Journal of Thermal Analysis and Calorimetry, Vol. 96 (2009) 2, 599–606

UO_2(VI), Sn(IV), Th(IV) AND Li(I) COMPLEXES OF 4-AZOMALONONITRILE ANTIPYRINE
Synthesis, characterization and thermal studies

H. A. El-Boraey[1*], *F. A. El-Saied*[1] *and S. A. Aly*[2]

[1]Department of Chemistry, Faculty of Science, El-Menoufia University, Shebin El-Kom, Egypt
[2]Department of Chemistry, Genetic Engineering and Biotechnology Research Institute, El-Menoufia University, Sadat City, Egypt

UO_2(VI), Sn(IV), Th(IV) and Li(I) complexes of 4-azomalononitrile antipyrine (L) have been isolated and characterized based on IR spectra, ^1H NMR, elemental analyses, molar conductance and thermal analysis (DTA/TG). The study revealed that the ligand behaves as a neutral bidentate one and coordination takes place via the carbonyl atom of pyrazolone ring >C=O and the azomethine nitrogen >C=N. The thermal stability of the metal complexes were investigated by thermogravimetry (TG), differential thermal analysis (DTA) techniques and infrared spectra, and correlated to their structure. The thermal study revealed that Th(IV) complexes show lower thermal stability than both UO_2(VI) and Sn(IV) complexes.

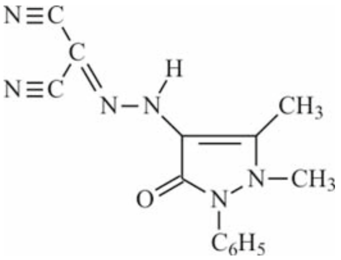
Keywords: *complexes, conductivity, IR, synthesis, thermal analysis (DTA/TG)*

Introduction

Antipyrine (2,3-dimethyl-1-phenyl-3-pyrazolin-5-one) and its derivatives possess a wide variety of potentially useful application, including biological [1, 2], clinical [3] and pharmacological areas [4]. They are also used as antipyretic, analgesic and anti-rheumatic materials [5–8]. Antipyrines have also been used as analytical reagents in determination of some metal ions [9]. Follow up literature indicate that considerable study has been devoted to Schiff bases and azo containing ligands derived from either 4-amino- or 4-formylantipyrine [10–12]. However, all the reported studies on this type of compounds are concerning with synthesis, structure and properties. However, comparatively less is known regarding their thermal behaviour. The present study extends to synthesis, characterization and thermal behaviour studies of UO_2(VI), Sn(IV), Th(IV) and Li(I) complexes with 4-azomalononitrile antipyrine (*L*).

Experimental

Reagent grade chemicals were used without further purification. The ligand 4-azomalononitrile antipyrine (Scheme 1) was prepared and characterized as described [13].



Scheme 1

The metal complexes were prepared by stirring magnetically at ca. 60°C an ethanolic solution (0.002 mol) of a metal salt of UO_2(VI) chloride, nitrate, acetate, Sn(IV) diphenyl chloride, Sn(IV) chloride, Th(IV) nitrate or Li(I) chlorate (VII) with (0.002 or 0.004 mol) 4-azomalononitrile antipyrine (*L*) in ca. 50 mL EtOH for periods of 5 h or more. The resulting solids were filtered off, washed several times with EtOH and dried under vacuum over P_4O_{10}. Elemental analysis (C, H and Cl) were performed by the Microanalytical unit of the University of Cairo, Egypt. Metal analyses were estimated using standard methods. IR spectra in the 4000–200 cm^{-1} range were performed as KBr discs using a PerkinElmer 1430 recording spectrophotometer. ^1H NMR spectra were recorded in DMSO-d_6 using a 300 MHz Varian NMR spectrometer. The molar conductivity measurements were made in DMF solutions (10^{-3} M) using a Tacussel conductometer type CD6N. Thermal analyses (DTA/TG) were carried out under N_2 atmosphere using a Schimadzu DT-50 thermal analyzer at a heating rate of 10°C min^{-1} in the temperature range 25–800°C using platinum crucibles.

