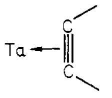
the chlorine atoms toward the tolane, and the coordinated pyridine molecule is 9.3° from coplanarity with the acetylenic unit, Ta(1)-C(20)-C(30). The pyridinium nitrogen atom, N(40), is 3.41 Å from Cl(3) and 3.51 Å from Cl(4). It is possible that the proton may be hydrogen bonded to these chlorine atoms.

Discussion

The most remarkable feature of this structure is the binding of the tolane to the tantalum atom, which is very strong and symmetrical. The Ta-C distances are 2.066 (8) and 2.079 (8) Å; the C-C distance is 1.325 (12) Å, and the two C-(phenyl)-C-C angles are 138.24 (80) and 141.16 (82)°. The benzyne complex[6] (η^5-C_5Me_5)Ta(C_6H_4)(CH_3)$_2$ is the only prior example of such a strongly bonded Ta(η-C≡C) moiety. The Ta-C distances are also very similar to that in the Ta═C bond found in the Ta-benzylidene complex (C_5H_5)$_2$Ta-(CHPh)(CH_2Ph),[7] where the bond length is 2.07(1) Å and the Ta-C_α-C_β angle is 135.2 (7)°. Thus a simple μ-bond representation, **3**, or one with two single bonds, **4**, does not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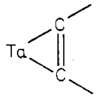
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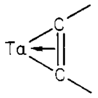
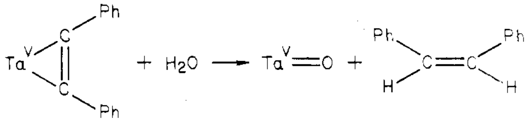

5

seem to account adequately for the structure. We may, therefore, in a purely formal way, consider an arrangement[8] in which even more electrons become involved in the bonding, namely, **5**. The actual electron distribution may, perhaps, be best represented by a combination of **4** and **5**.

The electronic structures implied by **4** and/or **5** are consistent with the hydrolysis of the compound to yield *trans*-stilbene and a whitish precipitate that appears to contain Ta^V:



To the extent that the tantalum bonding involves, at least in part, four-electron donation, it is pertinent to compare this case to the structure of W(CO)(S_2CNEt_2)$_2$(C_2H_2) reported by Ricard et al.[9] They find a W(HCCH) unit with W-C distances of 2.03 Å and a C-C distance of 1.29 Å and on the basis of these facts and other reasoning propose that the acetylene is acting as a four-electron donor. In their case this allows the metal to achieve an 18-electron configuration whereas for our compound Ta reaches only a 16-electron configuration.

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

Registry No. [pyH][$TaCl_4$(py)(PhC≡CPh)], 71763-72-9; $Ta_2Cl_6(SC_4H_8)_3$, 66758-43-8.

Supplementary Material Available: A table of thermal vibration parameters and a table of observed and calculated structure factors (13 pages). Ordering information is given on any current masthead page.

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[6] McLain, S. J.; Schrock, R. R.; Sharp, P. R.; Churchill, M. R.; Youngs, W. J. *J. Am. Chem. Soc.* **1979**, *101*, 263.

[7] Schrock, R. R.; Messerle, L. W.; Wood, C. D.; Guggenberger, L. J. *J. Am. Chem. Soc.* **1978**, *100*, 3793.

[8] We now suggest **5** rather than the structure **7** given in ref 1 since the latter implies too high a formal oxidation state, viz., VII, if taken as implying a four-covalent tolane ligand. Structure **5** would be consistent with a valence state of V for tantalum.

[9] Ricard, L.; Weiss, R.; Newton, W. E.; Chen, G.; McDonald, J. W. *J. Am. Chem. Soc.* **1978**, *100*, 1318.

