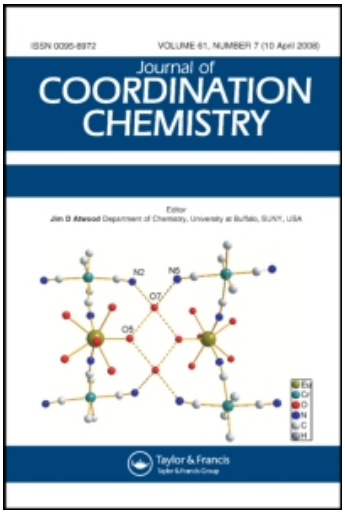

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COMPLEX FORMATION EQUILIBRIA FOR *S*-AMINO ACID AMIDES WITH NICKEL(II) IN AQUEOUS SOLUTION

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Solution equilibria of Ni^{II} with *S*-amino acid amides (alaninamide, valinamide, phenylalaninamide, prolinamide, tryptophanamide, (L)) were studied by potentiometry and spectrophotometry at 25°C and I = 0.1 mol dm^{-3} (KCl). The main species detected were $[NiL]^{2+}$, $[NiL_2]^{2+}$, and $[NiL_2H_{-2}]$. Simultaneous ionization of two amide protons from $[NiL_2]^{2+}$ yielded a square planar complex $[NiL_2H_{-2}]$ showing very different complexing behaviour of Ni^{II} with respect to Cu^{II} at high pH values (but not at low pH). These results are discussed with reference to literature data for other amino-amide ligands and oligopeptides.

Keywords: amino acid amides; nickel(II); stability constants; potentiometry; spectrophotometry

INTRODUCTION

Amino-amide ligands act as chelating agents towards divalent transition metal ions through the amine nitrogen and the carbonyl oxygen or deprotonated amide nitrogen atoms, depending on the pH.[1] Of particular interest is the ability of Cu^{II} and Ni^{II} to promote the ionization of the amide hydrogen in oligopeptides, though the behaviour of Cu^{II} is markedly different.[1-4] Solution equilibria of Cu^{2+} with *S*-amino acid amides have been exstensively studied, mainly by potentiometry and spectrophotometry, and complexes with neutral or deprotonated amide groups have been detected.[1,5-8] Moreover, the stereoselective formation of the

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ternary complexes Cu^{2+}/*S*-amino-acid amide/*R*- or *S*-amino acid has been investigated,[8] in order to shed some light on the mechanism responsible for the chiral discrimination of amino acids in reversed phase HPLC performed by Cu^{2+}/*S*-amino acid amide complexes added to the eluent.[9] Solid Cu^{2+} complexes of several amino acid amides, (L), of $[CuL_2]^{2+}$ and $[CuL_2H_{-2}]$ type, have been synthesized and characterized by spectroscopic techniques (IR, electronic, CD).[10,11]Crystal structure X-ray analysis of *trans*-$[CuL_2H_{-2}]$ for *S*-phenyla laninamide[12] and of *trans*-$[CuL_2H_{-2}].2H_2O$ for *S*-prolinamide[13] has confirmed the hypothesis of a tetrahedrally distorted square planar Cu^{II} coordination, $[(Cu(N_4)]$.

Literature data regarding equilibria of Ni^{2+} with amino acid amides, however, are scant, being restricted to glycinamide,[14,15] but they are contradictory both with respect to the species model and log ß values. More complete are literature reports on the synthesis and spectroscopic characterization of $[NiL_2]^{2+}$ and $[NiL_2H_{-2}]$ complexes of glycinamide, *S*-alaninamide, *S*-valinamide, *S*-leucinamide, *S*-prolinamide, and *S*-phenylalaninamide.[11,16] The structure of *trans-bis*[*S*-prolinamidato)]nickel(II) dihydrate has been determined by X-ray analysis; the Ni^{II} coordination is square planar.[17]

With the purpose of clarifying the complexation of Ni^{2+} with *S*-amino acid amides in aqueous solution, and also of a comparison with the well known behaviour of Cu^{2+}, we report here the results of a potentiometric and spectrophotometric investigation of solution equilibria between Ni^{2+} and five *S*-amino acid amides (alaninamide, Ala-NH_2, valinamide, Val-NH_2, phenylalaninamide, Phe-NH_2, prolinamide, Pro-NH_2, and tryptophanamide, Trp-NH_2).

