

*Acta Cryst.* (1995). **C51**, 2230–2232

## Chlorotrakis(2,2,6,6-tetramethyl-3,5-heptanedionato-*O,O'*)zirconium(IV)

MURIELLE JARDIN, YOUNG GAO, JOËLLE GUÉRY AND CHARLES JACOBONI

*Laboratoire des Fluorures URA 449, Faculté des Sciences, Université du Maine, 72017 Le Mans CEDEX, France*

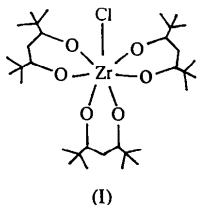
(Received 2 February 1995; accepted 16 May 1995)

### Abstract

The structure of [ZrCl(C<sub>11</sub>H<sub>19</sub>O<sub>2</sub>)<sub>3</sub>] has been solved from single-crystal X-ray diffraction data. Monomolecular units are associated two-dimensionally by intermolecular hydrogen bonds.

### Comment

At the present time, ZBLAN glass (52ZrF<sub>4</sub>, 23BaF<sub>2</sub>, 3LaF<sub>3</sub>, 3AlF<sub>3</sub>, 19NaF mol%) is the most studied glass for the development of optical fibres because of its low attenuation coefficient and good physical properties. Absorbing impurities and extrinsic scattering, however, limit the optical performance of the material (France, Drexhage, Parker, Moore, Carter & Wright, 1990). To increase chemical purity, metal-organic chemical vapour deposition (MOCVD) has been applied to the fluorination of volatile  $\beta$ -diketonate complexes, and fluoride components of the glass have been deposited individually or simultaneously (Jardin, Guéry & Jacoboni, 1995; Nishida, Fujiura, Sato, Sugawara, Kobayashi & Takahashi, 1992; Fujiura *et al.*, 1993). We have prepared and characterized (chemical analysis, TGA, IR, <sup>1</sup>H and <sup>13</sup>C NMR, X-ray powder diffraction) a number of  $\beta$ -diketonate complexes and in the case of [ZrCl(dpm)<sub>3</sub>], (I) (where dpmH is 2,2,6,6-tetramethyl-3,5-heptanedione), we have determined its crystal structure.



In the metal–ligand rings, the C–C and C–O distances are intermediate between single- and double-bond distances (C–C 1.54 and C=C 1.34; C–O 1.43 and C=O 1.23 Å). Because the rings are approximately coplanar, they have aromatic character with delocalized  $\pi$  electrons. The Zr<sup>4+</sup> ions are sevenfold co-

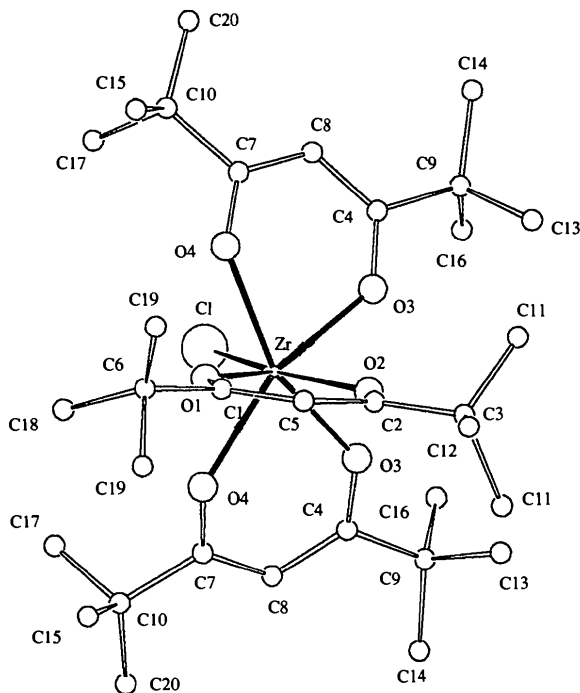


Fig. 1. Geometry of one [ZrCl(dpm)<sub>3</sub>] molecule with atomic labelling scheme.

