

Synthesis and Structures of Cobalt-Expanded Zirconium- and Cerium-Oxo Clusters as Precursors for Mixed-Metal Oxide Thin Films

Maximilian Seiß,^{a,b,‡} Jonas Lorenz,^{a,‡} Sebastian Schmitz,^a Marco Moors,^a Martin Börner,^b and Kirill Yu. Monakhov*^a

^a Leibniz Institute of Surface Engineering (IOM), Permoserstraße 15, 04318 Leipzig, Germany
E-mail: kirill.monakhov@iom-leipzig.de

^b Institut für Anorganische Chemie, Universität Leipzig, Johannisallee 29, 04103 Leipzig, Germany

‡ Authors contributed equally to this work.

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Additional experimental procedures

Synthesis of 1 at r.t. Freshly prepared $[\text{Ce}_6\text{O}_4(\text{OH})_4(\text{piv})_{12}]$ (0.195 g; 0.09 mmol; 1.0 eq), $\text{Co}(\text{piv})_2$ (0,200 g; 0.8 mmol; 8.9 eq), and *N*-butyldiethanolamine (0.17 mL; 1.0 mmol; 11 eq) were dissolved in MeCN (10 mL). Triethylamine (0.05 mL, 0.36 mmol; 4.0 eq) was added and the reaction mixture was stirred at r.t. for 2 h. No gas formation was observed during the reaction. The resulting dark-green solution was filtered off to remove undissolved starting material and the filtrate was stored in a sealed vial at ambient conditions. Compound **1** was obtained as brown-red crystals after one day. The product was collected by filtration, washed with ice-cold MeCN and a small amount of *n*-pentane, and dried in air. Yield of the air-dried product: 69 mg (21 % based on $[\text{Ce}_6\text{O}_4(\text{OH})_4(\text{piv})_{12}]$).

Synthesis of 1 without NEt_3 . Freshly prepared $[\text{Ce}_6\text{O}_4(\text{OH})_4(\text{piv})_{12}]$ (0.195 g; 0.09 mmol; 1.0 eq), $\text{Co}(\text{piv})_2$ (0,200 g; 0.8 mmol; 8.9 eq), and *N*-butyldiethanolamine (0.17 mL; 1.0 mmol; 11 eq) were dissolved in MeCN (10 mL). The reaction mixture was stirred under refluxing conditions for 2 h. The resulting dark-green solution was filtered off and the filtrate was stored in a sealed vial at ambient conditions. Compound **1** was obtained as brown-red crystals after one day. The product was collected by filtration, washed with ice-cold MeCN and a small amount of *n*-pentane, and dried in air. Yield of the air-dried product: 40 mg (12 % based on $[\text{Ce}_6\text{O}_4(\text{OH})_4(\text{piv})_{12}]$).

Synthesis of 1 under Ar atmosphere. The reaction was carried out under an atmosphere of dry, O_2 -free argon using standard dual manifold Schlenk line techniques with a rotary oil pump. Freshly prepared $[\text{Ce}_6\text{O}_4(\text{OH})_4(\text{piv})_{12}]$ (0.195 g; 0.09 mmol; 1.0 eq), $\text{Co}(\text{piv})_2$ (0,200 g; 0.8 mmol; 8.9 eq), and *N*-butyldiethanolamine (0.17 mL; 1.0 mmol; 11 eq) were dissolved in dry MeCN (10 mL). The reaction mixture was stirred under refluxing conditions for 2 h. A pink powder (**1a**, 42 mg) precipitated, and the resulting green-brown solution was filtered off and the filtrate was stored in a sealed vial at ambient conditions. Compound **1** was obtained as brown-red crystals after one day. The product was collected by filtration, washed with ice-cold MeCN and a small amount of *n*-pentane, and dried in air. Yield of the air-dried product: 51 mg (16 % based on $[\text{Ce}_6\text{O}_4(\text{OH})_4(\text{piv})_{12}]$).

Synthesis of 2 at r.t. Freshly prepared $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{ib})_{12}(\text{H}_2\text{O})]\cdot 3\text{Hib}$ (0.180 g; 0.09 mmol; 1.0 eq) and $\text{Co}(\text{ib})_2$ (0,200 g; 0.80 mmol; 9.0 eq) were dissolved in MeCN (10 mL). Triethylamine (0.05 mL; 0.36 mmol; 4.0 eq) was added and the reaction mixture was stirred at r.t. for 2 h. The resulting violet solution was filtered off and the filtrate was stored in a sealed vial at ambient conditions. Compound **2** was obtained as violet crystals after one day. The product was collected by filtration, washed with ice-cold MeCN and a small amount of *n*-pentane, and dried in air. Yield of the air-dried product: 0.19 g (69 % based on $[\text{Zr}_6\text{O}_4(\text{OH})_4(\text{ib})_{12}(\text{H}_2\text{O})]\cdot 3\text{Hib}$).