EXPERIMENTAL

Reagents

S-Alaninamide, *S*-valinamide, *S*-phenylalaninamide, *S*-prolinamide, and *S*-tryptophanamide hydrochlorides (*Sigma*), were all of high purity, and were used as received. Elemental analyses (C,H,N) of the ligands gave acceptable results. Their purity was also checked by means of potentiometric titrations with KOH solution. The ligands were dried over P_4O_{10} *in vacuo*, and stock solutions (*ca* 0.02 mol dm^{-3}) were prepared by weight and used within 2–3 days. Ni^{II}, KOH and HCl solutions were prepared and standardized as reported.[8] All solutions were prepared with freshly boiled, doubly distilled H_2O.

Potentiometric Measurements

Computer controlled titrations were performed using a 5 cm^3 Metrohm 655 Dosimat motor burette and a Radiometer PHM64 digital voltmeter equipped with B2905 glass and 363-S7 KCl sat. Ag/AgCl Ingold electrodes. The cell was standardized in terms of $[H^+]$ by titrating HCl solns. (0.01 mol dm^{-3}) in a starting volume of 50 cm^3 with standard KOH soln. (*ca* 0.2 mol dm^{-3} in 0.1 mol dm^{-3} KCl). The PC program BEATRIX,[18] based on the Gran method,[19] was used to calculate the equivalence volume, v_e, the electrode couple standard potential, $E°$, and pK_w (13.76(1)). The experiments were carried out at 25.0 ± 0.1°C and I = 0.1 mol dm^{-3} (KCl) under N_2 previously saturated with water vapour in 0.1 mol dm^{-3} KCl solution.

Appropriate aliquots of ligand, Ni^{II}, and HCl solutions were added to the cell, and the volume adjusted to 50 cm^3 with water.

For each of the systems considered, five or six titrations were performed with various Ni/L ratios (from 1/3 to 1/7) (C_{Ni} = 0.001–0.002 mol dm^{-3}). The pH range varied between 4.0 and 11.0.

Spectrophotometric Measurements

Absorption spectra were recorded on a Uvikon 941 Plus Kontron spectrophotometer between 300 and 600 nm, at 2 nm intervals, against a 0.1 mol dm^{-3} KCl soln. as reference. Solutions were passed from the potentiometric vessel to the spectrophotometric cell, using a peristaltic pump.

Calculations

Stability constants were calculated by the computer program HYPERQUAD,[20] which employs the sum of the weighted squares of the residuals between observed and calculated e.m.f. values as the optimization function. The weighting of the experimental observations takes into account the errors of both e.m.f. and titrant volume that were estimated as 0.2 mV and 0.008 cm^3, respectively. During the refinement of the trial log ß values for the metal complexes, the protonation constants of the ligands were fixed. For each system, the data from different titrations were treated in a unique batch.

RESULTS AND DISCUSSION

Potentiometric Determinations

Potentiometric data obtained for the various Ni^{II} / amino acid amide systems examined were processed using the protonation constants of the ligands previ-

