

A new type of face-sharing bioctahedral triply bonded diniobium cluster $(\text{PyH})[\text{Nb}_2(\mu\text{-Cl})_2(\mu\text{-THT})\text{Cl}_3(\text{Py})_3](\text{THF})(\text{C}_6\text{H}_6)_{0.5}$, made by a designed synthesis \star

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Abstract

A new type of triply bonded diniobium cluster compound $(\text{PyH})[\text{Nb}_2(\mu\text{-Cl})_2(\mu\text{-THT})\text{Cl}_3(\text{Py})_3](\text{THF})(\text{C}_6\text{H}_6)_{0.5}$, has been synthesized by the reaction of $\text{Nb}_2\text{Cl}_6(\text{THT})(\text{THF})_2$ with stoichiometric quantities of sodium amalgam and pyridine, followed by crystallization from a solvent diffusion system of THF–benzene/hexane. The crystallographic data are as follows: space group $P\bar{1}$, $a = 12.153(2)$, $b = 12.329(4)$, $c = 13.916(2)$ Å, $\alpha = 73.53(2)$, $\beta = 78.69(1)$, $\gamma = 68.99(2)^\circ$, $V = 1856(1)$ Å 3 , $Z = 2$. The Nb–Nb distance, 2.6054(5) Å, is the shortest among face-sharing bioctahedral diniobium and ditantalum clusters. The retention of the cluster core during the synthetic reaction is discussed.

Keywords: Crystal structures; Niobium complexes; Bioctahedral complexes; Triply bonded complexes; Dinuclear complexes; Cluster complexes

1. Introduction

Synthesis of discrete M_2X_8 type and/or face-sharing bioctahedral type diniobium and ditantalum compounds with triple metal–metal bonds remains a challenging topic. In sharp contrast to a wide spectrum of Group 6 chemistry of this kind [1], only recently has a general procedure been developed to synthesize the $\text{M}_2(\mu\text{-THT})_3\text{X}_6$ ($\text{M} = \text{Nb}, \text{Ta}$; $\text{X} = \text{Cl}, \text{Br}$) type compounds [2]. One major problem encountered in this preparative work is a strong tendency of the low-valent metal halides which are either intermediates or products of the reaction to oligomerize. Facile dimerization has been found for the above compounds [2], in which terminal halides become bridging ligands between two units. Larger aggregates, such as trinuclear [3,4], tetranuclear [5,6] and hexanuclear [7] compounds have also frequently been found with an oxidation state between 3 and 2, in which not only bridging but also capping halides exist. Recently a progressive transformation from

a dimer to a trimer and even larger aggregates has been observed [8] for face-sharing $\text{Nb}_2\text{Cl}_7\text{L}_2$ ($\text{L} = \text{PR}_3$) species under ambient conditions.

In the preparation of the $[\text{Cl}_3\text{M}(\mu\text{-THT})_3\text{MCl}_3]^{2-}$ compounds the possibility of oligomerization was probably reduced, or eliminated altogether, by the presence of three $\mu\text{-THT}$ ligands which, unlike bridging Cl^- ligands would not lend themselves to extending their reach to still other metal atoms. In the present work we have succeeded in preserving intact an $\text{Nb}(\mu\text{-THT})(\mu\text{-Cl})_2\text{Nb}$ core during the reduction of the niobium atoms from the III to the II oxidation state.

2. Experimental

2.1. General procedures

All synthetic work and sample handling were carried out under an atmosphere of argon or dinitrogen by using a dry-box or standard vacuum and Schlenk line techniques. Solvents THF, benzene, pyridine and hexane were dried and deoxygenated by refluxing over appropriate drying agents under an atmosphere of dinitrogen for at least 12 h and were distilled freshly before use. Sodium amalgam was prepared by dissolving

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0.46 g of sodium (22 mmol) in 20 ml of triply distilled mercury and was assumed to have a sodium content of 1.0 mmol/ml. $\text{Nb}_2\text{Cl}_6(\text{THT})(\text{THF})_2$ was prepared by the literature method [2,9]. Magnetic susceptibility measurements were carried out on a Johnson Matthey magnetic susceptibility balance at 26 °C.