IR spectra

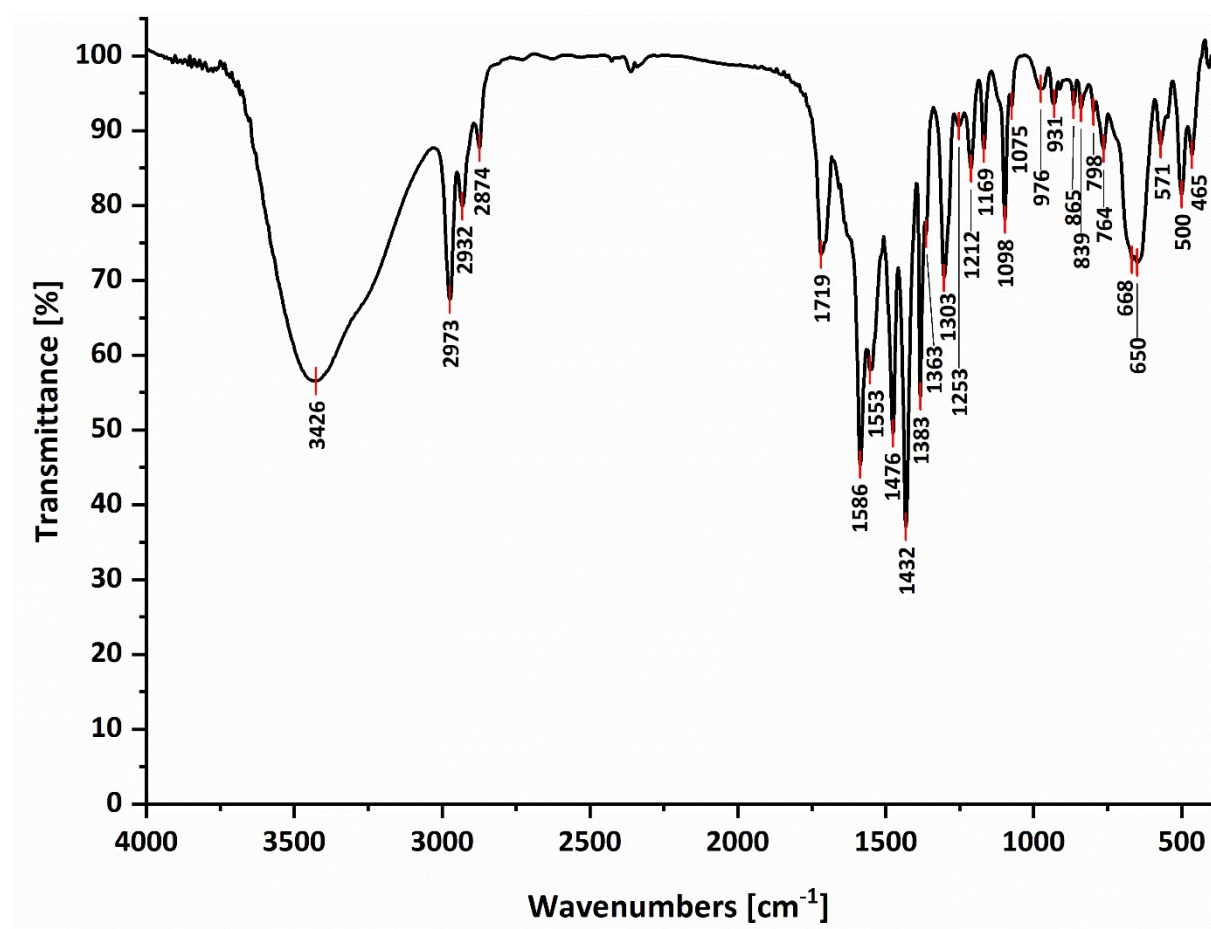


Figure S1: FTIR spectrum of the [Zr₆O₄(OH)₄(ib)₁₂(H₂O)]·3Hib precursor measured in KBr pellets in the range of 4000—400 cm⁻¹.

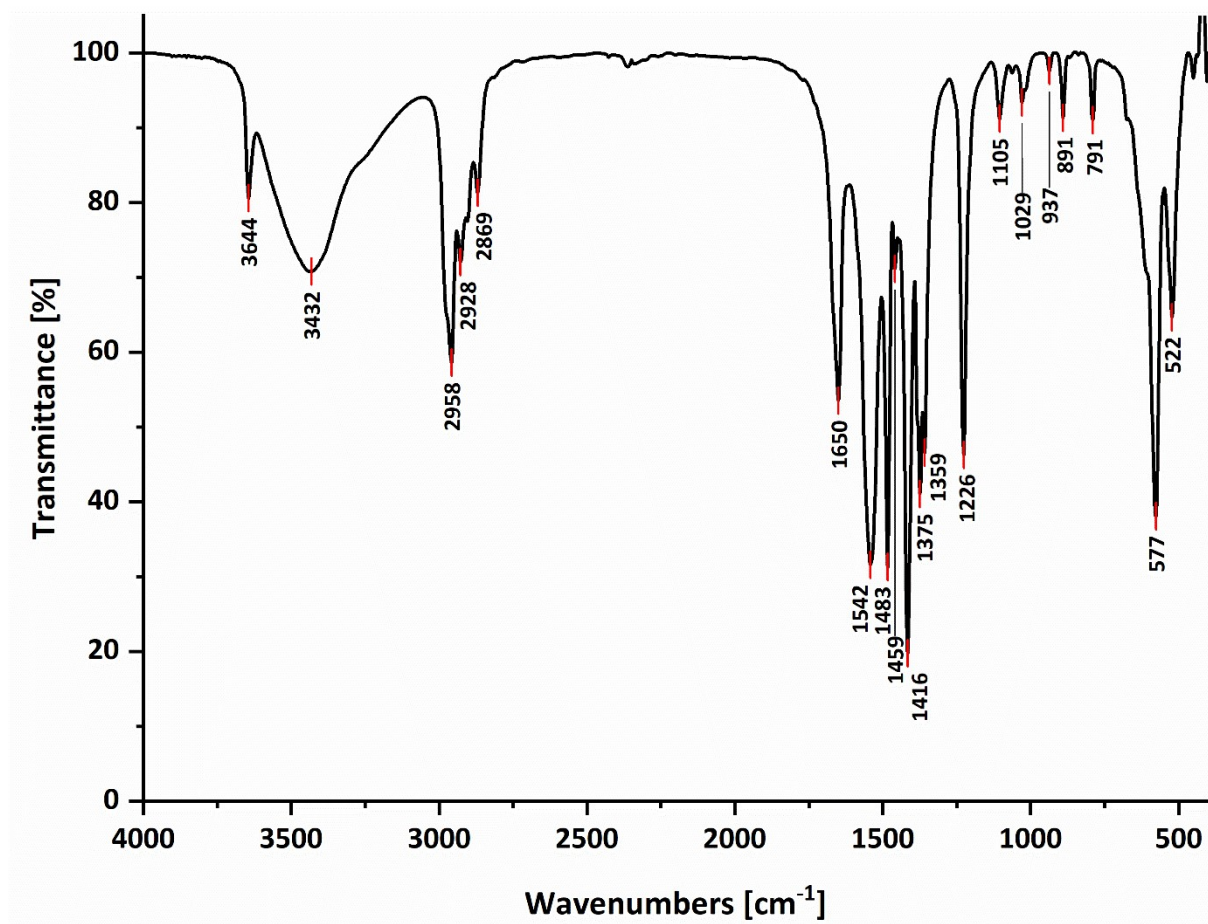


Figure S2: FTIR spectrum of the [Ce₆O₄(OH)₄(piv)₁₂] precursor measured in KBr pellets in the range of 4000—400 cm⁻¹.

