Cobalt(II), Nickel(II), Copper(II), and Zinc(II) Complexes with [3^5]Adamanzane, 1,5,9,13-Tetraazabicyclo[7.7.3]nonadecane, and [$(2.3)^2.2^1$]Adamanzane, 1,5,9,12-Tetraazabicyclo[7.5.2]hexadecane

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Isolation of the free bicyclic tetraamine, [3^5]adamanzane·H_2O (1,5,9,13-tetraazabicyclo[7.7.3]nonadecane·H_2O), is reported along with the synthesis and characterization of a copper(II) complex of the smaller macrocycle [$(2.3)^2.2^1$]-adamanzane (1,5,9,12-tetraazabicyclo[7.5.2]hexadecane) and of three cobalt(II), four nickel(II), one copper(II), and two zinc(II) complexes with [3^5]adamanzane. For nine of these compounds (**2**−**8**, **10b**, and **12**) the single-crystal X-ray structures were determined. The coordination geometry around the metal ion is square pyramidal in [Cu([$(2.3)^2.2^1$]adz)Br]ClO_4 (**2**) and trigonal bipyramidal in the isostructural structures [Cu([3^5]adz)Br]Br (**3**), [Ni([3^5]adz)Cl]Cl (**5**), [Ni([3^5]adz)Br]Br (**6**), and [Co([3^5]adz)Cl]Cl (**8**). In [Ni([3^5]adz)(NO_3)]NO_3 (**4**) and [Ni([3^5]adz)(ClO_4)]ClO_4 (**7**) the coordination geometry around nickel(II) is a distorted octahedron with the inorganic ligands at *cis* positions. The coordination polyhedron around the metal ion in [Co([3^5]adz)][$ZnCl_4$] (**10b**) and [Zn([3^5]adz)][$ZnCl_4$] (**12**) is a slightly distorted tetrahedron. Anation equilibrium constants were determined spectrophotometrically for complexes **2**−**6** at 25 and 40 °C and fall in the region 2−10 M^{-1} for the halide complexes and 30−65 M^{-1} for the nickel(II) nitrate complex (**4**). Rate constants for the dissociation of the macrocyclic ligand from the metal ions in 5 M HCl were determined for complexes **2**, **3**, **5**, **8**, **10**, and **12**. The reaction rates vary from half-lives at 40 °C of 14 min for the dissociation of the Zn([3^5]adz)$^{2+}$ complex (**12**) to 14−15 months for the Ni([3^5]adz)Cl^+ ion (**5**).

Introduction

Metal ion coordination compounds of macrocyclic polyamines are of current interest because of their applications in medicine and as catalysts and because of their importance as model systems within bioinorganic chemistry.[1−9] Recently, syntheses and studies of a new class of macrobi- and macrotricyclic ligands, adamanzanes, have been reported.[10−35] The so-called bowl and cage adamanzanes are cyclic tetraamines strapped by one or two alkylene chains, connecting two nonadjacent nitrogen atoms as illustrated for bowl adamanzanes in Figure 1. The smallest member is the classical compound urotropin or hexamethylenetetraamine. Large urotropin analogues with hexamethylene or octamethylene bridges, [6^6]adamanzane and [8^6]-adamanzane, were synthesized and studied by Schmidtchen,[10]

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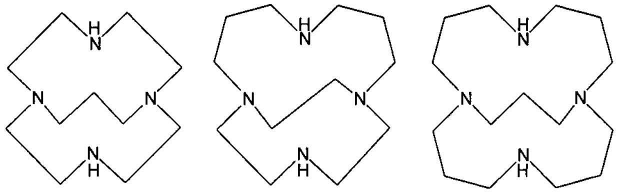

$[2^4.3^1]$adz $[(2.3)^2.2^1]$adz $[3^5]$adz

Figure 1. Bowl adamanzanes discussed in the present work.

and related compounds were reported by Takemura et al.[36] and Lehn and co-workers.[37]

Previously we have presented the syntheses and X-ray crystal structures of the inside protonated forms of the small tricyclic tetraamines $[2^4.3^2]$adamanzane,[17] $[(2.3)^3]$adamanzane,[28] and $[3^6]$-adamanzane,[18,23] for which all of the nitrogen lone pairs point into the cages. Along with the recent report by Miyahara et al.[27] concerning the synthesis of the highly symmetrical $[2^6]$-adamanzane, these are the first examples of adamanzanes containing only small chains ($n = 2$ or 3). The small cage adamanzanes act as proton sponges and have been the subject of recent ab initio studies involving calculations of properties such as basicity and strain energy.[25,26]

The syntheses of related bicyclic tetraamines have also been reported.[10−16,19,22,27,28,32,35] These bowl-shaped ligands may adopt conformations having all four nitrogen lone pairs pointing into the cavity, and despite this apparently relatively fixed spatial arrangement, tetrahedral, trigonal bipyramidal, or square pyramidal as well as octahedral coordination geometries may be obtained. Weisman et al.[11,19] and Busch and co-workers[24,31−34] have described coordination complexes between N-substituted adamanzanes and metal ions such as Li(I), Fe(II), Mn(II), Cu(I/II), and Pd(II). Furthermore Weisman and co-workers have reported copper(II) and zinc(II) complexes of $[2^2.3^2.2^1]$adamanzane,[19,30,35] and recently we published syntheses, crystal structures, and thermodynamical and kinetic studies of pentacoordinated copper(II) and hexacoordinated nickel(II) complexes of the bowl amine $[2^4.3^1]$adamanzane.[20,21,29] The present paper reports the syntheses and X-ray crystal structures of complexes of cobalt(II), nickel(II), copper(II), and zinc(II) with two different bowl-shaped adamanzane ligands. Thermodynamical and kinetic investigations are reported as well. Abbreviations used for the macrocycles are summarized in the Appendix.

Experimental Section

Materials. The halide salts of the protonated macrocyclic ligands $(H_3[(2.3)^2.2^1]adz)BrCl_2{\cdot}H_2O$ and $(H_4[3^5]adz)Br_4$ were prepared as previously described.[28,22] The remaining starting materials were commercially available and of reagent or analytical grade. Doubly deionized water was used for all spectral measurements. Solvents were used as purchased, with no further purification or drying. Deuterated solvents were purchased from Sigma-Aldrich.

Physical Measurements. Elemental analyses (C, H, N) were performed at the Microanalytical Laboratory, H. C. Ørsted Institute, Copenhagen. Bromide and chloride analyses were performed potentiometrically using standard procedures.

FAB mass spectra (positive mode) were recorded on a JEOL AZ505W mass spectrometer using glycerol or 3-nitrobenzyl alcohol (*m*-NBA) as the matrix.

A Cary 3 spectrophotometer was used for spectral measurements in the region 300−850 nm and a Zeiss DMR 21 spectrophotometer for the region 800−1200 nm.

^1H and ^{13}C NMR spectra were measured on a Bruker Avance 400 NMR spectrometer. In D_2O ^1H chemical shift values (δ) are reported in ppm and are referenced to internal dioxane (δ(dioxane) = 3.75 ppm), as are the ^{13}C chemical shift values (δ(dioxane) = 67.40 ppm). For $CDCl_3$ solutions chemical shift values (δ) are referenced to internal TMS (δ(TMS) = 0 ppm). ^{13}C DEPT NMR spectra were used to identify CH_2 carbon atoms, and HMBC spectra were used for the assignment of NH protons.

Calculations. Calculations involving the kinetic data were performed as previously described[38] except for one instant where linear regression was performed using the PC program Origin.[39] Nonlinear least-squares calculations for the determination of the thermodynamic constants were performed using the program PROC NLIN (DUD method) from the SAS Institute INC, Cary.[40]

CAUTION! Mechanical handling or heating of nitrates and perchlorates represents a potential hazard. In our hands, however, explosions with the present compounds have never occurred.

Preparations. $[3^5]adz{\cdot}H_2O$ (1). $(H_4[3^5]adz)Br_4$ (7.04 g, 11.9 mmol) was dissolved in warm water (35 mL). Following filtration, NaOH (35 mL, 40%) was added, leading to the formation of a pale precipitate. The solid was extracted into $CHCl_3$ (4 × 35 mL), and the combined extracts were dried by stirring overnight with Na_2SO_4. Filtration followed by rotatory evaporation of the filtrate at 40 °C and then at 80 °C yielded a slightly brownish waxy substance. The waxy solid was dissolved at 60 °C in the minimum volume of acetontrile (∼25 mL), and the warm solution was filtered to remove a small amount of a dark brown residue and then cooled to −18 °C, provoking massive precipitation of white crystals. These were filtered off and dried in the air. Yield: 2.25 g (66%). Anal. Calcd for $C_{15}H_{34}N_4O$: C, 62.89; H, 11.96; N, 19.56. Found: C, 63.3; H, 12.2; N, 19.7. ^{13}C NMR (100 MHz, $CDCl_3$), δ in ppm (assignment): 22.90, 25.23 (C−*C*H_2−C), 48.06, 53.63, 53.67 (*C*H_2−N). ^1H NMR (400 MHz, $CDCl_3$), δ in ppm (multiplicity, integration, assignment): 1.80 (m, 10.0 H, C−C*H*$_2$−C), 2.25 (s, broad, 2.8 H, N*H*), 2.50 (m, 16.5 H, C*H*$_2$−N), 2.80 (m, 4.0 H, C*H*$_2$−N), 3.89 (s, broad, 1.5 H, O*H*). 2D NMR (HMBC): cross peak between 2.25 ppm (^1H) and 53.6 ppm (^{13}C).

$[Cu([(2.3)^2.2^1]adz)Br]ClO_4{\cdot}H_2O$ (2). Crude $(H_3[(2.3)^2.2^1]adz)BrCl_2{\cdot}H_2O$ (225 mg, 0.57 mmol) was dissolved in 2 M NaOH (0.57 mL, 1.14 mmol), and 0.5 M $CuSO_4$ (2.75 mL, 1.37 mmol) and water (9 mL) were added. The blue solution was refluxed for 15 min, causing a change of color to a deeper blue. The pH of the solution was adjusted to neutral with 2 M NaOH, after which the reaction mixture was refluxed for another 10 min. The hot solution was filtered to remove insoluble residues stemming from the ligand. To the filtrate was added a mixture of saturated NaBr (5 mL) and saturated $NaClO_4$ (5 mL), and

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the resulting solution was cooled in ice. This gave a blue precipitate, and after cooling for a total of 10 min the crystals were filtered off, washed once with ice-cold water (1.5 mL) and twice with 1.5 mL portions of 96% ethanol, and dried in the air. Yield: 165 mg (60%). Anal. Calcd for $C_{12}H_{28}N_4BrClO_5Cu$: C, 29.58; H, 5.79; N, 11.50; Br, 16.40. Found: C, 29.12; H, 5.84; N, 11.36; Br, 16.20. UV−vis−near-IR [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: in 4 M NaBr, 980 (124), 592 (292); in 1 M perchloric acid containing 3 equiv of Hg^{2+}, 992 (69), 599 (74.8).

Crystals suitable for X-ray diffraction studies were grown by slow cooling of a hot (90−100 °C) solution of [Cu([$(2.3)^2.2^1$]adz)Br]ClO_4·H_2O (**2**) (86 mg) in water (3 mL). The crystals were washed with 96% ethanol and dried in the air.

