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Stability of Cu(II), Ni(II), and U(VI) Complexes with 2-Hydroxybenzohydroxamic Acid in Aqueous Solutions

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Complex formation between 2-hydroxybenzohydroxamic acid (salicylhydroxamic acid, H_2Sax) and metal ions Me^{2+} (with $Me^{2+} = Cu$, Ni, and UO_2^{2+}) was investigated using a potentiometric methodology at 25 °C, and in 1 M $NaClO_4$. The measurements have been performed using a glass electrode for Ni^{2+} and UO_2^{2+} and in the case of Cu^{2+} also an amalgam electrode. The molar concentrations of the metals ranged from $5.0 \cdot 10^{-4}$ mol·dm^{-3} to $1.0 \cdot 10^{-2}$ mol·dm^{-3}, whereas the concentration of salicylhydroxamic acid was chosen in the interval $1 \cdot 10^{-4}$ mol·dm^{-3} to 0.02 mol·dm^{-3}. The potentiometric data are consistent with the presence of species $CuH_{-1}(H_2Sax)^+$, $CuH_{-2}(H_2Sax)$, $NiH_{-1}(H_2Sax)^+$, $NiH_{-2}(H_2Sax)$, $NiH_{-3}(H_2Sax)_2^-$, $UO_2H_{-2}(H_2Sax)$, $UO_2H_{-3}(H_2Sax)^-$, and $UO_2H_{-4}(H_2Sax)^{-2}$. Medium effects on the constants were calculated using the specific interaction theory (SIT).

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1. Introduction

The hydroxamate group[1] has been found in many compounds isolated from fungi, yeast, and bacteria, as microbial iron transport molecules (siderochromes).[2] The investigation of these compounds is also of great analytical importance since various hydroxamic acids have been proposed as reagents for gravimetric and/or spectrophotometric determinations of cations,[3,4] such as U(VI), Fe(III), and Nb(V). This work reports the results of complexation equilibria between $Me^{2+} = Cu^{2+}, Ni^{2+}, UO_2^{2+}$, and 2-hydroxybenzohydroxamic acid (or salicylhydroxamic acid, H_2Sax).

The complexation equilibria were studied according to the reaction scheme

$$p\mathrm{Me}^{2+} + r\mathrm{H_2Sax} \rightleftharpoons \mathrm{Me}_p\mathrm{H}_{-q}(\mathrm{H_2Sax})_r^{\,2p-q} + q\mathrm{H}^+ \quad \beta_{pqr} \tag{1}$$

In spite of the interesting chemical properties of hydroxamic acids, few reliable data on the complexation equilibria with cations are available in the literature.[5] Previous works are summarized in Table 1.

The majority of the authors determined the stability constants in dilute solutions of metals and ligand, over a short range of pH. Wide discrepancies between the proposed model of speciation show that experimental conditions were not chosen adequately to provide reliable results. To obtain further information on the assumed complexes and on others not detectable in dilute reagent solutions, it was thought worthwhile to reinvestigate the metal−salicylhydroxamic acid system in 1 M $NaClO_4$.

2. Method

In this work, the complexing properties of salicylhydroxamic acid toward Cu^{2+}, Ni^{2+}, and UO_2^{2+} were studied at 25 °C and in 1 mol·dm^{-3} $NaClO_4$ by measuring $[H^+]$ in a series of metal perchlorate solutions containing perchloric acid and salicylhydroxamic acid, in various amounts. The hydrogen ion concentration was determined by the EMF of cell (A)

$$(-)\ \text{GE/Test Solution/RE}\ (+) \tag{A}$$

in which GE symbolizes a glass electrode and RE is the reference half-cell: RE = 1 M $NaClO_4$/0.01 M $AgClO_4$, 0.99 M $NaClO_4$/AgCl,Ag. The test solution had the general composition: C_M $Me(ClO_4)_2$, C_L H_2Sax, C_A $HClO_4$, C_B NaOH, $(1 - 2C_M - C_A - C_L)NaClO_4$.

