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A New Bis(μ-sulfido)ditantalum(IV) Edge-Sharing Bioctahedral Molecule and a Reassessment of Some Earlier "Bis(μ-chloro)" Molecules

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After reduction of $TaCl_5$ in toluene with Na/Hg, PhSSPh was added, followed by PMe_2Ph. After appropriate workup, orange crystalline $Ta_2(\mu\text{-}S)_2Cl_4(PMe_2Ph)_4$ was obtained and its crystal structure determined. The compound formed crystals in space group $P\bar{1}$ (a = 10.823 (2) Å, b = 10.991 (4) Å, c = 9.782 (3) Å, α = 107.77 (3)°, β = 113.86 (2)°, γ = 86.58(3)°, Z = 1), and the centrosymmetric molecule has a Ta–Ta distance of 2.8757 (4) Å and a mean Ta–S distance of 2.358 [4] Å. Previously reported $Nb_2Cl_6(EtSCH_2CH_2SEt)_2$ has been obtained in an isomeric form having different relative ring conformations. Crystals in space group $P2_1/a$ (a = 14.838 (5) Å, b = 10.396 (5) Å, c = 16.492 (5) Å, β = 95.4 (3)°, Z = 4) contain molecules in which the chelate rings, each with an anti arrangement of ethyl groups, are related by virtual D_2 symmetry. When the present results as well as several other structures are compared, we are led to propose that three compounds previously reported to be $Nb_2Cl_6(SMe_2)_4$, $Ta_2Cl_6(SMe_2)_4$, and $Ta_2Cl_6(EtSCH_2CH_2SEt)_2$ should be reformulated as having two μ-S groups rather than two μ-Cl groups. This changes the metal atom oxidation states from III to IV and the M–M bond orders from 2 to 1 and thus rationalizes the apparently long M–M bonds.

Introduction

In 1986 there were at least 53 structurally characterized binuclear complexes having edge-sharing bioctahedral structures, and the dependence of these structures on the metal atom oxidation states, number of electrons available for M–M bonding, and the identities of the ligands were reviewed.[1] Since then, no less than 40 new structures have been reported for compounds of this class.[2] While the additional data have in some cases allowed previous correlations to be refined and clarified,[3] there have not yet been any cases where new data have led to any revision of earlier interpretations. In this paper we report some new results that lead us to be virtually certain that some previously reported compounds[4] require reformulation in order to allow their structures to fit naturally into the pattern that accommodates all of the other structures. The point at issue concerns the possibility that sulfur-containing reagents *may* supply sulfur atoms to serve as μ-S groups, while X-ray crystallography cannot distinguish between these and μ-Cl groups insofar as their behavior under refinement is concerned.

Experimental Section

All reactions were carried out under an atmosphere of argon by using Schlenk glassware techniques. Toluene, THF, and hexane were dried over sodium–benzophenone ketyl and freshly distilled before use. Sodium amalgam was prepared in the glovebox by the addition of 1.15 g of sodium to 25 mL of previously deoxygenated mercury and transferred into the reaction flask by a syringe that was pretreated with the solvent used in the reaction. $TaCl_5$ was purchased from Aesar Chemicals; dithiaoctane was purchased from Fairfield Chemicals and freshly distilled prior to use; diphenyl disulfide was purchased from Aldrich Chemicals and pumped over vacuum for 30 min prior to use; PMe_2Ph was purchased from Strem Chemicals. $Nb_2Cl_6(THT)_3$[5] was prepared following the published procedures. Elemental analyses were performed by Galbraith Laboratories and the Microanalysis Laboratory in the Inorganic Chemistry Institution of the Technical University of Munich.

Preparation of $Ta_2S_2Cl_4(PMe_2Ph)_4$. A 2.00-g (5.56-mmol) sample of $TaCl_5$ was placed in a 100-mL three-neck round-bottom flask. A side arm containing 0.61 g (2.80 mmol) of PhSSPh was connected to the flask. After addition of 50 mL of toluene and 5.6 mL of 2 M Na/Hg, the mixture was stirred for approximately 10 min and PhSSPh was added to the flask. After 1.5 h of stirring, 1.60 mL (11.2 mmol) of PMe_2Ph, followed by 5 mL of THF, was added. The red-orange solution was stirred for an additional 40 h and then filtered through 2 cm of Celite; the mercury waste was washed with 20 mL of toluene and filtered. The filtrates were combined, and the solvent was removed under vacuum. The oily residue that remained was washed with 10 mL of hexane and the hexane solution decanted via cannula. The residue was pumped to dryness for 20 h. Addition of 6 mL of toluene completely dissolved the residue to give an orange solution. Subsequent dropwise addition of 50 mL of hexane resulted in the precipitation of an orange powder and some oily residue. The precipitate was collected on a filter stick and treated with a 1-mL toluene/9-mL hexane solution, which washed away an oily residue. The orange precipitate was then redissolved in 10 mL of toluene, and the solution was transferred into a Schlenk tube and layered with first 10 mL of toluene and then 14 mL of hexane. The orange crystalline product began to deposit along the walls of the Schlenk tube as the hexane layer slowly diffused into the toluene solution. Approximate yield: 800 mg, 26%. Anal. Calcd for $C_{32}H_{44}Cl_4P_4S_2Ta_2$: S, 5.72; Cl, 12.66. Found: S, 5.75; Cl, 13.60.

