Inorganica Chimica Acta, *85* (1984) 17–21

Reactions of Niobium(III) and Tantalum(III) Compounds with Acetylenes. 5. Preparation and Structure of $[NbCl_2(SC_4H_8)(PhCCPh)]_2(\mu\text{-}Cl)_2$ and its Relationship to Other Alkyne Complexes of Niobium(III) and Tantalum(III)

F. ALBERT COTTON* and WIESLAW J. ROTH

Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A & M University, College Station, Tex. 77843, U.S.A.

Received September 20, 1983

From the reaction of $Nb_2Cl_6(THT)_3$, *THT = tetrahydrothiophene, with tolane, PhCCPh, the compound* $[NbCl_2(THT)(PhCCPh)]_2(\mu\text{-}Cl)_2$, 1, *has been isolated. Its structure, which has been determined by X-ray crystallography, is very similar to that of the corresponding tantalum compound containing* CH_3-*CCBu in place of PhCCPh. It has been shown that* 1 *reacts smoothly with pyridine to give a product,* 2, *that is isomorphous with the previously reported* $(pyH)[TaCl_4py(PhCCPh)]$, 3. *Thus, the precursor of* 3, *previously suggested to be* $TaCl_3(THT)_2(PhCCPh)$, *is likely to be the Ta analog of* 1. *The relationship of* 1 *to the tetranuclear reaction product of* $NbCl_5$ *with tolane is discussed. The crystals of* 1 *belong to the triclinic system, space group* $P\bar{1}$, *and have unit cell dimensions* $a = 10.516(2)$ Å, $b = 12.663(3)$ Å, $c = 9.068(2)$ Å, $\alpha = 100.63(2)°$, $\beta = 91.71(2)°$, $\gamma = 68.36(2)°$, $V = 1102.1(6)$ Å^3, $Z = 1$.

Introduction

Previous work in this Laboratory has shown that complexes of Nb^{III} and Ta^{III} of the type $M_2Cl_6(THT)_3$ [1], where THT denotes tetrahydrothiophene, react readily with alkynes. In some cases polymerization or cyclotrimerization of the acetylene occurs [2], while in others mono- or dinuclear complexes containing the alkynes as ligands are obtained [3–5]. The alkyne can occupy either a bridging or a non-bridging position in dinuclear complexes. It appears that the non-bridging alkyne in a dinuclear complex is bonded in essentially the same way as it would be in a mononuclear complex. In the one binuclear complex with a non-bridging alkyne previously characterized structurally, *viz.*, $[TaCl_2(SC_4H_8)(MeC{\equiv}CBu^t)]_2(\mu\text{-}Cl)_2$, the molecule consists simply of two equivalent halves related by a center of symmetry and united by bridging Cl groups [5]. The one mononuclear complex previously characterized [4], *viz.*, $(pyH)[TaCl_4py(PhCCPh)]$, was not the primary product of the reaction between PhCCPh and $Ta_2Cl_6(THT)_3$, but instead resulted from a reaction between the initial product (not heretofore identified) and pyridine.

The work reported in this paper provides further insight into this area of chemistry in three different ways. (1) It establishes the (expected) homology between the behavior of Nb and Ta compounds of similar structure and composition. (2) It allows us to identify the initial product from which $(pyH)[TaCl_4py(PhCCPh)]$ was obtained. (3) It has an interesting chemical and structural relationship to a recently reported study of the reaction of PhCCPh with $NbCl_5$ [6].

Experimental

Preparations

All manipulations were performed under an atmosphere of argon using standard inert atmosphere techniques. $Nb_2Cl_6(THT)_3$ was prepared according to the literature method [1]. Tolane was purchased from Aldrich Chemical Company.

Preparation of 1

$Nb_2Cl_6(THT)_3$ (0.75 g, 1.1 mmol) and tolane (0.45 g, 2.5 mmol) were dissolved in 60 ml of toluene. A small amount of some insoluble material was removed by filtration and the solution stored in a refrigerator at –5 to 0 °C. Orange crystalline solid, which deposited in the flask within about one month,

---

*Author to whom correspondence should be addressed.

