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Supplementary Material Available: Figures of the molecular structure of **3** with a complete labeling scheme and an ORTEP stereoview of the cluster core and tables of distances and angles, general anisotropic temperature factor expressions, weighted least-squares planes, torsional angles, and observed and calculated structure factor amplitudes for **3** (26 pages). Ordering information is given on any current masthead page.

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Synthesis and Properties of Novel Cobalt(III) and Nickel(II) Complexes with Coordinated Azetidine Nitrogens: Crystal Structure of *mer*-Tris(3-(aminomethyl)-3-methylazetidine)cobalt(III) Chloride Trihydrate

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Syntheses of the new amine 3-(aminomethyl)-3-methylazetidine (ama) and the complexes *mer*-$[Co(ama)_3]^{3+}$ and $[Ni(ama)_3]^{2+}$ are described, and the crystal structure of the *mer*-$[Co(ama)_3]Cl_3{\cdot}3H_2O$ isomer is reported. This structure is triclinic, space group $P\bar{1}$, with a = 13.926 (5) Å, b = 10.303 (5) Å, c = 9.804 (4) Å, α = 116.51 (3)°, β = 91.41 (2)°, γ = 105.15 (2)°, and Z = 2. The final $R(F)$ = 0.043 for 2303 reflections with $(\sin\theta)/\lambda \leq 0.60$ Å^{-1}. The nitrogen atom configuration around Co is close to a regular octahedron with Co–N distances in the range 1.973 (5)–2.024 (5) Å. The ligand field absorption spectrum of the $[Co(ama)_3]^{3+}$ ion is shifted to exceptionally low energies, λ_{max} = 513 nm (crimson), compared with those of other tris(diamine)cobalt(III) complexes, $\lambda_{max} \approx$ 465–475 nm (yellow-orange), presumably because of the longer Co–N bonds and orbital constraints at the azetidine donor atoms. The cobalt complex is stable in ~5 M DCl over several days but is susceptible to base hydrolysis (pH >3). The coordinated azetidine ring of the chelate does not rupture under the hydrolysis conditions and is apparently stable to nucleophilic attack by OMe^- and CN^- prior to ligand substitution reactions.

Introduction

Cobalt(III) tris(diamine) complexes containing five-, six-, and seven-membered chelate rings have shown some variations in Co(III)–N bond lengths and significant distortions from octahedral symmetry.[2] Average cobalt–nitrogen distances for accurately determined crystal structures range from 1.964 (1) Å in (+)-$[Co(en)_3]Cl((+)\text{-}C_4H_4O_6){\cdot}5H_2O$[3] (en = ethylenediamine) to 1.991 (5) Å in $(+)_{589}$-$[Co(tmd)_3]Br_3$[4] (tmd = 1,4-butanediamine) and N–Co–N bond angles from 91.0° in $(-)_{589}$-$[Co(tn)_3]Cl_3{\cdot}H_2O$[5] (tn = 1,3-propanediamine) to 84.2° in $(+)_{589}$-$[Co((-)\text{-chxn})_3]Cl_3{\cdot}H_2O$ (chxn = *trans*-1,2-cyclohexanediamine).[6] Both the chelate ring size and flexibility appear to be important in determining the structural characteristics of the CoN_6 chromophore in a given complex. We supplement these results with a study of the synthesis, structure, and properties of a novel cobalt(III) tris(diamine) complex and the synthesis of its nickel(II) analogue in which the ligand (ama) contains a strained azetidine ring. Coordination of the azetidine ring nitrogen to the relatively inert Co(III) center might be expected to activate the adjacent strained ring carbons to nucleophilic attack. The ligand forms an unusually rigid six-membered chelate ring, which could be suitable for probing the reactivity and stereochemistry of nucleophilic addition to such carbon centers.

Experimental Section

All chemicals used were of analytical grade. ^1H NMR spectra were recorded with a JEOL JNM-FX-200 Fourier transform spectrometer or a JEOL JNM-PMX-60 spectrometer for the hydrolysis experiments at 25 °C with sodium 3-(trimethylsilyl)propanesulfonate (NaTPS) as internal standard. ^{13}C NMR spectra were recorded with a JEOL JNM-FX-200 Fourier transform spectrometer (INEPTR spectrum[7]) at 27 °C or a JEOL JNM-FX-60 Fourier transform spectrometer at 25 °C relative to 1,4-dioxane as internal standard (s denotes a singlet, br a broad, and m a multiplet resonance). Chemical shifts are reported as positive downfield from the standard. A Cary 118 spectrophotometer (UV/vis) and a Cary 17 spectrophotometer (near-IR) were used to measure absorption spectra.

A 6-L high-pressure autoclave suitable for reaction temperatures and pressures to 350 °C and 350 atm was employed for the ligand synthesis. Bio-Rad analytical Dowex 50W-X2 (200–400 mesh, H^+ form) and SP-Sephadex (C-25, Na^+ form) ion-exchange resins were used for the cation-exchange chromatography.

All evaporations were carried out under reduced pressure (≤20 torr) with Büchi rotary evaporators such that the temperature of the solution did not exceed 25 °C.

pK_a values were determined by pH titration[8] of ama·2HCl with 0.1 M KOH under nitrogen at 20 °C.

Syntheses. 3-(Aminomethyl)-3-methylazetidine (ama). Ethylidynetris(methylene benzenesulfonate) (500 g) was prepared as described previously[9] and slowly heated with liquid NH_3 (4 L) in a steel autoclave fitted with an enameled sleeve (6-L volume). After 12 h with intermittent stirring the temperature reached 100 °C and the pressure ~60 atm. These conditions were maintained for 12 h before the system was allowed to cool to ~20 °C. The temperature of the reaction mixture was monitored and regulated with a thermocouple probe attached to a temperature control unit incorporated in the heating circuit. *Caution*! It is mandatory to ensure that no significant area of the autoclave interior exceeds a temperature of 132.4 °C at any time (the critical temperature of NH_3) and rapid nonequilibrium heating is not advisable. The NH_3 was removed through a valve connected to an efficient water aspirator, and the autoclave was warmed to 30–40 °C during this period. The pale yellow syrupy residue was dissolved in H_2O (10 L), and HCl (~4 M)

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(1) (a) The Australian National University. (b) Aarhus Universitet.

(2) Saito, Y. *Top. Stereochem.* **1978**, *10*, 95.

(3) Templeton, D. H.; Zalkin, A.; Ruben, H. W.; Templeton, L. K. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1979**, *B35*, 1608. Magill, L. S.; Korp, J. D.; Bernal, I. *Inorg. Chem.* **1981**, *20*, 1187.

(4) Sato, S.; Saito, Y. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1975**, *B31*, 1378.

(5) Nagao, R.; Marumo, F.; Saito, Y. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1973**, *B29*, 2438.

(6) Kobayashi, A.; Marumo, F.; Saito, Y. *Acta Crystallogr., Sect. B: Struct. Crystallogr. Cryst. Chem.* **1972**, *B28*, 2709.

(7) "JEOL Application Note"; JEOL Analytical Instruments Inc.: Akishima, Japan, Jan 1981; No. 2.

(8) Albert, A.; Serjeant, E. P. "The Determination of Ionization Constants"; Chapman and Hall: London, 1971.

(9) (a) Fleisher, E. B.; Gebala, A. E.; Levey, A.; Tasker, P. A. *J. Org. Chem.* **1971**, *36*, 3042. (b) Geue, R. J.; Searle, G. H. *Aust. J. Chem.* **1983**, *36*, 927.

0020-1669/85/1324-2559$01.50/0

was slowly added until the pH was about 1. The solution was sorbed on Dowex 50W-X2 (60 × 12 cm, H^+ form) and washed with H_2O (5 L) and 1 M HCl (5 L). The 1 M HCl solution slowly separated the first light-colored ligand band (F_1), which was then rapidly eluted with 2 M HCl (10 L from band front). The second distinct ligand band (F_2) was eluted with 3 M HCl (7 L from band front), and the third band (F_3), together with more highly condensed species, was removed with 6 M HCl.

