Monatshefte für Chemie 124, 627–635 (1993)

Monatshefte für Chemie
Chemical Monthly

Structural Studies on 3-Acetyl-1,5-Diaryl and 3-Cyano-1,5-Diaryl Formazan Chelates with Cerium(III), Thorium(IV) and Uranium(VI)

O. E. Sherif[1], **Y. M. Issa**[1], **M. E. M. Hassouna**[2], and **S. M. Abass**[2]

[1] Chemistry Department, Faculty of Science, Cairo University, Giza, Egypt
[2] Chemistry Department, Faculty of Science, Cairo University, Beni Suef, Egypt

Summary. Solid complexes of 3-acetyl-1,5-diaryl and 3-cyano-1,5-diaryl formazans were prepared and characterized by elemental analysis, IR, NMR, TGA and DTA analyses. Based on these studies, the suggested general formula for the complexes is $[M(HL)_m(OH^-)_n$ or $(NO_3^-$ or $Cl^-)_x\cdot(H_2O)_y$ or $(C_2H_5OH$ or $DMSO)_z$, where HL = formazan $M = Ce^{3+}$, Th^{4+}, and UO_2^{2+}, m = 1–2, n = 0–3, x = 0–3, y = 0–4 and z = 0–3. The metal ions are expected to have coordination numbers 6–8.

Keywords. Complexes of 3-acetyl and 3-cyano formazans; Ce(III); Th(IV); U(VI).

Strukturuntersuchungen an 3-Acetyl-1,5-diaryl- und 3-Cyan-1,5-diaryl-formazan-Chelaten mit Cer(III), Thorium(IV) und Uran(VI)

Zusammenfassung. Die hergestellten Chelate wurden mittels Elementaranalyse, IR, NMR, TGA und DTA charakterisiert. Darauf basierend wird die generelle Formel $[M(HL)_m(OH^-)_n$ bzw. $(NO_3^-$ oder $Cl^-)_x\cdot(H_2O)_y$ oder $(C_2H_5OH$ bzw. $DMSO)_z]$ vorgeschlagen, wobei HL = Formazan, $M = Ce^{3+}$, Th^{4+} oder UO_2^{2+}, $m=1$–2, $n=0$–3, $x=0$–3, $y=0$–4 und $z=0$–3. Die Metallionen haben Koordinationszahlen von 6–8.

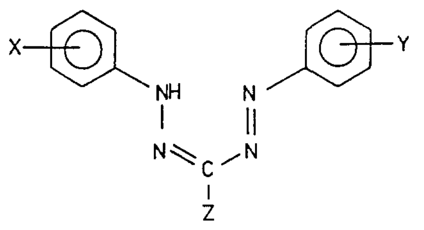
Introduction

Formazans are widely used as analytical reagents and dyestuffs [1–7]. They are also of great biological and industrial importance [8–10]. The use of formazans as ligands is of interest because of the considerable stability characteristic of some of the isolated complexes. However, there have been few investigations concerning the complexes of formazans. Uranium(VI) reacts with 1,5-bis(2-hydroxy-5-sulfophenyl)-3-cyanoformazans at *pH* 2.5–5.9 to form 1:1 complexes [11]. The IR spectrum indicates coordination of U(VI) via hydroxyl and imino groups of the formazan. The chelation of derivatives of 3-cyanoformazans with Th(IV) has been investigated [12].

Thermogravimetric studies on lanthanide complexes with 3-acetylformazans have been reported [13]. UV, IR and NMR have been carried out on some 3-acetylformazans and their complexes with lanthanide ions [14].

The present investigation is concerned with the study of the chelates of Ce(III), Th(IV) and U(VI) with substituted diaryl formazans. Elemental analysis, IR, NMR, TGA, and DTA of the solid chelates were performed to deduce their structures.

