Crystal and Molecular Structure of Dichlorobis-(*NN*-dicyclohexylacetamidinato)methyltantalum(v)

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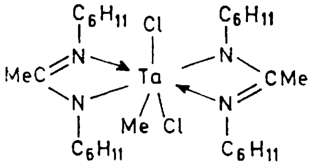
Crystals of the title compound are monoclinic, spacegroup $P2_1/c$ with a = 13·521(8), b = 13·084(8), c = 17·916(8) Å, β = 93·78(9)°, Z = 4. The intensities of 3198 independent reflections above background were collected by diffractometer methods and refined to R 0·080. The molecule is a seven-co-ordinate monomer, the tantalum being bonded to one methyl group [2·217(20) Å], two chlorine atoms [2·397(6), 2·430(6) Å], and four nitrogen atoms [2·160(7), 2·149(19), 2·040(17), 2·187(17) Å] of two bidentate ligands which are approximately perpendicular to each other. The geometry of the complex is considered in terms of a highly distorted pentagonal bipyramid but does not closely resemble any of the three ideal types of polyhedra usually found in seven-co-ordination.

We have been investigating the crystal structures of seven-co-ordinate complexes whose geometry was difficult to predict. In the course of this work, we have determined the structures of two complexes of general formula $Me_{3-n}MCl_nL_2$ (M = Nb or Ta, n = 2 or 3, L = bidentate ligand, R = alkyl) namely, (II), $NbCl_3[N(Me){\cdot}C(Me){\cdot}S]_2$ (ref. 1) and (III), $TaCl_3[Pr^i{\cdot}N{\cdot}C(Me){\cdot}N{\cdot}Pr^i]_2$.[2] Both structures are seven-co-ordinate monomers and have distorted pentagonal bipyramidal geometries with two chlorine atoms in the axial positions and one in the equatorial plane together with the two bidentate ligands. In an attempt to find a complex in this series with a different geometry, we chose $MeTaCl_2[C_6H_{11}{\cdot}N{\cdot}C(Me){\cdot}N{\cdot}C_6H_{11}]_2$, (I), prepared during a study of the reactions between Me_nMCl_{5-n} (M = Nb or Ta, n = 1—3) and disubstituted carbodi-imides,[3] and here report its crystal structure. We estimated that both the replacement of a chlorine atom by a methyl group and the presence of the bulky cyclohexane groups in the equatorial plane might well preclude (I) from having the pentagonal bipyramidal structure.



(I)

EXPERIMENTAL

The complex was prepared as stated in ref. 3 and crystallised from dichloromethane–petroleum.

Crystal Data.—$C_{29}H_{53}Cl_2N_4Ta$, M = 709·31, Monoclinic, a = 13·521(8), b = 13·084(8), c = 17·916(8) Å, β = 93·78(9)°, U = 3164·2 Å^3, D_m = 1·46(2), Z = 4, D_c = 1·49, $F(000)$ = 1448. Mo-K_α radiation, λ = 0·7107 Å, μ(Mo-K_α) = 38·34 cm^{-1}. Spacegroup $P2_1/c$ from systematic absences: $h0l$, $l = 2n + 1$; $0k0$, $k = 2n + 1$. A crystal with dimensions *ca.* 0·16 × 0·40 × 0·40 mm was mounted with the (011) planes perpendicular to the instrument axis of a General Electric XRD 5 apparatus which was used to measure diffraction intensities 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 for those reflections which were seriously affected by the streaking of other orders. For other reflections, backgrounds were taken from plots of background as a function of 2θ. Several standard reflections were measured repeatedly during the course of the experiment and their values decreased linearly with time. A correction factor (max. 1·50) was applied to each intensity to compensate for this crystal deterioration. 5650 Independent reflections were measured with 2θ < 50° by the stationary-crystal–stationary-counter method. The standard deviation $\sigma(I)$ of the reflections was taken to be $[I + 2E + (0{\cdot}03\, I^2)]^{\frac{1}{2}}$, where E is the estimated background of the reflection. 3198 Reflections with $I > \sigma(I)$ were used in subsequent calculations. An absorption correction was applied by use of the program ABSORB;[4] transmission factors varied between 0·25 and 0·55. No extinction correction was applied.

