Syntheses of Chromium and Copper Complexes of Hexaazamacrocycles. Crystal Structures of Chromium(III) Complexes of 1,4,7,10,13,16-Hexaazacyclooctadecane and 1,4,7,11,14,17-Hexaazacycloeicosane

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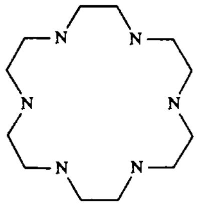
Chromium(III) complexes of two hexaazamacrocycles, 1,4,7,10,13,16-hexaazacyclooctadecane (**2**) and 1,4,7,11,14,17-hexaazacyloeicosane (**3**), have been prepared and the structures of the complex ions determined by single-crystal X-ray diffraction. For the 18-aneN_6 ring (**2**), a rare facial isomer has been identified. The complex crystallizes in the space group I_12/m_1 (No. 12). Refinement of the species $[Cr(\mathbf{2})]Br_3$ (a = 12.486(4) Å, b = 9.550(2) Å, c = 8.038(3) Å; β = 105.27(4)°) converged at R = 0.0639 (R_w = 0.0713) for 57 parameters using 751 reflections with $I > 2\sigma(I)$. The mean Cr–N bond length is 2.091(9) Å. However, the bite angle of the five-membered chelate ring subtended at the central chromium, 81.9(10)°, indicates significant distortion from octahedral symmetry. The complex $[Cr(\mathbf{3})]Br_3{\cdot}H_2O$ crystallizes in the monoclinic space group $P2_1/c$ (No.14). Refinement of the complex (a = 19.509(12) Å, b = 15.608(8) Å, c = 14.692(7) Å, β = 99.30(8)°) using a blocked-matrix approach converged at R = 0.0630 (R_w = 0.0617) for a total of 446 parameters using 2862 reflections with $I > 2\sigma(I)$. The average Cr—N bond distance is 2.095(15) Å, and the five-membered chelate angle is 83.5(6)°. Thus there is reduced strain within the ring compared to the smaller 18-membered macrocycle. This feature is also reflected in UV–visible spectroscopic and electrochemical measurements. The preparation, characterization, and electrochemistry of the analogous copper(II) complexes are also reported.

Introduction

There is considerable current interest in the complexes of hexadentate macrocyclic ligands, not least from the variety of geometrical forms available and the possible encapsulation of the metal ion. Such species may also be contrasted with those from the 1,4,7-triazamacrocycle, [9]-aneN_3 (**1**) (e.g., M([9]-aneN_3)$_2$), which have been studied extensively[1-3] with respect to their redox properties and stabilization of less common oxidation states. Maintainence of geometry is an important factor in the inner-sphere reorganization attendant upon electron transfer. In the bis(ligand)metal complexes of **1**, octahedral geometry is imposed as a result of the facial disposition of the donor atoms. These considerations have led to investigations on the hexadentate macrocyclic ligands 1,4,7,10,13,16-hexaazacyclooctadecane (**2**)



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and 1,4,7,11,14,17-hexaazacycloeicosane (**3**) and their metal complexes. Both Co(III) and Ni(II) ions form octahedral monomeric complexes with **2**, and in both cases, meridional isomers were isolated.[4-7] Mononuclear species have also been identified in solution in reactions with Co(II),[8] Zn(II),[9] and Cd(II)[10] ions. The hexaamine macrocycles also serve to bind two metal atoms, yielding discrete binuclear complexes.[11] Dicopper complexes of 20-, 22-, and 24- membered hexaamine macrocycles have been considered suitable in the activation of small molecules. The mode of substrate binding can be controlled by varying the size of the macrocyclic ligands in which the metal ions have otherwise similar ligand coordination environments. With [20]-aneN_6, tetranuclear clusters containing Cu of the type $[Cu_4(O_2)_2(H_2O)_4(L)_2](ClO_4)_6{\cdot}2CH_3NO_2$ have been obtained where each Cu atom is nearly square pyramidal in geometry.[12] The binuclear complex $Pd_2([20]\text{-ane}N_6)Br_4{\cdot}2H_2O$ was isolated in this laboratory.[13] This consists of two square planar Pd atoms, each coordinated to three N centers and one Br atom. The flexibility of the ligand thus allows for the formation of both mono- and dinuclear species. It was, therefore, of interest to study the complexation properties of these ligands with other transition metals ions. The ligand **3** has been obtained as a byproduct[13] during the synthesis of [10]-aneN_3 (**4**).[14] Both **4** and **3** have been synthesized directly, the latter in 30% yields.[15] We report here the synthesis of **3** in superior yields using a modified Richman and Atkins[16] synthesis. Chromium(III) complexes of both **2** and **3** were prepared and characterized structurally.

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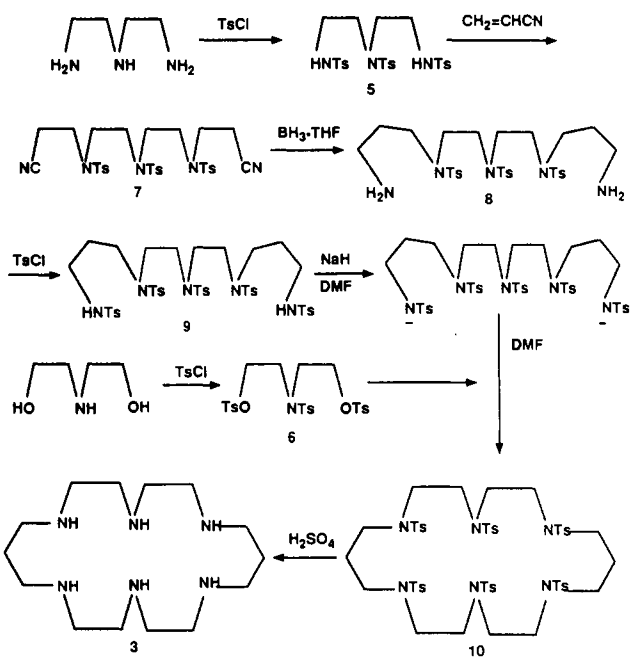
Scheme I



