

# Thermogravimetric study of the scandium nitrate hexahydrate thermolysis and computer modeling of intermediate oxynitrates

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**Abstract** The thermal decomposition of scandium nitrate is a complex process, which begins with the simultaneous condensation of 4 mol of the initial monomer  $\text{Sc}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ . The resulting cyclic tetramer  $\text{Sc}_4\text{O}_4(\text{NO}_3)_4 \cdot 2\text{H}_2\text{O}$  gradually loses azeotrope  $\text{H}_2\text{O}-\text{HNO}_3$ , and an intermediate oxynitrate  $\text{Sc}_4\text{O}_5(\text{NO}_3)_2$  is formed. At higher temperature, this oxynitrate is destroyed leaving behind unstable dimer  $\text{Sc}_4\text{O}_6$  which is transformed into scandium oxide. The molecular mechanics method used for comparison of the potential energies of consecutive products of thermal decomposition permits an evaluation of their stability and a proper interpretation of experimental data. The structural modeling was aimed to provide detailed information about the bond lengths and bond angles, filling the gap in what we know about amorphous oxynitrates. The models represent a reasonably good approximation to the real structures.

**Keywords** Rare earth · Scandium nitrate hexahydrate · Thermal decomposition · Oxynitrates · Computer modeling

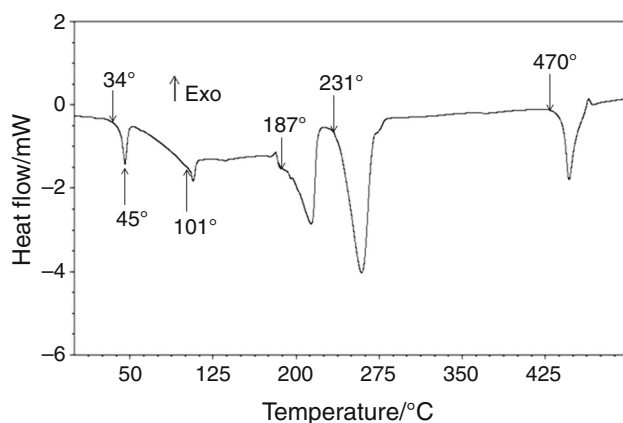
## Introduction

The properties and thermal decomposition of scandium nitrates were investigated with all the particulars for the last time in the 1960s–1970s. It was shown that  $\text{Sc}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$  melt below 100 °C and the end product of their thermal decomposition is  $\text{Sc}_2\text{O}_3$ . As for thermolysis products, several compounds were suggested as possible candidates, including  $\text{Sc}_4\text{O}(\text{NO}_3)_{10} \cdot 8\text{H}_2\text{O}$ ,  $\text{Sc}_4\text{O}_3(\text{NO}_3)_6 \cdot 6.5\text{H}_2\text{O}$ , and  $\text{Sc}_4\text{O}_5(\text{NO}_3)_2$  [1], with no attempts to suggest structural formulas. Actually, these compositions seem to be consistent with the thermolysis schemes recently proposed for metal nitrates,  $\text{Me}^{\text{III}}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ , where  $\text{Me}^{\text{III}} = \text{Ga}, \text{Y}, \text{Gd}, \text{Cr}$ . These works established that all attempts to prepare the anhydrous compounds in the presence of coordinated water are unsuccessful [2–7]. Therein, the researchers clearly pointed out that the intermediate oxynitrates contain a tetramer heterocycle, composed of four atoms of  $\text{Me}^{\text{III}}$ , alternating with four atoms of oxygen. The mechanism involved supposes a simultaneous condensation of four mol of the initial monomer into a cluster which is gradually denitrificated. In gadolinium, a cyclic cluster containing four gadolinium atoms has been isolated in crystalline form [4]. There are grounds to believe that the thermal behavior of scandium nitrate hexahydrate may have similar characteristics. The aim of the present study was to revert to the thermolysis of the title hydrate  $\text{Sc}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , and offer a different and more realistic scheme of events, by applying the hypothesis of tetramer structures and building up structural models for amorphous intermediate oxynitrates. On this basis, the stabilities of what we regard as the true intermediates can be compared.

