

1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol and *all-cis*-2,4,6-Trimethoxycyclohexane-1,3,5-triamine as Building Blocks for New Multidentate and Macrocyclic Ligands¹

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Treatment of the two Co^{III}-hexamine complexes [Co(taci)₂]³⁺ and [Co(tmca)₂]³⁺ (taci = 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol, tmca = *all-cis*-2,4,6-trimethoxycyclohexane-1,3,5-triamine) in CH₃CN with NEt₃ and excess paraformaldehyde gave the corresponding hexamethylideneimino (hmi) derivatives [Co(taci)₂-hmi]³⁺ and [Co(tmca)₂-hmi]³⁺ in excellent yield. Both hexaimines were stable in acidic aqueous solution and were isolated as solid compounds. They were characterized by elemental analyses, ¹³C NMR, ¹H NMR, IR, and visible spectroscopy, mass spectrometry, and single-crystal X-ray analyses. [Co(taci)₂-hmi]Cl₃·6H₂O crystallizes in the monoclinic space group *C2/m*, C₁₈Cl₃CoH₄₂N₆O₁₂, *Z* = 2, *a* = 13.046(2) Å, *b* = 9.802(2) Å, *c* = 12.332(2) Å, β = 118.42(1)°. [Co(tmca)₂-hmi](HSO₄)₃ crystallizes in the monoclinic space group *C2/c*, C₂₄CoH₄₅N₆O₁₈ S₃, *Z* = 4, *a* = 14.087(3) Å, *b* = 15.890(3) Å, *c* = 15.502(3) Å, β = 95.27(3)°. Subsequent treatment of [Co(taci)₂-hmi]³⁺ with nitromethane and base resulted in the formation of [Co(hebdoc)]⁺ (hebdoc = 8,10,18,20,21,22-hexahydroxy-9,19-bis(methylamino)-4,14-dinitro-2,6,12,16-tetraazatricyclo[15.3.1.1^{7,11}]docosa-2,12-diene-4,14-diate), where the two taci fragments were fused by two anionic N=CH–C(=NO₂[−])–CH₂–NH bridges. Two major diastereoisomers were formed from fifteen possibilities. They had different configurations at coordinated methylamino groups and were incorporated in a disordered manner in the crystal structure of [Co(hebdoc)]₂Cl₂·3.5H₂O: C₄₀Cl₂Co₂H₇₅N₁₆O_{23.50}, orthorhombic, space group *Pna2₁*, *Z* = 4, *a* = 33.835(2) Å, *b* = 15.356(2) Å, *c* = 9.967(2) Å. In the base-catalyzed reaction of [Co(tmca)₂]³⁺ with an appropriate mixture of formaldehyde and acetaldehyde, the condensation process was followed by a coupling reaction. After reduction with NaBH₄ and air oxidation, a Co^{III} complex with the novel hexadentate ligand *N*-(9'-amino-8',10',11'-trimethoxy-2',6',6'-diazabicyclo[5.3.1]undec-4'-yl-methyl)-2,4,6-trimethoxycyclohexane-1,3,5-triamine was formed as the major product. Direct treatment of [Co(taci)₂-hmi]³⁺ and [Co(tmca)₂-hmi]³⁺ with NaBH₄ resulted in the liberation of the new triamines 1,3,5-trideoxy-1,3,5-tris(methylamino)-*cis*-inositol and *all-cis*-2,4,6-trimethoxytris(*N*-methyl)cyclohexane-1,3,5-triamine.

Introduction

Organic polyamines are a well-known group of complexing agents for transition metal cations,³ and macrocyclic polyamines have been of particular interest in the last two decades owing to their ability to form metal complexes of exceptionally high thermodynamic and kinetic stability.⁴ Various synthetic routes

have been developed for the preparation of tailored polyamine ligands, and the use of suitable molecular building blocks of lower denticity, which can be coupled to give the target ligand, has been one useful strategy.⁵ This proved to be particularly successful, when a template method was used, in which the donor set is preorganized for the coupling reaction by coordination to a suitable metal cation. As an example, the condensation reactions of Co^{III} hexamine complexes with aldehyde or ketone components readily yield a variety of macrocycles and macropoly-cyclic cages.⁶

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- (1) The following acronyms were used for the ligands throughout this paper: taci, 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol; tmca, *all-cis*-2,4,6-trimethoxycyclohexane-1,3,5-triamine; tmaci, 1,3,5-trideoxy-1,3,5-tris(methylamino)-*cis*-inositol; tmca, *all-cis*-2,4,6-trimethoxytris(*N*-methyl)cyclohexane-1,3,5-triamine; hebdoc, 8,10,18,20,21,22-hexahydroxy-9,19-bis(methylamino)-4,14-dinitro-2,6,12,16-tetraazatricyclo[15.3.1.1^{7,11}]docosa-2,12-diene-4,14-diate; abuca, *N*-(9'-amino-8',10',11'-trimethoxy-2',6',6'-diazabicyclo[5.3.1]undec-4'-yl-methyl)-2,4,6-trimethoxycyclohexane-1,3,5-triamine. The Co^{III} complexes were abbreviated by the following numbering scheme: [Co(taci)₂]³⁺ (1); [Co(tmca)₂]³⁺ (2); the corresponding hexamethylideneimino (= hmi) derivatives, [Co(taci)₂-hmi]³⁺ (3); [Co(tmca)₂-hmi]³⁺ (4); [Co(hebdoc)]⁺ (5); and [Co(abuca)]³⁺ (6).
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In a series of recent papers, 1,3,5-triamino-1,3,5-trideoxy-*cis*-inositol (*taci*) has been shown to have some rather remarkable metal binding properties, which are attributed to the rigidity and versatility of this ligand.⁷⁻⁹ It follows that the complexes of this compound could serve as promising templates for the construction of novel hexadentate ligands. Previously, it has been demonstrated that the simple condensation of *taci* with 3 equiv of salicylic aldehyde, followed by hydrogenation, resulted in the formation of a potentially hexadentate chelator with a mixed N–O donor set.¹⁰ In the present investigation, the well-known hexamine complexes [Co(*taci*)₂]³⁺ (**1**)⁸ and its O-methylated derivative [Co(*tmca*)₂]³⁺ (**2**)¹¹ were used as templates along with formaldehyde and acetaldehyde or nitromethane to couple these tridentate ligands by nonaqueous procedures.^{12,13} The synthetic work is discussed in detail along with a comprehensive characterization of two new macrocyclic hexamine Co^{III} complexes.

Experimental Section

Physical Measurements and Analyses. UV–vis spectra were recorded with an Uvikon 820 spectrophotometer at 25 °C. IR spectroscopic measurements were performed with a Perkin-Elmer 883 IR spectrometer (KBr wafer). ¹H and ¹³C NMR spectra were measured at ambient temperature in D₂O with a Bruker DPX 300 Fourier transform NMR spectrometer at frequencies of 300.13 and 75.47 MHz, respectively. ¹³C, ¹H HMQC (heteronuclear multiple quantum coherence) and ¹³C DEPT (distortionless enhancement by polarization transfer) experiments were performed according to the literature.¹⁴ A Varian Gemini 300 MHz Fourier transform NMR spectrometer was used for the measurements of the DEPT spectra of complex **6**. Chemical shifts (in ppm) are given relative to sodium (trimethylsilyl)propionate-*d*₄ (=0 ppm) as internal standard. FAB⁺ mass spectra were recorded with a VG ZAB VSEQ instrument. Test solutions were prepared by dissolving the samples in water and mixing the resulting solutions with a glycerol matrix prior to introduction into the spectrometer. Deprotonation products of a complex [CoL₃]³⁺ are listed as [H_{−*y*}CoL₃]^{3−*y*}. Some of the ions found in the mass spectra must be interpreted as Co^{II} rather than Co^{III} complexes. It is well-known that Co^{III} can be reduced readily to Co^{II} in a glycerol matrix under FAB conditions.^{8,11}

C, H, N, Cl analyses were performed by D. Manser, Laboratorium für Organische Chemie, ETH Zürich. Co was analyzed by atomic

absorption spectroscopy (Microanalytical Laboratory, ANU). Semi-quantitative determinations of Co^{II} in solution were performed using the Merckoquant 10002 test strips (Merck).

Acidity constants (*K*_a) of the two triamines *tmca* and *tca* were determined by potentiometric titrations (25.0 ± 0.1 °C, 0.10 M KCl) as described previously.⁷ The electrode system was calibrated by titrating a 2 × 10^{−3} M HCl solution with 0.1 M KOH, using appropriate corrections for the liquid junction potentials. The constants given are concentration quotients, and pH is defined as −log[H⁺]. The p*K*_w was found to be 13.79(1). The amines used were analytically pure trihydrochlorides (total concentration, 10^{−3} M; total volume, 50 mL) and also pure stereoisomers (NMR). A small amount of additional HCl was added to ensure complete protonation at the beginning of the titration. Four independent measurements were made for each of the two compounds. A total of 31–71 data points in the range 3.0 < pH < 10.7 were considered for evaluation, using the computer program SUPERQUAD.¹⁵ The values for p*K*_w and for the total concentrations of all components were held fixed during the refinement. The final result was checked by using the computer program BEST,¹⁶ however, no significant differences were encountered by comparing the results of the two programs. Values of σ_{pH} = [Σw_{*i*}(pH_{*i*}^{obs} − pH_{*i*}^{calcd})²/Σw_{*i*}]^{1/2}, w_{*i*} = (pH_{*i−1*} − pH_{*i+1*})^{−2}, fell in the range 0.0035–0.0082. The estimated standard deviations of the evaluated p*K*_a (= −log *K*_a) values given by SUPERQUAD are less than 0.01.

Synthetic Work. Materials and General Remarks. CoCl₂·6H₂O, NEt₃, NaBH₄, NaHCO₃, Na₂CO₃, NaClO₄·H₂O, CH₃CN, and CH₃NO₂ were commercially available products (from Fluka and Merck) of reagent grade quality and were used without further purification. Further organic solvents (from Fluka) were distilled prior to use. CF₃SO₃H (from Fluka) was stored under N₂. Paraformaldehyde [polyoxymethylene (CH₂O)_{*n*}, mp 120–170 °C], and acetaldehyde (monomeric, bp 21 °C, from Merck) were used without further purification. The cation-exchange resin Dowex 50 W-X2, 100–200 mesh (from Fluka), was used in the H⁺ form and regenerated by eluting with 8 M HCl and with H₂O. The anion-exchange resin Dowex 2-X8, 20–50 mesh (Cl[−] form, Fluka) was converted to the OH[−] form by eluting with 0.2 M NaOH (until the eluent was free of Cl[−]) and then washed with H₂O (CO₂ free). SP-Sephadex C-25 (200 mesh) cation-exchange resin was from Pharmacia Biotech. [Co(*taci*)₂]Cl₃ and [Co(*tmca*)₂]Cl₃·H₂O were prepared according to published procedures.^{8,11} Both salts were insoluble in acetonitrile. The required solubility was achieved by converting [Co(*taci*)₂]Cl₃ into the corresponding trifluoromethanesulfonate salt (see below). [Co(*tmca*)₂]Cl₃·H₂O was dissolved by adding a large excess of NaClO₄·H₂O to the suspension, resulting in the precipitation of solid NaCl. **Caution!** Perchlorate salts of metal complexes with organic ligands are potentially explosive. The complex solution should not be heated nor evaporated to dryness. Condensation of the Co^{III}-hexamine complexes with paraformaldehyde and acetaldehyde and subsequent reductions with NaBH₄ were performed open to the air at ≈23 °C. Protection against moisture or oxygen was not necessary. **Caution!** Formaldehyde and HCl react readily to give the very toxic and volatile bis(chloromethyl)ether. Direct contact of formaldehyde and HCl should strictly be avoided. Excess paraformaldehyde should be removed prior to ion exchange chromatography. The exocyclic imines hydrolyze rapidly in alkaline aqueous media. They are, however, stable for at least several days in acidic conditions. A pH of ≤3 is required to avoid decomposition during the chromatographic procedures and the spectroscopic measurements described here.