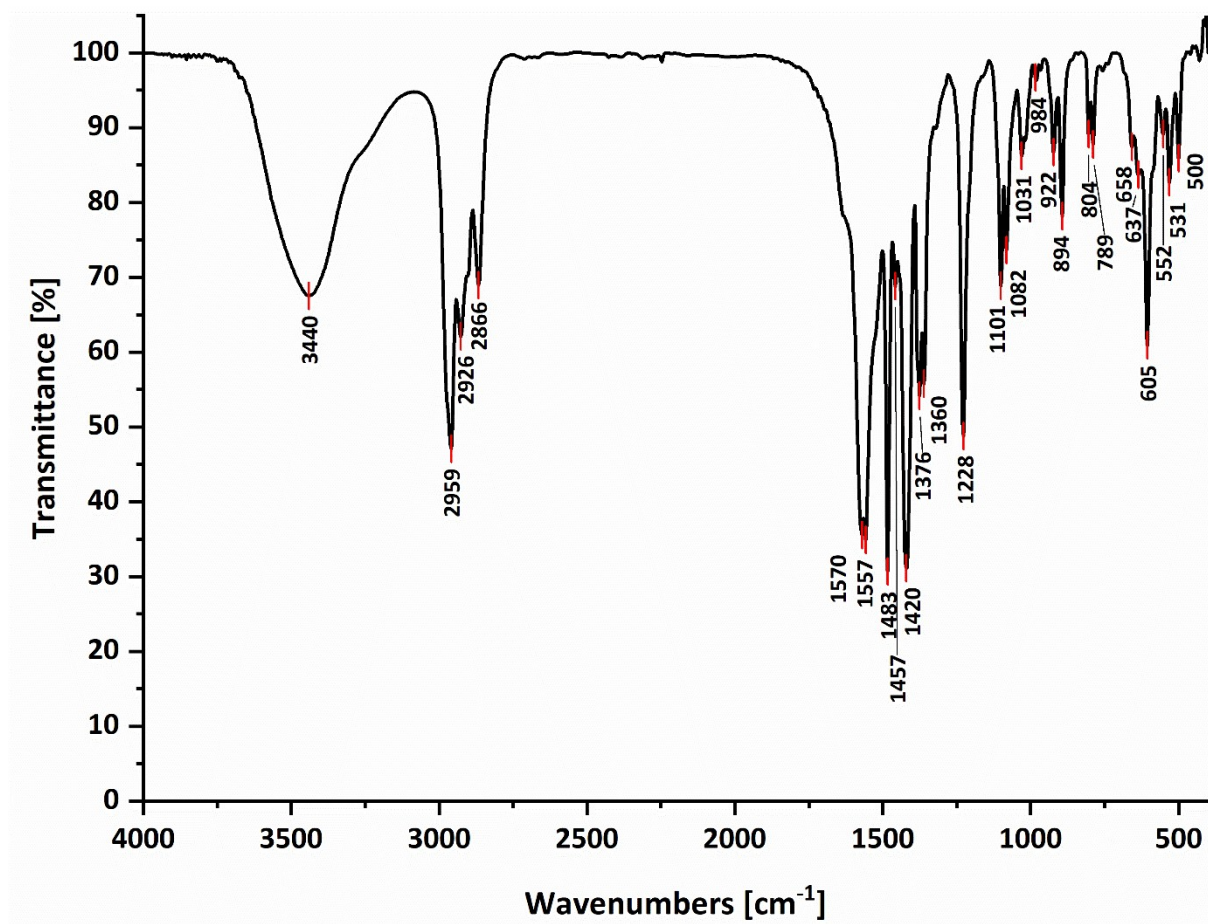


Figure S3: FTIR spectrum of **1** measured in KBr pellets in the range of 4000—400 cm⁻¹.

