Monatshefte für Chemie 125, 841–847 (1994)

Monatshefte für Chemie
Chemical Monthly
© Springer-Verlag 1994
Printed in Austria

Thermodynamics of Substituted Rhodanine II: Binary Complexes of Th(IV), UO_2(II), Ce(III), and La(III) with 3-Benzamidorhodanine and its Derivatives

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Summary. Th(IV), UO_2(II), Ce(III) and La(III) chelates with 3-benzamidorhodanine and its derivatives have been investigated potentiometrically in 0.1 *M* KCl and 20% (v/v) ethanol-water medium. The stability of the formed complexes increases in the order Th(IV) > UO_2(II) > Ce(III) > La(III). For the same metal ion, the stability of the chelates is found to increase with decreasing temperature, ionic strength, dielectric constant of the medium and by increasing the electron repelling property of the substituent. The thermodynamic parameters (ΔG, ΔH and ΔS) for complexation are evaluated and discussed. The formation of the complexes has been found to be spontaneous, exothermic and entropically favourable.

Keywords. 3-Benzamidorhodanine; Potentiometry; Thermodynamics; Stability constants; Complexation.

Thermodynamik von substituiertem Rhodanin II: Binäre Komplexe von Th(IV), UO_2(II), Ce(III) und La(III) mit 3-Benzamidorhodanin und seinen Derivaten

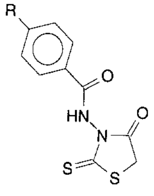
Zusammenfassung. Th(IV)-, UO_2(II)-, Ce(III)- und La(III)-Chelate mit 3-Benzamidorhodanin und seinen Derivaten wurden in 0.1 *M* KCl und 20% (v/v) Ethanol-Wasser potentiometrisch untersucht. Die Stabilität der gebildeten Komplexe steigt in der Reihenfolge Th(IV) > UO_2(II) > Ce(III) > La(III). Für ein- und dasselbe Metallion steigt die Stabilität der Chelate mit sinkender Temperatur, Ionenstärke und Dielektrizitätskonstante des Mediums und mit steigender Elektronenabstoßungsfähigkeit des Substituenten. Die thermodynamischen Parameter (ΔG, ΔH und ΔS) für die Komplexbildungsreaktion werden bestimmt und diskutiert. Die Bildung der Komplexe erweist sich als spontan, exotherm und entropisch begünstigt.

Introduction

Rhodanine and its derivatives are known to play an important role in biological reactions [1,2], *e.g.* in the inhibition of *mycobacterium tuberculosis* [3]. Although an extensive work has been done [4–6] on their solid complexes, nothing has been reported on the thermodynamics of their chelates with metal ions in solution. Therefore, and in continuation of our earlier work [7–10], we set out to report in the present paper the formation constants of Th(IV), UO_2(II), Ce(III) and La(III) complexes with 3-benzamidorhodanine and its substituted derivatives. Temperature, ionic strength, solvent composition, and substituent effects on the stability constants are also investigated. Furthermore, the corresponding thermodynamic functions of complexation are evaluated and discussed.

Experimental

The ligands discussed in this paper (**1**) are the same as in the first part of this series [11].



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R = H (*BR*), Cl (*PCBR*) or OCH_3 (*PTBR*)

For potentiometric and spectrophotometric measurements, the apparatus, general conditions and methods of calculation were described in detail in our previous work [7–10]. Three separate determinations were made and the average value was taken. There is a good agreement between the results obtained within 1% error. The *pH*-meter readings in different solvent compositions are corrected according to the *Van Uitert* and *Hass* relation [12].

