A THERMODYNAMIC AND SPECTROPHOTOMETRIC STUDY OF THE COMPLEX FORMATION OF COPPER(II) IONS WITH SULPHIDE-CONTAINING α,ω-AMINOPYRIDINES IN AQUEOUS SOLUTION

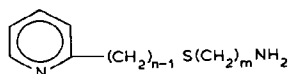C.T. HUYS, J. SCHAUBROECK and A.M. GOEMINNE *

Laboratory for General and Inorganic Chemistry-B, University of Ghent, Krijgslaan 281, B-9000 Ghent (Belgium)

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ABSTRACT

The complexation in aqueous solution of ligands of the type

$$\text{pyridine}-(CH_2)_{n-1}\,S(CH_2)_m NH_2$$

(n and m = 2 or 3) with Cu(II) has been investigated. The thermodynamic functions ΔG, ΔH and ΔS of complex formation have been determined at 25°C in 0.5 M KNO$_3$ solution by means of potentiometric and direct calorimetric titrations. They revealed that the ligands studied act as tridentates towards Cu(II).

It was found that the CuL^{2+} complexes having one or two six-membered chelate rings are more distorted than their analogues with only five-membered chelate rings.

The CuL$_2^{2+}$ complex with L =

$$\text{pyridine}-CH_2SCH_2CH_2NH_2$$
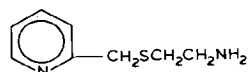
was found to be a strong covalent complex, in which both ligand molecules were completely coordinated.

INTRODUCTION

The complex formation in aqueous solution of transition metals with ligands containing terminal pyridyl groups has already been extensively studied [1]. It has been shown that the donor capacity of the aromatic nitrogen is lower than for the aliphatic analogue. Nevertheless differences in

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* To whom correspondence should be addressed.

stability constants of complexes with both types of nitrogen are smaller than expected from the differences in proton affinity between the aromatic and aliphatic nitrogen. Studies [1] of Cu(II) and Ni(II) complexes with tetradentate ligands
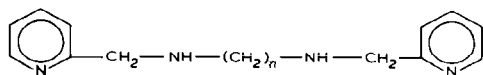
($n = 2$, 3 or 4) also revealed that ring alternation does not increase the stability of the complexes in the same way as was found for the aliphatic tetraamines [2].

In connection with our previous studies [3–5] on the complexation in aqueous solution of Cu(II and Ni(II) ions with sulphur-containing ligands, we have now undertaken a thermodynamic and spectrophotometric investigation on the complexation properties of a series of α,ω-thiaaminopyridines with Cu(II). The ligands studied are summarized in Table 1.

EXPERIMENTAL

Materials

The preparation of the three ligands has been given elsewhere [6]. Solutions of the aminopyridines, potassium hydroxide, nitric acid and copper(II) nitrate were obtained and standardized by the usual procedure [7].

Potentiometric titrations

Data on the pH were obtained by potentiometric titrations with the apparatus and [H$^+$] calibration method described previously [7]. Samples

TABLE 1
Ligands studied

Ligand	Formula	Abbreviation [a]
1-(2-Pyridyl)-4-amino-2-thiabutane	CH_2—S—$(CH_2)_2$—NH_2	2,2-N$_p$SN
1-(2-Pyridyl)-6-amino-3-thiapentane	$(CH_2)_2$—S—$(CH_2)_2$—NH_2	3,2-N$_p$SN
1-(2-Pyridyl)-6-amino-3-thiahexane	$(CH_2)_2$—S—$(CH_2)_3$—NH_2	3,3-N$_p$SN

[a] The abbreviation of the ligand contains the donor atoms in the chain preceded by the number of carbon atoms between the donors. The subscript p indicates the aromatic nitrogen.

containing known amounts of amine, nitric acid and metal salt were stepwise titrated with standard KOH (1.0 M in 0.5 M KNO_3). The ligand-to-metal ratio varied between 2 and 5. All measurements were carried out at $25°C \pm 0.05°C$.