[Cu([3^5]adz)Br]Br (3). The salt (H_4[3^5]adz)Br_4 (1.00 g, 1.69 mmol) was dissolved in 0.5 M $CuSO_4$ (4.30 mL, 2.15 mmol), and 1.9 M NH_3 (7 mL, 13.3 mmol) was added. The blue solution was refluxed for 10 min. After cooling in ice 4 M HBr (5.5 mL, 22 mmol) was added. This immediately gave a turquoise precipitate, and after cooling for another 5 min the crystals were filtered off, washed once with ice-cold water (1 mL) and three times with 2 mL portions of 96% ethanol, and dried in the air. Yield: 0.70 g (84%). Anal. Calcd for $C_{15}H_{32}N_4Br_2Cu$: C, 36.63; H, 6.56; N, 11.39; Br, 32.49. Found: C, 36.77; H, 6.12; N, 11.35; Br, 32.54. UV−vis−near-IR [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: in 4 M NaBr, 922 (270), 677 (472); in 0.003 M perchloric acid containing 3 equiv of Hg^{2+}, 891 (359), 674 (180, sh), 644 (183).

Crystals suitable for X-ray diffraction studies were grown by slow cooling to 25 °C of a hot (90−100 °C) solution of [Cu([3^5]adz)Br]Br (**3**) (76 mg) in water (2.8 mL). The crystals were washed with 96% ethanol and dried in the air.

[Ni([3^5]adz)(η^2-NO_3)]NO_3 (4). $Ni(NO_3)_2$·$6H_2O$ (815 mg, 2.8 mmol) was dissolved in absolute ethanol (5 mL). To the green solution was added a solution of [3^5]adz·H_2O (**1**) (285 mg, 1.0 mmol) in absolute ethanol (5 mL), instantly leading to the formation of a white precipitate. Stirring at reflux for 3 h gave complete conversion of this precipitate to a violet solid, which was filtered off and washed three times with absolute ethanol and twice with diethyl ether. Yield after drying in the air: 402 mg (89%). Anal. Calcd for $C_{15}H_{32}N_6O_6Ni$: C, 39.93; H, 7.15; N, 18.63. Found: C, 39.7; H, 7.13; N, 18.4. UV−vis [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: in methanol, 560 (33.9), 357 (68.6); in 0.3 M $NaNO_3$/0.7 M CF_3SO_3Na, 562 (36.0), 358 (82.0). FAB-MS: multiplets centered around *m*/*z* 325 [$NiC_{15}H_{31}N_4$]$^+$, 388 [$NiC_{15}H_{32}N_5O_3$]$^+$.

Crystals suitable for X-ray diffraction studies were grown at room temperature by slow dissolution of $NaNO_3$ (crystalline) in an aqueous solution of [Ni([3^5]adz)(NO_3)]NO_3 (**4**).

[Ni([3^5]adz)Cl]Cl (5). [3^5]adz·H_2O (**1**) (59 mg, 0.21 mmol) was dissolved in methoxyethanol (1 mL), and the solution was heated to 70 °C. To this was added a warm solution of $NiCl_2$·$6H_2O$ (52 mg, 0.22 mmol) in methoxyethanol (1 mL), instantly causing the green color of this solution to intensify. Within 5 min green crystals started to form. Heating at 70 °C was continued for 2 h, after which the mixture was allowed to cool to room temperature and then further cooled to 5 °C. Filtration followed by thorough washing with diethyl ether gave green crystals of a quality suitable for X-ray diffraction studies. Yield after drying in the air: 78 mg (95%). Anal. Calcd for $C_{15}H_{32}N_4Cl_2Ni$: C, 45.26; H, 8.10; N, 14.08; Cl, 17.81. Found: C, 46.0; H, 8.09; N, 14.0; Cl, 17.5. UV−vis [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: in methanol, 624 (62.5), 387 (186); in 5 M HCl, 615 (66.5), 382 (201). FAB-MS: multiplets centered around *m*/*z* 325 [$NiC_{15}H_{31}N_4$]$^+$, 361 [$NiC_{15}H_{32}N_4Cl$]$^+$.

[Ni([3^5]adz)Br]Br (6). [3^5]adz·H_2O (**1**) (57 mg, 0.20 mmol) was dissolved in methoxyethanol (1 mL), and the solution was heated to 70 °C. To this was added a warm solution of $NiBr_2$·$3H_2O$ (64 mg, 0.23 mmol) in methoxyethanol (1 mL), instantly causing the green color of this solution to intensify. Within 2 min a green precipitate started to form. The mixture was heated for a total of 15 min and then allowed to cool to room temperature followed by further cooling to 5 °C. The green microcrystalline solid was filtered off and washed thoroughly with diethyl ether. Yield after drying in the air: 87 mg (89%). Anal. Calcd for $C_{15}H_{32}N_4Br_2Ni$: C, 37.00; H, 6.62; N, 11.51. Found: C, 37.2; H, 6.50; N, 11.8. UV−vis [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: in methanol, 629 (75.6), 391 (254); in 5 M HBr, 620 (90.8), 386 (308). FAB-MS: multiplets centered around *m*/*z* 325 [$NiC_{15}H_{31}N_4$]$^+$, 407 [$NiC_{15}H_{32}N_4Br$]$^+$.

Crystals suitable for X-ray diffraction studies were grown at room temperature by gradual addition of 48% HBr (0.5 mL) to a blue-green saturated aqueous solution of [Ni([3^5]adz)Br]Br (**6**) (9 mg in 2.5 mL).

[Ni([3^5]adz)(η^2-ClO_4)]ClO_4 (7). [Ni([3^5]adz)Cl]Cl (**5**) (100 mg, 0.25 mmol) was dissolved in 0.01 M trifluoromethanesulfonic acid (3 mL). A solution of 0.5 M $Hg(ClO_4)_2$ in 2 M $HClO_4$ (1.5 mL), was added, causing immediate precipitation of a turquoise solid. This was filtered off and washed twice with trifluoromethanesulfonic acid (0.01 M), once with *tert*-butyl alcohol, and then twice with diethyl ether. Drying in the air provoked a color change to blue. Yield: 80 mg (61%). Anal. Calcd for $C_{15}H_{32}N_4Cl_2O_8Ni$: C, 34.25; H, 6.13; N, 10.65. Found: C, 34.2; H, 5.93; N, 10.6. UV−vis [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: in acetone, 580 (40.0), 365 (100); in 1 M CF_3SO_3Na, 600 (35.5), 374 (86.3). FAB-MS: multiplets centered around *m*/*z* 325 [$NiC_{15}H_{31}N_4$]$^+$ and 425 [$NiC_{15}H_{32}N_4ClO_4$]$^+$.

Crystals suitable for X-ray diffraction studies were grown at −18 °C by the diffusion of ether vapor into a solution of [Ni([3^5]adz)(ClO_4)]-ClO_4 (**7**) in acetone (30 mg in 6 mL).

[Co([3^5]adz)Cl]Cl (8). [3^5]adz·H_2O (**1**) (57 mg, 0.20 mmol) was dissolved in methoxyethanol (4 mL) and heated to 75 °C. Over a period of 35 min a solution of $CoCl_2$·$6H_2O$ (54 mg, 0.23 mmol) in methoxyethanol (2 mL) was added in portions of 35 μL. Between the additions the flask was shaken manually to provoke dissipation of the local blue coloring initially caused by each addition. Progressively through this process the color of the reaction mixture changed from red-violet to a more intense, darker violet. Approximately halfway through the addition violet crystals started to form. Gentle magnetic stirring was applied after addition of all of the cobalt solution, and heating at 75 °C was continued for a total of 2 h, after which the mixture was allowed to cool slowly to room temperature. Separation of the solid from the green mother liquor by filtration followed by thorough washing with absolute ethanol gave violet crystals. Yield after drying in the air: 66 mg (83%). Anal. Calcd for $C_{15}H_{32}N_4Cl_2Co$: C, 45.24; H, 8.10; N, 14.07. Found: C, 45.3; H, 8.17; N, 13.9. UV−vis [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: in methanol, 673 (17.8), 633 (18.4) (poorly separated), 505 (50.7); in 0.01 M trifluoromethanesulfonic acid at 1.0 °C, 763 (11.4, sh), 613 (17.9), 485 (29.0); in 12 M HCl at 1.0 °C, 766 (56.6), 573 (301). FAB-MS: multiplets centered around *m*/*z* 326 [$CoC_{15}H_{31}N_4$]$^+$ and 362 [$CoC_{15}H_{32}N_4Cl$]$^+$.

Crystals suitable for X-ray diffraction studies were synthesized in the same manner except for the lack of magnetic stirring and the employment of a nitrogen atmosphere during all the procedures up until the filtration.

[Co([3^5]adz)(H_2O)$_2$](ClO_4)$_2$·H_2O (9). [Co([3^5]adz)Cl]Cl (**8**) (100 mg, 0.25 mmol) was dissolved in ice-cold 0.01 M trifluoromethanesulfonic acid (3 mL). An ice-cold solution of 0.5 M $Hg(ClO_4)_2$ in 2 M $HClO_4$ (1.5 mL) was added causing immediate precipitation of a pale green solid. The solid was isolated by filtration and washed twice with ice-cold 0.01 M trifluoromethanesulfonic acid, once with *tert*-butyl alcohol, and three times with diethyl ether. Yield after drying in the air: 111 mg (76%). Anal. Calcd for $C_{15}H_{38}N_4O_{11}Cl_2Co$: C, 31.05; H, 6.60; N, 9.65. Found: C, 31.0; H, 6.61; N, 9.61. UV−vis in 0.01 M trifluoromethanesulfonic acid at 1.0 °C [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 760 (12, sh), 606 (19), 484 (28). FAB-MS: multiplets centered around *m*/*z* 326 [$CoC_{15}H_{31}N_4$]$^+$, 362 [$CoC_{15}H_{35}N_4O_2$]$^+$, and 426 [$CoC_{15}H_{32}N_4ClO_4$]$^+$.

[Co([3^5]adz)](PF_6)$_2$ (10a). [Co([3^5]adz)Cl]Cl (**8**) (81 mg, 0.20 mmol) was dissolved in water (2 mL) at room temperature over a period of 2−3 min. After an additional 4 min a freshly made, saturated NH_4PF_6 solution (ca. 0.8 mL) was added dropwise. This addition was performed over a period of 2 min. The resulting pink precipitate was filtered off and washed twice with ice-cold water. Redissolution of the crude product on the filter in water (25 mL) was followed by filtration, and solid NH_4PF_6 (grams) was then added until no further precipitation seemed to be occurring. The resulting pink solid was filtered off and washed four times with ice-cold water, twice with absolute ethanol (−18 °C), and then thoroughly with diethyl ether. All manipulations in the reprecipitation process were performed as quickly as possible. Yield after drying in the air: 62 mg (49%). Anal. Calcd for $C_{15}H_{32}N_4P_2F_{12}Co$: C, 29.19; H, 5.22; N, 9.08. Found: C, 29.0; H, 5.22; N, 9.01. UV−vis in 0.01 M trifluoromethanesulfonic acid at 2.3 °C

Table 1. Crystallographic Data for Compounds [Cu([(2.3)^2.2^1]adz)Br]ClO$_4$ (**2**), [Cu([3^5]adz)Br]Br (**3**), [Ni([3^5]adz)Cl]Cl (**5**), [Ni([3^5]adz)Br]Br (**6**), and [Co([3^5]adz)Cl]Cl (**8**)

