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STABILITY CONSTANTS AND THERMODYNAMICS OF COMPLEXATION OF SCHIFF BASE HYDRAZONES DERIVED FROM 3-HYDRAZINO-6-:PHENYL PYRIDAZINE AND ACETOPHENONE DERIVATIVES WITH UO_2^+, TH^{4+}, PR^{3+} AND YB^{3+} IONS

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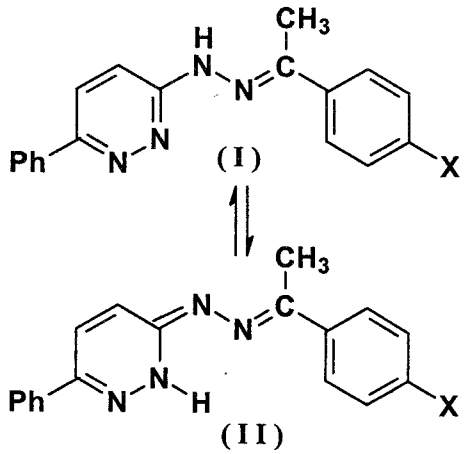
The stepwise stability constants of UO_2^{2+}, Th^{4+}, Pr^{3+} *and* Yb^{3+} ions with 3(acetophenonehydrazone)-6-phenyl pyridazine (AHP), 3-(p-chloroacetopheon-hydrazone)-6-phenyl pyridazine (ClAHP) and 3-p-aminoacetophenonehydrazone)-6-phenyl pyridazine (NH_2AHP) have been investigated potentiometrically in 75% (v/v) dioxane-water and 0.1 $MKNO_3$ at different temperatures (298,308 and 318K). For the same ligand, the order of stability decreases in the sequence; $Th^{4+} > UO_2^{2+} > Yb^{3+} > Pr^{3+}$. The thermodynamic functions (ΔG, ΔH and ΔS) for the dissociation and the complexation reactions have been evaluated and discussed. The higher negative values of ΔH suggest an octahedral environment around the metal ions in solution. AIso, the effect of the dielectric constant of the solvents, mole fraction and ionic strength of the medium on the stability of UO_2^{2+}-complexes were discussed.

Key words: 3-(acetophenonehydrazone)-6-phenyl pyridazine (AHP) and its derivatives ; Dissociation and stability constants ; Thermodynamic functions.

In our previous work, the thermodynamics of complexation of hydrazone-β-diketones[1-4], Schiff base hydrazones containing the pyridazine moiety [5-7] and the triazine moiety[8] have been investigated. Continuing our studies, we report herein the dissociation and stability constants as well as the thermodynamic functions for the complexation of UO_2^{2+}, Th^{4+}, Pr^{3}+ and Yb^{3+} ions with some Schiffbase hydrazones (NN-donors) derived from 3-hydrazino-6-phenyl pyridazine and acetophenone derivatives *(Str* I&II). Also, the effect of ionic strength, mole fraction of dioxane solvent and the dielectric constant of the medium was investigated and discussed for UO_2^{2+}-complexes as a typical example.



X	abbreviation
H	AHP
NH_2	NH_2AHP
Cl	ClAHP

Tautomeric structures of the Schiff-base hydrazone ligands

EXPERIMENTAL

All chemicals and solvents used were of reagent grade. Apparatus, general conditions, reagents and materials, purification of solvents and methods of calculation were the same as in previous investigations[1-8].

Potentiometric measurements

Appropriate aliquots of standard solutions of metal nitrates (0.001 M) and ligands (0.003M) were titrated potentiometrically with.0.09M *KOH* solution. For each mixture, the total volume was made up to 30ml by adding the organic solvent and water to attain the desired medium composition. The ionic strength of the medium *(KNO_3)* was kept virtually constant at the desired concentration. The values of pH' s were recorded on a *pH-meter(DIGI-520 Germany)* fitted with a combined glass-calomel electrode with an accuracy of ± 0.01 units. The temperature was maintained constant by using an ultrathermostat *(U3 Julabo-Germany).* Oxygen free nitrogen was bubbled through the titrating solutions to keep inert atmosphere. The correction for the measured pH-values was corrected according to the *Van Uitert* and *Hass* relation[9].