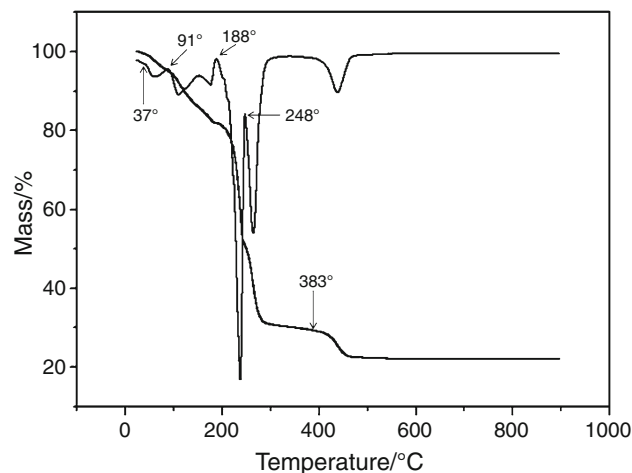
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**Fig. 1** DSC curve of  $\text{Sc}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$



**Fig. 2** TG curve of  $\text{Sc}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$

## Materials and methods

The starting reagent used was scandium nitrate hexahydrate  $\text{Sc}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ , of analytical grade purity (99.9 % on trace elements basis), purchased from Aldrich. Direct heating of the commercial reagent resulted in mass loss of 79.04 % confirming the water number slightly lower than six (calc. 79.64 %). Thermal gravimetric analysis (TG) and differential scanning calorimetry (DSC) were used to study thermal behavior, employing a 50H Shimadzu Instrumentation, and a Netsch STA Jupiter 449C Instrumentation. Test specimens, in the first case, were heated in a flux of nitrogen (temp. range  $-40$ – $500$  °C), and in the second case in a flux of argon (temp. range  $25$ – $500$  °C), always at a heating rate  $10$  °C  $\text{min}^{-1}$ . Mass losses during heating were analyzed and compared to previously calculated values. Melting point, gas liberation, and crystallization processes were monitored by visual observation. The evolution of volatiles was measured using a Netsch STA Jupiter 449C apparatus coupled with a FTIR spectrometer. Infrared spectroscopy of evolved gases was performed using a Tensor 27 Bruker spectrometer. The spectra were detected in a range  $400$ – $4,000$   $\text{cm}^{-1}$ . Temperature of the transport gas line was  $240$  °C. The spectra were taken for 12 s at a frequency accuracy of  $1$   $\text{cm}^{-1}$ . The identification of the IR spectra was done on the basis of NIST Chemistry Web-Book [8]. The samples were sealed in glass ampoules in a hot condition in order to avoid the impact of water vapors from the air. Compounds were simulated using the standard software package AVOGADRO, an open-source molecular builder and visualization tool, version 1.0.3 with the UFF force fields program [9, 10]. UFF is a force field widely used for the systems containing elements other than carbon, hydrogen, and nitrogen. It contains the energy terms for bond stretching, angle bending, dihedral torsion, van der

Waals, and electrostatic potential. Structures were found by minimizing the energy with respect to all geometrical variables, no assumptions being made other than that of appropriate symmetry. Angles and interatomic distances were evaluated by using special features of the program.

## Results and discussion

### Thermal analysis

The DSC analysis of  $\text{Sc}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  is presented in Fig. 1. At lower temperatures, no solid–solid phase transition was found, at least over  $-40$  °C. From approximately  $36$  °C on, a series of endothermic effects become evident, reflecting the dehydration/decomposition processes. Along with TG pattern, their analysis can be used for a rigorous interpretation of results.

