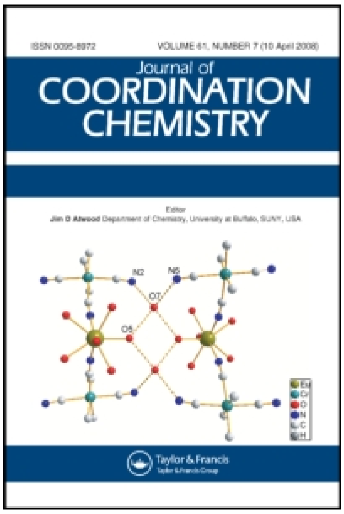

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A THERMOCHEMICAL AND SPECTROPHOTOMETRICAL STUDY OF COMPLEX FORMATION BETWEEN COPPER(II) ION AND α, π-THIADIAMINES

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A THERMOCHEMICAL AND SPECTROPHOTOMETRICAL STUDY OF COMPLEX FORMATION BETWEEN COPPER(II) ION AND α,ω-THIADIAMINES

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The enthalpies of formation of the complexes $[CuLH]^{3+}$ and $[CuL]^{2+}$ ($L = RR'N(CH_2)_nS(CH_2)_mNH_2$ with $R = CH_3$ or H; $R' = CH_3$; n,m = 2,3) have been determined at 25° and in 0.5 mol dm^{-3} KNO_3 by means of direct calorimetric titrations. The corresponding entropy changes have been calculated using the enthalpy changes and previously reported ΔG values. The absorption maxima of the d–d transitions of the $[CuL]^{2+}$ complexes have also been measured under the same conditions. For purposes of comparison the spectral investigation was extended to that of the 1:1 complexes between Cu(II) and 1,7-diaza-4-thiaheptane (2,2-NSN) and 1,8–diaza-4-thiaoctane (2,3-NSN). The exothermicity of the formation of the $[CuLH]^{3+}$ complexes is proportional to the distance between the free ammonium group and the central Cu^{2+} ion. The change of the state properties of the normal 1:1 complexes on increasing *N*-methyl substitution of the ligands suggests a decreasing solvation of the complex ion.

INTRODUCTION

We recently reported formation constants of Cu(II)-complexes with *N*-methyl substituted α,ω-thiadiamines[1] (abbreviated as n,m-(R′R)NSN; $R' = CH_3$ or H and $R = CH_3$). It was shown that for the $[Cu\,L]^{2+}$species the stability decreases with increasing substitution in contrast with what was expected from the positive inductive effect of an added methyl group. Furthermore the stabilizing effect of ring alternation was found to hold only when equally substituted α,ω-thiadiamines are compared.

We now have extended this investigation with spectrophotometric and calorimetric techniques. The ligands studied are listed in Table I.

EXPERIMENTAL

Materials

All ligands are prepared as previously described.[1,2] Solutions of the thiadiamines, potassium hydroxide, nitric acid and copper(II) were obtained and standardized as usual.[3] All solutions were made up to an ionic strength of 0.5 by adding KNO_3.

Calorimetric titrations

The calorimetric titrations were performed following Paoletti's method[4] with a LKB-8700/2 titration calorimeter, thermostated at 25 ± 0.001°. Samples containing known amounts of the substituted amine, nitric acid and copper(II) ions were titrated

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TABLE I
The α,ω-thiadiamines studied.

Ligand	Abbreviation
$NH_2(CH_2)_2S(CH_2)_2NH_2$	2,2-NSN
$NH_2(CH_2)_2S(CH_2)_3NH_2$	2,3-NSN
$CH_3NH(CH_2)_2S(CH_2)_2NH_2$	2,2-(Me)NSN
$CH_3NH(CH_2I_2)S(CH_2I_3)NH_2$	2,3-(Me)NSN
$(CH_3)_2N(CH_2)_2S(CH_2)_2NH_2$	2,2-(Me_2)NSN
$(CH_3)_2N(CH_2)_2S(CH_2)_3NH_2$	2,3-(Me_2)NSN
$NH_2(CH_2)_2S(CH_2)_3N(CH_3)_2$	2,3-NSN(Me_2)

with potassium hydroxide as reported.[1] Initial concentrations of amine and nitric acid were about 6×10^{-2} and 14×10^{-2} M respectively. Copper(II) concentrations depended on the metal/ligand ratio required to prevent the formation of insoluble hydrolysed species. All measured heats were corrected for dilution of the titrant and the formation of water as previously described.[5]

