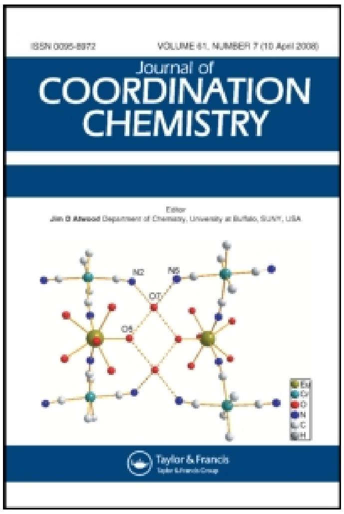

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COMPLEX FORMATION BETWEEN 1-AZA-4-THIAPENTANE, 1,4-DIAZA-7-THIAOCTANE AND 2-HYDROXYETHYLTHIOETHYLAMINE, AND HYDROGEN IONS, COPPER(II) AND NICKEL(II) IONS IN AQUEOUS SOLUTION A Potentiometric and Calorimetric Investigation

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COMPLEX FORMATION BETWEEN 1-AZA-4-THIAPENTANE, 1,4-DIAZA-7-THIAOCTANE AND 2-HYDROXYETHYLTHIOETHYLAMINE, AND HYDROGEN IONS, COPPER(II) AND NICKEL(II) IONS IN AQUEOUS SOLUTION

A Potentiometric and Calorimetric Investigation

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The behaviour of l-aza-4-thiapentane, 1,4-diaza-7-thiaoctane and 2-hydroxyethylthioethylamine in aqueous solution in equilibria with protons, and Cu(II) and Ni(II) ions has been investigated potentiometrically and calorimetrically. The protonation constants for the ligands, and the stability constants for their complexes at 25° C in 0.5 M KNO_3 are reported, together with the corresponding thermodynamic parameters ΔG°, ΔH° and ΔS°.

It is found that the presence of a thioether group in the aliphatic chain of the ligands lowers the basicity of the aminogroups. The complexes are less stable than their polyamine analogues: N-methylethylenediamine, diethylenetriamine and N-(2-hydroxyethyl)ethylenediamine. The reduced stability is due mainly to an unfavourable entropy change during complexation, although their heats of formation are also less exothermic.

INTRODUCTION

More than fifteen years ago, Fernelius and his coworkers[1,2] investigated potentiometrically the complexes formed in aqueous solution between 3d-metal ions and some amines containing sulphur.

They found that the sulphur atom was active in coordination, although the complexes formed were less stable than their polyamine analogues. From the temperature dependence of the stability constants, they calculated values for the thermodynamic quantities, and they found that the decreased stability of the complexes was mainly due to a less favourable entropy change during complexation.

Up to now, there has been no further systematical investigation reported of the 3d-metal ion complexes with sulphur containing amines or polyamines in aqueous solution. Therefore the present study deals with the reactions in aqueous solution of l-aza-4-thiapentane, 1,4-diaza-7-thiaoctane and 2-hydroxyethylthioethylamine with protons, Cu(II) and Ni(II) ions. The equilibrium constants are determined potentiometically, whereas the thermodynamic parameters ΔH° are derived from direct calorimetric experiments. ΔS° values were calculated from ΔG° and ΔH° values.

EXPERIMENTAL

Syntheses

1-aza-4-thiapentane, $NH_2CH_2CH_2SCH_3$, was prepared by a method already described.[2]

1,4-diaza-7-thiaoctane, $NH_2CH_2CH_2NHCH_2CH_2SCH_3$, was prepared as follows. A solution of 52 g (0.5 mole) N-(2-hydroxyethyl)-ethylenediamine in 500 ml 48% HBr solution was boiled for 48 h, while the azeotrope H_2O/HBr was distilled off dropwise. After cooling, the crude product N-(2-bromoethyl)-ethylenediamine.2HBr was filtered off and recrystallised from boiling ethanol. Anal. Calcd. for $C_4H_{13}Br_3N_2$: N, 8.5; Found: N, 8.4. Then 132g (0.4 mole) of this product, dissolved in 500ml ethanol, was slowly added to a cooled alcoholic solution containing 0.4 mole methylmercaptan (Aldrich) and 1.2 mole potassium hydroxide. After addition the reaction mixture was refluxed for 1 h, while potassium bromide precipitated. The mixture was kept overnight in the refrigerator. KBr was filtered off and the solvent was evaporated on a rotavapor. A yellow oil remained, which was distilled under reduced pressure through a Vigreux column. The fraction constantly boiling at 88°C/2 mm Hg was taken. This fraction was refractionated again and only the middle cut was used for the determination of the molecular weight by a potentiometric titration with standardized nitric acid (M.W.$_{found}$: 122.8, M.W.$_{calcd}$: 122.2).

