Contribution from the Department of Chemistry and the Molecular Structure Center, Indiana University, Bloomington, Indiana 47405

Chloro(dimethylamido) Compounds of Tantalum(V): Preparations, Properties, and Structures of $[Ta(NMe_2)_3Cl_2]_2$, $TaCl_3(NMe_2)_2(HNMe_2)$, $Ta(NMe_2)_3Cl_2(HNMe_2)$, and $[TaCl_2(NMe_2)_2(HNMe_2)]_2O$

MALCOLM H. CHISHOLM,* JOHN C. HUFFMAN, and LOON-SENG TAN

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$Ta(NMe_2)_5$ and Me_3SiCl (2 equiv) in pentane solvents react to give a microcrystalline precipitate of $[TaCl_2(NMe_2)_3]_2$ according to the stoichiometric reaction $Ta(NMe_2)_5 + 2Me_3SiCl \rightarrow {}^1/_2[TaCl_2(NMe_2)_3]_2 + 2Me_3SiNMe_2$. Addition of $HNMe_2$ to $[TaCl_2(NMe_2)_3]_2$ yields $TaCl_2(NMe_2)_3(HNMe_2)$ quantitatively. From the reaction between $TaCl_5$ and $HNMe_2$ (5 equiv) in benzene, $TaCl_3(NMe_2)_2(HNMe_2)$, $TaCl_2(NMe_2)_3(HNMe_2)$, and $[TaCl_2(NMe_2)_2(HNMe_2)]_2O$ have been isolated and characterized. The first compound was originally prepared by Carnell and Fowles; the latter two compounds are new ones and are formed as minor products in the reaction. The rapid (NMR time scale) and reversible reaction between $TaCl_3(NMe_2)_2(HNMe_2)$ and $HNMe_2$ to give $TaCl_2(NMe_2)_3(HNMe_2)$ and $Me_2NH_2^+Cl^-$ has been established. All the compounds have been characterized by elemental analyses, IR spectroscopy, variable-temperature 220-MHz ^1H NMR spectroscopy, and mass spectroscopy. The solid-state molecular structures of $[TaCl_2(NMe_2)_3]_2$, $TaCl_3(NMe_2)_2(HNMe_2)$, and $[TaCl_2(NMe_2)_2(HNMe_2)]_2O$ have been determined by single-crystal X-ray studies. In each compound, tantalum is in a distorted octahedral environment. The Ta–NMe_2 groups contain short Ta–N bond distances (1.96 Å averaged) and have planar Ta–NC_2 groups indicative of extensive nitrogen p to tantalum d π bonding. The disposition of Me_2N^- ligands about tantalum is such that tantalum achieves the maximum effect of this π donation, viz., *fac* in $[TaCl_2(NMe_2)_3]_2$, which has a planar central $Ta_2(\mu\text{-}Cl)_2$ moiety and *cis* in both $TaCl_3(NMe_2)_2(HNMe_2)$ and $[TaCl_2(NMe_2)_2(HNMe_2)]_2O$. The latter compound has a nearly linear Ta–O–Ta moiety (174°) with short Ta–O bond distances (1.92 Å averaged) indicative of oxygen p to tantalum d π bonding. The spectroscopic data are consistent with the view that $TaCl_2(NMe_2)_3(HNMe_2)$ adopts a similar structure with a *fac*-$Ta(NMe_2)_3$ group. Crystal data are as follows. For $[TaCl_2(NMe_2)_3]_2$: space group = $P2_1/n$, a = 10.464 (3) Å, b = 13.224 (4) Å, c = 8.450 (2) Å, β = 98.07 (1)°, Z = 2, V = 1157.6 (1) Å^3. For $TaCl_3(NMe_2)_2(HNMe_2)$: space group = $P2_1/c$, a = 9.750 (3) Å, b = 10.330 (2) Å, c = 14.300 (4) Å, β = 112.05 (1)°, Z = 4, V = 1335.0 (1) Å^3. For $[TaCl_2(NMe_2)_2(HNMe_2)]_2O$: space group = $P2_1/c$, a = 8.314 (1) Å, b = 20.480 (4) Å, c = 15.778 (3) Å, β = 112.22 (1)°, Z = 4, V = 1243.5 (1) Å^3.

Introduction

Though the group 6 transition elements are prolific in forming dinuclear compounds containing metal-to-metal multiple bonds of order 4 and 3, and to a lesser extent 2,[1] there are relatively few analogous compounds involving the group 5 transition elements. Indeed, the following provide the known examples which have been characterized by complete X-ray studies: tetrakis(2,6-dimethoxyphenyl)divanadium (M≡M);[2] $Cp_2V_2(CO)_5$ (M=M);[3] $Cp_2V_2(CO)_4PPh_3$;[3,4] $Cs_3Nb_2X_9$ (M=M), where X = Cl, Br, and I;[5] M_2Br_6(tetrahydrothiophene)$_3$ (M=M),[6] where M = Nb and Ta; $V_2(CO)_8(\mu\text{-}PMe_2)_2$ (M=M);[7] $Cp_2Nb_2(CO)_4$(PhC≡CPh)[8] and most recently Ta_2Cl_6(*t*-BuC≡C-*t*-Bu)$(THF)_2$.[9] We are inclined toward the view that tantalum in its lower oxidation states [+3 (d^2), +2 (d^3) and +1 (d^4)] could enter into interesting homodinuclear relationships and that the present paucity of such compounds reflects the lack of suitable precursor complexes. It is probably necessary to keep both the coordination number and the oxidation state low in order to maximize M–M interactions and tantalum tends to show most of its known chemistry with high coordination numbers and in high oxidation states.[10] We felt that mixed chloro(dimethylamido) compounds of tantalum(V) might be good starting materials for entry into the chemistry of the lower oxidation states and lower coordination numbers of tantalum. The dimethylamido ligand[11] is bulky and can act as a four-electron donor ($\sigma^2 + \pi^2$), and chloride ligands offer a number of possibilities for reduction. In this paper, we describe the preparation and characterization of several mixed chloro(dimethylamido) compounds of tantalum(V).

Results and Discussion

Syntheses. $[TaCl_2(NMe_2)_3]_2$. Previously we found that chlorotrimethylsilane reacted with the dinuclear compounds $M_2(NMe_2)_6$ (M = Mo, W) according to the stoichiometric equation (1).[12] The reaction proceeds via an amine-catalyzed

$$M_2(NMe_2)_6 + 2Me_3SiCl \rightarrow 1,2\text{-}Mo_2Cl_2(NMe_2)_4 + 2Me_3SiNMe_2 \quad (1)$$

sequence (see eq 2), and the 1,2-$M_2Cl_2(NMe_2)_4$ compounds

$$\text{(a) } Me_3SiCl + HNMe_2 \rightleftharpoons Me_3SiNMe_2 + HCl$$

$$\text{(b) } M_2(NMe_2)_6 + HCl \rightleftharpoons M_2(NMe_2)_5Cl + HNMe_2$$

$$\text{(c) } M_2(NMe_2)_5Cl + HCl \rightleftharpoons M_2Cl_2(NMe_2)_4 + HNMe_2 \quad (2)$$

may be isolated from reaction 1 because of (i) their relative low solubility and (ii) the high kinetic lability associated with these amine-catalyzed redistribution reactions.

When a similar reaction between $Ta(NMe_2)_5$ and Me_3SiCl was carried out in pentane, $TaCl_2(NMe_2)_3$ was obtained in

(1) For recent reviews, see: Cotton, F. A. *Acc. Chem. Res.* **1978**, *11*, 225. Chisholm, M. H.; Cotton, F. A. *Ibid.* **1978**, *11*, 356. Chisholm, M. H. *Transition Met. Chem.* **1978**, *3*, 356.
(2) Seidel, W.; Kreisel, G.; Mennenga, H. *Z. Chem.* **1976**, *12*, 492. Cotton, F. A.; Millar, M. *J. Am. Chem. Soc.* **1977**, *99*, 7886.
(3) Cotton, F. A.; Frenz, B. A.; Kruczynski, L. *J. Am. Chem. Soc.* **1973**, *95*, 951; *J. Organomet. Chem.* **1978**, *160*, 93.
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(6) (a) Mass, E. T., Jr.; McCarley, R. E. *Inorg. Chem.* **1973**, *12*, 1096. (b) Templeton, J. L.; Droman, W. C.; Clardy, J. C.; McCarley, R. E. *Ibid.* **1978**, *17*, 1263. (c) Templeton, J. L.; McCarley, R. E. *Ibid.* **1978**, *17*, 2293. (d) The following niobium(III) complexes are expected to contain (Nb=Nb) double bonds: $Nb_2Cl_6(SMe_2)_3$, $Nb_2Cl_6(L\text{-}L)_2$ (L-L = 1,1,1-tris(dimethylarsinomethyl)ethane (triars), *o*-phenylenebis(dimethylarsine) (diars), 1,2-bis(diphenylphosphino)ethane (diphos). See: Allen, A. D.; Naito, S. *Can. J. Chem.* **1976**, *54*, 2948.
(7) Vahrenkamp, H. *Chem. Ber.* **1978**, *111*, 3472.
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(10) Cotton, F. A.; Wilkinson, G. "Advanced Inorganic Chemistry", 4th ed.; Wiley-Interscience: New York, 1980.
(11) Bradley, D. C.; Chisholm, M. H. *Acc. Chem. Res.* **1976**, *9*, 273.
(12) Akiyama, M.; Chisholm, M. H.; Cotton, F. A.; Extine, M. W.; Murillo, C. A. *Inorg. Chem.* **1977**, *16*, 2407. The preparation of $[Ta(NMe_2)_3Cl_2]_2$ by the method described here was independently achieved by Dr. W. A. Nugent, Central Research and Development, Du Pont, and we are grateful for his helpful discussions and disclosures.

