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TRANSITION METAL COMPLEXES WITH THIOSEMICARBAZIDE-BASED LIGANDS

31. Dioxouranium(VI) complexes with N(1),N(4)-bis(salicylidene)- and N(1)-benzoylisopropylidene-N(4)-salicylidene-S-alkyl-isothio-semicarbazides

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Abstract

Solvate complexes of UO_2^{2+} and N(1), N(4)-bis(salicylidene)-S-methylisothiosemicarbazone, (H_2Me-L^1), of general formula [UO_2(Me-L^1)S] (*S*= H_2O, MeOH, EtOH, Py, DMF and DMSO) were synthesized. The methanolic UO_2^{2+} adducts of N(1)-benzoylisopropylidene-N(4)-salicylidene-S-alkylisothiosemicarbazone, (H_2R-L^2, *R*=Me, Pr^n) of general formula [UO_2(R-L^2)·MeOH], were also prepared. Thermal decomposition of the complexes was investigated in air and argon. The complexes decompose to α-U_3O_8 in air, while in argon the decomposition is not completed up to 1000 K. The temperature and the mechanism of decomposition of the complexes are a function of the solvent belonging to the inner coordination sphere.

Keywords: salicylaldehyde S-methylisothiosemicarbazone, thermogravimetry, uranyl complexes

Introduction

In our previous paper [1] the syntheses of pentagonal bipyramidal dioxouranyl complexes of a general formula [UO_2(Me-L^1)S] were described, where *Me-L^1* stands for the dianion of the ONNO-type N(1), N(4)-bis(salicydene)-S-methyl-isothiosemicarbazide ligand while *S*=MeOH, EtOH and DMF. In this paper we describe the thermal decomposition of these and some of the newlysynthesized (*S*=H_2O, Py and DMSO) complexes with the same ligand, as well as the synthesis and thermal decomposition of [UO_2(R-L^2)MeOH] complexes where *R-L^2* is the dianion of tetradentate ONNO N(1)-benzoylisopropylidene-N(4)-salicylidene-S-methyl/*n*-propylisothiosemicarbazide ligand.

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Experimental

Preparation of ligand percursors and complexes

The preparation of salicylaldehyde S-methylisothiosemicarbazone is described elsewhere [2].

Benzoylacetone S-methyl/*n*-propylisothiosemicarbazone was prepared by the reaction of cold ethanolic solutions of S-alkylisothiosemicarbazide hydrogeniodide [3] and benzoylacetone (10 mmol, 15 cm^3) in the presence of sodium hydroxide solution in water (15 mmol, 10 cm^3). 24 hours later a yellow crystalline product was obtained. The crystals were washed with water and dried at room temperature (yield: 50%).

The previously synthesized complexes [UO_2(Me-L^1)S] (*Me-*L^1=the dianion of the ONNO-type tetradentate N(1),N(4)-bis(salicydene)-S-methylisothiosemicarbazide ligand, *S*=MeOH, EtOH or DMF, (Samples 2, 3 and 5) were prepared by the reaction of salicylaldehyde with warm solutions of salicylaldehyde S-methylisothiosemicarbazone in MeOH, EtOH or DMF in the presence of UO_2^{2+} -ion as a template [1]. The solvate complexes with *S*=H_2O, Py and DMSO were synthesized in a similar way: The aqua complex, [UO_2(Me-L^1)H_2O], (Sample 1), of N(1),N(4)-bis(salicydene)-S-methyl- isothiosemicarbazide (H_2Me-L^1), was prepared by heating the ethanolic (EtOH-H_2O 70%, *v/v*) solution with equimolar amounts of salicylaldehyde S-methylisothiosemicarbazone, salicylaldehide and uranylacetate dihydrate. In the case of Sample 4, [UO_2(Me-L^1)Py], the methanolic solution of the ligand and uranylacetate was heated with salicylaldehyde and pyridine (equimolar ratio). The complex with DMSO, [UO_2(Me-L^1)DMSO], (Sample 6) was prepared by recrystallization of [UO_2(Me-L^1)MeOH] from the warm solution of MeOH-DMSO (1:1, *v/v*). The precipitate was separated, washed with EtOH and Et_2O and dried at room temperature. The yields, calculated on the basis of salicylaldehide S-methylisothiosemicarbazone, was 83%, 76% and 30%, respectively.

