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THE REACTION OF METHYLNIOBIUM(V) AND METHYLTANTALUM(V) CHLORIDES WITH NITROGEN OXIDE AND THE CRYSTAL AND MOLECULAR STRUCTURE OF ONE OF THE PRODUCTS, METHYLDICHLOROBIS-(*N*-METHYL-*N*-NITROSOHYDROXYLAMINATO) TANTALUM(V)

JOHN D. WILKINS*
Donnan Laboratories, University of Liverpool, Grove Street, P.O. Box 147, Liverpool L69 3BX (Great Britain)
MICHAEL G.B. DREW
Department of Chemistry, The University, Whiteknights, Reading RG6 2AD (Great Britain)
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Summary

The reaction of NO with Me_2MCl_3 and Me_3MCl_2 (M = Nb, Ta) yields complexes $MCl_3[ON(Me)NO]_2$ and $MeMCl_2[ON(Me)NO]_2$ respectively. The complexes have been characterised by measurements of IR and NMR spectra; the reactivity of the methyl group in the complex $MeTaCl_2[ON(Me)NO]_2$ is discussed. Crystals of this compound are monoclinic, spacegroup $P2_1/n$ with $a = 9.78(1)$, $b = 15.10(1)$, $c = 7.74(1)$ Å, $\beta = 97.18(6)°$, $Z = 4$. 1336 independent intensities were measured by counter methods and the structure refined to R 0.087. The co-ordination sphere of the tantalum atom is a slightly distorted pentagonal bipyramid with two chlorine atoms in axial positions [2.359(8), 2.357(10) Å]; four oxygens [2.090(17), 2.081(21), 2.108(18), 2.066(26) Å] and one methyl group [2.248(28) Å] in the pentagonal girdle.

Introduction

Insertion of nitrogen oxide into early transition metal—carbon bonds has been reported for Cp_2ZrMe_2 [1] (Cp = cyclopentadienyl) and WMe_6 [2,3]; the product of the latter reaction has been characterised by an X-ray study as $WMe_4[ON(Me)NO)]_2$ [3]. In each case the products arise from reaction of 2 moles of NO with each MCH_3 group. As part of a study of methylniobium(V) and methyltantalum(V) chlorides we have treated them with NO and the structure of the product derived from Me_3TaCl_2 has been established by a single

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* Present address: Christopher Ingold Laboratories, University College, 20 Gordon St, London WC1H OAJ.

crystal study, which we report here, as the seven-co-ordinate monomer methyldichlorobis (*N*-methyl-*N*-nitrosohydroxylamino)tantalum(V), (I). This complex is one of a series of seven-co-ordinate molecules whose structures we have been studying [4] to determine the factors involved in the choice of polyhedron between the three ideal types (capped octahedron, C_{3v}, capped trigonal prism, C_{2v}, and pentagonal bipyramid, D_{5h}).

Experimental

(a) Synthesis

All reactions were carried out in vacuo or under an atmosphere of dry oxygen-free nitrogen. Solutions of the alkyls Me_2NbCl_3, Me_3NbCl_2 and Me_3TaCl_2 in pentane were prepared by the literature methods [5,6]. Nitrogen oxide (Matheson) was purified by passage through concentrated sulphuric acid. Solvents were dried with potassium or phosphorus(V) oxide; methanol was dried with 3A molecular sieves. Analyses were carried out as previously described [5].

IR spectra were recorded using Perkin—Elmer 457 or 577 instruments; NMR spectra were recorded using a Perkin—Elmer R12B spectrometer. The complexes prepared together with appropriate analytical data are listed in Table 1.

Reactions of Me_2NbCl_3, Me_3NbCl_2 and Me_3TaCl_2 with NO. A solution of the alkyl (0.01 mole) in pentane (30 ml) was cooled to —80° in vacuo and then allowed to warm up to room temperature in an atmosphere of NO. The solid product was isolated by filtration, washed with pentane and pumped dry. The complex $MeTaCl_2[ON(Me)NO]_2$ was crystallised from a mixture of dichloromethane (80%) and 2,2,4-trimethylpentane (20%) by slow evaporation of the solvent mixture.

