Thermochimica Acta, 32 (1979) 27–31
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THERMOCHEMICAL STUDY OF THE COMPLEX FORMATION OF COPPER(II) AND OF NICKEL(II) IONS WITH 1,7-DIAZA-4-THIAHEPTANE AND 1,8-DIAZA-4-THIAOCTANE IN AQUEOUS SOLUTION

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(Received 30 August 1978)

ABSTRACT

The enthalpies of the reactions in 0.5 mole dm^{-3} (K)NO$_3$ at 25°C between 1,7-diaza-4-thiaheptane (2,2-NSN) and 1,8-diaza-4-thiaoctane (2,3-NSN) and Cu^{2+} and Ni^{2+} ions have been determined by direct calorimetric titrations. ΔG values reported elsewhere have been used to calculate the corresponding ΔS values. It is found that in all the complexes the co-ordination of the sulphur atom is achieved, and that in the 1:1 complexes of Cu^{2+} and Ni^{2+} both ligands are acting as tridentates. Evidence is found for the incomplete coordination of the second ligand molecule in the CuL$_2^{2+}$ complexes, whereas the NiL$_2^{2+}$ complexes are six coordinate.

INTRODUCTION

As indicated by a spectroscopic study of Taylor and Barefield[1], the ligand 1,7-diaza-4-thiaheptane (2,2-NSN)** is chelated by its three donor atoms (N, S and N) to Cu^{2+} and Ni^{2+} in solid state complexes. In aqueous solution however, it remained unclear as to whether 2,2-NSN acted as a bi- or as a tridentate towards these metal ions[2, 3].

Therefore, we recently reinvestigated potentiometrically the complex formation of Cu^{2+} and Ni^{2+} in aqueous solution with a series of sulphides containing α,ω-diamines, i.e. 1,7-diaza-4-thiaheptane (2,2-NSN), 1,8-diaza-4-thiaoctane (2,3-NSN), 1,9-diaza-4-thianonane (2,4-NSN) and 1,9-diaza-5-thianonane (3,3-NSN)[4].

In order to obtain a more reliable picture of the complex formation, we have now completed a calorimetric study of the coordinating properties of 2,2-NSN and 2,3-NSN towards Cu^{2+} and Ni^{2+}.

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** The abbreviation of the name of a ligand contains consecutively the donor atoms, preceded by the number(s) of methylene groups between two donor atoms.

EXPERIMENTAL

Materials

The preparation of the two ligands has already been described[5]. Solutions of the amines, potassium hydroxide, nitric acid, and copper(II) and nickel(II) nitrate were obtained and standardized as previously reported[6].

Calorimetric titrations

The calorimetric titrations were performed with a LKB-8700/2 titration calorimeter, thermostated at 25 ± 0.001 °C. The procedure for the determination of the reaction heats has already been described[7]. For the copper(II) complexes, the calorimetric measurements involved stepwise addition of KOH solution (C_{KOH} = 0.994 mole dm^{-3} in 0.5 mole dm^{-3} KNO_3) into solutions (ca. 0.080 dm^3) of copper(II) nitrate, ligand and nitric acid. The copper(II) ion concentrations were varied over a fourfold range (0.2–0.8 × 10^{-2} mole dm^{-3}) for four sets of solutions, in which the ligand-to-copper ion ratios were 2:1, 2.5:1, 3:1 and 4:1. For the nickel(II) complexes, the calorimetric vessel contained ca. 0.080 dm^3 of a solution of the complexes. The complexes were then decomposed by stepwise addition of a HNO_3 solution (C_{HNO_3} = 0.495 mole dm^{-3}). The nickel(II) ion concentration was varied over a four-fold range (0.25–1.0 × 10^{-2} mole dm^{-3}) for three sets of solutions in which the ligand-to-nickel ion ratios were 2:1, 2.5:1 and 4:1.

The $-\log[H^+]$ ranges covered in the titrations were 4.3–10.5 for copper and 10.8–3.5 for nickel. All the measurements were at I = 0.5 mole dm^{-3} (K)NO_3.