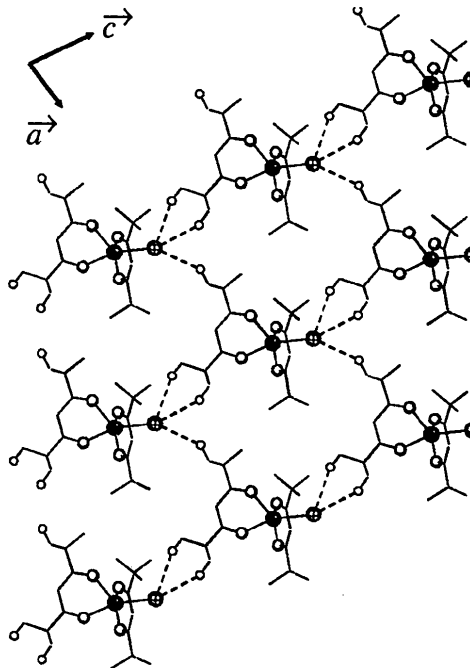


Fig. 2. Intermolecular hydrogen bonds in an (010) plane.

ordinated by six O atoms from three ligands and one Cl atom, forming monomolecular polyhedra (Fig. 1). This Zr environment and metal–ligand geometry is also observed in [ZrCl(acac)<sub>3</sub>] (acac = acetylacetonato) (Von-

Dreele, Stezowski & Fay, 1971). The polyhedra form planes based on Zr positions parallel to the (010) plane, in which each  $[\text{ZrCl}(\text{dpm})_3]$  molecule is linked to its four neighbours by ten intermolecular  $\text{Cl}\cdots\text{H}$  hydrogen bonds (to methyl groups), with distances in the range 3.06–3.30 Å (Fig. 2). Successive planes are reversed (Fig. 3) and the shortest  $\text{O}\cdots\text{H}$  interplane distance (3.62 Å) implies that only van der Waals bonds exist between planes.

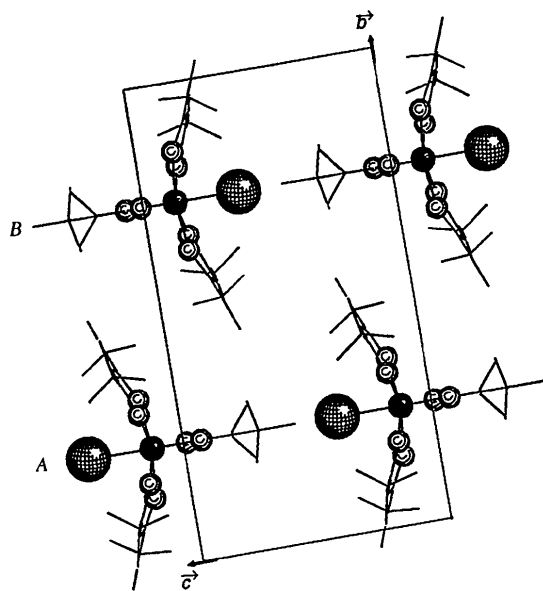


Fig. 3. Association of the  $[\text{ZrCl}(\text{dpm})_3]$  molecules along the  $a$  axis (plane A:  $x_{\text{Zr}} = 0.15$ ; plane B:  $x_{\text{Zr}} = -0.15$ ).

## Experimental

The title complex was prepared following the protocol described for the synthesis of  $[\text{Zr}(\text{dpm})_4]$  by Sievers, Eisenbraut, Springer & Meek (1967). Chemical analysis indicated a clear deviation from the  $[\text{Zr}(\text{dpm})_4]$  formula but was in good agreement with  $[\text{ZrCl}(\text{dpm})_3]$ . Single crystals were obtained by evaporation of a petroleum ether solution at room temperature.

### Crystal data

$[\text{ZrCl}(\text{C}_{11}\text{H}_{19}\text{O}_2)_3]$

$M_r = 676.48$

Monoclinic

$P2_1/m$

$a = 10.6883(6) \text{ \AA}$

$b = 18.270(2) \text{ \AA}$

$c = 10.9819(7) \text{ \AA}$

$\beta = 117.706(5)^\circ$

$V = 1898.5(2) \text{ \AA}^3$

$Z = 2$

$D_x = 1.183 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation

$\lambda = 0.71073 \text{ \AA}$

Cell parameters from 36 reflections

$\theta = 15.5\text{--}16^\circ$

$\mu = 0.366 \text{ mm}^{-1}$

$T = 293 \text{ K}$

Needle

$0.53 \times 0.23 \times 0.15 \text{ mm}$

Colourless

### Data collection

Stoe Siemens AED-2 diffractometer

$\theta/2\theta$  scans

Absorption correction:

SHELX76 Gaussian

(Sheldrick, 1976)

