Crystal and Molecular Structure of 2,2′-Bipyridyldichloro(trimethyl)-tantalum(V)

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Crystals of the title compound are monoclinic, space group $P2_1/m$, a = 7·549(8), b = 12·422(12), c = 8·558(9) Å, β = 109·7(2)°, Z = 2. The structure was solved from diffractometer data by Patterson and Fourier methods, and refined by least squares to R 0·08 for 762 independent reflections. A disordered structure model was refined in space group $P2_1/m$. In each individual molecule, the tantalum atom has a distorted capped trigonal prismatic environment, with one chlorine atom in the unique capping position [2·540(10) Å]; the nitrogen atoms [2·291(21) Å], one chlorine atom, and one methyl group form the capped quadrilateral face with two methyl groups [2·24(4) and 2·16(6) Å] occupying the remaining edge. The molecule was refined with imposed m symmetry, so that the two sites in the quadrilateral face occupied by a chlorine atom and a methyl group were given equivalent mean scattering factors. The choice of geometry for this seven-co-ordinate (with five unidentate ligands) complex has been rationalised by considering the ligand–ligand repulsions and the constraints imposed by the bidentate 2,2′-bipyridyl ligand.

DURING studies of the co-ordination chemistry of compounds of the type $\mathrm{Me}_n\mathrm{MCl}_{5-n}$ (n = 1—3; M = Nb or Ta), several complexes with bidentate ligands have been prepared and, on the basis of molecular-weight and conductivity measurements, have been assigned seven-co-ordinate structures.[1-3] As confirmation we have determined and report here the crystal and molecular structure of one of these compounds $\mathrm{Me_3TaCl_2(bipy)}$ (I) (bipy = 2,2′-bipyridyl). This crystal structure of a primarily unidentate seven-co-ordinate complex also provides further information in our studies[4-10] of the geometry of seven-co-ordinate polyhedra.

EXPERIMENTAL

2,2′-Bipyridyl (0·005 mol) in toluene (20 cm^3) was added to $\mathrm{Me_3TaCl_2}$ in pentane (25 cm^3), prepared from $\mathrm{TaCl_5}$ (0·01 mol) by the reported method.[2] The pale yellow solid was washed with pentane and pumped dry. A sample (0·5 g) was crystallised from dichloromethane (30 cm^3) by a slow evaporation of solvent (4 h).

Crystal Data.—$\mathrm{C_{13}H_{17}Cl_2N_2Ta}$, M = 453·5, Monoclinic, a = 7·549(8), b = 12·422(12), c = 8·558(9) Å, β = 109·7(2)°, U = 755·3 Å^3, D_c = 2·00, Z = 2, D_m = 2·02, $F(000)$ = 432. Space group $P2_1$ or $P2_1/m$ from systematic absences: $0k0$, $k = 2n + 1$. Mo-K_α radiation, λ = 0·7107 Å; μ(Mo-K_α) = 82·9 cm^{-1}.

In our original examination of this compound, we found that the crystals decomposed slowly over several days and that the rate of deterioration was accelerated by exposure to X-rays. After several attempts at obtaining a set of data had failed owing to crystal decomposition, the following procedure was adopted.

A crystal ca. 0·1 × 0·15 × 0·1 mm was chosen, from a freshly prepared sample and immediately sealed in a thin-walled Lindemann tube and mounted with the $(20\bar{1})$ planes perpendicular to the instrument axis of a General Electric XRD 5 apparatus, equipped with a manual goniostat, scintillation counter, and pulse-height discriminator. Zirconium-filtered molybdenum radiation was used. 1036 Independent reflections ($2\theta < 45°$) were then measured speedily by the stationary-crystal–stationary-counter method with a counting time of 10 s. During data collection, the intensities of standard reflections were measured at 30 min intervals. Plots showed that the intensity of these peaks were decreasing approximately linearly with time but at a rate independent of χ, ϕ, and 2θ. A linear isotropic factor was derived where the intensity of the nth reflection was multiplied by $(1 + 0{\cdot}5{*}n/1036)$. The final measurement of the standard reflections were ca. 0·66 of their original value. The standard deviation $\sigma(I)$ of the reflections was taken to be $[I + 2E + (0{\cdot}03I)^2]^{\frac{1}{2}}$, where I is the intensity and E the background. 762 Reflections with $I > 2\sigma(I)$ were used in the subsequent calculations. Neither absorption nor extinction corrections were applied.