Table I. Crystal Data for $Ta_2Cl_4S_2(PMe_2Ph)_4$ and $Nb_2Cl_6(EtSCH_2CH_2SEt)_2$

compd	$Ta_2Cl_4S_2(PMe_2Ph)_4$	$Nb_2Cl_6(EtSCH_2CH_2SEt)_2$
formula	$Ta_2Cl_4S_2P_4C_{32}H_{48}$	$Nb_2Cl_6S_4C_{12}H_{28}$
fw	1124.47	699.14
space group	$P\bar{1}$	$P2_1/a$
a, Å	10.823 (2)	14.838 (5)
b, Å	10.991 (4)	10.396 (5)
c, Å	9.782 (3)	16.492 (5)
α, deg	107.77 (3)	90.0
β, deg	113.86 (2)	95.4 (3)
γ, deg	86.58 (3)	90.0
V, Å^3	1011 (1)	2532 (3)
Z	1	4
d_{calc}, g/cm^3	1.847	1.833
μ(Mo Kα), cm^{-1}	58.927	18.228
radiation (monochromated in incident beam)	Mo Kα (λ = 0.71073 Å)	
temp, °C	21	21
transm factors: max, min	1.000, 0.761	1.0000, 0.7074
R^a	0.0334	0.0594
$R_w{}^b$	0.0443	0.0737

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

Preparation and Crystallization of $Nb_2Cl_6(EtSCH_2CH_2SEt)_2$. A 0.2-g sample of $Nb_2Cl_6(THT)_3$ was dissolved in 15 mL of toluene. The solution was filtered into a Schlenk tube through a filter stick containing 0.5 cm of Celite. In a separate Schlenk tube, 15 mL of toluene, 5 mL of hexane, and 0.2 mL (1.3 mmol) of $EtSCH_2CH_2SEt$ were mixed, and with a syringe, the mixture was gently placed in a layer over the solution of $Nb_2Cl_6(THT)_3$ in toluene. Slow diffusion of the hexane layer produced deep red crystals of the product. Yield: 130 mg, 79%. Anal. Calcd for $C_{12}H_{28}Cl_6S_4Nb_2$: C, 20.61; H, 4.01; Cl, 30.44; S, 18.32. Found: C, 21.16; H, 4.11; Cl, 29.48, 29.90; S, 16.53, 17.33.

X-ray Crystallography. The basic crystallographic data and the usual information about the collection of data and the refinement of the structure are presented in Table I. The solution and refinement proceeded without any problems. The crystals showed no decay during data

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Table II. Atomic Positional and Equivalent Isotropic Displacement Parameters and Their Estimated Standard Deviations for $Ta_2S_2Cl_4(PMe_2Ph)_4$