	2	**3**	**5**	**6**	**8**
formula	$C_{12}H_{26}BrClCuN_4O_4$	$C_{15}H_{32}Br_2CuN_4$	$C_{15}H_{32}Cl_2N_4Ni$	$C_{15}H_{32}Br_2N_4Ni$	$C_{15}H_{32}Cl_2CoN_4$
fw	469.27	491.81	398.06	486.98	398.28
temp, T/K	120(2)	120(2)	120(2)	120(2)	120(2)
cryst syst	monoclinic	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	$P2_1/n$	*Ibca*	*Ibca*	*Ibca*	*Ibca*
a/Å	8.498(2)	13.251(3)	12.693(3)	13.130(3)	12.738(3)
b/Å)	22.952(5)	13.951(3)	13.619(3)	13.859(3)	13.675(3)
c/Å	8.948(2)	20.374(4)	20.725(4)	20.645(4)	20.674(4)
β/deg	95.92(3)				
V/Å^3	1735.9(6)	3766.4(13)	3582.5(12)	3756.9(13)	3601.3(12)
Z	4	8	8	8	8
D_x/g cm^{-3}	1.796	1.735	1.476	1.722	1.469
μ(Mo Kα)/mm^{-1}	3.738	5.406	1.384	5.290	1.252
cryst color	blue	blue	blue-green	green	blue-violet
cryst size/mm	0.23 × 0.16 × 0.15	0.13 × 0.06 × 0.06	0.16 × 0.08 × 0.05	0.29 × 0.18 × 0.15	0.24 × 0.15 × 0.11
θ range/deg	1.77−29.56	2.91−29.50	1.97−34.06	1.97−33.96	1.97−29.55
meas reflns	11994	6220	26217	28100	11499
unique reflns	4448	2382	3472	3573	2355
reflns with [$I > 2\sigma(I)$]	3731	1568	2297	2919	1978
R(int)	0.0360	0.0478	0.0815	0.0287	0.0285
transm factors	1.0000−0.8565	1.0000−0.8915	1.0000−0.8605	1.0000−0.8235	1.0000−0.8080
refined params	221	102	102	102	103
R1^a (obs.data)	0.0651	0.0435	0.0630	0.0297	0.0348
wR2^b (all data)	0.1343	0.0893	0.1100	0.0738	0.0962
GOF	1.183	1.127	1.131	1.099	1.077
max, min $\Delta\rho$/e Å^{-3}	−0.962 and 2.483 (near Br)	−0.667 and 0.573	−0.582 and 0.668	−1.078 and 0.505	−0.527 and 0.737

^{a} $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. ^{b} $wR2 = [\sum w|F_o{}^2 - F_c{}^2|^2/\sum wF_o{}^4]^{1/2}$.

[λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 811 (71), 543 (314). FAB-MS: multiplets centered around m/z 326 [$CoC_{15}H_{31}N_4$]$^+$, 346 [$CoC_{15}H_{32}N_4F$]$^+$, and 472 [$CoC_{15}H_{32}N_4PF_6$]$^+$.

[Co([3^5]adz)][ZnCl$_4$] (10b). [Co([3^5]adz)Cl]Cl (**8**) (83 mg, 0.21 mmol) was dissolved in water (2 mL) at room temperature over a period of 2−3 min. After an additional 4 min 4 M $Li_2[ZnCl_4]$ (1 mL) was added. This addition was performed over a period of 2 min. Isolation by filtration of the resulting precipitate followed by thorough washing with absolute ethanol and then with diethyl ether gave an intensely pink microcrystalline solid. Yield after drying in the air: 93 mg (83%). Anal. Calcd for $C_{15}H_{32}N_4ZnCl_4Co$: C, 33.70; H, 6.03; N, 10.48. Found: C, 33.3; H, 5.92; N, 10.3. UV−vis in 0.01 M trifluoromethanesulfonic acid at 2.3 °C [λ_{max}, nm (ϵ, M^{-1} cm^{-1})]: 811 (61), 543 (273). FAB-MS: multiplets centered around m/z 326 [$CoC_{15}H_{31}N_4$]$^+$ and 362 [$CoC_{15}H_{32}N_4Cl$]$^+$.

Crystals of a quality suitable for X-ray diffraction studies were grown by slow evaporation at room temperature of an aqueous solution of this somewhat impure product.

Zn([3^5]adz)Br$_2$ (11). To a solution of (H_4[3^5]adz)Br_4 (1.00 g, 1.69 mmol) and NaOH (0.28 g, 7.0 mmol) dissolved in methanol (8 mL) at 60 °C was added a solution of $ZnBr_2$ (0.39 g, 1.73 mmol) in methanol (1 mL). The mixture was refluxed for 30 min and then cooled in ice. After 30 min colorless crystals were filtered off, washed twice with 2 mL-portions of 96% methanol, and dried in the air. Yield: 0.78 g (93%). Anal. Calcd for $C_{15}H_{32}N_4Br_2Zn$: C, 36.50; H, 6.53; N, 11.35; Br, 32.37. Found: C, 36.24; H, 6.33; N, 11.00; Br, 31.62.

[Zn([3^5]adz)][ZnCl$_4$]·H$_2$O (12). Zn([3^5]adz)Br_2 (**11**) (0.78 g, 1.58 mmol) was dissolved in water (31 mL) at 80 °C. The filtered solution was cooled in ice, and 4 M $Li_2[ZnCl_4]$ (2.5 mL, 10 mmol) was added. This gave a colorless precipitate, and after further cooling for 30 min the crystals were filtered off, washed twice with 2 mL portions of 96% ethanol, and dried in the air. Yield: 0.78 g (83%). Anal. Calcd for $C_{15}H_{32}N_4Cl_4Zn_2 \cdot H_2O$: C, 32.23; H, 6.13; N, 10.02; Cl, 25.37. Found: C, 32.29; H, 5.50; N, 9.94; Cl, 25.42. ^{13}C NMR (100 MHz, D_2O), δ in ppm (assignment): 21.6, 23.7 (C−*C*H$_2$−C) and 51.4, 53.8, 58.9 (*C*H$_2$−N). ^{1}H NMR (400 MHz, D_2O), δ in ppm (multiplicity, integration, assignment): 1.89 (m, 4 H, C−C*H*$_2$−C), 2.15 (m, 4 H, C−C*H*$_2$−C), 2.26 (q, 2 H, C−C*H*$_2$−C (bridge)), 2.98 (m, 8 H, N−C*H*$_2$ (tert) and 4 H, N−C*H*$_2$ (sec)), 3.08 (t, 4 H, N−C*H*$_2$ (bridge)), 3.28 (m, 4 H, N−C*H*$_2$ (sec)).

Crystals suitable for X-ray diffraction studies were obtained by the same method but using more dilute solutions and slow cooling. In this case an anhydrous salt was obtained.

X-ray Crystal Structure Determination. Crystal data for the compounds are listed in Table 1 and Table 2. The crystal of the compounds was cooled to 120 K using a Cryostream nitrogen gas cooler system. The data were collected on a Siemens SMART Platform diffractometer with a CCD area sensitive detector. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 of all data. In **2** the oxygen atoms are disordered with the population factors of 0.760(5) and 0.240(5), respectively. The structures of **3**, **5**, **6** and **8** are isostructural and rather disordered. In the [3^5]adamanzane ligand the site of each of the atoms C(2), C(3), C(4), C(5), and C(7) split into two equally populated positions. The atoms X(1), X(2), M, and C(8) are positioned on 2-fold axes (X = Cl or Br; M = Cu, Ni, or Co). The non-hydrogen atoms were refined anisotropically. In the [3^5]-adamanzane ligand of **4** the site of each of the atoms C(3), C(4), C(5), C(8), C(9), C(10), C(13), and C(15) splits into two equally populated positions. The hydrogen atoms in **2**, **3**, **5**, **6**, **8**, **4**, and **7** were at calculated positions using a riding model with C−H = 0.99 Å, N−H = 0.93 Å, and fixed thermal parameters [$U(H) = 1.2U$ for attached atom]. In **10b** and **12** the hydrogen atoms could all be located from electron-density difference maps and were refined isotropically. The Flack x-parameter is −0.010(12), 0.095(10), and 0.038(6) for **7**, **10b**, and **12**, respectively, indicating that this is the correct absolute structure.[41,42] Programs used for data collection, data reduction, and absorption were SMART, SAINT, and SADABS.[43,44] The program SHELXTL 95[45] was used to solve the structures and for molecular graphics. PLATON[46] was used for molecular geometry calculations.

Equilibrium Studies. The equilibrium constants were determined spectrophotometrically at two temperatures (25 and 40 °C), and

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Table 2. Crystallographic Data for Compounds [Ni([3^5]adz)(NO_3)]NO_3 (**4**), [Ni([3^5]adz)(ClO_4)]ClO_4 (**7**), [Co([3^5]adz)][$ZnCl_4$] (**10b**), and [Zn([3^5]adz)][$ZnCl_4$] (**12**)

	4	**7**	**10b**	**12**
formula	$C_{15}H_{32}N_6NiO_6$	$C_{15}H_{32}Cl_2N_4NiO_8$	$C_{15}H_{32}Cl_4CoN_4Zn$	$C_{15}H_{32}Cl_4N_4Zn_2$
fw	451.18	524.04	534.55	540.99
temp, T/K	120(2)	120(2)	120(2)	120(2)
cryst syst	orthorhombic	orthorhombic	orthorhombic	orthorhombic
space group	$Pcca$	$P2_12_12_1$	$Pna2_1$	$Pna2_1$
a/Å	27.468(6)	10.1453(4)	14.0833(2)	14.067(3)
b/Å)	10.663(2)	13.9663(6)	11.9845(2)	11.916(2)
c/Å	13.552(3)	14.5922(6)	12.6741(1)	12.600(3)
β/deg				
V/Å^3	3969.1(14)	2067.60(15)	2139.15(5)	2221.1(7)
Z	8	4	4	4
D_x/g cm^{-3}	1.510	1.683	1.660	1.701
μ(Mo Kα)/mm^{-1}	1.023	1.249	2.403	2.784
cryst color	blue	blue-violet	red-violet	colorless
cryst size/mm	0.20 × 0.13 × 0.13	0.25 × 0.18 × 0.15	0.35 × 0.25 × 0.08	0.28 × 0.21 × 0.09
θ range/deg	1.48−29.53	2.02−29.66	2.23−29.49	2.24−29.70
meas reflns	23916	14351	13884	13690
unique reflns	5164	5280	5160	5345
reflns with [$I > 2\sigma(I)$]	1974	4324	4838	4951
R(int)	0.1478	0.0444	0.0263	0.0232
transm factors	1.0000−0.8120	1.0000−0.8630	1.0000−0.5775	1.0000−0.8606
refined params	287	271	337	352
R1^a (obs data)	0.0977	0.0362	0.0305	0.0213
wR2^b (all data)	0.1671	0.0698	0.0818	0.0462
GOF	1.081	1.015	1.027	0.979
max, min $\Delta\rho$/e Å^{-3}	−0.377 and 0.416	−0.379 and 0.317	−0.505 and 1.140	−0.367 and 0.585

[a] $R1 = \sum||F_o| - |F_c||/\sum|F_o|$. [b] $wR2 = [\sum w|F_o^2 - F_c^2|^2/\sum wF_o^4]^{1/2}$.

nonlinear least-squares calculations were performed using the SAS program,[40] yielding equilibrium constants and thermodynamic parameters (Table 7).

