mm). Anisotropic thermal parameters were refined for all non-hydrogen atoms excepting disordered solvent fragments; x, y, z, and U_{iso} for H atoms were constrained at calculated values. Residuals at convergence were R,R' = 0.057, 0.066, reflection weights being $(\sigma^2(F_o) + 0.0005(F_o)^2)^{-1}$. Neutral complex scattering factors were used;[6] computation used the X-RAY 76 program system[7] implemented by S. R. Hall on a Perkin-Elmer 3240 computer.

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(7) Stewart, J. M., Ed. "The X-RAY System-Version of March, 1976", Technical Report TR-446; Computer Science Center, University of Maryland: College Park, MD, 1976.

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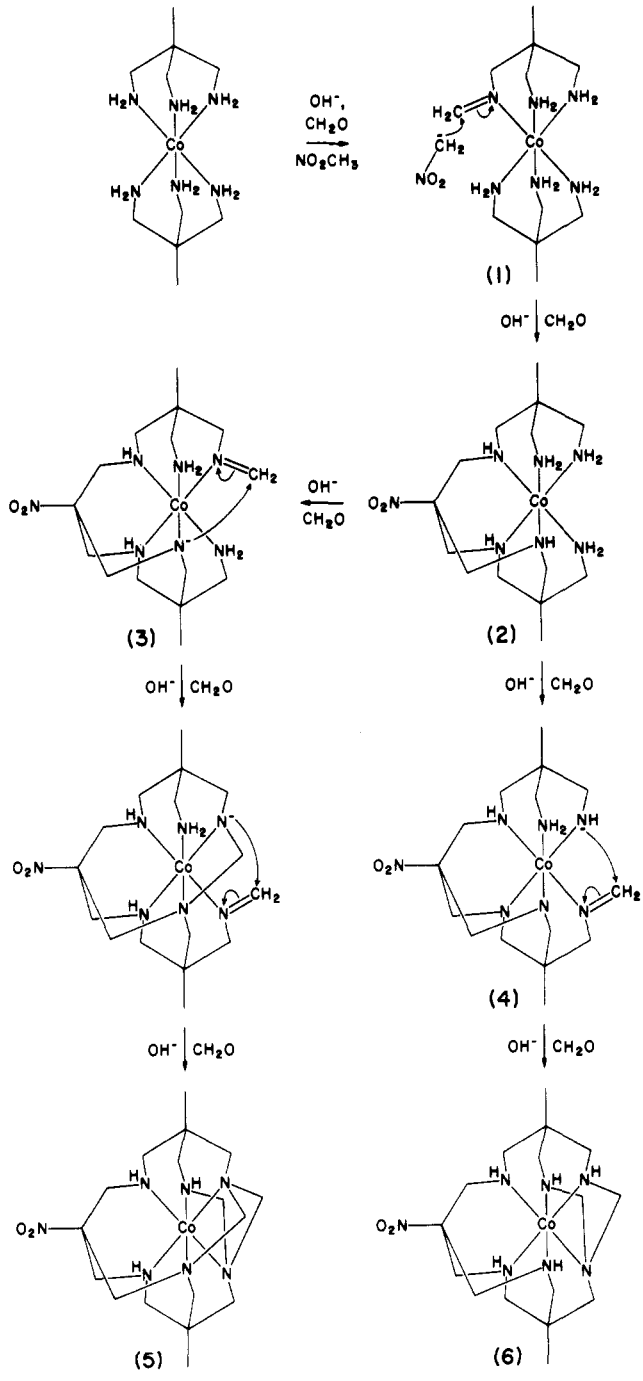
signals at δ 32.10, 31.45, 24.82 (3 broad singlets), δ 21.57 (singlet), δ −10.53 to 5.97 (9 singlets), δ −17.93 (broad singlet), δ −47.69 (singlet) relative to internal 1,4-dioxane]. The unusually low-field proton signals and the three lowest field ^{13}C signals appear to identify the strained methylene groups of the four-membered chelate rings uniquely, in both this molecule and related complexes.

Routes to the macrotetracyclic cage **5** and the principal macrotricyclic ion[1] **6** (ca. 30% here) are shown in Scheme I. The Co^{III}–imine intermediate **1** was identified and characterized by ^1H and $^{13}C\{^1H\}$ NMR data.[8] It is implied that the trigonally capped complex **2** appears prior to any four-membered ring closures although results obtained in the absence of nitromethane[9] suggest that in some instances one and possibly two of these may precede trigonal cap formation. This would partially account for the predominance of macrotricyclic products since the formation of an isolated four-membered ring at any stage of the reaction must preclude the syntheis of **5**. The imine **4** is also expected to lead to several macrotricyclic complexes, including the major one **6**, which was reported earlier.[1,2] The alternative intermediate **3** gives the macrotetracycle **5** exclusively if subsequent ring closures occur via three consecutive nucleophilic attacks of a deprotonated secondary nitrogen donor on a Co^{III}—N=CH_2 imine (Scheme I). In the case of **3** condensation with a deprotonated primary nitrogen is also feasible and this would again lead to macrotricyclic products. However, visual examination of a flexible scale model of **3** fails to reveal any marked regioselectivity between these two alternatives and in view of the generally enhanced rates of proton exchange on the secondary nitrogens of other $[Co(tame)_2]^{3+}$ derivatives[9] it is expected that **3** follows the path depicted.