A similar procedure was employed to synthesize the [UO_2(R-L^2)MeOH] complexes (*R-*L^2=dianion of N(1)-benzoylisopropylidene-N(4)-salicylidene-S-methyl/*n*-propylisothiosemicarbazide ligand) but instead of salicylaldehide S-methyl-isothiosemicarbazone benzoylacetone S-methyl/propylisothiosemicarbazone was used. The crystals were filtered off and washed with MeOH.

IR-spectra, X-ray diffraction

The IR spectra of the compounds have been recorded in the range of 4000–500 cm^{-1} on a Perkin-Elmer 457 spectrophotometer using KBr discs at room temperature.

The composition of the final product was determined on a HZG-4/C Diffractometer, Carl Zeiss, Jena, using CuK$_\alpha$ (λ=0.154 nm) radiation and a Ni filter. The speed of the goniometer was 1°/min.

Thermal analysis

The thermogravimetric measurements have been carried out on the thermobalance of a DuPont 990 TA system. The samples (about 5 mg) were heated in a platinum crucible in a flowing air and argon atmosphere to 973 K at a heating rate of 10 and 2 K min^{-1}.

DSC measurements were run in the DSC cell of a DuPont 1090 TA system. The samples (about 5 mg) were weighed in an open aluminum pan. As a reference an empty aluminum pan was used. Samples were heated at a rate of 10 K min^{-1} in a flowing argon atmosphere. DSC curves were recorded to 623 K.

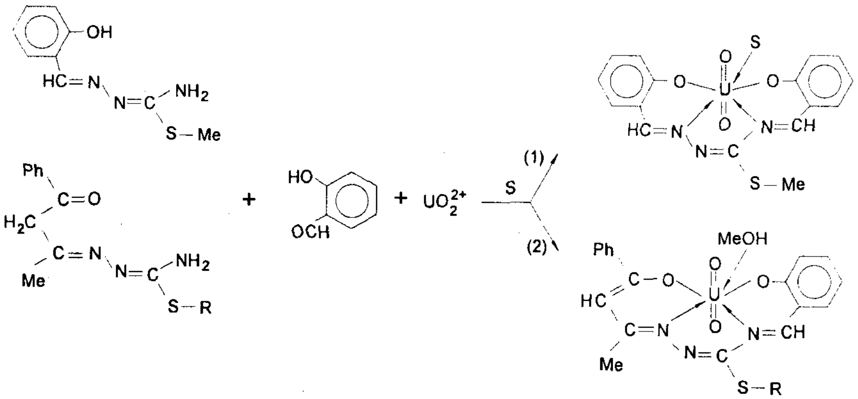
Molar conductivity measurements

The molar conductivity of the freshly prepared 10^{-3} mol dm^{-3} solution of the samples in DMF was measured at room temperature using a digital conductivity meter (Jenway 4010).

Results and discussion

Synthesis and general physico-chemical characteristics of the complexes

The synthesis of the complexes is presented in Scheme 1. The condensation reaction of the thioamidic $N(4)H_2$-group is possible only in the presence of metal ion [1]. As Scheme 1 shows, the tetradentate ligand is coordinated through the ONNO donor set to the UO_2^{2+} group. The usual pentagonal-planar arrangement of the ligands in the pentagonal-bipyramidal uranium(VI) complex is achieved by additional coordination of a monodentate solvent molecule (*S*). In the case of the DMF-adduct this was proved by X-ray diffraction analysis [1], too. The high temperature of the solvent evaporation (Table 2) also proves its strong coordination to the uranyl ion.



Scheme 1

Table 1 contains some of the physico-chemical characteristics and the results of elemental analyses (C, H, N) of the compounds.

The molar conductivity of the complexes in DMF (Table 1) is very low, which suggests their nonelectrolytic character. All the complexes are crystalline substances, soluble in DMF, Me_2CO, C_6H_6, $CHCl_3$, less soluble in MeOH, EtOH and Et_2O and insoluble in H_2O.