0020-1693/84/$3.00

was isolated by filtration and washed with toluene. The filtrate was then kept at room temperature for about two weeks yielding an additional crop of crystals (combined yield of the isolated product was *ca.* 0.70 g, 0.68 mmol, 62%). X-ray crystallographic analysis carried out on a selected crystal showed that composition of the product corresponded to the formula $Nb_2Cl_6(THT)_2(tolane)_2 \cdot C_6H_5CH_3$, *1*. When the initial mixture of reactants was not stored at lowered temperature the reaction was completed within several days but the product was microcrystalline.

Preparation of 2

$Nb_2Cl_6(THT)_2(tolane)_2 \cdot C_6H_5CH_3$ (0.3 g, 0.29 mmol) was dissolved in 4 ml of degassed pyridine which had been stored over KOH but not distilled to ensure that it was not completely anhydrous. The resulting bright red solution was filtered into a Schlenk tube and layered with *ca.* 10 ml of hexane. Red crystals which formed upon interdiffusion of the solvents were found to have the following triclinic unit cell parameters: a = 11.282(6) Å, b = 12.359(4) Å, c = 9.323(4) Å, α = 101.54(3)°, β = 105.97(7)°, γ = 87.69(5)° and V = 1224(2) Å^3. These values are almost identical with the unit cell parameters of $(pyH)[TaCl_4(py)(tolane)]$, *viz.*, a = 11.345(8) Å, b = 12.335(4) Å, c = 9.352(4) Å, α = 101.12(3)°, β = 106.82(4)°, γ = 87.07(4)°, and V = 1232(1) Å^3, indicating that the Nb complex has the same composition and structure.

X-ray Crystallography

Single crystal X-ray analyses have been carried out by application of general procedures that have already been fully described elsewhere [7]. The crystal parameters and basic information about data collection and structure refinement for $Nb_2Cl_6(THT)_2(tolane)_2$ are summarized in Table I. Corrections for polarization, Lorentz factor, absorption and loss of intensity (10%) were applied to the intensity data.

The position of the Nb atom was obtained from a three-dimensional Patterson function. The remaining non-hydrogen atoms were located by subsequent difference Fourier syntheses and least squares refinements. A molecule of the solvent, toluene, was found to be present in the crystal lattice. It was disordered two-fold around an inversion center. The two orientations were coplanar and related to each other by a rotation of 180° around an axis passing through two ortho carbon atoms (the inversion center was located at the intersection of this axis and the line incorporating the $C-CH_3$ bond). Consequently there were only five independent carbon atom positions in the asymmetric unit cell, three of them with a fractional occupancy ½. Apart from this disorder the solvent molecule refined well giving reasonable bond distances and angles. In the final cycles of refinement that produced the R values in Table I all atoms except those of toluene were treated anisotropically. No peaks of chemical significance were found in the final difference Fourier map.

TABLE I. Summary of Crystallographic Data for $Nb_2Cl_6(THT)_2(tolane)_2 \cdot C_6H_5CH_3$.

Formula	$Nb_2Cl_6S_2C_{43}H_{44}$
Formula weight	1023.5
Space group	$P\bar{1}$
a, Å	10.516(2)
b, Å	12.663(3)
c, Å	9.068(2)
α, degrees	100.63(2)
β, degrees	91.71(2)
γ, degrees	68.36(2)
V, Å^3	1102.1(6)
Z	1
d_{calc}, g/cm^3	1.542
Crystal size, mm	0.4 × 0.15 × 0.07
μ(MoKα), cm^{-1}	9.851
Data collection instrument	Enraf-Nonius CAD-4
Radiation	Mo Kα (λ = 0.71073 Å)
Scan method	$\omega-2\theta$
Data collection range	$0 \leq 2\theta \leq 50°$; ±h, ±k, +l
No. unique data,	2793
$F_o^2 \geq 3\sigma(F_o^2)$	2321
Number of parameters refined	228
R^a	0.058
$R_w{}^b$	0.071
Quality-of-fit indicator^c	1.881
Largest shift/esd, final cycle	0.09

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

Results and Discussion

Both molecules present in the crystal lattice of *1*, namely the complex and the disordered toluene reside on crystallographic inversion centers at ½, ½, ½ and 0, ½, 0, respectively. The former is represented by its ORTEP drawing in Fig. 1. The atomic positional parameters are given in Table II and the molecular dimensions are listed in Tables III and IV.