The formazans used are represented by the formula:



$Z = COCH_3$ (**I**) and $C{\equiv}N$ (**II**);
$X, Y =$ H, H (**a**); H, *o*-COOH (**b**); H, *p*-*As*O(OH)$_2$ (**c**);
and *p*-*As*O(OH)$_2$, *p*-*As*O(OH)$_2$ (**d**).

Experimental Part

Aryldiazonium chloride was prepared by diazotizing 0.05 mol of the arylamine in 15 ml of conc. hydrochloric acid with 3.7 g (0.053 mol) of sodium nitrite dissolved in 50 ml of water. The coupling of aryldiazonium chloride to acetylacetone and ethyl cyanoacetate (0.05 mol) in the presence of 14 g of sodium acetate yield the corresponding arylhydrazone with an initial molar ratio of the reactants of 1:1 (β-diketone or ethyl cyanoacetate to diazonium chloride). The product was kept in a refrigerator overnight, then acidified with 1:1 hydrochloric acid, filtered, washed several times with water and recrystallized from the proper solvent. The asymmetric formazans **Ib**, **IIb**, **Ic** and **IIc** were prepared by mixing a solution of (0.05 mol) of the prepared arylhydrazone in 400 ml *Et*OH with 500 ml aqueous NaOH (10.5 g of NaOH) solution. The solid was completely dissolved and the solution was cooled to below 5 °C. A diazonium chloride solution prepared from 0.05 mol of arylamine was then added dropwise with stirring. After the addition was completed, the solution was stirred for 0.5 h and left to stand overnight in a refrigerator, then it was acidified with 1:1 hydrochloric acid. The precipitate was filtered, washed with H_2O and recrystalized from the appropriate solvent.

The symmetric formazans **IIa**, **Id** and **IId** were prepared by coupling the aryldiazonium chloride with acetylacetone or ethyl cyanoacetate in a molar ratio of 2:1 in alkaline medium of sodium hydroxide. In this method, 0.02 mol of arylamine was dissolved in 6 ml conc. hydrochloric acid, then a cooled solution containing 0.023 mol sodium nitrite was added dropwise with continuous stirring. The diazonium chloride was then added slowly with stirring to an alkaline aqueous solution containing 0.01 mol acetylacetone or ethyl cyanoacetate and 6 g sodium hydroxide. The reaction mixture was kept in a refrigerator overnight, then it was acidified with 1:1 hydrochloric acid. The resulting solid was filtered and washed with water. The crude product was recrystallized from the proper solvent.

The symmetric formazan **Ia** was prepared by coupling of benzenediazonium chloride with acetylacetone in alkaline medium according to Ref. [15].

The solid complexes were prepared by mixing a hot alcoholic solution containing the metal ion with the requisite amount of formazans **Ia**, **Ib**, **Ic**, **Id**, **IIa**, and **IIb** sufficient to form 1:1 and 1:2 (*M*:*L*) complexes. Formazans **IIc** and **IId** were insoluble in ethanol so they were dissolved in a *DMSO*-alcohol mixture. The reaction mixture was stirred on a water bath. If the solid chelates did not separate on standing, ammonia solution was added until *pH* 7–8 was reached. The product was left overnight, filtered and then washed several times with ethanol until the filterate became colourless. The obtained complexes were kept in a vacuum desiccator.

Elemental analysis of carbon, hydrogen, nitrogen, and metal content of the complexes was performed in the microanalytical centre of Cairo University. The metal content of the complexes was determined after decomposition of the complex using the method described by Macdonald [16].

The IR spectra were recorded on a Perkin–Elmer 1430 infrared spectrometer using KBr discs. NMR spectra were obtained using the Varian Gemini 200 NMR spectrometer with dimethylsulfoxide (*DMSO*) as the solvent. The TGA and DTA were carried out using the Derivatograph OD 102 MOM Thermal analyzer (Budapest).