Experimental Section

Materials and Methods. All chemicals were of reagent grade except where otherwise indicated. Infrared spectra were obtained as KBr disks or as neat samples on NaCl plates with a Perkin-Elmer 283 grating spectrometer. ^{1}H NMR and ^{13}C NMR spectra were obtained with a Bruker WM250 or a Bruker 360 spectrometer. Electronic spectra were recorded on a Unicam SP800. EPR spectra were obtained with a Varian E6S spectrometer. The diphenylpicrylhydrazyl radical (dpph) was used as a field marker (g = 2.0037). Mass spectra were recorded with a Finnegan 330GC-MS instrument by using either electron impact or chemical ionization. Elemental analyses were performed by Microanalytical Services, Vancouver, BC, Canada. Electrochemical measurements were recorded with Princeton Applied Research equipment which included the Model 173/179 potentiostat–galvanostat and Model 175 programmer or a Princeton Applied Research Model 273 potentiostat–galvanostat, interfaced with an IBM/PC using the Princeton "Headstart" program. The electrochemical cell employed the standard three-electrode configuration. The reference electrode was a saturated calomel or Ag/AgCl electrode linked to the cell via a saturated KCl bridge. Ag/AgNO$_3$ (0.1 M) (or a Ag wire) was used as a reference electrode in nonaqueous systems containing 0.1 M NEt$_4$BF$_4$. Blank electrolyte solutions were scanned before each experiment and the ferrocenium/ferrocene couple (Fc$^+$/Fc) was used either as an internal or an external standard to calibrate the reference electrode, $E_{1/2}$(Fc$^+$/Fc) = 0.15 V vs Ag$^+$/Ag. Acetonitrile was distilled over CaH$_2$ prior to use for electrochemical purposes.

Syntheses. 1,4,7,10,13,16-Hexaazacyclooctadecane, [18]-aneN$_6$ (2). The ligand [18]-aneN$_6$·3H$_2$SO$_4$ used was supplied by Aldrich Chemical Co. The trisulfate salt was dissolved in water, and the solution was made basic (pH ~13) with sodium hydroxide solution. The free ligand was obtained as a colorless solid by continuous extraction with chloroform and subsequent removal of the solvent.

[Cr([18]-aneN$_6$)]Br$_3$. CrCl$_3$·6H$_2$O (0.124 g, 0.5 mmol) was dissolved in 10 mL of dmso at 190 °C. The volume of the solution was reduced to about 5 mL. A 0.5-mmol (0.134-g) solution of the ligand in ethanol (5 mL) was added to the metal containing solution at 60 °C. The temperature was raised slowly to 170 °C, during which time a yellow precipitate formed. Stirring was continued for 30 min at 170 °C. The yellow solid was filtered off, washed with small amounts of ethanol and ether, air-dried, and then dissolved in water (~4 mL) at 50 °C. A saturated solution of sodium bromide (2 mL) was added. Yellow-orange crystals, suitable for crystal structure determination, were obtained on slow evaporation. The crystals were filtered off and dried under vacuum. Yield: 0.28 g, 70%. Anal. Calcd for C$_{12}$H$_{30}$N$_6$CrBr$_3$: C, 26.19; H, 5.49; N, 15.27. Found: C, 26.23; H, 5.45; N, 15.29.

1,4,7,11,14,17-Hexaazacycloeicosane, [20]-aneN$_6$ (3). The synthetic route to the ligand is outlined in Scheme I.

N,N',N''-Tritosyldiethylenetriamine (5). This reagent was synthesized using the literature procedure[17] from diethylenetriamine and p-toluenesulfonyl chloride.

N-(p-Tolylsulfonyl)-2,2'-(p-tolylsulfonato)diethylamine (6). This material was prepared from p-toluenesulfonyl chloride and diethanolamine.[18]

3,6,9-Tritosyl-1,11-dicyano-3,6,9-triazaundecane (7). To a suspension of Na$_2$CO$_3$ (38 g) in acrylonitrile (200 mL) was added compound **5** (51 g, 0.09 mol) and stirring continued at reflux for 48 h. Excess acrylonitrile was then removed in vacuo. The solid residue was then partitioned between CH$_2$Cl$_2$ (600 mL) and water (500 mL). The aqueous layer was further extracted with CH$_2$Cl$_2$ (2 × 150 mL). The CH$_2$Cl$_2$ fractions were combined over Na$_2$SO$_4$ and taken to near dryness. Upon standing, a colorless solid was obtained, which was filtered off and dried under vacuum. Yield: 94% (57 g, 0.85 mol). Mp: 141–143 °C. MS (CI) (m/z): M + 1, 673; M + 29, 701. ^{1}H NMR (CDCl$_3$): δ 7.75–7.32 (12H, Ar), 3.38 (t, 4H), 3.36 (s, 8H), 2.74 (t, 4H), 2.42 (s, 9H). ^{13}C NMR (CDCl$_3$): δ 144.2, 144.0, 134.6, 134.4, 130.0, 129.9, 127.3 (Ar); 117.7 (–CN); 49.6, 49.4, 46.2, 21.4, 18.7 (aliphatic C). IR (KBr disk): ν_{CN} 2250 cm^{-1}. Anal. Calcd for C$_{31}$H$_{37}$N$_5$S$_3$O$_6$: C, 55.41; H, 5.55; N, 10.42; S, 14.31. Found: C, 55.47; H, 5.45; N, 10.49; S, 14.50.

1,13-Diamino-4,7,10-tritosyl-4,7,10-triazatridecane (8). To a solution of B$_2$H$_6$ in thf (700 mL, 1 M) under an atmosphere of nitrogen was added compound **7** (53 g, 0.079 mol). The solution was refluxed for 24 h, after which methanol (100 mL) was added carefully. After being taken to dryness in vacuo, the residue was dissolved in a solution of HCl in methanol (1 L, 2.5 M), and the mixture was refluxed for 3 h. The solution was again taken to dryness, the residue was partitioned between CH$_2$Cl$_2$ (750 mL) and aqueous NaOH (500 mL, 1 M), and the aqueous layer was further extracted with CH$_2$Cl$_2$ (2 × 500 mL). The organic fractions were combined, treated with anhydrous sodium sulfate, and taken to dryness under vacuum. A colorless oil was first obtained which then crystallized, yielding **8** (51 g, 0.075 mol) in 95% yield. Mp: 60 °C. MS (CI) (m/z): M + 1, 681; M + 29, 709; M + 41, 721. ^{1}H NMR (CDCl$_3$): δ 7.3–7.6 (12H, Ar); 3.2 (m, 16H); 2.69 (t, 4H); 2.38, 2.40 (2s, 6H + 3H); 1.64 (q, 4H). ^{13}C NMR (CDCl$_3$): δ 143.6, 135.6, 135.2, 129.9, 127.4 (Ar); 49.3, 48.3, 47.5; 37.9; 28.3; 21.4.

