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THERMOCHEMICAL STUDY OF THE STEPWISE PROTONATION OF 1,10-DIAZA-4,7-DITHIADECANE, AND ITS COMPLEX FORMATION WITH COPPER(II) AND NICKEL(II) IONS IN AQUEOUS SOLUTION

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ABSTRACT

The behaviour of 1,10-diaza-4,7-dithiadecane (2,2,2-NSSN) in aqueous solution in equilibria with protons, Cu^{2+} or Ni^{2+} ions has been investigated potentiometrically and calorimetrically. The protonation constants for the ligand, and the stability constants for its complexes at 25°C in 0.5 mole dm^{-3} $(K)NO_3$ are reported, together with the corresponding thermodynamic parameters ΔG, ΔH and ΔS. The results are compared with those for 1-aza-4-thiapentane and 1,7-diaza-4-thiaheptane. The ligand 2,2,2-NSSN forms complexes of formula ML^{2+} and MHL^{3+} with both Cu^{2+} and Ni^{2+}. It is found that in the non-protonated 1 : 1 complexes the ligand acts as a tetradentate. In the $CuHL^{3+}$ complex, the ligand is bound through one nitrogen and two sulphur donors, whereas in the $NiHL^{3+}$ complex the ligand is probably bound through only one nitrogen and one sulphur donor. Explanations are suggested.

INTRODUCTION

In previous studies, the stability constants and heats of stepwise formation of the complexes of Cu^{2+} and Ni^{2+} with the bidentate ligand 1-aza-4-thiapentane [1] (2-NS(Me)) ** and the tridentate ligand 1,7-diaza-4-thiaheptane [2] (2,2-NSN) were measured. This research has now been extended to the tetradentate ligand 1,10-diaza-4,7-dithiadecane, $NH_2(CH_2)_2S(CH_2)_2S(CH_2)_2NH_2$ (2,2,2-NSSN). The protonation constants of this ligand and the stability constants for its complexes with Cu^{2+} and Ni^{2+} have been determined at 25°C in 0.5 mole dm^{-3} $(K)NO_3$. The corresponding enthalpies of reaction have been determined calorimetrically under the same conditions. From these values and the values of the free-energy changes the corresponding entropy changes have been calculated.

The ligand 2,2,2-NSSN has been studied previously by several other workers [3—5] using a potentiometric method.

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** For the abbreviations of the names of the ligands, see ref. 1.

EXPERIMENTAL

Materials

The compound 2,2,2-NSSN was prepared according to the method already described [6]. It was purified as the hydrochloride which was recrystallized from ethanol and dried to constant weight. Solutions of potassium hydroxide, nitric acid, copper(II) nitrate and nickel(II) nitrate were obtained and standardized as previously described [1].

Potentiometric measurements

$-\log[H^+]$ data were obtained by potentiometric tritations with the apparatus and $[H^+]$-calibration method previously described [1]. For each titration the cell contained 80.0 ml of a solution in which known amounts of the amine · 2 HCl, nitric acid and, for metal—ligand equilibria, metal salt were present. The solution was then stepwise titrated with standardized KOH solution. All measurements were carried out at 25 ± 0.05°C in 0.5 mole dm^{-3} $(K)NO_3$.

Experimental details are given in Table 1. The calculation procedures for the protonation constants and the stability constants have been described elsewhere [7].

Calorimetric measurements

The calorimetric measurements were carried out in an LKB 8700/2 titration calorimeter, thermostatted at 25 ± 0.001°C. The procedure for the determination of the reaction heats has already been described [8]. For the protonation measurements, different volumes of a standard solution of nitric acid ($C_{HNO_3} = 0.501$ mole dm^{-3}) were added to ca. 80.0 ml of a 0.5 mole dm^{-3} KNO_3 solution containing the pure amine ($C_L = 4.04 \times 10^{-2}$ mole

TABLE 1

Experimental details of the potentiometric titrations (Initial concentrations mole $dm^{-3} \times 10^2$) [a]