Structure Determination.—The structure was solved by Patterson and Fourier methods and refined by full-matrix least-squares. The weighting scheme, chosen to give average values of $w\Delta^2$ for groups of reflections independent of the value of F_o and sin θ/λ, was $\sqrt{w} = 1$ for $F_o \leqslant 170$ and $\sqrt{w} = 170/F_o$ for $F_o > 170$. Calculations were made on a CDC 7600 computer at the University of London Computer Centre, with the programs described in ref. 4, and on an ICL 1904S computer at Reading University using our unpublished programs. Atomic scattering factors for tantalum, chlorine, nitrogen, and carbon were taken from ref. 5 as were corrections for the real and imaginary part of the anomalous dispersion of tantalum and chlorine. Scattering factors for hydrogen were taken from ref. 6. The structure was first refined with tantalum and chlorine atoms anisotropic and the remaining atoms isotropic to R 0·092. At this stage 44 hydrogen atoms were introduced in calculated tetrahedral positions bonded to the carbon atoms of the cyclohexane rings. Their positions coincided with positive areas in the difference Fourier map. Other hydrogen atoms on methyl groups were not unambiguously identified on the difference-Fourier map and positions were not included. The hydrogen atoms were given thermal parameters equivalent to those of the atom to which they were bonded and included in the structure factor calculation and not refined. R Was reduced to 0·089. Finally all

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[1] M. G. B. Drew and J. D. Wilkins, *J.C.S. Dalton*, 1974, 198.

[2] M. G. B. Drew and J. D. Wilkins, *J.C.S. Dalton*, 1974, 1579.

[3] J. D. Wilkins, *J. Organometallic Chem.*, in the press.

[4] '*X*-Ray' system of programs, ed. J. M. Stewart, University of Maryland, Technical Report TR 192, June 1972.

[5] 'International Tables for *X*-Ray Crystallography,' vol. III, Kynoch Press, Birmingham, 1965.

[6] R. F. Stewart, E. R. Davidson, and W. T. Simpson, *J. Chem. Phys.*, 1965, **42**, 3175.

atoms, except hydrogen, were given anisotropic thermal parameters and R was reduced to 0·080. Refinement was stopped when all shifts were $<0·050\sigma$. The anisotropic thermal parameters used were defined as exp $(-2\pi^2\sum_i\sum_j U_{ij}h_ih_jb_ib_j;\ i,j = 1,2,3)$, b_i being the ith reciprocal lattice dimension. The 2452 zero-weighted reflections showed no large discrepancies. The final difference Fourier map showed no significant peaks. Final positional co-ordinates and thermal parameters are given in Tables 1 and 2. The hydrogen atom positions and the final observed and calculated structure factors ($\times$ 1·00) are listed in a Supplementary Publication, No. SUP 21061 (12 pp., 1 microfiche.) *

TABLE 1

Atomic co-ordinates ($\times 10^4$) with estimated standard deviations in parentheses