Spectroscopy

The spectra of solutions containing mixtures of Cu^{2+} and ligand at several degrees of complexation were recorded in the region 12,800 to 17,900 cm^{-1} with a Cary model 14 spectrophotometer, connected *via* an interface to a Varian 620L-100 minicomputer. The concentrations of Cu^{2+} and ligand matched those of the calorimetric measurements and the ratio was chosen so that besides the hydrated copper ion only a minimum number of species contributed to the extinction of the solution. Different degrees of complexation were obtained by adding varying amounts of standardized KOH. The length (d) of the quartz cell used was chosen so as to obtain extinctions (E_i) between 0.3 and 0.7. All measurements were carried out at $25 \pm 0.05°$. The composition of each solution and the spectral data (d, E_i, ν) were stored on the computer disk.

Calculations

The enthalpy changes are calculated with Fortran IV programs based on minimisation procedures. The calculations methods have already been reported in detail.[3] The procedure for the calculation of the spectrum (molar extinction coefficient ϵ_j as a function of wavelength λ) for each complex species j from the spectra ($E_i(\lambda)$) of a number (M) of solutions i is based on the condition that the free ligand does not absorb in the region and on the Lambert-Beer's law. At each wavelength λ the extinction E_i of each solution i may then be written in (*1*),

$$E_i = d \cdot \epsilon_0 \cdot (Cu^{2+})_i + d \cdot \sum_{j=1}^{N} \epsilon_j \cdot (\text{complex j})_i \qquad (1)$$

where ϵ_0 is the molar extinction coefficient of the hydrated copper ion at the given wavelength, ϵ_j is the molar extinction coefficient of the j^{th} complex species at the same wavelength, N is the number of complex species, and (complex j)$_i$ is the concentration of the j^{th} complex species in solution i.

As ϵ_o may be determined separately and by division of each term by $C_{i,o}$, the analytical copper ion concentration in solution i, this equation may be transformed to (*2*),

$$\frac{E_i}{C_{i,o} \cdot d} - \alpha_{i,o} \cdot \epsilon_o = \sum_{j=1}^{N} \alpha_{i,j} \cdot \epsilon_j \qquad (2)$$

where $\alpha_{i,o}$ is the mole fraction of the hydrated copper ion in solution i and $\alpha_{i,j}$ is the mole fraction of the jth complex species in solution i. Using the previously determined stability constants[1,6] the mole fractions $\alpha_{i,o}$ and $\alpha_{i,j}$ may be calculated from the composition of solution i by means of the computer program EQUIL.[7] At each wavelength the N values ϵ_j may then be calculated from the M(>N) equations (*2*) by means of a least-squares program.

The whole spectrum of each component j may then be obtained by repeating the procedure every nm over the region of interest. In practice we tried to limit the number of complex species preferably to one by choosing an adequate composition of the solutions. This normally time consuming procedure was facilitated by use of the mini-computer, with the aid of appropriate EBASIC programmes.

RESULTS AND DISCUSSION

The thermodynamic functions for the complexation of Cu^{2+} with n,m-(R,R')NSN are given in Table II. Data for the systems 2,2-NSN/Cu^{2+} and 2,3-NSN/Cu^{2+} are taken from reference 8. The calorimetric study of these complexes has been restricted to the species formed at pH < 7 ($[CuLH]^{3+}$, $[CuL]^{2+}$). Indeed, in order to prevent hydrolysis, an excess of ligand is needed and at higher pH values the heat of deprotonation exceeds the heat due to complexation.

The absorption maxima of the d-d transitions of the normal 1:1 complexes together with their molar extinction coefficients are listed in Table III. The spectra each consist of one broad asymmetric band between 15,000 and 16,000 cm^{-1}.

