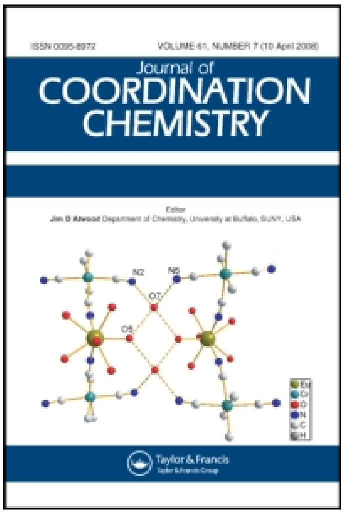

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Synthesis and characterization of some uranyl and zirconyl nitrilotriacetic acid (NTA) chelates

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Four new complexes $[UO_2(HNTA)(H_2O)] \cdot 3H_2O$, $Na[UO_2(NTA)] \cdot (H_2O)$, $[ZrO(HNTA)(H_2O)] \cdot 3H_2O$ and $Na[ZrO(NTA)] \cdot H_2O$ were obtained by the reactions of UO_2^{2+} and ZrO^{2+} salts with nitrilotriacetic acid (NTA) dissolved in water and NaOH aqueous solution. Infrared spectra of the solid complexes have been obtained and assigned on the basis of C_s symmetry. Octahedral and polymeric chain structures are adopted for the uranyl and zirconyl NTA complexes, respectively. Thermogravimetric (TG) and differential thermal analysis (DTA) data are in accordance with the proposed structures and show that the complexes decompose to metal oxides.

Keywords: Nitrilotriacetic acid; Zirconyl; Uranyl; Infrared spectra; Thermal analysis

1. Introduction

Nitrilotriacetic acid (NTA) is perhaps the most important chelating agent (after ethylenediaminetetraacetic acid, EDTA) among the family of amino polycarboxylic acids. Since it was first described by Schwarzenbach *et al.* [1], NTA has found extensive applications in the fields of water and soil treatment as well as in biological and medical research [2–8].

Infrared spectroscopy of metal–NTA chelates in aqueous solution and also in the solid state provides valuable information about the mode of NTA chelation to metal ions [9–14]. The anion of NTA is capable of forming 1 : 2 as well as 1 : 1 complexes with cations of rare earth metals. NTA behaves as a tetradentate ligand for divalent metals such as copper, nickel cobalt, zinc, cadmium and lead, and as a tridentate ligand for the alkaline earth metals. The stretching vibration $\nu(C{=}O)$ of the coordinated carboxylate group tends to correlate with the stability constant of complexes.

A literature survey has revealed that almost all of the work carried out on NTA complexes in aqueous solutions was mainly concerned with determination of their stability constants [15–19]. The aim of our work was to study the mode of chelation of NTA

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(which is known to be dependent on the pH of the solution and the nature of the metal ions [20]) with $UO_2^{2+}$and ZrO^{2+} ions and to investigate the type of bonding and structures of the complexes obtained as well as their thermal behavior.

2. Experimental

Reagent-grade chemicals were used throughout.

2.1. *Preparation of the complexes*

2.1.1. [UO_2(HNTA)(H_2O)]·3H_2O. The solid complex was isolated as a yellow precipitate by the addition of 100 mL of an aqueous solution (5×10^{-3} mol) of uranyl acetate [$UO_2(CH_3COO)_2 \cdot 2H_2O$; 2.120 g] or uranyl nitrate [$UO_2(NO_3)_2 \cdot 6H_2O$; 2.510 g] to 150 mL of an aqueous solution of NTA (0.9557 g, 5×10^{-3} mol). The mixture was stirred for about 2 h and then left overnight. The precipitate formed was filtered off, washed several times with minimum amounts of distilled water (4 × 2 mL), dried for about 30 min at *ca* 50°C in an oven and then under vacuum over $CaCl_2$ (yield: 74%, powder).

2.1.2. [ZrO(HNTA)(H_2O)]·3H_2O. A volume of 100 mL of an aqueous solution (5×10^{-3} mol) of zirconyl chloride [$ZrOCl_2 \cdot 8H_2O$; 1.6612 g] or zirconyl nitrate [$ZrO(NO_3)_2 \cdot 6H_2O$; 1.6962 g] was added to 100 mL of an aqueous solution of NTA (0.9557 g, 5×10^{-3} mol). The reaction mixture was stirred at room temperature for about 8 h and then refluxed for about 7 h. The white precipitate formed was filtered off, washed several times with minimum amounts of distilled water, dried for about 30 min at *ca* 50°C in an oven and then under vacuum over $CaCl_2$ (yield: 72%, powder).

