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▶ **To cite this version:**

Sarah Petit, Stéphanie Morlens, Zeming Yu, Dominique Luneau, Guillaume Pilet, et al.. Synthesis and thermal decomposition of a novel zirconium acetato-propionate cluster: [Zr12]. Solid State Sciences, 2011, 13, pp.665-670. 10.1016/j.solidstatesciences.2010.12.041 . hal-00714973

HAL Id: hal-00714973
https://hal.science/hal-00714973

Submitted on 6 Jul 2012

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Synthesis and Thermal Decomposition of a novel Zirconium Acetato-Propionate cluster: [Zr12]

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Abstract

This work reports a novel Zirconium acetato-propionate complex herein called [Zr12] obtained by reaction of zirconium acetylacetonate $Zr(acac)_4$ with propionic acid. The molecular structure has been determined by X-ray diffraction on single crystals and proposed to be $[Zr_{12}(\mu_3\text{-}O)_{16}(CH_3CH_2CO_2)_{12}(CH_3CO_2)_8(\mu_2\text{-}CH_3CH_2CO_2)_4]$. This cluster involves oxo/hydroxo bonds in the direct surrounding of the metallic center. The decomposition of [Zr12] has been studied by thermal analysis and compared to $Zr(acac)_4$. Its temperature of decomposition is much lower than for acetylacetonate derivative. In consequence, the formation of ZrO_2 is easier from [Zr12] than from

$Zr(acac)_4$. This phenomenon highlights the influence of the molecular structure on the process of decomposition. The local surrounding of Zr in [Zr12] and in ZrO_2 are very close, while it is markedly different in $Zr(acac)_4$.This difference of environment of the metallic ions is at the origin of the huge difference of thermal behavior of both compounds.

KEYWORDS: propionates, chemical solution deposition, $La_2Zr_2O_7$, Zirconium cluster, MOD,

1. Introduction

Metal-organic decomposition (MOD) is one of the less expensive methods to produce thin oxide films. MOD needs liquid precursors which are deposited then dried as a film on a substrate. This film is then pyrolysed to get an oxide film well crystallized [1]. Numerous oxide films have been made with success by this simple, economic and scalable processing. For example, MOD is extensively used to produce high temperature superconducting tapes of $YBa_2Cu_3O_7$ (YBCO) [2,3,4], where $La_2Zr_2O_7$ (LZO) is often used as an efficient buffer layer with great benefit [5,6,7]. $La_2Zr_2O_7$ concerns many other fields of applications: radiation tolerance, ionic conductivity in doped compositions and thermal barrier coating. Therefore great interest is devoted to precursors of Zirconium and Lanthanum usable in MOD.

Among the wide panel of available precursors, the most currently used for MOD are carboxylates, alkoxides or β-diketonates. Metal carboxylates present a wide variety of bonding arrangements and offer considerable opportunities to develop precursor's chemistry [7,8,9]. In that context, propionates derivatives are friendly compounds. Indeed, they are generally stable in air contrary to acetates or alkoxides which are often reactive with moisture. However propionates derivatives are not commercially available and must be prepared specially.

Syntheses of carboxylates by various methods have already been described such as interchange of carboxylic acid in the case of manganites [10] or reaction of alkoxides with carboxylic acids [11]. Up to date, several papers have reported the use of "Zr and La propionates", for the preparation of LZO thin films by chemical routes (MOD) [6,12,13,14]. The authors explain that the solutions of precursors are conveniently obtained by dissolving stoechiometric quantities of La and Zr acetylacetonates (acac) in

propionic acid. Note that "acac" ligands are often used [15,16] as precursors and supposed not to be modified during their solubilization. Only recently, at least for Lanthanum and Zirconium precursors, Yu *et al.* and Knoth *et al.* have shown that the real deposited metal precursors should be in fact metal-propionate derivatives and not simply the "acac" derivatives dissolved in propionic acid [6,14]. However, structure and composition of propionate derivatives are poorly known although these parameters are expected to play a crucial role in the transformation of the precursor into an oxide, a key stage of the MOD process. Indeed, the molecular structure and particularity the atomic arrangement of the precursor is very important. It imposes the local composition and is probably a major factor of the transformation and crystallization of the oxide. These factors greatly impact the temperature of formation and the final microstructure of the oxide. In the case of precursors obtained by dissolving acetylacetonates derivatives in propionic acid, the local composition, thermal decomposition and chemical properties are expected to differ from the initial one. Until now, few efforts were made to correlate the nature of the precursors (acetylacetonate, acetate, propionate…) with the final oxide, here we want to contribute to this topic [1].

In this paper, we focus on a zirconium acetato-propionate [Zr12] prepared from $Zr(acac)_4$. Its composition and structure have been established by structural determinations on single crystals and confirmed by thermal analysis. Finally, this study shows that structure and atmosphere are crucial to control the stage of pyrolysis.

2. Experimental section

Zirconium(IV) acetylacetonate (Zirconium(IV) 2,4-pentanedionate, or $Zr(acac)_4$), were commercial products of Aldrich grade. The purity of $Zr(acac)_4$ was controlled by elemental analysis and corresponded within 4 wt % to the stoichiometric $Zr(acac)_4 \equiv Zr(C_5H_7O_2)_4$. Complementary X-ray analysis proved that the compound was well crystallized and had to the expected structure. No adsorbed H_2O was detected by FT-IR spectroscopy. Propionic acid (99.5 %) (also from Aldrich grade) was used

as received without any special precaution, except when specified. All reactions and manipulations were performed under aerobic conditions.

2.1 Synthesis

Crystals named [Zr12] were obtained by dissolution of 10.25 mmole of $Zr(acac)_4$ in a large excess of distilled propionic acid (270 mmole, 20 mL) at room temperature. After few minutes of stirring, the dissolution was still uncompleted. This mixture was heated at 160 °C for 1 h in order to obtain a stable yellow solution. The excess of propionic acid was evaporated under vacuum. Removal of the solvent left a crude product (2.42 g). This product was dried at 60 °C and resulted in a white powder. Considering the final product as $Zr(prop)_4$ i.e. $\equiv Zr(CH_3CH_2COO)_4$, the yield would be 70 %. Colourless cubic shaped crystals suitable for X-ray diffraction were obtained after dissolution of the crude product into propionic acid and slow diffusion of added acetone. The crystals were cubic and stable in air. Further X-ray diffraction revealed that these crystals were built with units involving 12 Zr atoms surrounded by O, C and H atoms and called hereafter [Zr12].