[Co(*taci*)₂](CF₃SO₃)₃·CF₃SO₃H·6H₂O. [Co(*taci*)₂]Cl₃ (5.25 g, 10.1 mmol) was suspended in 100 mL of CF₃SO₃H and heated to 80 °C for 3 h while passing a stream of nitrogen through the reaction mixture. The clear orange solution was allowed to cool to ≈23 °C and was slowly poured into 1.5 L of diethyl ether. The pale orange precipitate was collected, washed carefully six times with diethyl ether, and dried in vacuo for 48 h over P₄O₁₀. Yield: 9.70 g (95%) of [Co(*taci*)₂](CF₃SO₃)₃·CF₃SO₃H. Anal. Calcd for C₁₆H₃₁CoF₁₂N₆O₁₈S₄: C, 19.02; H, 3.09; N, 8.32. Found: C, 18.84; H, 3.15; N, 8.23. The incorporation

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of one molecule of $\text{CF}_3\text{SO}_3\text{H}$ was verified by evaluating the pH of the product after dissolution in H_2O . ^1H NMR (D_2O): 5.14 ppm (br, $w_{1/2} = 9.5$ Hz; 12 H), 4.05 (t, $J = 3.8$ Hz; 6H), 2.85 (br, $w_{1/2} = 8$ Hz; 6H).¹⁷ $^{13}\text{C}\{^1\text{H}\}$ NMR: 122.7 (quartet, $J_{\text{F-C}} = 318$ Hz), 65.8, 52.3. Equilibration of the solid sample for 14 days at ambient conditions (60% atmospheric moisture, 23 °C) resulted in the formation of the hexahydrate $[\text{Co}(\text{taci})_2](\text{CF}_3\text{SO}_3)_3 \cdot \text{CF}_3\text{SO}_3\text{H} \cdot 6\text{H}_2\text{O}$. Anal. Calcd for $\text{C}_{16}\text{H}_{43}\text{CoF}_{12}\text{N}_6\text{O}_{24}\text{S}_4$: C, 17.18; H, 3.87; N, 7.51. Found: C, 17.10; H, 4.16; N, 7.55.

$[\text{Co}(\text{taci})_2\text{-hmi}]\text{Cl}_3 \cdot 6\text{H}_2\text{O}$.¹ $[\text{Co}(\text{taci})_2](\text{CF}_3\text{SO}_3)_3 \cdot \text{CF}_3\text{SO}_3\text{H}$ (9.50 g, 9.40 mmol) was dissolved in 500 mL of acetonitrile. Paraformaldehyde (37.5 g, 1.25 mol) and NEt_3 (64.4 g, 0.64 mol) were then added. The color turned to an intense brown within 20 s and to a pale yellowish-green after a few min. The suspension was stirred for 20 min, and the reaction quenched by pouring the mixture into a solution of H_2SO_4 (55 g), dissolved in 1.5 L of water. Excess paraformaldehyde was collected and the yellowish solution was sorbed on Dowex 50 W resin. The column was washed with 10^{-3} M H_2SO_4 and 0.5 M HCl. Further elution with 1.5 M HCl yielded a yellow fraction which was evaporated to dryness under reduced pressure. (The compound was only sparingly soluble in water and elution with a higher concentration of HCl resulted in its precipitation on the column.) The product was recrystallized from hot 0.1 M HCl and dried for 24 h under reduced pressure over P_4O_{10} . Yield: 4.70 g (7.71 mmol, 82%) of the trichloride monohydrate. Anal. Calcd for $\text{C}_{18}\text{H}_{32}\text{Cl}_3\text{CoN}_6\text{O}_7$: C, 35.46; H, 5.29; N, 13.78. Found: C, 35.53; H, 5.41; N, 13.70. ^1H NMR (D_2O , pD < 3): 8.14 (d, $J = 7.8$ Hz; 6H), 7.93 (d, $J = 7.8$ Hz; 6H), 4.65 (t, $J = 3.5$ Hz; 6H), 4.07 (t, $J = 3.5$ Hz; 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (D_2O , pD < 3): 187.1, 76.5, 68.4. IR (KBr, cm^{-1}): 1620 (s). UV-vis (10^{-3} M HCl): $\lambda_{\text{max}} = 451$ nm ($\epsilon = 78$ M^{-1} cm^{-1}). MS (FAB⁺, m/z): 484.0 (53%, $[\text{H}_{-1}\text{Co}(\text{taci})_2\text{-hmi}]^+$), 313.0 (13%, $[\text{Co}(\text{taci}-(\text{N-Me})_3)\text{Cl}]^+$), 277.1 (33%, $[\text{H}_{-1}\text{Co}(\text{taci}-(\text{N-Me})_3)]^+$). Single crystals of the trichloride hexahydrate, suitable for X-ray diffraction studies, were grown by slow evaporation of an acidic aqueous solution at ambient temperature. Anal. Calcd for $\text{C}_{18}\text{H}_{42}\text{Cl}_3\text{-CoN}_6\text{O}_{12}$: C, 30.89; H, 6.05; N, 12.01; Cl, 15.20; Co, 8.42. Found: C, 30.75; H, 5.88; N, 11.51; Cl, 15.11; Co, 8.31.

1,3,5-Trideoxy-1,3,5-tris(methylamino)-cis-inositol Trihydrochloride. NaHCO_3 (4.87 g, 58 mmol) was dissolved in 180 mL of water. The solution was stirred vigorously, and NaBH_4 (1.99 g, 52.6 mmol) and solid, ground $[\text{Co}(\text{taci})_2\text{-hmi}]\text{Cl}_3 \cdot \text{H}_2\text{O}$ (1.89 g, 3.1 mmol) were added. An immediate color change to purple was noted, and after a few min a black solid (elemental Co) precipitated. The mixture was stirred for 50 min, and the solid was then filtered off. The resulting clear solution was acidified with 4 M HCl to pH 1 and diluted to a total volume of 300 mL. It was then sorbed on Dowex 50 W resin and eluted in order with water, 0.5 M HCl, and 4 M HCl. The last fraction was evaporated to dryness, and the resulting colorless, hygroscopic solid was dried for 48 h over P_4O_{10} in vacuo. Yield: 1.43 g (4.3 mmol, 70%). ^1H NMR (D_2O , pD ≤ 2): 4.67 (t, $J = 3.3$ Hz; 3H), 3.60 (t, $J = 3.3$ Hz; 3H), 2.89 (s, 9 H); pD ≥ 12 : 4.27 (t, $J = 3.3$ Hz; 3H), 2.43 (t, $J = 3.3$ Hz; 3H), 2.40 (s, 9 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (D_2O , pD ≤ 2): 65.9, 60.2, 33.2; pD ≥ 12 : 71.2, 62.0, 34.2. MS (FAB⁺, m/z): 220.1 (100%, $[\text{HL}]^+$). Anal. Calcd for $\text{C}_9\text{H}_{24}\text{Cl}_3\text{N}_3\text{O}_3$: C, 32.89; H, 7.36; N, 12.78. Found: C, 32.67; H, 7.26; N, 12.65.

$[\text{Co}(\text{tmca})_2\text{-hmi}]\text{Cl}_3 \cdot 2\text{H}_2\text{O}$.¹ $[\text{Co}(\text{tmca})_2]\text{Cl}_3 \cdot \text{H}_2\text{O}$ (1 g, 1.61 mmol) was suspended in 75 mL of acetonitrile and $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (13 g), paraformaldehyde (4.0 g, 133 mmol), and NEt_3 (7 g, 69 mmol) were then added in order. The suspension was stirred vigorously, and the color turned immediately from yellow to an intense purple and after a few min to a pale yellow. The reaction was quenched after 15 min by pouring the mixture into a solution of H_2SO_4 (6 g) in 200 mL of water.¹⁸ After cooling, solid NaCl and excess of paraformaldehyde were filtered off. The yellow solution was diluted with water to a total volume of 600 mL, sorbed on Dowex 50 W resin, and eluted with 10^{-3} M H_2SO_4 , 0.5 M HCl, and 3 M HCl. The last fraction (yellow solution) was evaporated to dryness, yielding a yellowish green solid, which was allowed to dry in air for 48 h. Yield: 1.01 g (1.42 mmol, 88%). Anal. Calcd for $\text{C}_{24}\text{H}_{46}\text{Cl}_3\text{CoN}_6\text{O}_8$: C, 40.49; H, 6.51; N, 11.80. Found: C, 40.61; H, 6.38; N, 11.69. ^1H NMR (D_2O , pD < 3): 7.95 (d, $J = 7.5$ Hz; 6H), 7.83 (d, $J = 7.5$ Hz; 6H), 4.50 (t, $J = 3.3$ Hz; 6H), 4.21 (t, $J = 3.3$ Hz; 6H), 3.51 (s, 18 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (D_2O , pD < 3): 186.7, 76.8, 70.7, 60.0. IR (KBr, cm^{-1}): 1622 (s). UV-vis (10^{-3} M HCl): $\lambda_{\text{max}} = 453$ nm ($\epsilon = 83.3$ M^{-1} cm^{-1}). MS (FAB⁺, m/z): 604.1 (66%, $[\text{Co}(\text{tmca})_2\text{-hmi-Cl}]^+$), 569.1 (100%, $[\text{Co}(\text{tmca})_2\text{-hmi}]^+$). Single crystals of the tris(hydrogensulfate) salt, suitable for X-ray diffraction studies, were grown from an aqueous 1 M H_2SO_4 solution. Anal. Calcd for $\text{C}_{24}\text{H}_{45}\text{CoN}_6\text{O}_{18}\text{S}_3$: C, 33.49; H, 5.27; N, 9.76. Found: C, 33.67; H, 4.96; N, 9.61.

all-cis-2,4,6-Trimethoxytris(*N*-methyl)cyclohexane-1,3,5-triamine. NaHCO_3 (3.87 g, 46 mmol) was dissolved in 180 mL of water. The solution was stirred vigorously, and NaBH_4 (1.70 g, 45 mmol) and solid $4\text{Cl}_3 \cdot 2\text{H}_2\text{O}$ (2.11 g, 3.0 mmol), dissolved in 65 mL of MeOH was added. An immediate color change to blue was noted. After a few min the color turned to orange. The solution was stirred for 20 min, acidified with 4 M HCl to pH 1, diluted with H_2O to a total volume of 300 mL and sorbed on Dowex 50 W resin. Elution with water and 0.5 M HCl removed the organic solvents and Co^{II} . Further elution with 4 M HCl yielded a colorless fraction which was evaporated to dryness. The resulting colorless, hygroscopic solid was dried for 48 h over P_4O_{10} in vacuo. Yield: 1.51 g (4.1 mmol, 68%) of the trihydrochloride. Anal. Calcd for $\text{C}_{12}\text{H}_{30}\text{Cl}_3\text{N}_3\text{O}_3$: C, 38.88; H, 8.16; N, 11.33. Found: C, 38.67; H, 8.34; N, 11.08. The free triamine was obtained as a dihydrate by deprotonation of the trihydrochloride on Dowex 2 resin followed by sublimation (70 °C, 12 mbar) and equilibration in air. Anal. Calcd for $\text{C}_{12}\text{H}_{31}\text{N}_3\text{O}_5$: C, 48.46; H, 10.51; N, 14.13. Found: C, 48.65; H, 10.75; N, 14.28. ^1H NMR (D_2O , pD ≤ 2): 4.41 (t, $J = 3.1$ Hz; 3H), 3.66 (t, $J = 3.1$ Hz; 3H), 3.64 (s, 9 H), 2.97 (s, 9 H); pD ≥ 12 : 3.90 (t, $J = 3.1$ Hz; 3H), 3.55 (s, 9 H), 2.54 (t, $J = 3.1$ Hz; 3H), 2.45 (s, 9 H). $^{13}\text{C}\{^1\text{H}\}$ NMR (D_2O , pD ≤ 2): 75.6, 65.3, 61.0, 34.1; pD ≥ 12 : 80.9, 65.2, 62.7, 34.8. MS (FAB⁺, m/z): 262.1 (100%, $[\text{HL}]^+$).

