Crystal and Molecular Structures of Bis(η-cyclopentadienyl)di-isocyanato-titanium(IV) and -zirconium(IV)

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The crystal structures of the title complexes have been determined by *X*-ray crystallography. The complexes are isostructural with an orthorhombic unit cell and space group *Pbca*, $Z = 8$. For $[Ti(\eta\text{-}C_5H_5)_2(NCO)_2]$, $a = 9.689(3)$, $b = 13.265(4)$, $c = 17.500(6)$ and for $[Zr(\eta\text{-}C_5H_5)_2(NCO)_2]$, $a = 9.734(3)$, $b = 13.463$, and $c = 17.964(5)$ Å. Both complexes show distorted-tetrahedral co-ordination of the metal with the cyanate ligands clearly *N*-bonded.

THE group of complexes $[M(\eta\text{-}C_5H_5)_2(CNO)_2]$ (M = Ti, Zr, or Hf) are some of the few reported compounds which were originally formulated as having *O*-bonded cyanate linkages.[1] Assignments were based on mass-spectroscopic and i.r. spectral data, and subsequent ^{14}N n.m.r. measurements [2] indeed supported such a proposed structure for the titanium complex. However, Burmeister and his co-workers [3] who originally reported the complexes later found that dipole-moment measurements on the titanium and zirconium complexes were incompatible with both being *O*-bonded cyanates and favoured *N*-co-ordination for the titanium complex.

Preliminary *X*-ray analysis confirmed *N*-bonding for the titanium complex [4] and we have now made a full *X*-ray crystallographic study of both the titanium and zirconium analogues and have found that both complexes contain only *N*-bonded cyanate.

EXPERIMENTAL

Titanium Complex.—This was prepared by the method described by Burmeister *et al.*[1] Colourless crystals were obtained by slow cooling from chloroform solution. The crystal (0.20 × 0.15 × 0.15 mm) chosen for *X*-ray analysis was mounted on a glass fibre about the crystallographic *a* axis.

Crystal data. $C_{12}H_{10}N_2O_2Ti$, $M = 262.3$, Orthorhombic, $a = 9.689(3)$, $b = 13.265(4)$, $c = 17.500(6)$ Å, $U = 2\,249.18$ Å^3, $D_m = 1.57$, $Z = 8$, $D_c = 1.55$ g cm^{-3}, $F(000) = 1\,024$, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 7.6 cm^{-1}. Absent reflections, $0kl$ when $k \neq 2n$, $h0l$ when $l \neq 2n$, and $hk0$ when $h \neq 2n$, conform uniquely with space group *Pbca*.

The intensities and refined cell dimensions were obtained from a Hilger and Watts Y290 four-circle diffractometer with Mo-K_α radiation (zirconium filter and pulse-height analysis). 2 338 Reflections whose intensities were greater than 3σ of the background were monitored in the range $\theta \leqslant 30°$ and corrected for Lorentz and polarization effects but not for absorption or extinction.

The structure was solved by heavy-atom methods and refined by block-diagonal and full-matrix least-squares techniques. Initially, the cyanate groups were assumed to be *O*-bonded and refinement converged at a conventional *R* 0.108 with isotropic temperature factors for the light atoms and anisotropic temperature factors for the titanium atom. However, examination of the temperature factors in both cyanate groups showed them to be physically unlikely. Reversal of N and O gave an improved *R* of 0.101 and physically more reasonable temperature factors. Least-squares refinement of this structure allowing anisotropic thermal motion for all the non-hydrogen atoms resulted in a final *R* of 0.053. An identical refinement based on *O*-bonding gave a final *R* of 0.065. Scattering factors for Ti were taken from ref. 5, and those for C, N, and O from ref. 6. Weighting for the least-squares refinement were assigned as $w = 1$ if $F \leqslant 25$, otherwise $w = (25/F)^2$, and all calculations were carried out using the ' *X*-RAY '72 ' package of programs [7] as implemented at the University of Manchester Regional Computer Centre.

Zirconium Complex.—The complex was prepared by the method of Burmeister *et al.*[1] to give orthorhombic crystals. Since the crystals are unstable in air owing to reaction with oxygen, a suitable crystal (0.37 × 0.31 × 0.31 mm) for *X*-ray analysis was mounted in a Lindemann glass capillary tube with the crystallographic *a* axis parallel to the goniometer axis.