Atom	x	y	z
Ta	1592(1)	1492(1)	1354(1)
Cl(1)	2540(4)	1632(5)	0274(3)
Cl(2)	0792(4)	3067(4)	1707(4)
N(1)	1906(11)	1318(11)	2545(9)
N(2)	2872(14)	2248(15)	1870(11)
N(3)	1871(11)	−0039(13)	1334(10)
N(4)	0448(12)	0416(14)	1658(10)
C(1)	2778(17)	1853(17)	2580(11)
C(2)	3523(18)	2008(22)	3211(12)
C(3)	0952(14)	−0382(15)	1556(11)
C(4)	0697(17)	−1490(19)	1650(12)
C(5)	0461(15)	1674(16)	0410(11)
C(11)	1613(14)	0659(16)	3171(12)
C(12)	1376(13)	1232(16)	3895(12)
C(13)	0945(22)	0513(24)	4439(15)
C(14)	1620(21)	−0364(23)	4631(14)
C(15)	1849(16)	−0960(20)	3899(12)
C(16)	2270(16)	−0245(17)	3354(11)
C(21)	3628(16)	2984(18)	1761(14)
C(22)	3260(17)	3811(18)	1221(16)
C(23)	4069(17)	4627(20)	1110(14)
C(24)	4960(18)	4138(17)	0843(14)
C(25)	5379(18)	3278(21)	1389(14)
C(26)	4605(15)	2455(21)	1476(13)
C(31)	2672(19)	−0815(17)	1234(13)
C(32)	2605(17)	−1220(19)	0439(13)
C(33)	3438(21)	−1995(25)	0320(17)
C(34)	4455(22)	−1498(28)	0579(15)
C(35)	4533(20)	−1101(23)	1315(18)
C(36)	3650(17)	−0266(17)	1450(14)
C(41)	−0608(16)	0316(19)	1905(12)
C(42)	−0955(16)	1223(17)	2316(15)
C(43)	−1967(16)	1130(17)	2561(17)
C(44)	−2724(19)	0787(25)	1991(19)
C(45)	−2375(17)	−0140(30)	1597(18)
C(46)	−1355(17)	0016(19)	1292(15)
H(11) [a]	1006	0441	2926
H(21)	3782	3294	2240
H(31)	2593	−1366	1576
H(41)	−0540	−0248	2248

[a] Only hydrogen atoms bonded to C(n1) atoms are listed here. Co-ordinates for the others are listed in the Supplementary Publication.

Bond lengths and angles for (I), together with estimated standard deviations, are given in Table 3. Carbon atoms in the cyclohexane rings are numbered (1)—(6), the first number n being that of the ring, (1)—(4). Hydrogen atoms are numbered so that the first two digits are the same as those of the carbon atom to which they are bonded.

DISCUSSION

The molecule (I) is a seven-co-ordinate monomer with the tantalum atom bonded to two chlorine atoms, one methyl group, and to four nitrogen atoms from the two bidentate *NN*-dicyclohexylacetamidinato-ligands. The co-ordination sphere of (I), together with the atomic numbering scheme, is shown in Figure 1. Its geometry appears at first sight to bear little relationship to any of the three ideal seven-co-ordinate polyhedra. However, we have used the method of Britton and Dunitz [7] to investigate the polyhedra type. Figure 2 shows the co-ordination polyhedra of (I). The circles represent vertices, the numbers in the circles represent the number of edges (represented by lines) in which each vertex participates. In a molecule with different ligands it is difficult to define a polyhedron edge and so in Figure 2(a), this is where L–M–L $\leqslant 90°$, and in Figure 2(b) where L–M–L $\leqslant 115°$. These diagrams are compatible with Nos. 34 and 5 of the 34 non-isomorphic convex polyhedra with seven vertices listed.[7] No. 5 is a pentagonal bipyramid (PB) with N(3) and Cl(2) in axial sites: thus one bidentate ligand occupies an equatorial bite while the other spans axial and equatorial positions. Table 4 lists the deviations of atoms from the least-squares plane of the girdle, the maximum being 0·67, and the mean 0·36 Å. These high values and the L–M–L angles confirm that the geometry of (I), while having no close resemblance to any ideal polyhedron, can be described in terms of a highly distorted PB.

