

Diazidobis(η -cyclopentadienyl)titanium

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Abstract. $(C_5H_5)_2Ti(N_3)_2$, orthorhombic, $Pnma$, $a = 7.879$ (5), $b = 12.169$ (8), $c = 12.046$ (8) Å, $U = 1155$ Å³, $Z = 4$, $D_x = 1.51$ g cm⁻³. The structure was solved by Patterson methods and refined to an R of 0.072 for 456 unique diffractometer data. The molecule is bisected by a mirror plane. The Ti—N distance is 2.03 (1) Å.

Introduction. The chemistry of coordinated azides has received attention within the last decade. As a consequence, the crystal structures of several azide derivatives of transition metals have been determined. This work reports the first X-ray investigation of a coordinated azide of Ti.

Preparation of the title compound from aqueous solution has been reported by Langford & Aplington (1965) and Coutts & Wailes (1971). In this investigation the crystals were prepared by a different method with a non-aqueous solvent. A mixture of 0.8 g of Bu_3SnN_3 , 0.25 g of $(C_5H_5)_2TiCl_2$ and 15 ml of toluene

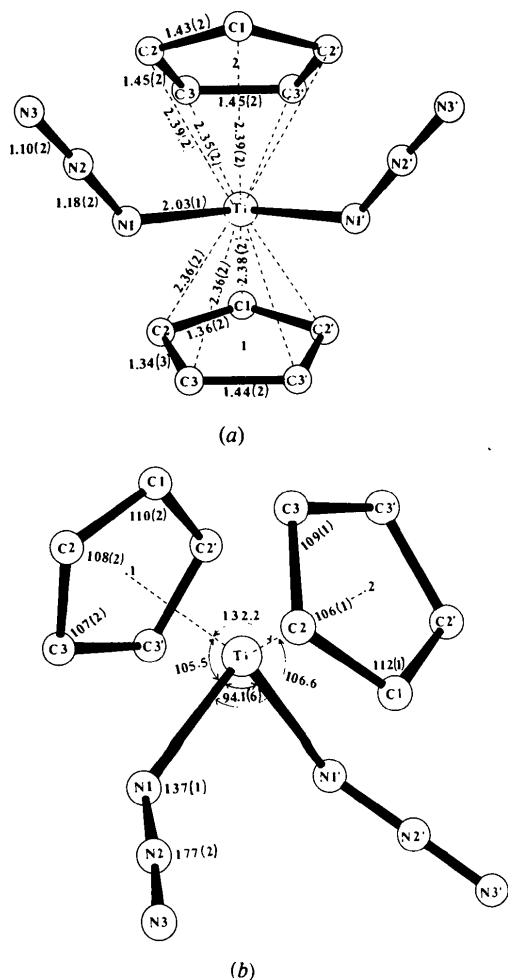


Fig. 1. The molecule of diazidobis(cyclopentadienyl)titanium. (a) Bond lengths. (b) Bond angles. Standard deviations are in parentheses.

Table 1. Atomic coordinates ($\times 10^4$) with standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>
Ti	1637 (5)	2500	-265 (2)
N(1)	1021 (16)	1282 (8)	-1337 (9)
N(2)	1683 (20)	792 (8)	-2058 (10)
N(3)	2251 (19)	307 (8)	-2732 (10)
C(11)	717 (44)	2500	1617 (19)
C(21)	74 (31)	1589 (14)	1125 (17)
C(31)	-1052 (26)	1907 (13)	351 (17)
C(12)	4355 (30)	2500	-1139 (15)
C(22)	4259 (21)	1526 (10)	-475 (12)
C(32)	4095 (22)	1906 (10)	662 (12)

Table 2. Anisotropic temperature factors (Å² $\times 10^3$) with standard deviations in parentheses

The temperature factor exponent takes the form:
 $-2\pi^2(U_{11}h^2a^{*2} + \dots + 2U_{12}hka^*b^*)$.