Calculations

The enthalpy changes ΔH for the formation of the complex species were calculated with a FORTRAN IV program. The details concerning the calculation procedure have already been reported[8].

The value for the entropy change ΔS for a complex formation reaction was calculated using the obtained ΔH value and the stability constant for the complex. Values for the stability constants were taken from material already published[4].

RESULTS AND DISCUSSION

Complexes of copper(II)

There are three complexes of Cu^{2+} with the ligand 2,2-NSN: CuL^{2+}, CuL_2^{2+} and $Cu(OH)L^+$, and five complexes with the ligand 2,3-NSN: CuL^{2+}, $CuHL^{3+}$, CuL_2^{2+}, $CuHL_2^{3+}$ and $Cu(OH)L^+$. The stability constants for the formation of these complexes have already been reported[4]. Their heats of formation have been measured and the results are shown in Table 1.

The heat of formation of $[Cu(2,3\text{-NSN})]^{2+}$ is not only appreciably more exothermic than that for the 1:1 complex of Cu^{2+} with 1-aza-4-thiapentane[6] (−33.3 kJ mole^{-1}), but is also more exothermic than that for the 1:1 complex of Cu^{2+} with

TABLE 1

THE STABILITY CONSTANTS[a] AND THE THERMODYNAMIC FUNCTIONS[b] OF THE COPPER(II) AND NICKEL(II) COMPLEXES WITH 1,7-DIAZA-4-THIAHEPTANE AND 1,8-DIAZA-4-THIAOCTANE

Reaction[c]	*2,2-NSN*[d]			*2,3-NSN*[e]		
	log K	*−ΔH*	*ΔS*	*log K*	*−ΔH*	*ΔS*
$Cu + L \rightleftharpoons CuL$	9.020	51.4(1)[f]	0.2(5)	10.035	59.0(1)	−5.8(5)
$Cu + HL \rightleftharpoons CuHL$				4.66	29.3(8)	−9(3)
$CuL + L \rightleftharpoons CuL_2$	5.238	33.7(3)	−12(1)	2.86	32.7(3)	−54(1)
$CuL + HL \rightleftharpoons CuHL_2$				2.44	31.8(9)	−59(3)
$CuL + OH \rightleftharpoons Cu(OH)L$	5.90	18.0(8)	52(4)	4.60	13.4(9)	43(4)
$Ni + L \rightleftharpoons NiL$	7.377	41.9(2)	0.7(6)	5.989	39.0(2)	−16.2(8)
$Ni + HL \rightleftharpoons NiHL$				2.75	21.3(5)	−18(2)
$NiL + L \rightleftharpoons NiL_2$	6.142	48.6(3)	−45(1)	3.86	38.9(3)	−56(1)
$NiL + HL \rightleftharpoons NiHL_2$				1.88	29.7(5)	−63(2)

[a] Data from ref. 4.

[b] 25 °C; 0.5 mole dm^{-3} $(K)NO_3$; ΔH in kJ $mole^{-1}$; ΔS in JK^{-1} $mole^{-1}$.

[c] Charges of ions are omitted.

[d] 2,2-NSN = 1,7-diaza-4-thiaheptane.

[e] 2,3-NSN = 1,8-diaza-4-thiaoctane.

[f] Values in parentheses are the standard deviations on the last significant figure; the reliability of the values is estimated to be better than four times the standard deviation.

ethylenediamine[9] (-52.6 kJ $mole^{-1}$) by an amount comparable with the strength of one Cu–S bond (about 6.7 kJ $mole^{-1}$)[6]. This is a strong indication that in $[Cu(2,3\text{-}NSN)]^{2+}$ the ligand is bound by its three donor atoms, thus acting as a tridentate.

The heat of formation of $[Cu(2,2\text{-}NSN)]^{2+}$ is lower than that of $[Cu(2,3\text{-}NSN)]^{2+}$. It is even slightly less exothermic than that for the 1:1 complex of Cu^{2+} with ethylenediamine. The difference is about 1.2 kJ $mole^{-1}$. That does not necessarily mean that the sulphur atom is not bound to the Cu^{2+} ion, but it rather indicates that the chelation of 2,2-NSN as a tridentate induces more strain in the two linked five membered chelate rings than is the case for 2,3-NSN where there is an alternation in the sizes of the two linked chelate rings. Supplementary to this may be the large nephelauxetic effect of the sulphur atom which may lead to an increase in the Cu–donor atom bond lengths. This is supported by the electronic[10] and EPR[11] spectral data reported for $[Cu(2,2\text{-}NSN)]^{2+}$.

