

METAL-ORGANIC COMPOUNDS

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Amidobis(pentamethylcyclopentadienyl)-titanium(III)

ELIZABETH BRADY, JASON R. TELFORD AND
GREG MITCHELL

*Department of Chemistry, University of California,
Berkeley, California 94720, USA*

WAYNE LUKENS*

*Chemical Sciences Division,
Lawrence Berkeley Laboratory, 1 Cyclotron Road,
Berkeley, California 94720, USA, and
Department of Chemistry, University of California,
Berkeley, California 94720, USA*

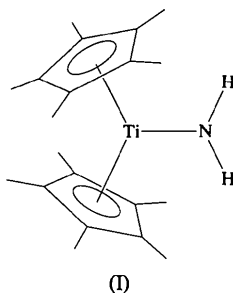
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Abstract

The title compound, $[\text{Ti}(\text{NH}_2)(\text{Me}_5\text{C}_5)_2]$ (I), is a bent metallocene with the NH_2 group oriented so as to maximize the π interaction between the N and Ti atoms. The Ti—N bond length is short [1.944 (2) Å], consistent with increased π bonding.

Comment

The title compound, (I), was synthesized as part of an investigation of metal–ligand π bonding in titanium(III) compounds. Since the electronically favored orientation of the NH_2 group is the most sterically hindered, the relative strength of the electronic and steric effects can be examined. If steric effects dominate, the plane of the NH_2 ligand should be perpendicular to the plane formed by the Ti atom and the centroids of the two pentamethylcyclopentadienyl ligands. On the other hand, if electronic effects dominate, the Ti atom, the two centroids and the NH_2 group (acting as a π donor) will all lie in the same plane.



An *ORTEP* (Johnson, 1965) drawing of $(\eta^5\text{-Me}_5\text{C}_5)_2\text{TiNH}_2$ is given in Fig. 1. The NH_2 ligand is in the appropriate orientation for the filled p orbital of the N atom to interact with the empty b_2 orbital of $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Ti}$, enabling the NH_2 ligand to act as a π donor. The Ti—N distance is also quite short at 1.944 (2) Å. Similar nitrogen to metal π bonding is seen in $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Hf}(\text{H})\text{NHMe}$ (Hillhouse, Bulls, Santarsiero & Bercaw, 1988) as evidenced by the similar orientation of the methylamido group. In the only other crystallographically characterized bis(pentamethylcyclopentadienyl)titanium(III) amide, (*N*-methyl-*N*-phenylamido)bis(pentamethylcyclopentadienyl)titanium(III) (Feldman & Calabrese, 1991), the amido ligand is perpendicular to the plane formed by the Ti atom and the centroids of the two cyclopentadienyl rings, thus preventing the p orbital of the N atom from interacting with the b_2 orbital of the $(\eta^5\text{-Me}_5\text{C}_5)_2\text{Ti}$ fragment. The Ti—N bond length [2.054 (2) Å] is considerably longer than that found in the title compound.

The titanium(IV) metallocene $(\eta^5\text{-C}_5\text{H}_5)_2\text{Ti}(\text{NC}_4\text{H}_4)_2$ (Bynum, Hunter, Rogers & Atwood, 1980) demonstrates nicely the difference in bond lengths caused by π bonding. The compound possesses two pyrrole ligands, one of which is in the correct orientation for the N-atom p -orbital to interact with the empty $1a_1$ orbital of the metallocene. The other pyrrole ring is perpendicular to the first and thus

