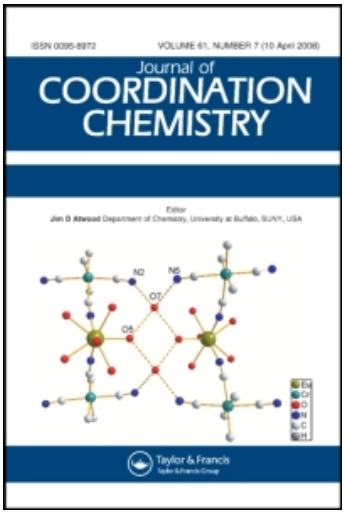

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AMINOHYDROXAMIC ACIDS AS METAL SEQUESTERING AGENTS: COPPER(II) AND NICKEL(II) COMPLEXES OF 2,6-DIAMINO-*N*-HYDROXYHEXANAMIDE, 2-AMINO-5-[(AMINOIMINOMETHYL)AMINO]-*N*-HYDROXYPENTANAMIDE, 2-AMINO-4-METHYLTHIO-*N*-HYDROXYBUTANAMIDE IN AQUEOUS SOLUTION

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Aqueous solution equilibria of the systems H^+, copper(II) and nickel(II) with L-lysinehydroxamic acid (2,6-diamino-*N*-hydroxyhexanamide) (dahhe), L-argininehydroxamic acid (2-amino-5-[(aminoiminomethyl)amino]-*N*-hydroxypentanamide) (aimahp), and DL-methioninehydroxamic acid (2-amino-4-methylthio-*N*-hydroxybutanamide)(amthb) have been investigated in the metal-ligand ratio range 1:1-1:4 using potentiometric and spectrophotometric methods. The protonation and metal-complex formation constants for each system were calculated using the SUPERQUAD program and are reported.

Complexation with copper(II) begins at pH *ca.* 3.0 for each system with simultaneous formation of $[CuA]^+$ and $[Cu_2A_2H_{-1}]^+$. Only copper-dahhe forms complexes with the terminal amino group in the protonated form. Between pH 5.5-9.5 the bis complex is dominant. Above pH 8 deprotonated complexes are detected. In the different bis complexes ($[CuA_2H_2]^{2+}$, $[CuA_2H]^+$, $[CuA_2]$ and $[CuA_2H_{-1}]^-$ in the case of dahhe, $[CuA_2]$ and $[CuA_2H_{-1}]^-$ with aimahp and amthb) only the nitrogens are coordinated but both the oxygen and the nitrogen donor atoms of the ligand are involved in the coordination in complexes $[CuAH]^{2+}$ and $[Cu_2A_2H]^{3+}$ formed with dahhe and in $[CuA]^+$ and $[Cu_2A_2H_{-1}]^+$ formed with the other two ligands. Spectroscopic evidence shows no significant coordination through the terminal group of the ligand for any of the systems investigated.

Complexation with nickel(II) starts at pH *ca.* 5.0 with simultaneous formation of 1:1 and 1:2 species. The $[NiA]^+$ ($[NiAH]^{2+}$ in the case of dahhe) is a very minor species. The $[NiA_2]$ ($[NiA_2H_2]^{2+}$ with dahhe) complex is the dominant species with a planar geometry. Deprotonation of one of the coordinated hydroxamates occurs above pH 8 and overlaps with deprotonation of the terminal NH_3^+ groups of the dahhe ligand.

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KEYWORDS: Aminohydroxamic acids, complex formation, potentiometry, spectrophotometry, SUPERQUAD, stability constants.