1,5,8,11,15-Pentatosyl-1,5,8,11,15-pentaazapentadecane (9). To a solution of **8** (51 g, 0.075 mol) in a mixture of thf (300 mL), CH$_2$Cl$_2$ (100 mL), and triethylamine (40 mL) was added dropwise a solution of p-toluenesulfonyl chloride (28.7 g, 0.15 mol) in thf (100 mL), and stirring was continued for 12 h at room temperature. The solvents were then removed under vacuum. Following partitioning of the residue between CH$_2$Cl$_2$ (500 mL) and water (500 mL), the aqueous layer was further extracted with CH$_2$Cl$_2$ (2 × 350 mL) and the organic layers were combined, dried over sodium sulfate, and evaporated under vacuum, yielding **9** as a colorless solid. This was recrystallized from hot CH$_2$Cl$_2$ and ethyl acetate (71 g, 72 mmoL, 96%). Anal. Calcd for C$_{45}$H$_{57}$N$_5$S$_5$O$_{10}$: C, 54.68; H, 5.81; N, 7.08. Found: C, 54.58; H, 5.89; N, 6.84. MS (negative ion methane CI) (m/z): M$^-$, 988. ^{1}H NMR (CDCl$_3$): δ 7.2–7.7 (m, 20H, Ar); 5.23 (2H); 3.26 (s, 8H); 3.13 (t, 4H); 2.98 (q, 4H); 2.45, 2.43, 2.40 (3s, 15H); 1.80 (q, 4H). ^{13}C NMR (CDCl$_3$): δ 143.8, 143.2, 137.0, 135.1, 129.9, 129.6, 127.3, 127.0 (Ar); 49.6, 48.7, 47.3, 40.1, 28.8, 21.4.

1,4,7,11,14,17-Hexatosyl-1,4,7,11,14,17-hexaazacycloeicosane (10). The disodium salt of the pentatosylate was prepared in situ by the addition of NaH (8 g of 60% dispersion, 0.16 mol) to a solution of **9** (61 g, 0.06 mol) in dmf (1 L). When the evolution of H$_2$ was complete, the solution was heated to 70 °C for 20–30 min, after which the excess NaH was filtered off. The solution was heated to 105 °C, and cyclization was achieved by dropwise addition of **6** (34.65 g, 0.06 mol) in dmf (400 mL) over 3 h, with stirring for a further 2 h. The dmf solution was taken to small volume (300 mL) and added dropwise to 1 L of water. Upon cooling, a precipitate formed, which was filtered off, rinsed with cold water, and air-dried. The solid was recrystallized from hot ethanol. Yield: 51 g, 70%. Mp: 281–284 °C. Anal. Calcd for C$_{56}$H$_{70}$N$_6$S$_6$O$_{12}$: C, 55.51; H, 5.82; N, 6.93; S, 15.87. Found: C, 55.27; H, 5.88; N, 6.99; S, 15.74. ^{1}H NMR (CDCl$_3$): δ 7.2–7.7 (m, 24H, Ar); 3.0–3.4 (m, 24H); 2.41, 2.39 (2s, 6H + 12H); 1.81 (q, 4H). ^{13}C NMR (CDCl$_3$): δ 143.7, 135.0, 129.9, 127.5, 127.4 (Ar); 50.0, 49.5, 48.4, 29.2, 21.5.

1,4,7,11,14,17-Hexaazacycloeicosane, [20]-aneN$_6$ (3). To a hot solution (140 °C) of concentrated sulfuric acid (50 mL) was added **10** (14 g, 11.6 mmol), and stirring was continued for 30 min. After the solution was cooled to 0 °C, ethanol (150 mL) was added slowly, followed

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Table I. Experimental Crystallographic Data for $[Cr([18]\text{-}aneN_6)]Br_3$ and $[Cr([20]\text{-}aneN_6)]Br_3{\cdot}H_2O$

formula	$CrBr_3N_6C_{12}H_{30}$	$CrBr_3N_6OC_{14}H_{36}$
MW	550.1	596.2
space group	I_12/m (No. 12)	$P2_1/c$ (No. 14)
cell dimens		
a (Å)	12.486(4)	19.509(12)
b (Å)	9.550(2)	15.608(8)
c (Å)	8.038(3)	14.692(7)
β (deg)	105.27(4)	99.30(8)
V (Å^3)	925	4415
Z	2	8
transm factors	0.286–0.413	0.292–0.309
D_{calcd} (g/cm^3)	1.976	1.794
D_{measd}	1.938	1.777
radiation (λ, Å)	Mo Kα (0.710 69)	Mo Kα (0.710 69)
T (°C)	22(2)	22(2)
μ (cm^{-1})	73.72	58.65
R^a	0.0639	0.0630
$R_w{}^b$	0.0713	0.0617
w	$4.02/(\sigma^2(F) + 0.001F^2)$	$1.68/(\sigma^2(F) + 0.001F^2)$

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

by ether (250 mL). The gray precipitate of $([20]\text{-}aneN_6){\cdot}3H_2SO_4$ was filtered off, rinsed with ethanol and ether, and air-dried. After dissolution of this precipitate in water (25 mL), it was made basic (to pH ~12) with NaOH and then extracted continuously (16 h) into $CHCl_3$. The organic fraction was treated with $MgSO_4$ and taken to dryness under vacuum, yielding **3** as a pale yellow oil. Yield: 2.5 g, 75%. MS (EI) (m/z): M$^+$, 286. ^{1}H NMR ($CDCl_3$): δ 2.73 (s, 16H), 2.73 (t, 8H), 2.39 (s, 6H), 1.71 (q, 4H). ^{13}C NMR ($CDCl_3$): δ 48.8, 48.2, 48.0, 29.1. The latter resonances are similar to those observed previously for this ligand.[15]