Results and Discussion

The structures of the complexes are in agreement with C, H, N, and metal analyses (Tables 1–3). The chemical analyses show that these complexes have the general formula:

$$[M(\mathrm{H}L)_m(\mathrm{OH}^-)_n, \quad \text{or} \quad (\mathrm{NO}_3^- \text{ or } \mathrm{Cl}^-)_x\cdot(\mathrm{H_2O})_y \quad \text{or} \quad (\mathrm{C_2H_5OH} \text{ or } DMSO)_z],$$

where: HL = formazans **Ia–d** and **IIa–d**, **M** = Ce^{3+}, Th^{4+}, and UO_2^{2+}, $m = 1–2$, n and $x = 0–3$, $y = 0–4$, and $z = 0–3$.

According to this formula, the metal ions are expected to have coordination numbers 6–8.

From the IR spectra of the complexes it is obvious that the N–H group is not observed in the spectra of the investigated metal formazan chelates. This indicates the replacement of the imino group proton by the central metal ion, or it can be attributed to its overlapping with the broad H_2O bands involved in chelation to satisfy the coordination centres of the metal ion (as in case of **Id** and **IId** complexes). The carboxylic OH bands for formazans **Ib** and **IIb** are replaced by the broad OH bands in their metal chelates which may be assigned to water molecules as well as some new bands which appeared on chelation at 1593, 1508, and 888 cm^{-1} [17] due to asymmetric COO^-, symmetric COO^-, and ν_{C-O}. This offers a proof that the COOH proton is removed in chelate formation while the C=O stretching band appeared at the same position as in free ligands indicating that it is not involved in chelation. In the spectra of **Ic**, **Id**, **IIc**, and **IId** complexes the OH group is still observed at the same position as in the free ligands because not all OH of the arsonic groups are participating in chelation.

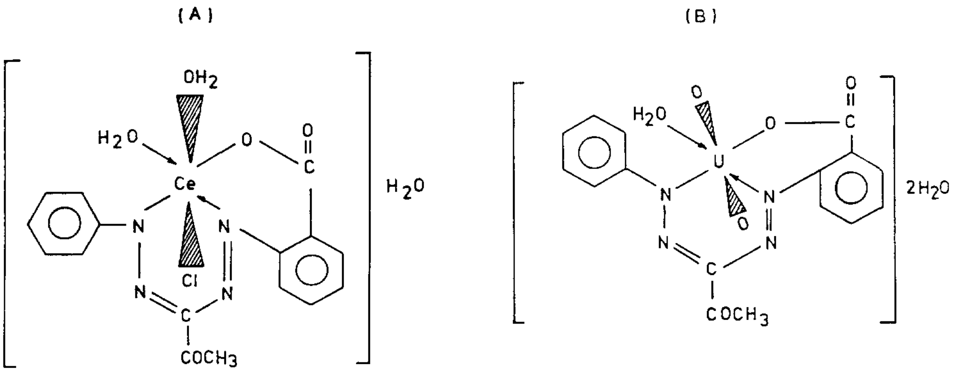


Fig. 1. (A) (1:1) Ce(III)-**Ib** complex; (B) (1:1) UO_2(VI)-**Ib** complex

Upon chelation, the C≡N and the acetyl C=O bands are still present in all complexes. The N=N band is shifted to lower wave numbers indicating its contribution in chelation with the central metal ion. The O–H stretching signal appears in the spectra of certain complexes as a broad band in the range 3660–2700 cm^{-1} instead of 3600 cm^{-1} in the case of a primary alcohol [18], confirming the participation of alcohol molecules (solvent) in the coordination. On the other hand, some complexes exhibit this band at 3400 cm^{-1} which may be attributed to ν_{OH} of water molecules present as water of hydration or as coordinated water.

In some Th(IV) chelates, the NO_3^- band appears within the range 1590–1520 cm^{-1}. The UO_2^{2+}-**IIc** chelate shows a band at 1050 cm^{-1} which is characteristic for the S=O band indicating the presence of a *DMSO* molecule in the coordination sphere. The *M*–Cl band for some Ce(III) chelates is observed around 500 cm^{-1}. The $M \leftarrow O$ and $M \leftarrow N$ stretching frequencies are also observed at 700–510 and 500–450 cm^{-1}.