Reaction of Me_2TaCl_3 with NO. $TaCl_5$ (0.01 mole) was allowed to react with Me_2Zn (0.0105 mole) in CCl_4 (30 ml) for 12 h at room temperature. The precipitated zinc chloride was removed by filtration and the resulting solution reacted with NO as above.

Preparation of $TaCl_2(OMe)[ON(Me)NO]_2$. $MeTaCl_2[ON(Me)NO]_2$ (0.01 mole) was allowed to react with MeOH (0.01 mole) in CH_2Cl_2 (30 ml) for 3 h at room temperature. The solvent was removed in vacuo, the residual white solid washed with pentane and pumped dry.

TABLE 1

COMPLEXES PREPARED

Complex	Colour	Found(%)		Calcd. (%)	
		Cl	M	Cl	M
$NbCl_3[ON(Me)NO]_2$	Orange	30.6	27.2	30.5	26.6
$MeNbCl_2[ON(Me)NO]_2$	Vermillion	21.3	28.7	21.6	28.3
$TaCl_3[ON(Me)NO]_2$	White	24.0	41.1	24.3	41.4
$MeTaCl_2[ON(Me)NO]_2$	Yellow	17.2	43.2	17.0	43.4
$TaCl_2(OMe)[ON(Me)NO]_2$	White	16.7	42.1	16.4	41.9

(b) Single crystal X-ray study

Crystal data. $C_3H_9N_4Cl_2TaO_4$, $M = 416.9$, $a = 9.78(1)$, $b = 15.10(1)$, $c = 7.74(1)$ Å, $\beta = 97.18(6)°$, $U = 1134.1$ Å^3, $D_m = 2.37$, $D_c = 2.44$, $F(000) = 788$, Mo—K_α radiation, $\lambda = 0.7107$ Å, $\mu = 108.1$ cm^{-1}, spacegroup $P2_1/n$ from the systematic absences $h0l$, $h + l = 2n + 1$, and $0k0$, $k = 2n + 1$. A General Electric XRD 5 apparatus, equipped with a manual goniostat, scintillation counter and pulse-height discriminator, was used in the experiment with zirconium-filtered X-radiation. Crystals were sealed in thin walled capillaries under nitrogen. Even so, they rapidly decomposed in X-rays and three crystals were required to measure the intensities of the 2008 independent reflections with $2\theta < 50°$. Each crystal was used to measure about 1/3 of the data by which time the standard intensities had dropped to 75% of the original value. The crystals which were of approximately equal size (0.25 × 0.10 × 0.25 mm) were all mounted with the a^* axis parallel to the instrument axis.

In the intensity measurement, the stationary-crystal—stationary-counter method was used with 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. The standard deviation $\sigma(I)$ of the reflections was taken to be $[I + 2E + (0.03I^2)]^{½}$ where E is the estimated background of the reflection. 1336 reflections with $I > 2\sigma(I)$ were used in subsequent calculations. A linear correction factor was applied to each reflection to account for the crystal decay. An absorption correction was applied using the program given in ref. 7. Transmission factors varied between 0.55 and 0.14.

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 $F_o < 25$ and $\sqrt{w} = 25/F_o$ for $F_o > 25$. Calculations were made on a 1906 A computer at S.R.C. Chilton, Berkshire with the programs described in ref. 7. Atomic scattering factors for tantalum, chlorine, oxygen, nitrogen and carbon were taken from ref. 8 as were the corrections for the real and imaginary part of the anomalous dispersion for

TABLE 2

ATOMIC CO-ORDINATES[a] WITH ESTIMATED STANDARD DEVIATIONS IN PARENTHESES

Atom	x	y	z
Ta	23679(11)	16248(5)	03833(14)
Cl(1)	0812(7)	0723(5)	1684(11)
Cl(2)	3906(10)	2520(5)	−0956(13)
O(1A)	2805(17)	2287(9)	2760(23)
O(2A)	1131(20)	2743(13)	0432(30)
N(1A)	2186(27)	3011(16)	3061(34)
N(2A)	1254(31)	3300(12)	1723(37)
C(1A)	2432(32)	3393(18)	4518(40)
O(1B)	2827(21)	0562(10)	−1212(24)
O(2B)	1037(27)	1628(12)	−1910(35)
N(1B)	2013(21)	0509(12)	−2756(29)
N(2B)	1145(32)	1093(15)	−3092(33)
C(1B)	2254(40)	−0180(22)	−3956(59)
C(2)	4189(29)	0883(19)	1730(42)

[a] × 10^5 for Ta, × 10^4 for other atoms.