Reference spectra were recorded for the copper complexes (**2**, **3**) in dilute perchloric acid containing 3 equiv of Hg^{2+} and in 4 M NaBr as well. The ionic strength for the equilibrium measurements was kept at 1.0 M, using $NaClO_4$ as the inert electrolyte for the measurements involving the Cu([$(2.3)^2.2^1$]adz)Br$^+$ complex (**2**) and $NaNO_3$ for the Cu([3^5]adz)Br$^+$ complex (**3**). The calculated spectra of CuLBr$^+$ (L = [$(2.3)^2.2^1$]adz/[3^5]adz) were identical to those of the dissolved bromide salts in 4 M NaBr, and the calculated spectra of the aqua complexes were identical to those of solutions of the bromide salts in excess Hg^{2+}.

The [Ni([3^5]adz)(ClO_4)]ClO_4 salt (**7**) was used for the measurements involving the nickel equilibria, adjusting the ionic strength to 1.0 M with CF_3SO_3Na.

For solubility reasons the perchlorate ions were removed in the nitrate experiment by running a solution of [Ni([3^5]adz)(ClO_4)]ClO_4 (**7**) through a Dowex 1-X8 anion exchange column on trifluoromethanesulfonate form. The blue eluate was diluted with water and 2.0 M CF_3SO_3Na to give a final trifluoromethanesulfonate concentration of 1.0 M; this solution was divided into suitable portions, which were stored in the freezer until needed for each measurement.

The spectrum of [Ni([3^5]adz)(ClO_4)]ClO_4 (**7**) in 1.0 M CF_3SO_3Na was assumed to equal that of the aqua complex and corresponded within the standard variations with the spectra calculated for this complex and with that of the solution from the anion exchange column.

Due to insufficient solubility of the [Ni([3^5]adz)X]X salts (X = NO_3, Cl, Br), spectra of these complexes could not be recorded in 4 M NaX solution for reference. However, comparison of the spectrum calculated for [Ni([3^5]adz)Cl]Cl (**5**) with that of the compound in 5 M HCl showed a variation of less than 5%, this being attributed to the difference in ionic activity. The spectrum calculated for [Ni([3^5]adz)(NO_3)]NO_3 (**4**) was equal within experimental error to that recorded at 25.0 °C in 0.300 M $NaNO_3$/0.700 M CF_3SO_3Na, in accordance with substantial conversion at this stage.

Direct determination of the anation equilibrium constant for the Ni([3^5]adz)Br$^+$ complex (**6**) was hindered by low solubility of the bromide salt of this species. However, due to what is surely a medium effect, the [Ni([3^5]adz)Br]Br salt is somewhat soluble in 5 M HBr. This spectrum was assumed to equal that of the Ni([3^5]adz)Br$^+$ complex (**6**) in aqueous solution and compared with those of [Ni([3^5]adz)Br]Br and [Ni([3^5]adz)(ClO_4)]ClO_4 in 1.0 M CF_3SO_3Na to yield an estimate for the equilibrium constant at 25 °C.

Kinetic Measurements. The rate constants were determined at two temperatures by ^1H NMR in 5 M DCl for the zinc complex (**12**) and spectrophotometrically in 5 M HCl for the rest. Linear least-squares calculations were performed for the zinc complex (**12**). For the rest, nonlinear least-squares calculations were performed as previously described,[38] yielding rate constants and activation parameters (Table 7).

For the copper(II) complex (**2**) of the smaller macrocycle, [$(2.3)^2.2^1$]-adamanzane, the calculations were performed from 450 to 750 nm, for the copper(II) and nickel(II) complexes of [3^5]adamanzane (**3**, **5**) from 400 to 800 nm, and for the cobalt(II) complexes (**8**, **10**) from 350 to 800 nm. The calculations for the zinc complex (**12**) were performed using the ^1H NMR integrals in the area around 1.89 ppm and from 2.1 to 2.5 ppm.

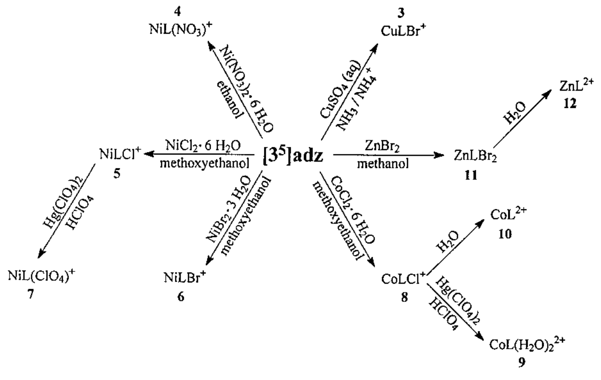
Generally, batch methods were employed except during the determination of the rate constants concerning the cobalt(II) complexes (**8**, **10**); here an external thermostat was used to keep the spectrophotometer sample block at constant temperature in between measurements. The experiments were continued until the elapse of at least 7 half-lives. For the zinc complex (**12**) the final NMR spectrum was compared with that of the free ligand (**1**) in 5 M DCl, and for the remainder the final UV−vis spectra were compared to those of an appropriate M^{2+} salt (M = Co, Ni, Cu) in 5 M HCl.

Results and Discussion

Synthesis, Characterization, and Reactivity. Twelve complexes of two different adamanzane bowl ligands were synthesized and characterized. In some cases halide salts of the ligands were used in the synthetic procedure, and in other cases employment of the free amine was necessary. An overview of the syntheses of the complexes (**3**−**12**) of the larger bowl, [3^5]-adamanzane, is presented in Scheme 1.

The synthesis of the bowl tetraamine, [3^5]adamanzane (1,5,9,13-tetraazabicyclo[7.7.3]nonadecane), was reported recently, and the ligand was isolated as the tetraprotonated bromide salt, (H_4[3^5]adz)Br_4.[22] In contrast to several other

Scheme 1. Overview of the Synthesis of Complexes of the Ligand [3^5]Adamanzane[a]



[a] L = [3^5]adz.

macrocyclic tetraamines[11,13,16,19,47] the free amine is not a proton sponge (pK_a(H[3^5]adz$^+$) = 12.09). This allows for the presence of the free amine in basic aqueous solutions. Isolation of a compound analyzing as [3^5]adz·H_2O (**1**) was afforded by the addition to the (H_4[3^5]adz)Br_4 salt of a strong NaOH solution followed by extraction with chloroform. Recrystallization in acetonitrile gave a crystalline off-white product, which is soluble in various organic solvents and somewhat soluble in water. This product was characterized by NMR, FAB-MS, and elemental analysis.

The two broad singlets observed at 2.25 and 3.89 ppm in the ^1H NMR spectrum were assigned with the aid of 2D NMR (HMBC) to the N*H* and O*H* protons, respectively. The water molecule must be partly hydrogen bonded to the amine in order to show up at the present position (3.89 ppm) in the $CDCl_3$ solution. This is equivalent to viewing the compound as an intermediate between the free amine with one crystal water, [3^5]adz·H_2O, and the hydroxide salt of the singly protonated amine, (H[3^5]adz)OH. The integrations point to the presence of more than two NH protons and less than two OH protons. This does not lead to an unambiguous interpretation; however, a structure resembling a proton complex could be proposed (Figure 2), with hydrogen bonds to some or all of the amine groups.

Two copper complexes (**2**, **3**) are described in this work differing in the size of the macrocyclic ligand. Both complexes are five-coordinated with bromide in the fifth position.

The blue copper(II) aqua complex of the ligand, [$(2.3)^2.2^1$]-adamanzane, was obtained by reaction between the monoprotonated bicyclic tetraamine H[$(2.3)^2.2^1$]adz$^+$ and copper(II) ions (in excess) in aqueous solution followed by addition of 1 equiv of base. Subsequent addition of bromide gave the bromo complex, which was isolated as a perchlorate salt, [Cu([$(2.3)^2.2^1$]-adz)Br]ClO_4·H_2O (**2**) (yield 60%).

The copper(II) complex with [3^5]adamanzane (**3**) was synthesized using the method described previously[20] for Cu([$2^4.3^1$]-adz)Br^+ by heating an excess of tetraamminecopper(II) ions with H_2[3^5]adz^{2+}/H[3^5]adz$^+$ in an ammonia/ammonium buffer solution resulting in the formation of a blue copper(II) complex with [3^5]adamanzane. From the acidified product solution turquoise crystals of [Cu([3^5]adz)Br]Br (**3**) were isolated in 84% yield.

The nitrate and halide nickel complexes (**4**−**6**) of the ligand [3^5]adamanzane were synthesized directly from the free amine ligand (**1**) and the appropriate hydrated nickel(II) salt. Maintaining an excess of the metal ion was crucial to the yields (89−95%), which were quite dependent on the choice of solvent as well. Ethanol was found to give the best result for the violet six-coordinated chelate nitrate complex (**4**) whereas the use of methoxyethanol optimized the syntheses of the green five-coordinated halide complexes (**5**, **6**). Employment of the latter solvent gave the added benefit of nicely crystalline products; in the case of the chloride complex (**5**) X-ray crystallographic measurements were performed directly on the bulk product.

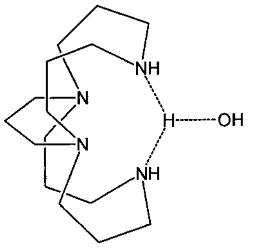


Figure 2. Proposed structure of [3^5]adz·H_2O (**1**). Weak interaction to the tertiary nitrogen atoms cannot be excluded.

The perchlorate nickel complex (**7**) of the [3^5]adamanzane ligand was synthesized in a 58% yield based on the ligand by dissolving the corresponding chloro complex (**5**) at room temperature in a solution containing $Hg(ClO_4)_2$ in dilute $HClO_4$. The initial turquoise color of the precipitate changed to blue upon drying, and microanalysis and the single-crystal X-ray structure reveal the compound to be anhydrous. It is a relatively rare example of a chelate coordination mode of the perchlorate ion in a transition metal complex.[48,49]

In aqueous solutions interconversion between the nitrate, chloro, and bromo complexes (**4**−**6**) is fast. The aqua species present in aqueous solutions of all the nickel complexes (**4**−**7**) displays visible decay according to the UV−vis spectra within days at neutral pH.

A cobalt(II) complex (**8**) of the large bowl adamanzane was synthesized as well (83% yield). The Co([3^5]adz)Cl^+ ion (**8**) is analogous to the five-coordinated complexes mentioned above (**3**, **5**, **6**), and the synthesis is similar to that of the nickel(II) halo complexes (**5**, **6**). With a little extra care crystals of a quality suitable for X-ray diffraction studies could be obtained directly from the bulk reaction.

A pale green compound (**9**) analyzing as Co([3^5]adz)$(ClO_4)_2$-$(H_2O)_3$ was also isolated. The color of the solid strongly resembles that of solutions of the compound in cold 0.01 M trifluoromethanesulfonic acid. Most likely, the complex ion is a diaqua species, and we have chosen to write it as such, i.e., [Co([3^5]adz)$(H_2O)_2$]$(ClO_4)_2$·H_2O (**9**). The solid product slowly deteriorates and should be stored in sealed vials in the freezer.

With time, aqueous solutions of the [Co([3^5]adz)Cl]Cl salt (**8**) and of the compound [Co([3^5]adz)$(H_2O)_2$]$(ClO_4)_2$·H_2O (**9**) display equilibration with the pink tetrahedral Co([3^5]adz)$^{2+}$ ion (**10**), which may be isolated by precipitation with various anions. The crystal structure was solved for this complex. Aqueous solutions of the Co([3^5]adz)$^{2+}$ cation (**10**) are unstable; thus timing is a crucial factor to the yields (41% based on the ligand for the pure hexafluorophosphate salt (**10a**)). The equilibration and decomposition rates vary nonlinearly with pH and the chloride ion concentration and are seemingly independent of the presence of air.

