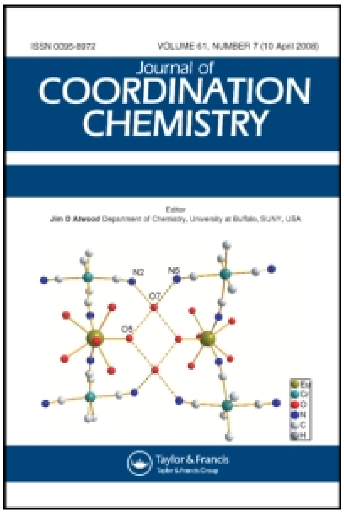

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THERMOCHEMICAL STUDY OF THE STEPWISE PROTONATION OF 1,4-DIAZA-7-THIANONANE, 1,4-DIAZA-7-THIA-8,8 ' -DIMETHYLNONANE AND 1,5-DIAZA-8-THIANONANE, AND OF THEIR COMPLEX FORMATION WITH COPPER(II) AND NICKEL(II) IONS IN AQUEOUS SOLUTION

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THERMOCHEMICAL STUDY OF THE STEPWISE PROTONATION OF 1,4-DIAZA-7-THIANONANE, 1,4-DIAZA-7-THIA-8,8'-DIMETHYLNONANE AND 1,5-DIAZA-8-THIANONANE, AND OF THEIR COMPLEX FORMATION WITH COPPER(II) AND NICKEL(II) IONS IN AQUEOUS SOLUTION

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The formation constants and the enthalpy changes of the reactions in 0.5 mol dm^{-3} ($K[NO_3]$) at 25°C between 1,4-diaza-7-thianonane (2,2-NNS(Et)), 1,4-diaza-7-thia-8,8'-dimethylnonane (2,2-NNS(t.But)) and 1,5-diaza-8-thianonane (3,2-NNS(Me)), and protons, copper(II) and nickel(II) ions in aqueous solution have been determined respectively by means of potentiometric and of direct calorimetric titrations. The corresponding ΔS values have also been calculated. For the reaction with protons, a tautomeric equilibrium between HL^+ species protonated on either the primary or the secondary aminogroup has been proposed. It is also shown that at the second protonation step, chain stiffening is increasingly weakened, when the alkyl substituent on the sulphur atom becomes larger. 2,2-NNS(Et) and 2,2-NNS(t.But) form both with copper(II) and nickel(II) the complexes ML^{2+} and $ML_2{}^{2+}$. 3,2-NNS(Me) forms with copper(II) the complexes CuL^{2+} and $Cu(OH)L^+$, whereas with nickel(II) only the formation of a NiL^{2+} complex could be detected.

The obtained values for the thermodynamic functions have been discussed. The three ligands act as tridentates in the 1:1 complexes with both Cu^{2+} and Ni^{2+}. In the 1:2 complexes with Cu^{2+} a pentacoordinative structure is proposed, whereas with Ni^{2+} there is complete coordination of the two ligand molecules. Finally, the complexes formed with 3,2-NNS(Me) are less stable than those with 2,2-NNS(Me).

INTRODUCTION

The study of the coordinating properties of sulphur containing polyamines towards copper(II) and nickel(II) ions in aqueous solution has now been extended with 1,4-diaza-7-thianonane, 1,4-diaza-7-thia-8,8'-dimethylnonane and 1,5-diaza-8-thianonane. As it was shown previously,[1] the sulphur atom in the aliphatic chain of polyamines can act as a donor to copper(II) and nickel(II) ions. In the investigation described here, we have turned our attention to the influence of the nature of the -S(Alkyl) group and to the influence of the chelate ring size on the thermodynamic behaviour of the complexes with ligands, in which there is a donor sequence N, N, S. The basic properties of these ligands are also reported and discussed.