Cation	$[M^{2+}]$	[L]	$[H^+]$	$-\log[H^+]$ range
H^+		4.0438	9.6175	3.62 [b]—11.02
		3.0012	6.1414	3.98—11.23
Cu^{2+}	1.1700	2.3529	7.0165	3.10—7.56
	0.8288	2.5000	7.4550	3.17—7.68
	0.6799	2.5641	7.6461	3.12—7.44
Ni^{2+}	1.4183	2.7777	7.7378	4.02—8.42
	0.7265	3.0487	8.4927	4.10—8.76
	0.5226	2.9762	8.2905	3.88—8.58

[a] Titer KOH solution : 1.0040 mole dm^{-3} KOH in 0.5 mole dm^{-3} KNO_3.
[b] Value for $-\log[H^+]$ after the first addition of strong base.

dm^{-3}). For the formation of the copper(II) complexes, different volumes of a standard solution of potassium hydroxide ($C_{KOH} = 1.0040$ mole dm^{-3} in 0.5 mole dm^{-3} KNO_3) were added to ca. 80.0 ml of a solution containing the amine · 2 HCl ($C_L = 2.500 \times 10^{-2}$ mole dm^{-3}), copper(II) nitrate ($C_{Cu} = 0.829 \times 10^{-2}$ mole dm^{-3}) and a slight excess of nitric acid (total $C_H = 7.455 \times 10^{-2}$ mole dm^{-3}). The heats of formation of the nickel(II) complexes were determined by adding different volumes of the standard nitric acid solution to ca. 80.0 ml of a solution containing the nickel(II) complexes ($C_{Ni} = 0.727 \times 10^{-2}$ mole dm^{-3}, $C_L = 3.049$ mole dm^{-3}) starting at $-\log[H^+] = 8.12$. The heats of formation of all the species were calculated using an appropriate program [9].

RESULTS AND DISCUSSION

The reaction constants and thermodynamic functions for the stepwise protonation of 2,2,2-NSSN and its complexation with Cu^{2+} and Ni^{2+} ions are represented in Table 2.

It can be seen that the values for the enthalpy change for both protonation stages are very close, so that the two amino groups hardly influence each other when they are protonated. The difference between the values for the free-energy change is much larger. This is due to the large difference between the two values for the entropy change, as a consequence of the different degree of "chain-stiffening" [10] between the mono- and the diprotonated form of the ligand.

2,2,2-NSSN forms two complexes with Cu^{2+}, of formula CuL^{2+} and $CuHL^{3+}$. The ΔH value of the reaction $Cu^{2+} + [H(2,2,2\text{-NSSN})]^+ \rightleftharpoons [CuH(2,2,2\text{-NSSN})]^{3+}$ is more negative than that obtained for the formation of the corresponding complex with 1,8-diaza-4-thiaoctane (2,3-NSN; −29.3 kJ $mole^{-1}$), in which only one Cu—N and one Cu—S bond are formed [2]. Moreover, the entropy change accompanying the formation of [CuH(2,2,2-

TABLE 2

Thermodynamic functions of protonation and complex formation with 2,2,2-NSSN [a]

Reaction	log K	$-\Delta G$ [b]	$-\Delta H$ [b]	ΔS [b]
$H^+ + L \rightleftharpoons HL^+$	9.637 (2) [c]	54.98 (1)	54.5 (2)	1.6 (7)
$H^+ + HL^+ \rightleftharpoons H_2L^{2+}$	8.965 (3)	51.15 (2)	53.9 (3)	−9 (1)
$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	10.911 (3)	62.25 (2)	67.9 (2)	−18.9 (7)
$Cu^{2+} + HL^+ \rightleftharpoons CuHL^{3+}$	5.05 (5)	28.8 (3)	35 (1)	−20 (4)
$Ni^{2+} + L \rightleftharpoons NiL^{2+}$	7.691 (3)	43.88 (2)	50.3 (3)	−21 (1)
$Ni^{2+} + HL^+ \rightleftharpoons NiHL^{3+}$	3.55 (6)	19.1 (3)	20 (1)	−3 (4)

[a] 25°C in 0.5 mole dm^{-3} $(K)NO_3$.

[b] ΔG and ΔH in kJ $mole^{-1}$; ΔS in J K^{-1} $mole^{-1}$. Standard state: 1 mole dm^{-3}.