In the case of Cu^{2+}, the free metal ion concentrations were also measured by cell (B)

$$(-)\ \text{Hg}-\text{Cu}(0.02\ \%)\text{/Test Solution/RE}\ (+) \tag{B}$$

It is useful to employ dilute copper amalgam to have a low metal concentration in the amalgam, so that the reactions with H^+ ions and with impurity of dissolved oxygen are negligible.

The measurements were carried out as potentiometric titrations. C_M ranged from $5 \cdot 10^{-4}$ mol·dm^{-3} to $2 \cdot 10^{-3}$ mol·dm^{-3}, whereas C_L was chosen to be less than 0.02 mol·dm^{-3}. $(C_A - C_B)$ was varied from $5 \cdot 10^{-3}$ mol·dm^{-3} to incipient formation of a solid phase. The EMF of cell (A) at 25 °C may be written as

$$E_G = E_{0G} - 0.05916\ \log[\mathrm{H}^+]y_H + E_j \tag{2}$$

where E_{0G} is a constant in each titration; y_H is the activity coefficient of the H^+ ion; and E_J represents the liquid junction potential of the test solution/1 mol·dm^{-3} $NaClO_4$ boundary. Activity coefficients tend to 1, and E_J tends to 0 as the composition of test solution approaches 1 mol·dm^{-3} $NaClO_4$.

Each titration consisted of two parts. In the first, E was measured in the absence of metal ions and H_2Sax ions. $(C_A - C_B) = [H^+]$ was varied between $2 \cdot 10^{-3}$ mol·dm^{-3} and $5 \cdot 10^{-5}$ mol·dm^{-3}. From these data, E_0 values constant to within ± 0.05 mV were calculated, assuming[13] $E_J = -0.064[H^+]$. The data were analyzed by the Gran function,[14] to refine the initial concentration of $HClO_4$. In the case of Cu^{2+}, the EMF of cell (B) may be represented by eq 3

$$E_M = E_{0M} - 0.02958\ \log[\mathrm{Cu}^{2+}]y_M + E_j \tag{3}$$

E_{0M} was determined by measuring E_M in solutions with known concentrations of metal, produced in situ stepwise coulometrically in test solution through the electrolysis cell (C)

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$$(+)\ \mathrm{Hg{-}Cu/Test\ Solution/AE}\ (-) \qquad \text{(C)}$$

in which Hg−Cu is another copper amalgam and AE is the auxiliary electrode: AE = 1 $\mathrm{mol \cdot dm^{-3}}$ $NaClO_4$/0.1 $\mathrm{mol \cdot dm^{-3}}$ NaCl, 0.9 $\mathrm{mol \cdot dm^{-3}}$ $NaClO_4$/AgCl,Ag. The acidity of the solution was high enough to suppress the hydrolysis of the Cu^{2+} ion. In the second part, in the presence of metal and H_2Sax, complex formation was followed by decreasing gradually the acidity on addition of NaOH solution to incipient precipitation of the solid phase. In a few experiments, alkaline solutions were back-titrated with $HClO_4$. The reason for the reverse titrations was to decide whether the equilibria were real. The data collected in the second part formed the basis of the evaluation of the stability constants of salicylhydroxamic acid−metal complexes. This required the protolytic equilibria of salicylhydroxamic acid, established in previous work[18]

$$\mathrm{H_2Sax + H_2O \rightleftharpoons HSax^- + H_3O^+} \quad -\log K_{a1} = 7.55_0 \pm 0.006$$

$$\mathrm{H_2Sax^- + 2H_2O \rightleftharpoons Sax^{2-} + 2H_3O^+} \quad -\log K_{a1}K_{a2} = 17.20 \pm 0.01$$

3. Experimental

3.1. Reagents and Analysis. Copper(II) perchlorate stock solutions[15] were prepared by dissolution of $CuO_{(s)}$ with $HClO_4$ added in a slight excess. $CuO_{(s)}$ was obtained by decomposition of $Cu(NO_3)_2 \cdot 4H_2O$ (crystallized from HNO_3concentrated) at 500 °C for 24 h. The copper(II) concentration of the stock solutions was analyzed gravimetrically by electrolytic deposition and by iodometry. The results agreed to within ± 0.2 %.