atom	x/a	y/b	z/c	B_{eqv},[a] Å^2
Ta(1)	-0.079	0.100	0.049	2.810 (5)
Cl(1)	-0.2977 (2)	-0.0043 (2)	-0.0680 (2)	4.11 (4)
Cl(2)	0.0858 (2)	0.2771 (2)	0.2002 (2)	4.41 (4)
S(1)	0.0434 (2)	-0.0432 (2)	0.1839 (2)	3.82 (4)
P(1)	-0.1448 (2)	0.1695 (2)	0.2982 (2)	3.79 (4)
P(2)	-0.2070 (2)	0.2910 (2)	-0.0610 (2)	3.30 (4)
C(11)	-0.2741 (7)	0.2793 (7)	0.3120 (7)	3.8 (1)
C(12)	-0.2401 (9)	0.4008 (8)	0.4235 (8)	5.0 (2)
C(13)	-0.344 (1)	0.4851 (9)	0.429 (1)	6.1 (2)
C(14)	-0.4772 (9)	0.4485 (9)	0.323 (1)	6.2 (2)
C(15)	-0.5105 (8)	0.3244 (9)	0.217 (1)	5.8 (2)
C(16)	-0.4070 (8)	0.2414 (8)	0.2095 (9)	4.9 (2)
C(17)	0.0027 (8)	0.236 (1)	0.4842 (8)	6.4 (3)
C(18)	-0.2107 (9)	0.0284 (9)	0.3219 (9)	6.0 (2)
C(21)	-0.3751 (7)	0.2475 (7)	-0.2215 (7)	3.7 (2)
C(22)	-0.3855 (9)	0.191 (1)	-0.3730 (9)	5.8 (2)
C(23)	-0.514 (1)	0.157 (1)	-0.493 (1)	7.0 (3)
C(24)	-0.6293 (9)	0.1759 (9)	-0.466 (1)	6.2 (3)
C(25)	-0.6163 (9)	0.232 (1)	-0.316 (1)	6.3 (3)
C(26)	-0.4896 (8)	0.2660 (9)	-0.1927 (9)	5.7 (2)
C(28)	-0.1123 (8)	0.3543 (8)	-0.1464 (8)	4.7 (2)
C(29)	-0.2252 (9)	0.4387 (8)	0.0784 (8)	4.9 (2)

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

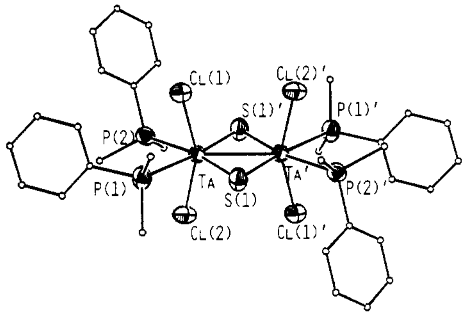

Figure 1. ORTEP drawing of $Ta_2S_2Cl_4(PMe_2Ph)_4$ with the thermal ellipsoids drawn at 50% probability level and carbon atoms assigned arbitrarily small thermal parameters for clarity.

collection, and no problems with disorder occurred during refinement. Absorption corrections were made in each case by the empirical method of ψ scans for several reflections with χ angles close to 90°. In the case of the Ta compound, the molecule resides on a crystallographic center of inversion, while the Nb compound has the molecule on a general position. The positional parameters and equivalent isotropic thermal parameters are listed in Tables II and III. Additional crystallographic information will be found in the supplementary material.

Results

$Ta_2S_2Cl_4(PMe_2Ph)_4$. A drawing of this centrosymmetric molecule is shown in Figure 1, and the principal bond distances and angles are listed in Table IV. It is significant that the four neutral terminal ligands occupy exclusively the equatorial positions, whereas in the majority of $M_2X_6L_4$ species, there are two equatorial ones on one end and two axial ones on the other end.

The main metrical features to note in this structure are as follows: (1) the Ta–Ta bond length of 2.8757 (4) Å, which is in accord with the existence of only a single bond between two Ta(IV) atoms; (2) the small Ta–S–Ta and large S–Ta–S angles, 75.15 (6) and 104.85 (6)°, respectively, which confirm the existence of a metal–metal bond; (3) the Ta–S distances, whose average value, 2.358 [4] Å, is slightly less than the mean Ta–Cl distance, 2.370 [16] Å. This reflects the inherently smaller covalent radius of the bridging sulfur atom compared to that of a bridging Cl atom, since typically (as in the structure below) the bridging M–Cl distances are longer than the terminal ones.

$Nb_2Cl_6(EtSCHCH_2SEt)_2$. The structure of this molecule is shown in Figure 2, and the important distances and angles are listed in Table V. The Nb–Nb distance is 2.682 (3) Å, which is very similar to Nb=Nb distances in several other edge-sharing bioctahedral compounds containing two Nb(III) atoms, bridged by Cl atoms, although it is the shortest one so far observed. The shortest one previously seen (2.696 (1) Å) is in $Nb_2Cl_6(dppm)_2$,[6] and the longest (2.764 (1) Å) is in $Nb_2Cl_6(Et_2NCH_2CH_2NEt_2)_2$.[7] The average Nb–Cl distances are 2.398 [8] Å for the terminal bonds and 2.418 [4] Å for the bridge bonds; the difference, 0.020 (9) Å, is significant at the 2σ level.