INTRODUCTION

The biological importance of hydroxamic acids has been proved beyond doubt and increased interest in their chemistry.[1] Hydroxamic acids are important Fe(III) transport agents in microbial systems (where they are termed siderophores). These naturally occurring compounds are widely used for different purposes. An example is desferrioxamine, which has been used for solid phase extraction of trace metals[2] as well as for treatment of iron-overload and aluminium-overload diseases.[3] In recent years, the hydroxamic acid derivatives of amino acids in particular have been investigated with great interest.[4] They have been shown to act as metal chelators which may function as tumour inhibitors, constituents of antibiotics and cell-division growth factors.[1,5] Some have also been shown to be potent inhibitors of thermolysin, elastase and aminopeptidase.[6] The hydroxamic acid derivatives of amino acids have also recently been used for liquid chromatographic analysis of metal ions. In this laboratory, aspartic acid β-hydroxamate and α-glutamic acid γ-monohydroxamate were used for the pre-column formation and separation of metal chelates of Al^{III}, Co^{II}, Cu^{II}, Fe^{III} and Mo^{VI}.[7,8] Moreover, presence of the α-amino group in aminohydroxamates increases the number of possible sites for chelation, since this group ($-NH_2$) could be involved in coordination as well as the nitrogen and oxygen of the hydroxamic function.[4]

In this work, a detailed potentiometric study of the equilibria of L-lysine-hydroxamic acid (2,6-diamino-*N*-hydroxyhexanamide) (dahhe), L-argininchydroxamic acid (2-amino-5-[(aminoiminomethyl)aminol]-*N*-hydroxypentanamide) (aimahp) and DL-methioninehydroxamic acid (2-amino-4-methylthio-*N*-hydroxybutanamide) (amthb) with protons as well as copper(II) and nickel(II) was undertaken. Spectrophotometric measurements were also used to determine the nature of complexation involved.

EXPERIMENTAL

Reagents

L-lysinehydroxamate hydrochloride, L-argininehydroxamate hydrochloride and DL-methioninehydroxamate were obtained from Sigma (Dorset, U.K.) and their purities were checked by potentiometric titration. 0.1 mol dm^{-3} copper(II) and nickel(II) stock solution were prepared from their chloride salts and standardized gravimetrically *via* precipitation of the quinolin-8-oxalate. All weights were measured with a Sartorius 2024MP balance to five decimal places. Doubly distilled water was used in all potentiometric and spectrophotometric experiments and titrations were carried out under an argon atmosphere. Titrations were carried out with carbonate-free KOH solutions of known concentrations (*ca.* 0.2 mol dm^{-3}). The concentration of both the KOH and the HCl solutions were determined using Gran's method.[9] Ionic strength was kept constant at 0.2 mol dm^{-3} using KCl.

Potentiometric Measurements

Potentiometric titrations were carried out on a Radiometer pHM 64 research pH meter equipped with a Radiometer GK 2421C combined electrode. A Radiometer ABU 13 autoburette was used to dispense the base solution. The electrode was calibrated for hydrogen ion concentration by the method of Irving *et al.*[10] A pK_w value of 13.76 was determined and used in the calculations. All solutions were prepared to a total volume of 25 cm^3 and thermostated at 25°C using an MLW Thermostat U10 circulating constant temperature water bath.

The concentrations of ligand solutions used were 0.004 mol dm^{-3} and 0.006 mol dm^{-3}. Metal ion-to-ligand molar ratios of 1:1, 1:2 and 1:4 were used. Titrations were performed over the pH range 2.0–11.0 and stability constants (β_{pqr}) defined by (**1**) (charges are omitted for simplicity) were calculated using the SUPERQUAD computer program.[11]

$$pM + qH + rL \rightleftharpoons M_pH_qL_r \quad (1)$$

$$\beta_{pqr} = [M_pH_qL_r]/[M]^p[H]^q[L]^r$$

Spectrophotometric Measurements

Absorption spectra in the range 800–400 nm were measured with a Varian DMS 100S UV-VIS spectrophotometer. Solutions containing the ligand and the metal ion were prepared at a ratio of 2:1 to an ionic strength of 0.2 mol dm^{-3} (KCl) under an atmosphere of argon. The spectra were measured from pH 2.5–11.0 at 25°C using 1 cm cells.