The molecular structure of **5** (Figure 1) exhibits gross angular distortions about the cobalt center and nitrogen donor atoms, with the CoN_6 configuration being largely constrained by the inflexible ligand geometry. The three fused 1,3-diazacobaltetidine rings result in distortions of 16–21° from octahedral values for five of the N–Co–N angles. A particularly interesting structural feature is apparent in the tightly bound nature of the three tertiary nitrogens which are held in close proximity to the metal center by the encapsulated ligand. The stereospecificity in the synthesis of **5** also merits some explanation in terms of the molecular structure. If the observed skeletal configuration about the metal center is maintained, the six chiral nitrogen donors and the chiral cobalt atom give rise to 2^7 possible stereoisomers or 2^6 diastereoisomers.[10] However, flexible models of the complex clearly indicate that for a given chirality about cobalt the rigid structure only permits two diastereoisomers, interconvertible by inversion at the secondary nitrogen center N(5). We have not yet detected any diastereoisomers of **5** by chromatographic or spectral analysis in acidic solutions, and the synthesis appears to yield just one pair of enantiomers.

The visible spectrum of **5** [λ_{max}, nm (ϵ_{max}, M^{-1} cm^{-1}) in H_2O: 470 (337), 342 (423)] shows a remarkable intensity enhancement for the visible absorption bands (derived from the $^1A_{1g} \rightarrow {}^1T_{1g}$ and $^1A_{1g} \rightarrow {}^1T_{2g}$ transitions of octahedral parentage) compared with the equivalent transitions of other cobalt(III) hexaamine complexes having near-octahedral nitrogen donor atom configurations[4,11,12] ($\epsilon_{max} \approx$ 50–150 M^{-1} cm^{-1}). It is apparent from detailed comparisons with the ultraviolet and visible spectra of the cobalt(III) hexaamines that the distortions from octahedral symmetry within the chromophore are largely responsible for the enhanced transition moments, rather than extra chromophoric field influences or position and intensity changes in the low-energy charge-transfer bands (λ_{max} for **5**: 259, 207 nm).

Scheme I



Reduction of **5** with Zn in HCl solution yields the amino-capped Co^{II} ion **7**, which further reacts with HCl to give the tripodal heptaamine **9** (Scheme II). The amino derivative of **5** (complex **8**) was isolated at an intermediate stage by reoxidation and ion-exchange chromatography and was characterized by ^1H NMR spectroscopy and analytical data. The two highly strained macrotetracyclic complexes **5** and **8** are remarkably stable to hydrolysis in acidic (6 M HCl at 60 °C) and mildly basic (pH <9 at 25 °C over several hours) solutions although the trigonal cap of **5** is slowly cleaved at pH >9 (25 °C).

Electrochemical analysis of the Co^{III}/Co^{II} reduction potentials in aqueous 0.1 M $NaClO_4$ (pH 6) media gave E values of −0.31

(8) The monoimine species **1** was recovered by quenching (with HOAc to pH ~3) either $[Co(tame)_2]Cl_3$–formaldehyde–nitromethane or $[Co(tame)_2]Cl_3$–formaldehyde reaction mixtures (aqueous, pH ~10.5) after 30 min. Cation-exchange chromatography using SP-Sephadex C-25 (Na^+ form) resin and 0.05 M trisodium citrate eluant was used to isolate **1**. ^1H NMR (0.1 M DCl, vs. sodium 3-(trimethylsilyl)propanesulfonate as internal standard): δ 7.96 (broad AB quartet, J = 6 Hz, N=CH_2), 4.7–5.3 (broad, NH_2), 3.58 (broad singlet, =N—CH_2–), 1.1–3.1 (broad complex multiplet, –CH_2–), 0.90, 0.96 (2 singlets). $^{13}C\{^1H\}$ NMR (0.1 M DCl, vs. 1,4-dioxane as internal standard): δ 109.2 (N=CH_2), −1.3, −2.4 (=N—CH_2–), −21.0, −21.4, −21.7 (–CH_2–), −28.3, −29.2 (quaternary C), −46.1, 46.5 (–CH_3).

