

1990a). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *ORTEPII* (Johnson, 1976) in *SHELXTL/PC* (Sheldrick, 1990b). Software used to prepare material for publication: *SHELXL93*.

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## A Tetrahydrofuran Ring-Opening Product: *trans*-Tetrachloro{4-[2-(phenylamino)pyridinio]butoxido-*O*}(tetrahydrofuran-*O*)-zirconium(IV)

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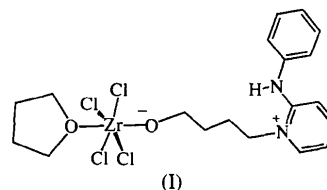
### Abstract

The title compound,  $[ZrCl_4(C_{15}H_{18}N_2O)(C_4H_8O)]$ , was formed *via* tetrahydrofuran (thf) ring opening when  $ZrCl_4$  and 2-(phenylamino)pyridine were heated in a thf-containing reaction medium. The molecule is zwitterionic, with distorted octahedral coordination at the negatively charged zirconium(IV) centre. A 2-(phenylamino)pyridinium cation is connected to the metal

centre by a residue formed through opening of a thf ring.

### Comment

We have recently synthesized chlorobis[2-(phenylamino)pyridinato] complexes by direct reaction of 2-(phenylamino)pyridine and the appropriate metal halide in toluene under reflux (Polamo & Leskelä, 1996). The direct reaction gave the desired bis complexes of Nb and Ta with reasonable yields, unlike zirconium chloride, which produced only a low yield. Nb and Ta complexes are monomeric in the solid state, whereas the corresponding monomeric Zr complex would be coordinatively unsaturated. The bis[2-(phenylamino)pyridinato]zirconium complex was found to be a dimer, with two bridging chloro ligands (Polamo & Leskelä, 1996). It is likely that the low yields of the Zr complex may be related to oligomerization. In order to obtain monomeric complexes, a tetrahydrofuran/toluene mixture was used as a reaction medium. The reaction between 2-(phenylamino)pyridine and zirconium tetrachloride resulted in a thf ring-opening product, (I), instead of the expected dichlorobis[2-(phenylamino)pyridinato]-(tetrahydrofuran)zirconium(IV).



Only a few thf ring-opening products have been previously reported. The formation of a pentamethylcyclopentadienyl complex of Sm (Ewans, Ulibarri,

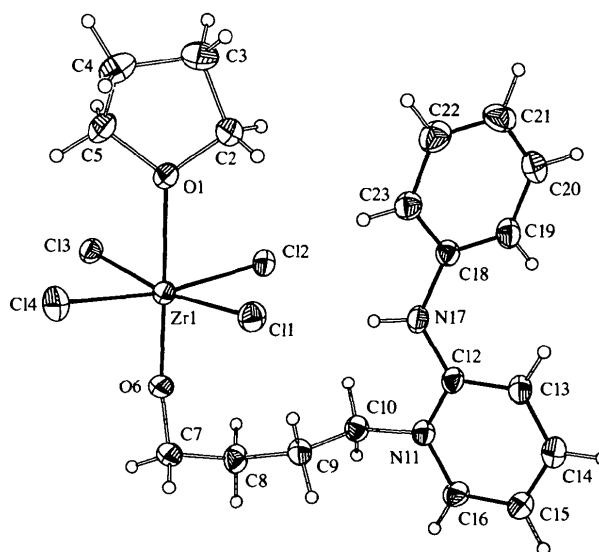


Fig. 1. The molecular structure of (I). Displacement ellipsoids are drawn at the 30% probability level.

Chamberlain, Ziller & Alvarez, 1990) and of a Zr–tri-cyclohexylphosphine complex (Breen & Stephen, 1992) indicates that the ring-opening reaction mechanism involves a step where the lone electron pair of the pyridine N atom attacks an  $\alpha$ -C atom of the thf ring coordinated to Zr. The electropositive metal atom polarizes the coordinated O atom and makes the  $\alpha$ -C atom more susceptible to nucleophilic attack.

The title compound can be regarded as a zwitterion, with six-coordinate anionic zirconate and a 2-phenylaminopyridinium cation connected by the thf residue resulting from the ring opening. The octahedral coordination around the Zr atom is slightly distorted. The more tightly coordinated butoxido group takes up more space around the metal, leading to O1—Zr—Cl angles of 84.21 (8)–86.29 (8)°, whereas the O6—Zr—Cl angles are all significantly greater than 90° [94.25 (9)–95.25 (9)°]. The angle between the pyridinium and phenyl planes is 52.77 (13)°.