2.2 Single crystal X-ray diffraction

Crystal structure of compound [Zr12] was obtained by X-ray diffraction (MoKα radiation) at room temperature using a Nonius Kappa CCD diffractometer by means of the collect program Nonius [17]. More than 16000 reflections were collected. Lorentz-polarization correction, peak integration and background determination were carried out with the *Denzo* program [18]. Frame scaling and unit-cell parameters refinements were made through the "*scalepack program*" [18]. No absorption corrections were applied to the data set. All structures were solved by direct methods using the *SIR97* program [19] combined with Fourier difference calculations and refined against *F* using reflections with [$I/\sigma(I)>3$] with the *crystals* program [19]. All atomic displacements parameters for non-hydrogen atoms have been

refined anisotropically. The hydrogen atoms were located on the basis of the conformation of the supporting molecule.

2.3 Powder X-Ray diffraction

Powder X-Ray diffraction (XRD) experiments were carried out on a Siemens D5000 diffractometer (θ-2θ Bragg-Brentano geometry) with CuKα radiation. Patterns were recorded over a range of 5-30 °, using a step-scanning mode (0.01 ° step, 8 s of counting time).

2.4 Thermogravimetric analysis and differential thermal analysis

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) of test samples were performed on a coupled SETARAM TAG 16 system (Lyon-France). The system has two symmetrical furnaces requiring only very small Archimede corrections of the weight variations. TGA and DTA measurements were carried out in dense alumina crucibles. The heating device allows to make measurements of thermal behavior (TGA/DTA) on heating up to 1600 °C at various rates (2-20 °C min^{-1}), in a dynamic atmosphere of Ar or Ar-20 %O_2 (10 L h^{-1}). Samples of 10-40 mg were typically used.

2.5 Elementary chemical analisys

Chemical analyses of test samples were performed on small quantities (10-100 mg) at the Central service of analysis of CNRS (CNRS-Vernaison Lyon, France). Zr element was determined by ICP in solution (with a relative error of 2%), C and H were quantified by catharometric detection (relative error 0.3 %), O was determined by measuring CO_2 produced by reaction of the pyrolysed products on an active C.

3. Results and discussion

3.1 Elemental analysis

Analytical data of [Zr12] are summarized in Table 1. Experimental values obtained for the cluster [Zr12] were compared with the calculated values for $Zr(prop)_4$ i.e. ≡ $Zr(CH_3CH_2COO)_4$. The comparison with experimental values shows that the re-crystallized product is consistent with the formulae $Zr_{12}C_{74}H_{122}O_{72}$ and not with $Zr(prop)_4$ as we thought initially. Note that the observed yield i.e. 93 % is close to 100 % while only 70 % would be received if one assumes the formation of $Zr(prop)_4$. The small differences between theoretical and experimental values obtained for [Zr12] can be accounted to the presence of solvent within the crystalline structure (propionic or acetic acid) and in the final product (residual solvent of reaction).

Table 1

3.2 Structure of [Zr12] crystals

The structure of the herein called compound [Zr12] was established by single crystal X-ray diffraction. The crystallographic data and structure refinement parameters for [Zr12] are summarized in Table 2.

Table 2

This compound is centrosymmetric and crystallizes in the monoclinic space group, $P2_1/c$. Its structure consists of dodecanuclear clusters made of hexanuclear $[Zr_6(\mu_3\text{-}O)_8(CH_3CH_2CO_2)_6(CH_3CO_2)_4]$ sub-units (Zr6), linked by four propionate ligands in a bidentate mode (Figure 1).

Figure 1

The Zr6 moieties are composed of six zirconium atoms, six propionate ligands, four acetate ligands and eight oxo/hydroxo groups. The [Zr12] cluster crystallizes with four molecules of free acid: two of propionic acid and two of acetic acid. All zirconium atoms in the structure of $[Zr_6(\mu_3\text{-}$

$O)_8(CH_3CH_2CO_2)_6(CH_3CO_2)_4]$ are eight-coordinated but exhibit five different types of surrounding. This characteristic was not previously described and observed in the literature.

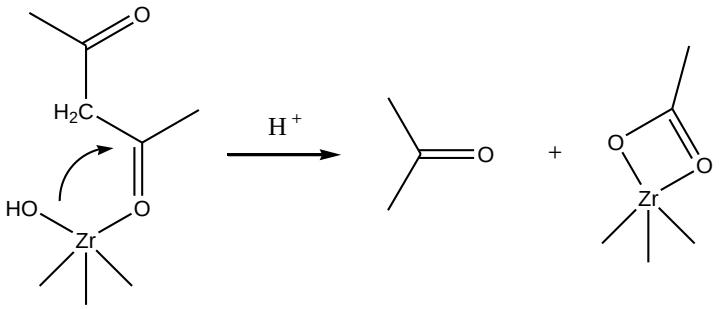
These characteristics are original and must be related to the synthesis procedure which has never been described in the literature yet. In this cluster, the assignment of the bridging oxygen atoms to μ_3-O or μ_3-OH groups is related to the different Zr-O bond lengths within $[Zr_6(\mu_3\text{-}O)_8(CH_3CH_2CO_2)_6(CH_3CO_2)_4]$. Several studies on Zr-O reveal some differences between Zr-(μ-O) and Zr-(μ-OH) lengths [20,21,22,23]. The O(23), O(24), O(26) and O(27) corresponding to the shortest Zr-O bond lengths [2.039(15)-2.136(12)Å)] constitute the μ_3-O (oxo) groups while the O(21), O(23), O(25) and O(28) with longer Zr-O bond lengths [2.193(15)-2.406(18)Å] represent the μ_3-OH (hydroxo) groups (Table 3). The full set of Zr-O bonds is listed in the electronic supplementary part. [Zr12] is similar to Zr(IV) clusters of general formula $[Zr_6O_4(OH)_4(RCO_2)_{12}]_2$ that were reported by others [11] using different ways of synthesis involving reaction of alkoxide (zirconium butoxide ≡ $Zr(OBu)_4$), with different carboxylic acids (acetic acid, propionic acid, vinylacetic acid…) in butanol. Hexanuclear zirconium complexes with formula $[Zr_6O_4(OH)_4(OOCR)_{12}]$ have also been synthesized by the same group with acrylic, methacrylic and benzoic acids [21]. No conversion was observed between the hexa and the dodecanuclear species but the nature of the ligand was found to influence the nuclearity of the clusters. Here the [Zr12] cluster is obtained by reacting $Zr(acac)_4$ with propionic acid. The propionate leads only to the dodecanuclear species.