$T_{\text{min}} = 0.90$ ,  $T_{\text{max}} = 0.95$

9716 measured reflections

7420 independent reflections

4125 observed reflections

$[I > 6\sigma(I)]$

$R_{\text{int}} = 0.0234$

$\theta_{\text{max}} = 35^\circ$

$h = -17 \rightarrow 15$

$k = 0 \rightarrow 29$

$l = 0 \rightarrow 17$

3 standard reflections

frequency: 60 min

intensity decay: 5%

### Refinement

Refinement on  $F$

$R = 0.041$

$wR = 0.041$

$S = 1.212$

4125 reflections

245 parameters

All H-atom parameters

refined

Unit weights applied

$(\Delta/\sigma)_{\text{max}} = 0.520$

$\Delta\rho_{\text{max}} = 0.79 \text{ e \AA}^{-3}$

$\Delta\rho_{\text{min}} = -0.39 \text{ e \AA}^{-3}$

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography*

(1974, Vol. IV, Table

2.2B)

Table 1. Fractional atomic coordinates and equivalent isotropic displacement parameters ( $\text{\AA}^2$ )

$$U_{\text{eq}} = (1/3)\sum_i\sum_j U_{ij}a_i^*a_j^*a_i\cdot a_j$$

	$x$	$y$	$z$	$U_{\text{eq}}$
Zr	0.15192 (4)	1/4	0.12551 (4)	0.041 (3)
Cl	0.2498 (1)	1/4	0.3810 (1)	0.07 (1)
O(1)	0.9310 (3)	1/4	0.9876 (3)	0.051 (3)
O(2)	0.1413 (3)	1/4	0.9286 (3)	0.056 (3)
O(3)	0.3205 (2)	0.1768 (1)	0.1563 (2)	0.056 (1)
O(4)	0.0753 (2)	0.1459 (1)	0.1480 (2)	0.053 (1)
C(1)	0.8519 (4)	1/4	0.8598 (4)	0.046 (3)
C(2)	0.0473 (4)	1/4	0.8022 (4)	0.047 (4)
C(3)	0.1049 (5)	1/4	0.6988 (4)	0.056 (4)
C(4)	0.3563 (3)	0.1124 (2)	0.2053 (3)	0.052 (3)
C(5)	0.9048 (4)	1/4	0.7653 (5)	0.057 (4)
C(6)	0.6925 (4)	1/4	0.8126 (5)	0.053 (4)
C(7)	0.1339 (3)	0.0859 (2)	0.2074 (3)	0.053 (3)
C(8)	0.2702 (3)	0.0675 (2)	0.2359 (4)	0.061 (3)
C(9)	0.5039 (3)	0.0891 (2)	0.2305 (4)	0.062 (3)
C(10)	0.0417 (4)	0.0365 (2)	0.2448 (4)	0.068 (4)
C(11)	0.2000 (4)	0.1824 (2)	0.7259 (4)	0.082 (4)
C(12)	0.9901 (7)	1/4	0.5502 (6)	0.092 (6)
C(13)	0.5165 (6)	0.1066 (4)	0.1026 (6)	0.155 (8)
C(14)	0.5335 (5)	0.0082 (3)	0.2608 (7)	0.128 (6)
C(15)	0.8954 (5)	0.0315 (4)	0.1256 (6)	0.149 (7)
C(16)	0.6080 (5)	0.1342 (3)	0.3453 (7)	0.167 (8)
C(17)	0.020 (1)	0.0754 (5)	0.3516 (7)	0.23 (1)
C(18)	0.6643 (7)	0.2797 (8)	0.9290 (8)	0.13 (1)
C(19)	0.6244 (6)	0.1895 (4)	0.721 (1)	0.27 (1)
C(20)	0.1062 (7)	0.9636 (3)	0.297 (1)	0.25 (1)

Table 2. Selected geometric parameters ( $\text{\AA}$ ,  $^\circ$ )

Zr—Cl	2.495 (1)	C(2 <sup>ii</sup> )—C(5 <sup>i</sup> )	1.382 (6)
Zr—O(1 <sup>i</sup> )	2.130 (2)	C(3)—C(11)	1.538 (5)
Zr—O(2 <sup>ii</sup> )	2.110 (3)	C(3 <sup>ii</sup> )—C(12 <sup>i</sup> )	1.518 (6)
Zr—O(3)	2.140 (2)	C(4)—C(8)	1.386 (6)
Zr—O(4)	2.129 (2)	C(4)—C(9)	1.531 (5)
O(1 <sup>i</sup> ) $\cdots$ O(2 <sup>ii</sup> )	2.611 (3)	C(5)—C(1)	1.393 (8)
O(1 <sup>i</sup> ) $\cdots$ O(4)	2.562 (3)	C(6)—C(1)	1.533 (6)
O(1)—C(1)	1.258 (4)	C(6)—C(19)	1.445 (8)
O(2)—C(2)	1.281 (4)	C(6)—C(18)	1.54 (1)
O(3) $\cdots$ Cl	3.189 (2)	C(7)—C(8)	1.383 (5)
O(3) $\cdots$ O(2 <sup>ii</sup> )	2.692 (3)	C(7)—C(10)	1.527 (6)
O(3) $\cdots$ O(3 <sup>iii</sup> )	2.676 (3)	C(9)—C(13)	1.507 (9)
O(3) $\cdots$ O(4)	2.638 (3)	C(9)—C(14)	1.516 (6)