Preparation of the organic ligands

The ligands were prepared according to our previous work[5-7], where an ethanolic solution of 3-hydrazino-6-phenyl pyridazine was refluxed for one hour with the stoichiometric amount of acetophenone or its *para* substituted derivatives to yield the corresponding Schiff base hydrazones (StrI&II). The yellow crude products were filtered off, washed with ethanol, air-dried and recrystallized from ethanol. The average yield range is approx. 75-85 %. The purity of the ligands was established from their melting points and elemental analyses (Table 1).

Table.1. Results of elemental analyses and melting points of the ligands .

Compound M,F,	Elemental analyses; (%) Found/(Calc.) C	H	N	Cl	m.p. °C
AHP ($C_{18}H_{16}N_4$)	74.70	5.40	19.20	-	200° C
	(75.0)	(5.56)	(19.44)	-	
NH_2AHP ($C_{18}H_{17}N_5$)	71.10	5.40	22.80	-	130°C
	(71.29)	(5.61)	(23.10)	-	
Cl AHP ($C_{18}H_{15}N_4Cl$)	66.80	4.70	17.20	10.90	206 °C
	(66.98)	(4.65)	(17.36)	(11.01)	

The mass spectra of *NH_2AHP* and *CIAHP* ligands (Fig.l) showed molecular ion peaks at m/z: 303 and 322 which coincide with their formulae weights, respectively and support their structures. The base peaks were observed at m/z: 115 and 307 for *NH_2AHP* and *CIAHP* ligands, respectively.

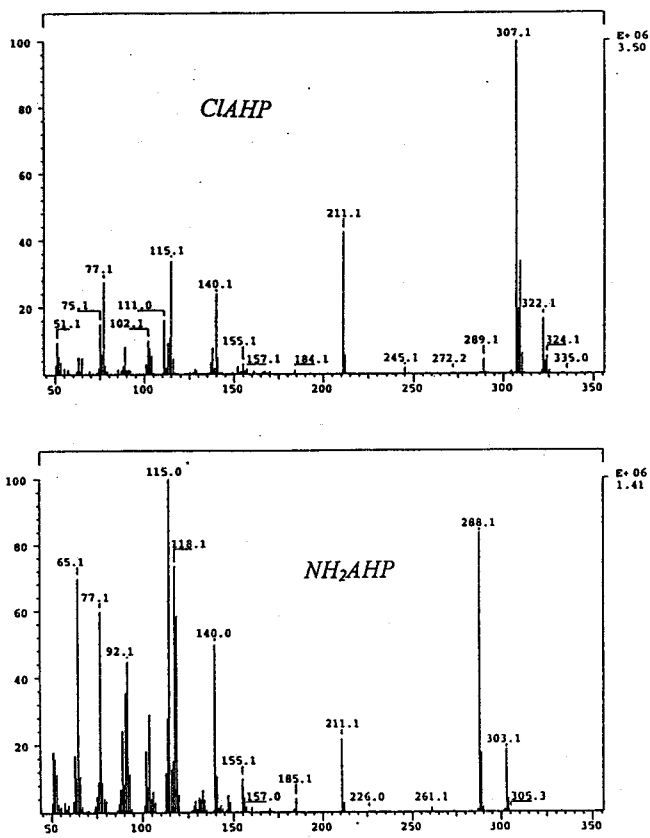


Fig. 1 Mass spectra of the ligands.

