

## Crystal Structure of the Orthorhombic Form of Trichlorobis-(*N,N'*-diisopropylacetamidinato)tantalum(V)

BY MICHAEL G. B. DREW

*Department of Chemistry, The University, Whiteknights, Reading RG6 2AD, England*

AND JOHN D. WILKINS

*Christopher Ingold Laboratories, University College, London WC1 0AJ, England*

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Crystals of the title compound are orthorhombic, space group  $Pna2_1$  with  $a=24.207$  (15),  $b=8.600$  (9),  $c=21.943$  (11) Å,  $Z=8$ . The intensities of 2831 independent reflexions above background were collected by counter methods and refined to  $R\ 0.056$ . In the asymmetric unit there are two independent seven-coordinate monomers both with highly distorted pentagonal bipyramidal geometries. Bond lengths for molecule *A* are Ta–Cl 2.379 (9), 2.400 (11), 2.411 (10); Ta–N 2.182 (20), 2.176 (23), 2.114 (19), 2.209 (21) Å and for molecule *B* Ta–Cl 2.409 (11), 2.388 (10), 2.410 (11); Ta–N 2.122 (18), 2.171 (22), 2.135 (18), 2.223 (20) Å. The distortions from ideal pentagonal bipyramidal geometry are similar in the two molecules but different in detail from those found in the monoclinic form of the same complex.

### Introduction

During our studies of the structures of seven-coordinate complexes, we prepared  $TaCl_3[C_3H_7-N-C(Me)-N-C_3H_7]_2$  by the published method (Wilkins, 1974) and determined its crystal and molecular structure (Drew & Wilkins, 1974*a*). The crystals were monoclinic, space group  $P2_1/a$ ,  $Z=4$ . Subsequently, we prepared an orthorhombic form of the same complex and we have determined its crystal and molecular structure.

We expected that a molecule of this stoichiometry would have a pentagonal bipyramidal geometry (= P.B.) and our object was to investigate whether the deviations from the ideal P.B. would be the same in the orthorhombic form as in the monoclinic form. If they were not the same, this would suggest that the energy differences between the various distortions from ideal symmetry were smaller than crystal packing effects.

Thompson & Bartell (1968) have attempted to predict the geometry of seven-coordinate complexes by minimizing the total repulsion energy of equivalent points on a sphere. This calculation leads to a number of minima on the potential energy surfaces which correspond to different stereochemistries, among them being the P.B. The potential well for the P.B. is very flat and shallow, requiring negligible energy to distort the pentagonal girdle. These calculations, while dependent upon the assumptions made, do suggest that the geometry of a P.B. could be fixed by small effects such as crystal packing. So we have taken the opportunity provided by the existence of two crystalline forms to compare the molecular structures of  $TaCl_3[C_3H_7-N-C(Me)-N-C_3H_7]_2$ .

### Experimental

We prepared  $MeTaCl_2[C_3H_7-N-C(Me)-N-C_3H_7]_2$  by the method of Wilkins (1974) with  $Me_3TaCl_2$  as starting material. The sample was suspended in petroleum spirit and sufficient dichloromethane added to dissolve the solid. The solvent was slowly removed *in vacuo* yielding only a small quantity of crystals which our X-ray examination revealed to be the trichloro complex  $TaCl_3[C_3H_7-N-C(Me)-N-C_3H_7]_2$ . We subsequently found an explanation for this; namely that the starting material  $Me_3TaCl_2$  was impure, containing *ca* 10%  $Me_2TaCl_3$ . Thus a small amount of the trichloro complex had been prepared which crystallized more readily than the bulk material, the dichloromethyl complex.\*

#### Crystal data

$C_{16}H_{34}N_4Cl_3Ta$ ,  $M=569.68$ , orthorhombic,  $a=24.207$  (15),  $b=8.600$  (9),  $c=21.943$  (11) Å,  $Z=8$ ,  $U=4567.0$  Å<sup>3</sup>,  $d_m=1.63$  (2),  $d_c=1.66$  g cm<sup>-3</sup>,  $F(000)=2256$ , Mo  $K\alpha$  radiation  $\lambda=0.7107$  Å,  $\mu=52.32$  cm<sup>-1</sup>, space group  $Pna2_1$ , No. 33, from the systematic absences  $0kl$ ,  $k+l=2n+1$  and  $h0l$ ,  $h=2n+1$ , and the successful structure determination. A crystal with dimensions *ca* 0.2 × 0.3 × 0.5 mm was mounted with the *b* axis perpendicular to the instrument axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities (*via* the stationary-

