



Full paper / Mémoire

Re-investigation of the $\text{Er}^{3+}-\text{C}_2\text{O}_4^{2-}-\text{H}_2\text{O}$ system: from the classical ceramic precursor to a new nanoporous molecular material potential precursor

Magatte Camara ^a, Carole Daiguebonne ^{a,*}, Kamal Boubekour ^b, Thierry Roisnel ^c,
Yves Gérard ^a, Christophe Baux ^a, Florence Le Dret ^a, Olivier Guillou ^{a,*}

^a Insa Rennes, GRCM, Laboratoire de chimie inorganique des lanthanides, 20, av. des Buttes-de-Coësmes,
CS 14315, 35043 Rennes cedex, France

^b IMN Jean-Rouxel, université de Nantes, 2, rue de la Houssinière, 44322 Nantes cedex 3, France

^c Laboratoire de chimie du solide et inorganique moléculaire, CNRS, université Rennes-1, 35042 Rennes cedex, France

Received 7 January 2003; accepted 4 March 2003

Abstract

This paper focuses on the crystallographic diversity observed for the compounds obtained, by reacting potassium oxalate with Er(III) chloride, in gel media. Three lanthanide and oxalate compounds are described two out of the three are simple lanthanide oxalate complexes while the other one is a mixed lanthanide–alkaline oxalate complex. All three have been structurally characterized. **1**, namely $\text{Er}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 4 \text{H}_2\text{O}$, crystallizes in the space group $P2_1/c$ (system monoclinic) with $a = 11.3590(2) \text{ \AA}$, $b = 9.6162(2) \text{ \AA}$, $c = 9.9401(2) \text{ \AA}$, $\beta = 118.723(9)^\circ$ and $Z = 4$. Its crystal structure has been found to be identical to the one already reported. It consists of parallel honeycomb-like molecular layers. **2**, namely $\text{KEr}(\text{C}_2\text{O}_4)_2 \cdot 4 \text{H}_2\text{O}$, has been found to be isostructural to the Y(III) homologous complex already reported. It crystallizes in the space group $I4_1/amd$ (tetragonal system) with $a = 11.4145(14) \text{ \AA}$, $c = 8.893(2) \text{ \AA}$ and $Z = 4$. Its structure consists of channels along the c axis spreading over the (ab) plane with a square cross section. **3**, namely $\text{Er}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 12 \text{H}_2\text{O}$, crystallizes in the space group $R\bar{3}$ (trigonal system) with $a = 30.8692(10) \text{ \AA}$, $c = 7.2307(2) \text{ \AA}$ and $Z = 12$. This compound has, to the best of our knowledge, never been structurally described. It is the first three-dimensional lanthanide oxalate ever reported. Its crystal structure exhibits channels with hexagonal cross-sections spreading along the $c \rightarrow$ axis. The diameter of the channels is as large as 12 \AA . They are filled with crystallization water molecules. **To cite this article:** M. Camara et al., C. R. Chimie 6 (2003).

© 2003 Académie des sciences. Published by Éditions scientifiques et médicales Elsevier SAS. All rights reserved.

Résumé

Cet article s'intéresse à la diversité structurale des composés obtenus par réaction en milieu gel de l'oxalate de potassium avec le chlorure d'erbium (III). Trois composés à base d'oxalate et d'erbium sont décrits : deux d'entre eux sont des oxalates de terre rare uniquement, alors que le troisième est un oxalate mixte de terre rare et de potassium. Tous trois ont été structuralement caractérisés. **1**, de formule chimique $\text{Er}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 4 \text{H}_2\text{O}$, cristallise dans le groupe d'espace $P2_1/c$ (système monoclinique)

* Corresponding author.

E-mail address: carole.daiguebonne@insa-rennes.fr (C. Daiguebonne).

avec $a = 11.3590(2)$ Å, $b = 9.6162(2)$ Å, $c = 9.9401(2)$ Å, $\beta = 118.723(9)^\circ$ et $Z = 4$. Sa structure cristalline est identique au composé déjà décrit et consiste en une superposition de plans moléculaires en nid d'abeilles. **2**, de formule chimique $\text{KEr}(\text{C}_2\text{O}_4)_2 \cdot 4 \text{H}_2\text{O}$, est isostructural à un complexe analogue à base d'Y(III) déjà décrit. Il cristallise dans le groupe d'espace $I4_1/amd$ (système quadratique) avec $a = 11.4145(14)$ Å, $c = 8.893(2)$ Å et $Z = 4$. Sa structure cristalline consiste en la juxtaposition de canaux à sections carrées suivant l'axe \vec{c} , se développant suivant le plan (ab) . **3**, de formule chimique $\text{Er}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 12 \text{H}_2\text{O}$, cristallise dans le groupe d'espace $R\bar{3}$ (système hexagonal), avec $a = 30.8692(10)$ Å, $c = 7.2307(2)$ Å et $Z = 12$. Ce composé n'a, à notre connaissance, jamais été structuralement caractérisé. Il constitue le premier exemple d'oxalate simple de terre rare tridimensionnel. Sa structure cristalline présente des canaux à sections hexagonales se développant suivant l'axe \vec{c} . Le diamètre de ces canaux est de l'ordre de 12 Å. Ils sont remplis de molécules d'eau de cristallisation. **Pour citer cet article** : M. Camara et al., C. R. Chimie 6 (2003).

© 2003 Académie des sciences. Published by Éditions scientifiques et médicales Elsevier SAS. All rights reserved.

Keywords: crystal growth; lanthanide; oxalate; coordination polymers; crystal structure

Mots clés : croissance cristalline ; lanthanide ; oxalate ; polymère de coordination ; structure cristalline

1. Introduction

For a few years, our group has been involved in the investigation of lanthanide containing coordination polymers. Many such polymeric compounds have been obtained by using polycarboxylate ligands [1–3]. All of them have been structurally characterized thanks to the single crystals obtained by slow diffusion of the reactants through gel media. Rather surprisingly, this synthesis pathway leads currently to numerous polymorphic phases [4, 5]. In order to check if the origin of this observed polymorphism lies in the use of gel media or not, we have recently undertaken the study of the system $\text{ErCl}_3 \cdot 6 \text{H}_2\text{O} - \text{K}_2(\text{C}_2\text{O}_4) \cdot 2 \text{H}_2\text{O} - \text{H}_2\text{O}$ in various gel media.

