

Thompson, 1988) and [Cu(O₄S)(C₅H₅N)₄].H₂O (Kožíšek, Hricov & Langfelderová, 1989).

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Structure of an Allotropic Form of [Bis(trimethylsilyl)amido]dichloro-(η^5 -cyclopentadienyl)titanium

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Abstract. [TiCl₂(C₆H₁₈NSi₂)(C₅H₅)], $M_r = 344.3$, triclinic, $P\bar{1}$, $a = 8.831(4)$, $b = 14.270(8)$, $c = 6.774(8)$ Å, $\alpha = 91.98(8)$, $\beta = 99.33(9)$, $\gamma = 85.13(5)^\circ$, $V = 839.2(8)$ Å³, $Z = 2$, $D_x = 1.36$ Mg m⁻³, $\lambda(\text{Mo } K\alpha) = 0.71069$ Å, $\mu = 0.95$ mm⁻¹, $F(000) = 360$, $T = 185$ K. Full-matrix least-squares refinement based on 1583 reflections led to $R(F_o)$ and $wR(F_w)$ values of 0.042 and 0.053, respectively. The room-temperature unit cell is also triclinic with consistent parameters. This triclinic form is an allotropic modification of the monoclinic [CpTiCl₂{N(SiMe₃)₂}] [Bai, Roesky & Noltemeyer (1991). *Z. Anorg. Allg. Chem.* **595**, 21–26]. No significant difference is observed in the molecular structure of both forms, characterized by a tetrahedral environment of the Ti atom and a noticeably short [1.881(6) Å] Ti—N bond.

Experimental. [CpTiCl₂{N(SiMe₃)₂}] from LiN-(SiMe₃)₂ and CpTiCl₃ in toluene under nitrogen, recrystallized from toluene solution at 255 K. A moisture-sensitive orange crystal of dimensions 0.40 × 0.20 × 0.05 mm was protected by a film of mineral oil, stuck with Apiezon grease and quickly transferred to the nitrogen gas flow of a cooling device. Intensity data were recorded at 185 K on an Enraf-Nonius CAD-4 diffractometer with graphite-monochromated Mo $K\alpha$ radiation. Cell dimensions

were determined from setting angles of 25 reflections having $3.5 < \theta < 14.1^\circ$. 2277 reflections were measured using $\omega/2\theta$ scans with 2θ from 3 to 44° ($-9 \leq h \leq 9$, $-15 \leq k \leq 15$, $0 \leq l \leq 7$) and scan width $(0.90 + 0.35 \tan \theta)^\circ$, with variable scan speed 0.97 – 8.24° min⁻¹. Intensities of three reflections ($\bar{1}01$, 141 , $0\bar{1}\bar{1}$) measured every 2 h showed 3.4% decay, for which correction was made. Corrections were applied for Lp effects, as well as for absorption by ψ scans (North, Phillips & Mathews, 1968); minimum and maximum relative transmission 0.83 and 0.99, respectively. 1925 reflections were unique; $R_{\text{int}} = 0.019$ for averaging redundant $\pm h \pm k 0$ reflections. Direct methods followed by Fourier and least-squares techniques using 1583 reflections having $F_o^2 > 3\sigma(F_o^2)$ based on counting statistics, were used to solve the structure. Full-matrix least-squares refinement was based on F_o , minimizing $\sum w(|F_o| - |F_c|)^2$, with anisotropic thermal parameters for non-H atoms. All H atoms were located by ΔF map and included with constrained geometry (C—H = 0.97 Å) and with isotropic U_H kept fixed to 0.05 Å². Final $R = 0.042$, $wR = 0.053$, $S = 1.45$, for 154 variables, and with unit weights.† Maximum parameter

† Lists of structure factors, H-atom parameters and anisotropic thermal parameters have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55570 (11 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: PA1006]

