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A POTENTIOMETRIC AND CALORIMETRIC STUDY OF THE PROTONATION AND COMPLEXATION WITH Cu^{2+} AND Ni^{2+} OF SOME SULPHUR-CONTAINING α,ω-AMINO ACIDS

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ABSTRACT

The behaviour in aqueous solution of some aminocarboxylates of the type $NH_2(CH_2)_nS(CH_2)_{m-1}COO^-$ (abbreviated as n,m-NSO; n and $m = 2$ or 3) in equilibria with H^+, Cu^{2+} and Ni^{2+} ions has been investigated potentiometrically and calorimetrically at 25°C in a 0.5 M KNO_3 medium.

The protonation of the amino function and especially the carboxylate function is attended by strong desolvation effects, which are characterized by low exothermic enthalpies and strongly positive entropies of protonation.

In $[Cu(n,m\text{-NSO})]^+$ and $[Ni(n,m\text{-NSO})]^+$ the aminocarboxylates act as tridentate ligands, forming complexes with a strong hard–hard character. The biligand species $[Ni(n,m\text{-NSO})_2]$ behave as six-coordinated complexes whereas in $[Cu(n,m\text{-NSO})_2]$ the second ligand is bound only through the N and S donor, forming a five-coordinated species.

Finally, the n,m-NSO ligands also form protonated species with the Cu^{2+} ion.

INTRODUCTION

In some previous studies [1–3] of Cu^{2+} and Ni^{2+} complexes with sulphur-containing α,ω-diamines n,m-NSN it was found that the $[Cu(2,2\text{-NSN})]^{2+}$ complex with two fused five-membered chelate rings was less stable than $[Cu(2,3\text{-NSN})]^{2+}$ with alternate five and six-membered chelate rings. The same extra stabilisation of alternating five and six-membered chelate rings was found by Paoletti et al. [4] for the copper (II) and nickel (II) complexes in a series of triamines, n,m-NNN.

We therefore thought it interesting to extend our investigation, on the interactions in aqueous solution between Cu^{2+} and Ni^{2+} and thioether-containing ligands to some sulphur-containing aminocarboxylates, $NH_2(CH_2)_nS(CH_2)_{m-1}COO^-$ (abbreviated as n,m-NSO) (see Table 1).

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TABLE 1

The ligands and their abbreviations

Name	Formula	Abbreviation [a]
S-2-Aminoethylmercaptoacetate	$NH_2CH_2CH_2SCH_2COO^-$	2,2-NSO
S-2-Aminoethyl-3′-mercaptopropionate	$NH_2CH_2CH_2SCH_2CH_2COO^-$	2,3-NSO
S-3-Aminoethylmercaptoacetate	$NH_2CH_2CH_2CH_2SCH_2COO^-$	3,2-NSO

[a] The abbreviations of the deprotonated amino acid contains first the numbers of carbon atoms between the donor groups, followed by the donor groups present in the aliphatic chain. The charge is omitted for simplicity.

EXPERIMENTAL

Reagents

The amino acids (2,3-NSO)H and (2,2-NSO)H are prepared by dropwise addition of 0.5 moles of cooled ethyleneimine to 0.5 moles of 3-mercaptopropionic and mercaptoacetic acid, respectively, dissolved in a small amount of water. The amino acids precipitate as zwitterions. They are recrystallised by dissolving them in a minimal amount of water followed by addition of ethanol until precipitation starts, and by cooling the mixture to 4°C. (2,2-NSO)H was found to be hygroscopic and had to be stored over P_2O_5.

The amino acid (3,2-NSO)H is prepared as described. To 0.5 moles of mercaptoacetic acid, dissolved in 0.2 dm^3 H_2O, 1 mole of NaOH and subsequently 0.5 moles of $Br(CH_2)_3NH_2 \cdot HBr$, dissolved in a minimal amount of ethanol, were added dropwise. The mixture was refluxed until the nitroprusside test for detection of mercaptans was negative. After cooling this mixture, the product, (3,2-NSO)H, was precipitated as a zwitterion by addition of an ethanol/ether mixture. It was recrystallised as described in the previous paragraph.