TABLE 2

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

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ta	28·4(4)	31·7(4)	41·3(4)	−01·9(5)	01·4(3)	01·2(5)
Cl(1)	58(3)	70(4)	50(3)	−02(3)	12(3)	−02(3)
Cl(2)	47(3)	47(3)	73(4)	04(3)	09(3)	−07(3)
N(1)	40(8)	24(9)	65(10)	00(7)	13(8)	−02(7)
N(2)	64(12)	50(11)	67(13)	−15(10)	−01(10)	−09(10)
N(3)	36(9)	49(10)	59(11)	−04(7)	20(9)	−20(9)
N(4)	39(9)	52(10)	48(10)	11(10)	00(10)	06(9)
C(1)	58(14)	44(12)	39(12)	−01(10)	00(10)	−06(9)
C(2)	58(15)	93(10)	38(12)	−14(14)	−14(11)	21(13)
C(3)	37(11)	39(11)	51(12)	12(9)	−10(9)	−13(10)
C(4)	64(14)	52(13)	60(13)	−19(14)	12(11)	−13(14)
C(5)	43(11)	52(15)	50(12)	02(10)	01(10)	−06(10)
C(11)	35(11)	40(11)	59(13)	12(9)	−06(10)	−10(10)
C(12)	19(9)	58(13)	58(15)	10(9)	05(8)	05(10)
C(13)	89(20)	80(20)	68(17)	−18(17)	39(15)	02(16)
C(14)	78(18)	88(20)	56(15)	−29(16)	04(13)	34(15)
C(15)	39(12)	93(18)	39(11)	29(12)	−11(10)	08(12)
C(16)	51(13)	57(14)	31(10)	07(11)	−00(9)	−07(10)
C(21)	39(12)	54(15)	69(16)	−02(11)	01(11)	14(12)
C(22)	40(13)	59(16)	95(19)	−06(11)	22(13)	01(14)
C(23)	47(14)	71(17)	64(15)	−12(13)	01(12)	10(14)
C(24)	60(15)	39(13)	74(16)	−27(13)	18(13)	10(12)
C(25)	55(15)	84(21)	63(15)	11(13)	09(12)	19(14)
C(26)	36(12)	84(18)	54(14)	−09(12)	03(11)	02(13)
C(31)	71(16)	38(13)	64(15)	24(11)	13(12)	06(11)
C(32)	51(13)	70(18)	62(14)	15(11)	−26(11)	−13(12)
C(33)	65(17)	94(21)	85(20)	17(16)	−07(15)	−20(17)
C(34)	80(19)	116(25)	59(16)	20(21)	−00(14)	−24(20)
C(35)	54(16)	90(21)	103(23)	29(15)	−04(15)	−24(17)
C(36)	55(14)	40(13)	62(15)	07(11)	10(11)	−01(11)
C(41)	43(12)	74(16)	41(11)	−02(11)	−04(10)	16(11)
C(42)	39(12)	43(14)	103(19)	−18(10)	11(12)	−20(12)
C(43)	35(12)	35(12)	131(24)	−06(9)	13(14)	−28(14)
C(44)	46(15)	92(22)	118(25)	−02(15)	29(16)	−26(19)
C(45)	21(12)	156(32)	102(23)	−19(16)	−02(13)	14(22)
C(46)	48(14)	56(14)	78(17)	−22(12)	24(12)	−07(13)

Whatever the geometry of (I) is called, its structure is

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* See Notice to authors No. 7 in *J.C.S. Dalton*, 1973, Index isssue.

[7] D. Britton and J. D. Dunitz, *Acta Cryst.*, 1973, **A29**, 362.

totally different from those of the other complexes of similar stoicheiometry, (II) [1] and (III),[2] for in (I) the two four-membered rings intersect at 88·9° compared with 6·5 and 25·4° for (II) and (III), both PB. So why the difference?

We have argued [1] that the three chlorine atoms in these other complexes determine the geometry as a PB, with the chlorine atoms in the T-formation such that Cl–Ta–Cl angles are $\geqslant$90°. In (I), the replacement of one chlorine atom by a methyl group removes this restriction * [Me–Ta–Cl 75·8(6) and 79·1(6)°, Cl · · · Me 2·84 and 2·96 Å] and allows the molecule to attain a geometry which maximises the intramolecular distances between the cyclohexyl groups. The arrangement in (I), where closest contacts between two hydrogen atoms in adjacent cyclohexane rings are H(111) · · · H(422) 2·35 and H(161) · · · H(311) 2·61 Å contains far less steric crowding than would a PB. Thus, all Cl–Ta–N–C and C(5)–Ta–N–C dihedral angles in Table 5 are greater than 35°, a considerable increase compared to the Cl–Ta–N–C angles in (III) which are *ca.* 15°. Cl · · · C Distances are thus *ca.* 3·4 instead of 3·2 Å as in (III). There is just one small dihedral angle involving adjacent ligands, namely N(4)–Ta–N(1)–C(11) which is −10·9°; allied to a N(4)–Ta–N(1) angle of 77·4(6)° this means a N(4) · · · C(11) contact of 3·06 Å and N(4) · · · H(11) 2·34 Å. However, as the two rings are perpendicular to each other the remaining atoms are kept apart. All Ta–N(*n*)–C(*n*1) angles are between 139 and 145°; strangely it is the Ta–N(1)–C(11) angle which is the smallest of the four at 139·5(12)°.

