

## Synthesis and crystal structure of tetra(quinolin-8-olato)thorium ethanol solvate, $\text{Th}(\text{C}_9\text{H}_6\text{NO})_4 \cdot \text{C}_2\text{H}_5\text{OH}$

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**Abstract:** Metal quinolinolates (also known as oxinates) have been widely used for gravimetric analysis and in recent days as materials for organic light emitting diodes (OLEDs). Recrystallisation of tetra(quinolin-8-olato)thorium(IV) ( $\text{ThQ}_4$ ) yielded yellow, translucent, prismatic crystals of the title compound,  $\text{ThQ}_4 \cdot \text{C}_2\text{H}_5\text{OH}$ , the single-crystal structure of which is described. Only one crystallographically distinct molecule is found, all ligands are crystallographically inequivalent. Thorium is coordinated by four 8-hydroxyquinolinato with average Th-O distances of 233.3 pm and average Th-N distances of 272.4 pm, and one ethanol ligand with a Th-O distance 256.7 pm. O and N surroundings around thorium can be described by a tricapped trigonal prism. In contrast to quinolinates of the trivalent metals,  $\text{ThQ}_4 \cdot \text{C}_2\text{H}_5\text{OH}$  does not fluoresce under UV irradiation, which is in accordance with the lack of  $\pi$ - $\pi$  overlap in the crystal structure.

**Keywords:** Thorium, metal hydroxyquinolinates, metal oxinates, single crystal X-ray diffraction.

### Introduction

8-hydroxyquinoline (= Q, Fig. 1), also known as oxine, has been extensively studied as a chelating ligand in analytical chemistry. 8-hydroxyquinolinato with one negative charge and having one nitrogen and one oxygen ligand atom, exhibits properties as a complex ligand between those of neutral 2, 2'-bipyridin with two nitrogen ligand atoms and the catecholate with two negative charges and two oxygen ligand atoms<sup>1</sup>. Its bonding properties to metal cations and the solubilities of the resulting complexes can be further varied by substitution on the aromatic rings, which is of importance in view of their applications<sup>2-6</sup>.

More recently, metal complexes  $\text{MQ}_n$  ( $2 \leq n \leq 4$ ) of main group, transition and rare earth metals have attracted considerable interest in supramolecular chemistry<sup>1</sup>, as materials for organic light emitting devices (OLEDs), especially  $\text{AlQ}_3$ <sup>2</sup>, as NIR emitters<sup>3</sup>, for medical applications<sup>4,5</sup>, and as precursors for chemical synthesis<sup>6</sup>. 8-hydroxyquinoline complexes of the actinides, however, have been studied to a much lesser extent.

Solvent free  $\text{ThQ}_4$  was found to be monoclinic, while the solvate  $\text{ThQ}_4 \cdot \text{Q}$  crystallizes with triclinic symmetry, the crystal structures, however, were not determined<sup>7</sup>. We have now prepared polycrystalline  $\text{ThQ}_4$  and recrystallised it in ethanol. This yielded yellow, translucent, prismatic crystals of the title compound,  $\text{ThQ}_4 \cdot \text{C}_2\text{H}_5\text{OH}$ , the single-crystal structure of which is discussed here.