The IR-spectra of the newly-prepared samples can serve as an additional proof of the solvent coordination (H_2O, Py and DMSO).

The IR-spectrum of the DMSO-adduct shows two characteristic IR absorption bands in the range of 990–945 cm^{-1} for the two S=O stretching vibrations. The ν(S=0) band appears at about 80 cm^{-1} lower energy compared to the corresponding band of the non-coordinated DMSO (1070 cm^{-1}) molecule [4], indicating the expected coordination of the solvent through the oxygen.

The band characteristic for the in-plane ring vibration of the noncoordinated pyridine [5] (≈600 cm^{-1}) in the spectrum of the $[UO_2(Me\text{-}L^1)Py]$ complex appears at a higher energy for 90 cm^{-1}, due to the pyridine nitrogen coordination to the central atom.

In the spectrum of H_2O solvate a broad, medium-intensity band in the range of 3600–3000 cm^{-1} stands for the O-H stretching vibration.

The characteristic bands for the UO_2^{2+} group are located at ≈900 cm–1 (ν_{as}, v.s.) and ≈800 cm^{-1} (ν_s, v.w.), i.e., in the ranges 950–870 cm^{-1} (ν_{as}) and 880–780 cm^{-1} (ν_s) usual for the $\nu(UO_2)$ vibrations of the dioxouranium(VI)-complexes [6, 7].

Thermal decomposition of the complexes

The TG and DTG curves of the aqua complex (Sample 1) in air and argon atmosphere are presented in Fig. 1. The course of the decomposition is the same in both cases up to about 700 K. In air, the decomposition is terminated at about 830 K by a rather fast burning process giving α-U_3O_8 as a final product. In argon atmosphere above 700 K the process of decomposition becomes slower and is not completed up to 1000 K. The measurements of all the other complexes were carried out in flowing air atmosphere.

The TG and DTG curves of Samples 1–6 are presented in Figs 1 and 2, while the DSC curves are given in Fig. 3. The first mass loss corresponds to the endothermic loss of the coordinated solvent molecule. In spite of the fact that all the complexes contain only one solvent molecule, the broad (50 K wide) DTG peak and the DSC curves (Fig. 3) indicate a rather complex desolvation process. To examine the mechanism of this process, the measurements were repeated with a heating rate of 2 K min^{-1}. In the case of the solvates with H_2O, MeOH and EtOH the DTG curves at the higher heating rate are broader, but the differences due to the different heating rates are not significant. The desolvation of the Py, DMF and DMSO solvates (Samples 4–6) takes place in several overlapping steps and

Table 1 Some physico-chemical characteristics and analytical data of the complexes

Complex	Colour	$\lambda_{(M)}$ (DMF)/ Ω^{-1} cm^2 mol^{-1}	Composition/% – measured (calculated)			
			U	C	H	N
$[UO_2(Me\text{-}L^1)H_2O]$	red	1.54	39.86 (39.71)	32.70 (32.06)	2.55 (2.52)	7.02 (7.01)
$[UO_2(Me\text{-}L^1)MeOH]$	orange-red	1.72	39.80 (38.80)	32.59 (33.28)	2.42 (2.79)	6.72 (6.85)
$[UO_2(Me\text{-}L^1)EtOH]$	red	1.53	38.02 (37.94)	34.72 (34.45)	3.16 (3.05)	6.62 (6.70)
$[UO_2(Me\text{-}L^1)Py]$	brick-red	1.62	36.43 (36.04)	38.38 (38.19)	3.06 (2.75)	8.31 (8.48)
$[UO_2(Me\text{-}L^1)DMF]$	brown	1.83	36.52 (36.37)	35.46 (34.84)	3.63 (3.08)	8.60 (8.56)
$[UO_2(Me\text{-}L^1)DMSO]$	dark-red	1.54		32.77 (32.78)	2.83 (2.90)	6.80 (6.37)
$[UO_2(Me\text{-}L^2)MeOH]$	dark-red	1.59		37.29 (36.74)	3.39 (3.08)	6.70 (6.43)
$[UO_2(Pr\text{-}L^2)MeOH]$	dark-red	1.50		38.46 (38.80)	3.62 (3.48)	6.32 (6.31)