In seven-co-ordinate polyhedra, it is often found that

TABLE 3

Bond lengths (Å) and angles (°) for (I)

Ta–Cl(1)	2·397(6)	Ta–N(1)	2·160(17)
Ta–Cl(2)	2·430(6)	Ta–N(2)	2·149(19)
Ta–C(5)	2·217(20)	Ta–N(3)	2·040(17)
		Ta–N(4)	2·187(17)
N(1)–C(1)	1·37(3)		
N(2)–C(1)	1·39(3)	N(1)–C(11)	1·49(3)
C(1)–C(2)	1·48(3)	N(2)–C(21)	1·43(3)
N(3)–C(3)	1·40(3)	N(3)–C(31)	1·50(3)
N(4)–C(3)	1·27(3)	N(4)–C(41)	1·53(3)
C(3)–C(4)	1·50(3)		

Cyclohexyl rings	(1)	(2)	(3)	(4)
C(1)–C(2)	1·55(3)	1·51(4)	1·52(3)	1·49(3)
C(2)–C(3)	1·50(4)	1·55(3)	1·54(4)	1·47(3)
C(3)–C(4)	1·49(4)	1·47(4)	1·57(4)	1·47(4)
C(4)–C(5)	1·57(4)	1·57(4)	1·41(4)	1·50(5)
C(5)–C(6)	1·49(3)	1·52(4)	1·65(4)	1·53(4)
C(6)–C(1)	1·49(3)	1·60(3)	1·53(3)	1·50(3)

L–Ta–L angles and L · · · L distances

	Cl(1)	Cl(2)	C(5)	N(1)	N(2)	N(3)	N(4)
Cl(1)		114·6(2)	75·8(6)	136·5(4)	81·6(5)	87·2(5)	132·4(5)
Cl(2)	4·06		79·1(6)	83·9(4)	81·8(5)	157·5(5)	98·4(5)
C(5)	2·84	2·96		147·7(7)	140·7(7)	102·2(7)	78·2(7)
N(1)	4·23	3·08	4·20		61·5(7)	83·7(6)	77·4(6)
N(2)	2·98	3·01	4·11	2·20		108·4(7)	138·7(7)
N(3)	3·07	4·38	3·31	2·80	3·40		60·4(6)
N(4)	4·20	3·50	2·78	2·72	4·06	2·13	

Ta–N(1)–C(1)	95·9(12)	Ta–N(3)–C(3)	98·1(12)
Ta–N(1)–C(11)	139·5(12)	Ta–N(3)–C(31)	143·2(13)
C(1)–N(1)–C(11)	122·2(16)	C(3)–N(3)–C(31)	118·5(17)
Ta–N(2)–C(1)	95·9(13)	Ta–N(4)–C(3)	95·6(13)
Ta–N(2)–C(21)	144·6(16)	Ta–N(4)–C(41)	144·8(14)
C(1)–N(2)–C(21)	119·1(19)	C(3)–N(4)–C(41)	119·6(18)
C(2)–C(1)–N(1)	130·3(19)	C(4)–C(3)–N(3)	123·7(18)
C(2)–C(1)–N(2)	123·4(20)	C(4)–C(3)–N(4)	130·5(19)
N(1)–C(1)–N(2)	106·2(17)	N(3)–C(3)–N(4)	105·8(17)

