New sulfido-bridged diniobium(IV) and ditantalum(IV) complexes and a related tetranuclear tantalum(IV) compound

Elizabeth Babaian-Kibala and **F. Albert Cotton***
Department of Chemistry and Laboratory for Molecular Structure and Bonding, Texas A&M University, College Station, TX 77843 (U.S.A.)

(Received October 4, 1990)

Abstract

Designed synthesis has led to the preparation of the compounds $M_2(\mu\text{-}S)_2Cl_4(PMe_3)_4$ (M = Nb, Ta) and an unexpected tetranuclear molecule, $Ta_4S_4Cl_8(PMe_3)_6$, has also been obtained in small yield. All three compounds have been conclusively identified and structurally characterized. The dinuclear compounds have Nb–Nb and Ta–Ta distances of 2.869(1) and 2.865(1) Å, respectively, indicative of single bonds between the metal atoms. $Ta_4S_4Cl_8(PMe_3)_6$ has a central pair of Ta atoms bridged by four S atoms (Ta–Ta = 2.891(1) Å) with square-antiprismatic eight-coordination on each one completed by two *trans* $Cl_2(PMe_3)_2$ sets of ligands. A $TaCl_2(PMe_3)$ unit is then attached to each central Ta atom (Ta–Ta′ = 3.091(1) Å) by two of the sulfur atoms and a terminal Cl atom, thus completing octahedral coordination about each Ta′ atom.

Introduction

In a recent publication [1], from this laboratory four compounds of the edge-sharing bioctahedral type in which Nb^{VI} or Ta^{IV} atoms were bridged by $\mu\text{-}S^{2-}$ ligands were described, and it was shown how these compounds can be distinguished from structurally similar M^{III} compounds with $\mu\text{-}Cl^-$ ligands, with which several of them had earlier been confused. In several of these μ-S compounds, including the three that had been mistaken for μ-Cl compounds, the μ-S atoms were of adventitious origin, that is to say, they had been extracted from organosulfur molecules.

We decided to explore the chemistry of these compounds by seeking synthetic methods designed expressly to produce $(\mu\text{-}S)_2$ compounds. In this we have been successful and we can report here the preparation and characterization of the homologous Nb and Ta compounds $M_2(\mu\text{-}S)_2Cl_4(PMe_3)_4$. In addition, it has also been found that a remarkable tetranuclear tantalum compound, $Ta_4S_4Cl_4(PMe_3)_6$, is formed in small quantities. As will be shown, the structure of this compound raises some interesting speculation as to whether it is simply a byproduct or perhaps a precursor to the binuclear one.

Experimental

All manipulations were carried out using standard Schlenk techniques or glove box procedures. $NbCl_5$ and $TaCl_5$ were purchased from Aesar Chemicals and used without further purification. PMe_3 was purchased from Strem Chemicals, and sodium metal was purchased from Fisher Scientific; mercury was triply distilled grade by D. F. Goldsmith Chemical and Metal Corporation and was degassed prior to use. Sodium amalgam for the reactions was measured and transferred into the reaction flask via a syringe which was pretreated with the solvent used during the reaction.

Benzene, toluene, tetrahydrofuran and hexane were kept over molecular sieves for at least four weeks then further dried over potassium–sodium benzophenone ketyl and were allowed to reflux over the drying agent at least 8 h before use. $NbCl_4(THF)_2$ was prepared following the published procedure [2].

Syntheses

$Ta_2S_2Cl_4(PMe_3)_4$ *(1) and* $Ta_4S_4Cl_8(PMe_3)_6$ *(2)*

$TaCl_5$ (1.0 g, 2.8 mmol), Li_2S (0.13 g, 2.28 mmol) and 20 ml toluene were placed in a 100 ml three neck flask, and 0.4 ml of 2 M Na/Hg was added. The mixture was stirred for 1 h. Addition of 10 ml of THF resulted in the formation of green solution

---

*Author to whom correspondence should be addressed.