Nuclear Magnetic Resonance

A substantial support for the results obtained from the IR spectra is gained by considering the NMR spectra of certain complexes.

The ^{1}H-NMR spectra of UO_2-**Ia** (1:1), UO_2-**Ib** (1:1), UO_2-**IIa** (1:1), and UO_2–**IIb** (1:1) showed a new signal at 3.5 ppm which is attributed to the presence of water in the coordination sphere of these complexes.

The disappearance of N–H and carboxylic COOH protons indicates their replacement by the metal ion. This can be taken as an evidence for the participation of -NH and COOH groups in chelation.

Thermogravimetric and Differential Thermal Analyses

The weight losses of 400 mg of each sample were measured, the heating rates were suitably controlled at 10 °C min^{-1} from ambient temperature up to 950 °C. The thermograms of some of the solid chelates are considered as representatives for the investigation. The found and calculated mass losses are listed in Table 4. The found mass loss calculations were based on thermogravimetric analysis data and the calculated mass losses were calculated using the results of microchemical analysis for the solid complexes (cf. Tables 1–3).

The initial weight loss in the temperature range 60–120 °C is referred to the loss of moisture and hygroscopic water during drying of the complexes while that at 140–200 °C is due to the coordinated water in the chelate and these steps are accompanied by endothermic peaks in the DTA curve. On further heating, the TGA curves show decomposition of the organic part of the chelates till a constant weight where the metal remains as oxide. This step is characterized by the presence of exothermic peaks in the DTA curve.

As indicated in Table 4 for the Ce-**Ib** complex (1:1), the first decomposition stage in the range 60–90 °C indicates a loss of one molecule of water of hydration and heating at 150–190 °C results in nearly 11.16% mass loss which corresponds to the loss of two coordinated water molecules. In the case of the Th(IV)-**IIb** (1:1) complex

Table 1. Elemental analysis of Ce(III) chelates with formazans **Ia–Id** and **IIa–IId**

Complex	Formula	C%		H%		N%		Cl%		Ce%	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Ia(1:1)	$Ce[C_{15}H_{13}N_4O\cdot 4H_2O]2Cl$	32.84	32.3	3.38	4.0	10.21	9.9	6.47	6.1	25.56	25.1
Ia(1:2)	$Ce[(C_{15}H_{13}N_4O)_2\cdot 2H_2O]Cl$	48.54	47.9	4.04	3.9	15.1	14.8	4.78	4.5	18.89	18.5
Ib(1:1)	$Ce[C_{16}H_{12}N_4O_3\cdot 3H_2O]Cl$	34.55	34.1	3.24	3.6	10.07	9.8	6.39	6.8	25.21	24.8
Ib(1:2)	$Ce[(C_{16}H_{12}N_4O_3)_2\cdot 2H_2O]H$	48.41	47.8	3.65	3.8	14.12	14.6	–	–	17.66	17.2
Ic(1:1)	$Ce[C_{15}H_{13}N_4O_4As\cdot 2C_2H_5OH\cdot Cl]$	34.77	35.1	3.81	3.7	8.54	8.9	5.41	5.2	21.37	21.6
Ic(1:2)	$Ce[(C_{15}H_{13}N_4O_4As)_2\cdot 2H_2O]H$	37.77	37.1	3.25	3.7	11.75	11.4	–	–	14.7	14.9
Id(1:1)	$Ce[C_{15}H_{13}N_4O_7As_2\cdot 2H_2O]$	26.2	26.4	2.47	2.4	8.15	7.9	–	–	20.39	20.9
Id(1:2)	$Ce[(C_{15}H_{14}N_4O_7As_2)_2]H$	30.87	30.5	2.57	2.4	9.61	9.3	–	–	12.02	12.2
IIa(1:1)	$Ce[C_{14}H_{10}N_5\cdot 4H_2O]2OH$	33.99	34.6	3.96	3.8	11.1	10.9	–	–	27.79	27.4
IIa(1:2)	$Ce[(C_{14}H_{10}N_5)_2\cdot 2H_2O]OH$	46.68	46.4	2.17	2.3	20.28	20.1	–	–	20.3	19.9
IIb(1:1)	$Ce[C_{15}H_9N_5O_2 2H_2O\cdot C_2H_5OH]\cdot OH$	38.48	38.2	3.77	4.1	13.2	13.5	–	–	26.43	26.1
IIb(1:2)	$Ce[(C_{15}H_9N_5O_2)_2\cdot 2H_2O]H$	47.42	47.8	1.84	2.1	9.22	8.9	–	–	18.45	18.1
IIc(1:1)	$Ce[C_{14}H_{10}N_5O_3As\cdot 3H_2O]Cl$	29.97	30.3	2.66	2.7	11.65	11.8	5.91	5.7	23.33	23.0
IIc(1:2)	$Ce[(C_{14}H_{10}N_5O_3As)_2\cdot 2H_2O]H$	36.55	36.8	2.72	2.7	7.6	7.8	–	–	15.24	15.1
IId(1:1)	$Ce[C_{14}H_{10}N_5O_6As_2\cdot 2H_2O]$	25.07	25.2	2.09	2.1	10.44	10.1	–	–	20.91	20.1
IId(1:2)	$Ce[C_{14}H_{11}N_5O_6As_2)_2]H$	29.7	29.5	2.03	2.2	12.37	12.2	–	–	12.38	12.4