The choice of the oxalate ligand was motivated by the fact that lanthanide oxalates have been extensively studied for more than 30 years due to their numerous industrial applications. For instance, lanthanide oxalate are extensively used as ceramics or mineral pigments precursors [6].

All these studies have led to the characterization and structural description of many compounds.

Lanthanide oxalates crystallize in two different ways, depending on the lanthanide ion. For lanthanide ions ranging from La to Er, the chemical formula is $\text{Ln}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 4 \text{H}_2\text{O}$ [7, 8], while for lanthanides ranging from Er to Lu, the chemical formula is $\text{Ln}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_4 \cdot 2 \text{H}_2\text{O}$ [9]. The structure of the lan-

thanide oxalate hexahydrate is closely related to that of the lanthanide oxalate decahydrate.

The mixed lanthanide–alkaline oxalates have also been largely studied. They can be classified into several families. We can uplift:

- $\text{K}_3\text{Ln}(\text{C}_2\text{O}_4)_3 \cdot 3 \text{H}_2\text{O}$ (Ln = Nd–Tb) [10];
- $\text{K}_8\text{Ln}_2(\text{C}_2\text{O}_4)_7 \cdot 14 \text{H}_2\text{O}$ (Ln = Tb, Er, Yb, Dy, Y) [11];
- $[\text{MLn}(\text{H}_2\text{O})_n](\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$ (M = Li, Ln = La–Gd, $n = 1$; M = Na, Ln = Ce–Nd, $n = 2$) [12];
- $\text{YM}(\text{C}_2\text{O}_4)_2 \cdot 4 \text{H}_2\text{O}$ (M = K, Rb) [13];
- $\text{Y}(\text{H}_2\text{O})\text{Na}(\text{C}_2\text{O}_4)_2 \cdot 3 \text{H}_2\text{O}$ [14].

A summary of the chemical formula, space group and cell parameters of these compounds is reported in Table 1. Considering the structural diversity and the stability of the reported phases, it was really a challenge to obtain, thanks to the use of gel media, a new phase yet unknown.

In this paper, we would like to report the results obtained by a set of synthesis realized with the same reactants (erbium(III) chloride and potassium oxalate) in the same solvent (water) and varying only the gel medium. Three different compounds were so obtained depending on the nature of the gel. One is of course the very stable oxalate decahydrate [7, 8]. Second is the $\text{KEr}(\text{C}_2\text{O}_4)_2 \cdot 4 \text{H}_2\text{O}$, which revealed to be isostructural to the $\text{KY}(\text{C}_2\text{O}_4)_2 \cdot 4 \text{H}_2\text{O}$ recently described [13]. The third is a new three-dimensional erbium oxalate compound.

Table 1

Summary of the unit cell parameters for selected well-known oxalate-containing compounds

| | Space group | <i>a</i> (Å) | <i>b</i> (Å) | <i>c</i> (Å) | α (°) | β (°) | γ (°) |
|--|-------------|--------------|--------------|--------------|--------------|-------------|--------------|
| $\text{Ln}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 4 \text{H}_2\text{O}$ (Ln = La–Er) [7, 8] | $P2_1/c$ | 11.516(250) | 9.631(30) | 10.081(400) | | 118.82(25) | |
| $\text{Ln}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_4 \cdot 2 \text{H}_2\text{O}$ (Ln = Er–Lu, Y, Sc) [9] | $P\bar{1}$ | 9.597(150) | 8.455(15) | 9.758(300) | 93.42(40) | 106.27(30) | 85.41(90) |
| $\text{K}_3\text{Ln}(\text{C}_2\text{O}_4)_3 \cdot 3 \text{H}_2\text{O}$ (Ln = Nd–Tb) [10] | $P\bar{1}$ | 9.383(50) | 8.484(20) | 9.751(50) | 88.86(50) | 81.76(50) | 96.55(30) |
| $\text{K}_8\text{Ln}_2(\text{C}_2\text{O}_4)_7 \cdot 14 \text{H}_2\text{O}$ (Ln = Tb, Er, Yb, Dy, Y) [11] | $C2/c$ | 16.079(50) | 11.773(60) | 23.371(120) | | 91.21(35) | |
| $[\text{LiLn}(\text{H}_2\text{O})_n](\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$ (Ln = La–Gd, $n = 1$) [12] | $P2/a$ | 9.399(100) | 7.666(80) | 12.877(140) | | 103.77(45) | |
| $[\text{NaLn}(\text{H}_2\text{O})_n](\text{C}_2\text{O}_4) \cdot \text{H}_2\text{O}$ (Ln = Ce–Nd, $n = 2$) [12] | $P2/a$ | 10.033(35) | 7.591(40) | 13.093(70) | | 102.02(20) | |
| $\text{YM}(\text{C}_2\text{O}_4)_2 \cdot 4 \text{H}_2\text{O}$ (M = K, Rb) [13] | $I4_1/a$ | 11.4612(8) | | 8.9040(8) | | | |
| $\text{Y}(\text{H}_2\text{O})\text{Na}(\text{C}_2\text{O}_4)_2 \cdot 3 \text{H}_2\text{O}$ [14] | Pc | 8.623(2) | 8.6310(8) | 14.896(3) | | 102.848(9) | |

2. Experimental part

2.1. Synthesis

The potassium oxalate salt has been purchased from Acros Organics and used without further purification. The gels have been purchased from Acros Organics and gelified according established procedures. The erbium oxide has been furnished by Rhodia Electronics and Catalysis.

Single crystals of each of the three phases are obtained by reaction of the same reactants (erbium chloride hexahydrate and potassium oxalate dihydrate salts), the crystallization occurring in different gel media. Three kinds of gels have been used: agar-agar, tetramethylorthosilicate (TMOS) and tetraethylorthosilicate (TEOS).

Dilute aqueous solutions of Er(III) chloride (0.25 mmol) and potassium salt of oxalate (0.25 mmol)

were allowed to slowly diffuse through the gel medium in an U-shaped tube. After a few weeks, single crystals were obtained.

Details of the different synthesis are listed in Table 2.

Anal. Calc. (found) for $\text{Er}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 4 \text{H}_2\text{O}$: Er 42.96% (42.90), C 9.25% (9.25), H 2.59% (2.60); for $\text{KEr}(\text{C}_2\text{O}_4)_2 \cdot 4 \text{H}_2\text{O}$: Er 36.80% (36.70), K 8.60% (8.65), C 10.57% (10.60), H 1.77% (1.80); for $\text{Er}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 12 \text{H}_2\text{O}$: Er 36.25% (36.25), C 7.81% (7.80), H 3.93% (3.95).