F_1 was evaporated to dryness and identified as 3-(aminomethyl)-3-methylazetidine dihydrochloride by ^1H NMR and analytical techniques. The off-white residue was stirred with methanol (1 L) and the solution cooled to about 5 °C. Slow addition of acetone completed crystallization of the white blocks, which were filtered off, washed with acetone and ether, and air-dried (60 g, 38%). Anal. Calcd for $C_5H_{12}N_2{\cdot}2HCl$: C, 34.70; H, 8.15; N, 16.18. Found: C, 34.6; H, 8.1; N, 16.0. ^1H NMR (D_2O): δ 1.47 (s, CH_3), 3.32 (s, CH_2), 4.00 (AB quartet, J = 11 Hz, ring CH_2's). $^{13}C\{^1H\}$ NMR (0.1 M DCl): δ −12.0 (ring CH_2's), −20.9 (CH_2), −31.3 (quaternary C), −46.0 (CH_3).

F_2 crystallized from the HCl solution as it was reduced in volume and was isolated and identified as 1,1,1-tris(aminomethyl)ethane (tame) (30 g, 15%) by ^1H NMR and analytical methods.[9] Anal. Calcd for $C_5H_{15}N_3{\cdot}3HCl$: C, 26.51; H, 8.01; N, 18.55. Found: C, 26.3; H, 7.9; N, 18.3.

The 6 M HCl eluate containing F_3 as well as some more strongly bound amines appeared, from preliminary ^1H NMR, ^{13}C NMR, and analytical work, to consist mainly of dimeric and trimeric species, some of which contained azetidine rings. They will be considered in more detail in a subsequent report.

$[Co(ama)_3]Cl_3{\cdot}3H_2O$. ama·2HCl (30 g, 0.174 mol) and $LiOH{\cdot}H_2O$ (12.25 g, 0.292 mol) were stirred in methanol (AR, 150 mL) until all the solid had dissolved. $CoCl_2$ (7.27 g, 0.056 mol) in methanol (AR, 150 mL) was slowly added, and air was bubbled through the stirred solution. After ~1 h a crimson solid began to precipitate, and after 5 h the solid was filtered, washed with ethanol and ether, and dried in the air (12.1 g). The crude chloride salt was recrystallized as the desired salt by dissolution in a minimum volume of water at ~30 °C and dropwise addition of the appropriate saturated sodium salt. In this way, large dark red crystals of the chloride, nitrate, or chloride perchlorate salts were obtained on standing for several hours. These were filtered, washed with ethanol and ether, and dried in the air. Anal. Calcd for $[(C_{15}H_{36}N_6)Co]Cl_3{\cdot}3H_2O$: C, 35.26; H, 8.09; N, 16.45; Cl, 20.82. Found: C, 35.4; H, 7.9; N, 16.1; Cl, 20.6. Calcd for $[(C_{15}H_{36}N_6)Co](NO_3)_3{\cdot}H_2O$: C, 31.80; H, 6.76; N, 22.25; Co, 10.40. Found: C, 31.8; H, 6.7; N, 22.1; Co, 10.3. Calcd for $[(C_{15}H_{36}N_6)Co]Cl(ClO_4)_2$: C, 30.34; H, 6.11; N, 14.15; Cl, 17.91. Found: C, 29.9; H, 6.3; N, 14.0; Cl, 17.8. ^1H NMR (0.1 M DCl): δ 1.05, 1.07 (s, CH_3's), 1.12 (s, CH_3), 2.3–3.2 (br m, ring CH_2's), 3.3–3.7 (br m, CH_2), 4.67 (br, NH_2's), 5.7–5.8 (br, NH's). $^{13}C\{^1H\}$ NMR (0.1 M DCl): δ −7.7, −8.2, −9.5, −9.8, −11.1, −11.6 (azetidine CH_2's), −19.2, −19.7, −20.4 (CH_2's), −29.4, −30.7, −31.7 (quaternary C's), −46.6, −46.7, −46.9 (CH_3's). UV/visible spectrum (λ_{max}, nm (ϵ_{max}, $M^{-1}\ cm^{-1}$), 10^{-3} M in 0.1 M CF_3SO_3H): 243 (22 680), 362 (134), 513 (145).

Symmetric *cis*-$[Co(ama)_2(OH_2)(Cl)](Cl)ClO_4{\cdot}H_2O$. ama·2HCl (22 g), $LiOH{\cdot}H_2O$ (9.06 g), and $CoCl_2$ (5.3 g) were reacted together in methanol (150 mL) as described above. After 10 h crude $[Co(ama)_3]Cl_3{\cdot}3H_2O$ solid (6.3 g) was filtered off and the filtrate was acidified (pH ~3) and sorbed on Sephadex resin (15 × 7 cm). The column was washed with 0.1 M $HClO_4$ and a large amount of purple material eluted, which was converted to the chloride form by treatment on Dowex resin. The purple species decomposed to Co^{2+} and ligand on evaporation in HCl solution. The column was then washed with 0.2 M $NaClO_4$/0.1 M $HClO_4$, which removed more purple species and a crimson band, which was resorbed on Dowex resin (8 × 5 cm), washed with water and 1 M HCl, eluted with 3 M HCl, and evaporated to low volume (~10 mL). A saturated $NaClO_4$ solution (~5 mL) was added, and when the mixture was allowed to stand, reddish crystals formed. The crystals of the mixed chloro/aquo species were filtered, washed on the frit with ethanol and ether, and dried in air (0.7 g). Anal. Calcd for $[Co(C_{10}H_{26}N_4ClO)](Cl)ClO_4{\cdot}H_2O$: C, 25.79; H, 6.06; N, 12.03; Cl, 22.84; Co, 12.66. Found: C, 25.7; H, 6.1; N, 11.9; Cl, 22.8; Co, 12.3. ^1H NMR (0.1 M DCl): δ 0.863 (s, CH_3's), 2.0–2.2, 2.4–2.6, 2.6–3.0 (br complex m, ring CH_2's), 3.41 (s, CH_2's), 5.08, 5.26, 5.74, 6.22 (br, NH's, NH_2's). UV/visible spectrum (λ_{max}, nm (ϵ_{max}, $M^{-1}\ cm^{-1}$), 2 × 10^{-3} M in 0.1 M $HClO_4$): 494 (78), 357 (82). ^1H NMR (sym *cis*-$[Co(ama)_2(OH_2)_2]^{3+}$, 0.1 M $DClO_4$): δ 0.84 (s, CH_3's), 2.0–3.0 (br complex m, ring CH_2's), 3.38 (s, CH_2's), 5.44, 5.65 (br NH's, NH_2's). $^{13}C\{^1H\}$ NMR (sym *cis*-$[Co(ama)_2(OH_2)_2]^{3+}$, 0.1 M $DClO_4$): δ +0.53 (CH_2's), −20.4, −21.7 (azetidine ring C's), −27.3 (quaternary C's), −48.3 (CH_3's) (assigned from an INEPTR spectrum).

$[Ni(ama)_3](ClO_4)_2{\cdot}H_2O$. ama·2HCl (3 g) was dissolved in methanol (AR, 50 mL) with $LiOH{\cdot}H_2O$ (1.45 g), and $NiCl_2{\cdot}6H_2O$ (1.37 g) in methanol (AR, 25 mL) was added dropwise. A concentrated solution of $NaClO_4$ in methanol (3 mL) was added to the green-blue solution, which was then left to stand at 5 °C. When it was cooled, the solution turned deep blue and NaCl precipitated. The solution was filtered, reduced in volume to ~10 mL by gentle warming on a steam bath, and cooled to 5 °C, whereupon large pale blue crystals formed over several days. These were filtered, washed with H_2O and ether, and dried in air. Anal. Calcd for $[Ni(C_{15}H_{36}N_6)](ClO_4)_2{\cdot}H_2O$: C, 31.27; H, 6.65; N, 14.59; Ni, 10.19. Found: C, 31.6; H, 6.3; N, 14.6; Ni, 9.9. Visible spectrum (λ_{max}, nm (ϵ_{max}, $M^{-1}\ cm^{-1}$), CH_3CN): 368 (15.2), 580 (9.0), 980 (8.1).