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Table 1. Fractional atomic coordinates and equivalent isotropic temperature factors ($\text{\AA}^2 \times 10^2$) with e.s.d.'s in parentheses

$$U_{\text{eq}} = \frac{1}{3}(\text{trace } U).$$

	x	y	z	U_{eq}
Ti	0.7923 (1)	0.33762 (8)	0.1263 (2)	2.25 (7)
Cl(1)	0.9798 (2)	0.2822 (1)	-0.0529 (2)	3.4 (1)
Cl(2)	0.6196 (2)	0.4008 (1)	-0.1284 (2)	3.3 (1)
Si(1)	0.8190 (2)	0.1346 (1)	0.3179 (3)	2.8 (1)
Si(2)	0.5010 (2)	0.2211 (1)	0.1435 (3)	2.7 (1)
N	0.7034 (6)	0.2305 (4)	0.1947 (8)	2.4 (3)
C(1)	0.8373 (9)	0.3868 (5)	0.4599 (9)	3.2 (4)
C(2)	0.9770 (8)	0.3879 (5)	0.387 (1)	3.3 (4)
C(3)	0.960 (1)	0.4601 (5)	0.246 (1)	4.3 (5)
C(4)	0.813 (1)	0.5009 (5)	0.229 (1)	4.1 (5)
C(5)	0.7329 (9)	0.4545 (5)	0.360 (1)	3.9 (5)
C(11)	0.8032 (9)	0.0317 (5)	0.143 (1)	4.4 (5)
C(12)	0.7611 (9)	0.1109 (5)	0.565 (1)	4.1 (5)
C(13)	1.0275 (9)	0.1546 (5)	0.385 (1)	4.6 (5)
C(21)	0.4387 (9)	0.1966 (5)	-0.130 (1)	3.9 (5)
C(22)	0.4351 (9)	0.1222 (5)	0.272 (1)	4.1 (5)
C(23)	0.3974 (8)	0.3283 (5)	0.233 (1)	3.7 (4)

Table 2. Bond lengths (\AA) and angles ($^\circ$) with e.s.d.'s in parentheses

Ti—Cl(1)	2.281 (2)	Cl(1)—Ti—Cl(2)	98.5 (1)
Ti—Cl(2)	2.266 (2)	Cl(1)—Ti—N	105.5 (2)
Ti—N	1.881 (6)	Cl(1)—Ti—Cp	112.8 (3)
Ti—C(1)	2.325 (7)	Cl(2)—Ti—N	104.3 (2)
Ti—C(2)	2.339 (7)	Cl(2)—Ti—Cp	111.5 (3)
Ti—C(3)	2.420 (8)	N—Ti—Cp	121.6 (2)
Ti—C(4)	2.422 (7)	Ti—N—Si(1)	121.1 (3)
Ti—C(5)	2.346 (8)	Ti—N—Si(2)	121.8 (3)
Ti—Cp	2.05 (1)	Si(1)—N—Si(2)	117.2 (3)
N—Si(1)	1.782 (5)	N—Si(1)—C(11)	107.3 (3)
N—Si(2)	1.780 (5)	N—Si(1)—C(12)	111.9 (3)
Si(1)—C(11)	1.855 (8)	N—Si(1)—C(13)	114.3 (3)
Si(1)—C(12)	1.877 (8)	C(11)—Si(1)—C(12)	112.6 (4)
Si(1)—C(13)	1.867 (8)	C(11)—Si(1)—C(13)	107.6 (4)
Si(2)—C(21)	1.875 (8)	N—Si(2)—C(21)	110.2 (3)
Si(2)—C(22)	1.865 (8)	N—Si(2)—C(22)	114.1 (3)
Si(2)—C(23)	1.850 (8)	N—Si(2)—C(23)	110.3 (3)
C(1)—C(2)	1.40 (1)	C(12)—Si(1)—C(13)	103.5 (4)
C(2)—C(3)	1.41 (1)	C(21)—Si(2)—C(22)	104.8 (4)
C(3)—C(4)	1.37 (1)	C(21)—Si(2)—C(23)	112.3 (3)
C(4)—C(5)	1.43 (1)	C(22)—Si(2)—C(23)	105.0 (4)
C(5)—C(1)	1.39 (1)	C(2)—C(1)—C(5)	108.2 (6)
		C(1)—C(2)—C(3)	107.9 (6)
		C(2)—C(3)—C(4)	108.2 (7)
		C(3)—C(4)—C(5)	108.5 (7)
		C(4)—C(5)—C(1)	107.1 (7)

