

Thattan Premkumar,<sup>a</sup> Subbiah Govindarajan,<sup>a</sup> Wojciech Starosta<sup>b</sup> and Janusz Leciejewicz<sup>b\*</sup><sup>a</sup>Department of Chemistry, Bharathiar University, Coimbatore 641 046, Tamilnadu, India, and <sup>b</sup>Institute of Nuclear Chemistry and Technology ul. Dorodna 16, 03-195 Warszawa, PolandCorrespondence e-mail:  
jlec@orange.ichtj.waw.pl

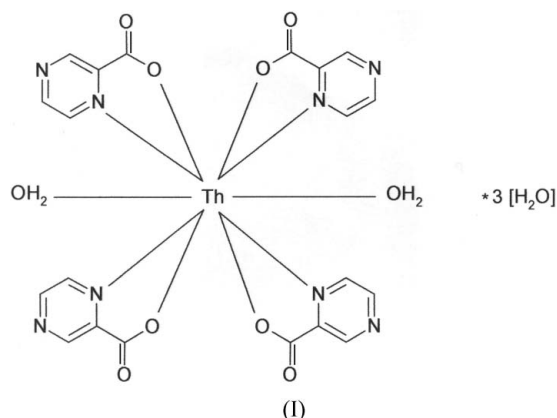
## Key indicators

Single-crystal X-ray study  
*T* = 293 K  
Mean  $\sigma(\text{C}-\text{C}) = 0.012 \text{ \AA}$   
*R* factor = 0.042  
*wR* factor = 0.124  
Data-to-parameter ratio = 14.9For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.Diaquatetrakis(pyrazine-2-carboxylato- $\kappa^2\text{O},\text{N}$ )-thorium(IV) trihydrate

The structure of the title compound,  $[\text{Th}(\text{C}_5\text{H}_3\text{N}_2\text{O}_2)_4(\text{H}_2\text{O})_2] \cdot 3\text{H}_2\text{O}$ , contains monomeric molecules composed of a thorium(IV) ion coordinated by *N,O*-chelating groups donated by four pyrazine-2-carboxylate ligands [mean Th–N = 2.773 (30) Å and mean Th–O = 2.391 (17) Å] and two water O atoms [mean Th–O = 2.517 (30) Å]. The coordination polyhedron around the Th<sup>IV</sup> ion is an irregular hexadecahedron.

## Comment

The structures and properties of divalent 3*d* transition metal complexes with the pyrazine-2-carboxylate ligand still attract much interest. In contrast, the structure of only one complex with the trivalent La<sup>III</sup> ion has been reported (Leciejewicz *et al.*, 2004). Its structure is polymeric, with three bridging pathways *via* the pyrazine-2-carboxylate ligands.



The structure of a complex with a tetravalent ion, Th<sup>IV</sup>, is described here. It contains monomeric molecules in which four pyrazine-2-carboxylate ligands are chelated to a Th<sup>IV</sup> ion using their *N,O*-bonding groups. Two water O atoms complete the ten-coordination. Fig. 1 shows the complex molecule with the ligand and atom numbering, and Fig. 2 is a packing diagram.

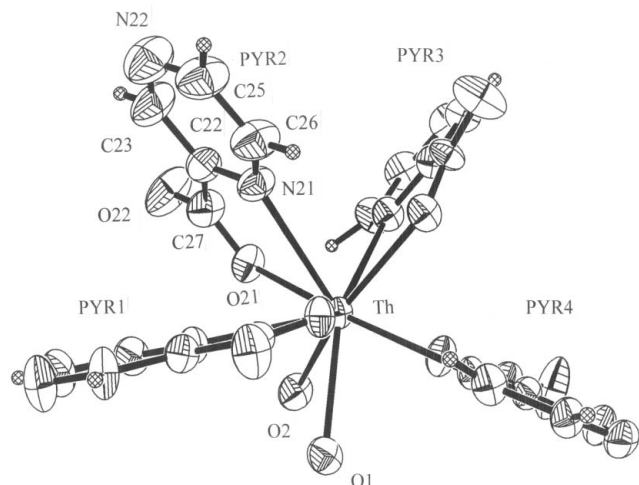
Each acid ligand is almost planar since the relevant r.m.s. deviations from the mean planes are 0.027 (1), 0.049 (1), 0.073 (1) and 0.040 (1) Å for the ligands PYR1, PYR2, PYR3 and PYR4, respectively (Fig. 1). The dihedral angles between ligand planes are PYR1/PYR2 = 63.0 (2)°, PYR2/PYR3 = 78.0 (2)°, PYR3/PYR4 = 75.9 (2)° and PYR4/PYR1 = 34.0 (2)°. The bond lengths and bond angles in the ligands are close to those reported for pyrazine-2-carboxylic acid (Taka-sagawa *et al.*, 1974).

