Nickel(II) Complexes with [2⁴.3¹]Adamanzane, 1,4,7,10-Tetraazabicyclo[5.5.3]pentadecane

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Nickel(II) complexes with the bicyclic tetraamine L=[2⁴.3¹]adamanzane (1,4,7,10-tetraazabicyclo[5.5.3]pentadecane) have been synthesized. The reaction of $NiBr_2$ with [2⁴.3¹]adz in dimethylformamide gives a dibromo-bridged dinuclear complex $[\{Ni(L)\}_2(\mu\text{-}Br)_2]Br_2$. From this crude product pure $[\{Ni(L)\}_2(\mu\text{-}Br)_2](ClO_4)_2$ and $[\{Ni(L)\}_2(\mu\text{-}Cl)_2](ClO_4)_2$ have been obtained. In aqueous solution these dinuclear species hydrolyse to the parent mononuclear diaqua species, which was isolated as $[Ni(L)(H_2O)_2]S_2O_6 \cdot 2H_2O$. The reaction of the diaqua complex with nitrite gives $[Ni(L)(NO_2)]ClO_4$ or $[Ni(L)(NO_2)]PF_6$ and with nitrate $[Ni(L)(NO_3)]ClO_4$ is obtained. Equilibrium studies of the formation of the nitrito and nitrato complexes are reported. The structures of $[\{Ni(L)\}_2(\mu\text{-}Cl)_2](ClO_4)_2$, $[Ni(L)(H_2O)_2]S_2O_6 \cdot 2H_2O$, $[Ni(L)(NO_2)]PF_6$ and $[Ni(L)(NO_3)]ClO_4$ have been determined by X-ray diffraction techniques. The coordination geometry about the nickel(II) ion is a distorted octahedron in all the structures.

Coordination compounds of macrocyclic and macrobicyclic polyamines are of current interest because of their importance as model systems within bioinorganic chemistry, their applications in medicine and as catalysts.[1–8] 'Cross-bridging' of macrocyclic amines such as cyclen (1,4,7,10-tetraazacyclododecane) and cyclam (1,4,8,11-tetraazacyclotetradecane), i.e. bridging of nonadjacent nitrogens, leads to bicyclic tetraamines, so-called bowl adamanzanes, and several synthetic methods for this class of amines have been reported.[9,10] Our own first successful preparation of a bowl adamanzane was achieved[9] by the reaction of *trans* ditosylated cyclen with the ditosylate of 1,3-propanediol, which after detosylation gave the small bowl [2⁴.3¹]adamanzane (Fig. 1). Subsequently we

reported[10] a synthesis of a larger bowl: [3⁵]adamanzane, 1,5,9,13-tetraazabicyclo[7.7.3]nonadecane (Fig. 1).

Complexation of Li^+, Cu^{2+} and Ni^{2+} with bowl adamanzanes has been reported.[11–14] Recently we published syntheses, crystal structures and detailed thermodynamical and kinetic studies of a series of copper(II) complexes of the bowl amine [2⁴.3¹]adamanzane (Fig. 1).[15,16] In this paper we present syntheses and crystal structures of some nickel(II) complexes with [2⁴.3¹]adz. Abbreviations used for the amine ligands are given below.

Experimental

Abbreviations and nomenclature. The simplified nomenclature suggested for adamanzanes (bowls and cages) has been discussed recently:[15,17]

[2⁴.3¹]adz = [2⁴.3¹]adamanzane
   = 1,4,7,10-tetraazabicyclo[5.5.3]pentadecane
[2⁴.3²]adz = [2⁴.3²]adamanzane
   = 1,4,8,11-tetraazatricyclo[6.6.2.2⁴,¹¹]octadecane
[3⁵]adz = [3⁵]adamanzane
   = 1,5,9,13-tetraazabicyclo[7.7.3]nonadecane
[3⁶]adz = [3⁶]adamanzane
   = 1,5,9,13-tetraazatricyclo[7.7.3.3⁵,¹³]docosane
The structures of [2⁴.3¹]adz and [3⁵]adz are shown in Fig. 1.
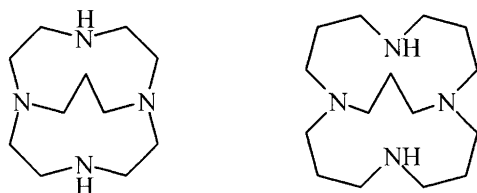
[2⁴.3¹]adamanzane   [3⁵]adamanzane

Fig. 1.

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Materials and instruments. $[H_3[2^4.3^1]adz]Br_3$ was synthesized as previously described.[9] All other chemicals were of analytical grade; and CO_2-free doubly deionized water was used for all measurements. A Cary 3 spectrophotometer was used for spectral measurements in the region 300–800 nm, and a Zeiss DMR 21 spectrophotometer for the region 800–1400 nm. IR spectra were recorded on a Perkin Elmer System 2000 FTIR spectrometer. For magnetic measurements a Johnson Matthey magnetic susceptibility balance (inverted Gouy balance) was used. Potentiometric pH measurements were performed using Metrohm equipment as described previously.[18] Cyclic voltammetry was performed using a glassy carbon working electrode, a Pt wire auxiliary electrode, and a Ag/AgCl reference electrode. A 5.06×10^{-3} M solution of the complex in 1 M $HClO_4$ was deoxygenated with Ar and measured at 20 °C. A scan rate of 100 mV/s was employed.

Calculations. Non-linear least-squares calculations for the determinations of the equilibrium and rate constants were performed using the program Origin from Microcal Software Inc., Northampton, USA.

Analyses. C, H and N analyses were made at the Microanalytical Laboratory, the H. C. Ørsted Institute, Copenhagen.

Syntheses. **Caution.** Mechanical handling or heating of perchlorates represent a potential danger. However, we have never experienced an explosion with the present compounds. Also it is noted that mixing of perchloric acid and organic solvents (e.g. ethanol) used for washing the samples should be avoided.