Table 2. Elemental analysis of Th(IV) chelates with formazans **Ia–Id** and **IIa–IId**

Complex	Formula	C%		H%		N%		Th%	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Ia(1:1)	$Th[C_{15}H_{13}N_4O \cdot 3OH \cdot C_2H_5OH]$	34.34	34.6	3.70	3.8	9.42	9.3	39.06	38.9
Ia(1:2)	$Th[(C_{15}H_{13}N_4O)_2 \cdot 2C_2H_5OH]2OH$	45.94	46.1	4.5	4.7	12.61	12.4	26.13	25.9
Ib(1:1)	$Th[C_{16}H_{12}N_4O_3 \cdot 3H_2O]2NO_3$	26.74	26.8	2.5	2.6	11.69	11.8	32.31	32.0
Ib(1:2)	$Th[(C_{16}H_{12}N_4O_3)_2 \cdot 2H_2O]$	43.43	43.1	3.16	3.2	12.67	12.8	26.24	26.1
Ic(1:1)	$Th[C_{15}H_{13}N_4O_4As \cdot 2C_2H_5OH \cdot H_2O]2OH$	29.84	29.5	3.79	3.9	7.33	7.1	30.37	30.1
Ic(1:2)	$Th[(C_{15}H_{13}N_4O_4As)_2 \cdot 2H_2O]$	34.48	34.6	2.87	2.6	10.72	10.5	22.22	22.1
Id(1:1)	$Th[C_{15}H_{13}N_4O_7As_2 \cdot 2H_2O]NO_3$	21.4	21.2	2.02	2.1	8.32	8.5	27.59	27.7
Id(1:2)	$Th[(C_{15}H_{14}N_4O_7As)_2]$	28.66	28.5	2.23	2.2	8.91	8.8	18.47	18.3
IIa(1:1)	$Th[C_{14}H_{10}N_5 \cdot 4H_2O]3NO_3$	22.76	22.7	1.35	1.5	15.17	15.5	31.44	31.6
IIa(1:2)	$Th[(C_{14}H_{10}N_5)_2 \cdot 2H_2O]2NO_3$	37.83	37.5	2.7	2.8	18.91	20.1	26.13	26.4
IIb(1:1)	$Th[C_{15}H_9N_5O_2 \cdot 3H_2O]2NO_3$	25.67	25.6	2.14	2.1	13.98	13.8	33.1	33.4
IIb(1:2)	$Th[(C_{15}H_9N_5O_2)_2 \cdot 2H_2O]$	42.35	42.6	2.58	2.6	16.47	16.4	27.29	27.5
IIc(1:1)	$Th[C_{14}H_{10}N_5O_3As \cdot 3H_2O]2OH$	24.31	24.5	2.60	2.8	10.13	10.3	33.57	33.5
IIc(1:2)	$Th[(C_{14}H_{10}N_5O_3As)_2 \cdot 2H_2O]$	33.27	35.5	2.37	2.5	13.86	13.6	22.97	22.7
IId(1:1)	$Th[(C_{14}H_{10}N_5O_6As_2) \cdot 2H_2O]OH$	21.56	21.0	1.92	2.1	8.98	9.1	29.78	29.3
IId(1:2)	$Th[(C_{14}H_{11}N_5O_6As_2)_2]$	27.49	27.3	1.8	2.0	11.45	11.6	18.98	19.2