This molecule is a geometric isomer of the one reported before.[4] In each case, the ethyl groups of each chelate ring have an anti

Table III. Atomic Positional and Equivalent Displacement Parameters and Their Estimated Standard Deviations for $Nb_2Cl_6(EtSCH_2CH_2SEt)_2$

atom	x	y	z	B_{eqv},[a] Å^2
Nb(1)	0.8512 (1)	0.1328 (2)	0.8011 (1)	3.86 (4)
Nb(2)	0.8421 (1)	0.3454 (2)	0.7086 (1)	4.04 (4)
Cl(1)	0.8444 (5)	-0.0259 (6)	0.6940 (4)	6.6 (2)
Cl(2)	0.8662 (4)	0.2346 (6)	0.9317 (3)	5.6 (2)
Cl(3)	0.9820 (4)	0.2380 (6)	0.7550 (4)	5.7 (2)
Cl(4)	0.7109 (4)	0.2425 (6)	0.7556 (4)	5.1 (1)
Cl(5)	0.8232 (5)	0.2422 (7)	0.5774 (4)	7.6 (2)
Cl(6)	0.8599 (5)	0.5044 (5)	0.8128 (4)	6.4 (2)
S(1)	0.9746 (5)	-0.0131 (6)	0.8788 (5)	7.0 (2)
S(2)	0.7428 (5)	-0.0337 (7)	0.8608 (5)	7.3 (2)
S(3)	0.9526 (5)	0.4743 (8)	0.6201 (5)	8.0 (2)
S(4)	0.7227 (4)	0.5167 (6)	0.6483 (4)	5.4 (2)
C(1)	1.118 (2)	-0.163 (4)	0.840 (2)	13 (1)
C(2)	1.041 (2)	-0.105 (3)	0.807 (2)	16 (1)
C(3)	0.905 (2)	-0.125 (3)	0.928 (2)	18 (1)
C(4)	0.825 (2)	-0.158 (3)	0.893 (2)	17 (1)
C(5)	0.688 (2)	0.031 (3)	0.952 (1)	9.2 (8)
C(6)	0.599 (2)	0.075 (3)	0.934 (2)	12 (1)
C(7)	1.092 (2)	0.639 (3)	0.628 (2)	11.5 (9)
C(8)	1.012 (3)	0.577 (3)	0.684 (2)	13 (1)
C(9)	0.870 (2)	0.584 (2)	0.565 (1)	7.1 (7)
C(10)	0.797 (1)	0.642 (2)	0.613 (1)	6.2 (6)
C(11)	0.659 (2)	0.470 (2)	0.553 (1)	6.9 (7)
C(12)	0.580 (1)	0.390 (3)	0.572 (2)	8.2 (8)

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

Table IV. Selected Bond Distances (Å) and Angles (deg) for $Ta_2Cl_4S_2(PMe_2Ph)_4$[a]

Distances			
Ta(1)–Ta(1)′	2.8757 (4)	P(1)–C(11)	1.813 (7)
Ta(1)–Cl(1)	2.354 (2)	P(1)–C(17)	1.835 (6)
Ta(1)–Cl(2)	2.386 (2)	P(1)–C(18)	1.858 (11)
Ta(1)–S(1)	2.362 (2)	P(2)–C(21)	1.828 (6)
Ta(1)–S(1)′	2.354 (2)	P(2)–C(28)	1.835 (10)
Ta(1)–P(1)	2.689 (2)	P(2)–C(29)	1.834 (8)
Ta(1)–P(2)	2.703 (2)		

Angles			
Cl(1)–Ta(1)–Cl(2)	155.28 (7)	P(1)–Ta(1)–P(2)	93.47 (6)
Cl(1)–Ta(1)–S(1)	99.62 (7)	Ta(1)–S(1)–Ta(1)′	75.15 (6)
Cl(1)–Ta(1)–S(1)′	95.70 (6)	Ta(1)–P(1)–C(11)	122.5 (3)
Cl(1)–Ta(1)–P(1)	80.23 (6)	Ta(1)–P(1)–C(17)	112.5 (3)
Cl(1)–Ta(1)–P(2)	84.76 (6)	Ta(1)–P(1)–C(18)	110.9 (3)
Cl(2)–Ta(1)–S(1)	95.85 (6)	C(11)–P(1)–C(18)	100.5 (4)
Cl(2)–Ta(1)–S(1)′	98.84 (7)	C(17)–P(1)–C(18)	104.2 (5)
Cl(2)–Ta(1)–P(1)	83.72 (7)	Ta(1)–P(2)–C(21)	116.3 (3)
Cl(2)–Ta(1)–P(2)	77.55 (6)	Ta(1)–P(2)–C(28)	110.8 (3)
C(11)–P(1)–C(17)	104.2 (4)	Ta(1)–P(2)–C(29)	118.9 (3)
S(1)–Ta(1)–P(1)	79.73 (6)	C(21)–P(2)–C(28)	102.8 (4)
S(1)–Ta(1)–P(2)	171.09 (5)	C(21)–P(2)–C(29)	105.1 (3)
S(1)–Ta(1)–P(1)′	174.40 (5)	C(28)–P(2)–C(29)	100.7 (4)
S(1)–Ta(1)–P(2)′	82.28 (6)	S(1)–Ta(1)–S(1)′	104.85 (6)