1. $[\{Ni([2^4.3^1]adz)\}_2(\mu\text{-}Br)_2]Br_2$. The preparation was carried out under N_2 to avoid contamination with water. A mixture of $[H_3[2^4.3^1]adz]Br_3$ (7.33 g, 16.1 mmol) and NaH dispersion (60% in mineral oil, 2.51 g, 62.8 mmol) in dry DMF (90 ml) in a two-necked flask equipped with an N_2 inlet and a drying tube was stirred and heated to 60 °C for about 1 h until no H_2 effervescence was observed. The solution was then added to a hot (ca. 60 °C) blue–green solution of $NiBr_2$ (3.52 g, 16.1 mmol) in dry DMF (40 ml) with stirring. The colour immediately changed to red and finally to purple. The mixture was stirred for an additional 30 min at 60 °C, then cooled to 5 °C, and HBr (47%, 2 ml) was added dropwise and with continued stirring. After cooling for 1 h a purple precipitate was filtered off, washed with a small volume of absolute ethanol, and dried at 60 °C for 15 min. Yield 6.26 g (90%). The product was purified by crystallisation as a perchlorate salt as described in the following preparation.

2. $[\{Ni([2^4.3^1]adz)\}_2(\mu\text{-}Br)_2](ClO_4)_2$. To a filtered solution of crude $[\{Ni([2^4.3^1]adz)\}_2(\mu\text{-}Br)_2]Br_2$ (300 mg, 0.7 mmol Ni) in water (2.4 ml) was added hydrobromic acid (47%, 0.5 ml) and then drop by drop perchloric acid (70%, 1.0 ml) with stirring, which led to

precipitation of the product. The mixture was left at room temperature overnight. The purple product was filtered off, washed with cold 1 M HBr/1 M $HClO_4$ (1 ml), then diethyl ether, and dried in the air. Yield 240 mg (76%) of a blue–purple powder. Calculated for $C_{11}H_{24}N_4BrClO_4Ni$: C, 29.33; H, 5.37; N, 12.44. Found: C, 29.61; H, 5.22; N, 12.50. IR: 3323 cm^{-1} [ν(N–H)], 1483 cm^{-1} [$\delta_s(CH_2)$], 1100, 626 cm^{-1} (ClO_4^-). The product is very soluble in water, slightly soluble in acetonitrile and nitromethane, but insoluble in nonpolar organic solvents such as diethyl ether or $CHCl_3$.

3. $[\{Ni([2^4.3^1]adz)\}_2(\mu\text{-}Cl)_2](ClO_4)_2$. To a filtered solution of $[\{Ni([2^4.3^1]adz)\}_2(\mu\text{-}Br)_2]Br_2$ (1.33 g, 3.09 mmol) in water (9.4 ml) was added hydrochloric acid (37%, 2.2 ml) and then drop by drop perchloric acid (70%, 2.6 ml) with stirring, which led to precipitation of the product. The mixture was left at room temperature overnight. The blue product was filtered off, washed with cold 1 M HCl/1 M $HClO_4$ (1 ml), then diethyl ether and dried at 60 °C for 20 min. Yield 1.06 g (85%) of a crystalline powder. Calculated for $C_{11}H_{24}N_4Cl_2O_4Ni$: C, 32.55; H, 5.96; N, 13.80. Found: C, 32.50; H, 5.77; N, 13.74. IR: 3334 cm^{-1} [ν(N–H)], 1483 cm^{-1} [$\delta_s(CH_2)$], 1100, 626 cm^{-1} (ClO_4^-). The product is very soluble in water, slightly soluble in acetonitrile and nitromethane, but insoluble in nonpolar organic solvents such as diethyl ether or $CHCl_3$. Crystals suitable for X-ray diffraction studies were grown by slow cooling to room temperature of a hot (90–100 °C) solution of the perchlorate salt (0.1 M) in aqueous 2 M HCl, 2 M $HClO_4$.

4. $[Ni([2^4.3^1]adz)(H_2O)_2](S_2O_6) \cdot 2H_2O$. To a filtered solution of crude $[\{Ni([2^4.3^1]adz)\}_2(\mu\text{-}Br)_2]Br_2$ (157 mg, 0.365 mmol) in H_2O (1.8 ml) was added finely powdered $Na_2S_2O_6 \cdot 2H_2O$ (265 mg, 1.10 mmol) at 80 °C with stirring, whereupon precipitation began. After heating for further 5 min the mixture was allowed to cool to room temperature. Pink crystals were filtered off, washed with a cold aqueous solution of 1 M $Na_2S_2O_6$ (1 ml), 50% ethanol, 96% ethanol and dried in the air. Yield 143 mg (78%) of a pink crystalline powder. Calculated for $C_{11}H_{32}N_4O_{10}S_2Ni$: C, 26.26; H, 6.41; N, 11.13. Found: C, 26.42; H, 6.15; N, 11.17. IR: 3510, 3401 cm^{-1} [ν(O–H)], 3298, 3187 cm^{-1} [ν(N–H)], 1478 cm^{-1} [$\delta_s(CH_2)$], 1238, 998, 580 cm^{-1} ($S_2O_6^{2-}$). The product is poorly soluble in water, better in 1 M $NaClO_4$ or $NaCF_3SO_3$, and nearly insoluble in organic solvents. Crystals suitable for X-ray crystallography were obtained by recrystallisation from hot water at a low concentration. The ligand-field spectrum of the diaqua species (1.00 M $NaCF_3SO_3$ at 25 °C) gave (ε/M^{-1}cm^{-1}, λ/nm)$_{max}$: (16, 880), (8.4, 529) and (8.4, 345).