Cyclohexyl ring	$n = 1$	$n = 2$	$n = 3$	$n = 4$
N(*n*)–C(*n*1)–C(*n*2)	115·5(16)	111·2(18)	110·4(18)	114·1(18)
N(*n*)–C(*n*1)–C(*n*6)	115·9(17)	111·3(19)	105·7(17)	110·0(19)
C(*n*2)–C(*n*1)–C(*n*6)	110·5(17)	110·3(20)	113·5(20)	110·7(19)
C(*n*1)–C(*n*2)–C(*n*3)	110·6(19)	111·7(19)	111·2(20)	114·4(19)
C(*n*2)–C(*n*3)–C(*n*4)	111·9(19)	110·0(20)	108·7(25)	115·9(26)
C(*n*3)–C(*n*4)–C(*n*5)	109·9(20)	112·2(21)	116·1(25)	110·4(22)
C(*n*4)–C(*n*5)–C(*n*6)	109·8(21)	110·5(19)	111·7(23)	112·4(26)
C(*n*5)–C(*n*6)–C(*n*1)	113·0(18)	108·3(21)	105·9(18)	110·7(22)

TABLE 4

Equations of least-squares planes for (I) in the form $Ax + By + Cz = D$, where x,y,z are the crystallographic fractional co-ordinates of the atoms. Distances (Å) of the relevant atoms from each plane are given in square brackets

	A	*B*	*C*	*D*
Plane (1): Ta, N(1), N(2)	−7·49	3·92	10·63	0·94
[C(11) −0·26, C(1) −0·10, C(2) −0·27, C(21) 0·19, H(11) −0·12, H(21) 0·56]				
Plane (2): Ta, N(3), N(4)	3·96	16·73	0·46	2·97
[C(31) 0·11, C(41) −0·01, C(3) −0·02, C(4) −0·03, H(31) 0·61, H(41) 0·55]				
Plane (3): Ta, Cl(1), N(1), N(2), N(4), C(5)	−5·75	2·74	11·72	1·15
[Ta 0·06, Cl(1) −0·62, N(1) 0·01, N(2) 0·35, N(4) −0·47, C(5) 0·67]				

Angle between (1) and (2) 88·9°.

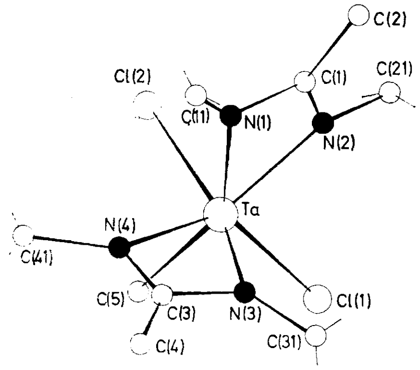

FIGURE 1 The molecule (I); cyclohexyl rings have been omitted for clarity

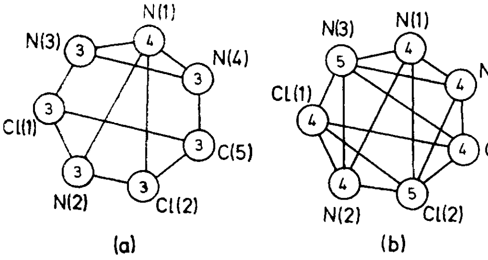

FIGURE 2 The co-ordination polyhedron of (I). Circles correspond to vertices; numbers in circles represent number of edges (represented by lines) in which each vertex participates. Edges are defined as in (a) where L–M–L $\leqslant$90°, and in (b) where L–M–L $\leqslant$115°. (a) is No. 34, C_{2v}, and (b) is No. 5, D_{5h}

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* A PB with two chlorine atoms axial and one methyl group equatorial is found for MeTaCl$_2$[ON(Me)NO]$_2$,[8] but there is little or no steric crowding in this molecule.

[8] M. G. B. Drew and J. D. Wilkins, *J. Organometallic Chem.*, 1974, **69**, 111.

