

The unit-cell packing, given in Fig. 3, is dominated by the tendency for the Br^+ ion to associate itself with both the negatively charged imidazolyl ring and the cyano nitrogen atom on neighboring molecules. The $\text{Br}-\text{N}(3)$ ($x, \frac{1}{2}-y, \frac{1}{2}+z$) separation is $2.912(6)$ Å, and the $\text{Br}-\text{N}(1)$ ($1-x, \frac{1}{2}+y, \frac{1}{2}-z$) distance is $3.094(6)$ Å; the next closest approach to Br is $\text{C}(3)$ ($1-x, -\frac{1}{2}+y, \frac{1}{2}-z$) at $3.665(8)$ Å. There are many intermediate non-bonding lengths not involving the bromine atom, the shortest of which is $\text{N}(3)-\text{N}(3)$ ($1-x, \bar{y}, \bar{z}$) at $3.08(2)$ Å.

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The Crystal and Molecular Structure of Dichlorobis-(*N,N*-diisopropylacetamidinato)methyltantalum(V)–1·0 Benzene

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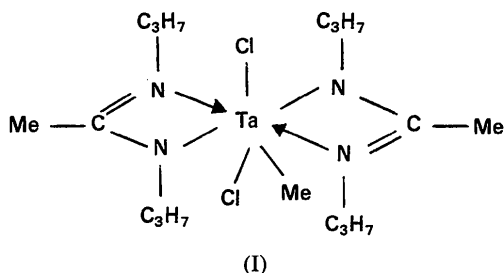
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Crystals of the title compound are monoclinic, space group $P2_1/n$, with $a=11.772$ (12), $b=16.250$ (13), $c=15.632$ (13) Å, $\beta=109.98$ (12)°, $Z=4$. The intensities of 1748 independent reflexions above background were collected by counter methods and refined to R 0.079. The structure of the molecule is disordered but it is clear that the seven-coordinate monomer has a distorted pentagonal bipyramidal geometry with the two bidentate ligands occupying the pentagonal girdle. While the two chlorine atoms occupy the axial positions and the methyl group the fifth equatorial position in most unit cells, there is evidence for interchange of position between the methyl group and the chlorine atoms in some unit cells. There is also evidence for disorder in the fifth equatorial position.

During our studies of the structure of seven-coordinate complexes, we have prepared the four compounds of formula $\text{Me}_n\text{TaCl}_{3-n}[\text{R}-\text{N}-\text{C}(\text{Me})-\text{N}-\text{R}]_2$ with $n=0, 1$ and $\text{R}=\text{C}_3\text{H}_7$, C_6H_{11} and have carried out crystal structure analyses of three; namely with $n=0$, $\text{R}=\text{C}_3\text{H}_7$ [monoclinic form, Drew & Wilkins (1974a),

orthorhombic form, Drew & Wilkins (1975a)], with $n=0$, $\text{R}=\text{C}_6\text{H}_{11}$ (Drew & Wilkins, 1975b) and with $n=1$, $\text{R}=\text{C}_6\text{H}_{11}$ (Drew & Wilkins, 1974b). In this paper we report the crystal structure of the fourth compound $\text{MeTaCl}_2[\text{C}_3\text{H}_7-\text{N}-\text{C}(\text{Me})-\text{N}-\text{C}_3\text{H}_7]_2$, (I)



The structure of both trichloro complexes showed distorted pentagonal bipyramidal geometries with the chlorine atoms in the T formation, two in axial and one in equatorial positions and the two four-membered rings in the girdle. On the other hand in the dichloromethyl complex, these two four-membered rings are perpendicular to each other and the coordination polyhedron was dissimilar from any of the ideal types. We wished to ascertain whether (I) had a similar structure to the trichloro complexes or to the other dichloromethyl complex.

Experimental

The compound was prepared by the method of Wilkins (1974) and recrystallized from benzene/ligroin.

Crystal data

$C_{17}H_{37}N_4Cl_2Ta \cdot C_6H_6$, $M = 549.38 + 78.10$, monoclinic, $U = 2791.7 \text{ \AA}^3$, $a = 11.772 (12)$, $b = 16.250 (13)$, $c = 15.632 (13) \text{ \AA}$, $\beta = 109.98 (12)^\circ$, $Z = 4$, $d_c = 1.49$ for 1.0 benzene, $\dagger F(000) = 1264$, Mo $K\alpha$ radiation $\lambda = 0.7107 \text{ \AA}$, $\mu = 44.4 \text{ cm}^{-1}$, space group $P2_1/n$ from systematic absences $h0l$, $h+l=2n+1$ and $0k0$, $k=2n+1$.