Contribution from Department of Chemistry,
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Reactions of Niobium(III) and Tantalum(III) Compounds with Acetylenes. 2. Preparation and Structure of $Ta_2Cl_4(\mu\text{-}Cl)_2(\mu\text{-}Me_3CC{\equiv}CCMe_3)(THF)_2$. The Shortest Known Ta-Ta Bond

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The reaction of $Ta_2Cl_6(SC_4H_8)_3$ with $(CH_3)_3CC{\equiv}CC(CH_3)_3$ (di-*tert*-butylacetylene, DTBA) in toluene gives a dark red solution after 2 days. Solvent was removed, and the solid residue recrystallized from THF to give orange crystals of the title compound, Ta_2Cl_6(DTBA)(THF)$_2$. These air-sensitive crystals belong to the monoclinic system with a = 15.181 (9) Å, b = 10.185 (8) Å, c = 17.301 (2) Å, β = 101.48 (6)°, and V = 2628.4 (4) Å^3. With a formula weight of 836.08, d(calcd) is 2.19 g cm^{-3} for Z = 4. The structure was solved and refined in space group $C2/c$ to R_1 = 0.031 and R_2 = 0.044, with hydrogen atoms omitted and all others treated anisotropically. The molecule lies on a crystallographic C_2 axis and has a structure similar to that of $Ta_2Cl_6(SC_4H_8)_3$, with the bridging SC_4H_8 replaced by the DTBA, which is oriented across but not exactly perpendicular to the Ta-Ta axis, and the terminal SC_4H_8 ligands replaced by THF molecules. The Ta-Ta distance, 2.677 (1) Å, is the shortest one known and is consistent with the postulated double bond. The tantalum atoms are seven-coordinate with the THF oxygen atom on one side and the acetylenic carbon atoms on the other side of a median $TaCl_4$ plane. The acetylene can be considered as a two-π-electron donor to each of the Ta atoms.

Introduction

The niobium(III) and tantalum(III) compounds $M_2X_6(SC_4H_8)_3$$^{1-3}$ are among the few readily available, well-defined substances with which to investigate the chemistry of Nb^{III} and Ta^{III}. We have already shown that interesting and novel products can be obtained by reacting them with alkyl cyanides[4a] and acetylenes.[4a,b] Their reactions with acetylenes, RC≡CR′, follow quite different courses depending on the identities of R and R′. In part 1 of this series[4b] we have

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[1] Maas, E. T., Jr.; McCarley, R. E. *Inorg. Chem.* **1973**, *12*, 1096.

[2] Templeton, J. L.; Dorman, W. C.; Clardy, J. C.; McCarley, R. E. *Inorg. Chem.* **1978**, *17*, 1263.

[3] Templeton, J. L., McCarley, R. E. *Inorg. Chem.* **1978**, *17*, 2293.

[4] (a) Cotton, F. A.; Hall, W. T. *J. Am. Chem. Soc.* **1979**, *101*, 5094; (b) *Inorg. Chem.*, preceding paper in this issue.

Table I. Positional Parameters for $Ta_2Cl_6(THF)_2(DTBA)$

atom	*x*	*y*	*z*
Ta(1)	0.44533 (3)	0.23924 (4)	0.17902 (3)
Cl(1)	0.4157 (2)	0.1024 (3)	0.2898 (2)
Cl(2)	0.2905 (2)	0.2892 (3)	0.1457 (2)
Cl(3)	0.4811 (3)	0.3198 (4)	0.0632 (2)
O(10)	0.3950 (5)	0.0607 (7)	0.1033 (4)
C(20)	0.4580 (6)	0.413 (1)	0.2576 (6)
C(22)	0.3235 (7)	0.445 (1)	0.3237 (7)
C(23)	0.3419 (9)	0.591 (1)	0.2096 (9)
C(21)	0.3960 (7)	0.513 (1)	0.2836 (8)
C(24)	0.4469 (9)	0.615 (1)	0.3435 (9)
C(11)	0.4180 (9)	−0.078 (1)	0.1203 (8)
C(13)	0.3297 (14)	−0.061 (1)	−0.0090 (9)
C(12)	0.3547 (12)	−0.155 (1)	0.0563 (9)
C(14)	0.3357 (11)	0.072 (1)	0.0238 (8)

reported in detail on the product obtained with tolane ($R = R' = C_6H_5$).

