

Bis[*N,N'*-diisopropyl-*N*-(trimethylsilyl)benzamidinium] di- μ -chloro-bis[tetrachlorozirconate(IV)] dichloromethane disolvate

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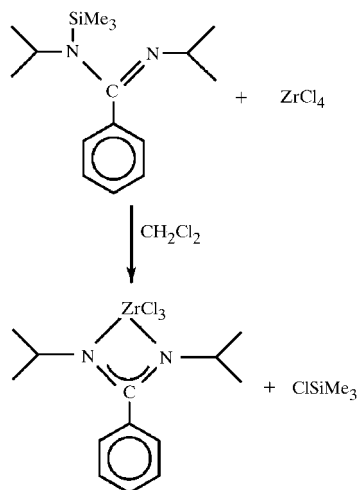
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The structure of the salt of the di- μ -chloro-bis[tetrachlorozirconate(IV)] anion and the *N,N'*-isopropyl-*N*-(trimethylsilyl)benzamidinium cation, (C₁₆H₂₉N₂Si)₂[Zr₂Cl₁₀]·2CH₂Cl₂, is reported. The anion lies about an inversion centre and shows a substantially octahedral coordination around Zr, while the structure of the cation is unequivocally assigned as that of a benzamidinium ion.

Comment

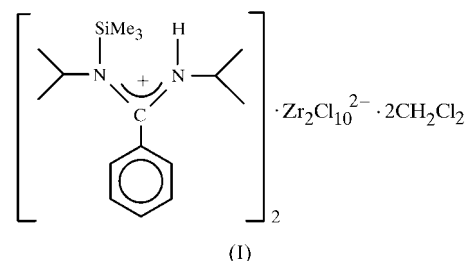
Monoamidinate complexes of group IV transition metals (Ti and Zr), when activated by methylaluminoxane, are active in the Ziegler–Natta polymerization of ethylene, propylene and styrene (Flores *et al.*, 1995*a,b*).



While trying to isolate the monoamidinate complex [C₆H₅-C{NCH(CH₃)₂}₂]ZrCl₃ from a CH₂Cl₂ solution of the reaction products, prepared as reported by Fenske *et al.* (1988) according to the reaction *Scheme* above, we obtained a crys-

talline compound as a by-product [¹H NMR (CD₂Cl₂ at room temperature): δ 0.07 (*s*, 9H), 1.33 (*d*, 6H), 1.69 (*d*, 6H), 3.51 (*m*, 1H), 4.18 (*m*, 1H), 6.59 (*s*, 1H), 7.2–8 (*m*, 5H)]. The singlet at 0.07 (chemical shift from tetramethylsilane), which is unequivocally attributable to a trimethylsilyl group, and the wide singlet at 6.59 suggest that an unexpected compound was isolated, probably as a result of partial hydrolysis of ZrCl₄ due to contamination of the reaction solvent with traces of water. Similar behaviour has been reported for the reaction of ZrCl₄ with 1,3,5-trimethoxybenzene (Coles *et al.*, 1999).

The crystal structure analysis of the new compound, (I), has shown that it corresponds to the chemical formula shown below.



An *ORTEP*-3 (Farrugia, 1997) diagram is shown in Fig. 1 (a partially disordered dichloromethane solvent molecule is also present in the crystallographically independent unit), and selected bond lengths and angles are reported in Table 1.

The [Zr₂Cl₁₀]²⁻ anion is dimeric through bridging Cl atoms across crystallographic inversion centres, and the coordination around the metal atom is substantially octahedral. As expected, the Zr–Cl bond distances are longer (~0.2 Å) in the case of bridging Cl atoms.

The cation differs from the case reported by Coles *et al.* (1999), in which protonation and cation formation were only inferred. In the present case, the location of the H atom is certain; in fact, it was clearly identified in a difference Fourier

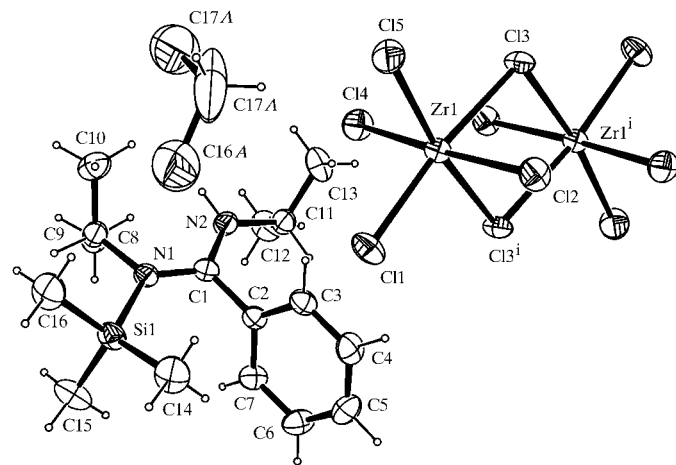


Figure 1

A view of the cation and anion of (I), with displacement ellipsoids shown at the 30% probability level. One of the three positions of the solvent molecule is also shown.

map as being bonded to atom N2, so that the cation can be individuated as an amidinium ion. The two C—N bond distances are equivalent, as reported in a similar amidinium cation (Schmidt & Arnold, 2002), and the N—Si bond length is considerably longer than, for example, the value reported for dimethyl(trimethylsilyl)amine (1.72 Å; Blake *et al.*, 1986). The latter observation suggests little evidence of $p\pi-d\pi$ bond contributions between N and Si atoms in the present case, so the double bond appears to be delocalized over the N1—C1—N2 system only (delocalization toward the phenyl ring can be excluded since the plane of the ring forms a dihedral angle of 72.8 (3)° with the C1/N1/N2 plane). Actually, the formation of the three-centred $p\pi-p\pi$ conjugated system is probably the reason why protonation occurs on atom N2 instead of atom N1.