A crystal with dimensions $0.4 \times 0.3 \times 0.3 \text{ mm}$ was mounted with the a^* axis parallel to the instrument

\dagger A batch of crystals showed a wide range of densities suggesting variable amounts of benzene in the lattice.

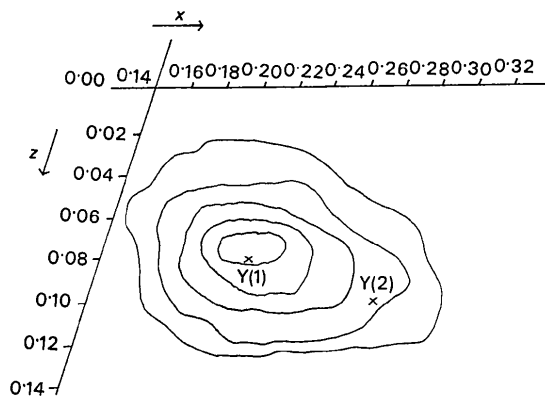


Fig. 1. A section at $y=0.300$ of the difference Fourier map showing the disorder in the fifth equatorial position. Contours are drawn for successive electron density of 1 e \AA^{-3} .

axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities (*via* the stationary-crystal stationary-counter method) and cell dimensions (*via* least-squares refinement of high-angle reflexions). 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 as a function of 2θ . Several standard reflexions were measured repeatedly during the experiment but no change in intensity was detected. 2631 independent reflexions with $2\theta < 40^\circ$ were measured. 1748 reflexions with $I > 2\sigma(I)$ were used in subsequent refinement. An absorption correction was applied with the program *ABSORB* (Stewart, 1972) with minimum and maximum transmission factors 0.23 and 0.33. No extinction correction was applied.

Structure determination

The position of the metal atom was found from the Patterson map. All atoms were located by subsequent Fourier syntheses and least-squares refinement was initiated with the tantalum atom given anisotropic and the remaining atoms isotropic thermal parameters. There were several exceptional features of the parameters obtained in this refinement. While the thermal parameters of the tantalum and nitrogen atoms were $ca 0.05 \text{ \AA}^2$, those of the axial chlorine atoms were $ca 0.10 \text{ \AA}^2$ and of the methyl carbon atom in the equatorial plane 0.02 \AA^2 . This suggested that the molecule was disordered and that both axial positions had some contribution from the carbon atom and that the equatorial position had some contribution from chlorine.* It is unusual to find disorder over two atoms in independent positions in a unit cell [for one example see La Placa & Ibers (1965)] as more frequently it is found over atoms whose positions are related by crystallographic symmetry [for example for Cl/Me in $Me_3TaCl_2(2,2'$ -bipyridyl) (Drew & Wilkins, 1973)]. In each axial position, we refined a chlorine atom and a carbon atom with equivalent positional parameters and thermal parameters, but with occupancy factors of x and $1-x$ respectively. The resulting refinement showed that the axial positions contained 0.78 and 0.91 of a chlorine atom respectively, thus leaving 0.31 of a chlorine atom in the equatorial site. [A similar refinement procedure was adopted by Albano, Ciani & Martinengo (1974).] We did not include in the refinement the fact that the Ta-C bond is expected to be $ca 0.2 \text{ \AA}$ shorter than the Ta-Cl bond, for the reason that it was unjustified to assume that all three atoms would be collinear and that in the absence of such an assumption refinement would be impossible. \dagger

* We could find no evidence that the space group was other than $P2_1/n$.

\dagger We attempted to allow for this by refining carbon and chlorine atoms in alternate cycles, but this did not converge even with fixed thermal parameters.

In the equatorial position, the situation is far more complicated than for the axial positions. When we refined a carbon atom in this equatorial site, the anisotropic thermal parameters were non-positive definite at 0.113, -0.021, 0.017, 0.014, 0.050, 0.000 Å². We then calculated a difference Fourier map omitting this atom and found a very broad peak with its longest axis approximately parallel to **a** and hence perpendicular to the plane of the girdle. From this peak (see Fig. 1), it is not clear whether the electron density can be adequately described in terms of two atomic positions named Y(1) and Y(2) either side of the girdle plane. Nevertheless we made this assumption and attempted to refine parameters of a Cl/C mixture. In site Y(1), the amounts of Cl and C were taken as *x* and *y* while in site Y(2) they were therefore 0.31 - *x* and 0.69 - *y* respectively. Positional parameters were refined but kept equivalent, and with fixed thermal parameters of 0.04 Å²* we obtained *x*=0.31 and *y*=0.09. Higher thermal parameters when used did not give reasonable values, nor was it possible to refine successfully models in which one site was exclusively carbon and the other chlorine. In the final model, Y(1) has 0.31 Cl+0.09 C and Y(2) 0.00 Cl+0.60 C.† A difference Fourier map showed no significant residual electron density in these positions suggesting that this distribution is about right.