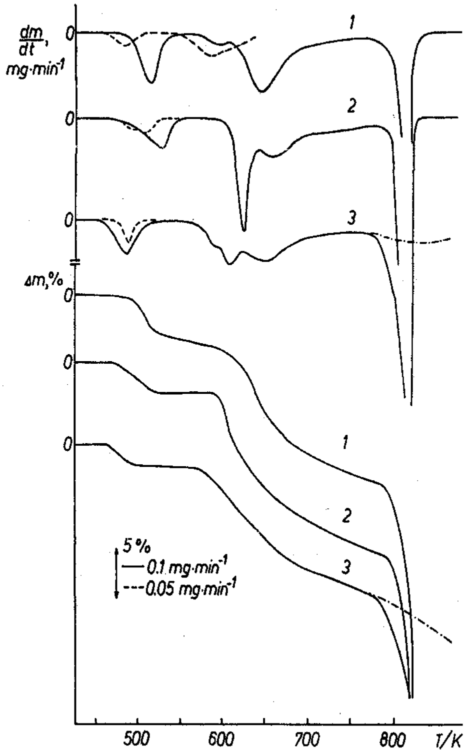


Fig. 1 TG, DTG and DSC curves of the samples: 1 – $[UO_2(Me\text{-}L^1)H_2O]$; 2 – $[UO_2(Me\text{-}L^1)MeOH]$; 3 – $[UO_2(Me\text{-}L^1)EtOH]$,
a) in air: heating rate 2 K min^{-1} (- - -) heating rate 10 K min^{-1} (—)
b) in argon: heating rate 10 K min^{-1} (–·–·–)

depends on the heating rate (Fig. 2). These samples lose the solvent at a temperature about 40 K higher than the H_2O, MeOH and EtOH solvates. The rather high temperature (>450 K) of the evaporation refers to the solvent molecule bond to the inner coordination sphere. The TG data for the solvent content of the freshly prepared samples were in agreement with the data of the elemental analysis. However, in spite of the high desolvation temperature the solvent content of some samples decreased with time. While the elemental analysis for the composition of the complexes gave a general formula of $[UO_2(Me\text{-}L^1)S]$, the mass loss for older Samples 2 and 3 corresponds to a lower solvent content and remains constant for a prolonged time.

The next step is the exothermic decomposition (Figs 2, 3 and 4) of the desolvated complex $[UO_2(Me\text{-}L^1)]$. The process of decomposition is a complex one in all the cases. As the DTG curves in Figs 2 and 3 show, the decomposition temperature of the samples and the mechanism of the decomposition depend on the solvent removed in the previous step. A higher decomposition temperature

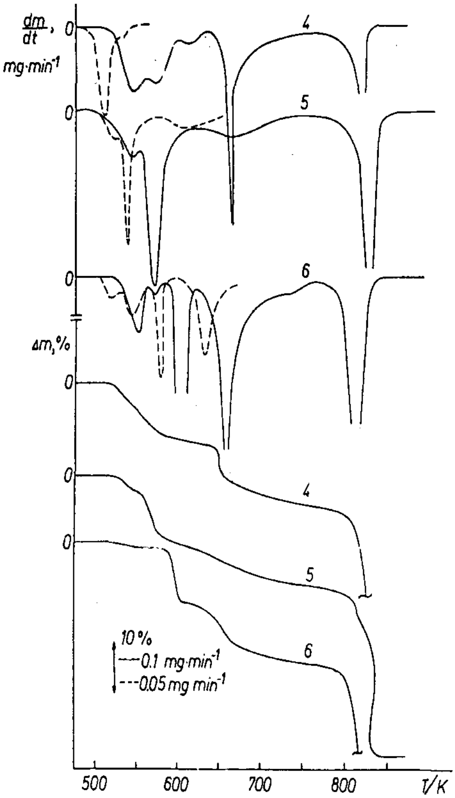


Fig. 2 TG and DTG curves of the samples in air: 4 – [UO$_2$(Me-L^1)Py]; 5 – [UO$_2$(Me-L^1)DMF]; 6 – [UO$_2$(Me-L^1)DMSO], heating rate 2 K min^{-} (- - -) heating rate 10 K min^{-1} (—)

