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Thermodynamic and structural study of coordination of the monodentate ligand ammonia in a square-planar nickel(II) complex with a tridentate amine

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Abstract

The octahedral nickel(II) complex of the tridentate ligand dachen (*N*-(2-aminoethyl)-1,4-diazacycloheptane), $[Ni(dachen)(H_2O)_3]^{2+}$, reacts with ammonia to yield the square-planar complex $[Ni(dachen)(NH_3)]^{2+}$, a rare example of coordination of the monodentate ammine ligand in a low-spin nickel(II) complex. The structure of $[Ni(dachen)(NH_3)](ClO_4)_2$ was determined by X-ray diffraction. Crystal data: orthorhombic space group *Pbca*, $a=13.402(3)$, $b=13.625(4)$, $c=17.118(4)$ Å, $V=3125.8(16)$ Å^3, $Z=8$. The structure was solved by direct methods and was refined to $R=0.053$. The stability constant of $[Ni(dachen)(NH_3)]^{2+}$ was determined by a spectrophotometric method. The log *K* value for addition of ammonia to $[Ni(dachen)(H_2O)_3]^{2+}$ to form square-planar $[Ni(dachen)(NH_3)]^{2+}$ was found to be 3.3 ± 0.1, an estimated 1.6 log units greater than for binding of ammonia in an analogous high-spin nickel(II) complex.

Introduction

Some time ago one of us reported [1] the synthesis of the tridentate ligand dachen (*N*-(2-aminoethyl)-1,4-diazacycloheptane) and the formation constants of its complexes with Cu(II) and Ni(II). Complexes of this ligand are of interest because the ligand, incorporating a mesocyclic diamine, is one of a class of ligands which have been termed ‘structurally reinforced’ [2]. Multiple bridging between donor atoms produces more rigid ligands which display increased stability and enhanced selectivity toward metal ion binding.

Like other polyamine ligands with steric bulk disposed above and below the plane of the complex, dachen stabilizes low-spin, square-planar nickel(II). In aqueous solution, the octahedral Ni(II) complex of dachen ionizes a proton from a coordinated water molecule to form the square-planar hydroxo complex (eqn. (1), $pK_a=8.84$ [1]) as evidenced by appearance of a band in the visible spectrum at 463 nm, characteristic of square-planar nickel(II) complexes. This high-spin to low-spin interconversion in solution involving nickel(II) complexed by a tridentate and hydroxide ion is extremely rare and to our knowledge has been observed previously only in the case of the complex of nickel(II) with glycylglycinamide [3].

$$\underset{\text{octahedral}}{[Ni(dachen)(H_2O)_3]^{2+}} \rightleftharpoons \underset{\text{square-planar}}{[Ni(dachen)(OH)]^{+}} + H^{+} + 2H_2O \qquad (1)$$

We now report the structure of the analogous complex involving ammonia as the monodentate ligand. Nickel(II)–nitrogen bond distances have been measured in a number of octahedral and square-planar complexes of linear and macrocyclic polyamines; the strain-free distance has been estimated by several workers to be 2.10 Å for high-spin nickel(II) and 1.89 Å for low-spin nickel(II) [4]. It was of interest to us to provide an example of low-spin nickel(II)–ammonia bond length, in a similar polyamine complex, for comparison. In addition, we report the binding constant of ammonia

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to the nickel(II) complex (eqn. (2)). We believe that this is the first measurement of the binding constant

$$\underset{\text{octahedral}}{[\mathrm{Ni(dachen)(H_2O)_3}]^{2+}} + \mathrm{NH_3} \rightleftharpoons \underset{\text{square-planar}}{[\mathrm{Ni(dachen)(NH_3)}]^{2+}} + 3\mathrm{H_2O} \qquad (2)$$

in aqueous solution of the monodentate ligand ammonia in a square-planar nickel(II) complex of a polyamine ligand. The difference between the binding constant of ammonia to low-spin nickel(II), and ammonia to high-spin nickel(II) (of which there are many examples), is also of interest; it was expected that the binding constant to low-spin nickel(II) would be significantly larger than that to high-spin nickel(II).