0020-1693/91/$3.50

TABLE 1. Crystal data for $Ta_2S_2Cl_4(PEt_3)_4$, (**1**), $Ta_4S_4Cl_8(PMe_3)_6$, (**2**) and $Nb_2S_2Cl_4(PEt_3)_4$, (**3**)

Compound	**1**	**2**	**3**
Formula	$C_{12}H_{36}Cl_4P_4S_2Ta_2$	$C_{22}H_{54}Cl_8P_6S_4Ta_4$	$C_{12}H_{36}Cl_4Nb_2P_4S_2$
Formula weight	872.15	1640.19	696.07
Space group	$P2_1/n$	$P2_1/n$	*Pbca*
a (Å)	9.921(2)	11.127(5)	14.035(4)
b (Å)	13.171(2)	10.230(2)	13.354(4)
c (Å)	10.991(3)	19.623(4)	15.117(4)
α (°)	90.0	90.0	90.0
β (°)	93.39(2)	97.02(2)	90.0
γ (°)	90.0	90.0	90.0
V (Å^3)	1433(1)	2217(1)	2836(1)
Z	2	2	4
D_{calc} (g/cm^3)	2.020	4.194	3.260
μ(Mo Kα) (cm^{-1})	82.775	212.60	30.378
Radiation (monochromated in incident beam)		Mo Kα (λ=0.71073 Å)	
Temperature (°C)	21	21	21
Transmission factors max, min.	1.0000, 0.8417	0.9999, 0.2707	0.9995, 0.9722
R^a	0.0309	0.0468	0.0335
$R_w{}^b$	0.0430	0.0772	0.0573

[a] $R = \Sigma||F_o| - |F_c||/\Sigma|F_o|$.

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

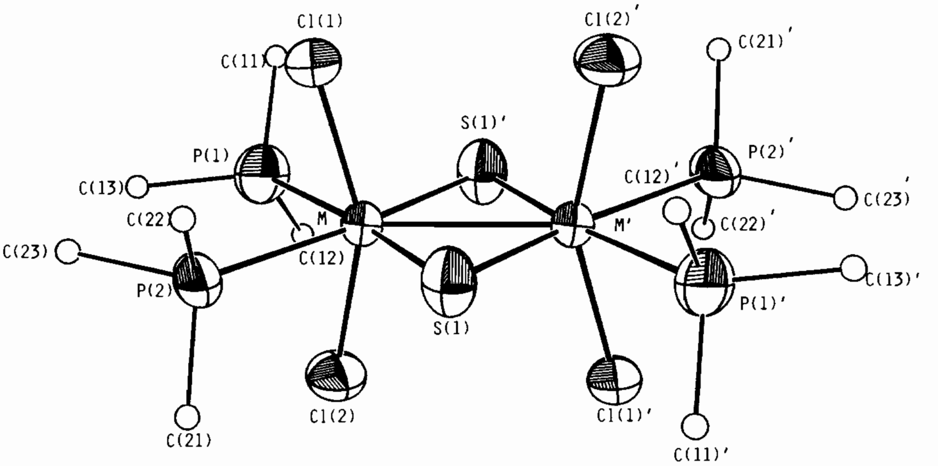

Fig. 1. A drawing depicting the isostructural $M_2(\mu\text{-}S)_2Cl_4(PMe_3)_4$ molecules (actually drawn with the dimensions of the Ta compound). Carbon atoms are represented by arbitrarily small circles for clarity, while the others are shown by thermal displacement ellipsoids drawn at the 30% probability level.

which within 2–3 min began to change into dark orange. After stirring for 6 h, PMe_3 (0.56 ml, 5.5 mmol) was added and the mixture stirred for 20 h at room temperature. The resulting solution was then filtered into a Schlenk tube and gently layered with 15 ml of isomeric hexanes. After two weeks the Schlenk tube contained orange crystals of $Ta_2S_2Cl_4(PMe_3)_4$ (*c.* 20%), small amounts of green crystals of $Ta_4S_4Cl_8(PMe_3)_6$ (~2%) and some green oil. In order to try to synthesize these two complexes separately many reactions were tried with different molar ratios of reactants (1:1:1.5, 1:1.5:1.5, 1:1.5:2; for Ta, S, PMe_3, respectively), different reaction times (2–20 h), and different temperatures (−15, −78°C). None of these experiments led to significantly different results. These reactions all resulted in 20–30% yields of **1**, a few crystals of **2** and an amount of the green oil that varied moderately from reaction to reaction.