Another reaction that we have studied is that between $Ta_2Cl_6(SC_4H_8)_3$ and $(CH_3)_3CC{\equiv}CC(CH_3)_3$, 2,2,5,5-tetramethylhex-3-yne (di-*tert*-butylacetylene, DTBA), which gives a dinuclear product. After recrystallization from tetrahydrofuran (THF), this product has the formula $Ta_2Cl_6(DTBA)(THF)_2$. We present here a detailed report on the preparation of this compound and its structural characterization by X-ray crystallography. This is the second of a series of papers describing the varied ways in which acetylenes react with the $M_2X_6(SC_4H_8)_3$ compounds.

Experimental Section

Synthesis and Crystal Preparation. $Ta_2Cl_6(SC_4H_8)_3$ (0.2 g, 0.24 mmol) was dissolved in toluene, and an excess of DTBA was added. The flask was left for 2 days at room temperature, during which time a subtle color change took place, giving a red solution. The solvent was removed under vacuum, and the solid was redissolved in a 10:1 toluene/THF mixture to give a dark orange solution. Cooling this solution to −10 °C overnight yielded well-formed crystals (0.14 g, 70% yield). One of these crystals was sealed in a capillary, in mineral oil, and used for data collection.

The product is very air sensitive, and all manipulations were performed under an inert atmosphere. Solvents were dried and deoxygenated by standard methods; DTBA was vacuum distilled from 4-Å molecular sieves.

X-ray Data Collection. Preliminary photographic examination indicated that the crystal is monoclinic, and ω scans of several reflections showed the crystal to be of good quality. The following cell constants were obtained by centering on 15 intense reflections in the range $16° < 2\theta < 27°$: $a = 15.181$ (9) Å, $b = 10.185$ (8) Å, $c = 17.301$ (2) Å, $\beta = 101.48$ (6), $V = 2628.4$ (4) Å^3. For $Z = 4$ and a formula weight of 836.08, the calculated density is 2.187.

Data were collected at 21 ± 2 °C on a Syntex P$\bar{1}$ diffractometer using Mo Kα radiation. The θ–2θ scan technique was employed by using a variable scan rate of 4.0–24.0°/min with a scan range of 0.9° below Kα_1 to 0.9° above Kα_2. Reflections were collected in the range $0° < 2\theta < 45°$, and a total of 1266 reflections having intensities greater than 3σ were obtained. The intensities of three standard reflections measured every 100 reflections showed no significant change with time. The usual Lorentz and polarization corrections were applied to the data. An empirical absorption correction based on Ψ scans of 5 reflections at $\chi = 90°$ was also applied.

Structure Solution. Systematic absences in the observed reflections were indicative of the space groups *Cc* or *C*2/*c*. The position of the tantalum atom was determined from the three-dimensional Patterson function and refined by the least-squares method, on the assumption of the space group being *C*2/*c*. Subsequent difference maps revealed the rest of the structure and justified the choice of this space group. It was found in this way that the molecular formula of the compound is $Ta_2Cl_6(OC_4H_8)_2[(CH_3)_3CC{\equiv}CC(CH_3)_3]$.

The structure was then refined by the full-matrix least-squares method, with all atoms treated anisotropically. The final values of R_1 and R_2 were 0.031 and 0.044, respectively, and the error in an observation of unit weight was 1.000. Anomalous dispersion effects were included in the calculated structure factors for all atoms. A table of structure factors is available as supplementary material.