We then refined all atoms anisotropically except for these Cl/Me atoms in the axial and equatorial sites. The thermal parameters of all atoms except for N(4) were reasonable. These parameters were non-positive definite at -0.00, 0.06, 0.07, -0.01, -0.01, 0.00 Å². This result suggests that this position must also be disordered, affected by the neighbouring equatorial site of Cl/Me. Attempts to refine this position as two sites *ca* 0.4 Å apart were not successful and it was included in the final refinement with isotropic thermal parameters.

We then calculated the positions of the four non-methyl hydrogen atoms of the isopropyl groups. The

position of H(41) was doubtful (see *Discussion*) and just three hydrogen atoms were included in the refinement, given thermal parameters equivalent to those of the atoms to which they were bonded, but not refined. The *R* value was 0.091. In a difference Fourier map, we located a benzene ring. Six carbon atoms were then included in the refinement and *R* dropped to 0.079. The average thermal parameter was 0.18 Å². With an occupancy factor of 0.5, the average thermal parameter became 0.07 Å². These results suggested that the actual occupancy factor could be less than 1.0 but when such a factor was allowed to refine, it converged back to 1.0. However variations in this factor made little difference to the geometry of (I).

In the full-matrix least-squares refinement in which four blocks were used, 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 $|w|=1$

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

	<i>x</i>	<i>y</i>	<i>z</i>
Ta	2577 (1)	1616 (1)	439 (1)
X(1) ^a	519 (10)	1509 (7)	331 (8)
X(2) ^b	4712 (9)	1798 (6)	744 (7)
Y(1) ^c	2257 (21)	3009 (13)	796 (14)
Y(2) ^d	3000 (39)	3042 (23)	995 (26)
N(1)	2427 (16)	2193 (14)	-850 (14)
N(2)	2001 (19)	939 (15)	-756 (16)
N(3)	3123 (19)	459 (13)	1057 (14)
N(4) ^e	2904 (15)	1497 (11)	1923 (12)
C(1)	1991 (28)	1468 (21)	-1318 (22)
C(2)	1721 (34)	1487 (21)	-2368 (20)
C(3)	3178 (24)	746 (19)	1933 (20)
C(4)	3535 (28)	95 (20)	2711 (18)
C(11)	2876 (28)	2948 (19)	-1144 (20)
C(12)	3850 (32)	2794 (23)	-1601 (29)
C(13)	1856 (34)	3532 (24)	-1692 (27)
C(21)	1186 (25)	189 (17)	-1074 (20)
C(22)	1687 (32)	-466 (20)	-1604 (22)
C(23)	-135 (28)	363 (21)	-1608 (25)
C(31)	3675 (23)	-275 (18)	816 (22)
C(32)	3074 (31)	-1066 (18)	861 (27)
C(33)	5030 (29)	-312 (19)	1299 (25)
C(41)	2782 (25)	1847 (20)	2684 (18)
C(42)	3696 (35)	2384 (27)	3141 (30)
C(43)	1646 (34)	1869 (32)	2801 (26)
C(101) ^f	6923 (69)	4610 (47)	13 (49)
C(102) ^f	8242 (58)	4644 (38)	173 (41)
C(103) ^f	9014 (58)	4062 (46)	486 (43)
C(104) ^f	8511 (63)	3269 (43)	716 (45)
C(105) ^f	7364 (51)	3240 (34)	534 (35)
C(106) ^f	6313 (62)	3772 (47)	164 (46)
H(31) ^g	3654	-146	106
H(21) ^g	1209	-184	-462
H(11) ^g	3397	3365	-554

(a) Population parameters Cl 0.78 (2), C 0.22 (2),* thermal parameter 0.09 (1) Å²; (b) for Cl 0.91 (2), for C 0.09 (2),* *U* 0.09 (1) Å²; (c) for Cl 0.31 (2),* for C 0.09 (2),* *U* 0.043 (5) Å²; (d) for C 0.60 (2),* *U* 0.032 (10) Å². (e) *U* 0.039 (5) Å². (f) Thermal parameters for the benzene ring are respectively 0.22 (3), 0.16 (2), 0.18 (2), 0.19 (2), 0.15 (2), 0.19 (3) Å². (g) Parameters fixed.

* Parameters not refined independently in the last cycle. Standard deviation is made equivalent to that of a related refined parameter.