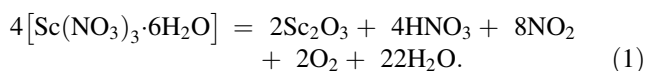
The representative TG curve of  $\text{Sc}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  is shown in Fig. 2. The first mass loss is due to water evaporation after fusion of the original hexahydrate at  $37$ – $48$  °C, similarly to yttrium hexahydrate [3]. This temperature is also confirmed by direct visual observation, when the melt loses gas bubbles and turns into a clear liquid. It is well known that the decomposition onset for the nitrates of trivalent metals is generally below  $100$  °C. In this respect, scandium nitrate is not an exception. Between  $37$  and  $188$  °C, the compound loses 22.4 % of mass, corresponding to 3 mol of water and 4 mol of nitric acid, taking into account the presence of four monomers at the start of decomposition process. At the same time, Table 1 shows the compositions of the reaction products with expected and experimentally found mass losses at different stages of thermal treatment.

**Table 1** Mass losses at different stages of  $\text{Sc}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  thermal decomposition in relation to the initial sum of four monomers

Steps	Compositions	Loss of volatile products/mol				Mass loss/%	
		Water	Nitric acid	Nitrogen dioxide	Oxygen	Exp.	Calc.
1	$\text{Sc}_4(\text{NO}_3)_{12} \cdot 24\text{H}_2\text{O}$	3	–	–	–	3.66	3.98
2	$\text{Sc}_4(\text{NO}_3)_{12} \cdot 21\text{H}_2\text{O}$	–	4	–	–	22.4	22.54
3	$\text{Sc}_4\text{O}_2(\text{NO}_3)_8 \cdot 19\text{H}_2\text{O}$	5	4	–	–	47.76	47.8
4	$\text{Sc}_4\text{O}_4(\text{NO}_3)_4 \cdot 12\text{H}_2\text{O}$	12	–	2	1	72.16	72.25
5	$\text{Sc}_4\text{O}_5(\text{NO}_3)_2$ 2 $\text{Sc}_2\text{O}_3$	–	–	2	1	79.06	79.6
Total: $20\text{H}_2\text{O}$ , $8\text{HNO}_3$ , $4\text{NO}_2$ , $2\text{O}$							
Final product: 2 $\text{Sc}_2\text{O}_3$							

The most significant losses of mass (25.36 and 24.34 %) occur between 188 and 292 °C. Later, in the range 383–700 °C, the remaining volatile products are lost (6.9 %), and the sample mass becomes practically constant. It can be seen that the above experimental mass losses really fit the values calculated for the formation of  $2\text{Sc}_2\text{O}_3$ . This is in accordance with the existing published data on the elements whose properties are close to scandium, i.e., gallium, gadolinium, and yttrium [2–4].

Calculations show that the hypothesis concerning clusters pre-existence in the solid state is quite applicable to the present case of scandium nitrate hydrate. Indeed, this suggests that at least four mol of  $\text{Sc}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  are involved in the condensation process. So, the whole condensation process may be described as

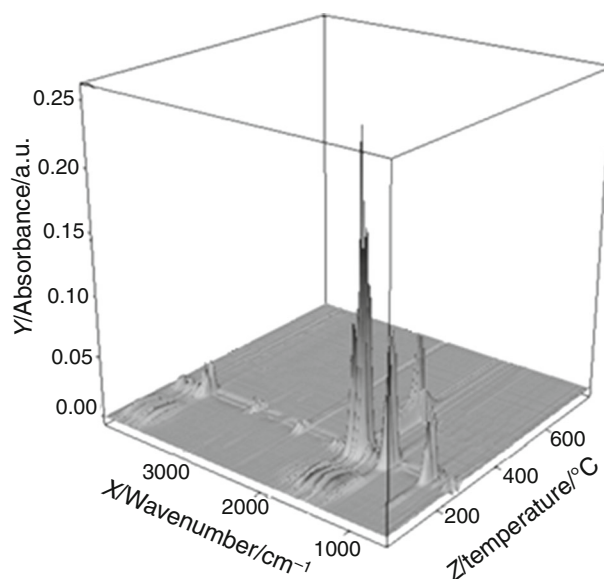


The DSC curve given in Fig. 1 confirms these considerations. One can see that between 40 and 300 °C, there exist at least three endothermic effects with the peaks at 45, 106, 212, and 260 °C, and a final effect at 446 °C. That seems to be an indication that water molecules stabilizing the intermediate structures, at least at the beginning, are removed step-by-step along with the release of nitrogen-containing compounds. The curve does not present indications of the crystallization processes.