Structure Determination.—The structure was determined from Patterson and Fourier syntheses 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 $\sin\theta/\lambda$, was $\sqrt{w} = 1$ for $F_o < 67$ and $\sqrt{w} = 67/F_o$ for $F_o > 67$. Calculations were made on an ATLAS computer at S.R.C. Chilton, Berkshire, with the program described in ref. 11. Atomic scattering factors for tantalum, chlorine, nitrogen, and carbon were taken from ref. 12 as were the corrections for the real and imaginary part of the anomalous dispersion for tantalum and chlorine. The anisotropic thermal parameter is defined as $\exp\,(-\,2\pi^2 \sum_i \sum_j U_{ij}h_ih_j;\ i,j = 1\text{—}3)$, and the isotropic thermal parameters as $\exp\,(-\,8\pi^2 U \sin^2\theta/\lambda^2)$.

The structure was first refined in space group $P2_1/m$ in which the molecule has imposed m symmetry with the tantalum atom, one chlorine atom, and two carbon atoms in

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[1] G. W. A. Fowles, D. A. Rice, and J. D. Wilkins, *J.C.S. Dalton*, 1972, 2313.

[2] G. W. A. Fowles, D. A. Rice, and J. D. Wilkins, *J.C.S. Dalton*, 1973, 961.

[3] G. W. A. Fowles, D. A. Rice, and J. D. Wilkins, to be published.

[4] M. G. B. Drew, J. D. Wilkins, and A. P. Wolters, *Chem. Comm.*, 1972, 1278.

[5] M. G. B. Drew and A. P. Wolters, *Chem. Comm.*, 1972, 457.

[6] M. G. B. Drew and J. D. Wilkins, to be published.

[7] M. G. B. Drew and R. Mandzczewsky, *Chem. Comm.*, 1970, 292.

[8] M. G. B. Drew, A. P. Wolters, and I. B. Tomkins, to be published.

[9] M. G. B. Drew, *J.C.S. Dalton*, 1972, 626.

[10] M. G. B. Drew, *J.C.S. Dalton*, 1972, 1329.

[11] 'X-Ray '67 ' system of programs, J. M. Stewart, University of Maryland Technical Report, 67 58 1967, revised July 1970.

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

special positions on the mirror planes ($y = 1/4, 3/4$) with the bipyridyl group straddling the mirror plane (*i.e.* the nitrogen and five carbon atoms in general positions). This leaves one chlorine atom and one methyl group unaccounted for. In a Fourier map, a peak was observed in a general position with a height approximately equivalent to the means of those of a chlorine and of a carbon atom.[‡] This atom, X, was given a scattering factor f_X which was equivalent to $\frac{1}{2}(f_{Cl} + f_C)$ and included in the refinement. We refined tantalum and chlorine with anisotropic and X, nitrogen and carbon with isotropic parameters to R 0·095. The decomposition factor was then applied to the observed data and further refinement gave R 0·082. The final positional co-ordinates and thermal parameters from this refinement are given in Table 1 and the dimensions of the molecule in Table 2. The molecular configuration is shown in Figure 1. For this model, the 274 zero reflections showed no serious discrepancies. A difference-Fourier map showed two peaks *ca.* 1 Å from the tantalum atom with a height of 1/2 a carbon atom, but no other peaks of any significance. In the final cycle of refinement, no shift was $>0{\cdot}040\sigma$. Final observed and calculated structure factors are listed in Supplementary Publication No. SUP 20741 (4 pp., 1 microfiche).[§]

TABLE 1

Final positional co-ordinates ($\times 10^4$), and thermal parameters ($\times 10^3$), with estimated standard deviations in parentheses

	x	y	z	U/Å^2
Ta	1272(3)	2500	1415(2)	*
Cl(1)	1731(13)	2500	4496(11)	*
X	−0311(18)	4120(10)	1572(16)	67(3)
N(1)	3911(29)	3534(18)	2541(26)	51(6)
C(1)	3927(40)	4667(25)	2252(37)	61(8)
C(2)	5439(44)	5272(25)	3049(39)	68(9)
C(3)	7068(42)	4834(25)	4036(37)	62(8)
C(4)	7080(41)	3683(25)	4252(36)	60(8)
C(5)	5477(35)	3110(21)	3477(31)	46(6)
C(6)	−1020(65)	2500	−1057(57)	71(13)
C(7)	2652(71)	2500	−0417(65)	83(15)