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high yield (>80%) according to eq 3 because it too precipitated

$$Ta(NMe_2)_5 + 2Me_3SiCl \rightarrow TaCl_2(NMe_2)_3 + 2Me_3SiNMe_2 \quad (3)$$

out of solution. When the reaction was carried out in toluene or benzene, a mixture of $TaCl_2(NMe_2)_3$ and $TaCl_3(NMe_2)_2$ was obtained because $TaCl_2(NMe_2)_3$ is more soluble in these solvents and it reacts further with chlorotrimethylsilane.

Attempts to prepare and isolate $TaCl(NMe_2)_4$ were unsuccessful because of the facile ligand redistribution reaction (4) and the lower solubility of $TaCl_2(NMe_2)_3$. The reaction

$$Ta(NMe_2)_5 + TaCl_2(NMe_2)_3 \rightleftharpoons 2TaCl(NMe_2)_4 \quad (4)$$

course between Me_3SiCl and $Ta(NMe_2)_5$ in toluene-d_8 solutions has been followed by ^1H NMR spectroscopy, and the distributions of products appears to follow closely that expected from statistics: no single product is favored by either kinetic or thermodynamic factors.

$TaCl_3(NMe_2)_2(HNMe_2)$, $TaCl_2(NMe_2)_3(HNMe_2)$, and $[TaCl_2(NMe_2)_2(HNMe_2)]_2O$. Carnell and Fowles reported[13] the preparation of an orange compound formed in the reaction between $TaCl_5$ and $HNMe_2$ in benzene. On the basis of analytical data, they formulated this as $TaCl_3(NMe_2)_2(HNMe_2)$. We have repeated their reaction sequence and have obtained $TaCl_3(NMe_2)_2(HNMe_2)$ as red cubic shaped crystals (85%), $TaCl_2(NMe_2)_3(HNMe_2)$ as a finely divided yellow powdery solid (6%), and $[TaCl_2(NMe_2)_2(HNMe_2)]_2O$ as orange, needlelike crystals (2%).

The compound $TaCl_2(NMe_2)_3(HNMe_2)$ can be prepared independently by the addition of dimethylamine (2 equiv) to $[TaCl_2(NMe_2)_3]_2$. It is also formed in the reaction between $TaCl_3(NMe_2)_2HNMe_2$ and free dimethylamine which produces an equilibrium mixture of compounds which interconvert rapidly on the NMR time scale. See eq 5.

$$TaCl_3(NMe_2)_2(HNMe_2) + 2HNMe_2 \rightleftharpoons TaCl_2(NMe_2)_3(HNMe_2) + Me_2NH_2^+Cl^- \quad (5)$$

The origin of the oxo-bridged product, $[TaCl_2(NMe_2)_2(HNMe_2)]_2O$, is not known. It could conceivably arise from an oxide impurity in the commercially available $TaCl_5$ or by trace hydrolysis during the course of these reactions and crystallizations. It is only a minor product, ca. 2% yield on the basis of tantalum, and might have gone unnoticed were it not to have had different crystalline morphology.

Physicochemical Properties. All of the new mixed chlorodimethylamido compounds of tantalum(V) are moisture sensitive and must be handled in dry solvents and atmospheres. They are volatile and may be sublimed, in vacuo, though not without some decomposition. Notable is the fact that the coordinated dimethylamine in the compounds $TaCl_2(NMe_2)_3(HNMe_2)$, $TaCl_3(NMe_2)_2(HNMe_2)$, and $[TaCl_2(NMe_2)_2(HNMe_2)]_2O$ is quite strongly bound and the mononuclear compounds sublime without evolution of amine. Thus, the rather simple preparation of $TaCl_2(NMe_2)_3(HNMe_2)$ described above does not afford access to the dimeric compound $[TaCl_2(NMe_2)_3]_2$. In the mass spectrometer, the mononuclear compounds show molecular ions; the dimeric compounds do not but show mononuclear ions formed by ligand bridge rupture. IR data, mass spectral data, NMR data, and analytical data are given in the Experimental Section.

Solid-State Structures. $TaCl_3(NMe_2)_2(HNMe_2)$. In the crystalline state, the compound is composed of discrete $TaCl_3(NMe_2)_2(HNMe_2)$ molecules. Final atomic positional parameters are given in Table I and bond distances and angles are given in Tables II and III, respectively. An ORTEP view of the molecule giving the atom numbering scheme is shown in Figure 1.

The molecule adopts a distorted octahedral geometry in the solid state: the trans angles are 168 ± 1°. The central $TaCl_3N_3$ moiety has a meridian disposition of ligands with a pair of cis dimethylamido ligands, one being trans to a chloride, the other trans to an amine. Further points of structural note are as follows: (i) the short Ta–NMe_2 bond distances 1.963 (5) and 1.954 (5) Å, though trans to Cl and $HNMe_2$, are essentially identical but *much shorter* than the Ta–$NHMe_2$ distance, 2.370 (6) Å; (ii) the tantalum atom is contained in the NC_2 planes of the dimethylamido ligands; (iii) the dihedral angle between the two Ta–NC_2 planes is 116°; (iv) the Ta–Cl bond distance trans to Ta–NMe_2 is 0.05 Å longer than the average Ta–Cl bond distance of the mutually trans Ta–Cl bonds.

$[TaCl_2(NMe_2)_2HNMe_2]_2O$. In the crystalline state the compound is composed of discrete $[TaCl_2(NMe_2)_2HNMe_2]_2O$ molecules. Final atomic positional parameters are given in Table IV, and bond distances and bond angles are given in

Table I. Fractional Coordinates[a] for the $[TaCl_3(NMe_2)_2(HNMe_2)]$ Molecule

atom	x	y	z	B_{iso}, Å^2
Ta(1)	7405.2 (3)	1804.1 (2)	1710.7 (2)	12
Cl(2)	7173 (2)	−130 (1)	744 (1)	18
Cl(3)	8213 (2)	3615 (2)	2847 (1)	16
Cl(4)	8421 (2)	495 (2)	3247 (1)	19
N(5)	9861 (6)	1519 (6)	1795 (5)	17
C(6)	11090 (7)	2140 (7)	2651 (6)	18
C(7)	10098 (8)	1741 (8)	836 (6)	22
N(8)	5368 (6)	1686 (5)	1658 (4)	16
C(9)	4745 (8)	577 (7)	1972 (6)	21
C(10)	4268 (8)	2719 (7)	1274 (6)	21
N(11)	7000 (6)	3047 (5)	610 (4)	14
C(12)	7661 (8)	4305 (7)	572 (6)	22
C(13)	5889 (9)	2725 (8)	−398 (5)	23
H(1)	982 (8)	52 (8)	194 (5)	14 (15)
H(2)	1123 (8)	204 (7)	333 (6)	12 (14)
H(3)	1213 (9)	171 (7)	271 (6)	21 (17)
H(4)	1106 (8)	292 (7)	248 (5)	5 (14)
H(5)	1130 (10)	139 (9)	100 (7)	43 (19)
H(6)	916 (9)	128 (8)	30 (6)	30 (17)
H(7)	1013 (8)	247 (8)	75 (5)	11 (14)
H(8)	454 (10)	73 (8)	276 (7)	34 (20)
H(9)	384 (9)	11 (8)	131 (6)	23 (17)
H(10)	529 (13)	4 (12)	208 (8)	53 (31)
H(11)	464 (8)	352 (7)	117 (5)	3 (13)
H(12)	338 (9)	248 (8)	64 (6)	24 (16)
H(13)	374 (10)	292 (8)	162 (7)	20 (19)
H(14)	875 (11)	436 (9)	118 (7)	64 (24)
H(15)	780 (6)	428 (5)	−9 (4)	8 (10)
H(16)	693 (9)	495 (9)	40 (6)	32 (19)
H(17)	529 (10)	339 (9)	−68 (7)	30 (20)
H(18)	623 (7)	255 (6)	−80 (5)	0 (11)
H(19)	516 (8)	193 (6)	−48 (5)	4 (13)

[a] Fractional coordinates are ×10^4 for nonhydrogen atoms and ×10^3 for hydrogens. All isotropic thermal parameters are ×10. The isotropic thermal parameters listed for those atoms refined anisotropically are the isotropic equivalent.