Base Hydrolysis of *mer*-$[Co(ama)_3]Cl_2ClO_4{\cdot}2H_2O$. The complex (1 g) was dissolved in water (30 mL) and mixed with a solution of 0.01 M NaOH (30 mL) (pH 11.83). After 40 s the solution was quenched to pH 1 with $HClO_4$ (70%), sorbed on Sephadex resin (9 × 4 cm), washed with dilute aqueous $HClO_4$ (pH 1), and eluted with 0.2 M $NaClO_4$/0.1 M $HClO_4$ solution. Two bands separated clearly on the column. The front crimson band (~70%) contained the starting material and a small amount of purple 3+ species (a symmetric cis form of the $[Co(ama)_2(OH_2)_2]^{3+}$ ion from NMR results). The second band (purple) was eluted with 0.3 M $NaClO_4$/0.1 M $HClO_4$. It was collected on Dowex resin (4 × 2 cm, H^+), washed with 1 M HCl, and eluted with 6 M HCl. The eluate was evaporated to dryness, and a final ^1H NMR spectrum on the residue indicated the presence of ama ligand as well as complex. The species appeared to decompose during evaporation at 25 °C in 6 M HCl. ^1H NMR (0.2 M DCl): δ 0.97, 1.03 (s, CH_3's), 1.33, 1.60 (br, CH_3's, total integration 1 CH_3), 2.0–4.0 (br CH_2's).

Separate experiments on a longer time scale produced a higher yield of $[Co(ama)_2(OH_2)_2]^{3+}$ isolated as the perchlorate salt of $[Co(ama)_2(OH)(OH_2)]^{2+}$. Anal. Calcd for $[(C_{10}H_{27}N_4O_2)Co](ClO_4)_2{\cdot}H_2O$: C, 23.50; H, 5.72; N, 10.96; Cl, 13.87. Found: C, 23.7; H, 6.0; N, 10.7; Cl, 14.0. ^1H NMR (0.1 M DCl): δ 1.07 (s, CH_3's), 1.9–2.1, 2.6–2.8, 2.9–3.5 (br complex m, CH_2's and ring CH_2's), 5.18, 5.74, 6.10 (br, NH's, NH_2's). ^1H NMR (1:1 Me_2SO-d_6/0.1 M $DClO_4$): δ 1.01 (s, CH_3's), 1.80–2.10, 2.85–3.35 (br complex m, CH_2's), 5.30, 5.81, 6.01 (br, NH's, NH_2's). $^{13}C\{^1H\}$ NMR (1:1 Me_2SO-d_6/0.1 M $DClO_4$): δ −9.9, −13.1, −19.1 (azetidine ring C's, CH_2's), −30.7 (quaternary C's), −46.1 (CH_3's). UV/visible spectrum (λ_{max}, nm (ϵ_{max}, $M^{-1}\ cm^{-1}$), 10^{-3} M in 10% CH_3CN in 0.1 M $HClO_4$): 320 (1496), 524 (110).

Acid Hydrolysis of *mer*-$[Co(ama)_3]Cl_2ClO_4{\cdot}2H_2O$. ^1H NMR spectra of *mer*-$[Co(ama)_3]^{3+}$ in 5 M DCl remained unchanged over a period of 24 h at 25 °C. After 43 h a new methyl peak appeared at δ 1.5, and after 9 days this accrued to ~5% of the total methyl integration.

Reactivity with Nucleophiles. *mer*-$[Co(ama)_3]Cl_3{\cdot}3H_2O$ (0.5 g) was stirred in methanol (50 mL) with NaCN (~0.5 g). After 10 min the solution turned yellow, and after 2 h the reaction mixture was quenched with HOAc, diluted, and chromatographed on SP-Sephadex resin (H^+ form) with 0.4 M HCl. *Caution!* It was necessary to perform these operations in a well-ventilated fume hood due to the evolution of HCN. Several yellow bands were eluted, and the major band was eluted as a 3+ ion. ^1H NMR: δ 0.96 (s, CH_3), 1.38, 1.46 (s, CH_3's), 2.8–4.0 (br, CH_2's). IR: ν(−CN) 2125 cm^{-1}.

A solution of *mer*-$[Co(ama)_3]^{3+}$ in methanol quickly turned purple on addition of NaOMe, indicating base solvolysis. A solution of *mer*-$[Co(ama)_3]^{3+}$ in H_2O (pH 1) did not change substantially over a period of weeks on addition of H_2O_2.

Attempted Isomer Separation and Resolutions. The complex (0.1 g) was chromatographed on a column of Sephadex resin (78 × 2 cm) with use of 0.2 M K_2SO_4 (pH 4.5) as eluant. No separation of the complex occurred although two minor bands due to decomposition hydrolysis (~10%) appeared.

Resolution. Resolution of *mer*-$[Co(ama)_3]^{3+}$ (0.1 g) was achieved by cation-exchange chromatography on SP Sephadex C-25 (Na^+ form, 78 × 2.5 cm) with 0.15 M $Na_2[Sb_2((+)\text{-tart})_2]$ (tart = tartrate, pH 4.5) as eluant (R_x 1.1). RD spectra (λ_{max}, nm (deg $M^{-1}\ m^{-1}$), 10^{-3} M in 0.1 M CF_3SO_4H): front band 554 (−9900), 470 (18 200); back band 554 (+7700), 470 (−13 700). CD spectra (λ_{max}, nm ($\Delta\epsilon$, $M^{-1}\ cm^{-1}$), 10^{-3} M in 0.1 M CF_3SO_3H): front band 500 (−4.47), 352 (+0.38).

X-ray Crystallographic Analysis of *mer*-$[Co(ama)_3]Cl_3{\cdot}3H_2O$. The compound crystallizes as prismatic crystals bounded by eight planes. A single crystal of the size and habit indicated in Table I was used for data collection at room temperature with Zr-filtered Mo Kα radiation on a Picker FACS-1 diffractometer. Unit cell dimensions were obtained by least-squares refinement of the centered angle settings of 16 reflections. Crystal data and details concerning the data collection are given in Table I. Integrated intensities were evaluated by the minimal $\sigma(I)/I$ criterion.[10] Periodical measurement of two reflections showed that their intensities

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[10] Lehmann, M. S.; Larsen, F. K. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1974**, *A30*, 580.

Table I. Crystal Data for Tris(3-(aminoethyl)-3-methylazetidine)cobalt(III) Chloride Trihydrate, $(CoN_6C_{15}H_{26})Cl_3 \cdot 3H_2O$

fw = 509.75
space group: $P\bar{1}$ (No. 2)
$Z = 2$
unit cell dimens: $a = 13.926$ (5) Å, $b = 10.303$ (5) Å, $c = 9.804$ (4) Å, $\alpha = 116.51$ (3)°, $\beta = 91.41$ (2)°, $\gamma = 105.15$ (2)°
$V = 1198.7$ Å^3
D(calcd) = 1.41 g/cm^3
μ(Mo Kα) = 11.05 cm^{-1}
cryst vol: 0.0196 mm^3
cryst boundary planes and dist (cm) to common point inside cryst: 1,0,0, 0.020; 1,–1,0, 0.012; 1,0,1, 0.012; –1,0,0, 0.0205; –1,0,–1, 0.0090; 0,–1,1, 0.0200; 0,1,–1, 0.0205; –4,0,0, 0.0090
data set: $-h, \pm k, \pm l$
no. of reflcns collected ($2\theta_{max} = 50°$): 4260
no. of unique reflcns with $I \geq 3\sigma(I)$: 2303
scan mode: ω–2θ
scan range: $2\theta(K\alpha_1) - 1.60°$ to $2\theta(K\alpha_2) + 1.60°$; step scanned, 0.04° in 2θ, 4 s/step