Results and Discussion

The formation curves for the metal complexes were obtained by plotting the average number of ligands attached per metal ion ($\bar{n}$) versus the free ligand exponent (*pL*). These curves were analyzed and the successive stability constants were determined using different computational methods [13, 14]. The mean values are listed in Table 1. The stability constants derived from different techniques are in good agreement within 1% error. It is evident that the degree of metal-ligand formation, $\bar{n}$, extends between 0.1 and 2.8, suggesting the formation of ML, ML_2 and ML_3 species in solution. This is assured by conductometric titration of 25 ml of 10^{-3} mol·l^{-1} metal ion with 10^{-2} mol·l^{-1} ligand solution. The increase of the conductance during the titration can be attributed to the liberation of protons through displacement by the metal ions during complex formation. This is in accordance with the results obtained potentiometrically, since the addition of the metal ion to the ligand solution causes a decrease of *pH* values. Furthermore, there exists a clear separation between the metal complexes and the ligands in the titration curves. The possibility of formation of metal hydroxide is excluded since no precipitate was observed in the titration vessel. Inspection of the results obtained in Table 1 reveals that in none of the investigated complexes $K_2 > K_1$ or $K_3 > K_2$, *i.e.* $\log(K_1/K_2)$ and $\log(K_2/K_3)$ are positive. This implies that the vacant sites of the metal ions are more freely available for the binding of a first ligand than for a second and consequently for a second ligand than for a third.

As can be seen from Table 1, the stability constants depend on the nature of both the ligand and the metal ion. For the same ligand, at constant temperature, ionic strength and dielectric constant of the medium, the stability of the chelates increases in the order Th(IV) > UO_2(II) > Ce(III) > La(III). A similar order was previously reported [15–18]. This is in accordance with the fact that the actinides are much more prone to complex formation than the lanthanides.

The Ce(III) complex has a higher stability than the La(III) one; this may be explained by the fact that with increasing reciprocal ionic radius (as a result of increasing atomic number) the ionic potential increases, thus leading to a higher covalent nature of the metal chelates [19].

Furthermore, with increasing electronegativity of the metals, the electronegativity difference between a metal atom and the donor atom of the ligand will decrease. Thus, the metal ligand bond would have more covalent character [20], which in turn results in a greater stability of Ce(III) chelates compared to La(III) ones. Moreover, the variation of the stability could be quantitatively accounted for by calculating the effective electric field strength F^* of the central metal ion ($F^* = Z^*/r^2$, where Z^* and r are the effective charge and radius of the investigated cation, respectively). It is found that F^* is higher for Ce(III) than for La(III), indicating its greater stability.

Effect of temperature on the stability of the complexes and the thermodynamic parameters of complexation

The stability constants of the complexes formed in 0.1 mol·l^{-1} KCl and 20% (v/v) ethanol-water mixture were calculated at 298.15, 308.15 and 318.15 K. The plots of

Table 1. Stepwise stability constants for the complexation of substituted rhodanine with Th^{4+}, UO_2^{2+}, Ce^{3+}, and La^{3+} in 20% (v/v) ethanol-water mixture and 0.1 *M* KCl at various temperatures

M^{n+}	Formation constant								
	298.15 K			308.15 K			318.15 K		
	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_1$	$\log K_2$	$\log K_3$	$\log K_1$	$\log K_2$	$\log K_3$
3-(*p*-Methoxybenzamido)-rhodanine (*PTBR*)									
Th^{4+}	11.74	9.60	6.60	11.51	9.45	6.51	11.31	9.32	6.41
UO_2^{2+}	10.70	6.80	5.10	10.53	6.71	5.02	10.38	6.63	4.96
Ce^{3+}	8.00	6.40	4.28	7.88	6.32	4.22	7.78	6.25	4.15
La^{3+}	7.80	5.90	3.09	7.69	5.83	3.03	7.60	5.77	2.98
3-Benzamidorhodanine (*BR*)									
Th^{4+}	11.35	9.23	6.29	11.14	9.08	6.21	10.96	8.95	6.14
UO_2^{2+}	10.43	6.40	4.78	10.27	6.31	4.70	10.13	6.23	4.63
Ce^{3+}	7.70	5.90	4.02	7.58	5.81	3.96	7.49	5.74	3.89
La^{3+}	7.30	5.63	2.90	7.19	5.55	2.84	7.11	5.49	2.79
3-(*p*-Chlorobenzamido)-rhodanine (*PCBR*)									
Th^{4+}	11.07	8.87	5.93	10.88	8.73	5.84	10.72	8.61	5.77
UO_2^{2+}	10.17	5.80	4.36	10.02	5.72	4.29	9.89	5.65	4.21
Ce^{3+}	7.39	5.53	3.70	7.28	5.44	3.63	7.19	5.37	3.57
La^{3+}	6.83	5.40	2.60	6.74	5.33	2.54	6.66	5.27	2.49