$Nb_2S_2Cl_4(PMe_3)_4$ (3)

$NbCl_4(THF)_2$ (0.76 g, 2.0 mmol), Li_2S (0.09 g, 2.0 mmol) and 25 ml THF were stirred for 1 h. To the resulting red solution, PMe_3 (0.41 ml, 4.0 mmol) was

TABLE 2. Positional and isotropic equivalent displacement parameters for $Ta_2S_2Cl_4(PMe_3)_4$

Atom	x	y	z	B_{eq} (Å^2)
Ta(1)	0.03673(4)	0.05044(3)	0.11260(3)	3.130(7)
Cl(1)	0.0881(3)	0.2173(2)	0.0469(3)	4.74(6)
Cl(2)	0.0134(3)	−0.0800(2)	0.2587(3)	5.29(7)
S(1)	0.1803(3)	−0.0389(3)	−0.0136(3)	4.92(6)
P(1)	−0.1080(4)	0.1505(3)	0.2119(3)	5.50(7)
P(2)	0.2729(3)	0.0773(2)	0.2425(3)	5.01(7)
C(11)	−0.195(2)	0.261(1)	0.208(2)	9.3(4)
C(12)	−0.245(2)	0.071(1)	0.323(2)	10.2(5)
(C13)	−0.037(2)	0.203(2)	0.417(2)	15.3(8)
C(21)	0.349(2)	−0.036(1)	0.303(2)	14.8(5)
C(22)	0.401(2)	0.133(2)	0.156(2)	11.5(5)
C(23)	0.301(2)	0.164(2)	0.371(2)	15.4(7)

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

TABLE 3. Positional and isotropic equivalent displacement parameters for $Nb_2S_2Cl_4(PMe_3)_4$

Atom	x	y	z	B_{eq} (Å^2)
Nb(1)	0.07596(4)	0.05196(4)	0.04376(3)	2.26(1)
Cl(1)	0.0732(1)	0.2128(1)	−0.0261(1)	3.68(3)
Cl(2)	0.1356(1)	−0.0688(1)	0.1457(1)	3.84(3)
S(1)	0.0873(1)	−0.0527(1)	−0.0812(1)	3.61(3)
P(1)	0.0855(1)	0.1583(1)	0.1956(1)	3.47(4)
P(2)	0.2616(1)	0.0832(1)	0.0048(1)	3.32(3)
C(11)	0.0362(9)	0.2838(6)	0.1938(6)	8.0(3)
C(12)	0.0177(6)	0.0959(7)	0.2845(4)	5.4(2)
C(13)	0.2005(6)	0.1761(8)	0.2504(6)	7.2(2)
C(21)	0.3454(6)	−0.0155(7)	0.0368(7)	7.3(3)
C(22)	0.2798(6)	0.0945(8)	−0.1160(6)	6.8(2)
C(23)	0.3200(6)	0.1978(6)	0.0425(6)	6.8(2)

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

added. After stirring for 20 h, the solution was filtered and layered with 20 ml of hexanes. Orange–brown crystals of $Nb_2S_2Cl_4(PMe_3)_4$ began to grow after 12 days (yield ~30%).

X-ray crystallography

All procedures for experimental and computational phases of the X-ray work were standard ones that have been referenced previously in publications from this laboratory, see, for example, ref. 1.

These air sensitive Nb and Ta crystals were examined under a layer of mineral oil which was previously treated with sodium and degassed for at least 8 h. The intensity data were all corrected for Lorentz and polarization effects and empirical absorption corrections were made in each case by the method of psi scans for several reflections with χ angle close to 90°. A summary of the data collection parameters for all the crystal structures is listed in Table 1. The three standard reflections monitored throughout the data collection showed no decomposition of any of the crystals. In each case Patterson interpretation employing the SHELXS-86 program revealed the Ta, S, Cl and P atoms. Alternate least-squares refinements and difference Fourier syntheses located the carbon atoms of the PMe_3. Ultimately, all the atoms were refined anisotropically.