2.2. Synthesis

$\text{Nb}_2\text{Cl}_6(\text{THT})(\text{THF})_2$ (0.615 g, 1.0 mmol), Na/Hg (2 ml, 2 mmol) and pyridine (0.32 ml, 4.0 mmol) were stirred in THF (20 ml) for 10 h. The solution gradually changed from purple to greenish brown, and some brown precipitate was formed. The solution was filtered through a fine fritted funnel into a long Schlenk tube. After layering 5 ml of benzene, the solution was further layered with 30 ml of hexane. In a fortnight purple–red column-shaped crystals grew on the bottom along with a flocculent brown precipitate. The light brown solution was decanted. The crystalline compound was separated from the precipitate by adding 30 ml of hexane, shaking up the contents, and decanting the suspension after the crystals settled down. Yield 0.18 g, ~20%. It was diamagnetic. NMR characterization was hampered by poor solubility of the compound in common organic solvents, such as hydrocarbons, THF and even dichloromethane.

2.3. X-ray crystallography

Crystals for X-ray diffraction experiments were examined under a layer of mineral oil that had been dried and degassed for at least 1 day by stirring it with several blocks of sodium metal on a vacuum line. A suitable crystal was wedged inside a thin-walled capillary in a steam of argon and sealed by flame.

Unit cell parameters were obtained by indexing 25 reflections which were located and centered in the 2θ range 12–16°, and refined by centering and least-squares fitting of 25 reflections from a preliminary data collection in the 2θ range 36–40°. Axial photography confirmed the cell parameters and the Laue symmetry. Three intensity standards were checked after every 2 h of X-ray exposure, which showed that after an initial ~9% decay there was essentially no further decay. Three orientation standards were checked after every 300 data points, which showed no alteration of the crystal alignment. Apart from conventional corrections for Lorentz and polarization effects, the data set was also corrected for an anisotropic decay, and an empirical absorption correction based on ψ scan data of seven reflections with their χ angles near 90° was applied.

Positions of the two crystallographically independent niobium atoms were deduced from a three-dimensional Patterson map². An ensuing combination of least-

squares refinements and difference Fourier syntheses revealed all the other non-hydrogen atoms. One puckered five-membered ring and two planar six-membered rings were observed in the structure. The five-membered ring and one six-membered ring, which was located on an inversion center, were assigned to a THF molecule and a benzene molecule, respectively.

Since the compound was isolated in only 20% yield, we cannot discount the possibility that this centrosymmetric ‘benzene’ site might be at least partially occupied by disordered molecules of pyridine. The other six-membered ring was located in a general position. The possible assignments of this ring were as a pyridine molecule, a pyridinium ion or a benzene molecule, since X-ray diffraction generally could not conclusively distinguish a carbon atom from a nitrogen atom. However, based on the diamagnetism provided by a magnetic susceptibility measurement, the ring would have to be a pyridinium ion so that the bimetallic center would have an even number of d electrons. The assignment of the nitrogen atom in the pyridinium ring and the oxygen atom in the THF ring was based on their smaller thermal parameters, as compared with those of the other ring atoms, after all these ring atoms had been refined isotropically as carbon atoms to convergence. In the final least-squares refinement all these non-hydrogen atoms were refined anisotropically. The final difference Fourier map was nearly featureless with the two highest peaks in the vicinity of the two metal atoms (<0.5 Å). Since so few peaks which could be assigned as hydrogen atoms had showed up in the final difference Fourier map, no further effort was made to locate and refine hydrogen atoms. All the crystallographic data are listed in Table 1. Positional and equivalent isotropic thermal parameters are listed in Table 2.