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## Results and Discussion

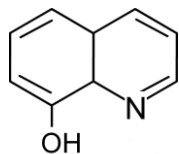
The crystal structure of the new compound tetra(quinolin-8-olato)thorium(IV) ethanol,  $\text{Th}(\text{C}_9\text{H}_6\text{NO})_4 \cdot \text{C}_2\text{H}_5\text{OH}$  was solved from single crystal X-ray diffraction data using the crystallographic software SHELX-97<sup>8</sup>. Thorium is coordinated by four crystallographically inequivalent 8-hydroxyquinolinato ligands with average Th-O distances of 233.3 pm and average Th-N distances of 272.4 pm and one ethanol ligand at a Th-O distance 256.7 pm, i. e. it exhibits a coordination number of nine with four nitrogen and five oxygen ligand atoms. Bond angles O-Th-N within one quinolinate ligand molecule vary from 62.4° to 64.5°. The surroundings of thorium by oxygen and nitrogen can be described by distorted monocapped quadratic antiprism or tricapped trigonal prism, respectively. High coordination numbers are well known in actinide chemistry with ligands from the pnictogen and chalcogen groups in genera<sup>19-13</sup>, and similar coordination is found for other bidentate ligands coordinating thorium by oxygen and nitrogen in particular<sup>14,15</sup>. The four 8-hydroxyquinolinato ligands in  $\text{ThQ}_4 \cdot \text{C}_2\text{H}_5\text{OH}$  are at a closer distance to the central thorium atom than the uncharged solvate ethanol molecule (Table 1). While many crystal structures of 8-hydroxyquinolinate complexes with main group, transition and rare earth metals are known, tetra(quinolin-8-olato)thorium ethanol,  $\text{Th}(\text{C}_9\text{H}_6\text{NO})_4 \cdot \text{C}_2\text{H}_5\text{OH}$  represents one of the first such complex with an actinide metal.

Two molecules of the title compound are arranged around an inversion centre (Fig. 2), forming an elongated unit, i. e., while a single  $\text{Th}(\text{C}_9\text{H}_6\text{NO})_4 \cdot \text{C}_2\text{H}_5\text{OH}$  exhibits the symmetry 1 or  $C_1$ , in Hermann-Mauguin or Schönflies notation, respectively, such a two molecule unit is of higher symmetry,  $-1$  or  $C_i$ . These building blocks are arranged in a distorted cubic primitive packing within the crystal structure. Hereby, ligands of neighboring  $\text{ThQ}_4 \cdot \text{C}_2\text{H}_5\text{OH}$  molecules are inclined at a 100° angle with respect to each with the shortest intermolecular C-C contacts between C6 and C10 (363 pm, dotted line in Fig. 3).  $\pi$ - $\pi$  interaction can therefore considered to be negligible in the title compound. This is in sharp contrast to many other metal 8-hydroxyquinolates, in which closest intermolecular C-C contacts are shorter (350 pm for  $\text{AlQ}_3$ <sup>16</sup>, 337 pm for  $\text{InQ}_3$ <sup>17</sup> and  $\text{ZnQ}_2$ <sup>18</sup>, and the overlap of the quinolinate rings is significant, which has been shown to be crucial for the luminescence properties observed<sup>16-18</sup>. The absence of  $\pi$ - $\pi$  stacking of the quinolinate rings in the title compound is thus in accordance with the observation that it does not fluoresce under UV light irradiation, in contrast to the hydroxyquinolates of aluminium<sup>16</sup>, indium<sup>17</sup> or zinc<sup>18</sup>.

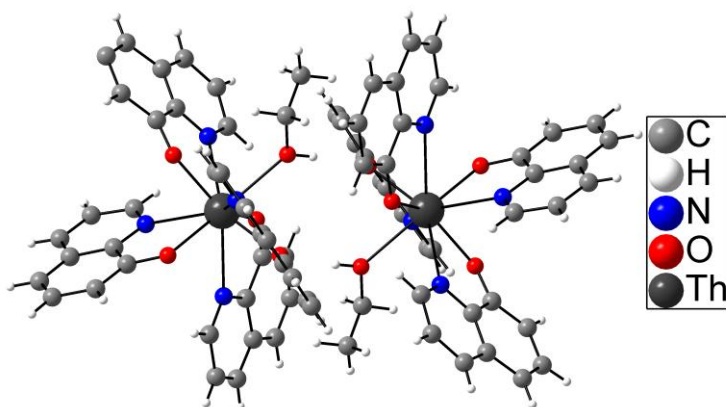
**Table 1:** Bond distances in  $\text{ThQ}_4 \cdot \text{C}_2\text{H}_5\text{OH}$  in pm.

atoms	distance / pm	mean distance /pm
Th-O11D	230.9(3)	Th – O(oxine): 233.3
Th-O11A	232.2(3)	
Th-O11B	233.1(4)	
Th-O11C	237.1(3)	
Th-O88	256.7(4)	Th – O(solvent): 256.7
Th-N1A	268.8(3)	Th – N(oxine): 272.4
Th-N1C	271.6(4)	
Th-N1D	274.0(4)	
Th-N1B	275.1(4)	