[Cr([20]-aneN$_6$)]Br$_3$·H$_2$O. The procedure was identical to that described above for Cr(**2**)$^{3+}$ with use of $CrCl_3{\cdot}6H_2O$ (0.6 g, 2.2 mmol) and the ligand (2.2 mmol, 0.64 g) as reagents. The yellow solid formed was dissolved in a saturated aqueous solution of NaBr; evaporation yielded yellow crystals of $[Cr([20]aneN_6)]Br_3{\cdot}H_2O$ suitable for crystal structure determination. Yield: 0.9 g, 66%. Anal. Calcd for $C_{14}H_{34}N_6$-$CrBr_3{\cdot}H_2O$: C, 28.33; H, 6.11; N, 14.17. Found: C, 28.29; H, 6.02; N, 14.11.

Caution: Perchlorate salts of transition metal ions are potentially explosive and must be handled with caution. Only small amounts of these materials should be prepared.

[Cu([20]-aneN$_6$)](ClO$_4$)$_2$. The ligand [20]-aneN$_6$ (0.35 g, 1.2 mmol) was dissolved in methanol (10 mL) at 50 °C, and a solution of $Cu(ClO_4)_2{\cdot}6H_2O$ (0.37 g, 0.98 mmol) in methanol (10 mL) was added with stirring. A blue precipitate formed immediately. After a further 30 min, the solid was filtered off and dried under vacuum. The material was recrystallized from an acetonitrile solution containing sodium perchlorate. Yield: 0.41 g, 71%. Anal. Calcd for $C_{14}H_{34}N_6CuCl_2O_8$: C, 30.63; H, 6.24; N, 15.31; Cl, 12.91. Found: C, 30.92; H, 6.18; N, 15.38; Cl, 12.82.

Crystallography. Suitable crystals were mounted in glass Lindemann tubes, and Weissenberg photography and precession photography were used to obtain the space groups and to determine initial unit cell dimensions. The diffraction data were obtained on a Picker four-circle diffractometer automated with a PDP11/10 computer scanning in the θ–2θ mode. Background counting was introduced at each end of the scan. A set of three standard reflections preceded each batch of 50 measurements, with no noticeable change in intensity observed during the collection in all cases. The data collection was carried out at 22 ± 2 °C. The atomic scattering factors used were those included in the SHELX76[19] program together with the Cr f curve from ref 20. The completion of the structure and the refinement were carried out by difference electron density maps and the method of least squares. The crystal data for both Cr complexes are given in Table I.

[Cr([18]-aneN$_6$)]Br$_3$. The unit cell dimensions were refined using 24 pairs of reflections in the 2θ range 17–49°. The solution of the phase problem was achieved via direct methods, using MULTAN,[21] which revealed the positions of chromium and bromine atoms. Subsequent Fourier syntheses using SHELX76[19] provided locations of the carbon and nitrogen atoms. The hydrogen atoms could not be located. All non-hydrogen atoms were refined anisotropically. Of 872 reflections collected, 751 ($I > 2\sigma(I)$) were used, with 57 parameters to be refined in the final cycle. The refinement converged to $R = 0.0639$ and $R_w = 0.0713$ with a maximum shift/esd of 0.023 on the final cycle. The final difference map had a maximum peak of 0.73 e Å^{-3}.

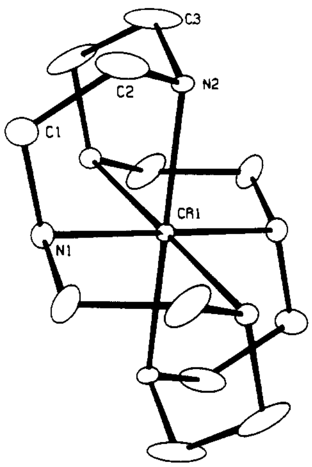

Figure 1. ORTEP diagram of Cr([18]-aneN$_6$)$^{3+}$ showing the atomic numbering scheme.

[Cr([20]-aneN$_6$)]Br$_3$·H$_2$O. The unit cell was refined using 20 pairs of reflections in the range $2\theta = 10$–$40°$. A total of 4118 reflections were measured, from which 2862 ($I > 2\sigma(I)$) were used. The solution of the phase problem was achieved by direct methods by use of SHELX-76.[19] The asymmetric unit was composed of two molecules of the complex containing 50 atoms. All non-hydrogen atoms except one carbon atom were refined with anisotropic thermal parameters. Since there were 446 parameters to be refined, a block matrix procedure was adopted. The bromine, chromium, and oxygen atoms were common to all blocks. The carbon and nitrogen atoms of the respective cations were refined in independent blocks. The refinement converged with a maximum shift/esd of 0.034 in the final cycle, to $R = 0.0630$ and $R_w = 0.0617$. The largest peak in the final difference map was 0.74 e Å^{-3}.

[Cu([20]-aneN$_6$)](ClO$_4$)$_2$. Crystals of the complex were isolated by slow evaporation of ethanolic solutions. Analysis showed the presence of a CuN$_5$ core in a distorted trigonal bipyramidal geometry. The structure was solved to a value of $R = 0.13$. However, the sixth nitrogen in the macrocycle and the propane carbon atoms were disordered and the structure could not be refined further.

Discussion

Synthesis. The preparation of the 20-aneN$_6$ ligand (Scheme I) afforded good yields of all intermediates. Detosylation of the cyclized [20]-aneN$_6$-tosylate was carried out either by hydrolysis in sulfuric acid or using H_3PO_4 dried with P_2O_5.[22] Good yields of the ligand (~60%) were obtained with both methods. Chromium complexes of both **2** and **3** were prepared by a modification of Pedersen's method.[23] The dmso solution containing $CrCl_3{\cdot}6H_2O$ was heated to facilitate the formation of the $Cr(dmso)_6Cl_3$ complex. The labile dmso ligand was then replaced by the N atoms of the hexadentate macrocyclic ligand to form the monomeric species containing a CrN$_6$ core.