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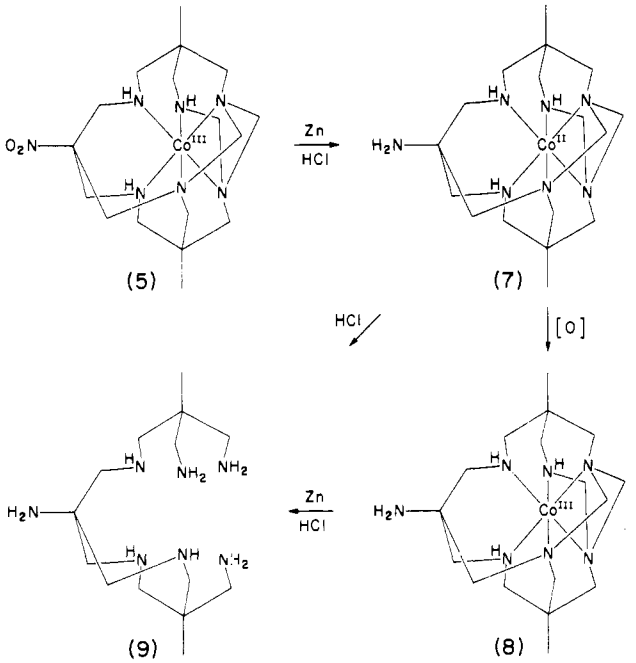
Scheme II



and −0.38 V (vs. the standard hydrogen electrode) for the nitro-capped complex **5** and the amino derivative **8**, respectively, and both reductions were quasi-reversible. The potentials are higher than that found for the macrotricyclic ion **6** (E = −0.51 V[9]), but it is clear from a comparison of the structures of **5** (Figure 1) and **6**[1] that the additional methylene bridge in **5** induces a further distortion of the nitrogen donor atoms over the cobalt sphere without significantly increasing the CoN_6 core size (Co–N distances are similar). This effectively opens up one side of **5** relative to the equivalent side of the macrotricyclic cage **6** and could be conceived to allow more favorable accommodation of the larger but more readily distorted Co^{2+} ion.

Registry No. 1, 95674-09-2; **2**, 95674-10-5; **5**·Cl_3·$3H_2O$, 95674-08-1; **7**, 95674-11-6; **8**, 95674-12-7; **9**, 95674-13-8; tame, 15995-42-3; $[Co(tame)_2]Cl_3$, 60909-16-2; CH_2O, 50-00-0; NO_2CH_3, 75-52-5.

Supplementary Material Available: Listings of atomic coordinates, cobalt atom environments, ligand geometries, and anisotropic thermal parameters for the two independent molecules in the asymmetric unit (11 pages). Ordering information is given on any current masthead page.

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Metalloporphyrin Coordination Chemistry of Highly Oxidizing Oxyanions: The Chromate Complex of Iron(III) Tetraphenylporphyrin

Sir:

Iron (III) porphyrin coordination of a variety of unusual oxyanion ligands is possible as a consequence of the oxophilic character of iron(III) and the seemingly universal requirement for at least one axial ligand on the macrocyclic complex. Five-coordinate iron porphyrin complexes have been reported for the following: ClO_4^-,[1] NO_3^-,[2] SO_4^{2-},[2,3] OH^-,[4] O_2^{2-},[5] O^{2-},[6] μ-oxo,[7] μ-peroxo,[8] and various organic sulfonate,[2,9] carboxylate,[9,10] phenoxide,[10b,11] and alkoxide[10b,12] ligands. The general strategy for inducing coordination of weak-field oxyanions involves using a noncoordinating solvent and making only the ligand of interest available to the iron porphyrin. Thus, a wide variety of additional oxyanionic complexes conceivably are possible, and this preliminary report describes a group of newly prepared adducts with potentially strongly oxidizing oxyanions. Synthesis and spectroscopic properties of the novel μ-chromato dimeric complex are discussed in the greatest detail. Previous use of CrO_4^{2-} as a ligand has been largely restricted to generation of monomeric cobalt(III) ammine chromate complexes.[13]

Oxyanionic complexes were prepared by metathesis of the chloroiron(III) porphyrin with the respective silver salt or by hydrolysis of the μ-oxo dimeric iron(III) porphyrin with the oxyacid. Preparation of the chromate complex was carried out by stirring a 10% excess of solid Ag_2CrO_4 (Alfa) with chloroiron(III) tetraphenylporphyrin ((TPP)FeCl) in dry THF for 24 h. The mixture was protected from light by a foil wrap, and manipulations were conducted in a nitrogen-filled glovebox to preclude water contamination and subsequent μ-oxo dimer formation. Completion of reaction was judged by monitoring loss of the band at 380 nm characteristic of the (TPP)FeCl species. Removal of solid AgCl by filtration, evaporation of the THF to half the original volume, and addition of two volumes of heptane resulted in a microcrystalline product (the yield ranged to 75% if the heptane–THF solution was allowed to stand 24 h).

Variable amounts of solvent were retained in the presumably dimeric (μ-chromato)iron(III) tetraphenylporphyrin complex. Elemental analysis[14] revealed a chromium/iron ratio of 0.49 ±

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