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The Reactivity of $M_2(\mu\text{-Cl})_2(\mu\text{-SMe}_2)Cl_4(SMe_2)_2$: Formation of $Ta_2(\mu\text{-SEt})_2(\mu\text{-Cl})Cl_4(SMe_2)_2$ and $NbCl_3(S_2CNEt_2)_2$

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Abstract

The reaction of $Ta_2Cl_6(SMe_2)_3$ with diethyl disulfide and $Nb_2Cl_6(SMe_2)_3$ with tetraethylthiuram disulfide has produced two distinct products. In the former case, oxidative addition of the disulfide across the Ta=Ta bond and loss of one chlorine and one dimethyl sulfide ligand, produces the complex of mixed Ta(III)–Ta(IV) oxidation state, $Ta_2(\mu\text{-SEt})_2(\mu\text{-Cl})Cl_4(SMe_2)_2$ (**1**). In the latter case, use of tetraethylthiuram disulfide affords complete oxidation of the Nb=Nb bond, forming a monomeric Nb(V) seven-coordinate complex, $NbCl_3(S_2CNEt_2)_2$ (**2**). Crystallographic data for the new compounds are as follows: **1**, $P2_1/n$, $a = 10.696(4)$, $b = 13.730(2)$, $c = 14.927(4)$ Å, $\beta = 103.28(2)°$, $Z = 4$, Ta=Ta = 2.758(1) Å; **2**, *Pnam*, $a = 14.921(4)$, $b = 8.385(2)$, $c = 15.585(3)$ Å, $Z = 4$. Compound **2** has a pentagonal bipyramidal structure, with the equatorial plane defined by four S atoms and one Cl atom.

Introduction

The reaction chemistry of the niobium and tantalum d^2–d^2 face-sharing bioctahedral complex, $M_2(\mu\text{-Cl})_2(\mu\text{-L})Cl_4L_2$ [L = dimethyl sulfide or tetrahydrothiophene (tht)], has been heavily explored in several areas. Included are the oxidative addition reactions of these unsaturated species. A number of these reactions have been investigated and diverse product types have been seen. Some of these are quite understandably formed while others seem strikingly unconventional. Predicting whether a particular product will form even within a class of reactions appears quite difficult if not impossible. Cases in point include the reactions of $Nb_2(\mu\text{-Cl})_2(\mu\text{-tht})Cl_4(tht)_2$ with alcohols which have lead to a variety of products. In the reaction with methanol, the Nb(III) starting material is oxidized to Nb(IV) giving the edge-sharing bioctahedral complex, $Nb_2(\mu\text{-OMe})_2(OMe)_2(HOMe)_2Cl_4$. With ethanol, the Nb(IV) complex $[Nb_2(\mu\text{-Cl})(\mu\text{-OEt})(OEt)(thf)_2Cl_3O]_2$, is formed which consists of two edge-sharing bioctahedra coupled together via oxygen bridges [1].

Even more diverse are the reactions with alkynes. When MeCC-tBu reacts with $Ta_2(\mu\text{-Cl})_2(\mu\text{-tht})Cl_4(tht)_2$ or PhCCPh reacts with $Nb_2(\mu\text{-Cl})_2(\mu\text{-tht})Cl_4(tht)_2$, the respective complexes, $Nb_2(\mu\text{-Cl})_2Cl_2(tht)_2(MeCC\text{-tBu})_2$ and $Ta_2(\mu\text{-Cl})_2Cl_2(tht)_2(PhCCPh)_2$, are formed [2]. Here the metal centers have been oxidized to the +5 state leaving no direct bonding interaction between them. Other reactions with alkynes have given a variety of products including monomers [3], dimers with alkene bridges [4], and even trimers and polymers [5].