---

[*] Author for correspondence: helboraey@yahoo.com

1388–6150/$20.00

Akadémiai Kiadó, Budapest, Hungary
Springer, Dordrecht, The Netherlands

Results and discussion

The reaction of UO_2(VI), Sn(IV), Th(IV) and Li(I) salts with 4-azomalononitrile antipyrine ligand (L) results in the formation of three types (1:1, 1:2 and 1:3) metal complexes. All the complexes are stable under ordinary conditions; they are only freely soluble in strong coordinating solvents like DMF and DMSO. The values of molar conductivities in DMF (10^{-3} M) solution (Table 1) show that the complexes are essentially nonelectrolytes indicating non coordination of the anions except complexes (2, 7 and 8) that behave as 1:2 electrolyte [14]. The chlorato(VII) complex (9) behaves as 1:1 electrolyte [14].

^{1}H NMR

A review of the literature revealed that the ^{1}H NMR spectroscopy has been proven to be useful in establishing the nature and structure of many organic ligands as well as their complexes in solutions. The ^{1}H NMR of 4-azomalononitrile antipyrine ligand (L) is reported [13]. The ^{1}H NMR spectra of the complexes are examined in comparison with that of the free ligand. It was found that for all complexes the NH signal that appeared in the spectrum of the free ligand at 8.8 ppm (s, 1H, NH) does not change upon complexation. New signals at 14–15 ppm in the spectra of the complexes, (**5** and **6**), assigned to (s, 1H, OH). The signal observed at 1.82 ppm for acetato complex (**4**) with an integration corresponding to 6 protons, assigned to acetate anions. Also, complexes (1–9) except (**3** and **6**) show a signal at 3.4 ppm attributed to water molecules.

The infrared spectra and mode of bonding:

A study and comparison of the IR spectra of the 4-azomalononitrile antipyrine ligand (L) and its metal complexes imply that the ligand is bidentate in nature. With carbonyl-oxygen and azomethine nitrogen, as two coordination sites. The IR data are presented in Table 2. Generally, the infrared spectrum of the free ligand shows four bands at 3190, 2215, 1630 and 1590 cm^{-1}, assigned to $\nu_{N–H}$, $\nu_{C≡N}$, $\nu_{C=O}$ and $\nu_{C=N}$, respectively. The infrared spectra of all metal complexes show a decrease in the energy of $\nu_{C=O}$ and $\nu_{C=N}$ on complexation, consistent with coordination of the carbonyl oxygen and azomethine nitrogen atoms [15–17]. The spectra of all complexes show that the bands corresponding to $\nu_{N–H}$ and $\nu_{C≡N}$ remain at the same frequency or are slightly shifted to lower frequencies compared to that of the free ligand, indicating that the N–H and C≡N groups do not participate in coordination.

However some new bands with medium to weak intensities appear in the 520–450 and 450–380 cm^{-1} in the spectra of complexes under study, are tentatively assigned to $\nu_{M–O}/\nu_{M–N}$ modes [14, 15, 17]. The chloro-complexes (1, 5 and 6) show an additional band at 345–325 cm^{-1} due to $\nu_{M–Cl}$ mode [14, 18]. The IR spectra of UO_2(VI) complexes show a strong absorption band near 925–910 cm^{-1}, assigned to antisymmetric $\nu_{3O=U=O}$ [19].

The IR spectra of nitrato complexes (3, 7 and 8) show two bands $\bar{\nu}$=1006–1103 and 1290–1319 cm^{-1} which may be assigned to asymmetric and symmetric stretches ν_1 and ν_2 of coordinated nitrate group. We can conclude that the NO_3 group is coordinated in

Table 1 Colour, elemental analysis data and molar conductivities results of 4-azomalononitrile