$[\text{Co}(\text{abuca})]\text{Cl}_3 \cdot 2.5\text{H}_2\text{O}$.¹ $[\text{Co}(\text{tmca})_2]\text{Cl}_3 \cdot \text{H}_2\text{O}$ (1.75 g, 2.81 mmol) was suspended in 60 mL of acetonitrile. $\text{NaClO}_4 \cdot \text{H}_2\text{O}$ (12 g), paraformaldehyde (550 mg, 18.3 mmol), and acetaldehyde (24 g, 545 mmol) were then added. The condensation was started by the addition of NEt_3 (6 g). An immediate color change to brown occurred. This color turned to dark green and finally to black. The reaction was quenched after 30 min by pouring the mixture into an aqueous solution of H_2SO_4 (18 g) in 200 mL of H_2O . The resulting, clear, orange-brown solution (pH ≈ 1) was diluted with H_2O to a total volume of 400 mL and sorbed on Dowex 50 W resin. Four fractions (300 mL each) were collected by eluting with H_2O , 0.5 M HCl, 2 M HCl, and 6 M HCl, respectively. The third fraction (orange) was evaporated to dryness, redissolved in water, and sorbed on Sephadex C-25 resin. Elution with 0.2 M Na_2SO_4 gave one major, reddish-orange band which was collected, desalted on Dowex 50 W resin and evaporated to dryness again. Remaining *exo*-imino groups were removed by dissolving the product in 50 mL of H_2O , adjusting the pH to 8.3 (NaHCO_3 - Na_2CO_3 buffer) and stirring the solution for 14 h. Solid NaBH_4 (800 mg) was then added to reduce *endo*-imino groups. The color changed immediately to a deep reddish purple. The solution was stirred for further 30 min, and excess NaBH_4 was destroyed by adding solid NaHCO_3 until the pH was below 8. The solution was stirred for 3 days and bubbled with air to reoxidize Co^{II} to Co^{III} . This solution was then acidified with 4 M HCl to about pH 1, sorbed on Dowex 50 W resin and eluted with water, 0.5 M HCl, 2 M HCl, and 6 M HCl, respectively. The second fraction contained a considerable amount of Co^{II} . The third fraction was evaporated to dryness yielding a pinkish red solid. The last fraction contained a very dark brownish material which was discarded. The red solid of the third fraction was suspended in EtOH and filtered. The resulting clear solution was evaporated to dryness again, redissolved in water, sorbed on Sephadex C-25 resin and eluted with 0.2 M sodium citrate. Beside several very minor bands, only one major band with a pinkish red color was collected. It was desalted on Dowex 50 W resin and evaporated to dryness, giving a red solid which

(17) The signal at 5.14 ppm originates from the N-H protons. Due to a slow exchange reaction with D_2O , this signal disappeared upon heating the sample. In addition, the signal at 2.85 ppm now appeared as a sharp triplet ($J = 3.8$ Hz).

(18) It is important to stop the reaction precisely 15 min after the addition of NEt_3 . Shorter or longer reaction times resulted in a significantly diminished yield.

Table 1. Crystallographic Data for **3**, **4**, and **5**

	3Cl ₃ ·6H ₂ O	4(HSO ₄) ₃	5 ₂ Cl ₂ ·3.5H ₂ O
empirical formula	C ₁₈ Cl ₃ CoH ₄₂ N ₆ O ₁₂	C ₂₄ CoH ₄₅ N ₆ O ₁₈ S ₃	C ₄₀ Cl ₂ Co ₂ H ₇₅ N ₁₆ O _{23.50}
fw	699.85	860.77	1344.91
space group	C2/m (No. 12)	C2/c (No. 15)	Pna2 ₁ (No. 33)
a, Å	13.046(2)	14.087(3)	33.835(2)
b, Å	9.802(2)	15.890(3)	15.356(2)
c, Å	12.332(2)	15.502(3)	9.967(2)
α, deg	90	90	90
β, deg	118.42(1)	95.27(3)	90
γ, deg	90	90	90
V, Å ³	1386.8(4)	3455(1)	5178(2)
Z	2	4	4
T, °C	23(1)	20(2)	23(1)
λ, Å	0.710 73 (Mo Kα)	0.710 73 (Mo Kα)	1.541 78 (Cu Kα)
ρ _{calc} , g cm ⁻³	1.676	1.655	1.725
μ, cm ⁻¹	9.78 (Mo Kα)	7.66 (Mo Kα)	71.1 (Cu Kα)
R ^a	0.028 ^b	0.060 ^c	0.057 ^b
R _w ^d	0.028 ^b		0.071 ^b
wR ₂ (all data) ^e		0.209	

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|. \quad ^b I > 3\sigma(I). \quad ^c I > 2\sigma(I). \quad ^d R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w F_o^2]^{1/2}. \quad ^e wR_2 = [\sum w(F_o^2 - F_c^2)^2 / \sum w F_o^4]^{1/2}.$$

was soluble in H₂O, MeOH, EtOH, and PrOH. Yield 0.75 g (38%). Anal. Calcd for C₂₂H₅₁Cl₃CoN₆O_{8.5}: C, 37.70; H, 7.33; N, 11.99. Found: C, 37.41; H, 6.99; N, 12.25. ¹H NMR (D₂O): 7.6 [br, 1 H(-N)], 6.4 [br, 1 H(-N)], 5.9 [br, 1 H(-N)], 5.3 [br, 1 H(-N)], 5.1 [br, 1 H(-N)], 5.0 [br, 2 H(-N)], 4.4 [br, 2 H(-N)], 3.55 (s, 3 H), 3.54 (s, 3 H), 3.52 (s, 3 H), 3.50 (s, 3 H), 3.48 (s, 3 H), 3.45 (s, 3 H), 2.60–3.85 m (19 H). ¹³C{¹H} NMR (D₂O), 77.6 (CH), 76.1 (CH), 75.8 (CH), 75.2 (CH), 75.1 (CH), 73.8 (CH), 60.8 (CH₂), 60.7 (CH₃), 60.6 (CH₃), 60.3 (CH₃), 59.9 (CH₃), 59.8 (CH₃), 59.5 (CH₃), 57.3 (CH), 55.7 (CH), 55.6 (CH₂), 54.9 (CH), 49.9 (CH₂), 47.5 (CH), 47.4 (CH), 45.8 (CH), 37.0 (CH). MS (FAB⁺, *m/z*): 548.3 (100%, [H₂-Co(abuca)]⁺). UV-vis (H₂O): λ_{max} = 357 nm (ε = 165 M⁻¹ cm⁻¹), λ_{max} = 508 nm (ε = 137 M⁻¹ cm⁻¹). Dissolution of the product in 2-PrOH (20 mL), followed by the addition of ZnCl₂ (2 g, dissolved in 5 mL of 2-PrOH and 2 mL of concentrated HCl) resulted in the almost complete precipitation of the tetrachlorozincate salt [Co(abuca)]₂[ZnCl₄]₃·7H₂O·2-PrOH. The presence of 1 mol of 2-PrOH was confirmed by NMR spectroscopy. Anal. Calcd for C₄₇H₁₁₄Cl₁₂Co₂N₁₂O₂₆Zn₃: C, 29.60; H, 6.03; N, 8.81. Found: C, 29.67; H, 6.04; N, 8.73. An analogous procedure with ZnBr₂ and HBr was used to prepare the corresponding tetrabromozincate salt. Drying in vacuo over P₄O₁₀ resulted in the formation of [Co(abuca)]₂[ZnBr₄]₃·2-PrOH. The incorporated 2-propanol (which was verified by NMR spectroscopy), however, was not removed. Anal. Calcd for C₄₇H₁₀₀Br₁₂Co₂N₁₂O₁₃Zn₃: C, 24.39; H, 4.36; N, 7.26. Found: C, 24.52; H, 4.58; N, 7.19. Attempts to grow single crystals, suitable for X-ray diffraction studies, using either the trichloride, the tetrachlorozincate, or the tetrabromozincate salt of [Co(abuca)]³⁺ were not successful.

[Co(hebdoc)]Cl·2H₂O·2HCl. [Co(taci)₂](CF₃SO₃)₃·CF₃SO₃H (2.0 g, 1.98 mmol) was dissolved in 130 mL of acetonitrile. Paraformaldehyde (7.74 g, 258 mmol) and NEt₃ (17.7 g, 175 mmol) were added, and the reaction mixture was stirred for 20 min. Excess paraformaldehyde was then filtered off, and the resulting clear solution was added to a solution of NEt₃ (13.3 g, 131 mmol) and CH₃NO₂ (8.85 g, 145 mmol) in 45 mL of acetonitrile. An immediate color change to a brilliant bluish green was observed and a green solid precipitated within 5–10 min. After 30 min, the solid was filtered off and carefully washed several times with acetonitrile to remove traces of base. The solid was dissolved in 400 mL of water and acidified with HCl to a pH of about 2. The brown solution was sorbed on Dowex 50 W and eluted with water, 0.5 M HCl, and 2 M HCl, respectively. The brownish-green second fraction (0.5 M HCl) was evaporated to dryness and dried for 2 days at 25 °C over P₄O₁₀. Yield: 800 mg (1.07 mmol, 54%) of a dark brownish green solid. Anal. Calcd for C₂₀H₄₀Cl₃CoN₈O₁₂: C, 32.03; H, 5.38; N, 14.94; Cl, 14.18. Found: C, 32.07; H, 5.25; N, 14.97; Cl, 14.20. ¹H NMR (D₂O/NaOD, pD = 13): 9.17 (d, *J* = 2.0 Hz; 2H), 4.03 (d, *J* = 13.9 Hz; 2H), 4.00 (t, *J* = 3.8 Hz; 2H), 3.83 (t, *J* = 2.7 Hz; 2H), 3.77 (m, 2 H), 3.26 (m, 4H), 2.92 (m, 2H), 2.62 (m, 2H), 2.40 (s, 6H). ¹³C{¹H} NMR (D₂O/NaOD, pD = 13): 169.3, 121.4,

Table 2. Bond Lengths (Å) and Selected Bond Angles (deg) of **3** with Esd's in Parentheses^a

Co–N(1)	1.964(2)	Co–N(3)	1.962(2)
N(1)–C(1)	1.479(3)	N(1)–C(11)	1.270(3)
N(3)–C(3)	1.482(2)	N(3)–C(13)	1.272(3)
O(2)–C(2)	1.417(2)	O(4)–C(4)	1.423(3)
C(1)–C(2)	1.517(3)	C(2)–C(3)	1.529(3)
C(3)–C(4)	1.521(2)		
N(1)–Co–N(3)	89.74(6)	N(1)–Co–N(1a)	180.00
N(1)–Co–N(3a)	90.26(6)	N(3)–Co–N(3a)	180.00
N(3)–Co–N(3b)	89.11(9)	N(3)–Co–N(3c)	90.89(9)
Co–N(1)–C(11)	123.0(2)	Co–N(1)–C(1)	120.2(2)
C(11)–N(1)–C(1)	116.8(2)	Co–N(3)–C(3)	120.2(1)
Co–N(3)–C(13)	122.8(1)	C(3)–N(3)–C(13)	117.0(2)

^a Symmetry operations used to generate equivalent atoms: a, $-x, -y, -z$; b, $x, -y, z$; c, $-x, y, -z$.