* Anisotropic thermal parameters ($\times 10^3$):

	U_{11}	U_{22}	U_{33}	U_{13}
Ta	57(1)	44(1)	39(1)	18(1)
Cl(1)	60(6)	36(5)	41(5)	18(5)

TABLE 2

Molecular dimensions (distances, Å; angles, °) *

Ta–Cl(1)	2·540(10)	Cl(1)–Ta–X	80·5(3)	3·17 †
Ta–X	2·367(14)	Cl(1)–Ta–N(1)	76·7(6)	3·00
Ta–N(1)	2·291(21)	Cl(1)–Ta–C(6)	140·6(15)	4·50
Ta–C(6)	2·24(4)	Cl(1)–Ta–C(7)	145·6(12)	4·49
Ta–C(7)	2·16(6)	C(6)–Ta–C(7)	73·8(19)	2·64
N(1)–C(1)	1·43(4)	C(6)–Ta–X	79·0(8)	2·93
N(1)–C(5)	1·30(3)	C(6)–Ta–N(1)	133·1(11)	4·15
C(1)–C(2)	1·34(4)	C(7)–Ta–X	114·7(5)	3·81
C(2)–C(3)	1·35(4)	C(7)–Ta–N(1)	75·0(12)	2·71
C(3)–C(4)	1·44(4)	N(1)–Ta–N(1^{I})	68·2(8)	2·57
C(4)–C(5)	1·37(4)	X–Ta–X^{I}	116·4(5)	4·02
C(5)–C(5^{I})	1·52(4)	N(1)–Ta–X	83·3(6)	3·10
		N(1)–Ta–X^{I}	146·8(6)	4·46

Ta–N(1)–C(1)	122·4(15)	C(3)–C(4)–C(5)	119·2(24)
Ta–N(1)–C(5)	121·0(18)	C(4)–C(5)–N(1)	124·2(26)
C(1)–N(1)–C(5)	116·6(22)	C(4)–C(5)–C(5^{I})	121·4(23)
N(1)–C(1)–C(2)	121·3(25)	N(1)–C(5)–C(5^{I})	114·0(21)
C(1)–C(2)–C(3)	121·9(30)		
C(2)–C(3)–C(4)	116·5(27)		

* Roman numeral I as superscript refers to an atom in position $x, \frac{1}{2} - y, z$ relative to the reference co-ordinates at x, y, z. † Non-bonded distances in the co-ordination sphere appropriate to the adjacent listed angle.

This refined structure model does not represent the contents of an individual unit cell. We conclude from the successful refinement that individual unit cells are ordered in space group $P2_1$ with a fraction x of them ($0 \leqslant x \leqslant 1$) having the chlorine atom on the positive side of the $y = \frac{1}{4}$ mirror plane and a methyl group on the negative side [structure (A)] with the remaining unit cells ($1 - x$ of them) having the reverse arrangement [structure (B)]. The refinement in space group $P2_1/m$ gives no indication as to the value of x.

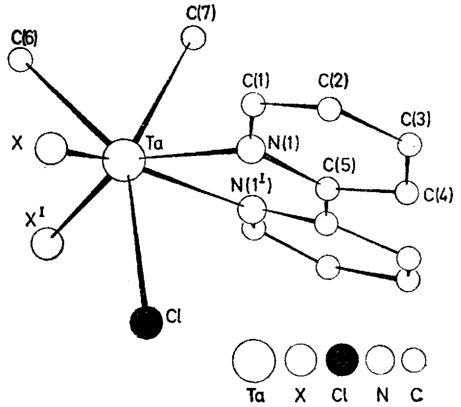

FIGURE 1 The structure of (I)

Whatever the value of x, the structure model has a surprising feature. It is to be expected that the positions of the remaining atoms in the molecule would be different in structures (A) and (B), owing to variations between Cl $\cdots$ L and Me $\cdots$ L repulsions (L = ligand), and therefore that the refined positions of all atoms would be the mean of the two positions in structures (A) and (B). It is considered reasonable[13] that ligand–ligand contacts are slightly less than the sum of van der Waals radii. The radii of the chlorine atom and the methyl groups are usually taken as 1·8 and 2·0 Å.[14] However the positions of the hydrogen atoms make this value for the methyl group sensitive to direction. For example, in (I), C $\cdots$ C contacts of 2·64 Å are found, an acceptably short value only if we consider the hydrogen atoms to be mutually staggered. Cl $\cdots$ Cl contacts of 2·95 and 3·05 Å are found in $WOCl_4$-(diars) [diars = *o*-phenylenebis(dimethylarsine)],[7] but the more usual values are of the order of 3·4 Å.[8,15]

