

Tetrachloro(*N,N,N',N'*-tetramethylethylenediamine)zirconium(IV)Clifton E. F. Rickard,<sup>a\*</sup> Mark W. Glenny<sup>a</sup> and Alastair J. Nielson<sup>b</sup><sup>a</sup>Department of Chemistry, University of Auckland, Private Bag 92019, Auckland, New Zealand, and <sup>b</sup>Institute of Fundamental Sciences, Massey University at Albany, Private Bag 102 904, North Shore Mail Center, Auckland, New Zealand

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## Key indicators

Single-crystal X-ray study

 $T = 203\text{ K}$ Mean  $\sigma(\text{C}-\text{C}) = 0.005\text{ \AA}$  $R$  factor = 0.018 $wR$  factor = 0.045

Data-to-parameter ratio = 24.9

For details of how these key indicators were automatically derived from the article, see <http://journals.iucr.org/e>.

The crystal structure of the title compound,  $[\text{ZrCl}_4(\text{C}_6\text{H}_{16}\text{N}_2)]$ , has a distorted octahedral coordination geometry. The chloro ligands *trans* to the nitrogen donors have significantly shorter bonds than the chloro ligands which are mutually *trans*.

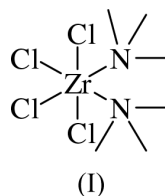
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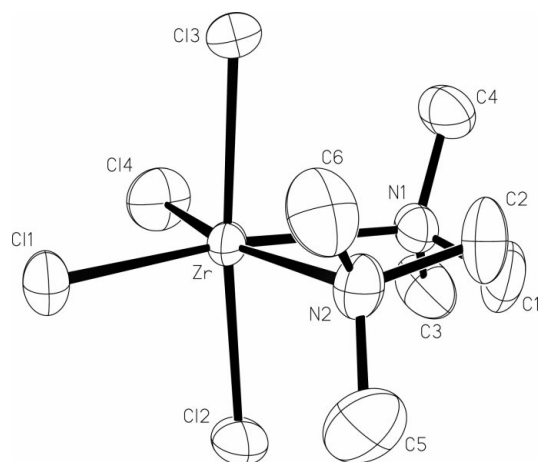
## Comment

Simple coordination compounds of titanium and zirconium are known to be active catalysts for 1-alkene polymerizations (Pino & Mulhaupt, 1980). Titanium complexes containing the *N,N,N',N'*-tetramethylethylenediamine (tmeda) ligand have been found to be catalytically active when heterogeneous systems are used. For example, when  $[\text{TiCl}_4(\text{tmeda})]$  is slurried with  $\text{MgCl}_2$ , the ethylene polymerization activity is above  $5800\text{ g mmol}^{-1}\text{ h}^{-1}$  at 0.5 MPa (Giannini *et al.*, 1980) and the components  $[\text{TiCl}_4(\text{tmeda})]/\text{Et}_3\text{Al}/\text{MgCl}_2$  have been shown to be active in propene polymerization (Sobota *et al.*, 1997).  $[\text{TiCl}_4(\text{tmeda})]$  has been structurally characterized and shown to be a monomeric six-coordinate species (Sobota *et al.*, 1997). Tmeda has been used as a solubilizing reagent for reactions involving the insoluble  $[\text{ZrCl}_4]$  (Strickler & Power, 1996, 1998, 1999) and  $[\text{ZrCl}_4(1.5\text{tmeda})]$  has been prepared and characterized by spectroscopic methods (Gordon & Wallbridge, 1986), but little is known of the structures of these complexes.



We have found that, when slightly more than one equivalent of tmeda in  $\text{CH}_2\text{Cl}_2$  is added to  $[\text{ZrCl}_4]$  in  $\text{CH}_2\text{Cl}_2$ , the insoluble zirconium chloride compound slowly dissolves, producing a colourless solution which gives rise to a highly crystalline complex analysing as  $[\text{ZrCl}_4(\text{tmeda})]$ . Given the propensity for zirconium to form complexes with coordination numbers greater than 6 (Fay, 1986), a crystal structure determination of  $[\text{ZrCl}_4(\text{tmeda})]$ , (I), was undertaken to establish the coordination geometry.