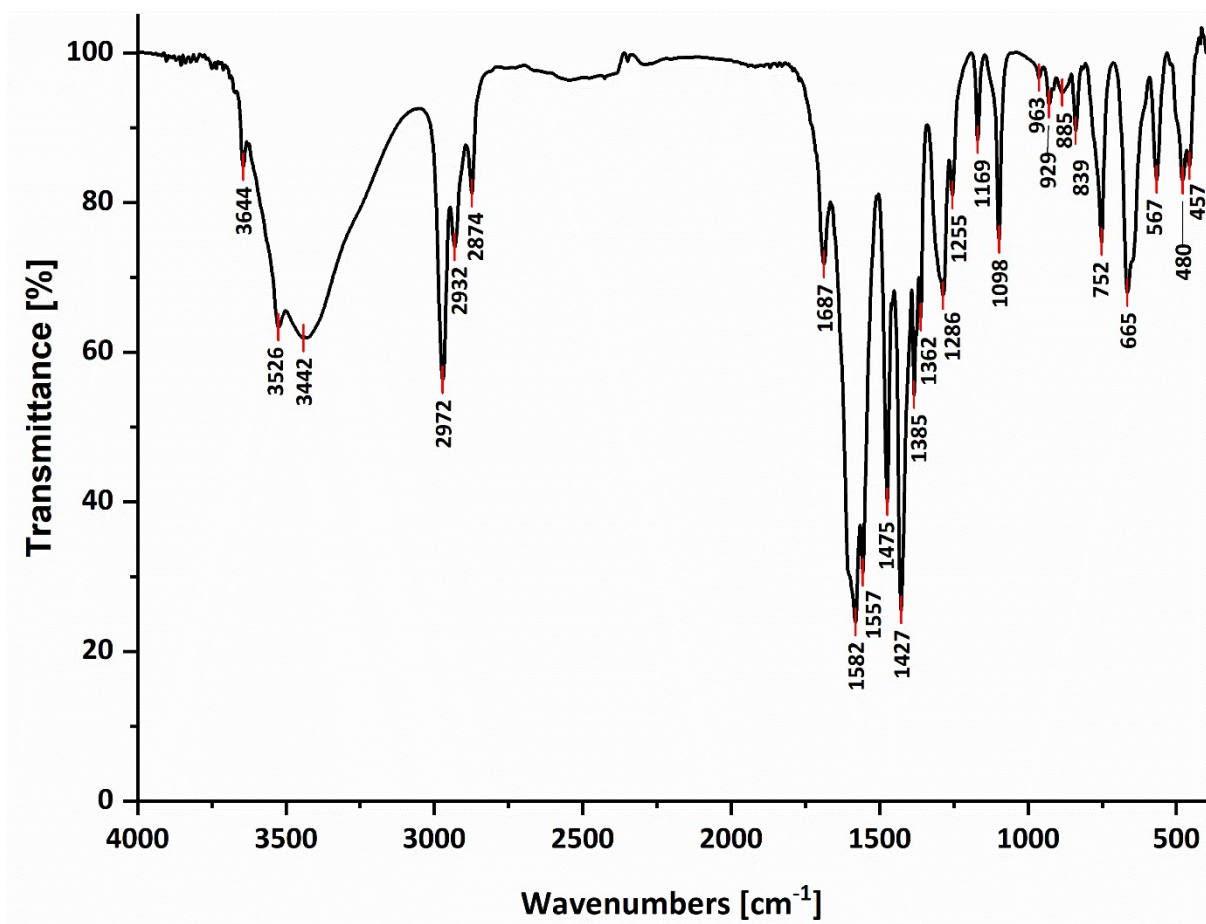


Figure S4: FTIR spectrum of **2** measured in KBr pellets in the range of 4000—400 cm⁻¹.

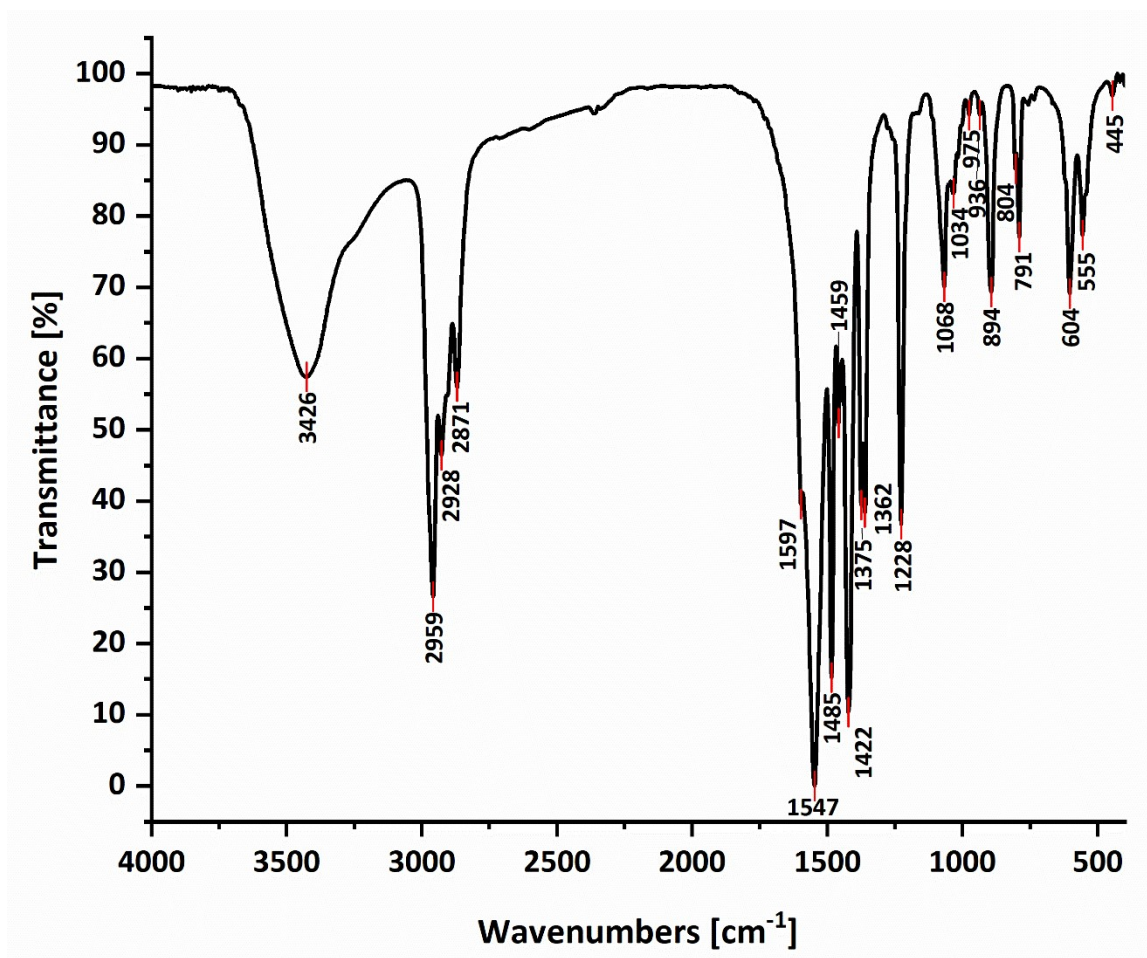


Figure S5: FTIR spectrum of the freshly isolated by-product **1a** measured in KBr pellets in the range of 4000—400 cm⁻¹.