The coordination geometry of the niobium atoms in *1* is virtually identical to that in $Ta_2Cl_6(THT)_2(Bu^t-C{\equiv}C-Me)_2$ [5]. There is a close match between corresponding bond distances and angles confirming

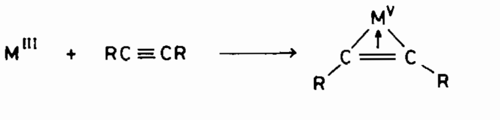
TABLE II. Positional and Isotropic Equivalent Thermal Parameters for $Nb_2Cl_6(THT)_2(tolane)_2 \cdot C_6H_5CH_3$.[a]

Atom	*x*	*y*	*z*	*B (A²)*
Nb	0.40753(8)	0.67838(7)	0.5408(1)	2.28(2)
Cl(1)	0.3779(2)	0.5080(2)	0.6106(3)	2.76(5)
Cl(2)	0.4776(2)	0.7814(2)	0.3900(3)	3.78(6)
Cl(3)	0.5683(2)	0.6721(2)	0.7313(3)	3.70(6)
S	0.2708(2)	0.6311(2)	0.3064(3)	2.94(6)
C(1)	0.2095(8)	0.7729(7)	0.619(1)	2.5(2)
C(2)	0.2860(8)	0.8303(7)	0.673(1)	2.7(2)
C(3)	0.0657(8)	0.7877(7)	0.616(1)	2.8(2)
C(4)	0.0249(9)	0.6939(8)	0.603(1)	4.1(3)
C(5)	−0.1163(10)	0.7093(10)	0.591(2)	5.7(3)
C(6)	−0.2115(10)	0.8185(10)	0.585(1)	5.5(3)
C(7)	−0.1710(10)	0.9157(10)	0.600(1)	5.2(3)
C(8)	−0.0323(9)	0.9003(9)	0.616(1)	3.9(3)
C(9)	0.2870(9)	0.9349(7)	0.776(1)	3.0(2)
C(10)	0.3926(11)	0.9741(8)	0.767(1)	4.7(3)
C(11)	0.3945(13)	1.0707(9)	0.871(2)	6.5(4)
C(12)	0.2924(13)	1.1253(10)	0.983(1)	6.3(4)
C(13)	0.1846(12)	1.0853(9)	0.990(1)	5.6(3)
C(14)	0.1795(11)	0.9905(9)	0.884(1)	4.6(3)
C(15)	0.3755(10)	0.5880(9)	0.131(1)	4.5(3)
C(16)	0.3041(14)	0.6782(11)	0.036(1)	7.4(4)
C(17)	0.1781(17)	0.7558(12)	0.094(1)	10.1(5)
C(18)	0.1518(10)	0.7675(9)	0.260(1)	4.4(3)
C(19)	0.091(1)	0.462(1)	0.085(2)	6.7(3)*
C(20)	0.987(2)	0.525(2)	0.197(3)	5.6(6)*
C(21)	0.856(2)	0.595(1)	0.179(2)	9.8(5)*
C(22)	0.831(3)	0.591(2)	0.047(3)	8.1(8)*
C(23)	0.038(3)	0.473(2)	−0.065(3)	6.3(6)*

[a] Starred atoms were refined isotropically. Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $4/3[a^2B_{11} + b^2B_{22} + c^2B_{33} + ab(\cos\gamma)B_{12} + ac(\cos\beta)B_{13} + bc(\cos\alpha)B_{23}]$.

the above stated exceptation that no significant difference would be observed between Nb and Ta systems.