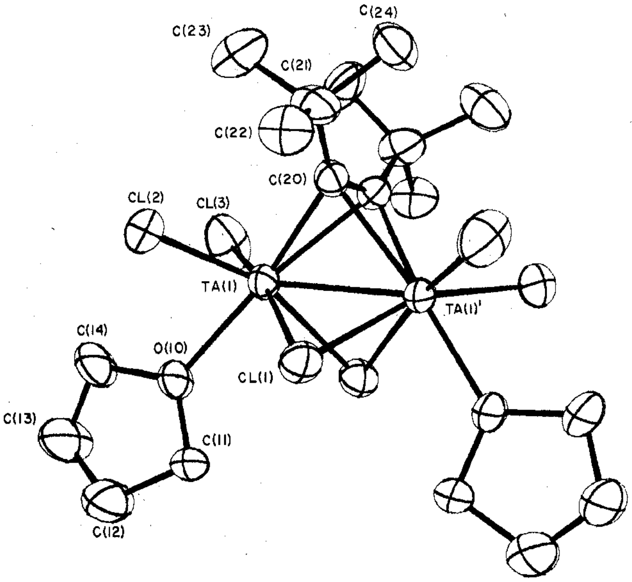

Figure 1. ORTEP computer drawing of the $Ta_2Cl_6(DTBA)(THF)_2$ molecule. Unlabeled atoms are related to those with labels by the twofold rotation axis which is a perpendicular bisector of the acetylenic C–C bond and the Ta–Ta′ bond. Ellipsoids of thermal vibration enclose 40% of the electron density of each atom.

Table II. Selected Bond Distances (Å)

Ta(1)–Ta(1)′	2.677 (1)	C(21)–C(22)	1.574 (16)
–Cl(1)	2.482 (3)	–C(23)	1.591 (20)
–Cl(1)′	2.496 (3)	–C(24)	1.557 (18)
–Cl(2)	2.362 (3)	O(11)–C(11)	1.470 (14)
–Cl(3)	2.327 (4)	–C(14)	1.491 (16)
–O(10)	2.282 (8)	C(11)–C(12)	1.529 (19)
–C(20)	2.214 (11)	C(12)–C(13)	1.470 (21)
–C(20)′	2.416 (11)	C(13)–C(14)	1.470 (20)
C(20)–C(20)′	1.351 (21)		
–C(21)	1.517 (15)		

Computer programs used in solving and refining this structure were those of the Enraf-Nonius structure determination package, on a PDP 11/45 computer. All procedures, definitions, and sources of data required in the structure solution and refinement have been discussed elsewhere.[5]

Results and Discussion

Positional parameters for all atoms are listed in Table I, and the thermal parameters are listed in a table which is available as supplementary material. Figure 1 shows the overall structure and defines the numbering scheme. The bond distances and angles are listed in Tables II and III, respectively.

The molecule resides on a crystallographic twofold symmetry axis that bisects both the C≡C and Ta=Ta bonds. Each Ta atom is seven-coordinate if the acetylenic carbon atoms are each counted separately. The four chlorine atoms form a meridional set, and the oxygen of the THF and the acetylenic carbons complete the coordination. The coordination is similar to that in the $[TaCl_4(py)(PhC{\equiv}CPh)]$ anion[4] where there is also a meridional set of four chlorine atoms about the Ta with a pyridine molecule and the tolane molecule on opposite sides.

The Ta is formally in the oxidation state III if the DTBA is considered to be a neutral donor, and the two Ta centers, each having two 5d electrons, form a metal–metal double bond with a bond length of 2.677 (1) Å. This will be discussed further below.

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(5) Cotton, F. A.; Frenz, B. A.; Stultz, B. R.; Webb, T. R. *J. Am. Chem. Soc.* **1976**, *98*, 2768.

Table III. Selected Bond Angles (Deg)