The reaction of $Ta_2(\mu\text{-Cl})_2(\mu\text{-tht})Cl_4(tht)_2$ with RCN leads to the formation of $(RCN)_2Cl_3Ta{=}N(R)C{=}C(R)N{=}TaCl_3(RCN)_2$ when R is methyl, ethyl, isopropyl, but not tert-butyl or phenyl [6]. Other nitrogen containing oxidizing species have provided for interesting and diverse product types. A metathesis reaction occurs between tantalum or niobium $M_2(\mu\text{-Cl})_2(\mu\text{-SMe}_2)Cl_4(SMe_2)_2$ with azobenzene producing the M(V) species $M_2(\mu\text{-Cl})_2Cl_4({=}NPh)_2(SMe_2)_2$ [7]. The reaction of $Ta_2(\mu\text{-Cl})_2(\mu\text{-SMe}_2)Cl_4(SMe_2)_2$ with PhHNNHPh produces a Ta(IV) complex, $Ta_2(\mu\text{-NPh})(\mu\text{-Cl})_2(H_2NPh)_2$ while $Nb_2(\mu\text{-Cl})_2(\mu\text{-SMe}_2)Cl_4(SMe_2)_2$ with PhHC=NN=CHPh yields $Nb_2(\mu\text{-Cl})_2Cl_4(SMe_2)[PhHC(\mu\text{-N})PhHCNHN{=}CHPh]$ [8]. Interestingly and unexpectedly, both of the latter complexes have nitrogen ligands which do not correspond to the nitrogen containing reactants used, and the routes to these products are not understood.

The reaction of $Ta_2(\mu\text{-Cl})_2(\mu\text{-SMe}_2)Cl_4(SMe_2)_2$ with diphenyl disulfide cleanly produces the edge-sharing bioctahedral complex, $Ta_2(\mu\text{-SPh})_2Cl_6(SMe_2)_2$ [9]. One might have expected that other disulfides would lead to similar Ta(IV)–Ta(IV) species. This, however, is not the case. In this paper, we report the reaction of $Ta_2(\mu\text{-Cl})_2(\mu\text{-SMe}_2)Cl_4(SMe_2)_2$ with diethyl disulfide to give a mixed oxidation state face-sharing bioctahedral complex, $Ta_2(\mu\text{-SEt})_2(\mu\text{-Cl})Cl_4(SMe_2)_2$, and the reaction of $Nb_2(\mu\text{-}$

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$Cl)_2(\mu\text{-}SMe_2)Cl_4(SMe_2)_2$ with tetraethylthiuram disulfide to produce the seven-coordinate monomeric complex $NbCl_3(S_2CNEt_2)_2$.

Experimental

All manipulations were carried out under an inert atmosphere of argon using standard Schlenk and vacuum line techniques. Commercial grade solvents were distilled from benzophenone ketyl prior to use. The compounds, $Ta_2Cl_6(SMe_2)_3$ and $Nb_2Cl_6(SMe_2)_3$ were prepared by literature methods [10]*. Diethyl disulfide and tetraethylthiuram disulfide were purchased from Aldrich Chemical Company. The infrared spectra were recorded on a Perkin-Elmer 783 spectrophotometer. Samples were obtained as Nujol mulls between CsI plates. Peaks coinciding with Nujol are not reported.

Preparation and Crystallization of $Ta_2(\mu\text{-}SEt)_2(\mu\text{-}Cl)Cl_4(SMe_2)_2$ (1)

To a 100 ml round bottom Schlenk flask, 0.30 g of $Ta_2Cl_6(SMe_2)_3$ (0.39 mmol) dissolved in 15 ml of toluene was filtered. To this, 0.097 ml of EtSSEt (0.79 mmol) in 15 ml of toluene and 10 ml of hexane was added. Over a period of one day, the initial brown reaction mixture turned bright purple in color. Within one week, a deep blue solid precipitated out. The solvent was decanted off, and the remaining solid was washed with two 10 ml aliquots of hexane to give $Ta_2(\mu\text{-}SEt)_2(\mu\text{-}Cl)Cl_4(SMe_2)_2$ in a 40% yield. IR cm^{-1}: 1265(w), 1242(m), 1053(w), 1032(m), 981(m), 965(m), 772(w), 728(br, m), 688(w), 635(m), 442(m), 404(w), 390(w), 335(vs), 303(s).

Crystals for X-ray diffraction were obtained by dissolving 0.15 g of $Ta_2Cl_6(SMe_2)_3$ (0.20 mmol) in 5 ml toluene which was filtered into a Schlenk tube. A hexane solution (10 ml) of EtSSEt (0.05 ml, 0.41 mmol) was layered on top. Slow diffusion provided for deep blue block shaped crystals.