Table 3

The presence in the same structure of acetato and propionato ligands [24] raises the question of their origin. Acetylacetone is one of the most probable sources of the acetato ligands. Splitting of acetylacetone to give acetic acid and acetone was previously reported for metallic acetylacetonate derivatives but it was described in basic medium [25,26]. In our case, the medium is acidic but zirconium can be hydrolyzed [26,27] and it has been suggested that this can initiate splitting of acetylacetone (Equation 1). The source of hydroxo and oxo groups may be questionable. Then a source

of water should explain the hydrolysis and condensation into $[Zr_{12}(\mu_3\text{-}O)_{16}(CH_3CH_2CO_2)_{12}(CH_3CO_2)_8(\mu_2\text{-}CH_3CH_2CO_2)_4]$ clusters.

As described in the experimental section, the propionic acid was distilled before use but this step was probably insufficient to remove all the water. Moreover the synthesis was carried out under aerobic conditions. Both factors contribute to the presence of water and thus to the hydrolysis of Zr(IV).



Equation 1

Nevertheless, these phenomena seem insufficient to complete the chemical formula, so the water may also come from *in situ* reaction. The (1:1) reaction of acetylacetonate with propionic acid suggests the formation of an ester and water as an internal source of hydrolysis of Zr. This reaction is suspected to be at the origin of the yellow color of the solution resulting from the reaction of acetylacetone with propionic acid while the [Zr12] crystals are colorless. This characteristic indicates clearly the formation of a yellow under-product during the formation of [Zr12].

3.3 X-ray powder diffraction

XRD were perfomed on the [Zr12] cluster and $Zr(acac)_4$ for comparison. The measured powder diffraction of [Zr12] and $Zr(acac)_4$ are showed on Figure 2. The measured diagrams of [Zr12] cluster and $Zr(acac)_4$ are completely different. This study confirms the conversion of the acetylacetonate into acetato- propionate.

Figure 2

3.4 Thermal decomposition of $Zr(acac)_4$ and [Zr12]

It was important to study the thermal decomposition of [Zr12], and to compare it with the initial source of Zirconium. The thermal decomposition of $Zr(acac)_4$ under Ar flow is plotted versus temperature in Figure 3.

Figure 3

It is composed of a melting process at 195°C prior a sharp decomposition where ~ 39 % of the total weight loss occurs (noted I in Table 4). This process ends up at 280 °C (end of the endothermic peak) and is followed by two progressive steps (300-500 °C). The last step proceeds at 507 °C (step III) and is characterized by a small exothermic peak associated with the onset of crystallization. Then a progressive weight loss is detected extending up to 1350 °C where a last step is observed (step IV). The expected weight loss corresponding to the stoechiometric formulae (74.7 %) is slightly different (3 %) from the measured weight loss at 1500 °C due to non decomposed part and/or residual carbon. It is important to stress that the weak weight decrease of the step IV extending from 500 °C to 1350°C is misleading. This step is not the end of the decomposition of $Zr(acac)_4$ which is completed only over 1500°C. This very flat step corresponds to an amorphous product with a composition deduced from the weight loss close to $ZrOCO_3$.

Table 4

It is interesting to note that the thermal decomposition performed under Ar is significantly different from the thermal behavior under Ar-20%O_2. In this latter case, the decomposition ends up at 580 °C by the formation of ZrO_2 (weight loss 74.5 %), Figure 3. The thermal weight evolution is very close to results of other study suggesting that a small quantity of residual oxygen was present in this last experiment [28]. It also proves that oxygen has a tremendous effect on the decomposition of $Zr(acac)_4$ with a complete conversion to ZrO_2 at rather low temperature. In absence of oxygen in the gaseous

phase, the formation of a very stable compound under neutral conditions is favored where as the oxolation of Zr is prevented.

The thermal decomposition of the complex [Zr12] performed under Ar versus temperature is given on Figure 4. It is characterized by a first decomposition step (26 % of the total weight loss) at 194 °C occurring simultaneously with the melting process of the compound (the melting at this temperature was also confirmed by the Köfler method). A second step is visible at 331 °C with a weight loss of 25.3 % followed by the crystallization at 515 °C where almost all the weight loss has been achieved. No variation of mass is detected from 600 to 1100 °C indicating that the decomposition is total above 600 °C. It is a characteristic difference with regard to $Zr(acac)_4$.

Figure 4

The total weight loss is 56.1 % which is not compatible with $Zr(acac)_4$ and proves that $Zr(acac)_4$ has been modified during the preparation of the solution in agreement with the results of the previous sections. Considering the formation of a "simple Zr propionate" ≡ $Zr(CH_3CH_2COO)_4$, the decomposition of this compound would give a total weight loss of 67.8 %, which is considerably larger than the observed value. This clearly indicates that [Zr12] does not have the composition of "the simple propionate". Another indication along the same direction is the temperature at which decomposition ends up. By analogy with $Zr(acac)_4$ treated under oxygenated atmosphere, the rather low temperature at which the weight loss finishes suggests that Zr has already been oxolated in the [Zr12] precursor. The transformation of [Zr12] into ZrO_2 at low temperature occurs without requiring oxygen in the gaseous phase.

As already mentioned, it is useful to underline the big difference between $Zr(acac)_4$ and [Zr12]. In the first one, the metal atom is not oxolated like in [Zr12]. In the later, Zr^{4+} ions adopt a configuration close

to ZrO_2 and therefore changes to the oxide at a rather low temperature compared to $Zr(acac)_4$. Oxygen presents in the gas phase has got a huge effect in this later case, probably inducing faster oxolation in the temperature range 200-400 °C resulting in the crystallization of ZrO_2 at low temperature.