Investigation of **1a** using IR-spectroscopy

Reactions in an inert Ar atmosphere were performed to determine if the Ce₆ core could be maintained in the presence of a Co^{II} source under otherwise identical conditions. Under an inert atmosphere, the reaction of [Ce₆O₄(OH)₄(piv)₁₂], Co(piv)₂, and *N*-butyldiethanolamine proceeded as usual, resulting in the formation of **1** (see Additional experimental procedures) until additionally a pink precipitate (**1a**) was observed. This new by-product was filtered off and stored separately under inert conditions. The compound was observed to decompose rapidly upon addition of water and organic solvents, including methanol, acetonitrile, dichloromethane, dimethyl sulfoxide, and dimethyl formamide. It also oxidizes slowly under aerobic conditions, resulting in the formation of a brown powder within days. In order to investigate the air-sensitive compound **1a**, IR-spectroscopy investigations were performed to obtain insights into the coordination environment. Therefore, we compared freshly isolated **1a** with the brown powder obtained from **1a** after one week in air, and with the desired compound **1**. The by-product **1a** (**Figure S6**, black curve) exhibits distinct vibrational bands below 1000 cm⁻¹ compared to the [Ce₆O₄(OH)₄(piv)₁₂] precursor (**Figure S2**). This suggests that **1a** has a different coordination environment of the metal cluster. After one week of oxidation under aerobic conditions (**Figure S6**, blue curve), significant changes in the IR spectrum are observed below 1700 cm⁻¹ (**Figure S7**), indicating a change in the coordination assembly of the by-product. It is important to note that **1a**, after one week under aerobic conditions, is not a purified new complex and still contains the byproduct **1a**. The appearance of new vibrational bands around 1100 cm⁻¹, 900 cm⁻¹, and between 500 cm⁻¹ to 700 cm⁻¹ correspond to complex **1**. Therefore, we suggest that **1a** is a reduced precursor of **1**, which was formed under inert conditions in the absence of O₂.

It can be concluded that the decomposition of the hexanuclear {Ce₆} precursor occurs during both, the reaction with the Co^{II} source under aerobic conditions and under inert conditions, respectively. The synthesis under Ar conditions allows for the isolation of the air-sensitive precursor of **1**. However, due to the rapid oxidation in solution, recrystallization has not yet been successful, and the final structure is not yet known. Further research with strict control of the atmosphere is necessary to gain insight into the structure and oxidation pathway of the reaction.

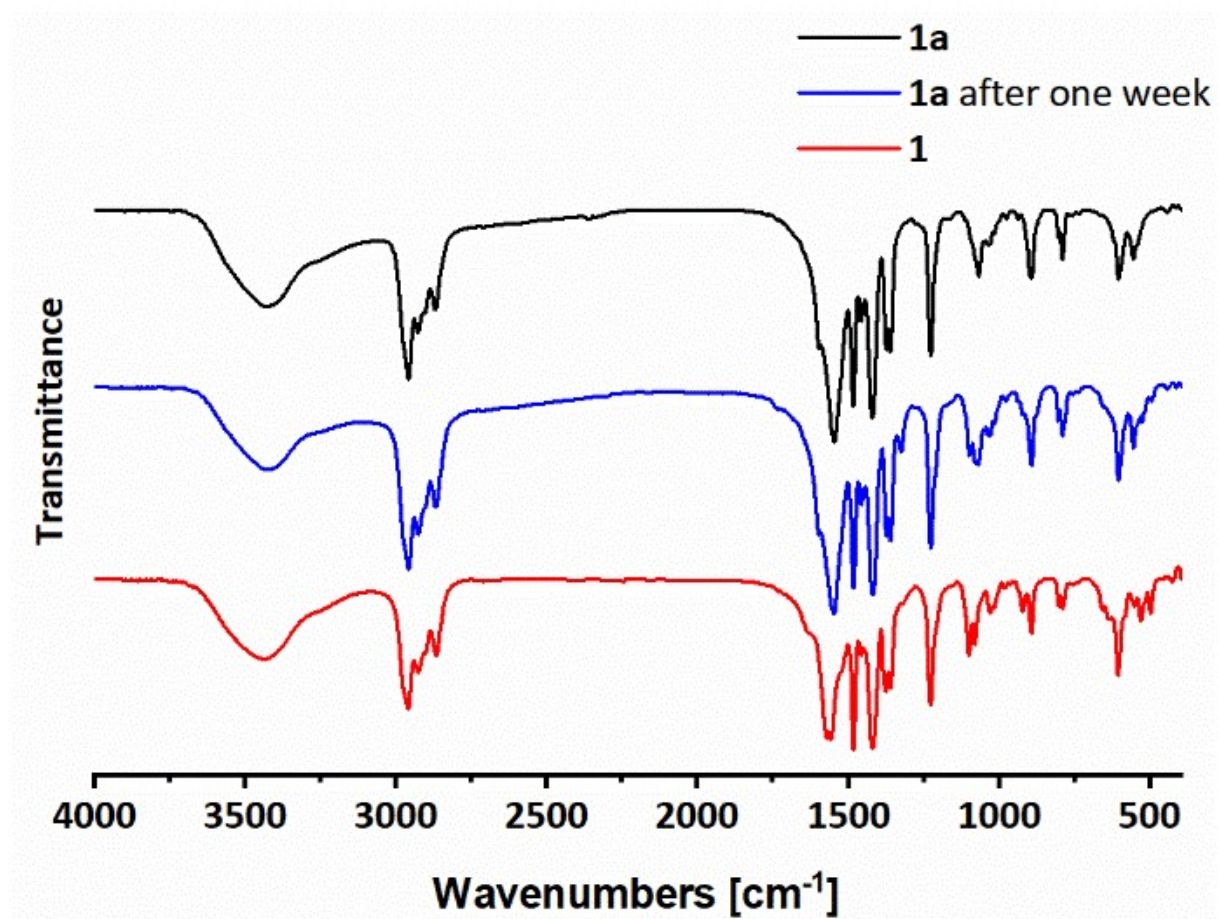


Figure S6: FTIR spectrum of the freshly isolated by-product **1a** (black), after one week under aerobic conditions (blue), and **1** (red) measured in KBr pellets in the range of 4000—400 cm^{-1} .