TABLE 3

ANISOTROPIC THERMAL PARAMETERS (X 10^3) WITH STANDARD DEVIATIONS IN PARENTHESES

Atom	U_{11}	U_{22}	U_{33}	U_{12}	U_{13}	U_{23}
Ta	525(7)	325(6)	477(7)	065(4)	095(6)	—074(4)
Cl(1)	58(4)	59(4)	—07(3)	−69(3)	14(4)	—04(3)
Cl(2)	97(6)	54(4)	89(6)	05(4)	44(5)	06(4)
O(1A)	57(10)	30(7)	60(11)	—01(7)	10(8)	—02(7)
O(2A)	62(12)	75(12)	89(15)	08(10)	—08(12)	09(12)
N(1A)	82(17)	61(14)	67(16)	−38(14)	05(15)	22(13)
N(2A)	110(21)	33(11)	76(17)	11(12)	33(16)	—18(11)
C(1A)	78(21)	61(18)	59(18)	08(15)	27(15)	—45(15)
O(1B)	82(12)	43(8)	52(10)	−12(9)	25(9)	05(8)
O(2B)	116(19)	58(11)	107(20)	49(12)	−51(18)	−27(12)
N(1B)	48(11)	39(10)	59(13)	11(9)	17(10)	—07(9)
N(2B)	126(23)	55(13)	56(14)	49(15)	—07(17)	—12(12)
C(1B)	101(27)	61(18)	100(24)	−23(19)	37(22)	19(20)
C(2)	53(15)	64(15)	68(19)	—06(14)	−16(16)	09(14)

tantalum and chlorine. The anisotropic thermal parameter is defined as exp($-2\pi^2\Sigma\Sigma U_{ij}h_ih_j$) ($i,j$ = 1—3). Three scale factors were refined as were all atoms anisotropically to R 0.087. In the final cycle of refinement all shifts were $< 0.040\sigma$. The 672 reflections given zero weight showed no serious discrepancies. A difference Fourier map showed no significant peaks but we were unable to locate the methyl hydrogen atoms unambiguously. The final list of co-ordinates and thermal parameters is given in Tables 2 and 3. The molecular dimensions are listed in Table 4. The final observed and calculated structure factors can be obtained from the authors on request.

TABLE 4

MOLECULAR DIMENSIONS FOR (I), BOND DISTANCES (Å) AND ANGLES (°)