Calorimetric titrations

The calorimetric titrations were performed with a LKB-8700/2 titration calorimeter, thermostated at $25°C \pm 0.001°C$, following the procedure proposed by Paoletti et al. [8].

The copper(II) complexes were titrated following the procedure used for the potentiometric titrations. The order of magnitude of the total concentrations of ligand and metal salts was about 6.5×10^{-2} and 2.5×10^{-2} M, respectively. All measured heats were corrected for dilution of the titrant and the formation of water as previously described [4].

Spectroscopy

Spectra in the visible region of solutions containing the Cu(II) complexes were obtained with a Cary Model 14 Spectrophotometer connected with a Varian 620L-100 minicomputer. For each Cu^{2+}/ligand system several solutions were prepared. Typical initial concentrations of the components in
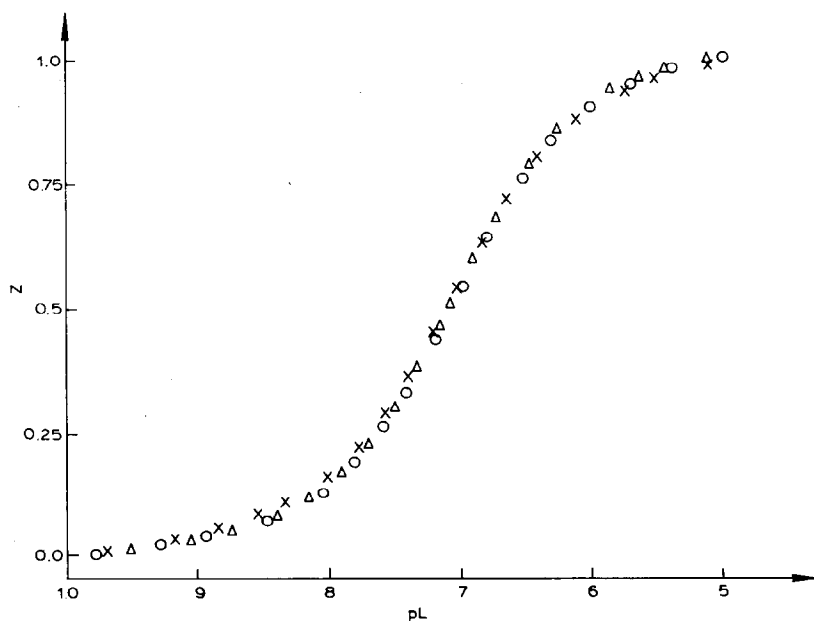

Fig. 1. The formation curve for the complexation of Cu^{2+} with 3,3-N_pSN. $T_L : T_m$ ratios: $\times$, 4:1; $\bigcirc$, 2.5:1; $\triangle$, 3:1.

solution are $c_L = 2 \times 10^{-2}$ M, $c_H = 4.5 \times 10^{-2}$ M, and $c_{Cu^{2+}} = 1 \times 10^{-2}$ M. Different degrees of complexation were obtained by adding varying amounts of KOH. The spectra of these solutions were measured following a procedure which has been extensively reported elsewhere [5(b)].

Calculations

The stability constants and the enthalpy changes are calculated using

TABLE 2

Stability constants [a] and thermodynamic [a,b] functions for the reaction of n,m-N$_p$SN with H$^+$ and Cu(II) ions