Table II. Fractional Coordinates ($\times 10^4$) and Equivalent Isotropic Thermal Parameters ($\times 10^3$) for Non-Hydrogen Atoms

atom	x	y	z	U_{eq},^{a} Å^2
Co	2509.3 (5)	1568.9 (8)	7796.7 (7)	26.7 (4)
N11	2665 (3)	2852 (5)	6724 (5)	33 (3)
N21	3971 (3)	1830 (5)	7743 (5)	32 (2)
C11	4445 (3)	2768 (6)	6235 (5)	36 (3)
C21	5321 (5)	3336 (8)	5546 (7)	51 (4)
C31	3451 (4)	2935 (7)	5711 (6)	42 (3)
C41	4270 (4)	1210 (6)	6156 (6)	40 (3)
C51	4606 (4)	3372 (6)	7988 (6)	33 (3)
N12	2898 (3)	3383 (5)	9900 (5)	31 (3)
N22	1109 (3)	1678 (5)	8029 (5)	35 (3)
C12	1102 (4)	3326 (5)	10314 (5)	34 (3)
C22	501 (5)	4142 (7)	11495 (7)	50 (4)
C32	2202 (4)	3813 (7)	11029 (6)	37 (3)
C42	700 (4)	1592 (6)	9418 (6)	40 (3)
C52	1010 (4)	3280 (7)	8750 (6)	39 (3)
N13	1966 (3)	–337 (5)	5745 (5)	38 (3)
N23	2429 (3)	161 (5)	8675 (5)	37 (3)
C13	2094 (4)	–2107 (6)	6849 (6)	40 (3)
C23	1900 (5)	–3766 (7)	6354 (8)	58 (5)
C33	2038 (5)	–1856 (7)	5434 (7)	49 (4)
C43	1492 (4)	–1246 (6)	8008 (7)	41 (3)
C53	3010 (4)	–945 (6)	8050 (7)	45 (4)
O1	6721 (4)	3950 (5)	623 (5)	49 (3)
O2	1888 (6)	877 (10)	1917 (8)	82 (5)
O3	4418 (4)	–152 (6)	2086 (7)	96 (5)
Cl1	4635 (1)	2625 (2)	1337 (2)	55 (1)
Cl2	552 (1)	1661 (2)	4582 (2)	58 (1)
Cl3	7829 (2)	1997 (2)	8133 (2)	90 (2)

^{a} $U_{eq} = {}^1/_3 \sum_i \sum_j a_i^* \cdot a_j^* \, a_i \cdot a_j \, U_{ij}$.

were decaying in a fashion that could be described by a second-order polynomial. All reflections were corrected for the decrease in intensities, which totaled 30% during the data collection period of 3 weeks. Observed step counts were corrected for coincidence loss, and correction for the Lorentz and polarization effects was applied. Data were corrected for absorption by Gaussian numerical integration.[11] Transmission factors range from 0.74 to 0.81.

Structure Determination and Refinement. The structure was solved by the direct-methods program system MULTAN.[12] All non-hydrogen atoms were located in the first E map, and hydrogen atoms even for the water molecules could be picked out as the highest peaks in the subsequent difference Fourier. Atomic positions and thermal parameters—anisotropic for non-hydrogen atoms and isotropic for hydrogen atoms—were determined in a full-matrix least-squares refinement, which also included a parameter for isotropic extinction.[13] The final refinement based on the 2303 reflections with $(\sin \theta)/\lambda \leq 0.60$ Å^{-1} and $I > 3\sigma(I)$ converged to discrepancy factors

$$R = (\sum ||F_o| - |F_c||)/\sum |F_o| = 0.045$$

$$R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w |F_o|^2]^{1/2} = 0.042$$

and goodness of fit, GOF = $[\sum w(F_o^2 - F_c^2)^2/(N_o - N_v)]^{1/2} = 1.20$, where the weighting factor w is determined by $1/w = \sigma(F^2) + 0.02F^2$. F_o and F_c are the observed and calculated structure factors; N_o is the number of structure factors, and N_v is the number of variables. Atomic scattering factors were taken from ref 14. Atomic coordinates and the equivalent isotropic thermal parameters[15] are given for non-hydrogen atoms in Table II. Atomic coordinates for hydrogen atoms, anisotropic thermal parameters for non-hydrogen atoms, and observed and calculated structure factor amplitudes are available as supplementary material.

Results

Syntheses and NMR Spectra. The ligand 3-(aminomethyl)-3-methylazetidine (ama) has been synthesized as a major coproduct in the condensation between ethylidynetris(methylene benzenesulfonate) and ammonia at 100 °C and ~60 atm.

The pK_a values of ama determined by pH titration gave pK_{a1} (primary amine) = 7.94 ± 0.03 and pK_{a2} (secondary amine) = 10.92 ± 0.03 at 20 °C.

The strained metal complexes $[M(ama)_3]^{n+}$ (M = Co(III), Ni(II)) were isolated in moderate yields under relatively anhydrous conditions (<5% H_2O). The ^1H NMR spectra of the *mer*-$[Co(ama)_3]^{3+}$ ion showed methyl proton resonances at δ 1.05, 1.07, and 1.12 (relative to NaTPS). The methylene proton resonances at δ 2.3–3.7 were complex multiplets, and the broad peaks, due to protons bound to the nitrogens, were centered at δ 4.67 and 5.63.

The ^{13}C NMR spectrum showed a distinct resonance for each individual carbon atom, revealing the true asymmetry of the molecule. The azetidine ring methylene carbon signals appeared between δ –7.70 and –11.56, and the pendant methylene carbons displayed peaks at δ –19.24, –19.74, and –20.38. The three quarternary carbon and three methyl carbon resonances occurred at δ –29.37, –30.67, –31.71 and –46.63, –46.69, –46.89, respectively. Assignment of these resonances was aided by the use of an INEPTR program (INEPT = insensitive nuclei enhanced by polarization transfer) which distinguished between methyl, methylene, and quarternary carbon atoms.[7]

Chromatography on the filtrate from the synthesis of $[Co(ama)_3]^{3+}$ was conducted in order to detect the possible presence of the *fac*-$[Co(ama)_3]^{3+}$ ion, which may be soluble under the reaction conditions. However only a reddish bis complex was isolated which gave a ^1H NMR spectrum (0.1 M DCl) with a methyl singlet at δ 0.863, a singlet for the pendant methylene protons at δ 3.41 (weak coupling occurs with the NH_2 protons), and five nitrogen proton resonances. The number of NH resonances suggests that the compound was in the chloro/aquo form. The diaquo species gave two broad nitrogen proton signals and a ^{13}C NMR spectrum with five peaks, which were assigned with the aid of an INEPTR spectrum.

The C_2 symmetric cis isomer has the possible forms in which the azetidine ring nitrogens may be arranged either cis or trans to each other. Both the two trans and the two C_2 symmetric cis isomers of $[Co(ama)_2(OH_2)_2]^{3+}$ can give rise to this observed C_2 symmetry. However, the possibility that the compound is trans is precluded since both trans forms have a mirror plane, which would result in four peaks in the $^{13}C\{^1H\}$ NMR spectrum and not five as observed.

With use of ion-exchange chromatography and sodium antimony tartrate as eluant, the racemic *mer*-$[Co(ama)_3]^{3+}$ ion has been resolved into its chiral forms and the UV/visible, circular dichroism, and rotatory dispersion spectra of the enantiomer that

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(11) Coppens, P.; Leiserowitz, L.; Rabinovich, D. *Acta Crystallogr.* **1965**, *18*, 1035.
(12) Germain, G.; Main, P.; Woolfson, M. M. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1971**, *A27*, 368.
(13) Becker, P. J.; Coppens, P. *Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr.* **1974**, *A30*, 129.
(14) "International Tables for X-ray Crystallography"; Kynoch Press: Birmingham, England, 1974; Vol. IV.
(15) Willis, B. T. M.; Pryor, A. W. "Thermal Vibrations in Crystallography"; Cambridge University Press: New York, 1975; p 101.
(16) Johnson, C. K. *Oak Ridge Natl. Lab.*, [*Rep.*] *ORNL* (*U.S.*) **1965**, *ORNL-3894*.