5. $[Ni([2^4.3^1]adz)(NO_2)]ClO_4$. Pure $[\{Ni([2^4.3^1]adz)\}_2(\mu\text{-}Cl)_2](ClO_4)_2$ (122 mg, 0.3 mmol Ni) was dissolved in water (10 ml) at 80 °C. To the stirred purple solution was added a solution of $NaNO_2$ (138 mg, 2.0 mmol) in water (2 ml), whereupon the colour changed to pink. Then a saturated aqueous solu-

458

tion of $LiClO_4$ (0.5 ml) was added to the hot solution. Slow cooling to room temperature produced a red crystalline product, which was filtered off, washed with ethanol, diethyl ether and dried in the air. Yield 99 mg (79%). Calculated for $C_{11}H_{24}N_5ClNiO_6$: C, 31.72; H, 5.81; N, 16.82. Found: C, 31.91; H, 5.69; N, 16.73. IR: $3316\ cm^{-1}$ [v(N–H)], $1479\ cm^{-1}$ [$\delta_s(CH_2)$], $1208\ cm^{-1}$ [$v_s(NO_2)$], 1092, $624\ cm^{-1}$ (ClO_4^-). The ligand-field spectrum of the nitrito species was measured using a solution of [Ni($[2^4.3^1]$adz)(NO_2)]ClO_4 (0.014 M) in 0.32 M $NaNO_2$, 0.68 M $NaCF_3SO_3$ at 25 °C, which gave $(\varepsilon/M^{-1}\ cm^{-1}, \lambda/nm)_{max}$: (20, 840), (27, 504), the band expected for Ni^{2+} around 330 nm was obscured by a NO_2^- absorption band.

6. [Ni([2⁴.3¹]adz)(NO₂)]PF₆. To a filtered solution of crude [{Ni($[2^4.3^1]$adz)}$_2$(μ-Br)$_2$]Br$_2$ (86 mg, 0.2 mmol Ni) in water (8 ml) a solution of $NaNO_2$ (55 mg, 0.8 mmol) in water (0.5 ml) was added at 80 °C, followed by the dropwise addition of a solution of $NaPF_6$ (102 mg, 0.6 mmol) in water (1 ml). After cooling to room temperature, the pink product was collected by filtration, washed with 96% ethanol, and dried at 80 °C for 10 min. Yield 49 mg (53%). Calculated for $C_{11}H_{24}N_5F_6NiO_2P$: C, 28.60; H, 5.24; N, 15.16. Found: C, 28.87; H, 5.16; N, 15.11. Recrystallisation from hot water (10 mg in 0.7 ml, slow cooling) gave red crystals suitable for X-ray structure determination.

7. [Ni([2⁴.3¹]adz)(NO₃)]ClO₄. To a solution of [{Ni($[2^4.3^1]$adz)}$_2$(μ-Cl)$_2$](ClO_4)$_2$ (81 mg, 0.2 mmol Ni) in water (1.5 ml) was added a solution of $NaNO_3$ (595 mg, 7.0 mmol) in H_2O (1.2 ml). The pink solution was stirred and heated to 100 °C for 5 min, then filtered while hot. To the hot filtrate was added a saturated aqueous solution of $NaClO_4$ (0.6 ml) and the solution was allowed to cool to room temperature. Pink crystals were filtered off, washed with diethyl ether and dried in the air. Yield 71 mg (82%). Calculated for $C_{11}H_{24}N_5ClNiO_7$: C, 30.55; H, 5.59; N, 16.19; Found: C, 28.59; H, 5.10; N, 15.37. Though the sample was finely ground and dried, no better agreement with the calculated values could be achieved. However, the experimentally determined ratios C/N = 2.170 and H/C = 2.126, respectively, agree with the calculated ratios C/N = 2.200 and H/C = 2.182. IR: 3300, $3146\ cm^{-1}$ [v(N–H)], 1510, $1276\ cm^{-1}$ [v(NO_3)], $1476\ cm^{-1}$ [$\delta_s(CH_2)$], 1089, $625\ cm^{-1}$ (ClO_4^-). By cooling the reaction solution very slowly crystals suitable for X-ray structure determination could be obtained. The ligand-field spectrum of the nitrato species was calculated using the spectrum of [Ni($[2^4.3^1]$adz)(NO_3)]ClO_4 in 1.00 M $NaNO_3$ and the spectrum of Ni($[2^4.3^1]$adz)(H_2O)$_2^{2+}$ in 1 M $NaCF_3SO_3$ using the equilibrium constant $K(NO_3^-)$ (see Results) and this gave $(\varepsilon/M^{-1}\ cm^{-1}, \lambda/nm)_{max}$: (21, 840), (26, 510) and (43, 333).

8. Ni₃([2⁴.3¹]adz)₃(CO₃)(H₂O)₃(ClO₄)₄. To a solution of [{Ni($[2^4.3^1]$adz)}$_2$(μ-Cl)$_2$](ClO_4)$_2$ (27 mg, 0.06 mmol Ni) in water (3 ml) were added 1 M NaOH (0.3 ml) and saturated $NaClO_4$ (0.1 ml) and the purple

solution was allowed to take up CO_2 from the air. Within a period of 2 weeks pink–purple crystals formed and were collected by filtration, washed with 96% ethanol and dried in the air. Yield 16 mg (60%). Calculated for $C_{34}H_{78}N_{12}Cl_4Ni_3O_{22}$: C, 30.82; H, 5.93; N, 12.69. Found: C, 30.98; H, 5.64; N, 12.45. IR: $3437\ cm^{-1}$ [v(O–H)], 3340, $3228\ cm^{-1}$ [v(N–H)], 1520, $1392\ cm^{-1}$ [$v_{as}(CO_3)$], $1478\ cm^{-1}$ [$\delta_s(CH_2)$], 1120, 1090, 626 cm^{-1} (ClO_4^-). The complex could also be obtained by adding 1/3 equiv. of Na_2CO_3 to a solution of [{Ni($[2^4.3^1]$adz)}$_2$(μ-Cl)$_2$](ClO_4)$_2$ in 1 M NaOH, 1 M $NaClO_4$. This sample exhibits an infrared spectrum which is identical to that obtained from the product above.