* When we allowed the thermal parameters *U* to refine as well as the occupancy factors *p* of these atoms, we found that both became unreasonably high. A similar effect occurred in the final model when for Y(2), *p* and *U* were refined together and converged to give values of 0.73 (7) and 0.054 (15) Å². These results contradict those from the original refinement which suggested that with 0.31 Cl and 0.69 C spread over the two sites, it was necessary to have *U*=0.04 Å² as with higher values a total occupancy of >1 would be required to describe the electron density. Thus we suggest that the best method of refinement is with fixed thermal parameters. After all, the results obtained from the above refinement of Y(2) are within 2σ of these values, the high standard deviations reflecting the correlation between *p* and *U*. As noted previously, for the axial atoms, refinement of *p* and *U* was more successful. It is possible that the lack of success in refining *p* and *U* for Y(1) and Y(2) is due to their close proximity and/or to inadequacies in the model in that other sites should be considered.

† Having obtained this distribution of occupancy factors, we fixed them and refined the thermal parameters only but there was no significant change.

for $F_o < 77$ and $\sqrt{w} = 77/F_o$ for $F_o > 77$. Calculations were made on a C.D.C. 7600 computer at the University of London Computer Centre, with the X-RAY system of programs (Stewart, 1972) and on an I.C.L. 1904S computer at Reading University. Atomic scattering factors for tantalum, chlorine, nitrogen and carbon were taken from *International Tables for X-ray Crystallography* (1965), as were values for the anomalous dispersion of tantalum, and for hydrogen from Stewart, Davidson & Simpson (1965). The anisotropic thermal parameters used were defined as $\exp(-2\pi^2 \sum_i \sum_j U_{ij} h_i h_j b_i b_j)$; $i, j = 1, 2, 3$, b_i being the i th reciprocal lattice dimension. The isotropic thermal parameter was $\exp(-8\pi^2 U \sin^2 \theta / \lambda^2)$. The 883 zero-weighted reflexions showed no large discrepancies. The refinement was stopped when all shifts were $< 0.10\sigma$. The final difference Fourier map showed no significant peaks. Final positional coordinates and thermal parameters are given in Tables 1 and 2.* Bond lengths and angles for (I), together with estimated standard deviations are given in Table 3.

Discussion

The molecule (I) is a seven-coordinate monomer with the tantalum atom bonded to two chlorine atoms, one methyl group and to four nitrogen atoms from the two bidentate *N,N*-diisopropylacetamidinato ligands. Its geometry is a distorted pentagonal bipyramid with both bidentate ligands in the pentagonal girdle. The two chlorine atoms and the methyl group occupy the two axial sites and the disordered equatorial site. The two axial sites [called X(1) and X(2)] contain 78 and

* A list of structure factors has been deposited with the British Library Lending Division as Supplementary Publication No. SUP 31079 (6 pp.). Copies may be obtained through The Executive Secretary, International Union of Crystallography, 13 White Friars, Chester CH1 1NZ, England.

91% chlorine respectively with the remainder carbon. In the equatorial position, two atoms Y(1) and Y(2) were refined, Y(1) containing 0.31 of a chlorine atom and 0.09 of a carbon atom, while Y(2) contained 0.60 of a carbon atom. The molecule is shown in Fig. 2, together with the atomic numbering scheme.

No attempt was made to account for the differences between Ta-C and Ta-Cl bond lengths in the refinement and therefore the Ta-X and Ta-Y bond lengths are of little significance, values being Ta-X(1) 2.38 (1), Ta-X(2) 2.41, Ta-Y(1) 2.39 (2) and Ta-Y(2) 2.47 (4) Å. The four Ta-N bond lengths are within the range of values found in previous structures (Drew & Wilkins, 1974*a,b*, 1975*a,b*).

As the remaining dimensions in the molecule are as expected, it is clear that the interchange of positions between the methyl group and the chlorine atoms has little effect upon the overall geometry of the molecules. The three possible arrangements of the chlorine atoms and the methyl group are shown in Fig. 3.*

The geometry of (I) is thus similar to that found in the trichloro complexes

$\text{TaCl}_3[\text{C}_6\text{H}_{11}\text{N}-\text{C}(\text{Me})-\text{N}-\text{C}_6\text{H}_{11}]_2$
and $\text{TaCl}_3[\text{C}_3\text{H}_7\text{N}-\text{C}(\text{Me})-\text{N}-\text{C}_3\text{H}_7]_2$ which leaves $\text{MeTaCl}_2[\text{C}_6\text{H}_{11}\text{N}-\text{C}(\text{Me})-\text{N}-\text{C}_6\text{H}_{11}]_2$ as the odd one out in the series of four. In our description of this latter structure (Drew & Wilkins, 1974*b*), we showed that its geometry contains less steric crowding than would a pentagonal bipyramid (P.B.). However, in this arrangement Me-Ta-Cl angles are 75.8 and 79.1°, and we argued that in the trichloro complexes, the geometry is a P.B. because Cl...Cl repulsions require Cl-Ta-Cl angles to be $\geq 90^\circ$. From these arguments it can be predicted that the structure of (I) would be similar to that of $\text{MeTaCl}_2[\text{C}_6\text{H}_{11}\text{N}-\text{C}(\text{Me})-\text{N}-\text{C}_6\text{H}_{11}]_2$ and not have the distorted P.B. structure that it has. It seems

* It is surprising that in the n.m.r. spectrum, at -70°C , we were unable to find more than one methyl group environment.

