Preparation and Structure of Hexachlorotetrapyridine Ditantalum(III)

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Abstract

The title compound, $Ta_2Cl_6py_4$, has been prepared and structurally characterized. It is very similar to its tungsten analog, from which some inferences concerning the M–M bonding in both compounds may be drawn. The principal dimensions of the molecule are: Ta–Ta, 2.740(1); Ta–Cl_b, 2.44[1]; Ta–Cl_{ax}, 2.400[6]; Ta–Cl_{eq}, 2.46[1]; Ta–N_{ax}, 2.216[3]; Ta–N_{eq}, 2.31[2] Å.

Introduction

Binuclear transition metal compounds of the edge-sharing bioctahedron type are numerous [1]. They have been closely examined from a structural and magnetic point of view because they present an important opportunity to study metal-to-metal bonding [2] within a flexible and more or less designable structural framework. One of the earliest edge-sharing bioctahedral complexes to be structurally characterized was $W_2Cl_6py_4$ [3]. The type of structure displayed by this compound, in which the two pyridine ligands are axial on one metal atom and equatorial on the other, has since been seen in many other cases [1], but there are also numerous $M_2X_6L_4$ compounds in which all the neutral ligands, L, are equatorial [4].

We have been able to prepare and structurally characterize the tantalum analog, $Ta_2Cl_6py_4$, of the tungsten compound. In addition to determining the ligand arrangement, we have also obtained the Ta–Ta distance which may be compared with the W–W distance to give insight into the electronic structures of both compounds.

Experimental

Tantalum(V) chloride was purchased from Aesar Chemicals and used as received. All operations were conducted in an atmosphere of argon. Solvents were freshly distilled before use. Benzene was dried over sodium-benzophenone ketyl; pyridine was dried over calcium hydride.

Preparation of $Ta_2Cl_6py_4$

A slurry of 4.00 g (11.2 mmol) $TaCl_5$ and 70 ml benzene was placed in a 250 ml round bottom flask containing a gas inlet, and 0.49 g (22 mmol) of $LiBH_4$ was directly added to the flask. The mixture was stirred for 2 days, after which an orange solution and a light green precipitate were present. The precipitate was filtered, washed with 20 ml benzene and dried *in vacuo*. This intermediate was isolated in a 4.4 g yield. A total of 0.5 g of the precipitate was placed in a 50 ml round bottom flask containing a gas inlet and cooled with liquid nitrogen. After addition of 20 ml of pyridine the flask was allowed to warm to room temperature. As the flask was warmed a purple solution was formed which was stirred at room temperature for 1 day, filtered, and layered with 20 ml hexane. Upon slow diffusion of the hexane layer purple crystals of $Ta_2Cl_6(py)_4$ were formed. Approximate yield: 400 mg. Overall yield based on $TaCl_5$: *c.* 70%.

Structure Determination

A single crystal was mounted inside a capillary. The data were collected on a Syntex P3 diffractometer. Three standards monitored throughout the data collection showed 22.4% decay in intensity for which an appropriate correction was made. The data collection parameters are listed in Table 1.

Direct methods (SHELXS-86) revealed the locations of the Ta, Cl and N atoms immediately. From consecutive least-squares refinements and difference Fourier maps the carbon atoms of the pyridine rings coordinated to the dimer were found. The interstitial solvent molecules (pyridine) were located with the aid of SHELX-76 where they were refined as six carbon atoms, since it was not possible to distinguish between carbon and nitrogen atoms. It was concluded that the nitrogen and the carbon atoms of the pyridine rings are disordered over all six positions. The final atomic positional and equivalent isotropic displacement parameters are listed in Table 2.