9. [{Ni([2⁴.3¹]adz)}₂(C₂O₄)]Br₂. A filtered solution of crude [{Ni($[2^4.3^1]$adz)}$_2$(μ-Br)$_2$]Br$_2$ (172 mg, 0.4 mmol Ni) in H_2O (2.5 ml) was heated to ca. 95 °C followed by addition of a solution of $K_2C_2O_4 \cdot H_2O$ (92 mg, 0.5 mmol) in H_2O (0.5 ml) with stirring. After 10 min the mixture was allowed to cool to room temperature and the product was filtered off, washed with ethanol and dried at 60 °C for 30 min. Yield 129 mg (82%) pink needles. The complex has a low solubility in cold water. Calculated for $C_{24}H_{48}N_8Br_2Ni_2O_4$: C, 36.49; H, 6.13; N, 14.19. Found: C, 36.61; H, 6.04; N, 14.06. IR: 3218, $3186\ cm^{-1}$ [v(N–H)], $1646\ cm^{-1}$ [$v_{as}(C–O)$], $1478\ cm^{-1}$ [$\delta_s(CH_2)$], 794, $482\ cm^{-1}$ [δ(O–C–O)].

X-Ray techniques. Crystal data for the compounds are listed in Table 1. The crystals of the three mononuclear compounds were cooled to 120 K using a Cryostream nitrogen gas cooler system.[19] The crystals of [{Ni($[2^4.3^1]$adz)}$_2$(μ-Cl)$_2$](ClO_4)$_2$ were damaged when cooled to 120 K. The data were collected on a Siemens SMART Platform diffractometer with a CCD area-sensitive detector. The intensities were corrected for Lorenz, polarization and absorption effects. The structures were solved by direct methods and refined by the full-matrix least-squares technique. The counter anions of the structures, except for [Ni($[2^4.3^1]$adz)(NO_2)]PF_6, are disordered. The non-hydrogen atoms were refined anisotropically. The hydrogen atoms of the compounds [Ni($[2^4.3^1]$adz)(H_2O)$_2$]$S_2O_6 \cdot 2H_2O$ and [Ni($[2^4.3^1]$adz)(NO_3)]ClO_4 were all located from electron-density difference maps and refined isotropically. The hydrogen atoms of the other two structures were all at calculated positions using a riding model with fixed thermal parameters [U(H) = 1.2 × U for attached atom]. The space group $C2/c$ was assumed in all calculations in three of the structures. The refinements confirmed that this choice was correct. The scattering factors were taken from the literature.[20] Programs used for data collection, data reduction and absorption were SMART, SAINT and SADABS.[21,22] The program SHELXTL 95[23] was used to solve the structures and for molecular graphics. PLATON[24] was used for molecular geometry calculations. The atomic coordinates and further crystallo-

Table 1. Crystal data for the four compounds [L = ([2⁴.3¹]adz)].

Crystal data	[{NiL}₂(μ-Cl)₂](ClO₄)₂	[NiL(H₂O)₂]S₂O₆ · 2H₂O	[NiL(NO₂)]PF₆	[NiL(NO₃)]ClO₄
	All data were collected on a SMART CCD diffractometer using Mo Kα radiation ($\lambda = 0.71073$ Å)			
Formula	$C_{22}H_{48}Cl_4N_8Ni_2O_8$	$C_{11}H_{32}N_4NiO_{10}S_2$	$C_{11}H_{24}F_6N_5NiO_2P$	$C_{11}H_{24}ClN_5NiO_7$
MW	405.95	503.24	462.03	432.51
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$C2/c$	$C2/c$	$C2/c$	$Pbca$
a/Å	11.328(2)	17.064(3)	26.3649(8)	14.586(3)
b/Å	12.713(3)	16.537(3)	8.9488(3)	14.973(3)
c/Å	22.794(5)	15.372(3)	30.7694(10)	15.218(3)
β/°	101.42(3)	111.77(3)	102.3280(10)	–
V/Å³	3217.6(11)	4028.5(14)	7092.2(4)	3323.5(11)
Z	4	8	16	8
$F(000)$	1696	2128	3808	1808
D_x/g cm⁻³	1.676	1.659	1.731	1.729
Linear absorption coefficient/mm⁻¹	1.560	1.228	1.262	1.376
Temperature, T/K	296	120	120	120
Crystal description	Violet	Violet, old rose	Pale pink	Pink
Crystal size/mm	0.05 × 0.13 × 0.15	0.08 × 0.23 × 0.25	0.03 × 0.08 × 0.21	0.10 × 0.10 × 0.23
θ-Range/°	1.82–27.00	1.78–29.52	1.35–29.61	2.36–29.70
Range of h	−17–16	−23–22	−35–23	−13–19
Range of k	−16–19	−22–15	−11–12	−17–19
Range of l	−28–34	−19–20	−40–42	−20–20
Measured reflections	17 433	13 758	22 781	17 851
Total no. of unique reflections	3516	5110	8946	4295
Observed reflections [$I > 2\sigma(I)$]	2334	4360	4509	3331
R (int)	0.0764	0.0212	0.0987	0.0416
Corrections	Lorenz, polarization and absorption	Lorenz, polarization and absorption	Lorenz, polarization and absorption	Lorenz, polarization and absorption
Transmission factors	1.0000–0.2648	1.0000–0.8383	1.0000–0.7364	1.0000–0.8448
Minimization of:	$\Sigma w(|F_o|^2 - |F_c|^2)^2$	$\Sigma w(|F_o|^2 - |F_c|^2)^2$	$\Sigma w(|F_o|^2 - |F_c|^2)^2$	$\Sigma w(|F_o|^2 - |F_c|^2)^2$
Anisotropic thermal parameters	All non-hydrogen atoms	All non-hydrogen atoms	All non-hydrogen atoms	All non-hydrogen atoms
Isotropic thermal parameters	Hydrogen atoms (pos. cal.; $U = 1.2 \times U$ for attached atom)	Hydrogen atoms	Hydrogen atoms (pos. cal.; $U = 1.2 \times U$ for attached atom)	Hydrogen atoms
No. of refined parameters	212	388	471	329
Weighting scheme	[$\sigma^2(F^2_o) + (0.0870P)^2 + 16.8980P]^{-1}$, $P = (F_o^2 + 2F_c^2)/3$	[$\sigma^2(F^2_o) + (0.0256P)^2 + 5.3834P]^{-1}$, $P = (F_o^2 + 2F_c^2)/3$	[$\sigma^2(F^2_o) + (0.0105P)^2 + 20.0953P]^{-1}$, $P = (F_o^2 + 2F_c^2)/3$	[$\sigma^2(F^2_o) + (0.0282P)^2 + 6.8798P]^{-1}$, $P = (F_o^2 + 2F_c^2)/3$
R (obs. data)[a]	0.0671	0.0275	0.0689	0.0409
wR (all data)[b]	0.1865	0.0678	0.1222	0.0916
S^c	1.067	1.059	1.048	1.059
Final $(\Delta/\sigma)_{max}$	0.131	0.061	0.122	0.089
Final $\Delta\rho_{min}$ and $\Delta\rho_{max}$/e Å⁻³	−0.785 and 1.531 less than 1 Å from Ni	−0.468 and 0.481 less than 1 Å from Ni and O(3)	−0.653 and 1.026 about 1 Å from C(10A)	−0.499 and 0.979 less than 1 Å from Cl and C(10)