ln K versus $1/T$ were utilized to evaluate the enthalpy change, ΔH, and the entropy change, ΔS, for the complexation according to the relation $\ln K = (\Delta S/R) - (\Delta H/RT)$. The free energy change, ΔG, was calculated by the relation $\Delta G = -RT \ln K$. The resulting values are given in Table 2. Inspection shows that the decrease in ln K values with increasing temperature suggests that the complex formation is exothermic and favourable at lower temperatures. This is verified from the negative values of ΔH. The negative values of ΔG reveal that all complexes under investigation are formed spontaneously in solution. The entropy values, ΔS, for all complexes are positive, indicating that the disorder of the system increases much more rapidly than the increase in the order taking place in the chelation. This stems from the fact that the order of the arrangement of the solvent around the ligand and the metal ion is lost when the complex is formed.

Effect of the substituent R on the stability of the complexes

For the same metal ion, on plotting $\log K_1$ versus *Hammett*'s constant (σ_R), a linear correlation with a correlation coefficient of *ca.* 1, was obtained. The statistical results are summarized in Table 3. The linear correlation and the negative values of the slopes reveal that the complexation of *BR* and its substituted derivatives is susceptible to the effect of the substituent R and is also favoured by high electron densities at the coordination sites.

In an attempt to gain further information about the dependence of the stability of chelates on the basicity of the ligand, a plot of $\log K_1$ for *PTBR* chelates *vs.* the corresponding $\log K_1$ values for *BR* or *PCBR* was constructed and analyzed

Table 2. Thermodynamic functions for the complexation of substituted rhodanine with Th^{4+}, UO_2^{2+}, Ce^{3+} and La^{3+} at 308.15 K

M^{n+}	Free energy change (kJ·mol^{-1})			Enthalpy change (kJ·mol^{-1})			Entropy change (JK^{-1}·mol^{-1})		
	$-\Delta G_1$	$-\Delta G_2$	$-\Delta G_3$	$-\Delta H_1$	$-\Delta H_2$	$-\Delta H_3$	$-\Delta S_1$	$-\Delta S_2$	$-\Delta S_3$
3-(*p*-Methoxybenzamido)-rhodanine (*PTBR*)									
Th^{4+}	67.91	55.76	38.41	39.06	25.43	17.24	93.70	98.50	68.60
UO_2^{2+}	62.13	39.59	29.62	29.07	15.44	12.73	107.35	78.40	54.90
Ce^{3+}	46.49	37.29	24.90	19.99	13.63	13.79	86.09	76.80	42.40
La^{3+}	45.43	34.40	17.88	18.18	11.81	10.00	88.34	73.30	25.60
3-Benzamidorhodanine (*BR*)									
Th^{4+}	65.73	53.57	36.64	35.53	25.44	13.63	98.42	91.38	74.70
UO_2^{2+}	60.65	37.23	27.73	27.25	15.44	13.63	108.26	65.30	45.80
Ce^{3+}	44.78	34.28	23.36	19.09	14.54	11.79	83.32	64.10	37.50
La^{3+}	42.54	32.75	16.76	17.28	12.73	10.00	81.75	65.10	21.90
3-(*p*-Chlorobenzamido)-rhodanine (*PCBR*)									
Th^{4+}	64.19	51.33	34.46	31.80	23.62	14.54	105.24	90.57	64.70
UO_2^{2+}	60.65	33.75	25.31	25.44	13.63	13.61	109.37	65.30	37.90
Ce^{3+}	42.89	32.10	21.42	18.18	14.54	11.81	80.49	57.10	31.20
La^{3+}	39.71	31.44	14.99	15.44	11.81	10.00	78.97	63.80	16.20

statistically by the linear regression method. The following relations were obtained at 298.15 K with a correlation coefficient of *ca.* 1:

$$\log K_1(PTBR \text{ chelates}) = 0.51 + 0.98 \log K_1(BR \text{ chelates})$$
$$\log K_1(PTBR \text{ chelates}) = 1.07 + 0.96 \log K_1(PCBR \text{ chelates})$$