The coordination polyhedron around the Th<sup>IV</sup> ion is an irregular hexadecahedron and the geometry is composed of

Received 21 November 2005

Accepted 28 November 2005

Online 14 December 2005



**Figure 1**

The molecule of (I) with ligand and atom labelling schemes. Non-H atoms are shown as 50% probability displacement ellipsoids. For clarity, ligand molecules are marked as PYR1, PYR2, PYR3 and PYR4.

two monocapped square pyramids rotated by *ca* 45° around the O21–Th–N41 axis [O21–Th–N41 = 171.28 (18)°].

Fig. 3 shows the atom alignment in the polyhedron viewed along the O21–Th–N41 axis. The base of the upper pyramid consists of atoms N11, N21, N31 and O2; its apex is atom O21. The base of the lower pyramid is formed by atoms O11, O31, O41 and O1, the apex being atom N41. The bond distances and bond angles observed within this polyhedron are listed in Table 1.

The same coordination geometry has been reported in the structure of the Th<sup>IV</sup> complex with pyridine-2,6-dicarboxylate and water, in which the metal ion is coordinated by the *O,O',N*-bonding groups donated by two pyridine-2,6-dicarboxylate ligands and four water O atoms, forming a monomeric molecule (Degetto *et al.*, 1978).

## Experimental

An aqueous solution of thorium nitrate pentahydrate (0.570 g in 25 ml) was added to a solution of pyrazine-2,3-dicarboxylic acid (0.745 g in 25 ml H<sub>2</sub>O) and 10% hydrazine hydrate (2 ml). The pH of the resulting solution was maintained at 3 by adding a few drops of 10% hydrazine hydrate. After concentration over a steam bath to one-half of the initial volume, the turbid solution was filtered and the clear filtrate was left for crystallization at room temperature. Pale-yellow block-shaped crystals were found in the mother liquid after a week. They were washed with a cold (1:1) water–ethanol mixture and dried in air.

### Crystal data

[Th(C<sub>5</sub>H<sub>3</sub>N<sub>2</sub>O<sub>2</sub>)<sub>4</sub>(H<sub>2</sub>O)<sub>2</sub>]<sub>2</sub>·3H<sub>2</sub>O