Table 3. Elemental analysis of UO_2(VI) chelates with formazans **Ia–Id** and **IIa–IId**

Complex	Formula	C%		H%		N%		U%	
		Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found
Ia(1:1)	$UO_2[C_{15}H_{13}N_4O\cdot 3H_2O\cdot OH]$	29.7	29.9	3.30	3.2	9.24	9.3	39.27	39.4
Ia(1:2)	$UO_2[(C_{15}H_{13}N_4O)_2\cdot 2H_2O]$	43.06	42.9	3.58	3.6	13.39	13.7	28.46	28.1
Ib(1:1)	$UO_2[C_{16}H_{12}N_4O_3\cdot 3H_2O]$	31.21	31.3	2.92	3.1	9.1	9.5	38.69	38.5
Ib(1:2)	$UO_2[(C_{16}H_{13}N_4O_3)_2\cdot 2H_2O]$	41.58	41.5	3.24	3.5	12.12	11.9	25.75	25.4
Ic(1:1)	$UO_2[C_{15}H_{13}N_4O_4As\cdot C_2H_5OH\cdot 2H_2O]$	27.56	27.9	3.24	3.4	7.56	7.1	32.16	32.3
Ic(1:2)	$UO_2[(C_{15}H_{14}N_4O_4As)_2\cdot 2H_2O]$	33.21	33.1	2.95	3.1	10.33	10.1	21.9	21.7
Id(1:1)	$UO_2[C_{15}H_{14}N_4O_7As_2\cdot 2H_2O]$	22.00	22.2	2.2	2.4	6.84	6.7	29.09	29.2
Id(1:2)	$UO_2[(C_{15}H_{15}N_4O_7As_2)_2]$	27.79	27.8	2.31	2.4	8.64	8.7	18.36	18.7
IIa(1:1)	$UO_2[C_{14}H_{10}N_5\cdot OH\cdot 2H_2O\cdot C_2H_5OH]$	31.11	31.4	3.40	3.4	11.34	11.6	38.57	38.6
IIa(1:2)	$UO_2[(C_{14}H_{10}N_5)_2\cdot 2C_2H_5OH]$	44.75	44.1	3.73	3.8	16.31	16.5	27.73	27.6
IIb(1:1)	$UO_2[C_{15}H_9N_5O_2\cdot 2H_2O\cdot C_2H_5OH]$	31.77	31.2	2.96	3.1	10.9	10.7	37.07	37.5
IIb(1:2)	$UO_2[(C_{15}H_{10}N_5O_2)_2\cdot 2H_2O]$	40.45	40.6	2.69	2.8	15.73	15.6	26.74	26.5
IIc(1:1)	$UO_2[C_{14}H_{10}N_5O_3As\cdot 3DMSO]$	27.42	28.5	3.2	3.4	8.00	7.4	27.2	27.5
IIc(1:2)	$UO_2[(C_{14}H_{11}N_5O_3As)_2\cdot 2H_2O]$	32.00	32.1	2.47	2.6	13.33	13.1	22.66	22.7
IId(1:1)	$UO_2[(C_{14}H_{11}N_5O_6As_2)\cdot 2H_2O]$	20.97	20.8	1.87	1.9	8.73	8.8	29.87	29.9
IId(1:2)	$UO_2[(C_{14}H_{12}N_5O_6As_2)_2]$	26.62	26.3	1.9	2.1	11.09	10.9	18.85	18.7