Table II. Bond Distances (A) for the $TaCl_3(NMe_2)_2(HNMe_2)$ Molecule[a]

A	B	dist	A	B	dist
Ta(1)	Cl(2)	2.391 (2)	N(5)	C(6)	1.499 (9)
Ta(1)	Cl(3)	2.408 (2)	N(5)	C(7)	1.491 (9)
Ta(1)	Cl(4)	2.450 (2)	N(8)	C(9)	1.445 (9)
Ta(1)	N(5)	2.370 (6)	N(8)	C(10)	1.466 (9)
Ta(1)	N(8)	1.963 (5)	N(11)	C(12)	1.460 (8)
Ta(1)	N(11)	1.954 (5)	N(11)	C(13)	1.480 (9)

[a] Bond distances to hydrogen atoms and nonbonding distances to 3.0 A are available as supplementary material.

(13) Carnell, P. J. H.; Fowles, G. W. *J. Chem. Soc.* **1959**, 4113.

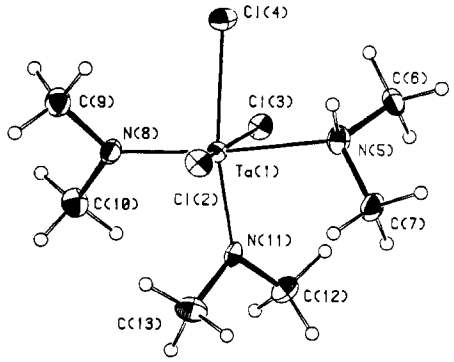


Figure 1. ORTEP view of the $TaCl_3(NMe_2)_2(HNMe_2)$ molecule showing the atom numbering scheme used in the tables. Ellipsoids of thermal vibration enclose 50% of the electron density.

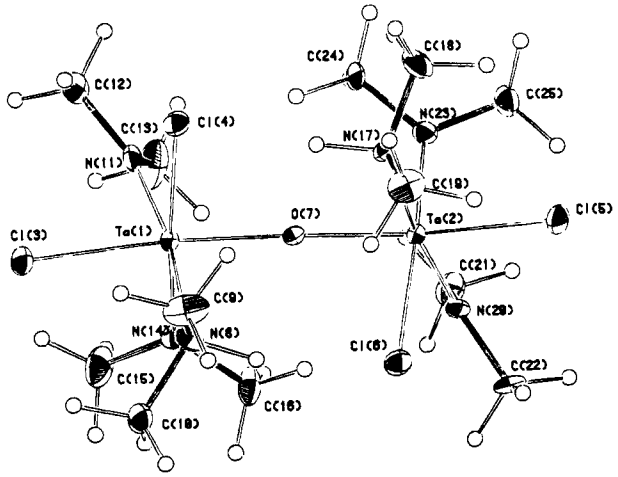


Figure 2. ORTEP view of the $[TaCl_2(NMe_2)_2HNMe_2]_2O$ molecule showing the atom numbering scheme used in the tables. Ellipsoids of thermal vibration enclose 50% of the electron density.

Tables V and VI, respectively. An ORTEP view of the molecule giving the atom numbering scheme is shown in Figure 2. This view of the molecule also emphasizes that the molecule has a virtual but not crystallographically imposed C_2 axis of symmetry. Each tantalum atom is in a distorted octahedral environment being coordinated to a pair of mutually cis NMe_2 ligands, a pair of cis Cl ligands, a dimethylamine molecule, and a bridging oxo ligand. The central Ta–O–Ta angle (174°) is close to linearity,[14] and the view of the molecule down the Ta–Ta axis, shown in Figure 3, reveals the nearly eclipsed geometry of the ligands. In part, this may be a result of intramolecular hydrogen bonding between the hydrogen atom of a dimethylamine coordinated to one tantalum atom and a chloride ligand bound to the other tantalum atom. These two NH---Cl distances are extremely short: 2.20 (2) and 2.24 (2) Å. Other points of structural note are as follows: (i) the short Ta–NMe_2 bond distances are 1.97 Å (averaged), and the long Ta–$NHMe_2$ bond distances are 2.37 Å (averaged); (ii) the tantalum atoms lie in the NC_2 planes of the dimethylamido groups, and the dihedral angle between the NC_2 planes of the two NMe_2 ligands bound to each tantalum atom is close to 90°; (iii) the Ta–Cl distances are longer by 0.1 Å when they are trans to dimethylamido groups than when they are trans to the bridging oxo ligand; (iv) the dimethylamido and bridging oxo ligands occupy a facial arrangement in both octahedra.

(14) The near linear Ta–O–Ta group found here may be compared to the linear Ta–N–Ta group, Ta–N = 1.849 (2) Å, reported in $[TaBr_5]_2^{3-}$: Frank, K. P.; Strähle, J.; Weidlen, J. *Z. Naturforsch. B: Anorg. Chem., Org. Chem.* **1980**, *356B*, 300.

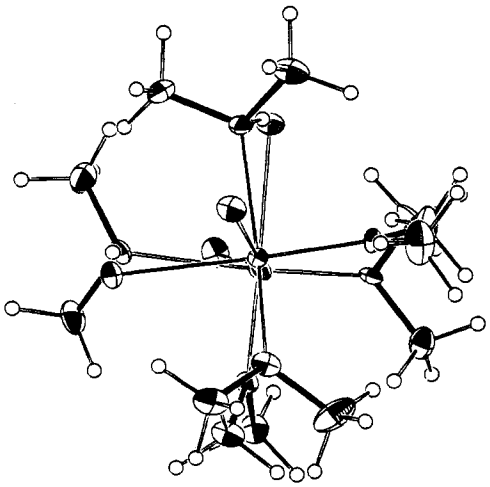


Figure 3. ORTEP view of the $[TaCl_2(NMe_2)_2HNMe_2]_2O$ molecule looking almost down the Ta–Ta axis showing the nearly eclipsed conformation which results from N–H···Cl bonding. Ellipsoids of thermal vibration enclose 50% of the electron density.

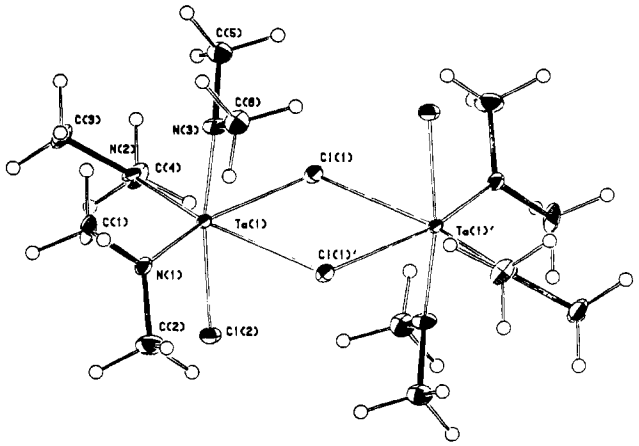


Figure 4. ORTEP view of the $[TaCl_2(NMe_2)_3]_2$ molecule showing the atom numbering scheme used in the tables. Ellipsoids of thermal vibration enclose 50% of the electron density.

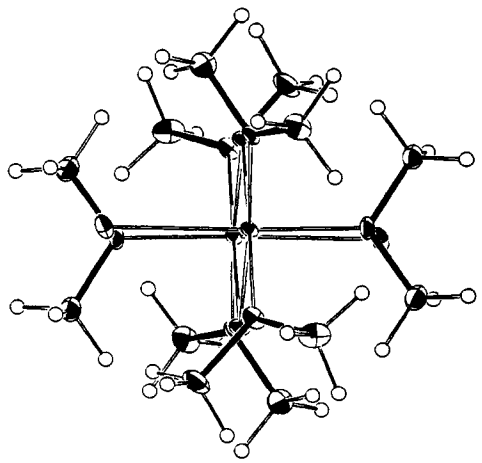


Figure 5. ORTEP view of the $[TaCl_2(NMe_2)_3]_2$ molecule looking almost down the Ta–Ta axis showing the edge-shared bioctahedron of the central $Ta_2Cl_4N_6$ unit. Ellipsoids of thermal vibration are drawn to enclose 50% of the electron density.