*M<sub>r</sub>* = 814.50

Monoclinic, *P*2<sub>1</sub>/*n*

*a* = 7.9080 (16) Å

*b* = 18.014 (4) Å

*c* = 19.391 (4) Å

β = 95.70 (3)°

*V* = 2748.7 (10) Å<sup>3</sup>

*Z* = 4

*D<sub>x</sub>* = 1.968 Mg m<sup>-3</sup>

Mo Kα radiation

Cell parameters from 25 reflections

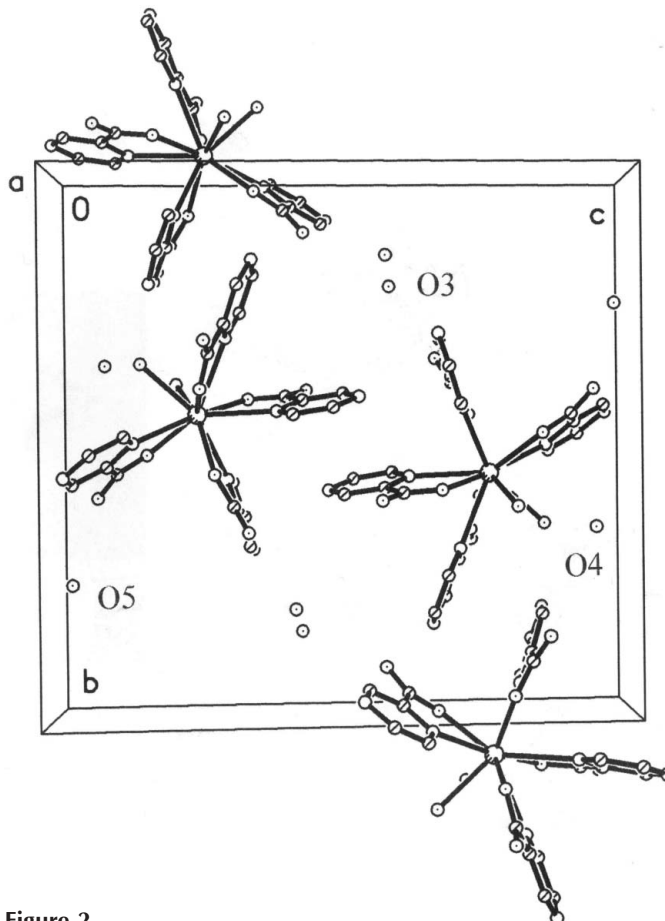
θ = 6–15°

μ = 5.50 mm<sup>-1</sup>

*T* = 293 K

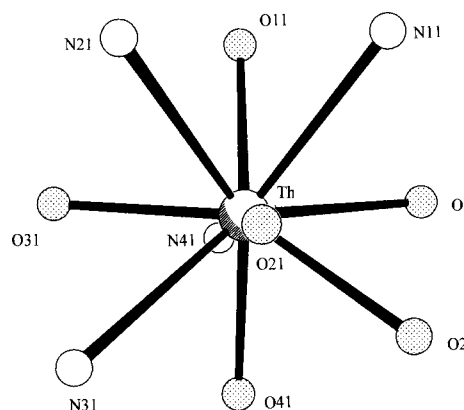
Rectangular block, pale yellow

0.41 × 0.31 × 0.19 mm



**Figure 2**

A packing diagram of (I). Solvent water O atoms are marked as O3, O4 and O5. H atoms have been omitted.



**Figure 3**

The coordination polyhedron around the Th<sup>IV</sup> ion in (I), viewed along the O21–Th–N41 axis.

### Data collection

Kuma KM-4 diffractometer

ω/2θ scans

Absorption correction: analytical  
(*CrysAlis RED*; Oxford  
Diffraction, 2000)

*T*<sub>min</sub> = 0.241, *T*<sub>max</sub> = 0.379

7144 measured reflections

5768 independent reflections

4872 reflections with *I* > 2σ(*I*)

*R*<sub>int</sub> = 0.067

θ<sub>max</sub> = 30.1°

*h* = 0 → 11

*k* = 0 → 25

*l* = -26 → 26

3 standard reflections

every 200 reflections

intensity decay: 9.7% (allowed  
for in data processing)

Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0835P)^2 + 2.9776P]$
$R[F^2 > 2\sigma(F^2)] = 0.042$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.124$	$(\Delta/\sigma)_{\max} = 0.002$
$S = 1.10$	$\Delta\rho_{\max} = 1.54 \text{ e } \text{\AA}^{-3}$
5768 reflections	$\Delta\rho_{\min} = -3.93 \text{ e } \text{\AA}^{-3}$
388 parameters	
H atoms treated by a mixture of independent and constrained refinement	

**Table 1**  
Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ ).

Th1—O41	2.369 (6)	Th1—O1	2.545 (6)
Th1—O31	2.388 (5)	Th1—N11	2.742 (6)
Th1—O11	2.405 (6)	Th1—N21	2.766 (7)
Th1—O21	2.409 (5)	Th1—N31	2.781 (6)
Th1—O2	2.466 (6)	Th1—N41	2.804 (5)
O41—Th1—O31	85.0 (2)	O31—Th1—N31	61.43 (19)
O41—Th1—O1	83.3 (2)	O11—Th1—N31	136.5 (2)
O11—Th1—O1	73.3 (2)	O2—Th1—N31	90.8 (2)
O2—Th1—O1	65.1 (2)	O41—Th1—N41	60.34 (17)
O2—Th1—N11	80.4 (2)	O21—Th1—N41	171.28 (18)
N11—Th1—N21	65.6 (2)		