RESULTS AND DISCUSSION

The calculation of the stability constants of the investigated metal complexes is based on the fact that the pH-measurements during the titration of a ligand solution and in presence and in absence of a metal ion could be used to calculate the free ligand exponent *(pL)* and the number of ligand molecules attached per metal ion ($\bar{n}$). The experimental formation curves were constructed by plotting $\bar{n}$ *vs. pL* . It is evident that the degree of metal-ligand formation $\bar{n}$ extends between 0.1-2.6 for UO_2^{2+} and Th^{4+}-complexes and between 0.2-1.8 for Pr^{3+} and Yb^{3+}-complexes, suggesting that the higher species is 1:3; M:L for actinide complexes and is 1:2; M:L for lanthanide complexes in solution. The stepwise stability constants; *logK1, logK2 or logK3* were determined from the *constructed* $\bar{n}$*-pL* formation curves, where at $\bar{n}$= 0.5,1.5 or 2.5; *pL* = $\log K_1$, $\log K_2$ or $\log K_3$; respectively. Also, the Irving-Rossotti[10] relations;

$$\log\left(\frac{\bar{n}}{1-\bar{n}}\right) = \log K_1 - pL \; ; \; \log\left(\frac{\bar{n}-1}{2-\bar{n}}\right) = \log K_2 - pL \text{ and } \log\left(\frac{\bar{n}-2}{3-\bar{n}}\right) = \log K_3 - pL$$

have been constructed and analyzed to determine *logK1, logK2 or logK3;* respectively. The average of these two methods was taken as the stability constants. Inspection of the results obtained in Table 2 reveals that;

(i) $logK_1 \approx logK_2$ *except* for UO_2^{2+}-complexes where $\log K_1 > \log K_2$.AIso, $logK_2 > logK_3$ for both UO_2^{2+} and Th^{4+} -complexes. This implies that there is some steric hindrance for the second coordination in case of UO_2^{2+}-complexes only and a greater steric hindrance for the third coordination in both UO_2^{2+} and *Th4+*-complexes.

(ii) For the same metal ion, the values of $logK_1$, $logK_2$ *or* $logK_3$ increase in the order; *CIAHP < AHP < NH2AHP* and this is the order of increasing electron-repelling and decreasing electron-withdrawing effects of the substituent *X* (Str I&II). AIso, the above order is the same order of increasing the basicity of these ligands.

(iii)For the same ligand, the values of $logK_1$, $logK_2$ or $logK_3$ increase in the order; $Pr^{3+} < Yb^{3+} < UO_2^{2+} < Th^{4+}$ and this is consistent with the fact that the actinides $(UO_2^{2+}$ and $Th^{4+})$ are much more prone to complex formation than the lanthanides $(Pr^{3+}$ and $Yb^{3+})$. The higher stability of Th^{4+}*-complexes* is expected on the basis of the higher charge and consequently the higher ionization potential of Th^{4+} ion, in addition to larger gain in entropy[3] (see Table 4). On the other side, the Yb^{3+} -complexes have higher stability than the Pr^{3+} -ones, this may be explained by the fact that with increasing reciprocal ionic radius (1/r) as a result of increasing atomic number, the ionic potential increases, thus leading to a higher covalent nature of the metal chelates[11]. AIso, the polarizing power (Z^*/r^2; Z* and r are the effective charge and radius of the cation, respectively) is higher for Yb^{3+} ion than for Pr^{3+} ion, indicating its greater stability (Table 2).

A number of attempts have been made to find general relationships which affect the overall stability of the chelates :

(a)Effect of Substituents (X) on the stability of the chelates

For the same metal ion, a linear regression analysis of $\log K_n$ (n = 1, 2 or 3) vs. the Hammett' s constant (σ_x) yields a linear correlation with a negative slope (ρ) and a correlation coefficient (r) of ca.1 (Table2). The negative slopes of the Hammett' s equation; $logK_x = logK_H + \rho\sigma_x$ mean that with increasing electron repelling effect of the substituent *X* (StrI&II)-paralleled by increasing Lewis basicity of the ligands-the stability constants are increased. The additivity rule holds also for changes on both ligands; *NH_2AHP and ClAHP* with reference to the *AHP* ligand as the unsubstituted species[12]. In summary, the electron releasing *(p-NH_2)* group increases the electron density on the coordination sites leading to higher stability, while the electron attracting *(p-Cl)* substituent decreases the electron density on the coordination sites leading to lower stability (Table 2). :