We attempted to locate the two positions for each atom in several ways. First, all atoms were refined anisotropically in space group $P2_1/m$ and R was reduced to

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[‡] The CH_3/Cl type of disorder has been found in other structures, *e.g.* 2-amino-6-chloro-4-methylpyrimidine (C. J. B. Clews and W. Cochran, *Acta Cryst.*, 1948, **1**, 4).

[§] For details see Notice to Authors No. 7 in *J.C.S. Dalton*, 1972, Index issue. (Items less than 10 pp. are sent as full sized copies.)

[13] V. W. Day and J. L. Hoard, *J. Amer. Chem. Soc.*, 1970, **92**, 3626.

[14] L. Pauling, 'The Nature of the Chemical Bond,' Cornell University Press, 3rd edn., Ithaca, New York, 1960.

[15] A. Mawby and G. E. Pringle, *J. Inorg. Nuclear Chem.*, 1972, **34**, 517.

0·080, a decrease which, in view of the increased number of parameters, did not appear significant. The anisotropic thermal parameters for all atoms except the two methyl groups on the mirror planes were approximately spherical. Those of the two methyl groups could be interpreted as indicating two disordered positions slightly off the mirror planes but attempts to prove this through refinement were unsuccessful, presumably because of the small increments involved. Although each pyridine ring was planar, the planes of the two pyridine rings intersected each other at 14·9°. This is most unusual * [*cf.* 5·0° in $Mo(CO)_3(bipy)(pyridine)$,[16] 4·7° in $Mo(CO)_3(bipy)Cl(SnMeCl_2)$,[17] and 3·1° in $W(CO)_3(bipy)Br(GeBr_3)$ [18]]. The size of this angle indicated that there might be two possible positions of a planar bipy group but this would mean (*inter alia*) two C(2) positions 0·85 Å apart, a splitting of peaks which would have shown up on a difference-Fourier map, which showed no alternative ring-atom positions.

We are therefore forced to conclude that the bipy group is significantly non-planar in each individual molecule, that the two positions for each atom in structures (A) and (B) are very close, and therefore that the orientation of the hydrogen atoms in the methyl group is such that the effect of the methyl group and the chlorine atom in fixing the molecular configuration and on intermolecular packing are very similar.

As a final check on the validity of this structure model, we refined atom X as an ordered chlorine atom and alternatively as an ordered carbon atom. The two refinements led to thermal parameters of U 0·121 Å^2 for chlorine and $-0·004$ Å^2 for carbon and no change in R. In the original refinement, X had a thermal parameter of U 0·058 Å^2 which was far more comparable with those of other atoms in the molecule. The Ta–X bond length was intermediate between the other Ta–C and Ta–Cl bond lengths in the molecule. This confirms that (I) is $Me_3TaCl_2(bipy)$.

We were unable to ascertain the value of x. We attempted refinements for $x = 0·0$ and $1·0$ which represent ordered structures in space group $P2_1$ but even taking into account the considerable anomalous dispersion of the tantalum atom, no model refined to $R < 0·080$ with reasonable dimensions. This was not surprising in view of the high correlation between parameters caused by such a large percentage of the scattering being compatible with a mirror plane.

DISCUSSION

It has often been observed [19] that the energy differences between the three basic polyhedra [(1 : 5 : 1) pentagonal bipyramidal (PB), D_{5h}; (1 : 3 : 3) capped octahedral (CO), C_{3v} and (1 : 4 : 2) capped trigonal prismatic (CTP), C_{2v}] in seven-co-ordinate molecules are very low. It is however noticeable that the majority of such molecules do have geometries which are very close to one of these three types and that any distortions from the ideal polyhedra can be related to variations in the ligands.[9,20] The choice of polyhedron for a given complex is dictated by a variety of factors including symmetry, ligand–ligand repulsions, the steric constraints of multidentate ligands, the electronic structure of the metal and crystal packing energies. There is not enough structural data available for these last two factors to be understood. However, the first three factors can be used to predict the stability and geometry of a complex of known stoicheiometry.† The geometry of (I) is best described as a distorted capped trigonal prism with a chlorine atom in the unique capping position, two nitrogen atoms, one chlorine atom and one methyl group making up the capped quadrilateral face, and two methyl groups in the remaining edge.