3. Results and discussion

Fig. 1 shows the configuration of the cluster anion, in which the two metal atoms are bridged by two chlorine atoms and one THT ligand. One of the Nb atoms is further coordinated by two chlorine atoms and one pyridine ligand, and the other by one chlorine atom and two pyridine ligands to complete an octahedral environment for each metal atom. The stoichiometry indicates that this is a d^3 – d^3 type $\text{Nb}_2(\text{II,II})$ cluster, and the metal–metal distance of 2.6054(5) Å (see Table 3) indicates a strong metal–metal interaction. For comparison, all face-sharing bioctahedral diniobium and ditantalum compounds found so far are listed in Table 4 along with some important average bond lengths. While the above metal–metal bond distance is comparable to those of other triply bonded structures, it is the shortest among the face-sharing bioctahedral diniobium and ditantalum structures.

² Computation was done on a local area VAX cluster, employing the VAX/VMS V5.4 and Enraf-Nonius SDP/VAX software.

Table 1
Crystallographic data for (PyH)[Nb₂Cl₅(THT)(Py)₃](THF)(C₆H₆)_{0.5}

Formula	Nb ₂ Cl ₅ SON ₄ C ₃₁ H ₄₀
Formula weight	879.83
Space group	P $\bar{1}$
Systemic absence	none
<i>a</i> (Å)	12.153(2)
<i>b</i> (Å)	12.329(4)
<i>c</i> (Å)	13.916(2)
α (°)	73.53(2)
β (°)	78.69(1)
γ (°)	68.99(2)
<i>V</i> (Å ³)	1856(1)
<i>Z</i>	2
<i>D</i> _{calc} (g cm ⁻³)	1.573
Crystal size (mm)	0.40 × 0.25 × 0.15
μ (Mo K α) (cm ⁻¹)	10.375
Data collection instrument	Enraf-Nonius CAD4
Radiation (monochromated in incident beam); λ (Å)	Mo K α ; 0.71073
Orientation reflections no.; range, 2θ (°)	25; 36–40
Temperature (°C)	20
Scan method	ω - 2θ
Data collection range, 2θ (°)	4–50
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	6529; 5495
No. parameters refined	397
Transmission factors; max., min.	0.9997, 0.6852
<i>R</i> ^a	0.050
<i>R</i> _w ^b	0.065
Quality-of-fit indicator ^c	1.606
Largest shift/e.s.d., final cycle	0.03
Largest peak (e Å ⁻³)	1.158

$$^a R = \sum ||F_o| - |F_c|| / \sum |F_o|$$

$$^b R_w = [\sum w(|F_o| - |F_c|)^2 / \sum w|F_o|^2]^{1/2}; w = 1/\sigma^2(|F_o|)$$

$$^c \text{Quality-of-fit} = [\sum w(|F_o| - |F_c|)^2 / (N_{\text{obs}} - N_{\text{param}})]^{1/2}$$

Since a number of new members have joined the face-sharing bioctahedral cluster family recently, it can be seen from the comparison presented in Table 4 that in clusters with chloride and thioether ligands, metal–metal distances seem to drop uniformly with the increase of the metal–metal bond order. The following values or average values 2.81, 2.76, 2.70 and 2.61 Å correspond well to bond orders 1(*d*¹–*d*¹), 1.5(*d*¹–*d*²), 2(*d*²–*d*²), and 3(*d*³–*d*³), respectively, which means a decrease of about 0.1 Å for an increase of bond order of one. It is also evident that substitution of chloride for thioether in bridging positions has no major influence on the metal–metal bond, although M–S_{bridging} distances are a little shorter than M–Cl_{bridging} distances. In sharp contrast, nitrogen and oxygen bridges seem to have a much larger influence on the metal–metal distance, which, as compared with chloride and thioether, amounts to 0.17 Å in shortening metal–metal distances and is indicative of the size influence of the ligands. It is interesting to note that in the title structure three terminal sites are occupied by nitrogen, which does not seem to have any discernable effect on the metal–metal bond.