$HClO_4$ stock solutions were prepared by diluting a 72 % Merck p.a. product and analyzed by titration with $KHCO_3$ and Tl_2CO_3, with a reproducibility of 0.1 % or better.

Nickel(II) perchlorate stock solutions[16] were prepared from pure 4N5 metal purchased from Sigma-Aldrich. An exactly weighed amount of metal was dissolved in a known amount of $HClO_4$ in excess of 10 %. In the final product, no halogenide ions could be detected. The nickel(II) concentration of the stock solutions was analyzed gravimetrically by electrolytic deposition.

Uranium(VI) perchlorate solutions[17] were prepared by $U_3O_{8(s)}$, obtained by ignition at 900 °C of $UO_2(NO_3)_2(H_2O)_6$ (Merck, p.a.). The oxide was dissolved by HIO_3 (Merck, p.a.), and the iodine was removed by heating. The uranium(VI) concentration in the stock solution was determined gravimetrically as $U_3O_{8(s)}$, obtained by precipitation with ammonia and igniting at 900 °C.

Copper amalgam, 0.2 % (weight) was made by bringing pure copper into contact with distilled mercury under an inert atmosphere. A weighed amount of mercury was introduced into a small well, built in the bottom of the titration vessel containing the test solution. Then copper, deposited by electrolysis on a Pt wire, was introduced.

Salicylhydroxamic acid (Sigma-Aldrich of pure grade) was recrystallized twice from methanol–water mixtures, as described elsewhere.[18]

NaOH solutions were prepared by generating an OH^- ion at the cathode of the electrolysis cell, described elsewhere.[18]

Sodium perchlorate (Merck p.a., as $NaClO_4 \cdot H_2O$) stock solutions[19] were standardized gravimetrically after evaporation of aliquots of the stock solutions and drying at 120 °C. Silver perchlorate[19] was synthesized from Ag_2O (Sigma-Aldrich product) and $HClO_4$. The silver concentration in the stock solution was determined by potentiometric titrations with NaCl.

Table 1. Survey of Previous Works for the Me^{2+}−H_2Sax Systems

ref	medium	method	species	log β_{pqr}
		Cu^{2+}		
6	0.1 M $NaNO_3$	Poten.	CuSax	−4.10
7	0.1 M $NaNO_3$	Poten.	CuSax	−4.19
			$Cu(Sax)_2^{2-}$	−16.93
8	0.5 M KCl	Spectr.	CuSax	−3.89
			$Cu(Sax)_2^{2-}$	−8.62
9	50 % dioxane/0.1 M $NaClO_4$	Poten.	CuSax	−9.21
10	75 % dioxane/0.5 M KCl	Spectr.	CuSax	−7.60
			$Cu(Sax)_2^{2-}$	−16.61
		Ni^{2+}		
6	0.1 M $NaNO_3$	Poten.	NiSax	−11.13
7	0.1 M $NaNO_3$	Poten.	NiSax	−11.16
			$Ni(Sax)_2^{2-}$	−24.41
			$Ni(HSax)(Sax)^-$	−22.55
9	50 % dioxane/0.1 M $NaClO_4$	Poten.	NiSax	−12.65
		UO_2^{2+}		
7	0.1 M $NaNO_3$	Poten.	UO_2Sax	−5.27
			$UO_2(Sax)_2^{2-}$	−16.62
9	50 % dioxane/0.1 M $NaClO_4$	Poten.	UO_2Sax	−9.89
11	0.1 M $LiClO_4$/0.1 M $NaClO_4$	Poten.	UO_2Sax	−9.49
			$UO_2(Sax)_2^{2-}$	−19.89
12	50 % acetone/0.5 M $NaClO_4$	Poten.	UO_2Sax	−10.5
			$UO_2(Sax)_2^{2-}$	−22.24

Sodium chloride and potassium bromide (Baker) were dried at 110 °C.