It is obvious that these considerations must be corroborated by additional experimental techniques.

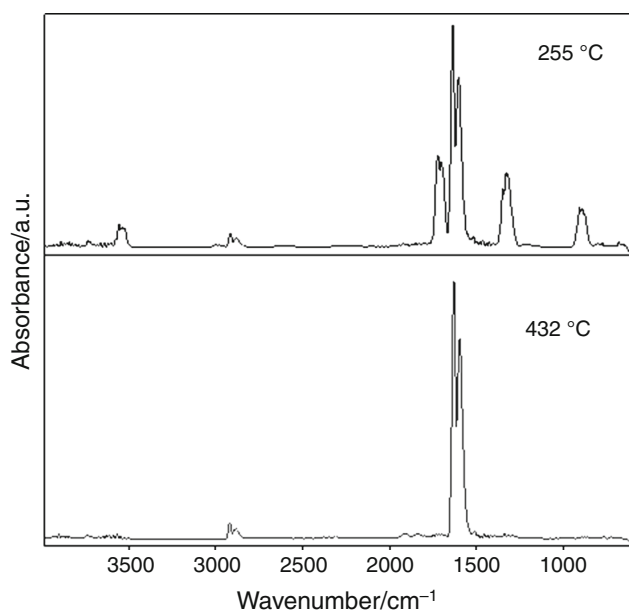
#### Identification of volatile products

Our working hypothesis was that scandium nitrate is hydrolyzed by the crystallization water, and as a result, nitric acid should have been produced. Indeed, this acid, or rather the azeotrope 68 %  $\text{HNO}_3$ –32 %  $\text{H}_2\text{O}$ , is detected by the IR sensor of the volatile products from the very beginning of the thermal treatment.

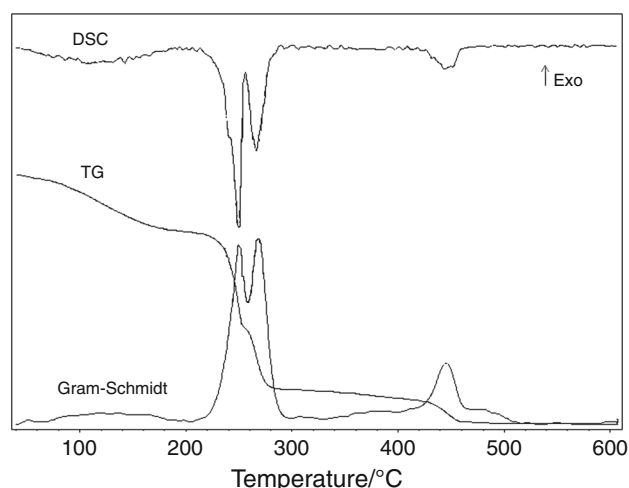
**Fig. 3** Temperature-dependent 3D diagram of IR spectra of the  $\text{Sc}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  thermal decomposition

The 3D diagram of IR–spectrum shown in Fig. 3 gives a general view of absorption at sequential temperatures. The main mass loss up to 50 °C is clearly attributed to the water. From 120 °C on, significant contributions come from the water and nitric acid. The IR spectrum of the product corresponding to 255 °C (Fig. 4) confirms this identification by the presence of the main nitric acid absorbance bands at 895, 1,508, 1,598, 1,629, 1,698, and 1,715  $\text{cm}^{-1}$ . According to the Gram-Schmidt curve, which describes integrated spectral absorbance, this effect starts at 120 °C (Fig. 5), exactly corresponding to the boiling point of the azeotrope with the composition 36.6 %  $\text{H}_2\text{O}$ –67.4 %  $\text{HNO}_3$  [11].