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

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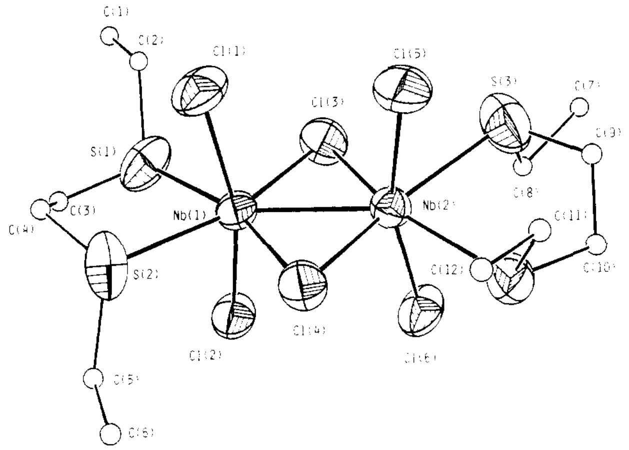

Figure 2. ORTEP drawing of $Nb_2Cl_6(EtSCH_2CH_2SEt)_2$ with the thermal ellipsoids drawn at 50% probability level and the carbon atoms assigned arbitrarily small thermal parameters for clarity.

Table V. Selected Bond Distances (Å) and Angles (deg) for $Nb_2Cl_6(EtSCH_2CH_2SEt)_2$[a]

Distances			
Nb(1)-Nb(2)	2.682 (3)	Nb(2)-Cl(3)	2.416 (6)
Nb(1)-Cl(1)	2.412 (7)	Nb(2)-Cl(4)	2.412 (6)
Nb(1)-Cl(2)	2.391 (6)	Nb(2)-Cl(5)	2.409 (7)
Nb(1)-Cl(3)	2.412 (6)	Nb(2)-Cl(6)	2.380 (6)
Nb(1)-Cl(4)	2.430 (6)	Nb(2)-S(3)	2.657 (8)
Nb(1)-S(1)	2.617 (7)	Nb(2)-S(4)	2.639 (6)
Nb(1)-S(2)	2.618 (8)		

Angles			
Nb(2)-Nb(1)-Cl(1)	98.7 (2)	Nb(1)-Nb(2)-Cl(6)	99.5 (2)
Nb(2)-Nb(1)-Cl(2)	98.2 (2)	Nb(1)-Nb(2)-S(3)	136.7 (2)
Nb(2)-Nb(1)-S(1)	138.7 (2)	Nb(1)-Nb(2)-S(4)	140.0 (2)
Nb(2)-Nb(1)-S(2)	139.4 (2)	Cl(3)-Nb(2)-Cl(4)	112.8 (2)
Cl(1)-Nb(1)-Cl(2)	163.0 (2)	Cl(3)-Nb(2)-Cl(5)	95.9 (2)
Cl(1)-Nb(1)-Cl(3)	93.4 (2)	Cl(3)-Nb(2)-Cl(6)	93.4 (2)
Cl(1)-Nb(1)-Cl(4)	96.9 (2)	Cl(3)-Nb(2)-S(3)	81.4 (2)
Cl(1)-Nb(1)-S(1)	86.6 (2)	Cl(3)-Nb(2)-S(4)	163.1 (2)
Cl(1)-Nb(1)-S(2)	80.7 (2)	Cl(4)-Nb(2)-Cl(5)	93.6 (2)
Cl(2)-Nb(1)-Cl(3)	94.3 (2)	Cl(4)-Nb(2)-Cl(6)	96.5 (2)
Cl(2)-Nb(1)-Cl(4)	94.3 (2)	Cl(4)-Nb(2)-S(3)	163.4 (2)
Cl(2)-Nb(1)-S(1)	79.3 (2)	Cl(4)-Nb(2)-S(4)	83.5 (2)
Cl(2)-Nb(1)-S(2)	87.8 (2)	Cl(5)-Nb(2)-Cl(6)	162.4 (2)
Cl(3)-Nb(1)-Cl(4)	112.4 (2)	Cl(5)-Nb(2)-S(3)	75.9 (3)
Cl(3)-Nb(1)-S(1)	82.6 (2)	Cl(5)-Nb(2)-S(4)	86.8 (2)
Cl(3)-Nb(1)-S(2)	163.7 (2)	Cl(6)-Nb(2)-S(3)	90.8 (2)
Cl(4)-Nb(1)-S(1)	164.3 (2)	Cl(6)-Nb(2)-S(4)	80.1 (2)
Cl(4)-Nb(1)-S(2)	83.5 (2)	S(3)-Nb(2)-S(4)	83.1 (2)
S(1)-Nb(1)-S(2)	81.9 (2)	Nb(1)-Cl(3)-Nb(2)	67.5 (2)
Nb(1)-Nb(2)-Cl(5)	98.0 (2)	Nb(1)-Cl(4)-Nb(2)	67.3 (2)