$[TaCl_2(NMe_2)_3]_2$. In the crystalline state, the compound is composed of discrete $[TaCl_2(NMe_2)_3]_2$ molecules. Final atomic positional parameters are given in Table VII, and bond distances and angles are given in Tables VIII and IX, re-

Table III. Bond Angles (Deg) for the $TaCl_3(NMe_2)_2(HNMe_2)$ Molecule[a]

A	B	C	angle
Cl(2)	Ta(1)	Cl(3)	167.2 (1)
Cl(2)	Ta(1)	Cl(4)	88.6 (1)
Cl(2)	Ta(1)	N(5)	78.5 (1)
Cl(2)	Ta(1)	N(8)	92.9 (2)
Cl(2)	Ta(1)	N(11)	97.9 (2)
Cl(3)	Ta(1)	Cl(4)	84.5 (1)
Cl(3)	Ta(1)	N(5)	89.6 (1)
Cl(3)	Ta(1)	N(8)	98.3 (2)
Cl(3)	Ta(1)	N(11)	87.1 (2)
Cl(4)	Ta(1)	N(5)	79.2 (2)
Cl(4)	Ta(1)	N(8)	93.6 (2)
Cl(4)	Ta(1)	N(11)	167.6 (2)
N(5)	Ta(1)	N(8)	169.3 (2)
N(5)	Ta(1)	N(11)	91.0 (2)
N(8)	Ta(1)	N(11)	96.6 (2)
Ta(1)	N(5)	C(6)	118.1 (4)
Ta(1)	N(5)	C(7)	115.9 (4)
C(6)	N(5)	C(7)	109.5 (6)
Ta(1)	N(8)	C(9)	125.1 (5)
Ta(1)	N(8)	C(10)	123.8 (4)
C(9)	N(8)	C(10)	111.1 (6)
Ta(1)	N(11)	C(12)	131.0 (4)
Ta(1)	N(11)	C(13)	119.3 (4)
C(12)	N(11)	C(13)	109.6 (5)

[a] Bond angles involving hydrogen atoms are available as supplementary material.

spectively. ORTEP views of the molecule are shown in Figures 4 and 5. The molecule has a rigorous and crystallographically imposed center of inversion relating the halves of the dimer. The coordination geometry about tantalum is again that of a distorted octahedron: the three dimethylamido groups occupy one face of each of the octahedra which are joined along a common edge by a pair of chloride bridges. The Ta–N distances trans to the bridging chloride ligands, 1.96 Å (averaged), are slightly shorter than the Ta–N distance, 1.989 (5) Å, which is trans to the terminal Ta–Cl bond distance. Conversely, the terminal Ta–Cl bond distance is shorter than those associated with bridges by ca. 0.15 Å.

Remarks on Structure and Bonding. In all three structures, tantalum achieves an octahedral geometry, either by coordination of a molecule of dimethylamine or by the formation of chloride bridges. This is in contrast to the situation observed for $Ta(NMe_2)_5$ which, being isostructural with $Nb(NMe_2)_5$, has a square based pyramidal TaN_5 unit.[15] This preference for an octahedral geometry can readily be understood in terms of electronic considerations. In all the structures, there are planar $Ta–NC_2$ units associated with the Me_2N^- ligands. This, taken together with the short Ta–N distances and the observed dihedral planes between the $Ta–NC_2$ units, provides direct evidence for nitrogen p to Ta d π bonding.[16] The Me_2N^- ligand in each of these molecules can be considered to act as a four-electron donor ($\sigma^2 + \pi^2$). Thus in $[TaCl_2(NMe_2)_3]_2$, each tantalum achieves an 18 valence shell of electrons as a result of forming six metal–ligand σ bonds and three π bonds with the NMe_2 ligands. The *fac*-TaN_3Cl_3 skeleton is reminiscent of the *fac*-WN_3O_3 skeleton found in $W(NMe_2)_3(O_2CNMe_2)_3$.[17]

Table IV. Fractional Coordinates[a] for the $[TaCl_2(NMe_2)_2(HNMe_2)]_2O$ Molecule

atom	x	y	z	B_{iso}, Å^2
Ta(1)	2610.5 (4)	4392.8 (2)	2318.0 (2)	9
Ta(2)	4240.8 (4)	2750.8 (2)	3508.1 (2)	9
Cl(3)	1458 (3)	5491 (1)	2080 (1)	16
Cl(4)	5222 (3)	4856 (1)	3571 (1)	14
Cl(5)	5551 (3)	1971 (1)	4724 (1)	17
Cl(6)	1920 (3)	2913 (1)	4153 (1)	16
O(7)	3456 (7)	3556 (3)	2865 (4)	11
N(8)	1152 (9)	4391 (4)	3346 (5)	13
C(9)	1941 (15)	4719 (6)	4236 (7)	25
C(10)	−695 (13)	4576 (5)	2948 (7)	21
N(11)	3742 (9)	4549 (4)	1441 (5)	14
C(12)	4796 (13)	5098 (5)	1434 (7)	20
C(13)	3485 (19)	4144 (6)	641 (7)	29
N(14)	562 (9)	3965 (4)	1408 (4)	13
C(15)	9401 (16)	4293 (6)	589 (7)	28
C(16)	−35 (14)	3288 (5)	1390 (7)	21
N(17)	6016 (11)	3455 (4)	4695 (5)	13
C(18)	7886 (12)	3371 (5)	4915 (7)	21
C(19)	5704 (15)	3487 (6)	5564 (7)	24
N(20)	2792 (9)	2072 (4)	2672 (5)	11
C(21)	2869 (14)	1906 (5)	1788 (7)	20
C(22)	1665 (12)	1614 (5)	2893 (8)	23
N(23)	6062 (9)	2671 (4)	3009 (5)	12
C(24)	6657 (13)	3170 (4)	2530 (7)	17
C(25)	7083 (13)	2074 (5)	3099 (7)	18
H(1)	131 (14)	390 (6)	348 (7)	23
H(2)	307 (17)	467 (6)	452 (8)	35
H(3)	203 (16)	520 (6)	418 (8)	35
H(4)	127 (16)	468 (6)	471 (8)	35
H(5)	−112 (15)	498 (6)	266 (7)	31
H(6)	−111 (15)	434 (6)	229 (8)	31
H(7)	852 (15)	445 (6)	329 (8)	31
H(8)	602 (15)	491 (6)	139 (7)	31
H(9)	440 (15)	533 (6)	96 (8)	31
H(10)	513 (15)	530 (6)	200 (8)	31
H(11)	301 (17)	378 (7)	64 (8)	41
H(12)	284 (17)	445 (7)	4 (9)	41
H(13)	462 (17)	403 (7)	53 (8)	41
H(14)	−51 (16)	478 (7)	57 (8)	38
H(15)	−83 (16)	422 (6)	−1 (9)	38
H(16)	−198 (17)	420 (6)	50 (8)	38
H(17)	−146 (15)	328 (6)	136 (7)	32
H(18)	7 (15)	303 (6)	97 (8)	32
H(19)	50 (15)	305 (6)	189 (8)	32
H(20)	578 (15)	365 (5)	458 (8)	23
H(21)	840 (15)	288 (6)	530 (8)	31
H(22)	815 (15)	343 (6)	433 (7)	31
H(23)	838 (15)	364 (6)	534 (8)	31
H(24)	658 (15)	366 (6)	607 (8)	33
H(25)	451 (16)	353 (6)	537 (8)	33
H(26)	585 (16)	310 (7)	581 (8)	33
H(27)	170 (15)	189 (6)	131 (7)	30
H(28)	329 (16)	228 (6)	170 (8)	30
H(29)	321 (15)	155 (6)	177 (7)	30
H(30)	178 (15)	155 (6)	349 (8)	33
H(31)	34 (16)	171 (6)	243 (8)	33
H(32)	208 (15)	118 (6)	300 (8)	33
H(33)	819 (15)	323 (6)	283 (7)	27
H(34)	645 (14)	294 (6)	196 (7)	27
H(35)	612 (14)	356 (6)	254 (7)	27
H(36)	663 (15)	176 (6)	329 (7)	29
H(37)	692 (15)	200 (6)	246 (8)	29
H(38)	826 (16)	219 (6)	343 (8)	29

[a] Fractional coordinates are $\times 10^4$ for nonhydrogen atoms and $\times 10^3$ for hydrogens. All isotropic thermal parameters are $\times 10$. The isotropic thermal parameters listed for those atoms refined anisotropically are the isotropic equivalent.

In both $TaCl_3(NMe_2)_2(HNMe_2)$ and $[TaCl_2(NMe_2)_2(NHMe_2)]_2O$, there are cis Me_2N ligands coordinated to each tantalum. The dihedral angles between the $TaNC_2$ planes of

(15) Heath, C. E.; Hursthouse, M. B. *Chem. Commun.* **1971**, 143. Rather interestingly, the closely related diethylamido compound $Ta(NEt_2)_5$ has a trigonal-bipyramidal TaN_5 unit: Smallwood, R. J. Ph.D. Thesis, London University, 1975. The change in TaN_5 structure on going from NMe_2 to NEt_2 probably arises because the D_{3h} structure is favored on steric grounds: Orioli, P. L. *Coord. Chem. Rev.* **1971**, *6*, 285.

(16) Ta—$HNMe_2$ and Ta—NMe_2 bond distances reported here may be compared with Ta—CH_3 (2.246 (2) Å) and Ta=CH_2 (2.026 (10) Å) reported for $Cp_2Ta(=CH_2)(CH_3)$: Guggenberger, L. J.; Schrock, R. R. *J. Am. Chem. Soc.* **1975**, *97*, 6578.

(17) Chisholm, M. H.; Extine, M. W. *J. Am. Chem. Soc.* **1974**, *96*, 6214; **1977**, *99*, 782.