Could this geometry have been predicted from the molecular formula? Four factors seem important. First, the geometry of (I) could correspond to its stoicheiometry, $MX_3Y_2Z_2$. Such correspondence is often found in seven-co-ordinate complexes, *e.g.* $[W(CO)_4Br_3]^-$,[5] $MoBr_4(PMe_2Ph)_3$,[4] and aquotris-(1-phenylbutane-1,3-dionato)yttrium [21] have CO symmetry, $[UO_2F_5]^{3-}$ has PB symmetry,[22] and $[Mo(diars)_2(CO)_2Cl]^+$ (ref. 6) and $[Mo(CNR)_6I]^+$ (ref. 23) have CTP symmetry. Secondly, the bite of the bidentate ligand (72, ref. 18, and 72·6°, ref. 16) must fit a polyhedron edge. Thirdly, the bulk of the pyridine rings ensure that no other ligands will be coplanar with them. Fourthly, one would expect ligand–ligand repulsions to be minimised. These are not well understood, even for equivalent ligands in an ML_7 molecule,[24] but from a study of L ··· L distances in other seven-co-ordinate molecules,[5,9,10,17,18] in conjunction with van der Waals' radii, we conclude that although C ··· C, C ··· N, and N ··· N repulsions are such as to allow these pairs of atoms to occupy any bite of any polyhedron,‡ this is not the case for the Cl ··· Cl repulsions § and Cl ··· Cl contacts of *ca.* 3·4 Å are required (*cf.* 3·46, ref. 8, and 3·39 Å, ref. 15, corresponding to Cl–M–Cl angles of 86·7 and 84·4°). It is, therefore, probable that in (I), as in any other monomeric complex of ML_5X_2 stoicheiometry (X = halogen, L = smaller ligand), the two halogen atoms will occupy the

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* However, in the crowded octahedral molecule $Cu(bipy)_3$ (O. P. Anderson, *J.C.S. Dalton*, 1972, 2597), angles between pyridine rings are 13·6, 11·2, and 31·3° for the three bipy groups.

† Because of the similarity between the three basic polyhedra a ligand, occupying a site in a polyhedron for which it is unsuited, will cause distortions to occur in order to accommodate it, thus changing the polyhedron to another of the three.

‡ A bite is usually defined by L ··· L distance along a polyhedron edge. However it is often helpful to quote the L–M–L angle, which is related to the bite *via* the M–L bond length. It is logical to assume the most stable geometry of a seven-co-ordinate complex to be that which allows as many M–L bonds as possible to be comparable in length to similar bonds in six-co-ordinate molecules. Thus C ··· C, C ··· N, and N ··· N distances of *ca.* 2·50 Å can be equated with angles of 70°, assuming M–L 2·10 Å.

§ There is not much data on C ··· Cl and N ··· Cl contacts, but it is probable that they would fit bites intermediate between those suitable for C ··· C and Cl ··· Cl contacts.

[16] A. Griffiths, *J. Cryst. Mol. Structure*, 1971, **1**, 75.

[17] M. Elder and D. Hall, *Inorg. Chem.*, 1969, **8**, 1268.

[18] E. M. Cradwick and D. Hall, *J. Organometallic Chem.*, 1970, **25**, 91.

[19] E. L. Muetterties and C. M. Wright, *Quart. Rev. Chem. Soc.*, 1967, **21**, 109.

[20] R. B. Van Dreele, J. J. Stezowski, and R. C. Fay, *J. Amer. Chem. Soc.*, 1971, **93**, 2887.

[21] F. A. Cotton and P. Legzdins, *Inorg. Chem.*, 1968, **7**, 1777.

[22] W. H. Zachariasen, *Acta Cryst.*, 1954, **7**, 783.

[23] D. F. Lewis and S. J. Lippard, *Inorg. Chem.*, 1972, **11**, 621.

[24] H. B. Thompson and L. S. Bartell, *Inorg. Chem.*, 1968, **7**, 488.

two least-crowded sites in a polyhedron with the other atoms [in (I), nitrogen and carbon] occupying the more crowded sites. In Figure 2, the three polyhedra are shown, together with the most likely sites for chlorine atoms in a ML_5Cl_2 molecule.