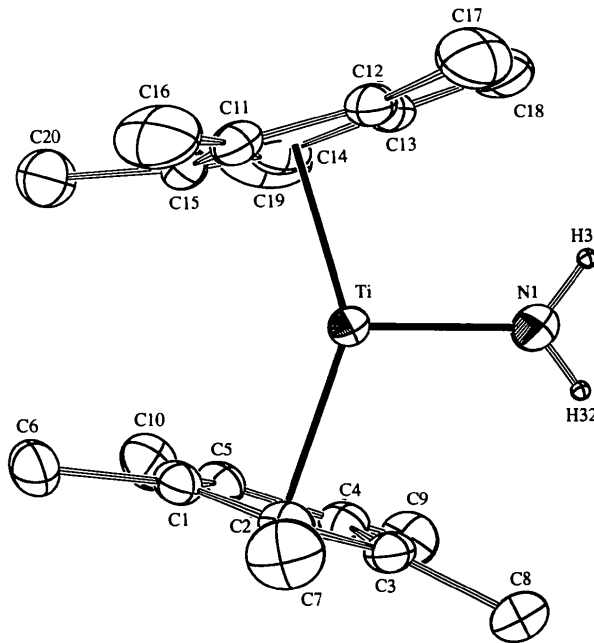


Fig. 1. *ORTEP* (Johnson, 1965) drawing of the molecule with 50% probability displacement ellipsoids.

unable to act a π donor towards the low-lying $1a_1$ orbital. The Ti—N bond length for the pyrrole acting as a π donor is 2.070 (5) Å while it is 2.100 (4) Å for the non- π -bonding pyrrole. Curiously, in the analogous zirconium compound (Bynum, Hunter, Rogers & Atwood, 1980), the bond lengths are almost identical.

Experimental

The title compound was synthesized from $(\eta^5\text{-C}_5\text{Me}_5)_2\text{TiCH}_3$ and NH_3 . Crystals were grown by slowly cooling a saturated hexane solution. An air-sensitive crystal was mounted on the end of a quartz capillary tube with a drop of Paratone N oil.

Crystal data

[Ti(NH₂)(C₁₀H₁₅)₂]

$M_r = 334.38$

Monoclinic

$P2_1/n$

$a = 9.601$ (2) Å

$b = 13.690$ (2) Å

$c = 14.808$ (2) Å

$\beta = 100.83$ (1)°

$V = 1911.6$ (9) Å³

$Z = 4$

$D_x = 1.162$ Mg m⁻³

Mo $K\alpha$ radiation

$\lambda = 0.71073$ Å

Cell parameters from 24

reflections

$\theta = 14\text{--}16^\circ$

$\mu = 0.44$ mm⁻¹

$T = 183$ K

Block

$0.50 \times 0.50 \times 0.30$ mm

Dark purple

Data collection

CAD-4 diffractometer

$\omega/2\theta$ scans

Absorption correction:

refined from ΔF

(DIFABS; Walker & Stuart, 1983)

4844 measured reflections

4393 independent reflections

3571 observed reflections

$[F^2 > 3\sigma(F^2)]$

$\theta_{\text{max}} = 27.5^\circ$

$h = 0 \rightarrow 12$

$k = 0 \rightarrow 17$

$l = -19 \rightarrow 18$

3 standard reflections

frequency: 60 min

intensity decay: not significant

Refinement

Refinement on F

$R = 0.0353$

$wR = 0.0447$

$S = 1.988$

3571 reflections

328 parameters

All H-atom parameters

refined

$w = 1/\sigma^2(F_o)$

$(\Delta/\sigma)_{\text{max}} < 0.1$

$\Delta\rho_{\text{max}} = 0.29$ e Å⁻³

$\Delta\rho_{\text{min}} = -0.10$ e Å⁻³

Extinction correction:

secondary (Stout & Jensen, 1968)

Extinction coefficient:

7×10^{-7}

Atomic scattering factors

from *International Tables*

for *X-ray Crystallography* (1974, Vol. IV)

Table 1. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters (Å²)

B_{iso} for H atoms; $B_{\text{eq}} = (1/3)\sum_i\sum_j B_{ij}a_i^*a_j^*$ for others.

	x	y	z	$B_{\text{iso}}/B_{\text{eq}}$
Ti	0.11498 (1)	0.23016 (1)	0.40310 (1)	1.529 (5)
N1	0.1327 (2)	0.1761 (1)	0.5261 (1)	3.69 (4)
C1	0.1354 (2)	0.1684 (1)	0.2533 (1)	2.01 (3)