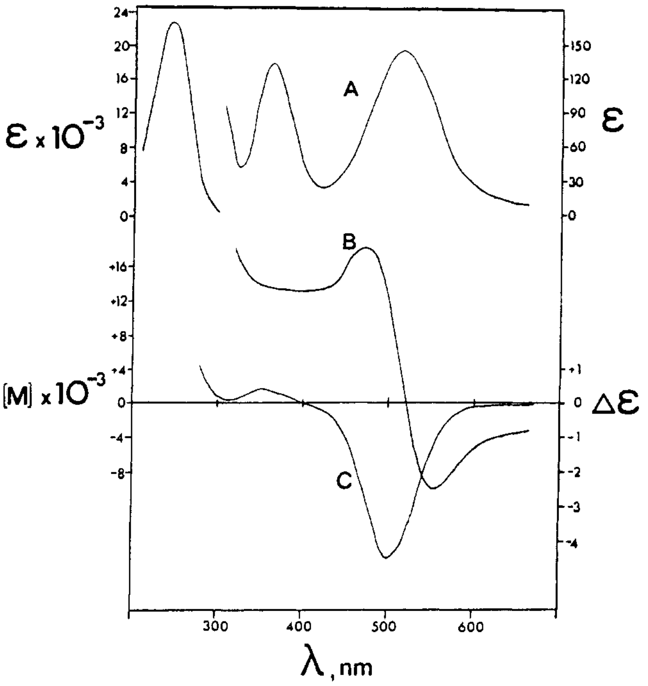


Figure 1. UV/visible (A), RD (B), and CD (C) spectra of resolved *mer*-$[Co(ama)_3]^{3+}$ (front band) (10^{-3} M in 0.1 M CF_3SO_3H).

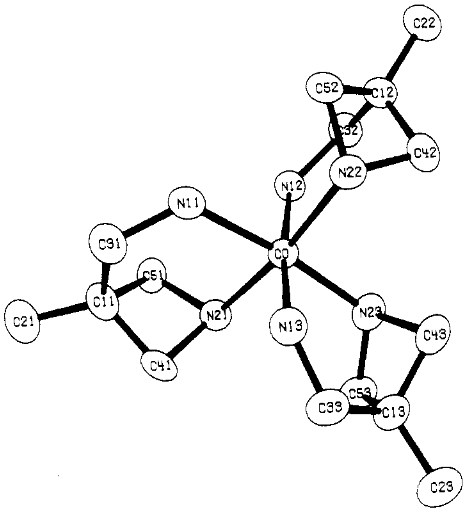


Figure 2. Crystal structure of *mer*-$[Co(ama)_3]^{3+}$.

separated first are given in Figure 1.

Chemical resolution methods showed no prospect for the enantiomeric resolution of the $[Co(ama)_3]^{3+}$ ion or the presence of both facial and meridional forms. ^{13}C NMR and ^1H NMR spectra were also consistent with the existence of only the meridional diastereoisomer.

Hydrolysis of *mer*-$[Co(ama)_3]^{3+}$ in 0.05 M NaOH initially yielded a 4+ ion after acid quenching. It gave a ^1H NMR spectrum with only two sharp methyl resonances and subsequently decomposed in strong acid. A symmetric cis form isolated as $[Co(ama)_2(OH)(OH_2)](ClO_4)_2{\cdot}H_2O$ appeared to be the main product when the hydrolysis was continued for a longer period. Its symmetric cis identity was confirmed by the ^1H NMR spectrum (Me_2SO-d_6/0.1 M $DClO_4$), which gave a singlet due to the methyl protons and three nitrogen proton resonances, and the $^{13}C\{^1H\}$ NMR spectrum (Me_2SO-d_6/0.1 M $DClO_4$), which gave only five signals. The tris(diamine) complex was stable in ~5 M DCl over a period of 2 days, after which some slight decomposition became noticeable.

Description of the Structure of *mer*-$[Co(ama)_3]Cl_3{\cdot}3H_2O$. Figure 2 shows the *mer*-$[Co(ama)_3]^{3+}$ group and the numbering system adopted. The three ligands are chemically equivalent but do not conform with a pseudothreefold axis in the structural arrangement around the central Co atom. Distances and angles within the cation are given in Tables III and IV. The nomenclature and the construction of Tables III and IVb are such that similar distances and angles can be compared along the rows.

Least-squares planes defined by the atoms Co–N1*i*–C3*i*–C1*i*–C2*i*–N2*i* show very similar puckering for *i* = 1 and *i* = 2, while puckering goes in the opposite direction for ligand 3. Table V gives deviations from the least-squares planes. This difference in the conformation of the ligands is also evident as a difference in bond torsion angles Co–N1*i*–C3*i*–C1*i*, which are given in Table VI along with the dihedral angles of the azetidine groups C1*i*–C4*i*–C5*i*–N2*i*. Identical puckering of the ligands would bring the hydrogen atoms on C43 in close contact with the hydrogen atoms on C42. Interchanging N12 and N22 would give a potential threefold axis and an isomer that has been designated the *facial* form.

Table III. Interatomic Distances (Å) Not Involving Hydrogen Atoms within the Ligand Complex

	ligand 1	ligand 2	ligand 3
Co–N1*i*	2.001 (5)	2.004 (5)	2.024 (5)
Co–N2*i*	1.988 (4)	1.995 (5)	1.973 (5)
N1*i*–C3*i*	1.507 (7)	1.483 (7)	1.487 (8)
N2*i*–C4*i*	1.512 (7)	1.519 (7)	1.534 (7)
N2*i*–C5*i*	1.510 (7)	1.525 (7)	1.487 (8)
C1*i*–C2*i*	1.519 (8)	1.515 (8)	1.498 (8)
C1*i*–C3*i*	1.543 (7)	1.524 (7)	1.524 (8)
C1*i*–C4*i*	1.525 (8)	1.527 (8)	1.522 (8)
C1*i*–C5*i*	1.531 (7)	1.514 (8)	1.522 (8)

Table IV

(a) N–Co–N Angles (deg)

	N21	N12	N22	N13	N23
N11	85.0 (2)	93.0 (2)	89.7 (2)	90.2 (2)	173.6 (2)
N21		87.7 (2)	170.6 (2)	98.1 (2)	90.9 (2)
N12			84.8 (2)	173.8 (2)	91.8 (2)
N22				89.6 (2)	95.0 (2)
N13					85.4 (2)

(b) Bond Angles (deg) within the Ligands

	ligand 1	ligand 2	ligand 3
Co–N1*i*–C3*i*	123.7 (4)	124.9 (4)	123.9 (4)
Co–N2*i*–C4*i*	116.0 (3)	117.3 (4)	115.6 (3)
Co–N2*i*–C5*i*	115.8 (3)	115.2 (3)	117.0 (4)
C2*i*–C1*i*–C3*i*	112.7 (5)	111.0 (5)	109.9 (5)
C2*i*–C1*i*–C4*i*	118.4 (5)	117.5 (5)	118.8 (5)
C2*i*–C1*i*–C5*i*	117.2 (5)	119.2 (5)	119.7 (5)
C3*i*–C1*i*–C4*i*	110.8 (5)	109.7 (5)	110.5 (5)
C3*i*–C1*i*–C5*i*	109.8 (5)	111.4 (4)	111.0 (5)
C4*i*–C1*i*–C5*i*	84.8 (4)	85.7 (4)	84.7 (5)
C1*i*–C3*i*–N1*i*	113.6 (4)	114.8 (4)	115.1 (5)
C1*i*–C4*i*–N2*i*	89.2 (4)	88.5 (4)	88.4 (4)
C1*i*–C5*i*–N2*i*	89.0 (4)	88.8 (4)	90.1 (4)