According to the IR absorbance at higher temperatures, the next mass loss is due to forming of nitrogen dioxide with the most characteristic bands at 1,314, 1,595, and

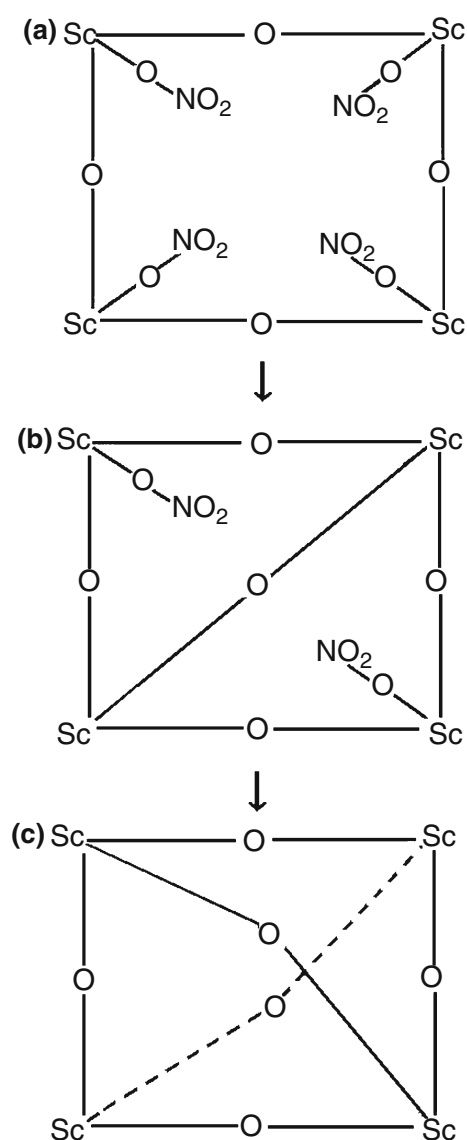


**Fig. 4** IR spectra of the volatile compounds corresponding to 255 and 432 °C



**Fig. 5** Comparison of integrated spectral absorbance with TG and DCS curves

$1,629\text{ cm}^{-1}$ . Besides the traces of nitric acid and water, no other gas with changing dipole moment has been detected (Fig. 4). The presence of nitrogen dioxide suggests a mechanism involving  $\text{N}_2\text{O}_5$  formation with immediate disproportionation into  $2\text{NO}_2 + \text{O}$ . The curves of simultaneous equilibrium of  $\text{NO}$ ,  $\text{NO}_2$ ,  $\text{N}_2\text{O}_3$ , and  $\text{N}_2\text{O}_4$  show that above  $300\text{ °C}$  nitrogen dioxide is the only existing phase [12]. Nevertheless, it should be borne in mind that oxygen is not active in IR spectrum region and consequently undetectable by this technique. Thus, the only volatile products of the whole process of  $\text{Sc}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  thermolysis are water, nitric acid, nitrogen dioxide, and

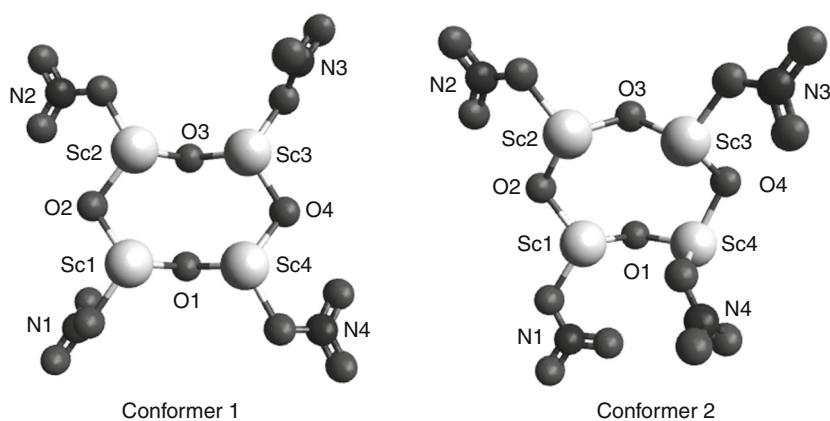


**Fig. 6** Scheme illustrating the denitrification process of  $\text{Sc}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$  (water molecules are not shown). **a**  $\text{Sc}_4\text{O}_4(\text{NO}_3)_4 \cdot 24\text{H}_2\text{O}$ , **b**  $\text{Sc}_4\text{O}_4(\text{NO}_3)_4$ , **c** hypothetical  $\text{Sc}_4\text{O}_6$

oxygen. Returning to the Gram-Schmidt curve, one can see that it mirrors the DTG curve confirming that no other gaseous products are unaccounted for Fig. 5.