Molecular Structures. Crystal Structure of [Cr([18]-aneN$_6$)]Br$_3$. The ORTEP diagram of the complex cation, Cr([18]-aneN$_6$)$^{3+}$, with atomic labeling for the non-hydrogen atoms is shown in Figure 1. The fractional atomic coordinates and the isotropic temperature factors are given in Table II. Selected bond lengths and angles are listed in Table III. The species crystallized in the space group I_12/m_1. The mean Cr–N bond length is 2.091(9) Å, which is similar to that observed in Cr(en)$_3{}^{3+}$ [24] (2.075(2) Å)

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Table II. Fractional Atomic Coordinates and Temperature Parameters for $[Cr([18]\text{-aneN}_6)]Br_3$[a]

atom	x/a	y/b	z/c	U_{eq}, Å^2
Cr(1)	50000(0)	0(0)	0(0)	185(9)
Br(1)	0(0)	0(0)	0(0)	384(7)
Br(2)	27929(11)	0(0)	55857(17)	330(5)
N(1)	3310(8)	100000(0)	−96(14)	29(4)
N(2)	5042(6)	1669(7)	1697(9)	28(2)
C(1)	3036(8)	1195(13)	751(18)	57(5)
C(2)	3976(12)	1669(13)	2268(17)	66(6)
C(3)	5261(15)	2961(12)	625(18)	80(7)

[a] Estimated standard deviations are given in parentheses. Coordinates × 10^n where n = 5, 5, 4, 4 for Cr, Br, N, C. Temperature parameters × 10^n where n = 4, 4, 3, 3 for Cr, Br, N, C. U_{eq} (equivalent isotropic temperature parameter) = $^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*(a_i \cdot a_j)$. $T = \exp[-(8\pi^2U_{iso}(\sin^2\theta)/\lambda^2]$.

Table III. Selected Interatomic Distances and Angles for $[Cr([18]\text{-aneN}_6)]Br_3$[a]

	Distances (Å)		
N(1)–Cr(1)	2.091(9)	N(2)–Cr(1)	2.090(6)
	Angles (deg)		
N(2)–Cr(1)–N(1)	82.8(3)	C(1)–N(1)–Cr(1)	110.6(6)
C(2)–N(1)–Cr(1)	108.7(6)	N(2)–Cr(1)–N(2)	80.6(4)
C(3)–N(2)–Cr(1)	110.3(6)	N(2)–Cr(1)–N(2)	99.5(4)

[a] Estimated standard deviations are given in parentheses.

and in $Cr(NH_3)_6^{3+}$ (2.064(3) Å).[25] The bite angle of the five-membered chelate ring subtended at the central Cr atom in the present complex is 81.9(10)°, showing significant distortion from octahedral symmetry. In the $Cr(en)_3^{3+}$ complex the corresponding value was found to be 82.4(10)°. Ideal six-coordinate chelate complexes with regular geometry about the C_3 axis have a twist angle $\phi = 60°$. However, many complexes adopt stable structures in which the ML_6 coordination unit is significantly distorted from the usual octahedral symmetry.[26,27] For the $[Cr([18]\text{-aneN}_6)]Br_3$ complex the twist angle is 50 ± 1°. This value is identical to that obtained[24] for the $Cr(diamsar)^{3+}$ ion[27] (diamsar = 1,8-diamino-3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane).

Both facial and meridional isomers may be formed for metal complexes of **2**. With Co(III) and Ni(II) complexes of **2**, meridional isomers are obtained preferentially.[4–7] Yoshikawa[4] obtained <1% of the facial isomer of the $Co([18]\text{-aneN}_6)^{3+}$ complex cation. It has been suggested that the presence of large nonbonded hydrogen–hydrogen interactions in the facial isomer may result in the preferential formation of the meridional isomer. Indeed, in the crystal structure of the meso cobalt(III) complex,[4b] bond length differences are observed in the chelate rings such that the H–H repulsions inherent in the symmetry may be avoided. However, in the present case, the hexadentate ligand **2** wraps around the larger central Cr^{3+} ion in a preferred facial manner. This is a rare example of the isolation and characterization of such a structure in [18]-aneN$_6$ complexes. In the case of **3** (vide infra), there is a significant change of structure which may reflect the greater flexibility of the molecule owing to the presence of the two trimethylene units. Structural differences have also been observed between the 18- and 20-membered-ring complexes of Pd(II).[13]

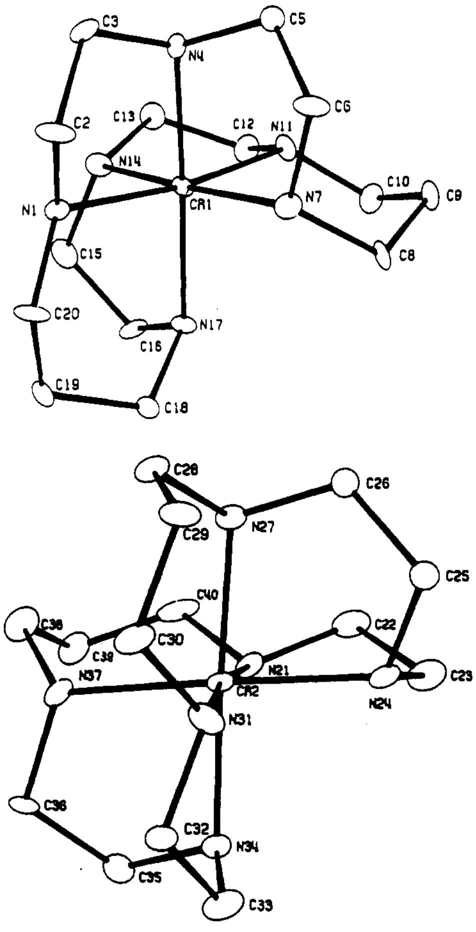

Figure 2. ORTEP diagram of $Cr([20]\text{-aneN}_6)^{3+}$ with two molecules in the asymmetric unit: (a, top) molecule 1; (b, bottom) molecule 2.