Preparation and Crystallization of $NbCl_3(S_2CNEt_2)_2$ (2)

In a 100 ml round bottom Schlenk flask, 0.25 g of $Nb_2Cl_6(SMe_2)_3$ (0.43 mmol) and 0.25 g of $(Et_2NCS_2)_2$ (0.84 mmol) were dissolved in 24 ml of toluene. The reaction mixture was stirred for one day to give a red–orange precipitate which was filtered, washed with 10 ml of hexane and vacuum dried. The product, $NbCl_3(S_2CNEt_2)_2$, was obtained in a 47% yield. IR cm^{-1}: 2780(br, s), 2485(m), 2390(mw), 1725(br, mw), 1525(s), 1517(sh, s), 1507(sh, m), 1355(m), 1297(m), 1280(2), 1209(m), 1154(m), 1100(mw), 1073(br, m), 1052(mw), 922(m), 853(s), 811(s), 798(s), 784(s), 692(br, vs), 614(m), 586(ms), 426(w), 404(w), 374(ms), 357(ms), 342(m), 331(m), 315(m), 295(br, s), 282(br, s).

X-ray diffraction quality crystals were obtained by dissolving 0.12 g of $Nb_2Cl_6(SMe_2)_3$ (0.21 mmol) in 12 ml of toluene, filtering the solution into a Schlenk tube, and then layering it with a 25/75 mixture of toluene/hexane. A third layer, 0.12 g of $(Et_2NCS_2)_2$ (0.40 mmol) in 12 ml of hexane, was placed on top. Slow diffusion between layers allowed for the formation of large red–orange crystalline blocks.

Crystallographic Study

Crystals of 1 and 2 were grown as described above, and were mounted in a glass capillary tube using epoxy resin. Single crystal diffraction experiments were conducted on a Syntex P3 four circle X-ray diffractometer equipped with monochromated Mo Kα radiation. Routine unit cell identification and intensity data collection procedures have been described previously [11]. Crystal quality and dimensions were obtained through axial photographs. Three standard reflections were monitored throughout the data collection, and showed no significant variation in intensity. Empirical absorption corrections based on azimuthal scans of reflections with Eulerian angle chi near 90° were applied to the data sets. Both data sets were corrected for Lorentz and polarization effects. Standard computational procedures were used to solve and refine the structures using the VAX-SDP or Enraf-Nonius SDP software packages on the VAX-11/780 and PDP-11/60 computers, respectively.

Structure Solution and Refinement for $Ta_2(\mu\text{-}SEt)_2(\mu\text{-}Cl)Cl_4(SMe_2)_2$ (1)

The space group, $P2_1/n$, for the monoclinic cell was uniquely determined from the systematic absences in the intensity data. The two independent tantalum atoms were located from the three dimensional Patterson function. The remaining non-hydrogen atoms were located by employing a series of alternating difference Fourier maps and least-squares refinement cycles. All atoms were refined anisotropically.

Structure Solution and Refinement for $NbCl_3(S_2CNEt_2)_2$ (2)

The unique niobium atom was located from the Patterson map. The systematic absences in the intensity data narrowed the choice of space groups between $Pna2_1$ and $Pnam$. The non-centrosymmetric space group was initially chosen and used. The non-hydrogen atoms were located via a series of alternating difference Fourier maps and least-squares refinements. At this point it became apparent that a mirror plane existed in the $NbCl_3$ plane and the space group was changed from $Pna2_1$ to $Pnam$. The z coordinate

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*The procedure for the bulk preparation of $Ta_2Cl_6(SMe_2)_3$ and $Nb_2Cl_6(SMe_2)_3$ has been adapted from ref. 10b.