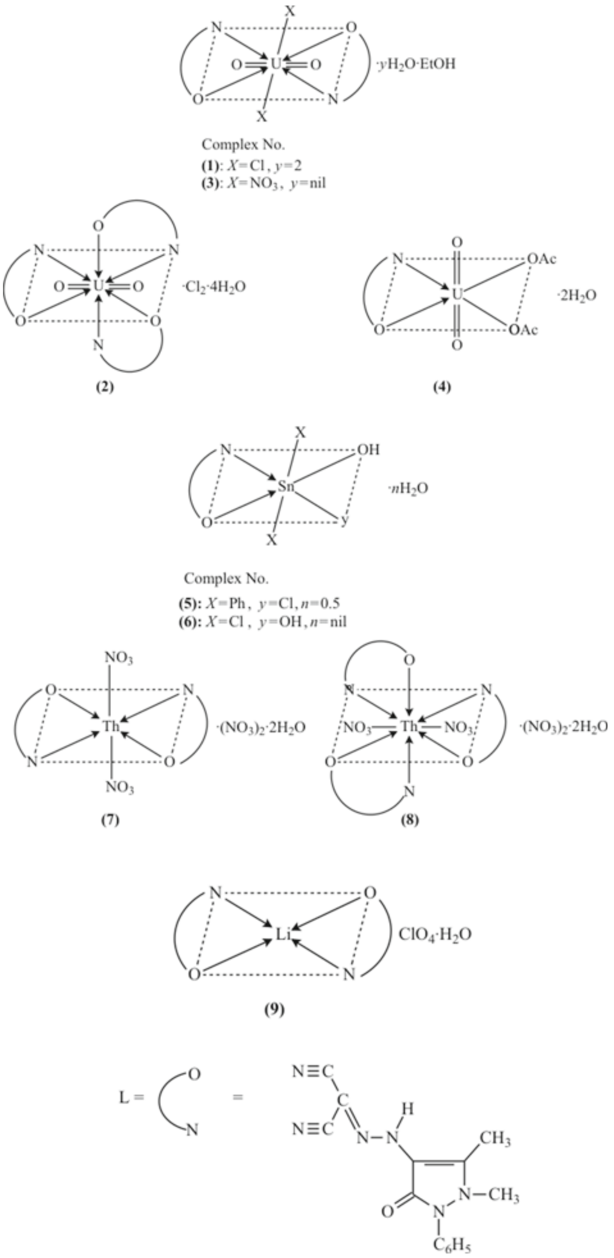
No.	Compound	Colour	Decomp. temp./°C	Analysis/%				Λ_M*
				Calc. (F)				
				C	H	M	Cl	
	L ($C_{14}H_{12}N_6O$)	Orange yellow	–	56.4(56.1)	4.7(4.4)	–	–	–
1	$[UO_2L_2CL_2]·2H_2O·EtOH$	Dark brown	240	36.3(36.5)	3.3(3.2)	24.2(24.5)	7.2(7.2)	31
2	$[UO_2L_3]·CL_2·4H_2O$	Brown	256	40.2(40.1)	3.5 (3.4)	18.9(18.9)	5.7(5.7)	136
3	$[UO_2L_2(NO_3)_2]·EtOH$	Brown	277	36.0(36.7)	3.0(3.0)	23.8(23.8)	–	12
4	$[UO_2L(OAc)_2]·2H_2O$	Brown	235	30.6(31.0)	3.1(3.0)	33.8(32.8)	–	16
5	$[SnL(Ph)_2Cl(OH)]·0.5H_2O$	Yellow	252	50.8(50.8)	3.9(3.9)	19.2(19.20)	5.7(5.7)	11
6	$[SnLCl_2(OH)_2]$	Yellow	250	33.1(33.3)	2.6(2.8)	23.4(23.4)	14.1(14.0)	13.3
7	$[ThL_2(NO_3)_2]·(NO_3)_2·2H_2O$	Dark red	170	30.9(31.2)	2.9(2.6)	21.5(21.3)	–	141
8	$[ThL_3(NO_3)_2]·(NO_3)_2·2H_2O$	Red	152	37.1(37.1)	2.9(2.9)	17.1(17.9)	–	126
9	$[LiL_2]CLO_4·H_2O$	Brown	290	49.1(48.7)	3.8(4.1)	1.0(1.0)	5.2(5.0)	70

*Ω^{-1} cm^2 mol^{-1} in 10^{-3} M DMF Soln

Table 2 Infrared spectral bands (cm^{-1}) for 4-azomalononitrile antipyrine ligand and its metal complexes