Table V. Bond Distances (Å) for the $[TaCl_2(NMe_2)_2(HNMe_2)]_2O$ Molecule[a]

A	B	dist	A	B	dist
Ta(1)	Cl(3)	2.417 (2)	N(8)	C(9)	1.468 (12)
Ta(1)	Cl(4)	2.505 (2)	N(8)	C(10)	1.472 (12)
Ta(1)	O(7)	1.928 (6)	N(11)	C(12)	1.428 (13)
Ta(1)	N(8)	2.364 (7)	N(11)	C(13)	1.458 (13)
Ta(1)	N(11)	1.971 (7)	N(14)	C(15)	1.452 (12)
Ta(1)	N(14)	1.970 (7)	N(14)	C(16)	1.470 (12)
Ta(2)	Cl(5)	2.416 (2)	N(17)	C(18)	1.469 (12)
Ta(2)	Cl(6)	2.521 (2)	N(17)	C(19)	1.490 (12)
Ta(2)	O(7)	1.917 (6)	N(20)	C(21)	1.461 (12)
Ta(2)	N(17)	2.382 (8)	N(20)	C(22)	1.459 (11)
Ta(2)	N(20)	1.981 (7)	N(23)	C(24)	1.464 (11)
Ta(2)	N(23)	1.960 (7)	N(23)	C(25)	1.464 (11)

[a] Bond distances to hydrogen atoms and nonbonding distances to 3.0 Å are available as supplementary material.

Table VI. Bond Angles (Deg) for the $[TaCl_2(NMe_2)_2(HNMe_2)]_2O$ Molecule[a]

A	B	C	angle
Cl(3)	Ta(1)	Cl(4)	86.8 (1)
Cl(3)	Ta(1)	O(7)	162.3 (2)
Cl(3)	Ta(1)	N(8)	80.3 (2)
Cl(3)	Ta(1)	N(11)	90.4 (2)
Cl(3)	Ta(1)	N(14)	96.7 (2)
Cl(4)	Ta(1)	O(7)	85.6 (2)
Cl(4)	Ta(1)	N(8)	88.6 (2)
Cl(4)	Ta(1)	N(11)	89.5 (2)
Cl(4)	Ta(1)	N(14)	174.9 (2)
O(7)	Ta(1)	N(8)	83.5 (2)
O(7)	Ta(1)	N(11)	105.6 (3)
O(7)	Ta(1)	N(14)	90.0 (3)
N(8)	Ta(1)	N(11)	170.6 (3)
N(8)	Ta(1)	N(14)	88.5 (3)
N(11)	Ta(1)	N(14)	94.1 (3)
Cl(5)	Ta(2)	Cl(6)	87.2 (1)
Cl(5)	Ta(2)	O(7)	161.9 (2)
Cl(5)	Ta(2)	N(17)	79.4 (2)
Cl(5)	Ta(2)	N(20)	92.5 (2)
Cl(5)	Ta(2)	N(23)	94.5 (2)
Cl(6)	Ta(2)	O(7)	86.6 (2)
Cl(6)	Ta(2)	N(17)	86.8 (2)
Cl(6)	Ta(2)	N(20)	89.7 (2)
Cl(6)	Ta(2)	N(23)	177.2 (2)
O(7)	Ta(2)	N(17)	83.2 (2)
O(7)	Ta(2)	N(20)	104.6 (3)
O(7)	Ta(2)	N(23)	91.1 (3)
N(17)	Ta(2)	N(20)	171.3 (3)
N(17)	Ta(2)	N(23)	91.3 (3)
N(20)	Ta(2)	N(23)	92.4 (3)
Ta(1)	O(7)	Ta(2)	174.3 (3)
Ta(1)	N(8)	C(9)	119.7 (6)
Ta(1)	N(8)	C(10)	115.5 (6)
C(9)	N(8)	C(10)	107.9 (8)
Ta(1)	N(11)	C(12)	126.2 (6)
Ta(1)	N(11)	C(13)	124.3 (7)
C(12)	N(11)	C(13)	109.3 (8)
Ta(1)	N(14)	C(15)	122.9 (6)
Ta(1)	N(14)	C(16)	128.7 (6)
C(15)	N(14)	C(16)	108.3 (7)
Ta(2)	N(17)	C(18)	113.6 (6)
Ta(2)	N(17)	C(19)	118.6 (6)
C(18)	N(17)	C(19)	108.9 (8)
Ta(2)	N(20)	C(21)	124.3 (6)
Ta(2)	N(20)	C(22)	125.2 (6)
C(21)	N(20)	C(22)	110.1 (8)
Ta(2)	N(23)	C(24)	127.7 (6)
Ta(2)	N(23)	C(25)	122.5 (6)
C(24)	N(23)	C(25)	109.7 (7)

[a] Bond angles to hydrogen atoms are available as supplementary material.

these cis ligands are close to 90°. This situation allows for the formation of strong σ bonds because the groups are not

Table VII. Fractional Coordinates[a] for the $[TaCl_2(NMe_2)_3]_2$ Molecule

atom	*x*	*y*	*z*	B_{iso}, Å^2
Ta(1)	3526.4 (2)	5866.3 (2)	−1150.3 (2)	6
Cl(1)	4907 (1)	5570 (1)	1668 (2)	9
Cl(2)	5309 (1)	6994 (1)	−1617 (2)	12
N(1)	2759 (5)	5801 (3)	−3399 (6)	10
N(2)	2638 (4)	6967 (4)	−191 (5)	9
N(3)	2283 (4)	4853 (4)	−530 (6)	11
C(1)	1388 (6)	5663 (6)	−4077 (8)	16
C(2)	3518 (7)	5845 (6)	−4734 (8)	18
C(3)	1258 (6)	7194 (5)	9395 (8)	16
C(4)	3256 (6)	7706 (5)	970 (8)	16
C(5)	1795 (6)	4860 (5)	1012 (8)	14
C(6)	1980 (6)	3895 (5)	−1372 (8)	15
H(1)	93 (7)	548 (6)	−333 (9)	19 (15)
H(2)	119 (6)	628 (5)	−467 (7)	6 (12)
H(3)	145 (6)	506 (5)	−469 (8)	11 (13)
H(4)	437 (8)	590 (4)	−443 (8)	11 (14)
H(5)	341 (6)	522 (5)	−527 (7)	5 (12)
H(6)	327 (7)	646 (6)	−534 (9)	21 (15)
H(7)	117 (7)	786 (5)	−124 (8)	17 (14)
H(8)	88 (5)	667 (4)	−141 (7)	0 (10)
H(9)	77 (6)	721 (5)	26 (8)	12 (13)
H(10)	408 (7)	758 (5)	111 (8)	16 (14)
H(11)	294 (11)	859 (9)	−12 (13)	79 (30)
H(12)	269 (10)	769 (8)	184 (11)	59 (25)
H(13)	195 (6)	551 (5)	151 (7)	2 (10)
H(14)	89 (7)	467 (5)	90 (8)	13 (13)
H(15)	221 (6)	445 (5)	161 (8)	8 (13)
H(16)	103 (7)	376 (5)	−148 (8)	18 (14)
H(17)	231 (6)	386 (4)	774 (8)	2 (11)
H(18)	262 (8)	338 (6)	931 (9)	30 (17)

[a] Fractional coordinates are $\times 10^4$ for nonhydrogen atoms and $\times 10^3$ for hydrogens. All isotropic thermal parameters are $\times 10$. The isotropic thermal parameters listed for those atoms refined anisotropically are the isotropic equivalent.

Table VIII. Bond Distances (Å) for the $[TaCl_2(NMe_2)_3]_2$ Molecule[a]

A	B	dist	A	B	dist
Ta(1)	Cl(1)′	2.586 (1)	N(1)	C(1)	1.480 (8)
Ta(1)	Cl(1)	2.635 (2)	N(1)	C(2)	1.469 (8)
Ta(1)	Cl(2)	2.463 (1)	N(2)	C(3)	1.468 (7)
Ta(1)	N(1)	1.958 (5)	N(2)	C(4)	1.470 (7)
Ta(1)	N(2)	1.962 (5)	N(3)	C(5)	1.465 (8)
Ta(1)	N(3)	1.989 (5)	N(3)	C(6)	1.466 (8)

[a] Bond distances to hydrogen atoms and nonbonding distances to 3.0 Å are available as supplementary material. The Ta-to-Ta distance is 4.1 Å.

competing for the same hybrid metal orbitals to form σ bonds[18] and allows for noncompetitive use of tantalum t_{2g} type d orbitals for π bonding. In $TaCl_3(NMe_2)_2(HNMe_2)$, tantalum achieves a 16 valence electron shell as a result of forming six metal–ligand σ bonds and two π bonds to the two NMe_2 ligands. It is possible for the chloride ligands to π bond, Cl 3p to Ta 5d, but there is no compelling structural evidence to suggest that any such interaction is significant. In the oxo-bridged dimer, oxygen-to-tantalum π bonding is possible and indicated by the short Ta–O distance, and thus tantalum can again achieve an 18 valence shell of electrons. Note the oxo ligand is cis to both Ta–NMe_2 groups.

Though the structure of $TaCl_2(NMe_2)_3(HNMe_2)$ was not determined by an X-ray study, it can fairly safely be assumed to once again contain six-coordinate tantalum with a *fac*-$Ta(NMe_2)_3$ moiety. This structure is arrived at by replacing

(18) Ligands having a high trans influence always prefer a mutual cis configuration, irrespective of their π-acceptor or -donor properties: Appleton, T. G.; Clark, H. C.; Manzer, L. E. *Coord. Chem. Rev.* **1973**, *10*, 335.

