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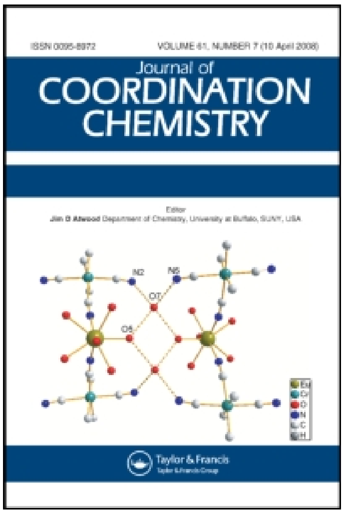

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EQUILIBRIUM STUDIES OF COPPER(II) AND OF NICKEL(II) COMPLEXES WITH SULPHIDE CONTAINING α,ω-DIAMINES

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EQUILIBRIUM STUDIES OF COPPER(II) AND OF NICKEL(II) COMPLEXES WITH SULPHIDE CONTAINING α,ω-DIAMINES

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The complex formation of Cu^{2+} and Ni^{2+} with 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) has been studied potentiometrically at 25°C in 0.5 mol dm^{-3} (K)NO_3 medium. The formation constants of the CuL^{2+} complexes with the four ligands are 9.02, 10.03, 9.49 and 9.79 respectively. In these 1:1 complexes the ligands can be facially disposed. 2,2-NSN and 2,3-NSN also form a $CuL_2{}^{2+}$ complex with log K_2 = 5.24 and 2.86 respectively, whereas the hydrolysis constants of the $[Cu(OH)L]^+$ species with the same ligands are 5.90 and 4.60. 2,3-NSN also forms the species $CuHL^{3+}$ and $CuHL_2{}^{3+}$, with protonation constants 4.77 and 9.7 respectively. With Ni^{2+} only 5,5- and 5,6-membered chelate ring systems are formed. With 2,2-NSN log K_1 = 7.377 and log K_2 = 6.142. With 2,3-NSN log K_1 = 5.989 and log K_2 = 3.86. There is a six co-ordinate environment about the metal ion in the $NiL_2{}^{2+}$ complexes. The Ni(II) complexes of the latter ligand may be protonated to $NiHL^{3+}$ and $NiHL_2{}^{3+}$ with protonation constants of 6.9 and 8.2 respectively.

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INTRODUCTION

Much attention has been paid to some transition metal ion complexes with linear aliphatic triamines forming complexes with two condensed chelate rings with varying ring sizes.[1,2,3,4] For the normal 1:1 complexes with Cu^{2+} and Ni^{2+} it was found that the complexes containing two five membered chelate rings are more stable than those containing two six membered ones. However, when the complex contains two alternate 5,6 membered chelate rings, the cumulative ring strain is decreased[1] and the complex gains an additional stability. The 1:1 complexes of Cu^{2+} and Ni^{2+} with triamines containing either two alternate 5,7 membered or two alternate 6,7 membered chelate rings are less stable than those with diethylenetriamine.[4] This has been ascribed to the low stability of the seven membered chelate ring, due to the repulsion which occurs between adjacent polar aminogroups when they must be brought closer together in order to effect co-ordination to the metal ion.[5] Moreover the aminogroup at the end of the tetramethylene chain is even not co-ordinated to the Ni^{2+} ion in the case of 1,4,9-triazanonane.[2]

In this work we have turned our attention to the co-ordination ability of a series of α,ω-diamines containing a sulphur atom in their skeleton. The series investigated, 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), was chosen to determine the relative stability in function of the sizes of the chelate rings formed in their complexes with Cu^{2+} and Ni^{2+}. The stability constants were determined by a potentiometric method at 25°C in 0.5 mol dm^{-3} (K)NO_3. Comparison of the results with those of the triamines would make it possible to assess the influence of the sulphide donor on the stability sequence of condensed chelate ring systems.