Table 3. Selected Bond Lengths (Å) and Angles (deg) of **4** with Esd's in Parentheses^a

Co–N(1)	1.968(4)	N(3)–C(3)	1.472(7)
Co–N(3)	1.972(4)	N(3)–C(13)	1.262(7)
Co–N(5)	1.959(4)	N(5)–C(5)	1.484(7)
N(1)–C(1)	1.467(7)	N(5)–C(15)	1.261(7)
N(1)–C(11)	1.266(7)		
N(1)–Co–N(3)	90.0(2)	C(1)–N(1)–Co	119.3(4)
N(1)–Co–N(5)	89.7(2)	C(11)–N(1)–Co	122.9(4)
N(1)–Co–N(1a)	180.0	C(11)–N(1)–C(1)	117.8(5)
N(1)–Co–N(3a)	90.0(2)	C(3)–N(3)–Co	119.7(3)
N(1)–Co–N(5a)	90.3(2)	C(13)–N(3)–Co	123.3(4)
N(3)–Co–N(5)	89.9(2)	C(13)–N(3)–C(3)	117.1(5)
N(3)–Co–N(3a)	180.0	C(3)–N(5)–Co	120.1(3)
N(3)–Co–N(5a)	90.2(2)	C(15)–N(5)–Co	123.5(4)
N(5)–Co–N(5a)	180	C(15)–N(5)–C(5)	116.4(5)

^a Symmetry operations used to generate equivalent atoms: a, $^3/2 - x, ^1/2 - y, -z$.

76.0, 69.9, 69.2, 68.2, 67.7, 66.4, 46.6, 38.4. MS (FAB⁺): analysis of the intensities in the range *m/z* 605.1–608.1 revealed overlap of two major signals assignable to [Co(hebdoc)]⁺ (60%) and [Co(H-hebdoc)]⁺ (100%). IR (KBr, cm⁻¹): 1626 (m), 1561 (s). UV-Vis (H₂O): λ_{max} = 560 nm (ε = 382 M⁻¹ cm⁻¹). Crystals of the composition [Co(hebdoc)]₂Cl₂·3.5H₂O, suitable for single-crystal X-ray analysis were grown from aqueous solution.

Crystal Structure Determination. Crystal data for 3Cl₃·6H₂O, 4(HSO₄)₃, and 5₂Cl₂·3.5H₂O are presented in Table 1.¹ Atomic coordinates are available as Supporting Information. Selected bond distances and bond angles are listed in Tables 2–4. Additional information on data collection, structure solution, and refinement is summarized in the following three paragraphs.

Table 4. Selected Bond Lengths (Å) and Angles (deg) of **5** with Esd's in Parentheses

N(11)–Co(1)	2.06(1)	N(31)–Co(2)	2.06(1)
N(12)–Co(1)	1.99(1)	N(32)–Co(2)	1.98(1)
N(13)–Co(1)	2.01(1)	N(33)–Co(2)	2.03(1)
N(21)–Co(1)	2.06(1)	N(41)–Co(2)	2.03(1)
N(22)–Co(1)	1.97(1)	N(42)–Co(2)	1.98(1)
N(23)–Co(1)	2.00(1)	N(43)–Co(2)	2.02(1)
C(11)–N(11)	1.51(2)	C(31)–N(31)	1.51(2)
C(13)–N(12)	1.51(2)	C(33)–N(32)	1.43(2)
C(15)–N(13)	1.52(2)	C(35)–N(33)	1.53(2)
C(17)–N(11)	1.45(2)	C(37)–N(31)	1.45(1)
C(18)–N(12)	1.29(2)	C(38)–N(32)	1.29(2)
C(19)–N(14)	1.36(2)	C(39)–N(34)	1.38(2)
C(19)–C(18)	1.38(2)	C(39)–C(38)	1.40(2)
C(20)–N(23)	1.51(2)	C(40)–N(43)	1.48(2)
C(21)–N(21)	1.47(2)	C(41)–N(41)	1.50(2)
C(23)–N(22)	1.47(2)	C(43)–N(42)	1.47(2)
C(25)–N(23)	1.51(2)	C(45)–N(43)	1.51(2)
C(27)–N(21)	1.47(1)	C(47)–N(41)	1.47(1)
C(28)–N(22)	1.31(2)	C(48)–N(42)	1.33(2)
C(29)–N(24)	1.36(2)	C(49)–N(44)	1.35(2)
C(30)–N(13)	1.50(2)	C(50)–N(33)	1.53(2)
C(29)–C(28)	1.42(2)	C(49)–C(48)	1.41(2)
N(11)–Co(1)–N(12)	91.5(6)	N(31)–Co(2)–N(32)	92.3(5)
N(11)–Co(1)–N(13)	90.1(6)	N(31)–Co(2)–N(33)	88.3(4)
N(11)–Co(1)–N(21)	89.3(5)	N(31)–Co(2)–N(41)	89.3(4)
N(11)–Co(1)–N(22)	87.7(5)	N(31)–Co(2)–N(42)	88.0(5)
N(11)–Co(1)–N(23)	173.0(5)	N(31)–Co(2)–N(43)	174.6(5)
N(12)–Co(1)–N(13)	86.0(5)	N(32)–Co(2)–N(33)	84.6(5)
N(12)–Co(1)–N(21)	90.1(5)	N(32)–Co(2)–N(41)	92.7(5)
N(12)–Co(1)–N(22)	178.5(5)	N(32)–Co(2)–N(42)	179.4(4)
N(12)–Co(1)–N(23)	95.3(5)	N(32)–Co(2)–N(43)	93.1(5)
N(13)–Co(1)–N(21)	176.0(5)	N(33)–Co(2)–N(41)	176.4(5)
N(13)–Co(1)–N(22)	95.2(5)	N(33)–Co(2)–N(42)	95.0(5)
N(13)–Co(1)–N(23)	88.7(5)	N(33)–Co(2)–N(43)	91.8(4)
N(21)–Co(1)–N(22)	88.7(5)	N(41)–Co(2)–N(42)	87.7(5)
N(21)–Co(1)–N(23)	92.3(5)	N(41)–Co(2)–N(43)	90.8(5)
N(22)–Co(1)–N(23)	85.5(5)	N(42)–Co(2)–N(43)	86.5(5)
Co(1)–N(11)–C(11)	117(1)	Co(2)–N(31)–C(31)	118.0(9)
Co(1)–N(11)–C(17)	121(1)	Co(2)–N(31)–C(37)	124(1)
Co(1)–N(11)–C(17)	115(1)	C(31)–N(31)–C(37)	111(1)
Co(1)–N(12)–C(13)	120(1)	Co(2)–N(32)–C(33)	121.1(8)
Co(1)–N(12)–C(18)	125(1)	Co(2)–N(32)–C(38)	124(1)
C(13)–N(12)–C(18)	114(1)	C(33)–N(32)–C(38)	114(1)
Co(1)–N(13)–C(15)	118(1)	Co(2)–N(33)–C(35)	118.3(8)
Co(1)–N(13)–C(30)	116.7(9)	Co(2)–N(33)–C(50)	115.2(9)
C(15)–N(13)–C(30)	110(1)	C(35)–N(33)–C(50)	111(1)
C(19)–N(14)–O(14)	119(2)	C(39)–N(34)–O(34)	119(1)
C(19)–N(14)–O(15)	119(1)	C(39)–N(34)–O(35)	122(1)
O(14)–N(14)–O(15)	122(1)	O(34)–N(34)–O(35)	119(1)
Co(1)–N(21)–C(21)	117.7(9)	Co(2)–N(41)–C(41)	119.9(9)
Co(1)–N(21)–C(27)	119(1)	Co(2)–N(41)–C(47)	120(1)
C(21)–N(21)–C(27)	112(1)	C(41)–N(41)–C(47)	111(1)
Co(1)–N(22)–C(23)	120.9(9)	Co(2)–N(42)–C(43)	122.4(8)
Co(1)–N(22)–C(28)	126(1)	Co(2)–N(42)–C(48)	124(1)
C(23)–N(22)–C(28)	112(1)	C(43)–N(42)–C(48)	113(1)
Co(1)–N(23)–C(20)	116.6(9)	Co(2)–N(43)–C(40)	119(1)
Co(1)–N(23)–C(25)	117.4(9)	Co(2)–N(43)–C(45)	117.2(9)
C(20)–N(23)–C(25)	111(1)	C(40)–N(43)–C(45)	112(1)
C(29)–N(24)–O(24)	121(2)	C(49)–N(44)–O(44)	121(1)
C(29)–N(24)–O(25)	118(2)	C(49)–N(44)–O(45)	120(1)
O(24)–N(24)–O(25)	121(1)	O(44)–N(44)–O(45)	119(1)

An orange, block-shaped crystal of $3\text{Cl}_3 \cdot 6\text{H}_2\text{O}$ having approximate dimensions of $0.25 \times 0.15 \times 0.11$ mm was used for data collection (23 ± 1 °C, Rigaku AFC6S four-circle diffractometer with graphite-monochromated Mo K α radiation, maximum 2θ value of 55.1°). Three standard reflections were checked after every 150 reflections, but no loss of intensity was noted. The data were corrected for Lorentz and polarization effects and an analytical absorption correction was applied, yielding transmission factors ranging from 0.86 to 0.91. Based on systematic absences of hkl : $h + k \neq 2n$, packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be

$C2/m$. Of the 1774 reflections which were collected, 1700 were unique ($R_{\text{int}} = 0.012$). The structure was solved by Patterson methods¹⁹ and expanded using Fourier techniques.²⁰ The non-hydrogen atoms were refined anisotropically. All hydrogen atoms were located in a difference Fourier map and their coordinates were refined with fixed isotropic displacement parameters. One of the OH hydrogen atoms is disordered over two symmetry-related sites. The final cycle of full-matrix least-squares refinement was based on 1430 observed reflections [$I > 3\sigma(I)$] and 141 parameters.²¹

A yellow block of $4(\text{HSO}_4)_3$ having approximate dimensions of $0.3 \times 0.25 \times 0.2$ mm was used for data collection (20 ± 2 °C, Siemens Stoe AED 2 four-circle diffractometer, graphite monochromated Mo K α radiation). Checking of 3 standard reflections every 90 min revealed no loss of intensities during measurement. The data were corrected for Lorentz and polarization effects and an empirical absorption correction was applied yielding transmission factors ranging from 0.905 to 0.999. The structure was solved by direct methods using the computer program SHELXS-97.²² One of the HSO_4^- counterions lies on an axis of 2-fold rotation and must therefore be disordered (a 2-fold rotational symmetry is possible for SO_4^{2-} but not for HSO_4^- ; however, the presence of the protonated monoanion is clearly indicated by the charge balance and elemental analysis). The oxygen positions of this disordered HSO_4^- ion were refined using isotropic displacement parameters. All other non-hydrogen atoms were refined in the anisotropic mode (2271 unique reflections, 227 parameters, full-matrix least-squares refinement on F^2 , SHELXL-97).²³ The hydrogen atoms of the complex cation were placed at calculated positions (riding model). The protons of the HSO_4^- counterions were not considered.