The concentration of the amino acid solutions was determined by potentiometric titrations, using Gran plots [5] and the calculation method of Briggs and Stuehr [6].

Solutions of potassium hydroxide, nitric acid, copper (II) and nickel (II) nitrate were obtained and standardized as previously reported [1]. To all the solutions an appropriate amount of solid potassium nitrate was added, so that the total nitrate concentration was 0.5 M dm^{-3}.

TABLE 2

The thermodynamic functions of protonation [a,b]

	Protonation of					
	2,3-NSO	2,2-NSO	3,2-NSO	2-NS(Me) [c]	3-NS(Me) [c]	2-(Et)SO [d]
NH_2 group						
$\log K_1^H$	9.498 (4)	9.534 (4)	10.191 (6)	9.472 (2)	10.102 (2)	
$-\Delta G_1$	54.20 (2)	54.41 (2)	58.16 (3)	54.02 (4)	57.61 (4)	
$-\Delta H_1$	51.3 (2)	49.3 (2)	54.7 (2)	53.89 (4)	55.98 (4)	
$T\Delta S_1$	2.9 (2)	5.1 (2)	3.5 (2)	0.13 (4)	1.63 (4)	
Carboxylate group						
$\log K_2^H$	3.938 (7)	3.181 (6)	3.348 (8)			3.65 (1)
$-\Delta G_2$	22.47 (4)	18.15 (3)	19.11 (5)			20.80 (6)
$-\Delta H_2$	0.3 (3)	−0.2 (3)	−1.6 (5)			−1.08 (4)
$T\Delta S_2$	22.2 (3)	18.3 (3)	20.7 (6)			19.7 (1)

[a] 298 K, 0.5 M KNO_3; $-\Delta G$, $-\Delta H$ and $T\Delta S$ in kJ $mole^{-1}$.

[b] Values in parentheses are the standard deviations on the last significant figure.

[c] 298 K, 0.5 M KNO_3; data given for comparison, see ref. 9.

[d] 298 K, 1.0 M KCl; ethylthioacetate, given for comparison, see ref. 13.

TABLE 3

The thermodynamic functions [a,b] of complex formation of Cu^{2+} and Ni^{2+} with some sulphur-containing α,ω-amino acids and some previously investigated bidentates

Thermodynamic functions for the reactions	2,2-NSO	2,3-NSO	3,2-NSO	2-NS(Me) [c]	2(Et)SO [d]
$Ni^{2+} + L \rightleftharpoons NiL^{+}$					
log K	6.14 (1)	3.739 (4)	4.157 (6)	3.299 (4)	1.04 (1)
$-\Delta G$	35.00 (6)	21.34 (2)	23.70 (3)	18.82 (5)	5.94 (6)
$-\Delta H$	22.6 (2)	13.6 (2)	14.6 (2)	23.3 (1)	1.4 (8)
$T\Delta S$	12.4 (2)	7.7 (2)	9.1 (2)	−4.5 (1)	4.5 (8)
$NiL^{+} + L \rightleftharpoons NiL_2$					
log K	5.393 (8)	3.178 (4)	3.247 (6)	2.807 (7)	0.77 (2)
$-\Delta G$	30.74 (5)	18.14 (2)	18.47 (3)	16.02 (8)	4.39 (8)
$-\Delta H$	22.7 (2)	15.9 (2)	17.6 (3)	25.3 (4)	1.3 (2)
$T\Delta S$	8.1 (2)	2.2 (2)	0.9 (3)	−9.3 (4)	3.1 (2)
$Cu^{2+} + L \rightleftharpoons CuL^{+}$					
log K	7.25 (2)	6.24 (1)	6.867 (6)	5.572 (3)	2.57 (1)
$-\Delta G$	41.3 (1)	35.59 (6)	39.16 (3)	31.79 (1)	14.64 (6)
$-\Delta H$	20.0 (3)	15.4 (2)	14.2 (2)	33.3 (1)	−2.30 (4)
$T\Delta S$	21.4 (3)	20.2 (2)	25.0 (3)	1.5 (1)	16.9 (1)