2.1.3. Na[UO_2(NTA)]·H_2O. A volume of 100 mL of an aqueous solution of uranyl acetate (0.848 g, 2×10^{-3} mol) was added to 60 mL of a solution of NTA (0.38228 g, 2×10^{-3} mol) in sodium hydroxide (0.24 g, 6×10^{-3} mol). The reaction mixture was stirred for about 5 h at 60°C. A dark yellow precipitate started to appear after concentration of the solution to half its volume. The precipitate was left in its mother liquor overnight, filtered off, washed several times with distilled water and then dried under vacuum over P_2O_5 (yield: 87%, powder).

2.1.4. Na[ZrO(NTA)]·H_2O. A volume of 100 mL of an aqueous solution of zirconyl chloride (0.64 g, 2×10^{-3} mol) was added to 60 mL of a solution of NTA (0.38228 g, 2×10^{-3} mol) in sodium hydroxide (0.24 g, 6×10^{-3} mol). The mixture was stirred for about 7 h at 60–70°C. A white precipitate started to appear after evaporation of the solution to half its volume. The precipitate was left in its solution overnight, filtered off, washed several times with distilled water and then dried under vacuum over P_2O_5 (yield: 85%, powder).

2.2. *Characterization of the complexes*

C, H and N contents of the uranyl and zirconyl complexes were determined by elemental analysis using a Perkin Elmer CHN 2400 instrument. Uranium and zirconium were

Table 1. Elemental analysis data for uranyl and zirconyl complexes.

	%C		%N		%H		%U		%Zr		%Na	
Complex	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.	Found	Calc.
$[UO_2(HNTA)(H_2O)] \cdot 3H_2O$	13.52	13.57	2.72	2.64	2.93	2.82	43.63	44.82	–	–	–	–
$[ZrO(HNTA)(H_2O)] \cdot 3H_2O$	19.27	19.60	3.43	3.84	3.74	4.07	–	–	24.65	24.78	–	–
$Na[UO_2(NTA)] \cdot H_2O$	14.53	14.42	2.82	2.85	2.31	1.63	46.89	47.70	–	–	4.71	4.61
$Na[ZrO(NTA)] \cdot H_2O$	19.81	21.42	3.96	4.16	2.53	2.37	–	–	26.98	27.14	6.78	6.84

determined from thermogravimetric (TG) curves by ignition of the complexes to oxides at 800°C. The sodium content was determined by atomic absorption spectroscopy, using a PYE-UNICAM SP 1900 instrument fitted with a sodium lamp. Elemental analyses of the complexes are summarized in table 1.

Infrared spectra were measured in the range 4000–400 cm^{-1} from KBr disks using a Perkin-Elmer 1430 ratio-recording IR spectrophotometer. Thermal analysis [TG and differential thermal analysis (DTA)] was carried out using a Shimadzu TGA-50 H computerized thermal analysis system, which includes a program that processes data with ChromotPac C-R3A. The rate of heating of the samples was kept at 10°C min^{-1}. Sample masses varied between 2.00 and 4.98 mg and were analyzed under N_2 flow at 30 mL min^{-1}. α-Alumina powder was used as DTA standard.

3. Results and discussion

The four new complexes were isolated as solids and formulated as $[UO_2(HNTA)(H_2O)] \cdot 3H_2O$, $[ZrO(HNTA)(H_2O)] \cdot 3H_2O$, $Na[UO_2(NTA)] \cdot H_2O$ and $Na[ZrO(NTA)] \cdot H_2O$, based on their elemental analysis, IR spectra and thermal analysis.

3.1. *Infrared spectra*

3.1.1. $[UO_2(HNTA)(H_2O)] \cdot 3H_2O$ and $[ZrO(HNTA)(H_2O)] \cdot 3H_2O$. Infrared spectra of these two complexes were obtained and vibrational assignments of the well-defined IR bands are given in table 2.