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TABLE 1. Crystal data for $Ta_2Cl_6py_4 \cdot 2C_5H_5N$

Formula	$Ta_2Cl_6N_6C_{30}H_{30}$
Formula weight	1049.23
Space group	$P\bar{1}$
Systematic absences	none
a (Å)	11.931(2)
b (Å)	16.622(2)
c (Å)	9.327(2)
α (°)	105.72(1)
β (°)	95.33(2)
γ (°)	81.57(2)
V (Å^3)	1758(1)
Z	2
D_{calc} (g/cm^3)	1.981
Crystal size (mm)	0.20 × 0.30 × 0.30
μ(Mo Kα), cm^{-1}	66.361
Data collection instrument	Syntex P3
Radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)
Orientation reflections: no., range (2θ) (°)	25, $12 < 2\theta < 24$
Temperature (°C)	21
Scan method	$\omega - 2\theta$
Data collection range, 2θ (°)	$4 \leqslant 2\theta \leqslant 45$
No. unique data, total	4018
with $F_o^2 > 3\sigma(F_o^2)$	3045
No. parameters refined	397
Transmission factors, max., min.	0.9989, 0.8304
R [a]	0.0322
R_w [b]	0.0414
Quality-of-fit indicator[c]	0.886
Largest shift/e.s.d. final cycle	0.03
Largest peak (e/Å^3)	0.687

[a] $R = \Sigma ||F_o| - |F_c|| / \Sigma |F_o|$. [b] $R_w = [\Sigma w(|F_o| - |F_c|)^2 / \Sigma w |F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality-of-fit $= [\Sigma w(|F_o| - |F_c|)^2 / (N_{obs} - N_{parameters})]^{1/2}$.

TABLE 2. Atomic positional and equivalent isotropic displacement parameters and their e.s.d.s for $Ta_2Cl_6py_4$

Atom	x/a	y/b	z/c	B_{eq} (Å^2)
Ta(1)	0.58048(4)	0.27635(3)	0.36819(5)	2.86(1)
Ta(2)	0.37010(4)	0.25592(3)	0.22915(5)	2.65(1)
Cl(1)	0.5408(2)	0.1640(2)	0.1442(3)	3.37(6)
Cl(2)	0.4047(3)	0.3652(2)	0.4539(3)	3.81(7)
Cl(3)	0.7743(3)	0.2006(2)	0.3321(3)	4.22(7)
Cl(4)	0.6591(3)	0.3791(2)	0.5792(4)	4.96(8)
Cl(5)	0.3158(3)	0.1649(2)	0.3650(3)	4.20(7)
Cl(6)	0.3774(3)	0.3450(2)	0.0678(3)	3.77(7)
N(1)	0.6210(8)	0.3539(6)	0.225(1)	3.4(2)
N(2)	0.5649(8)	0.1967(6)	0.5190(9)	3.2(2)
N(3)	0.1886(8)	0.3222(6)	0.259(1)	3.7(2)
N(4)	0.2978(8)	0.1636(6)	0.019(1)	3.9(2)
C(11)	0.672(1)	0.3167(7)	0.094(1)	3.9(3)
C(12)	0.690(1)	0.3636(8)	−0.006(1)	4.8(3)
C(13)	0.656(1)	0.4476(8)	0.029(1)	5.4(3)
C(14)	0.606(1)	0.4857(7)	0.167(1)	4.9(3)
C(15)	0.589(1)	0.4382(7)	0.258(1)	4.4(3)
C(21)	0.603(1)	0.1132(7)	0.481(1)	3.6(3)
C(22)	0.597(1)	0.0621(8)	0.574(1)	5.0(3)
C(23)	0.555(1)	0.0964(8)	0.713(1)	5.0(3)
C(24)	0.518(1)	0.1808(9)	0.755(1)	5.5(4)
C(25)	0.525(1)	0.2295(8)	0.655(1)	4.4(3)
C(31)	0.163(1)	0.4069(7)	0.296(1)	4.0(3)
C(32)	0.056(1)	0.4499(8)	0.314(1)	5.0(4)
C(33)	−0.030(1)	0.402(1)	0.284(2)	7.2(4)
C(34)	−0.010(1)	0.314(1)	0.243(2)	6.4(4)
C(35)	0.099(1)	0.2767(8)	0.230(1)	4.3(3)
C(41)	0.312(1)	0.0801(7)	0.003(1)	3.6(3)
C(42)	0.267(1)	0.0247(8)	−0.118(2)	5.0(3)
C(43)	0.201(1)	0.0534(9)	−0.226(2)	6.0(4)
C(44)	0.182(1)	0.1412(9)	−0.210(2)	5.9(4)
C(45)	0.235(1)	0.1951(8)	−0.084(1)	5.0(3)
C(51)	0.906(2)	0.596(1)	0.120(2)	7.7(5)
C(52)	1.011(2)	0.610(1)	0.122(2)	8.5(5)
C(53)	1.056(1)	0.654(1)	0.239(2)	8.1(5)
C(54)	0.999(2)	0.6885(9)	0.367(2)	7.6(5)
C(55)	0.889(2)	0.673(1)	0.367(2)	7.8(5)
C(56)	0.841(1)	0.6278(9)	0.240(2)	6.7(4)
C(61)	0.135(2)	−0.150(1)	0.161(3)	11.5(8)
C(62)	0.114(2)	−0.092(2)	0.080(3)	12.0(8)
C(63)	0.096(2)	−0.009(1)	0.164(2)	10.2(6)
C(64)	0.093(2)	0.014(2)	0.316(2)	11.3(8)
C(65)	0.103(2)	−0.043(2)	0.387(2)	11.5(7)
C(66)	0.131(2)	−0.126(1)	0.314(3)	16.4(8)