Table 2
Positional and equivalent isotropic thermal parameters for (PyH)[Nb₂Cl₅(THT)(Py)₃](THF)(C₆H₆)_{0.5}

Atom	<i>x</i>	<i>y</i>	<i>z</i>	<i>B</i> _{eq} (Å ²)
Nb(1)	0.27304(3)	0.40579(3)	0.23051(2)	3.362(7)
Nb(2)	0.47217(3)	0.37415(3)	0.29509(2)	3.281(7)
Cl(1)	0.41286(8)	0.51817(8)	0.13001(7)	3.94(2)
Cl(2)	0.44798(8)	0.21962(8)	0.22291(7)	4.03(2)
Cl(3)	0.14989(9)	0.2795(1)	0.31200(9)	5.15(3)
Cl(4)	0.1073(1)	0.5926(1)	0.20434(9)	5.26(3)
Cl(5)	0.5250(1)	0.52471(9)	0.34415(8)	4.96(2)
S	0.28293(9)	0.43210(9)	0.39416(7)	4.04(2)
C(1)	0.2307(4)	0.3455(5)	0.5141(3)	5.7(1)
C(2)	0.1815(6)	0.4321(6)	0.5832(4)	8.7(2)
C(3)	0.1424(7)	0.5569(6)	0.5251(5)	10.9(2)
C(4)	0.2206(5)	0.5776(4)	0.4296(4)	5.9(1)
N(1)	0.2498(3)	0.3876(3)	0.0752(2)	3.88(8)
C(5)	0.1436(4)	0.3882(4)	0.0584(3)	4.8(1)
C(6)	0.1219(4)	0.3874(5)	–0.0359(4)	5.8(1)
C(7)	0.2097(5)	0.3829(5)	–0.1140(4)	5.9(1)
C(8)	0.3189(5)	0.3801(4)	–0.0973(3)	5.5(1)
C(9)	0.3353(4)	0.3805(4)	–0.0018(3)	4.6(1)
N(2)	0.6615(3)	0.3224(3)	0.2132(3)	4.08(8)
C(10)	0.6841(4)	0.3113(4)	0.1171(3)	4.7(1)
C(11)	0.7962(5)	0.2819(5)	0.0682(4)	5.9(1)
C(12)	0.8899(5)	0.2662(5)	0.1196(5)	6.9(2)
C(13)	0.8689(4)	0.2771(5)	0.2168(5)	6.4(1)
C(14)	0.7540(4)	0.3061(4)	0.2619(4)	5.1(1)
N(3)	0.5447(3)	0.2282(3)	0.4298(2)	4.12(8)
C(15)	0.5927(5)	0.1117(4)	0.4269(4)	5.7(1)
C(16)	0.6405(5)	0.0231(5)	0.5088(4)	6.7(2)
C(17)	0.6369(5)	0.0521(5)	0.5959(4)	6.6(1)
C(18)	0.5883(5)	0.1694(5)	0.6024(4)	6.5(2)
C(19)	0.5429(4)	0.2561(4)	0.5173(3)	5.1(1)
N(4)	0.3489(8)	0.8327(6)	0.1241(6)	13.5(3)
C(20)	0.4089(8)	0.9124(8)	0.1072(8)	12.0(3)
C(21)	0.3562(8)	1.0195(7)	0.1175(6)	11.8(3)
C(22)	0.2490(9)	1.0538(7)	0.1525(6)	12.0(3)
C(23)	0.1812(9)	0.978(1)	0.1771(8)	14.2(4)
C(24)	0.2335(8)	0.8622(8)	0.1617(7)	11.7(3)
O	0.7554(9)	0.9020(8)	0.2900(5)	18.8(4)
C(25)	0.873(1)	0.902(1)	0.2391(9)	20.2(6)
C(26)	0.866(1)	0.911(1)	0.136(1)	18.2(6)
C(27)	0.736(1)	0.949(1)	0.1321(8)	15.7(5)
C(28)	0.686(1)	0.898(1)	0.2259(7)	13.9(4)
C(29)	0.921(1)	0.107(1)	0.4682(9)	16.2(5)
C(30)	0.967(1)	0.031(1)	0.4153(9)	19.3(6)
C(31)	1.015(2)	–0.084(1)	0.462(1)	22.2(8)