In PB symmetry, these two sites (marked A,A in Figure 2) are mutually *trans* (the axial positions), while in the other two polyhedra, they are mutually *cis*. For (I), there seems no reason why either arrangement of chlorine atoms is to be preferred. This is not always the case, since molecules containing π-accepting ligands[8,9,10,15] (carbonyl groups, phosphorus, and arsenic atoms) have these mutually *cis* so as to avoid competition for the metal electrons. Such an arrangement naturally leads to mutually *cis* halogen atoms.

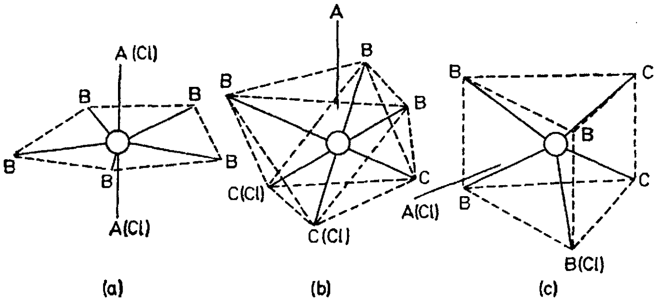

FIGURE 2 The three ideal polyhedra for seven-co-ordinate complexes. Probable positions for two halogen atoms in ML_5X_2 complexes (X = halogen, L = smaller ligand) are shown for each polyhedron. (a) Pentagonal bipyramid, D_{5h}, mean angles: B–M–B 72, A–M–B 90°; (b) capped octahedron, C_{3v}, mean angles:[5] A–M–B 74, B–M–C(*cis*) 80, C–M–C 90°; and (c) capped trigonal prism, C_{2v}, mean angles:[23] A–M–B 81·5, C–M–C 70, B–M–C(*cis*) 75, B–M–B(*cis*) 85·5, 90° (only angles $\leqslant 90°$ are listed)

It is also possible that the geometry of a particular complex can be related to that of its precursor. This is not the case for (I) as Me_3TaCl_2 is the precursor of both (I) and $MeTaCl_2(MeN_2O_2)_2$. This latter molecule has a PB structure with chlorine atoms in the axial positions.[25]

The PB geometry is not possible for (I) as the bulk of the bipy group cannot fit into the equatorial plane without giving unreasonable repulsions to neighbouring atoms.* In general, it is unlikely that the bipy group would occupy any bite which necessitated dihedral angles L–M–N(1)–C(1) being close to zero. This leaves the CO and the CTP as possible geometries for (I). In the CO arrangement, the chlorine atoms would occupy two sites (marked C,C in Figure 2) in the uncapped face, where the L–M–L angles are *ca.* 90°. Such an arrangement is often found[9,10] for the larger halogens, bromine and iodine. In a CTP structure, one of the chlorine atoms would occupy the unique capping position (A) and the other, one of the positions in the capped quadrilateral face (B). The bite between these two sites is 81·5° in $[Mo(CNR)_6I]^+$.[23] In $MoCl_2(CO)_2(dpm)_2$[8] [dpm = bis(diphenylphosphino)methane] and in $MoCl_2(CO)_2(PMe_2Ph)_3$,[15] Cl–Mo–Cl angles are intermediate between 90 and 81·5, being 86·7 and 84·4°, and indeed the geometry of these molecules is intermediate between that for CO and CTP. From models (and a study of the angles listed in Figure 2), it would appear that the remaining five atoms in (I) would fit into both polyhedra without any unlikely close contacts. In the CO arrangement, the bipy group would occupy a bite between sites B and C (ideal angle 80°). This would leave one methyl group in the unique capping position (A) and two in B sites. In the CTP arrangement, the bipy group would occupy a bite in the capped quadrilateral face (ideal angles 85 and 90°) and the polyhedron would be completed by one methyl group in site B and two in sites C. In both geometries, the bites occupied by the bipy groups lead to L–M–N(1)–C(1) dihedral angles which are significantly non-zero.

This analysis of the factors involved in the fixing of the geometry of (I) has led to two possible structures, one of which, the CTP, is found to be correct from the *X*-ray analysis. One possible reason for this is that, while both configurations have no symmetry, CTP approximates to *m* symmetry such that the refined structure model (representing the statistical average) has *m* symmetry and thus one of the factors involved in deciding this geometry may be the crystal-packing energy. It is possible, of course, that the disorder is masking a particular molecular dimension which would provide a further clue to the factors involved.