2-hydroxyethylthioethylamine, $NH_2CH_2CH_2SCH_2$-CH_2OH, was prepared by addition of 1 mole ethyleneimine to an alcoholic solution of 1 mole 2-mercaptoethanol. When the reaction was completed, the solvent was evaporated on a rotavapor, and the remaining oil was distilled under reduced pressure through a Vigreux column. The fraction constantly boiling at 137 °C/10 mm Hg was taken. This fraction was refractionated again and only the middle cut was used for the determination of the molecular weight by a potentiometric titration with standardized nitric acid (M.W.$_{found}$: 121.3, M.W.$_{calcd}$: 121.9).

Solutions

Solutions of the three amines were prepared with CO_2-free twice distilled water under a flow of nitrogen. They were standardized by potentiometric titration with standard acid.[3] Solutions of potassium hydroxide, nitric acid, copper(II)nitrate and nickel(II)nitrate were standardized by conventional methods.[4] To all the solutions an appropriate amount of solid potassium nitrate was added, so that the total nitrate concentration was 0.5 M.

Potentiometric Titrations

The potentiometric titrations were performed using a Radiometer PHM 64 digital potentiometer, an Ingold HA 201 glass electrode, an Ingold 3 M KCl calomel electrode and an Ingold salt bridge containing 0.5 M KNO_3. Before and after each titration the electrode system was calibrated in terms of hydrogen ion concentration by direct titration of nitric acid with potassium hydroxide in 0.5 M KNO_3. The standard potential of the electrode system, E_0, and the stoichiometric ionic product of water were calculated following the principles of Gran.[5] The value found for pK_W (= 13.72) is in good agreement with that determined previously by other workers.[6]

For each titration, the cell contained 70.0 to 80.0 ml of a solution in which known amounts of amine, nitric acid, and, for metal–ligand equilibria, metal salt were present. For each metal–ligand system, several titrations were performed at different total ligand concentrations (0.013 M to 0.006 M), different total metal ion concentrations (0.0066 M to 0.0019 M) and at a total acid concentration of about 0.03 M. The solutions were titrated with standardized potassium hydroxide (1.0040 M in 0.5 M KNO_3), while $-\log[H^+]$ varied from about 3 to 11. All measurements were carried out at 25°C ± 0.05°C.

Calorimetric Titrations

The calorimetric titrations were performed with a LKB-8700/2 calorimeter, thermostatted at 25.000°C ± 0.001°C, following the procedure, proposed by P. Paoletti and coworkers,[7] for the study of reactions of metal ions with basic ligands in aqueous solution. The concentration level was about 1×10^{-2} M. Details concerning the procedure for determining the heats of formation are found in a publication of Wadsö.[8]

Abbreviations

For the ligands used in this work and for those mentioned further in the text, we have used abbreviations, which differ from those currently used. The abbreviation for the name of a ligand contains consecutively the donor atoms present in the aliphatic chain, preceded by the number(s) of methylene groups between two donor atoms. Such abbreviations visualize more easily the structure of the ligands: 2-NS(Me) for 1-aza-4-thiapentane; 2,2-NNS(Me) for 1,4-diaza-7-thiaoctane; 2,2-NSOH for 2-hydroxyethylthioethylamine; 2-NN for ethylenediamine; 2-NN(Me) for N-methylethylenediamine; 2,2-NNN for diethylenetriamine, and so on.