3.2. Apparatus. During the EMF measurements, the cell assembly, automatic burette, and gas washing bottles were placed in an air thermostat kept at 25.00 ± 0.02 °C.

Glass electrodes manufactured by Metrohm Ltd. (Switzerland) were employed. Bridge solutions and reference electrodes were lodged in Wilhelm-type bridges.[20] Silver electrodes were prepared according to Brown.[21]

Potentiometric titrations were carried out with a programmable computer controlled data acquisition unit 34970A, supplied by Agilent Technologies (USA). The potentials were read with a precision of $1 \cdot 10^{-5}$ V. The EMF of cell (A) was read with a Keithley 642 type Digital Electrometer.

Test solutions were purged of oxygen by bubbling purified and presaturated nitrogen gas.

The X-ray powder patterns were obtained with an automatic Philips diffractometer using Cu Kα radiation (λ = 1.544 Å, Ni-filtered) and settings of 40 kV and 20 mA.

The Fourier transform infrared spectra of KBr pellets were measured by a Jasco FT/IR-430 spectrometer (Jasco Corporation, Japan), in trasmission mode. About 500 mg of KBr was pressed with 5 mg of the solid, and the spectra were measured in the regions (400 to 4000) cm^{-1}, with a resolution of 4 cm^{-1}. The signals were collected as averages of 50 summations to improve signal−noise ratio. Identification of band maxima frequencies was performed by inspection of smoothed absorbance spectra using Gaussian curve fitting.

4. Treatment of the Data and Results

On the basis of free metal ion measurements of the Cu^{2+}−H_2Sax system, we evaluated $\log(C_M/[Cu^{2+}])$ as a function of $\log[H^+]$ (Figure 1). Since data of forward titrations pratically coincide with those of back-titrations, the equilibria were truly attained.

For the Ni^{2+}−H_2Sax system, the function Z_H can be determined by

$$Z_H = ([H^+] - C_H)/C_A \qquad (4)$$

which represents the average number of released protons per ligand. Examples of experimental curves (Z_H, $-\log[H^+]$) are reported in Figure 2.

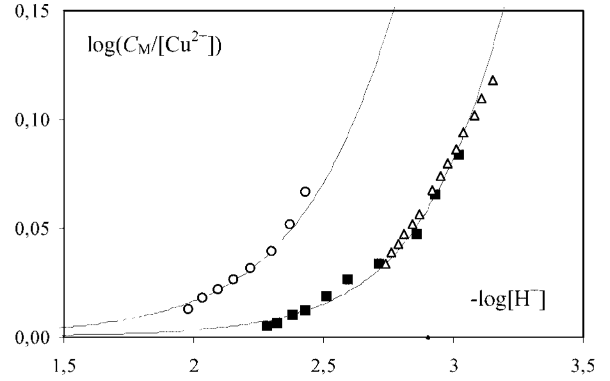


Figure 1. log(C_M/[Cu^{2+}]) as a function of log[H^+], for some titrations, in the Cu(II)−H_2Sax system. Experimental conditions (C_M10^3 mol·dm^{-3}, C_A10^3 mol·dm^{-3}): circles, (9.71, 10.30); filled rhombs, (0.30, 2.0) (back-titration); triangles, (1.38, 2.11). The continuous curves were drawn using the stability constants of Table 2.