ously determined.[7,8] Formation constants for the species $[NiL]^{2+}$, $[NiL_2]^{2+}$, $[NiL_3]^{2+}$, and $[NiL_2H_{-2}]$, namely those reported in the literature for glycinamide,[15] were initially considered in the calculation. The complex $[NiL_3]^{2+}$ was found only for Ala-NH_2, Phe-NH_2, and Trp-NH_2, but its concentration reached *ca* 10–15% of total Ni^{II} when the ligand to metal ratio was 7/1. Moreover, since the precision of its log ß is significantly lower than those of the other species, $[NiL_3]^{2+}$ can be considered uncertain. When the constants of additional complexes, $[NiLH_{-1}]^{+}$, $[NiL_2H_{-1}]^{+}$, $[NiL_2H_{-3}]^{-}$, were included in the model, they were rejected. The cumulative formation constants obtained are reported in Table I. A species distribution diagram, as a function of pH, for the system Ni^{2+}/*S*-Pro-NH_2 is shown in Figure 1. All five amino acid amides examined form relatively weak $[NiL]^{2+}$ and $[NiL_2]^{2+}$ complexes, where the neutral ligand chelates through the amine nitrogen and the carbonyl oxygen. Values of stepwise constants can be correlated with the basicity of the amino group and are quite similar to those of $[NiL]^{+}$ and $[NiL_2]$ formed by dipeptides,[1–4,15] which chelate in the same way. Above pH 8 simultaneous dissociation of the two amide protons from $[NiL_2]^{2+}$ occurs and the colour of the solution changes from pale green to yellow, indicating the formation of a square planar species $[NiL_2H_{-2}]$ which reaches 100% of total nickel at pH *ca* 10. This concerted ionization of two amide protons is the result of a particularly enhanced stability of the diamagnetic square planar *bis*-amino amidato complex, which disfavours the formation of the high spin complexes $[NiLH_{-1}]^{+}$ and $[NiL_2H_{-1}]^{+}$. These species are observed with copper(II), instead.[1,5–8] This behaviour resembles that of diamino-diamide ligands such as *N,N'*-diglycylethylenediamine[21] and *S,S-N,N'*-diphenylalanylethylenediamine,[22] which also release in a single step the two amide protons with Ni^{II}, but not with Cu^{II},[21,23,24] yielding yellow solutions of a square planar complex, *cis*-$[NiLH_{-2}]$. In the same way, triglycine (three N donors plus carboxylate O) and tetraglycine (four N donor atoms) form square planar Ni^{II} complexes with simultaneous ionization of two and three peptide protons, respectively.[14,25] Dipeptides, however, behaving as terdentates ($-NH_2$, $=N^-$, COO^-), give rise to a very stable complex $[NiLH_{-1}]$ which prevents the formation of the yellow species in solution,[1–4,14] and in the solid only a blue octahedral $[NiL_2H_{-2}]^{2-}$ anion has been obtained for diglycine.[26]

TABLE I Logarithms of protonation and Ni^{II} complex formation constants ($ß_{pqr} = [Ni_pL_qH_r]/[Ni]^q[L]^q[H]^r$ for *S*-amino acid amides in aqueous solution at 25°C and $I = 0.1$ mol dm^{-3} (KCl). Standard deviations are given in parentheses. Data for glycinamide (Gly-NH_2) are taken from the literature

	$[HL]^{+}$	$[NiL]^{2+}$	$[NiL_2]^{2+}$	$[NiL_3]^{2+}$	$[NiL_2H_{-2}]$	s^2 [a]	n [a]
S-Ala-NH_2	7.96(1)	3.18(2)	5.80(2)	7.64(7)	−11.64(1)	1.00	297
S-Val-NH_2	7.72(1)	2.77(2)	4.93(2)		−11.60(1)	1.77	436

TABLE I *(Continued).*

	$[HL]^+$	$[NiL]^{2+}$	$[NiL_2]^{2+}$	$[NiL_3]^{2+}$	$[NiL_2H_{-2}]$	s^2 [a]	n [a]
S-Phe-NH_2	7.26(1)	2.57(1)	4.69(3)	6.41(7)	−11.86(1)	0.67	313
S-Pro-NH_2	8.69(1)	3.85(1)	7.16(1)		−9.75(1)	1.56	404
S-Trp-NH_2	7.49(1)	2.85(3)	5.37(6)	7.66(7)	−11.21(1)	1.44	290
Gly-NH_2 [b]	8.05	4.20	7.60	9.70	−11.41		
[c]	7.95(1)	3.80(4)	6.88(4)	9.3(1)	−12.13(2)		

[a] $S^2 = \Sigma\ w_i(E_i^o - E_i^c)^2/(n - m)$ = sample variance; $1/\sigma_i^2$ where σ_i is the expected error of each experimental e.m.f. value (E_i^o); n = number of observations; m = number of parameters refined. [b]Ref. 14; other species $[NiLH_{-1}]^+$ (log ß = −5.60), $[NiLH_{-2}]$ (log ß = − 15.70).[c]Ref. 15.