Crystal Structure of $[Cr([20]\text{-aneN}_6)]Br_3\cdot H_2O$. The chromium complex crystallized in the monoclinic space group $P2_1/c$, with a = 19.509 Å, b = 15.608 Å, c = 14.692 Å, β = 99.3°, and two molecules in the asymmetric unit. The molecular structures of these two molecules are shown in Figure 2. The fractional atomic coordinates for the Cr complex are given in Table IV for two crystallographically independent formula units. Each formula unit consists of a triply charged Cr(III) cation, three bromide anions, and a water molecule. The complex shows an octahedral microsymmetry with the six nitrogen atoms from the ligand coordinated to the central chromium atom. Selected interatomic distances and the bond angles for the chromium complex are given in Table V. The atomic labeling scheme of molecule 1 is shown in Figure 2a. Molecule 2 (Figure 2b) is labeled in a similar way (add 20 to each label except for the chromium which is labeled Cr(2)). The carbon atom labeled C(5) was not made anisotropic because of a poor thermal ellipsoid. The bite angle of the five-membered chelate ring subtended at the central Cr atom for the chromium complex of **3** has a mean of 84 ± 2°, similar to that of the chromium complex of **2**, thus showing significant distortion from octahedral symmetry. The angles subtended by the six-membered chelate ring at the center have a mean of 92 ± 2°. The twist angle for the $[Cr([20]\text{-aneN}_6)]Br_3$ complex is 56 ± 1°, somewhat larger than that for the [18]-aneN$_6$ complex owing to reduced strain in the 20-membered ring where there are two six-membered chelate rings present. This is in keeping with the observation that the $E_{1/2}$ for the $Cr([18]\text{-aneN}_6)^{3+/2+}$ couple is greater than that for the corresponding [20]-aneN$_6$ complex and the ligand field strength of the $[Cr([20]\text{-aneN}_6)]Br_3$ complex is also larger (vide infra).

The two complex ions present are structurally identical; however their disposition within the unit cell is unique. Transformation between cations does not appear to be symmetry related, although the crystals are racemic owing to the presence of an inversion center. Three isomers are possible for complexes of [20]-aneN$_6$,[14] depending upon the relative dispositions of the trimethylene linkages. The trimethylene bridging groups in the $[Cr([20]\text{-aneN}_6)]Br_3$ complex isolated are cis to one another. Utilizing

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Table IV. Fractional Atomic Coordinates and Temperature Parameters for [Cr([20]-aneN$_6$)]Br$_3$·H$_2$O^a

atom	x/a	y/b	z/c	U_{eq}
Br(1)	66618(10)	3808(11)	10262(12)	404(7)
Br(2)	99820(10)	11744(11)	44178(13)	470(8)
Br(3)	33414(11)	46788(14)	1493(15)	638(9)
Br(4)	11321(11)	14132(12)	7946(13)	516(8)
Br(5)	45035(12)	21237(12)	33208(15)	612(9)
Br(6)	79316(10)	31019(12)	10924(14)	539(8)
Cr(1)	62999(13)	41398(15)	26439(17)	242(9)
Cr(2)	−12273(14)	−9716(15)	25999(17)	275(10)
O(1)	8845(10)	2720(10)	4457(10)	112(8)
O(2)	3915(9)	2691(9)	337(10)	106(8)
N(1)	6422(7)	2888(7)	2167(8)	29(5)
N(4)	5817(7)	4336(7)	1289(8)	28(5)
N(7)	5275(7)	3944(8)	2871(9)	37(5)
N(11)	6241(7)	5448(7)	2940(9)	32(5)
N(14)	7305(7)	4466(8)	2446(9)	37(6)
N(17)	6761(7)	3847(8)	3990(8)	31(5)
C(2)	4871(10)	2731(11)	1333(11)	47(8)
C(3)	5866(8)	3542(11)	719(10)	34(7)
C(5)	5098(9)	4632(10)	1290(11)	34(4)
C(6)	4760(9)	4119(11)	1990(11)	43(7)
C(8)	5087(9)	4432(9)	3711(12)	35(7)
C(9)	5150(9)	5429(10)	3623(12)	41(7)
C(10)	5912(10)	5718(10)	3737(13)	49(8)
C(12)	6965(9)	5858(11)	3077(12)	42(7)
C(13)	7370(10)	5431(10)	2391(12)	46(8)
C(15)	7813(10)	4077(11)	3229(13)	52(8)
C(16)	7523(9)	4071(11)	4143(11)	42(7)
C(18)	6662(9)	2926(10)	4322(11)	40(7)
C(19)	6890(9)	2229(10)	3697(12)	40(7)
C(20)	6411(10)	2106(10)	2785(12)	48(8)
N(21)	−1323(7)	293(8)	3038(9)	38(6)
N(24)	−1571(7)	−1260(9)	3832(9)	43(6)
N(27)	−2288(7)	−1084(7)	2035(9)	32(5)
N(31)	−1060(7)	−2282(8)	2364(10)	43(6)
N(34)	−172(7)	−997(8)	3196(9)	40(6)
N(37)	−846(7)	−594(7)	1414(9)	37(6)
C(22)	−1806(10)	314(11)	3749(13)	51(8)
C(23)	−1627(11)	−454(12)	4399(13)	58(8)
C(25)	−2280(9)	−1713(10)	3635(11)	37(7)
C(26)	−2709(9)	−1300(10)	2764(11)	39(7)
C(28)	−2438(9)	−1651(10)	1167(11)	40(7)
C(29)	−2220(9)	−2594(9)	1399(12)	39(7)
C(30)	−1437(9)	−2703(10)	1487(11)	42(7)
C(32)	−297(9)	−2437(11)	2423(11)	39(7)
C(33)	74(10)	−1911(11)	3254(12)	54(8)
C(35)	211(9)	−439(11)	2612(13)	46(8)
C(36)	−54(8)	−534(11)	1575(12)	42(8)
C(38)	−1179(10)	205(10)	941(12)	51(8)
C(39)	−1068(11)	999(11)	1580(13)	56(8)
C(40)	−1537(10)	989(10)	2320(14)	54(8)

^{a} Estimated standard deviations are given in parentheses. Coordinates × 10^n where n = 5, 5, 4, 4, 4 in Br, Cr, O, N, C. Temperature parameters × 10^n where n = 4, 4, 3, 3, 3 for Br, Cr, O, N, C. U_{eq} (equivalent isotropic temperature parameter) $= {}^1/_3\sum_i\sum_j U_{ij}a_i^*a_j^*(a_i\cdot a_j)$. $T = \exp[-8\pi^2U_{iso}(\sin^2\theta)/\lambda^2]$.