No.	Compound	$\nu_{H_2O/EtOH}$	ν_{M-OH}	ν_{N-H}	$\nu_{C\equiv N}$	$\nu_{C=O}$	$\nu_{C=N}$	ν_{M-O}	$\nu_{M\leftarrow N}$	ν_{M-Cl}
	L($C_{14}H_{12}N_6O$)	–		3190(w)	2215(s)	1630(s)	1590(s)	–	–	–
1	$[UO_2L_2CL_2]\cdot 2H_2O\cdot EtOH$	3420(br)	–	3190(w)	2210(s)	1600(s)	1560(s)	490(w)	445(w)	345(w)
2	$[UO_2L_3]\cdot CL_2\cdot 4H_2O$	3420(br)	–	3190(w)	2215(s)	1610(s)	1560(s)	450(m)	380(w)	–
3	$[UO_2L_2(NO_3)_2].EtOH$	3420(br)	–	3190(w)	2190(s)	1600(s)	1550(s)	515(w)	410(w)	–
4	$[UO_2L(OAc)_2]\cdot 2H_2O$	3420(br)	–	3200(w)	2210(s)	1600(s)	1570(s)	480(m)	450(m)	–
5	$[SnL(Ph)_2Cl(OH)]\cdot 0.5H_2O$	3400(br)	3390(m)	3200(w)	2210(s)	1600(s)	1570(s)	520(m)	440(w)	330(s)
6	$[SnLCl_2(OH)_2]$	–	3390–3270(m)	3210(w)	2210(s)	1600(s)	1565(s)	480(m)	450(w)	325(s)
7	$[ThL_2(NO_3)_2]\cdot(NO_3)_2\cdot 2H_2O$	3430(br)	–	3180(w)	2215(s)	1605(s)	1570(s)	470(m)	420(m)	–
8	$[ThL_3(NO_3)_2]\cdot(NO_3)_2\cdot 2H_2O$	3420(br)	–	3220(s)	2200(s)	1610(s)	1580(s)	470(m)	440(m)	–
9	$[LiL_2]CLO_4\cdot H_2O$	3400(br)	–	3190(w)	2210(s)	1615(w)	1560(s)	510(m)	430(w)	–

unidentate manner [19, 20]. Complexes (7 and 8) also show new bands at 1380 and 1385 cm^{-1}, respectively, assigned to the ionic nitrate group [19, 21]. The acetato ligand may coordinate to a metal center in a monodentate, bidentate or bridging manner. The $\nu_{a(COO^-)}$ and $\nu_{s(COO^-)}$ of the free acetate ions are at ~1560 and 1416 cm^{-1}, respectively. In the monodentate coordination $\nu_{aC=O}$ is found at higher energy than $\nu_{a(COO^-)}$ and ν_{C-O} is lower than $\nu_{a(COO^-)}$. As a result the separation between the two (C–O) bands is much larger in monodentate complexes than that of free ion, the acetato complex (4), reveals two new bands $\nu_{a(CO_2)}$ at 1615–1605 and $\nu_{s(CO_2)}$ at 1375 cm^{-1}, respectively. Indicating monodentate acetates [22, 23]. In chlorato(VII) complex (9), the presence of (ν_3) at 1120 and (ν_4) at 630 cm^{-1} indicates that the T_d symmetry of ClO_4^- is maintained and suggests the presence of ClO_4^- outside the coordination sphere [22, 24].



Scheme 2 Structural formulae of ligand (L) metal complexes

The infrared spectra of hydroxo-complexes 5 and 6 show one or two new bands at 3390–3270 cm^{-1}, assigned to ν_{M-OH} [14]. The appearance of the broad strong absorption band at about 3430–3400 cm^{-1} can be reasonably attributed to the presence of lattice water molecules and/or ethanolic OH group, another bands observed at 900–844 cm^{-1} due to bending vibration of H_2O [17], indicating that these complexes (except **3**, **6**) are hydrated and was supported from thermal analysis study [25–28]. The above arguments indicate that the ligand in all complexes behaves as a neutral bidentate ligand and coordination occurs via the carbonyl oxygen and azomethine nitrogen atoms.

Based on the obtained results the coordination behaviour of the ligand is shown in Scheme 2.

Thermal studies (TG and DTA)

Thermal behaviour of the obtained complexes was investigated by thermogravimetric and differential thermal analysis. Figure 1 shows the recorded DTA and TG curves of the complexes under nitrogen atmosphere; important data are summarized in Table 3. Due to the explosive nature of chlorato(VII) complexes, the thermal behaviour of lithium chlorato(VII) complex, (**9**) has not been investigated. The correlations between the different decomposition steps of the complexes with the corresponding mass losses are discussed in terms of the proposed formulae of the complexes.

DTA curves (Fig. 1) are generally characterized by endothermic peaks in the temperature range of 25–270°C (except for complex **6**), assigned to loss of solvents of crystallization as results from TG mass loss in that temperature range. The lower and wide range of temperature of desolvation indicates that, the solvents of crystallization are physically bound [29]. As shown from DTA curves (Fig. 1), the desolvation process was followed by other asymmetric exothermic peaks, assigned to material decomposition. The initial decomposition temperature has been used as an indication on the thermal stability of complexes [30].