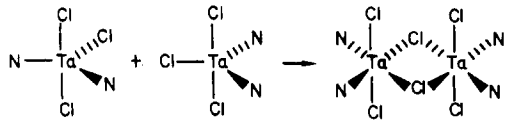
Table IX. Bond Angles (Deg) for the $[TaCl_2(NMe_2)_3]_2$ Molecule[a]

A	B	C	angle
Cl(1)′	Ta(1)	Cl(1)	76.3 (0)
Cl(1)	Ta(1)	Cl(2)	84.6 (1)
Cl(1)′	Ta(1)	Cl(2)	84.5 (0)
Cl(1)′	Ta(1)	N(1)	165.6 (1)
Cl(1)	Ta(1)	N(1)	89.3 (1)
Cl(1)′	Ta(1)	N(2)	164.4 (1)
Cl(1)	Ta(1)	N(2)	88.2 (1)
Cl(1)	Ta(1)	N(3)	90.2 (2)
Cl(1)	Ta(1)	N(3)	87.6 (1)
Cl(2)	Ta(1)	N(1)	95.0 (1)
Cl(2)	Ta(1)	N(2)	91.7 (1)
Cl(2)	Ta(1)	N(3)	171.3 (1)
N(1)	Ta(1)	N(2)	106.2 (2)
N(1)	Ta(1)	N(3)	91.8 (2)
N(2)	Ta(1)	N(3)	91.5 (2)
Ta(1)	Cl(1)	Ta(1)′	103.7 (0)
Ta(1)	N(1)	C(1)	128.6 (4)
Ta(1)	N(1)	C(2)	123.4 (4)
C(1)	N(1)	C(2)	107.9 (5)
Ta(1)	N(2)	C(3)	124.1 (4)
Ta(1)	N(2)	C(4)	125.4 (4)
C(3)	N(2)	C(4)	110.4 (5)
Ta(1)	N(3)	C(5)	123.6 (4)
Ta(1)	N(3)	C(6)	124.0 (4)
C(5)	N(3)	C(6)	111.0 (5)

[a] Bond angles involving hydrogen atoms are available as supplementary material.

either a bridging chloride in $[TaCl_2(NMe_2)_3]_2$ or one of the mutually trans chloride ligands in $TaCl_3(NMe_2)_2(HNMe_2)$ by a dimethylamido ligand. Here tantalum achieves an 18 valence shell of electrons. This structure is also consistent with the ^1H NMR data presented later.

For $TaCl_3(NMe_2)_2$, a dimeric structure with a pair of chloride bridges and two pairs of *cis*-$Ta(NMe_2)_2$ groups seems likely. Here, as in $TaCl_3(NMe_2)_2(HNMe_2)$, tantalum would achieve only 16 valence electrons. This contrasts with the monomeric structure found for $TaCl_3(NSi_2Me_6)_2$ which has a trigonal-bipyramidal $TaCl_3N_2$ unit with *cis*-$TaNSi_2Me_6$ groups. The latter compound is no doubt monomeric because of the voluminous silylamide ligands. The structure we are predicting for a dimeric $TaCl_3(NMe_2)_2$ compound represents the association of two trigonal-bipyramidal TaN_2Cl_3 units: the chloride ligands in the equatorial positions of the trigonal-bipyramidal $TaCl_3N_2$ groups form bridging groups of the two octahedral $TaCl_4N_2$ moieties. This is shown schematically by



^1H NMR Studies. $TaCl_3(NMe_2)_2(HNMe_2)$ contains a meridian disposition of TaCl bonds: there are two types of Ta–NMe_2 groups, one being trans to Ta–Cl, the other trans to Ta–$NHMe_2$. At 16 °C and 220 MHz, the solution ^1H NMR spectrum, recorded in toluene-d_8, is entirely consistent with this structure. There are two single lines at δ 3.96 and 3.54 assignable to the coordinated dimethylamido ligands and a doublet at δ 2.15 (J_{HH} = 6.8 Hz) corresponding to the methyl resonance of the coordinated dimethylamine. In addition, there is a broad resonance (1 H) at δ 2.32 assignable to the N–H group. When the temperature is lowered to −45 °C, the only observable change in the spectrum is that the NH proton resonance becomes a fairly well-resolved septet (J_{HH} = 6.8 Hz) due to coupling to the six methyl protons of the coordinated dimethylamine. Evidently, rotations about Ta–N bonds are still rapid on the NMR time scale.

$TaCl_2(NMe_2)_3(HNMe_2)$ is predicted to have a *fac*-$Ta(NMe_2)_3$ group (see Remarks on Structure and Bonding) which generates two equivalent Ta–NMe_2 groups, those trans to Ta–Cl bonds, and one Ta–NMe_2 group trans to Ta–$NHMe_2$. The low-temperature (−45 °C) ^1H NMR spectrum shows two dimethylamido resonances at δ 3.84 and 3.34 in the integral ratio 1:2. In addition, there is a doublet at δ 2.07 with J_{HH} = 6.8 Hz and a broad resonance at δ 2.38 which are assignable to the methyl and amine protons, respectively, of the coordinated dimethylamine. The low-temperature spectrum is thus entirely consistent with the predicted structure. It should be noted, however, that the same pattern would be expected for a *mer*-$Ta(NMe_2)_3Cl_2(HNMe_2)$ compound, and this is only discounted on the basis of electronic considerations. When the temperature is raised, the two dimethylamido resonances coalesce to a singlet at δ 3.57 above 16 °C at 220 MHz. Evidently, the molecule is fluxional on the NMR time scale.

$TaCl_2(NMe_2)_3(L)$. The spectra of $[TaCl_2(NMe_2)_3]_2$ dissolved in pyridine-d_5 are analogous to those associated with $TaCl_2(NMe_2)_3(HNMe_2)$ in toluene-d_8. At 16 °C and 220 MHz, there is a single resonance for the dimethylamido protons at δ 3.82. When the sample is cooled to −22 °C and below, two resonances are observed at δ 3.93 and 3.64 in the integral ratio 1:2, respectively. A similar situation is found when 4-picoline is added to a toluene-d_8 solution of $[TaCl_2(NMe_2)_3]_2$ which suggests that the dimer is readily cleaved by nitrogen donor ligands to form $TaCl_2(NMe_2)_3L$ compounds.

$[TaCl_2(NMe_2)_3]_2$. A freshly prepared sample of $[TaCl_2(NMe_2)_3]_2$ in toluene-d_8 showed four resonances in the dimethylamido region at 16 °C (220 MHz): δ 3.95, 3.70, 3.62, and 3.54. The resonance at δ 3.62 was initially the most intense and was slightly broad. With time (on the order of hours if the sample was kept cold ca. −20 °C or within 30 min if maintained in the probe of the NMR spectrometer at +16 °C) the other resonances increased in intensity at the expense of the resonance at δ 3.62. We believe this situation arises from the distribution reaction shown in eq 6. However, an

$$TaCl_2(NMe_2)_3 \rightleftharpoons TaCl(NMe_2)_4 + TaCl_3(NMe_2)_2 \quad (6)$$

unequivocal assignment of the observed spectrum is not possible at this time. If the ^1H NMR spectrum of a freshly prepared sample of $[TaCl_2(NMe_2)_3]_2$ is recorded at temperatures below −22 °C, several additional resonances are observed. Presumably, not only are there several species present in solution but also at least some of these are fluxional on the NMR time scale.

Experimental Section

General Data. All manipulations were performed under a dry and oxygen-free nitrogen atmosphere with use of standard Schlenk and vacuum line procedures and/or a Vacuum Atmospheres Co. Dri-Lab assembly. Solvents were distilled from sodium–benzophenone ketyl solutions and stored over calcium hydride under a nitrogen atmosphere prior to use.

Chemicals. $TaCl_5$ (99% purity) from Apache Chemical Co., anhydrous dimethylamine from Matheson Co., and *n*-butyllithium (ca. 2.4 M in hexane) from Ventron Corp. were used without purification. Chlorotrimethylsilane, from Aldrich Chemical Co., was distilled and stored over 10-Å molecular sieves prior to use. $Ta(NMe_2)_5$ was prepared according to the method of Bradley and Thomas.[19]

Physical and Analytical Measurements. Elemental analyses were obtained from Alfred Bernhardt Mikroanalytisches Laboratorium, Elbach, West Germany, and Canadian Microanalytical Services, Vancouver, BC, Canada, using drybox sampling techniques.

Infrared spectra were obtained from Nujol or Fluorolube mulls between CsI and KBr plates, respectively, with use of a Perkin-Elmer 283 spectrophotometer.

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^{1}H NMR spectra were recorded with use of a Varian HR-220 instrument equipped with variable-temperature accessories.

Mass spectra were obtained on an AEI MS-902 spectrometer courtesy of Mr. Peter Cook, Department of Chemistry, Queen Mary College, London E1 4NS, England.