2.2. Single-crystal X-ray diffraction data

All crystals have been sealed in glass capillaries for X-ray single crystal data collection in order to avoid potential dehydration.

Table 2

Summary of the results of the synthesis

| | Gel density | Chemical formulae and crystal cell parameters | Ref. |
|-----------|------------------|--|-----------|
| Agar-agar | 0.1% | $\text{Er}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 4 \text{H}_2\text{O}$ | [7–8] |
| | 0.25% | $P2_1/c$ | |
| | 0.5% | $a = 11.3590(2) \text{ \AA}; b = 9.6162(2) \text{ \AA}; c = 9.9401(2) \text{ \AA}; \beta = 118.723(9)^\circ$ | |
| | 1/19 1.5/18.5 | | |
| TMOS | 3/17 | $\text{Er}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 12 \text{H}_2\text{O}$ $R\bar{3}$ $a = 30.8692(10) \text{ \AA}; c = 7.2307(2) \text{ \AA}$ | This work |
| | 1/19 | $\text{Er}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 4 \text{H}_2\text{O}$ $P2_1/c$ $a = 11.3590(2) \text{ \AA}; b = 9.6162(2) \text{ \AA}; c = 9.9401(2) \text{ \AA}; \beta = 118.723(9)^\circ$ | [7–8] |
| TEOS | 1.5/18.5 | $\text{KEr}(\text{C}_2\text{O}_4)_2 \cdot 4 \text{H}_2\text{O}$ $I4_1/amd$ | This work |
| | 3/17 | $a = 11.4145(14) \text{ \AA}; c = 8.893(2) \text{ \AA}$ | |

2.2.1. Crystal 1

A plate-like pale-pink transparent single crystal has been mounted on a Nonius KappaCCD diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å).

The unit cell parameters found after 10 frames are: $\alpha = 11.3590(2)$ Å, $b = 9.6162(2)$ Å, $c = 9.9401(2)$ Å, $\beta = 118.723(9)^\circ$. These parameters are the same that those already found for the $\text{Er}_2(\text{C}_2\text{O}_4)_3(\text{H}_2\text{O})_6 \cdot 4 \text{H}_2\text{O}$ compound [7,15–20].

2.2.2. Crystal 2

A block-like pale-pink transparent single crystal has been mounted on a Enraf Nonius CAD-4 four circle diffractometer equipped with Mo K α radiation and a graphite monochromator. Accurate unit cell parameters were derived from least-squares refinement of the setting angles of 25 machine-centred reflections in the range $4.59 \leq \theta \leq 13.29^\circ$ and have for values: $a = 11.4145(14)$ Å, $c = 8.893(2)$ Å. Data collection was performed in the ω - 2θ scan mode. Intensities of three standard reflections were measured every 60 min and showed no decrease during the data collection. The data were corrected for Lorentz and polarization effects and for absorption using the psi-scan method [21]. The structure was solved by direct methods and refined by full-matrix least-squares methods, which were performed using the SHELXS-97 and SHELXL-97 software packages [22, 23]. All non-hydrogen atoms were refined anisotropically. Hydrogen atoms of water molecules have been localized and have not been refined.

2.2.3. Crystal 3

A diamond-like pale-pink transparent single crystal has been mounted on a Nonius KappaCCD diffractometer with Mo K α radiation ($\lambda = 0.71073$ Å). The crystal data collection has been performed at room temperature.

A crystal-to-detector distance of 25.0 mm has been used and data collection strategy (determination and optimisation of the detector and goniometer positions) have been performed with the help of the COLLECT program [24] to measure Bragg reflections of the unique volume in reciprocal space until $\theta = 27.48^\circ$.

A total of 166 frames were recorded, using $\Delta\omega = 2.0^\circ$ rotation scans to fill the asymmetric zone of the reciprocal space (exposition time = 50 s deg^{-1}).

Finally, 25 796 reflections have been indexed, Lorentz polarization corrected and then integrated in the trigonal symmetry ($R3$ point group) by the DENZO program of the KappaCCD software package [25].

Numerical absorption corrections have been performed using the analytical facilities [26] included in the WinGX program suite [27].

Structure determinations have been performed with the solving program SIR97 [28], that revealed all the non hydrogen atoms. All non-hydrogen atoms were refined anisotropically using the SHELXL program [23]. Hydrogen atoms of water molecules have not been localized.

Crystal and final structure refinement data of the three compounds are listed in Table 3.

3. Result and discussion

3.1. Description of the structures.

3.1.1. Description of the structure of compound 1

This compound, isostructural to the already well-described lanthanide oxalate decahydrate, exhibits a 2D framework, based on an honeycomb-like molecular motif (Fig. 1).

3.1.2. Description of the structure of compound 2

This compound is original because it has never been characterized before. However the Y(III) containing homogenous compound (with K or Rb counter cations) has already been described in the literature [13]. In this paper its crystal structure had been solved on the basis of powder X-ray diffraction diagram. The crystal structure determination reported here, based on single crystal X-ray diffraction data, has allowed us to refine the space group determination ($I4_1/amd$) and the location of the water molecules.

The asymmetric unit, along with the atomic numbering scheme (Fig. 2), shows that the erbium(III) ions are eight coordinated by eight oxygen atoms from four oxalato groups, so forming a slightly distorted dodecahedron (Fig. 3). It can be noticed that this coordination polyhedron is free of water molecule. The distances between the Er(III) ion and the oxygen atoms belonging to oxalato groups are 2.318(1) and 2.357(1) Å. In Fig. 2, one can also notice that the O1 atom is also