	2,2-N$_p$SN	3,2-N$_p$SN	3,3-N$_p$SN
H$^+$ + L → HL$^+$			
log K	9.280(4)	9.351(4)	10.030(4)
$-\Delta G$	52.96(2)	53.37(2)	57.24(2)
$-\Delta H$	52.1(2)	52.7(3)	55.3(2)
$T\Delta S$	0.9(2)	0.7(3)	1.9(2)
Cu^{2+} + LH$^+$ → CuLH^{3+}			
log K	1.92(2)		1.63(3)
$-\Delta G$	11.0(1)		9.3(2)
$-\Delta H$	16.7(8)		7.3(4)
$T\Delta S$	$-5.7(9)$		2.0(6)
CuL^{2+} + H$^+$ → CuLH^{3+}			
log K	3.40		4.52
$-\Delta G$	19.4		25.8
$-\Delta H$	23.9		20.3
$T\Delta S$	-4.5		5.5
Cu^{2+} + L → CuL^{2+}			
log K	7.81(1)	8.161(4)	7.133(4)
$-\Delta G$	44.57(6)	46.57(2)	40.71(2)
$-\Delta H$	44.9(9)	44.9(3)	42.3(4)
$T\Delta S$	$-0.4(1)$	1.7(3)	$-1.6(4)$
CuL^{2+} + HL$^+$ → CuL$_2$H^{3+}			
log K	1.26(3)		
$-\Delta G$	7.2(2)		
$-\Delta H$	21(2)		
$T\Delta S$	$-14(2)$		
CuL^{2+} + L → CuL$_2^{2+}$			
log K	6.001(6)		
$-\Delta G$	34.25(3)		
$-\Delta H$	65(2)		
$T\Delta S$	$-31(2)$		

[a] Values in parentheses are standard deviations on the last significant figure.
[b] All values in kJ mol^{-1} at 25°C.

Fortran IV programs, based upon minimization procedures [7]. The procedure for the calulations of the spectrum (molar extinction coefficient as a function of wavelength) for each complex species has been described in a preceding paper [5(b)].

RESULTS AND DISCUSSION

Preliminary information about the complexation model and estimates of the complex stabilities were obtained from the formation curves [9], an example of which is given in Fig. 1. The refined stability constants and the thermodynamic functions for the step-wise complexation of Cu(II) are listed in Table 2. The spectroscopic part has been limited to the study of the d-d transitions of the CuL^{2+} and CuL_2^{2+} complexes. Band maxima together with their molar extinction coefficients are summarized in Table 3.

1 : 1 complexes

The stability constants, as well as the enthalpy changes, for the formation of the normal CuL^{2+} complexes ($L = \alpha, \omega$-thiaaminopyridine) are more favorable than those of $Cu(2$-$NS(Me))^{2+}$ (log $K = 5.572$; $-\Delta H = 33.2$ kJ mol^{-1}) [7]. This suggests that all investigated α, ω-thiaaminopyridines act as tridentate in the 1 : 1 complexes. Consider the sequences for $-\Delta G$ and $-\Delta H$

$-\Delta G: 3,2$-$N_pSN > 2,2$-$N_pSN \gg 3,3$-N_pSN

$-\Delta H: 3,2$-$N_pSN \simeq 2,2$-$N_pSN > 3,3$-N_pSN

It can be readily deduced that:

(i) The 1 : 1 complexes having a five-membered chelate ring, which includes the amino function, are at an advantage or, in other words, the amino function predominantly determines the stability of these 1 : 1 complexes, in agreement with its greater donor capacity.

(ii) The stability and exothermicity gain due to ring alternation when

TABLE 3

Maxima [a] for the d-d transition of Cu(II)-complexes with α, ω-thiaaminopyridines

Species	ν_{d-d} [b]
$[Cu(2,2$-$N_pSN)]^{2+}$	15.25(70)
$[Cu(3,2$-$N_pSN)]^{2+}$	16.00(182)
$[Cu(3,3$-$N_pSN)]^{2+}$	15.75(182)
$[Cu(2,2$-$N_pSN)_2]^{2+}$	16.70(46)

[a] All values in kJ.
[b] Values in parentheses are the molar extinction coefficients.

