We believe that the inertness of these complexes to further modification is a function of both the steric constraints that the ligand imparts on the metal derivative and an electronic effect. From the X-ray structure of the zirconium derivative **4b**, both the chloride ligands are surrounded by bulky $SiMe_2$ or PMe_2 groups, which can shield the Zr–Cl (or Hf–Cl) bonds from incoming nucleophilic reagents. In addition, the electronic effect of the weak C–H···Cl interactions may further reduce the tendency for substitution.

Conclusion

Our strategy in the design of these hybrid ligands is clearly effective since we have been able to generate a new family of group 4B derivatives that contain phosphine ligands. Although the particular hybrid ligands described here are capable of tridentate coordination, we observe only a bidentate mode of chelation both in solution and in the solid state; presumably, steric effects are the major factor in this behavior.

All of the zirconium and hafnium complexes are chiral as evidenced by solution ^1H NMR and the solid-state single-crystal X-ray structure of **4b**. This particular type of chirality is a result of the cis silylamide ligands interacting as two constrained, *geared* molecular propellers.[26] Without the chelating phosphine to constrain each molecular propeller, gear slipping[27] would occur, resulting in stereoisomerization; the ^1H NMR indicates diastereotopic nuclei up to 60 °C (>60 °C results in decomposition), thus providing additional evidence for the robust nature of the metal–phosphine linkage.

Acknowledgment. Financial support for this research was generously provided by the Department of Chemistry, the Natural, Applied and Health Sciences Fund (UBC), and the Natural Sciences and Engineering Research Council of Canada. Computing funds were provided for by Xerox Corp. and the UBC Computing Centre.

Registry No. **4a**, 84173-97-7; **4b**, 84173-98-8; **5a**, 84192-51-8; **5b**, 84236-32-8.

Supplementary Material Available: Listings of calculated coordinates and thermal parameters for hydrogen atoms (Table III), anisotropic thermal parameters (Table IV), observed and calculated structure factor amplitudes (Table V), and torsion angles (Table IX) (43 pages). Ordering information is given on any current masthead page.

---

(26) Mislow, K. *Acc. Chem. Res.* **1976**, *9*, 26.
(27) Johnson, C. A.; Guenzi, A.; Mislow, K. *J. Am. Chem. Soc.* **1981**, *103*, 6240.

Contribution from the Department of Chemistry,
Texas A&M University, College Station, Texas 77843

An Unusual Ditantalum (Ta=Ta) Compound with a Bridging Oxo Ligand

F. ALBERT COTTON* and WIESLAW J. ROTH

Received June 21, 1982

As a minor product in the preparation of $Ta_2Cl_6(dmpe)_2$ a compound of composition $Ta_2Cl_4(dmpe)_2(\mu\text{-}O)(\mu\text{-}Me_2S)\cdot HCl\cdot C_6H_5CH_3$ has been isolated and structurally characterized. It consists of two distorted $TaCl_2P_2OS$ octahedra sharing an edge defined by the μ-Me_2S and μ-O ligands. The μ-O ligand is strongly hydrogen bonded to a Cl atom, O···Cl = 2.893 (7) Å, which may alternatively be formulated as O···H–Cl or O–H···Cl. The Ta–Ta distance of 2.726 (1) Å, together with the fact that the tantalum atoms are formally Ta^{III} (d^2), implies the presence of a double bond between the metal atoms. This compound presumably arises because of hydrolysis by traces of water coupled with the availability of the $(CH_3)_2S$ ligand, which was present in the starting material, $Ta_2Cl_6(Me_2S)_3$. The compound crystallizes in space group $P2_1/c$ with a = 14.159 (2) Å, b = 12.487 (3) Å, c = 21.174 (3) Å, β = 108.95 (2)°, V = 3540 (2) Å^3, and Z = 4.