Dioxouranium(VI) chelates

Careful analysis of DTA and TG curves of UO_2(VI) chelates (1, 3 and 4) (Fig. 1) show the presence of an endothermic DTA peak in the temperature range of 25–270°C, This peak is assigned to desolvation of the complexes as results from TG mass loss in that temperature range (Table 3). The DTA curve of complex (**2**) shows that it loses its water of crystallization during decomposition process as indicated from TG data (Table 3). The higher temperature of dehydration of complex (**2**) may be due to strong interaction of water molecules in the crystal lattice. The desolvation process was followed by number of exothermic events in the temperature range of 231–604°C, assigned to the material decomposition as demonstrated from IR spectra of the complexes and their thermoproducts in that temperature range. As it results from TG mass loss, the final residue of thermal decomposition is UO_2Cl_2+carbon residue [29, 31] for complex (**1**), UO_2 for complex (**2**) and UO_2+carbon residue [29, 31] for complexes (**3**), (4). It is clear that the acetato complex (**4**) has lower thermal stability (231°C) than the chloro one (1) (240° C), which may be interpreted to the presence of two six-membered chelate rings in complex (1) relative to one in complex (**4**). Also, the anions (Cl, OAc) play an important role in the thermal stability of the two complexes. The nitrato complex (**3**) shows higher thermal stability (270°C), than the chloro complex (**2**) (240°C) this

Table 3 DTA and TG data of the investigated complexes

No.	Complex	Temp./°C		Mass loss/%	Reaction	Leaving species
		DTA	TG	Calc.(F)		
1	$[UO_2L_2CL_2]\cdot 2H_2O\cdot EtOH$	25–50*	25–50	4.7(4.7)	b	EtOH
		50–240*	50–240	3.6(3.6)	a	$2H_2O$
		240–552•	240–552	49.8(50.0)	d	1.75L
			at 552	42.0(41.6)^o		UO_2Cl_2+0.25L (≡6C)
2	$[UO_2L_3]\cdot CL_2\cdot 4H_2O$	256–300	256–300	16.9(16.8)	a+b	$4H_2O$+0.5L
		300–604•	300–604	61.5(62.0)	d	(Cl_2+2.5L)
			at 604	21.5(21.2)^o		≡UO_2
3	$[UO_2L_2(NO_3)_2]\cdot EtOH$	25–270*	25–270	4.6(4.6)	b	EtOH
		270–307	270–307	40.4(40.3)	d	($2NO_3$+L)
		307–557	307–557	21.0(21.2)	d-	0.75L
			at 646	34.0(33.9)^o		UO_2+0.25L (≡6C)
4	$[UO_2L(OAc)_2]\cdot 2H_2O$	25–100	25–231	5.1(5.0)	a	$2H_2O$
		231–310	231–310	9.4(9.3)	d	1.5 (CO_2)
		310–600	310–600	40.0(40.6)	d	L
			at 600	46.0(45.1)^o		UO_2+Carbon residue (≡4C)
5	$[SnL(Ph)_2Cl(OH)]\cdot 0.5H_2O$	25–74*	25–74	1.4(1.4)	a	$0.5H_2O$
		252–329	252–329	17.4(17.3)	d	(HCL+0.25L)
		329–600	329–585	34.2(34.3)	d	Completion of decomposition reaction
			at 585	46.9(47.0)^o		≡$Sn(Ph)_2O$
6	$[SnLCl_2(OH)_2]$	250–310	250–310	14.5(14.5)	d	2HCL
		310–670•	310–670	55.66(55.7)	d	L
			at 670	29.8(29.8)^o		≡SnO_2
7	$[ThL_2(NO_3)_2]\cdot (NO_3)_2\cdot 2H_2O$	25–170*	27–170	3.3(3.3)	a	$2H_2O$
		170–300	170–300	11.5(11.6)	d	$2NO_3$=($2NO_2$+O_2)
		300–340	300–340	26.0(26.2)	d	L
		340–483	340–483	26.2(26.2)	d	L
			at 483	33.0(32.7)^o		≡$Th(NO_3)_2$
8	$[ThL_3(NO_3)_2]\cdot (NO_3)_2\cdot 2H_2O$	25–152*	25–152	2.7(2.6)	a	$2H_2O$
		152–270	152–270	9.1(9.1)	d	$2NO_3$=($2NO_2$+O_2)
		270–500	270–500	68.7(69.0)	d	3L+$2NO_2$
			at 468	19.5(19.3)^o		≡ThO_2