In an attempt to gain further information about the dependence of the stability of the chelates on the basicity of the ligands, a linear regression analysis of $logK_1$ for the substituted derivatives *versus* $logK_1$ for the unsubstituted compound, *AHP* was constructed and analyzed. The following relations were obtained in 75% (v/v) dioxane-water medium at 298 K with a correlation coefficient (r) of *ca.* 1 and a slope amounting to unity;

$log\ K_1\ (NH_2AHP) = 0.509 + 1.0\ log\ K_1\ (AHP);$

r=0.9997

$log\ K_1(ClAHP) = -0.629 + 1.04\ log\ K_1\ (\Delta HP);$

$r=0.9999$

However, these data effectively validate the *Irving-Rossotti*[13] *equation* when .structurally similar ligands are to be compared.

(b)Effect of temperature on the stability of the chelates

The dissociation and stability constants of the ligands and their complexes with UO_2^{2+}, Th^{4+}, Pr^{3+} and Yb^{3+} ions have been evaluated at 298, 308 and 318 K potentiometrically in 75 % (v/v) dioxane-water. A linear regression analysis of *logK versus 1/T* was utilized to evaluate both the enthalpy change *(ΔH);* Table 4 and the stability constants; *log K* at the *ice-point temperature(273K);* Table3. The free energy change ΔG) and the entropy change (ΔS) were calculated from the well-known relationships;

$\Delta G = -RTlnK$ *and* $\Delta S = (\Delta H - \Delta G)/T.$

The resulting values are given in Tables 3 and 4. Inspection shows that the dissociation of the ligands is non spontaneous, endothermic and entropically unfavourable while their complexation is spontaneous, exothermic and entropically favourable. This means that the dissociation of the ligands is favourable at higher temperatures, while their complexation is favourable at lower temperatures. This is

in accordance with our previous studies [1-8].The positive entropy values (ΔS) for all complexes in solution indicate that the disorder of the system increases much more rapidly than the increase in the order taking place in the chelation. This is consistent with the hypothesis that a large number of water molecules are released upon chelation. AIso, this stems from the fact that the order of arrangement of the solvent molecules around the ligand and the water molecules around the metal ion is lost when the chelate is formed.

The positive entropy change (ΔS) upon complexation is a composite of :(a) a negative contribution due to the conversion of translational entropy of the free ligands, (b) a positive entropy due to release of coordinated water molecules and (c) a decrease in entropy of translation by the formation of one chelate ML from two species *(M^{n+} &L)*. Therefore, the positive entropy change associated with (b) predominates.

From Table 4, it can be seen that $\Delta H_1 \approx \Delta H_2$ and $\Delta S_1 \approx \Delta S_2$ for all systems but both the enthalpic and entropic contributions (ΔH_3 & ΔS_3) differ strongly. The higher values of ΔS for *Th^{4+}, Pr^{3+} and Yb^{3+}-complexes* compared to that one of *UO_2^{2+}*-complexes is attributed to the fact that the highest charged ion has a large and more ordered hydration sphere. As a consequence, in complexation reactions this involves a higher favourable entropy term (higher positive ΔS values). The values of *ΔH* reflect the changes in the number and strength of the bonds formed and broken during the complexation process. Also, the values of *ΔH* are correlated to the type of bonding between the metal ions and the ligand molecules, and to the structural features of the complexes. On the basis of this, and the fact that the formation of octahedral species is more exothermic[14], one could conclude an octahedral environment around the *Th^{4+},Pr^{+3}* and *Yb^{3+}* ions in solution (higher negative values of *ΔH;*Table 4). This is in a good agreement with the formation of tris chelates of *Th^{4+}* ions (1:3; *M:L*).In case of UO_2^{2+}-complexes, a hexagonal bipyramid geometry would be expected (3 ligands +2 oxygens make the coordination number =8).