shift was 0.001σ . Maximum and minimum heights in the final ΔF map were 0.44 and -0.69 e \AA^{-3} , respectively. Scattering factors including real and imaginary parts of anomalous dispersion were obtained from *International Tables for X-ray Crystallography* (1974, Vol. IV, pp. 99–101, 149) for non-H atoms and from Stewart, Davidson & Simpson (1965) for H atoms. A MicroVAX 3400 DEC computer was used with programs *MolEN* (Fair, 1990), *SHELX76* (Sheldrick, 1976), *SHELXS86* (Sheldrick, 1986) and *ORFFE* (Busing, Martin & Levy, 1964). Room-temperature cell parameters were measured using another crystal from a different batch mounted in a Lindemann-glass tube. Least-squares calculations based on the setting angles of 25 reflections having

$14 < \theta < 17^\circ$ gave $a = 8.915 (2)$, $b = 14.471 (5)$, $c = 6.842 (3) \text{ \AA}$, $\alpha = 90.92 (4)$, $\beta = 98.63 (4)$, $\gamma = 85.96 (3)^\circ$, $V = 870.5 (5) \text{ \AA}^3$.

Related literature. The final positional and equivalent isotropic thermal parameters are listed in Table 1, and bond lengths and angles are given in Table 2. A thermal-ellipsoid plot of the $[\text{CpTiCl}_2\{\text{N}(\text{SiMe}_3)_2\}]$ complex (*ORTEP*; Johnson, 1965) is shown in Fig. 1 with atomic labelling. Fig. 2 is a stereoview of the molecular packing. $[\text{CpTiCl}_2\{\text{N}(\text{SiMe}_3)_2\}]$ is used as a precursor for chemical vapour deposition (CVD) of thin films of the ceramic TiN onto various substrates (Laurent, Zhao, Valade, Choukroun & Cassoux, 1992). The present structural determination was undertaken to ascertain the molecular structure of the precursor in order to study its decomposition process. Before completion of the CVD experiments (and thus before publication of our results) a paper by Bai, Roesky & Noltemeyer (1991) reported the crystal structure of a monoclinic form of $[\text{CpTi-}$

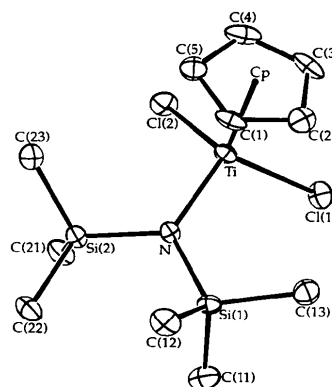


Fig. 1. *ORTEP* (Johnson, 1965) plot of $[\text{CpTiCl}_2\{\text{N}(\text{SiMe}_3)_2\}]$ with atomic numbering, showing 35% probability thermal ellipsoids. H atoms are omitted for clarity.

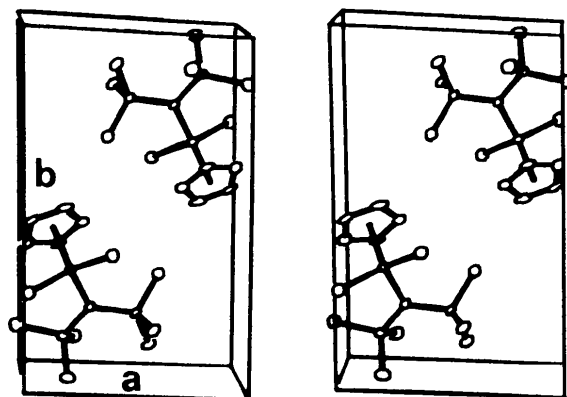


Fig. 2. Stereoview of the molecular packing.