The pink color of the Co([3^5]adz)$^{2+}$ ion stems from the much higher ligand field strength of the amine macrocycle compared to that of the anionic ligands present in the more prevalent blue

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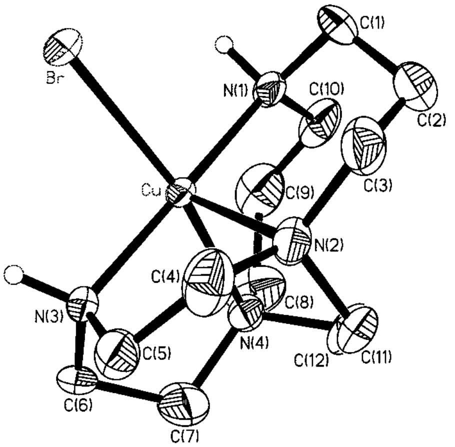

Figure 3. View of the cation in $[Cu([(2.3)^2.2^1]adz)Br]Br$ (**2**). In this and the following four figures the thermal ellipsoids are drawn at the 50% probability level. With exception of H(1) and H(3), bound to N(1) and N(3), respectively, the hydrogen atoms have been omitted for clarity.

Table 3. Bond Lengths (Å) and Bond Angles (deg) for the Coordination Sphere around the Metal Ion in $[Cu([(2.3)^2.2^1]adz)Br]ClO_4$ (**2**)

Br−Cu	2.4796(8)	Cu−N(4)	2.128(4)
Cu−N(3)	1.997(4)	Cu−N(2)	2.176(5)
Cu−N(1)	2.008(5)		
N(3)−Cu−N(1)	176.3(2)	N(4)−Cu−N(2)	83.9(2)
N(3)−Cu−N(4)	83.2(2)	N(3)−Cu−Br	91.49(13)
N(1)−Cu−N(4)	95.0(2)	N(1)−Cu−Br	89.66(13)
N(3)−Cu−N(2)	85.0(2)	N(4)−Cu−Br	167.64(13)
N(1)−Cu−N(2)	98.0(2)	N(2)−Cu−Br	106.86(13)

tetrahedral cobalt(II) complexes. The position of the visible absorption band (543 nm) is nearly identical to that of the reported tetrahedral $Co([16]aneN_4)^{2+}$ ion (540 nm).[50]

Analogous to the pink $Co[3^5]adz^{2+}$ complex (**10**) is the colorless tetrahedral $Zn([3^5]adz)^{2+}$ ion (**12**). This zinc(II) complex was prepared by heating a basic solution containing a mixture of [3^5]adamanzane (free amine) and $Zn(OH)_4{}^{2-}$ (in slight excess) in methanol. This gave colorless crystals analyzing as $Zn([3^5]adz)Br_2$ (**11**). The constitution of this compound was not established, but preliminary experiments indicate the presence of at least one coordinated bromide ligand. Dissolution of this salt in hot water followed by addition of $Li_2[ZnCl_4]$ gave $[Zn([3^5]adz)][ZnCl_4]\cdot H_2O$ (**12**) in high yield (83% based upon the ligand).

Crystal Structures. Structure of $[Cu([(2.3)^2.2^1]adz)Br]ClO_4$ (2). Compound **2** consists of $Cu([(2.3)^2.2^1]adz)Br^+$ and $ClO_4{}^-$ ions. Bond lengths and angles of the coordination sphere around the copper ion are listed in Table 3. The labeling of the atoms of the cation is shown in Figure 3. For five-coordinated compounds two basic idealized geometric forms, the D_{3h} trigonal pyramid (TBP) and the C_{4v} square pyramid (SP), exist. The two forms are most simply and symmetrically related by the Berry intramolecular ligand exchange process with the trigonal bipyramid as reference. The coordination geometry around the copper ion in the present structure is best described as square pyramidal, the percentage (TBP → SP) being 86.6. The apical position is occupied by N(2). In $[Cu([2^4.3^1]adz)Br]ClO_4$[20] and in $[\{Cu([2^4.3^1]adz)\}_3(\mu_3\text{-}CO_3)](ClO_4)_4$[21] the coordination was best described as being about halfway between the two idealized structures, trigonal bipyramidal and square pyramidal, the percentages (TBP → SP) being 52.3 and 56.9, respectively. In the present structure the hydrogen atoms attached to N(1) and N(3) are oriented toward the Br atom and away from the ligand. The same result is found for the copper(II) and nickel(II) complexes with [2^4.3^1]adamanzane.[20,21,29] The Cu−N bonds involving the bridgehead nitrogen atoms are longer than the other two Cu−N bonds. This result is opposed to what was found for the five-coordinated Cu complexes of [2^4.3^1]adz.[20,21] The distance between the bridgehead nitrogen atoms N(2)···N(4) is 2.876(7) Å, and the N(1)···N(3) distance is 4.002(6) Å. In $H[(2.3)^3]adz^+$ [28] the distance between the bridgehead nitrogen atoms [ethylene bridge] are 2.73(2) and 2.91(1) Å for the two independent cations.

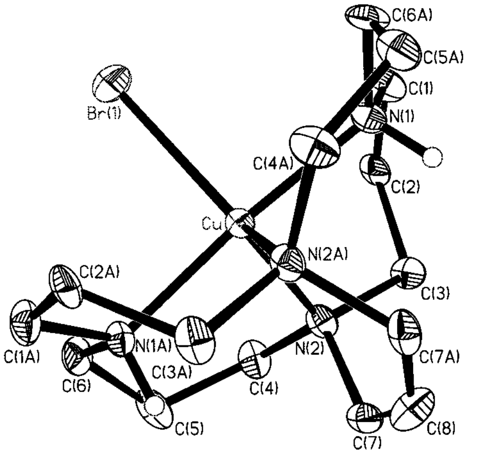

Figure 4. View of the cation in $[Cu([3^5]adz)Br]Br$ (**3**). Five of the carbon atoms are disordered. Only one position of these atoms is presented. $[Ni([3^5]adz)Cl]Cl$ (**5**), $[Ni([3^5]adz)Br]Br$ (**6**), and $[Co([3^5]adz)Cl]Cl$ (**8**) are isostructural with **3**.

Table 4. Bond Lengths (Å) and Bond Angles (deg) of the Coordination Sphere around the Metal Ions in $[Cu([3^5]adz)Br]Br$ (**3**), $[Ni([3^5]adz)Cl]Cl$ (**5**), $[Ni([3^5]adz)Br]Br$ (**6**), and $[Co([3^5]adz)Cl]Cl$ (**8**)[a]

	3	**5**	**6**	**8**
X(1)−M	2.4978(11)	2.3140(11)	2.4706(6)	2.3051(9)
M−N(1)	2.035(3)	2.116(2)	2.108(2)	2.170(2)
M−N(2)	2.130(3)	2.086(2)	2.090(2)	2.100(2)
N(1)^i−M−N(1)	174.8(2)	173.87(12)	174.15(8)	173.08(9)
N(1)−M−N(2)^i	88.12(12)	87.90(8)	87.95(6)	87.78(6)
N(1)−M−N(2)	88.91(13)	88.48(8)	88.59(6)	88.30(7)
N(2)^i−M−N(2)	109.9(2)	107.54(12)	107.44(9)	111.04(9)
N(1)−M−X(1)	92.59(10)	93.06(6)	92.92(4)	93.46(4)
N(2)−M−X(1)	125.05(10)	126.23(6)	126.28(4)	124.48(5)

[a] Symmetry code: (i) $-x, -y + {}^1/_2, z$. (M, X) in **3**, **5**, **6**, and **8** = (Cu, Br), (Ni, Cl), (Ni, Br), and (Co, Cl).

The six-membered ring, Cu(1)−N(1)−C(1)−C(2)−C(3)−N(2), has a chair conformation, whereas the other one has a twist-boat form. All three five-membered rings are in a twist conformation. The hydrogen attached to N(3) is involved in a weak hydrogen bond to O(1) (${}^1/_2 - x, -{}^1/_2 + y, {}^1/_2 - z$) of the $ClO_4{}^-$ ion. The N(3)−H···O(1) bond is 3.038(7) Å (D···A).

Structure of $[Cu([3^5]adz)Br]Br$ (3), $[Ni([3^5]adz)Cl]Cl$ (5), $[Ni([3^5]adz)Br]Br$ (6), and $[Co([3^5]adz)Cl]Cl$ (8). **3**, **5**, **6**, and **8** are isostructural, and the compounds consist of $M([3^5]adzX)^+$ and X^- ions (M = Cu, Ni, or Co; X = Cl or Br). The cations have 2-fold symmetry, the metal ion, X(1), and C(8) being positioned on a 2-fold axis. Bond lengths and angles of the coordination sphere around the copper ion are listed in Table 4. The labeling of the atoms of the cation is shown in Figure 4. The coordination geometry around the copper ion is trigonal bipyramidal, the percentages (TBP → SP) being 8.1, 10.2, 10.5,

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(50) Chen, L.; Cotton, F. A. *Inorg. Chim. Acta* **1997**, *263*, 9 and references therein.

Table 5. Bond Lengths (Å) and Bond Angles (deg) of the Coordination Sphere around the Metal Ions in [Ni([3^5]adz)(NO$_3$)]NO$_3$ (**4**) and [Ni([3^5]adz)(ClO$_4$)]ClO$_4$ (**7**)

	4	**7**
Ni−N(1)	2.083(6)	2.066(2)
Ni−N(2)	2.094(6)	2.101(2)
Ni−N(3)	2.074(6)	2.072(2)
Ni−N(4)	2.095(6)	2.084(2)
Ni−O(1)	2.195(5)	2.260(2)
Ni−O(2)	2.180(5)	2.258(2)
N(3)−Ni−N(1)	176.5(2)	177.34(10)
N(3)−Ni−N(2)	89.2(3)	88.28(9)
N(1)−Ni−N(2)	88.6(3)	89.99(9)
N(3)−Ni−N(4)	89.6(3)	88.69(9)
N(1)−Ni−N(4)	88.3(2)	89.87(9)
N(2)−Ni−N(4)	105.9(2)	106.41(9)
N(3)−Ni−O(2)	91.4(2)	92.87(8)
N(1)−Ni−O(2)	91.6(2)	89.48(8)
N(2)−Ni−O(2)	157.5(2)	158.61(8)
N(4)−Ni−O(2)	96.6(2)	94.97(8)
N(3)−Ni−O(1)	91.7(2)	92.67(8)
N(1)−Ni−O(1)	91.4(2)	89.54(8)
N(2)−Ni−O(1)	98.3(2)	96.67(8)
N(4)−Ni−O(1)	155.7(2)	156.91(8)
O(2)−Ni−O(1)	59.2(2)	61.94(6)

and 5.1 for [Cu([3^5]adz)Br]Br (**3**), [Ni([3^5]adz)Cl]Cl (**5**), [Ni([3^5]adz)Br]Br (**6**), and [Co([3^5]adz)Cl]Cl (**8**), respectively, whereas a square pyramidal coordination was found in [Cu([(2.3)^2.2^1]adz)Br]ClO$_4$ (**2**). The geometry around the metal ion depends on the metal ion, the anions, and the size of the tetraamine cavity.

