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Hexachloro(dimethylsulfide)bis(hexamethyltriaminophosphine)ditantalum-(Ta=Ta), $[(Me_2N)_3P]Cl_2Ta(\mu\text{-}Cl)_2(\mu\text{-}Me_2S)TaCl_2[(Me_2N)_3P]$: Preparation and Structure

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The reaction of $Ta_2Cl_6(SMe_2)_3$ with $(Me_2N)_3P$ in CH_2Cl_2 affords the title compound, which was crystallized from hexane. The structure of the molecule was determined from single-crystal X-ray diffraction data. The compound crystallizes in space group $P2_1/n$ with a = 14.98(1) Å, b = 13.319(7) Å, c = 17.592(8) Å, β = 109.95(7)°, V = 3298(2) Å^3 and Z = 4. The molecule is derived from the starting material by replacement of the terminal Me_2S ligands with $(Me_2N)_3P$ ligands; the bridging Me_2S ligand is retained. The $Ta_2Cl_6SP_2$ skeleton has effectively C_{2v} symmetry and the Ta=Ta bond length is 2.704(1) Å. The compound is diamagnetic and gives a sharp proton NMR spectrum with signals at 3.092 and 2.665 ppm (downfield from Me_4Si) in an intensity ratio of 1:6 and assignable to SMe_2 (singlet) and $(Me_2N)_3P$ (doublet, J = 8.82 Hz), respectively.

Introduction

In this paper we report a study that continues our exploration [1–6] of the chemistry of niobium and tantalum in their lower oxidation states (≤III) with particular interest in compounds containing Nb=Nb and Ta=Ta bonds. It is also important to call attention to the pioneering work of McCarley and coworkers [7–10], which we shall have occasion to cite later in this report.

Experimental

All materials were handled under argon using Schlenk or vacuum line techniques. Dichloromethane and hexane were distilled over P_2O_5 and potassium benzophenone ketyl, respectively. Tantalum pentachloride (99+%) was purchased from Alfa Division of Ventron Corp. Tris(dimethylamino)phosphine, $(Me_2N)_3P$, was obtained from Pressure Chemical Company. The preparation of $Ta_2Cl_6(SMe_2)_3$ has been reported previously [6]. The ^{1}H NMR spectrum was obtained on a Varian XL 200 (200 MHz) NMR spectrometer using de-gassed C_6D_6/TMS as a solvent. The infrared spectrum was recorded on a Unicam SP1100 spectrophotometer.

Preparation

$Ta_2Cl_6(SMe_2)_3$ (3.0 g, 3.9 mmol) was dissolved in dichloromethane (100 ml). An addition funnel was charged with $(Me_2N)_3P$ (2.6 ml, 16 mmol) and dichloromethane (20 ml). The contents of the addition funnel was added dropwise to the stirred orange-brown tantalum solution at 20 °C. The solution had become red-orange in color when the addition was complete. The solvent was removed under vacuum yielding a red-brown solid. Hexane (50 ml) was stirred over the solid for 4 hours. A red solution over a maroon oil was obtained. The red solution was filtered through a celite pad. The oil was again extracted with hexane (50 ml) and the two hexane extracts were combined. After two days, red crystals suitable for X-ray analysis formed from the saturated hexane solution at room temperature in *ca.* 35% yield. The crystals are moderately air-sensitive (approx. 15 min in air) and form very air-sensitive (<1 min in air) solutions. IR (mull): 2492 (br), 1411 (s), 1309 (w), 1271 (s), 1182 (sh), 966 (sh), 934 (w), 869 (m), 809 (s), 633 (s), 591 (sh).

X-ray Crystallography. Collection of Data

Crystals used for data collection were sealed in capillaries under nitrogen. Data were collected on a Syntex P$\bar{1}$ diffractometer at 26 ± 1 °C using Mo Kα radiation (λ = 0.71073 Å) with a graphite-crystal monochromator in the incident beam. A summary of data collection and refinement parameters is presented in Table I. Other details concerning the collection and processing of data have been discussed previously [10]. Lorentz and polarization corrections were applied to the data. An empirical absorption correction based on ψ scans of six reflections at χ near 90° was also applied [11]. The intensities

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TABLE I. Crystallographic Parameters for $Ta_2Cl_6(SMe_2)[P(NMe_2)_3]_2$.