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $wR2 = [\Sigma w|F^2_o - F^2_c|^2/\Sigma wF_o^4]^{1/2}$. [c] $S = [\Sigma w(|F_o|^2 - |F_c|^2)^2/(N_{obs} - N_{var})]^{1/2}$.

graphic details may be obtained from one of the authors (I.S.) on request.

Results and discussion

Synthesis of the complexes. The monoprotonated form of the bowl amine H[2⁴.3¹]adz⁺ is a very weak acid ($pK_a > 15$)[9] and replacement of the inside bound proton with a metal ion is therefore thermodynamically and possibly also kinetically hindered. In the case of Cu^{II} it

was found[15] that heating a mixture of $Cu(NH_3)_4^{2+}$ and H[2⁴.3¹]adz⁺ in an ammonia/ammonium buffer solution leads to a high yield of $Cu([2^4.3^1]adz)(H_2O)^{2+}$. Several attempts using this method for nickel(II) failed. Instead it was found that heating anhydrous nickel(II) bromide in DMF with the free ligand, made *in situ* by deprotonation using sodium hydride, affords a dibromo-bridged dinuclear species which was isolated as a crude bromide salt in high yield. This bromide salt has a purity suitable for further synthetic work. An analytically pure

compound was obtained as a perchlorate salt, [{Ni([2⁴.3¹]adz)}₂(μ-Br)₂](ClO₄)₂. Treatment of the crude bromide salt with hydrochloric acid affords the corresponding dichloro-bridged dinuclear species, which was isolated as a pure perchlorate salt, [{Ni([2⁴.3¹]adz)}₂(μ-Cl)₂](ClO₄)₂. The structure of the dichloro-bridged species was established by a crystal structure determination. Comparison of the IR data for the two species strongly suggests that the bromo complex also has a di-bridged structure. The values of the magnetic moments for the bromo and chloro complexes (3.15μ_B and 3.08μ_B, respectively, 296 K) are as expected[25] for octahedral high-spin Ni^{II}, indicating that there is no magnetic coupling between the two Ni^{II} centers.

In dilute aqueous solution both dinuclear species form the corresponding mononuclear diaqua species as illustrated in Scheme 1. The aqua complex was isolated from the crude dibromide as [Ni([2⁴.3¹]adz)(H₂O)₂]S₂O₆ · 2H₂O in a relatively high yield and its structure was established as described below.

Several complexes have been synthesized from the diaqua species, which for practical reasons was always made *in situ* from either the dibromo- or dichloro-bridged species. Reaction with nitrate affords a chelate coordinated nitrato complex isolated as a perchlorate salt and similarly reaction with nitrite gives a chelate coordinated nitrito complex isolated as a perchlorate salt and as a hexafluorophosphate salt. The crystal structures of [Ni([2⁴.3¹]adz)(NO₃)]ClO₄ and [Ni([2⁴.3¹]adz)(NO₂)]PF₆ are described below.

Reaction with oxalate gives a salt analyzing as [{Ni([2⁴.3¹]adz)}₂(C₂O₄)]Br₂, thus indicating that in the solid two Ni^{II} ions are bound to one oxalate ion, which is in agreement with the infrared data.