Experimental

Single crystals of (I) were obtained by cooling a CH₂Cl₂ solution at 253 K. The crystal used in the analysis was sealed in a Lindemann capillary under a nitrogen atmosphere.

Crystal data

(C ₁₆ H ₂₉ N ₂ Si) ₂ [Zr ₂ Cl ₁₀]·2CH ₂ Cl ₂	Mo K α radiation
$M_r = 1261.80$	Cell parameters from 25 reflections
Orthorhombic, <i>Pbca</i>	$\theta = 28.2-29.4^\circ$
$a = 19.61 (5) \text{ \AA}$	$\mu = 1.09 \text{ mm}^{-1}$
$b = 17.350 (2) \text{ \AA}$	$T = 293 (2) \text{ K}$
$c = 16.832 (2) \text{ \AA}$	Prism, white
$V = 5727 (15) \text{ \AA}^3$	$0.60 \times 0.50 \times 0.30 \text{ mm}$
$Z = 4$	
$D_x = 1.463 \text{ Mg m}^{-3}$	

Data collection

Enraf–Nonius MACH3 diffractometer	$\theta_{\text{max}} = 28.0^\circ$
Non-profiled $\omega/2\theta$ scans	$h = 0 \rightarrow 25$
Absorption correction: φ scan (North <i>et al.</i> , 1968)	$k = 0 \rightarrow 22$
$T_{\text{min}} = 0.503$, $T_{\text{max}} = 0.721$	$l = 0 \rightarrow 22$
6872 measured reflections	1 standard reflection
6872 independent reflections	frequency: 126 min
4109 reflections with $I > 2\sigma(I)$	intensity decay: none

Table 1

Selected geometric parameters (Å, °).

Zr1—Cl1	2.389 (5)	Zr1—Cl5	2.398 (6)
Zr1—Cl2	2.408 (6)	Si1—N1	1.833 (4)
Zr1—Cl3	2.622 (5)	N1—C1	1.325 (5)
Zr1—Cl3 ⁱ	2.610 (7)	N2—C1	1.329 (6)
Zr1—Cl4	2.419 (6)	C1—C2	1.474 (6)
Cl1—Zr1—Cl5	99.58 (5)	Cl3 ⁱ —Zr1—Cl3	79.09 (12)
Cl5—Zr1—Cl3 ⁱ	169.46 (5)	Zr1 ⁱ —Cl3—Zr1	100.91 (12)
Cl1—Zr1—Cl3	169.82 (5)		
N2—C1—C2—C3	72.1 (6)	N1—C1—C2—C7	73.6 (6)

Symmetry code: (i) 2 - x, -1 - y, -z.

Refinement

Refinement on F^2	$w = 1/[\sigma^2(F_o^2) + (0.0624P)^2 + 7.0008P]$
$R[F^2 > 2\sigma(F^2)] = 0.049$	where $P = (F_o^2 + 2F_c^2)/3$
$wR(F^2) = 0.147$	$(\Delta/\sigma)_{\text{max}} = 0.002$
$S = 1.02$	$\Delta\rho_{\text{max}} = 0.67 \text{ e \AA}^{-3}$
6872 reflections	$\Delta\rho_{\text{min}} = -0.55 \text{ e \AA}^{-3}$
261 parameters	
H-atom parameters constrained	

Reflections corresponding to systematic absences were not collected. All H atoms were positioned stereochemically, with the exception of H atoms bonded to atoms N2 and C10, which were found from a difference Fourier synthesis. All H atoms were refined as riding, with U_{iso} values equal to the U_{eq} value of the carrier atom. The disorder of the CH₂Cl₂ solvent molecule was modelled without constraints on the basis of three partially superimposed sites (*A*, *B* and *C*) with occupancy factors of 0.4, 0.4 and 0.2, respectively. Seemingly, site *B* is obtained from site *A* by rotation around the Cl6*A*—C17*A* bond, and site *C* is obtained from site *A* by rotation around the Cl7*A*—C17*A* bond. Furthermore, if the solvent molecule and its nearest centrosymmetrically related molecule are considered, some of the possible relative orientations are not allowed because of the close contacts between Cl atoms.

Data collection: MACH3/PC and CAD-4/PC (Nonius, 1996); cell refinement: CELLFIT (Centore, 2002); data reduction: XCAD4 (Harms & Wocadlo, 1995); program(s) used to solve structure: SHELXS97 (Sheldrick, 1990); program(s) used to refine structure: SHELXL97 (Sheldrick, 1997); molecular graphics: ORTEP-3 for Windows (Farrugia, 1997); software used to prepare material for publication: WinGX (Farrugia, 1999).

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Supplementary data for this paper are available from the IUCr electronic archives (Reference: NA1614). Services for accessing these data are described at the back of the journal.

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