\* We subsequently obtained crystals of the dichloromethyl complex. A crystal-structure analysis has shown its geometry to be a P.B. with two chlorine atoms in axial positions and two bidentate ligands and one methyl group in the girdle. The structure is however distorted and the distortions from ideal geometry are difficult to assess (Drew & Wilkins, 1974*b*).

crystal stationary-counter method) and cell dimensions. It was equipped with a manual goniostat, scintillation counter and pulse-height discriminator. Zirconium-filtered molybdenum X-radiation was used with a 4° take-off angle and a counting time of 10 s. Individual backgrounds were taken from plots of background as a function of  $2\theta$ . Several standard reflexions were measured repeatedly during the course of the experiment and showed no change in intensity. 4132 independent reflexions were measured with  $2\theta < 50^\circ$ . 2831 reflexions with  $I > \sigma(I)$  were used in subsequent refinement. An absorption correction was applied with the program *ABSORB* (Stewart, 1972) with minimum and maximum transmission factors 0.27 to 0.39. No extinction correction was applied.

### Structure determination

A Patterson function was calculated and it was clear that the space group was *Pna*2<sub>1</sub>, as there were no interatomic vectors consistent with the mirror plane of *Pnam*. The positions of two independent tantalum atoms were obtained. Fourier syntheses were then calculated to determine the positions of the remaining atoms. The structure was refined by full-matrix least-squares calculations. The weighting scheme, chosen to give average values of  $w\Delta^2$  for groups of reflexions independent of the value of  $F_o$  and  $\sin \theta/\lambda$ , was  $\sqrt{w} = 1$  for  $F_o < 100$  and  $\sqrt{w} = 100/F_o$  for  $F_o > 100$ . Calculations were made on a C.D.C. computer at the University of London Computer Centre with the X-RAY system of programs (Stewart, 1972), and with some of our own programs on an ICL 1904S at this university. Atomic scattering factors for tantalum, chlorine, nitrogen and carbon were taken from *International Tables for X-ray Crystallography* (1965) with corrections for the real and imaginary part of the anomalous dispersion for tantalum and chlorine. Hydrogen scattering factors were taken from Stewart, Davidson & Simpson (1965). The anisotropic thermal parameters were defined as  $\exp[-2\pi^2 \sum_i \sum_j U_{ij} h_i h_j b_i b_j]$ ; ( $i, j = 1, 2, 3$ ) where  $b_i$  is the  $i$ th reciprocal cell dimension and the isotropic thermal parameter was  $\exp(-8\pi^2 U' \sin^2 \theta/\lambda^2)$ . The tantalum and chlorine atoms were refined anisotropically and the nitrogen and carbon atoms isotropically to  $R$  0.056. (Refinement with the opposite enantiomorphs gave  $R$  0.057.) The refinement of atoms C(41*A*), C(42*A*), C(43*A*) was unsatisfactory (see *Discussion*). Ignoring H(41*A*), the other seven non-methyl hydrogen atom positions were calculated assuming  $sp^3$  carbon; these corresponded to the positive regions in the difference Fourier map and were included in the structure factor calculations, with thermal parameters equivalent to those of the atom to which they were bonded, but were not refined. Methyl hydrogen atoms were not unambiguously discernible in the difference map and were not included. In the final cycle of refinement no shift was  $> 0.10\sigma$ . The 1301 re-

flexions given zero weight showed no large discrepancies. The final difference Fourier map showed no significant peaks. The final list of positional coordinates and thermal parameters, together with their

Table 1. *Positional parameters* ( $\times 10^4$ ) and *thermal parameters* ( $\times 10^3$ ) with estimated standard deviations in parentheses