comparing the 5,5-membered $[Cu(2,2-N_pSN)]^{2+}$ complex with the 6,5-membered $[Cu(3,2-N_pSN)]^{2+}$ complex is small in comparison with the gains found when comparing $[Cu(2,2-NSN)]^{2+}$ (log $K = 9.02$; $-\Delta H = 51.4$ kJ mol^{-1}) to $[Cu(2,3-NSN)]^{2+}$ (log $K = 10.03$; $-\Delta H = 59.0$ kJ mol^{-1})[3]. This may be connected with the greater destabilizing effect when substituting an aliphatic by an aromatic amino group in complexes with one or more six-membered chelate rings in comparison with those having only 5-membered rings. This may be seen from Table 4. This different behavior as a function of chelating type may be explained [1(c)] by assuming a greater distortion when a pyridine group forms part of a six-membered chelate ring. A more distorted structure for $[Cu(3,2-N_pSN)]^{2+}$ and $[Cu(3,3-N_pSN)]^{2+}$ is also in agreement with their $d-d$ transition band maxima, which occur at higher energies than for $[Cu(2,2-N_pSN)]^{2+}$. Nevertheless further investigation is needed to confirm this assumption. Finally, it is remarkable that a good estimate of log K for $[Cu(3,3-N_pSN)]$ ($= 7.133$) can be obtained when taking half the sum of log K for $[Cu(3,3-N_pSN_p)]^{2+}$ ($= 4.3$) [11] and log K for $[Cu(3,3-NSN)]^{2+}$ ($= 9.8$) [3(a)]. This may indicate that the corresponding donors in these three CuL^{2+} complexes are bound in a comparable way.

Protonated complexes

The protonation of the amino function in $[Cu(2,2-N_pSN)]^{2+}$ and $[Cu(3,3-N_pSN)]^{2+}$ gives rise to the formation of stable $[CuLH]^{3+}$ complexes. The values of the thermodynamic functions $-\Delta G$ and $-\Delta H$ for these protonations are compared to those for the corresponding protonation in the free amine in Table 2. It can be seen that the protonation of the amino function in the CuL^{2+} complex is appreciably less favorable than in the free ligand, indicating that it occurs with loss of a strong Cu–N bond. This is in agreement with what was expected for a completely coordinated CuL^{2+} complex.

The existence of a stable six-membered chelate ring as in $[Cu(3,3-N_pSN)H]^{3+}$ may be surprising. No such species has been shown to exist for the system $Cu^{2+}/\alpha,\omega$-thiadiamines [3(a)]. Uhlig and Hepp [11], however,

TABLE 4

The effect of substitution of an aliphatic by an aromatic nitrogen

	$\delta(-\Delta G_{CuL})$ [a]	Ref.
$[Cu(2,2-NSN)]^{2+} \rightarrow [Cu(2,2-N_pSN)]^{2+}$	-6.9	3
$[Cu(2,3-NSN)]^{2+} \rightarrow [Cu(3,2-N_pSN)]^{2+}$	-10.7	3
$[Cu(3,3-NSN)]^{2+} \rightarrow [Cu(3,3-N_pSN)]^{2+}$	-15.2	3
$[Cu(2-NN)]^{2+} \rightarrow [Cu(2-N_pN)]^{2+}$	-4.7	10
$[Cu(3-NN)]^{2+} \rightarrow [Cu(3-N_pN)]^{2+}$	-12.0	10

[a] kJ mol^{-1} at 25°C.

have already found a similar $[Cu(3,3-N_pSN_p)H]^{3+}$ complex. The stability constant for the latter complex (2.1) is somewhat larger than the one for $[Cu(3,3-N_pSN)H]^{3+}$ (see Table 2), which means that the destabilizing effect due to electronic repulsion between the protonated donor and the positive metal center is smaller for a pyridinium ion than for an ammonium group.

Finally, the thermodynamic quantities for protonation of the amino function in $[Cu(2,2-N_pSN)_2]^{2+}$ ($-\Delta G = 25.94$ kJ mol^{-1}; $-\Delta H = 8.74$ kJ mol^{-1}) are also much lower than those for protonation of the NH_2 group in the free ligand (Table 2). This proves again that protonation must occur with loss of a fairly strong Cu–N bond or otherwise the original CuL_2^{2+} complex must have been a six-coordinated species.

1 : 2 complexes

Only $[Cu(2,2-N_pSN)_2]^{2+}$ could be identified. The heat exchange in the second complexation step is much larger than for the coordination of the first ligand molecule. The entropy change, however, is more unfavorable in comparison with that in the first step. Both these results are characteristic of the fact that the second complexation step results in the formation of a strong covalently-bound six-coordinated complex. This is in agreement with the previous section.

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