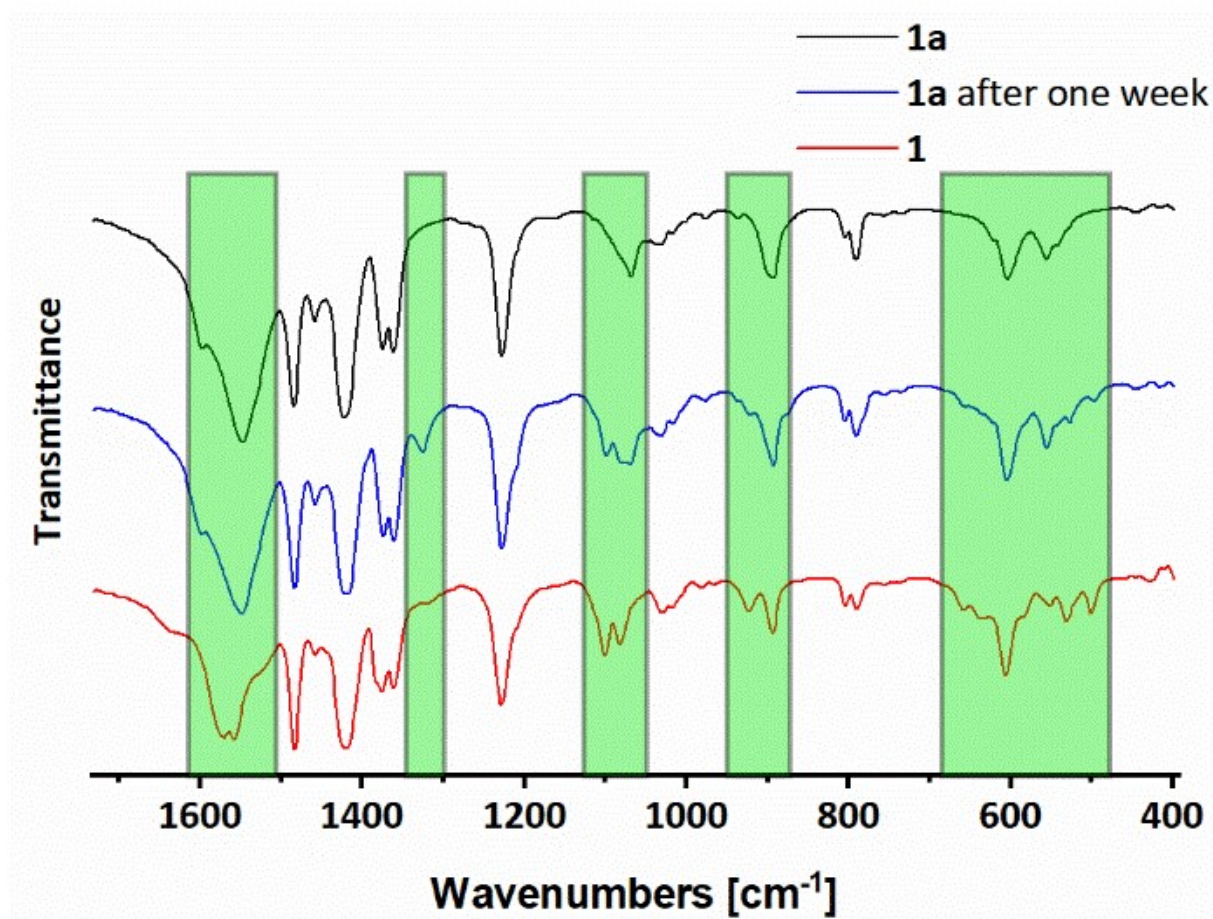


Figure S7: FTIR spectrum of the freshly isolated by-product **1a** (black), after one week under aerobic conditions (blue), and **1** (red) measured in KBr pellets in the range of 1700–400 cm⁻¹. Green boxes highlight areas of significant change.