In each of the present structures the M−N bonds are of almost the same length. The N(1) and N(1)^i (i = $-x$, $-y + {}^1/_2$, z) atoms occupy the axial positions. The N(2)···N(2)^i distance between the bridgehead nitrogen atoms is 3.487(6), 3.366(4), 3.369(3), and 3.461(3) Å, and the N(1)···N(1)^i distance is 4.065(6), 4.226(4), 4.211(3), and 4.332(3) Å for [Cu([3^5]adz)Br]Br (**3**), [Ni([3^5]adz)Cl]Cl (**5**), [Ni([3^5]adz)Br]Br (**6**), and [Co([3^5]adz)Cl]Cl (**8**), respectively. The hydrogen atom attached to N(1) is oriented away from the X(1) atom and is involved in a weak hydrogen bond with X(2) (X = Cl or Br). The N(1)−H(1)···X(2) bond is 3.528(4), 3.447(2), 3.522(2), and 3.398(2) Å (D···A) for [Cu([3^5]adz)Br]Br (**3**), [Ni([3^5]adz)Cl]Cl (**5**), [Ni([3^5]adz)Br]Br (**6**), and [Co([3^5]adz)Cl]Cl (**8**), respectively.

Structure of [Ni([3^5]adz)(NO$_3$)]NO$_3$ (4) and [Ni([3^5]adz)(ClO$_4$)]ClO$_4$ (7). Compound **4** consists of Ni([3^5]adz)(NO$_3$)$^+$ and NO$_3^-$ ions, and compound **7** consists of Ni([3^5]adz)(ClO$_4$)$^+$ and ClO$_4^-$ ions. Bond lengths and angles of the coordination sphere around the nickel ion are listed in Table 5. The labeling of the atoms of the cations is shown in Figures 5 and 6. The NO$_3^-$ and ClO$_4^-$ ligands are bidentately coordinated, giving a *cis* configuration as found in the Ni complexes with the ligand [2^4.3^1]adamanzane.[29] In octahedral complexes the adamanzanes constrain the configuration to *cis* as opposed to the related macrocyclic ligand, 1,5,9,13-tetraazacyclohexadecane ([16]aneN$_4$), which forms *cis* as well as *trans* complexes.[48] In the present structures the angles around the nickel ion show distortions with respect to those of a regular octahedron. This is mainly due to the very small angle O(1)−Ni−O(2) of 59.2(2)° and 61.94(6)° for [Ni([3^5]adz)(η^2-NO$_3$)]NO$_3$ (**4**) and [Ni([3^5]adz)(η^2-ClO$_4$)]ClO$_4$ (**7**), respectively. These values are in agreement with those of 60.19(12)° and 61.0(2)° found in *cis*-(nitrato-*O*,*O*′)[(1*RS*,4*SR*,5*SR*,8*RS*,11*SR*,12*SR*)-*C*-*rac*-1,5,8,12-tetramethyl-1,4,8,11-tetraazacyclotetradecane-κ^4N]nickel(II) nitrate[51] and nickel(II) complexes with the bidentate perchlorate.[49]

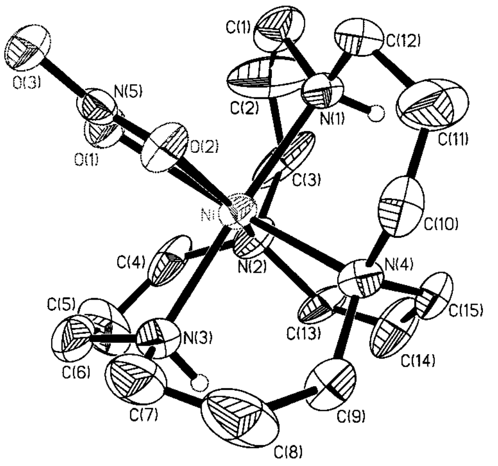

Figure 5. View of the cation in [Ni([3^5]adz)(NO$_3$)]NO$_3$ (**4**). Eight of the carbon atoms are disordered. Only one position of these atoms is presented.

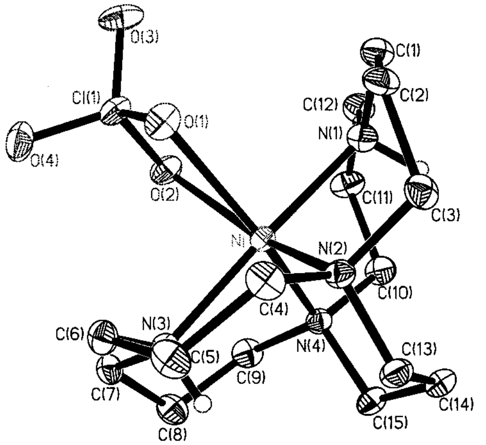

Figure 6. View of the cation in [Ni([3^5]adz)(ClO$_4$)]ClO$_4$ (**7**).

As a consequence the NO$_3^-$ ligand in [Ni([3^5]adz)(NO$_3$)]NO$_3$ (**4**) and the ClO$_4^-$ ligand in [Ni([3^5]adz)(ClO$_4$)]ClO$_4$ (**7**) show distortion from regular triangle and tetrahedron symmetry, respectively, the O(1)−N(5)−O(2) angle being 116.0(4)° and the O(1)−Cl(1)−O(2) angle being 104.97(12)°.

The Ni−N and Ni−O bonds in both structures are similar to those of other six-coordinated Ni(II) complexes. As with other coordinated perchlorates[49] the Cl−O bond lengths in [Ni([3^5]adz)(ClO$_4$)]ClO$_4$ (**7**) are shorter to the noncoordinating oxygens (1.425(2), 1.426(2) Å) than to the coordinated oxygens (1.464(2), 1.468(2) Å).

In the perchlorate compound (**7**) the two six-membered rings containing N(1) are in a twist-boat conformation, whereas the other three rings are in a chair form. The N(2)···N(4) distance between the bridgehead nitrogen atoms is 3.344(7) Å in [Ni([3^5]adz)(NO$_3$)]NO$_3$ (**4**) and 3.351(3) Å in [Ni([3^5]adz)(ClO$_4$)]ClO$_4$ (**7**), and the N(1)···N(3) distance is 4.156(7) Å in the nitrate compound (**4**) and 4.136(3) Å in the perchlorate compound (**7**). In both structures the hydrogen atoms attached to N(1) and N(3) are oriented away from the inorganic ligand. In [Ni([3^5]adz)(NO$_3$)]NO$_3$ (**4**) the hydrogen atom of N(3) is involved in a weak hydrogen bond of 3.009(9) Å (D···A) with O(6) (1 − x, 1 − y, −z) of one of the NO$_3^-$ anions, and in

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(51) Panneerselvam, K.; Lu, T.-H.; Chi, T.-Y.; Liao, F.-L.; Chung, C.-S. *Acta Crystallogr.* **1999**, *C55*, 724 and references therein.

Table 6. Bond Lengths (Å) and Bond Angles (deg) of the Coordination Sphere around the Metal Ions in $[Co([3^5]adz)][ZnCl_4]$ (**10b**) and $[Zn([3^5]adz)][ZnCl_4]$ (**12**)[a]

	10b	**12**
M−N(1)	2.005(3)	1.990(2)
M−N(3)	2.011(3)	1.995(2)
M−N(2)	2.018(3)	2.021(2)
M−N(4)	2.025(3)	2.021(2)
N(1)−M−N(3)	126.22(11)	125.44(8)
N(1)−M−N(2)	107.19(10)	107.54(7)
N(3)−M−N(2)	104.58(10)	104.86(7)
N(1)−M−N(4)	104.84(10)	104.84(7)
N(3)−M−N(4)	107.84(10)	108.24(7)
N(2)−M−N(4)	104.31(11)	104.14(7)

[a] M in **10b** is Co and in **12** is Zn.

$[Ni([3^5]adz)(ClO_4)]ClO_4$ (**7**) there is a weak hydrogen bond between the hydrogen atoms attached to N(1) and O(7) of the ClO_4^- anions of 3.226(4) Å.

Structure of $[Co([3^5]adz)][ZnCl_4]$ (10b) and $[Zn([3^5]adz)][ZnCl_4]$ (12). The compounds **10b** and **12** are isostructural and consist of $M([3^5]adz)^{2+}$ and $ZnCl_4^{2-}$ ions (M = Co or Zn). Bond lengths and angles of the coordination sphere around the metal ion are listed in Table 6. The labeling of the atoms of the cation is shown in Figure 7. The coordination polyhedron around the metal ion, M, is a slightly distorted tetrahedron. The angles around the metal ion are in the range 104.31(11)−107.84(10)° (M = Co, **10b**) and 104.14(7)−108.24(7)° (M = Zn, **12**) except for the angle between the nonbridging nitrogen atoms, N(1)−M−N(3), which in $[Co([3^5]adz)][ZnCl_4]$ (**10b**) is 126.22(11)° and in $[Zn([3^5]adz)][ZnCl_4]$ (**12**) is 125.44(8)°. These values are very close to those found in the two isostructural and tetrahedral complexes, $[Co([16]aneN_4)](ClO_4)_2$[50] and $[Zn([16]aneN_4)](ClO_4)_2$.[52] In $Co([16]aneN_4)^{2+}$ the angles N−Co−N range from 98.9(9)° to 124.6(8)°, and in $Zn([16]aneN_4)^{2+}$ the angles N−Zn−N range from 101.9(5)° to 123.4(4)°. In the present structures, the N(1)···N(3) distance is 3.581(4) and 3.542(3) Å and the N(2)···N(4) distance between the bridgehead nitrogen atoms is 3.192(4) and 3.188(3) Å in the cobalt (**10b**) and zinc (**12**) compounds, respectively. The Zn−N(1) and Zn−N(3) bonds are slightly shorter than the two other Zn−N bonds (**12**), whereas in **10b** the Co−N bonds are of equal length. In both structures, the six-membered ring containing N(1) and N(2) and the ring containing N(3) and N(4) have the envelope conformation. The ring involving N(2) and N(3) and the one with N(1) and N(4) are both in a chair form. The fifth ring with N(2) and N(4) has a twist-boat conformation. The hydrogen atoms attached to N(1) and N(3), both being oriented away from the ligand, are involved in a weak hydrogen bond with $ZnCl_4^{2-}$ ions, the N(1)−H(1)···Cl(1) (*x*, *y*, *z* − 1) and the N(3)−H(3)···Cl(2) (*x*, *y*, *z* − 1) bonds being 3.312(3) ($[Co([3^5]adz)][ZnCl_4]$, **10b**), 3.298(2) ($[Zn([3^5]adz)][ZnCl_4]$, **12**) and 3.266(3) ($[Co([3^5]adz)][ZnCl_4]$, **10b**), 3.236(2) ($[Zn([3^5]adz)][ZnCl_4]$, **12**) Å (D···A), respectively.

In the investigation of these small bicyclic tetraamines we find the N−H bonds to be oriented away from the adamanzane ligand in the complexes of $[2^4.3^1]$adamanzane and of $[(2.3)^2.2^1]$adamanzane and in the four-coordinated complexes of $[3^5]$adamanzane, whereas in the five- and six-coordinated complexes of $[3^5]$adamanzane the N−H bonds are oriented in the opposite direction.

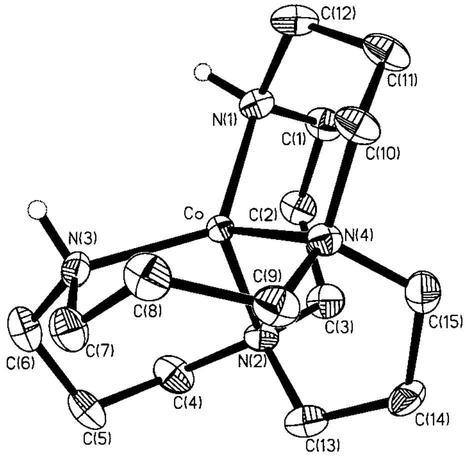

Figure 7. View of the cation in $[Co([3^5]adz)][ZnCl_4]$ (**10b**). $[Zn([3^5]adz)][ZnCl_4]$ (**12**) is isostructural with **10b**.