	<i>x</i>	<i>y</i>	<i>z</i>	<i>U</i>
Ta( <i>A</i> )	194 (1)	580 (1)	0000 <sup>a</sup>	<i>b</i>
Ta( <i>B</i> )	2648 (1)	763 (1)	2540 (1)	<i>b</i>
Cl(1 <i>A</i> )	232 (4)	-1184 (10)	-834 (4)	<i>b</i>
Cl(2 <i>A</i> )	99 (4)	1887 (12)	961 (5)	<i>b</i>
Cl(3 <i>A</i> )	941 (4)	-939 (11)	418 (6)	<i>b</i>
Cl(1 <i>B</i> )	2666 (4)	-1032 (12)	3383 (5)	<i>b</i>
Cl(2 <i>B</i> )	2538 (5)	2216 (13)	1620 (5)	<i>b</i>
Cl(3 <i>B</i> )	3380 (4)	-835 (13)	2139 (6)	<i>b</i>
N(1 <i>A</i> )	873 (8)	2245 (22)	-48 (13)	49 (5)
N(2 <i>A</i> )	159 (9)	2377 (24)	-697 (12)	47 (6)
N(3 <i>A</i> )	-678 (8)	711 (22)	-14 (12)	53 (5)
N(4 <i>A</i> )	-313 (8)	-1238 (25)	439 (10)	51 (5)
N(1 <i>B</i> )	3321 (7)	2319 (20)	2643 (12)	41 (5)
N(2 <i>B</i> )	2642 (9)	2565 (22)	3232 (11)	44 (5)
N(3 <i>B</i> )	1773 (8)	1020 (22)	2618 (12)	52 (5)
N(4 <i>B</i> )	2086 (8)	-972 (23)	2115 (9)	46 (5)
C(11 <i>A</i> )	1359 (12)	2664 (32)	301 (13)	54 (7)
C(21 <i>A</i> )	-146 (13)	2506 (35)	-1228 (14)	61 (7)
C(31 <i>A</i> )	-1064 (11)	1985 (33)	-106 (13)	57 (7)
C(41 <i>A</i> )	-209 (17)	-2751 (49)	692 (20)	96 (12)
C(1 <i>A</i> )	645 (11)	2969 (34)	-533 (12)	52 (6)
C(2 <i>A</i> )	947 (11)	4309 (33)	-873 (13)	55 (6)
C(3 <i>A</i> )	-784 (10)	-594 (31)	264 (12)	51 (6)
C(4 <i>A</i> )	-1349 (14)	-1329 (40)	356 (16)	74 (9)
C(12 <i>A</i> )	1357 (15)	4260 (42)	526 (17)	80 (9)
C(13 <i>A</i> )	1906 (14)	2218 (38)	-45 (17)	79 (9)
C(22 <i>A</i> )	-396 (12)	4133 (35)	-1351 (14)	60 (7)
C(23 <i>A</i> )	235 (14)	1987 (40)	-1801 (16)	74 (9)
C(32 <i>A</i> )	-1519 (14)	1688 (41)	-616 (15)	73 (9)
C(33 <i>A</i> )	-1352 (13)	2586 (37)	504 (15)	66 (8)
C(42 <i>A</i> )	-94 (15)	-2783 (42)	1352 (17)	79 (8)
C(43 <i>A</i> )	-263 (18)	-4145 (48)	252 (23)	107 (13)
C(11 <i>B</i> )	3822 (13)	2679 (37)	2258 (14)	64 (8)
C(21 <i>B</i> )	2382 (10)	2766 (28)	3867 (11)	44 (5)
C(31 <i>B</i> )	1411 (15)	2281 (43)	2765 (27)	80 (10)
C(41 <i>B</i> )	2049 (15)	-2450 (43)	1782 (17)	39 (5)
C(1 <i>B</i> )	3138 (10)	3166 (28)	3073 (11)	43 (5)
C(2 <i>B</i> )	3384 (14)	4493 (39)	3386 (16)	73 (8)
C(3 <i>B</i> )	1649 (12)	-353 (33)	2294 (13)	55 (7)
C(4 <i>B</i> )	1060 (13)	-852 (37)	2205 (14)	65 (8)
C(12 <i>B</i> )	3824 (15)	4476 (43)	1973 (17)	80 (9)
C(13 <i>B</i> )	4359 (11)	2284 (33)	2602 (16)	65 (7)
C(22 <i>B</i> )	2160 (13)	4344 (37)	3953 (15)	69 (8)
C(23 <i>B</i> )	2747 (12)	2079 (36)	4353 (14)	62 (7)
C(32 <i>B</i> )	982 (13)	1854 (37)	3269 (15)	67 (8)
C(33 <i>B</i> )	1123 (12)	3059 (36)	2197 (13)	59 (7)
C(42 <i>B</i> )	2284 (18)	-2322 (55)	1181 (21)	106 (14)
C(43 <i>B</i> )	2264 (28)	-3768 (79)	2127 (33)	169 (26)
H(11 <i>A</i> )	1382	1880	690	<i>c</i>
H(21 <i>A</i> )	-476	1668	-1235	<i>c</i>
H(31 <i>A</i> )	-826	2983	-257	<i>c</i>
H(11 <i>B</i> )	3808	1956	1834	<i>c</i>
H(21 <i>B</i> )	2045	1940	3926	<i>c</i>
H(31 <i>B</i> )	1662	3197	2968	<i>c</i>
H(41 <i>B</i> )	1601	-2777	1726	<i>c</i>