RESULTS AND DISCUSSION

Protonation Equilibria

A maximum of three protons can be released from dahhe while two protons can be released from both aimahp and amthb. It may be noted in Figure 1, that aimahp appears to have an additional dissociable proton besides the hydroxamic (-NH-OH) and the ammonium functional groups. Leporati *et al.*[12] calculated the pKa of the guanidino amino proton in aimahp to be 13.23 ± 0.08. In a recent paper, Noszál *et al.*[13] suggested that the guanidino group of arginine is much less acidic and reported a pKa~15, which was 2–4 log units lower than previous literature data.[14] In order to clarify the question, the dissociation of aimahp at high ligand concentration (0.05 mol dm^{-3}) up to high pH (~13.4) was studied. It was found that the ligand titration curve runs with the titration curve for the strong acid of the same concentration. Accordingly, it can be stated that the guanidino group does not dissociate in the measurable pH range, its pKa is certainly >14 and therefore cannot be determined by pH-metric methods. Our data relating to H^+-amthb are in agreement with that published by El-Ezaby *et al.*[15] The overall protonation constants, $\log\beta_{011}$, $\log\beta_{021}$, $\log\beta_{031}$ (dahhe) and $\log\beta_{011}$, $\log\beta_{021}$ (aimahp, amthb) determined for each ligand are given in Table 1. The derived stepwise constants (pKa: 6.90; 8.82; 10.59 for dahhe, 6.82; 8.86 for aimahp and 6.87; 8.96 for amthb) indicate somewhat overlapping protonation processes. By comparing the data for

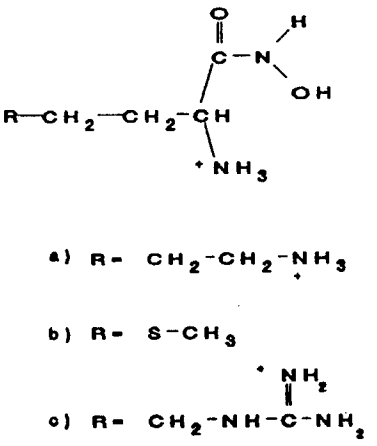


Figure 1 a) Lysine Hydroxamic Acid (dahhe); b) Methionine Hydroxamine Acid (amthb); c) Arginine Hydroxamic Acid (aimahp)

TABLE 1 Stability constant data ($\log\beta_{pqr}$) for proton and copper(II) and nickel(II) complexes of dahhe, aimahp and amthb. (T = 25°C; I = 0.2 mol dm^{-3} KCl).

	H^+ – dahhe	H^+ – aimahp	H^+ – amthb	Cu^{II} – dahhe	Cu^{II} – aimahp	Cu^{II} – amthb	Ni^{II} – dahhe	Ni^{II} – aimahp	Ni^{II} – amthb
$\log\beta_{011}$	10.59(1)[a]	8.86(2)	8.96(3)						
$\log\beta_{021}$	19.41(2)	15.68(3)	15.83(5)						
$\log\beta_{031}$	26.31(2)								
$\log\beta_{111}$				20.72(3)			16.73(2)		
$\log\beta_{122}$				40.06(2)			34.56(1)		
$\log\beta_{112}$				30.62(3)			26.40(2)		
$\log\beta_{102}$				20.22(3)	18.98(3)	19.41(2)	16.12(3)	13.30(2)	13.55(1)
$\log\beta_{1\text{-}12}$				9.30(5)	9.01(5)	9.85(3)	5.43(3)	5.52(3)	5.15(1)
$\log\beta_{212}$				40.95(2)					
$\log\beta_{101}$					10.26(4)	10.48(2)		5.90(13)	6.53(2)
$\log\beta_{2\text{-}12}$					19.82(4)	20.20(3)			

[a] Figures in parentheses are the computed standard deviations.

H^+-dahhe with the appropriate data for lysine,[14] the $\log\beta_{011}$ value can be assumed to belong to protonation of the terminal amino group.

Metal-Complex Equilibria

Titration data for different ligand-to-metal ratios were evaluated using estimates of formation constants and the stoichiometries of possible complexes to find the best agreement between calculated and observed data. Protonation constants previously calculated were kept constant and SUPERQUAD was used to refine the formation constants.