Table 2. Anisotropic thermal parameters ($\times 10^3$) in (I), with estimated standard deviations in parentheses

	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ta	61.9 (8)	45.5 (8)	47.6 (8)	-1.2 (8)	25.5 (5)	-0.0 (8)
N(1)	33 (11)	84 (17)	50 (13)	17 (11)	18 (10)	11 (12)
N(2)	61 (16)	88 (19)	78 (17)	16 (13)	37 (13)	59 (15)
N(3)	67 (15)	53 (14)	52 (14)	-5 (11)	19 (12)	-00 (11)
C(1)	76 (22)	91 (26)	65 (21)	-02 (19)	-04 (17)	-47 (20)
C(2)	139 (31)	82 (25)	44 (18)	-23 (22)	28 (20)	-04 (18)
C(3)	45 (18)	81 (22)	71 (21)	-48 (17)	25 (16)	-19 (19)
C(4)	92 (23)	85 (23)	36 (16)	27 (20)	24 (16)	12 (18)
C(11)	84 (23)	68 (19)	68 (21)	24 (18)	43 (18)	19 (18)
C(12)	90 (26)	105 (29)	159 (37)	13 (22)	98 (28)	39 (28)
C(13)	104 (29)	97 (30)	112 (31)	04 (24)	32 (24)	59 (25)
C(21)	66 (20)	48 (17)	84 (21)	-34 (16)	44 (16)	-15 (17)
C(22)	99 (27)	75 (24)	63 (22)	-03 (20)	10 (20)	-25 (19)
C(23)	56 (21)	84 (25)	107 (27)	00 (18)	18 (19)	-03 (21)
C(31)	35 (16)	69 (21)	93 (23)	02 (15)	19 (15)	-01 (19)
C(32)	87 (24)	41 (19)	139 (32)	-18 (17)	41 (22)	20 (20)
C(33)	76 (24)	60 (21)	127 (31)	02 (18)	46 (22)	-21 (21)
C(41)	41 (17)	101 (26)	49 (18)	-30 (17)	04 (15)	-30 (18)
C(42)	94 (30)	126 (34)	150 (39)	-09 (26)	60 (28)	-78 (32)
C(43)	81 (28)	205 (51)	90 (29)	15 (29)	23 (22)	-68 (32)

unlikely that the differences between the alkyl groups C_3H_7 and C_6H_{11} could affect the geometry of the coordination sphere in these molecules. Close contacts involving atoms bonded to $C(n1)$ atoms are important in fixing molecular geometry but in both alkyl groups $C(n1)$ is bonded to two carbon atoms and a hydrogen atom. In addition the two trichloro complexes with these alkyl groups have equivalent geometries.

It is possible that we have to seek a reason for the present geometry of (I) in the disorder. It is clear that in the $MeTaCl_2[C_6H_{11}-N-C(Me)-N-C_6H_{11}]_2$ structure if a methyl group and a chlorine atom were inter-

changed, the geometry would contain very short $Cl \cdots Cl$ contacts. This is not the case for the P.B. where interchange of position makes little difference to the overall repulsive energy and the positions of all other atoms in the molecule would be relatively unchanged. Thus, given disorder,* we can see why a distorted P.B. structure is found.

* This begs the question of why disorder is found. It would be interesting to see whether another crystal form exists for this complex (with possibly a different solvent) in which an ordered structure is found.