O(3)—C(4)	1.275 (4)	C(9)—C(16)	1.484 (6)
O(4)···Cl	3.032 (2)	C(10)—C(15 <sup>iv</sup> )	1.505 (5)
O(4)—C(7)	1.281 (4)	C(10)—C(17)	1.48 (1)
C(2)—C(3)	1.523 (8)	C(10)—C(20 <sup>v</sup> )	1.485 (7)
Cl—Zr—O(2 <sup>ii</sup> )	161.0 (2)	O(2)—C(2)—C(3)	115.0 (4)
Cl—Zr—O(4)	81.5 (1)	C(5 <sup>i</sup> )—C(2 <sup>ii</sup> )—C(3 <sup>ii</sup> )	123.6 (3)
Cl—Zr—O(1 <sup>i</sup> )	123.0 (1)	C(11)—C(3)—C(11 <sup>iii</sup> )	106.8 (4)
Cl—Zr—O(3)	86.6 (1)	C(12 <sup>i</sup> )—C(3 <sup>ii</sup> )—C(11 <sup>iii</sup> )	109.8 (3)
O(1 <sup>i</sup> )—Zr—O(2 <sup>ii</sup> )	76.0 (2)	O(3)—C(4)—C(8)	123.1 (3)
O(1 <sup>i</sup> )—Zr—O(4)	74.0 (2)	O(3)—C(4)—C(9)	114.5 (3)
O(3)—Zr—O(2 <sup>ii</sup> )	78.6 (2)	C(8)—C(4)—C(9)	122.4 (3)
O(3)—Zr—O(4 <sup>iii</sup> )	151.7 (2)	C(2 <sup>ii</sup> )—C(5 <sup>i</sup> )—C(1 <sup>i</sup> )	123.7 (4)
O(3)—Zr—O(4)	76.3 (2)	C(19)—C(6)—C(19 <sup>iii</sup> )	99.9 (6)
O(3)—Zr—O(1 <sup>i</sup> )	133.2 (2)	C(19)—C(6)—C(18)	128.1 (5)
O(3)—Zr—O(3 <sup>iii</sup> )	77.4 (2)	O(4)—C(7)—C(8)	122.6 (3)
O(4)—Zr—O(2 <sup>ii</sup> )	106.1 (2)	O(4)—C(7)—C(10)	114.8 (3)
O(4)—Zr—O(4 <sup>iii</sup> )	126.5 (2)	C(8)—C(7)—C(10)	122.6 (3)
C(1)—O(1 <sup>i</sup> )—Zr	137.7 (3)	C(7)—C(8)—C(4)	123.3 (3)
C(2)—O(2 <sup>ii</sup> )—Zr	138.7 (3)	C(16)—C(9)—C(13)	108.5 (4)
C(4)—O(3)—Zr	135.0 (2)	C(16)—C(9)—C(14)	111.0 (3)
C(7)—O(4)—Zr	134.4 (2)	C(13)—C(9)—C(14)	108.1 (5)
O(1)—C(1)—C(5)	122.5 (4)	C(17)—C(10)—C(20 <sup>v</sup> )	110.1 (6)
O(1)—C(1)—C(6)	116.2 (4)	C(17)—C(10)—C(15 <sup>iv</sup> )	103.5 (5)
C(5)—C(1)—C(6)	121.4 (4)	C(20 <sup>v</sup> )—C(10)—C(15 <sup>iv</sup> )	112.8 (4)
O(2 <sup>ii</sup> )—C(2 <sup>ii</sup> )—C(5 <sup>i</sup> )	121.4 (5)		

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

The refinement was performed in the centrosymmetric space group  $P2_1/m$ . The Zr<sup>4+</sup> ions were found from the Patterson map and a Fourier calculation was used to locate the Cl<sup>-</sup> positions. The coordinates of the other non-H atoms were obtained from difference Fourier syntheses. Initially, atom C(18) was placed on the 2(e) site and had a very high anisotropic displacement parameter along the *b* axis [ $U_{22} = 0.73(13) \text{ \AA}^2$ ]. By setting it on the 4(*f*) site, the  $U_{22}$  coefficient was reduced to  $0.25(3) \text{ \AA}^2$ . A tetrahedral geometry was imposed on the H atoms of the methyl radicals using *SHELX76 AFIX* (Sheldrick, 1976).