Experimental

The ligand was synthesized as described previously [1] and isolated as the trihydrobromide salt. The salt was recrystallized repeatedly from HBr solution until free from contamination by the disubstituted ligand, as demonstrated by pH titration. Nickel perchlorate and sodium perchlorate were recrystallized repeatedly; solutions were standardized as previously described [5].

Absorbance measurements were made using Cary 14, Cary 2300 or Perkin–Elmer Lambda 3B spectrophotometers. The complex $[\mathrm{Ni(dachen)(NH_3)}]^{2+}$ has $\lambda_{max} = 448$ nm, $\epsilon = 93$. The hydroxo complex $[\mathrm{Ni(dachen)(OH)}]^+$ has $\lambda_{max} = 463$ nm, $\epsilon = 95$ [1].

Equilibrium constant determination

For determination of the binding constant (eqn. (2)), solutions of the nickel(II) complex were prepared by mixing stoichiometric amounts of a solution of the ligand trihydrobromide, nickel(II) perchlorate solution and 3 equiv. of sodium hydroxide solution. In some experiments aliquots of an ammonia solution (standardized by acid–base titration) were added to the complex solution by means of a calibrated Gilmont micrometer syringe; absorbance and pH of the solution were recorded after each addition. In other experiments ammonium chloride solution was added to the complex solution and the pH adjusted by addition of sodium hydroxide solution. Experimental conditions were: $[\mathrm{Ni}]_T = 2.4$ or 4.0 mM, $[\mathrm{NH_3}]_T = 4.5$ to 40 mM (titration experiments), 20 mM (ammonium chloride experiments). The pH range of the measurements was 7.7–9.4. All measurements were carried out on solutions adjusted to ionic strength 0.10 with sodium perchlorate and thermostatted to 25 °C. Measurements of pH were converted to hydrogen ion concentration by means of the equation $-\log [\mathrm{H}^+] = \mathrm{pH} - 0.10$ [5].

X-ray crystallography

Yellow crystals of $[\mathrm{Ni(dachen)(NH_3)}](\mathrm{ClO_4})_2$ suitable for X-ray analysis were prepared by evaporation of an aqueous solution of $[\mathrm{Ni(dachen)(NH_3)}]^{2+}$ to which excess $\mathrm{NaClO_4}$ had been added. *Anal.* Found: C, 20.36; H, 4.61; N, 13.78. Calc.: C, 20.12; H, 4.82; N, 13.41%. A total of 2301 reflections was collected in the range $3.5 < 2\theta < 47°$ with a Siemens P3/P4 crystallographic system using the θ:2θ scan routine and graphite monochromated Mo Kα radiation ($\lambda = 0.71073$ Å). After Lorentz and polarization corrections the structure was solved by direct methods with the SHELXTL PC programs and refined with full-matrix least-squares. Scattering factors and anomalous dispersion coefficients were taken from the literature [6]. All non-hydrogens were refined anisotropically. The approximated locations of all hydrogen atoms were placed in calculated positions and allowed to ride with the atom to which they were attached. Face-indexed numerical absorption corrections were applied, resulting in the final agreement factors of $R = 0.0526$ and $R_w = 0.0540$ for 1793 unique observed reflections $[F_0 > 2\sigma(F_o)]$ and 199 independent parameters. Cl–O bond distances and O–Cl–O angles for the second perchlorate ion were found to be distorted. Application of positional distortion corrections did not improve the alignment of the perchlorate ion and thus were not applied in the final solution. The crystal data of $[\mathrm{Ni(dachen)(NH_3)}](\mathrm{ClO_4})_2$ are tabulated in Table 1. The atomic coordinates and equivalent isotropic thermal parameters for non-hydrogen atoms are listed in Table 2.