Copper(II)-dahhe system

Stoichiometries of the complexes and the formation constants, $\log\beta_{pqr}$, yielding the

best fit of the pH-metric experimental data for the copper(II)-dahhe system are given in Table 1. The only difference between the equilibrium models for systems containing dahhe or other simple amino hydroxamic acids[4] as ligands is the formation of different protonated complexes containing the side chain amino group in protonated form. Representative species distribution curves and visible spectra as a function of pH are shown in Figures 2 and 3, respectively. The species distribution curves relate to a 1:2 metal to ligand ratio. An increase in the ligand concentration causes a decrease in the amount of the 1:1 species formed. As can be seen in Fig. 2, complexation begins at pH *ca.* 3.0 with formation of $[CuAH]^{2+}$ (maximum concentration of 20% total copper at pH 4.0 and under the conditions given in Fig. 2) and the polynuclear complex $[Cu_2A_2H]^{3+}$. The latter reaches a maximum concentration of 83% total copper at pH 4.75. The visible spectrum at pH 5.0 has a λ_{max} value of 650 nm. According to the semi-empirical equations of Sigel and Martin[16] for estimating the absorption maximum of copper complexes, this λ_{max} value is consistent with both oxygen and nitrogen being involved in coordination. The formation of an epr silent binuclear species with the composition $[Cu_2A_2H_{-1}]$ was already proved in the case of simpler aminohydroxamates.[4,17-21] Formerly, the polynuclear complex was considered to be a mixed hydroxo species in which monomeric units are joined *via* one OH^- bridge,[17-19] but the assumption[20] that the hydroxamate oxygens also take part in bonding was proved by X-ray analysis in the case of copper(II)-β-alaninehydroxamic acid.[21] Based on complete agreement with visible spectra recorded for other simple aminohydroxamates and dahhe containing systems in the pH-range 4–6, the same type of bonding as in Cu(II)-β-alaninehydroxamic acid can be assumed. (The terminal amino groups are protonated in the complex formed with dahhe). The proposed structure of the polynuclear species, shown in Scheme 1, is not complete. The ratio in $[Cu_2A_2H]^{3+}$ is known but the species may also be $(Cu_2A_2H)_n$. Between pH 5.6–9.5, $[CuA_2H_2]^{2+}$

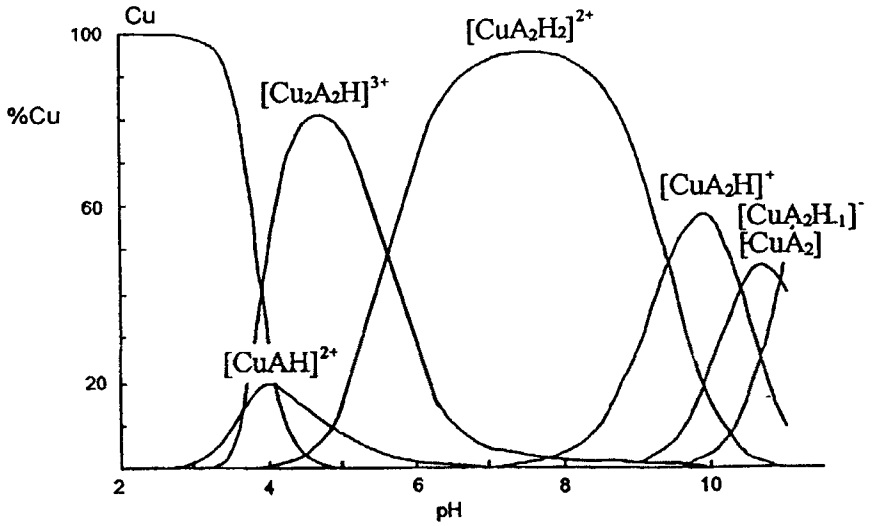


Figure 2 Species distribution curves for complexes present in the copper(II)-dahhe system. Concentrations (mol dm^{-3}): Cu^{II}, 2×10^{-3}; dahhe, 4×10^{-3}.