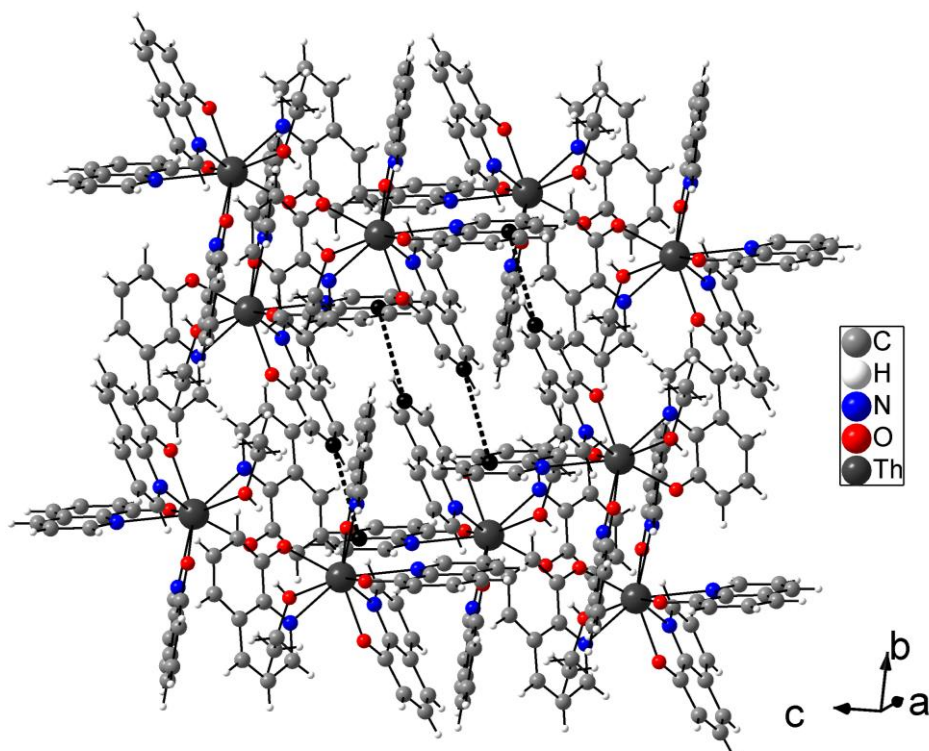
**Figure 1:** Molecular structure of 8-hydroxyquinoline (= HQ, also known as oxine).



**Figure 2:** Two molecules of the title compound with an inversion center in between, Th atoms at a distance of 604.7(5) pm.



**Figure 3:** Packing of  $\text{ThQ}_4 \cdot \text{C}_2\text{H}_5\text{OH}$  molecules in the crystal structure, shortest intermolecular C-C contacts (363 pm) highlighted by dotted lines between blackened C atoms. Note the absence of  $\pi$ - $\pi$  stacking of quinolate ligands.



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## Experimental Section

*Synthesis:* 240 mg of thorium metal powder was dissolved in aqua regia, boiled down a couple of times with hydrochloric acid, and diluted with deionised water. After adjusting to pH  $\approx$  5 by adding sodium acetate, a solution of 14.5 g 8-hydroxyquinolin in 1 L glacial acetic acid was added until no more of the yellow-brown precipitate was formed. After filtration, it was washed several times with hot water and dissolved in ethanol, to give a green solution, which turned yellow after a while. Slow evaporation of the solvent over ten days yielded yellow translucent crystals with prismatic habitus. Crystals of the title compound did not show fluorescence under UV light irradiation.