As before [4, 5] the bond lengths and bond angles in the metal–alkyne unit signify to us that the effective oxidation state of the metal atom is V. We thus regard the reaction of the alkyne with the Nb^{III} as an oxidative addition, as shown schematically in eqn. (1), where electron density in the



$$\mathrm{M^{III}} + \mathrm{RC{\equiv}CR} \longrightarrow \overset{\mathrm{M^{V}}}{\overset{\uparrow}{\mathrm{RC{=}CR}}} \qquad (1)$$

second C–C π bond may be partially donated to a metal *d* orbital, thus strengthening the metal–alkyne interaction and reducing the polarity of the grouping. This mode of bonding, to a metal atom in a high formal oxidation state, is quite different from that found [8] in compounds such as $CpNbCO(PhCCPh)_2$ and $[CpNbCO(PhCCPh)]_2$. In these compounds the Nb–C bond lengths are 2.2 Å, and greater and the mode of bonding is presumably similar to that found in the classical metal–alkene and metal–alkyne complexes formed by elements in group VIII.

From the similarity of unit cell parameters of *2* and $(pyH)[TaCl_4py(PhCCPh)]$, there seems to be no doubt that *2* is $(pyH)[NbCl_4py(PhCCPh)]$. By further analogy between the two systems, it seems highly probable that the reaction of $Ta_2Cl_6(THT)_3$ with tolane first produces the tantalum analog of

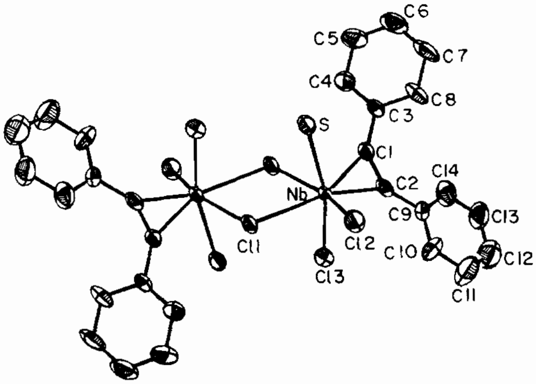


Fig. 1. ORTEP drawing of the $Nb_2Cl_6(THT)_2PhC{\equiv}CPh)_2$ molecule. Atoms are represented by ellipsoids of thermal vibration corresponding to 40% probability. THT carbon atoms have been omitted for clarity. There is a crystallographic inversion center relating the two halves of the molecule.

TABLE III. Interatomic Distances (Å) in the Molecule of $Nb_2Cl_6(THT)_2(tolane)_2$.[a]

Nb–Nb′	4.137(1)[b]	C(4)–C(5)	1.427(10)
Nb–Cl(1)′	2.483(2)	C(5)–C(6)	1.386(12)
Nb–Cl(1)	2.758(2)	C(6)–C(7)	1.427(13)
Nb–Cl(2)	2.354(2)	C(7)–C(8)	1.405(10)
Nb–Cl(3)	2.372(2)	C(9)–C(10)	1.382(10)
Nb–S	2.632(2)	C(9)–C(14)	1.403(10)
Nb–C(1)	2.052(6)	C(10)–C(11)	1.407(11)
Nb–C(2)	2.047(6)	C(11)–C(12)	1.388(14)
S–C(15)	1.839(7)	C(12)–C(13)	1.409(13)
S–C(18)	1.836(7)	C(13)–C(14)	1.410(11)
C(1)–C(2)	1.301(9)	C(15)–C(16)	1.519(12)
C(1)–C(3)	1.453(9)	C(16)–C(17)	1.375(13)
C(2)–C(9)	1.476(9)	C(17)–C(10)	1.506(13)
C(3)–C(4)	1.389(10)		
C(3)–C(8)	1.419(9)		

[a] Numbers in parentheses are estimated standard deviations in the least significant digits. [b] Nonbonding contact.