Finally, with carbonate a complex analyzing for three Ni^{II} per carbonate was isolated as a perchlorate salt; however, the structure has not yet been established.
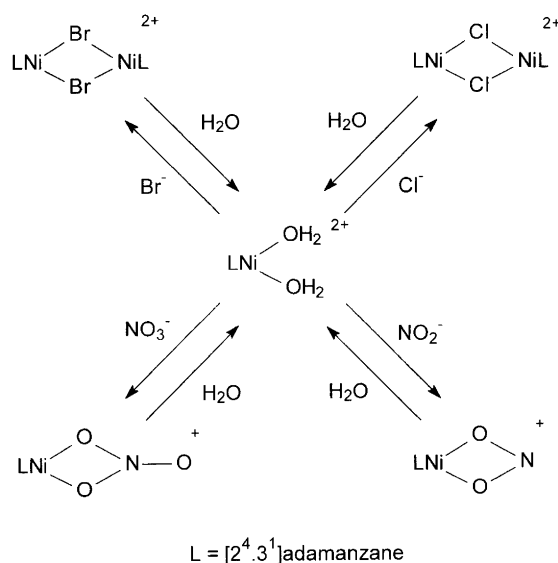
Crystal structures of [{Ni([2⁴.3¹]adz) }₂(μ-Cl)₂](ClO₄)₂, [Ni([2⁴.3¹]adz)(H₂O)₂]S₂O₆ · 2H₂O, [Ni([2⁴.3¹]adz)- (NO₂)]PF₆ and [Ni([2⁴.3¹]adz)(NO₃)]ClO₄. Selected bond lengths and bond angles are given in Table 2. The labelling of the atoms in the cations are shown in Figs. 2–5. The cation of [{Ni([2⁴.3¹]adz)}₂(μ-Cl)₂](ClO₄)₂ is dimeric containing a crystallographic centre of symmetry, whereas the other cations are monomers. In [Ni([2⁴.3¹]adz)(NO₂)]PF₆ the two independent cations are almost identical. The angles around the nickel atoms show distorsions with respect to those of a regular octahedron. In the Ni([2⁴.3¹]adz)(NO₂)$^+$ and Ni([2⁴.3¹]adz)(NO₃)$^+$ ions the equatorial N(2)–Ni–N(4) angles are in the range 98.46(8)–99.0(2)° and the axial N(1)–Ni–N(3) angles are in the range 170.0(2)–170.6(2)°. In the {Ni([2⁴.3¹]adz)}₂(μ-Cl)₂$^{2+}$ and Ni([2⁴.3¹]adz)(H₂O)₂$^+$ ions the N(2)–Ni–N(4) angles are 94.3(2) and 94.88(5)° and the N(1)–Ni–N(3) angles 166.2(2) and 168.43(5)°, respectively. The larger N(2)–Ni–N(4) angles of the Ni([2⁴.3¹]adz)(NO₂)$^+$ and Ni([2⁴.3¹]adz)(NO₃)$^+$ ions are due to the O(1)–Ni–O(2) angles of 59.1(2)–60.54(7), which are smaller than the Cl(1)–Ni–Cl(2) angle of 75.91(6), and the O(1)–Ni–O(2) angle of 82.07(5)° found in {Ni([2⁴.3¹]adz)}₂(μ-Cl)₂$^{2+}$ and Ni([2⁴.3¹]adz)(H₂O)₂$^+$, respectively. In the {Ni([2⁴.3¹]adz)}₂(μ-Cl)₂$^{2+}$ ion the Ni–N bond lengths vary as much as 0.06 Å, whereas in
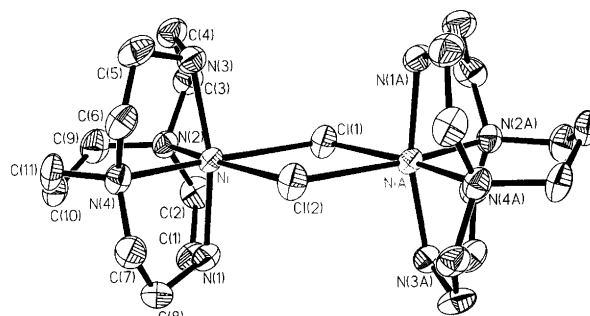
Fig. 2. View of the cation in [{Ni([2⁴.3¹]adz)}₂(μ-Cl)₂](ClO₄)₂. In this and the following three figures thermal ellipsoids are drawn at the 50% probability level, and H atoms are omitted for clarity.

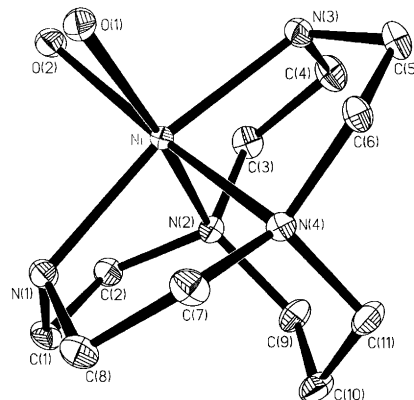*Fig. 3.* View of the cation in [Ni([2⁴.3¹]adz)(H₂O)₂]S₂O₆ · 2H₂O.

L = [2⁴.3¹]adamanzane

Scheme 1.

Table 2. Selected bond lengths (in Å) and bond angles (in °).

[{Ni ([2⁴.3¹]adz)}₂(μ-Cl)₂](ClO₄)₂

Ni–N(3)	2.040(5)	Ni–N(2)	2.104(5)
Ni–N(1)	2.043(4)	Ni–Cl(2)	2.550(2)
Ni–N(4)	2.102(5)	Ni–Cl(1)	2.551(2)
N(3)–Ni–N(1)	166.2(2)	N(4)–Ni–Cl(2)	94.99(14)
N(3)–Ni–N(4)	85.5(2)	N(2)–Ni–Cl(2)	170.51(13)
N(1)–Ni–N(4)	85.2(2)	N(3)–Ni–Cl(1)	94.95(14)
N(3)–Ni–N(2)	85.4(2)	N(1)–Ni–Cl(1)	95.92(14)
N(1)–Ni–N(2)	85.2(2)	N(4)–Ni–Cl(1)	170.88(14)
N(4)–Ni–N(2)	94.3(2)	N(2)–Ni–Cl(1)	94.77(14)
N(3)–Ni–Cl(2)	97.04(14)	Cl(2)–Ni–Cl(1)	75.91(6)
N(1)–Ni–Cl(2)	93.90(13)		

[Ni([2⁴.3¹]adz)(H₂O)₂]S₂O₆ · 2H₂O

Ni–N(1)	2.0610(14)	Ni–N(2)	2.0948(13)
Ni–N(3)	2.0655(14)	Ni–O(2)	2.1219(12)
Ni–N(4)	2.0771(13)	Ni–O(1)	2.1295(12)
N(1)–Ni–N(3)	168.43(5)	N(4)–Ni–O(2)	172.44(5)
N(1)–Ni–N(4)	86.80(5)	N(2)–Ni–O(2)	92.58(5)
N(3)–Ni–N(4)	85.36(5)	N(1)–Ni–O(1)	90.80(5)
N(1)–Ni–N(2)	85.92(6)	N(3)–Ni–O(1)	97.76(6)
N(3)–Ni–N(2)	86.29(6)	N(4)–Ni–O(1)	90.56(5)
N(4)–Ni–N(2)	94.88(5)	N(2)–Ni–O(1)	173.47(5)
N(1)–Ni–O(2)	94.96(5)	O(2)–Ni–O(1)	82.07(5)
N(3)–Ni–O(2)	93.93(5)		