	U_{11}	U_{22}	U_{33}	U_{23}	U_{13}	U_{12}
Ti	52 (2)	35 (2)	33 (1)	0	6 (2)	0
N(1)	76 (11)	66 (7)	70 (8)	-21 (6)	-2 (6)	-4 (6)
N(2)	100 (10)	46 (7)	74 (8)	-14 (5)	2 (9)	-13 (9)
N(3)	127 (14)	83 (9)	105 (10)	-52 (8)	29 (9)	-20 (8)
C(11)	141 (31)	234 (38)	49 (15)	0	34 (16)	0
C(21)	121 (19)	102 (15)	93 (14)	26 (10)	45 (14)	6 (13)
C(31)	74 (16)	159 (16)	118 (12)	-19 (11)	31 (11)	-46 (9)
C(12)	74 (17)	99 (15)	73 (14)	0	6 (12)	0
C(22)	96 (15)	108 (11)	70 (13)	13 (8)	0 (9)	22 (9)
C(32)	82 (18)	105 (10)	74 (9)	8 (7)	-12 (8)	14 (7)

was heated at 60°C for 1 h. Evaporation gave orange-red crystals (0.25 g) which were recrystallized from toluene–heptane. Composition: calculated for $C_{10}H_{10}N_6Ti$: C 45.3, H 3.4, N 31.7%; found: C 45.39, H 3.58, N 31.4%.

The crystals are prismatic and moderately air sensitive. A crystal $0.15 \times 0.20 \times 0.35$ mm was mounted in a Lindemann capillary in an argon atmosphere. Lattice parameters and integrated intensities were measured on a Norelco Pailred diffractometer with graphite-monochromatized Mo $K\alpha$ radiation. 2323 reflexions with $2\theta < 45^\circ$ were measured and averaged after application of an Lp correction to give 456 unique reflexions with $I > 3\sigma(I)$. The structure was elucidated by Patterson and Fourier methods. Atomic positions and thermal parameters were refined by full-matrix least squares. Complex neutral-atom scattering factors were employed, and the weighting scheme was $w = 1/\sigma^2(F)$. The refinement, with anisotropic thermal motion and an anomalous-dispersion correction for Ti, converged to $R_w = \sum w^{1/2} \Delta / \sum w^{1/2} |F_o| = 0.062$ and $R = 0.072$. No absorption corrections were made. Final atomic coordinates and thermal parameters are given in Tables 1 and 2, and the bond lengths and angles in Fig. 1.*

Discussion. The structure consists of discrete molecules with m symmetry. The coordination around the Ti atom is distorted tetrahedral with N(1)–Ti–N(1') 94.1; N(1)–Ti–CtCp(1) (Ct centroid, Cp cyclopentadienyl) 105.5; N(1)–Ti–CtCp(2) 106.6; and CtCp(1)–Ti–CtCp(2) 132.2°.

The bent $(C_5H_5)_2Ti$ moiety is similar to those found in $(C_5H_5)_4Ti$ (Calderon, Cotton & Legzdins, 1969),

$(C_5H_5)_2Ti(C_6H_5)_2$ (Kocman, Rucklidge, O'Brien & Santo, 1971), $(C_5H_5)_2TiS_5$ (Epstein, Bernal & Köpf, 1971) and $(C_5H_5)_3Ti$ (Lucas, Green, Forder & Prout, 1973). The two cyclopentadienyl rings are in staggered configuration with the Ti atom 2.06 and 2.03 Å from CtCp(1) and CtCp(2) respectively. The Ti–C distances are in the range 2.35–2.39 Å and the C–C distances 1.34–1.45 Å.

The N_3 ligand is linear within experimental error. The N–N distances are 1.10(2) and 1.18(2) Å; the longer distance is closer to the Ti–N bond. The angle N(2)–N(1)–Ti is 137(1)°. This geometrical arrangement is similar to those present in the equivalent $M(N_3)_2$ portion of $[Co(NH_3)_5N_3]^{2+}$ (Palenik, 1964), [1,2-bis(diphenylphosphinato)ethane] $Cu_2(N_3)_2$ (Gaughan, Ziolo & Dori, 1971) and $[Pd_2(N_3)_6]^{2-}$ (Fehlhammer & Dahl, 1972).

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* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 32170 (3 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.