The complex is almost isostructural with  $[\text{TiCl}_4(\text{tmeda})]$ , except that the bite angle for the two N atoms of the tmeda ligand is slightly smaller in the zirconium complex [ $75.44(7)$  versus  $78.5(3)^\circ$ ]. Other angles are very similar to those in the titanium complex. The Zr–Cl bond distances *trans* to the tmeda N atoms are significantly shorter than the two Zr–Cl



**Figure 1**  
The structure of (I), showing 50% probability displacement ellipsoids. The H atoms have been omitted for clarity.

bonds where the chloro ligands are mutually *trans*, due to the greater degree of  $\pi$ -donation to the metal from these ligands. In the absence of any  $\pi$ -donation the complex achieves an electron count of only 12, but this increases to 16 if the chloro ligands *trans* to the N atoms each donate two electrons into two separate metal orbitals. For the *trans* chloro ligands, competitive  $\pi$ -donation would not allow this electron count to be maximized. The chelate ring has the commonly encountered *gauche* conformation.

## Experimental

All preparations and manipulations were carried out under dry oxygen-free nitrogen using standard bench-top techniques for air-sensitive substances.  $\text{ZrCl}_4$  and  $N,N,N',N'$ -tetramethylethylenediamine (tmeda) were used as received from commercial sources. Dichloromethane was dried over and distilled from freshly ground  $\text{CaH}_2$  immediately prior to use. Tmeda (0.97 g, 8.35 mmol) in  $\text{CH}_2\text{Cl}_2$  (20 ml) was added to a suspension of  $\text{ZrCl}_4$  (1.91 g, 8.2 mol) in  $\text{CH}_2\text{Cl}_2$  (30 ml) and the mixture was stirred for 30 min, during which time the solid completely dissolved. The colourless solution was filtered and the volume reduced to about 30 ml. On standing at 253 K, the complex was obtained as a colourless crystalline solid which was filtered off. The solution volume was reduced further to ca 15 ml and, on standing, further crystalline product was obtained. Yield: 2.7 g, 94%. Found: C 20.96, H 4.70, N 8.05%;  $\text{C}_6\text{H}_{16}\text{Cl}_4\text{N}_2\text{Zr}$  requires: C 20.64, H 4.62, N 8.02%. Once isolated, the complex is insufficiently soluble in  $\text{CD}_2\text{Cl}_2$  to obtain NMR spectra.

### Crystal data

$[\text{ZrCl}_4(\text{C}_6\text{H}_{16}\text{N}_2)]$   
 $M_r = 349.23$   
 Orthorhombic,  $Pna2_1$   
 $a = 14.6419(3) \text{ \AA}$   
 $b = 7.6642(2) \text{ \AA}$   
 $c = 12.0660(2) \text{ \AA}$   
 $V = 1354.03(5) \text{ \AA}^3$   
 $Z = 4$   
 $D_x = 1.713 \text{ Mg m}^{-3}$

Mo  $K\alpha$  radiation  
 Cell parameters from 5543 reflections  
 $\theta = 2\text{--}25^\circ$   
 $\mu = 1.57 \text{ mm}^{-1}$   
 $T = 203(2) \text{ K}$   
 Irregular fragment, colourless  
 $0.42 \times 0.28 \times 0.18 \text{ mm}$

### Data collection

Siemens SMART diffractometer  
 $\omega$  scans  
 Absorption correction: multi-scan (Blessing, 1995)  
 $T_{\min} = 0.559$ ,  $T_{\max} = 0.766$   
 13246 measured reflections  
 3059 independent reflections

2927 reflections with  $I > 2\sigma(I)$   
 $R_{\text{int}} = 0.027$   
 $\theta_{\max} = 28.1^\circ$   
 $h = 0 \rightarrow 19$   
 $k = 0 \rightarrow 10$   
 $l = -15 \rightarrow 15$