The structures of these complexes can be considered in the light of the infrared spectra obtained for the carboxylate group both in NTA (the free acid) and in the M–NTA chelates. For both complexes, two very strong absorption bands are observed in the region 1725–1625 cm^{-1}. The first band is observed at 1715 cm^{-1} for $[UO_2(HNTA)(H_2O)] \cdot 3H_2O$ and at 1725 cm^{-1} for the corresponding zirconyl complex, $[ZrO(HNTA)(H_2O)] \cdot 3H_2O$. This band is also observed (1730 cm^{-1}) in the spectrum of the free acid, where the absorption band of the free carboxylic acid group is expected [12,21]. This band is therefore assigned in both complexes to the stretching vibration ν(C=O) of the uncoordinated carboxylic acid group, COOH. The other band, which appeared as a very strong absorption at 1630 and at 1625 cm^{-1} for the uranyl and zirconyl complexes, respectively, is not observed in the spectrum of the free acid and can be assigned to the stretching vibration, ν(C=O), of the coordinated carboxylate group, COOM.

Carboxylate ions give rise to another band in the region of 1420–1390 cm^{-1} that is assigned to the stretching vibration, ν(C–O). The infrared spectra of these complexes

Table 2. Infrared wavenumbers (cm^{-1}) and assignments for the complexes $[UO_2(HNTA)(H_2O)] \cdot 3H_2O$ (**1**), $[ZrO(HNTA)(H_2O)] \cdot 3H_2O$ (**2**), $Na[UO_2(NTA)] \cdot H_2O$ (**3**) and $Na[ZrO(NTA)] \cdot H_2O$ (**4**).

1	2	3	4	Assignment
3568 (br)	3435 (br)	3431 (br)	3455 (br)	ν(OH); H_2O
3479 (br)	3390 (br)			
2964 (w)	2961 (w)	2976 (w)	2977 (w)	ν(CH); $-CH_2-$ of NTA
2358 (vw)	2357 (w)	2368 (w)	2366 (w)	
1715 (vs)	1725 (vs)	–	–	ν(C=O); free COOH
1630 (vs)	1625 (vs)	1630 (vs)	1641 (vs)	ν(C=O); COO–M
1415 (s)	1410 (s)	1395 (vs)	1390 (vs)	ν(C–O); COO^-
1380 (s)	1385 (s)			
1125 (w)	1132 (m)	1120 (m)	1122 (m)	ν(C–N)
927 (vs)	905 (vs)	913 (s)	911 (s)	ν_{as}(U=O), ν_{as}(Zr=O)
849 (w)	831 (m)	–	–	$\delta_r(H_2O)$
734 (w)	743 (w)	745 (w)	743 (w)	ν_s(U=O), ν_s(Zr=O)
548 (w)	559 (w)	554 (w)	585 (w)	ν(U–N), ν(Zr–N)
409 (m)	488 (m)	468 (m)	436 (m)	ν(U–O), ν(Zr–O)

m, medium; s, strong; vs, very strong; w, weak; br, broad.
ν, stretching; s, symmetric; as, asymmetric; δ_r, rocking.

show two bands for each complex; at 1415 and 1380 cm^{-1} for the uranyl complex, and at 1410 and 1385 cm^{-1} for the zirconyl complex. This group of bands is also observed at almost the same region in the spectrum of the free acid NTA. This group of bands is therefore probably associated with the stretching vibrations, ν(CO), of the carboxylate groups. From these observations, it is clear that in these two complexes, one of the three carboxyl groups does not coordinate with the central metal ion, but remains as free carboxylic acid.

The stretching vibration associated with the C–N bond is observed at 1145 cm^{-1} in the spectrum of NTA, the free acid, while the corresponding vibration, ν(CN), appeared at 1125 and 1132 cm^{-1} for the uranyl and zirconyl chelates, respectively. The assignment of this vibration is consistent with the expected lowering of the stretching wavenumber value of the C–N bond upon coordination of nitrogen to the metal ion and also with the assignment of ν(CN) vibrations of some related divalent metal–NTA chelates [12]. The metal–N bond stretching vibrations, ν(U–N) and ν(Zr–N), are observed as expected [20] at 548 and 559 cm^{-1} for the two complexes, respectively.