The intercepts obtained (0.51 and 1.07) correspond approximately to the basicity difference ΔpK^{H} for the amidic proton. These differences were found to be 0.50 and 0.89, respectively [11]. This confirms that the basicity of the ligands is the main factor governing the stabilization of chelates of *BR* and its substituted derivatives.

Table 3. Statistical data for the UO_2^{2+} complexes with 3-benzamidorhodanine and its substituted derivatives in different ionic strengths and solvents at various temperatures; correlation coefficients in all cases $\geqslant 0.98$

Solvent	%	KCl (mol·l^{-1})	Temp. (K)	LogK_1			logK_2			logK_3		
				Exp.[a]	Calc.[b]	$-\rho$[c]	Exp.[a]	Calc.[b]	$-\rho$[c]	Exp.[a]	Calc.[b]	$-\rho$[c]
Ethanol	20	0.05	298.15	10.54	10.52	1.047	6.50	6.40	2.033	4.84	4.79	1.507
Ethanol	20	0.10	298.15	10.43	10.42	1.069	6.40	6.31	2.004	4.78	4.73	1.486
Ethanol	20	0.10	308.15	10.27	10.26	1.029	6.31	6.22	1.985	4.70	4.65	1.466
Ethanol	20	0.10	318.15	10.13	10.12	0.988	6.23	6.14	1.965	4.63	4.58	1.507
Ethanol	20	0.15	298.15	10.30	10.30	1.091	6.31	6.23	1.986	4.71	4.67	1.467
Ethanol	20	0.20	298.15	10.20	10.21	1.092	6.22	6.13	1.965	4.66	4.61	1.507
Ethanol	40	0.10	298.15	10.85	10.88	1.137	6.51	6.46	1.750	4.94	4.88	1.445
Ethanol	50	0.10	298.15	10.13	11.15	1.115	6.60	6.56	1.751	5.00	4.95	1.446
Ethanol	60	0.10	298.15	11.43	11.43	1.171	6.73	6.69	1.730	5.06	5.00	1.465
Ethanol	70	0.10	298.15	11.85	11.85	1.273	6.92	6.90	1.774	5.17	5.12	1.446
Methanol	50	0.10	298.15	10.83	10.80	1.107	6.41	6.39	1.612	4.89	4.84	1.446
Acetone	50	0.10	298.15	11.68	11.72	1.461	6.81	6.83	2.205	5.26	5.20	1.525
Dioxane	50	0.10	298.15	12.11	12.10	1.210	7.13	7.13	1.880	5.42	5.38	1.448

[a] Potentiometrically; [b] These values were obtained by linear regression of log *K* versus *Hammett*'s constant (σ_R); [c] Slope of *Hammett*'s equation ($\log K_R = \log K_H - \rho\sigma_R$)

Table 4. Formation constants for UO_2^{2+} complexes with substituted rhodanine in different concentrations of KCl at 298.15 K and 20% (v/v) ethanol-water mixture

KCl (mol·l^{-1})	*PTBR*			*BR*			*PCBR*		
	logK_1	logK_2	logK_3	logK_1	logK_2	logK_3	logK_1	logK_2	logK_3
0.20	10.50	6.62	4.99	10.20	6.22	4.66	9.96	5.64	4.24
0.15	10.59	6.72	5.04	10.30	6.31	4.71	10.05	5.73	4.31
0.10	10.70	6.80	5.10	10.43	6.40	4.78	10.17	5.80	4.36
0.05	10.79	6.89	5.17	10.54	6.50	4.84	10.27	5.88	4.22
0.00[a]	11.09	7.16	5.35	10.90	6.79	5.03	10.59	6.12	4.60

[a] These values were obtained by linear regression of log *K* *vs.* the square root of the concentration of KCl

In summary, the complexation increases by increasing the electron density on the coordination site. The electron donor substituent (p-OCH_3) increases the charge density leading to higher stability, while the electron-attracting one (p-Cl) decreases the charge density leading to less stable complexes.