The equivalent isotropic displacement parameter, B_{eq}, is calculated as: $\frac{1}{3}[a^2a^{*2}B_{11} + b^2b^{*2}B_{22} + c^2c^{*2}B_{33} + 2ab(\cos\gamma)a^*b^*B_{12} + 2ac(\cos\beta)a^*c^*B_{13} + 2bc(\cos\alpha)b^*c^*B_{23}]$.

Results and Discussion

The Structure

An ORTEP drawing of the molecular structure is shown in Fig. 1. A list of the principal bond lengths and angles is presented in Table 3. It can be seen that the overall structure is of the same type as that previously found for $W_2Cl_6py_4$; in fact, the two are almost identical. The molecule has no crystallographic symmetry so that all bond lengths and angles are independent. They can be averaged according to idealized C_{2v} symmetry. Such average values are listed in Table 4 for comparison with those in other structures.

Preparative Method

Most of the reduction reactions of Nb and Ta pentahalides reported in the past used sodium amalgam as the reducing agent. Investigation of $LiBH_4$ as a reducing agent resulted in the isolation of crystals of $Ta_2Cl_6py_4$. When $TaCl_5$ is reduced with two equivalents of $LiBH_4$ in benzene a very slow color change is observed. The reaction is completed after the mixture is stirred for about two days at room temperature. A green precipitate, the nature of which is not known, is recovered from the reaction. We suggest that this precipitate may be similar to the black precipitate formed when $TaCl_5$ is reduced with

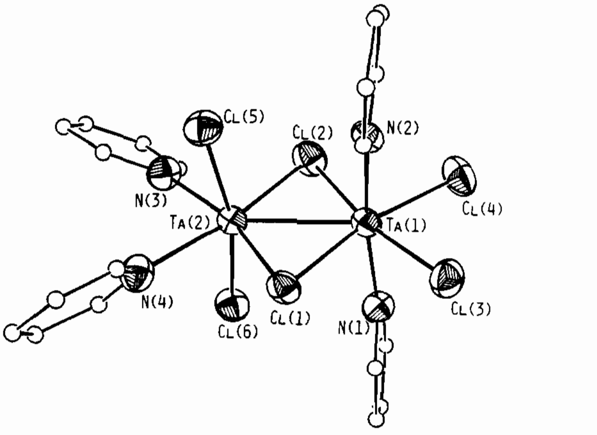

Fig. 1. An ORTEP drawing of the $Ta_2Cl_6(py)_4$ molecule with the thermal ellipsoids drawn at 50% probability level and carbon atoms assigned arbitrarily small thermal parameters for clarity. The atom numbering employed in the Tables is defined.

two equivalents of Na/Hg in aromatic solvents, since both are very reactive towards simple electron donating solvents. However, this green precipitate reacts exothermically with THF and only an oily residue is recovered from the reaction, whereas the black precipitate from Na/Hg reduction forms trinuclear clusters containing THF as the coordinating ligand. These THF clusters will be discussed in future publications.

To our surprise the addition of pyridine to this green precipitate was not as exothermic as the addition of THF and upon slow diffusion of hexane into this pyridine solution purple crystals of $Ta_2Cl_6py_4$ were formed. Clay and Brown previously reported the preparation of this compound by addition of pyridine to $Ta_2Cl_6(THT)_3$ but it was characterized only by its magnetic susceptibility. It was found to be diamagnetic [5].