Results and discussion

The energy of the d–d transition ($\lambda = 448$ nm) for the $[\mathrm{Ni(dachen)(NH_3)}]^{2+}$ complex is very similar to that for complexes of nickel(II) with a number of other polyamine ligands, e.g. [Ni(*N*,*N*′-bis(2-aminoethyl)-1,3-

TABLE 1. Crystal data for $[\mathrm{Ni(dachen)(NH_3)}](\mathrm{ClO_4})_2$

Empirical formula	$\mathrm{C_7H_{20}Cl_2N_4NiO_8}$
Color; habit	orange plate
crystal size (mm)	0.08 × 0.38 × 0.60
Crystal system	orthorhombic
Space group	*Pbca*
Unit cell dimensions	
a (Å)	13.402(3)
b (Å)	13.625(4)
c (Å)	17.118(4)
Volume (Å^3)	3125.8(16)
Z	8
Formula weight	417.9
Density (calc.) (Mg/m^3)	1.763
Absorption coefficient (mm^{-1})	1.615
F(000)	1728

TABLE 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement coefficients ($\text{Å}^2 \times 10^3$) for $[\mathrm{Ni(dachen)(NH_3)}](\mathrm{ClO_4})_2$[a]

	x	y	z	U_{eq}
Ni(1)	1078(1)	7331(1)	1777(1)	39(1)
Cl(1)	−2069(1)	4868(1)	1468(1)	61(1)
Cl(2)	−920(1)	7057(1)	3361(1)	56(1)
N(1)	536(3)	7328(4)	743(3)	43(2)
N(2)	941(5)	8717(5)	1643(3)	73(3)
N(3)	1034(4)	5932(4)	1746(3)	57(2)
N(4)	1671(4)	7393(4)	2792(3)	54(2)
O(1)	−2402(5)	4219(5)	880(3)	120(3)
O(2)	−2176(4)	5853(4)	1216(4)	106(3)
O(3)	−1051(4)	4674(4)	1649(3)	101(3)
O(4)	−2647(4)	4703(4)	2159(3)	94(2)
O(5)	−131(4)	6432(5)	3543(4)	133(3)
O(6)	−1014(4)	7161(6)	2549(3)	130(3)
O(7)	−631(7)	7948(6)	3653(6)	182(5)
O(8)	−1796(4)	6725(5)	3686(4)	103(3)
C(1)	−368(5)	7996(6)	764(4)	66(3)
C(2)	−100(6)	8916(6)	1299(6)	105(4)
C(3)	1670(8)	9051(7)	1166(7)	105(5)
C(4)	1560(7)	8752(7)	387(7)	115(5)
C(5)	1329(5)	7738(5)	226(4)	57(3)
C(6)	287(6)	6303(5)	513(4)	68(3)
C(7)	1009(5)	5633(5)	914(4)	61(3)

[a]Numbers in parentheses are e.s.d.s in the last digit. Equivalent isotropic U defined as one-third of the trace of the orthogonalized U_{ij} tensor.

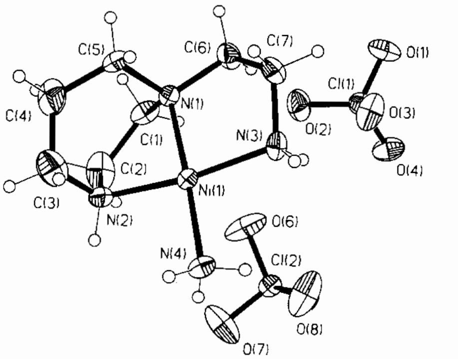

Fig. 1. X-ray structure of $[\mathrm{Ni(dachen)(NH_3)}](\mathrm{ClO_4})_2$. For clarity the hydrogen atoms are shown as small circles. Thermal ellipsoids are at 50% probability.

propanediamine)]$^{2+}$, 448 nm [5], [Ni(cyclam)]$^{2+}$, 445 nm [7a], [Ni(1,5-diazacyclooctane)$_2$]$^{2+}$, 442 nm [7b], [Ni(ethylenediamine)$_2$]$^{2+}$, 450 nm [7c]. Thus the ammonia ligand appears to be as effective a donor as either a primary or secondary amine.