Cl₂{N(SiMe₃)₂}, space group $P2_1/n$ at room temperature. Our results indicate the existence of a triclinic form at 185 and 295 K. This polymorphism may result from the crystallization method: the monoclinic form was obtained by sublimation while the triclinic form was crystallized from toluene solution; other details of the synthesis are quite similar in both cases. No significant difference is noticed between the two molecular structures. However, the bond lengths are systematically longer (by a mean of 0.020 Å) in the low-temperature triclinic structure than in the room-temperature monoclinic structure. This difference (Δl) results from the reduction of libration motion upon cooling (Willis & Pryor, 1975); it is much more pronounced for the Cp group (mean Δl for C—C 0.048 Å, mean Δl for Ti—C 0.021 Å) than for other atoms (mean Δl excluding Cp 0.007 Å).

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Bis(tetraethylammonium) Nickel Tetrakis thiophenolate: a New Polymorph

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Abstract. Tetraethylammonium tetrakisbenzenethiolatonicelate(2-), [(C₂H₅)₄N]₂[Ni(C₆H₅S)₄], $M_r = 755.86$, orthorhombic, $P2_12_12_1$, $a = 14.145(7)$, $b = 16.482(8)$, $c = 17.589(8)$ Å, $V = 4101(3)$ Å³, $Z = 4$, $D_x = 1.224$ g cm⁻³, $\lambda(\text{Mo } K\alpha) = 0.71073$ Å, $\mu = 6.98$ cm⁻¹, $F(000) = 1624$, $T = 296$ K, $R_F = 0.0509$ for 2675 observed reflections and 377 least-squares parameters. As expected, the anion contains four thiophenolate ligands tetrahedrally coordinated to the Ni atom. The average Ni—S bond distance is 2.296(4) Å. The structure is similar to a previously reported monoclinic form [Yamamura, Miyamae, Katayama & Sasaki (1985). *Chem. Lett.* pp. 269–272] for which $R = 0.088$.

Experimental. Violet crystals were grown from acetonitrile (0.40 × 0.40 × 0.40 mm). Data were collected on a Nicolet R3m diffractometer with graphite monochromator, using ω scans. Lattice parameters were determined from least-squares fit of 25 reflections ($20 \leq 2\theta \leq 25^\circ$). An absorption correction was required ($T_{\text{max}}/T_{\text{min}} = 0.847/0.633$; $\mu = 6.98$ cm⁻¹). $2\theta_{\text{max}} = 50^\circ$ ($h = \pm 18$, $k = \pm 21$, $l = +22$). Three standard reflections (703, 194 and 039), for 4202

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reflections collected, showed less than 2% decay. Of 4176 unique reflections, 2678 were observed with $F_o > 5\sigma(F_o)$ (1498 unobserved reflections). Direct methods (*SOLV*; Sheldrick, 1983) were used for structure solution. Least-squares refinement of 377 parameters, with all non-H atoms anisotropic, all H atoms calculated (C—H = 0.960 Å, $U = 1.2U$ for attached C) and phenyl rings constrained as rigid planar hexagons (C—C = 1.395 Å), converged at $R_F = 5.09\%$, $wR_F = 5.17\%$ [$w^{-1} = \sigma^2(F_o) + gF_o^2$, $g = 0.001$], $S = 1.231$; $(\Delta/\sigma)_{\text{max}} = 0.045$; $(\Delta\rho)_{\text{max}} = 0.579$, $\Delta\rho_{\text{min}} = -0.265$ e Å⁻³. Atomic scattering factors were taken from *International Tables for X-ray Crystallography* (1974, Vol. IV). *SHELXTL* computer programs (Sheldrick, 1983) were used in the structure determination.

Atomic coordinates and equivalent isotropic thermal parameters are given in Table 1. Selected bond lengths and bond angles are given in Table 2.† The anion is shown in Fig. 1 and the packing in Fig. 2.

† Lists of structure factors, bond lengths and angles, anisotropic thermal parameters and H-atom coordinates have been deposited with the British Library Document Supply Centre as Supplementary Publication No. SUP 55588 (19 pp.). Copies may be obtained through The Technical Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England. [CIF reference: HH1015]

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