For the second complexation step, the heats of formation of $[Cu(2,2\text{-}NSN)_2]^{2+}$ and of $[Cu(2,3\text{-}NSN)_2]^{2+}$ are not very different, but they are appreciably less exothermic than for the first complexation step. In fact, their values are comparable with the value for the heat of formation of the 1:1 complex of Cu^{2+} with 1-aza-4-thiapentane[6] in which one Cu–N and one Cu–S bond are formed. From this comparison we can deduce that in the two former complexes there is incomplete coordination of the second molecule of ligand, leaving one amino group free.

The two protonated species, $[CuH(2,3\text{-}NSN)]^{3+}$ and $[CuH(2,3\text{-}NSN)_2]^{3+}$, have values for their heat of formation very close to that for $[Cu(2,3\text{-}NSN)_2]^{2+}$. Their coordination occurs consequently through one nitrogen and one sulphur donor. The protonated aminogroup is probably the one on the trimethylene arm, since it has the largest basicity[5].

The entropy changes accompanying the formation of the normal and the protonated complex species are all appreciably less favourable than for the corresponding complexes with triamine ligands. The main reason for this is the greater degree of hydration of the triamines relative to the sulphur containing diamines, so that more hydrated water is released when the former ligands coordinate to a metal ion[6].

Finally, the greater stability of the hydroxo-complexes $[Cu(OH)(2,2\text{-}NSN)]^+$ and $[Cu(OH)(2,3\text{-}NSN)]^+$ relative to the hydroxo-complexes with the corresponding triamines[12], is also reflected by their greater heat of formation. It is therefore possible that the hydroxo-complexes with the sulphur containing ligands have a different structure from those with the triamines.

Complexes of nickel(II)

There are two complexes of Ni^{2+} with the ligand 2,2-NSN: NiL^{2+} and NiL_2^{2+}, and four complexes with the ligand 2,3-NSN: NiL^{2+}, $NiHL^{3+}$, NiL_2^{2+} and $NiHL_2^{3+}$. The stability constants for the formation of these complexes have already been communicated[4]. Their thermodynamic functions are reported in Table 1. It was found that the stability of the complexes $[Ni(2,2\text{-}NSN)]^{2+}$ and $[Ni(2,3\text{-}NSN)]^{2+}$ was lower than for the analogous complexes with diethylenetriamine[13] and ethylenediamine[14]. Their heats of formation, however, are more exothermic than that for the 1:1 complex of Ni^{2+} with ethylenediamine (-38.7 kJ $mole^{-1}$)[15]. Then let us assume that the sulphur atom is coordinated to the Ni^{2+} ion in both complexes. With 19.3 kJ $mole^{-1}$ as the value for the exothermic contribution of one Ni–N bond[6] in the formation of the two complexes, it becomes clear that the strength of the Ni–S bond in $[Ni(2,2\text{-}NSN)]^{2+}$ (about 3.3 kJ $mole^{-1}$) and in $[Ni(2,3\text{-}NSN)]^{2+}$ (about 0.5 kJ $mole^{-1}$) is smaller than in the 1:1 complex of Ni^{2+} with 1-aza-4-thiapentane (about 4.2 kJ $mole^{-1}$)[6]. The donor strength of the sulphide group appears to be weakened when linking the two chelate rings present in the complex.