Description of the [Ni(dachen)(NH$_3$)](ClO$_4$)$_2$ structure

The $[\mathrm{Ni(dachen)(NH_3)}]^{2+}$ cation is shown in Fig. 1. The crystal structure consists of approximately square-planar $[\mathrm{Ni(dachen)(NH_3)}]^{2+}$ cation and non-interacting perchlorate ions. Bond distances and angles are listed in Table 3. The angles about the nickel(II) ion are significantly distorted from the ideal square-planar angles, with N(1)–Ni–N(2) reduced to 81.6°, the result of the reduced bite of the bicyclic chelate ring. The deviations of the nitrogen atoms from the best least-squares plane through the nickel and four surrounding nitrogen atoms are +0.0491, −0.0491, −0.0471, +0.0401 Å for N1–N4, respectively, and +0.0069 Å for Ni. All four Ni–N bonds are essentially identical, 1.91 Å, despite the fact that the nitrogen donors are 'zeroth', primary, secondary and tertiary amines. The ethylenediamine ring in the bicyclic system adopts an approximately eclipsed conformation, while the six-membered ring and the C(6)–C(7) ethylenediamine ring are in their lowest energy conformations, approximately 'chair' and 'gauche', respectively.

Discussion of the Ni(dachen)(NH$_3$)(ClO$_4$)$_2$ structure

A search of the Cambridge Crystallographic Database yielded four structures of square-planar nickel(II) containing ammonia as a ligand [8]: complexes of salicylaldehyde semicarbazone (N, O, S donors), benzoylacetone-*S*-methylisothiosemicarbazone (N, N, O do-

TABLE 3. Bond lengths (Å) and angles (°) for $[\mathrm{Ni(dachen)(NH_3)}](\mathrm{ClO_4})_2$[a]

Bond lengths (Å)			
Ni(1)–N(1)	1.912(5)	Ni(1)–N(2)	1.911(6)
Ni(1)–N(3)	1.908(5)	Ni(1)–N(4)	1.913(5)
Cl(1)–O(1)	1.412(6)	Cl(1)–O(2)	1.417(6)
Cl(1)–O(3)	1.424(5)	Cl(1)–O(4)	1.432(5)
Cl(2)–O(5)	1.393(7)	Cl(2)–O(6)	1.403(6)
Cl(2)–O(7)	1.368(9)	Cl(2)–O(8)	1.375(6)
N(1)–C(1)	1.515(9)	N(1)–C(5)	1.492(8)
N(1)–C(6)	1.489(8)	N(2)–C(2)	1.538(11)
N(2)–C(3)	1.352(13)	N(3)–C(7)	1.482(9)
C(1)–C(2)	1.594(12)	C(3)–C(4)	1.403(17)
C(4)–C(5)	1.443(12)	C(6)–C(7)	1.496(10)
Bond angles (°)			
N(1)–Ni(1)–N(2)	81.6(2)	N(1)–Ni(1)–N(3)	87.8(2)
N(2)–Ni(1)–N(3)	168.8(3)	N(1)–Ni(1)–N(4)	176.7(2)
N(2)–Ni(1)–N(4)	96.0(2)	N(3)–Ni(1)–N(4)	94.7(2)
O(1)–Cl(1)–O(2)	110.1(4)	O(1)–Cl(1)–O(3)	109.9(4)
O(2)–Cl(1)–O(3)	109.8(4)	O(1)–Cl(1)–O(4)	108.6(4)
O(2)–Cl(1)–O(4)	110.3(4)	O(3)–Cl(1)–O(4)	108.0(3)
O(5)–Cl(2)–O(6)	110.6(4)	O(5)–Cl(2)–O(7)	104.2(5)
O(6)–Cl(2)–O(7)	107.3(5)	O(5)–Cl(2)–O(8)	111.0(4)
O(6)–Cl(2)–O(8)	110.8(4)	O(7)–Cl(2)–O(8)	112.7(5)
Ni(1)–N(1)–C(1)	106.3(4)	Ni(1)–N(1)–C(5)	106.2(4)
C(1)–N(1)–C(5)	111.0(5)	Ni(1)–N(1)–C(6)	109.4(4)
C(1)–N(1)–C(6)	113.0(5)	C(5)–N(1)–C(6)	110.7(5)
Ni(1)–N(2)–C(2)	107.9(5)	Ni(1)–N(2)–C(3)	109.6(6)
C(2)–N(2)–C(3)	111.4(7)	Ni(1)–N(3)–C(7)	107.6(4)
N(1)–C(1)–C(2)	107.8(5)	N(2)–C(2)–C(1)	106.6(6)
N(2)–C(3)–C(4)	113.6(9)	C(3)–C(4)–C(5)	118.8(9)
N(1)–C(5)–C(4)	113.5(6)	N(1)–C(6)–C(7)	107.9(6)
N(3)–C(7)–C(6)	106.7(5)		