Ta—Cl(1)	2.359(8)		
Ta—Cl(2)	2.357(10)		
Ta—O(1A)	2.090(17)	Ta—O(1B)	2.108(18)
Ta—O(2A)	2.081(21)	Ta—O(2B)	2.066(26)
Ta—C(2)	2.248(28)		
O(1A)—N(1A)	1.28(3)	O(1B)—N(1B)	1.35(3)
O(2A)—N(2A)	1.30(3)	O(2B)—N(2B)	1.24(4)
N(1A)—N(2A)	1.36(4)	N(1B)—N(2B)	1.23(3)
N(1)—C(1A)	1.26(4)	N(1B)—C(1B)	1.43(5)
Cl(1)—Ta—Cl(2)	179.2(3)		
Cl(1)—Ta—O(1A)	88.4(5)	Cl(1)—Ta—O(1B)	90.4(6)
Cl(1)—Ta—O(2A)	93.1(6)	Cl(1)—Ta—O(2B)	89.8(7)
Cl(1)—Ta—C(2)	91.7(8)		
Cl(2)—Ta—O(1A)	92.4(5)	Cl(2)—Ta—O(1B)	89.1(6)
Cl(2)—Ta—O(2A)	86.9(6)	Cl(2)—Ta—O(2B)	89.4(7)
Cl(2)—Ta—C(2)	88.7(8)		
O(1A)—Ta—O(2A)	69.6(7)	O(1B)—Ta—O(2B)	69.9(8)
O(1A)—Ta—O(1B)	147.7(7)		
O(2A)—Ta—O(2B)	73.0(9)		
O(1A)—Ta—O(2B)	142.4(8)	O(1B)—Ta—O(2A)	142.7(8)
C(2)—Ta—O(1A)	76.6(9)	C(2)—Ta—O(1B)	71.2(10)
C(2)—Ta—O(2A)	145.6(10)	C(2)—Ta—O(2B)	141.0(10)
Ta—O(1A)—N(1A)	121.2(15)	Ta—O(1B)—N(1B)	114.7(14)
Ta—O(2A)—N(2A)	122.7(17)	Ta—O(2B)—N(2B)	122.1(20)
O(1A)—N(1A)—C(1A)	120.7(25)	O(1B)—N(1B)—C(1B)	119.2(22)
O(1A)—N(1A)—N(2A)	114.8(23)	O(1B)—N(1B)—N(2B)	117.3(31)
C(1A)—N(1A)—N(2A)	124.5(26)	C(1B)—N(1B)—N(2B)	123.3(25)
N(1A)—N(2A)—O(2A)	111.5(27)	N(1B)—N(2B)—O(2B)	115.7(25)

Results and Discussion

The alkyls Me_2MCl_3 and Me_3MCl_2 (M = Nb, Ta) react with 4 moles of NO at temperatures above −80° to give $MCl_3[ON(Me)NO]_2$ and $MeMCl_2[ON(Me)NO]_2$ respectively. The structure of the latter compound, for M = Ta^{I}, as established by the structure determination is shown in Fig. 1 together with the atomic numbering scheme. The tantalum atom is seven-coordinate being bonded to two chlorine atoms, four oxygens of the two bidentate ligands and one methyl group. IR and NMR spectra suggest that the other three complexes have similar structures.

Thus, the IR spectra in the 4000 — 700 cm^{-1} region are essentially the same for all 4 complexes and moreover very similar to those reported for other complexes containing the *N*-methyl-*N*-nitrosohydroxylamine (dinom) moiety [1,3]. The complexes $MeMCl_2[ON(Me)NO]_2$ each show a band at ca. 500 cm^{-1} attributable to ν(M—C) (Table 5). As well as metal—carbon stretches the complexes would be expected to show bands attributable to metal—oxygen stretching modes. The complexes show a strong band at ca. 595 cm^{-1} which is tentatively assigned to a metal—oxygen stretch, niobium and tantalum alkoxides show ν(M—O) in the same region [9,10]. The metal chloride stretching modes were present as strong, rather broad bands in the 300 — 400 cm^{-1} region.

The NMR spectra (Table 5) are similar to those in refs. 1, 3 and moreover like other complexes containing the dinom group, the MeN resonance was found to be appreciably solvent dependent; thus in benzene solution (I) shows resonances at τ7.27 (NMe) and 7.68 (TaMe) (cf. values in Table 5 for CH_2Cl_2 solution). The shift of the methyl-metal resonance to lower field in benzene solution is noteworthy as the methyl-metal resonance of the parent methyls Me_nMCl_{5-n} shift to higher field in benzene solution, thus $MeTaCl_4$ shows a resonance at τ 7.22 in CH_2Cl_2 solution and τ 7.78 in benzene solution.