EXPERIMENTAL

Materials

The three ligands were prepared by a method, analogue to that for 1,4-diaza-7-thiaoctane[1] (abbrev. 2,2-NNS (Me)), using different starting materials. For the preparation of 1,4-diaza-7-thianonane (abbrev. 2,2-NNS(Et)) and 1,4-diaza-7-thia-8,8'-dimethylnonane (abbrev. 2,2-NNS(t.But)) N-(-2-hydroxyethyl)-ethylene diamine (Fluka Chem.) was used as the starting alcohol and ethylmercaptan, respectively tert. butylmercaptan (Fluka Chem.) as the mercaptans. For the preparation of 1,5-diaza-8-thianonane (abbrev. 3,2-NNS(Me)), N-(-2-hydroxyethyl)-propane-1,3-diamine (Ega Chem.) and methylmercaptan (Fluka Chem.) were used. The final products were distilled three times under reduced pressure through a Vigreux column, and only the middle fractions were taken. Their molecular weight was determined by potentiometric titration with standardized nitric acid. Anal. 2,2-NNS(Et): b.p. 112°C/2 mm Hg, $M.W._{calcd.}$: 148.27, $M.W._{exp.}$:

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147.9; 2,2-NNS(t.But): b.p. 130°C/2 mm Hg, M.W.$_{calcd.}$: 176.33, M.W.$_{exp.}$: 176.2; 3,2-NNS(Me): b.p. 109°C/2 mm Hg, M.W.$_{calcd.}$: 148.27, M.W.$_{exp.}$: 148.4.

The solutions of the amines, copper(II) nitrate, nickel(II) nitrate, nitric acid and of potassium hydroxide were prepared and standardized as previously described.[1] To all the solutions an appropriate amount of solid potassium nitrate was added to bring the total nitrate concentration up to 0.5 mol dm^{-3}.

Potentiometric Titrations

pH Data were obtained by potentiometric titrations with the apparatus and [H$^+$]-calibration method previously described.[1] For each titration, the cell contained 70.0 or 80.0 cm^3 of a solution in which known amounts of amine, nitric acid and, for metal-ligand equilibria, metal salt were present. The solution was then stepwise titrated with standardized KOH solution (1.0040 mol dm^{-3} in 0.5 mol dm^{-3} KNO$_3$). For each ligand, several titrations were performed at different total ligand concentrations (1.1 to 2.8 x 10^{-2} mol dm^{-3}), different total metal ion concentrations (0.3 to 0.8 x 10^{-2} mol dm^{-3}) and at a total acid concentration of about 8.2 x 10^{-2} mol dm^{-3}. The ligand: metal ion ratio was varied between 2.1 and 6.1. All measurements were carried out at 25° ± 0.05°C.

Calorimetric Titrations

The calorimetric titrations were performed with a LKB-8700/2 titration calorimeter, thermostatted at 25° ± 0.001°C, following the procedure proposed by P. Paoletti and coworkers.[2]

For the protonation of the ligands, solutions of the ligand (C_L = ca. 1 x 10^{-2} mol dm^{-3}) were titrated in the calorimeter with standard nitric acid (C_{HNO_3} = 1.0124 mol dm^{-3}).

For the nickel(II) complexes, the calorimetric measurements involved stepwise addition of standard nitric acid into an alkaline nickel(II)-ligand buffer solution (C_L = ca. 2.1 x 10^{-2} mol dm^{-3}, C_{Ni} = ca. 0.7 x 10^{-2} mol dm^{-3}), starting at -log[H$^+$] = ca. 8.5.

For the copper(II) complexes, a reversed procedure was preferred to avoid precipitation of copper(II) hydrolyse products, when mixing a copper(II) solution with an alkaline ligand solution. Therefore, standard KOH solution (C_{KOH} = 1.0040 mol dm^{-3} in 0.5 mol dm^{-3} KNO$_3$) was added stepwise up to -log[H$^+$] = ca. 10.5 into a mixture of copper(II) (C_{Cu} = ca. 0.8 x 10^{-2} mol dm^{-3}), ligand (C_L = ca. 2.4 x 10^{-2} mol dm^{-3}) and nitric acid (C_H = ca. 6 x 10^{-2} mol dm^{-3}). The heats of dilution of the titrant were determined by stepwise addition of standard HNO$_3$ or KOH into a 0.5 mol dm^{-3} KNO$_3$ solution. The heat of formation of water was determined by adding standard KOH to a solution of HNO$_3$ in 0.5 mol dm^{-3} KNO$_3$.

The formation enthalpy of water, ΔH_W, was found to be –55.73 kJ mol^{-1}.