* – Endo, • – Splitted, ^{o} – Final product percent, a – Dehydration, b – Desolvation, d – Decomposition, L=($C_{14}H_{12}N_6O$)

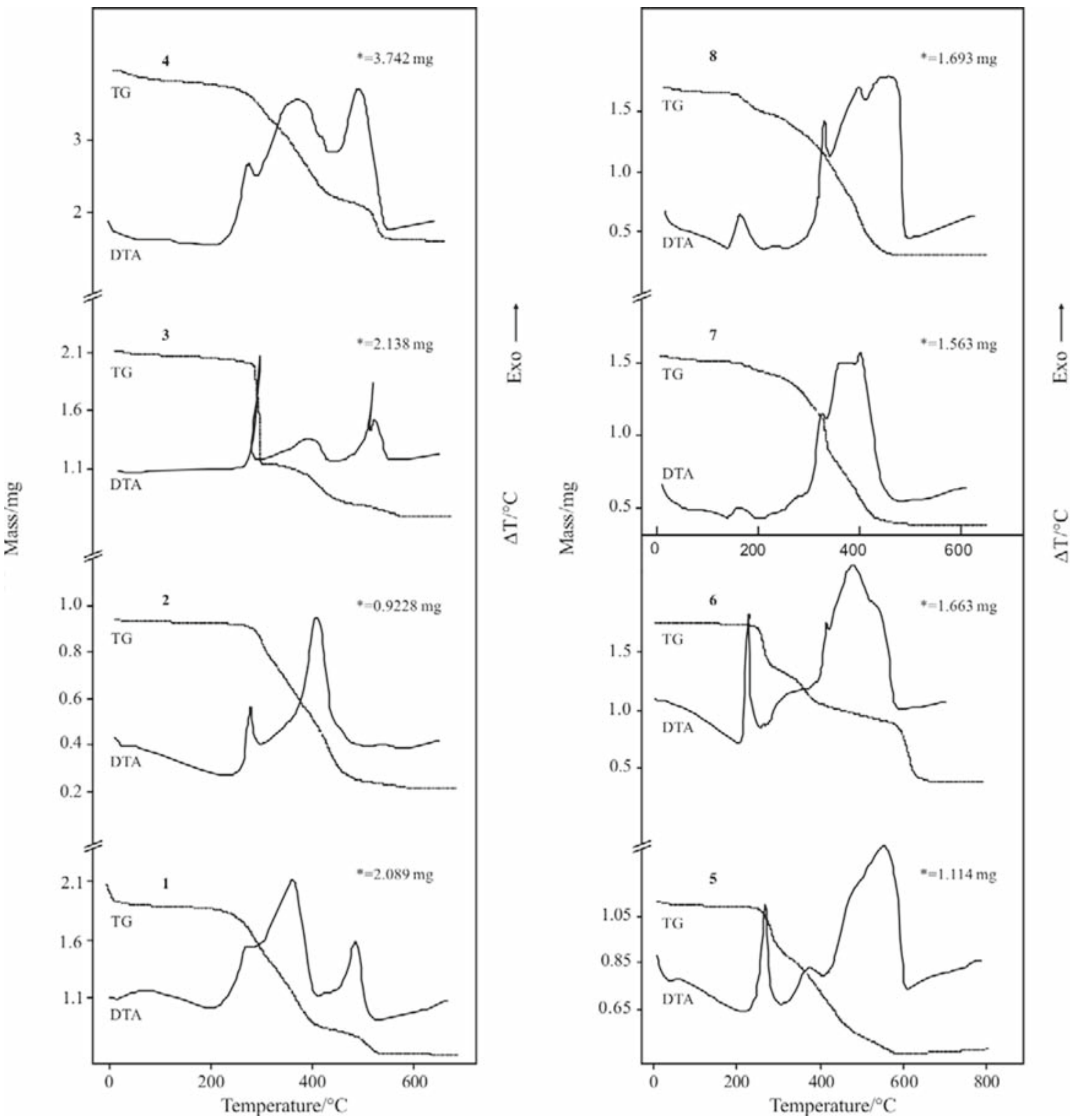
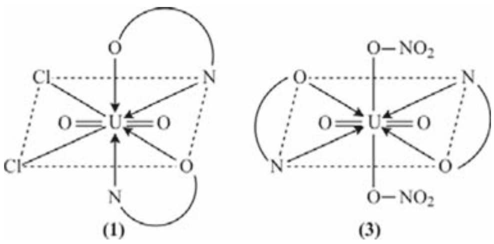


Fig. 1 DTA and TG curves of **1**–**4** – dioxouranium(VI) complexes, **5**, **6** – tin(IV) complexes and **7**, **8** – thorium(IV) complexes *Mass of sample

may be attributed to the distribution of the ligands around the metal ion as shown in Scheme 3.