Table 2. Survey of the Formation Constants (Equation 1) of the Me^{2+}−H_2Sax Systems at 25 °C in 1 mol·dm^{-3} $NaClO_4$ (Calculated by HYPERQUAD)

Me^{2+}	Cu^{2+}	Ni^{2+}	UO_2^{2+}
log $\beta_{111} \pm 3\sigma$	-1.54 ± 0.05	-3.71 ± 0.01	-
log $\beta_{121} \pm 3\sigma$	-4.04 ± 0.01	-11.31 ± 0.06	-5.77 ± 0.03
log $\beta_{131} \pm 3\sigma$	-	-	-10.35 ± 0.03
log $\beta_{132} \pm 3\sigma$	-	-15.43 ± 0.09	-
log $\beta_{141} \pm 3\sigma$	-	-	-19.79 ± 0.08
U_{min}	13.1	15.3	55.58
σ_u^2	0.32	0.64	0.82
χ^2	15.5	12.4	17.12

In an analogous way, to visualize the experimental results for the UO_2^{2+}−H_2Sax system, the function Z_H was constructed (Figure 3).

The best equilibrium model was sought by systematically testing *pqr* combinations, using the HYPERQUAD program.[22] As a criterion for the best explanation, we employed the weighted variance of the residuals $\sigma_U^2 = \sum w_i(E_i^{obsd} - E_i^{calcd})^2/(N - n)$, where w_i is the weight assigned to the generic point *i*, inversely proportional to the variance of that point connected with the errors of *E* and the titrant volume. $E_i^{obsd} = E_0 + 0.05916\log[H+]$ was deduced from eq 1. E_i^{calcd} is a value calculated with a given set of β_{pqr}; *N* is the number of observationsp; and *n* is the number of parameters to be refined. Hydrolysis constants (log Q_{mn}) in 1 mol·dm^{-3} $NaClO_4$ corresponding to the formation of $Me_m(OH)_n^{2m-n}$ species are[23]

$$Cu^{2+}{:}-7.22(CuOH^+),\ -10.75(Cu_2(OH)_2^{2+})$$

$$Ni^{2+}{:}-10.50(NiOH^+)$$

$$UO_2^{2+}{:}-4.80((UO_2)OH^{3+}),\ -5.91((UO_2)_2(OH)_2^{2+}),\ -16.43((UO_2)_3(OH)_5^{+}$$

Equilibrium analysis has revealed the formation of the complex species reported in Table 2.

5. Discussion

To visualize the amounts of the different species, some distribution diagrams were constructed. These are given in Figures 4–6 and show that each of the complexes corresponds to at least 10 % of the total metal.

In dilute solutions of metals, the predominanting species at −log[H^+] > 6 are $CuH_{-2}(H_2Sax)$, $NiH_{-1}(H_2Sax)$, and $UO_2H_{-3}(H_2Sax)^-$. It is evident that species bearing two hydroxamic groups attain appreciable concentrations only in solutions with high concentrations of ligand. The stability constants for the reaction

$$Me^{2+} + Sax^{2-} \rightleftharpoons MeSax$$

characteristic of the interaction of the metal ion with the hydroxamate binding site, were derived from the protolytic equilibria of salicylhydroxamic acid and the constants given in Table 2. The stability scale of the complex is (Me(log const.)): Cu (13.16) > UO_2 (11.85) > Ni (5.89).

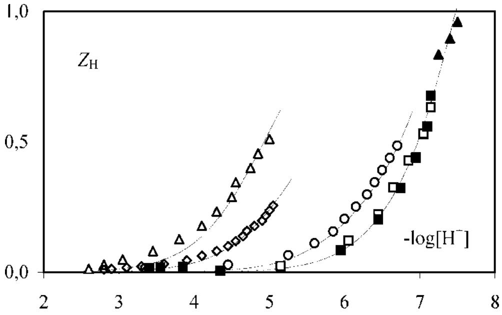


Figure 2. Z_H (−log[H^+]) in function of −log[H^+] for the system Ni(II)−H_2Sax. The symbols refer to (C_M10^3 mol·dm^{-3}, C_A10^3 mol·dm^{-3}): triangles, (9.19, 20.56); rhombs, (27.58, 23.52); circles, (1.5, 3.0); filled squares, (0.54, 1.06); squares, (1.0, 4.00); filled triangles, (0.919, 2.94) (back-titration). The curves have been calculated by assuming the constants given in Table 2.