belongs to the complexes which contained Py, DMF and DMSO previously (Samples 4–6), while the complex with ethanol (Sample 3) has the lowest thermal stability. The most probable explanation of this phenomenon is that during the desolvation the structure of the complexes does not change. The DTG curves have a minimum at about 750 K, where the rate of mass loss is almost zero (<0.01 mg min^{-1}). The molar mass of the evolved fragments in the temperature interval from the beginning of the decomposition of the desolvated complex to the minimum of curve is (79±8) g mol^{-1}, e.g., the molar mass of benzene.

The thermal decomposition data for all the samples are presented in Table 2.

The thermal stability of the methanolic UO$_2^{2+}$ complexes with benzoylacetone S-methylisothiosemicarbazone, [UO$_2$(Me-L^2)MeOH], or benzoylacetone S-propyl-isothiosemicarbazone, [UO$_2$(Pr-L^2)MeOH], was also investigated (Fig. 4, Samples 7 and 8). While UO$_2^{2+}$ complexes with the Me-L^1 ligand lose the solvent above 470 K, the complexes [UO$_2$(Me-L^2)MeOH] and [UO$_2$(Pr-L^2)MeOH] lose

Table 2 Thermoanalytical data of the samples

Sample	Complex	T_{range}/K	Mass loss/%		T_{range}/K	Mass loss/%	T_{range}/K	Mass loss/%	
			calcd.	found				calcd.	found
1	$[UO_2(Me\text{-}L^1)H_2O]$	485–530	3.00	4.0 4.0*	575–775	14.5 86.9**	775–830	53.17	54.5
2	$[UO_2(Me\text{-}L^1)MeOH]$	485–550	5.22	5.2 3.2*	600–750	14.5 89.0**	775–815	54.24	53.5
3	$[UO_2(Me\text{-}L^1)EtOH]$	465–510	7.34	7.5 2.9*	565–750	12.0 75.9**	775–840	55.26	54.3
4	$[UO_2(Me\text{-}L^1)Py]$	505–600	11.97	11.7	620–720	12.0 79.3**	775–825	57.50	57.2
5	$[UO_2(Me\text{-}L^1)DMF]$	510–600	11.17	13.0	670–720	10.0 65.5**	800–830	57.11	56.3
6	$[UO_2(Me\text{-}L^1)DMSC]$	505–620	11.99	12.0	625–745	12.0 79.1**	775–820	57.44	55.5
7	$[UO_2(Me\text{-}L^2)MeOH]$	420–480	4.90	4.9 3.4*	550–640	17.5 114.4**	650–830	57.07	57.1
8	$[UO_2(Pr\text{-}L^2)MeOH]$	325–475	4.81	4.6	560–650	16.4 116.2**	650–850	57.82	57.8

* Mass change for older samples

**Average molar weight of the fragments

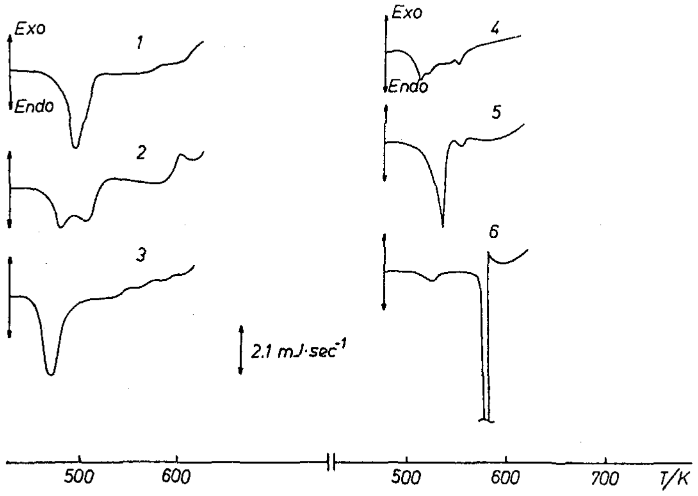


Fig. 3 DSC curves of the samples: 1 – [UO_2(Me-L^1)H_2O]; 2 – [UO_2(Me-L^1)MeOH]; 3 – [UO_2(Me-L^1)EtOH]; 4 – [UO_2(Me-L^1)Py]; 5 – UO_2(Me-L^1)DMF]; 6 – [UO_2(Me-L^1)DMSO]