As shown, the chloro complex (**1**) suffers from steric hindrance than the nitrato one (**3**). On the other hand, the chloro complex (**2**) shows higher thermal stability (256°C) than the chloro complex (**1**) (240°C), which may be due to the increasing number of chelate rings, however, it still shows lower thermal stability than the nitrato complex (**3**), which may be related to the presence of three organic ligands around the metal ion.



Scheme 3

Tin(IV) chelates

The DTA curves of tin(IV) complexes are shown in Fig. 1. The data of the thermal analysis are also collected in Table 3. Inspection of the DTA curves show that Sn complex (**5**) exhibits an endothermic DTA peak in the temperature range of 25–74°C, assigned to loss of 0.5 molecule of water which is in good agreement with calculated value (Table 3). The DTA/TG curves also reveal that the thermal stability of tin(IV) complexes (**5** and **6**) is about the same. Complex (**5**) starts to decompose around 252°C through losing of one HCl molecule with partial elimination of the organic ligand, while complex (**6**) starts to decompose at nearly 250°C through losing of two HCl molecules per-complex molecule. The final thermoproducts were analyzed by IR spectroscopy and were identified as $Sn(Ph)_2O$ and SnO_2 for complexes (**5**) and (**6**), respectively. The higher temperature of the formation of final product for complex (**6**) (670°C) relative to that of complex (**5**) (585°C) may be attributed to the presence of two strong M–Cl bonds in complex (**6**) which are characterized by their high covalent character.

Thorium(IV) complexes

DTA and TG curves of thorium(IV) complexes (**7** and **8**) (Fig. 1 and Table 3), show a broad endothermic peak in the temperature range of 25–170°C, assigned to loss of two water molecules for both complexes as indicated from TG mass loss. That was followed by an exothermic peak (170–300°C), assigned to loss of nitrate moiety (as $2NO_2+O_2$) which is in good agreement with the calculated value (Table 3). This peak is followed by exo-DTA peaks, assigned to departure of the organic ligand and formation of $Th(NO_3)_2$ and ThO_2 as final thermoproducts for the complexes (**7**) and (**8**), respectively as indicated from IR spectra. The formation of different final thermoproduct as well as the different nature of the decomposition of the two complexes (vide TG data) may confirm the different structure of the two complexes.

In all of the studied complexes, the metal percentage calculated from the remain residue were compared with those determined by the analytical metal content determination [32].

Conclusions

We have synthesized and structurally characterized UO_2(VI), Sn(IV), Th(IV) and Li(I) complexes with 4-azomalononitrile antipyrine (L) in the same way as that in first row transition metals complexes preliminary reported [13]. It should be pointed out that 4-azomalononitrile antipyrine (L), acts as bidentate ligand coordinating to the metal ion through the carbonyl atom of pyrazolone ring and azomethine nitrogen. The thermal behaviour of the investigated complexes have also been studied, the thermal study reveals the following points.

- The thermal stability of dioxouranium(VI) chelates increase with increasing number of chelate rings in the complexes.
- The dioxouranium(VI) nitrato complex (**3**) shows higher thermal stability than the chloro-analogous (1), which may be attributed to the distribution of the ligands around the central metal ion and its effect on the thermal stability of chelate. Also, the anions (ligands) Cl, and OAc play an important role in the thermal stability of the two complexes.
- Tin(IV) complexes have nearly the same thermal stability and start their decomposition by the same manner.
- Thorium(IV) complex (**8**) show lower thermal stability than thorium(IV) complex (**7**), which may correspond to the presence of three organic ligands around metal ion in complex (**8**).
- Thorium(IV) complexes decomposed at lower temperature than both UO_2(VI) and Sn(IV) complexes.