Table 3
Crystal and final structure refinement data of the three compounds

| Compound | 1 | 2 | 3 |
|--|--|--|--|
| Molecular formula | ErC ₃ O ₁₁ H ₁₀ | ErKC ₄ O ₁₂ H ₈ | Er _{1.5} C _{4.5} O _{22.5} H ₂₇ |
| Formula weight | 389.37 | 454.46 | 692.15 |
| Size (mm) | 0.08 × 0.08 × 0.08 | 0.14 × 0.16 × 0.29 | 0.07 × 0.08 × 0.10 |
| Temperature (K) | 293 | 293 | 293 |
| Crystal system | monoclinic | tetragonal | trigonal |
| Space group | <i>P</i> 2 ₁ / <i>c</i> | <i>I</i> 4 ₁ / <i>amd</i> | <i>R</i> $\bar{3}$ |
| <i>a</i> (Å) | 11.3590(2) | 11.4145(14) | 30.8692(10) |
| <i>b</i> (Å) | 9.6162(2) | 11.4145(14) | 30.8692(10) |
| <i>c</i> (Å) | 9.9401(2) | 8.893(2) | 7.2307(2) |
| α (°) | 90 | 90 | 90 |
| β (°) | 118.723(9) | 90 | 90 |
| γ (°) | 90 | 90 | 90 |
| <i>V</i> (Å ³) | 952.2(3) | 1158.7(3) | 5967.1(3) |
| <i>Z</i> | 4 | 4 | 12 |
| <i>D</i> _{calc} (g cm ⁻³) | | 2.605 | 2.311 |
| <i>F</i> (000) | | 860 | 4032 |
| μ (cm ⁻¹) | | 7.661 | 6.405 |
| Data collected | | 2893 | 3036 |
| Observed data | | 390 | 2419 |
| Parameters refined | | 39 | 172 |
| <i>R</i> (%) | | 4.99 | 4.24 |
| <i>R</i> _w (%) | | 12.03 | 11.18 |
| Goodness of fit | | 1.072 | 1.164 |
| Final shift/error | | 0.002 | 0 |

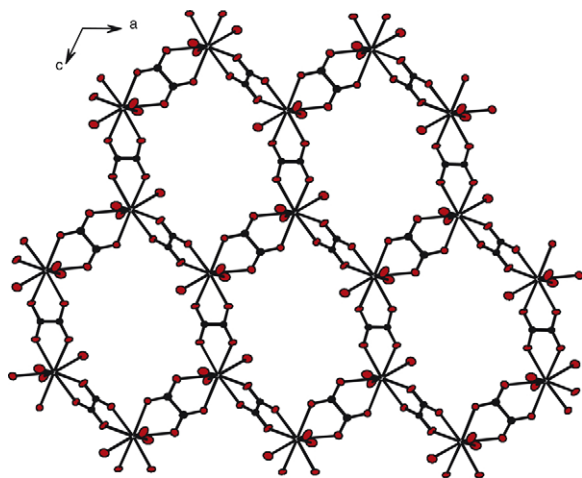


Fig. 1. Honeycomb-like molecular motif for compound **1**. Crystallization water molecules have been omitted for clarity.

bounded to the K⁺ ion. The coordination polyhedron of the K⁺ ion is also a dodecahedron, formed by four oxygen atoms from four oxalato groups and four oxygen atoms from crystallization water molecules.

The crystal structure exhibits a 3D open framework. Along the *c*→ axis, the structure presents channels with square-cross sections, the erbium ions occupying the corners of the squares (Fig. 4). The distances between Er(III) ions are all 6.125(1) Å and so the surface of the square-cross section is 37 Å². These channels are filled with disordered crystallization water molecules. A deeper study of the location of the crystallization water molecules shows that they are forming two screws translated by \vec{c} and rotated by 45° from each other (Fig. 5). The distances between two oxygen atoms from adjacent crystallization water molecules belonging to a given screw are 2.901(1) Å.

The square cross-section channels can also be described as helixes, as shown in Fig. 6.

The crystal structure presents also channels spreading along the \vec{a} or \vec{b} axis. These channels present an irregular chair-like hexagonal section with six lanthanide ions localized at the corners and six oxalato groups forming the edges. Their surface is roughly 45 Å² large. They are filled with crystallization water molecules and with the potassium ions (Fig. 7).

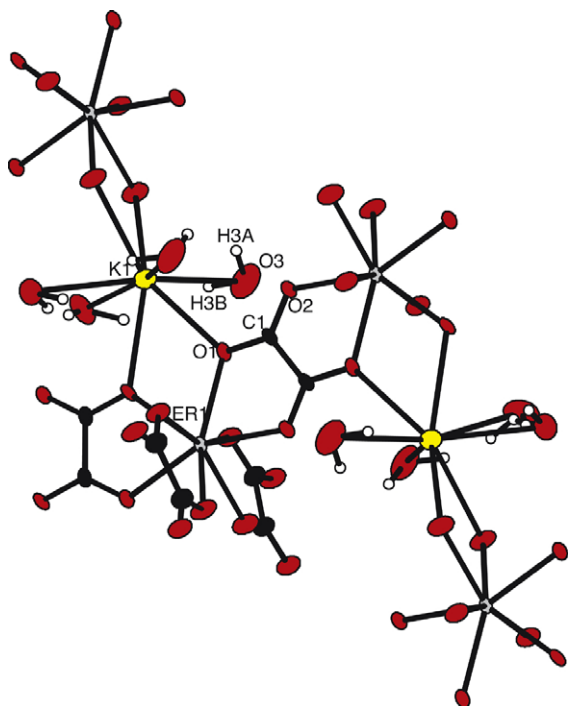


Fig. 2. Extended asymmetric unit along with the atomic numbering scheme for compound **2**.

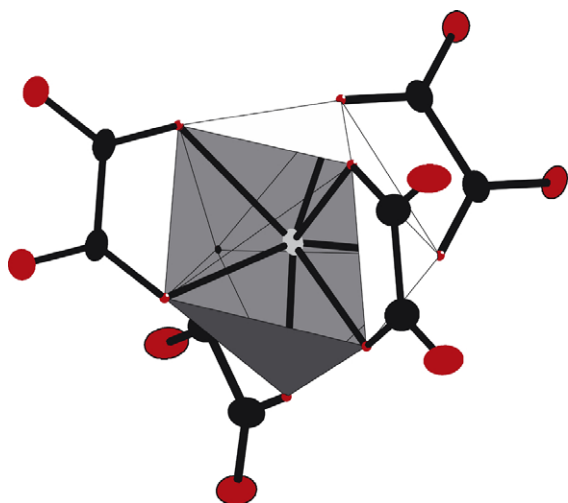


Fig. 3. Coordination polyhedron of the Er(III) ion in compound **2**.

3.1.3. Description of the structure of compound **3**

This compound is, to the best of our knowledge, the first octadecahydrate lanthanide oxalate ever crystallographically characterized and the first lanthanide, only containing oxalate, exhibiting a 3D framework.