the M–L bond length is dependent upon which site in which polyhedron is occupied by L. The result most often found is that M–L(ax) < M–L(eq) in a PB by *ca.* 0·05 Å. This is considered to be due to the greater crowding in the equatorial sites[2] and/or electronic effects.[9] Of the four Ta–N bonds, Ta–N(3) [2·040(17)] is shorter than the others [2·160(17), 2·149(9), and 2·187(17) Å] and also than the bonds in (III). As already stated, the site of N(3) resembles an axial site in a PB and is less sterically crowded than any of the other nitrogen atoms. The other Ta–N bonds in (I) are equivalent in length to the longer pair of bonds in (III) which were described as being lengthened by steric crowding.[2] The Ta–Cl bond lengths are longer than those found for axial bonds in (III) [2·386(6) and 2·370(6) Å] and in $MeTaCl_2[ON(Me)NO]_2$ [2·359(8), 2·357(10) Å],[8] but slightly shorter than Ta–Cl(eq) in (III) [2·436(6) Å]. The Ta–Cl(1) bond [2·397(6) Å] is shorter than the Ta–Cl(2) bond [2·430(6) Å]. From the PB description of the molecule Cl(2) is axial, but the L–M–L angles show that the distortions from an ideal PB make this site more crowded than that occupied by Cl(1).* The Ta–C(5) bond length [2·217(20) Å] is comparable in length with that [2·248(28) Å] reported in ref. 8.

TABLE 5

Dihedral angles (°)

(*a*) Angles pertaining to close L · · · L contacts *

Cl(1)–Ta–N(2)–C(21)	−35·1	C(5)–Ta–N(4)–C(3)	−111·0
Cl(1)–Ta–N(2)–C(1)	152·2	C(5)–Ta–N(4)–C(41)	67·7
Cl(1)–Ta–N(3)–C(31)	−43·6	N(1)–Ta–N(3)–C(3)	−79·6
Cl(1)–Ta–N(3)–C(3)	143·1	N(1)–Ta–N(3)–C(31)	93·8
Cl(2)–Ta–N(1)–C(11)	−111·0	N(1)–Ta–N(4)–C(3)	90·3
Cl(2)–Ta–N(1)–C(1)	87·8	N(1)–Ta–N(4)–C(41)	−91·0
Cl(2)–Ta–N(2)–C(21)	81·4	N(3)–Ta–N(1)–C(1)	−111·0
Cl(2)–Ta–N(2)–C(1)	−91·3	N(3)–Ta–N(1)–C(11)	50·2
C(5)–Ta–N(3)–C(3)	68·4	N(4)–Ta–N(1)–C(1)	−172·1
C(5)–Ta–N(3)–C(31)	−118·4	N(4)–Ta–N(1)–C(11)	−10·9

(*b*) Other dihedral angles

Ta–N(1)–C(11)–C(12)	134·5	Ta–N(3)–C(31)–C(32)	98·3
Ta–N(1)–C(11)–C(16)	−93·9	Ta–N(3)–C(31)–C(36)	−24·8
Ta–N(1)–C(11)–H(11)	21·0	Ta–N(3)–C(31)–H(31)	−141·8
Ta–N(2)–C(21)–C(22)	−31·0	Ta–N(4)–C(41)–C(42)	26·8
Ta–N(2)–C(21)–C(26)	92·6	Ta–N(4)–C(41)–C(46)	−101·7
Ta–N(2)–C(21)–H(21)	−148·1	Ta–N(4)–C(41)–H(41)	143·1

	(1)	(2)	(3)	(4)
C(5)–C(6)–C(1)–C(2)	−55·4	−57·1	57·0	53·8
C(6)–C(1)–C(2)–C(3)	54·6	57·0	−60·0	−50·3
C(1)–C(2)–C(3)–C(4)	−57·4	−57·4	52·5	48·9
C(2)–C(3)–C(4)–C(5)	57·9	57·0	−53·8	−48·7
C(3)–C(4)–C(5)–C(6)	−56·1	−59·4	55·3	52·4
C(4)–C(5)–C(6)–C(1)	55·8	56·5	−54·4	−56·6

* Restricted to A–Ta–B–C angles where the A–Ta–B angle is <90°.