References

1 T. P. Popova, R. I. Alexandrova, R. Tudose, E. M. Mosoarca and O.Costrisor, Bulgarian J. Vert. Med., 9 (2006) 265.
2 N. Raman, J. D. Raja and A. Saklhivel, J. Chem. Sci., 119 (2007) 303.
3 D. Chiaramonte, J. M. Steiner, J. D. Broussard, K. Baer, S. Gumminger, E. D Moller, D. A. Williams and R. Shumway, Can. J. Vet. Res., 67 (2003) 183.
4 T. Hitoshi, N. Tamao, A. Hideyuki, F. Manabu and M. Takayuki, Polyhedron, (1997) 3787.
5 A. Kandil and A. Hamid, J. Dry Res., 12 (1980) 27.
6 A. M. Farghaly and A. Hozza, Pharmazie, 35 (1980) 596.
7 I. D. Capel, M. Jenner and M. H. Pinnock, Biochem. Pharm., 27 (1978) 3.
8 E. M. Mosoarca, R. Tudose, R. Alexandrova and O. Costisor, Chem. Bull., 50 (2005) 1.
9 K. Saraswathi, N. V. S. Naidu, K. M. Kumari and K. P. Padmaja, Chem. Environ. Res., 8 (1999) 271.
10 P. M. Selvakumar, E. Suresh and P. S. Subramanian, Polyhedron, 26 (2007) 749.
11 S. A. Abdel-Latif, H. B. Hassib and Y. M. Issa, Spectrochim. Acta, 67 (2007) 950.
12 T. Rosu, S. Pasculescu, V. Lazar, C. Chifiriuc and R. Cernat, Molecules, 11 (2006). 904.
13 F. A. El-Saied, M. I. Ayad, R. M. Issa and S. A. Aly, Pol. J. Chem., 74 (2000) 919.
14 F. A. El-Saied and S. A. Aly, Afinidad, 61 (2004) 516.
15 M. P. Sathisha, V. K. Revankar and K. S. R. Pai, Metal-based Drugs, (2008) 1.
16 K. B. Gudasi, R. V. Shenoy, R. S. Vadavi, M. S. Pattil and S. A. Patil, Chem. Pharm. Bull., 53 (2005) 1077.
17 Z. H. Abd El- Wahab, Spectrochim. Acta, A (67) (2007) 25.
18 K. Nakamoto, Infrared Spectra of Inorganic and Coordination Compounds, 2nd Ed., NY: Wiley Interscience, New York 1970.
19 Z. H. Abd El-Wahab, M. M. Mashaly and A. A. Faheim, Chem. Pap., 59 (2005) 25.

20 T. A. Khan, M. A. Rather, N. Jaham, S. P. Vankey and M. Shakir, Synth. React. Inorg. Met. Org. Chem., 27 (1997) 843.

21 A. A. Alemi and B. Shaabani, Acta, Chem. Solv., 47 (2000) 363.

22 R. K. Agarwal, L. Singh and D. K. Sharma, Bioinorg. Chem. Appl., (2006) 1.

23 I. S. Ahuja, C. L. Yadav and S. Tripath, Asian., J. Chem., 1 (1989) 195.

24 K. Nakamoto, Infrared and Raman Spectra of Inorganic and Coordination Compounds, Wiley-Interscience, New York 1997.

25 H. A. El-Boraey, A. M. Donia and M. F. El- Samalehy, J. Anal. Appl. Pyrol., 73 (2005) 204.

26 A. M. Donia, H. A. El-Boraey and M. F. El-Samalehy, J. Therm. Anal. Cal., 73 (2003) 987.

27 C. K. Modi, S. H. Patel and M. N. Patel, J. Therm. Anal. Cal., 87 (2007) 441.

28 R. Olar, M. Badea, M. N. Grecu, D. Marinescu, V. Lazar and C. Balotescu, J. Therm. Anal. Cal., 92 (2008) 239.

29 H. A. El-Boraey, J. Therm. Anal. Cal., 81 (2005) 339.

30 M. Nath and P. Arora, Synth. React. Inorg. Met-Org. Chem., 23 (1993) 1523.

31 N. N. Dass and S. Sarmah, J. Therm. Anal. Cal., 58 (1999) 137.

32 A. M. G. Macdonald and P. Sirichanya, J. Micro Chem., 14 (1969) 199.

Received: April 23, 2008
Accepted: July 10, 2008
Online First: November 11, 2008

DOI: 10.1007/s10973-008-9197-6