Solution Studies. X-ray crystal structures were not obtained for any of the aqua species of the presently reported complexes. The values of the absorption coefficients were used to assign the coordination numbers.

Previously reported crystal structures of copper(II) aqua complexes with macrocyclic tetraamines all display five-coordination.[53] The bromo complexes in the present work (**2**, **3**) are five-coordinated, and the extinction coefficients for the corresponding aqua species (acidic, aqueous solutions containing Hg^{2+} in excess) vary by less than a factor of 3 from those for the bromo complexes. This moderate change suggests roughly identical coordination geometries; accordingly, five-coordination is assigned to the aqua species, i.e., $Cu([(2.3)^2.2^1]adz)(H_2O)^{2+}$ and $Cu([3^5]adz)(H_2O)^{2+}$.

The similar lack of a significant reduction in the extinction coefficients for the nickel aqua species (aqueous solutions of $[Ni([3^5]adz)(ClO_4)]ClO_4$ (**7**)) supports a formulation as a five-coordinated complex as well, i.e., $Ni([3^5]adz)(H_2O)^{2+}$. The high extinction coefficients found for the six-coordinated nitrate and perchlorate complexes (**4**, **7**) are attributed to the distortion from regular octahedral geometry imposed by the small bite angle of the anionic ligands. The distortion is apparently severe enough to disrupt the presence of parity selection rules. Complexes of this type have previously been described as pseudo-five-coordinated with the chelately bound oxo ligand occupying only one, mean coordination site.[54]

The opposite is true for aqueous solutions of the cobalt(II) complexes (**8**, **10**), which at low chloride ion concentrations appear to contain substantial amounts of a species with very low absorption coefficients: ca. $^1/_{10}$ of those of the five-coordinated and tetrahedral species. The absorption spectrum of the pale green product $[Co([3^5]adz)(H_2O)_2](ClO_4)_2\cdot H_2O$ (**9**) is very similar to that of the $Co([3^5]adz)Cl^+$ ion (**8**) in cold 0.01 M trifluoromethanesulfonic acid (a medium in which the various reactions of the present cobalt(II) system are slow). These facts are taken as evidence for the presence of a six-coordinated, pseudo-octahedral $Co([3^5]adz)(H_2O)_2^{2+}$ ion.

In aqueous solutions of high chloride concentration the five-coordinated $Co([3^5]adz)Cl^+$ ion (**8**) presents itself as a highly absorbing species as is seen from the reported spectrum of $[Co([3^5]adz)Cl]Cl$ (**8**) in 12 M HCl. This is in conflict with the absorption bands of very low extinction coefficients observed for solutions of the same compound in organic solvents. The spectra are interpreted as evidence of six-coordination in the organic solvents, afforded either by coordination of the ionic

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(52) Luckay, R.; Chantson, T. E.; Reibenspeis, J. H.; Hancock, R. D. *J. Chem. Soc., Dalton Trans.* **1995**, 1363.

(53) Chang, C.-C.; Chung, C.-S. *J. Chem. Soc., Dalton Trans.* **1991**, 1685.

(54) Mathew, M.; Palenik, G. J.; Clark, G. R. *Inorg. Chem.* **1973**, *12*, 446.

Table 7. Thermodynamic Data for the Equilibrium Constants, $K(\mathrm{X}^-)/\mathrm{M}^{-1}$, for the Formation of $\mathrm{M^{II}LX^+}$ Complexes in Aqueous Solution and Kinetic Data for the Dissociation in 5 M HCl of the Macrocyclic Ligand from the Metal Ion at 25 °C[a]

	K/M^{-1}	$\Delta H°/\mathrm{kJ{\cdot}mol^{-1}}$	$\Delta S°/\mathrm{J{\cdot}mol^{-1}\,K^{-1}}$	k/s^{-1}	$\Delta H^{\ddagger}/\mathrm{kJ{\cdot}mol^{-1}}$	$\Delta S^{\ddagger}/\mathrm{J{\cdot}mol^{-1}\,K^{-1}}$
$\mathrm{Cu([2^4.3^1])adz)Br^+}$	8.3(2)[b]	−8.4(1.8)	−11(6)	$1.48(2) \times 10^{-6}$	89(6)[j]	−60(14)[j]
$\mathrm{Cu([(2.3)^2.2^1]adz)Br^+}$	4.8(3)[c]	1.7(9)	19(3)	$1.79(5) \times 10^{-6}$	93(4)	−42(9)
$\mathrm{Cu([3^5]adz)Br^+}$	4.55(2)[d]	−4.5(3)	−2.6(1)	$2.28(6) \times 10^{-7}$	121(4)	32(14)
$\mathrm{Ni([3^5]adz)Cl^+}$	9.1(4)[e]	−7.9(2.7)	−8.1(8.7)	$1.4(6) \times 10^{-9}$ [g]	126(6)[g]	8(17)[g]
$\mathrm{Ni([3^5]adz)(NO_3)^+}$	62(4)[e]	−33(4)	−75(15)			
$\mathrm{Ni([3^5]adz)Br^+}$	1.0(3)[f]					
$\mathrm{Co([3^5]adz)^{2+}}$				$1.12(2) \times 10^{-4}$ [h]	84(2)	−39(5)
$\mathrm{Zn([3^5]adz)^{2+}}$				$1.60(6) \times 10^{-4}$ [i]	82(2)	−44(7)

[a] Equilibrium and rate constants at 40 °C are given in Tables S1 and S2 (available as Supporting Information). [b] 1.00 M $\mathrm{Na(Br,ClO_4)}$, ref 20. [c] 1.00 M $\mathrm{Na(Br,ClO_4)}$. [d] 1.00 M $\mathrm{Na(Br,NO_3)}$. [e] 1.00 M $\mathrm{Na(X,CF_3SO_3)}$ (X = Cl, $\mathrm{NO_3}$). [f] Rough estimate, see text. [g] The rate constants at 25 °C have been calculated from the values of $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ determined in this study from rate constants $k = 4.81(9) \times 10^{-6}\ \mathrm{s}^{-1}$ at 80 °C and $k = 5.04(50) \times 10^{-5}\ \mathrm{s}^{-1}$ at 100 °C. [h] Equilibrium mixture containing $\mathrm{Co([3^5]adz)^{2+}}$ and $\mathrm{Co([3^5]adz)Cl^+}$, see text. [i] 5 M DCl. [j] Activation parameters calculated from an earlier determination of k at 25 °C and k at 40 °C determined in this study (Table S2).

chloride ion to form a neutral species or by coordination of a solvent molecule.

Equilibrium Studies. No aqua species has made itself evident for the adamanzane complexes of zinc(II) (**11**, **12**), but for the remainder (**2**−**10**), equilibration with the aqua complexes is observed in aqueous solutions, and for the five- and six-coordinated complexes (**2**−**8**) the reaction is fast.

In the present work the equilibria involving the copper(II) (**2**, **3**) and three of the nickel(II) (**4**−**6**) complexes were studied spectrophotometrically. Omission of the $\mathrm{Ni([3^5]adz)ClO_4^+}$ ion (**7**) from this study was justified by the weak donor capabilities of the perchlorate ligand and by spectral measurements of the complex in water/acetone solutions of varying composition. The complex interconversions of the cobalt(II) system have not been examined here.

In all five cases studied, interpretation of the spectral changes in terms of the equilibria shown in eq 1 was unambiguous for the entire wavelength region, with no indications of the presence of other species. The equilibrium constants, $K(\mathrm{X}^-)$, were determined as described in the Experimental Section (Table 7).

$$\mathrm{ML(H_2O)^{2+} + X^- \xrightleftharpoons{K(X^-)} MLX^+ + H_2O} \qquad (1)$$

$$\mathrm{M = Cu:\ \ L = [(2.3)^2.2^1]adz,\ [3^5]adz,\ X = Br^-}$$

$$\mathrm{M = Ni:\ \ L = [3^5]adz,\ X = NO_3^-,\ Cl^-,\ Br^-}$$

The equilibrium constants for the copper(II) complexes correspond well with those reported for $\mathrm{Cu([2^4.3^1]adz)Br^+}$ and for copper(II) complexes with other macrocyclic tetraamines, all having values of $K(\mathrm{Br}^-)$ in the region 2−20 M^{-1}.[20,55−58]

A 9-fold increase in the equilibrium constants for the formation of the nickel(II) anion complexes (**4**−**6**) is seen when crossing from bromide (**6**) to chloride (**5**) and a further approximate 5-fold increase upon changing to nitrate (**4**). The nitrate ion is generally considered to be of weak ligating power. However, the results obtained for the present complexes correlate with the acidity of the corresponding strong acids; the stronger the acid, the weaker the anion is bound to the positively charged nickel−adamanzane moiety. Accordingly, the binding of the perchlorate ion appears to be insignificant in aqueous solution.

The binding of the nitrate ion is 25 times more efficient in the present species, $\mathrm{Ni([3^5]adz)(\eta^2\text{-}NO_3)^+}$ (**4**), than was the case for the analogous $\mathrm{Ni([2^4.3^1]adz)(\eta^2\text{-}NO_3)^+}$ complex.[29] For the $[3^5]$adamanzane species (**4**) weak hydrogen bonding is possible between the hydrogen atoms of the methylene groups directly attached to the nonbridged nitrogen atoms and the coordinated oxo groups of the inorganic ligand. Such interaction is prohibited with complexes of the smaller macrocycle, which display an inverted geometry around the nonbridged nitrogen atoms. This hydrogen bonding might aid slightly to greater stability of the present nitrate complex (**4**) and also toward formation of the rather unusual chelate perchlorate complex (**7**). However, the X-ray data shows the interaction to be weak, and Table 7 shows the standard enthalpy change for the complexation reaction to be dramatically more favorable for the nickel(II) nitrate complex (**4**) than for the remainder of the adamanzane complexes. Clearly, other effects must be present as well.

Hydrolysis Kinetics. In hydrochloric acid the adamanzane complexes are cleaved slowly to form the hexaaquametal(II) ions or the tetrachlorometalate(II) anions plus the corresponding protonated amines. The kinetics were studied as described in the Experimental Section, and the obtained kinetic parameters are listed in Table 7. In the case of the copper(II) species (**2**, **3**) and following previous studies[20] of the $[2^4.3^1]$adamanzane complexes, it is assumed that transformation of the bromo complexes into the corresponding chloro complexes is fast and quantitative. The overall reaction is shown in eq 2.

$$\mathrm{CuLCl^+ + 4H^+ + 3Cl^- \xrightarrow{k_{obs}} CuCl_4^{2-} + H_4L^{4+}} \qquad (2)$$

$$\mathrm{L = [(2.3)^2.2^1]adz,\ [3^5]adz}$$

For nickel(II), measurements were performed directly on the chloro species. Due to the extreme inertness of the five-coordinated chloro complex (**5**), the experiments were conducted at 80 and 100 °C. The overall reaction is shown in eq 3.

$$\mathrm{Ni([3^5]adz)Cl^+ + 4H^+ + 6H_2O \xrightarrow{k_{obs}} Ni(H_2O)_6^{2+} + H_4[3^5]adz^{4+} + Cl^-} \qquad (3)$$

The NMR data obtained for the analogous reaction involving the tetrahedral zinc(II) complex (**12**) also followed the expression for a first-order reaction, and the overall reaction is shown in eq 4.