A red platelet of $5_2\text{Cl}_2 \cdot 3.5\text{H}_2\text{O}$ having approximate dimensions of $0.15 \times 0.11 \times 0.02$ mm was used for data collection on a Rigaku AFC6R diffractometer (23 ± 1 °C, graphite-monochromated Cu K α radiation, 12 kW rotating anode generator) using the ω - 2θ scan technique to a maximum 2θ value of 120.6° . Based on the systematic absences $0kl$, $k+l \neq 2n$ and $h0l$, $h \neq 2n$, packing considerations, a statistical analysis of intensity distribution, and the successful solution and refinement of the structure, the space group was determined to be $Pna2_1$. A total of 4392 reflections was collected. The intensities of three standard reflections were measured after every 150 reflections. Over the course of data collection, the standards decreased by 9.7%, and a linear correction factor was applied to the data to account for this phenomenon. An analytical absorption correction was performed and the data were corrected for Lorentz and polarization effects. The structure was solved by direct methods²⁴ and expanded using Fourier techniques.²⁰ A stage of refinement was reached in which anisotropic displacement factors were being used for cobalt, chlorine and oxygen atoms (with the exception of O(34), O(35), and O(w4)), and isotropic displacement factors for all other atoms. Hydrogen atoms for the cation were included at calculated positions but not refined. Full-matrix least-squares refinement²¹ with this model was based on 2322 observed reflections [$I > 2.0\sigma(I)$] and 461 variable parameters and converged with agreement factors of $R = 0.064$, $R_w = 0.058$. Refinement of a model with inverse coordinates gave $R = 0.081$ and $R_w = 0.071$, indicating that the original coordinates correspond to the correct polarity of the crystal. This model, however, had several unsatisfactory features. The N(11)–C(17) and N(31)–C(37) distances were shorter than

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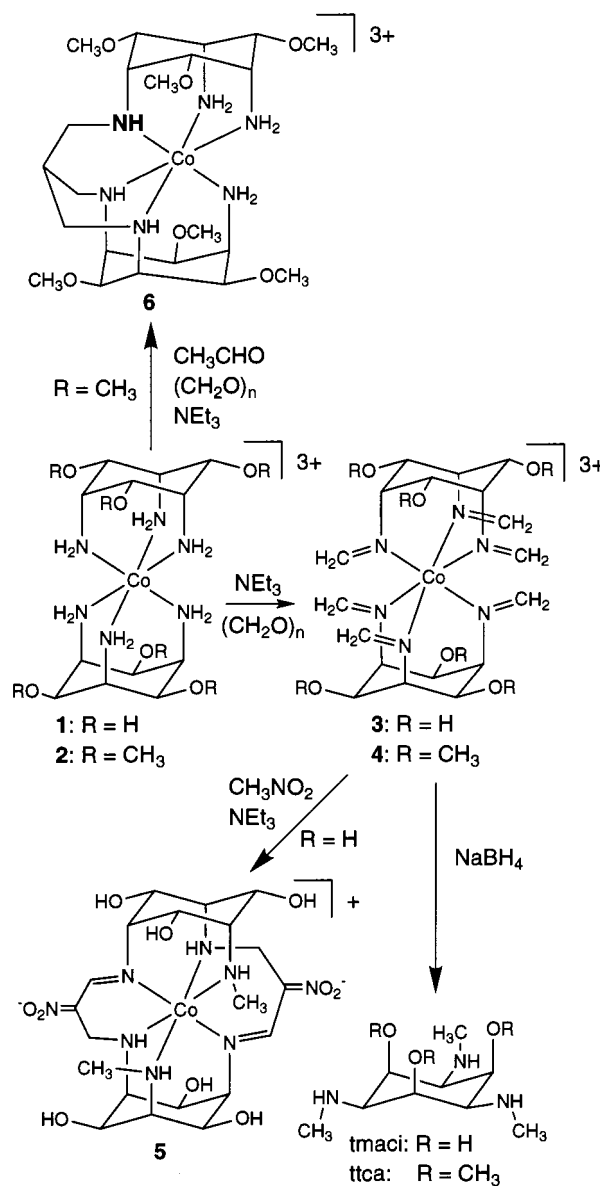
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expected for single bonds, and the thermal factors for C(17) and C(37) were atypically large. To a lesser extent, this also applied to C(27) and C(47). The alternative, that C(17) and C(37) were involved as methylideneimine carbon atoms rather than methylamine carbon atoms, would involve C–N distances that are unusually long for double bonds and was also in disagreement with the NMR and MS data. A rational explanation is a disorder of the terminal methyl groups corresponding to inversion about the nitrogen atoms. In addition, attempts to allow oxygen and carbon atoms to have unconstrained anisotropic refinement ran into difficulties because the observation:parameter ratio for such refinement was less than 3:1. Consequently, refinement was continued using the RAELS system.²⁵ The two inequivalent cations were allowed anisotropic atomic thermal parameters, each defined by a 15 variable TLX model.²⁶ The chloride anions and water oxygen atoms were refined as individual anisotropic atoms. Refinement of atom positional parameters was unrestrained except for restraints on the minor components of the disordered atoms [designated by C(17'), C(27'), C(37'), C(47')]. These lesser occupancy sites were restrained so that C(*n*') approaches a mirror relationship to the unconstrained C(*n*) atom (*n* = 1, 2, 3, 4) using the plane of the adjacent N(*n*1) (*n* = 1, 2, 3, 4) and the other two atoms coordinated to N(*n*1) [viz. C(*n*1) and either Co(1) for *n* = 1, 2 or Co(2) for *n* = 3, 4]. The differences in occupancies between the two component sites were refined for each disordered atom pair to give C(*n*7)/C(*n*7') ratios of 0.74(2):0.26, 0.95(2):0.05, 0.83(2):0.17, and 0.90(2):0.10 for *n* = 1 to 4, respectively, and distances N(*n*1)–C(*n*7) of 1.45(2), 1.47(1), 1.45(1), and 1.47(1) Å for the major components. In addition, the occupancy of O(w4) was refined to be 0.52(4). The cobalt atoms were allowed to have an additional anisotropic vibration in excess of that implied by the TLX model but this amount was less than 3σ for all the additional parameters. Hydrogen atoms were inserted to obey sensible geometry. A feasible hydrogen-bonding scheme is included as Supporting Information. It is worthy of note that out-of-plane angles²⁷ calculated for the major occupancy methyl atoms were of the same sign for the first cation (implying an effective 2-fold rotation symmetry in the molecule) but of opposite sign for the second cation. This justifies the model that assumes an inversion of environment about the N(*n*1) atoms (*n* = 1, 2, 3, 4). N(31) has the mirror environment to N(11), N(21), and N(41). The final full-matrix least-squares refinement²⁸ was based on 2261 observed reflections [*I* > 3.0σ(*I*)] and 347 variable parameters and converged with *R* = 0.057 and *R*_w = 0.071. The maximum and minimum peaks in the final difference Fourier map corresponded to 0.58 and –0.50 e[–]/Å³, respectively.

Results and Discussion

Preparation and Characterization of Hexamethylideneimine-Co^{III} Complexes. The two hexamine-Co^{III} complexes [Co(taci)₂]³⁺ (**1**) and [Co(tmca)₂]³⁺ (**2**) used as the starting materials were prepared by well-established standard procedures.^{8,11} In the presence of base, they both reacted readily with an excess of paraformaldehyde to form the corresponding hexaimines **3** and **4** (Scheme 1).²⁹ In aqueous alkaline media, the condensation of **1** and **2** with formaldehyde resulted in the formation of complex mixtures, containing a variety of species. The reaction was, however, readily driven toward the hexaimine formation by using CH₃CN as solvent, and NEt₃ as the base. Since the trichloride salts of **1** and **2** were not sufficiently soluble in CH₃CN, more suitable counterions such as CF₃SO₃[–] and

Scheme 1



ClO₄[–] were used.³⁰ Small amounts of water in the reaction mixture did not affect this reaction adversely, even though both products hydrolyzed rapidly in alkaline aqueous media. In acidic aqueous solution, **3** and **4** were stable for many hours and could be handled without problems.

The two hexaimines **3** and **4** were isolated as trichloride salts and were characterized by IR spectroscopy (C=N stretch vibrations at 1620 and 1622 cm^{–1}, respectively) and FAB mass spectrometry (through the observation of a variety of pseudo-molecular ions, see Experimental Section). In the electronic spectrum, the expected absorptions (origin ¹A_{1g}–¹T_{1g}) appeared at 451 and 453 nm, respectively. Compared to the two parent hexamines **1** and **2**, this corresponds to a hypsochromic shift of about 20 nm and indicates a significantly stronger ligand field. In solution, the hexaimines **3** and **4** showed rather simple ¹H and ¹³C NMR spectra characteristic of D_{3d} symmetry and the formation of the methylidene groups were readily verified by specific signals in the low-field range of the spectra.³¹ Single crystals of the hydrated trichloride salts were grown for X-ray

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(28) Least-squares in RAELS. Function minimized: $\sum w(|F_o| - |F_c|)^2$, where $w = [(\sigma_c(F_o))^2 + 0.0009F_o^2]^{-1}$, $\sigma_c(F_o) = \text{esd}$ based on counting statistics.

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analysis. However, the crystals of the chloride salt of **4** were not high enough in quality.³² Complex **4** was therefore converted into the corresponding tris(hydrogensulfate) salt which was suitable for an X-ray study. A view of the two cations **3** and **4** is presented in Figure 1. The crystallographically imposed point group symmetry is C_{2h} for **3** and C_i for **4**. However, deviation from D_{3d} symmetry for both cations is not significant. Furthermore, little or no deviation from octahedral geometry was observed for the coordination sphere within the significance of the measurements (all N–Co–N bond angles fall in the range 89.1–90.9°). The average Co–N bond distances of 1.963(1) and 1.966(7) Å are somewhat shorter than those of the parent hexamine complexes **1** and **2**,^{8,11} which is consistent with the hypsochromic shift observed in the visible spectrum. The C=N double bonds have mean distances of 1.271(1) and 1.263(3) Å, whereas the mean distances of the C–N single bonds are 1.481(2) and 1.474(9) Å, respectively. The sums of the three bond angles around the nitrogen atoms are 360.0(2) for **3** and 360.0(5) for **4**, indicating a strictly planar geometry for the sp^2 hybridized donor atoms.

Reaction of **3 and **4** with $NaBH_4$.** It was expected that the coordinated methyldeneimino groups of **3** and **4** would react readily with a variety of nucleophiles. They are therefore promising synthons for novel ligands.^{12,29} In an initial screening, the reactivity of these two complexes toward a hydride donor was investigated. Addition of $NaBH_4$ to an aqueous or methanolic solution of these two complexes resulted in rapid hydrogenation of the C=N double bonds. However, the reaction was also coupled with the reduction of Co^{III} and subsequent decomposition of the complex. This follows from a dramatic increase of non bonding repulsion energy in the coordination sphere. Due to the sp^2 hybridization of the nitrogen donors, the methyldene substituents of **3** and **4** have an ideal, “staggered” orientation which probably receives some additional stabilization by C–H···O hydrogen bonding (Figure 2). However, due to the rigid geometry of the double adamantane structure of the complex, the *N*-methyl groups of the hydrogenated complexes point directly toward N-hydrogen atoms of the other ligand. Molecular modeling studies confirmed a large increase in interligand repulsion energy which would obviously lead to an elongation of the Co^{III} –N bond, and an increased stabilization of the Co^{II} state. It was not surprising therefore to observe facile reduction to the labile Co^{II} analogues and subsequently decomposition of the complexes.