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

In the new structure M–N distances for pyridine ligands *trans* to the bridging THT ligand are 2.312[2] Å, which is about 0.05 Å longer than the one *trans* to a bridging chloride. Similar *trans* influences can be found elsewhere among the compounds listed in Table 4. In these face-sharing bioctahedral structures, when bridging and terminal THT ligands are *trans* to each other, M–S_{bridging} distances can be shorter than

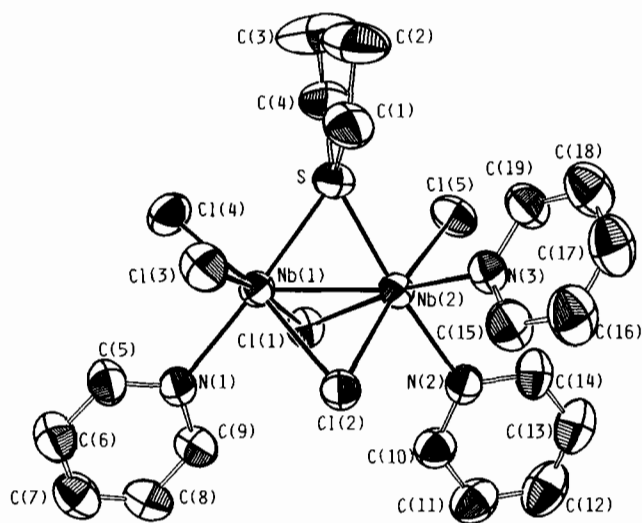


Fig. 1. Configuration of $[\text{Nb}_2\text{Cl}_5(\text{THT})(\text{Py})_3]^-$, showing the atom-labeling scheme and 40% probability thermal ellipsoids.

$\text{M}-\text{S}_{\text{terminal}}$ distances by more than 0.23 \AA . Contrary to the above observation, $\text{M}-\text{Cl}$ bridging distances in these structures are longer than $\text{M}-\text{Cl}$ terminal distances by about 0.05 \AA . It is obvious that the bonding characters of sulfur and halogen are quite different. These bond length data tend to support the following bond strength order: $\text{M}-\text{S}_b > \text{M}-\text{X}_t > \text{M}-\text{X}_b > \text{M}-\text{L}_t$ ($\text{M} = \text{Nb}, \text{Ta}$; $\text{S}_b =$ bridging THT and SMe_2 ; $\text{X}_t =$ terminal halides; $\text{X}_b =$ bridging halides; $\text{L}_t =$ terminal ligands *trans* to S_b).

These bond strength considerations are consistent with experience in the preparative chemistry. For example, from $\text{M}_2\text{X}_6(\text{S}_b)_3$ ($\text{M} = \text{Nb}, \text{Ta}$; $\text{X} = \text{Cl}, \text{Br}$; $\text{S}_b = \text{THT}, \text{SMe}_2$) a number of compounds with the formula $\text{M}_2\text{X}_6(\text{S}_b)_2\text{L}_2$ ($\text{L} =$ halides [16], THF [9,21], PR_3 [21], $\text{P}(\text{R}_2\text{N})_3$ [19]) have been prepared by ligand sub-