**Table 2**  
Hydrogen-bond geometry ( $\text{\AA}$ ,  $^\circ$ ).

$D-H \cdots A$	$D-H$	$H \cdots A$	$D \cdots A$	$D-H \cdots A$
O1—H11 $\cdots$ N32 <sup>i</sup>	0.85 (2)	2.22 (6)	2.994 (9)	152 (10)
O1—H12 $\cdots$ O4	0.86	1.86	2.718 (10)	179
O2—H21 $\cdots$ O12 <sup>ii</sup>	0.84 (2)	1.87 (3)	2.696 (8)	167 (11)
O2—H22 $\cdots$ O3 <sup>iii</sup>	0.85 (2)	1.86 (5)	2.668 (9)	159 (11)
O3—H301 $\cdots$ O4	0.83	2.05	2.783 (12)	148
O3—H302 $\cdots$ N42 <sup>iii</sup>	0.83	2.11	2.886 (9)	155
O4—H402 $\cdots$ O32 <sup>iv</sup>	0.91	2.01	2.919 (14)	179
O4—H401 $\cdots$ O5	0.89	2.01	2.574 (19)	120
O5—H502 $\cdots$ O22 <sup>v</sup>	0.85	2.03	2.871 (15)	174
O5—H501 $\cdots$ O42 <sup>vi</sup>	0.85	2.36	3.051 (15)	138

Symmetry codes: (i)  $-x + \frac{5}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (ii)  $x + 1, y, z$ ; (iii)  $-x + 1, -y + 2, -z + 1$ ; (iv)  $-x + \frac{3}{2}, y - \frac{1}{2}, -z + \frac{1}{2}$ ; (v)  $x - \frac{1}{2}, -y + \frac{3}{2}, z + \frac{1}{2}$ ; (vi)  $-x + 2, -y + 2, -z + 1$ .

The positions of H atoms attached to the coordinated water O atoms (O1 and O2) and to the uncoordinated water O atoms (O3, O4 and O5) were not observed directly in Fourier maps. To include them and construct the hydrogen-bond network, the method of Nardelli (1999), as implemented in the *WinGX* software (Farrugia, 1999), has been adopted. The full structure of (I) was then refined using constraints on the O—H distances and H—O—H angles (using restraints on the O—H distances of 0.84  $\text{\AA}$  and H—O—H angles of 105 $^\circ$ ). Pyrazine ring H atoms were positioned geometrically at a distance of 0.93  $\text{\AA}$  from the respective C atom and refined with a riding model.

Data collection: *KM-4 Software* (Kuma, 1996); cell refinement: *KM-4 Software*; data reduction: *DATAPROC* (Kuma, 2001); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1997); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *XP* (Siemens, 1992); software used to prepare material for publication: *SHELXL97*.

References

Degetto, S., Baracco, L., Graziani, R. & Celon, E. (1978). *Transition Met. Chem.* **3**, 351–354.  
 Farrugia, L. J. (1999). *J. Appl. Cryst.* **32**, 837–838.  
 Kuma (1996). *KM-4 Software*. Kuma Diffraction, Wroclaw, Poland.  
 Kuma (2001). *DATAPROC*. Version 10.0.7. Kuma Diffraction, Wroclaw, Poland.  
 Leciejewicz, J., Ptasiwicz-Bak, H., Premkumar, T. & Govindarajan, S. (2004). *J. Coord. Chem.* **57**, 97–103.  
 Nardelli, M. (1999). *J. Appl. Cryst.* **32**, 563–571.  
 Oxford Diffraction (2000). *CrysAlis RED*. Version 1.69. Oxford Diffraction Ltd, Abingdon, Oxfordshire, England.  
 Sheldrick, G. M. (1997). *SHELXS97* and *SHELXL97*. University of Göttingen, Germany.  
 Siemens (1992). *XP*. Version 4.3. Siemens Analytical X-ray Instruments Inc., Karlsruhe, Germany.  
 Takusagawa, F., Higuchi, T., Shimada, A., Tamura, C. & Sasada, Y. (1974). *Bull. Chem. Soc. Jpn*, **47**, 1409–1412.