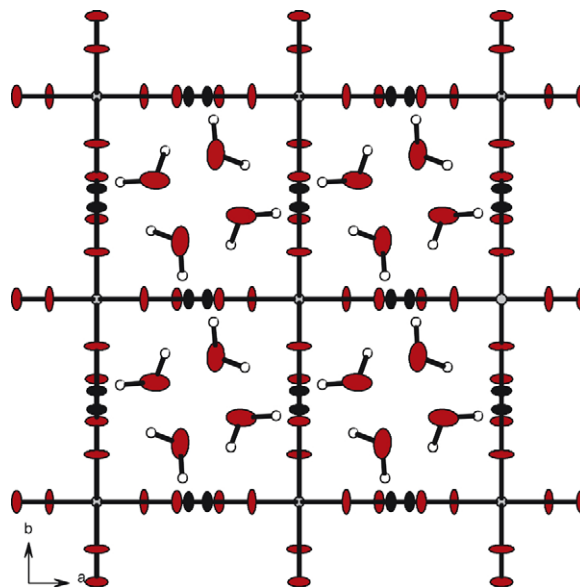


Fig. 4. Square cross-section channels: projection along the \vec{c} axis of a double-cell content. Potassium ions have been omitted for clarity. Also for clarity, only one water molecule over two has been represented.

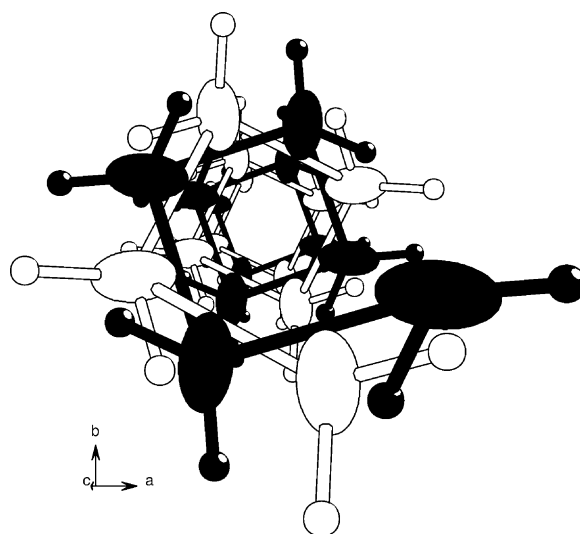


Fig. 5. Perspective view of the two disordered screws formed by crystallization water molecules in compound **2**. One is drawn in black while the other is in white. Oxygen atoms belonging to a same screw have been formally linked for clarity.

The asymmetric unit, along with the atomic numbering scheme (Fig. 8), shows that the erbium(III) ions are nine-coordinated by six oxygen atoms from three oxalato groups, according to a bidentate coordination

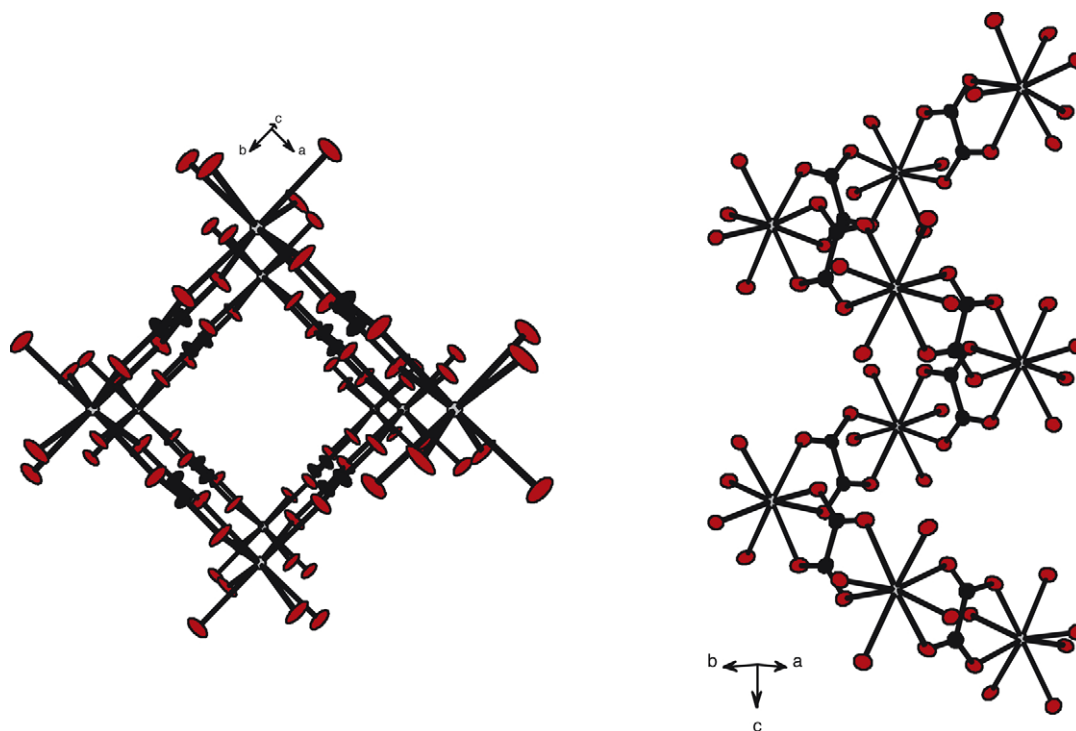


Fig. 6. Perspective views along $\vec{c}/2$ axis (left) and along $\vec{a} + \vec{b}$ direction (right).