$[CuLH]^{3+}$ complexes

The enthalpy values of the $[CuLH]^{3+}$ complexes generally confirm the conclusions drawn from the stability constants.[1] These complexes with the asymmetric thiadiamines

TABLE II
The stability constants[a] and thermodynamic functions[b] of the Cu^{2+} complexes with the thiaamines.

Reaction	$Cu^{2+} + LH^+ \rightleftharpoons CuLH^{3+}$			$Cu^{2+} + L \rightleftharpoons CuL^{2+}$		
L	log K	−ΔH	TΔS	log K	−ΔH	TΔS
2-NS(Me)[c]	5.572(3)	33.2(2)	−1.5(2)			
2,2-NSN[d]				9.020(2)	51.4(1)	0.1(1)
2,3-NSN[d]	4.66(1)	29.3(8)	−2.7(8)	10.035(2)	59.0(1)	−1.7(1)
2,2-(Me)NSN				8.619(6)	41.0(3)	8.2(3)
2,3-(Me)NSN	4.46(3)	32.6(8)	−7. (1)	9.601(2)	48.8(5)	6.0(5)
2,2-(Me_2)NSN	3.70(6)	19. (1)	2. (1)	7.24(1)	28.8(3)	12.5(4)
2,3-(Me_2)NSN				7.93(1)	32.4(3)	12.9(4)
2,3-NSN(Me_2)	4.41(2)	27.4(8)	−2. (1)	7.60(1)	49.2(5)	−5.8(6)

[a] 0.5M KNO_3, 298 K; previously determined values, see refs. 1 and 6. [b] 0.5M KNO_3, 298 K; −ΔH and TΔS in kJ mol^{-1}. [c] 0.5M KNO_3, 298 K; data for the normal CuL^{2+} complex of 1-aza-4-thiapentane, given for comparison, see ref. 3. [d] 0.5M KNO_3, 298 K; previously determined values, see ref. 8.

TABLE III
The absorption maxima[a] (kK) of the electronic spectra of the 1:1 complexes of Cu^{2+} with α,ω-thiadiamines.

	$\nu_{d\text{-}d}$
$[Cu(2,2\text{-NSN})]^{2+}$	15.19(100)
$[Cu(2,3\text{-NSN})]^{2+}$	15.93(180)
$[Cu(2,2\text{-(Me)NSN})]^{2+}$	15.29(116)
$[Cu(2,3\text{-(Me)NSN})]^{2+}$	15.80(185)
$[Cu(2,2\text{-(Me}_2\text{)NSN})]^{2+}$	14.33(146)
$[Cu(2,3\text{-NSN(Me}_2\text{)})]^{2+}$	16.00(152)
$[Cu(2,3\text{-(Me}_2\text{)NSN})]^{2+}$	15.68(199)

[a] Values in parentheses are the molar extinction coefficients (M^{-1} cm^{-1}).

n,m-(R,R′)NSN are formed through chelation of Cu^{2+} by a sulphur atom and one of the nitrogen donors, the other nitrogen being protonated. Which nitrogen will be bound is determined by the following criteria:

1) A five membered chelate ring is more stable than a six-membered one; this was proven by the absence of a 1:1 complex of Cu^{2+} with 3-NS(Me) as contrasted with 2-NS(Me).[13]

2) Although the donor capacity of a nitrogen atom is expected to increase with increasing substitution, complexes with tertiary amines usually are less stable than those with primary amines.

3) The positively charged ammonium group exerts a destabilizing effect that increases with decreasing distance from the positive chelate centre.

4) The nitrogen most remote from the sulphur atom is more easily protonated.[2]

5) For equal distances between both amino groups and S, the protonation ability follows the sequence sec > prim > tert.[11]

As a consequence of the third criterion neither 2,2-NSN nor 2,2-(Me)NSN forms a $[CuLH]^{3+}$ species. Nevertheless with the analogous ligand 2,2-(Me_2)NSN a protonated chelate is formed and this indeed shows the lowest stability and the smallest exothermic enthalpy value ($-\Delta H$) within the whole series. Considering the second criterion, and in spite of the fifth one, the primary nitrogen will here be bound whereas the destabilizing effect of the nearby tertiary ammonium group is obviously lower than that of a secondary or primary one.