The two new *N*-methylated derivatives 1,3,5-trideoxy-1,3,5-tris(methylamino)-*cis*-inositol (tmaci) and *all-cis*-2,4,6-trimethoxytris(*N*-methyl)cyclohexane-1,3,5-triamine (ttca) were readily isolated as trihydrochlorides from such reaction mixtures. Since the introduction of only one methyl group at each primary amine is not a routine task, this reaction is a convenient high-yield method for the preparation of such compounds. Both these novel methylated ligands were characterized by elemental analysis and spectroscopic methods. A series of potentiometric titrations was also performed to determine a set of pK_a values (Table 5). It is interesting to note that the lowest pK_a value of H_3ttca^{3+} is remarkably low compared with other methylated derivatives of taci. We attribute this effect to the observation,

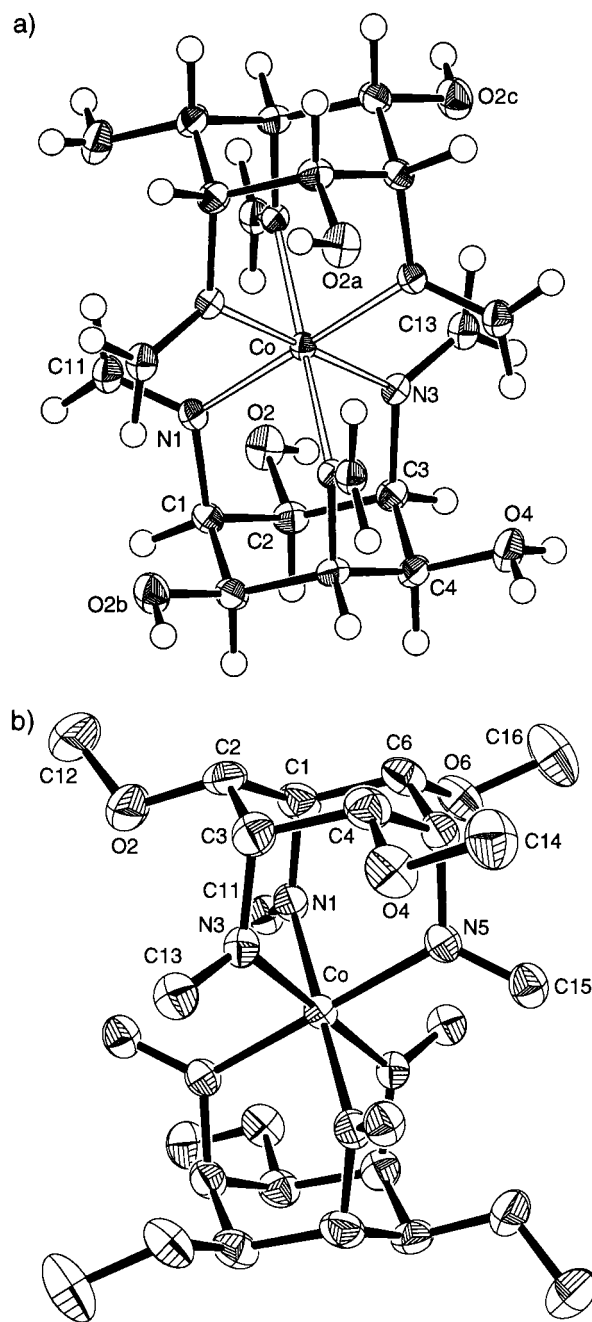


Figure 1. ORTEP drawing of (a) $[Co(taci)_2-hmi]^{3+}$ (**3**) and (b) $[Co(tmca)_2-hmi]^{3+}$ (**4**) with numbering scheme and vibrational ellipsoids at the 50% probability level. The hydrogen atoms of **3** are shown as spheres of arbitrary size (the hydrogen atom on O(4) is disordered over two sites). The hydrogen atoms of **4** are omitted for clarity. The crystallographically imposed C_{2h} point group symmetry of **3** is shown by corresponding labels for the symmetry related atoms of O(2) using the symmetry operations as listed in Table 2.

that for a fully protonated taci derivative, the three positively charged ammonium groups will have an equatorial orientation to minimize steric and electrostatic repulsion energies. This enforces an axial orientation for the three oxygen atoms. For taci, tmaci, and tdc, this arrangement is stabilized by intramolecular O–H···O hydrogen bonding. For ttca, however, a stabilization by such hydrogen bonds is of course not possible and the formation of a conformer with three axial methoxy groups would require some additional energy. Similar arguments have recently been used to explain the low basicity of *all-cis*-2,4,6-trimethylcyclohexane-1,3,5-triamine.³³ However,

(31) The chemical shifts of the methyldeneimino groups in a related Co^{III} complex reported in ref 29 are 7.34 and 7.87 ppm (1H) and 177.2 ppm (^{13}C).

(32) $[Co(tmca)_2-hmi]Cl_3 \cdot 8H_2O$ (yellow prisms) crystallizes in the triclinic space group $P1$, $a = 8.70(1)$ Å, $b = 9.34(1)$ Å, $c = 13.06(2)$ Å, $\alpha = 103.3(1)^\circ$, $\beta = 101.6(1)^\circ$, $\gamma = 109.5(1)^\circ$, $Z = 1$ (for $C_{24}Cl_3CoH_{58}N_6O_{14}$), $R = 4.66\%$, $R_w = 6.43\%$ for 813 observed reflections [$I > 2\sigma(I)$] and 227 refined parameters. The mean Co–N distance is 1.96(1) Å.

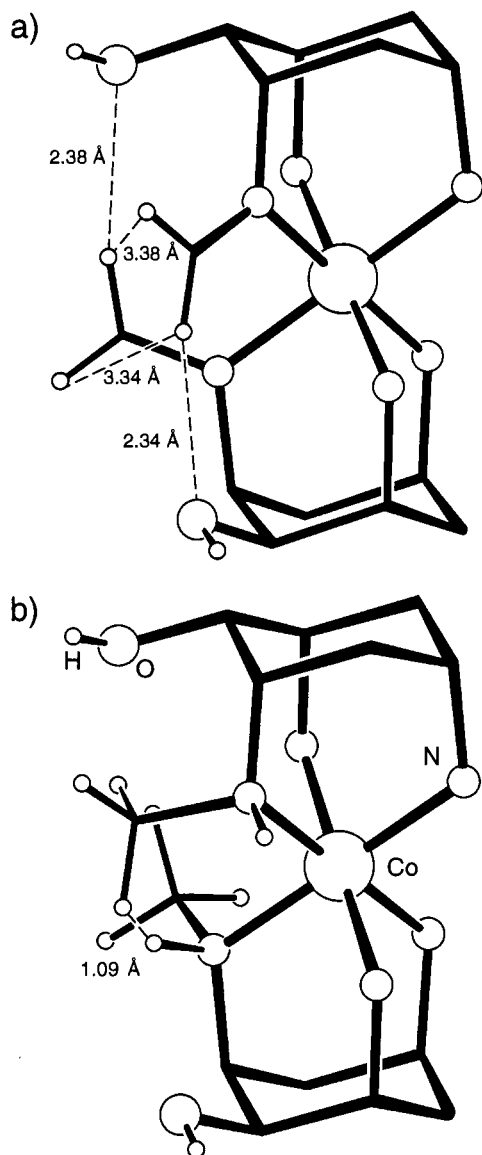


Figure 2. (a) Ball and stick model of a part of the hexamethyldeneimine **3** and (b) a hypothetical product where the $\text{CH}_2=\text{N}$ groups were reduced to corresponding CH_3-NH groups. The structures are drawn using the X-ray data of **3** and assuming an sp^3 hybridization for the reduced CH_3-NH donor with bond angles of 110° and an $\text{N}-\text{C}$ distance of 1.48 \AA . The model clearly shows the unstrained, ideal arrangement for the $\text{CH}_2=\text{N}$ substituents in **3**, which is further stabilized by $\text{C}-\text{H}\cdots\text{O}$ hydrogen bonds (a) and the considerable increase in $\text{N}-\text{H}\cdots\text{H}_3\text{C}$ steric repulsion for the hydrogenated product (b).

Table 5. pK_a Values (25.0°C , 0.1 M KCl) of the Two Triamines *tmaci* and *ttca* and of Some Related Cyclohexane-Based Triamines

ligand	pK_1^a	pK_2^a	pK_3^a	ligand	pK_1^a	pK_2^a	pK_3^a
<i>tach</i> ^b	10.16	8.66	7.17	<i>tdci</i> ^e	9.68	7.62	5.89
<i>taci</i> ^c	8.91	7.42	5.96	<i>ttca</i> ^f	9.15	7.03	4.99
<i>tmaci</i> ^d	9.28	7.66	6.08				

^a $\text{pK}_i = -\log K_i$, $K_i = [\text{H}_{i-1}\text{L}]\cdot[\text{H}]\cdot[\text{H}_i\text{L}]^{-1}$. ^b *all-cis*-Cyclohexane-1,3,5-triamine (ref 38). ^c 1,3,5-Triamino-1,3,5-trideoxy-*cis*-inositol (ref 9a). ^d 1,3,5-Trideoxy-1,3,5-tris(methylamino)-*cis*-inositol (this work). ^e 1,3,5-Trideoxy-1,3,5-tris(dimethylamino)-*cis*-inositol (ref 39). ^f *all-cis*-2,4,6-Trimethoxy-tris(*N*-methyl)cyclohexane-1,3,5-triamine (this work).

all of the ligands shown in Table 5 are considerably more basic than this trimethylcyclohexanetriamine.

Coupling Reaction with Nitromethane. The treatment of the hexamine **3** (prepared in situ) with an excess of nitromethane and triethylamine in CH_3CN resulted in a rapid condensation reaction. The resulting green product eluted with a remarkably low concentration of acid from the cation resin which indicated a low charge for the complex cation. Mass spectrometric measurements were consistent with the formation of a monocation of the composition $[\text{Co}(\text{C}_{20}\text{H}_{34}\text{N}_8\text{O}_{10})]^+$.

The ^1H and ^{13}C NMR data provided evidence that the new complex contained two CH_3-NH groups and two $\text{N}=\text{CH}-\text{C}(\text{NO}_2^-)-\text{CH}_2-\text{NH}$ bridges. The spectra of the crude material, obtained directly after evaporation of the fraction eluted with 0.5 M HCl , were exceedingly complicated. In the ^{13}C NMR spectrum, for instance, at least 30 resonances were visible. A total of three resonances in the range of $169-173 \text{ ppm}$ and three resonances at about 121 ppm were indicative of delocalized $-\text{N}=\text{CH}-\text{C}(\text{NO}_2^-)-$ fragments. These data implied that at least two different isomers were formed. However, in strongly alkaline solution the 30 resonances collapsed to 10 with single resonances at 121.4 and 169.3 ppm for the above-mentioned $-\text{N}=\text{CH}-\text{C}(\text{NO}_2^-)-$ bridges. Analogous observations were made for the ^1H NMR spectra. Initially, a total of three resonances of $(\text{N}=\text{C}-)\text{H}$ protons appeared in the range of $8.3-8.5 \text{ ppm}$, and a complicated and poorly resolved pattern was found for the aliphatic $\text{H}(-\text{C})$ protons in the range of $2.3-4.4 \text{ ppm}$. Upon addition of base, only one signal was observed for the $(\text{N}=\text{C}-)\text{H}$ protons at 9.17 ppm and in the aliphatic range one dominant singlet at 2.40 ppm was found for the $\text{CH}_3(-\text{NH})$ groups (Figure 3). A series of two-dimensional NMR measurements allowed a complete assignment of the ^{13}C and ^1H resonances of the sample in 1 M NaOD .