$CuL^+ + L^- \rightleftharpoons CuL_2$								
log K	6.15	(1)	4.51	(1)			5.082 (4)	2.20 (2)
$-\Delta G$	35.07	(6)	25.72	(6)			29.00 (2)	12.5 (1)
$-\Delta H$	46.6	(3)	38.6	(2)			38.1 (3)	−0.17 (4)
$T\Delta S$	−11.5	(3)	−12.9	(2)			−9.1 (3)	12.7 (1)
$Cu^{2+} + LH \rightleftharpoons CuLH^{2+}$								
log K	1.42	(2)	1.19	(3)	1.63	(2)		
$-\Delta G$	8.1	(1)	6.8	(1)	9.3	(1)		
$-\Delta H$	0.0	(4)	−1.8	(4)	−1.6	(3)		
$T\Delta S$	8.1	(5)	8.6	(5)	10.9	(4)		
$CuLH^{2+} + LH \rightleftharpoons CuL_2H_2^{2+}$								
log K					1.11	(5)		
$-\Delta G$					6.3	(3)		
$-\Delta H$					−9.6	(4)		
$T\Delta S$					15.9	(7)		
$CuL + LH \rightleftharpoons CuL_2H$								
log K	1.19	(9)						
$-\Delta G$	6.8	(5)						
$CuL^+ + H^+ \rightleftharpoons CuLH^{2+}$								
log K^H	3.70	(4)	4.45	(2)	4.95	(3)		

[a] 298 K, 0.5 M KNO_3; $-\Delta G$, $-\Delta H$ and $T\Delta S$ in kJ mole^{-1}.

[b] Values in parentheses are the standard deviations on the last significant figure.

[c] 298 K, 0.5 M KNO_3; previously determined values, see ref. 9.

[d] 298 K, 1.0 M $NaNO_3$; (ethylthio)aceticacid, given for comparison, see ref. 14.

Potentiometric titrations

Potentiometric titrations were performed at 25 ± 0.05°C with a Radiometer PHM64 digital potentiometer, equipped with an Ingold HA 201 glass electrode, a 0.5 mole dm^{-3} KNO_3 salt bridge and an Ingold 3 mole dm^{-3} KCl calomel electrode. The electrode system was calibrated following the usual procedure in our laboratory [1,7].

Samples containing known amounts of amino acid, nitric acid and, for metal–ligand equilibria studies, metal salt were titrated with standardized KOH (1.0 M) in the pH range 2.0–9.5. The initial concentration of amino acid in the titration vessel was about 4×10^{-2} M. Ligand to metal ratios varied between 2 and 5. The system Cu(II)–(3,2-NSO) gave rise to insoluble hydrolysed Cu(II) species above pH = 6.

Calorimetric titrations

Calorimetric measurements were carried out with an LKB 8700/2 titration calorimeter, thermostatted at 25.000 ± 0.001°C. The procedure for the determination of the heats of reactions has already been described [8].

Calorimetric titrations for the determination of the enthalpy of protonation of the NH_2 group and the enthalpies of formation of the Ni^{2+} complexes involved stepwise addition of a standardized HNO_3 solution (0.5 M) to the fully deprotonated respective complexed amino acid (initial ligand concentrations were about 6×10^{-2} M).

For the calorimetric study of the protonation of the carboxylate group and the complexation with Cu^{2+}, a standardized KOH solution (1.0 M) was added stepwise to a solution of the fully protonated amino acid ($\sim 6 \times 10^{-2}$ M) and eventually copper(II) nitrate ($\sim 2 \times 10^{-2}$ M).

Calculations and results

All calculations were performed with appropriate FORTRAN IV programs. Details have been given elsewhere [9–11]. The results are given in Table 2 (protonation) and Table 3 (complexation).