At first sight it is surprising that 2,3-(Me_2)NSN does not form a protonated five-membered chelate *via* the tertiary amine group. Obviously the constraint of the second criterion prevents this whereas chelation *via* the primary amino group is inhibited according to the first criterion. The remaining thiaamines all form a five-membered chelate with Cu^{2+} and their stability sequence

2-NS(Me) > 2,3-NSN > 2,3-(Me)NSN > 2,3-NSN(Me_2) > 2,2-(Me_2)NSN

is in accord with the above-mentioned criteria. The $-\Delta H$ sequence is parallel except that the higher donor capacity of the secondary nitrogen in 2,3-(Me)NSN, as compared with 2,3-NSN, is reflected in a reversal of their mutual position. The protonated $[CuLH]^{3+}$

species can also be considered to be formed by the protonation of the normal CuL^{2+} complex:

$$CuL^{2+} + H^{+} \rightleftharpoons CuLH^{3+}.$$

The difference in proton affinity ($-\Delta H$) between the complexed and free amine is equal to the difference in the exothermic heat of complexation between the protonated and normal complex. From Table II it can be seen that this difference amounts to several kJ mol^{-1}. This proves that the protonated nitrogen was originally bound in the normal complex.

$[CuL]^{2+}$ complexes

The $-\Delta H$ sequence for these complexes is $[Cu(2,3\text{-}NSN)]^{2+} > [Cu(2,2\text{-}NSN)]^{2+} > [Cu(2,3\text{-}NSN(Me_2))]^{2+} \simeq [Cu(2,3\text{-}(Me)NSN)]^{2+} > [Cu(2,2\text{-}(Me)NSN)]^{2+} > [Cu(2,3\text{-}(Me_2)NSN)]^{2+} > [Cu(2,2\text{-}(Me_2)NSN)]^{2+}$. Apart from the strange behaviour of $[Cu(2,3\text{-}NSN(Me_2)]^{2+}$, two general conclusions may be drawn from this sequence. First, comparing equally substituted ligands, the complexes with alternating five-six membered chelate rings are always more stable than those with two fused five-membered rings. This means that chelation of 2,2-(R′,R)NSN) is attended with greater strain than in the case of 2,3-(R′,R)NSN. The low $-\Delta H$ value for $[Cu(2,2\text{-}(Me)NSN)]^{2+}$ (41.0 kJ mol^{-1}) relative to that for $[Cu(N\text{-}methylethylenediamine)]^{2+}$ (48.2 kJ mol^{-1}),[9] which might suggest incomplete coordination of the ligand, must also partly be ascribed to the above mentioned strain. Indeed, the protonation of the $[Cu(n,m\text{-}(Me)NSN)]^{2+}$ complexes (see foregoing section) really indicates complete coordination of the n,m-(Me)NSN ligands.

A second conclusion from the enthalpy sequence is that, comparing complexes with equal-membered chelate rings, the heats of formation ($-\Delta H$) decrease with increasing methyl-substitution on one nitrogen. This means that the effect of increased donor capacity of the nitrogen upon substitution with one or two methyl groups has been overshadowed by increasing steric hindrance and decreasing solvation of the complex ion. Indeed, with increasing substitution on N, the values of $T\Delta S$ (see Table II) increase, indicating an increasing release of water molecules. This lowered hydration of the *N*-methyl substituted copper complexes is further reflected in a lower value of the $-\Delta H$ values. The change of $-\Delta H$ *versus* ΔS upon substitution is very similar for each series of complexes and parallels the analogous change of the enthalpy and entropy of protonation of the free ligands upon *N*-methyl substitution.[11] This suggests that the observed differences in enthalpy and entropy of complexation, and hence also the thermodynamic properties of the reaction (*3*)