RESULTS

The equilibrium constants for the protonation of the three ligands were calculated with a computer programme using the minimization procedure of Davidon.[9–12] The calculations were performed using more than 75 selected data points from different titrations for each ligand. The results are given in the Tables I, II and III.

Preliminary values for the stability constants of the complexes were obtained from the formation curves.[13] It was found that these curves were coincident for different values of the total metal ion concentration. It was also evident from these curves that with the ligands 2-NS(Me) and 2,2-NSOH only the complexes CuL^{2+} and CuL_2^{2+} were formed. There was also a close resemblance between the formation curves of the Ni(II) complexes of 2-NS(Me) and 2,2-NSOH, but for the former ligand the formation curve raised above $\bar{n} = 2$ (for symbols, see Ref. 13), indicating the presence of a NiL_3^{2+} complex. With 2,2-NNS(Me) the formation curves for both the Cu(II) and the Ni(II) complexes were consistent with the formation of 1:1

TABLE I

The formation constants and the thermodynamic functions[a] for the ligand species and the complex species of 2-NS(Me)

Reaction	log K	$-\Delta G°$	$-\Delta H°$	$\Delta S°$
$H^+ + L \rightleftharpoons HL^+$	9.472(2)[b]	12.914(3)	12.88(2)	0.1(1)
$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	5.572(3)	7.598(4)	7.95(4)	−1.2(1)
$CuL^{2+} + L \rightleftharpoons CuL_2^{2+}$	5.082(4)	6.930(6)	9.10(9)	−7.3(3)
$Ni^{2+} + L \rightleftharpoons NiL^{2+}$	3.299(4)	4.499(7)	5.57(4)	−3.6(2)
$NiL^{2+} + L \rightleftharpoons NiL_2^{2+}$	2.805(7)	3.83(2)	6.05(9)	−7.4(4)
$NiL_2^{2+} + L \rightleftharpoons NiL_2^{2+}$	1.63(1)	2.22(2)	6.1(2)	−13.0(9)

[a] $\Delta G°$ and $\Delta H°$ in kcal.mole^{-1}, $\Delta S°$ in cal.mole^{-1}, degree^{-1}, Standard state of 1 mole. 1^{-1}.

[b] Value in parentheses is the standard deviation on the last significant figure, calculated with Eq. 14 in Ref. 14. The reliability of the values is estimated to be better than four times the standard deviation.

TABLE II

The formation constants and the thermodynamic functions for the ligand species and the complex species of 2,2-NNS(Me)[a]

Reaction	log K	$-\Delta G°$	$-\Delta H°$	$\Delta S°$
$H^+ + L \rightleftharpoons HL^+$	9.596(2)	13.086(3)	11.40(2)	5.6(1)
$H^+ + HL^+ \rightleftharpoons H_2L^{2+}$	6.631(2)	9.042(3)	10.31(4)	−4.3(2)
$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	11.377(1)	15.514(2)	13.98(6)	5.1(2)
$CuL^{2+} + L \rightleftharpoons CuL_2^{2+}$	6.306(3)	8.599(4)	10.82(14)	−7.5(5)
$Ni^{2+} + L \rightleftharpoons NiL^{2+}$	7.063(3)	9.632(5)	8.67(4)	3.2(2)
$NiL^{2+} + L \rightleftharpoons NiL_2^{2+}$	5.858(7)	7.99(1)	10.6(1)	−8.8(4)

[a] For footnotes, see Table I.

TABLE III

The formation constants and the thermodynamic functions for the ligand species and the complex species of 2,2-NSOH[a]

Reaction	log K	$-\Delta G°$	$-\Delta H°$	$\Delta S°$
$H^+ + L \rightleftharpoons HL^+$	9.369(2)	12.776(3)	12.66(3)	0.4(1)
$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	5.243(2)	7.150(4)	7.56(3)	−1.4(1)
$CuL^{2+} + L \rightleftharpoons CuL_2^{2+}$	4.765(8)	6.50(1)	8.62(8)	−7.1(3)
$CuL_2^{2+} + OH^- \rightleftharpoons Cu(OH)L_2^+$	4.39(1)	5.99(3)	5.7(6)	1(2)
$Ni^{2+} + L \rightleftharpoons NiL^{2+}$	3.208(8)	4.37(1)	4.81(5)	−1.5(2)
$NiL^{2+} + L \rightleftharpoons NiL_2^{2+}$	2.55(1)	3.47(2)	5.42(8)	−6.5(3)