TABLE IV. Bond Angles (deg.) for $Nb_2Cl_6(THT)_2(tolane)_2$.[a]

Nb'–Nb–Cl(1)'	40.30(4)	Nb–S–C(15)	111.6(3)
Nb'–Nb–Cl(1)	35.61(4)	Nb–S–C(18)	108.8(3)
Nb'–Nb–Cl(2)	118.24(5)	C(15)–S–C(18)	94.7(4)
Nb'–Nb–Cl(3)	84.97(5)	Nb–C(1)–C(2)	71.3(4)
Nb'–Nb–S	81.09(4)	Nb–C(1)–C(3)	149.0(5)
Nb'–Nb–C(1)	126.0(2)	C(2)–C(1)–C(3)	139.4(6)
Nb'–Nb–C(2)	150.8(2)	Nb–C(2)–C(1)	71.7(4)
Cl(1)'–Nb–Cl(1)	75.90(6)	Nb–C(2)–C(9)	144.0(5)
Cl(1)'–Nb–Cl(2)	156.73(6)	C(1)–C(2)–C(9)	144.0(6)
Cl(1)'–Nb–Cl(3)	89.19(7)	C(1)–C(3)–C(4)	121.5(6)
Cl(1)'–Nb–S	82.63(6)	C(1)–C(3)–C(8)	117.9(6)
Cl(1)'–Nb–C(1)	87.5(2)	C(4)–C(3)–C(8)	120.4(7)
Cl(1)'–Nb–C(2)	112.1(2)	C(3)–C(4)–C(5)	120.7(7)
Cl(1)–Nb–Cl(2)	83.25(6)	C(4)–C(5)–C(6)	118.9(8)
Cl(1)–Nb–Cl(3)	83.18(6)	C(5)–C(6)–C(7)	120.9(8)
Cl(1)–Nb–S	83.29(5)	C(6)–C(7)–C(8)	119.7(8)
Cl(1)–Nb–C(1)	157.0(2)	C(3)–C(8)–C(7)	119.3(8)
Cl(1)–Nb–C(2)	165.9(2)	C(2)–C(9)–C(10)	120.7(7)
Cl(2)–Nb–Cl(3)	98.59(7)	C(2)–C(9)–C(14)	117.7(7)
Cl(2)–Nb–S	84.81(7)	C(10)–C(9)–C(14)	121.6(7)
Cl(2)–Nb–C(1)	109.2(2)	C(9)–C(10)–C(11)	119.7(9)
Cl(2)–Nb–C(2)	90.5(2)	C(10)–C(11)–C(12)	120(1)
Cl(3)–Nb–S	165.56(6)	C(11)–C(12)–C(13)	119.7(9)
Cl(3)–Nb–C(1)	112.7(2)	C(12)–C(13)–C(14)	120.6(9)
Cl(3)–Nb–C(2)	85.3(2)	C(9)–C(14)–C(13)	118.2(8)
S–Nb–C(1)	78.9(2)	S–C(15)–C(16)	106.2(5)
S–Nb–C(2)	108.8(2)	C(15)–C(16)–C(17)	114.1(8)
C(1)–Nb–C(2)	37.0(3)	C(16)–C(17)–C(18)	116.1(9)
Nb'–Cl(1)–Nb	104.10(6)	S–C(18)–C(17)	104.5(6)

[a]Numbers in parentheses are estimated standard deviations in the least significant digits.

1, namely $[TaCl_2(THT)(PhCCPh)]_2(\mu\text{-}Cl)_2$. Our previous speculation [4] that the initial product may have been $TaCl_3(THT)_2(PhCCPh)$ is one we would now retract. It is then reasonable to suppose that the Cl-bridged dimer reacts with pyridine to split the bridges, giving, perhaps, $TaCl_3(THT)py(PhCCPh)$ or $TaCl_3py_2(PhCCPh)$ which can then react with (pyH)-Cl, present adventitiously, to afford crystals of (pyH)-$[TaCl_4py(PhCCPh)]$.

An attempt to intercept and identify the second postulated intermediate was made using the niobium system. When *1* was dissolved in CH_2Cl_2-pyridine 9:1) a compound with a monoclinic unit cell having dimensions $a = 7.575(2)$ Å, $b = 31.688(9)$ Å, $c = 10.156(3)$ Å, $\beta = 109.13(2)°$ and $V = 2303(2)$ Å^3 was obtained. Its structure was not refined satisfactorily because of poor crystal quality and rapid decomposition of the crystal. The partially solved structure indicated that the compound is very probably $TaCl_3py_2(PhCCPh)$ or $TaCl_3py(THT)(PhCCPh)$.