EXPERIMENTAL

Materials

The preparation of the four ligands has already been described.[6] Solutions of the amines, potassium hydroxide, nitric acid, and copper(II) and nickel(II) nitrate were obtained and standardized as previously described.[7]

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E.M.F. Measurements

All the potentiometric titrations were done with a Radiometer PHM 64 digital potentiometer equipped with an Ingold HA 201 glass electrode, an 0.5 mol dm^{-3} KNO_3 salt bridge and an Ingold 3 mol dm^{-3} KCl calomel electrode, following the procedure previously described.[7] The measurements were carried out at 25°C in 0.5 mol dm^{-3} $(K)NO_3$. For each metal-ligand system several titrations were performed. The metal to ligand ratios varied between 1:2 and 1:20. The initial total concentrations varied between 2×10^{-2} mol dm^{-3} and 5×10^{-3} mol dm^{-3} for the ligands, and between 1×10^{-2} mol dm^{-3} and 0.9×10^{-3} mol dm^{-3} for the metal ions. Appropriate volumes of a nitric acid solution were added. The solutions were titrated with 0.9975 mol dm^{-3} KOH in 0.5 mol dm^{-3} KNO_3 so that the $-\log [H^+]$ range varied from ca. 3 to ca. 10.5. No potentiometric titration data could be obtained for the complexation of Ni^{2+} with 1,9-diaza-4-thianonane and 1,9-diaza-5-thianonane at the concentration levels used, since insoluble hydrolyse products were always present as soon as the excess of mineral acid was neutralized.

The complex formation constants were calculated with the program LEAST.[8] The protonation constants of the ligands and the experimentally measured ionic product of water ($-\log K_W = 13.72$) were held constant during the calculations.

Abbreviations

The abbreviation for the name of a ligand contains consecutively the donor atoms present in the aliphatic chain, preceeded by the number(s) of methylene groups between two donor atoms. The names of other ligands, used further in the text, are abbreviated in the same way: e.g. 2,2-NNN for diethylenetriamine, 2-NN for ethylenediamine.

RESULTS

The basicity constants of the ligands and the stability constants of their metal complexes are reported in Table I. Preliminary values for the stability constants of the 1:1 complexes of Cu^{2+} with 2,2-NSN, 2,3-NSN and 3,3-NSN and of the 1:1 and 1:2 complexes of Ni^{2+} with 2,2-NSN and 2,3-NSN were obtained from their formation curves ($\bar{n}$ versus $-\log [L]$).

Species selection and least squares refinement of the stability constants with the program LEAST (R– factors[9] of 0.3–0.5% were achieved) further revealed that (i) 2,2-NSN and 2,3-NSN form with Cu^{2+} a 1:2 complex and a hydroxo complex $[Cu(OH)L]^+$, (ii) 2,3-NSN forms both with Ni^{2+} and with Cu^{2+} the protonated species MHL^{3+} and $MHL_2{}^{3+}$, (iii) 2,4-NSN forms only the complexes CuL^{2+} and $CuHL^{3+}$.

TABLE I
The basicity constants of the ligands[a] and the stability constants of their metal complexes[b]

Ion	Reaction	2,2-NSN	2,3-NSN	2,4-NSN	3,3-NSN
H^+	$H^+ + L \rightleftharpoons HL^+$	9.682	10.139	10.440	10.365
	$H^+ + HL^+ \rightleftharpoons H_2L^{2+}$	8.821	9.161	9.249	9.628
Cu^{2+}	$Cu^{2+} + L \rightleftharpoons CuL^{2+}$	9.020(2)[c]	10.035(2)	9.490(2)	9.792(5)
	$CuL^{2+} + H^+ \rightleftharpoons CuHL^{3+}$		4.77(1)	5.99(4)	
	$CuL^{2+} + L \rightleftharpoons CuL_2{}^{2+}$	5.238(8)	2.86(1)		
	$CuL_2{}^{2+} + H^+ \rightleftharpoons CuHL_2{}^{3+}$		9.7(1)		
	$CuL^{2+} + OH^- \rightleftharpoons Cu(OH)L^+$	5.90(2)	4.60(1)		
Ni^{2+}	$Ni^{2+} + L \rightleftharpoons NiL^{2+}$	7.377(2)	5.989(3)		
	$NiL^{2+} + H^+ \rightleftharpoons NiHL^{3+}$		6.9(1)		
	$NiL^{2+} + L \rightleftharpoons NiL_2{}^{2+}$	6.142(4)	3.86(1)		
	$NiL_2{}^{2+} + H^+ \rightleftharpoons NiHL_2{}^{3+}$		8.2(3)		

[a] Data taken from Ref. 6.