stitution reactions, in which L is always in the position *trans* to the S_b ligand. For the $\text{M}_2^{\text{III,III}}(\mu\text{-THT})(\mu\text{-X})_2$ ($\text{X} = \text{Cl}, \text{Br}$) type compounds THT can readily replace $\mu\text{-X}$ to form a $\text{M}_2^{\text{II,II}}(\mu\text{-THT})_3$ core during the reduction reaction [2], while the opposite reaction, i.e., replacement of a $\mu\text{-THT}$ by a halide is much more difficult. So far, only by using a large excess of R_4NCl and taking advantage of low solubility of the product, has $\text{Nb}_2(\mu\text{-THT})(\mu\text{-Cl})_2(\text{THT})_2\text{Cl}_2$ been converted to $[\text{Nb}_2\text{Cl}_9]^{3-}$ in CH_2Cl_2 [16]. Moreover, for the Ta derivative, the reaction can only go as far as $[\text{Ta}_2(\mu\text{-THT})(\mu\text{-Cl})_2\text{Cl}_6]^{2-}$, no matter how much R_4NCl is used or how long the reaction is carried out [16]. In our preparative process, two pyridine ligands have replaced the two THF ligands *trans* to the $\mu\text{-THT}$ ligand, as expected, while the third has replaced a terminal halide ligand instead of a bridging one, so that the skeleton $\text{Nb}_2(\mu\text{-THT})(\mu\text{-Cl})_2$ remains intact. While this result may at first seem bizarre, considering that pyridine cannot be a bridging ligand, the retention of the third THT is understandable. It is also reasonable to assume that if more pyridine were used, a chloride bridge might be ruptured by two pyridine ligands to create an edge-sharing structure, and that further replacement would eventually result in a monomer, such as $\text{MCl}_2(\text{Py})_4$ [22].

As we mentioned above, the $\text{Nb}_2(\mu\text{-THT})(\mu\text{-Cl})_2$ skeleton survives the reduction. One may wonder why the two bridging chlorides do not extend their bridges to form a larger aggregate. As can be seen from the drawing of the configuration, pyridine is a large ligand and its ring atoms can reach the periphery of the two chloride bridges. Thus steric hindrance may prevent other $\text{M}-\text{L}$ entities having easy access to the bridging chlorides. It is fair to note that in our synthetic effort, although the process is reproducible, the yield is rather

Table 3

Selected bond distances (\AA) and angles ($^\circ$) for $(\text{PyH})[\text{Nb}_2\text{Cl}_5(\text{THT})(\text{Py})_3](\text{THF})(\text{C}_6\text{H}_6)_{0.5}$

Bond distances					
Nb(1)–Nb(2)	2.6054(5)	Nb(1)–S	2.420(1)	Nb(2)–S	2.417(1)
Nb(1)–Cl(1)	2.534(1)	Nb(1)–N(1)	2.313(4)	Nb(2)–N(2)	2.310(3)
Nb(1)–Cl(2)	2.5225(9)	Nb(2)–Cl(1)	2.5242(9)	Nb(2)–N(3)	2.265(3)
Nb(1)–Cl(3)	2.440(1)	Nb(2)–Cl(2)	2.515(1)		
Nb(1)–Cl(4)	2.448(1)	Nb(2)–Cl(5)	2.462(1)		
Bond angles					
Cl(1)–Nb(1)–Cl(2)	85.63(3)	Cl(3)–Nb(1)–N(1)	89.52(9)	Cl(2)–Nb(2)–N(2)	84.1(1)
Cl(1)–Nb(1)–Cl(3)	172.29(4)	Cl(4)–Nb(1)–S	89.15(4)	Cl(2)–Nb(2)–N(3)	89.0(1)
Cl(1)–Nb(1)–Cl(4)	89.49(4)	Cl(4)–Nb(1)–N(1)	87.44(8)	Cl(5)–Nb(2)–S	88.47(4)
Cl(1)–Nb(1)–S	97.37(4)	S–Nb(1)–N(1)	176.08(7)	Cl(5)–Nb(2)–N(2)	86.6(1)
Cl(1)–Nb(1)–N(1)	84.55(9)	Cl(1)–Nb(2)–Cl(2)	86.00(4)	Cl(5)–Nb(2)–N(3)	93.5(1)
Cl(2)–Nb(1)–Cl(3)	88.76(4)	Cl(1)–Nb(2)–Cl(5)	90.46(4)	S–Nb(2)–N(2)	174.0(1)
Cl(2)–Nb(1)–Cl(4)	169.53(4)	Cl(1)–Nb(2)–S	97.69(3)	S–Nb(2)–N(3)	89.52(8)
Cl(2)–Nb(1)–S	100.65(3)	Cl(1)–Nb(2)–N(2)	85.87(8)	N(2)–Nb(2)–N(3)	87.3(1)
Cl(2)–Nb(1)–N(1)	82.88(7)	Cl(1)–Nb(2)–N(3)	171.89(8)	Nb(1)–Cl(1)–Nb(2)	62.01(2)
Cl(3)–Nb(1)–Cl(4)	95.17(4)	Cl(2)–Nb(2)–Cl(5)	170.30(3)	Nb(1)–Cl(2)–Nb(2)	62.29(3)
Cl(3)–Nb(1)–S	88.86(4)	Cl(2)–Nb(2)–S	100.95(4)	Nb(1)–S–Nb(2)	65.19(3)