Space group	$P2_1/n$
a, A	14.98(1)
b, A	13.319(7)
c, A	17.592(8)
β, deg.	109.95(7)
V, A^3	3298(2)
ρ_{calcd}, g/cm^3	2.548
Z,	4
fw	1265.5
Cryst. size, mm	0.1 × 0.2 × 0.2
μ(Mo Kα), cm^{-1}	73.449
Range 2*θ*, deg.	0–45
No. unique data	2205
No. data, $F_o^2 > 3\sigma(F_o^2)$	2118
No. variables	260
R_1[a]	0.036
R_2[a]	0.046
esd	0.985
Largest shift/esd ratio[b]	0.05
Largest peak[c]	0.97

[a] $R_1 = \Sigma||F_o|-|F_c||/\Sigma|F_o|$, $R_2 = [\Sigma w(|F_o|-|F_c|)^2/\Sigma w|F_o|^2]^{1/2}$. [b] For any parameter in final refinement cycle. [c] Largest peak in a final difference Fourier, e/A^3.

TABLE II. Table of Positional and Isotropic Thermal Parameters and Their Estimated Standard Deviations.

Atom	x	y	z	B, A^2
Ta(1)	0.43919(5)	0.25328(6)	0.19304(4)	
Ta(2)	0.52599(5)	0.07305(5)	0.20462(4)	
Cl(1)	0.4230(3)	0.1179(4)	0.2849(2)	
Cl(2)	0.6066(3)	0.2220(3)	0.2860(2)	
Cl(11)	0.4930(3)	0.3921(4)	0.1368(3)	
Cl(12)	0.2719(3)	0.2593(4)	0.1271(3)	
Cl(21)	0.6566(3)	0.0532(4)	0.1583(3)	
Cl(22)	0.4289(4)	−0.0679(4)	0.1477(3)	
S(1)	0.4456(3)	0.1581(4)	0.0794(2)	
P(1)	0.4268(3)	0.3858(3)	0.3073(2)	
P(2)	0.6243(4)	−0.0413(4)	0.3347(3)	
N(11)	0.3977(11)	0.499(1)	0.2705(8)	
N(12)	0.5308(9)	0.410(1)	0.3808(7)	
N(13)	0.3627(9)	0.349(1)	0.3640(8)	
N(21)	0.6588(12)	−0.151(1)	−0.3692(10)	
N(22)	0.5619(14)	−0.067(1)	0.3973(9)	
N(23)	0.7289(16)	0.010(1)	0.3972(9)	
C(1)	0.336(1)	0.111(2)	0.0040(11)	
C(2)	0.508(1)	0.199(2)	0.0121(10)	
C(3)	0.322(2)	0.515(1)	0.1894(12)	
C(4)	0.411(2)	0.594(1)	0.3196(12)	
C(5)	0.605(1)	0.464(1)	0.3559(11)	
C(6)	0.572(1)	0.338(1)	0.4484(9)	
C(7)	0.276(1)	0.290(2)	0.3296(10)	
C(8)	0.362(2)	0.409(2)	0.4370(10)	
C(9)	0.648(2)	−0.191(2)	0.2287(12)	
C(10)	0.716(3)	−0.222(2)	0.3732(17)	
C(11)	0.465(2)	−0.113(2)	0.362(2)	10.9(8)
C(12)	0.601(4)	−0.096(4)	0.474(3)	24.9(22)
C(13)	0.798(2)	0.054(2)	0.368(2)	10.7(8)
C(14)	0.701(2)	0.077(3)	0.462(2)	15.3(12)

TABLE III. Table of Bond Distances in Angstroms.[a]