Ta–Ta and W–W Bonding

With the structures of both compounds now available, it is possible to draw some inferences about

TABLE 3. Selected bond distances (Å) and angles (°) for $Ta_2Cl_6py_4{\cdot}2C_5H_5N$

Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance	Atom 1	Atom 2	Distance
Ta(1)	Ta(2)	2.740(1)	Ta(1)	N(1)	2.219(11)	Ta(2)	Cl(6)	2.394(3)
Ta(1)	Cl(1)	2.458(2)	Ta(1)	N(2)	2.213(10)	Ta(2)	N(3)	2.287(9)
Ta(1)	Cl(2)	2.447(3)	Ta(2)	Cl(1)	2.418(3)	Ta(2)	N(4)	2.323(9)
Ta(1)	Cl(3)	2.472(3)	Ta(2)	Cl(2)	2.422(3)			
Ta(1)	Cl(4)	2.445(3)	Ta(2)	Cl(5)	2.406(4)			

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Ta(2)	Ta(1)	Cl(1)	55.12(7)	Ta(1)	Ta(2)	Cl(2)	56.18(7)
Ta(2)	Ta(1)	Cl(2)	55.32(7)	Ta(1)	Ta(2)	Cl(5)	97.72(8)
Ta(2)	Ta(1)	Cl(3)	135.95(7)	Ta(1)	Ta(2)	Cl(6)	96.35(8)
Ta(2)	Ta(1)	Cl(4)	135.89(8)	Ta(1)	Ta(2)	N(3)	137.5(2)
Ta(2)	Ta(1)	N(1)	93.2(2)	Ta(1)	Ta(2)	N(4)	135.8(2)
Ta(2)	Ta(1)	N(2)	94.2(2)	Cl(1)	Ta(2)	Cl(2)	112.7(1)
Cl(1)	Ta(1)	Cl(2)	110.42(9)	Cl(1)	Ta(2)	Cl(5)	94.0(1)
Cl(1)	Ta(1)	Cl(3)	80.85(9)	Cl(1)	Ta(2)	Cl(6)	94.8(1)
Cl(1)	Ta(1)	Cl(4)	168.7(1)	Cl(1)	Ta(2)	N(3)	166.0(2)
Cl(1)	Ta(1)	N(1)	89.7(2)	Cl(1)	Ta(2)	N(4)	79.3(2)
Cl(1)	Ta(1)	N(2)	92.6(2)	Cl(2)	Ta(2)	Cl(5)	93.1(1)
Cl(2)	Ta(1)	Cl(3)	168.36(9)	Cl(2)	Ta(2)	Cl(6)	93.7(1)
Cl(2)	Ta(1)	Cl(4)	80.7(1)	Cl(2)	Ta(2)	N(3)	81.4(2)
Cl(2)	Ta(1)	N(1)	95.4(2)	Cl(2)	Ta(2)	N(4)	168.0(2)
Cl(2)	Ta(1)	N(2)	90.7(2)	Cl(5)	Ta(2)	Cl(6)	165.9(1)
Cl(3)	Ta(1)	Cl(4)	88.1(1)	Cl(5)	Ta(2)	N(3)	85.1(3)
Cl(3)	Ta(1)	N(1)	87.3(2)	Cl(5)	Ta(2)	N(4)	85.5(3)
Cl(3)	Ta(1)	N(2)	85.8(2)	Cl(6)	Ta(2)	N(3)	83.7(3)
Cl(4)	Ta(1)	N(1)	87.1(2)	Cl(6)	Ta(2)	N(4)	85.3(3)
Cl(4)	Ta(1)	N(2)	89.2(2)	N(3)	Ta(2)	N(4)	86.7(3)
N(1)	Ta(1)	N(2)	172.3(3)	Ta(1)	Cl(1)	Ta(2)	68.38(7)
Ta(1)	Ta(2)	Cl(1)	56.50(6)	Ta(1)	Cl(2)	Ta(2)	68.50(7)

Numbers in parentheses are e.s.d.s in the least significant digits.