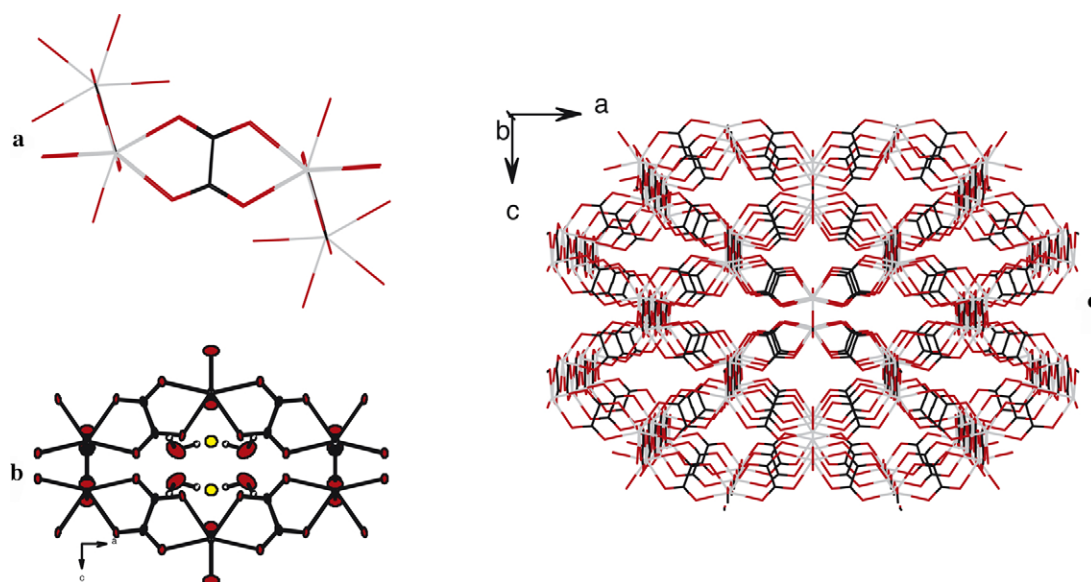


Fig. 7. Chair-like hexagonal cross-section channels in compound **2**. (a): Wire-model representation of the chair-like hexagonal molecular motif. (b): Projection along the \vec{b} axis of an hexagonal cross-section molecular motif. (c): Perspective view along the \vec{b} axis of the molecular skeleton of the crystal structure.

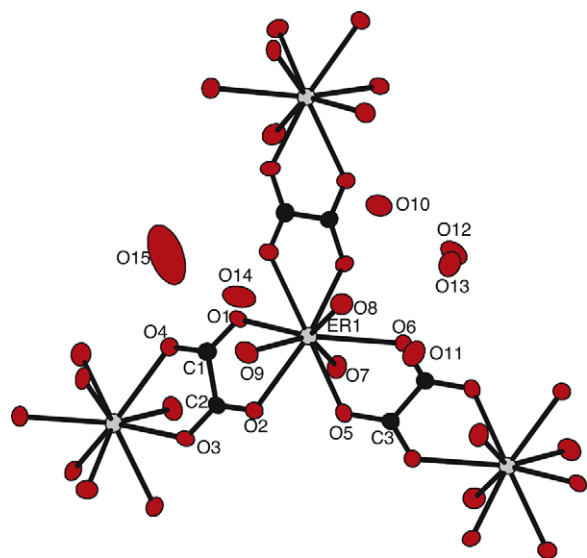


Fig. 8. Extended asymmetric unit along with the atomic numbering scheme for compound **3**.

mode, as well as by three coordination water molecules, so forming a tricapped trigonal prism (Fig. 9). The distances between the lanthanide ions and the bounded oxygen atoms are 2.415(10) Å and 2.275(65) Å for oxygen atoms belonging to water molecules and to oxalato groups respectively.

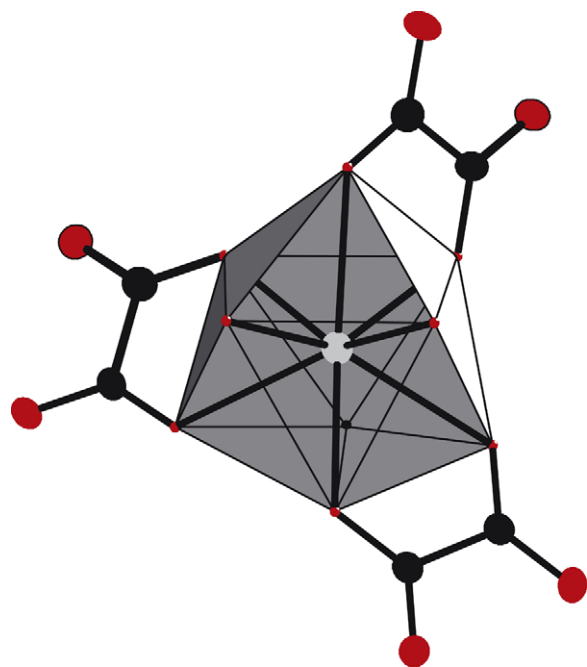


Fig. 9. Coordination polyhedron of the Er(III) ion in compound **3**.

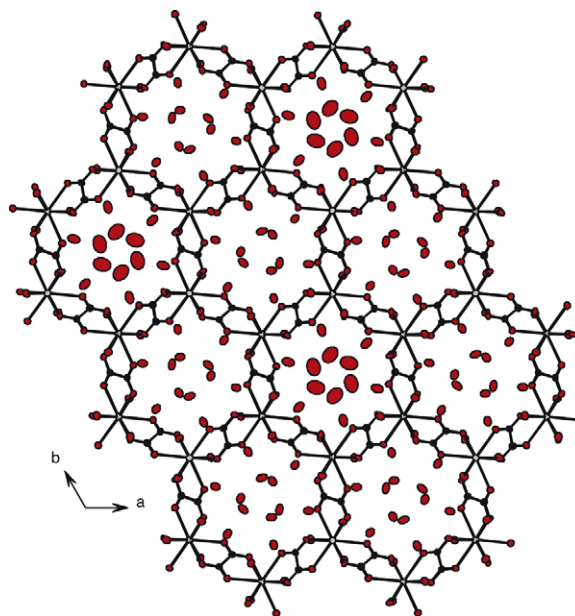


Fig. 10. Honeycomb-like molecular motif for compound **3**: projection along the $c \rightarrow$ axis.

The projection view along the \vec{c} axis shows channels with hexagonal sections roughly 100 \AA^2 large. Each section is formed by six lanthanide ions at the corners connected by six oxalato groups forming the edges. These channels are filled with crystallization water molecules (Fig. 10). One channel out of two is, actually, an helix spreading along the \vec{c} axis (Fig. 11). Each such channel is connected to three other helical channels in such a way that if one turns right, adjacent others turn left (Fig. 12). The connection between helices is insured by a common Er(III)–C₂O₄²⁻–Er(III) molecular fragment. Six connected helices form another hexagonal cross-section channel filled by crystallization water molecules too. The crystallization water molecules occupying these channels present bigger thermal agitation factors than those occupying the helical channels.