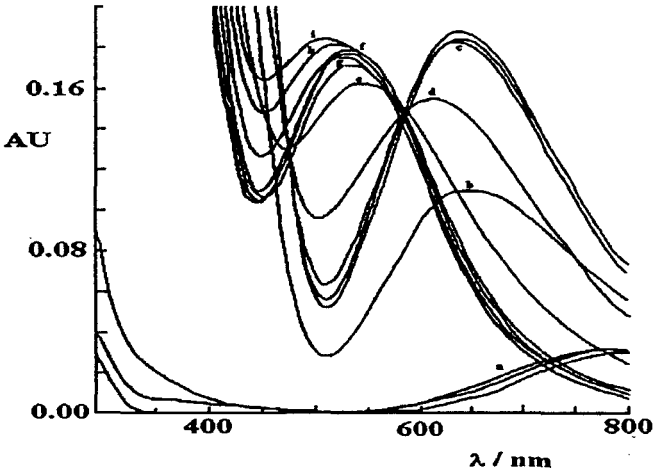
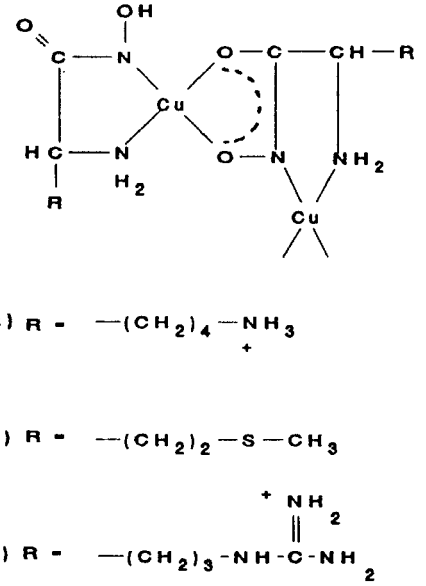


Figure 3 Visible absorption spectra for the copper(II)-dahhe system at various pH values: 3.5(a), 4.0(b), 5.0(c), 5.5(d), 6.0(e), 8.0(f), 10.0(g), 10.5(h), 11.0(i). Concentrations (mol dm^{-3}): Cu^{II}, 2×10^{-3}; dahhe, 4×10^{-3}.



a) R = $-(CH_2)_4-\overset{+}{N}H_3$

b) R = $-(CH_2)_2-S-CH_3$

c) R = $-(CH_2)_3-NH-\overset{\overset{+NH_2}{\|}}{C}-NH_2$

Scheme 1 a) Lysine Hydroxamic Acid (dahhe); b) Methionine Hydroxamic Acid (amthb); c) Arginine Hydroxamic Acid (aimahp).

is the dominant species with a maximum concentration of 96% total copper at pH 7.6. There is general agreement that bis complexes formed in copper(II)-aminohydroxamate systems[4,18–21] involved coordination of both the α-amino group and the deprotonated hydroxamate nitrogens *i.e.*, 4N coordination. This is reflected

in the visible spectra where formation of the above complex, beginning at pH 6.0, results in a significant blue shift to ~520 nm (see Fig. 3). Above pH 8.0, three more complexes were detected, resulting from successive deprotonation of the $[CuA_2H_2]^{2+}$ complex. Protons can be removed from the non-coordinated terminal ammonium groups, the coordinated -N-OH groups or a coordinated water molecule. The change of λ_{max} in the absorption spectra from 530 nm (at pH 8.0) to 515nm (at pH 11.0) suggests deprotonation of the hydroxamate hydroxyl proton. Stabilization by hydrogen bonding between the hydroxy groups increases the planarity of the complex and strengthens the nitrogen coordination causing a blue shift in the visible spectrum. On the other hand, the spectrophotometric results and the derived stepwise pK values (9.44, 10.40 and 10.92 respectively) show that the three successive deprotonation processes overlap. This means that different isomers of the $[CuA_2H]^+$ and $[CuA_2]$ exist in the systems.