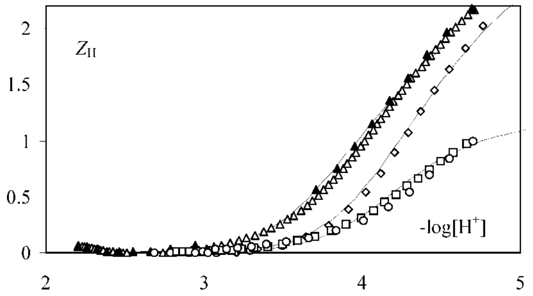


Figure 3. Z_H (−log[H^+]) in function of −log[H^+] for the system UO_2^{2+}−H_2Sax. The symbols refer to (C_M10^3 mol·dm^{-3}, C_A10^3 mol·dm^{-3}): triangles, (3.01, 3.00); filled triangles, (3.00, 3.01) (back-titration); rhombs, (0.69, 0.69); circles, (0.353, 0.706); squares, (0.690, 1.38). The curves have been calculated by assuming the constants given in Table 2.

Table 3. Frequency Values of the C−O, C−N, and N−O Stretching Bands of Solids $UO_2(HSax)_2{\cdot}2H_2O_{(s)}$, $Cu(HSax)_{2(s)}$, and $Ni(HSax)_{2(s)}$

solid	ν_{C-O}, cm^{-1}	ν_{C-N}, cm^{-1}	ν_{N-O}, cm^{-1}
$UO_2(HSax)_2{\cdot}2H_2O_{(s)}$	1606	1485	1165
$Cu(HSax)_{2(s)}$	1605	1476	1146
$Ni(HSax)_{2(s)}$	1604	1485	1156

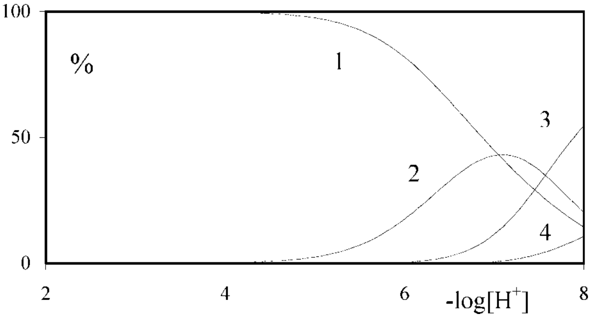


Figure 4. Distribution of the nickel ion over the various complexes, as a function of −log[H^+] in solution with $C_M = 1{\cdot}10^{-4}$ mol·dm^{-3} and $C_A = 1{\cdot}10^{-4}$mol·dm^{-3}. Species: 1, Ni^{2+}; 2, $NiH_{-1}(H_2Sax)^+$; 3, $NiH_{-2}(H_2Sax)$; 4, $NiH_{-3}(H_2Sax)_2^-$.

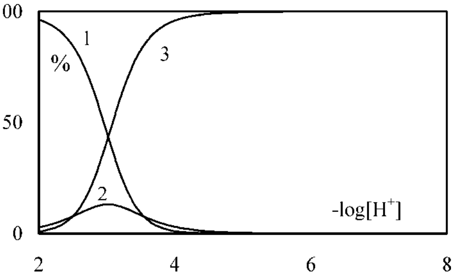


Figure 5. Species distribution diagram of the $Cu^{2+}-H_2Sax$ system. Diagram for $C_M = 1.0 \cdot 10^{-4}$ mol·dm^{-3} and $C_A = 0.01$ mol·dm^{-3}. The constants employed are those given in Table 3. Species: 1, Cu^{2+}; 2, $CuH_{-1}(H_2Sax)^+$; 3, $CuH_{-2}(H_2Sax)$.