Calculations

The protonation constants for each amine, and the enthalpy changes for the formation of both protonated and complex species were calculated with appropriate FORTRAN IV programmes, based upon the minimisation procedure of Davidon.[3] The details concerning these calculation procedures have already been reported.[1] The stability constants of the metal complexes were calculated with the programme LEAST.[4] R-factors[5] of 0.3–0.5% were achieved. The values for the protonation constants and for the stoichiometric ionic product of water (pK$_W$ = 13.72)[1] were kept constant. Starting values for the free concentration of metal ion and of ligand at each titration point were calculated with the programme EQUIL,[6] using estimates for the stability constants and available concentration data.

RESULTS

The protonation constants and the thermodynamic functions of the stepwise protonation of the ligands are reported in Table I. The calculations were consistent with a two step protonation scheme:

$$H^+ + L \rightleftharpoons HL^+;\ \log K_{1p}, \Delta H_{1p}, \Delta S_{1p}$$

$$H^+ + HL^+ \rightleftharpoons H_2L^{2+};\ \log K_{2p}, \Delta H_{2p}, \Delta S_{2p}$$

The overall stoichiometry of the complexation reactions and preliminary values for the stability constants of the complexes were established from their formation curves. It was found that these curves were coincident for different values of the total metal ion concentration. The formation curves for the copper(II) and nickel(II) complexes with 2,2-NNS(Et) and 2,2-NNS(t.But) indicated the formation of only two complexes : ML^{2+} and ML$_2$$^{2+}$ ($\bar{n}_{max}$ = 2).[7] The preference of Cu^{2+} to form 4-coordinated square planar complexes[8] makes it probable that not

TABLE I
The protonation constants and the thermodynamic functions of the stepwise protonation of 2,2-NNS(Me)[a], 2,2-NNS(Et), 2,2-NNS(t.But) and 3,2-NNS(Me)[b]

Ligand	$\log K_{1p}$	$\log K_{2p}$	$-\Delta H_{1p}$	$-\Delta H_{2p}$	ΔS_{1p}	ΔS_{2p}
2,2-NNS(Me)	9.596	6.631	47.7	43.1	23	–18
2,2-NNS(Et)	9.610(3)[c]	6.605(4)	47.6(1)	42.5(3)	24(1)	–16(1)
2,2-NNS(t.But)	9.605(3)	6.532(4)	48.4(2)	40.5(3)	21(1)	–11(2)
3,2-NNS(Me)	10.259(2)	8.190(4)	53.7(2)	47.7(2)	16(1)	– 3(1)

[a] Data from Ref. 1.

[b] 25°C, 0.5 mol dm^{-3} (K[NO$_3$]); ΔH in kJ mol^{-1}, ΔS in JK^{-1} mol^{-1}; Standard State : 1 mol dm^{-3}.

[c] Value in parentheses is the standard deviation on the last significant figure. The reliability of the values is estimated to be better than four times the standard deviation.

all six donor atoms in the CuL_2^{2+} complexes are coordinated.

For the Cu^{2+}/3,2-NNS(Me) system, the formation curve raised above $\bar{n} = 1$, showing a horizontal part at $\bar{n} = 1$ for $-\log[L]$ between 9 and 5. There was no symmetry about $\bar{n} = 1$. The calculations with the potentiometric data revealed a best fit for a set containing a mononuclear 1:1 complex and a hydroxo-complex $[Cu(OH)L]^+$. For the Ni^{2+}/3,2-NNS(Me) system, only the formation of a NiL^{2+} complex was found ($\bar{n}_{max} = 1$).

The stability constants and the thermodynamic functions of the stepwise complexation of Cu^{2+} and Ni^{2+} with the three ligands are reported in Table II and III. The data concerning the ligand 2,2-NNS(Me) are also given.

DISCUSSION

Protonation of the Ligands

Protonation of 2,2-NNS(Et), 2,2-NNS(t.But) and 3,2-NNS(Me) may occur at both the primary and the secondary nitrogen atoms. Therefore, the HL^+ ion can exist in two tautomeric forms, the one protonated on the primary aminogroup and the other on the secondary aminogroup:

$$\overset{+}{N}H_3(CH_2)_nNH(CH_2)_2S(Alk) \rightleftharpoons NH_2(CH_2)_n\overset{+}{N}H_2(CH_2)_2S(Alk)$$