Introduction

As part of our continuing studies on the chemistry of niobium and tantalum in their III oxidation states, we recently reported[1] the preparation of $Ta_2Cl_6(dmpe)_2$, a molecule whose structure consists of two octahedra sharing an edge and united by a Ta=Ta (double) bond, of length 2.710 (1) Å. This compound was obtained in 85% yield by the reaction of $Ta_2Cl_6(SMe_2)_3$[2] with bis(dimethylphosphino)ethane, dmpe, in CH_2Cl_2. We have now found that by appropriate workup of the mother liquor a very small amount of another binulcear tantalum(III) compound can be obtained. In this paper we report the identification and structural characterization of that compound by X-ray crystallography.

Experimental Procedures

Preparation. All manipulations were performed under an atmosphere of argon. $Ta_2Cl_6(SMe_2)_3$ was prepared according to the literature method.[2] Dmpe was purchased from Strem Chemicals, Inc., and used without further purification as a 10% w/v solution in toluene.

The title compound is a minor product obtained during the preparation of $Ta_2Cl_6(dmpe)_2$. A 1-mL quantity of the toluene solution of dmpe (0.1 g) was added to 100 mg of $Ta_2Cl_6(SMe_2)_3$ in 10 mL of CH_2Cl_2. After several hours of stirring a precipitate (accounting for ca. 85% of Ta) of red $Ta_2Cl_6(dmpe)_2$,[1] an unidentified white solid and a dark green solution were obtained. The solution was filtered and evaporated nearly to dryness. The residue was redissolved in a mixture of 5 mL of toluene and 2 mL of CH_2Cl_2, and the solution was filtered into a Schlenk tube and carefully layered with 10 mL of hexane. Upon slow diffusion of hexane into the solution layer, about 10 mg of dark green, plate-shaped crystals was formed.

X-ray Crystallography. A crystal of approximate dimensions 0.4 × 0.3 × 0.15 mm was mounted in a glass capillary with the use of epoxy cement. Unit cell parameters and intensity data were obtained on an Enraf-Nonius CAD-4 diffractometer by using standard procedures.[3] The summary of crystallographic data is presented in Table I. Polarization, Lorentz, and absorption corrections were applied to the intensity data.

Structure Solution and Refinement.[4] Positions of the two Ta atoms were obtained from a three-dimensional Patterson function. Three cycles of isotropic least-squares refinement gave values of R_1 = 0.25 and R_2 = 0.34. Subsequent series of Fourier syntheses and isotropic least-squares refinements revealed the positions of 27 non-hydrogen atoms, namely, the $Ta_2Cl_4(dmpe)_2(SMe_2)O$ molecule and a separate Cl atom. The values of R_1 and R_2 at that point were equal to 0.076 and 0.105, respectively. Following anisotropic least-squares refinement a difference Fourier map was obtained, showing 14 peaks, which were interpreted as two poorly defined toluene molecules. The refinement

---

(1) Cotton, F. A.; Falvello, L. R.; Najjar, R. C. *Inorg. Chem.* **1983**, *22*, 375.
(2) Cotton, F. A.; Najjar, R. C. *Inorg. Chem.* **1981**, *20*, 2716.
(3) Bino, A.; Cotton, F. A.; Fanwick, P. E. *Inorg. Chem.* **1979**, *18*, 3558.
(4) All crystallographic computing was performed on a PDP 11/60 computer at B. A. Frenz and Associates, Inc., College Station, TX, equipped with a modified version of the Enraf-Nonius structure determination package.

Table I. Crystallographic Data Collection Parameters

formula	$Ta_2Cl_5SP_4OC_{21}H_{47}$
fw	1016.73
space group	$P2_1/c$
a, Å	14.159 (2)
b, Å	12.487 (3)
c, Å	21.174 (3)
α, deg	90.0
β, deg	108.95 (2)
γ, deg	90.0
V, Å^3	3540 (2)
Z	4
d_{calcd}, g/cm^3	1.907
cryst size, mm	0.4 × 0.3 × 0.15
μ(Mo Kα), cm^{-1}	67.377
data collection instrument	CAD-4
radiation	Mo Kα
scan method	ω–2θ
data collection range, deg	$0 < 2\theta < 50$; $+h, +k, \pm l$
no. of unique data	5020
no. of data with $F_o^2 \geqslant 3\sigma(F_o^2)$	4163
no. of parameters refined	256
R_1[a]	0.0496
R_2[b]	0.0602
quality-of-fit indicator[c]	1.672
largest shift/esd, final cycle	0.16