$$CuA^{2+} + B \rightleftharpoons CuB^{2+} + A \qquad (3)$$

must be mainly due to differences in solvation of the less (A) and more (B) *N*-methyl-substituted ligand. From the thermodynamic cycle in Scheme 1, it can be concluded that the relative differences between the exothermic heats of complexation in the gas phase ($-\Delta H_g$) and in solution ($-\Delta H$) arise from the differences between the heats of hydratation of the free ($-\Delta H_L^h$) and of the complexed ligands ($-\Delta H_{CuL}^h$). Since the differences in alkyl amine hydration depend primarily on differences in the alkyl group interactions,[10] and as these hydrophobic effects will cancel each other in the free and complexed ligand, it can be shown that the differences in the heat of complexation in solution of reaction (*3*) reduce to that in (*4*),

$$\delta[-\Delta H] \simeq \delta[-\Delta H_g] + \delta[-\Delta H(Cu\,L^{2+})^{el}] \qquad (4)$$

SCHEME 1

Thermodynamic cycle of complexation.

$$\begin{tikzcd}
Cu^{2+}_{(g)} \arrow[d, "-\Delta H^{h}_{Cu}"] & + & L_{(g)} \arrow[d, "-\Delta H^{h}_{L}"] \arrow[r, "-\Delta H_g"] & CuL^{2+}_{(g)} \arrow[d, "-\Delta H^{h}_{CuL}"] \\
Cu^{2+}_{(aq)} & + & L_{(aq)} \arrow[r, "-\Delta H"'] & CuL^{2+}_{(aq)}
\end{tikzcd}$$

where $-\Delta H(CuL^{2+})^{el}$ is a solvation term responsible for the electrostatic interaction between the charged complex ion and the surrounding solvent molecules. Just as the charge density of an ammonium ion decreases with increasing substitution on the nitrogen atom,[10] it can be expected that the same holds for the charge density around an amine group coordinated to a Cu^{2+} ion. Hence according to equation (*4*) the change in the heat of formation $\delta(-\Delta H)$ of a copper complex upon increasing *N*-methylsubstitution of the coordinated ligand is due to three effects:

(1) The positive inductive effect of the methyl group that increases the exothermic heat of complexation in the gas phase ($\delta(-\Delta H_g) > 0$), (2) steric hindrance of these methyl groups on the other hand that will lower this heat of complexation $\delta(-\Delta H_g) < 0$, and, (3) the decreased charge density around nitrogen that will decrease the electrostatic solvation term $\delta(-\Delta H(CuL^{2+})^{el}) < 0$. As the experimental $-\Delta H$ values decrease with increasing substitution, the latter effects obviously dominate the first one.

The importance of solvation effects to the exothermicity of these complexes may further be deduced from their d-d spectra. These are supposed to be less sensitive to such solvation effects and are shown (see Table III) to vary only slightly with increasing substitution. This means that the first and second effects nearly cancel each other, whereas the third effect lowers the experimental heat of complexation in solution. On the other hand, comparing complexes with equally *N*-substituted ligands, it is always found that the extra stability of alternating five- and six-membered chelate rings compared with two fused five-membered rings leads to a remarkable change of both the $\nu_{d\text{-}d}$ absorption maxima and the complexation enthalpy in solution. The changes in both properties clearly indicate that solvation effects may alter complex forming ability in solution and that heats of complexation in solution should be interpreted with care.

The complex $[Cu(2,3\text{-}NSN(Me_2))]^{2+}$

As may be seen from the sequences of $-\Delta H_{CuL}$ and $\nu_{d\text{-}d}$, the interaction of 2,3-NSN(Me_2) with Cu^{2+} is much stronger than might be expected for a disubstituted ligand. In previous papers[1,6,12] we have mentioned that the α,ω-thiadiamines are probably facially arranged in their 1:1 complexes with copper(II). The complex $[Cu(2,3\text{-}NSN(Me_2))]^{2+}$ might however be an exception. Indeed, if we assume a meridional rather than a facial arrangement of the α,ω-thiadiamine in the latter complex, the high energy of its d-d transition might be explained by a high degree of tetragonal distortion. It remains however unclear why the α,ω-thiadiamine 2,3-NSN(Me_2) would prefer to coordinate in the equatorial plane.

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