4. Conclusions

A new zirconium acetato-propionate cluster bas been produced by reacting $Zr(acac)_4$ with propionic acid. Its structure has been identified and discussed. The proposed formulae $[Zr_{12}(\mu_3\text{-}O)_{16}(CH_3CH_2CO_2)_{12}(CH_3CO_2)_8(\mu_2\text{-}CH_3CH_2CO_2)_4]$ shows differences compared to propionates synthesized by other methods. The thermal decomposition of this cluster has been studied, it shows great differences with $Zr(acac)_4$. This difference has been ascribed to the presence of oxo/hydroxo bridges in the cluster offering to the Zr metallic ion a surrounding closed to the oxide.

Acknowledgments

This work has been supported by a European Found for Regional Developments (FEDER: Superfacts n° 2009-017-000008). Financial support from the ANR Madisup is also acknowledged. Single crystal X-ray diffraction studies were performed at the "Centre de Diffractométrie Henri Longchambon", Université Claude Bernard Lyon 1-France.

Additional data

X-ray crystallographic files in CIF format for the structure determinations of $[Zr_{12}(\mu_3\text{-}O)_{16}(CH_3CH_2CO_2)_{12}(CH_3CO_2)_8(\mu_2\text{-}CH_3CH_2CO_2)_4]$ (Zr12). This material is available free of charge via the Internet at http://pubs.acs.org.

Figures caption

Figure 1. Structure of [Zr12], hydrogen atoms have been removed for clarity.

Figure 2. XRD patterns: (a) [Zr12] and (b) $Zr(acac)_4$.

Figure 3. TGA and DTA of $Zr(acac)_4$, heating rate 10 °C.min^{-1} : (a) under Ar flow; (b) under Ar-20%O_2.

Figure 4. TGA and DTA of [Zr] under Ar, heating rate 10 °C.min^{-1}.

Tables

Table 1. Elemental analysis of [Zr12] compared to $Zr(prop)_4 \equiv Zr(CH_3CH_2COO)_4$.

Table 2. Crystal data and structure refinement parameters for [Zr12].

Table 3. Selected interatomic distances (Å) for [Zr12]

Table 4. Thermal analysis of $Zr(acac)_4$and [Zr12]. The analysis is made under Ar flow, heating rate 10 °C.min^{-1}.

References

[1] R. W. Schwartz, Chem. Mater. 9 (1997) 2325.

[2] M. P. Siegal, P. G. Clem, J. T. Dawley, R. J. Ong, M. A. Rodrigez, D. L. Overmyer, Appl. Phys. Lett. 80 (2002) 2710.

[3] T. Araki, Y. Takahashi, K. Yamahiwa, T. Yuasa, Y. Iijima, K. Yakeda, S. B. Kim, Y. Yamada, I. Hirabayashi, IEEE Trans. App. Supercond., 11 (2001) 2869.

[4] X. Obradors, T. Puig, A. Pomar, F. Sandiumenge, N. Mestres, M. Coll, A. Cavallaro, N. Romà, J. Gázquez, J. C. González, J. Gutierrez, A. Palau, K. Zalamova, S. Morlens, A. Hassini, M. Gibert, S. Ricart, J. M. Moreto, S. Piñol, D. Isfort, J. Bock, Sci. Technol. 19 (2006) S13-S26.

[5] J. W. Seo, J. Fompeyrine, A. Guiller, G. Norga, C. Marchiori, H. Siegwart, J. P. Locquet, Appl. Phys. Lett. 83 (2003) 5211.

[6] K. Knoth, R. Hühne, S. Oswald, L. Schultz, B. Holzapfel, Acta Mater. 55 (2007) 517.

[7] T. Caroff, S. Morlens, A. Abrutis, M. Decroux, M. Z. Saltyte, P. Chadouet, L. Porcar, C. Jimenez, P. Odier, F. Weiss, Supercond. Sci. and Technol. 21 (2008) 075007.

[8] X. Obradors, T. Puig, A. Pomar, F. Sandiumenge, S. Piñol, N. Mestres, O. Castaño, M. Coll, A. Cavallaro, A. Palau, J. Gázquez, J. C. González, J. Gutiérrez, N. Romà, S. Ricart, J. M. Moretó, M. D.Rossell, G. Van. Tendeloo, Supercond. Sci. and Technol. 17 (2004) 1055.

[9] M. Paranthaman, S. Sathyamurthy, L. Heatherly, P. M. Martin, A. Goyal, T. Kodenkandatha, X. Li, C. L. H. Thieme, M. Rupich, W. Physica C 529 (2006) 445.

[10] U. Hasenkox, C. Mitze, R. J. Waser, J. Am. Ceram. Soc. 80 (1997) 2709.

[11] M. Puchberger, F. R. Kogler, M. Jupa, S. Gross, H. Fric, G. Kickelbick, U. Schubert, Eur. J. Inorg. Chem. 16, (2006) 3283.

[12] L. Molina, K. Knoth, S. Engel, B. Holzapfel, O. Eibl, Supercond. Sci. Technol. 19 (2006) 1200.

[13] S. Engel, K. Knoth, R. Hühme, L. Schultz, B. Holzapfel, Supercond. Sci. Technol. 18 (2005)

1385.

[14] Z. M. Yu, P. Odier, L. Ortega, L. Zhou, P. X. Chang, A. Girard, Materials Sci. Engineering B 130 (2006) 126.

[15] O. Castaño, A. Palau, J. C. Gonzàlez, S. Piñol, T. Puig, N. Mestres, F. Sandiumenge, X. Obradors, Physica C 372 (2002) 806.

[16] A. Cavallaro, O. Castaño, A. Palau, J. C. Gonzalez, M. D. Rossel, T. Puig, F. Sanduimenge, N. Mestres, S. Pinol, X. Obradors, J. European Ceram. Soc. 24 (2004) 1831.

[17] Nonius; COLLECT, B. V. Nonius, Delft, The Netherland, 1997-2001.

[18] Otwinowski, Z.; Minor, W.; *Methods in Enzymology*; Academic Press, New York, 1997.