[a] $R_1 = \Sigma||F_o| - |F_c||/\Sigma|F_o|$. [b] $R_2 = [\Sigma w(|F_o| - |F_c|)^2/\Sigma w|F_o|^2]^{1/2}$; $w = 1/\sigma^2(|F_o|)$. [c] Quality of fit $= [\Sigma w(|F_o| - |F_c|)^2/(N_{\text{observns}} - N_{\text{parameters}})]^{1/2}$.

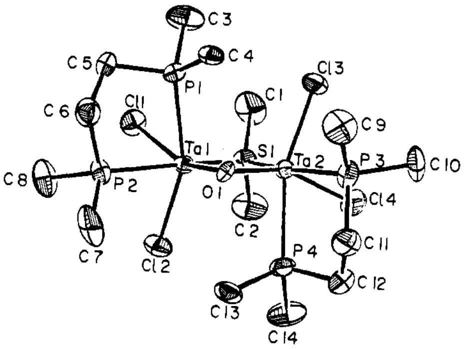

Figure 1. Molecular structure and atom-labeling scheme for the $Ta_2Cl_4(dmpe)_2(\mu\text{-}O)(\mu\text{-}SMe_2)$ molecule. Atoms are represented by their ellipsoids of thermal vibration scaled to enclose 40% of the electron density.

Table II. Atomic Positional Parameters and Equivalent Isotropic Thermal Parameters for $Ta_2Cl_4(dmpe)_2(\mu\text{-}O)(\mu\text{-}SMe_2)\cdot HCl\cdot C_6H_5CH_3$[a]

atom	x	y	z	B, Å^2
Ta(1)	0.29640 (3)	0.22386 (4)	0.50016 (2)	2.06 (1)
Ta(2)	0.18589 (4)	0.29208 (4)	0.37583 (2)	2.14 (1)
Cl(1)	0.4450 (3)	0.1126 (3)	0.5450 (2)	3.81 (8)
Cl(2)	0.3705 (3)	0.3810 (3)	0.5620 (2)	4.01 (8)
Cl(3)	0.1543 (3)	0.1359 (3)	0.3051 (2)	3.72 (8)
Cl(4)	0.2139 (3)	0.4128 (3)	0.2923 (2)	4.17 (8)
Cl(5)	0.9691 (3)	0.2563 (3)	−0.0047 (2)	3.91 (8)
S(1)	0.3628 (2)	0.2649 (3)	0.4122 (2)	3.04 (7)
P(1)	0.2222 (3)	0.0282 (3)	0.4816 (2)	2.58 (7)
P(2)	0.2569 (3)	0.1820 (3)	0.6108 (2)	2.89 (8)
P(3)	−0.0056 (3)	0.3231 (3)	0.3144 (2)	3.32 (8)
P(4)	0.1526 (3)	0.4816 (3)	0.4183 (2)	3.12 (8)
O(1)	0.1474 (5)	0.2531 (6)	0.4570 (4)	2.0 (2)
C(1)	0.423 (1)	0.160 (2)	0.3775 (8)	6.0 (4)
C(2)	0.450 (1)	0.375 (1)	0.4170 (9)	5.5 (4)
C(3)	0.279 (1)	−0.076 (1)	0.4422 (9)	5.2 (4)
C(4)	0.0896 (9)	0.013 (1)	0.4364 (6)	2.9 (3)
C(5)	0.235 (1)	−0.029 (1)	0.5646 (7)	3.5 (3)
C(6)	0.191 (1)	0.054 (1)	0.6058 (7)	3.9 (4)
C(7)	0.187 (1)	0.276 (2)	0.6430 (7)	5.3 (4)
C(8)	0.370 (1)	0.167 (2)	0.6824 (7)	4.8 (4)
C(9)	−0.094 (1)	0.218 (1)	0.3181 (9)	4.9 (4)
C(10)	−0.033 (1)	0.344 (1)	0.2249 (7)	4.8 (4)
C(11)	−0.047 (1)	0.446 (1)	0.3461 (8)	4.1 (4)
C(12)	0.032 (1)	0.531 (1)	0.3583 (7)	4.3 (4)
C(13)	0.131 (1)	0.490 (1)	0.4990 (6)	3.8 (3)
C(14)	0.240 (1)	0.595 (1)	0.424 (1)	6.0 (5)
C(21)	0.605	0.109	0.250	19 (2)*
C(22)	0.620	0.204	0.254	11 (1)*
C(23)	0.638	0.252	0.315	6.4 (7)*
C(24)	0.661	0.361	0.342	12 (1)*
C(25)	0.665	0.436	0.284	8.0 (9)*
C(26)	0.645	0.368	0.218	7.8 (8)*
C(27)	0.627	0.270	0.198	10 (1)*
C(28)	0.605	0.139	0.209	5 (1)*
C(29)	0.625	0.250	0.250	4 (1)*
C(30)	0.375	0.721	0.207	7 (2)*
C(31)	0.666	0.305	0.346	7 (2)*
C(32)	0.687	0.416	0.332	9 (2)*
C(33)	0.666	0.416	0.250	6 (1)*
C(34)	0.637	0.315	0.217	4 (1)*