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(55) Liang, B.-F.; Margerum, D. E.; Chung, C.-S. *Inorg. Chem.* **1979**, *18*, 2001.
(56) Liang, B.-F.; Chung, C.-S. *Inorg. Chem.* **1980**, *19*, 572.
(57) Wu, S.-Y.; Lee, C.-S.; Chung, C.-S. *Inorg. Chem.* **1984**, *23*, 2548.
(58) Chen, J.-W.; Chang, C.-C.; Chung, C.-S. *Inorg. Chem.* **1987**, *26*, 335.

$$\mathrm{Zn([3^5]adz)^{2+} + 4H^+ + 4Cl^-} \xrightarrow{k_{\mathrm{obs}}} \mathrm{ZnCl_4{}^{2-} + H_4[3^5]adz^{4+}} \quad (4)$$

The stoichiometries of the reactions of the cobalt(II) complexes (**8** and **10**) in 5 M HCl are shown in eqs 5 and 6. At 25 °C both reactions showed biphasic kinetics, which was interpreted in terms of two consecutive reactions, k_{fast} being 10 times larger than k_{slow}.

$$\mathrm{Co([3^5]adz)Cl^+ + 4H^+ + 6H_2O} \xrightarrow{k_{\mathrm{obs}}} \mathrm{Co(H_2O)_6{}^{2+} + H_4[3^5]adz^{4+} + Cl^-} \quad (5)$$

$$\mathrm{Co([3^5]adz)^{2+} + 4H^+ + 6H_2O} \xrightarrow{k_{\mathrm{obs}}} \mathrm{Co(H_2O)_6{}^{2+} + H_4[3^5]adz^{4+}} \quad (6)$$

The slow/fast ambiguity was resolved by looking at the calculated spectra of the intermediates, and it was unambiguously concluded that k_{fast} corresponds to the first reaction. As discussed in the following, the kinetic data can be interpreted in terms of a fast pre-equilibration followed by a slow ligand extrusion reaction(s) (eqs 5 and 6). The pre-equilibration is

$$\mathrm{Co([3^5]adz)^{2+} + Cl^-} \underset{k_{-1}}{\overset{K}{\underset{}{\overset{k_1}{\rightleftharpoons}}}} \mathrm{Co([3^5]adz)Cl^+} \quad (7)$$

proposed to be an equilibration between the complexes **8** and **10** as shown from the kinetic data (eq 7). The calculated intermediate spectra for solutions starting with either **8** or **10** were identical, confirming that equilibrium has been attained. Furthermore, the observed pseudo-first-order rate constants, k_{fast}, for reactions starting with either **8** or **10** were identical (1.41(3) × 10^{-3} and 1.38(3) × 10^{-3} $\mathrm{s^{-1}}$, respectively) as expected for equilibration kinetics (eq 7). From the calculated equilibrium spectrum and the spectra of the starting compounds, the concentration equilibrium constant $K = [\mathrm{Co([3^5]adz)Cl^+}]/[\mathrm{Co([3^5]adz)^{2+}}][\mathrm{Cl^-}] = 0.2\ \mathrm{M^{-1}}$ was calculated, i.e., the equilibrium mixture contains approximately equal amounts of the two species in 5 M HCl. Assuming that $k_{\mathrm{fast}} = k_1 + k_{-1}[\mathrm{Cl^-}]$ and using the value for $K = k_1/k_{-1}$, the rate constants $k_1 = 7 \times 10^{-4}\ \mathrm{s^{-1}}$ and $k_{-1} = 1.4 \times 10^{-4}\ \mathrm{s^{-1}}$ (25 °C) are calculated.

The observed pseudo-first-order rate constants for the second reaction, k_{slow}, were identical for the two compounds **8** and **10**. This corresponds well to the proposal that for both complexes the second reaction corresponds to the ligand extrusion reaction for an equilibrium mixture of the two species (eq 7). At present we have no indication as to whether the rate-determining step(s) in the extrusion process mainly involves either **8** or **10** or both species.

At 40 °C the time required to dissolve the samples in 5 M HCl prohibited a reliable determination of the first and fast reaction, but well-defined values for the ligand extrusion, k_{slow}, could be obtained. Data for this reaction are given in Table 7.

The dissociation of the macrocyclic ligand from the metal ion is a multistep process for which the nature of the rate-determining step remains unknown. Furthermore, the products of the dissociation reactions differ, from tetrachloro to hexaaqua ions. These facts dictate extreme caution when attempting comparison of the rates and kinetic parameters. However, a few observations merit comment.

There is no trend in the variation of the dissociation rates for the three copper(II) complexes. The activation parameters, on the other hand, display a general increase in both parameters with the increase in ligand size, ending up with a change of sign for the activation entropy concerning the dissociation of the [3^5]adamanzane complex (**3**).

When comparing only the [3^5]adamanzane complexes the general expectation[59] is for the cleavage of nickel(II) complexes to be the slowest followed by cobalt(II), copper(II), and finally zinc(II) as the fastest.

In accordance with this, the dissociation of the five-coordinated nickel(II) complex (**5**) is by far the slowest. However, the order is reversed for the next two metal ions (Table 7). The reaction in 5 M HCl is slower for the [3^5]adamanzane complex of copper(II) (**3**) than for the cobalt(II) system (**8**, **10**). Apart from the difference in the products of the dissociation reactions this may relate to the preequilibrium (eq 7) established for the cobalt complexes (**8**/**10**). As mentioned earlier, comparison with the five- and six-coordinated species of [3^5]-adamanzane (**3**−**8**) reveals an inverted geometry for the tetrahedral complexes (**10**, **12**) around the nonbridged nitrogen atoms. Also, the coordination polyhedron for the latter complexes (**10**, **12**) forms a *flattened* tetrahedron (HN−M−NH ∼ 126°, Table 6). In combination these two structural features cause the metal ion to be less embedded in the cavity formed by the organic framework of the macrocycle, leaving more room for attack. Thus the presence of substantial amounts of the tetrahedral species (**10**) in the equilibrium mixture concurs with an enhanced dissociation rate for the cobalt(II) system. The result is faster cleavage for cobalt(II) (**8**/**10**) than that observed for the five-coordinated copper(II) complex (**3**), contrary to the order expected just from the nature of the metal ions.[59]

Faster yet is the dissociation of the zinc(II) complex (**12**). This complex is isostructural with the tetrahedral cobalt(II) ion (**10**). Furthermore, no ligand field stabilization exists for zinc(II), rendering obsolete the contribution to the activation energy barrier from the difference in LFSE between the starting complex and the product(s) for reactions involving this particular metal ion.

The dissociation reactions of the [3^5]adamanzane complexes of copper(II) and nickel(II) (**3**, **5**) in 5 M HCl are much more temperature dependent than is the case for the remainder of the complexes (Table 7). Furthermore, comparison of the enthalpies and entropies of activation for the dissociation process (Table 7) shows the parameters for these two to be identical within the standard variation but quite different from the parameters of the rest. Again structural differences might constitute an explanation. The only systems which involve the cleavage of five-coordinated [3^5]adamanzane species solely are precisely those involving the mentioned copper and nickel complexes (**3**, **5**). The previously discussed inversion around the nonbridged nitrogen atoms is observed when comparing the five- and six-coordinated complexes of [3^5]adamanzane (**3**−**8**) with *all* of the rest of the adamanzane complexes and may be responsible for a different mechanism for the dissociation of the macrocyclic ligand from the metal ion.

Concluding Remarks

A range of transition metal complexes (**3**−**12**) with the bowl-shaped macrocyclic ligand [3^5]adamanzane were synthesized and characterized, along with a copper(II) complex (**2**) of the smaller ligand [(2.3)^2.2^1]adamanzane. Equilibrium constants for the complexation with various anions as the fifth ligand were

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[59] Wilkins, R. G. *Kinetics and Mechanism of Reactions of Transition Metal Complexes*, 2nd ed.; VCH Publisher: New York, 1991.

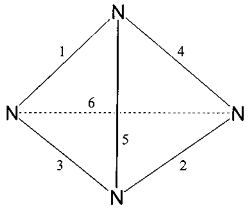

Figure 8. Order of listing the five and six carbon chains, respectively, in bowl and cage adamanzanes.

determined, as were decomposition rates in 5 M HCl. The obtained thermodynamic and kinetic parameters were discussed in light of the structural data, particularly the observed inversion in the conformation of the nonbridged nitrogen atoms of the macrocyclic ligands. Complexes of $[2^4.3^1]$adamanzane,[20,21,29] $[(2.3)^2.2^1]$adamanzane (**2** in this study), and the tetrahedral complexes (**10**, **12**) of the larger $[3^5]$adamanzane macrocycle displayed a conformation with the hydrogen atoms of the secondary amine groups pointing upward from the rim of the bowl-shaped macrocycle, in the direction of the site for the potential fifth ligand. Inversion was observed for all of the five- and six-coordinated complexes of $[3^5]$adamanzane (**3**−**8**) yielding a configuration where the metal ion seems much more deeply embedded in the cavity of the ligand. In general these latter complexes showed a tendency toward greater stability, i.e., lower decomposition rates.

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Appendix

We have previously suggested a simplified nomenclature for this series of bi- and tricyclic tetraamines.[18,22,23] The nomenclature corresponds to that used for the series of bicyclic systems in which the numbers of carbon (and hetero) atoms in the three chains are given as a prefix in a square bracket.[1] The cages and bowls may be considered as nitrogen analogues to the tetrahedral carbon cage whose smallest member is adamantane, tricyclo-$[3.3.1.1^{3,7}]$decane. We name the series of tetraaza bowls and cages **adamanzanes** (**adaman**tane + tetraa**za** + ami**ne**) and follow the rules above with the additional rule that the carbon chains are listed in the order as shown in Figure 8. The cages and bowls are named as indicated below (an additional short notation for cases with several carbon chains of equal length in sequence is also given), and the notation is illustated in Figure 1 for bowl adamanzanes (adz = adamanzane).

Bowls:
1,5,9,13-tetraazabicyclo[7.7.3]nonadecane = [3.3.3.3.3]adamanzane = $[3^5]$adz.
1,4,7,10-tetraazabicyclo[5.5.3]pentadecane = [2.2.2.2.3]adamanzane = $[2^4.3^1]$adz.
1,5,9,12-tetraazabicyclo[7.5.2]hexadecane = [2.3.2.3.2]adamanzane = $[(2.3)^2.2^1]$adz.
Cages:
1,3,5,7-tetraazatricyclo$[3.3.1.1^{3,7}]$decane = [1.1.1.1.1.1]adamanzane = $[1^6]$adz.
1,4,8,11-tetraazatricyclo$[6.6.2.2^{4,11}]$octadecane = [2.2.2.2.3.3]adamanzane = $[2^4.3^2]$adz.

Formulas for the protonated species may be written as, for instance $H_4[3^5]adz^{4+}$.

Supporting Information Available: Nine X-ray crystallografic files, in CIF format. One table giving the equilibrium constants, $K(X^-)$, and thermodynamic data for the formation of $M^{II}LX^+$ complexes in aqueous solution at 40 °C and a table giving the rate constants, k_{obs}, for the dissociation in 5 M HCl of the macrocyclic ligand from the metal ion. This material is available free of charge via the Internet at http://pubs.acs.org.

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