Copper(II)-aimahp and -amthb Systems

The complex formation constants for copper(II)-amthb and copper(II)-aimahp are given in Table 1. Both of these systems display very similar behaviour indicating that involvement of either the guanidino moiety of aimahp or the sulphur group of amthb is unlikely. Complexation begins at pH *ca.* 3.0 with simultaneous formation of $[CuA]^+$ and $[Cu_2A_2H_{-1}]^{\bullet}$. Like the copper-dahhe system, these complexes are in equilibrium with each other, the polynuclear complex being dominant. The $[Cu_2A_2H_{-1}]^+$ complex reaches a maximum concentration of 78% total copper at pH 4.6. The dominant species between pH 5.5–9.5 for both systems is the $[CuA_2]$ complex, reaching a maximum concentration of 99% total copper at pH 7.7. The only deprotonated species detected was $[CuA_2H_{-1}]^-$ above pH 8.0. This confirms that the amino group at the guanidino moiety of aimahp is not deprotonated in the pH range 2–12.$[CuA_2H_{-1}]^-$ is formed by deprotonation of one of the hydroxy protons of the hydroxamate functional group. The visible spectra for copper(II)-aimahp and copper(II)-amthb are very similar to that for copper(II)-dahhe indicating similar bonding.

The visible spectra show no evidence for coordination through the terminal amino groups (dahhe, aimahp) and sulphur group (amthb) for the three systems under investigation. If there was any significant coordination through these positions, it would weaken co-oordination in the plane, and cause a red shift in the visible spectrum. Since no red shift is observed, we can conclude that these groups have no significant role in the coordination of the complexes.

Nickel(II)-dahhe system

The complex formation constants, $\log\beta_{pqr}$, for the nickel(II)-dahhe system are given in Table 1. Complexation, as can be seen in Figure 4 showing the species distribution curves for the nickel(II)-dahhe system, begins at pH *ca.* 5.0 with a simultaneous formation of $[NiAH]^{2+}$ and $[NiA_2H_2]^{2+}$. (The colour of the solution becomes yellow indicating formation of species with planar geometry). The complex $[NiAH]^{2+}$ is present as a very minor species and only reaches a maximum concentration of 13% total nickel at pH 6.0 under the conditions shown in Fig. 4. Between pH 6.0 and 8.2, $[NiA_2H_2]^{2+}$ is the dominant species. Above pH 7.0, deprotonation of this complex occurs, resulting in overlapping processes for the

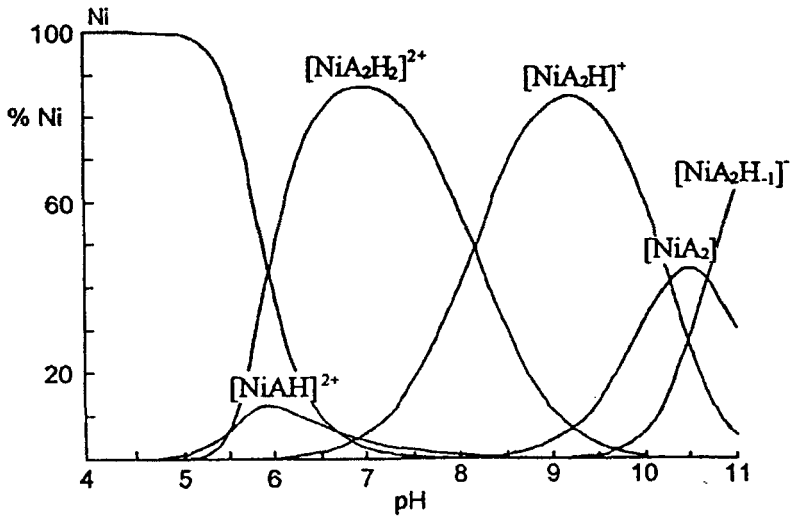
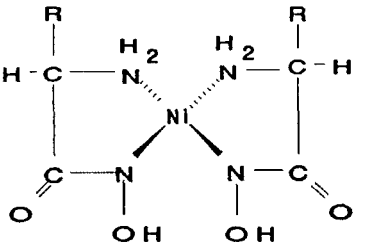