[a] Atoms marked with an asterisk were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as $^4/_3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

Table III. Bond Distances (Å) for the $Ta_2Cl_4(dmpe)_2(\mu\text{-}O)(\mu\text{-}SMe_2)$ Molecule

Ta(1)–Ta(2)	2.726 (1)	P(1)–C(3)	1.86 (1)
–Cl(1)	2.442 (3)	–C(4)	1.82 (1)
–Cl(2)	2.403 (3)	–C(5)	1.85 (1)
–P(1)	2.639 (3)	P(2)–C(6)	1.84 (1)
–P(2)	2.631 (3)	–C(7)	1.80 (1)
–S(1)	2.399 (3)	–C(8)	1.82 (1)
–O(1)	2.042 (6)	C(5)–C(6)	1.60 (2)
Ta(2)–Cl(3)	2.411 (3)	P(3)–C(9)	1.83 (1)
–Cl(4)	2.453 (3)	–C(10)	1.83 (1)
–P(3)	2.627 (3)	–C(11)	1.84 (1)
–P(4)	2.628 (3)	P(4)–C(12)	1.87 (1)
–S(1)	2.394 (3)	–C(13)	1.83 (1)
–O(1)	2.025 (6)	–C(14)	1.86 (1)
S(1)–C(1)	1.84 (1)	C(11)–C(12)	1.51 (2)
–C(2)	1.83 (1)		

of their occupancy with positional and thermal parameters fixed gave average fractional values of $^1/_3$ and $^2/_3$. Upon least-squares refinements of their positions the atoms shifted away, resulting in an unacceptable arrangement. Their x, y, and z coordinates were therefore fixed, and only isotropic thermal parameters were refined. The final R_1 and R_2 values were equal to 0.049 and 0.060, respectively. In the last difference Fourier map there were four peaks having heights ca. 3 e/Å^3 and located about 1.2 Å from the Ta atoms. All remaining peaks were below 1 e/Å^3. The refined positional parameters and equivalent isotropic thermal parameters are listed in Table II. The components of the anisotropic thermal vibration tensors and the structure factors are available as supplementary material.

Results and Discussion

The formula of the new compound was established by the X-ray crystallographic structure determination. With four formula units in a unit cell belonging to space group $P2_1/c$, no crystallographic symmetry is imposed. Aside from the toluene molecules, which appear to be distributed over two positions to give partial occupation of each, and to be disordered as well, the structure is very clean and precise. It consists of the binuclear unit shown in Figure 1 plus one chlorine atom that lies 2.893 (7) Å away from the oxygen atom. The bond lengths and angles are listed in Tables III and IV.