### Structural modeling

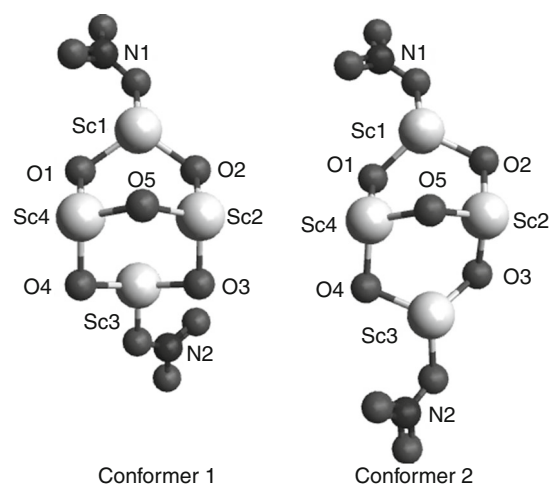
To the best of our knowledge, the X-ray structure determination for scandium oxynitrates has never been performed. So structural modeling is aimed to provide detailed information about the bond lengths and bond angles, filling the gap in what we know about these intermediate amorphous compounds. The removal of  $\text{HNO}_3$  and water leads to creation of oxygen bridges between the scandium atoms,

**Fig. 7** Models of tetramer conformers containing 4NO<sub>3</sub>

obliging 4Sc(NO<sub>3</sub>)<sub>4</sub> to condense into a tetramer structure Sc<sub>4</sub>O<sub>4</sub>(NO<sub>3</sub>)<sub>4</sub>·24H<sub>2</sub>O (scheme Fig. 6a). Simultaneously, the entire system of hydrogen bonds is rebuilt. Both DTG and DSC curves show that this is a complex step-wise process, so the water molecules must belong to differently bonded species. These are involved in intermolecular hydrogen bonding making the monomers stand together. At the following stage, tetramer loses 2 mol of nitrogen dioxide, 1 mol of oxygen, and the remaining water, so the composition of the resulting solid product will correspond to Sc<sub>4</sub>O<sub>5</sub>(NO<sub>3</sub>)<sub>2</sub> (scheme Fig. 6b). Finally, the latter will lose 1 mol of nitrogen dioxide, and 1 mol of oxygen, and there are no further thermal transformations. At this stage, the oxygen-containing bridges are unable to withstand the strain and collapse, leaving behind the unstable dimer Sc<sub>4</sub>O<sub>6</sub> (scheme Fig. 6c) which is transformed into 2 mol of Sc<sub>2</sub>O<sub>3</sub>. The total mass loss 79.06 % matches the calculated value. These features are reminiscent of the process of gadolinium nitrate thermolysis, where the intermediate oxynitrates were shown to be identical in composition [4].

We did not perform any systematic energy sampling for searching conformational energy space. Two conformers for each composition were chosen at random for structural comparisons. The models obtained by using the molecular mechanics technique are shown in Figs. 7 and 8. As can be seen, the base of the tetramer Sc<sub>4</sub>O<sub>4</sub>(NO<sub>3</sub>)<sub>4</sub> is formed by an inorganic heterocycle composed of four atoms of scandium, alternating with four atoms of oxygen, which, to simplify things, are numbered from 1 to 4. The interatomic distances and bond angles for both conformers are presented in Tables 2 and 3.

At the first glance, this cycle seems symmetric as all distances Sc–O are almost identical: 2.056–2.059 Å. The comparison shows that these distances are shorter than those refined from X-ray diffraction data for other scandium compounds (oxyfluoride, vanadate, tungstate, etc.), that is 2.08–2.22 Å. As for the angles Sc–O–Sc, they are slightly different, being in the range 104.2–104.5°, which is similar to the angle in Sc<sub>2</sub>O<sub>3</sub> [1]. The deformation of the

**Fig. 8** Models of tetramer conformers containing 2NO<sub>3</sub>

cycle becomes evident considering the distances Sc–Sc. These distances between the opposite scandium atoms in the cycle, e.g., Sc(2)–Sc(4) and Sc(1)–Sc(3), are not equal: 4.551 and 4.649 Å, respectively, so the scandium and oxygen atoms are not located in the same planes as can appear from the Fig. 6a.