Crystal data. $C_{12}H_{10}N_2O_2Zr$, $M = 305.4$, Orthorhombic, $a = 9.734(3)$, $b = 13.463(4)$, $c = 17.964(5)$ Å, $U = 2\,354.16$ Å^3, $Z = 8$, $D_c = 1.723$ g cm^{-3}, $F(000) = 1\,216$, Mo-K_α radiation, $\lambda = 0.710\,7$ Å, μ(Mo-K_α) = 8.7 cm^{-1}. Absent reflections, $0kl$ when $k \neq 2n$, $h0l$ when $l \neq 2n$, and $hk0$ when $h \neq 2n$, conform uniquely with space group *Pbca*.

Intensity data were collected under the same conditions as before, allowing the measurement of 2 414 unique observed reflections. Similarity of cell dimensions and space group indicated that the zirconium and titanium complexes might be isostructural and a successful refinement was carried out using the co-ordinates of the titanium complex as a starting point. As before, the *O*-bonded possibility gave physically unreasonable temperature factors and a slightly higher *R* value. Refinement of the *N*-bonded case using all the non-hydrogen atoms and allowing anisotropic thermal motion gave a final *R* of 0.038. Scattering factors for Zr, which were corrected for anomalous dispersion, were obtained from ref. 5 and those for the light atoms from ref. 6. The final weighting scheme in the least-squares analysis was given by $W = 1/[1 + (F - 20)/10]^2$ and calculations were carried out using ' *X*-Ray '72 ' as before.

RESULTS AND DISCUSSION

The final positional parameters are listed for both structures in Table 1, with the atom numbering and molecular structure shown in Figure 1. Structure factors and temperature parameters have been deposited as Supplementary Publication No. SUP 22368 (18 pp.).* Bond lengths and bond angles are listed in Tables 2 and 3 and deviations from least-squares planes through the cyclopentadienyl rings are given in Table 4. The unit-cell contents, projected down *a*, are shown in Figure 2.

The most important result of this investigation is the

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* For details see Notices to Authors No. 7, *J.C.S. Dalton*, 1978, Index issue.

TABLE 1

Fractional co-ordinates and their standard deviations ($\times 10^5$)

	M = Ti			M = Zr		
Atom	*x*	*y*	*z*	*x*	*y*	*z*
M	15 417(5)	37 338(3)	61 097(2)	15 082(2)	37 603(2)	60 981(1)
C(1)	−2 455(38)	33 807(31)	52 163(21)	−3 508(38)	33 037(32)	52 022(20)
C(2)	8 683(42)	27 388(31)	50 412(21)	7 519(40)	26 684(32)	50 551(20)
C(3)	10 937(48)	20 863(28)	56 517(25)	9 559(47)	20 537(27)	56 750(25)
C(4)	689(45)	23 092(29)	62.241(23)	−511(49)	22 930(31)	62 032(24)
C(5)	−7 433(36)	30 960(32)	59 516(23)	−8 577(39)	30 601(33)	59 095(24)
C(6)	24 501(46)	42 743(37)	73 233(20)	24 629(54)	42 472(38)	73 486(19)
C(7)	35 000(41)	43 678(32)	67 934(21)	35 256(40)	43 674(36)	68 420(23)
C(8)	38 185(41)	34 017(42)	65 201(25)	38 787(43)	34 463(41)	65 583(25)
C(9)	29 415(57)	27 191(32)	68 978(32)	30 267(51)	27 494(34)	69 006(30)
C(10)	20 739(47)	32 677(39)	73 744(23)	21 427(49)	32 492(41)	73 731(22)
N(1)	3 869(33)	49 486(21)	63 796(17)	2 971(32)	50 168(22)	63 746(17)
N(2)	25 276(32)	44 140(25)	52 428(16)	25 568(34)	44 185(25)	52 032(16)
C(11)	−3 007(41)	55 843(25)	66 158(20)	−3 923(42)	56 372(24)	65 900(21)
C(12)	30 807(28)	47 519(28)	47 160(20)	31 075(36)	47 583(29)	46 926(19)
O(1)	−10 016(43)	62 577(22)	68 462(23)	−10 997(56)	62 779(24)	68 131(33)
O(2)	36 345(38)	51 131(30)	41 788(20)	36 534(40)	51 206(31)	41 756(20)