TABLE 1. Crystallographic Data for $Ta_2(\mu\text{-}SEt)_2(\mu\text{-}Cl)Cl_4(SMe_2)_2$ (**1**) and $NbCl_3(S_2CNEt_2)_2$ (**2**)

Compound	1	2
Formula	$Ta_2Cl_5S_4C_8H_{22}$	$NbCl_3S_4N_2C_{10}H_{20}$
Formula weight	785.66	495.81
Space group	$P2_1/n$	$Pnam$
a (Å)	10.696(4)	14.921(4)
b (Å)	13.730(2)	8.385(2)
c (Å)	14.927(4)	15.585(3)
β (°)	103.28(2)	
V (Å^3)	2133.6	1949.9
Z	4	4
D_{calc} (g/cm^3)	2.446	1.689
Crystal size (mm)	0.60 × 0.35 × 0.15	0.4 × 0.4 × 0.15
μ(Mo Kα) (cm^{-1})	117.8	14.111
Data collection instrument	Syntex P3	Syntex P3
Radiation (monochromated in incident beam)	Mo Kα (λ_α = 0.71073 Å)	
Orientation reflections, number, range (2θ)	25, $20.00 \leq 2\theta \leq 29.23$	25, $20.28 \leq 2\theta \leq 29.97$
Temperature (°C)	22	22
Scan method	$\omega - 2\theta$	$\omega - 2\theta$
Data collection range, 2θ (°)	$4 \leq 2\theta \leq 45$	$4 \leq 2\theta \leq 50$
No. unique data, total with $F_o^2 > 3\sigma(F_o^2)$	2806, 2065	1791, 872
No. parameters refined	172	97
Transmission factors, max., min.	0.9981, 0.6304	0.9997, 0.9282
R [a]	0.03148	0.0521
R_w [b]	0.04462	0.0660
Quality-of-fit indicator[c]	0.970	1.1736
Largest shift/e.s.d., final cycle	0.00	0.00
Largest peak (e/Å^3)	0.748	0.666

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

of the four atoms, Nb, Cl(1), Cl(2) and Cl(3), was fixed. All atoms were refined anisotropically with convergence at 0.0521 (R_w = 0.0660).

Pertinent crystallographic parameters for both compounds are summarized in Table 1. Final atomic positional and isotropic equivalent thermal parameters for **1** and **2** are listed in Tables 2 and 3, respectively. A complete list of bond distances and bond angles are found in Tables 4 and 5 for **1** and **2**, respectively. ORTEP views, which also define the labeling scheme used in the Tables, are shown in Figs. 1 and 2.

Results and Discussion

Synthetic Reaction

The reaction between $Ta_2Cl_6(SMe_2)_3$ and EtSSEt is obviously not straightforward. The reaction initially produces a purple colored complex which is isolable. This complex has not been fully characterized, but we believe it to be the edge-sharing bioctahedral complex, $Ta_2(\mu\text{-}SEt)_2Cl_6(SMe_2)_2$ [12]*.

TABLE 2. Final Atomic Positional and Isotropic Equivalent Thermal Parameters for $Ta_2(\mu\text{-}SEt)_2(\mu\text{-}Cl)Cl_4(SMe_2)_2$ (**1**)

Atom	x	y	z	B (Å^2)
Ta(1)	0.16474(5)	0.19572(4)	0.29748(4)	2.53(1)
Ta(2)	−0.05988(5)	0.26473(4)	0.33511(4)	2.53(1)
S(1)	0.1517(3)	0.2668(2)	0.4516(2)	2.76(7)
S(2)	0.0278(3)	0.0960(2)	0.3790(2)	2.73(7)
Cl(1)	0.0104(4)	0.2909(3)	0.2002(3)	4.04(8)
Cl(2)	0.1582(4)	0.0706(3)	0.1895(2)	3.89(8)
Cl(3)	0.3385(4)	0.2986(3)	0.2886(3)	4.20(8)
Cl(4)	−0.2579(4)	0.1967(3)	0.2602(3)	4.53(9)
Cl(5)	−0.0901(4)	0.4315(3)	0.3607(3)	4.02(8)
S(3)	0.3662(4)	0.0936(3)	0.3970(3)	3.61(8)
S(4)	−0.1675(4)	0.2409(3)	0.4806(3)	4.38(9)
C(1)	−0.061(1)	−0.001(1)	0.305(1)	4.1(3)
C(2)	−0.145(2)	−0.051(1)	0.359(1)	6.4(4)
C(3)	0.218(1)	0.3927(9)	0.462(1)	3.5(3)
C(4)	0.356(1)	0.390(1)	0.520(1)	5.3(4)
C(5)	0.470(2)	0.060(1)	0.321(1)	5.6(4)
C(6)	0.313(2)	−0.027(1)	0.420(1)	4.7(4)
C(7)	−0.077(2)	0.309(1)	0.577(1)	5.3(4)
C(8)	−0.315(1)	0.309(1)	0.458(1)	6.5(5)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos\text{gamma})B(1,2) + ac(\cos\text{beta})B(1,3) + bc(\cos\text{alpha})B(2,3)]$.