DISCUSSION

Protonation of the amino acids

Comparing the thermodynamic functions of protonation of the amino group of 2,2-NSO with those of 3,2-NSO, it is seen from Table 2 that insertion of a CH_2 group between S and N obviously reduces the electron-withdrawing effect of the thioether group, leading to a greater basicity

$(-\Delta G_1)$ in 3,2-NSO ($\delta = 3.75$ kJ mole^{-1}). About the same increase in basicity ($\delta = 3.47$ kJ mole^{-1}) is found between 2-NS(Me) and 3-NS(Me). However, the differences in protonation enthalpy and entropy between both pairs of amines (or amino acids) are not similar. For the amino acids the increase in proton affinity $(-\Delta H_1)$ is 5.4 kJ mole^{-1} whereas for the monoamines it is only 2.1 kJ mole^{-1}. Moreover, whereas the protonation entropy decreases in going from 2,2-NSO and 3,2-NSO, it increases for the set 2-NS(Me) and 3-NS(Me). This different behaviour may be ascribed to the formation of a zwitterion by protonation of the aminoacetate. As was pointed out earlier [12] the difference in proton affinity in solution $\delta(-\Delta H)$ between a related pair of amines reduces mainly to

$$\delta\{-\Delta H\} = \delta\{-\Delta H_g\} + \delta\{-\Delta H_s(BH^+)^{el}\} \quad (1)$$

where $-\Delta H_g$ is the proton affinity in the gas phase and $-\Delta H_s(BH^+)^{el}$ is the heat responsible for the electrostatic interaction of the charge of the ammonium ion with the solvent. Insertion of a CH_2 group between N and S in *n*-NS(Me) reduces the electron-withdrawing effect of the thioether group, increases the proton affinity in the gas phase $(-\Delta H_g)$ and causes the ammonium ion to have a lower charge density at nitrogen. This leads to a relative desolvation, inducing a decrease in $-\Delta H_s(BH^+)^{el}$, an attenuation of the heat of protonation in solution and an increase in protonation entropy [compare, e.g., 2-NS(Me) and 3-NS(Me)].

Protonation of the amino group in *n*,*m*-NSO, however, gives rise to a zwitterion. The electrostatic solvation around the positively charged ammonium ion may then be influenced by the nearby negatively charged carboxylate part of the same zwitterion. On comparison with an analogous *n*-NS(Me) amine this leads to a smaller degree of solvation of the ammonium ion in *n*,*m*-NSO, resulting in a lower $-\Delta H$ value and a higher protonation entropy, ΔS [compare, e.g., 2,2-NSO and 2-NS(Me)].

Insertion of a CH_2 group between N and S in 2,2-NSO reduces the mutual influence of both oppositely charged parts of the zwitterion. As a consequence, the solvation of the zwitterion in 3,2-NSO is higher than in 2,2-NSO, leading to a higher increase in heat of protonation $(-\Delta H_1)$ in comparison with *n*-NS(Me) and a decrease in protonation entropy.

Insertion of a CH_2 group between the thioether and carboxylate group is also attended by an increase in $-\Delta H$ and a decrease in ΔS. This again may be ascribed to an increase in solvation of the zwitterion due to a smaller mutual influence of both opposite charges.

The protonation of the carboxylate anion is characterized by large $T\Delta S_2$ values. This is in accordance with the great loss of water molecules, when neutralizing the charge of the carboxylate group. The thermodynamic values for the protonation of the carboxylate group of 2,2-NSO and 3,2-NSO are very similar to those of 2-(Et)SO and the slight variations between them are determined by the inductive influence of the nearby ammonium group and

the zwitterion solvation effect. In 2,3-NSO the same effects are active but increased by a decrease (in comparison with 2,2-NSO) in the electron-withdrawing effect of the thioether group. This results in a stronger proton affinity ($-\Delta H$).