Table V. Deviations (Å) from Least-Squares Planes Defined by the Atoms Co–N1*i*–C3*i*–C1*i*–C2*i*–N2*i*

	ligand 1	ligand 2	ligand 3
Co	−0.104	−0.070	0.081
N1*i*	0.199	0.157	−0.155
C3*i*	−0.165	−0.147	0.135
C1*i*	−0.022	0.007	0.006
C2*i*	0.038	0.028	−0.026
N2*i*	0.054	0.025	−0.041

Table VI. Torsion Angles (deg) Defined by Co–N1*i*–C3*i*–C1*i* and Dihedral Angles between the Planes C1*i*–C4*i*–C5*i* and C4*i*–C5*i*–N2*i* of the Azetidine Groups

	ligand 1	ligand 2	ligand 3
Co–N1*i*–C3*i*–C1*i*	−33.0 (7)	−28.8 (7)	26.8 (8)
dihedral angle	34.5 (5)	35.4 (5)	35.0 (6)

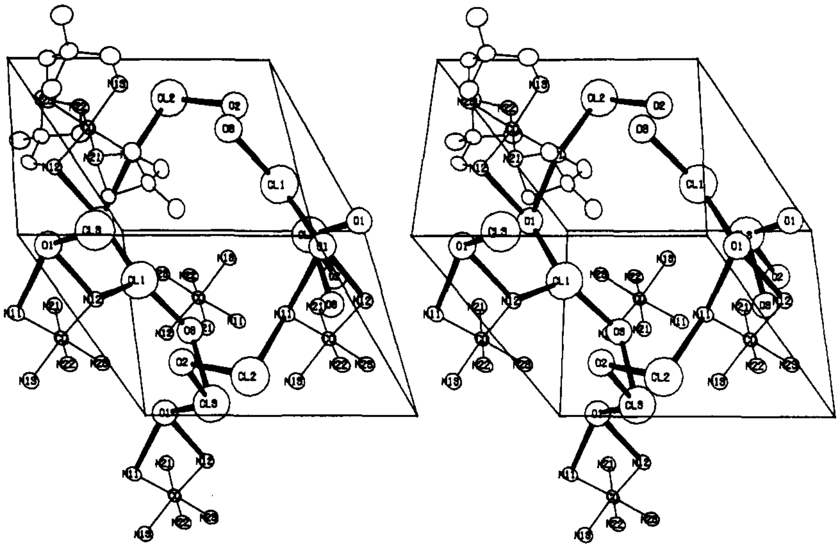


Figure 3. ORTEP[16] stereo drawing of molecular packing. Thermal ellipsoids are at the 50% probabiity level with O and Cl atoms drawn as spheres of arbitrary size.

Table VII. Short Intermolecular Contacts

O1---H-N12	2.933 (7)	O1---H-N11	3.020 (7)
Cl1---H-O1	3.111 (6)	Cl1---N21	3.288 (5)
Cl1---H-O3	3.201 (7)	Cl1---N23	3.508 (5)
Cl1---H-N12	3.201 (5)		
Cl2---H-O2	3.175 (8)	Cl2---H-N22	3.380 (5)
Cl2---H-N11	3.177 (5)	Cl2---H-N13	3.363 (5)
Cl3---H-O1	3.067 (9)	Cl3---H-O3	3.154 (7)
Cl3---H-O2	3.132 (6)		

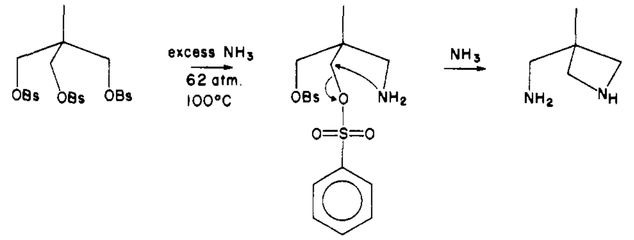
The structure has a three-dimensional network of hydrogen bonds, which is marked in heavy lines in Figure 3. Hydrogen atoms are not shown, and only one *mer*-$[Co(ama)_3]^{3+}$ cation is completed in the drawing; other cations are represented by the CoN_6 chromophores only. Figure 3 illustrates how chains of alternating oxygen and chlorine atoms hydrogen bond the *mer*-$[Co(ama)_3]^{3+}$ cations. One chain, N12[cation(*x*,*y*,*z*)]-O1-Cl3-O3-Cl1-N12[cation(1 + *x*, *y*, *z*)], winds through the structure along the *a* axis. Cl1 is also hydrogen bonded to O1. Another chain, N12[cation(*x*, *y*, *z*)]-O1-Cl3-O2-Cl2-N11-[cation(*x*, 1 + *y*, 1 + *z*)], winds through the structure approximately along the [011] diagonal. A list of short intermolecular contacts is given in Table VII. In the cases where H is indicated in Table VII, the hydrogen atom is found close to the line of the contact given, indicating some hydrogen bonding. In Figure 3 only distances within limits usually accepted for indication of hydrogen bonding are drawn in heavy lines. N11-O1-N12 possibly constitutes intramolecular hydrogen bonds, which may also be evidenced by the mean-square amplitude of O1 being much smaller than those of O2 and O3. Note that Cl1 is almost equally spaced to N12, N21, and N23 of the same molecule. The distance Cl1-Co is 4.054 (4) Å. Cl2 is close to the three other nitrogen atoms, but of two different cations. The third chlorine atom has close distances only to the water molecules, which makes it understandable that Cl3 has a considerably higher mean-square amplitude of vibration than Cl1 and Cl2, which are bonded to nitrogen atoms of the heavy chromophore.

The CoN_6 Chromophore. The cobalt atom is at a general position in the triclinic space group, but nevertheless the CoN_6 chromophore is close to being a regular octahedron.

The Co(III)-N bond lengths range from 1.973 (5) to 2.024 (5) Å around the average 1.998 Å. The distribution in distances is suggestive, but barely significantly, of a difference in bond lengths $\langle Co\text{-}N1i \rangle = 2.010\ (7)$ Å and $\langle Co\text{-}N2i \rangle = 1.985\ (6)$ Å.

The longer Co-N distances involve nitrogen bonded to a single carbon atom, and the shorter Co-N distances involve nitrogen bonded to two carbon atoms of the azetidine moiety. Some measures are calculated which describe the deviation of the chromophore atoms from positions corresponding to a best-fitted regular octahedron with the same N-N distances of 2.825 Å, as the average found in the *mer*-$[Co(ama)_3]^{3+}$ cation. The octahedron is centered on the mass center of the cation and has a threefold axis almost perpendicular to planes N11-N22-N13 and N12-N23-N21. The distance from the cobalt atom to the mass center is 0.026 Å. N11, N22, N13 are turned an average 8.9° relative to N12, N23, N21 around the ideal threefold axis, which has the consequence that the angles N1*i*-Co-N2*i* become less than 90° (see Table IVa). The angle between planes N11-N22-N13 and N12-N23-N21 is 2.0 (2)° and the distance between the mass centers of these two planes is practically identical with the similar distance in the ideal, regular octahedron.

Scheme I



Discussion

The diamine ligand 3-(aminomethyl)-3-methylazetidine has been isolated in moderate yield by the direct ammonolysis of ethylidynetris(methylene benzenesulfonate) with liquid ammonia (Scheme I).

Despite the extensive studies on azetidin-2-one derivatives in relation to β-lactam antibiotics,[17] comparatively little effort has been devoted to the chemistry of azetidines.[18] Several methods of synthesis have been developed,[18c,19,20] and some studies of ring-opening reactivity have been made.[18b]

The reactivity of the ring 2- and 4-positions in 3,3-disubstituted azetidines with unsubstituted ring nitrogens does not appear to have been investigated. Although azetidine itself ring opens in

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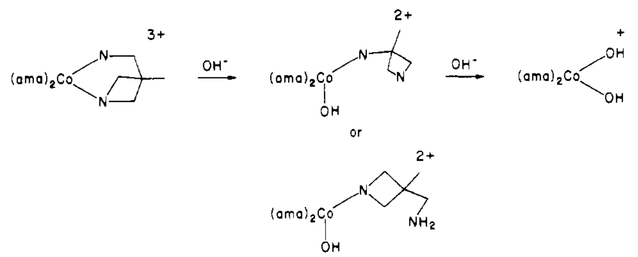
(17) Elks, J., Ed. "Recent Advances in the Chemistry of β-Lactam Antibiotics"; The Chemical Society: London, 1980.