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*The corresponding tungsten species are isolated in the same reaction, e.g., $WCl_4(SMe_2)_2 + SiMe_3(SPh) \rightarrow W_2Cl_4(\mu\text{-}Cl)(\mu\text{-}SPh)(SMe_2)_2 + W_2Cl_6(\mu\text{-}SPh)_2(SMe_2)_2$.

TABLE 3. Final Atomic Positional and Isotropic Equivalent Thermal Parameters for $NbCl_3(S_2CNEt_2)_2$ (2)

Atom	x	y	z	B (Å^2)
Nb(1)	0.5998(1)	0.1666(2)	0.250	2.43(2)
Cl(1)	0.4449(3)	0.0803(7)	0.250	4.7(1)
Cl(2)	0.6510(3)	−0.1012(6)	0.250	4.0(1)
Cl(3)	0.5580(4)	0.4326(6)	0.250	4.9(1)
S(1)	0.5621(2)	0.1391(4)	0.0932(2)	3.36(6)
S(2)	0.7319(2)	0.2390(4)	0.1548(2)	3.17(6)
C(1)	0.6685(7)	0.204(1)	0.0656(7)	2.7(2)
N(1)	0.6961(7)	0.225(1)	−0.0134(5)	3.3(2)
C(2)	0.6397(9)	0.182(2)	−0.0896(8)	4.3(3)
C(3)	0.598(1)	0.331(2)	−0.1278(9)	5.8(3)
C(4)	0.7879(7)	0.291(1)	−0.0307(8)	3.6(3)
C(5)	0.8546(9)	0.157(2)	−0.047(1)	6.2(4)

Anisotropically refined atoms are given in the form of the isotropic equivalent thermal parameter defined as: $(4/3)[a^2B(1,1) + b^2B(2,2) + c^2B(3,3) + ab(\cos \text{gamma})B(1,2) + ac(\cos \text{beta})B(1,3) + bc(\cos \text{alpha})B(2,3)]$.

An infrared spectrum of this compound, while not identical to that of $Ta_2(\mu\text{-}SEt)_2(\mu\text{-}Cl)Cl_4(SMe_2)_2$, is very similar, indicating the presence of the same ligand types, but in different environments about the metal center. If the reaction mixture is allowed to stand for several days, the blue, structurally characterized compound, $Ta_2(\mu\text{-}SEt)_2(\mu\text{-}Cl)Cl_4(SMe_2)_2$ is formed.

TABLE 4. Complete List of Bond Distances (Å) and Angles (°) for $Ta_2(\mu\text{-}SEt)_2(\mu\text{-}Cl)Cl_4(SMe_2)_2$ (1)[a]

Atom 1	Atom 2	Distance
Ta(1)	Ta(2)	2.758(1)
Ta(1)	S(1)	2.532(3)
Ta(1)	S(2)	2.514(3)
Ta(1)	Cl(1)	2.333(4)
Ta(1)	Cl(2)	2.345(3)
Ta(1)	Cl(3)	2.362(4)
Ta(1)	S(3)	2.711(4)
Ta(2)	S(1)	2.517(4)
Ta(2)	S(2)	2.529(3)
Ta(2)	Cl(1)	2.334(4)
Ta(2)	Cl(4)	2.350(4)
Ta(2)	Cl(5)	2.356(3)
Ta(2)	S(4)	2.701(4)
S(1)	C(3)	1.861(13)
S(2)	C(1)	1.848(14)
S(3)	C(5)	1.816(15)
S(3)	C(6)	1.811(15)
S(4)	C(7)	1.80(2)
S(4)	C(8)	1.79(2)
C(1)	C(2)	1.50(2)
C(3)	C(4)	1.53(2)