unequivocal demonstration that in the crystalline state the cyanate groups are *N*-bonded to both the titanium and zirconium atoms. The metal–isocyanate linkages are approximately linear with M–N–C angles of 171.8(3) and 175.7(3)° when M = Ti and 172.6(3) and 177.5(3)° when M = Zr. The N–C–O angles are 178.3(4) and 178.8(4)° for the titanium complex and 179.9(5) and 178.6(5)° for the zirconium complex. Slight deviations from linearity have also been observed in other isocyanato-complexes such as $Me_4NAg(CNO)_2$ [8] where angles of *ca.* 170° were found. In both complexes, C–N distances are significantly shorter than C–O distances, and in each case the shortness of the bonds implies some triple-bond character. This has been observed in other isocyanato-species, for example $[Cr(\eta\text{-}C_5H_5)(NCO)(NO)_2]$ [9] where C–N and C–O bond lengths of 1.126 and 1.179 Å have been found. The average Ti–N distance is 2.012 and the corresponding Zr–N distance is 2.110 Å.

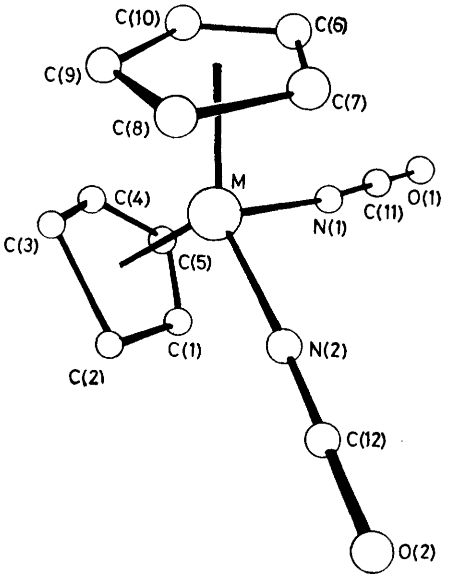

FIGURE 1 Molecular structure showing the metal co-ordination and the atom-numbering system

TABLE 2

Bond distances (Å) and their standard deviations

	M			M	
Bond	Ti	Zr	Bond	Ti	Zr
M–C(1)	2.380(4)	2.498(4)	C(1)–C(2)	1.409(6)	1.398(6)
M–C(2)	2.380(4)	2.494(4)	C(2)–C(3)	1.392(6)	1.403(6)
M–C(3)	2.368(4)	2.480(4)	C(3)–C(4)	1.441(6)	1.410(6)
M–C(4)	2.377(4)	2.501(4)	C(4)–C(5)	1.391(6)	1.391(6)
M–C(5)	2.386(4)	2.512(4)	C(1)–C(5)	1.425(5)	1.403(6)
M–A *	2.503	2.194	C(6)–C(7)	1.382(6)	1.390(6)
M–C(6)	2.408(4)	2.517(4)	C(7)–C(8)	1.402(7)	1.381(7)
M–C(7)	2.396(4)	2.513(4)	C(8)–C(9)	1.407(7)	1.398(7)
M–C(8)	2.361(4)	2.485(4)	C(9)–C(10)	1.389(7)	1.381(7)
M–C(9)	2.357(5)	2.471(5)	C(6)–C(10)	1.387(7)	1.380(7)
M–C(10)	2.355(4)	2.469(4)	N(1)–C(11)	1.151(5)	1.140(5)
M–B *	2.058	2.915	N(2)–C(12)	1.157(5)	1.156(5)
M–N(1)	2.018(3)	2.119(3)	C(11)–O(1)	1.192(5)	1.176(6)
M–N(2)	2.007(3)	2.101(3)	C(12)–O(2)	1.184(5)	1.175(5)

* A and B are the centroids of the cyclopentadienyl rings represented by C(1)—C(5) and C(6)—C(10) respectively.