O(10)-Ta(1)-Cl(1)	84.53 (21)	C(20)'-Ta(1)-Cl(1)	110.26 (28)
-Cl(1)'	81.44 (22)	-Cl(2)	116.01 (25)
-Cl(2)	80.10 (23)	-Cl(3)	84.73 (30)
-Cl(3)	84.00 (23)	-Cl(1)'	84.22 (25)
-C(20)	165.15 (34)	Ta(1)-Cl(1)-Ta(1)'	65.04 (7)
-C(20)'	161.26 (34)	C(20)'-C(20)-C(21)	136.26 (64)
Cl(1)-Ta(1)-Cl(1)'	78.19 (13)	C(20)-C(21)-C(22)	129.91 (83)
-Cl(2)	89.14 (12)	-C(23)	107.47 (92)
-Cl(3)	166.42 (14)	-C(24)	96.00 (79)
Cl(2)-Ta(1)-Cl(3)	96.02 (15)	C(22)-C(21)-C(23)	106.3 (1.0)
-Cl(1)'	158.50 (11)	-C(24)	107.3 (1.2)
Cl(3)-Ta(1)-Cl(1)	92.92 (14)	C(23)-C(21)-C(24)	108.2 (1.2)
C(20)-Ta(1)-Cl(1)	88.91 (29)	C(11)-O(10)-C(14)	109.65 (88)
-Cl(2)	86.51 (11)	O(10)-C(11)-C(12)	105.0 (1.0)
-Cl(3)	103.91 (30)	C(11)-C(12)-C(13)	104.6 (1.2)
-Cl(1)'	104.31 (29)	C(12)-C(13)-C(14)	108.5 (1.3)
		C(13)-C(14)-O(10)	105.2 (1.2)

Table IV. Compounds with Double Bonds between Niobium or Tantalum Atoms

	M-M, Å	ref
$Cs_3Nb_2Cl_9$	2.70	6
$Ta_2Br_6(THT)_3$	2.710 (2)	3
$Nb_2Br_6(SC_4H_8)_3$	2.728 (5)	3
$Cp_2Nb_2(CO)_2(PhC{\equiv}CPh)_2$	2.74	7
$Ta_2Cl_6(THF)_2(DTBA)$	2.677 (1)	this work

The acetylenic carbon atoms, C(20) and C(20)', are not bound symmetrically to the Ta atoms; the bond lengths are 2.416 (11) and 2.214 (11) Å. Although this difference in Ta–C bond lengths is large, it corresponds to a twist of only about 7° from a perfectly perpendicular projection of the C(20)–C(20)' bond upon the Ta–Ta' bond. We believe that this twist can be ascribed entirely to steric factors. Two of the carbon atoms of the *tert*-butyl group, C(22) and C(23), are oriented to minimize contact with Cl(2); this, however, directs C(24) toward Cl(3)'. The acetylenic residue twists so as to increase the C(20)–Ta' distance and thus necessarily to decrease the C(20)–Ta distance to lessen the repulsive interaction between C(24) and Cl(3)'.

The overall structure of this compound is similar to that of the $Ta_2Cl_6(SC_4H_8)_3$ starting material, where the DTBA has replaced the bridging THT. The coordinated THF molecules are labile and can be replaced by a variety of donors.

The short Ta–Ta internuclear distance implies the existence of a bond. In the $M_2Cl_6(SC_4H_8)_3$ compounds and related bromo and iodo analogues, it has been presumed that double bonds are present, and the same assumption seems equally pertinent here. In fact, of all the previously known examples of putative Ta=Ta or Nb=Nb bonds, listed in Table IV, this one is the shortest. It is interesting to note that the Ta=Ta distance here is appreciably longer than that in $W_2S_2(S_2CNEt_2)_4$, 2.530 (2) Å, where a W=W bond has been proposed.[8]

The mean Ta–C bond length, 2.31 Å, the C≡C bond length, 2.35 Å, and the $Me_3CC{\equiv}C$ angle, 136.3°, are all consistent with the view that the bridging acetylene is serving as a two-π-electron donor to each of the metal atoms. They are insignificantly different from those found in a series of $(\eta\text{-}C_5H_5)_2Mo_2(CO)_4(RCCR)$ molecules[9] where such a formulation seems natural and not subject to debate.

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

Registry No. $Ta_2Cl_6(DTBA)(THF)_2$, 73770-95-3; $Ta_2Cl_6(SC_4H_8)_3$, 66758-43-8.

Supplementary Material Available: A table of thermal vibration parameters and a table of observed and calculated structure factors (7 pages). Ordering information is given on any current masthead page.

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(6) Broll, A.; von Schnering, H. G.; Schäfer, H. *J. Less-Common Met.* **1978**, *22*, 243.

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(8) Bino, A.; Cotton, F. A.; Dori, Z.; Sekutowski, J. C. *Inorg. Chem.* **1978**, *17*, 2946.

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