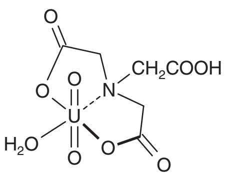
The infrared spectra of the two complexes show a group of bands in the region of 3568–3435 cm^{-1}, where H_2O is expected to absorb. Although there is no a definite borderline between coordinated and lattice water, the former is expected to show other modes such as rocking and metal–oxygen stretching vibrations. The infrared spectrum of the uranyl complex shows two absorption bands at 849 and 409 cm^{-1}, which can be assigned to the rocking, $\delta_r(H_2O)$, mode and stretching vibration, ν(U–O), respectively. The corresponding two vibrations for the zirconyl complex are observed at 831 and 488 cm^{-1}, respectively. The assignments of these two bands to these frequencies agree fairly well with those reported previously for aqua complexes [22]. The presence of one H_2O molecule inside and three H_2O molecules outside the coordination sphere of these complexes is confirmed by thermal analysis (table 3).

According to the above discussion, NTA in these two complexes behaves as a tridentate ligand through two oxygen atoms of two carboxylate groups and a nitrogen atom. Assuming an octahedral geometry for the uranyl complex and a square pyramidal for

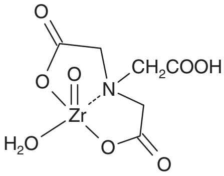
Table 3. Maximum temperature values for the decomposition along with the species lost in each step of the decomposition reactions of the uranyl and zirconyl complexes.

Complex	Decomposition	T_{max}/°C	Lost species	%Weight loss	
				Found	Calc.
$[UO_2(HNTA)(H_2O)] \cdot 3H_2O$	First step	82	$3H_2O$ uncoord.	10.00	10.16
	Second step	170–180	H_2O coord.	3.70	3.38
	Third step	240–750	NTA	34.20	35.95
	Total loss			47.90	49.49
	Residue			52.10	50.51
$[ZrO(HNTA)(H_2O)] \cdot 3H_2O$	First step	70	$3H_2O$ uncoord.	14.15	14.76
	Second step	170–180	H_2O coord.	5.10	4.89
	Third step	240–750	NTA	50.18	51.35
	Total loss			69.43	71.00
	Residue			30.57	29.00
$Na[UO_2(NTA)] \cdot H_2O$	First step	70	H_2O uncoord.	3.66	3.60
	Second step	200–800	NTA	36.63	37.80
	Total loss			40.29	41.40
	Residue			59.71	58.60
$Na[ZrO(NTA)] \cdot H_2O$	First step	70	H_2O uncoord.	5.84	5.34
	Second step		NTA	54.63	56.08
	Total loss			60.47	61.42
	Residue			39.53	38.58

the zirconyl complex, the structures of the two complexes are shown as **I** and **II**, respectively.



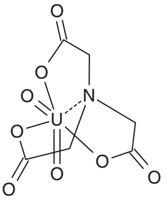
(I)



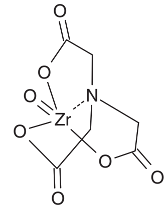
(II)

3.1.2. $Na[UO_2(NTA)] \cdot H_2O$ and $Na[ZrO(NTA)] \cdot H_2O$ complexes.

In contrast to the uranyl and zirconyl HNTA chelates, the infrared spectra of the sodium uranyl and zirconyl NTA chelates (table 2) show only one carbonyl stretching vibration, ν(C=O). This band is observed at 1630 cm^{-1} for $Na[UO_2(NTA)] \cdot H_2O$ and at 1641 cm^{-1} for $Na[ZrO(NTA)] \cdot H_2O$. Both are observed as very strong bands in a region typical for coordinated carboxylate. The spectra also show an absorption band at 1395 and 1390 cm^{-1} for the uranyl and zirconyl complexes, respectively, which can be assigned to the stretching vibration, ν(C–O), of the coordinated carboxylate group. The C–N stretching vibration, ν(C–N), is observed at 1120 and 1122 cm^{-1}, while the ν(U–N) and ν(Zr–N) stretching motions are observed at 554 and 585 cm^{-1} for the sodium uranyl and zirconyl complexes, respectively. The spectra of both complexes also reveal broad absorption bands around 3430 cm^{-1} due to the O–H stretching vibration of lattice water. This band for the sodium uranyl complex is observed at 3431 cm^{-1} and for the sodium zirconyl complex at 3455 cm^{-1}.