(18) See, for example: (a) Elderfield, R. C. *Chem. Heterocycl. Compounds* **1950**, *1*. (b) Moore, J. A. In *Chem. Heterocycl. Compounds* **1964**, *19*, Part 2. Ayes, R. S.; Moore, J. A. *Chem. Heterocycl. Compounds* **1983**, *42*, Part 2. (c) Cromwell, N. H.; Phillips, B. *Chem. Rev.* **1979**, *79*, 331.

(19) Yamashita, M.; Ojima, J. *J. Am. Chem. Soc.* **1983**, *105*, 6339 and references therein.

(20) Okutani, T.; Kaneko, T.; Masuda, K. *Chem. Pharm. Bull.* **1974**, *22*, 1490 and references therein.

Scheme II



dilute acidic solution,[18a] it is stable under strongly basic conditions.[18] Other 3,3-disubstituted azetidines are stable in strongly acid solutions,[18b] and ama was expected to be relatively stable in both strongly acidic and strongly basic media. However, we have observed a significant decrease (from ca. 37% to less than 5%) in the yield of ama when the amination is conducted over a longer period (48 h), and it is probable that subsequent ring opening occurs under the conditions used for the synthesis. An increased yield of tame, the major product, over the longer period is consistent with this proposal.

The $[Co(ama)_3]^{3+}$ and $[Ni(ama)_3]^{2+}$ complexes have two possible diastereomeric forms consistent with the three ligands being arranged in the asymmetric meridional (*mer*) or the C_3 symmetric facial (*fac*) configuration. The ^1H NMR and ^{13}C NMR spectra for the cobalt species indicate an asymmetric species arising from a *mer* arrangement, and the crystal structure confirms this assignment. Attempts to prepare the *fac*-$[Co(ama)_3]^{3+}$ ion by conducting the synthesis with ama/$CoCl_2$/methanol/O_2 at 0 °C or using ama plus $[Co(py)_4(Cl)_2]Cl\cdot6H_2O$ as reactants were unsuccessful. Ion-exchange chromatography on the reaction products of the $[Co(ama)_3]^{3+}$ syntheses did not reveal any *fac* form of the complex. The *fac*-$[Co(ama)_3]^{3+}$ form may conceivably be prepared by reacting the unsymmetric form of *cis*-$[Co(ama)_2(CF_3SO_3)_2](CF_3SO_3)$[21] with ama in a noncoordinating solvent, although we did not observe this species in the present investigation.

The symmetric nature of *cis*-$[Co(ama)_2(OH_2)_2]^{3+}$ isolated from the reaction for the $[Co(ama)_3]^{3+}$ synthesis is clearly shown by its ^1H NMR and ^{13}C NMR spectra.

The hydrolysis of *mer*-$[Co(ama)_3]^{3+}$ proceeds (on a time scale of hours) above about pH 3, and the isolation and partial characterization of intermediates supports the pathway given in Scheme II for the process. The monodentate ligand in Scheme II is proposed on the basis of a 4+ charge for the intermediate in acid solution and the ^1H NMR spectrum, which shows only two resonances at $\delta \sim 1.0$ for the methyl groups at a chemical shift similar to those for the tris complex. Other work also supports the argument that the complex with the bound primary nitrogen in Scheme II is the more likely intermediate.[22]

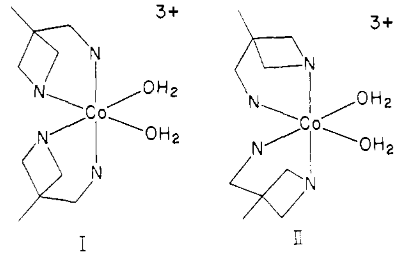


Figure 4. Isomers of symmetric *cis*-$[Co(ama)_2(OH_2)_2]^{3+}$.

Table VIII. Dissociation Constants of Amines at 20 °C

compd	pK_{a1}	pK_{a2}	μ, M
NH_3[a]	9.40		
CH_3NH_2[b]	10.79		0.05–0.2
$(CH_3)_2NH$[b]	10.92		0.05–0.2
$CH_3NH(CH_2)_2NH_2$[b]	7.13	10.44	0.002
ama	7.94	10.92	0.1

[a] Bates, R. G.; Pinching, G. D. *J. Am. Chem. Soc.* **1950**, *72*, 1393.
[b] Reference 24.

The ^1H and ^{13}C NMR spectra of the $[(ama)_2Co(OH_2)_2]^{3+}$ hydrolysis product (Me_2SO-d_6/0.1 M $DClO_4$) are consistent with a cis arrangement of the ligands having C_2 symmetry. Additionally, the NMR spectral results clearly distinguish between the symmetric *cis*-$[Co(ama)_2(OH_2)_2]^{3+}$ isomeric form isolated from the synthesis of *mer*-$[Co(ama)_3]^{3+}$ and the symmetric cis form isolated from the base hydrolysis reaction. A stability difference between the two forms, expected to arise largely from inter-ring steric interactions, is reflected in their visible spectral differences in the ligand field absorption regions. Indeed, the purple isomer obtained from the base hydrolysis is quite unstable to aquation whereas the red form from the synthesis appears to be stable in acidic and neutral aqueous solutions. Models of the two C_2 cis isomers I and II (Figure 4) indicate that isomer I, in which the azetidine rings are cis, has stronger inter-ring repulsions than does II, where the azetidine rings are trans. It can then be argued that I is more likely to be unstable to dissociation and hydrolysis than II, and we propose that the C_2 symmetric *cis*-$[Co(ama)_2(OH_2)_2]^{3+}$ isomer isolated from the synthesis of *mer*-$[Co(ama)_3]^{3+}$ is II whereas the unstable hydrolysis product is I.

The *mer*-$[Co(ama)_3]^{3+}$ complex is stable to aquation in ~5 M DCl over an extended period at low temperature (<20 °C). This indicates that the Co(III)–N bonds are still rather inert even though they are longer than normal and the chelate rings are strained.

Because of the susceptibility of *mer*-$[Co(ama)_3]^{3+}$ to hydrolysis, experiments involving addition of nucleophiles resulted in substitution at the cobalt center without any observable addition to the 2- and 4-positions of the azetidine ring. For NaOMe addition, solvolysis was rapid in methanol, and when CN^- was used as the nucleophile, the cyanide binds to the Co(III) center, facilitating the release of one or more amine donors.

A surprising property of the *mer*-$[Co(ama)_3]^{3+}$ ion is its crimson color when most other $[Co(diamine)_3]^{3+}$ complexes are orange to yellow. This surprising spectroscopic change bears some discussion. The effect of N-methylation of diamines on the electronic spectra of $[Rh(diamine)_3]^{3+}$ complexes has been evaluated.[23] N-methylation of the amine donor increases its basicity for primary amines[24] as shown by the examples in Table VIII, and the pK_a values for ama also follow this trend. On this basis, *N*-methyl diamine chelates should impose a stronger ligand field than unsubstituted diamines in their metal complexes. However, the steric effect of the *N*-methyl group more than offsets the increased basicity and the result is that the absorption maxima are shifted to lower energies for the *N*-methyl derivatives.[23] This is the case for the $[Rh(N\text{-methyl diamine})_3]^{3+}$ complexes,[23] and it can also be seen from the comparison between the absorption maxima for $[Co(en)_3]^{3+}$ and $[Co(meen)_3]^{3+}$ (meen = *N*-methyl-1,2-ethanediamine) (Table IX).