Attempts to insert NO into the remaining metal—carbon bond of the complexes $MeMCl_2[ON(Me)NO]_2$ have not yielded pure products. The complexes are inert to nitrogen oxide at room temperature but in refluxing dichlo-

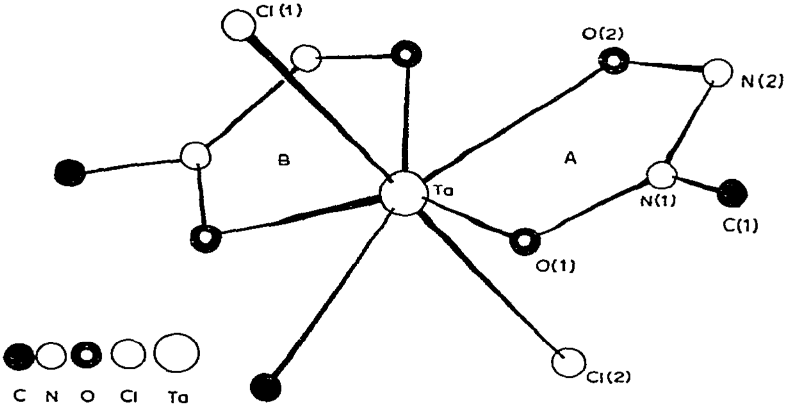

Fig. 1. Structure of $MeTaCl_2[ON(Me)NO]_2$, (I).

TABLE 5

IR AND NMR SPECTRA[a]

Complex	τ(MeN)	τ(MeM)	ν(M—C)(cm^{-1})[b]
$NbCl_3[ON(Me)NO]_2$	5.51		
$MeNbCl_2[ON(Me)NO]_2$	5.49	7.64	496w
$TaCl_3[ON(Me)NO]_2$	5.55		
$MeTaCl_2[ON(Me)NO]_2$	5.52	8.20	503m
$TaCl_2(OMe)[ON(Me)NO]_2$[c]	5.57		

[a] Dichloromethane solution (CH_2Cl_2, τ = 4.67). [b] w = weak, m = medium. [c] τ(MeO) = 5.37.

romethane further reaction took place yielding non-stoichiometric products which did not contain a methyl-metal group. The IR spectrum, in addition to bands arising from the dinom groups showed a broad band at ca. 750 cm^{-1} [ν(M—O—M)] suggesting that the complex $MCl_2[ON(Me)NO]_3$, which is probably the primary reaction product, decomposed under the conditions used.

(I) was found to be much less reactive than other compounds previously reported containing methyl-tantalum and methyl-niobium groups [5,6] thus it was inert to dry oxygen over a period of 2 h at room temperature, contrasting with alkyls such as Me_2NbCl_3 which react explosively with pure oxygen. The methyl-metal groups can however be cleaved by reagents such as Et_2NH, C_2H_5-CO_2H, HCl and MeOH, the latter reagent yielding the complex $TaCl_2(OMe)$-$[ON(Me)NO]_2$. The IR spectrum of this complex shows band typical of the dinom groups and additional strong bands at 1100 cm^{-1}, ν(C—O) and 547 cm^{-1}, ν(Ta—OMe) and no band at ca. 500 cm^{-1} attributable to ν(Ta—C).

(I) was stable indefinitely at room temperature under nitrogen while the corresponding niobium complex decomposed slowly. However, their thermal stability was greater than that of six-coordinate complexes of the type $MeMCl_4 \cdot L$ (L = unidentate ligand) consistent with the idea that an increase in co-ordination number results in reduced lability of the metal—carbon bond.

The crystal structure of (I) shows that the geometry of the co-ordination sphere (see Fig. 1) is a slightly distorted pentagonal bipyramid with the two chlorine atoms in the axial positions. The atoms in the girdle follow the sequence C(2), O(1), O(2), O(2), O(1); thus the molecule has approximate *m* symmetry. The two *N*-methyl groups are thus mutually *cis*, an arrangement which is found in other molecules containing two bidentate ligands formed by insertion reactions into early transition metal—methyl bonds, viz. $WMe_4[ON(Me)$-$NO]_2$ [3] and $NbCl_3[NMeC(S)Me]_2$ [11], and this may therefore be due to the mechanism of the reaction.