(I) (II) n = 2,3

An analogue tautomeric equilibrium has also been suggested for the first protonation step of N-methylethylenediamine,[9] N-(-2-hydroxyethyl)-ethylenediamine[10] and of 1,4-diaza-7-thiaoctane (2,2-NNS(Me)).[1] For the series 2,2-NNS(Alk), the values for $\log K_{1p}$, ΔH_{1p} and ΔS_{1p} do not differ appreciably. We assume therefore that the percentage of the two tautomeric forms is similar for the three ligands. At the second protonation stage, there is a distinct decrease in both basicity and protonation heat, when going from methyl to tert. butyl. The thermodynamic behaviour at the second protonation stage, is thus clearly influenced by the nature of the alkyl substituent on the sulphur atom. We suggest therefore that at the first protonation step the tautomeric species I will be dominant. Consequently, the secondary aminogroup will be protonated largely at the second protonation step, and, in its protonated form, it will exercise a "chain-stiffening" effect[11] on the $-(CH_2)_2S(Alk)$ branch of the ion. This effect, however, should become negligible for that part of the chain further than four atoms away from the ammonium group. This could be deduced from an analysis of the thermodynamic data on the protonation of primary n-alkyl amines,[12] since the decrease in the positive entropy change for the protonation of these amines levels out, when going from methylamine to n-pentylamine. For the series 2,2-NNS(Alk) however, the entropy change ΔS_{2p} becomes less unfavourable in the sequence methyl, ethyl, tert. butyl. Therefore, we assume that the alkyl substituent on the sulphur atom is no longer stiffened, but increasingly weakens the stiffening of the chain part between the secondary ammonium group and the sulphide group, when the alkyl substituent becomes larger. As this effect is undoubtedly endothermic, the values for $-\Delta H_{2p}$ decrease steadily with increasing size of the alkyl substituent.

For 3,2-NNS(Me), an increased basicity and a larger value for $-\Delta H_p$ is found for both protonation steps, relative to 2,2-NNS(Me). This is also the case when comparing log K and -ΔH values for the protonation of 1,3-propanediamine with those of ethylenediamine and an explanation for this has already been given.[13] The observation that for 3,2-NNS(Me) ΔS_{1p} is less favourable and ΔS_{2p} is less unfavourable than for 2,2-NNS(Me), is in complete agreement with the "chain stiffening" explanation given for diamines with increasing chain length between the two aminogroups.[13]

Copper(II) Complexes

Since 2,2-NNS(Et) and 2,2-NNS(t.But) only differ from 2,2-NNS(Me) in the nature of the alkyl substituent on the sulphur atom, one can expect an analogue complexation behaviour of the three ligands towards the copper(II) ion. Indeed for the complexes $Cu[2,2\text{-}NNS(Alk)]^{2+}$ the values for $-\Delta H_1$ are between the corresponding values for the 1:1 complexes of Cu^{2+} with diethylenetriamine[14] and with N-methylethylenediamine,[15] respectively 75.3 kJ mol^{-1} and 48.3 kJ mol^{-1}. We assume therefore that in the 1:1 complexes with Cu^{2+}, the three ligands are acting as tridentates and are bound through their donor atoms N, N and S, with the Cu–S bond being much weaker than the Cu–N bonds. $-\Delta H_1$ for $Cu[2,2\text{-}NNS(Et)]^{2+}$ is somewhat larger than for $Cu[2,2\text{-}NNS(Me)]^{2+}$. Although ligand solvation effects contribute to differences in complex formation enthalpies, the enhanced donor strength of the sulphide group by the greater electron donating power of the ethyl substituent relative to methyl must also be considered. On the other hand, $-\Delta H_1$ for $Cu[2,2\text{-}NNS(t.But)]^{2+}$ is appreciably lower than for the two other complexes, while ΔS_1 is more positive. This should indicate that more water molecules are expelled from the hydration sphere of the copper(II) ion when tert. butyl is the substituent on the sulphide group. Since the liberation of water molecules is an endothermic process, the formation of the complex $Cu[2,2\text{-}NNS(t.But)]^{2+}$ will be accompanied by the lowest enthalpy change. The enthalpy change $-\Delta H_2$ for the second complexation step is for the three complexes lower than for the first step. For the complex $Cu[2,2\text{-}NNS(Me)]_2^{2+}$ incomplete coordination of the second ligand molecule has already been suggested.[1] Since hexacoordination of the copper(II) ion can generally be excluded,[8] we propose a pentacoordinative structure for the three 1:2 complexes (Figure 1). The total enthalpy change ($-\Delta H_T$) for the two complexation steps is also more positive for $Cu[2,2\text{-}NNS(Me)]_2^{2+}$ and $Cu[2,2\text{-}NNS(Et)]_2^{2+}$ than for the 1:2 complex of Cu^{2+} with N-methylethylenediamine[15] respectively 103.8, 103.0 and 99.3 kJ mol^{-1}.