(III)

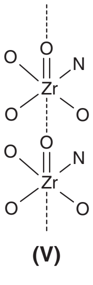


(IV)

NTA in these complexes acts as a tetradentate ligand and coordinates to UO_2^{2+} and ZrO^{2+} ions through its three oxygen atoms of the carboxylate groups and the nitrogen atom. X-ray structural determinations [23–27] for some M–NTA–heteroaromatic N-base ternary complexes, where NTA is tetracoordinated to the central metal atom (through its nitrogen and three oxygens), indicate that NTA occupies four positions of the octahedral sphere around the central atom. Accordingly, the structures of the two complexes may be shown schematically as **III** and **IV**, where the uranyl complex retains a distorted octahedral geometry with *cis*-UO_2, consistent with the structure of $(NH_4)_2[VO_2NTA]$ determined by X-ray crystallography [28].

According to the proposed octahedral structures of the two uranyl complexes, their symmetry is C_s. Four vibrations for the uranyl unit, UO_2, are expected for the two complexes under this symmetry. These four vibrations are three A′ and one A″, namely ν_s(U=O); A′, ν_{as}(U=O); A′, $\delta(UO_2)$; A′ and δ (UO_2); A″. The data given in table 2 show that the ν_{as}(U=O) in these complexes occurs as a very strong band at 927 and 905 cm^{-1}, while ν_s(U=O) is observed at 734 and 745 cm^{-1} for the $[UO_2(HNTA)(H_2O)]\cdot 3H_2O$ and $[UO_2(NTA)]^-$ complexes, respectively. These assignments for ν(U=O) stretching vibration are in the usual range observed dioxouranium(VI) complexes [29].

The infrared spectra of the two zirconyl complexes show two strong absorption bands at 913 and 911 cm^{-1} for $[ZrO(HNTA)(H_2O)]$ and $[ZrO(NTA)]^-$, respectively. This band can be assigned to the Zr=O bond stretching vibration. Spectroscopic studies of some related metal(IV) complexes [30] indicate that a large number of complexes exhibit a strong M=O stretching vibration around 1000 cm^{-1}. However, in some cases a large shift in the M=O value towards lower wavenumbers is observed, with some tetradentate ligands forming dimeric or polymeric structures via M–O–M bridges [31]. The large shift in the Zr=O stretch to lower wavenumber may be explained in terms of an oxygen bridging, Zr–O–Zr, polymeric chain formation, as shown in structure **V**. However, the shift of ν(Zr=O) to a lower value in the proposed polymeric structure compared with that of the monomer could be attributed to the expected increase in reduced mass values of both Zr and O upon polymerization decreasing ν(Zr=O).



(V)

Change in the coordination mode of NTA towards uranyl and zirconyl ions on changing the pH is clear. NTA reacts with metal ions in aqueous solution either as a tri- or tetradentate ligand and the extent of interaction is governed by the solution pH value and the kind of metal ion used. This behavior of NTA can be explained on the basis of known titration data [24]. For example, chelate formation between NTA and magnesium ions occurs in the pH region above 4.8, and the main equilibria involved in the pH region of 4.2 or higher are:

$$\mathrm{HNTA}^{2-} + \mathrm{M}^{2+} = \mathrm{MNTA}^{-} + \mathrm{H}^{+} \tag{1}$$

$$\mathrm{NTA}^{3-} + \mathrm{M}^{2+} = \mathrm{MNTA}^{-} \tag{2}$$

However, equation 2 will be valid only in the relatively high pH region, as the third dissociation constant of NTA is $10^{-9.73}$.

3.2. *Thermal analysis*

3.2.1. $[UO_2(HNTA)(H_2O)]\cdot 3H_2O$ and $[ZrO(HNTA)(H_2O)]\cdot 3H_2O$. Thermal analyses were carried out under nitrogen flow. TG, DTG and DTA curves obtained for the complexes are shown in figure 1(a,b). Table 3 gives the maximum temperature values for the decomposition along with the species lost in each step of the decomposition reaction. The data obtained indicate that the decomposition modes of the two complexes are the same and occur in three main degradation steps.