Table V. Interatomic Distances and Angles for [Cr([20]-aneN$_6$)]Br$_3$·H$_2$O^a

	Distances (Å)		
N(1)–Cr(1)	2.102(12)	N(21)–Cr(2)	2.094(13)
N(4)–Cr(1)	2.082(12)	N(24)–Cr(2)	2.079(15)
N(7)–Cr(1)	2.102(14)	N(27)–Cr(2)	2.109(13)
N(11)–Cr(1)	2.095(12)	N(31)–Cr(2)	2.109(13)
N(14)–Cr(1)	2.091(14)	N(34)–Cr(2)	2.103(13)
N(17)–Cr(1)	2.087(12)	N(37)–Cr(2)	2.087(14)
	Angles (deg)		
N(4)–Cr(1)–N(1)	82.9(5)	N(37)–Cr(2)–N(27)	98.9(5)
N(7)–Cr(1)–N(1)	94.6(5)	N(37)–Cr(2)–N(31)	92.9(5)
N(7)–Cr(1)–N(4)	83.0(5)	N(37)–Cr(2)–N(34)	84.1(5)
N(11)–Cr(1)–N(1)	171.2(5)	C(2)–N(1)–Cr(1)	108.4(9)
N(11)–Cr(1)–N(4)	91.3(5)	C(20)–N(1)–Cr(1)	122.2(10)
N(11)–Cr(1)–N(7)	91.3(5)	C(3)–N(4)–Cr(1)	110.5(8)
N(14)–Cr(1)–N(1)	91.2(5)	C(5)–N(4)–Cr(1)	109.1(9)
N(14)–Cr(1)–N(4)	96.9(5)	C(6)–N(7)–Cr(1)	110.6(10)
N(14)–Cr(1)–N(7)	174.2(5)	C(8)–N(7)–Cr(1)	114.2(9)
N(14)–Cr(1)–N(11)	82.9(5)	C(10)–N(11)–Cr(1)	119.0(10)
N(17)–Cr(1)–N(1)	93.3(5)	C(12)–N(11)–Cr(1)	110.7(9)
N(17)–Cr(1)–N(4)	175.7(5)	C(13)–N(14)–Cr(1)	109.7(11)
N(17)–Cr(1)–N(7)	95.4(5)	C(15)–N(14)–Cr(1)	108.0(10)
N(17)–Cr(1)–N(11)	92.7(5)	C(16)–N(17)–Cr(1)	110.7(9)
N(17)–Cr(1)–N(14)	85.1(5)	C(18)–N(17)–Cr(1)	116.6(9)
N(24)–Cr(2)–N(21)	83.1(5)	C(22)–N(21)–Cr(2)	109.1(9)
N(27)–Cr(2)–N(21)	93.9(5)	C(40)–N(21)–Cr(2)	119.2(10)
N(27)–Cr(2)–N(24)	83.7(5)	C(23)–N(24)–Cr(2)	111.0(11)
N(31)–Cr(2)–N(21)	171.4(5)	C(25)–N(24)–Cr(2)	110.1(9)
N(31)–Cr(2)–N(24)	90.8(6)	C(26)–N(27)–Cr(2)	110.9(9)
N(31)–Cr(2)–N(27)	91.3(5)	C(28)–N(27)–Cr(2)	114.6(10)
N(34)–Cr(2)–N(21)	91.1(5)	C(30)–N(31)–Cr(2)	119.3(9)
N(34)–Cr(2)–N(24)	93.7(5)	C(32)–N(31)–Cr(2)	109.1(9)
N(34)–Cr(2)–N(27)	174.0(5)	C(33)–N(34)–Cr(2)	108.9(10)
N(34)–Cr(2)–N(31)	83.3(5)	C(35)–N(34)–Cr(2)	107.1(9)
N(37)–Cr(2)–N(21)	93.0(5)	C(36)–N(37)–Cr(2)	112.1(9)
N(37)–Cr(2)–N(24)	175.4(5)	C(38)–N(37)–Cr(2)	115.4(11)

^{a} Estimated standard deviations are given in parentheses.

Table VI. Absorption Data and Redox Potentials

complex	λ_{max} (nm) (ϵ (L mol^{-1} cm^{-1}))^a	ref
[Cr([9]-aneN$_3$)$_2$]$^{3+}$	439 (88), 340 (64)	2
[Cr([18]-aneN$_6$)]$^{3+}$	466 (227), 361 (103)	PW^c
[Cr([20])-aneN$_6$)]$^{3+}$	456 (104), 350 (85)	PW
[Cu([18]-aneN$_6$)]$^{2+}$	699 (140)	33
[Cu([9]-aneN$_3$)$_2$]$^{2+}$	618^b	31
[Cu([20]-aneN$_6$)]$^{2+}$	672 (150)^b	PW

complex	$E_{1/2}$ (V) vs NHE	ΔE_p (mV)^d		ref
[Cr([9]-aneN$_3$)$_2$]$^{3+/2+}$	−1.14^e	63	rev^f	2
[Cr(diamsar)]$^{3+/2+}$	−1.11	70	ref^f	24
[Cr([20]-aneN$_6$]$^{3+/2+}$	−1.02^e	80	quasi-rev^f	PW
[Cr([18]-aneN$_6$]$^{3+/2+}$	−0.92^e	120	quasi-rev^f	PW
[Cu([9]-aneN$_3$)$_2$]$^{2+/+}$	−1.41^g		irrev	31
[Cu([18]-aneN$_6$)]$^{2+/+}$	−0.44^h		rev	PW, 33
[Cu([20]-aneN$_6$)]$^{2+/+}$	1.07^g		quasi-rev	PW

^{a} H$_2$O. ^{b} CH$_3$CN. ^{c} PW = present work. ^{d} 50 mV s^{-1}. ^{e} 0.1 M LiClO$_4$. ^{f} Hanging-mercury-drop electrode. ^{g} CH$_3$CN, Fc$^+$/Fc. ^{h} SCE.