Preparation of $[TaCl_2(NMe_2)_3]_2$. $Ta(NMe_2)_5$ (7.04 g, 17.5 mmol) was placed in a 100-mL round-bottomed flask, together with a magnetic follower (spin bar). Pentane (50 mL) was added to afford a clear orange solution. The solution was then frozen in a liquid-nitrogen bath and subjected to three cycles of freeze–pump–thaw before attaching the reaction vessel to a calibrated vacuum manifold. Me_3SiCl (4.34 g, 40 mmol) was condensed into the flask containing the frozen solution of $Ta(NMe_2)_5$. The reaction vessel was then allowed to warm slowly to room temperature, and the solution was stirred vigorously for 6 h. A bright yellow precipitate formed. The solvent was stripped, and the resulting yellow solids were washed with hexane (4 × 25 mL) in a Dri-Lab until the filtrate was colorless. The solids were collected and dried in vacuo. The yield was 6.05 g (90% on the basis of eq 3). Anal. Calcd for $TaCl_2(NMe_2)_3$: C, 18.76; H, 4.72; N, 10.94; Cl, 18.48. Found: C, 18.44; H, 4.91; N, 11.17; Cl, 18.06. $[TaCl_2(NMe_2)_3]_2$ is insoluble in aliphatic hydrocarbon solvents, slightly soluble in aromatic hydrocarbon solvents, and very soluble in coordinating solvents such as pyridine and tetrahydrofuran. IR data in cm^{-1} are as follows. (i) Fluorolube: 2988 m, 2895 s br, 2865 s, 2820 w, 2775 m, 1453 s, 1440 s, 1423 vw, 1408 w, 1385 w. (ii) Nujol: 2773 m, 1443 s, 1425 vw, 1408 m, 1384 vw, 1244 s, 1127 vs, 1145 s sh, 1136 vs, 967 vs, 949 vs, 737 m, br, 560 s, br, 545 s sh, 373 s, 328 vw, 321 m, 293 vs, 255 m, 222 m. In the mass spectrometer, the ion of highest m/e corresponded to $TaCl_2(NMe_2)_3^+$ and was followed by (loss of HCl) $TaCl(NMe_2)_2(N(CH_2)CH_3)^+$. Analogous reactions involving $Ta(NMe_2)_5$ and Me_3SiCl (2 equiv) in toluene yielded orange, hexane-insoluble products having higher chloride and lower nitrogen contents, e.g., 21.7% Cl and 8.83% N. Recrystallization from hot toluene gave a mixture of two crystalline products of similar solubility: red crystals and orange crystals. The latter are known to be $[TaCl_2(NMe_2)_3]_2$ from the X-ray study. The former are presumed to be $[TaCl_3(NMe_2)_2]_2$.

Preparation of $TaCl_3(NMe_2)_2(HNMe_2)$, $TaCl_2(NMe_2)_3(HNMe_2)$, and $[TaCl_2(NMe_2)_2(HNMe_2)]_2O$. These three products were all isolated from the reaction between $TaCl_5$ and $HNMe_2$ which followed closely the procedure described by Carnell and Fowles.[13]

$TaCl_5$ (12.9 g, 36.0 mmol) was partially dissolved in degassed benzene (125 mL) in a 250-mL round-bottomed flask to give a yellow-green solution. Dimethylamine (185 mmol) was added to this frozen solution at ca. −178 °C, with use of a calibrated vacuum manifold. The reaction vessel was then slowly allowed to warm to room temperature. The solution initially became orange and then turned rose red. The solution was stirred with a magnetic follower for 24 h at room temperature. A fine white crystalline precipitate ($Me_2NH_2^+Cl^-$) was removed by filtration, and the filtrate was concentrated to ca. 30 mL. Pentane (100 mL) was then added slowly, which initiated crystallization. After 24 h, the first crop of crystals (red cubic crystals) were filtered and dried: 12.9 g of $Ta(NMe_2)_2Cl_3(HNMe_2)$ (85% yield on the basis of Ta). Anal. Calcd: C, 17.1; H, 4.55; N, 9.99; Cl, 25.3. Found: C, 17.6; H, 4.82; N, 9.94; Cl, 25.0. IR data in cm^{-1} are as follows. (a) Obtained in Fluorolube: 3252 s, 3002 w, 2982 m, 2900, 2880, 2860 s, br, 2830 w, 2782 m, 2768 vw, 1469 m sh, 1456 s, 1443 s, 1422 ms, 1412 m, 1400 w, 1392 w sh. (b) Obtained in Nujol: 3252 s, 3010 w, 2782 m, 2768 w, 1443 s, br, 1422 s, 1412 m, 1400 m, 1392 w sh, 1375 m, 1258 s, 1243 s, 1209 ms, 1127 s, 1110 vs, 1039 vs, 1009 s, 958 vs, 936 vs, 886 vs, 740 ms, br, 610 ms, 556 vs, 440 s, 375 s, 292 vs, 267 s. In the mass spectrometer, the ion of highest mass corresponded to $TaCl_2(NMe_2)_3^+$, i.e., $[M - HCl]^+$. Further loss of HCl yielded $TaCl(NMe_2)_2(N(CH_2)CH_3)^+$. The orange-red filtrate was let stand for a further 10 days during which time orange-red needle-shaped crystals were formed along with yellow rodlike crystals. The latter grew in clusters. In addition, a few red cubic crystals were formed. The supernatant liquid was decanted, the crystals were washed with pentane and dried in vacuo. The yellow rodlike crystals were easily separated by hand in the drybox and identified as $Ta(NMe_2)_3Cl_2(HNMe_2)$ (0.25 g (1.6% yield on the basis of Ta)). Anal. Calcd: C, 22.4; H, 5.64; N, 13.3; Cl, 16.5. Found: C, 22.0; H, 5.25; N, 12.6; Cl, 16.8. IR data in cm^{-1} are as follows. (a) Obtained Fluorolube mull: 3234 s, 2982 ms, 2852 s, br, 2812 m, 2770 ms, 1450 s, 1415 ms, 1398 w. (b) Obtained Nujol mull: 3220 s, 2760 ms, 1408 w, 1391 w, 1257 m, 1232 ms, 1120 s, 1083 s, br, 1034 ms, 1010 s, 965 s, 945 vs, 887 s, 733 w, br, 604 ms, 542 ms, br, 282 ms, br, 246 m, br. Separation of the orange-red needles from the red cubic crystals was more difficult but was attempted, yielding $[TaCl_2(NMe_2)_2(HNMe_2)]_2O$ (0.96 g (6.3% on the basis of Ta)). Anal. Calcd: C, 18.31; H, 4.84; N, 10.7; Cl, 18.1. Found: C, 18.7; H, 4.57; N, 10.2; Cl, 24.1. The chloride analysis was not repeated since the orange-red needlelike crystals were unequivocally identified by the X-ray study. IR data in cm^{-1} are as follows. (a) Obtained from Fluorolube: 3255 s, 3185 s, 3170 s, 3010 w, 2980 m, 2900 s, br, 2828 vw, 2780 m, 1458 s, br, 1446 s sh, 1422 w, 1413 w, 1398 m, br. (b) Obtained from Nujol: 3252 s, 3184 ms, 3168 ms, 3010 w, 2780 m, 1422 w, 1414 w, 1400 w, br, 1374 ms, 1258 s, 1241 s, 120 m, 1127 s sh, 1110 vs, 1041 vs, 1020 ms, 963 vs, 950 vs, 936 vs, 888 vs, 736 vs, br, 608 m, br, 556 s, br, 440 ms, br, 370 ms, br, 295 s, br, 268 m. In the mass spectrometer, the most intense ion corresponded to $Ta(NMe_2)_3O^+$.

Thermal Stability of $TaCl_3(NMe_2)_2(HNMe_2)$. (a) An NMR tube containing $TaCl_3(NMe_2)_2(HNMe_2)$ (ca. 10 mg) dissolved in toluene-d_8 (1.2 mL) was sealed in vacuo and placed in an oil bath at 70 °C. After 30 h, there was no visual sign of change, and the ^{1}H NMR spectrum showed no sign of decomposition. (b) $TaCl_3(NMe_2)_2(HNMe_2)$ was sealed in a Pyrex tube in vacuo and placed in an oil bath. Upon heating to 110–112 °C, the sample melted to give a red liquid. After 29 h at 120 °C, there was a deep red liquid at the bottom of the tube and some microcrystalline orange sublimate at the upper part of the tube. Both the sublimate and the solids formed on cooling were identified as $TaCl_3(NMe_2)_2(HNMe_2)$ by NMR spectroscopy. (c) $TaCl_3(NMe_2)_2(HNMe_2)$ (3.0 g) was placed in a sublimation apparatus, and the solids were heated to 90 °C at 10^{-4} torr. After 36 h, the orange sublimate was collected (2.01 g, 67%) and was shown by ^{1}H NMR spectroscopy to be $TaCl_3(NMe_2)_2(HNMe_2)$. The ^{1}H NMR spectrum of the unsublimed brown solids (0.92 g, 31%) showed evidence of other products in addition to unreacted $TaCl_3(NMe_2)_2(HNMe_2)$.