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

relationship. However, previously the two rings were related so as to give virtual C_{2h} symmetry (C_2 coinciding with the Nb-Nb axis), while in the present case they are related by the three C_2 axes of the group D_2. This is only the second reported example of such isomers based on different combinations of ring conformations, the previous pair being provided by $Ta_2Cl_6(Et_2PCH_2CH_2PEt_2)_2$.[8]

The two conformational isomers of $Nb_2Cl_6(EtSCH_2CH_2SEt)_2$ show very similar bond lengths. For the C_{2h} and D_2 structures, in that order, we have Nb–Nb = 2.688 (2), 2.682 (3) Å, Nb–Cl_b = 2.440 (3), 2.418 [4] Å, Nb–Cl_t = 2.400 (3), 2.398 [8] Å, and Nb–S = 2.64 [1], 2.63 [1] Å. On the other hand there are significant differences in certain angles, most notably in the Cl_t–Nb–Cl_t angles, which are 152.5 (1) and 162.7 [4]°, respectively. This is not surprising, since the different structures give rise to different sets of nonbonded contacts between Cl_t atoms and ethyl groups, and bond angles are less rigid than bond lengths.

Table VI. Comparison of Bond Distances (Å) in Related Structures

compd	M-M dist	M-X_b dist	ref
1. Nb(IV)-Nb(IV) Compounds with Two μ-S Atoms			
$Nb_2(\mu\text{-}S)_2Cl_4(MeCN)_4$	2.866 [3]	2.343 [2]	9
$Nb_2(\mu\text{-}S)_2Cl_4(THT)_4$	2.868 (2)	2.350 (3)	10
$Ta_2(\mu\text{-}S)_2Cl_4(PMe_2Ph)_4$	2.8757 (4)	2.358 [4]	this work
2. M(III)-M(III) Compounds with Two μ-Cl Atoms			
$Ta_2(\mu\text{-}Cl)_2Cl_4(depe)_2$	2.737 (1)	2.441 [5]	8
$Nb_2(\mu\text{-}Cl)_2Cl_4(dppm)_2$	2.696 (1)	2.454 [3]	6
$Ta_2(\mu\text{-}Cl)_2Cl_4(dmpe)_2$	2.710 (1)	2.460 [1]	11
$Nb_2(\mu\text{-}Cl)_2Cl_4(dppe)_2$	2.729 [9]	2.450 [6]	12
$Ta_2(\mu\text{-}Cl)_2Cl_4(dmpm)_2$	2.692 (2)	2.433 (6)	13
$Nb_2(\mu\text{-}Cl)_2Cl_4(dmpm)_2$	2.711 (3)	2.438 [5]	14
$Ta_2(\mu\text{-}Cl)_2Cl_4(PMe_3)_4$	2.721 (1)	2.452 [14]	15
$Nb_2(\mu\text{-}Cl)_2Cl_4(EtSCH_2CH_2SEt)_2$	2.682 (3)	2.418 [4]	this work
3. Four Compounds To Be Reexamined			
$Ta_2(\mu\text{-}Cl)_2Cl_4(SMe_2)_4$	2.829 (1)	2.338 [4]	4
$Nb_2(\mu\text{-}Cl)_2Cl_4(SMe_2)_4$	2.836 [2]	2.336 [2]	4
$Ta_2(\mu\text{-}Cl)_2Cl_4(EtSCH_2CH_2SEt)_2$	2.846 [5]	2.356 [3]	4
$Nb_2(\mu\text{-}Cl)_2Cl_4(EtSCH_2CH_2SEt)_2$	2.688 (2)	2.440 (3)	4

Discussion

The major importance of the results reported here is not in the new compounds themselves but in the light they throw on some previous results, which now require reinterpretation. We shall begin with structural comparisons and the conclusions we draw from them and then discuss the chemical implications.