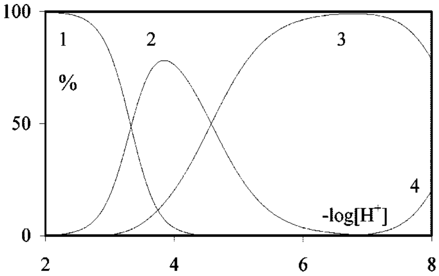


Figure 6. Distribution of uranium over the various complexes, with $C_M = 1 \cdot 10^{-4}$ mol·dm^{-3} and $C_L = 5 \cdot 10^{-2}$ mol·dm^{-3}: 1, UO_2^{2+}; 2, $UO_2H_{-2}(H_2Sax)$; 3, $UO_2H_{-3}(H_2Sax)^-$; 4, $UO_2H_{-4}(H_2Sax)^{-2}$.

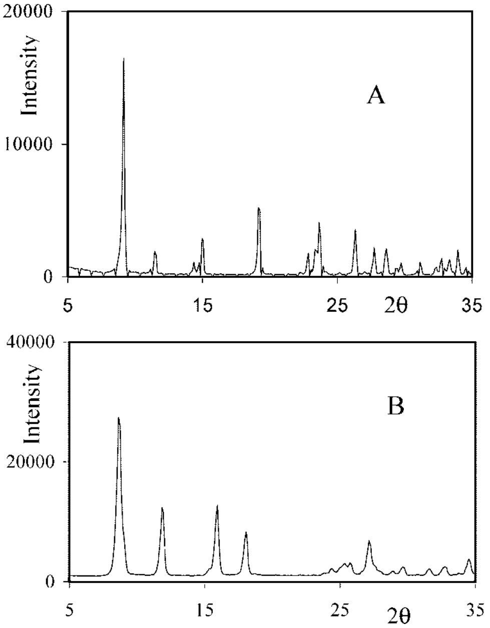


Figure 7. X-ray diffraction pattern of $UO_2(HSax)_2 \cdot 2H_2O_{(s)}$ (A) and $Cu(HSax)_{2(s)}$ (B).

The discrepancy of the $NiH_{-3}(H_2Sax)_2$ stability constant is explainable in terms of additional species in the $Ni^{2+}-H_2SAX$ model (ref 7) that can modify the value of constants of the other species and in terms of different ionic media.

Table 4. Survey of the Formation Constants (Equation 1) of the $Me^{2+}-H_2Sax$ Systems at 25 °C at Infinite Dilution

Me^{2+}	Cu^{2+}	Ni^{2+}	UO_2^{2+}
$\log \beta_{111} \pm 3\sigma$	-1.3 ± 0.2	-3.5 ± 0.1	-
$\log \beta_{121} \pm 3\sigma$	-3.8 ± 0.1	-11.1 ± 0.2	-5.3 ± 0.1
$\log \beta_{131} \pm 3\sigma$	-	-	-9.6 ± 0.2
$\log \beta_{132} \pm 3\sigma$	-	-14.8 ± 0.2	-
$\log \beta_{141} \pm 3\sigma$	-	-	-18.6 ± 0.2

The X-ray powder diffraction patterns (Figure 7) show that the precipitated solids have a crystalline structure, except for the nickel compound that was obtained in an amorphous state. Single crystal structural analysis of the uranyl compound was performed successfully.[24]

The ligand acts both as a chelate, forming five-membered rings, and as a bridge between two U atoms. The coordination around each U atom is a distorted hexagonal bipyramid.

Infrared spectroscopic data on solid compounds are shown in Table 3. The investigation was focused mainly within the (1700 to 1400) cm^{-1} range because this region is potentially most informative to assign coordination sites.

The FT-IR spectra of solids are characterized by C−O stretching around 1600 cm^{-1}, C−N vibrations at 1480 cm^{-1}, and N−O stretching around 1150 cm^{-1}. The compounds presented the similar frequency values of stretching bands. This suggests that the coordination sites around the metal are the same.