TABLE 3

Bond angles (°) and their standard deviations

	M			M	
Angle	Ti	Zr	Angle	Ti	Zr
N(1)–M–N(2)	94.7(2)	96.4(1)	C(3)–C(4)–C(5)	107.8(3)	107.9(4)
M–N(1)–C(11)	171.8(3)	172.6(3)	C(4)–C(5)–C(1)	108.5(3)	108.7(4)
M–N(2)–C(12)	175.7(3)	177.5(3)	C(5)–C(1)–C(2)	107.2(3)	107.4(3)
A–M–B *	132.8	130.9	C(6)–C(7)–C(8)	107.9(4)	108.7(4)
N(1)–C(11)–O(1)	178.3(4)	179.9(5)	C(7)–C(8)–C(9)	107.2(4)	107.2(4)
N(2)–C(12)–O(2)	178.8(4)	178.6(4)	C(8)–C(9)–C(10)	108.0(4)	108.1(4)
C(1)–C(2)–C(3)	109.2(3)	108.6(3)	C(9)–C(10)–C(6)	107.9(4)	108.4(4)
C(2)–C(3)–C(4)	107.3(4)	107.3(4)	C(10)–C(6)–C(7)	108.9(4)	107.6(4)

* A and B are the centroids of the cyclopentadienyl rings represented by C(1)—C(5) and C(6)—C(10) respectively.

The co-ordination of the metal in each case is that of a distorted tetrahedron with N^1–M–N^2 angles of 94.7(2) and 96.4(1)° for M = Ti and Zr respectively. The angles between the lines joining the metals to the η-C_5H_5 centroid are 132.8 and 130.9° and are typical for bis(η-cyclodienyl) complexes.[10] The cyclopentadienyl rings are virtually planar as expected (Table 4) with Ti–C distances ranging from 2.368(4) to 2.386(4) Å and Zr–C distances in the range 2.480(4)—2.501(4) Å. The average distance of the centroid to Ti is 2.055 Å and to Zr 2.194 Å. Again these distances are in accord with published values.[10,11] The tetrahedral entities are held in the crystal lattice by normal van der Waals forces between the light atoms; no abnormal contacts have been detected.

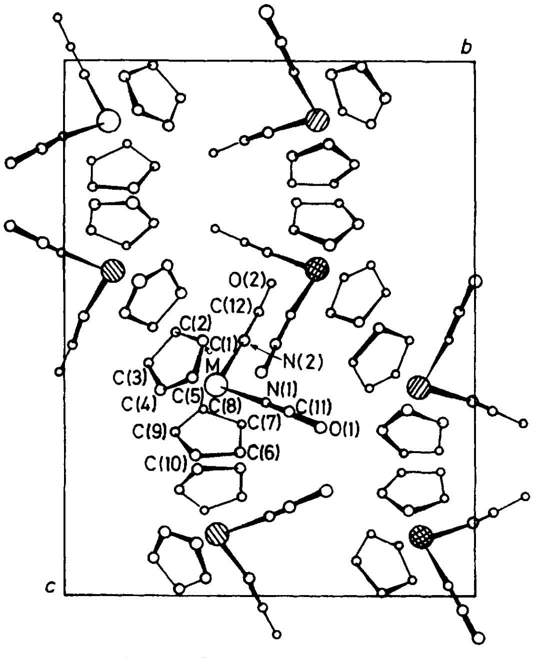

FIGURE 2 Unit-cell contents viewed down the crystallographic *a* axis

TABLE 4

Least-squares planes through the cyclopentadienyl rings expressed as $PX + QY + RZ = S$ in direct space where X, Y, Z are fractional co-ordinates of the atoms in the plane

Atoms	Plane	P	Q	R	S	M
C(1)–C(5)	A	6.0522	8.7428	7.3295	6.6233	Ti
		6.0266	9.0589	7.2732	6.5565	Zr
C(6)–C(10)	B	6.4732	−1.4784	12.8744	10.3694	Ti
		6.4467	−1.5927	13.2907	10.6721	Zr

Distances of atoms from planes (Å):

	Plane A			Plane B	
Atoms	M = Ti	Zr	Atoms	M = Ti	Zr
C(1)	0.007	0.008	C(6)	0.013	0.006
C(2)	−0.008	−0.010	C(7)	−0.004	0.000
C(3)	0.005	0.007	C(8)	−0.006	−0.006
C(4)	−0.009	−0.002	C(9)	0.013	0.010
C(5)	−0.004	−0.004	C(10)	−0.016	−0.010