(*a*) Parameter fixed. (*b*) Thermal parameters in Table 2. (*c*) Hydrogen atom thermal parameters were set equal to that of the atom to which they were bonded. Hydrogen atom parameters were not refined.



Table 3 (cont.)

	Molecule <i>A</i>	Molecule <i>B</i>
C(21)–N(2)–C(1)	131.9 (25)	123.7 (21)
C(31)–N(3)–C(3)	126.0 (22)	128.2 (20)
C(41)–N(4)–C(3)	130.0 (26)	118.3 (24)
N(1)–C(1)–N(2)	113.4 (24)	106.4 (21)
N(1)–C(1)–C(2)	121.8 (23)	130.9 (24)
N(2)–C(1)–C(2)	124.7 (24)	122.7 (24)
N(3)–C(3)–N(4)	109.1 (22)	109.6 (23)
N(3)–C(3)–C(4)	126.7 (24)	120.5 (24)
N(4)–C(3)–C(4)	124.2 (25)	129.9 (27)
N(1)–C(11)–C(12)	114.2 (24)	113.8 (24)
N(1)–C(11)–C(13)	111.5 (24)	111.0 (24)
C(12)–C(11)–C(13)	113.3 (26)	112.8 (25)
N(2)–C(21)–C(22)	115.3 (26)	111.5 (21)
N(2)–C(21)–C(23)	109.1 (25)	111.4 (21)
C(22)–C(21)–C(23)	109.7 (24)	118.6 (24)
N(3)–C(31)–C(32)	115.0 (24)	112.8 (21)
N(3)–C(31)–C(33)	114.1 (24)	114.5 (21)
C(32)–C(31)–C(33)	109.9 (23)	111.4 (21)
N(4)–C(41)–C(42)	115.4 (33)	111.5 (32)
N(4)–C(41)–C(43)	116.5 (34)	113.0 (38)
C(42)–C(41)–C(43)	128.0 (36)	113.3 (42)

standard deviations are given in Tables 1 and 2. Molecular dimensions are given in Table 3.\*

### Discussion

In the orthorhombic crystal, there are two independent molecules in the asymmetric unit. The structures of these two molecules ( $O_A$  and  $O_B$ ) are shown in Fig. 1(a) and (b), together with the atomic numbering scheme. The molecules are opposite enantiomorphs. As in the monoclinic form (= *M*), in the orthorhombic form the *N,N'*-diisopropylacetamidinato ligands are bidentate, bonding to the metal atom *via* the two nitrogen atoms. The tantalum atom is thus seven-coordinate being bonded to three chlorine and four nitrogen atoms. The coordination sphere is a distorted pentagonal bipyramid with two chlorine atoms Cl(1) and Cl(2) in axial positions. The atoms in the girdle follow the sequence Cl(3), N(1), N(2), N(3), N(4). In an ideal P.B., the girdle is planar and angles of 72° are subtended by adjacent pairs of atoms but the presence of the four isopropyl groups in the girdle make this ideal symmetric arrangement impossible in the present complex and large distortions from ideal geometry are required to minimize repulsions between the isopropyl groups and adjacent atoms.