Atom 1	Atom 2	Distance
Ta(1)	Ta(2)	2.704(1)
Ta(1)	Cl(1)	2.487(5)
Ta(1)	Cl(2)	2.517(4)
Ta(1)	Cl(11)	2.365(5)
Ta(1)	Cl(12)	2.377(4)
Ta(1)	S(1)	2.397(4)
Ta(1)	P(1)	2.729(4)
Ta(2)	Cl(1)	2.492(4)
Ta(2)	Cl(2)	2.502(4)
Ta(2)	Cl(21)	2.376(5)
Ta(2)	Cl(22)	2.377(5)
Ta(2)	S(1)	2.403(5)
Ta(2)	P(2)	2.724(5)
S(1)	C(1)	1.84(2)
S(1)	C(2)	1.82(2)
P(1)	N(11)	1.636(15)
P(1)	N(12)	1.681(13)
P(1)	N(13)	1.676(15)
P(2)	N(21)	1.67(2)
P(2)	N(22)	1.70(2)
P(2)	N(23)	1.72(2)
N(11)	C(3)	1.50(2)
N(11)	C(4)	1.51(2)
N(12)	C(5)	1.50(2)
N(12)	C(6)	1.49(2)
N(13)	C(7)	1.46(2)
N(13)	C(8)	1.52(2)
N(21)	C(9)	1.47(3)
N(21)	C(10)	1.50(3)
N(22)	C(11)	1.50(4)
N(22)	C(12)	1.34(6)
N(23)	C(13)	1.43(4)
N(23)	C(14)	1.61(4)

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

of three standard reflections, measured every 47 reflections, showed an average loss in intensity of 5.8%, and an appropriate correction was applied to the data [12].

TABLE IV. Table of Bond Angles in Degrees.

Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle	Atom 1	Atom 2	Atom 3	Angle
Ta2	Ta1	Cl1	57.2(1)	Cl1	Ta2	Cl2	75.9(2)	N11	P1	N13	112.1(9)
Ta2	Ta1	Cl2	57.1(1)	Cl1	Ta2	Cl21	164.0(2)	N12	P1	N13	99.6(8)
Ta2	Ta1	Cl11	120.1(1)	Cl1	Ta2	Cl22	91.1(2)	Ta2	P2	N21	113.2(7)
Ta2	Ta1	Cl12	117.8(1)	Cl1	Ta2	S1	101.1(2)	Ta2	P2	N22	113.3(7)
Ta2	Ta1	S1	55.8(1)	Cl1	Ta2	P2	85.4(2)	Ta2	P2	N23	115.4(7)
Ta2	Ta1	P1	132.1(1)	Cl2	Ta2	Cl21	89.5(2)	N21	P2	N22	107.(1)
Cl1	Ta1	Cl2	75.8(2)	Cl2	Ta2	Cl22	166.8(2)	N21	P2	N23	103.(1)
Cl1	Ta1	Cl11	164.0(2)	Cl2	Ta2	S1	98.3(2)	N22	P2	N23	104.(1)
Cl1	Ta1	Cl12	91.3(2)	Cl2	Ta2	P2	86.9(2)	P1	N11	C3	121.(1)
Cl1	Ta1	S1	101.5(2)	Cl21	Ta2	Cl22	103.0(2)	P1	N11	C4	125.(1)
Cl1	Ta1	P1	86.8(2)	Cl21	Ta2	S1	87.2(2)	C3	N11	C4	109.(2)
Cl2	Ta1	Cl11	89.7(2)	Cl21	Ta2	P2	87.3(2)	P1	N12	C5	117.(1)
Cl2	Ta1	Cl12	166.8(2)	Cl22	Ta2	S1	86.7(2)	P1	N12	C6	121.(1)
Cl2	Ta1	S1	98.0(2)	Cl22	Ta2	P2	89.4(2)	C5	N12	C6	114.(1)
Cl2	Ta1	P1	86.1(1)	S1	Ta2	P2	172.5(2)	P1	N13	C7	121.(1)
Cl11	Ta1	Cl12	102.9(2)	Ta1	Cl1	Ta2	65.8(1)	P1	N13	C8	122.(1)
Cl11	Ta1	S1	87.0(2)	Ta1	Cl2	Ta2	65.2(1)	C7	N13	C8	112.(2)
Cl11	Ta1	P1	85.5(2)	Ta1	S1	Ta2	68.6(1)	P2	N21	C9	129.(2)
Cl12	Ta1	S1	86.9(2)	Ta1	S1	C1	120.3(7)	P2	N21	C10	120.(2)
Cl12	Ta1	P1	90.7(2)	Ta1	S1	C2	123.9(8)	C9	N21	C10	110.(2)
S1	Ta1	P1	171.4(2)	Ta2	S1	C1	123.0(9)	P2	N22	C11	119.(2)
Ta1	Ta2	Cl1	57.0(1)	Ta2	S1	C2	121.9(7)	P2	N22	C12	124.(3)
Ta1	Ta2	Cl2	57.7(1)	C1	S1	C2	99.(1)	C11	N22	C12	109.(4)
Ta1	Ta2	Cl21	120.2(2)	Ta1	P1	N11	112.2(6)	P2	N23	C13	123.(2)
Ta1	Ta2	Cl22	117.4(2)	Ta1	P1	N12	114.3(5)	P2	N23	C14	106.(2)
Ta1	Ta2	S1	55.6(1)	Ta1	P1	N13	116.4(5)	C13	N23	C14	115.(2)
Ta1	Ta2	P2	131.9(1)	N11	P1	N12	100.5(8)				