[a]Numbers in parentheses are e.s.d.s in the last digit.

nors), a hydroxyphenyl formazan ligand (N, N, O donors) and a hydroxyphenyl 3-oxobutenamine ligand (O, N, O donors). No structures containing a tridentate amine ligand in addition to ammonia were found. The Ni–N(ammonia) bond distances in these compounds are listed in Table 4.

In $[Ni(dachen)(NH_3)](ClO_4)_2$, the Ni–N(tridentate amine ligand) distances (all 1.91 Å) are close to the 'ideal' Ni–N distance of 1.89 Å suggested for low-spin Ni(II) [4]. The Ni–N(amine) distance was expected to be somewhat longer, because of the slightly weaker donor strength of ammonia relative to chelating polyamines (as measured by proton basicity or from a quantitative spectrochemical series, for example Jorgensen's *f* factors for ligands [9]). Yet it also is 1.91 Å. Two of the four examples in Table 4 have distances essentially identical to that observed here. Thus the ideal 1.89 Å bond distance observed in complexes of polyamine ligands with low-spin nickel(II) does not appear to be affected (i.e. shortened) by chelation.

Binding constant of ammonia

The formation constant K_{NiLNH3} of the ternary complex $[Ni(dachen)(NH_3)]^{2+}$ (eqn. (2)) was determined by means of absorbance and pH measurements on solutions prepared either by addition of standard ammonia solution to a solution of $[Ni(dachen)(H_2O)_3]^{2+}$ or by addition of standard base to a solution containing $[Ni(dachen)(H_2O)_3]^{2+}$ plus ammonium ion. The formation constant was calculated from eqn. (3), where A_{corr} represents the absorbance measured at 448 nm

$$K_{NiLNH3}=\frac{\{A_{corr}/b\epsilon\}\{1+K_1{}^H[H^+]\}\{1+K_{NiLOH}[OH^-]\}}{\{[Ni]_T-A_{corr}/b\epsilon\}\{[NH_3]_T-A_{corr}/b\epsilon\}} \qquad (3)$$

(corrected for the absorbance contribution of $[Ni(dachen)(OH)]^+$, *vide infra*), b is the cell path length and ϵ is the molar absorptivity of $[Ni(dachen)(NH_3)]^{2+}$ at 448 nm. $[Ni]_T$ and $[NH_3]_T$ are the analytical concentrations of $[Ni(dachen)(H_2O)_3]^{2+}$ and NH_3, respectively. $K_1{}^H$ is the protonation constant of ammonia (log $K_1{}^H=9.29$ at $I=0.10$, 25 °C) [10], and K_{NiLOH} is the formation constant of the hydroxo complex (log $K_{NiLOH}=4.92$ at $I=0.10$, 25 °C) [1}. The absorbance readings were corrected for the contribution from $[Ni(dachen)(OH)]^+$ by an iterative procedure, using Microsoft Excel 3.0, according to eqns. (4) and (5). The concentration of $[Ni(dachen)(OH)]^+$ was initially set equal to zero, and eqn. (3) was used to calculate K_{NiLNH3}.