[b] 25°C, 0.5 mol dm^{-3} $(K)NO_3$.

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

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DISCUSSION

The 1:1 Complexes

As can be seen from Table I, the stability constants for the 1:1 complexes of Cu^{2+} with the four S-α, ω-diamines are all smaller than the stability constant for the complex $[Cu(2,2\text{-NNN})]^{2+}$ ($\log K_1 = 15.80$).[10] The same holds for the 1:1 complexes of Ni^{2+} with 2,2-NSN and 2,3-NSN relative to the complex $[Ni(2,2\text{-NNN})]^{2+}$ ($\log K_1 = 10.60$).[10] This can probably be attributed to the lower donor strength of the sulphur atom, relative to the aminogroup.[7] However, different possibilities for the S-α, ω-diamines to co-ordinate either to Cu^{2+} or Ni^{2+} might be considered.

The first possibility is that these ligands are only co-ordinated through the two terminal aminogroups, which would lead to the formation of chelate rings with considerable ring sizes : an eight membered chelate ring in the complexes with 2,2-NSN, and even larger ones in the complexes with the other homologues. This possibility is rather improbable, since it is known that diamines like tetramethylenediamine and hexamethylenediamine seem to act as non-chelating ligands.[11]

The second possibility is that the ligands are only co-ordinated through one aminogroup and the sulphide group, leaving a free end with one aminogroup unco-ordinated. This possibility can also be excluded, when we consider that the four 1:1 complexes with Cu^{2+} and the two 1:1 complexes with Ni^{2+} are all considerably more stable than the complexes $[Cu(2\text{-NS(Me)})]^{2+}$ or $[Ni(2\text{-NS(Me)})]^{2+}$.[7] It is then reasonable to assume that the S-α,ω-diamines act as tridentates at the first complexation step. W. C. Fernelius *et al.*[12] already suggested from the complete parallel between the characteristic co-ordination number in the complexes of ethylenediamine and 1-aza-4-thiapentane, diethylenetriamine and 1,4-diaza-7-thiaheptane, and of triethylenetetramine and 1,10-diaza-4,7-dithiadecane, that the sulphur atom was active in the co-ordination. Moreover, we can also deduce some evidence for complete co-ordination of 2,2-NSN in the 1:1 complex with Ni^{2+} from the enthalpy values, determined from temperature coefficient measurements by the same authors,[12] since the enthalpy change for the formation of $[Ni(2,2\text{-NSN})]^{2+}$ ($-41.8\ \text{kJ mol}^{-1}$) was found to be more negative than the corresponding enthalpy change for $[Ni(2\text{-NN})]^{2+}$ ($-36.8\ \text{kJ mol}^{-1}$) and for $[Ni(2\text{-NN(Me)})]^{2+}$ ($-35.6\ \text{kJ mol}^{-1}$).

As one can see from Table I, $[Ni(2,2\text{-NSN})]^{2+}$ is more stable than $[Ni(2,3\text{-NSN})]^{2+}$, and, since there is no complex formation between Ni^{2+} and 2,4-NSN or 3,3-NSN under comparable concentration conditions, the stability of the nickel(II) complexes decreases with increasing distance between the two terminal aminogroups.

The following sequence was found for the stabilities of the 1:1 complexes with Cu^{2+}: $[Cu(2,3\text{-NSN})]^{2+} > [Cu(3,3\text{-NSN})]^{2+} > [Cu(2,4\text{-NSN})]^{2+} > [Cu(2,2\text{-NSN})]^{2+}$. This sequence is different from that found for the corresponding triamines:[2,13] $[Cu(2,3\text{-NNN})]^{2+}$ ($\log K_1 = 16.601$) $>$ $[Cu(2,2\text{-NNN})]^{2+}$ ($\log K_1 = 15.80$) $>$ $[Cu(3,3\text{-NNN})]^{2+}$ ($\log K_1 = 14.20$) $>$ $[Cu(2,4\text{-NNN})]^{2+}$ ($\log K_1 = 13.05$).