Nickel(II) complexes

The sulphur-containing aminocarboxylates form two successive complexes with Ni^{2+} $[Ni(n,m\text{-NSO})]^{+}$ and $[Ni(n,m\text{-NSO})_2]$, the stabilities of which follow the sequence: 2,2-NSO $\gg$ 3,2-NSO > 2,3-NSO. The steep drop in stability between 2,2-NSO and 3,2- or 2,3-NSO could raise doubts regarding the coordination of all three donor atoms in the latter ligands. However, the stability of both nickel species for all ligands is greater than that of the corresponding complex with 1-aza-4-thiapentane [abbreviated as 2-NS(Me)] or with (ethylthio)acetate [abbreviated as 2-(Et)SO] (see Table 3). This suggests complexation via the three donor atoms. The relatively high $T\Delta S$ values [as compared to 2-NS(Me)] and the relatively low values of the heat of complexation ($-\Delta H$) reflect the destructuring process of the solvent as a consequence of the association of the negatively charged carboxylate groups and the positive nickel ion.

In contrast with the greater stability of $[Ni(2,3\text{-NNN})]^{2+}$ with respect to $[Ni(2,2\text{-NNN})]^{2+}$, ring alternation [4] does not produce an extra stability with these n,m-NSO ligands. On the contrary, the complex $[Ni(2,2\text{-NSO})]^{+}$ with two fused five-membered chelate rings is much more stable than its analogues with alternating five-six membered rings, by several kilojoules in both $-\Delta G$ and $-\Delta H$.

Copper(II) complexes

The ligands under investigation form a normal $[Cu(n,m\text{-NSO})]^{+}$ complex with Cu^{2+} having the same stability sequence as was found for the nickel complexes. Here too the stability for each complex is greater than that with 2-NS(Me) or 2-(Et)SO, indicating complexation via the three donor atoms. Coordination of the carboxylate group is again reflected in the low $-\Delta H$ and high $T\Delta S$ values [as compared to 2-NS(Me)]. Neither the stability nor the enthalpy sequences give an indication of extra stabilisation due to ring alternation in contrast with that stated for $[Cu(n,m\text{-NNN})]^{2+}$ [4] and $[Cu(n,m\text{-NSN})]^{2+}$ [2,3].

In the second complexation step the n,m-NSO ligands obviously coordinate only via the N and S donors, forming five-coordinated $[Cu(n,m\text{-NSO})_2]$ species. The absence of a biligand species with 3,2-NSO may then be explained by the fact that also with 3-NS(Me) no copper complexes in solution could be detected [15]. The lack of coordination via the carboxylate group is further reflected by the relatively low $T\Delta S$ values as compared to

those for the formation of the CuL species and the six-coordinated NiL_2 species. Moreover, the entropy and exothermic enthalpy value compare well with those of the corresponding copper(II) complex of 2-NS(Me).

Besides the normal complexes, a series of complexes may be formed in which the amino function is protonated and where chelation occurs through the thioether and carboxylate group only. The stability and the endothermicity of these $[CuH(n,m\text{-NSO})]^{2+}$ species may be compared to that of the corresponding copper (II) complex with (ethylthio)acetate (see Table 3). The sequence in stability is $[Cu(2\text{-(Et)SO})]^{+} > [CuH(3,2\text{-NSO})]^{2+} > [CuH(2,2\text{-NSO})]^{2+} > [CuH(2,3\text{-NSO})]^{2+}$ which shows that chelates with a five-membered ring are the most stable and that the stability increases with increasing distance between the protonated nitrogen and the chelate center. As a consequence, it is clear that only $[CuH(3,2\text{-NSO})]^{2+}$ is able to add a second ligand with formation of a $[CuH_2(3,2\text{-NSO})_2]^{2+}$ species.

Finally, the protonation constants for the normal complexes

$$CuL^{+} + H^{+} \rightarrow CuLH^{2+}$$

are much smaller (see Table 3) than those for the protonation of the amino group in the free ligands (Table 2), and prove that the nitrogen atom was coordinated in the CuL^{+} complex.

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