$$[Ni(dachen)(OH)^+]=K_{NiLOH}[OH^-][Ni]_T/\{1+K_{NiLOH}[OH^-]+K_{NiLNH3}[NH_3]\} \qquad (4)$$

$$A_{corr}=A-b\epsilon_{NiLOH}[Ni(dachen)(OH)^+] \qquad (5)$$

The value of K_{NiLNH3} was then used, together with the previously determined value of K_{NiLOH} to calculate, by means of eqn. (4), the concentration of the hydroxo species. This was then used in eqn. (5) to calculate the correction to the absorbance (4–23% of the measured absorbance). In eqn. (5), ϵ_{NiLOH} is the molar absorptivity of the hydroxo complex $[Ni(dachen)(OH)]^+$ at 448 nm, the λ_{max} of $[Ni(dachen)(NH_3)]^{2+}$ ($\epsilon=80$). A_{corr} was then used in eqn. (3) to calculate a new value for K. A total of 19 measurements from four separate experiments was used to calculate the equilibrium constant.

The stability constant obtained for reaction (2) is log $K_{NiLNH3}=3.3\pm0.1$. For comparison, we estimated the stability constant for the binding of ammonia to a $Ni(II)(N\text{-}N\text{-}N)(H_2O)_3{}^{2+}$ complex (where N-N-N represents three amine donors) to form the analogous high-spin nickel(II) complex $Ni(N\text{-}N\text{-}N)(NH_3)(H_2O)_2{}^{2+}$. The constant was estimated (i) by using the equation of Jackobs and Margerum [11], from which log $K=1.65$, (ii) by using log K_4 for $Ni^{2+}+NH_3$ (log $K_4=1.1$) [12] and including a statistical factor of 4, from which log $K=1.7$, or (iii) by using the value determined for $Nidien^{2+}+NH_3$ ($I=0.25$, 25 °C) for which log $K=1.7$ [13]. Thus Δlog K, the increase in K in the binding of NH_3 to low-spin nickel(II) compared to high-spin nickel(II), is approximately 1.6 log units, significantly smaller than the value which we had intuitively expected.

This Δlog K is the estimated equilibrium constant for the reaction (6). The temperature dependence

TABLE 4. Ni–N(ammine) bond distances in ammine-tridentate ligand–nickel(II) complexes

Tridentate ligand	Ni–N (Å)	Ref.
Salicylaldehyde thiosemicarbazonato-N,O,S	1.919	8a, 8b
Benzoylacetone-*S*-methylisothiosemicarbazonato-N,N′,O	1.918	8c
1-(2-Hydroxyphenyl)-3,5-diphenylformazanato	1.937	8d
N-(2-Hydroxyphenyl)-2-ethoxycarbonyl-3-oxobutenamine-N,O,O′	1.952	8e
N-(2-Aminoethyl)-1,4-diazacycloheptane	1.913	this work

$$\underset{\text{(high spin)}}{[\mathrm{Ni(dachen)(NH_3)(H_2O)_2}]^{2+}} \rightleftharpoons \underset{\text{(low spin)}}{[\mathrm{Ni(dachen)(NH_3)}]^{2+}} + 2\mathrm{H_2O} \quad (6)$$

of log K for a number of similar nickel(II) high-spin to low-spin equilibria has been examined [5, 14], providing the $\Delta G°$, $\Delta H°$ and $\Delta S°$ for these 'blue-to-yellow' interconversions. The $\Delta S°$ for the loss of the two water molecules has been shown to be approximately 16–20 cal K^{-1} mol^{-1} for trans-to-planar interconversions [5]. For the present system, in which $\Delta G° = -2.2$ kcal mol^{-1}, and assuming a similar value to that observed for other systems for $\Delta S°$ for the loss of the two water molecules, $\Delta H°$ is approximately 4 kcal mol^{-1}, in agreement with the range of ΔH values observed for other trans-to-planar interconversions (3–6 kcal mol^{-1}) [5].

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