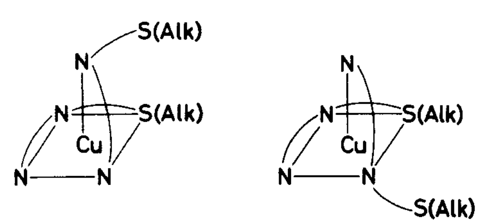

FIGURE 1 Two possible isomeric pentacoordinative structures for the $Cu[2,2\text{-}NNS(Alk)]_2^{2+}$ complexes.

The possibility of two uncoordinated ligand arms in these 1:2 complexes can therefore be excluded. For $Cu[2,2\text{-}NNS(t.But)]_2^{2+}$ the value for $-\Delta H_T$ (98.6 kJ mol^{-1}) is somewhat lower than 99.3 kJ mol^{-1}. The reason for this can be a steric effect due to the bulkiness of 2,2-NNS(t.But), when a second ligand molecule enters the coordination sphere of the copper(II) ion.

Relative to 2,2-NNS(Me), the complexation of Cu^{2+} with 3,2-NNS(Me) occurs with a smaller heat of formation but with a more favourable entropy change. The same has been observed when comparing the complex formation of 1,3-diaminopropane

TABLE II
The stability constants and the thermodynamic functions of the stepwise complexation of Cu^{2+} with 2,2-NNS(Me)[a], 2,2-NNS(Et), 2,2-NNS(t.But) and 3,2-NNS(Me)[b]

Ligand	$\log K_1$	$\log K_2$	$-\Delta H_1$	$-\Delta H_2$	ΔS_1	ΔS_2
2,2-NNS(Me)	11.377	6.306	58.5	45.3	24.4	−31
2,2-NNS(Et)	11.596(5)	6.299(7)	59.7(2)	43.3(4)	21.7(8)	−24(1)
2,2-NNS(t.But)	10.843(4)	6.388(6)	53.7(1)	44.9(3)	27.2(8)	−28(1)
3,2-NNS(Me)[c]	11.009(5)	–	55.1(2)	–	26(1)	–

[a] Data from Ref. 1.

[b] For the remarks, see Table I.

[c] For the reaction $CuL^{2+} + OH^- \rightleftharpoons Cu(OH)L^+$: log K = 5.147(16), $-\Delta H$ = 12.1(7) kJ mol^{-1}, ΔS = 57(4) JK^{-1} mol^{-1}.

relative to ethylenediamine.[16] Since the formation of the complex $Cu[3,2\text{-NNS(Me)}]^{2+}$ is more exothermic than the formation of the corresponding complex with 1,3-propanediamine ($-\Delta H_1 = 46.1$ kJ mol^{-1}), we may assume that 3,2-NNS(Me) is bound to the copper(II) ion through its three donor atoms. It is therefore interesting to observe that in the complex $Cu[3,2\text{-NNS(Me)}]^{2+}$, where a six-membered chelate ring is linked to a five-membered one, there is apparently no extra stabilization relative to the complex $Cu[2,2\text{-NNS(Me)}]^{2+}$, in which two five-membered chelate rings are linked. This is in contrast to what was found for the 1:1 complexes of Cu^{2+} with triamines, where 1,4,8-triazaoctane (2,3-NNN) forms a more stable complex with Cu^{2+} than diethylenetriamine (2,2-NNN) or 3,3′-diaminodipropylamine (3,3-NNN).[17] This was attributed to the presence of two alternate chelate 5,6-membered rings in the complex $Cu[2,3\text{-NNN})]^{2+}$, which decreases the cumulative ring strain.[18] As the strength of the Cu–N bond (about 26.3 kJ mol^{-1}) is much greater than that of a Cu–S bond (about 9.6 kJ mol^{-1}), the stability of the complexes $Cu[2,2\text{-NNS(Me)}]^{2+}$ and $Cu[3,2\text{-NNS(Me)}]^{2+}$ will be determined predominantly by the strength of the chelate ring formed through the two nitrogen donors. The lower stability of $Cu[3,2\text{-NNS(Me)}]^{2+}$ than agrees with the fact that the five-membered N-Cu-N chelate ring is more stable than the six-membered one.[16] It is also found that Cu^{2+} cannot coordinate a second molecule of 3,2-NNS(Me). Instead, it readily coordinates a hydroxide ion. The enthalpy change for the reaction $Cu[3,2\text{-NNS(Me)}]^{2+} + OH^- \rightleftharpoons Cu[(OH)\text{-}3,2\text{-NNS(Me)}]^+$ is not very different from the values found for the corresponding reaction of Cu(triamine)$^{2+}$ complexes.[17] It is therefore reasonable to assume that all these hydroxo complexes have the same structure: i.e. a square planar coordination of the tridentate ligand and the hydroxide ion to the copper(II) ion.