Two general observations can be made, when comparing the two series: (i) $[Cu(2,2\text{-NSN})]^{2+}$ is less stable than $[Cu(3,3\text{-NSN})]^{2+}$ and $[Cu(2,4\text{-NSN})]^{2+}$; (ii) the $\log K_1$ values for the triamine complexes span a range of 3.55 log K units, whereas for the S-α,ω-diamine complexes the range is only 1.02 log K units. The latter observation let us assume that the stability of the 1:1 complexes of Cu^{2+} with the S-α,ω-diamine ligands is not so dependent on the bulkiness of the ligand and of the sizes of the chelate rings formed, as this is the case for the triamine complexes.[1] This tends to suggest that the structure of the S-α,ω-diamine complexes is more flexible, which could arise from different degrees of tetragonal distortion in these complexes. A different co-ordination mode between the S-α,ω-diamines and the triamines in their 1:1 complexes with Cu^{2+} is therefore not improbable. Polyamine ligands are generally equatorially disposed in their complexes with Cu^{2+}.[1,14,15] A facial co-ordination mode is only more likely with the triamine 2,4-NNN.[2] Although only few structural information about complexes with S-α,ω-diamines is available, there is indeed some indication that their structure might be different from those with triamines.

From comparisons of the CD spectra of $[Co(2,2\text{-NSN})_2]^{3+}$ with the spectra of the isomers of the complex $[Co(2,2\text{-NNN})_2]^{3+}$, the former was assigned the unsymmetric-facial geometry.[16] Infrared evidence indicated that the complexes $[Cu(2,2\text{-NSN})OAc]ClO_4$[17] and $[Cu(2,3\text{-NSN})OAc]ClO_4$[18] are five co-ordinate in the solid state with symmetric bidentate co-ordination of the acetate ion. On the other hand, N. F. Curtis[19] has shown that the complexes $[Cu(2,2\text{-NNN})OAc]ClO_4$ and $[Cu(3,3\text{-NNN})OAc]ClO_4$ are also five co-ordinate in the solid state, but with assymetrical chelate acetate. So, if these four complexes are assumed to have the same stereochemistry, i.e. a distorted square

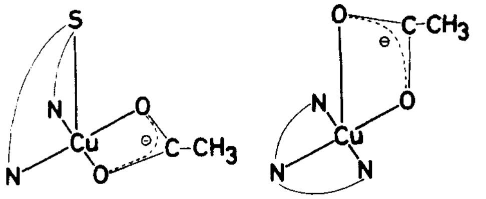

FIGURE 1 The facial arrangement of the NSN ligand and the equatorial arrangement of the NNN ligand in the complexes of general type $[CuLOAc]ClO_4$

pyramidal structure, then the ligands 2,2-NSN and 2,3-NSN are facially disposed, whereas the ligands 2,2-NNN and 3,3-NNN are equatorially disposed in these complexes (see Figure 1). No structural information about complexes with 3,3-NSN and 2,4-NSN is yet available. However, it cannot be excluded that in their 1:1 complexes with Cu^{2+} they are also facially arranged, since the small range for the stability constants of the four complexes tends to suggest a similar structure.

The 1:2 Complexes

The formation of 1:2 complexes was only found for Cu^{2+} and Ni^{2+} with 2,2-NSN and 2,3-NSN. The log K_2 value for the formation of $[Cu(2,2\text{-}NSN)_2]^{2+}$ is appreciably lower than the log K_1 value, but it is still comparable with the log K_2 value (= 5.082) for the formation of $[Cu(2\text{-}NS(Me))_2]^{2+}$.[7] It is therefore quite probable that the second molecule of the ligand 2,2-NSN is only co-ordinated through two donor atoms, preferably N and S.