Following the arguments of Bailey and Kozak[12] in assigning *O*-bonding in hexacyanates of Mo^{III}, Re^{IV}, and Re^{V}, the bands at 1 254 and 1 070 cm^{-1} in the i.r. mull spectra of the zirconium and hafnium complexes were attributed to Fermi resonance occurring between ν(CO) and 2δ(NCO) for *O*-co-ordination.[1] However, we have examined the laser Raman spectra of the titanium and zirconium complexes (Table 5) and have found that a strong band at 1 363 and 1 377 cm^{-1} for the two complexes respectively can be assigned to the CO stretching vibration in the region typical of *N*-bonding. Furthermore, the CN vibrations in the Raman spectra of these complexes are weak compared to the CO stretching mode. This behaviour has been observed in a number of *N*-bonded cyanate complexes of Pt^{II}.[13] Unfortunately, the complexes were too insoluble to measure their Raman spectra in solution but the integrated absorption intensities of the CN vibrations observed in the i.r. spectra from KBr pellets (see Table 5) are similar to values from solution measurements[1,3] and are typical of values found for other *N*-bonded cyanato-complexes.[14] Since the i.r. spectrum of [Hf(η-C_5H_5)$_2$(CNO)$_2$] is very similar to the zirconium and titanium analogues it seems likely, therefore, that this complex also has *N*-bonded cyanate linkages.

TABLE 5

Infrared and Raman spectral data (cm^{-1})

Spectral band	[Ti(η-C_5H_5)$_2$(CNO)$_2$] I.r. [a]	[Ti(η-C_5H_5)$_2$(CNO)$_2$] Raman [b]	[Zr(η-C_5H_5)$_2$(NCO)$_2$] I.r. [a]	[Zr(η-C_5H_5)$_2$(NCO)$_2$] Raman [b]
ν(CN)	2 220 (13 × 10^4) [c]	2 214w	2 217 (14 × 10^4)	2 216w
	2 195 (16 × 10^4)	2 174m	2 197 (17 × 10^4)	2 186m
ν(CO)		1 363s		1 377vs
δ(NCO)	625m	600w	630m	627w
	585m		605m	614w

[a] Measured as KBr disc. [b] Measured as solid. [c] Figures in parentheses are peak areas (mol^{-1} cm^{-2})

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REFERENCES

[1] J. L. Burmeister, E. A. Deardorff, A. Jensen, and V. H. Christiansen, *Inorg. Chem.*, 1970, **9**, 58.

[2] W. Becker and W. Beck, ref. 311 in ' Nitrogen-containing Pseudohalide Ligands,' by W. Beck in *M.T.P. Internat. Rev. Sci.*, 1972, **2**.

[3] A. Jensen, V. H. Christiansen, J. F. Hansen, T. Likowski, and J. L. Burmeister, *Acta Chem. Scand.*, 1972, **26**, 2898.

[4] S. J. Anderson, D. S. Brown, and A. H. Norbury, *J.C.S. Chem. Comm.*, 1974, 996.

[5] ' International Tables for *X*-Ray Crystallography,' Kynoch Press, Birmingham, vol. 3, 1968.

[6] D. Cromer and J. Mann, *Acta Cryst.*, 1968, **A24**, 321.

[7] ' *X*-Ray '72,' Technical Report TR-192, the Computer Science Center, University of Maryland, June 1972.

[8] K. Aarflot and K. Åse, *Acta Chem. Scand.*, 1974, **A28**, 137.

[9] M. A. Bush and G. A. Sim, *J. Chem. Soc.* (*A*), 1970, 605.

[10] K. Prout, T. S. Cameron, R. A. Forder, S. R. Critchley, B. Denton, and G. V. Rees, *Acta Cryst.*, 1974, **B30**, 2290.

[11] J. L. Attwood, K. Barker, J. Holton, W. E. Hunter, M. F. Lappert, and R. Pearce, *J. Amer. Chem. Soc.*, 1977, **99**, 6645.

[12] R. A. Bailey and S. L. Kozak, *J. Inorg. Nuclear Chem.*, 1969, **31**, 689.

[13] S. J. Anderson, P. L. Goggin, and R. J. Goodfellow, *J.C.S., Dalton*, 1976, 1959.

[14] A. H. Norbury and A. I. P. Sinha, *J. Chem. Soc.* (*A*), 1968, 1598.