[a] For footnotes, see Table I.

and 1:2 complexes. However, for former ion the formation of the two complexes was distinctly separated (d n̄/d log a = 0 for n̄ = 1). The main chemical reason is evidently the greater preference of Cu(II), relative to Ni(II), for 4-coordinated square planar complexes. The stability constants were refined by minimisation of the titration data with the programme LEAST.[14] R-factors[15] of 0.2 – 0.4% were achieved. For the system Cu(II)/2,2-NSOH the presence of the species $Cu(OH)L_2^+$ was also revealed. Introduction of other species remained unsuccessful.

The values for the enthalpy changes during protonation and complexation were calculated with a modified version[16] of the minimization procedure of Davidon.[9] The thermodynamic functions ΔG°, ΔH° and ΔS° are represented in the Tables I, II and III. In the Tables IV, V and VI the thermodynamic functions for the reactions of some polyamines with protons, Cu(II) and Ni(II) ions are given for comparison.

DISCUSSION

Protonation of the Ligands

From Table I and IV it can be seen that 2-NS(Me) is less basic than n-butylamine. The decreased basicity is due to a lower value for both $-\Delta H^{H,L}_{HL}$ and $\Delta S^{H,L}_{HL}$. The character of the sulphur atom, which attracts electrons more than a $-CH_2-$ group,[19] and a greater loss of rotational entropy by "chain-stiffening"[20] during protonation, can be responsible. 2,2-NSOH (Table III) is even a weaker base than 2-NS(Me). The presence of the alcoholic group seems to produce a further lowering of the electron density on the nitrogen atom compared with 2-NS(Me). This can also account for the less exothermic enthalpy change for 2,2-NSOH during protonation.

TABLE IV
The thermodynamic functions for the protonation of n-butylamine and N-methylethylenediamine.
Comparison table.

	N(n-But)	2-NN(Me)[c]
$-\Delta G^{H,L}_{HL}$	13.72[a]	13.83
$-\Delta G^{H,HL}_{H_2L}$		9.90
$-\Delta H^{H,L}_{HL}$	13.98[b]	11.25
$-\Delta H^{HL}_{H_2L}$		10.34
$\Delta S^{H,L}_{HL}$	1.8[b]	8.7
$\Delta S^{H,HL}_{H_2L}$		−1.5

[a] ref. 17 ($\mu \rightarrow 0$, 25°C)
[b] ref. 18 ($\mu \rightarrow 0$, 25°C)
[c] ref. 21 (0.5 M KNO_3, 25°C)

The thermodynamic functions for the protonation of 2,2-NNS(Me) might be compared with those for N-methylethylenediamine (Table IV). As for this ligand, there will be a tautomeric equilibrium at the first protonation step of 2,2-NNS(Me).[21]

$$\overset{+}{N}H_3CH_2CH_2NHCH_2CH_2SCH_3 \quad (I)$$

$$NH_2CH_2CH_2\overset{+}{N}H_2CH_2CH_2SCH_3 \quad (II)$$

However, as the percentages of the tautomeric protonated species are not known, it is preferable to compare only the overall thermodynamic functions for the reaction $2H^+ + L \rightleftharpoons H_2L^{2+}$. Consequently, one can see from Table II and IV that 2,2-NNS(Me) is also less basic than 2-NN(Me). The decreased basicity is due to a less favourable entropy change, respectively 1.3 e.u. for 2,2-NNS(Me) and 7.2 e.u. for 2-NN(Me). As it is reasonable to assume that the degree of hydratation of both fully protonated ligands will not be very different, the lower positive entropy change for the former ion must be explained by a greater loss of rotational entropy during protonation. The enthalpy change $-\Delta H^{2H,L}_{H_2L}$ is almost equal for 2,2-NNS(Me) and for 2-NN(Me). One can also see that both $-\Delta H^{H,L}_{HL}$ and $-\Delta H^{H,HL}_{H_2L}$ for 2,2-NNS(Me) are not very different from the corresponding values obtained for 2-NN(Me),[21] so that the nature of the aliphatic branch, substituted on the secondary nitrogen, has only a minor influence on the tautomeric equilibrium.