the description[28] where *f* describes a facial coordination of a tridentate ligand and *m* the meridional analogue, one may view the present complexes as follows. Commencing at N(1), the N(1)–N(4)–N(7) sequence may be described as *f*(en,en) and in series *f*(en,tn), *m*(tn,en), *f*(en,en), *f*(en,tn), *m*(tn,en). An identical pattern is found for both cations with the sequence commencing at N(21) in the second ion. Similar meridional isomers were obtained for the Ni([20]-aneN$_6$)$^{2+}$ and Co([20]-aneN$_6$)$^{3+}$ complexes with the six-membered chelate rings cis to one another.[14,29]

Spectroscopic Studies. Details of the UV–visible spectra for the various complexes are presented in Table VI. The spectra of the chromium complexes obtained are similar to those of known octahedral MN$_6$ systems. The spectrum of the Cr([18]-aneN$_6$)$^{3+}$ complex ion exhibits two bands (ϵ, L mol^{-1} cm^{-1}) at 466 nm (227) and 361 nm (103) while the 20-membered-ring analogue has features at 456 nm (104) and 350 nm (85), respectively. The lower energy band has been assigned to the $^4T_{2g} \leftarrow {}^4A_{2g}$ transition and that at higher energy to the $^4T_{1g} \leftarrow {}^4A_{2g}$ transition. The 10*Dq* value for the Cr complex of [20]-aneN$_6$ (21 930 cm^{-1}) is greater than that for the [18]-aneN$_6$ complex (21 460 cm^{-1}) and is attributed to the strain-free 20-membered ring as opposed to the strained 18-membered macrocycle in the Cr complex. However, both field strengths are lower than that for the Cr(**1**)$_2^{3+}$ ion (22 780 cm^{-1}).[2] The occurrence of λ_{max} at 670 nm for [Cu([20]-aneN$_6$)](ClO$_4$)$_2$ is consistent with a distorted CuN$_6$ or a CuN$_5$ core. The energy of the absorption band for the Cu(II) complex of **3** (14 881 cm^{-1}) is greater than that for the complex

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of **2** (14 300 cm^{-1}), again indicating greater stability of the relatively strain-free 20-membered ring. The electron spin resonance spectrum of the Cu(II) complex based on **3**, in CH_3NO_2 solutions, shows three features: $g_{zz} = 2.437$; $g_{xx} = 1.996$; $g_{yy} = 2.066$. The g_{zz} feature is split into four lines by the copper nuclear hyperfine interaction ($I = {}^3/_2$). There is also a suggestion of superhyperfine interaction with the nitrogen nucleus ($I = 1$) on the high field side of the spectrum.

Electrochemistry. The redox behavior of the Cr and Cu complexes was studied by cyclic voltammetry. Although the peak current ratios (i_a/i_c) were close to unity, some variation in ΔE with the scan rate for the Cr(III) complexes was observed, suggestive of quasi-reversibility. The ratio of the anodic and the cathodic currents for the Cr complexes were obtained by using a semiempirical procedure.[30] Formal redox potentials for the present and related complexes are summarized in Table VI. Comparison of the redox potential of $[Cr(\mathbf{1})_2]^{3+/2+}$ with those of the corresponding complexes of **2** and **3** indicates a stability order of $Cr(\mathbf{1})_2^{3+} > Cr(\mathbf{3})_2^{3+} > Cr(\mathbf{2})_2^{3+}$. In all cases the Cr(II) complex ions may be viewed as strong reductants. A similar stability order was obtained from absorption spectroscopy.

All of the data collected for these complexes to date are consistent with a release in strain energy as a result of the incorporation of one or more six-membered chelate rings into the macrocycle. Thus in the complex of **2**, the metal atom is subjected to a constrained octahedral environment. Kinetic observations indicate that the strained $Ni([18]\text{-ane}N_6)^{2+}$ complex is more rapidly hydrolyzed than $Ni([20]\text{-ane}N_6)^{2+}$.[11]

Cyclic voltammograms of the $[Cu(\mathbf{3})]^{2+/+}$ complex in CH_3CN showed a quasi-reversible wave at $E_{1/2} = -1.08$ V vs Fc^+/Fc (Fc = ferrocene). The flexibility of the macrocyclic ring allows for the formation of the $Cu(\mathbf{3})^+$ ion, although the resulting complex is of limited kinetic stability. The corresponding redox wave for $[Cu([9]\text{-ane}N_3)_2]^{2+/+}$ is irreversible.[31]

The redox potential, $E_{1/2}$, may be related to the ligand field splitting, $10Dq$.[32] Miyoshi et al.[33] have obtained a linear relationship between the absorption maxima (λ_{max}) and the redox potentials ($E_{1/2}$ values) for the Cu(II) complexes of macrocyclic polyamines. The data for both $[Cu(L)]^{2+/+}$ couples fit this correlation well. The $E_{1/2}$ values are most negative for square planar Cu(II) complexes with a large in-plane ligand field strength and increase to more positive values in distorted octahedral complexes. Very recently, a similar correlation has been observed[34] for Cr(III)–cyclam and –tetramethylcyclam derivatives of various charges. After allowance has been made for $E°$ values in differing conditions of ionic strength, the present data fall in a cluster of points for $Cr(N_6)^{3+}$ ions, confirming that ligand field stabilization effects are operative. It has been observed that stereochemical factors may be important in determining the photophysical behavior of Cr(III) complexes.[35,36] Ligand-promoted trigonal distortions may facilitate the nonradiative relaxation of the (^2E) Cr(III) state. Endicott et al.[35] found that the ambient lifetime of this state is dependent upon the strain within the Cr(III) complexes. The systems described herein may provide further evidence for effects of this kind.

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Supplementary Material Available: Table S1, containing experimental crystallographic data for the Cr(III) complexes of $[18]\text{-ane}N_6$ and $[20]\text{-ane}N_6$, and Tables S2–S8, containing bond lengths and angles, anisotropic temperature parameters, and intermolecular distances for both the complexes (9 pages). Ordering information is given on any current masthead page.

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