Results

Compounds **1** and **3** are the intended synthetic targets, $M_2(\mu\text{-}S)_2Cl_4(PMe_3)_4$ with M=Ta and Nb, respectively. A drawing showing both structures and the atom numbering scheme used in the Tables is presented in Fig. 1. The atomic positional parameters for these compounds are listed in Tables 2 and 3. Surprisingly, these very similar compounds do not form isomorphous crystals, but in each case the molecules reside on crystallographic inversion centers that lie at the midpoints of the M–M bonds. Table

TABLE 4. Selected bond distances and angles in the $M_2(\mu\text{-}S)_2Cl_4(PMe_3)_4$ molecule

	M = Nb	M = Ta
Distances (Å)		
M–M′	2.869(1)	2.865(1)
M–Cl(1)	2.395(2)	2.378(3)
M–Cl(2)	2.384(2)	2.373(3)
M–S(1)	2.356(2)	2.361(3)
M–S(1)′	2.362(2)	2.360(3)
M–P(1)	2.703(2)	2.676(4)
M–P(2)	2.704(2)	2.696(3)
Angles (°)		
Cl(1)–M–Cl(2)	153.96(6)	155.0(1)
Cl(1)–M–S(1)	100.38(6)	97.8(1)
Cl(1)–M–S(1)′	94.96(6)	97.2(1)
Cl(1)–M–P(1)	84.45(6)	82.9(1)
Cl(1)–M–P(2)	77.35(5)	81.0(1)
Cl(2)–M–S(1)	95.33(6)	97.1(1)
Cl(2)–M–S(1)′	100.87(6)	98.2(1)
Cl(2)–M–P(1)	77.85(5)	80.5(1)
Cl(2)–M–P(2)	84.66(6)	81.6(6)
S(1)–M–S(1)′	105.10(6)	105.3(1)
S(1)–M–P(1)	171.77(6)	174.7(1)
S(1)–M–P(2)	81.45(5)	80.8(1)
S(1)–M–P(1)	89.94(6)	79.8(1)
S(1)′–M–P(2)	170.83(6)	173.9(1)
P(1)–M–P(2)	93.22(5)	94.1(1)
M–S(1)–M′	74.90(5)	74.75(8)

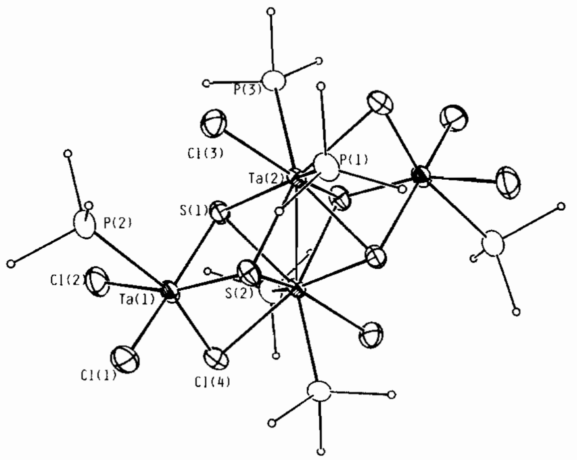

Fig. 2. The structure of the centrosymmetric $Ta_4S_4Cl_8(PMe_3)_6$ molecule. Most atoms are represented by ellipsoids of thermal displacement at the 10% probability level, while carbon atoms are arbitrarily small.

4 lists the principal bond lengths and angles for **1** and **3**.

Compound **2** forms centrosymmetric molecules which reside on inversion centers in space group $P2_1/n$, with the positional parameters listed in Table 5. A drawing of the molecule is shown in Fig. 2, and principal distances and angles are listed in Table 6.

TABLE 5. Positional and isotropic equivalent displacement parameters for $Ta_4S_4Cl_8(PMe_3)_6$

Atom	*x*	*y*	*z*	B_{eq} (Å^2)
Ta(1)	0.26107(6)	0.11588(7)	0.05932(3)	2.03(1)
Ta(2)	0.39287(5)	−0.03984(6)	−0.04432(3)	1.57(1)
S(1)	0.4312(4)	0.1915(4)	0.0045(2)	1.99(7)
S(2)	0.4147(4)	−0.0483(4)	0.0870(2)	2.06(7)
Cl(1)	0.1418(4)	0.0201(5)	0.1399(2)	3.33(9)
Cl(2)	0.1563(4)	0.3192(5)	0.0336(3)	3.43(9)
Cl(3)	0.3736(4)	−0.1756(4)	−0.1510(2)	2.87(8)
Cl(4)	0.1685(4)	0.0101(4)	−0.0343(2)	2.76(8)
P(1)	0.2987(4)	0.1151(5)	−0.1517(2)	2.46(9)
P(2)	0.3123(4)	0.2647(5)	0.1764(3)	3.0(1)
P(3)	0.2726(4)	−0.2647(4)	−0.0196(2)	2.41(8)
C(11)	0.398(2)	0.147(3)	−0.216(1)	7.3(6)
C(12)	0.169(2)	0.047(2)	−0.205(1)	4.1(4)
C(13)	0.247(2)	0.275(2)	−0.136(1)	4.5(4)
C(21)	0.394(2)	0.421(2)	0.167(1)	3.8(4)
C(22)	0.389(2)	0.185(2)	0.2537(9)	3.7(4)
C(23)	0.167(2)	0.323(2)	0.2064(9)	4.3(5)
C(31)	0.367(2)	−0.412(2)	−0.018(1)	5.3(6)
C(32)	0.145(2)	−0.304(2)	−0.082(1)	4.5(5)
C(33)	0.201(2)	−0.286(2)	0.0592(8)	3.4(4)