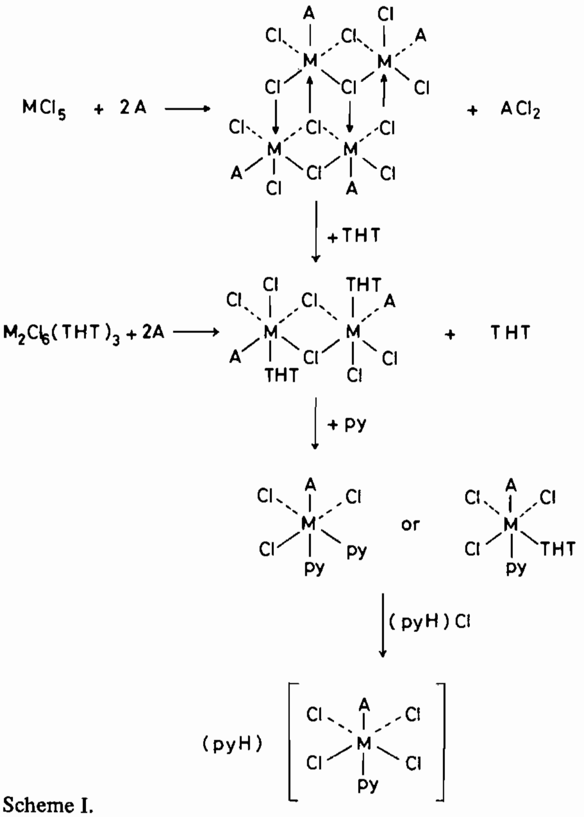
It has recently been reported [6] that the reaction of $NbCl_5$ with tolane follows eqn. (2), so that one mole of tolane serves

$$NbCl_5 + 2PhCCPh \longrightarrow \tfrac{1}{4}[NbCl_3(PhCCPh)]_4 + PhClCCClPh \qquad (2)$$

as a dechlorinating agent while the second one adds to the niobium atom. The authors of this work appear to prefer an oxidation state assignment of III in their product, but, as already noted, we would consider V to be more apt. In any event, we recognize their tetranuclear product to be closely related to the compounds we have been studying, as shown in Scheme I. In the absence of any other donor molecules (*e.g.*, THT or py), '$NbCl_3(PhCCPh)$' tetramerizes so as to allow each metal atom to achieve its preferred coordination number of 6. Reaction with THT, in a molar ratio of THT to Nb of 1 should lead to the formation of our compound *1*.

Acknowledgement

We thank the National Science Foundation for financial support.



Scheme I.

Supplementary Material Available

Tables of anisotropic thermal parameters and structure factors (11 pages). These are available from FAC on request.

References

1 J. L. Templeton and R. E. McCarley, *Inorg. Chem., 17,* 2293 (1978) and references cited therein.

2 F. A. Cotton, W. T. Hall, K. J. Cann and F. J. Karol, *Macromolecules, 14,* 233 (1981).

3 F. A. Cotton and W. T. Hall, *J. Am. Chem. Soc., 101,* 5094 (1979).

4 F. A. Cotton and W. T. Hall, *Inorg. Chem., 19,* 2352, 2354 (1980).

5 F. A. Cotton and W. T. Hall, *Inorg. Chem., 20,* 1285 (1981).

6 E. Hey, F. Weller and K. Dehnicke, *Naturwissenschaften, 70,* 41 (1983).

7 A. Bino, F. A. Cotton and P. E. Fanwick, *Inorg. Chem., 18,* 3558 (1979).

8 A. N. Nesmeyanov, A. I. Gusev, A. A. Pasinskii, K. N. Anisimov, N. E. Kolobova and Y. T. Struchov, *J. Chem. Soc. Comm.,* 1365 (1968), 277 (1969).