Contrary to that observed for the 1:1 complexes with Cu^{2+}, both the stability and the heat of formation of $[Ni(2,3\text{-}NSN)]^{2+}$ are lower than for $[Ni(2,2\text{-}NSN)]^{2+}$. A possible explanation can be looked for in different percentages of the facial and meridional isomers in a tetragonal ligand field for both 1:1 complexes[16]. As for the 1:2 complexes, one can notice that the addition of the second ligand molecule takes place with a ΔH_2 value greater than ΔH_1 for 2,2-NSN, but equal, within the standard deviation, to ΔH_1 for 2,3-NSN. Differences in ligand solvation and/or steric hindrance between the two molecules of 2,3-NSN can therefore be an explanation. It remains, however, very probable that the 1:2 complexes with both ligands are six coordinate. The heat of formation relative to the reaction

$$Ni^{2+} + H(2,3\text{-}NSN)^{+} \rightleftharpoons [NiH(2,3\text{-}NSN)]^{3+}$$

is about 17.7 kJ $mole^{-1}$ less exothermic than the enthalpy change for the formation of $Ni(2,3\text{-}NSN)^{2+}$, but only 2.1 kJ $mole^{-1}$ less exothermic than the heat of formation of the 1 : 1 complex of Ni^{2+} with 1-aza-4-thiaheptane ($NH_2CH_2CH_2SCH_2CH_2CH_3$)[17]. The latter difference can be attributed to the destabilising effect exercised by the protonated aminogroup upon the stability of the chelate ring in the complex.

Finally, it can be noticed that the low stability of $[NiH(2,3\text{-}NSN)_2]^{3+}$ is due to the very negative value for the entropy change, although the heat of formation is more exothermic than for $[NiH(2,3\text{-}NSN)]^{3+}$. The more unfavourable entropy changes for the formation of both $[NiH(2,3\text{-}NSN)]^{3+}$ and $[NiH(2,3\text{-}NSN)_2]^{3+}$ relative to the corresponding normal complexes can be explained by the greater solvent orientating power of the protonated complexes[12] and by the greater rigidity of the aliphatic chain bound to the ammonium group[18].

ACKNOWLEDGEMENTS

The authors wish to thank Prof. Dr. Ir. Z. Eeckhaut for helpful discussions and Mr. W. Lippens and Mrs. W. Schaubroeck for technical assistance.

REFERENCES

1 L. T. Taylor and E. K. J. Barfield, *J. Inorg. Nucl. Chem.*, 31 (1969) 3831.
2 E. Gonick, W. C. Fernelius and B. E. Douglas, *J. Am. Chem. Soc.*, 76 (1954) 4671.
3 A. May and D. J. MacDonald, *U.S. Bur. Mines, Rep. Invest.*, 7825 (1974).
4 G. G. Herman, A. M. Goeminne and Z. Eeckhaut, *J. Coord. Chem.*, in press.
5 G. G. Herman and A. M. Goeminne, *J. Coord. Chem.*, 7 (1977) 75.
6 G. G. Herman, A. M. Goeminne and Z. Eeckhaut, *J. Coord. Chem.*, 7 (1977) 53.
7 L. Wadsö, *Sci. Tools*, 13 (1966) 33.
8 J. J. Tombeux, A. M. Goeminne and J. Schaubroeck, *Thermochim. Acta*, 19 (1977) 327.
9 R. Barbucci, L. Fabbrizzi, P. Paoletti and A. Vacca, *J. Chem. Soc., Dalton Trans.*, (1972) 740.
10 A. M. Goeminne and L. C. Van Poucke, unpublished results.
11 R. Barbucci and M. J. H. Campbell, *Inorg. Chim. Acta*, 16 (1976) 113.
12 R. Barbucci, L. Fabbrizzi and P. Paoletti, *J. Chem. Soc., Dalton Trans.*, (1974) 2403.
13 M. Ciampolini, P. Paoletti and L. Sacconi, *J. Chem. Soc.*, (1961) 2994.
14 M. Ciampolini, P. Paoletti and L. Sacconi, *J. Chem. Soc.*, (1960) 4553.
15 F. Holmes and D. R. Williams, *J. Chem. Soc. A*, (1967) 1702.
16 L. C. Van Poucke and G. G. Herman, unpublished results.
17 G. G. Herman, to be published.
18 D. H. Everett and B. R. W. Pinsent, *Proc. R. Soc. (London), Ser. A*, 215 (1952) 416.