(c)Effect of ionic strength (μ) on the stability of the chelates

In an attempt to investigate the nature of interactions between the metal ions (*M^{n+}*) and the investigated ligands (HL), the metal-ligand formation constants for *UO_2^{2+}*-complexes-as an example- at 298K in 75 % (v/v) dioxane-water were determined at different ionic strengths viz. 0.20, 0.15, 0.1 and 0.05 mol.L^{-1} *KNO_3* (Table 5). Inspection of the results shows that the stability constants *(logK)* for *UO_2^{2+}*-complexes decrease with increasing the ionic strength *(μ)* of the medium i.e. the tendency of the *UO_2^{2+}* ions to form complexes decreases in presence of other ions e.g. K^+ ions in the medium. This is due to the fact that the metal ion is screened or competed by other ions and this is consistent with the *Debye-Hückel* equation. According to *Irving and Rossotti*[13], the complexation process is a competition between protons *(H^+)* and metal ions *(M^{n+})* on the free chelating species *(L^-)*. Hence, in presence of other ions e.g. K^+ ions, this competitive effect would be increased.

However, a linear regression analysis of log*K vs.* $(\mu)^{1/2}$ was used to evaluate the stability constants *(logK)* at zero ionic strength (Table 5) i.e. in absence of such ions.

(d)Effect of dielectric constant (D) of the medium on the stability of the chelates
Effect of the selected organic solvents on the stability of the chelates was represented by UO_2^{2+}- NH_2AHP complex -as a typical example-in 75 % (v/v) solvent (dioxane, isopropanol, ethanol, methanol)-water at 298K and 0.10 mol/L (KNO_3). The values of the stability constants for this system are presented in Table 6 with those in different ratios; 30, 40, 50, 60 and 75 % (v/v) dioxane-water. Inspection of the results shows that the stability constants in 75 % (v/v) solvent-water increase in the sequence;
methanol < ethanol < isopropanol < dioxane and at various dioxane-water (v/v) composition, the order is; 30 < 40 < 50 < 60 < 75 which is the same order of increasing basicity of the ligands; decreasing the dielectric constant of the medium and decreasing the coordinating ability of the solvents. Thus, one can conclude that the coordinating ability of the solvents may retard the ligand-metal intcraction.
Moreover, the dissociation constant (pK^H) of NH_2AHP ligand and its stability constants $(log\ K_1,\ logK_2$ and $logK_3)$ with UO_2^{2+} ion were determined in aqueous medium by two different methods based on linear regression analysis (Table 6). The results obtained are in good agreement with each other.
In conclusion, the stability of the chelates increases by; (i) increasing both the electron repelling property of the substituents and the organic solvent content, and (ii) decreasing the temperature, the ionic strength and the dielectric constant of the medium. This conclusion was supported by . EI-Bindary and Shehatta studies[15] on substituted rhodanines with La^{3+}, Ce^{3+}, UO_2^{2+} and Th^{4+} ions.

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Table 2. Statistical data for the M^{n+} - XAHP chelates at 298I in 75 % (v/v) dioxane-water and 0.1 M KNO_3

logK	AHP		CIAHP		NH_2AHP		$-\rho^c$	$-r^d$
	Exp.[a]	Calc.[b]	Exp.[a]	Calc.[b]	Exp.[a]	Calc.[b]		
PK^H	12.93	12.94	12.79	12.78	13.39	13.39	0.679	0.999
UO_2^{2+}-complexes								
$LogK_1$	10.96	10.93	10.70	10.72	11.54	11.55	0.929	0.998
$logK_2$	10.71	10.67	10.43	10.46	11.27	11.28	0.923	0.997
$logK_3$	9.60	9.56	9.30	9.33	10.20	10.21	0.989	0.997
Th^{4+}-complexes								
$logK_1$	12.85	12.86	12.68	12.68	13.37	13.37	0.778	0.999
$logK_2$	12.77	12.78	12.60	12.60	13.30	13.30	0.790	0.999
$logK_3$	1190	11.91	11.72	11.71	12.50	12.50	8840	0.999
Pr_3^{3+}-complexes								
$logK_1$	9.50	9.45	9.21	9.25	10.00	10.01	0.859	0.993
$logK_2$	9.43	9.36	9.10	9.16	9.91	9.93	0.870	0.986
Yb^{3+}-complexes								
$logK_1$	10.47	10.44	10.22	10.24	11.02	11.03	0.884	0.998
$logK_2$	10.40	10.37	10.15	10.17	10.96	10.97	0.896	0.999

[a]Potentiometrically; [b]These volues were obtained by linear regression of *logK* vs. Hammmett's constant (σ_x); [c]Slope of Hammett' equation *($logK_x = logK_H + p\sigma_x$)*; [d]Correlation coefficient.