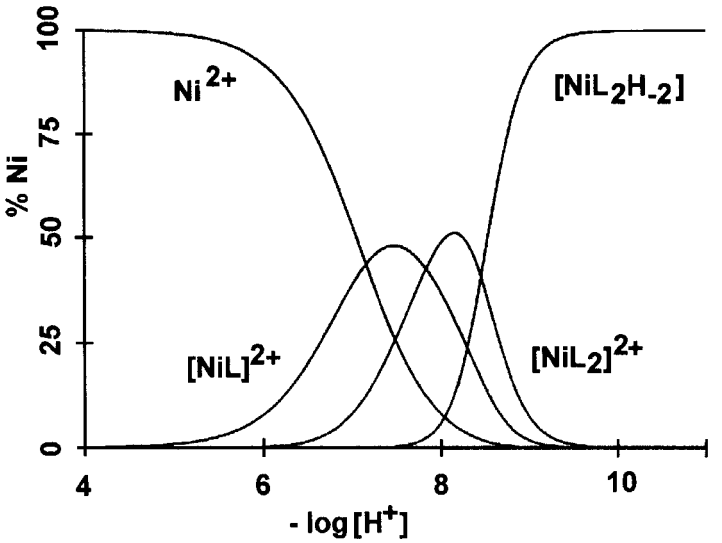

FIGURE 1 Species distribution for the Ni^{II}/*S*-Pro-NH_2 system as a function of -log $[H^+]$; C_{Ni} = 0.001 mol dm^{-3}, C_L = 0.004 mol dm^{-3}.

Spectrophotometric Determinations

The solutions employed for the spectrophotometric measurements had a ligand to metal ratio of 3/1 in order to minimize the presence of the species $[NiL_3]^{2+}$ for Ala-NH_2, Phe-NH_2, and Trp-NH_2. The absorption spectra were measured at appropriate pH values and then resolved using the SQUAD program.[27] Concentrations of individual species were calculated from the stability constants obtained by potentiometry (Table I). Molar absorptivities for the complex $[NiL]^{2+}$ could not be determined with any degree of accuracy, and indeed negative values were sometimes obtained. The spectroscopic characteristics (λ_{max}, ε) of the complexes $[NiL_2]^{2+}$ and $[NiL_2H_{-2}]$ are reported in Table II,

TABLE II Absoption maxima (λ_{max}/nm) and molar absorptivities (ε/M^{-1} cm^{-1}), in parentheses, for $[NiL_2]^{2+}$ and $(NiL_2\ H_{-2}]$ complexes of *S*-amino acid amides at 25°C and I = 0.1 mol dm^{-3} (KCl)

	Ala-NH_2	Val-NH_2	Pro-NH_2	Phe-NH_2	Trp-NH_2	Gly-NH_2
$[NiL_2]^{2+}$	376 (13.6 378[a]	388 (28.2)	382 (17.6)	388 (28.3)	384(16.8)	377 (9.3)[a]
$[NiL_2H_{-2}]$	432 (61.7)	432 (62.0)	436 (69.3) 35 (67.6)[c]	436 (56.3)	440 (60.1)	438 (61.0)[b]

together with some literature data for comparison.[11,14,16] The species $[NiL_2H_{-2}]$ show absorption maxima in the range 432–440 nm and this is reasonable for a square planar complex with two chelate rings ($-NH_2$, $-NH^-$). The 'corresponding' tetradentate ligands, *N,N'*-diglycylethylenediamine[21] and *S,S-N,N'*-diphenylalanylethylenediamine[22] form a square planar complex $[NiLH_{-2}]$, but with three chelate rings, thus exerting a somewhat stronger ligand field, and they have absorption maxima at 414 and 416 nm, respectively. Similarly, the species $[NiLH_{-3}]^{2-}$ of tetraglycine,[14] with four nitrogen donors, shows almost identical spectroscopic characteristics, λ_{max} = 412 nm.

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