TGA curves

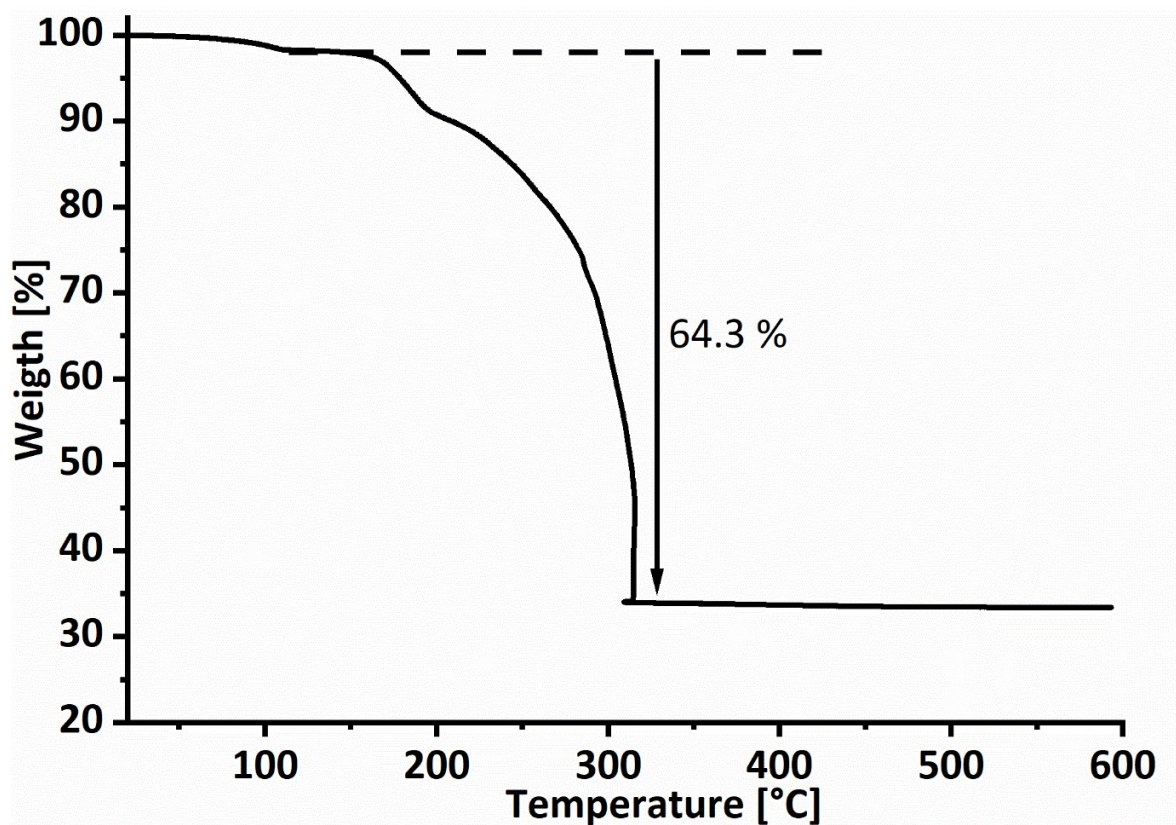


Figure S8: TGA curve of **1** measured using dry air as purge gas and a heating rate of 5 K min⁻¹.

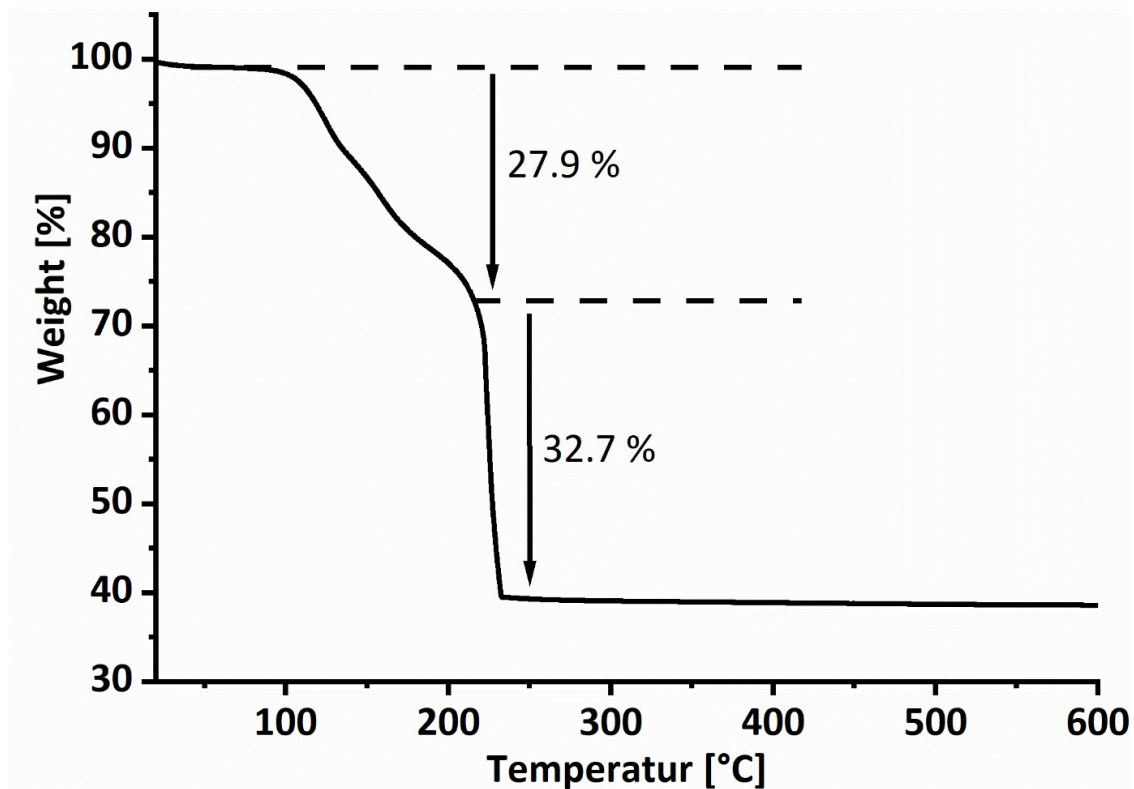


Figure S9: TGA curve of **1** measured using dry air as purge gas and a heating rate of 5 K min⁻¹.