The views along the \vec{a} or \vec{b} axis are similar. The molecular skeleton can be described as a juxtaposition of channels with a square cross-section. These small channels are filled by crystallization water molecules (Fig. 13). The molecular motifs correspond to each other via the translation $1/3 \vec{c} - 1/3 \vec{b}$ (or $1/3 \vec{c} - 1/3 \vec{a}$).

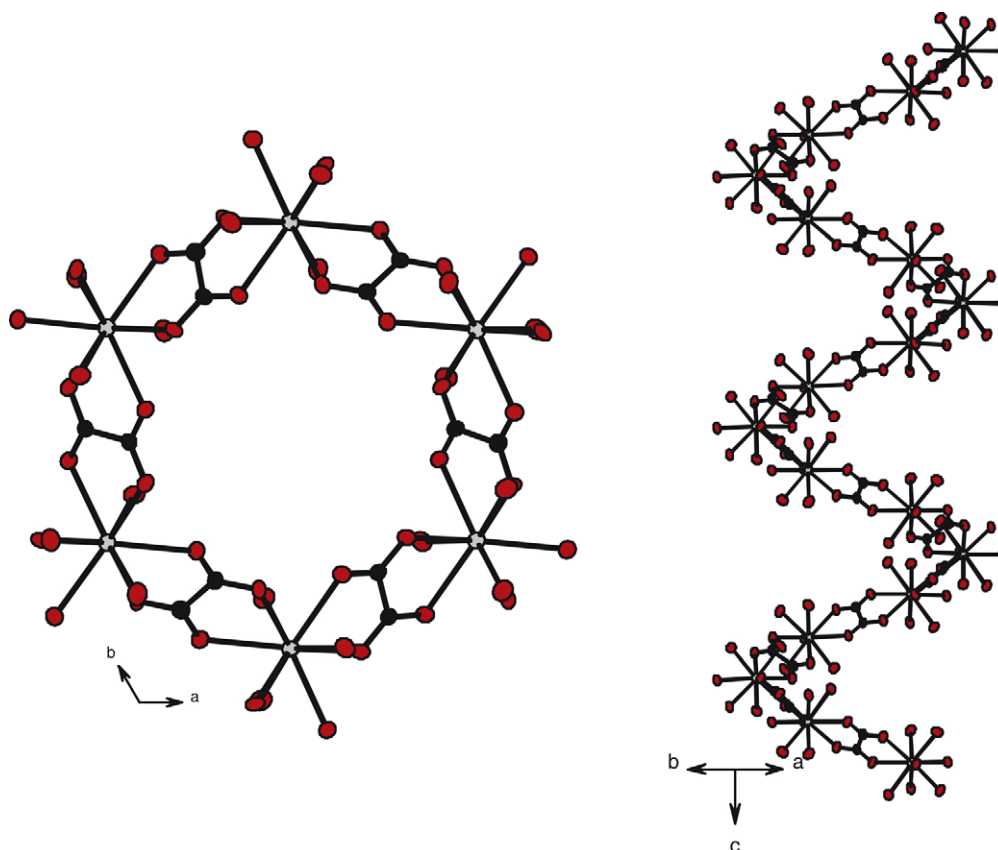


Fig. 11. Projection views along \vec{c} axis (left) and along $\vec{a} + \vec{b}$ direction (right) of a helical molecular channel in compound **3**.

3.2. Discussion and conclusion

This study confirms that the polymorphism already observed on other systems [5] is most probably due to the use of gel media. The crystallogenesis in gel medium, using the same reactants (erbium chloride hexahydrate and potassium oxalate dihydrate salts) in the same solvent (water), allows one to obtain three crystallographically different structures.

The most often obtained is, of course, the well-known very stable decahydrate erbium oxalate (namely compound **1**).

The second compound described here before is isostructural to a recently characterized Y(III) containing compound.

The third, at last, is the new octadecahydrate erbium oxalate. The existence of this compound had already been suggested on the basis of an elemental analysis in 1971 [29]. We have compared the X-ray powder dif-

fraction diagram reported in this paper with the one calculated [30] from our atomic parameters obtained for compound **3**. The two diagrams, the experimental reported one and the calculated one, are rather similar. However, they present some discrepancies that do not allow us to be sure that the two samples are exactly the same.

The compounds **2** and **3** seem to be interesting because of their potentiality in heterogeneous catalysis or optical systems. The rest of our discussion will so focus on them.

Indeed both are three-dimensional compounds, both exhibit an open molecular framework and both are containing Er(III) ions.

The presence of erbium ions is very important as far as optical applications are concerned. For instance, the silica-doped optical fibres used in telecommunications as amplifier for transcontinental transmissions do contain Er(III) ions. We are currently investigating the

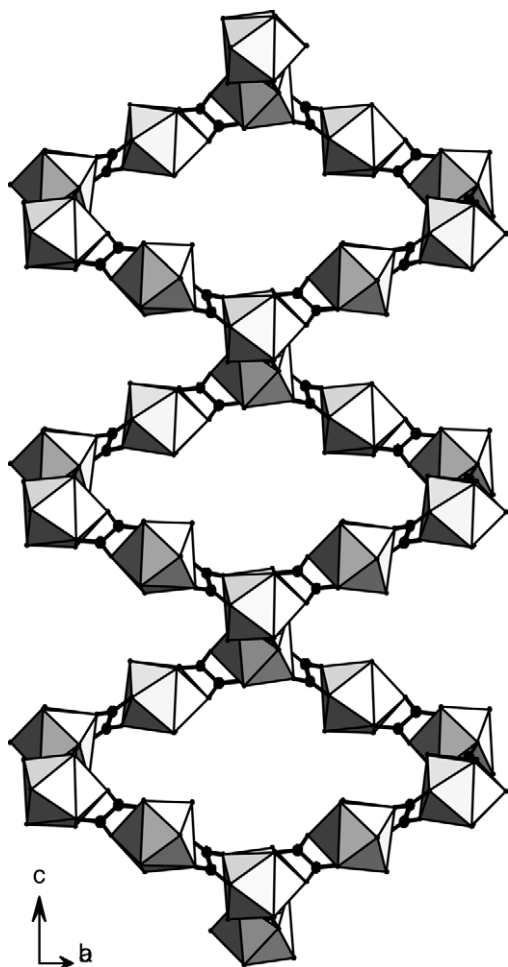


Fig. 12. Projection view along the $\vec{a} - \vec{b}$ direction of two adjacent helical molecular motifs in compound **3**.

efficiency of both systems as molecular laser amplifiers at 1.54 μm . The anhydrous character of the Er(III) coordination sphere in compound **2** is an obvious advantage. However, the relatively short Er–Er distances could make vanish the emission of the Er(III) ions by spin–phonon coupling. This has to be checked.