TABLE 4. Important distances of some $M_2Cl_6L_4$ complexes

	$Ta_2Cl_6(Py)_4$	$Ta_2Cl_6(PMe_3)_4$ [6]	$W_2Cl_6(Py)_4$ [3]	$Ru_2Cl_6(PBu_3)_4$ [7]
M–M	2.740(1)	2.721(1)	2.737(3)	3.733(2)
$M-Cl_b$	2.44[1]	2.45[2]	2.392[0]	2.414(3)
$M-Cl_{ax}$	2.400[6]	2.399[1]	2.397(8)	2.331(2)
$M-Cl_{eq}$	2.46[1]	2.479[7]	2.430(8)	2.324(3)
$M-L_{ax}$	2.226[7]	2.607[9]	2.18(2)	2.397(3)
$M-L_{eq}$	2.30[2]	2.565[9]	2.24(2)	2.321(3)

metal–metal bonding from a comparison of the two. It should be noted first that according to the literature both the tantalum [5] and the tungsten [3] compounds are diamagnetic.

For the tantalum compound, the short Ta–Ta distance, 2.740(1) Å, and the average internal angles in the Ta(μ-Cl)$_2$Ta bridge structure, (Cl–Ta–Cl, 112°; Ta–Cl–Ta, 68°) show that substantial Ta–Ta bonding occurs. This coupled with the diamagnetism of the compound leads to the firm conclusion that there is a Ta–Ta double bond, based on a $\sigma^2\pi^2$ configuration. This, of course, is what would have been expected.

We may now turn to the question of the W–W interaction in the tungsten compound. Since it, too, is diamagnetic and shows all the structural earmarks of metal–metal bonding, the question before us is whether the electron configuration is $\sigma^2\pi^2\delta^2$ or $\sigma^2\pi^2\delta^{*2}$. It has been shown [2] in other edge-sharing bioctahedral complexes of molybdenum(III) and tungsten(III) that the M–M bond lengths, when properly compared with those in adjacent group V and group VII compounds favor the $\sigma^2\pi^2\delta^{*2}$ configuration. The same result is obtained in this case.

As pointed out before [2], on going from a Ta–Ta to a W–W bond, all other things being equal, the distance would decrease by *c.* 0.06 Å simply because of the smaller size of the W atoms. If the W–W bond had a δ component in addition to the σ and π components, we would expect the W–W distance to be >0.06 Å shorter than the Ta–Ta distance. In fact, the W–W bond (Table 4) is <0.06 Å shorter; it is actually the same length within experimental error (0.003 Å). This can be attributed to the occurrence of a δ^{*2} antibonding contribution.

Our final conclusions, therefore, are: (1) the Ta–Ta bond in $Ta_2Cl_6py_4$ is based on a $\sigma^2\pi^2$ electron configuration; (2) the W–W bond in $W_2Cl_6py_4$ is based on a $\sigma^2\pi^2\delta^{*2}$ configuration and is weaker than that in the tantalum compound; (3) the $M_2Cl_6py_4$ type compounds follow the same pattern of M–M interactions as previously established for $M_2Cl_6(PR_3)_4$ type compounds.

With regard to the larger size of the Ta versus the W atom, it may be noted in Table 4 that all Ta–ligand distances are an average of 0.04 Å longer than the W–ligand distances. On the other hand, the comparable Ta–ligand distances in $Ta_2Cl_6py_4$ and $Ta_2Cl_6(PMe_3)_4$ are equal within experimental error.

Supplementary Material

Full lists of bond distances, bond angles, anisotropic displacement parameters and a table of observed and calculated structure factors are available from author F.A.C.

Acknowledgements

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References

1 F. A. Cotton, *Polyhedron, 6* (1987) 667.
2 J. A. M. Canich, F. A. Cotton, L. M. Daniels and D. B. Lewis, *Inorg. Chem., 26* (1987) 4046.
3 R. B. Jackson and W. E. Streib, *Inorg. Chem., 10* (1971) 1760.
4 F. A. Cotton, M. P. Diebold and P. A. Kibala, *Inorg. Chem., 27* (1988) 779.
5 A. E. Clay and T. M. Brown, *Inorg. Chim. Acta, 58* (1982) 1.
6 A. P. Sattelberger, R. B. Wilson and J. C. Huffman, *Inorg. Chem., 21* (1982) 2392.
7 F. A. Cotton, M. Matusz and R. C. Torralba, *Inorg. Chem., 28* (1989) 1516.