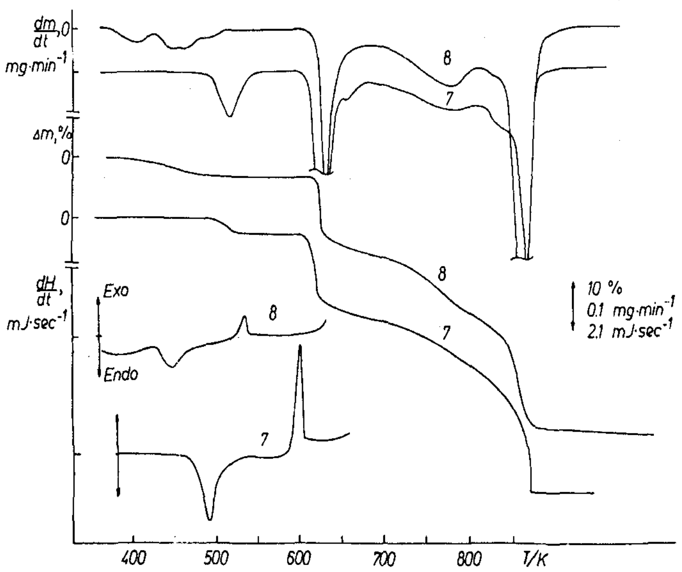


Fig. 4 TG, DTG and DSC curves for the samples: 7 – [UO_2(Me-L^2)MeOH]; 8 – [UO_2(Pr-L^2)MeOH]

methanol at lower temperatures. As can be seen in Fig. 4, the onset temperature of methanol evaporation from Sample 7 is at 425 K, while the mass loss of Sample 8 begins almost at room temperature. Both processes are rather complex. The methanol content of the freshly prepared Sample 7 corresponds to the composition given by elemental analysis, [UO_2(Me-L^2)MeOH], but decreases in the course of time to [UO_2(Me-L^2)0.7MeOH], which remains canstant for a while. The solvent content of Sample 8 was constant all the time and agreed with the composition given by elemental analysis, [UO_2(Pr-L^2)MeOH] in spite of the fact that the thermal stability of the solvate is low. Usually, the solvent is lost in an endothermic process (DSC curves in Fig. 4). When the evaporation of the solvent is completed, the exothermic decomposition of the complex begins. In the range from the beginning of this step to the minimum of the DTG curve (550–650 K) the average molar mass of the leaving fragments is 115 g mol^{-1}, which corresponds to the molar mass of a salicyliminic group. This means that in spite of the fact that the S-alkyl group of the ligand is different, the process of decomposition is similar for both samples. The DSC curve of Sample 8 shows an exothermic maximum at 477 K, probably due to a configurational change.

Conclusion

Samples 1–6 differ only in the coordinately bond solvent molecule. The desolvation of the complexes takes place at relatively high temperatures, owing to the strong bonding of the solvent to the central ion. In spite of the fact that after desolvation the composition of the products is the same for all of the complexes, the temperature of the following decomposition is different for different solvates, probably because during the desolvation the complexes retain the original structure. The average molar mass of the fragments departing to the minimum of the DTG curve (about 750 K) agree with the molar mass of benzene. The final product of the decomposition in air is α-U_3O_8.

The thermal stability of Samples 7 and 8 is somewhat lower. The decomposition temperature (550 K) and the course of the decomposition of the desolvated complex is very similar for both solvates. In spite of the fact that the S-alkyl group of these complexes is different, the average molar mass of the leaving fragments to the minimum of the DTG curve is about the same and consistent with the molar mass of a salicylimine group which means that the S-alkyl-group remained untouched in this step of the decomposition.

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