The O···Cl distance can only be understood by assuming it to be a hydrogen-bonded contact. It is, of course, notoriously difficult to detect the hydrogen atoms in hydrogen bonds, the more so if one of the atoms, Cl in this case, is a second-row atom. In the present case, the strongest peak in the final difference map (except for the ghosts very close to the tantalum atoms) was found close to the line between the O and Cl atoms at a distance of about 2.2 Å from O and 1.0 Å from Cl. This would seem to imply that the unit should be described as O···H–Cl, but we doubt if this residual peak can be taken so

Table IV. Bond Angles (deg) for the $Ta_2Cl_4(dmpe)_2(\mu\text{-}O)(\mu\text{-}SMe_2)$ Molecule

Ta(2)-Ta(1)-Cl(1)	134.84 (7)	P(4)-Ta(2)-S(1)	107.6 (1)
-Cl(2)	106.46 (8)	-O(1)	78.4 (2)
-P(1)	93.98 (6)	S(1)-Ta(2)-O(1)	103.6 (2)
-P(2)	134.47 (6)	Ta(1)-S(1)-Ta(2)	69.32 (7)
-S(1)	55.25 (7)	-C(1)	120.5 (5)
-O(1)	47.7 (2)	-C(2)	123.1 (5)
Cl(1)-Ta(1)-Cl(2)	94.8 (1)	Ta(2)-S(1)-C(1)	122.9 (5)
-P(1)	77.41 (9)	-C(2)	122.0 (5)
-P(2)	86.9 (1)	C(1)-S(1)-C(2)	99.4 (7)
-S(1)	85.3 (1)	Ta(1)-O(1)-Ta(2)	84.2 (2)
-O(1)	155.6 (2)	Ta(1)-P(1)-C(3)	120.4 (4)
Cl(2)-Ta(1)-P(1)	156.9 (1)	-C(4)	118.0 (3)
-P(2)	81.9 (1)	-C(5)	107.6 (4)
-S(1)	92.1 (1)	C(3)-P(1)-C(4)	102.2 (5)
-O(1)	107.6 (2)	-C(5)	103.6 (6)
P(1)-Ta(1)-P(2)	76.08 (9)	C(4)-P(1)-C(5)	103.0 (5)
-S(1)	108.63 (9)	P(1)-C(5)-C(6)	109.7 (7)
-O(1)	78.2 (2)	P(2)-C(6)-C(5)	108.1 (8)
P(2)-Ta(1)-S(1)	169.72 (9)	Ta(1)-P(2)-C(6)	111.9 (4)
-O(1)	86.9 (2)	-C(7)	120.6 (5)
S(1)-Ta(1)-O(1)	102.9 (2)	-C(8)	112.4 (4)
Ta(1)-Ta(2)-Cl(3)	106.26 (7)	C(6)-P(2)-C(7)	104.8 (6)
-Cl(4)	135.42 (8)	-C(8)	104.4 (6)
-P(3)	134.47 (7)	C(7)-P(2)-C(8)	101.0 (6)
-P(4)	93.53 (7)	Ta(2)-P(3)-C(9)	118.8 (4)
-S(1)	55.43 (7)	-C(10)	111.8 (4)
-O(1)	48.2 (2)	-C(11)	110.0 (4)
Cl(3)-Ta(2)-Cl(4)	95.1 (1)	C(9)-P(3)-C(10)	103.3 (6)
-P(3)	81.9 (1)	-C(11)	106.1 (6)
-P(4)	157.4 (1)	C(10)-P(3)-C(11)	106.0 (6)
-S(1)	92.8 (1)	P(3)-C(11)-C(12)	109.9 (8)
-O(1)	106.7 (2)	P(4)-C(12)-C(11)	110.3 (8)
Cl(4)-Ta(2)-P(3)	86.3 (1)	Ta(2)-P(4)-C(12)	106.9 (4)
-P(4)	77.4 (1)	-C(13)	118.1 (4)
-S(1)	85.5 (1)	-C(14)	121.3 (5)
-O(1)	155.7 (2)	C(12)-P(4)-C(13)	103.0 (6)
P(3)-Ta(2)-P(4)	76.4 (1)	-C(14)	103.6 (6)
-S(1)	169.75 (9)	C(13)-P(4)-C(14)	101.8 (6)
-O(1)	86.4 (2)		