*Crystal structure determination:* Several yellow translucent crystals of the title compound with prismatic habitus were used for X-ray single crystal diffraction experiments on a Bruker X8 Apex diffractometer equipped with a CCD detector and using MoK $\alpha$  radiation. The one described in the following had the dimensions 50\*75\*125  $\mu\text{m}^3$  and diffraction data were taken up to  $2\theta = 60^\circ$  within a total data collection time of 48h and a redundancy of 16. The metrics was found to be triclinic with  $a = 1186.76(2)$  pm,  $b = 1198.89(2)$  pm,  $c = 1278.33(2)$  pm,  $\alpha = 86.600(1)^\circ$ ,  $\beta = 75.684(1)^\circ$ ,  $\gamma = 66.585(1)^\circ$ . A multiscan absorption correction was performed. The crystal structure could be solved with SHELXS-97 [8] in space group  $P-1$  with two ThQ $_4$ \* C $_2$ H $_5$ OH molecules in the unit cell. The crystal structure was freely refined using SHELXL-97 [8] with hydrogen positions constrained (AFIX 43 for H riding on the aromatic ring, AFIX 23 for the secondary CH $_2$  group of the ethanol solvent molecule) or restrained (rigid body refinement for the methyl group, AFIX 137, and for the hydroxyl group of the ethanol solvent molecule, HFIX 147) to an  $R$  factor of 2.6% for all reflections (see CIF in the supplementary material). Analysis of the X-ray single crystal data of four other crystals of the title compound did not show significant differences as for the refined crystal structure.

## References

### References

- 1 - M. Albrecht, M. Fiege, O. Osetska, Coord. Chem. Rev., **2008**, 252, 812-824.
- 2 - M. Cölle, W. Brütting, Phys. Status Solidi A, **2004**, 201, 1095-1115.
- 3 - N. M. Shavaleev, R. Scopelliti, F. Gummy, J.C.G. Bünzli, Inorg. Chem., **2009**, 48, 7937-7946.
- 4 - C. Deraeve, M. Pitié, H. Mazarguil, B. Meunier, New J. Chem., **2007**, 31, 193-195.
- 5 - M. A. Green, J. C. Huffman, J. Nucl. Med., **1988**, 29, 417-420.
- 6 - G. M. da Costa, E. van San, E. De Grave, R. E. Vandenberghe, V. Barrón, L. Datas, Phys. Chem. Miner., **2002**, 29, 122-131.
- 7 - J. H. Van Tassel, W. W. Wendtland, E. Sturm, J. Am. Chem. Soc., **1961**, 83, 810-812
- 8 - G. M. Sheldrick, <i>SHELXL97</i> and <i>SHELXS97</i>, University of Göttingen, Germany, **1997**.
- 9 - A. J. Freeman, C. Keller (Eds.), Handbook on the Physics and Chemistry of the Actinides, Vol. 4, North-Holland Physics-Publishing, Amsterdam, **1986**.

- 10 - U. Benedict, *J. Less-Common Met.*, **1987**, 128, 7-45.
- 11 - H. Kohlmann, H. P. Beck, *Z. Anorg. Allg. Chem.*, **1997**, 623, 785-790.
- 12 - H. Kohlmann, H. P. Beck, *Z. Kristallogr.*, **1999**, 214, 341-345.
- 13 - Z. Szabó, T. Toraiishi, V. Vallet, I Grenthe, *Coord. Chem. Rev.*, **2006**, 250, 784-815.
- 14 - R. K. Agarwal, P. C. Jain, V. Kapur, S Sharma, A. K. Srivastava, *Transition Met. Chem.*, **1980**, 5, 237-239.
- 15 - P. Thuery, *Inorg. Chem.* **2011**, 50, 1898–1904.
- 16 - M. Brinkmann, G. Gadret, M. Muccini, C. Taliani, N. Masciocchi, A. Sironi, *J. Am. Chem. Soc.* **2000**, 122, 5147-5157.
- 17 - L. S. Sapochak, A. Ranasinghe, H. Kohlmann, K. F. Ferris, P. E. Burrows, *Chem. Mater.*, **2004**, 16, 401-406.
- 18 - L. S. Sapochak, F. E. Benincasa, R. S. Schofield, J. L. Baker, K. K. C. Riccio, D.Fogarty, H. Kohlmann, K. F. Ferris, P. E. Burrows, *J. Am. Chem. Soc.*, **2002**, 124, 6119-6125.