[19] C. Cascarano, A. Altomare, C. Giacovazzo, A. Guagliardi, A. G. G. Moliterni, D. Sliliqi, M. C. Burla, G. Polidori, M. Camlli, Acta. Crystallogr. A52 (1996) C-79.

[20] D. J. Watkin, C. K. Prout, J. R. Carruthers, P. W. Betteridge, Cristal Issue 11, Chemical Cristallography Laboratory, Oxford, UK, 1999.

[21] G. Kickelbick, P. Wiede, U. Schuber, Inorg. Chim. Acta. 284 (1999) 1.

[22] M. Y. Reza, H. Matsushima, M. Koikawa, M. Nakashima, T. Tokii, Polyhedron 18 (1999) 787.

[23] P. Piszczek, A. Radtke, A. Wojtczak, T. Muziol, J. Chojnacki, Polyhedron 28 (2009) 279.

[24] P. Piszczek, A. Radtke, A. Wojtczak, T. Muziol, J. Chojnacki, Polyhedron 26 (2009) 679.

[25] O. Poncelet, L. G. Hubert-Pfalzgraf, J. C. Daran, Polyhedron 9 (1990) 1305.

[26] G. A. Seisenbaeva, E. V. Suslova, M. Kritikos, V. G. Kessler, L. Rapenne, M. Andrieux, F. Chassagneux, S. Parola, J. Mater. Chem. 14 (2004) 3150.

[27] M. Henry, J.-P. Jolivet, J. Livage, Structure and Bonding 77 (1992) 153.

[28] H. M. Ismail, Powder Technol. 85 (1995) 253.

Table

Table 1 Elemental analysis of [Zr12] compared to $Zr(prop)_4 \equiv Zr(CH_3CH_2COO)_4$

	C	**H**	**Zr**
[Zr12][a]	**30.54**	**4.67**	**28.8**
	27.27	*3.77*	*33.59*
$Zr(prop)_4$	*37.58*	*5.25*	*23.78*

[a] From composition of [Zr12] (see section Structure of [Zr12])

[b] Bold measured data, italic from steochiometric formulea

Table 2 Crystal data and structure refinement parameters for[Zr12]

	[Zr12]
Formula	$C_{74}H_{122}O_{72}Zr_{12}$
M / g mol^{-1}	3258.38
Cryst. Syst.	Monoclinic
Space group	$P2_1/c$ (N°14)
a / Å	19.42 (2)
b / Å	21.95 (2)
c / Å	17.59 (2)
α / deg.	90
β / deg.	100.99 (2)
γ / deg.	90
V / Å^3	7363 (14)
Z	2
T / K	298
λ (MoKα) / Å	0.71073
D / g cm^{-3}	1.563
μ / mm^{-1}	0.90
Collected Reflections	16496
Independent Reflections	9720
R(F²), I>2σ(Fo)	0.1193
R_w (F²)	0.1299
S	1.15
Δρmax/Δρmin (e Å^{-3})	2.48/-1.33

Table 3 Selected interatomic distances (Å) for [Zr12]

Zr1—O2i	2.237 (13)	Zr4—O22	2.257 (17)
Zr1—O12i	2.231 (13)	Zr4—O24	2.101 (17)
Zr1—O21	2.363 (15)	Zr4—O25	2.25 (2)
Zr1—O23	2.112 (12)	Zr4—O27	2.077 (13)
Zr1—O26	2.064 (14)	Zr4—O31	2.26 (2)
Zr1—O28	2.297 (13)	Zr4—O32	2.32 (2)
Zr1—O72	2.201 (14)	Zr4—O82	2.23 (2)
Zr1—O92	2.248 (14)	Zr4—O122	2.22 (2)
Zr2—O21	2.194 (17)	Zr5—O1	2.203 (16)
Zr2—O24	2.136 (16)	Zr5—O22	2.397 (15)
Zr2—O25	2.209 (17)	Zr5—O23	2.067 (13)
Zr2—O26	2.060 (13)	Zr5—O27	2.093 (14)
Zr2—O51	2.33 (2)	Zr5—O28	2.323 (13)
Zr2—O52	2.31 (2)	Zr5—O102	2.245 (16)
Zr2—O62	2.226 (18)	Zr5—O111	2.229 (16)
Zr2—O71	2.24 (2)	Zr5—O121	2.207 (17)
Zr3—O21	2.193 (15)	Zr6—O11	2.233 (16)
Zr3—O22	2.241 (16)	Zr6—O25	2.406 (18)
Zr3—O23	2.083 (12)	Zr6—O26	2.103 (14)
Zr3—O24	2.128 (17)	Zr6—O27	2.039 (15)
Zr3—O41	2.29 (2)	Zr6—O28	2.295 (14)
Zr3—O43	2.335 (17)	Zr6—O61	2.248 (16)
Zr3—O91	2.203 (19)	Zr6—O81	2.199 (19)
Zr3—O112	2.221 (19)	Zr6—O101	2.253 (16)

[a] Symmetry operators for the generated atoms: -*x*, -y + 1, -z + 1.

Table 4 Thermal analysis of $Zr(acac)_4$ and [Zr12]. The analysis is made under Ar flow, heating rate 10 $K.min^{-1}$[a].

		I	II	III	IV	V
$Zr(acac)_4$	T peak (°C)	197		524		
	Weight loss (%)	39	16.8	3	4.5	8.3
[Zr12]	T peak (°C)	194	331	515		
	Weight loss (%)	26	25.3	4.5	0.3	