Table 4. TGA results of some solid chelates with Ce^{3+}, Th^{4+}, and UO_2^{2+} ions

Suggested formula	M:L	Dehydration stage			Decoordination stage			% Metallic residue*		
		Temp. range °C	% Weight loss		Temp. range °C	% Weight loss		Temp. °C	% Weight loss	
			Calc.	Found		Calc.	Found		Calc.	Found
Ce(III)-**Ib** $CeL\cdot 3H_2O\cdot Cl$	1:1	60–90	3.72	3.75	150–190	11.16	11.00	720	64.41	75.00
Th(IV)-**IIb** $ThL\cdot 2NO_3\cdot 3H_2O$	1:1	60–100	7.67	7.25	–	–	–	–	–	–
UO_2(VI)-**Ib** $UO_2L\cdot 3H_2O$	1:1	80–120	5.69	5.4	120–200	8.54	8.75	680	57.27	57.25

* Ce as CeO_2; U as UO_2

Table 5. Data of some solid chelates with Ce^{3+}, Th^{4+}, and UO_2^{2+} ions

Complex	M:L	Endothermic peaks	Exothermic peaks
Ce(III)-**Ib** $CeL\cdot 3H_2O\cdot Cl$	1:1	80 (w), 100 (w), 225 (w), 300 (w)	180 (vw), 220 (m), 340–790 (vs)
Th(IV)-**IIb** $ThL\cdot 2NO_3\cdot 3H_2O$	1:1	60 (vw), 420 (vw), 520 (vw)	200 (m), 820 (m)
UO_2(VI)-**Ib** $UO_2L\cdot 3H_2O$	1:1	80 (w), 120 (vw)	200–680 (vs)

w weak, m medium, s strong, vs very strong

the initial mass loss in the temperature range 60–100 °C is attributed to the loss of 3 water molecules of hydration, while for the UO_2(VI)-**Ib** (1–1) complex the mass loss in the temperature range 80–120 °C involves the loss of two hydrated water molecules and the following decomposition stage comprises the loss of one coordinated molecule.

The Ce(III)-**Ib** and UO_2-**Ib** complexes show additional inflections in the ranges 225–650 °C and 340–790 °C, which may be attributed to the formation of unstable intermediates (e.g. aryl carboxylate, carbonate...etc.) while in case of the Th-**IIb** complex the thermogram shows abnormal behaviour: no decomposition steps are observed after the dehydration stage. This is due to the sublimation of the complex which might be based on the high covalent bond character in this complex. The final stage includes the conversion of such intermediates to the stable metal oxide where U(VI) is reduced to the stable UO_2 while Ce(III) is oxidized to ceric oxide CeO_2.