There have been two previous reports of edge-sharing bioctahedral Nb(IV) compounds with bridging S atoms.[9,10] Table VI lists the results for these and for $Nb_2S_2Cl_4(PMe_2Ph)_4$ reported here. It is clear that there is close agreement among the Nb–Nb and Nb–S distances for all three. In the next section of Table VI are listed several compounds containing Nb(III) or Ta(III) with Cl bridges, including the one reported here. Once again, it is evident that these all have fairly similar M–M and M–Cl_b distances. It is also evident that there are marked differences in these dimensions for the two types of compounds: M(III)–M(III) distances are in the range 2.68–2.74 Å.

Now let us look at the four compounds listed in the last section of Table VI. It is clear that $Nb_2Cl_6(EtSCH_2CH_2SEt)_2$ has dimensions in good accord with those in section 2 of the table and there is no reason to question its formulation. When we turn to the other three compounds in the last section, however, it is obvious that they cry out to be reformulated as M(IV)–M(IV) compounds with S bridges, and that is exactly what we now propose to do with them.

While it is obvious that on a structural basis this reformulation has everything in its favor, it is also necessary to rationalize it on a chemical basis. As a last observation before doing that, it should be emphasized that it is a practical impossibility to discriminate between Cl^- and S^{2-} on the basis of their behavior during refinement of the structure. They are isoelectronic and so close to having identically shaped electron densities that they are indistinguishable in that way.

From a chemical point of view, it is now evident that the abstraction of sulfur atoms from sulfur-containing reagents of all types plays an important role in the preparation of all compounds in which the intention is to place the sulfur-containing ligands *intact* in the product. In preparing $Nb_2(\mu\text{-}S)_2Cl_4(PMe_2Ph)_4$, it was our intention to employ PhSSPh as a source of PhS^- ligands,

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but instead, S–C bonds were broken and S atoms became the bridges. Similarly, in the previous preparations of the last three compounds in Table VI, sulfur atoms were completely removed from the sulfur reagents employed. In the case of $Ta_2(\mu\text{-}S)_2Cl_4(EtSCH_2CH_2SEt)_2$ the source of the μ-S atoms might have been either the Me_2S ligands in the starting material, $Ta_2Cl_6(SMe_2)_3$, or the $EtSCH_2CH_2SEt_2$. For the two $M_2(\mu\text{-}S)_2Cl_4(SMe_2)_4$ compounds, the source might have been either MeSSMe or Me_2S. There has recently been a report showing directly that S can be abstracted from Me_2S in the reaction of a diphosphine with $Ta_2Cl_6(SMe_2)_3$.[16]

A question clearly arises as to why the reaction of $Nb_2Cl_6(SMe_2)_3$ with $EtSCH_2CH_2SEt$ did not lead to a compuond with μ-S groups, as in the case of the tantalum analogue. The answer is that it probably did, but not as a major product. As noted in ref 4, it was thought that in addition to the main form of $Nb_2Cl_6(EtSCH_2CH_2SEt)_2$, for which the structure was there reported, a second form was obtained in small amounts. It was shown to have a unit cell nearly identical with that of what we now recognize to be one form of $Ta_2(\mu\text{-}S)_2Cl_4(EtSCH_2CH_2SEt)_2$. We have now obtained, and described here, an authentic second form of this compound.

The observation that both $M^{III}{}_2(\mu\text{-}Cl)_2$ and $M^{IV}{}_2(\mu\text{-}S)_2$ products can be formed in the same reaction is in accord with another observation we have made. When the preparation[4,17] of "$Ta_2Cl_6(EtSCH_2CH_2SEt)_2$" was carried out on a fairly large scale, the product gave a microanalysis inconsistent with either the $(\mu\text{-}Cl)_2$ or the $(\mu\text{-}S)_2$ product, but indicative of a mixture of both. Evidently the process of transferring sulfur from an organosulfur molecule to the bridge positions in the dinuclear complex proceeds at different relative rates for different cases. There is also the question of which product crystallizes most readily if both are present.

It is clear that considerable work will have to be done to discover how to obtain either the $M^{III}{}_2(\mu\text{-}Cl)_2$ or the $M^{IV}{}_2(\mu\text{-}S)_2$ product in any given system cleanly, in good yield, and with certainty beforehand as to which it will be. Whether Clay and Brown,[17] who used $M_2Cl_6(c\text{-}C_4H_8S)_3$ as starting material, really obtained $M_2Cl_6(EtSCH_2CH_2SEt)_2$ products as they presumed is uncertain. Our repetition of one of their preparations gave a mixture according to the elemental analysis. One might suppose that tetrahydrothiophene would be more resistant to sulfur abstraction than SMe_2, but $Et_2SCH_2CH_2SEt_2$ must also be considered as a sulfur source in these reactions.