Table 3. *Molecular dimensions, distances (Å), angles (°)*

Ta-X(1)	2.376 (12)	Ta-N(1)	2.174 (22)	
Ta-X(2)	2.411 (10)	Ta-N(2)	2.073 (24)	
Ta-Y(1)	2.391 (22)	Ta-N(3)	2.112 (20)	
Ta-Y(2)	2.466 (37)	Ta-N(4)	2.226 (19)	
X(1)-Ta-X(2)	172.6 (4)	Y(1)-Ta-N(1)	80.7 (8)	
X(1)-Ta-Y(1)	81.3 (7)	Y(1)-Ta-N(2)	133.1 (8)	
X(1)-Ta-Y(2)	99.9 (11)	Y(1)-Ta-N(3)	141.6 (8)	
X(1)-Ta-N(1)	102.0 (6)	Y(1)-Ta-N(4)	79.9 (7)	
X(1)-Ta-N(2)	83.4 (7)	Y(2)-Ta-N(1)	82.2 (11)	
X(1)-Ta-N(3)	96.4 (7)	Y(2)-Ta-N(2)	141.4 (11)	
X(1)-Ta-N(4)	82.9 (5)	Y(2)-Ta-N(3)	133.1 (10)	
X(2)-Ta-Y(1)	94.3 (6)	Y(2)-Ta-N(4)	76.9 (11)	
X(2)-Ta-Y(2)	75.2 (11)	N(1)-Ta-N(2)	59.7 (9)	
X(2)-Ta-N(1)	83.1 (5)	N(1)-Ta-N(3)	136.3 (9)	
X(2)-Ta-N(2)	103.9 (7)	N(1)-Ta-N(4)	159.0 (7)	
X(2)-Ta-N(3)	83.4 (7)	N(2)-Ta-N(3)	83.9 (8)	
X(2)-Ta-N(4)	90.4 (5)	N(2)-Ta-N(4)	141.2 (8)	
Y(1)···Y(2)	0.82	N(3)-Ta-N(4)	61.9 (8)	
N(1)-C(1)	1.39 (4)	N(3)-C(3)	1.43 (4)	
N(2)-C(1)	1.23 (4)	N(4)-C(3)	1.26 (4)	
C(1)-C(2)	1.56 (5)	C(3)-C(4)	1.56 (4)	
N(1)-C(1)-N(2)	107.8 (27)	N(3)-C(3)-N(4)	112.2 (25)	
N(1)-C(1)-C(2)	116.3 (28)	N(3)-C(3)-C(4)	116.0 (25)	
N(2)-C(1)-C(2)	135.6 (30)	N(4)-C(3)-C(4)	131.8 (28)	
Ta-N(1)-C(1)	91.3 (13)	Ta-N(3)-C(3)	93.1 (16)	
Ta-N(2)-C(1)	101.1 (20)	Ta-N(4)-C(3)	92.9 (17)	
C(11)-N(1)-C(1)	130.5 (26)	C(31)-N(3)-C(3)	129.4 (22)	
C(21)-N(2)-C(1)	118.4 (23)	C(41)-N(4)-C(3)	119.6 (24)	
	<i>n</i> = 1	<i>n</i> = 2	<i>n</i> = 3	<i>n</i> = 4
N(<i>n</i>)-C(<i>n1</i>)	1.47 (4)	1.53 (4)	1.47 (4)	1.37 (4)
Ta-N(<i>n</i>)-C(<i>n1</i>)	136.5 (16)	133.9 (21)	134.3 (20)	146.7 (17)
C(<i>n1</i>)-C(<i>n2</i>)	1.57 (6)	1.58 (5)	1.48 (4)	1.38 (5)
C(<i>n1</i>)-C(<i>n3</i>)	1.54 (5)	1.52 (4)	1.51 (4)	1.41 (5)
N(<i>n</i>)-C(<i>n1</i>)-C(<i>n2</i>)	114 (3)	114 (3)	116 (3)	115 (3)
N(<i>n</i>)-C(<i>n1</i>)-C(<i>n3</i>)	113 (3)	116 (3)	113 (2)	121 (3)
C(<i>n2</i>)-C(<i>n1</i>)-C(<i>n3</i>)	113 (3)	110 (3)	112 (2)	121 (2)
C(101)-C(102)	1.49 (11)	C(101)-C(102)-C(103)		127 (7)
C(102)-C(103)	1.29 (8)	C(102)-C(103)-C(104)		116 (6)
C(103)-C(104)	1.51 (10)	C(103)-C(104)-C(105)		117 (6)
C(104)-C(105)	1.28 (9)	C(104)-C(105)-C(106)		139 (6)
C(105)-C(106)	1.46 (9)	C(105)-C(106)-C(101)		102 (6)
C(106)-C(101)	1.60 (11)	C(106)-C(101)-C(102)		120 (6)