Nickel(II) Complexes

The enthalpy change for the formation of the complexes $Ni[2,2\text{-NNS(Et)}]^{2+}$ and $Ni[2,2\text{-NNS(t.-But)}]^{2+}$ is almost equal to the value for the formation of $Ni[2,2\text{-NNS(Me)}]^{2+}$, for which complete coordination of the ligand through its three donor atoms has been suggested.[1] It is therefore reasonable to assume that in the two former complexes the ligands are also completely coordinated to the nickel(II) ion. In contrast to the 1:1 complexes with Cu^{2+}, the value for ΔS_1 decreases with increasing volume of the alkyl substituent on the sulphur atom. This decrease can be attributed to different percentages of the facial and meridional isomers of the 1:1 complex for the three ligands. As the meridional isomer has a smaller dipole moment than the facial one,[19] it will be able to orientate fewer water molecules. The trend in the ΔS_1 - values therefore indicates that the percentage of the facial isomer increases when the volume of alkyl substituent on the sulphur increases.

At the second complexation step $-\Delta H_2$ is higher than $-\Delta H_1$ for the three ligands. This behaviour is usually encountered for successive coordination of Ni^{2+} in the absence of steric hindrance.[18] However, the difference ($\Delta H_1 - \Delta H_2$) is appreciably smaller for 2,2-NNS(t.But) (0.3 kJ mol^{-1}) than for 2,2-NNS(Me) (8.1 kJ mol^{-1}) and 2,2-NNS(Et) (7.9 kJ mol^{-1}). This is indicative of steric hindrance between the two molecules of 2,2-NNS(t.But) in the 1:2 complex with Ni^{2+}. Nevertheless, complete coordination of the two ligand molecules through the six donor atoms in the complexes $Ni[2,2\text{-NNS(Alk)}]_2^{2+}$ can be put forward. The structure of these 1:2 complexes is probably octahedral, with a certain degree of tetragonal distorsion, since all the six donor atoms are not equivalent. As it was the case with Cu^{2+}, 3,2-NNS(Me) forms with Ni^{2+} a less stable 1:1 complex than 2,2-NNS(Me). It is also found that the complex formation of Ni^{2+} with the former ligand is less exothermic,

TABLE III
The stability constants and the thermodynamic functions of the stepwise complexation of Ni^{2+} with 2,2-NNS(Me)[a] 2,2-NNS(Et), 2,2-NNS(t.But) and 3,2-NNS(Me)[b]

Ligand	log K_1	log K_2	$-\Delta H_1$	$-\Delta H_2$	ΔS_1	ΔS_2
2,2-NNS(Me)	7.063	5.858	36.3	44.4	13.4	–37
2,2-NNS(Et)	7.230(9)	5.63(1)	37.7(2)	45.6(1)	11.8(8)	–45(1)
2,2-NNS(t.But)	6.516(4)	4.659(6)	36.2(3)	36.5(6)	3(1)	–33(2)
3,2-NNS(Me)	6.881(2)	–	34.0(1)	–	17(1)	–

[a] Data from Ref. 1.

[b] For remarks, see Table I.

while the entropy change is more favourable. So, the ring size of the chelate ring formed by the two nitrogen donors and the central ion also determines the overall stability of the two 1:1 complexes involved, and is in agreement with the fact that nickel(II) complexes with a single five-membered chelate ring are more stable than those with a six-membered one.[16]

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