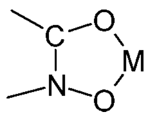
5.1. Effect of Medium Change. Modeling of natural systems requires a knowledge of formation constants relevant to the infinite dilution reference state. Extrapolation to zero ionic strength was carried out assuming the validity of the specific interaction theory (SIT).[25,26] The activity coefficient of a given species "*i*", γ_i (molal scale), can be expressed in the activity scale by

$$\log \gamma_i = -z^2 D + \sum_j b(i,j) m_j$$

in which $D = 0.5109 I^{1/2}/(1 + 1.5 I^{1/2}) = 0.2044$ in 1 mol·dm^{-3} $NaClO_4$ (equal to 1.05 mol·kg^{-1}), at 25 °C. $b(i,j)$ represents the specific interaction coefficient between *i* and *j* ions present in molality m_j.

A few $b(i,j)$ values have been deduced from experiments from various sources: $b(Na^+, OH^-) = 0.04$, $b(H^+, ClO_4^-) = 0.14$, $b(UO_2^{2+}, ClO_4^-) = 0.46$, $b(Cu^{2+}, ClO_4^-) = 0.32$ (ref 25), $b(Na^+, HSax^-) = 0.12$, $b(Na^+, Sax^{2-}) = 0.17 \pm 0.02$ (ref 18), $b(Ni^{2+}, ClO_4^-) = 0.37 \pm 0.032$ (ref 27).

On the basis of empirical rules, suggested elsewhere,[26] the $b(i,j)$ values for the complexes can be estimated. If interaction coefficients result from short-range forces, in a complex the metal and the ligand interact with the medium ions in a reduced amount according to the contact area accessible for interaction. Recent studies have proved that the hydroxamate group behaves as a bidentate (O,O) ligand,



forming a five-membered chelate. For the species $MeH_{-1}(H_2Sax)$, which may be written MeHSax, the interaction of the ligand group with the medium ions is approximately reduced by ½ that of the free ion. If $Me^{2+} = Cu^{2+}, Ni^{2+}$, assuming that the coordination number of the metal remains 4, the surface contact is reduced by 2/4. Hence: $b(MeHSax^+, NaClO_4) = (2/4)b(Me^{2+}, ClO_4^-) + (1/2)b(HSax^-, Na^+)$.

Therefore: $b(CuHSax^+, NaClO_4) = 0.22$, $b(NiHSax^+, NaClO_4) = 0.23$.

In an analogous way, for the species $MeH_{-2}(H_2Sax)$, that may be written MeSax, the interaction coefficients are: $b(CuSax, NaClO_4) = 0.24$, $b(NiSax, NaClO_4) = 0.26$.

Hence: $b(Ni(HSax)(Sax)^-, NaClO_4) = 0.29$.

If one assumes that UO_2^{2+} shows a coordination number of 6, the contact area is reduced by (4/6), whereas for each Sax^{-2} the interaction with Na^+ ions is $(1/2)b(Sax^{-2}, Na^+)$. The interaction coefficient for the complex UO_2Sax may be written

$$b(UO_2Sax, NaClO_4) = (4/6)b(UO_2^{2+}, ClO_4^-) + (1/2)b(Sax^-, Na^+) = 0.39$$

Similarly

$$b(UO_2(OH)_2Sax^{-2}, NaClO_4) = 0.26, b(UO_2OH(Sax)_2^{-3}, NaClO_4) = 0.25$$

Conversion constants on the molality scale were performed taking for the density of 1 $mol \cdot dm^{-3}$ $NaClO_4$ the value 1.052 $g \cdot cm^{-3}$. According to the Brönsted postulate,[25] we assumed $b(i,j) = 0$ between ions bearing the same charge type. A survey of the proposed stability constants in the infinite dilution reference state is given in Table 4.

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