[a] Weight loss is taken at the end of the peak

Figure

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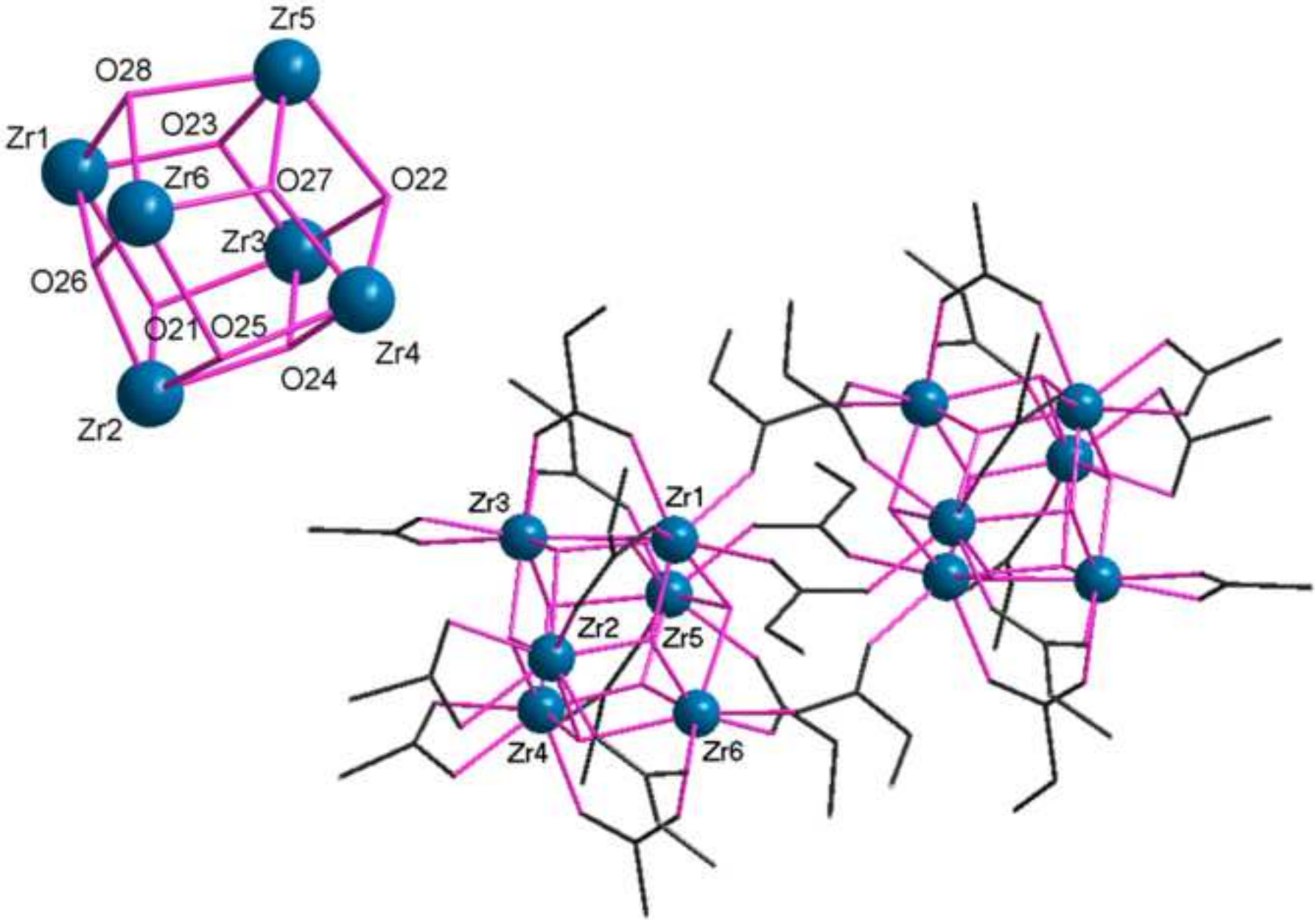

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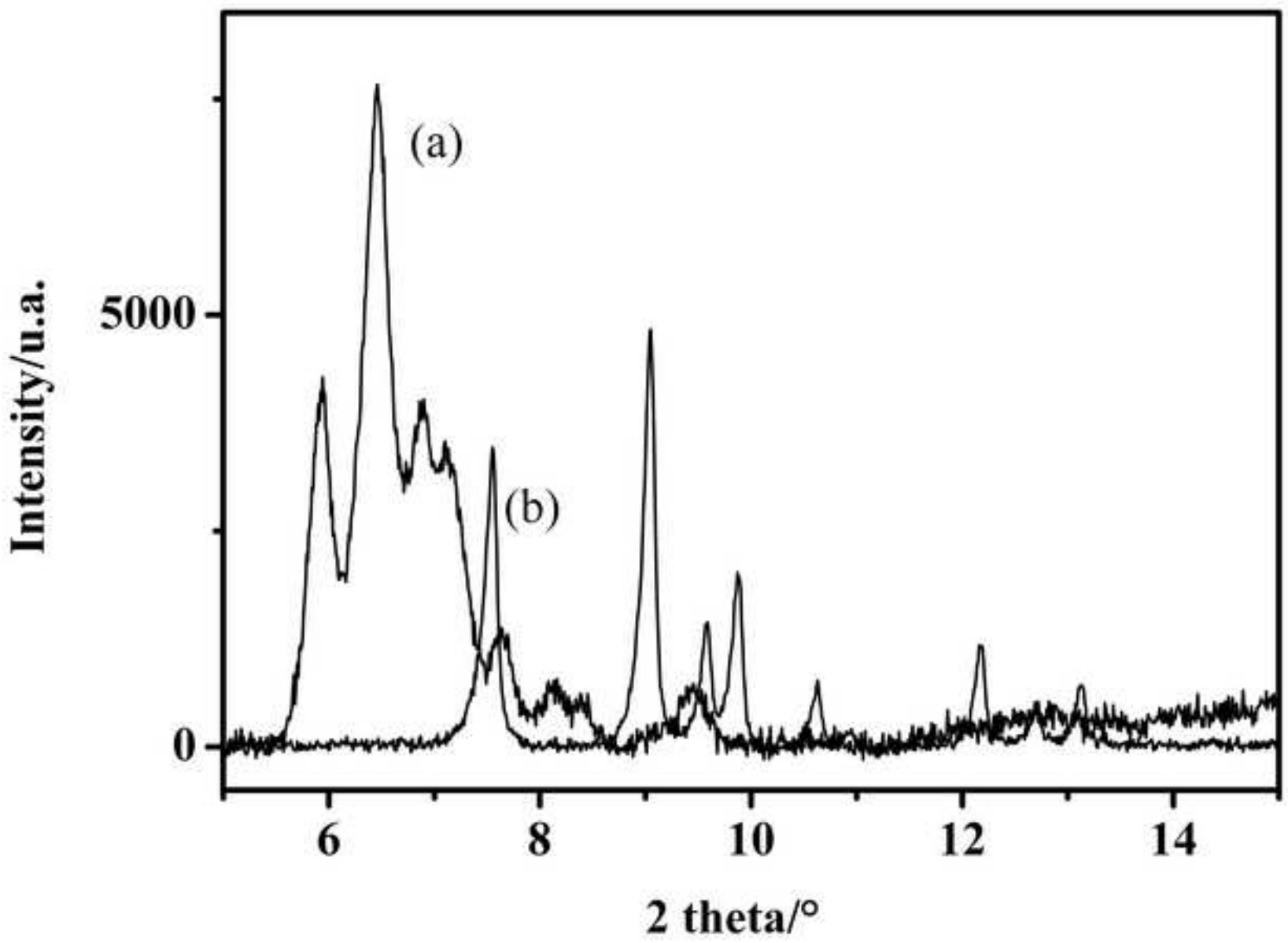