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

Table 4
Comparison of bond distances of face-sharing bioctahedral dinioibium and ditantalum compounds

	M–M	M–X _b ^a	M–L _b ^b	M–X _t ^c	M–L _t ^d	Ref.
d¹–d¹						
[Nb ₂ (OMe) ₉] [–]	2.640[6] ^e		2.069[2] _O		1.996[5]	[10]
Sn[Ta ₂ Cl ₉] ₂ ·C ₆ H ₆	2.812(3)	2.47[1]		2.33[2]		[11]
(Ph ₄ P)[Nb ₂ (OMe) ₃ (SPrS) ₃]	2.901(1)		2.090[2] _O 2.55[2] _S		1.853[7] _O 2.47[2] _S	[12]
Ta ₂ Cl ₂ (NPh)(NH ₂ Ph) ₂ Cl ₄	2.644(1)	2.469[9]	1.98(1) _N	2.35[1]	2.36[1] _N	[13]
d¹–d²						
Ta ₂ Cl(SEt) ₂ (SMe ₂) ₂ Cl ₄	2.758(1)	2.334[1]	2.523[8] _S	2.353[6]	2.706[5] _S	[14]
d²–d²						
Cs ₃ Nb ₂ Cl ₉	2.70(1)					[15]
Cs ₃ Nb ₂ Br ₉	2.77(3)					[15]
Cs ₃ Nb ₂ I ₉	2.96(9)					[15]
(Et ₄ N) ₃ [Nb ₂ Cl ₉]·5CH ₂ Cl ₂	2.7413(3)	2.508[7]		2.456[9]		[16]
(Pr ₄ N) ₃ [Nb ₂ Cl ₉]·6CH ₂ Cl ₂	2.691(2)	2.50[1]		2.45[2]		[16]
Ta ₂ Cl ₆ (THT) ₃	2.681(1)	2.503[9]	2.390[1] _S	2.366[4]	2.629[7] _S	[17]
Ta ₂ Br ₆ (THT) ₃	2.710(2)	2.63[1]	2.393[3] _S	2.516[3]	2.624[3] _S	[18]
Nb ₂ Br ₆ (THT) ₃	2.728(5)	2.63[1]	2.49[3] _S	2.534[6]	2.63[4] _S	[18]
(Et ₄ N) ₂ [Nb ₂ Cl ₈ (THT)]	2.707(2)	2.496[5]	2.415[3] _S	2.44[4]		[16]
(Et ₄ N) ₂ [Ta ₂ Cl ₈ (THT)]	2.6875(8)	2.497[9]	2.382[4] _S	2.42[4]		[16]
Ta ₂ Cl ₆ (SMe ₂) ₃	2.691(1)	2.50[2]	2.378(5) _S	2.372[7]	2.618(5) _S	[17]
Ta ₂ Cl ₆ (SMe ₂)(THF) ₂	2.6695(5)	2.494[1]	2.370[1] _S	2.368[1]	2.23[1] _O	[9]
Nb ₂ Cl ₆ (SMe ₂)(THF) ₂	2.684(2)	2.489[2]	2.406[1] _S	2.375[5]	2.234[1] _O	[9]
Ta ₂ Cl ₆ (SMe ₂)(Me ₂ N) ₃ P ₂	2.704(1)	2.500[7]	2.400[3] _S	2.347[3]	2.726[3] _P	[19]
[Ta ₂ Cl ₆ (THT)] ₂ (dpppe) ₂	2.704(2)	2.50[2]	2.395[7] _S	2.369[6]	2.753[7] _P	[20]
Nb ₂ Cl ₆ (THT)(PEt ₃) ₂	2.718(1)	2.51[2]	2.459[3] _S	2.399[7]	2.677[2] _P	[21]