The dimensions of the structure model must be treated with caution (see earlier). The Ta–Cl bond length is similar to those obtained for Mo–Cl distances in similar sites in seven-co-ordinate structures, *i.e.* 2·575 Å,[6] 2·486,[15] and 2·484 Å.[8] The two ordered methyl groups give Ta–C bond lengths of 2·24(4) and 2·16(6) Å which are comparable with a mean value of 2·20 Å for the W–C bond length[26] in the eight-co-ordinate $Me_4W(MeN_2O_2)_2$ and 2·16 Å for $Nb–CH_2$ in the $[Nb(CSiMe_3)(CH_2SiMe_3)_2]_2$ dimer.[27]

In the quadrilateral face, two of the sites are disordered between a chlorine atom and a methyl group, the refined Ta–X bond distance being 2·367(14) Å. For the two ordered sites, the N–Ta–N angle is 68·2(8)° (N · · · N 2·57 Å). The angle is comparable with that found for bipy in other molecules.[16-18] However, the bite is considerably less than is usually found in a capped trigonal prism [90° in $Mo(CNR)_6I$[23]]. The space made available in the capped quadrilateral face is occupied by an expansion of the X–Ta–X′ angle to 116·4(5)° not by an expansion of the X–Ta–N angles (83·3(6)°] which are equivalent to those reported in ref. 23. Following this variation in the *cis*-angles, the *trans*-angles in the face

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* In the PB molecule, $Mn(NO_3)_3(bipy)$ (F. W. B. Einstein, D. W. Johnson, and D. Sutton, *Canad. J. Chem.*, 1972, **50**, 3332), the bipy group occupies an axial and one equatorial site. Such an arrangement is acceptable owing to the smaller size of the remaining ligands, compared with those in (I).

[25] M. G. B. Drew and J. D. Wilkins, unpublished work.

[26] S. R. Fletcher, A. Shortland, A. C. Skapski, and G. Wilkinson, *J.C.S Chem. Comm.*, 1972, 922.

[27] F. Huq, W. Mowat, A. C. Skapski, and G. Wilkinson, *Chem. Comm.*, 1971, 1477.

are 146·8(6), less than the ideal 163·0.[23] The Ta–N bond length [2·29(2) Å] is slightly longer than those reported (2·20, 2·21 Å) for W–N.[18] In addition to these variations, the C(6)–Ta–N angle at 133·1(11)° and the C(7)–Ta–X angle at 114·7(5)° are respectively 13° greater and 5° less than similar angles reported in ref. 23, in accord with the shifts in position contained in the quadrilateral face. The remaining angles in (I) are similar to those found in the ideal geometry.

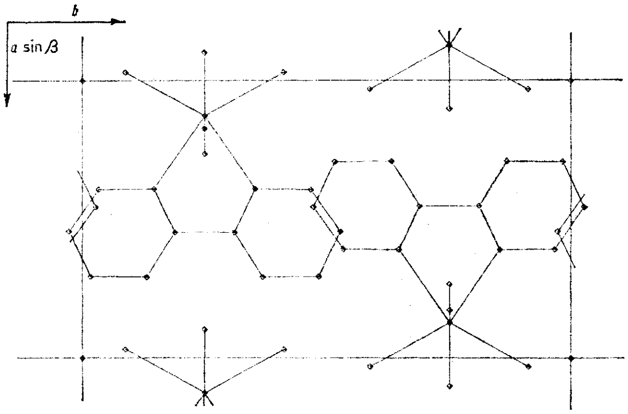

FIGURE 3 The unit cell of (I) in the *c* projection

It is possible that the bend in the bipy group (the two pyridine rings intersect at 14·9°) is due to the need to increase the X–Ta–N(1)–C(1) dihedral angle and hence the X ··· C(1) and X ··· H(1) distances, particularly when X is Cl. In fact, the X ··· Cl(1) contact is only 3·17 Å, presumably the Cl ··· Cl(1) contact is greater than this and the Me ··· Cl(1) contact is less.

The packing diagram for (I) is shown in Figure 3, which is the *c* projection. There are no abnormally short contacts, a C ··· C contact of 3·45 and a C ··· Cl(1) contact of 3·57 Å being the minimum values.

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