The data of Table 9 imply a link between the weakening of the ligand field and an increase in the average Co–N bond length for a number of cobalt tris(diamine) complexes.[25] The data for *mer*-$[Co(ama)_3]^{3+}$ ion also correlate and in fact show the longest bond lengths and lowest energy d–d and charge-transfer bands for any of the known $[Co(diamine)_3]^{3+}$ complexes. The weak ligand field and long Co–N bonds of *mer*-$[Co(ama)_3]^{3+}$ are likely to arise from at least two sources. Steric interactions between

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(21) Dixon, N. E.; Jackson, W. G.; Lancaster, M. J.; Lawrance, G. A.; Sargeson, A. M. *J. Am. Chem. Soc.* **1981**, *20*, 470.
(22) Ogino, H.; Orchara, Y.; Tanaka, N. *Inorg. Chem.* **1980**, *19*, 3179.
(23) Watt, G. W.; Alexander, P. W. *J. Am. Chem. Soc.* **1967**, *89*, 1814.
(24) Perrin, D. D. "Dissociation Constants of Organic Bases in Aqueous Solution"; Butterworths: London, 1967.
(25) Kojuma, M.; Yamada, H.; Ogino, H.; Fujita, J. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2325 and references therein.
(26) Arakawa, S.; Kashiwabara, K.; Fujita, J.; Saito, K. *Bull. Chem. Soc. Jpn.* **1977**, *50*, 2108.

Table IX. Absorption Spectra and Co–N Bond Lengths of $[Co(diamine)_3]^{3+}$ Complexes

complex[a]	λ, nm	log ε, M^{-1} cm^{-1}	av Co–N dist, Å[e]
$[Co(en)_3]^{3+}$ [b]	467	1.97	1.964 (1)[f]
	339	1.93	
	212	4.36	
$[Co(meen)_3]^{3+}$ [c]	492	2.06	
	351	2.01	
	231	4.36	
$[Co(tn)_3]^{3+}$ [b]	490	1.88	1.979 (5)[g]
	351	1.88	
	231	4.38	
$[Co(tmd)_3]^{3+}$ [b]	502.5	1.92	1.991 (5)[h]
	357	1.87	
	232	4.38	
Λ-$[Co(S,S\text{-}dppn)_3]^{3+}$ [d]	506	2.06	
mer-$[Co(ama)_3]^{3+}$	514	2.14	1.998 (7)
	365	2.10	
	243	4.35	

[a] All solutions 10^{-3} M in H_2O. Abbreviations: en = 1,2-ethanediamine; meen = *N*-methyl-1,2-ethanediamine; tn = 1,3-propanediamine; tmd = 1,4-butanediamine; dppn = 1,3-diphenyl-1,3-propanediamine. [b] Reference 25. [c] Reference 23. [d] Reference 26. [e] Errors were calculated as the estimated standard deviations in the derived mean Co–N values. [f] Reference 3. [g] Reference 5. [h] Reference 4.

the chelating ligands are expected to make the dominant contribution to the expansion of the CoN_6 chromophore. Additionally, the azetidine moieties inhibit the conformational freedom of the chelate rings. Both factors could constrain the orbital orientation and overlap of the nitrogen donors and weaken the metal/donor atom interactions.

No other $[Co(diamine)_3]^{3+}$ ions with six-membered chelate rings and secondary nitrogen donors appear to have been reported, although a range of complexes $[Co(N\text{-}Ren)_3]^{3+}$ (*N*-Ren = *N*-alkylethylenediamine) have been prepared.[27] The $[M(ama)_3]^{n+}$ species constitute a novel addition to the known series of $[M(diamine)_3]^{n+}$ complexes.

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Registry No. ama·2HCl, 96308-73-5; *mer*-$[Co(ama)_3]Cl_3·3H_2O$, 96308-74-6; *cis*-$[Co(ama)_2(OH_2)(Cl)](Cl)ClO_4$, 96326-16-8; *cis*-$[Co(ama)_2(OH_2)_2]^{3+}$, 96308-75-7; $[Ni(ama)_3](ClO_4)_2$, 96326-20-4; $[Co(ama)_2(OH)(OH_2)_2](ClO_4)_2$, 96326-18-0; ethylidynetris(methylenebenzenesulfonate), 31044-85-6.

Supplementary Material Available: Fractional coordinates for hydrogen atoms (Table IIa), anisotropic thermal parameters for non-hydrogen atoms (Table IIb), interatomic distances involving hydrogen atoms within the ligand complex (Table IIIa), and a listing of observed and calculated structure factor amplitudes (15 pages). Ordering information is given on any current masthead page.

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[27] Keller, R. N.; Edwards, L. J. *J. Am. Chem. Soc.* **1952**, *74*, 215.

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Reactions of $W(CO)_5$ Adsorbed onto Porous Vycor Glass with Various Ligands

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UV photolysis of $W(CO)_6$ physisorbed onto porous Vycor glass, PVG, leads to the corresponding pentacarbonyl. Electronic and EPR spectra indicate that the latter has a square-pyramidal, C_{4v}, structure with either a silanol group or chemisorbed water occupying the vacated coordination site. Exposing the pentacarbonyl to various ligands, either as gases or in a solution of degassed *n*-hexane, leads to displacement of the PVG surface functionality and formation of adsorbed $W(CO)_5L$ or $W(CO)_4L$ when L is bidentate. The pressure dependence of the reactions with gaseous ligands suggests that, at higher pressure, the predominant mode of reaction is between $W(CO)_5$ and a mobile, coadsorbed ligand. The activation parameters of the reaction with CO, which is weakly adsorbed onto PVG, indicate that the $W(CO)_5$–PVG interaction energy is ≤7 kcal/mol.

Introduction

Photolysis of the group 6[1] hexacarbonyls physisorbed onto porous Vycor glass, PVG, yields the corresponding pentacarbonyls.[2a] UV–visible spectra of the latter, particularly the W analogue, resemble spectra of $W(CO)_5L$ species, where L is an O-donor ligand.[2b] Since hydroxylated silica supports can be viewed as polydentate ligands,[3–6] the spectral similarity suggests that the long lifetime of the adsorbate, designated $W(CO)_5$(ads), is due to coordination to PVG. Stability gained through coordination to the support is advantageous with respect to spectroscopic characterization, but breaking this bond, which may be a necessary prerequisite to further reactivity, could represent a costly, endergonic activation step.

Previous studies of the thermal activation of these complexes physisorbed onto SiO_2 or Al_2O_3 indicate that formation of surface carbonyl species is reversible, although, in general, reversibility requires elevated temperatures. Howe, for example, reports that warming the complexes on SiO_2 above 10 °C in vacuo causes IR bands characteristic of the hexacarbonyl to disappear.[8] The

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[1] In this paper the periodic group notation is in accord with recent actions by IUPAC and ACS nomenclature committees. A and B notation is eliminated because of wide confusion. Groups IA and IIA become groups 1 and 2. The d-transition elements comprise groups 3 through 12, and the p-block elements comprise groups 13 through 18. (Note that the former Roman number designation is preserved in the last digit of the new numbering: e.g., III → 3 and 13.)

[2] (a) Simon, R. C.; Morse, D. L.; Gafney, H. D. *Inorg. Chem.* **1983**, *22*, 573. (b) Wrighton, M. S. *Chem. Rev.* **1974**, *74*, 401.

[3] Ahrland, S.; Grenthe, I.; Noren, B. *Acta Chem. Scand.* **1960**, *14*, 1059.

[4] Wolf, F.; Renger, P.; Janowski, F.; Heyer, W. *Z. Anorg. Allg. Chem.* **1977**, *432*, 249.

[5] Stanton, J. H.; Maatman, J. *J. Phys. Chem.*, **1964**, *68*, 757.

[6] Burwell, R. L. *CHEMTECH* **1974**, 370.

[7] Bailey, D. C.; Langer, S. H. *Chem. Rev.* **1981**, *81*, 109.

[8] Howe, R. F. *Inorg. Chem.* **1976**, *15*, 486.