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Supplementary Material Available: For both compounds, tables listing full crystallographic data, bond distances and angles, and anisotropic thermal parameters (13 pages); tables of calculated and observed structure factors (25 pages). Ordering information is given on any current masthead page.

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The Dinuclear Palladium(II) Complex of Pyridine-2-thiol. Synthesis, Structure, and Electrochemistry

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Reaction of pyridine-2-thiol (pytH) with $Pd_3(CH_3COO)_6$ gives $[Pd_2(pyt)_4]$ (**1**), but that with $PdCl_2(CH_3CN)_2$ gives $[Pd(pytH)_4]Cl_2$ (**2**), the alkalization of which yields **1**. Reaction of **1** with iodine yields neither a dinuclear $Pd^{II}Pd^{III}$ nor $Pd^{III}Pd^{III}$ complex but tetranuclear $[Pd_4I_2(pyt)_6]$ (**3**). The structures **1**–**3** have been investigated by X-ray crystallography. Two Pd atoms in **1** are bridged by four pyt ligands in such way that two *cis*-PdS_2N_2 units centrosymmetrically face each other. The Pd⋯Pd distance is 2.677 (1) Å. The cation of **2** has a square-planar coordination by four S atoms. All pyridine N atoms are protonated and linked to chloride ions by N–H⋯Cl hydrogen bonds. The tetranuclear complex **3** has C_2 symmetry. Four Pd atoms are disposed in a rhombic configuration and bridged by the pyt ligands, diagonal Pd⋯Pd distances being 3.009 (2) and 7.024 (6) Å. There are two kinds of Pd coordination spheres: PdS_3N and *trans*-$PdISN_2$. Cyclic voltammetry showed that $[Pd_2(pyt)_4]$ undergoes an irreversible one-electron oxidation (E_{pa} = 0.61 V vs Ag/Ag^+) in CH_2Cl_2 containing only TBAP as a supporting electrolyte. In the presence of halide ion, however, the compound undergoes a quasi-reversible two-electron oxidation at much more lower potential ($E_{1/2}$ = 0.13 V for Cl^- and 0.15 V for Br^-) with the uptake of one halide ion. These electrochemical results indicate that one electron per Pd atom is removed from the metal-based MO. Crystal data: $[Pd_2(pyt)_4]\cdot 2CHCl_3$, monoclinic, space group $P2_1/c$, a = 12.518 (2) Å, b = 6.587 (1) Å, c = 18.878 (3) Å, β = 99.09 (1)°, Z = 2; $[Pd(pytH)_4]Cl_2$, triclinic, space group $P\bar{1}$, a = 9.006 (2) Å, b = 10.059 (3) Å, c = 8.329 (2) Å, α = 115.17 (2)°, β = 75.03 (2)°, γ = 113.09 (2)°, Z = 1; $[Pd_4(pyt)_6I_2]\cdot C_3H_7NO$, monoclinic, space group $P2/c$, a = 14.335 (9) Å, b = 9.030 (2) Å, c = 17.401 (9) Å, β = 108.30 (8)°, Z = 4.

Introduction

In contrast to the many dinuclear $Pt^{III}{}_2$ complexes with d^7–d^7 bonds reported in the last decade, no corresponding $Pd^{III}{}_2$ complex has been synthesized as yet. The Pd^{III} oxidation state is unusual but is stabilized by appropriate donor atoms as demonstrated by the isolation of some mononuclear Pd^{III} complexes.[2] Several dinuclear complexes of the [Pd(bridge)$_4$Pd] type have been synthesized and structurally characterized,[3–7] some of which have been electrochemically investigated in order to probe the generation of $[Pd^{III}(bridge)_4Pd^{III}]^{n+}$ complexes. Cotton and co-workers isolated an intriguing complex, $[Pd_2(form)_4]PF_6$ (form = $(p\text{-}CH_3C_6H_4)NCHN(p\text{-}CH_3C_6H_4)^-$), but concluded that both Pd atoms in this seemingly $Pd^{II}Pd^{III}$ dimer are divalent and the odd electron occupies a ligand-based MO,[3] whereas Bear and co-workers detected $[Pd^{II}(\mu\text{-}dpb)_4Pd^{III}]^+$ (dpb = *N*,*N'*-diphenylbenzamidinate) in the electrolyzed solution of $[Pd(\mu\text{-}dpb)_4Pd]$.[7]

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