(continued)

TABLE 4. *(continued)*

Atom 1	Atom 2	Atom 3	Angle
Ta(2)	Ta(1)	S(1)	56.63(8)
Ta(2)	Ta(1)	S(2)	57.11(8)
Ta(2)	Ta(1)	Cl(1)	53.8(1)
Ta(2)	Ta(1)	Cl(2)	120.1(1)
Ta(2)	Ta(1)	Cl(3)	122.6(1)
Ta(2)	Ta(1)	S(3)	133.33(9)
S(1)	Ta(1)	S(2)	67.1(1)
S(1)	Ta(1)	Cl(1)	99.8(1)
S(1)	Ta(1)	Cl(2)	155.1(1)
S(1)	Ta(1)	Cl(3)	91.6(1)
S(1)	Ta(1)	S(3)	84.5(1)
S(2)	Ta(1)	Cl(1)	101.5(1)
S(2)	Ta(1)	Cl(2)	90.3(1)
S(2)	Ta(1)	Cl(3)	155.0(1)
S(2)	Ta(1)	S(3)	86.0(1)
Cl(1)	Ta(1)	Cl(2)	94.4(1)
Cl(1)	Ta(1)	Cl(3)	94.8(2)
Cl(1)	Ta(1)	S(3)	172.3(1)
Cl(2)	Ta(1)	Cl(3)	107.4(1)
Cl(2)	Ta(1)	S(3)	83.8(1)
Cl(3)	Ta(1)	S(3)	78.7(1)
Ta(1)	Ta(2)	S(1)	57.16(8)
Ta(1)	Ta(2)	S(2)	56.59(8)
Ta(1)	Ta(2)	Cl(1)	53.8(1)
Ta(1)	Ta(2)	Cl(4)	119.9(1)
Ta(1)	Ta(2)	Cl(5)	121.7(1)
Ta(1)	Ta(2)	S(4)	132.4(1)
S(1)	Ta(2)	S(2)	67.1(1)
S(1)	Ta(2)	Cl(1)	100.2(1)
S(1)	Ta(2)	Cl(4)	154.5(1)
S(1)	Ta(2)	Cl(5)	90.7(1)
S(1)	Ta(2)	S(4)	85.8(1)
S(2)	Ta(2)	Cl(1)	101.0(1)
S(2)	Ta(2)	Cl(4)	90.0(1)
S(2)	Ta(2)	Cl(5)	154.8(1)
S(2)	Ta(2)	S(4)	83.2(1)
Cl(1)	Ta(2)	Cl(4)	94.8(2)
Cl(1)	Ta(2)	Cl(5)	94.2(1)
Cl(1)	Ta(2)	S(4)	173.6(1)
Cl(4)	Ta(2)	Cl(5)	108.7(1)
Cl(4)	Ta(2)	S(4)	80.3(2)
Cl(5)	Ta(2)	S(4)	83.6(1)
Ta(1)	S(1)	Ta(2)	66.21(9)
Ta(1)	S(1)	C(3)	109.4(5)
Ta(2)	S(1)	C(3)	109.3(5)
Ta(1)	S(2)	Ta(2)	66.30(8)
Ta(1)	S(2)	C(1)	112.5(5)
Ta(2)	S(2)	C(1)	113.6(5)
Ta(1)	Cl(1)	Ta(2)	72.4(1)
Ta(1)	S(3)	C(5)	108.1(7)
Ta(1)	S(3)	C(6)	109.6(6)
C(5)	S(3)	C(6)	98.7(8)
Ta(2)	S(4)	C(7)	109.1(6)
Ta(2)	S(4)	C(8)	107.8(7)
C(7)	S(4)	C(8)	100.(1)
S(2)	C(1)	C(2)	108.(1)
S(1)	C(3)	C(4)	109.(1)

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

TABLE 5. Complete List of Bond Distances (Å) and Angles (°) for $NbCl_3(S_2CNEt_2)_2$ (2)[a]