Since the bonds Sc–O forming the cycles are not covalent, but rather ionic in nature, it becomes quite clear that, in contrast to the planar benzene ring, these cycles can easily become corrugated. Moreover, as the angle of this “folding” may vary within certain limits, one can expect to find the presence of conformational isomers with slightly differing values of potential energy. In a real solid, this degree of freedom is unlikely to be preserved due to the requirements imposed by the densest packing. At this stage, we can only suppose that this model corresponds to a distorted crown conformation.

The same is true of the degree of freedom of rotation about the bonds between scandium and oxygen of NO<sub>3</sub> groups attached to scandium atoms. Their rotation about the Sc–N bond is clearly the source of numerous

**Table 2** Interatomic distances (Å) calculated for tetramer models

Distances	Sc <sub>4</sub> O <sub>4</sub> (NO <sub>3</sub> ) <sub>4</sub>		Sc <sub>4</sub> O <sub>5</sub> (NO <sub>3</sub> ) <sub>2</sub>	
	Conformer 1	Conformer 2	Conformer 1	Conformer 2
Sc(1)–O(1)	2.057	2.057	2.055	2.057
Sc(2)–O(2)	2.058	2.059	2.055	2.057
Sc(3)–O(3)	2.057	2.057	2.055	2.057
Sc(4)–O(4)	2.058	2.057	2.057	2.056
Sc(1)–O(2)	2.057	2.057	2.055	2.056
Sc(2)–O(3)	2.057	2.057	2.057	2.058
Sc(3)–O(4)	2.057	2.057	2.055	2.056
Sc(4)–O(1)	2.057	2.056	2.057	2.058
Sc(1)–Sc(2)	3.254	3.251	3.352	3.248
Sc(2)–Sc(3)	3.253	3.254	3.251	3.252
Sc(3)–Sc(4)	3.254	3.249	3.251	2.249
Sc(4)–Sc(1)	3.252	3.246	3.252	3.252
Sc(1)–Sc(3)	4.649	4.271	4.592	5.422
Sc(2)–Sc(4)	4.551	4.882	3.297	3.268
N(1)–N(3)	10.157	9.375	–	–
N(2)–N(4)	10.319	8.937	–	–
N(1)–N(2)	7.689	7.968	9.309	10.552
N(3)–N(4)	7.070	6.175	–	–
Sc(1)–N(1)	2.924	2.923	2.924	2.924
Sc(2)–N(2)	2.939	2.939	2.924	2.924
Sc(3)–N(3)	2.924	2.924	–	–
Sc(4)–N(4)	2.939	2.924	–	–

conformers. These groups, as in the case of gallium nitrate [2], behave as normal nitrate anions with N–O distances in the range 1.192–1.318 Å [13], that is slightly larger than the interatomic distances in the groups of solid nitrates established by X-ray methods (1.20–1.22 Å) [14]. The large, but different distances between nitrogen atoms in *trans*-positions (Table 1) illustrate the non-equivalence between the NO<sub>3</sub> groups present. Meanwhile, the bond angles O–N–O found for the model are equal to the angles

**Table 3** Bond angles (°) calculated for tetramer models

Angles	Sc <sub>4</sub> O <sub>4</sub> (NO <sub>3</sub> ) <sub>4</sub>		Sc <sub>4</sub> O <sub>5</sub> (NO <sub>3</sub> ) <sub>2</sub>	
	Conformer 1	Conformer 2	Conformer 1	Conformer 2
Sc(1)–O(2)–Sc(2)	104.50	104.4	104.50	104.5
Sc(2)–O(3)–Sc(3)	104.50	104.5	104.40	104.4
Sc(3)–O(4)–Sc(4)	104.50	104.3	104.40	104.3
Sc(4)–O(1)–Sc(1)	104.50	104.2	104.50	104.7
Sc(4)–O(5)–Sc(2)	No bridge	No bridge	104.60	104.6

in solid nitrates (all 120.0°) in accordance with the actual structure of the polyatomic ion, which has trigonal planar geometry.