## Experimental

For the preparation of the title compound, the ligand precursor 2-(phenylamino)pyridine (5.20 g, 30.5 mmol), was dissolved in 50 ml of toluene/tetrahydrofuran (3:1 mixture) and cooled to 223 K. Zirconium(IV) chloride (6.20 g, 26.8 mmol) was added to the solution. The temperature of the continuously stirred suspension was allowed to rise to room temperature over a period of 60 min. The mixture was refluxed vigorously for 2 h. The reaction mixture was then filtered and crystals were obtained in 48 h. The crystal for the X-ray measurements was attached to a glass fibre using the oil-drop method (Kottke & Stalke, 1993). All reaction steps were carried out under an atmosphere of argon using standard Schlenk techniques.

### Crystal data

[ZrCl <sub>4</sub> (C <sub>15</sub> H <sub>18</sub> N <sub>2</sub> O)(C <sub>4</sub> H <sub>8</sub> O)]	Mo K $\alpha$ radiation
$M_r = 547.44$	$\lambda = 0.71073 \text{ \AA}$
Monoclinic	Cell parameters from 25 reflections
$P2_1/c$	$\theta = 3\text{--}20^\circ$
$a = 14.251 (5) \text{ \AA}$	$\mu = 0.954 \text{ mm}^{-1}$
$b = 11.548 (5) \text{ \AA}$	$T = 193 (1) \text{ K}$
$c = 14.280 (7) \text{ \AA}$	Prismatic
$\beta = 99.89 (3)^\circ$	$0.45 \times 0.35 \times 0.15 \text{ mm}$
$V = 2315.1 (17) \text{ \AA}^3$	Colourless
$Z = 4$	
$D_x = 1.571 \text{ Mg m}^{-3}$	
$D_m$ not measured	

### Data collection

Rigaku AFC-7S diffractometer	2766 reflections with $I > 2\sigma(I)$
$\omega$ -2 $\theta$ scans	$\theta_{\max} = 25.0^\circ$
Absorption correction: $\psi$ scan (North, Phillips & Mathews, 1968)	$h = -16 \rightarrow 16$
$T_{\min} = 0.755$ , $T_{\max} = 0.867$	$k = -13 \rightarrow 0$
3560 measured reflections	$l = -16 \rightarrow 0$
3560 independent reflections	3 standard reflections every 200 reflections
	intensity decay: none

### Refinement

Refinement on $F^2$	$w = 1/[\sigma^2(F_o^2) + (0.0475P)^2 + 1.7287P]$
$R[F^2 > 2\sigma(F^2)] = 0.044$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.106$	$(\Delta/\sigma)_{\max} = 0.013$
$S = 1.079$	$\Delta\rho_{\max} = 0.61 \text{ e \AA}^{-3}$
3560 reflections	$\Delta\rho_{\min} = -0.49 \text{ e \AA}^{-3}$
253 parameters	Extinction correction: none
H atoms riding with $U(H) = 1.3U_{eq}$ of parent atom	Scattering factors from <i>International Tables for Crystallography</i> (Vol. C)

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

Zr1—O6	1.896 (3)	Zr1—Cl1	2.4777 (12)
Zr1—O1	2.281 (3)	Zr1—Cl3	2.4899 (12)
Zr1—Cl4	2.4581 (12)	Zr1—Cl2	2.5226 (11)
O6—Zr1—O1	178.98 (11)	Cl4—Zr1—Cl3	90.87 (4)
O6—Zr1—Cl4	95.25 (9)	Cl1—Zr1—Cl3	170.04 (4)
O1—Zr1—Cl4	84.21 (8)	O6—Zr1—Cl2	94.25 (9)
O6—Zr1—Cl1	94.60 (9)	O1—Zr1—Cl2	86.29 (8)
O1—Zr1—Cl1	86.28 (8)	Cl4—Zr1—Cl2	170.48 (4)
Cl4—Zr1—Cl1	91.81 (4)	Cl1—Zr1—Cl2	88.09 (4)
O6—Zr1—Cl3	94.70 (9)	Cl3—Zr1—Cl2	87.68 (4)
O1—Zr1—Cl3	84.45 (8)		

In the monoclinic indexing used,  $a$  and  $c$  are nearly equal and a  $B$ -centred lattice with  $\beta = 90^\circ$  could be chosen; however, transformations to this cell and averaging in point group  $mmm$  gave  $R_{\text{int}} = 0.45$ , confirming that the Laue symmetry is no higher than  $2/m$ .

Data collection: *MSCIAFC Diffractometer Control Software* (Molecular Structure Corporation, 1992a). Cell refinement: *MSCIAFC Diffractometer Control Software*. Data reduction: *TEXSAN* (Molecular Structure Corporation, 1992b). Program(s) used to solve structure: *SHELXTL/PC* (Sheldrick, 1990). Program(s) used to refine structure: *SHELXL93* (Sheldrick, 1993). Molecular graphics: *SHELXTL/PC*. Software used to prepare material for publication: *SHELXL93*.

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