Copper Complexes

Starting from $-\Delta H^{Cu,L}_{CuL} = 12.56$ kcal.mole^{-1} for ethylenediamine,[22] we can take 6.3 kcal.mole^{-1} as an estimate for the contribution of one $Cu-N_{pr}$ bond to the enthalpy change $-\Delta H^{Cu,L}_{CuL}$ for 2-NS(Me). We can see then (Table I) that the sulphur atom is active in the coordination of the 1:1 complex, although the Cu–S bond gives a considerable less exothermic contribution to the enthalpy change (about 1.6 kcal.mole^{-1}). For $Cu(2\text{-}NS(Me))^{2+}$, the entropy change $\Delta S^{Cu,L}_{CuL}$ is much smaller, and even negative compared with the corresponding value for 2-NN or 2-NN(Me).[22] For $Cu(2\text{-}NS(Me))^{2+}$.a fewer number of water molecules will be liberated during the first complexation step, since it has been shown[23] that a polyamine has in its primary hydratation sphere as many water molecules bound by hydrogen bonding as the number of nitrogen atoms present in the molecule. As the sulphur atom is probably not hydrated, there will be at least

TABLE V
The thermodynamic functions of the Cu(II)-complexes with some polyamines. Comparison table.

	2-NN[a]	2-NN(Me)[b]	2,2-NNN[c]	2,2-NNOH[d]
$-\Delta G^{Cu,L}_{CuL}$	14.435	14.210	21.55	14.09
$-\Delta G^{CuL,L}_{CuL_2}$	12.482	11.872	7.10	10.57
$-\Delta H^{Cu,L}_{CuL}$	12.56	11.53	18.00	11.09
$-\Delta H^{CuL,L}_{CuL_2}$	12.64	12.2	8.15	1.06
$\Delta S^{Cu,L}_{CuL}$	6.3	9.0	12.0	10.06
$\Delta S^{CuL,L}_{CuL_2}$	−0.5	−1.0	−3.5	31.9

[a] ethylenediamine (0.5 M KNO_3, 25°C) ref. 22
[b] N-methylethylenediamine (0.5 M KNO_3, 25°C) ref. 22
[c] diethylenetriamine (0.1 M KCl, 25°C) ref. 26
[d] N-hydroxyethylethylenediamine (0.5 M $NaClO_4$, 25°C) ref. 28

one molecule of water less released at the first complexation step compared with 2-NN or 2-NN(Me), resulting in a less positive value for $\Delta S^{Cu,L}_{CuL}$. Another effect could be a greater loss in configurational entropy for the sulphur containing ligand by chelation. Finally, the sulphur containing ligands are more water structure-breaking compared with their polyamine analogues. By complex formation, it will be possible for the water to attain a more well-ordered structure[24] and this, consequently, will lower the positive entropy contribution.

Concerning the second complexation step, it can be seen (Table I and V) that the difference $\Delta H^{Cu,L}_{CuL} - \Delta H^{CuL,L}_{CuL_2}$ for 2-NS(Me) is greater than for 2-NN and 2-NN(Me) (resp. 1.15, 0.08 and 0.67 kcal.mole^{-1}). The presence of the sulphur donor makes 2-NS(Me) a softer ligand[25] than its nitrogen analogues, and therefore increases the covalent character of the metal–ligand bonds in the 1:2 complex. $\Delta S^{CuL,L}_{CuL_2}$ is also much more unfavourable for 2-NS(Me) than for its nitrogen analogues. The differences, however, between the entropy changes for 2-NS(Me) and 2-NN are almost equal for both complexation steps (7.5 e.u. for the first step; 6.8 e.u. for the second one). This seems to support the hypothesis that the unfavourable entropy change for the sulphur containing ligand is entirely due to the nature of the ligand itself.