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

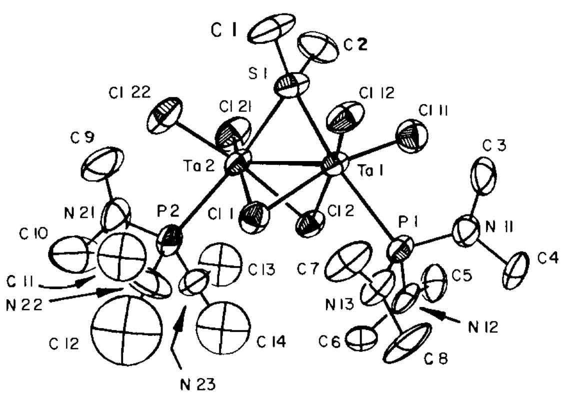

Fig. 1. Ortep drawing of $Ta_2Cl_6(SMe_2)[P(NMe_2)_3]_2$ with thermal ellipsoids at the 40% probability level.

Structure Solution

Data were collected for a monoclinic unit cell having a volume consistent with $Z = 4$. The data exhibited systematic absences for h0l, h + l = 2n, and 0k0, k = 2n which uniquely determined the space group as $P2_1/n$. The positions of all nonhydrogen atoms were determined from a three-dimensional Patterson function and a sequence of alternating difference Fourier maps and least-squares refinements. Anisotropic thermal parameters were assigned to all non-hydrogen atoms except C(11), C(12), C(13) and C(14), which appear to be disordered although no simple disorder model was found. These four carbon atoms were refined to convergence with isotropic thermal parameters. The refinement proceeded smoothly otherwise to final discrepancy factors listed in Table I. A final difference map showed no peaks of structural significance. Tables of structure factors and anisotropic thermal parameters are available upon request from F.A.C.

Results

Crystal Structure

The positional parameters for all nonhydrogen atoms and the isotropic thermal parameters for C(11)–C(14) are listed in Table II. Bond distances and angles are compiled in Tables III and IV, respectively. Four molecules of $Ta_2Cl_6(SMe_2)[P(NMe_2)_3]_2$

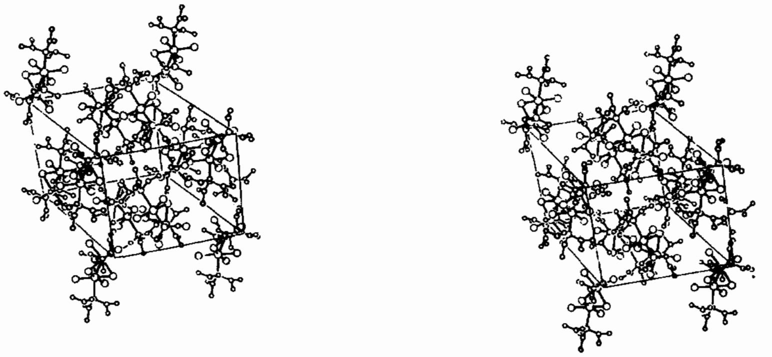

Fig. 2. A stereoscopic view of the packing in the unit cell of $Ta_2Cl_6(SMe_2)[P(NMe_2)_3]_2$.