Seven-coordinate monomers of stoichiometry MX_2L_5, where X is a halogen and larger than ligand L, have previously been found to have capped octahedral [$MoBr_2(CO)_3$(dpe), dpe = 1,2-bis(diphenylphosphino)ethane [12] $MoBr_2(CO)_2(dam)_2$, dam = bis(diphenylarsino)methane [13]] or capped trigonal prismatic geometry [Me_3TaCl_2bipy [4], bipy = 2,2'-bipyridine, $Mo(CO)_2Cl_2(dpm)_2$ [14], dpm = bis(diphenylphosphino)methane] and thus the present molecule, being a pentagonal bipyramid, completes the series of the three ideal geometries. As was discussed in ref. 4 these three geometries have in common the requirement that the two chlorine atoms occupy the least crowded sites in the particular polyhedron. While the present molecule is the first example of a pentagonal bipyramid, one estimates that a whole series of compounds of this stoichiometry will have this geometry whenever the five ligands L can fit into a pentagonal girdle.

In (I), the Ta—Cl bond lengths at 2.359(8), 2.357(10) Å are comparable with those found in the $TaCl_6^-$ anion which range between 2.29 and 2.37 Å [15]. They are also equivalent to those found for the axial Nb—Cl bonds in the pentagonal bipyramidal $NbCl_3[MeNC(S)Me]_2$ [11] molecule which are 2.359(6) and 2.338(6) Å. The Ta—O distances range between 2.07(3) and 2.10(2) Å, differences not significant. Comparisons with Nb—O bond lengths in girdles show that these lengths are short: cf. [2.10, 2.12, 2.17 Å] in oxobisoxalatobisaquoniobate(V) [16] and 2.11 — 2.15 Å in ammonium oxotrioxalatoniobate monohydrate [17]. The O...O contacts in the present structure are very short at 2.38, 2.39 in the chelate rings (O(1)—Ta—O(2) 69.6, 69.9°) and 2.47 Å between rings. The inter-ring bite is the same as that found for the inter-ring bite in $Zr(acac)_3Cl$, acac = acetylacetone [18] which is 2.46 Å. We conclude that the small chelate bite in (I) permits both strong Ta—O bonds and a relatively unstrained pentagonal girdle. The Ta—C(2) bond [2.248(28) Å] is similar to those found in Me_3TaCl_2bipy [4] which are 2.24(5) and 2.16(6) Å.

In (I), the five atoms in the planar girdle are all small enough to fit easily into the girdle where the ideal L—M—L angle is 72°. The chelate angles O(1)—Ta—O(2) angles are 69.6(7), 69.9(8) while the O(2A)...O(2B) inter-ring angle is 73.0(9)°. The C(2)—Ta—O(1) angles are different at 76.6(9) and 71.2(10)°, but this may not be significant in view of the high standard deviations (vide infra). However, it would not be surprising for the molecule not to have perfect *m* symmetry in the girdle for two possible reasons: (i) Distortions, such as adjacent atoms alternatively above and below the least squares plane, will increase ligand...ligand contacts and (ii) the positions of the hydrogen atoms of the methyl group C(2), which are unknown, may be asymmetrically placed and thus affect O(2A) and O(2B) differently.

The distortions from *m* symmetry are however slight. Least-squares plane

TABLE 6

INTRAMOLECULAR CONTACTS <3.35 Å AND INTERMOLECULAR CONTACTS <3.75 Å

Cl(1)...O(1A)	3.11	Cl(1)...O(1B)	3.17
Cl(1)...O(2A)	3.23	Cl(1)...O(2B)	3.13
Cl(1)...C(2)	3.31		
Cl(2)...O(1A)	3.21	Cl(2)...O(1B)	3.14
Cl(2)...O(2A)	3.06	Cl(2)...O(2B)	3.12
Cl(2)...C(2)	3.22		
O(1A)...O(2A)	2.38	O(1B)...O(2B)	2.39
O(2A)...O(2B)	2.47		
C(2)...O(1A)	2.69	C(2)...O(1B)	2.54
Cl(1)...C(1B)^a	3.75	Cl(2)...N(2A)^e	3.33
C(2)...O(1B)^b	3.70	Cl(2)...C(1A)^e	3.69
Cl(1)...Cl(1)^c	3.61	C(1A)...O(1B)^f	3.55
N(2B)...Cl(1)^c	3.51	Cl(2)...C(1B)^g	3.65
N(1B)...Cl(1)^c	3.59		
O(1A)...O(2A)^d	3.63	N(2)...C(1B)^g	3.57
O(1A)...O(2B)^d	3.54		
Cl(2)...N(2B)^d	3.59		
Cl(2)...N(1A)^e	3.48		