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

NSSN)]$^{3+}$ is much more unfavourable than that of [CuH(2,3-NSN)]$^{3+}$ (—9 J K^{-1} mole^{-1}) [2]. These comparisons can support the suggestion that in the complex [CuH(2,2,2-NSSN)]$^{3+}$ the ligand is bound to the Cu^{2+} ion by one nitrogen and two sulphur donor atoms.

Compare the enthalpy change of the reaction Cu^{2+} + [H(2,2,2-NSSN)]$^{+}$ $\rightleftharpoons$ [CuH(2,2,2-NSSN)]$^{3+}$ with that of the reaction Cu^{2+} + 2,2,2-NSSN $\rightleftharpoons$ [Cu(2,2,2-NSSN)]$^{2+}$; let us assume that in the simple 1 : 1 complex the ligand is coordinated to the central Cu^{2+} ion by its four donor atoms. Some evidence for this assumption can also be found in the observation that the enthalpy change for the formation of Cu(2,2,2-NSSN)$^{2+}$ is more exothermic than for the formation of the 1 : 1 complex of Cu^{2+} with 1,7-diaza-4-thiaheptane (2,2-NSN), in which two Cu—N and one Cu—S bonds are formed [2]. However, the $-\Delta H$ value for [Cu(2,2,2-NSSN)]$^{2+}$ is lower than the value $-(\Delta H_1 + \Delta H_2)$ for the formation of the 1 : 2 complex with 1-aza-4-thiapentane [1] (2-NS(Me)) (67.9 and 71.3 kJ mole^{-1}, respectively). In the former complex there are three consecutive five-membered rings, whereas the latter contains two unconnected five-membered rings. Thus the formation of a five-membered ring between the two adjacent sulphur atoms in [Cu(2,2,2-NSSN)]$^{2+}$ presumably leads to a destabilization of the coordinate bonds by introduction of steric strain. However, no structural data exist which could confirm this hypothesis.

2,2,2-NSSN also forms two complexes with Ni^{2+}, of formula NiL^{2+} and NiHL^{3+}. As for the Cu^{2+} complexes, the higher $-\Delta H$ value for the formation of the 1 : 1 complex of Ni^{2+} with 2,2,2-NSSN, relative to the corresponding values with 2,2-NSN and 2,3-NSN (50.3, 41.9 and 39.0 kJ mole^{-1}, respectively) can account for the complete coordination of 2,2,2-NSSN by its four donor atoms. The enthalpy change for the formation of [Ni(2,2,2-NSSN)]$^{2+}$ is also more exothermic than that for the formation of the 1 : 2 complex of Ni^{2+} with 2-NS(Me) (—48.6 kJ mole^{-1}). However, this cannot be a rigorous comparison, since in solution the 1 : 1 complexes of Ni^{2+} with linear tetradentate ligands can exist as octahedral paramagnetic or planar diamagnetic species. In turn, the paramagnetic species can exist in *cis* α, *cis* β and *trans* forms [11]. It is therefore possible that in solution at equilibrium the complex [Ni(2,2,2-NSSN)]$^{2+}$ can exist in those four different forms, but the percentage of each form cannot be established from the single value of the enthalpy change alone.

However, it has been shown [12] that the ligand 1,6-bis(2-pyridyl)-2,5-dithiahexane forms a 1 : 1 complex with Ni^{2+} in the solid state; this complex also has three consecutive five-membered rings, involving the sulphur atoms and the pyridine nitrogens. Models indicated that steric requirements prevented coordination of this ligand to the metal ion in a planar arrangement, since the two sulphur atoms, separated by only two carbon atoms, enteracted sterically. Therefore, it might be possible that for the complex [Ni(2,2,2-NSSN)]$^{2+}$ the octahedral *cis* α and *cis* β forms are dominant.

The enthalpy change for the reaction Ni^{2+} + [H(2,2,2-NSSN)]$^{+}$ $\rightleftharpoons$ [NiH(2,2,2-NSSN)]$^{3+}$ is less exothermic than for the corresponding reaction with 2,3-NSN as ligand (20 and 21 kJ mole^{-1}, respectively) [2]. The entropy change for the former reaction is also less unfavourable than that for the latter (−3 and −18 J K^{-1} $mole^{-1}$, respectively). This might indicate that in the complex $[NiH(2,2,2\text{-}NSSN)]^{3+}$ the ligand is only coordinated through one nitrogen and one sulphur atom.

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