Nb ₂ Cl ₆ (THT)(THF) ₂	2.684(2)	2.496[1]	2.401(1) _S	2.39[2]	2.401(4) _O	[21]
Ta ₂ Cl ₆ (THT)(PMe ₃) ₂	2.682(3)	2.50[1]	2.422[6] _S	2.375[9]	2.623[8] _P	[21]
(Bu ₄ N)[Nb ₂ Cl ₇ (PEt ₃) ₂]	2.708(3)	2.50[2]		2.403(5)	2.617(6) _P	[8]
(Bu ₄ N)[Nb ₂ Cl ₇ (PMe) ₂]·THF	2.683(1)	2.51[2]		2.40[1]	2.584[7] _P	[8]
d³–d³						
(Et ₄ N) ₂ [Nb ₂ Cl ₆ (THT) ₃]·MeCN	2.632(1)		2.431[4] _S	2.540[9]		[2]
[Na(THF) ₃] ₂ [Nb ₂ Cl ₅ (THT) ₃] ₂	2.610(3)		2.425[9] _S	2.53[3]		[2]
[Na(THF) ₃] ₂ [Nb ₂ Br ₅ (THT) ₃] ₂	2.607(2)		2.424[8] _S	2.70[3]		[2]
[Li(THF) ₂] ₂ [Nb ₂ Cl ₆ (THT) ₃]	2.626(1)		2.392[8] _S	2.52[2]		[2]
Na ₂ [Ta ₂ Cl ₆ (THT) ₃]·1.5THF	2.6156(5)		2.399[7] _S	2.53[2]		[2]
(PyH)[Nb ₂ Cl ₅ (THT)(Py) ₅]·(THF)(C ₆ H ₆) _{0.5}	2.6054(5)	2.524[7]	2.419[2] _S	2.450[9]	2.30[2] _N	this work

^a X_b denotes bridging halides.

^b L_b denotes bridging ligands other than halides.

^c X_t denotes terminal halides.

^d L_t denotes terminal ligands other than halides.

^e Square brackets denote mean deviation from the unweighted arithmetic mean.

poor. The major product is a large amount of intractable precipitate, which, according to our observation on a similar oligomerization system [8], may also consist of large aggregates. Thus, while pyridine has some capacity to keep a chloride-bridged cluster core intact in a designed synthesis for a triply bonded dinioibium cluster, a search for more effective derivatives should be made.

4. Supplementary material

For the crystal structure full tables of bond distances and angles, anisotropic thermal parameters (5 pages); table of observed and calculated structure factors (28

pages); and ORTEP drawings of unit cell contents (2 pages) are available on request from author F.A.C.

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