Figure 4 Species distribution curves for complexes present in the nickel(II)-dahhe system. Concentrations (mol dm^{-3}): Ni^{II}, 2×10^{-3}; dahhe, 4×10^{-3}.

formation of $[NiA_2H]^+$, $[NiA_2]$ and $[NiA_2H_{-1}]^-$. The coordination mode for all the above bis complexes can be supposed to be through four nitrogens with planar geometry as shown in Scheme 2. This assumption is in agreement with other nickel(II)-aminohydroxamate systems[4] and with the results of the visible spectrum (Figure 5) for various pH values. Coordination of the hydroxamic acid group through nitrogen rather than oxygen was first reported by Brown *et al.*[22] in the case of Ni(II)-glycine hydroxamic acid and Ni(II)-serine hydroxamic acid in both solution and the solid state. There was no change observed in the geometry of the complexes formed in the system above pH 6.0. However, an increase of the λ_{max} at 425nm can be found in spectra registered above pH 7.0. A similar result was reported where hydrogen bond formation caused increased planarity of complexes containing the hydroxy moiety of one of the coordinated ligands in the deprotonated form. This result clearly shows that deprotonation of the terminal NH_3^+-groups of lysine hydroxamate and of the hydroxy group in one of the ligands overlap (as was found in the copper(II)-dahhe system). The complex $[NiA_2H_{-1}]^-$ contains



Scheme 2

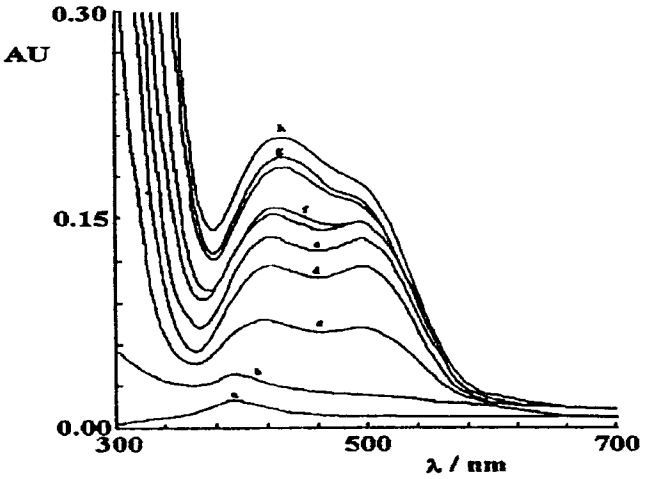


Figure 5 Visible absorption spectra for the nickel(II)-dahhe system at various pH values: 3.5(a), 5.5(b), 6.0(c), 6.5(d), 7.0(e), 8.0(f), 9.5(g), 10.0(h). Concentrations (mol dm^{-3}): Ni^{II}, 2×10^{-3}; dahhe, 4×10^{-3}.

both terminal amino groups and one of the hydroxy groups in the deprotonated form.

Nickel(II)-amthb and -aimahp systems

The complex formation constants for nickel(II)-amthb and nickel(II)-aimahp are given in Table 1. For both systems, complexation begins at pH *ca.* 5.0 with simultaneous formation of $[NiA]^+$ and $[NiA_2]$. Again, $[NiA_2]$ is the dominant species reaching a maximum concentration of 89% total nickel at pH 7.2 for the nickel(II)-amthb system and 85% total nickel at pH 6.7 for the nickel(II)-aimahp system. $[NiA]^+$ is present in both systems as a minor complex, reaching a maximum concentration of 22% total nickel at pH 5.9 for nickel(II)-amthb and 9% total nickel at pH 6.0 for the nickel(II)-aimahp system. Above pH 8.5, the only species detected is $[NiA_2H_{-1}]^-$, formed by deprotonation of one of the hydroxy protons of the hydroxamate functional group of $[NiA_2]$. The visible spectra for nickel(II)-amthb and nickel(II)-aimahp were similar to that for nickel(II)-dahhe with a λ_{max} value of ~425nm, again indicating co-ordination through nitrogens for all species detected (see scheme 2).

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