Table 4. *Dihedral angles (°)*

Y(1)-Ta-N(1)-C(11)	42.9	Y(2)-Ta-N(1)-C(11)	23.2	
Y(1)-Ta-N(4)-C(41)	15.2	Y(2)-Ta-N(4)-C(41)	34.9	
C(2)-C(1)-N(2)-C(21)	-27.2	C(4)-C(3)-N(3)-C(31)	-19.6	
C(2)-C(1)-N(1)-C(11)	-11.6	C(4)-C(3)-N(4)-C(41)	-6.2	
N(3)-Ta-N(2)-C(21)	53.2	N(2)-Ta-N(3)-C(31)	39.0	
	<i>n</i> = 1	<i>n</i> = 2	<i>n</i> = 3	<i>n</i> = 4
Ta-N(<i>n</i>)-C(<i>n1</i>)-H(<i>n1</i>)	-4.2	-26.5	-8.2	-
Ta-N(<i>n</i>)-C(<i>n1</i>)-C(<i>n2</i>)	110.4	-137.4	-130.3	-85.6
Ta-N(<i>n</i>)-C(<i>n1</i>)-C(<i>n3</i>)	-118.0	94.2	98.5	74.4

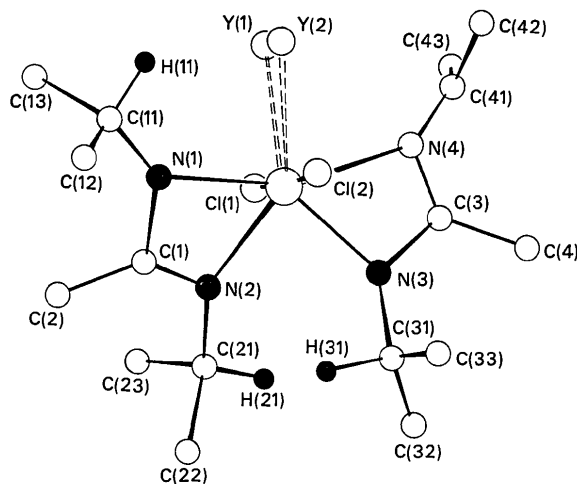


Fig. 2. The molecule of (I).

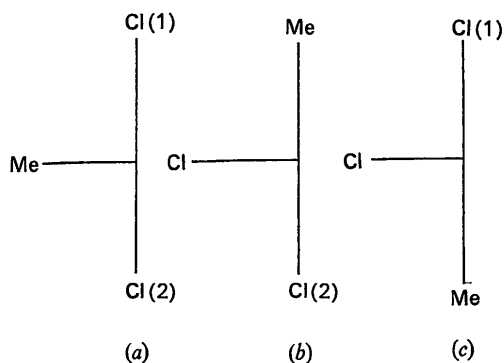
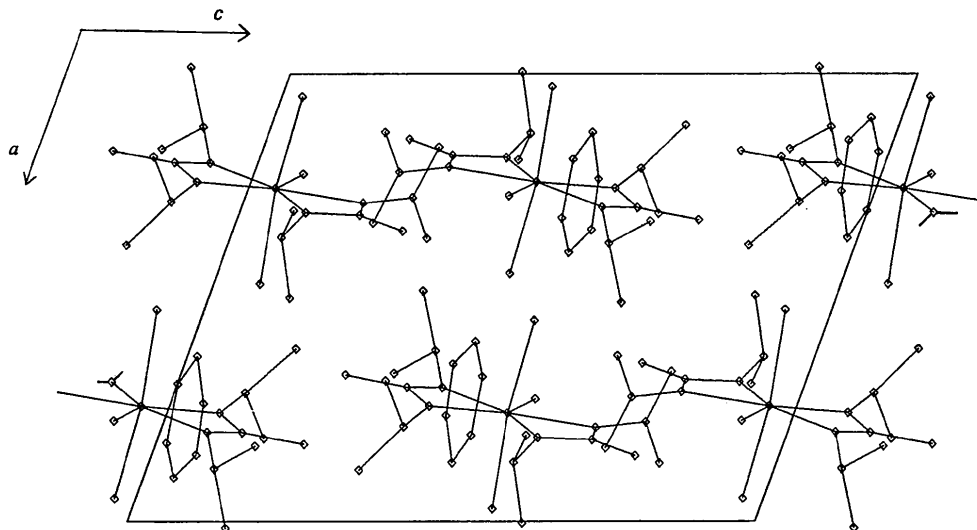


Fig. 3. Possible arrangements of the two chlorine atoms and one methyl group around the tantalum atom. Percentages obtained from the refinement are (a) 69%, (b) 22%, (c) 9%.

Of the three structures (Fig. 3) for (I), (a) with two chlorine atoms axial and the methyl group equatorial is the most frequently found. This is to be expected as the two chlorine atoms occupy the least crowded axial sites in the P.B. as in $\text{MeTaCl}_2[\text{ON}(\text{Me})\text{NO}]_2$ (Drew & Wilkins, 1974c). Structures (b) and (c) with methyl group axial have no precedents and it seems unlikely that they would be found in the solid state except in the present arrangement where they are stabilized by having equivalent unit cells to structure (a).