Table 3. Stepwise stability constants for M^{n+}-XAHP chelates in 75%(v/v)dioxane-water and and 0.1 M KNO_3 at different temperatures.

M^{n+}	298			308 K			318 K			273 K*		
	$logK_1$	$logK_2$	$logK_3$	$logK_1$	$logK_2$	$logK_3$	$logK_1$	$logK_2$	$logK_3$	$logK_1$	$logK_2$	$logK_3$
3-(acetophenonehydrazone)-6-phenyl pyridazine (AHP)												
H^+	12.93	-	-	12.60	-	-	12.20	-	-	-	-	-
UO_2^{2+}	10.96	10.71	9.60	10.70	10.45	9.45	10.48	10.25	9.28	11.66	11.37	10.07
Th^{4+}	12.85	12.77	11.90	12.53	12.50	11.72	12.29	12.20	11.55	13.66	13.61	12.41
Pr^{3+}	9.50	9.43	-	9.35	9.26	-	9.17	9.14	-	9.99	9.85	-
Yb^{3+}	10.47	10.40	-	10.26	10.21	-	10.10	10.06	-	11.0	10.89	-
3(p-chloroacetophenohenydrazone)-6-phenyl pyridazine (ClAHP)												
H^+	12.79	-	-	12.46	-	-	12.15	-	-	-	-	-
UO_2^{2+}	10.70	10.43	9.30	10.49	10.19	9.17	10.25	10.0	9.0	11.36	11.057	9.74
Th^{4+}	12.68	12.60	11.72	12.40	12.34	11.51	12.155	12.12	11.35	13.45	13.30	12.25
Pr^{3+}	9.21	9.10	-	9.07	8.95	-	8.90	8.77	-	9.67	9.59	-
Yb^{3+}	10.22	10.15	-	10.02	10.0	-	9.87	9.83	-	10.72	10.62	-
3(p-aminoacetophenonehydrazone)-6-phenyl pyridazine(NH_2AHP)												
H^+	13.39	-	-	13.10	-	-	12.87	-	-	-	-	-
UO_2^{2+}	11.54	11.27	10.20	11.30	11.01	10.00	11.00	10.79	9.83	12.34	11.97	10.74
Th^{4+}	13.37	13.30	12.50	13.02	13.00	12.23	12.77	12.75	12.10	14.23	14.10	13.06
Pr^{3+}	10.0	9.91	-	9.80	9.73	-	9.62	9.50	-	10.55	10.52	-
Yb^{3+}	11.02	10.96	-	10.95	10.89	-	10.68	10.60	-	15.55	11.52	-

*These values were obtained by linear regression analysis of logK vs. 1/T.

Table 4. Thermodynamic functions for M^{n+}-XAHP chelates in 75%(v/v)dioxane-water and 0.1 M KNO_3