seriously. We believe that either an O···H–Cl or an O–H···Cl bond might be present and that we cannot choose between these possibilities. The overall O···Cl distance is close to the low end of the known range of hydrogen bonds between this pair of atoms,[5] but it is certainly not without precedent. For example, O···Cl distances of 2.84 (3) and 2.88 (2) Å have been reported in an $[O(H\cdots Cl)_3]^{2-}$ ion[6] and an O···Cl distance of 2.78 Å is found in $(NH_4)_5[Mo_2Cl_8]Cl\cdot H_2O$.[7]

Given that this O···H···Cl hydrogen bond is present, it is then straightforward to formulate the rest of the structure as a dinuclear tantalum(III) complex. The Ta–Cl distances, with an average value of 2.427 [12] Å, which may be compared with the Ta^{III}–Cl terminal distances in $Ta_2Cl_6(dmpe)_2$, which have an average value of 2.415 [7] Å, are supportive of the assignment of oxidation state III to the metal atoms. Furthermore, the characteristic tendency of Ta^{III} to form Ta=Ta bonds with lengths of about 2.70 Å is displayed here. The central Ta–O–Ta–S bridge structure, with its acute angles at the bridging atoms, 84.2 (2)° at O and 69.32 (7)° at S, and highly obtuse angles, 103.6 (2) and 102.9(2)°, at the metal atoms, with a Ta to Ta distance of 2.726 (1) Å shows unambiguously that a Ta to Ta bond is present. The distance, as noted already, is consistent with its being a double bond. In $Ta_2Cl_6(dmpe)_2$ the Ta=Ta bond length is 2.710 (1) Å and there are a number of other Ta=Ta distances[2] ranging from 2.68 to 2.72 Å.

The oxo- or hydroxo-bridged compound described here is evidently the result of partial hydrolysis, due to traces of water in the solvent or glassware, or otherwise adventitously introduced. It is interesting that the pronounced tendency of Ta^{III} to form dinuclear complexes in which the Ta atoms are joined by a Ta=Ta double bond is again manifested. It is also interesting that in this case the other ligands, apart from the bridging ones, that complete the octahedron about each metal atom, two Cl and one dmpe, are arranged differently from those in $Ta_2Cl_6(dmpe)_2$. In the latter, the two phosphorus atoms are equatorial, i.e., each one is trans to the bridging atoms, whereas here one phosphorus atom is equatorial and the other axial. We do not see any simple electronic explanation for this.

Acknowledgment. We thank the National Science Foundation for financial support.

Registry No. $Ta_2Cl_4(dmpe)_2(\mu\text{-}O)(\mu\text{-}Me_2S)\cdot HCl\cdot C_6H_5CH_3$, 84433-29-4; $Ta_2Cl_6(SMe_2)_3$, 77827-59-9; Ta, 7440-25-7.

Supplementary Material Available: Tables of observed and calculated structure factors and anisotropic thermal vibration parameters (23 pages). Ordering instructions are given on any current masthead page.

---

(5) Pimentel, G. C.; McClellan, A. L. *Annu. Rev. Phys. Chem.* **1971**, *22*, 2532.

(6) Davis, A. R.; Einstein, F. W. B. *Inorg. Chem.* **1975**, *14*, 3030.

(7) Brencic, J. V.; Cotton, F. A. *Inorg. Chem.* **1970**, *9*, 346.