As the model is based on the real relationship of the ionic radii provided by force field, there is one further point to consider in connection with the anions NO<sub>3</sub>. It seems reasonable to assume that under no circumstances can relatively large anions be located inside the cycle which can be seen in simplified form in Fig. 6b,d in the model representation in Fig. 7. This inner space is too small to accommodate even a single anion, so the anions are “looking” outward, some parallel the sheet plane, other perpendicular to it. For this reason, further condensation with removal of the distant NO<sub>3</sub> groups becomes difficult to achieve; hence the slow kinetics.

Figure 8 shows the structure Sc<sub>4</sub>O<sub>5</sub>(NO<sub>3</sub>)<sub>2</sub> that might be formed after the removal of the penultimate 2 mol of NO<sub>2</sub> and 1 mol of oxygen, so only a pair of NO<sub>3</sub> groups would be bonded to the cycle. In this instance, a newly formed cross-bridge Sc–O–Sc connects scandium atoms 2 and 4. As can be concluded from the Table 2 and Fig. 8, the distances Sc(2)–Sc(4) become shorter, while those between Sc(1)–Sc(3) and N(1)–N(2) get larger, especially in the case of the second conformer. This means that the cycle is substantially elongated, the remaining two nitrogen atoms set at the distance 9.309–10.552 Å. This model appears to correspond to a distorted chair conformation. In view of the exceptional narrowness of the internal space, the formation of a second bridge does not seem probable. That is why the elimination of the last 2NO<sub>3</sub> instead of metastable dimer Sc<sub>4</sub>O<sub>6</sub> will produce 2 mol of Sc<sub>2</sub>O<sub>3</sub>, in agreement with the experimental data.

The calculation of minimal potential energies for the aforementioned models shows that the difference between their numerical values for both tetramers, Sc<sub>4</sub>O<sub>4</sub>(NO<sub>3</sub>)<sub>4</sub> and Sc<sub>4</sub>O<sub>5</sub>(NO<sub>3</sub>)<sub>2</sub>, is, in an arbitrary scale, very small, that is –3.15 and –2.48 kJ mol<sup>–1</sup>, respectively. This is a clear indication that the corresponding compounds may be readily formed, and possess a certain stability, conclusion that is in agreement with the experimental curve of thermal analysis. The exceptionally high level of potential energy

for a hypothetical  $\text{Sc}_4\text{O}_6$  ( $305.0 \text{ kJ mol}^{-1}$ ) shows that the formation of a second bridge is practically impossible; hence the existence of such a compound is questionable. As to the final product,  $\text{Sc}_2\text{O}_3$ , as expected, its potential energy is the lowest of all compounds considered, that is  $-0.073 \text{ kJ mol}^{-1}$ . It is clear that the levels of potential energy, calculated by means of molecular mechanics, must not necessarily have any definite physical meaning in themselves. However, when considering a series of related structures, the method may be of help when interpreting the experimental findings in the absence of X-ray data for the interatomic distances and bond angles.

## Conclusions

1. The thermal decomposition of scandium nitrate is a complex process, which begins with the simultaneous condensation of 4 mol of the initial monomer  $\text{Sc}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$ .
2. The resulting cyclic tetramer  $\text{Sc}_4\text{O}_4(\text{NO}_3)_4 \cdot 24\text{H}_2\text{O}$  gradually loses azeotrope  $\text{H}_2\text{O}-\text{HNO}_3$ , and an intermediate oxynitrate  $\text{Sc}_4\text{O}_5(\text{NO}_3)_2$  is formed.
3. At higher temperature, this oxynitrate is destroyed leaving behind unstable dimer  $\text{Sc}_4\text{O}_6$  which is transformed into scandium oxide.
4. The molecular mechanics method used for comparison of the potential energies of consecutive products of thermal decomposition permits an evaluation of their stability and a proper interpretation of experimental data.
5. The models of intermediate oxynitrates represent a reasonably good approximation to the real structures.

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