Atom 1	Atom 2	Distance
Nb(1)	Cl(1)	2.422(4)
Nb(1)	Cl(2)	2.372(5)
Nb(1)	Cl(3)	2.316(5)
Nb(1)	S(1)	2.519(3)
Nb(1)	S(2)	2.540(3)
S(1)	C(1)	1.730(10)
S(2)	C(1)	1.707(11)
C(1)	N(1)	1.311(13)
N(1)	C(2)	1.499(14)
N(1)	C(4)	1.503(13)
C(2)	C(3)	1.51(2)
C(4)	C(5)	1.52(2)

Atom 1	Atom 2	Atom 3	Angle
Cl(1)	Nb(1)	Cl(2)	91.4(2)
Cl(1)	Nb(1)	Cl(3)	91.8(2)
Cl(1)	Nb(1)	S(1)	76.10(7)
Cl(1)	Nb(1)	S(2)	144.26(6)
Cl(2)	Nb(1)	Cl(3)	176.8(2)
Cl(2)	Nb(1)	S(1)	89.15(9)
Cl(2)	Nb(1)	S(2)	88.6(1)
Cl(3)	Nb(1)	S(1)	91.61(9)
Cl(3)	Nb(1)	S(2)	88.8(1)
S(1)	Nb(1)	S(1)	152.1(1)
S(1)	Nb(1)	S(2)	68.17(9)
S(1)	Nb(1)	S(2)	139.6(1)
S(2)	Nb(1)	S(2)	71.5(1)
Nb(1)	S(1)	C(1)	90.4(4)
Nb(1)	S(2)	C(1)	90.2(4)
S(1)	C(1)	S(2)	111.1(6)
S(1)	C(1)	N(1)	124.3(8)
S(2)	C(1)	N(1)	124.5(8)
C(1)	N(1)	C(2)	122.3(9)
C(1)	N(1)	C(4)	120.4(9)
C(2)	N(1)	C(4)	117.3(9)
N(1)	C(2)	C(3)	110.(1)
N(1)	C(4)	C(5)	110.7(9)

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

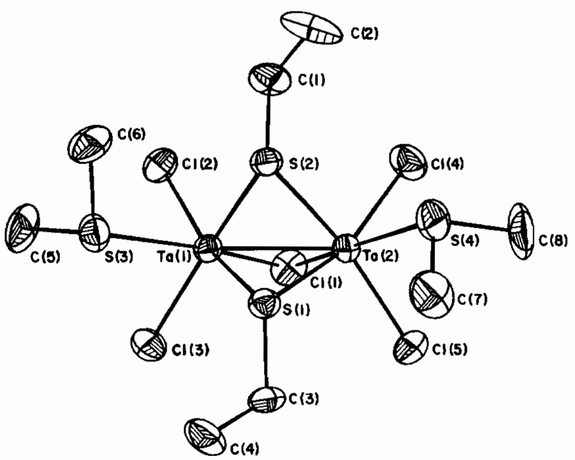

Fig. 1. ORTEP view of $Ta_2(\mu\text{-}SEt)_2(\mu\text{-}Cl)Cl_4(SMe_2)_2$ (1) with thermal ellipsoids drawn at the 50% probability level.

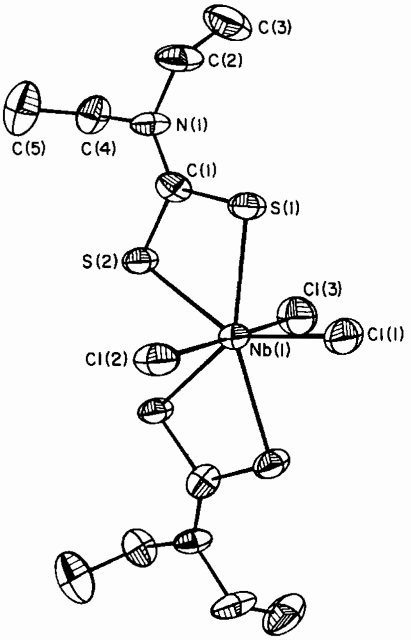

Fig. 2. ORTEP view of $NbCl_3(S_2CNEt_2)_2$ (2) with thermal ellipsoids drawn at the 50% probability level.