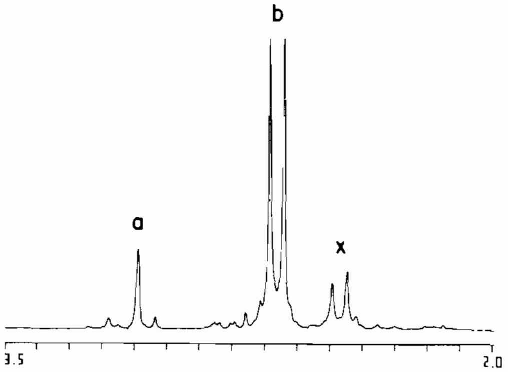

Fig. 3. ^1H NMR spectrum of $Ta_2Cl_6(SMe_2)[P(NMe_2)_3]_2$ in C_6D_6. Resonances (a) and (b) are centered at δ 3.092 and 2.665 ppm downfield from TMS, respectively. The relative intensities of (a) and (b) are 1:6, and the splitting in (b) is 8.82 Hz. Resonance (X) is due to free $(NMe_2)_3$. Base-line peaks are due to decomposition products.

occupy the unit cell with no crystallographically imposed symmetry. The molecular structure is depicted and the atom numbering scheme defined in Fig. 1. Four carbon atoms, C(11)–C(14), have high thermal parameters indicative of a disorder problem, although no satisfactory model for the disorder was established.

The volume of the unit cell appears to be larger than necessary (26.6 $Å^3$ per atom) to contain four molecules with 31 non-hydrogen atoms each. An examination of the crystal packing (Fig. 2) gives some insight into the reason. The arrangement of molecules is dominated by the bulky $(Me_2N)_3P$ ligands. In each molecule one $(Me_2N)_3P$ moiety (which includes C(11) to C(14)) points into the center of the unit cell. The packing in this region appears to be loose and disordered, thus accounting for the large volume of the unit cell.

NMR Spectrum

The ^1H NMR spectrum (Fig. 3) consisted of two resonance peaks, a singlet (a) at δ 3.092 and a doublet (b) at (δ 2.687, δ2.643), *vs.* TMS. The doublet "X" is due to $P(NMe_2)_3$ as free ligand located at δ 2.492 and δ 2.448. Remaining baseline peaks in the spectrum were decomposition products.

The relative intensities of peaks (a) and (b) were 1:6 consistent with the assignment of (a) to the bridging SMe_2 and (b) to the two terminal $(Me_2N)_3P$ ligands. The ^{31}P–^1H coupling for both peaks, (b) and X, was J = 8.82 Hz.

Discussion

The preparation of this compound involves a reaction in which the two terminal L groups of an $M_2Cl_6L_3$ (M = Nb, Ta) molecule have been substituted, while leaving the bridging L group in place, and in this sense it is complementary to some previously reported reactions in which the bridging L group has been replaced while leaving the terminal ones. There are, of course, also cases in which all bridges have been broken to give mononuclear products.

In the starting materials used here and in previous work, the ligands L have been of the dialkylsulfide type, either $(CH_3)_2S$ or $\overline{CH_2CH_2CH_2CH_2S}$ (THT), and these are capable of serving both as bridging and terminal ligands since they have two lone pairs available. When the $M_2Cl_6L_3$, molecules reacts under mild conditions with a ligand, L′, that is not capable of filling a bridging position, it is not surprising that the product is the molecule in which only the terminal L ligands have been replaced by L′ to give $M_2Cl_6LL'_2$. On the other hand, when L′ is an acetylene, which can replace the bridging ligand and perhaps serve as an even better bridging group, this is the preferred course of reaction [3].

The details of the structure of $Ta_2Cl_6(\mu\text{-}Me_2S)[P(NMe_2)_3]_2$ are not unusual. The Ta=Ta distance of 2.704(1) Å is about the same as those previously found in similar compounds [6–9] and may particularly be compared with that in $Ta_2Cl_6(Me_2S)_3$

where it is 2.691(1) Å [6]. The conformation of the $P(NMe_2)_3$ ligand is of the type recently found by Cowley, *et al.* [13] in other coordination compounds.

Acknowledgements

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