In *M*, the distortions give a geometry of  $C_2$  symmetry, the rotation axis being coincident with the Ta–Cl(3) bond. The two planar four-membered rings Ta, N, N, C intersect the equatorial girdle [defined as the least-squares plane of atoms Ta, Cl(3), N(1), N(2), N(3), N(4)] at angles of 10.7 and –15.5°. Thus C(*n*) atoms are respectively –0.71, 1.04, –1.04, 0.60 Å (for *n* = 1–4) from the equatorial plane.

\* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 30613 (9 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

The distortions of  $O_A$  and  $O_B$  from ideal P.B. geometry are equivalent but much less symmetrical than in *M*. This is shown by the distances of atoms from the least-squares planes of the girdle which are shown in Fig. 1(a), (b) and listed in Table 4. The planar four-membered ring Ta, N(1), N(2), C(1) intersects the plane of the equatorial girdle at an angle of 24.3, 22.8°\* while the planar ring Ta, N(3), N(4), C(3) intersects that girdle plane at an angle of –7.1, –4.1°. This asymmetry is also shown by the Cl(3)–Ta–N(3) angles [141.5, 144.9°] being much larger than the Cl(3)–Ta–N(2) angles [132.9, 131.8°] in contrast to *M* where both angles are equivalent at 139.2, 138.4°.

Table 4. Equations of least-squares planes in the form  $Ax + By + Cz = D$ , where *x, y, z* are the crystallographic fractional coordinates of the atoms

Distances (Å) of relevant atoms from each plane are given in square brackets.

### Plane

- Ta(*A*), Cl(3*A*), N(1*A*), N(2*A*), N(3*A*), N(4*A*)  
 $A = -2.68, B = 4.78, C = 18.08, D = 0.27$   
 [Ta(*A*) –0.05, Cl(3*A*) –0.22, N(1*A*) 0.48, N(2*A*) –0.44, N(3*A*) 0.22, N(4*A*) 0.01, C(11*A*) 1.18, C(21*A*) –1.26, C(31*A*) 0.78, C(41*A*) –0.28, C(1*A*) 0.01, C(2*A*) –0.05, C(3*A*) 0.13, C(4*A*) 0.10]
  - Ta(*B*), Cl(3*B*), N(1*B*), N(2*B*), N(3*B*), N(4*B*)  
 $A = 2.00, B = -4.83, C = 18.07, D = 4.74$   
 [Ta(*B*) 0.01, Cl(3*B*) 0.20, N(1*B*) –0.42, N(2*B*) 0.39, N(3*B*) –0.15, N(4*B*) –0.03, C(11*B*) –1.18, C(21*B*) 1.39, C(31*B*) –0.56, C(41*B*) 0.07, C(1*B*) –0.09, C(2*B*) –0.12, C(3*B*) –0.10, C(4*B*) –0.13]
  - Ta(*A*), N(1*A*), N(2*A*), C(1*A*)  
 $A = -11.62, B = 5.24, C = 13.84, D = 0.08$   
 [Ta(*A*) 0.01, N(1*A*) –0.01, N(2*A*) 0.01, C(1*A*) –0.02, C(2*A*) –0.14, C(11*A*) 0.15, C(21*A*) –0.30]
  - Ta(*A*), N(3*A*), N(4*A*), C(3*A*)  
 $A = -0.01, B = 4.39, C = 18.87, D = 0.27$   
 [Ta(*A*) 0.01, N(3*A*) –0.01, N(4*A*) 0.02, C(3*A*) –0.03, C(4*A*) –0.18, C(31*A*) 0.41, C(41*A*) –0.17]
  - Ta(*B*), N(1*B*), N(2*B*), C(1*B*)  
 $A = 10.48, B = -5.35, C = 14.30, D = 6.01$   
 [Ta(*B*) –0.01, N(1*B*) 0.01, N(2*B*) 0.01, C(1*B*) –0.02, C(2*B*) –0.03, C(11*B*) –0.20, C(21*B*) 0.54]
  - Ta(*B*), N(3*B*), N(4*B*), C(3*B*)  
 $A = 0.49, B = -4.60, C = 18.53, D = 4.48$   
 [Ta(*B*) 0.01, N(3*B*) –0.01, N(4*B*) –0.01, C(3*B*) 0.01, C(4*B*) 0.05, C(31*B*) –0.33, C(41*B*) 0.05]
- Angles between planes:
- |         |       |
|---------|-------|
| 1 and 3 | 24.3° |
| 2 and 5 | 22.8  |
| 1 and 4 | 7.1   |
| 2 and 6 | 4.1   |