TABLE 6

Intramolecular contacts <3·75 Å involving non-hydrogen atoms *

Cl(1) · · · C(21)	3·45	C(5) · · · C(3)	3·42
Cl(1) · · · C(22)	3·43	C(5) · · · C(41)	3·60
Cl(1) · · · C(26)	3·58	N(1) · · · C(3)	3·07
Cl(1) · · · C(32)	3·75	C(5) · · · C(46)	3·71
Cl(1) · · · C(31)	3·63	N(1) · · · C(41)	3·75
Cl(1) · · · C(36)	3·53	N(2) · · · C(36)	3·55
Cl(2) · · · C(1)	3·41	N(3) · · · C(11)	3·46
Cl(2) · · · C(22)	3·64	N(4) · · · C(11)	3·06
Cl(2) · · · C(42)	3·60	N(3) · · · C(16)	3·63
N(3) · · · C(1)	3·50		
C(1) · · · C(36)	3·67		
C(3) · · · C(16)	3·58		
C(3) · · · C(11)	3·27		
C(11) · · · C(41)	3·67		

* Distances (*a*) between atoms bonded to the same atom, and (*b*) between atoms in the same bidentate ligand have been omitted.

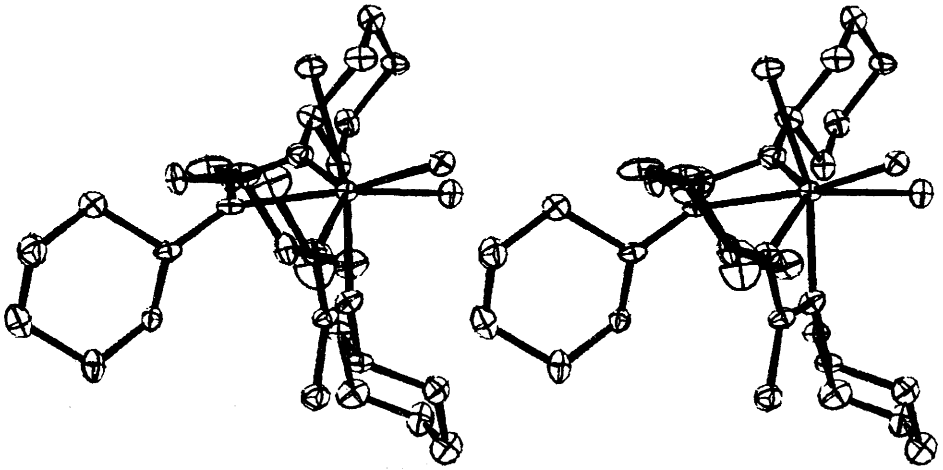

FIGURE 3 Stereopair for (I)

The cyclohexyl C(*n*1) carbon atoms are far nearer to the plane of the four-membered rings than in (III) where the crowding of both ligands into the equatorial plane led to large deviations of *ca.* 0·3 Å. In (I), C(31) and C(41) are 0·11 and −0·01 Å respectively from one plane, and C(11) and C(21) are −0·26 and −0·19 Å from the other. C(11) is the farthest from a plane, no doubt because of the close N(4) · · · C(11) contact. Unlike the situation in (III), the H(*n*1)–C(*n*1) bonds are not rotated such that the Ta–N(*n*)–C(*n*1)–H(*n*1) dihedral angle is close to zero. Again this is true only for C(11) where steric effects are

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* Shortest contacts <4·0 Å are, for Cl(1): C(5) 2·84, N(2) 2·98, and N(3) 3·07 Å; and for Cl(2): C(5) 2·96, N(1) 3·08, N(2) 3·01, and N(4) 3·50 Å.

[9] T. F. Brennan and I. Bernal, *Inorg. Chim. Acta*, 1973, **7**, 283.

greatest. For the others, the C(n2) and C(n6) groups are as close to the plane of the ring as are the H(n1) atoms.

All cyclohexyl rings are in the chair formation with C–C–C–C dihedral angles *ca.* 55°; a slight flattening from the ideal 60°. As in (III) the N–C lengths in the rings are probably equivalent, the mean value of 1·35 Å representing a bond order of 1·5. All C–C bonds and C–C–C angles are close to expected values. Intramolecular contacts $<3·85$ Å are listed in the Supplementary Publication. No value is significantly less than the sum of van der Waals radii. Figure 3 shows the molecular configuration in a stereopair, drawn by use of ORTEP.[10]

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[4/422 *Received, 4th March,* 1974]

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[10] C. K. Johnson, ORTEP, A Fortran Thermal Ellipsoid Plot Program for Crystal Structure Illustrations, Report ORNL 3794, Oak Ridge National Laboratory, 1965.