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

Discussion

The homologous $M_2(\mu\text{-}S)_2(PMe_3)_4$ molecules have the type of structure in which all four neutral ligands occupy equatorial sites, making the two metal atoms equivalent and allowing the $M_2S_2Cl_4P_4$ core to have D_{2h} symmetry. This type of structure is common for $M_2(\mu\text{-}X)_2Y_4L_4$ molecules, but there are also many that have the structure in which there are two axial L ligands on one metal atom and two equatorial ones on the other. There is no way known to predict in general which one will occur in any given case. For example $Ta_2Cl_6(PMe_3)_4$ has the ax, ax, eq, eq structure [3]. It is noteworthy, however, that all of the group 5 molecules of the $M_2(\mu\text{-}S)_2Cl_4L_4$ type (with L = Me_2S, $PhMe_2P$ and now Me_3P) have the all-equatorial arrangement.

As pointed out previously, the M–M and M–S distances are characteristic of the $M^{IV}(\mu\text{-}S)_2M^{IV}$ unit. In the present cases, these are very similar to those previously found. The established ranges are now: Nb–Nb, 2.84–2.87; Ta–Ta, 2.83–2.87; Nb–S, 2.33–2.36; Ta–S, 2.33–2.36 Å.

We now discuss **2**, the tetranuclear tantalum compound. This has a central $Ta(\mu\text{-}S)_4Ta$ unit with *trans* $Cl_2(Me_3P)_2$ sets of ligands on each end. To this are

TABLE 6. Selected bond distances (Å) and angles (°) for $Ta_4S_4Cl_8(PMe_3)_6$

Distances					
Ta(1)–Ta(2)	3.091(1)	Ta(1)–P(2)	2.757(5)	Ta(2)–Cl(3)	2.499(4)
Ta(1)–S(1)	2.416(4)	Ta(2)–Ta(2)′	2.891(1)	Ta(2)–Cl(4)	2.580(4)
Ta(a)–S(2)	2.410(4)	Ta(2)–S(1)	2.569(4)	Ta(2)–P(1)	2.740(4)
Ta(1)–Cl(1)	2.395(5)	Ta(2)–S(1)′	2.544(4)	Ta(2)–P(3)	2.734(5)
Ta(1)–Cl(2)	2.407(5)	Ta(2)–S(2)	2.561(4)		
Ta(1)–Cl(4)	2.268(4)	Ta(2)–S(2)′	2.557(4)		
Angles					
S(1)–Ta(1)–S(2)	75.6(1)	Ta(1)–Ta(2)–Ta(2)′	83.20(2)	S(2)–Ta(2)–Cl(3)	144.3(1)
S(1)–Ta(1)–Cl(1)	162.3(1)	S(1)–Ta(2)–S(1)′	111.1(1)	S(2)–Ta(2)–Cl(4)	84.4(1)
S(1)–Ta(1)–Cl(2)	90.9(2)	S(1)–Ta(2)–S(2)	70.4(1)	S(2)–Ta(2)–P(1)	140.7(1)
S(1)–Ta(1)–Cl(4)	95.5(1)	S(1)–Ta(2)–S(2)′	71.9(1)	S(2)–Ta(2)–P(3)	77.4(1)
S(1)–Ta(1)–P(2)	95.8(1)	S(1)–Ta(2)–Cl(3)	144.9(1)	S(2)′–Ta(1)–Cl(3)	84.9(1)
S(2)–Ta(1)–Cl(1)	90.1(2)	S(1)–Ta(2)–Cl(4)	84.7(1)	S(2)′–Ta(2)–Cl(4)	144.3(1)
S(2)–Ta(1)–Cl(2)	163.9(2)	S(1)–Ta(2)–P(1)	77.6(1)	S(2)′–Ta(2)–P(1)	78.5(1)
S(2)–Ta(1)–Cl(4)	95.1(1)	S(1)–Ta(2)–P(3)	140.5(1)	S(2)′–Ta(2)–P(3)	143.3(1)
S(2)–Ta(1)–P(2)	97.3(1)	S(1)′–Ta(2)–S(2)	72.3(1)	Cl(3)–Ta(2)–Cl(4)	100.9(1)
Cl(1)–Ta(1)–Cl(2)	101.5(2)	S(1)′–Ta(2)–S(2)	70.8(1)	Cl(3)–Ta(2)–P(1)	72.0(1)
Cl(1)–Ta(1)–Cl(4)	96.1(2)	S(1)′–Ta(2)–Cl(3)	84.4(1)	Cl(3)–Ta(2)–P(3)	71.8(1)
Cl(1)–Ta(1)–P(2)	75.5(2)	S(1)′–Ta(2)–Cl(4)	144.4(1)	Cl(4)–Ta(2)–P(1)	70.2(1)
Cl(2)–Ta(1)–Cl(4)	94.7(2)	S(1)′–Ta(2)–P(1)	142.7(1)	Cl(4)–Ta(2)–P(3)	69.7(1)
Cl(2)–Ta(1)–P(2)	75.1(2)	S(1)′–Ta(2)–P(3)	78.9(1)	P(1)–Ta(2)–P(3)	118.3(1)
Cl(4)–Ta(1)–P(2)	164.9(2)	S(2)–Ta(2)–S(2)′	111.2(1)		