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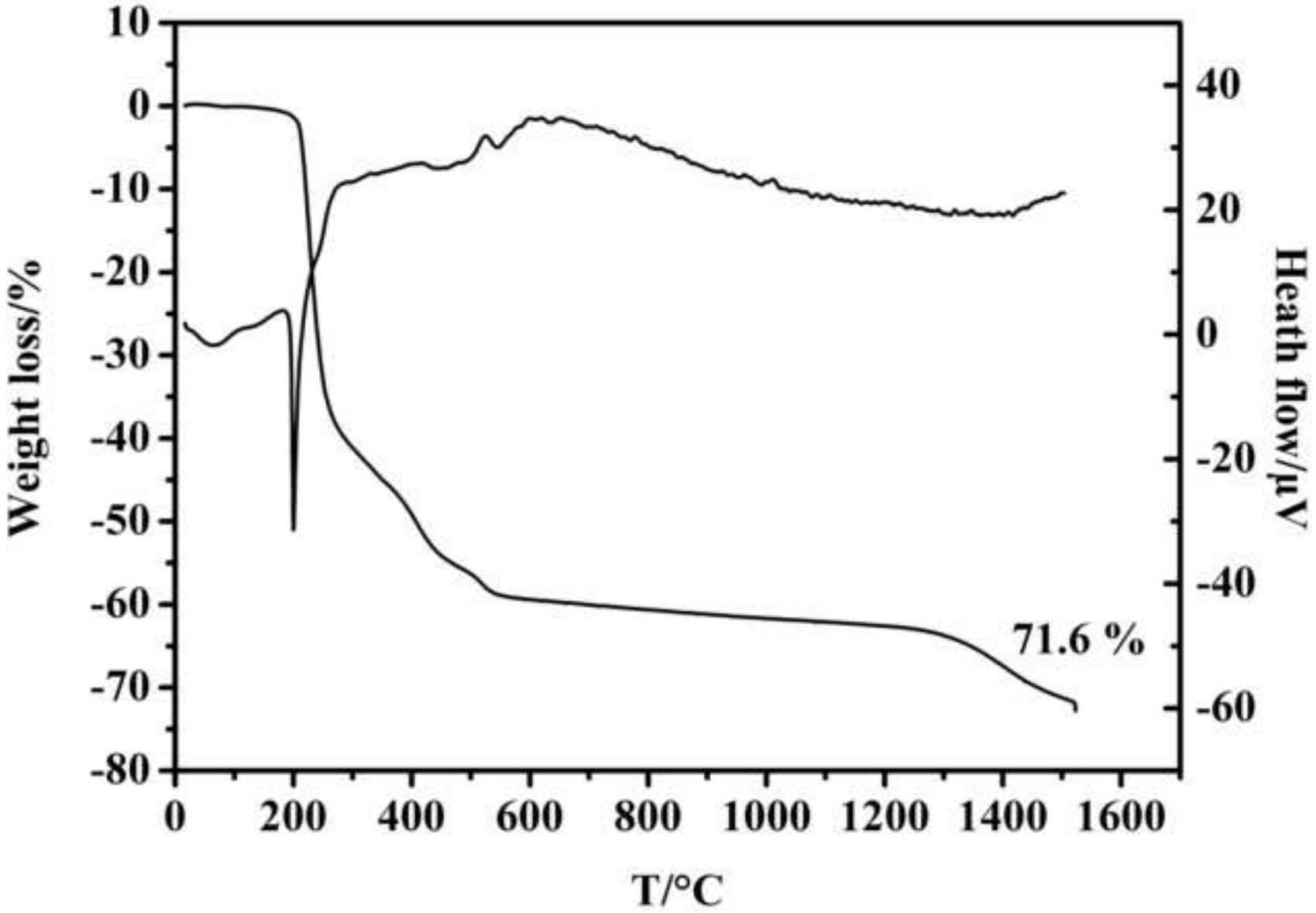