The first stage of decomposition occurs at a maximum temperature of 82 and 70°C for the complexes $[UO_2(HNTA)(H_2O)]\cdot 3H_2O$ and $[ZrO(HNTA)(H_2O)]\cdot 3H_2O$ and is associated with a weight loss of 10.0 and 14.15%, respectively. Theoretically, the loss of the three lattice water molecules in these complexes corresponds to a weight loss of 10.16 and 14.76%, respectively, in good agreement with the experimental values.

The second stage of decomposition occurs at a maximum temperature in the range 170–180°C for both of the complexes. The weight loss value associated with this stage is 3.70% for the uranyl complex and 5.10% for the zirconyl complex. These values agree fairly well with the calculated weight loss of 3.38 and 4.89% and may attributed to the loss of the coordinated water molecule in the two complexes, respectively.

The third stage of decomposition is observed at a maximum temperature in the range 240–750°C. The weight loss values associated with this stage are 34.20 and 50.18% for the uranyl and zirconyl complexes, respectively. The loss in weight associated with this stage of decomposition is due to the loss of the organic part (NTA) of these complexes, which agrees well with the theoretical values of 35.95 and 51.35% for the complexes, respectively.

3.2.2. $Na[UO_2(NTA)]\cdot H_2O$ and $Na[ZrO(NTA)]\cdot H_2O$. The thermal data obtained for these two complexes [figure 1(c,d) and table 3] indicate that decomposition occurs in two stages.

The first stage of decomposition proceeds with weight loss values of 3.66% and 5.84% for the uranyl and zirconyl complexes, respectively. This stage of decomposition occurs at a maximum temperature of approximately 70°C and may be associated with loss of the water molecule in good agreement with the

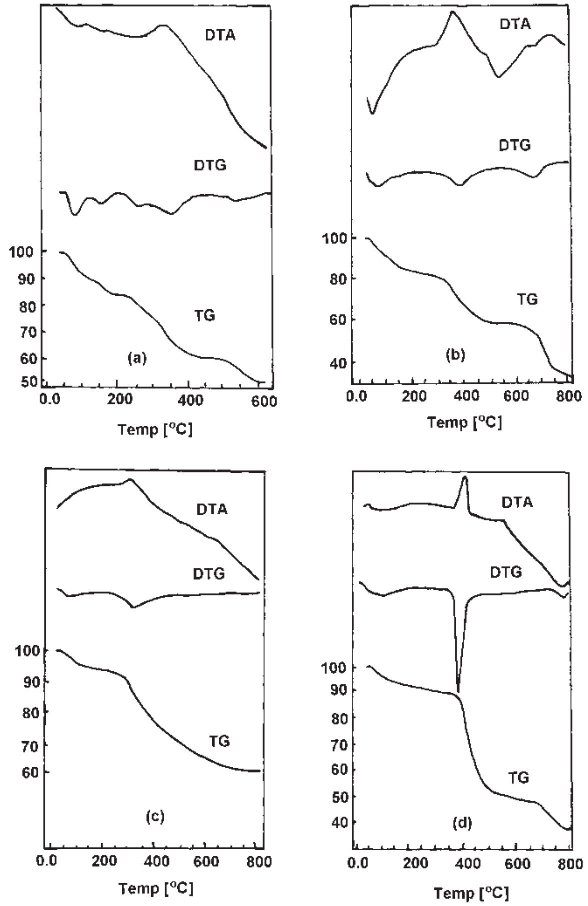


Figure 1. TG, DTG and DTA curves of (a) $[UO_2(HNTA)(H_2O)] \cdot 3H_2O$, (b) $[ZrO(HNTA)\text{-}(H_2O)] \cdot 3H_2O$, (c) $Na[UO_2(NTA)] \cdot H_2O$ and (d) $Na[ZrO(NTA)] \cdot H_2O$.

calculated values of 3.60 and 5.34% for the uranyl and zirconyl complexes, respectively.

The second stage of decomposition is distributed among two steps at a maximum temperature extending from 200 to 800°C. The weight loss values associated with this stage of decomposition are 36.63% for the uranyl complex and 54.63% for the zirconyl complex due to loss of the organic ligand, NTA. These values are in good agreement with the calculated values of 37.80 and 56.08% for the two complexes, respectively.

Finally, infrared spectra of the final thermal decomposition products show the absence of any bands due to NTA, but instead reveal the characteristic spectra of uranium and zirconium oxides.

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