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

added two $TaCl_2PMe_3$ units so that octahedral coordination is completed about each one by two μ-S atoms and a terminal Cl atom. The central Ta–Ta distance, Ta(2)–Ta(2)′, 2.891(1) Å, is consistent with a single bond between them. The other two, equivalent Ta–Ta distances, 3.091(1) Å, are significantly longer, but, on the other hand, probably not as long as one might have expected (>3.3 Å) if no Ta–Ta bonding occurred.

The problem we face in reconciling these distances with the bonding possibilities is that with a mean tantalum oxidation state of +4, we have only four electrons available for Ta–Ta bonding. In a purely formal sense, of course, we might assign two bonds of order 0.5 and one (in the center) of order 1.0. However, this does not give a very satisfying explanation of the bonding in orbital terms and leaves the question of magnetic properties somewhat open. In view of the present unavailability of this compound in large enough quantities for more complete characterization, we have not attempted to explore the electronic structure in any more detail.

From a chemical point of view $Ta_4S_4Cl_8(PMe_3)_6$ poses some interesting questions. It is, of course, simply related in a chemical sense to the dinuclear compound

$$Ta_4S_4Cl_8(PMe_3)_6 + 2PMe_3 = 2Ta_2S_2Cl_4(PMe_3)_4$$

Thus, it could be a precursor, or a subsequent condensation product of the dinuclear compound. It could also be neither of these, but simply a byproduct arising by an unrelated pathway. At present we have no firm evidence to decide among these possibilities. As noted in 'Experimental', our efforts to control the product ratio by varying reaction conditions were not very successful and thus afforded no clues as to how the two products might be related synthetically. We have also not observed any formation of the tetranuclear species from the dinuclear one when the latter is in solution under comparable conditions to those used in the synthetic reaction. We have not had a sufficient quantity of the tetranuclear compound to determine whether it would undergo the above reaction in the forward direction.

Supplementary material

Tables of structure factors, anisotropic thermal ellipsoids and complete bond lengths and angles for all three compounds are available from author F.A.C.

Acknowledgement

We thank the Robert A. Welch Foundation for support under Grant No. A-494.

References

1 E. Babaian-Kibala, F. A. Cotton and P. A. Kibala, *Inorg. Chem.*, *29* (1990) 4002.

2 L. Manzer, *Inorg. Chem.*, *16* (1977) 595.

3 A. P. Sattelberger, R. B. Wilson, Jr. and J. C. Huffman, *Inorg. Chem.*, *21* (1982) 2392.