From the thermal analyses of the complexes, the following schemes of decomposition can be suggested:

$$\mathrm{Ce}L\cdot 3\mathrm{H_2O}\cdot\mathrm{Cl} \xrightarrow[\text{endothermic}]{90\,^{\circ}\mathrm{C}} \mathrm{Ce}L\cdot 2\mathrm{H_2O}\cdot\mathrm{Cl} \xrightarrow[\text{endothermic}]{90\,^{\circ}\mathrm{C}} \mathrm{Ce}L\cdot\mathrm{Cl} \xrightarrow[\text{exothermic}]{340\text{–}790\,^{\circ}\mathrm{C}} \mathrm{CeO_2}$$

$$\mathrm{Th}L\cdot 2\mathrm{NO_3}\cdot 3\mathrm{H_2O} \xrightarrow[\text{endothermic}]{60\text{–}100\,^{\circ}\mathrm{C}} \mathrm{Th}L\cdot 2\mathrm{NO_3}$$

$$\mathrm{UO_2}L\cdot 3\mathrm{H_2O} \xrightarrow[\text{endothermic}]{80\text{–}120\,^{\circ}\mathrm{C}} \mathrm{UO_2}L\cdot\mathrm{H_2O} \xrightarrow[\text{endothermic}]{120\text{–}200\,^{\circ}\mathrm{C}} \mathrm{UO_2}L\cdot \xrightarrow[\text{exothermic}]{200\text{–}680\,^{\circ}\mathrm{C}} \mathrm{UO_2}.$$

Accordingly, the structure of Ce(III)-**Ib** (1:1) and UO_2-**Ib** (1:1) chelates, which were confirmed by thermal analysis, may be represented by the formulae shown in Fig. 1. The metal ion is expected to have a coordination number 6 for the Ce-**Ib** and UO_2-**Ib** chelates.

References

[1] Vozisova V. G., Podchainova V. N. (1970) Zh. Anal. Khim. **25**: 1361 [C.A. (1970) **73**: 136880b]
[2] Vasileva N. L., Ermakova M. I. (1964) Zh. Analit. Khim. **19**: 1305
[3] Zolotavin V. L., Fedorova N. D. (1964) Pcredovye Metody Khim. Technol. i Kontrolya Proizv. Sb.: 223
[4] Vasileva N. L., Ermakova M. I., Postovskii I. Ya. (1960) Zh. Vsesoyuz. Khim. Obshch. im D.I. Mendeleeva **5**: 110
[5] Vasileva N. L., Ermakova M. I. (1963) Zh. Analit. Khim. **18**: 43
[6] Vessely M., Muzik F., Poskocil J. (1961) Coll. Czech. Chem. Commun. **26**: 2530
[7] Von Robel H. R., Wizinger R. (1962) Rec. Prog. Chem. Nat. Synth. Color. Matters, p. 495
[8] Nesynov E. P., Karabanov Yu. V., Forsyuk V. P., Pel'kis P. S. (1974) Fiziol. Akt. Veschestva **6**: 22
[9] Balut D., Zawistowska M., Eckstein Z. (1966) Bull. Acad. Polon. Sci., Ser. Chim. **14**: 11
[10] Grote M., Schwalk A., Huppe U., Kettrup A. (1983) Fresenius' Z. Anal. Chem. **316**: 247
[11] Sergovskaya V. V., Ermakova M. I. (1974) Tezisy Dokivses. Knof. Khim. Uran. 1 (in Russian) Akad. Nauk SSSR, Gos. Kom. Ispol'z At. Energ. SSSR: Moscow, USSR. [C.A. (1978) **88**: 83100y]
[12] Budesinsky B., Svecova J. (1971) Inorg. Chem. **10**: 313
[13] Badawy S. S., Issa Y. M., Abdel Fattah H. M. (1989) Thermochem. Acta **144**: 249
[14] Badawy S. S., Issa Y. M., Abdel Fattah H. M. (1989) Trans. Met. Chem. **14**: 401
[15] Yao H. C. (1964) J. Org. Chem. **29**: 2959
[16] Macdonald A. M. G., Sirichanya P. (1969) Microchem. J. **14**: 199
[17] Bellamy L. J. (1975) The Infrared Spectra of Complex Molecules, 3rd Ed. Chapman and Hall, London
[18] Rao C. N. R. (1963) Chemical Application of Infrared Spectroscopy. Academic Press, New York, London

Received May 13, 1992. Accepted June 15, 1992