Data collection: *DIF4* (Stoe & Cie, 1988*a*). Cell refinement: *DIF4*. Data reduction: *REDU4* (Stoe & Cie, 1988*b*). Program(s) used to solve structure: *SHELX76*. Program(s) used to refine structure: *SHELX76*. Molecular graphics: *SCHAKAL92* (Keller, 1992).

Lists of structure factors, anisotropic displacement parameters, H-atom coordinates and complete geometry have been deposited with the IUCr (Reference: DU1125). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

## References

- France, P. W., Drexhage, M. G., Parker, J. M., Moore, M. W., Carter, S. F. & Wright, J. V. (1990). *Fluoride Glass Optical Fibres*, pp. 12, 65–66, 132, 186. Glasgow: Blackie.
- Fujiura, K., Nishida, Y., Sato, H., Sugawara, H., Kobayashi, K., Terunuma, Y. & Takahashi, S. (1993). *J. Non-Cryst. Solids*, **161**, 14–17.
- Jardin, M., Guéry, J. & Jacoboni, C. (1995). *J. Non-Cryst. Solids*. In the press.
- Keller, E. (1992). *SCHAKAL92. Computer Program for the Graphic Representation of Molecular and Crystallographic Models*. Univ. of Freiburg, Germany.
- Nishida, Y., Fujiura, K., Sato, H., Sugawara, H., Kobayashi, K. & Takahashi, S. (1992). *Jpn. J. Appl. Phys.* **31**, L1692–L1694.
- Sheldrick, G. M. (1976). *SHELX76. Program for Crystal Structure Determination*. Univ. of Cambridge, England.

- Sievers, R. E., Eisentraut, K. J., Springer, C. S. & Meek, D. W. (1967). *Adv. Chem. Ser.* **71**, 141–154.
- Stoe & Cie (1988*a*). *DIF4. Diffractometer Control Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.
- Stoe & Cie (1988*b*). *REDU4. Data Reduction Program*. Version 6.2. Stoe & Cie, Darmstadt, Germany.
- VonDreele, R. B., Stezowski, J. J. & Fay, R. C. (1971). *J. Am. Chem. Soc.* **93**, 2887–2892.

*Acta Cryst.* (1995). **C51**, 2232–2235

## Inclusion Complex of *N,N'*-(1,1'-Dimethylene-3,3'-biisoquinoline 2,2'-dioxide)-4,13-diaza-18-crown-6 with Sodium Bromide

KINGA SUWIŃSKA

*Institute of Physical Chemistry, Polish Academy of Sciences, Kasprzaka 44/52, PL-01 224 Warszawa, Poland*

(Received 27 October 1994; accepted 16 May 1995)

## Abstract

In the title compound, {25,28,33,36-tetraoxa-1,22,39,40-tetraazahexacyclo[20.8.8.1<sup>3,11</sup>.1<sup>12,20</sup>.0<sup>4,9</sup>.0<sup>14,19</sup>]tetraconta-3(40),4,6,8,10,12(39),13,15,17,19-decaene 39,40-dioxide-O,O',O'',O''',O''''}sodium bromide monohydrate, [Na(C<sub>32</sub>H<sub>38</sub>N<sub>4</sub>O<sub>6</sub>)]Br·H<sub>2</sub>O, the Na<sup>+</sup> cation is located in the geometrical centre of the ligand molecule and is octahedrally coordinated by the six O atoms [Na<sup>+</sup>—O distances vary from 2.391(1) to 2.673(1) Å] in a distorted octahedral arrangement. The water molecules are located in channels formed by cryptate cations and Br<sup>-</sup> anions along the [111] direction of the unit cell.

## Comment

Macrocyclic and macrobicyclic ligands containing heterocyclic *N*-oxide groups are able to bind lanthanide cations and form photoactive cryptates that display strong luminescence and, thus, are of interest both as new luminescent materials and potential labels for time-resolved photoimmunoassays (Alpha, Lehn & Mathis, 1987; Alpha, Balzani, Lehn, Perathoner & Sabbatini, 1987; Lehn, 1987; Sabbatini, Perathoner, Balzani, Alpha & Lehn, 1987). The syntheses of the title ligand, (I), and its lithium and europium(III) cryptates were reported by Lehn, Pietraszkiwicz & Karpiuk (1990). In order to study the details of the cryptate structures and the ligand conformation in the complex, these cryptates were crystallized and their X-ray analyses were undertaken. The present paper reports on the 'Li<sup>+</sup> cryptate'. However, in accordance with some concern regarding the quality of