Crystal refinement data

Table S1: Crystallographic details for compounds **1** (CCDC 2328391) and **2** (CCDC 2328390).

| Sample | 1 | 2 |
|---|---|--|
| Empirical formula | C ₅₉ H ₁₁₀ Ce ₃ Co ₂ N ₄ O ₂₄ | C ₈₈ H ₁₆₈ Co ₆ O ₅₈ Zr ₆ |
| Formular weight /g/mol | 1797.72 | 3055.11 |
| Temperature / K | 180(2) | 180(2) |
| Wavelength / pm | 154.186 | 154.186 |
| Crystal system | triclinic | monoclinic |
| Space group | <i>P</i> -1 | <i>P</i> 2 ₁ / <i>c</i> |
| <i>a</i> / pm | 1488.20(2) | 1608.07(2) |
| <i>b</i> / pm | 1526.96(2) | 2083.26(3) |
| <i>c</i> / pm | 1941.27(3) | 2022.15(2) |
| α / ° | 66.8650(10) | 90 |
| β / ° | 75.4190(10) | 112.1870(10) |
| γ / ° | 79.6030(10) | 90 |
| Volume / 10 ⁶ pm ³ | 3909.46(10) | 6272.67(14) |
| <i>Z</i> | 2 | 2 |
| Density ρ / g/cm ³ | 1.527 | 1.618 |
| Absorption coefficient μ / mm ⁻¹ | 17.049 | 10.708 |
| <i>F</i> (000) | 1824 | 3124 |
| Crystal size / mm | 0.05 · 0.08 · 0.08 | 0.09 · 0.12 · 0.16 |
| θ range / ° | 3.57 to 71.01 | 3.649 to 71.308 |
| | -18 ≤ <i>h</i> ≤ 16 | -7 ≤ <i>h</i> ≤ 19 |
| Index ranges | -18 ≤ <i>k</i> ≤ 16 | -23 ≤ <i>k</i> ≤ 25 |
| | -19 ≤ <i>l</i> ≤ 23 | -24 ≤ <i>l</i> ≤ 21 |
| Reflections collected | 63541 | 95970 |
| Independent reflections | 14579 [R _{int} = 0.0272] | 12024 [R _{int} = 0.0311] |
| Completeness to θ_{\max} | 96.3 % | 98.7 % |
| Absorption correction | multi-scan | multi-scan |
| T _{min} / T _{max} | 0.0101 / 0.0369 | 0.0222 / 0.0543 |
| Data/restraints/parameters | 14579 / 226 / 912 | 12024 / 556 / 806 |
| Goodness-of-fit on <i>F</i> ² | 1.040 | 1.051 |
| Final <i>R</i> indexes [<i>I</i> >= 2 σ (<i>I</i>)] | R1 = 0.0364 wR2 = 0.0954 | R1 = 0.0500 wR2 = 0.1199 |
| Final <i>R</i> indexes [all data] | R1 = 0.0448 wR2 = 0.1015 | R1 = 0.0592 wR2 = 0.1267 |
| Largest diff. peak/hole / e·Å ⁻³ | 1.473 / -0.693 | 0.822 / -0.696 |

Crystal cell parameter of $[\text{Ce}_6\text{O}_4(\text{OH})_4(\text{piv})_{12}]$

Table S2: Comparison of the crystal cell parameter of $[\text{Ce}_6\text{O}_4(\text{OH})_4(\text{piv})_{12}]$ with the literature data.

| Sample | This work | Powell <i>et al.</i> ¹ |
|---------------------------------|-------------|-----------------------------------|
| Wavelength / pm | 154.186 | 71.073 |
| Temperature / K | 180(2) | 100 |
| Crystal system | trigonal | trigonal |
| Space group | <i>R</i> -3 | <i>R</i> -3 |
| <i>a</i> / pm | 2201.64(3) | 2182.20(4) |
| <i>b</i> / pm | 2201.64(3) | 2182.20(4) |
| <i>c</i> / pm | 1533.17(3) | 1522.95(6) |
| α / ° | 90 | 90 |
| β / ° | 90 | 90 |
| γ / ° | 120 | 120 |
| Volume / 10^6 pm ³ | 6436.0(2) | 6280.7(3) |

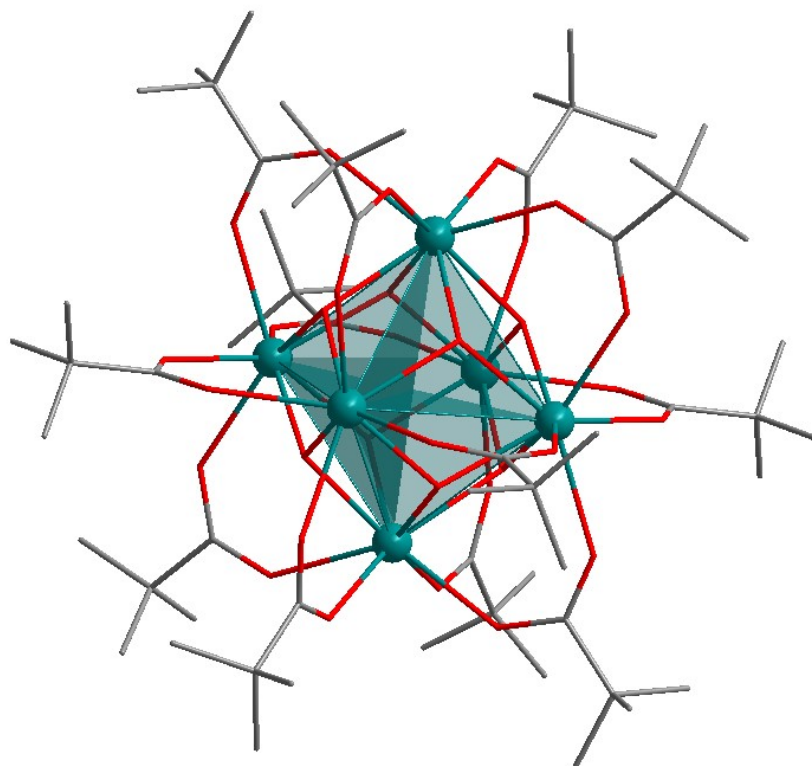


Figure S10: Molecular structure of $[\text{Ce}_6\text{O}_4(\text{OH})_4(\text{piv})_{12}]$. Color code: Ce^{IV} , teal; C, gray and O, red. The cavity of the Ce_6 octahedron is shown in transparent teal. H atoms are omitted for clarity.

References

- 1 V. Mereacre, A. M. Ako, M. N. Akhtar, A. Lindemann, C. E. Anson, A. K. Powell, *Helv. Chim. Acta*, 2009, **92**, 2507–2524.