Crystal and Molecular Structure of Bis(η-cyclopentadienyl)bis-(*N*-cyanato)titanium(IV)

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Summary *X*-Ray diffraction methods show that crystals of $[Ti(\eta\text{-}C_5H_5)_2(NCO)_2]$ contain discrete molecules with titanium in a distorted tetrahedral environment, and *N*-bonded cyanate groups.

It is only recently that the first example of linkage isomerism of the co-ordinated cyanate has been reported.[1] *O*-Bonded cyanate complexes are characterised with difficulty, partly because of the absence of authenticated structures for comparative purposes. The title compound was originally reported as $[Ti(\eta\text{-}C_5H_5)_2(OCN)_2]$ on the basis of spectral measurements,[2] and the assignment was further supported by ^{14}N n.m.r. chemical shifts.[3] Later, dipole moment measurements[4] seemed to suggest that the compound should be formulated as $[Ti(\eta\text{-}C_5H_5)_2(NCO)_2]$, which supposition we now confirm by *X*-ray analysis.

The title compound was prepared as previously described[2] and gives orthorhombic crystals from $CHCl_3$; $C_{12}H_{10}N_2O_2Ti$, $a = 9{\cdot}689(3)$, $b = 13{\cdot}265(4)$, $c = 17{\cdot}500(6)$ Å; space group *Pbca*, $Z = 8$; $D_m = 1{\cdot}57$, $D_c = 1{\cdot}55$ g cm^{-3}. The structure was solved by Patterson and heavy-atom methods using 2338 observed independent reflections ($\theta < 30°$) measured on a Hilger-Watts four circle diffractometer with Mo-K_α radiation, and refined to the present R value of 0·053. A parallel refinement, based on the assumption that the cyanate groups are *O*-bonded, yielded a higher R factor (0·065) and physically unreasonable temperature factors. The molecular structure of [Ti (η-C_5H_5)$_2$(NCO)$_2$] is shown in the Figure. The co-ordination about the central titanium is that of a distorted tetrahedron not unlike that found in other bis(cyclopentadienyl)titanium(IV) compounds;[5] the C–C distances within the rings, and the distances of the titanium atom from the mean planes (2·053 and 2·058 Å from rings A and B respectively) are also in accord with previous results.[5] The data for the co-ordinated isocyanate groups show them to be linear with Ti–N–C bond angles which are also close to linearity, and with interatomic distances which are similar to those reported for the few other isocyanate complexes to have been studied by *X*-ray crystallography.[6]

The determination of this structure clarifies the fact that the compound contains *N*-cyanato-groups only in the solid state but whether or not *O*-bonding occurs in solution, particularly in view of the ^{14}N n.m.r. results,[3] remains a subject for further study: the nature of the solvent has been shown to affect which linkage isomer of [Rh(PPh$_3$)$_3$NCO] is formed.

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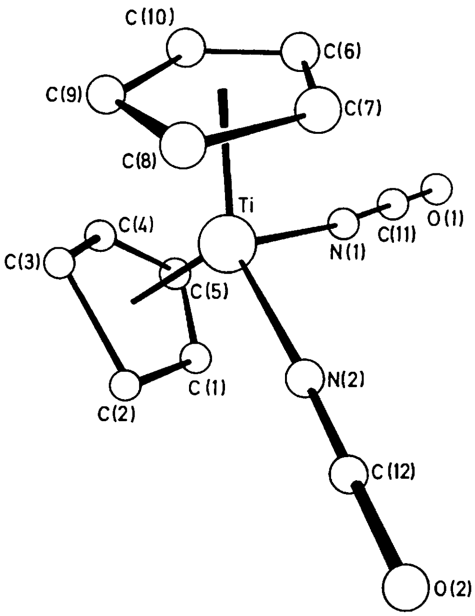

FIGURE. Structure of [Ti(η-C_5H_5)$_2$(NCO)$_2$];Ti–N(1) 2·018(3), Ti–N(2) 2·007(3), N(1)–C(11) 1·151(5), C(11)–O(1) 1·192(5), N(2)–C(12) 1·157(5), C(12)–O(2) 1·184(5) Å; ∠ Ti–N(1)–C(11) 171·8(3), Ti–N(2)–C(12) 175·7(3), N(1)–C(11)–O(1) 178·3(4), N(2)–C(12)–O(2) 178·4(4), N(1)–Ti–N(2) 94·7(2)°.

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