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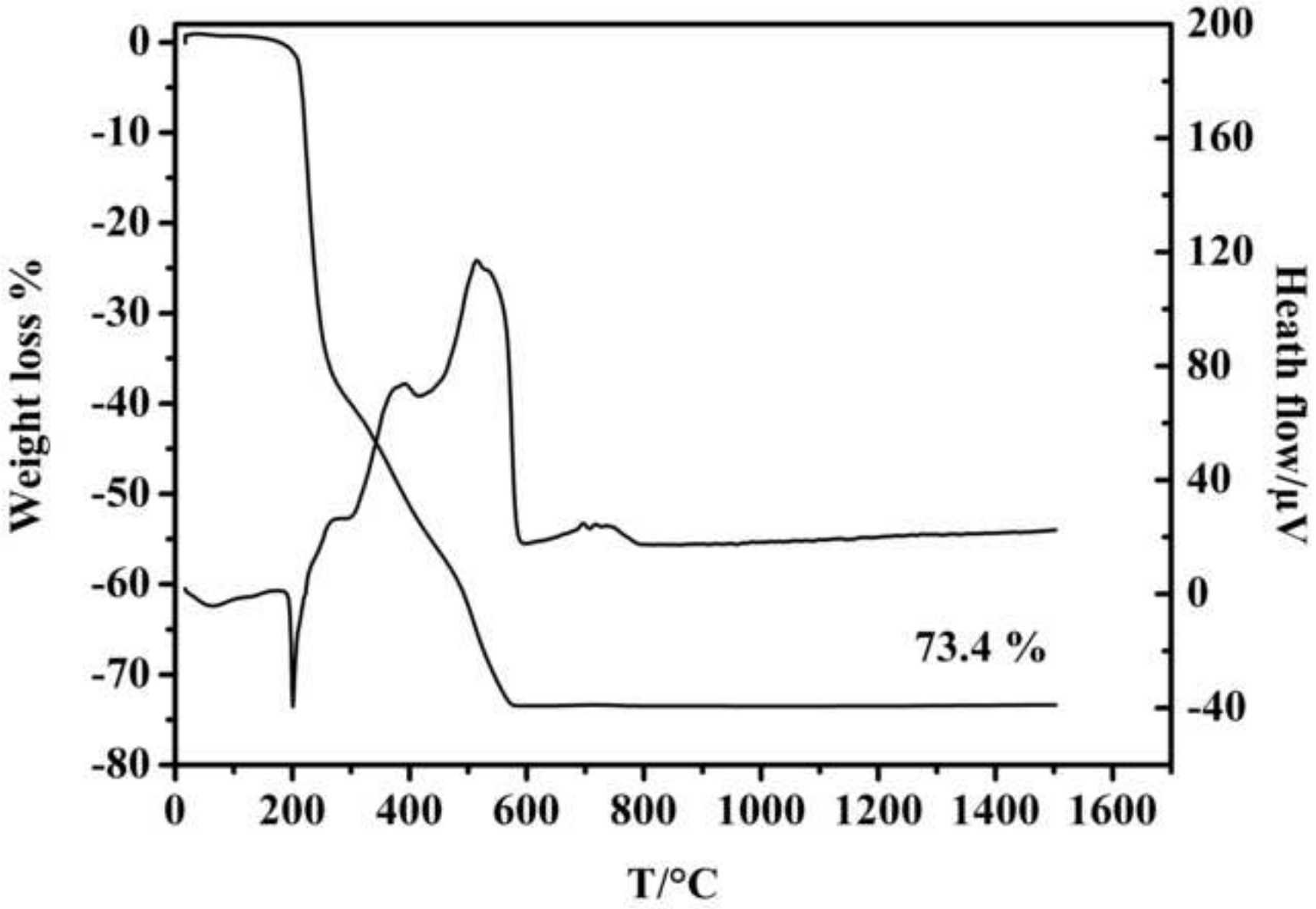

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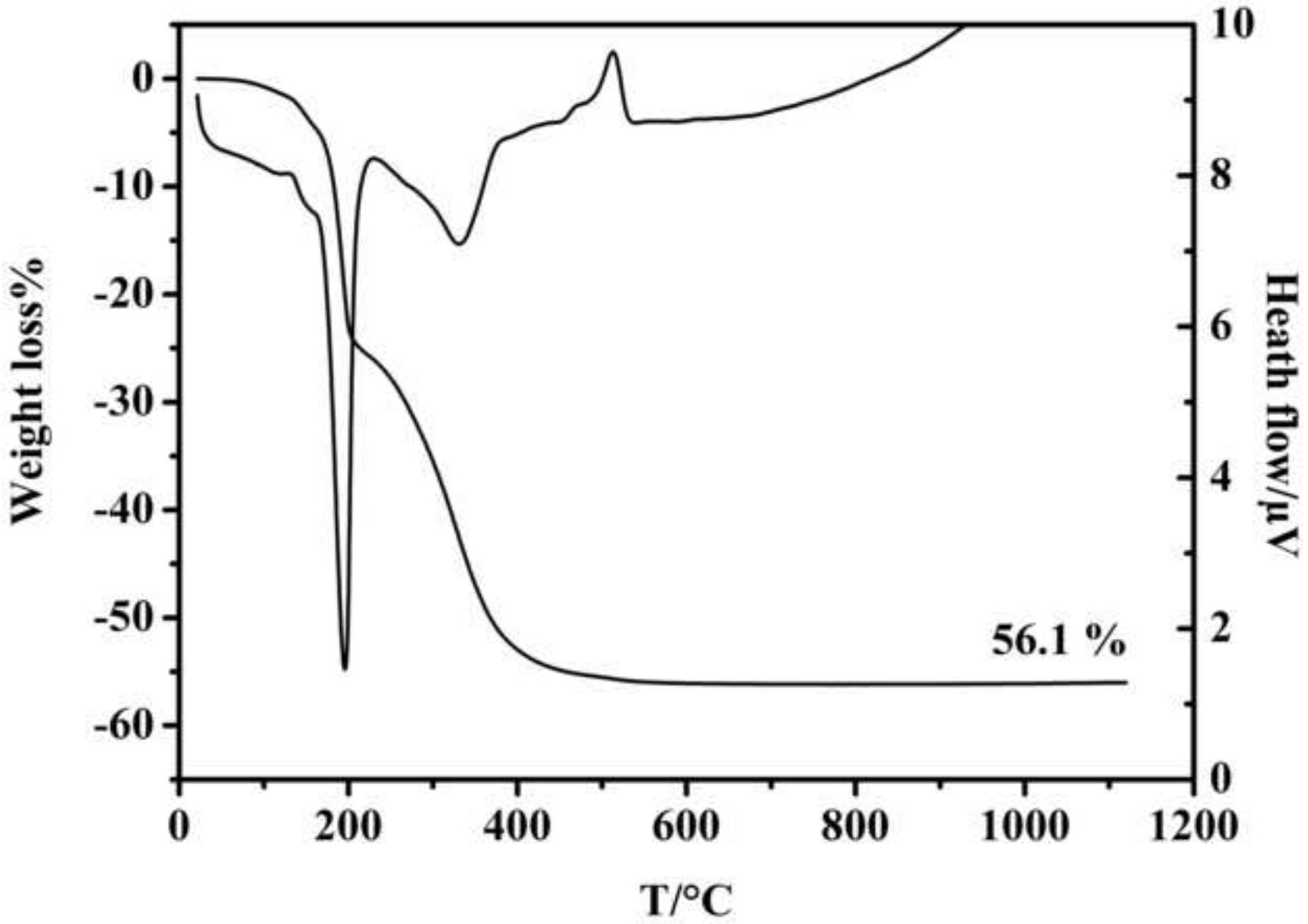

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