As N(1) is tilted out of the girdle by a much larger amount than N(4), the dihedral angle Cl(3)–Ta–N(4)–C(41) is –14.3, 4.2° (Table 5). To compensate for the

\* When two dimensions are given, the first refers to molecule  $O_A$  and the second to molecule  $O_B$ .

latter small dihedral angle and to decrease the Cl(3)···C(41) repulsions, Cl(3)–Ta–N(4) > Cl(3)–Ta–N(1) angles and the Ta–N(4) bonds are the longest Ta–N bonds in both molecules. The conformation of the Pr<sup>1</sup>(1) group\* relative to the N(1)–C(11) bonds are equivalent in both molecules and to that in *M* as H(11) is in the most sterically crowded position adjacent to Cl(3), the dihedral angles Ta–N(1)–C(11)–H(11) being 1.8, 1.2°. In molecule *B* the Ta–N(4)–C(41) angle is 145.8°, a good 7° larger than all the other angles of this type. The conformation of Pr<sup>1</sup>(4*B*) is opposite to that found for all other Pr<sup>1</sup> groups in *O<sub>A</sub>*, *O<sub>B</sub>* and *M* in that the Ta–N(4*B*)–C(41*B*)–H(41*B*) dihedral angle is *ca*

180 and not *ca* 0° [see Fig. 1(*b*)]. Thus the two methyl groups are staggered with respect to the Ta–N(4) bond. The methyl to Cl(3) contacts are 3.62, 3.70 Å. It is clear that the small Cl(3)–Ta–N(4*B*)–C(41*B*) dihedral angle is a consequence of this conformation of Pr<sup>1</sup>(4*B*) as with a larger angle, one of the methyl to Cl(3) contacts would be decreased.

The conformation of Pr<sup>1</sup>(4*A*) is not clearly determined. Taking the refined positions of the atoms from Table 1, the three angles subtended at C(41*A*) by N(4*A*) C(42*A*), C(43*A*) add up to 359.9°, an unlikely value for tetrahedral carbon. A difference Fourier map omitting C(41*A*), C(42*A*), C(43*A*) was then calculated. All three peaks were elongated in the *x* direction with spreads of *ca* 1.2 Å. We then refined molecule *O<sub>A</sub>* anisotropically. The thermal ellipsoids of all atoms except N(4*A*), C(41*A*), C(42*A*), C(43*A*) were approximately spherical but these four all had exceptionally large *U*<sub>11</sub> terms. We then refined two sites separated by *ca* 0.8 Å with ½ occupancy for each of the three carbon atoms but the resulting dimensions were not reasonable. The most likely explanation for these facts is that there are several possible sites for the isopropyl group. It was not possible to determine whether the conformation of Pr<sup>1</sup>(4*A*) has a dihedral angle for Ta–N(4*A*)–C(41*A*)–H(41*A*) of 0° (as in *M*) or 180° (as in *O<sub>B</sub>*). Although the latter seems the most likely, particularly as the configuration of the rest of the molecule is more similar to that in *O<sub>B</sub>* rather than in *M*, we have not proved this. We therefore quote in the tables the parameters obtained from the isotropic refinement for Pr<sup>1</sup>(4*A*).

The minimizing of repulsions between adjacent Pr<sup>1</sup>(2) and Pr<sup>1</sup>(3) groups is achieved in *O<sub>A</sub>* and *O<sub>B</sub>* in a manner equivalent to that found in *M*. The twists in the two rings out of the pentagonal girdle ensure that the N(2)···N(3) contacts are 2.90, 2.83 Å with N(2)–Ta–N(3) angles of 85.0, 82.2°. Unlike C(11) and C(41), the carbon atoms C(21) and C(31) are a significant distance from the four-membered ring plane [–0.30, 0.54 Å for C(21) and 0.41, –0.33 Å for C(31)]. These deviations are concomitant with large dihedral angles for N(3)–Ta–N(2)–C(21) and N(2)–Ta–N(3)–C(31) of –48.5, 55.3 and –34.6, 30.4°. The C(21)···C(31) contacts are 3.35, 3.40 Å. As in *M*, in both *O<sub>A</sub>* and *O<sub>B</sub>*, H(21) and H(31) are in the most sterically crowded positions (see Fig. 1). Close contacts between Pr<sup>1</sup>(2) and Pr<sup>1</sup>(3) are comparable with those in *M*.