The log K_2 value for the formation of $[Cu(2,3\text{-}NSN)_2]^{2+}$ is even lower than the corresponding value for $[Cu(2,2\text{-}NSN)_2]^{2+}$. This observation and the fact that the ligands 2,4-NSN and 3,3-NSN do not form a 1:2 complex under comparable concentration conditions, let us assume that the possibility for the 1:1 complexes to take up a second molecule of ligand decreases with increasing length of the ligand. This behaviour has also been shown in the Cu(II) complexes with the triamines 2,2-NNN, 2,3-NNN and 3,3-NNN.[13]

For the 1:2 complexes of 2,2-NSN and of 2,3-NSN with Ni^{2+}, one can see that, as it was the case for the complexes with Cu^{2+}, log K_2 is smaller than log K_1 and that log K_2 for $[Ni(2,3\text{-}NSN)_2]^{2+}$ is smaller than for $[Ni(2,2\text{-}NSN)_2]^{2+}$. It has been found[12] that the enthalpy change for the second complexation step of Ni^{2+} with 2,2-NSN was more exothermic than for the first one (resp. −50.2 and −41.8 kJ mol^{-1}), and from the room temperature electronic spectrum of $[Ni(2,2\text{-}NSN)_2]^{2+}$ it was found[17] that its structure was symmetric facial with trans sulphide groups. It can therefore be assumed that the two molecules of ligand are completely co-ordinated in this complex. Neither thermodynamic nor spectroscopic data are available for the complex $[Ni(2,3\text{-}NSN)_2]^{2+}$, but as its log K_2 value is still larger than the log K_1 value for the formation of $[Ni(2\text{-}NS(Me))]^{2+}$ [7] (resp. 3.86 and 3.30), a six co-ordinate structure for $[Ni(2,3\text{-}NSN)_2]^{2+}$ is also very likely.

Protonated Complexes

It can be noticed from Table I that the ligand 2,3-NSN forms both with Cu^{2+} and Ni^{2+} two protonated complex species: MHL^{3+} and $MHL_2{}^{3+}$, whereas the ligand 2,4-NSN forms with Cu^{2+} only the protonated species $CuHL^{3+}$. If we suppose that the protonated complexes are formed by protonation of the normal complexes, ML^{2+} or $ML_2{}^{2+}$, it is evident that their formation will depend on both the stability of the normal complexes and the basicity of the ligand. Considering the stability of the complexes $[Cu(2,3\text{-}NSN)]^{2+}$, $[Cu(2,4\text{-}NSN)]^{2+}$ and $[Ni(2,3\text{-}NSN)]^{2+}$, one can see that their protonation occurs easier when they are less stable. Moreover, the basicity of the normal complex is always much smaller than that of the ligand itself. This means that the nitrogen atom to be protonated in the three 1:1 complexes was co-ordinated to the metal ion. This is in agreement with the hypothesis, previously considered, of the complete co-ordination of these ligands in their normal 1:1 complexes.

The constants for the protonation of $[Cu(2,3\text{-}NSN)_2]^{2+}$ and of $[Ni(2,3\text{-}NSN)_2]^{2+}$ are higher than for the protonation of the corresponding 1:1 complexes. For the reaction $[Cu(2,3\text{-}NSN)_2]^{2+} + H^+ \rightleftharpoons [CuH(2,3\text{-}NSN)_2]^{3+}$ the constant lies between the first and the second protonation constant of the free ligand. That means that the nitrogen atom to be protonated in the complex $[Cu(2,3\text{-}NSN)_2]^{2+}$ was free, and this is in agreement with the hypothesis of incomplete co-ordination of the second molecule of ligand in the latter complex. For the reaction $[Ni(2,3\text{-}NSN)_2]^{2+} + H^+ \rightleftharpoons [NiH(2,3\text{-}NSN)_2]^{3+}$ the constant is somewhat smaller than the second protonation constant of the ligand. Therefore, the aminogroup to be protonated in the complex $[Ni(2,3\text{-}NSN)_2]^{2+}$ was probably very weakly bound to the Ni^{2+} ion.

Hydro Complexes

Both 2,2-NSN and 2,3-NSN form with Cu^{2+} an

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hydroxo complex of formula $[Cu(OH)L]^+$. This complex is formed in a –log $[H^+]$ range where the hydroxide ion competes with the second molecule of either 2,2-NSN or 2,3-NSN to be co-ordinated to the 1:1 complex. The constant for the complex $[Cu(OH)(2,2\text{-NSN})]^+$ is appreciably higher than that for $[Cu(OH)(2,3\text{-NSN})]^+$. Since $[Cu(2,2\text{-NSN})]^{2+}$ is less stable than $[Cu(2,3\text{-NSN})]^{2+}$, the tendency for hydrolysis might therefore be greater in the former than in the latter complex.

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