C2	0.0893 (2)	0.0911 (1)	0.3043 (1)	2.00 (3)
C3	0.2006 (2)	0.0696 (1)	0.3794 (1)	1.98 (3)
C4	0.3126 (2)	0.1360 (1)	0.3768 (1)	2.00 (3)
C5	0.2730 (2)	0.1971 (1)	0.2989 (1)	2.01 (3)
C6	0.0606 (2)	0.1994 (2)	0.1592 (1)	2.85 (4)
C7	-0.0451 (2)	0.0339 (2)	0.2768 (1)	3.22 (4)
C8	0.2035 (2)	-0.0152 (1)	0.4433 (1)	2.84 (4)
C9	0.4533 (2)	0.1383 (2)	0.4415 (1)	3.08 (4)
C10	0.3702 (2)	0.2698 (2)	0.2667 (1)	3.09 (4)
C11	-0.0822 (2)	0.3342 (1)	0.3476 (1)	2.31 (3)
C12	-0.0692 (2)	0.3286 (1)	0.4440 (1)	2.04 (3)
C13	0.0605 (2)	0.3724 (1)	0.4849 (1)	2.16 (3)
C14	0.1296 (2)	0.4031 (1)	0.4135 (1)	2.57 (3)
C15	0.0385 (2)	0.3828 (1)	0.3287 (1)	2.58 (3)
C16	-0.2126 (2)	0.3043 (2)	0.2800 (2)	1.53 (5)
C17	-0.1803 (2)	0.2856 (2)	0.4914 (2)	3.76 (4)
C18	0.1126 (2)	0.3910 (2)	0.5854 (1)	3.71 (4)
C19	0.2647 (3)	0.4613 (2)	0.4263 (2)	5.52 (6)
C20	0.0541 (3)	0.4264 (2)	0.2375 (2)	5.38 (5)
H31	0.093 (2)	0.201 (2)	0.572 (2)	5.4 (6)
H32	0.172 (2)	0.125 (2)	0.545 (1)	5.0 (6)

Table 2. Bond lengths (Å) and angles (°)

Cp1 and Cp2 are the centroids of the cyclopentadienyl rings.

Ti—N1	1.944 (2)	Ti—Cp1	2.071
Ti—Cp2	2.070	Ti—Cp	2.40 (1)
Ti—C1	2.415	Ti—C11	2.388 (2)
Ti—C2	2.385 (2)	Ti—C12	2.390 (2)
Ti—C3	2.396 (2)	Ti—C13	2.402 (2)
Ti—C4	2.386 (2)	Ti—C14	2.375 (2)
Ti—C5	2.402 (2)	Ti—C15	2.412 (2)
H31—N1—H32	108 (2)	H31—N1—Ti	126 (2)
H32—N1—Ti	126 (2)	Cp1—Ti—Cp2	144.3
Cp1—Ti—N1	108.7	Cp2—Ti—N1	107.0

Structure refinement was performed using *MolEN* (Fair, 1990) and local unpublished programs.

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Lists of structure factors, anisotropic displacement parameters, H-atom coordinates, complete geometry and least-squares-planes data have been deposited with the IUCr (Reference: MU1104). Copies may be obtained through The Managing Editor, International Union of Crystallography, 5 Abbey Square, Chester CH1 2HU, England.

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Hexaaquatitanium(III) Tris(*p*-Toluenesulfonate) Trihydrate

MANUEL A. S. AQUINO, WILLIAM CLEGG,* QIU-TIAN LIU
AND A. GEOFFREY SYKES

*Department of Chemistry, University of Newcastle
upon Tyne, Newcastle upon Tyne NE1 7RU, England*

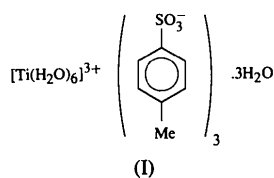
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Abstract

The crystal structure of [Ti(H₂O)₆](*p*-CH₃C₆H₄SO₃)₃·3H₂O consists of discrete cations, anions and solvate water molecules, all linked by a hydrogen-bonding network. Each Ti ion lies on an inversion centre and shows essentially octahedral coordination with Ti—O bonds in the range 2.018 (5)–2.046 (6) Å.