The asymmetric distortions from P.B. symmetry in *O<sub>A</sub>* and *O<sub>B</sub>* have resulted in no systematic variations in metal–ligand bond lengths as was found in *M*. There the Ta–N(1) and Ta–N(4) bond lengths [2.193 (15), 2.180 (20) Å] were longer than the Ta–N(2) and Ta–N(3) bond lengths [2.098 (14), 2.058 (16) Å] and the Ta–Cl(1) and Ta–Cl(2) bond lengths are 0.05 Å shorter than the Ta–Cl(3) equatorial bond at 2.436 (6) Å. These variations were ascribed to the differences in ligand···ligand repulsions between different polyhedra sites. In *O<sub>A</sub>*, *O<sub>B</sub>* the Ta–Cl bond lengths are all between the values found for the equatorial and axial

Table 5. Dihedral angles (°)

	Molecule <i>A</i>	Molecule <i>B</i>
Ta—N(1)–C(11)–H(11)	1.8	1.2
Ta—N(1)–C(11)–C(12)	–118.9	113.9
Ta—N(1)–C(11)–C(13)	111.1	–117.7
Ta—N(2)–C(21)–H(21)	14.0	–18.3
Ta—N(2)–C(21)–C(22)	137.2	–138.5
Ta—N(2)–C(21)–C(23)	–98.8	86.4
Ta—N(3)–C(31)–H(31)	9.8	–17.0
Ta—N(3)–C(31)–C(32)	127.6	–129.7
Ta—N(3)–C(31)–C(33)	–104.1	101.4
Ta—N(4)–C(41)–H(41)	—	175.2
Ta—N(4)–C(41)–C(42)	92.9	–66.3
Ta—N(4)–C(41)–C(43)	–90.3	62.7
Cl(3)–Ta—N(1)–C(11)	–35.2	38.2
Cl(3)–Ta—N(4)–C(41)	–14.3	4.2
C(2)–C(1)–N(2)–C(21)	14.2	–22.9
C(2)–C(1)–N(1)–C(11)	10.7	–12.0
C(4)–C(3)–N(3)–C(31)	22.8	–17.0
C(4)–C(3)–N(4)–C(41)	6.2	–2.5
N(3)–Ta—N(2)–C(21)	–48.5	55.3
N(2)–Ta—N(3)–C(31)	–34.6	30.4

\* The Pr<sup>1</sup>(*n*) group consists of atoms C(*n*1), C(*n*2), C(*n*3), H(*n*1).

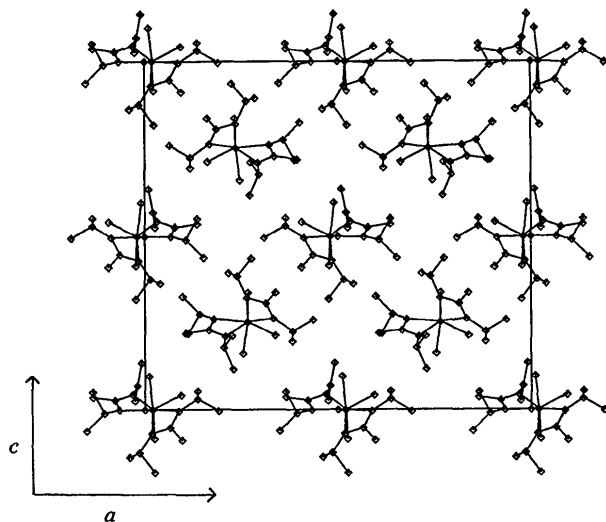


Fig. 2. The unit cell in the *b* projection.

bonds in *M*. This would suggest that the distinction between axial and equatorial sites is much less definite in *O<sub>A</sub>* and *O<sub>B</sub>* than in *M*. Indeed there are 10 close contacts between the axial chlorine atoms Cl(1) and Cl(2) and atoms in the two ligands, *viz* Cl(1)···C(21) 3·41, 3·50 Å; Cl(1)···C(3) 3·48, 3·48 Å; Cl(2)···C(11) 3·44, 3·43 Å; Cl(2)···C(3) 3·39, 3·42 Å; Cl(1)···C(23) 3·45, 3·44 Å. While it is difficult to show precisely that the variations in bond lengths in *O<sub>A</sub>* and *O<sub>B</sub>* are affected by these close contacts, it is noticeable that in *M* with short M–Cl axial bonds, there is only one comparable Cl···C contact < 3·5 Å.