Reaction of $TaCl_3(NMe_2)_2(HNMe_2)$ with $HNMe_2$. $TaCl_3(NMe_2)_2(HNMe_2)$ (10 mg, 0.094 mmol) was dissolved in toluene-d_8 (1.2 mL) in an NMR tube. $HNMe_2$ (0.067 mmol) was added by use of a calibrated vacuum manifold. The tube was sealed, and the sample was examined by variable-temperature ^{1}H NMR spectroscopy. At −45 °C, both $TaCl_3(NMe_2)_2(HNMe_2)$ and $TaCl_2(NMe_2)_3(HNMe_2)$ were identified. In addition, a fine crystalline precipitate, $Me_2NH_2^+Cl^-$, was present. When the temperature was raised to +70 °C, the methyl signals assignable to $TaCl_3(NMe_2)_2(HNMe_2)$, $TaCl_2(NMe_2)_3(HNMe_2)$, $Me_2NH_2^+Cl^-$, and free Me_2NH coalesced to a single resonance, indicating that the equilibrium reaction $TaCl_3(NMe_2)_2(HNMe_2) + 2HNMe_2 \rightleftharpoons TaCl_2(NMe_2)_3(HNMe_2) + Me_2NH_2^+Cl^-$, is rapid on the NMR time scale.

Reaction of $[TaCl_2(NMe_2)_3]_2$ with $HNMe_2$. $[TaCl_2(NMe_2)_3]_2$ (0.2 g, 0.52 mmol) was placed in a glass ampule and dissolved in liquid $HNMe_2$ (3 mL), which was added by use of a vacuum manifold, to give a clear orange solution. After 2 h, $HNMe_2$ was pumped off, and the resulting yellow solids were dried in vacuo. The ^{1}H NMR spectra of the yellow solids recorded in toluene-d_8 at +16 and −45 °C were identical with those of $TaCl_2(NMe_2)_3(HNMe_2)$. The reaction between $[TaCl_2(NMe_2)_3]_2$ and $HNMe_2$ apparently gives $TaCl_2(NMe_2)_3(HNMe_2)$ quantitatively and irreversibly.

X-ray Structural Determinations. General operating procedures were as described previously.[4]

$[Ta(NMe_2)_3Cl_2]_2$. An orange crystal of dimensions 0.14 × 0.15 × 0.12 mm was examined. The cell dimensions obtained from 28 reflections at −165 °C with Mo Kα (λ 0.71069 Å) were a = 10.464 (3) Å, b = 13.224 (4) Å, c = 8.450 (2) Å, β = 98.07 (1)°, V = 1157.6 (5) Å^3, Z = 2, d_{calcd} = 2.204 g cm^{-3}, with space group $P2_1/n$.

A total of 3873 reflections were collected with use of standard moving-crystal moving-detector techniques with the following values: scan speed = 3° min^{-1}, scan width = 2.0 + dispersion, single background time at extremes of scan = 8 s, aperture size = 3.0 × 4.0 mm. The limits of data collection were $5° < 2\theta < 50°$. Of 2051 unique intensities, the number of reflections with $F > 2.33\sigma_F$ was 1880. The linear absorption coefficient was 98.12 cm^{-1}.

The structure was solved by direct methods and refined by full-matrix techniques, including all hydrogen atoms, to give final residuals R_F = 0.030 and R_{wF} = 0.031. The goodness of the fit for the last cycle was 1.223, and the maximum Δ/σ was 0.05.

$TaCl_3(NMe_2)_2(HNMe_2)$. An orange crystal of dimensions 0.16 × 0.21 × 0.31 mm was examined. The cell dimensions obtained from 27 reflections at −171 °C with Mo Kα (λ 0.71069 Å) were a = 9.750

(3) Å, b = 10.330 (2) Å, c = 14.300 (4) Å, β = 112.05 (1)°, V = 1335.0 Å^3, Z = 4, d_{calcd} = 2.092 g cm^{-3}, with space group $P2_1/c$.

A total of 3523 reflections were collected with use of standard moving-crystal moving-detector techniques with the following values: scan speed = 4.0° min^{-1}, scan width = 2.0 + dispersion, single background time at extremes of scan = 4 s, aperture size = 3.0 × 4.0 mm. The limits of data collection were $5° < 2\theta < 50°$. The number of reflections with $F > 2.33\sigma_F$ was 2758. The data were corrected for absorption: the linear absorption coefficient was 87.135 cm^{-1} with minimum and maximum corrections of 0.152 and 0.311, respectively.

The structure was solved by direct methods and refined with use of full-matrix techniques, including all hydrogen atoms, to give final residuals R_F = 0.038 and R_{wF} = 0.040. The goodness of fit for the last cycle was 1.057, and the maximum Δ/σ was 0.05.

$[TaCl_2(NMe_2)_2(HNMe_2)]_2O$. A yellow crystal of dimensions 0.14 × 0.16 × 0.24 mm was examined. The orange crystals selected at ambient temperatures all exhibited reversible chromic behavior, turning yellow upon cooling to −171 °C. The cell dimensions obtained from 29 reflections at −171 °C with Mo Kα (λ 0.71069 Å) were a = 8.314 (1) Å, b 20.480 (4) Å, c = 15.778 (3) Å, β = 112.22 (1)°, V = 1243.6 Å^3, Z = 4, d_{calcd} = 2.241 g cm^{-3}, with space group $P2_1/c$.

A total number of 11 996 reflections were collected with use of standard moving-crystal moving-detector techniques with the following values: scan speed = 4.0° min^{-1}, scan width = 2.0 + dispersion, single background time at extremes of scan = 5 s, aperture size = 3.0 × 4.0 mm. The limits of data collection were $5° < 2\theta < 50°$. Of 5718 unique intensities, the number of reflections with $F > 2.33\sigma_F$ was 5064. The data were corrected for absorption: the linear absorption coefficient was 91.390 cm^{-1} with minimum and maximum corrections of 0.195 and 0.377, respectively.

The structure was solved by direct methods and refined by full-matrix techniques, including hydrogen atoms with fixed thermal parameters, to give final residuals R_F = 0.047 and R_{wF} = 0.044. The goodness of fit for the last cycle was 1.155, and the maximum Δ/σ was 0.05.

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Registry No. $[TaCl_2(NMe_2)_3]_2$, 77071-68-2; $TaCl_3(NMe_2)_2(HNMe_2)$, 77071-69-3; $[TaCl_2(NMe_2)_2(HNMe_2)]_2O$, 77071-70-6; $TaCl_2(NMe_2)_3(HNMe_2)$, 77071-71-7; $Me_2NH_2^+Cl^-$, 506-59-2; $Ta(NMe_2)_5$, 19824-59-0; Me_3SiCl, 75-77-4; $TaCl_5$, 7721-01-9.

Supplementary Material Available: Tables of observed and calculated structure factors (98 pages). Ordering information is given on any current masthead page. The complete structural reports, MSC Reports 7941, 8004, and 8007, are available upon request, in microfiche form only, from the Indiana University Library.

Contribution from the Department of Chemistry, Texas A&M University, College Station, Texas 77843

The μ-Oxo-decachloroditantalum(V) Ion

F. ALBERT COTTON* and ROBERT C. NAJJAR

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The compound $[P(CH_3)_3C_6H_5]_2[Ta_2Cl_{10}O]$ was prepared serendipitously and the structure determined by X-ray crystallography. The compound crystallizes in space group $P2_1/c$ with Z = 2. The unit cell dimensions are a = 8.479 (3) Å, b = 19.577 (5) Å, c = 10.285 (4) Å, and β = 103.87 (8)°. The $[Ta_2Cl_{10}O]^{2-}$ ion has a crystallographic inversion center but approximates very closely to D_{4h} ($4/mmm$) symmetry. The important bond lengths and angles are as follows: Ta–O, 1.880 (1) Å; Ta–Cl(trans), 2.381 (6) Å; average Ta–Cl(cis), 2.336 ± 0.004 Å; average O–Ta–Cl(cis), 90.9 ± 0.5°. This is the first species of its kind lacking metal d electrons, and comparisons are made with structurally similar species of W, Re, Ru, and Os with 4–8 metal d electrons.

Introduction

Linear oxo bridges, X–O–X, have long been of interest with respect to the problem of correlating their linearity with the character of the X–O bonds. Simple σ bonds, as in H_2O, ethers, etc., are in general best formed by using two orbitals of mainly 2p character, leaving one lone pair in a very low-energy orbital of mainly 2s character and the other lone pair in an orbital of nearly pure 2p character that has a node in the plane defined by the bent, symmetrical X–O–X triad. In some cases the X–O–X angle becomes quite large, allegedly because of increased π contributions to the X–O bonds. In the limit of a linear X–O–X triad, the opportunity for X–O π bonding is maximal and also governed by symmetry restrictions in a way that is helpful in discussing the pertinent orbital overlaps.

The most intensively studied examples of linear X–O–X containing systems are those anions in which X is a Cl_5M moiety, where M is a transition metal. These anions have D_{4h} symmetry, which makes qualitative analysis of the bridge bonding simple and convenient. The first such anion to be characterized structurally[1] and analyzed theoretically[2] was $[Cl_5RuORuCl_5]^{4-}$. The accuracy of the structure determination of this anion has since been increased.[3] In addition, the four ions containing $W^{IV}W^{IV}$, $Re^{IV}Re^{IV}$, $Re^{IV}Re^{V}$, and $Os^{IV}Os^{IV}$ have been discovered and extensively studied by X-ray crystallography,[4-7] spectroscopy,[8-12] and magnetic measurements.[13] Actually, $[Cl_5ReOReCl_5]^{4-}$ was the first

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