[Ni([2⁴.3¹]adz)(NO₂)]PF₆

Ni(1)–N(4)	2.038(4)	Ni(2)–N(2A)	2.038(4)
Ni(1)–N(2)	2.038(4)	Ni(2)–N(4A)	2.042(4)
Ni(1)–N(1)	2.047(4)	Ni(2)–N(1A)	2.046(4)
Ni(1)–N(3)	2.051(4)	Ni(2)–N(3A)	2.052(4)
Ni(1)–O(2)	2.113(4)	Ni(2)–O(1A)	2.128(3)
Ni(1)–O(1)	2.126(4)	Ni(2)–O(2A)	2.134(3)
N(4)–Ni(1)–N(2)	99.0(2)	N(2A)–Ni(2)–N(4A)	98.6(2)
N(4)–Ni(1)–N(1)	86.5(2)	N(2A)–Ni(2)–N(1A)	86.7(2)
N(2)–Ni(1)–N(1)	86.5(2)	N(4A)–Ni(2)–N(1A)	86.5(2)
N(4)–Ni(1)–N(3)	87.0(2)	N(2A)–Ni(2)–N(3A)	87.7(2)
N(2)–Ni(1)–N(3)	86.9(2)	N(4A)–Ni(2)–N(3A)	86.9(2)
N(1)–Ni(1)–N(3)	170.0(2)	N(1A)–Ni(2)–N(3A)	170.6(2)
N(4)–Ni(1)–O(2)	100.6(2)	N(2A)–Ni(2)–O(1A)	100.37(15)
N(2)–Ni(1)–O(2)	160.4(2)	N(4A)–Ni(2)–O(1A)	160.86(15)
N(1)–Ni(1)–O(2)	95.2(2)	N(1A)–Ni(2)–O(1A)	92.06(15)
N(3)–Ni(1)–O(2)	93.4(2)	N(3A)–Ni(2)–O(1A)	96.41(15)
N(4)–Ni(1)–O(1)	159.7(2)	N(2A)–Ni(2)–O(2A)	159.55(15)
N(2)–Ni(1)–O(1)	101.3(2)	N(4A)–Ni(2)–O(2A)	101.83(15)
N(1)–Ni(1)–O(1)	94.3(2)	N(1A)–Ni(2)–O(2A)	93.6(2)
N(3)–Ni(1)–O(1)	94.5(2)	N(3A)–Ni(2)–O(2A)	94.3(2)
O(2)–Ni(1)–O(1)	59.1(2)	O(1A)–Ni(2)–O(2A)	59.18(13)

[Ni([2⁴.3¹]adz)(NO₃)]ClO₄

Ni–N(2)	2.035(2)	Ni–N(1)	2.055(2)
Ni–N(4)	2.039(2)	Ni–O(1)	2.138(2)
Ni–N(3)	2.051(2)	Ni–O(2)	2.146(2)
N(2)–Ni–N(4)	98.46(8)	N(3)–Ni–O(1)	95.01(9)
N(2)–Ni–N(3)	86.60(9)	N(1)–Ni–O(1)	93.29(9)
N(4)–Ni–N(3)	87.08(9)	N(2)–Ni–O(2)	98.98(8)
N(2)–Ni–N(1)	87.48(8)	N(4)–Ni–O(2)	162.56(8)
N(4)–Ni–N(1)	86.01(9)	N(3)–Ni–O(2)	93.87(9)
N(3)–Ni–N(1)	170.14(9)	N(1)–Ni–O(2)	94.83(8)
N(2)–Ni–O(1)	159.51(8)	O(1)–Ni–O(2)	60.54(7)
N(4)–Ni–O(1)	102.02(8)		
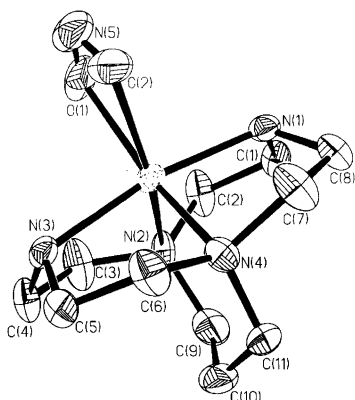
Fig. 4. View of the cation in [Ni([2⁴.3¹]adz)(NO₂)]PF₆.
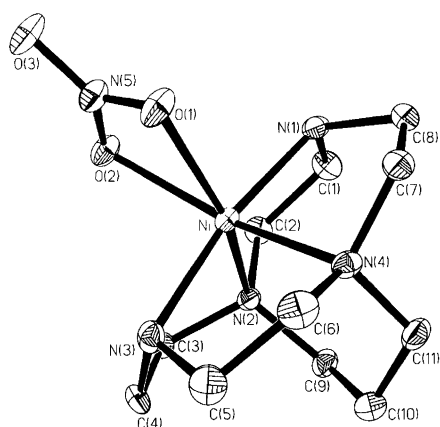
Fig. 5. View of the cation in [Ni([2⁴.3¹]adz)(NO₃)]ClO₄.

the three other complex ions the variations are less than 0.04 Å. The conformation of the ligand in all the cations is the same and similar to the conformations in the Cu([2⁴.3¹]adz)Br⁺ and the {Cu([2⁴.3¹]adz)}₃(μ₃-CO₃)⁴⁺ complexes.[15,16] In the 12-membered ring the eight carbon atoms are nearly coplanar, with N(1) and N(3) about 0.7 Å above and N(2) and N(4) about 0.5 Å below the plane. The ring has an approximate *mm* symmetry with respect to the two planes through Ni, N(1), N(3) and Ni, N(2), N(4). The N(2)–N(4) distances between the bridgehead nitrogen atoms are in the range 3.07–3.10 Å and the N(1)–N(3) distances are 4.05–4.10 Å. In the [Cu([2⁴.3¹]adz)Br]⁺ and the {Cu([2⁴.3¹]adz)}₃(μ₃-CO₃)⁴⁺ ions the N(2)–N(4) distances are 3.16(1) and 3.164(10) Å, whereas the N(1)–N(3) distances are 3.97(1) and 3.969(6) Å, respectively.[15,16]

In all four Ni complex ions the two 10-membered rings in the ligand both have approximate *m* symmetry with respect to the plane through N(1), Ni, C(10) and through N(3), Ni, C(10), respectively. The six-membered chelate ring has a half boat conformation, and all five-membered chelate rings are in a twist form.