In a discussion of the structures of $\text{TaCl}_3[\text{C}_3\text{H}_7\text{-N-C}(\text{Me})\text{-N-C}_3\text{H}_7]_2$ in the two crystal forms, Drew & Wilkins (1975a) have shown that of the many ways of distorting the ideal P.B. to accommodate the isopropyl groups in the girdle, two are the most likely. The first of these (with C_2 symmetry) is found in the monoclinic form and differs from the second (with C_1 symmetry) found in the orthorhombic form by rotation of one isopropyl group by 180° about the N-C bond. However, in (I) there is some doubt as to the orientation of one of the isopropyl groups. As stated in the experimental section, we calculated the positions of four $\text{H}(n1)$ atoms assuming tetrahedral geometry for C(1). However the three angles subtended at C(41) by N(4), C(42) and C(43) are up to 357° , an unlikely value for tetrahedral carbon. (A similar unlikely value was found for one of the molecules of $\text{TaCl}_3[\text{C}_3\text{H}_7\text{-N-C}(\text{Me})\text{-N-C}_3\text{H}_7]_2$ in the orthorhombic form.) It is possible that both orientations of the group are found and that the refined positions are the average of two. This could account for the disorder in the adjacent equatorial position and in the difficulty found in refining N(4). Dihedral angles are shown in Table 4.

As stated in the *Experimental* section, we refined two sites for this equatorial position Y(1) and Y(2) which are situated above and below the plane of the metal

Fig. 4. The unit cell in the *b* projection.

atom and the four nitrogen atoms by -0.49 and 0.31 Å respectively (see Table 5). Angles subtended at the metal atom including Y(1) or Y(2) are for the most part reasonable though values of 81.2° for X(1)–Ta–Y(1) and 75.2° for X(2)–Ta–Y(2) are smaller than normal. However Y(2) is all carbon and it is noticeable that it is concerned with closer contacts than Y(1). It may well be that our treatment of the disorder is an oversimplification and that the Cl/Me atom can occupy intermediate sites between Y(1) and Y(2) particularly as such sites would not be too close to non-bonded atoms in the molecule. Variations in the position of Y are presumably correlated with the conformation of the isopropyl group N(4), H(41), C(41), C(42), C(43) but not in any simple way. It is clear from the refinement that one explanation for disorder namely a chlorine atom in one site, a carbon atom in the other, each concomitant with one of the possible orientations of the isopropyl group can be ruled out.

Table 5. *Least-squares planes in the form*

$$Ax + By + Cz = D,$$

where x, y, z are crystallographic coordinates of the atoms

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

Plane 1 Ta, N(1), N(2), N(3), N(4)

$$A = 11.67, B = 0.38, C = -3.44, D = 2.97$$

[Ta -0.05 , Y(1) -0.49 , Y(2) 0.31 , N(1) 0.24 , N(2) -0.34 , N(3) 0.33 , N(4) -0.18 , C(1) -0.14 , C(2) -0.09 , C(3) 0.10 , C(4) 0.23 , C(11) 0.89 , C(21) -1.21 , C(31) 1.03 , C(41) -0.57]

Plane 2 Ta, N(1), N(2)

$$A = 11.29, B = -4.06, C = -3.13, D = 2.11$$

[Ta, N(1), N(2) 0.00 , C(1) -0.05 , C(2) -0.05 , C(11) 0.29 , C(12) 1.59 , C(13) -0.93 , C(21) -0.52 , C(22) 0.48 , C(23) -1.91]

Plane 3 Ta, N(3), N(4)

$$A = 11.14, B = 4.13, C = -2.12, D = 3.45$$

[Ta, N(3), N(4) 0.00 , C(3) -0.01 , C(4) -0.04 , C(31) 0.36 , C(32) -0.64 , C(33) 1.75 , C(41) -0.15 , C(42) 0.99 , C(43) -1.44]

•Angles between planes 1 and 2 15.8° ; 1 and 3 14.1° ; 2 and 3 29.5°

The geometry of the distorted P.B.'s of the trichloro complexes was described with reference to the plane of the equatorial girdle which was calculated from the least-squares plane of the ML_5 atoms. In view of the uncertainty about the fifth site, we cannot compare (I) with those structures by this means. In Table 5, it is shown that the plane of the TaN_4 atoms intersect the two planar four-membered rings at angles of 15.8 and 14.1° respectively. The angle between the two planes is 29.5° .

The dimensions of the benzene ring are acceptable given the high thermal parameters. Packing between molecules and solvent in the unit cell is not particularly efficient, there being only four intermolecular distances less than 3.75 Å, all involving one atom in the benzene ring and one in the molecule.

Fig. 4 shows the unit cell in the b projection.

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