M^{n+}	$\Delta G(KJmol^{-1})$			$\Delta H(KJmol^{-1})$						$\Delta S(JK^{-1}mol^{-1})$		
	$-\Delta G_1$	$-\Delta G_2$	$-\Delta G_3$	$-\Delta H_1$	r_1	$-\Delta H_2$	R_2	$-\Delta H_3$	r_3	ΔS_1	ΔS_2	ΔS_3
	3 -(acetophenonehydrazone)-6-phenyl pyridazine (AHP)											
H^+	-73.8	-	-	-66.12	0.997	-	-	-	-	-25.76	-	-
UO_2^{2+}	62.56	61.13	54.79	43.56	0.999	41.77	0.998	29.0	0.998	63.73	64.93	86.50
Th^{4+}	73.34	72.89	67.92	50.86	0.999	51.66	0.999	31.75	0.999	75.40	71.21	121.31
Pr^{3+}	54.22	53.82	-	29.89	0.998	26.34	0.997	-	-	81.60	92.17	-
Yb^{3+}	59.76	59.36	-	33.60	0.998	30.87	0.999	-	-	87.74	95.56	-
	3(p-chloroacetophenohenydrazone)-6-phenyl pyridazine (ClAHP)											
H^+	-73.0	-	-	-58.05	-	-	-	-	-	-50.16	-	-
UO_2^{2+}	61.07	59.53	53.08	40.77	0.999	39.04	0.999	27.16	0.995	68.09	68.72	86.94
Th^{4+}	72.37	71.92	66.89	48.09	0.998	43.56	0.999	33.60	0.998	81.44	95.12	111.66
Pr^{3+}	52.57	51.94	-	28.08	0.997	29.89	0.997	-	-	82.14	73.96	-
Yb^{3+}	58.33	57.93	-	31.79	0.998	29.00	0.998	-	-	89.02	97.03	-
	3(p-aminoacetophenonehydrazone)-6-phenyl pyridazine(NH_2AHP)											
H^+	-76.43	-	-	-47.21	0.999	-	-	-	-	-98.05	-	-
UO_2^{2+}	65.87	64.33	58.22	48.91	0.997	43.56	0.999	33.58	0.999	56.88	69.66	82.64
Th^{4+}	76.31	75.91	71.35	54.54	0.993	49.92	0.999	36.41	0.984	73.02	87.17	117.19
Pr^{3+}	57.08	56.56	-	34.48	0.999	37.13	0.996	-	-	75.80	65.17	-
Yb^{3+}	62.90	62.56	-	30.63	0.941	32.43	0.937	-	-	108.23	101.06	-

Table 5. Stepwise stability constants for the UO_2^{2+}-XAHP chelates in 75%(v/v)dioxane-water and different ionic strengths.

KNO_3	AHP				CIAHP				NH_2AHP			
mol/L	pK^H	$logK_1$	$logK_2$	$logk_3$	pK^H	$logK_1$	$logK_2$	$logk_3$	pK^H	$logK_1$	$logK_2$	$logK_3$
0.20	12.75	10.77	10.48	9.32	12.63	10.46	10.20	9.03	13.25	11.36	11.05	10.04
0.15	12.84	10.84	10.58	9.46	12.70	10.59	10.32	9.15	13.31	11.44	11.18	10.13
0.10	12.93	10.96	10.71	9.60	12.79	10.70	10.43	9.30	13.39	11.54	11.27	10,20
0.05	13.00	11.07	10.85	9.81	12.85	10.85	10.57	9.50	13.44	11.69	11.43	10.32
0.00*	13.26	11.38	11.23	10.29	13.09	11.24	10.94	9.97	13.64	12.01	11.80	10.59

*These values were obtained by linear regression analysis of pK^H or log K vs. the square root of the concentration ofKNO_3 (r = 0.996-0.999).

Table 6. Stepwise stability constants for the UO_2^{2+}-NH_2AHP chelates in 298 and 0.1 KNO_3 in different solvent-water (v/v) composition.

LogK	Solvent Composition % (v/v)									
	Dioxane							Isopropanol	Ethanol	Methanol
	0.00[a]	0.00[b]	30	40	50	60	75	75	75	75
PK^H	11.57	11.13	11.58	11.80	12.25	12.67	13.39	12.25	12.04	11.92
$LogK_1$	9.49	9.22	9.73	9.90	10.29	10.77	11.54	10.57	9.90	9.81
$LogK_2$	9.47	9.12	9.56	9.78	10.14	10.49	11.27	10.23	9.85	9.79
$LogK_3$	8.57	8.12	8.48	8.83	9.10	9.63	10.20	9.26	9.00	8.84

[a]These values were obtained (at 0.0127; 1/D) by linear regression analysis of log K or pK^H vs. 1/D of the 75 % (v/v) solvent-water (r = 0.981-0.999).

[b]These values were obtained by linear regression analysis of logK or pK^H vs. the mole fraction of the dioxane-water mixtures (r = 0.987-0.999).

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