### Refinement

Refinement on  $F^2$   
 $R[F^2 > 2\sigma(F^2)] = 0.018$   
 $wR(F^2) = 0.045$   
 $S = 1.02$   
 3059 reflections  
 123 parameters  
 H-atom parameters constrained

$w = 1/[\sigma^2(F_o^2) + (0.0236P)^2 + 0.3332P]$   
 where  $P = (F_o^2 + 2F_c^2)/3$   
 $(\Delta/\sigma)_{\max} = 0.362$   
 $\Delta\rho_{\max} = 0.30 \text{ e \AA}^{-3}$   
 $\Delta\rho_{\min} = -0.27 \text{ e \AA}^{-3}$   
 Absolute structure: Flack (1983),  
 1331 Friedel pairs  
 Flack parameter = 0.44 (4)

**Table 1**

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

Zr—Cl4	2.4066 (7)	Zr—Cl3	2.4298 (6)
Zr—Cl1	2.4111 (5)	Zr—N1	2.4319 (17)
Zr—Cl2	2.4281 (6)	Zr—N2	2.4337 (19)
Cl4—Zr—Cl1	104.50 (3)	Cl2—Zr—N1	86.12 (5)
Cl4—Zr—Cl2	91.46 (3)	Cl3—Zr—N1	89.23 (5)
Cl1—Zr—Cl2	90.96 (2)	Cl4—Zr—N2	166.27 (5)
Cl4—Zr—Cl3	91.52 (3)	Cl1—Zr—N2	89.21 (5)
Cl1—Zr—Cl3	92.75 (2)	Cl2—Zr—N2	88.99 (5)
Cl2—Zr—Cl3	174.52 (2)	Cl3—Zr—N2	87.03 (5)
Cl4—Zr—N1	90.90 (5)	N1—Zr—N2	75.44 (7)
Cl1—Zr—N1	164.40 (5)		

The space group is polar and the structure is a twin composed of the two components with opposite polar directions for the  $c$  axis; the twin components have contributions of 0.44 (4) and 0.56 (4). H atoms were placed geometrically and refined with a riding model (including free rotation about C—C bonds for methyl groups), and with  $U_{\text{iso}}$  values constrained to be 1.2 (1.5 for methyl groups) times  $U_{\text{eq}}$  of the carrier atom.

Data collection: *SMART* (Siemens, 1995); cell refinement: *SMART*; data reduction: *SAINT* (Siemens, 1995); program(s) used to solve structure: *SHELXS97* (Sheldrick, 1990); program(s) used to refine structure: *SHELXL97* (Sheldrick, 1997); molecular graphics: *SHELXTL* (Siemens, 1994); software used to prepare material for publication: *SHELXL97*.

## References

- Blessing, R. H. (1995). *Acta Cryst.* **A51**, 33–38.  
 Fay, R. C. (1986). *Coord. Chem. Rev.* **71**, 113–000.  
 Flack, H. D. (1983). *Acta Cryst.* **A39**, 876–881.  
 Giannini, U., Cassita, A., Longi, P. & Mazzocchi, R. (1980). US Patent 4 226 963.  
 Gordon, D. & Wallbridge, M. G. H. (1986). *Inorg. Chim. Acta*, **111**, 77–00.  
 Pino, P. & Mulhaupt, R. (1980). *Angew. Chem. Int. Ed. Engl.* **19**, 857–000.  
 Sheldrick, G. M. (1990). *Acta Cryst.* **A46**, 467–473.  
 Sheldrick, G. M. (1997). *SHELXL97*. University of Göttingen, Germany.  
 Siemens (1994). *SHELXTL*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Siemens (1995). *SMART* and *SAINT*. Siemens Analytical X-ray Instruments Inc., Madison, Wisconsin, USA.  
 Sobota, P., Utton, J. & Szczegot, S. (1997). *J. Chem. Soc. Dalton Trans.* pp. 679–000.  
 Strickler, J. R. & Power, J. M. (1996). US Patent 5 556 997.  
 Strickler, J. R. & Power, J. M. (1998). US Patent 5 847 175.  
 Strickler, J. R. & Power, J. M. (1999). US Patent 5 883 278.