The 3D character of both structures is also of interest as far as heterogeneous catalysis is concerned. Indeed, may be it is possible to dehydrate them without destroying the molecular skeleton. This would lead to 3D open molecular framework with large channels and low density (1.5 g cm^{-3} and 2.2 g cm^{-3} for dehydrated compounds **3** and **2**, respectively). We are currently investigating this. Our idea is to evaluate the potentiality of these compounds as nanoporous molecular mate-

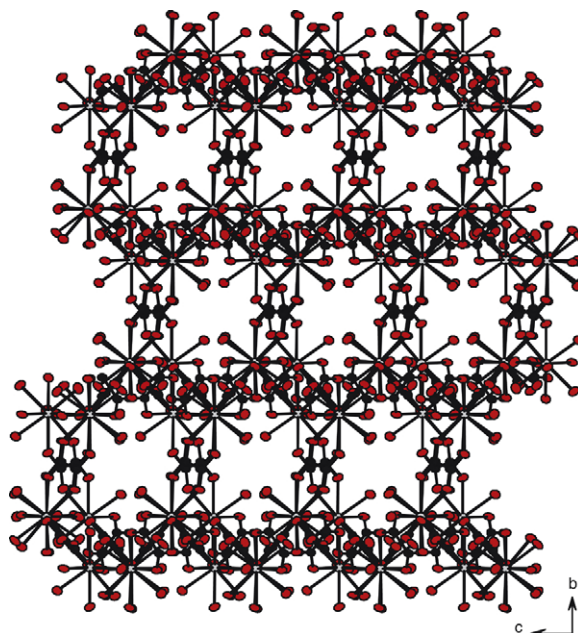


Fig. 13. Projection view along the \vec{a} axis of compound **3**. The crystallization water molecules have been omitted for clarity.

rials. We have so to perform BET measurement in order to determine their catalytic potentiality.

At last, we have just obtained the Gd(III) containing analogous compound of compound **3**. We are currently investigating its magnetic properties.

4. Supplementary material

Full details of the X-ray structure determination of compounds **2** and **3** have been deposited with the Cambridge Crystallographic Data Centre under the depository numbers CCDC-199967 and CCDC-199964 respectively and can be obtained, on request, from the authors with reference to this publication.

References

- [1] C. Daiguebonne, Y. Géralt, O. Guillou, A. Lecerf, K. Boubekeur, O. Kahn, M. Kahn, *J. Alloys Comps* 275–277 (1998) 50.
- [2] C. Daiguebonne, O. Guillou, Y. Géralt, A. Lecerf, K. Boubekeur, *Inorg. Chim. Acta* 284 (1999) 139.
- [3] C. Daiguebonne, O. Guillou, K. Boubekeur, *J. Alloys Comps* 324 (2001) 199.

- [4] C. Daiguebonne, O. Guillou, K. Boubekeur, *Inorg. Chim. Acta* 304 (2000) 161.
- [5] C. Daiguebonne, O. Guillou, K. Boubekeur, Structural Diversity in Lanthanide Complex Chemistry: the Ln^{3+} -TMA $^{3-}$ -H $_2$ O System, Transworld Research Network (2000) 165.
- [6] K.V. Krishnamurty, G.M. Harris, *Chem. Rev.* 61 (1961) 213.
- [7] E. Hansson, *Acta Chem. Scand.* 24 (1970) 2969.
- [8] E. Hansson, *Acta Chem. Scand.* 27 (1973) 823.
- [9] E. Hansson, *Acta Chem. Scand.* 26 (1970) 1337.
- [10] I.A. Kahwa, F.R. Fronczek, J. Selbin, *Inorg. Chim. Acta* 82 (1984) 161.
- [11] I.A. Kahwa, F.R. Fronczek, J. Selbin, *Inorg. Chim. Acta* 82 (1984) 167.
- [12] S. Romero, A. Mosset, J.-C. Trombe, *Eur. J. Inorg. Chem.* 32 (1995) 1053.
- [13] T. Bataille, J.-P. Auffrédic, D. Louër, *Chem. Mat.* 11 (1999) 1559.
- [14] T. Bataille, D. Louër, *Acta Crystallogr. C* 55 (1999) 1760.
- [15] W. Ollendorff, F. Weigel, *Inorg. Nucl. Chem. Lett.* 5 (1969) 263.
- [16] A.W. Wylie, *J. Chem. Soc.* (1947) 1687.
- [17] V. Gilpin, W.C. McCrone, *Anal. Chem.* 24 (1952) 225.
- [18] I.L. Jenkins, F.H. Moore, M.J. Waterman, *J. Inorg. Nucl. Chem.* 27 (1965) 77.
- [19] F. Weigel, W. Ollendorff, V. Scherer, R. Hagenbruch, *Z. Anorg. All. Chem.* 345 (1966) 119.
- [20] F. Weigel, W. Ollendorff, *Acta Crystallogr.* 22 (1967) 923.
- [21] D.C. Phillips, F.S. Mathews, *Acta Crystallogr. A* 24 (1968) 351.
- [22] G.M. Sheldrick, *Acta Crystallogr. D* 49 (1993) 18.
- [23] G.M. Sheldrick, T.R. Schneider, *Macromol. Crystallogr. B* (1997) 319.
- [24] Delft, The Netherlands. Nonius COLLECT: KappaCCD software, 1998.
- [25] Z. Otwinowski, W. Minor, *Methods Enzymol.* (1997) 307.
- [26] N.W. Alcock, *Cryst. Comput.* (1970) 271.
- [27] L.J. Farrugia, *J. Appl. Crystallogr.* 32 (1999) 837.
- [28] A. Altomare, M.C. Burla, M. Camalli, G. Cascarano, C. Giacovazzo, A. Guagliardi, A.G.G. Moliterni, G. Polidori, R. Spagna, *J. Appl. Crystallogr.* 32 (1999) 115.
- [29] M. Watanabe, K. Nagashima, *J. Inorg. Nucl. Chem.* 33 (1971) 3604.
- [30] W. Kraus, G. Nolze, *J. Appl. Crystallogr.* 29 (1996) 301.