Therefore, the order of decreasing stability constants for the ligands with the same metal ion at constant temperature, ionic strength and the dielectric constant of the medium is *PTBR* > *BR* > *PCBR*.

Effect of the ionic strength and the dielectric constant of the medium on the stability of the complexes

The variation of log K values with the ionic strength of the medium was investigated at 298.15 K and in 20% (v/v) ethanol-water. These values are listed in Table 4. An inspection shows that the stability constants of the complexes of these ligands with UO_2(II), as a typical example, decrease with increasing ionic strength of the medium which is consistent with the *Debye–Hückel* equation [21], i.e. the tendency of the metal ion to form complexes decreases in the presence of other ions in the system where the metal ion is screened or competed by other ions.

On the other hand, as indicated from Table 5, the order of increasing stability constants at various ethanol-water compositions is 20 < 40 < 50 < 60 < 70%, which is the same trend of increasing basicity of the ligands [11]and decreasing dielectric constant of different aquo-organic solvents. The decrease in the dielectric constants with increasing the organic content in the solvent increases the stability of complexes

Table 5. Formation constants for UO_2^{2+} substituted rhodanine complexes in various aquo-organic mixtures at 298.15 K and 0.1 M KCl

log K	Solvent composition % (v/v)								
	Ethanol						Methanol	Acetone	Dioxane
	0[a]	20	40	50	60	70	50	50	50
3-(p-Methoxybenzamido)-rhodanine (*PTBR*)									
log K_1	10.44	10.70	11.20	11.46	11.74	12.19	11.09	12.13	12.42
log K_2	6.65	6.80	6.91	7.01	7.13	7.36	6.81	7.43	7.64
log K_3	5.04	5.10	5.24	5.31	5.37	5.49	5.20	5.58	5.75
3-benzamidorhodanine (*BR*)									
log K_1	10.15	10.43	10.85	11.13	11.43	11.85	10.83	11.68	12.11
log K_2	6.27	6.40	6.51	6.60	6.73	6.92	6.41	6.81	7.13
log K_3	4.73	4.78	4.94	5.00	5.06	5.17	4.89	5.26	5.42
3-(p-Chlorobenzamido)-rhodanine (*PCBR*)									
log K_1	9.93	10.17	10.64	10.91	11.16	11.56	10.54	11.41	11.82
log K_2	5.69	5.80	6.04	6.14	6.27	6.48	6.01	6.34	6.71
log K_3	4.30	4.36	4.52	4.59	4.64	4.77	4.48	4.82	5.03

[a] These values were obtained by linear regression of log K versus the mole fraction of the ethanol-water mixtures

containing either O–M or O–H links [22,23]. This may be due to the increase in the ion–ion interaction between the metal ion (or proton) and the anionic oxygen donor, surpassing the ion–dipole interaction between metal ion (or proton) and solved complexes.

Moreover, for a particular composition (50% v/v) of the solvent-water mixture, these values decrease as follows: dioxane-water > acetone-water > ethanol-water > methanol-water. This order is in accordance with decreasing $1/D$ and increasing basicity of the ligands [11].

In conclusion, the complexation of 3-benzamidorhodanine and its substituted derivatives with Th(IV), UO_2(II), Ce(III) and La(III) is spontaneous, exothermic and entropically favourable. The stability of these complexes increases with increasing electron-repelling property of the substituent and the organic content in the media, while the rise of temperature and the increase of ionic strength of the medium decrease their stabilities. Furthermore, the present ligands may be used as an analytical reagent for the determination of the present metal ions. This is due to the high overall stability constants which reflect the stability of the formed complexes over the studied temperature range.

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Received October 11, 1993. Accepted January 3, 1994