The crystal packing of the structures are influenced by hydrogen bonds. In [{Ni([2⁴.3¹]adz)}₂(μ-Cl)₂](ClO₄)₂ N(1) and N(3) are hydrogen bonded to O(1) of the ClO₄⁻ ions. The hydrogen bonds (D–A) are 3.08–3.16 Å.

In [Ni([2⁴.3¹]adz)(NO₂)]PF₆ the hydrogen bonds between the cations and the PF₆⁻ ions are in the range 3.05–3.13 Å. In [Ni([2⁴.3¹]adz)(H₂O)₂]S₂O₆·2H₂O the shortest hydrogen bonds are between the water ligands and the water molecules. They are 2.67–2.70 Å. In [Ni([2⁴.3¹]adz)(NO₃)]ClO₄ the hydrogen bonds between the cations and the ClO₄⁻ ions are in the range 3.05–3.21 Å.

Equilibrium constants. In aqueous solution both the nitrato and the nitrito complexes give an equilibrium mixture with the parent diaqua complex, which is a weak acid, $pK_a > 6$.

$$Ni([2^4.3^1]adz)(H_2O)_2^{2+} + X^-$$

$$\xrightleftharpoons{K(X^-)} Ni([2^4.3^1]adz)X^+ + 2H_2O \quad (1)$$
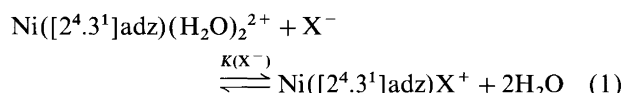
The concentration equilibrium constants $K(X^-)$ were determined as described[15] for Cu^{II} complexes with [2⁴.3¹]adz by spectrophotometric studies in the wavelength region 300–900 nm. This gave $K(NO_2^-) = 3.8(2) \times 10^2$ M^{-1} and $K(NO_3^-) = 2.5(3)$ M^{-1} [25 °C, $I = 1.0$ M using Na(CF₃SO₃,NO₂) and Na(CF₃SO₃,NO₃), respectively]. Spectral data for the nitrato and nitrito complexes, respectively, are given in the Experimental section. The observation that nitrite coordinates about 10^2 times better than nitrate corresponds to the lower acidity of HNO₂ compared to HNO₃.

Acid hydrolysis. In concentrated hydrochloric acid the present Ni^{II} complexes undergo hydrolysis of the bowl amine as illustrated in eqn. (2). for the diaqua complex.

$$Ni([2^4.3^1]adz)(H_2O)_2^{2+} + 3H^+ + 4H_2O$$

$$\xrightarrow{k_{cleavage}} Ni(H_2O)_6^{2+} + H_3[2^4.3^1]adz^{3+} \quad (2)$$
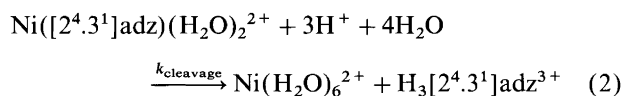
The visible absorption spectra of the reactant solution showed that the aqua complex is the dominant species in 5 M HCl, but the presence of minor amounts of chloro species can not be excluded. The reaction in 5 M HCl at 80 °C was studied spectrophotometrically in the region 300–870 nm. The change of absorption with time followed the expression for a first-order reaction, and $k_{cleavage} = 2.0(2) \times 10^{-6}$ s^{-1}. The cleavage of Ni(cyclam)$^{2+}$, which is reported to be extremely slow at room temperature,[27] was investigated in this study in 5 M HCl (80 °C) and this gave $k_{cleavage} = 2.3(3) \times 10^{-3}$ s^{-1}. Thus, the adamanzane complex is cleaved about 10^3 times slower than the cyclam complex. The additional inertness can be attributed to the rigid framework of the bowl-shaped ligand, which hinders dissociation of a protonated nitrogen donor atom. The hydrolysis of Cu([2⁴.3¹]adz)(H₂O)$^{2+}$ in 5 M HCl has been studied[15,26] at 25 and 40 °C, and by extrapolation it is calculated that $k_{cleavage} = 4.5 \times 10^{-4}$ s^{-1} at 80 °C. The nickel(II) complex therefore reacts more than 200 times slower than the copper complex, which follows the generally more labile character of copper(II) complexes relative to Ni^{II}. A better accessibility in the five-coordinate copper(II) complex for attack of protons compared to the

six-coordinate nickel(II) complex might also contribute to the observed difference in reactivity.

Cyclic voltammetry. Cyclic voltammetry of $\{Ni([2^4.3^1]adz)(H_2O)_2\}S_2O_6 \cdot 2H_2O$ was carried out in strongly acidic solution (1 M $HClO_4$) in order to suppress water oxidation. The voltammogram obtained with a scan rate of 100 mV/s and an Ag/AgCl reference electrode showed a quasi-reversible redox behaviour for the couple Ni^{II}/Ni^{III} with a peak separation of $\Delta E = 83$ mV and a halfwave potential of $E_{1/2} = 1.07$ V. The quasi-reversibility shows that no fast decomposition reactions of the formed Ni^{III} complex occur, although attempts to isolate a Ni^{III} complex failed. The observed potential of $E_{1/2} = 1.07$ V is very high compared to the potentials of macrocyclic nickel(II)/(III) couples: Reported values[28] for octahedral $Ni([9]aneN_3)_2^{2+/3+}$ and $Ni([16]aneN_5)(H_2O)^{2+/3+}$ ($[9]aneN_3 = 1,4,7$-triaza-cyclononane and $[16]aneN_5 = 1,4,7,10,13$-pentaazacyclohexadecane) are 0.72 and 0.79 V, respectively (in 3.5 M $NaClO_4$, pH 2, relative to Ag/AgCl).

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