For 2,2-NNS(Me) the value for $-\Delta H^{Cu,L}_{CuL}$ is greater than for the bidentate 2-NN(Me), but smaller than for the tridentate 2,2-NNN.[26] We assume therefore that 2,2-NNS(Me) acts as a tridentate at the first complexation step, the sulphur atom being active in the coordination. Again $\Delta S^{Cu,L}_{CuL}$ is much more unfavourable than for 2,2-NNN, the difference being about 7 e.u. $\Delta H^{CuL,L}_{CuL_2}$ is lower than for the first complexation step of 2,2-NNS(Me). Consequently, it is possible that in the complex $Cu(2,2\text{-}NNS(Me))_2^{2+}$ the six donor atoms of the two ligand molecules are not all coordinated. The value for $-\Delta H^{Cu,2L}_{CuL_2}$ is only about 1 kcal mole^{-1} greater than the corresponding value for 2-NN(Me): respectively 24.8 kcal mole^{-1} for 2,2-NNS(Me) and 23.73 kcal.mole^{-1} for 2-NN(Me). It is therefore reasonable to assume that in the complex $Cu(2,2\text{-}NNS(Me))_2^{2+}$ there is one branch of the ligand uncoordinated: probably the $-CH_2CH_2SCH_3$ branch. This penta-coordination effect has also been suggested for the complexes $Cu(2,2\text{-}NNN)_2^{2+}$[26] and $Cu(2,3\text{-}NNN)_2^{2+}$,[27] for which $\Delta H^{CuL,L}_{CuL_2}$ is also less negative than $\Delta H^{Cu,L}_{CuL}$.

For the 1:1 complex of Cu(II) with 2,2-NSOH, one can see (Table III) that the values for $-\Delta G^{Cu,L}_{CuL}$ and $-\Delta H^{Cu,L}_{CuL}$ are lower than for the complex $Cu(2\text{-}NS(Me))^{2+}$. The presence of an alcoholic group at the end of an aliphatic chain in a ligand molecule, lowers the stability of the corresponding 1:1 complex with Cu(II) ions. The same conclusions can be drawn from a comparison of the stabilities of the complexes $Cu(2\text{-}NN(Me))^{2+}$ and $Cu(2,2\text{-}NNOH)^{2+}$[28] (Table V). We can roughly calculate the impact of an alcoholic group on the formation enthalpy from the following comparisons.

$$\Delta H^{Cu,L}_{CuL}\ (L = 2,2\text{-}NNOH) - \Delta H^{Cu,L}_{CuL}\ (L = 2\text{-}NN(Me)) = -11.09 + 11.53 = 0.44\ \text{kcal.mole}^{-1}.$$

$$\Delta H^{Cu,L}_{CuL}\ (L = 2,2\text{-}NSOH) - \Delta H^{Cu,L}_{CuL}\ (L = 2\text{-}NS(Me)) = -7.56 + 7.95 = 0.39\ \text{kcal.mole}^{-1}.$$

We can conclude that in the complexes $Cu(2,2\text{-}NNOH)^{2+}$

and $Cu(2,2\text{-}NSOH)^{2+}$ the presence of an alcoholic group lowers the formation enthalpy of these complexes with an amount of about 0.4 kcal $mole^{-1}$, compared with their analogues without the OH-group. $\Delta H^{CuL,L}_{CuL_2}$ for 2,2-NSOH is also less negative than for 2-NS(Me). Taking into account the preference of Cu(II) to form 4-coordinated complexes and the close resemblance of the formation curves of Cu(II) with 2-NS(Me) and 2,2-NSOH, we may conclude that the alcoholic groups are uncoordinated. The formation enthalpy for the complex $Cu(OH)L_2^+$ has a value comparable with those for analogue Cu(II)-hydroxo-complexes with polyamines. However, the low positive value for $\Delta S^{CuL_2,OH}_{Cu(OH)L_2}$ is rather surprising.