The reaction between $Nb_2Cl_6(SMe_2)_3$ and $(Et_2NCS_2)_2$ cleanly produces $NbCl_3(S_2CNEt_2)_2$. It is interesting to note that while excess disulfide is typically used in these oxidative addition reactions, this is the first example of monomer formation. Unlike the other disulfides used, the Et_2NCS_2 fragment has two accessible sulfur atoms for bonding to the metal. This allows the formation of a stable seven-coordinate Nb(V) monomer. The corresponding unknown monomeric compounds formed from disulfides such as EtSSEt or PhSSPh would be five-coordinate and would naturally tend to take dimeric forms such as those found in $[NbCl_5]_2$ and $[Nb(OMe)_5]_2$ [13]. These corresponding disulfide species have not been obtained since oxidation appears to stop at the formation of the Ta(IV)–Ta(IV) or Ta(IV)–Ta(III) dimers as in $Ta_2Cl_6(\mu\text{-}SPh)_2(SMe_2)_2$ and $Ta_2(\mu\text{-}SEt)_2(\mu\text{-}Cl)Cl_4(SMe_2)_2$, respectively.

Molecular Structure: $Ta_2(\mu\text{-}SEt)_2(\mu\text{-}Cl)Cl_4(SMe_2)_2$

The structure of $Ta_2(\mu\text{-}SEt)_2(\mu\text{-}Cl)Cl_4(SMe_2)_2$ is based on a face-sharing bioctahedral configuration of the core atoms. A metal–metal interaction is structurally indicated by the acute angles subtended at the atoms which bridge the tantalum centers [Ta(1)–S(1)–Ta(2), 66.21(9); Ta(1)–S(2)–Ta(2), 66.30(8); Ta(1)–Cl(1)–Ta(2), 72.4(1); average Ta(1)–X–Ta(2), 68(2)]. The wider than average Ta(1)–Cl(1)–Ta(2) angle is in part due to the unusually short Ta–Cl(1) bridge distances of 2.333(0) Å. If no metal–metal interaction was present, the Ta(1)–X–Ta(2) angles would be expected to be 70.5° or greater [14]. Thus, the average of the three angles at 68(2)° is consistent with metal–metal bonding. The actual bond distance of 2.758(1) Å is reasonable for the mixed Ta(IV)–Ta(III) complex and is only 0.067 Å longer than the Ta(III)–Ta(III) bond length in the starting material, $Ta_2(\mu\text{-}Cl)_2(\mu\text{-}SMe_2)Cl_4(SMe_2)_2$.

As mentioned, $Ta_2(\mu\text{-}SEt)_2(\mu\text{-}Cl)Cl_4(SMe_2)_2$ is a complex of mixed oxidation state. Whether the 'extra' electron is shared equally between both tantalum atoms (directly or via ligand bridges) or resides on one atom is not ascertainable from the structure alone. The ligand-to-Ta(1) and ligand-to-Ta(2) bond distances are equivalent within experimental error. This would be expected if the 'extra' electron was shared equally between the two tantalum atoms, or if the complex with non-equivalent tantalum atoms were crystallographically disordered.

Molecular Structures: $NbCl_3(S_2CNEt_2)_2$

The $NbCl_3(S_2CNEt_2)_2$ molecule is situated on a mirror plane which passes through the metal center and all three chlorine atoms. Perpendicular to this mirror plane is a pentagon defined by the atoms, S(1), S(2), S(2)′, S(1)′, Cl(1) with Nb(1) at its center. This pentagon and the apical atoms Cl(2) and Cl(3) define a pentagonal bipyramid. The apex atoms, Cl(2) and Cl(3) subtend an angle about the metal center at 176.8(2)°. The structure of this compound is a familiar one for complexes of the type $MX_3(LL)_2$ whenever the bidentate ligand, LL, does not have steric requirements that are incompatible with the formation of the pentagonal equatorial plane. Numerous prior examples are known and have been discussed by Drew [15].

Supplementary Material

Available from author (F.A.C.): the crystal structures of $Ta_2(\mu\text{-}SEt)_2(\mu\text{-}Cl)Cl_4(SMe_2)_2$ and $NbCl_3(S_2CNEt_2)_2$ including anisotropic displacement parameters (2 pages); observed and calculated structure factors (16 pages).

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