Comment

There is general interest in completing the structural characterization of the first-row transition metal *M*^{III} hexaaqua ions. The V^{III}, Cr^{III}, Mn^{III}, Fe^{III} and Co^{III} hexaaqua ions, for example, have all been structurally characterized as the alums Cs[M(H₂O)₆](SO₄)₂·6H₂O (Beattie, Best, Skelton & White, 1981), as has that of Ti^{III} (Sygusch, 1974). However, full structural data for only one first-row transition metal ion, V^{III} (Cotton, Fair, Lewis, Mott, Ross, Schultz & Williams, 1984), and one second-row transition metal ion, Ru^{III} (Bernhard, Bürgi, Hauser, Lehmann & Ludi, 1982), forming [M(H₂O)₆]X₃ complexes have been reported. The *p*-toluenesulfonate anion (pts[−]) has proved successful in the past in crystallizing hexaaqua ions such as those of Ru^{II} and Ru^{III} (Bernhard *et al.*, 1982), Cu^{II} (Couldwell, Prout, Robey, Taylor & Rossotti, 1978) and Zn^{II} (Hargreaves, 1957). We report here the structure of the *p*-toluenesulfonate salt of [Ti(H₂O)₆]³⁺, [Ti(H₂O)₆](*p*-CH₃C₆H₄SO₃)₃·3H₂O, (I).



The structure contains discrete [Ti(H₂O)₆]³⁺ cations, pts[−] anions and solvate water molecules (Fig. 1). Each of the two crystallographically independent Ti ions lies on an inversion centre and is coordinated in an essentially octahedral geometry by six water molecules as ligands. Bond lengths and angles within the cations are unexceptional, with a small range of Ti—O distances [2.018 (5)–2.046 (6) Å], similar to the lengths observed for the caesium titanium alum (Sygusch, 1974). The Ti—O bonds are longer than the V—O bonds in the corresponding cation, where the mean distance is 1.995 Å (Cotton *et al.*, 1984). A decrease in the *M*^{III}—O distance such as this is expected on changing the configuration of the central metal ion from *d*¹ to *d*² (Cotton & Wilkinson, 1988).

Two-thirds of the coordinated water molecules were refined with similarity restraints on their geometry; the H atoms of the others were not located in difference syntheses. The orientations of these ligands were allowed to refine freely, but in each case the result placed the Ti—O bond essentially in or close to the ligand

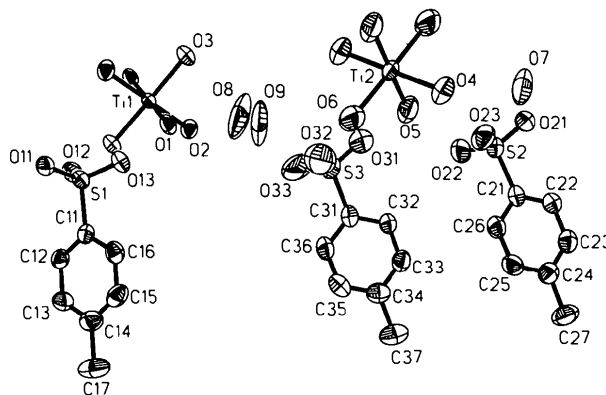


Fig. 1. The atom-labelling scheme for the cations, anions and water molecules, showing 50% probability displacement ellipsoids.

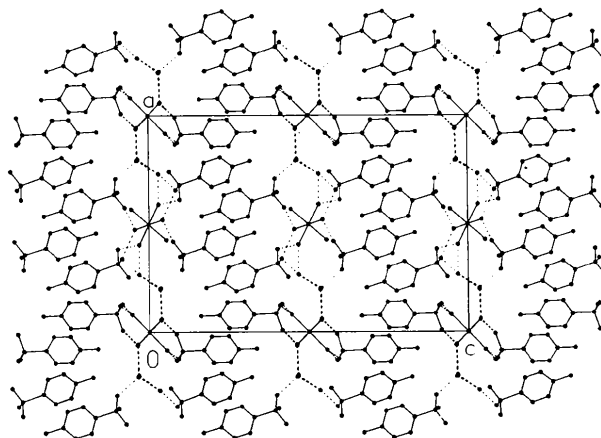


Fig. 2. The packing seen in parallel projection along the *y* axis.