Nickel Complexes

Starting from $-\Delta H^{Ni,L}_{NiL} = 9.25$ kcal $mole^{-1}$ for ethylenediamine,[29] we can take 4.6 kcal $mole^{-1}$ as an estimate for the contribution of one $Ni-N_{pr}$ bond to the enthalpy change $-\Delta H^{Ni,L}_{NiL}$ for 2-NS(Me). So we can see (Table I) that the sulphur atom is coordinated in the complex $Ni(2\text{-}NS(Me))^{2+}$. However, a single Ni–S bond gives only an exothermic contribution to the enthalpy change of circa 1 kcal $mole^{-1}$. The value for $-\Delta H^{NiL,L}_{NiL_2}$ is greater than for $-\Delta H^{Ni,L}_{NiL}$. This sequence has been found for Ni(II)-complexes, when steric influences or changes in structure are absent.[30] The NiL_2^{2+} complex can also bind a third ligand molecule.[1] This reaction, however, is only as exothermic as for the formation of the 1:2 complex. As it was the case for the Cu(II)-complexes, the entropy changes at each complexation step, are less favourable than for the polyamine analogues. For both the first and the second complexation step, the difference is about 6 or 7 e.u. These lower entropy values may be ascribed to the same causes as those mentioned for the Cu(II)-complexes.

The complex $Ni(2,2\text{-}NNS(Me))^{2+}$ is less stable than the $Ni(2,2\text{-}NNN)^{2+}$ complex (Table VI). However, the value for $-\Delta H^{Ni,L}_{NiL}$ is slightly more exothermic (8.67 kcal $mole^{-1}$) than the value, roughly calculated by adding the enthalpy contributions of a $Ni-N_{pr}$, a $Ni-N_{sec}$ and Ni–S bond (about 8.3 kcal $mole^{-1}$). We therefore assume that the ligand 2,2-NNS(Me) acts as a tridentate in the 1:1 complex with Ni(II). The value for $\Delta S^{Ni,L}_{NiL}$ is also less favourable than for 2,2-NNN, the difference being 5.3 e.u.

The second stage of complex formation with 2,2-NNS(Me) is appreciable more exothermic than the first one, so that we may conclude that in the 1:2 complex all six donor atoms are coordinated to the Ni(II)-ion. However, it is surprising that the values for $\Delta S^{NiL,L}_{NiL_2}$ are almost equal for 2,2-NNS(Me) and 2,2-NNN. Different values for the thermodynamic parameters for the isomerisation reaction meridional ⇌ facial in the 1:1 complex[28] can be an explanation.

TABLE VI

The thermodynamic functions of the Ni(II)-complexes with some polyamines. Comparison table.

	2-NN[a]	2,2-NNN[b]	2,2-NNOH[c]
$-\Delta G^{Ni,L}_{NiL}$	10.22	14.45	9.50
$-\Delta G^{NiL,L}_{NiL_2}$	8.79	10.90	7.95
$-\Delta G^{NiL_2,L}_{NiL_3}$	5.61		
$-\Delta H^{Ni,L}_{NiL}$	9.25	11.85	7.78
$-\Delta H^{NiL,L}_{NiL_2}$	9.19	13.45	8.31
$-\Delta H^{NiL_2,L}_{NiL_3}$	9.46		
$\Delta S^{Ni,L}_{NiL}$	3.3	8.5	5.8
$\Delta S^{NiL,L}_{NiL_2}$	−1.3	−8.5	−1.2
$\Delta S^{NiL_2,L}_{NiL_3}$	−12.9		

[a] ethylenediamine (0.3 M ClO_4^-, 25°C) ref. 29

[b] diethylethylenediamine (0.1 M KCl, 25°C) ref. 26

[c] N-hydroxyethylethylenediamine (0.5 M $NaClO_4$, 25°C) ref. 28

The enthalpy changes for both complexation steps of 2,2-NSOH with Ni(II) are less exothermic than for 2-NS(Me). So, the presence of the alcoholic group exercises a destabilising effect upon complex formation. The values for $\Delta S^{Ni,L}_{NiL}$ and $\Delta S^{NiL,L}_{NiL_2}$ are less negative for 2,2-NSOH than for 2-NS(Me). Therefore it is most probable that 2,2-NSOH acts as a bidentate with Ni(II), as it was proposed with Cu(II).

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