Superscripts refer to the following equivalent positions relative to *x*, *y*, *z* for the second atom: $^a x, y, 1+z$; $^b 1-x, -y, -z$; $^c -x, -y, -z$; $^d \frac{1}{2}+x, \frac{1}{2}-y, \frac{1}{2}+z$; $^e \frac{1}{2}+x, \frac{1}{2}-y, -\frac{1}{2}+z$; $^f \frac{1}{2}-x, \frac{1}{2}+y, \frac{1}{2}-z$; $^g \frac{1}{2}-x, \frac{1}{2}+y, -\frac{1}{2}-z$.

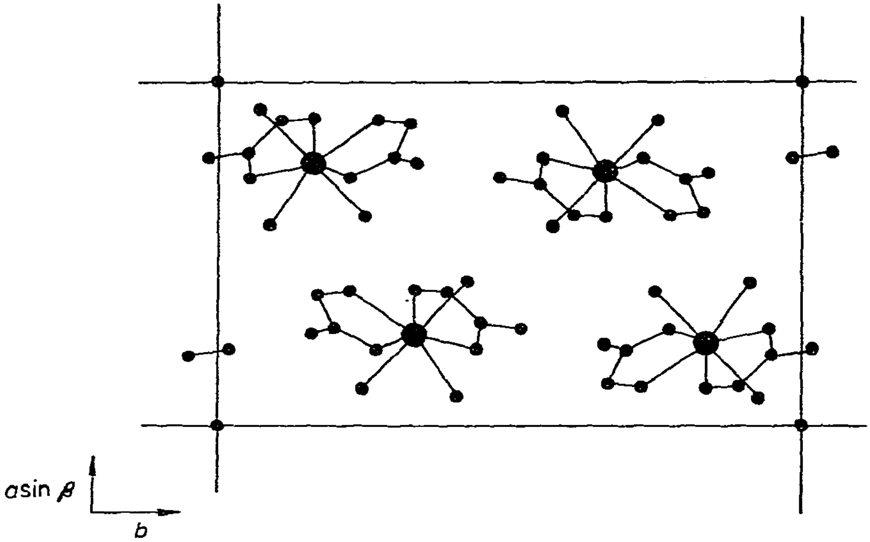

Fig. 2. Unit cell of (I) in the *c* projection.

calculations show that for tantalum and the five ligands, the maximum distance of an atom from the least-squares plane is 0.08 Å with a mean deviation of 0.04 Å. [Ta −0.02, O(1A) −0.08, O(2A) 0.08, C(2) 0.06, O(1B) −0.01, O(2B) −0.04 Å]. When a least-squares plane is calculated for all twelve atoms in the equatorial plane, the maximum deviation is 0.11 Å and the mean deviation 0.04 Å [Ta −0.03, O(1A) − 0.07, O(2A) 0.05, O (1B) −0.01, O(2B) −0.07, C(2) 0.08, N(1A) −0.00, N(2A) 0.11, N(1B) −0.02, N(2B) 0.00, C(1A) −0.06, C(1B) 0.02 Å]. Thus, O(2A) and O(2B) are alternatively above and below the plane, thus increasing their interatomic distance.

Of the internal ring dimensions and the amount of double bonding in the O—N and N—N bonds, little useful information has been gained from this structure analysis. The dimensions differ considerably between the two rings and as one would expect on chemical grounds that dimensions should be equivalent, it can be concluded that the differences are not significant and therefore that the standard deviations as calculated from the least-squares refinement are too small. These differences may thus be a result of the difficulties encountered in data collection.

All intermolecular contacts less than 3.75 Å are shown in Table 6. There are some particularly short N...Cl contacts, viz. Cl(2)...N(2A)^e 3.33, Cl(2)...N(1A)^e 3.48 but in general all close contacts are similar to the sum of the van der Waals radii. The unit cell in the *c* projection is shown in Fig. 2.

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