Assuming that both $\text{N}=\text{CH}-\text{C}(\text{NO}_2^-)-\text{CH}_2-\text{NH}$ bridges connect both *taci* fragments and that the $\text{N}-\text{CH}_3$ groups are attached to different *taci* fragments, a total of 15 diastereomers must be considered. This number originates from the possibility that (i) the two sp^2 nitrogen atoms of the bridges may be bound to the same or to different *taci* fragments, and (ii) the two sp^2 nitrogen atoms or (iii) the two $\text{N}-\text{CH}_3$ groups have a *cis* or *trans* orientation with respect to the CoN_6 octahedron. Of these 15 isomers, 9 have no point symmetry at all (C_1), 4 others have 2-fold rotational symmetry (C_2), and a further 2 have a center of inversion (C_i). The entire complex cation has a total of 20 carbon atoms and consequently, 20 resonances would be expected in the ^{13}C NMR spectrum of a C_1 isomer. Since the 2-fold axes of the C_2 isomers are never coincident with any carbon atom, the C_i and C_2 isomers are each expected to show a total of 10 lines in their ^{13}C NMR spectra. The initially observed 30 signals could thus readily be explained by the presence of two major components in the crude product, one having C_1 and the other C_2 or C_i symmetry. The observation of only 10 signals in the alkaline solution together with the simple ^1H NMR characteristics may be interpreted either by the formation of only one dominant species of higher symmetry or in terms of a rapid equilibrium where the observed signals represent the average of a variety of species. On reacidification, however, the spectra showed one new major component (Figure 3). This result implies a rapid equilibrium at high pH that was not reached in the reaction mixture. A new low-energy isomer is formed at high pH. According to the ^{13}C characteristics, it has C_2 or C_i symmetry (its ^{13}C NMR spectrum showed a total of 10 signals). Although of lowest energy, it was obviously not a major product of the original synthesis process.

The reaction mixture, containing the two initially formed isomers, was used to grow single crystals of $[\text{Co}(\text{hebdoc})]^+$ (**5**).

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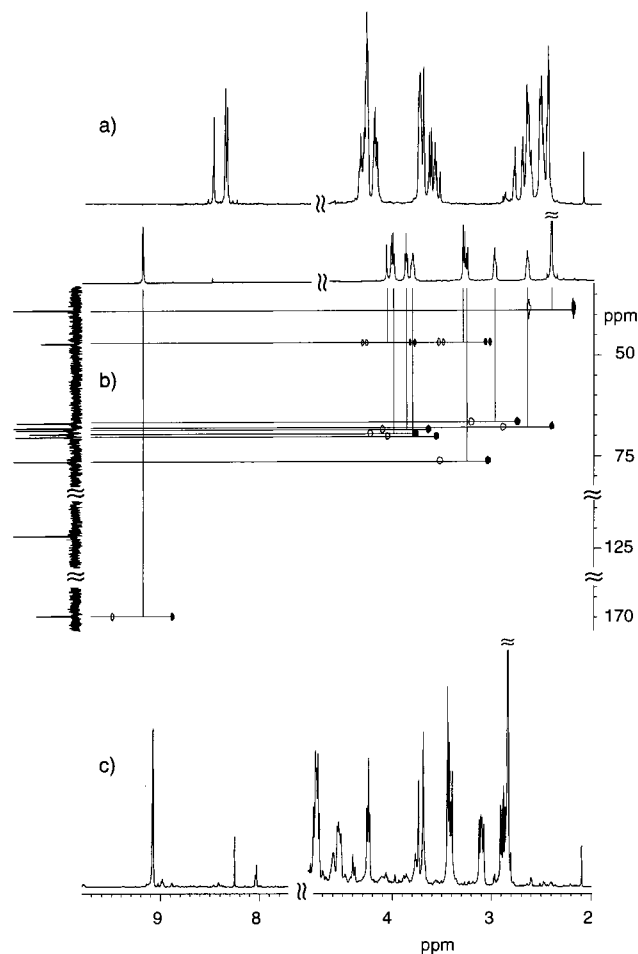


Figure 3. NMR characteristics of the $[\text{Co}(\text{hebdoc})]^+$ complex **5**. (a) ^1H spectrum of the primary reaction product. (b) Section of the ^1H – ^{13}C HMQC spectrum of the same sample in 1 M NaOD. (c) The ^1H NMR spectrum after reacidification with DCl (pD 1).

The X-ray analysis revealed two crystallographically inequivalent complex cations. However, both of the cation positions were occupied in a disordered manner and the structure was solved assuming a superposition of two different isomers. The isomers have C_1 and effective C_2 point group symmetry and differ in the configuration about the $\text{N}(-\text{CH}_3)$ nitrogen atoms (Figure 4). Attempts to grow single crystals from a solution of the third isomer, after treatment with base (see previous section), were not successful.

The crystal structure confirmed the formation of the novel macrocyclic hebdoc ligand. In both cations, the two *taci* fragments were fused by two $\text{NH}-\text{CH}_2-\text{C}(\text{=NO}_2^-)-\text{CH}=\text{N}$ bridges, where the $\text{O}_2\text{N}=\text{C}-\text{C}=\text{N}$ moiety represents a delocalized π -stabilized anion as indicated by the short C–N and C–C bonds and by the sums of the bond angles around each of the atoms N(12), C(19), N(14), N(22), C(29), N(24) and N(32), C(39), N(34), N(42), C(49), N(44) which all fall in the range of 357 – 360° . A distorted octahedral coordination is found for Co(1) and Co(2) with rather long Co–N($-\text{CH}_3$) bonds [mean value: $2.050(13)$ Å]. The sp^2 nitrogen donors of the bridges form significantly shorter Co–N distances [mean value: $1.980(7)$ Å], while the Co–N bonds of the remaining sp^3 nitrogen donors in the bridges fall in an intermediate range [mean value: $2.017(14)$ Å]. Overall, the cavity formed by the six nitrogen donors of this ligand is actually too large to accommodate the Co^{III} cation without considerable strain. This analysis is consistent with the pronounced bathochromic shift observed for the low energy ligand field band ($\lambda_{\text{max}} = 560$ nm).

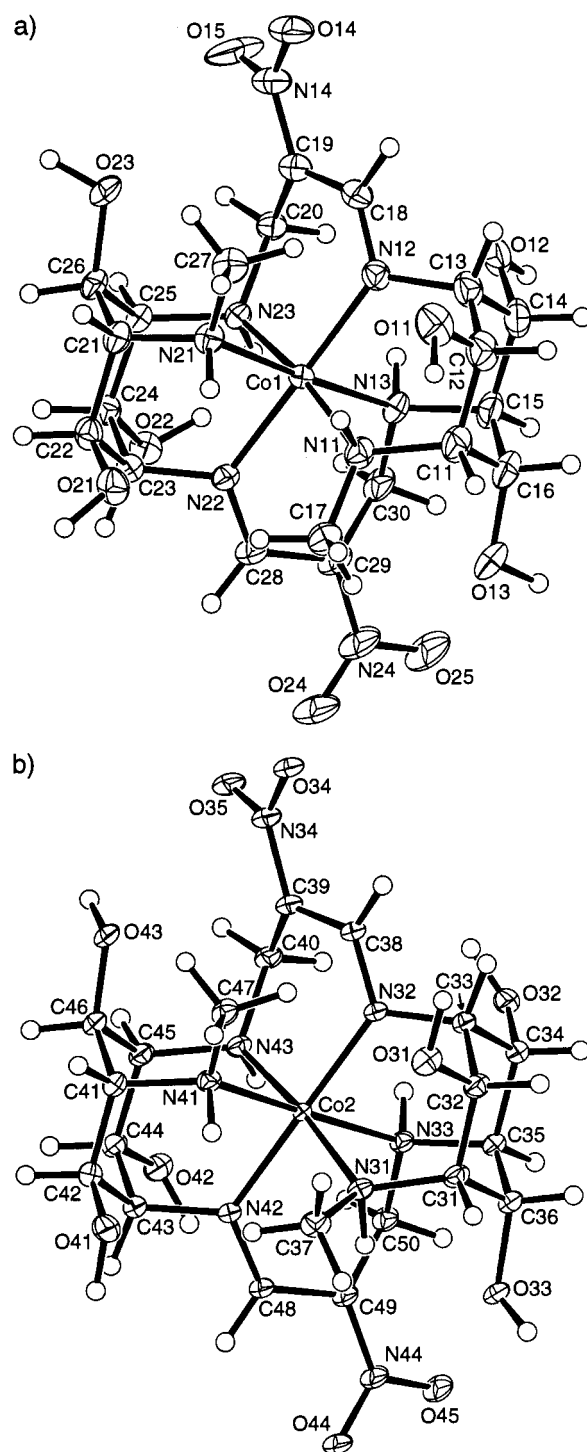


Figure 4. ORTEP drawing of the two cations $[\text{Co}(\text{hebdoc})]^+$ of $5_2\text{Cl}_2 \cdot 3.5\text{H}_2\text{O}$ with numbering scheme and vibrational ellipsoids at the 50% probability level. The hydrogen atoms are shown as spheres of arbitrary size. Only the major positions of the four disordered methyl groups are shown for clarity.

Condensation Reactions with Formaldehyde–Acetaldehyde Mixtures. By using a mixture of formaldehyde and acetaldehyde, the base-catalyzed condensation reaction with the hexamine complex **2** resulted in the formation of mixed methylideneimine–ethylideneimine derivatives. Such products are of particular interest, since the methyl group of a condensed acetaldehyde moiety is still acidic, and after deprotonation, addition of the carbanion to an adjacent methylideneimine group can occur.^{12,34} The condensation reaction with acetaldehyde is significantly slower than that with formaldehyde but the slower

rate can be compensated to some extent by supplying a sufficiently large excess of acetaldehyde. In our investigation, the ratio of the two aldehydes was varied systematically to find the optimal conditions for which the formation of one ethylideneimine moiety was followed by an attack (i.e. C–C bond formation) to two adjacent methylideneimines. Any remaining exocyclic imines were then hydrolyzed and the endocyclic imine was reduced with NaBH₄. This procedure resulted in a reduction of Co^{III} as well, and the resulting Co^{II} center had to be reoxidized with O₂ to get to the final [Co^{III}(abuca)]³⁺ (**6**) product. The complex was isolated as a chloride, a [ZnCl₄]²⁻ and a [ZnBr₄]²⁻ salt. Attempts to grow single crystals suitable for X-ray studies were not successful. However, the structure was assigned unambiguously by a series of NMR measurements and is consistent with FAB mass spectrometric data (observation of the pseudo molecular ion [H₋₁Co(abuca)]⁺ as the Co^{II} complex following reduction by the matrix) and with elemental analyses. The expected total of 22 lines was observed in the ¹³C NMR spectrum, and the absence of any signal above 80 ppm clearly indicated the lack of any imine function. A DEPT experiment allowed discrimination between CH, CH₂, and CH₃ groups and revealed a total of six CH(O) carbon atoms (73–78 ppm), six methoxy groups (59–61 ppm) and six CH(N) carbon atoms (46–57 ppm) of the two cyclohexane rings (Figure 5). The three CH₂ resonances at 49.9, 55.6, and 60.8 ppm together with the high-field CH resonance at 37.0 ppm were indicative of the trigonal H–C(–CH₂)₃ cap. In the ¹H NMR spectrum, the six methoxy groups were also observed as 6 individual singlets in the range 3.45–3.55 ppm, and the ring H(–C) protons together with the protons of the capping fragment were revealed as a group of poorly resolved signals in the range 2.6–3.9 ppm. In addition, a total of 9 H(–N) protons were assigned to signals in the range 4.4–7.6 ppm. As expected, these latter signals disappeared at pD values >7 as a result of H⁺ for D⁺ exchange.