In the orthorhombic form, there are considerable variations in N–C bond lengths particularly for molecule *B*, but these are probably not significant. The C–C bond lengths and the angles in the four-membered rings are about as expected. The intermolecular contacts less than 3·80 Å not involving hydrogen atoms are given in Table 6. These seem comparable with corresponding contacts in *M*. The *b* projection of the unit cell is shown in Fig. 2.

Table 6. Intermolecular distances < 3·85 Å not including hydrogens

Roman numeral superscripts refer to atoms in the following equivalent positions relative to the reference molecule at *x, y, z*.

I	<i>x, 1+y, z</i>	IV	$\frac{1}{2}+x, \frac{1}{2}-y, z$
II	$-x, 1-y, \frac{1}{2}+z$	V	$\frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}+z$
III	$-x, -y, \frac{1}{2}+z$	VI	$\frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}+z$
C(42 <i>B</i> )···Cl(3 <i>A</i> )	3·85	C(33 <i>B</i> )···C(22 <i>A</i> <sup>II</sup> )	3·82
C(32 <i>B</i> )···Cl(2 <i>A</i> )	3·81	C(33 <i>B</i> )···Cl(1 <i>A</i> <sup>III</sup> )	3·58
C(4 <i>B</i> )···C(42 <i>A</i> )	3·75	Cl(1 <i>B</i> )···C(32 <i>A</i> <sup>III</sup> )	3·58
N(2 <i>A</i> )···C(43 <i>A</i> <sup>I</sup> )	3·78	Cl(2 <i>B</i> )···C(33 <i>A</i> <sup>IV</sup> )	3·64
C(1 <i>A</i> )···C(43 <i>A</i> <sup>I</sup> )	3·73	C(13 <i>B</i> )···C(33 <i>A</i> <sup>IV</sup> )	3·70
C(22 <i>A</i> )···C(43 <i>A</i> <sup>I</sup> )	3·83	C(2 <i>B</i> )···Cl(1 <i>A</i> <sup>V</sup> )	3·81
Cl(2 <i>B</i> )···C(43 <i>B</i> <sup>I</sup> )	3·69	C(12 <i>B</i> )···Cl(1 <i>A</i> <sup>V</sup> )	3·81
		C(2 <i>A</i> )···Cl(1 <i>B</i> <sup>VI</sup> )	3·74

Two conclusions can be drawn from the comparison of *O<sub>A</sub>*, *O<sub>B</sub>* and *M*: first that there is a strong requirement for the molecular geometry of this complex to be a P.B. with the chlorine atoms in the *T* formation, and that this is more important than packing considerations; second that there are two ways\* of distorting the ideal P.B. to fit the isopropyl groups into the girdle, namely those found in *M* (with *C<sub>2</sub>* symmetry) and in *O<sub>A</sub>*, *O<sub>B</sub>* and that packing forces may well affect the choice of one type of distortion over another.

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\* It is unlikely that there are any others. There are two possible conformations for Pr<sup>I</sup>(1) and Pr<sup>I</sup>(4) with Ta–N–C–H dihedral angles of 0 or 180°. However a consequence of a dihedral angle of 180° is that the four-membered ring is almost coplanar with the girdle such that the Cl···Me contacts are equivalent. Thus an arrangement with both dihedral angles *ca* 180° is unlikely as Pr<sup>I</sup>(2)···Pr<sup>I</sup>(3) contacts would be too close. A conformation of Pr<sup>I</sup>(2) or Pr<sup>I</sup>(3) with Ta–N–C–H dihedral angles *ca* 180° rather than *ca* 0° is also unlikely as C···C contacts would be too close. Thus the two most likely conformations are *M* and *O<sub>A</sub>*, *O<sub>B</sub>*.

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