Complex **6** had limited stability compared with other Co^{III} hexaamine complexes. Prolonged standing in D₂O resulted in the emergence of additional signals, indicating the formation of a decomposition product of unknown structure. This decomposition is rather slow in acid but became more rapid in strongly alkaline solution (pH >13). At pH 12, the complex was, however, sufficiently stable to observe characteristic changes in NMR spectra. In the ¹³C spectrum, the number of signals was reduced from 22 to 15; four signals each for the methoxy groups, the C(H–O) carbon atoms, and the C(H–N) carbon atoms. In addition one CH and two CH₂ resonances were found for the C₄H₇ cap. Similarly, four singlets were located for the methoxy groups in the ¹H spectrum. This is consistent with the lack of symmetry of complex **6** based on the asymmetric configuration about a single nitrogen atom (indicated as bold faced **NH** in Scheme 1) and the proposal that the complex adopts an averaged C_s symmetry by rapid deprotonation at this coordinated NH group.

Mechanistic Aspects. The introduction of a trigonal cap by condensing 1 equiv of acetaldehyde and 2 equiv of formaldehyde on one octahedral face of a hexaamine Co^{III} complex, followed by the subsequent base-catalyzed C–C bond formation is well established and straightforward.^{12,34} It is, however, interesting that in such a reaction with complex **2**, the mono-capped species is formed as a major product and the formation of a second trigonal cap was not observed, even though the reaction condi-

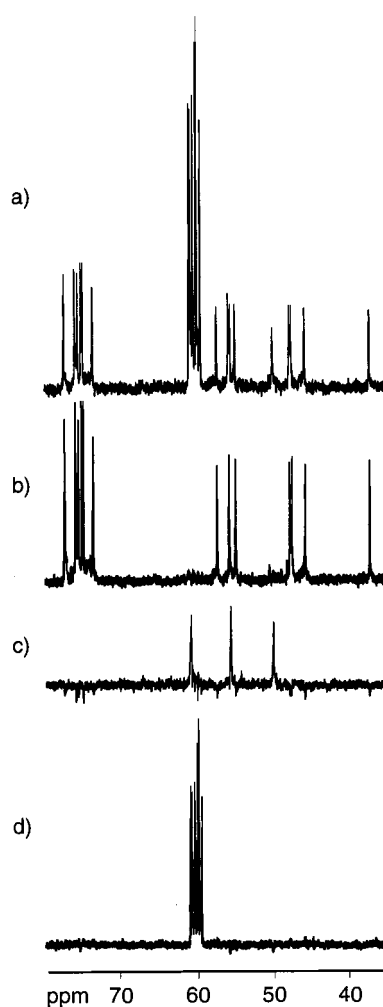


Figure 5. DEPT experiment of the [Co(abuca)]³⁺ complex **6**. The signals could be assigned as follows (values for the parent complex **2** in parentheses). (a) The entire ¹³C NMR spectrum with a total of 22 lines. (b) The 13 CH carbon atoms: 6 O-bonded cyclohexane C atoms at about 76 ppm (**2**: 74.9 ppm); 3 NH₂-bonded cyclohexane C atoms at about 47 ppm (**2**: 46.8 ppm); 3 additional N-bonded cyclohexane C atoms at about 56 ppm (the well-known downfield shift is caused by the additional substituent [trigonal cap] attached to the nitrogen atoms); the CH signal at 37 ppm of the trigonal cap. (c) The 3 CH₂ carbon atoms of the trigonal cap. (d) The 6 methoxy groups at 59.5–60.7 ppm (**2**, 60.1 ppm).

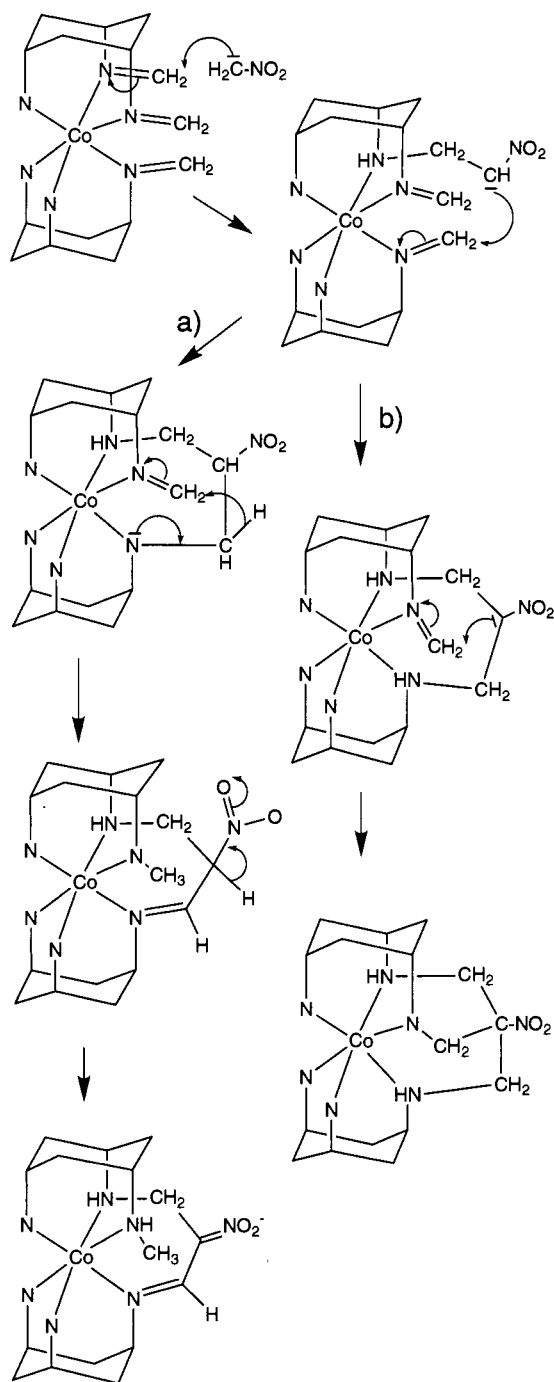
tions were varied over a wide range. This result is in contrast to analogous systems with simple 1,2-diamine ligands and nitromethane or aliphatic aldehydes as the coupling reagent, where the formation of two trigonal caps is well established.³⁵ We attribute this result to the rigidity of the two *taci* frames and the oversize dimension of the cavity for the metal ion.³⁶ The bathochromic shift observed in going from **2** to **6** indicates that already the coordination sphere of the mono-capped product is significantly strained and the introduction of a second cap would make the complex even more strained. Note that in the structure of **5**, a trigonal cap is not present at all. Analogous treatment

(34) Behm, C. A.; Creaser, I. I.; Korybut-Daszkiwicz, B.; Geue, R. J.; Sargeson, A. M.; Walker, G. W. *J. Chem. Soc., Chem. Commun.* **1993**, 1844.

(35) (a) Geue, R. J.; Hambley, T. W.; Harrowfield, J. M.; Sargeson, A. M.; Snow, M. R. *J. Am. Chem. Soc.* **1984**, *106*, 5478. (b) Walker, G. W. Ph.D. Thesis, Australian National University, 1997.

(36) It is noteworthy that the reaction between [Co(en)₃]³⁺ (en = ethane-1,2-diamine), formaldehyde, and nitromethane rapidly produced the bicapped complex whereas for the corresponding analogue with the more rigid *trans*-cyclohexane-1,2-diamine ligand, the reaction proceeded more slowly and in equivalent conditions only the monocapped species was formed: Geue, R. J.; McCarthy, M. G.; Sargeson, A. M. *J. Am. Chem. Soc.* **1984**, *106*, 8282.

Scheme 2



of $[\text{Co}(\text{tach})_2]^{3+}$ ($\text{tach} = \text{all-cis-cyclohexane-1,3,5-triamine}$) led to one trigonal cap and one $\text{NH-CH}_2\text{-C(=NO}_2\text{)}-\text{CH=N}$ bridge.³⁷ The formation of one cap in the tach complex generates unusually long Co–N bonds and it does seem that the introduction of a second cap is inhibited in this system. The taci complex with its additional hydroxy substituents is even more sterically demanding and the incorporation of a trigonal cap is not observed in the nitromethane condensation reaction either.

(37) Geue, R. J.; McCarthy, M. G.; Sargeson, A. M.; Horn, E.; Snow, M. *R. J. Chem. Soc., Chem. Commun.* **1986**, 848.

(38) Childers, R. F.; Wentworth, R. A. D.; Zompa, L. *J. Inorg. Chem.* **1971**, *10*, 302.

(39) Hegetschweiler, K.; Kradolfer, T.; Gramlich, V.; Hancock, R. D. *Chem. Eur. J.* **1995**, *1*, 74.

It is significant that the generation of such a $\text{N=CH-C(=NO}_2\text{)}-\text{CH}_2\text{-NH}$ bridge is coincident with the formation of one adjacent *N*-methyl group. This finding also supports the previously postulated mechanism, namely, an intramolecular hydride shift from the bridge methylene group to the adjacent *N*-methylideneimine group.³⁷ Two different pathways must be considered after the second addition of the nitromethane fragment to an imino group (Scheme 2): (a) a hydride transfer from a deprotonated Co–N–CH₂ moiety to an adjacent methylideneimine, along with deprotonation of the NO₂–CH group or (b) a C–C bond formation by adding the nitromethane carbanion to the methylideneimine. The hydride shift leads to an extended delocalized carbanion which is stabilized by the nitro and the imino groups. Extended π -stabilization is not possible for the intermediate preceding **6** and consequently the addition reaction (generation of the trigonal cap) occurs. It seems clear now that in the less strained systems with the open chain amine ligands, the formation of a trigonal cap is also the faster process for the condensation reaction with nitromethane. However, in more strained systems such as **5**, the attack of the remaining methylideneimine by the carbanion (b) is slow and the alternative hydride shift (a) thus becomes the dominant pathway.

Conclusions

In the present contribution, it has been demonstrated that the two hexamethylideneimines **3** and **4** are useful synthons for a variety of new compounds. They can be prepared readily from the parent hexamine complexes **1** and **2** in high yields and are surprisingly stable. Two different reaction pathways have been established in this investigation.

(i) The simple addition of a hydride ion to the C=N double bonds, followed by a protonation of the coordinated nitrogen donors, gives rise to a substantial increase of strain in the coordination sphere. The addition is followed by rapid decay of the complex and the subsequent liberation of the *N*-alkylated triamine. This procedure is simply a metal ion promoted version of the well-known reductive alkylation of primary amines. It represents, however, a very efficient and convenient route to the new tris(monoalkylamine) derivatives of taci and tmca.

(ii) Reagents with a moderately acidic methyl or methylene group such as nitroalkanes or aliphatic aldehydes may undergo multiple addition of the same atom to two or three adjacent imino groups, resulting in the formation of a linear bridge or a trigonal cap that connects the two taci fragments. This procedure is a promising tool for the synthesis of novel, hexadentate, macrocyclic ligands of high rigidity. Such ligands are interesting with respect to the specific modulation of electronic properties such as the redox potential, the electron-transfer rate, magnetic properties (spin state) and the energy of the d–d transitions.

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Supporting Information Available: Listings of crystallographic data, anisotropic displacement parameters, positional parameters of hydrogen atoms, bond distances and bond angles and a hydrogen bonding scheme of $[\text{Co}(\text{hebdoc})_2\text{Cl}_2 \cdot 3.5\text{H}_2\text{O}$ (15 pages). Ordering information is given on any current masthead page.