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Bis(dimethylamido)tris(*N*,*N*-dimethylcarbamato)tantalum(V). Structure and Dynamical Solution Behavior of a Compound Containing Seven-Coordinate Tantalum

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Bis(dimethylamido)tris(*N*,*N*-dimethylcarbamato)tantalum(V), $Ta(NMe_2)_2(O_2CNMe_2)_3$, crystallizes in the monoclinic system with $a = 15.488$ (3) Å, $b = 8.214$ (1) Å, $c = 17.808$ (3) Å, $\beta = 115.25$ (1)°, $V = 2049$ (1) Å^3, $Z = 4$, and space group $P2_1/c$. The structure was solved and refined to $R_1 = 0.070$ and $R_2 = 0.088$ using 2247 reflections having $I > 3\sigma(I)$. Tantalum is seven-coordinate and the central TaN_2O_5 moiety corresponds closely to a pentagonal bipyramid. Two bidentate O_2CNMe_2 ligands occupy four of the sites of the pentagonal plane while the fifth is occupied by a dimethylamido ligand. The other dimethylamido ligand and a monodentate O_2CNMe_2 ligand occupy the axial positions. The short Ta–N bond distances (1.96 (1) and 1.97 (1) Å), the planar $Ta-NC_2$ units, and the 90° dihedral angle between the two $Ta-NC_2$ planes are indicative of N-to-Ta π bonding, which, together with the formation of the seven σ bonds, allow tantalum to achieve an 18-valence shell electronic configuration. The compound shows an interesting dynamical solution behavior. Above 0 °C intramolecular site exchange is rapid on the NMR time scale (^1H and ^{13}C) and leads to the appearance of one type of NMe_2 ligand and one type of O_2CNMe_2 ligand. At low temperature (<–60 °C) there are two types of NMe_2 groups and two types of O_2CNMe_2 ligands. If certain assumptions are made, the latter observation may be reconciled with the adoption in solution of a structure akin to that found in the crystal.

Introduction

Previous work has shown[1-4] that early transition metal dimethylamides react with carbon dioxide to give *N*,*N*-dimethylcarbamato compounds according to eq 1, where M =

$$M(NMe_2)_n + nCO_2 \rightarrow M(O_2CNMe_2)_n \qquad (1)$$

Ti or Zn for $n = 4$ and M = Nb or Ta for $n = 5$. In some cases it was possible to detect and even isolate intermediates $M(NMe_2)_{n-m}(O_2CNMe_2)_m$ in these reactions. In a study of the reactions between $M(NMe_2)_5$ (M = Nb and Ta) and CO_2 we found that no single $M(NMe_2)_{5-n}(O_2CNMe_2)_n$ compound was favored exclusively by kinetic and thermodynamic factors.[4] For M = Ta the compound $Ta(NMe_2)_2(O_2CNMe_2)_3$ was the only mixed dimethylamido(carbamato)tantalum compound which could be isolated in a pure state.[4] We report here the crystal and molecular structure of $Ta(NMe_2)_2(O_2CNMe_2)_3$ together with the results of a variable-temperature NMR study (^1H and ^{13}C).

Results and Discussion

Solid-State Structure of $Ta(NMe_2)_2(O_2CNMe_2)_3$. The compound is composed of discrete molecules of $Ta(NMe_2)_2(O_2CNMe_2)_3$ in the solid state. A perspective drawing showing the coordination geometry of the tantalum atom and the atom labeling scheme is shown in Figure 1. The final atomic coordinates and thermal parameters are given in Table I. Pertinent bond distances and angles are given in Table II. Table III lists a number of least-squares planes calculated for this molecule.

$Ta(NMe_2)_2(O_2CNMe_2)_3$ contains seven-coordinate tantalum. Two of the carbamato ligands are bidentate and one is monodentate. The TaO_5N_2 moiety can be described as a distorted pentagonal bipyramid, with O(5) and N(5) occupying the axial coordination sites. The tantalum and remaining five atoms are approximately planar (see Table III). All three *N*,*N*-dimethylcarbamato ligands are planar; note that the tantalum atom lies in the planes defined by the bidentate carbamato ligands. The two $TaNC_2$ moieties are also planar.

Bonding Considerations. Among the higher coordination numbers, seven-coordinate species represent a commonly found

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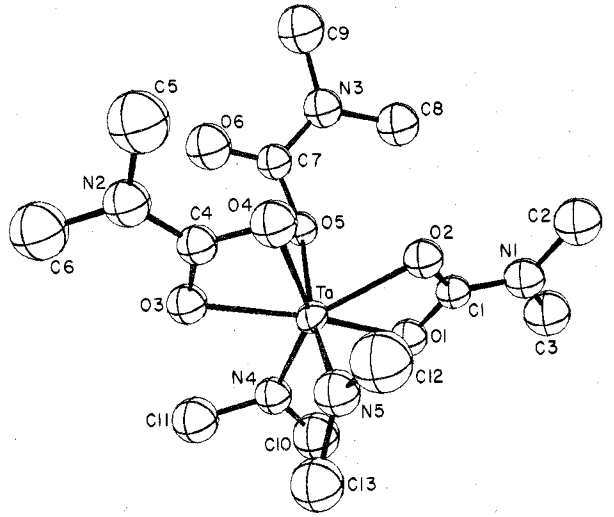

Figure 1. ORTEP view of the molecule $Ta(NMe_2)_2(O_2CNMe_2)_3$ showing the atomic numbering scheme. Atoms are represented as 40% probability ellipsoids.

Table I. Positional and Thermal Parameters and Their Estimated Standard Deviations

Atom	*x*	*y*	*z*	*B*, Å^2
Ta	0.29138 (3)	0.09561 (6)	0.02456 (2)	
O(1)	0.4033 (6)	−0.045 (1)	0.1027 (5)	3.6 (2)
O(2)	0.2622 (6)	−0.147 (1)	0.0645 (5)	3.5 (2)
O(3)	0.1943 (6)	0.304 (1)	−0.0310 (5)	3.7 (2)
O(4)	0.1286 (7)	0.081 (1)	−0.0125 (6)	4.6 (2)
O(5)	0.2817 (6)	0.165 (1)	0.1354 (5)	3.0 (2)
O(6)	0.1605 (7)	0.316 (1)	0.1297 (6)	5.4 (2)
N(1)	0.3880 (8)	−0.299 (2)	0.1511 (7)	4.1 (2)
N(2)	0.0329 (8)	0.302 (2)	−0.0717 (7)	4.4 (2)
N(3)	0.2088 (9)	0.105 (1)	0.2172 (7)	4.1 (3)
N(4)	0.3811 (7)	0.240 (1)	0.0218 (6)	3.7 (2)
N(5)	0.2568 (8)	−0.012 (2)	−0.0818 (7)	4.6 (3)
C(1)	0.3511 (8)	−0.165 (2)	0.1067 (7)	2.9 (2)
C(2)	0.3285 (13)	−0.429 (2)	0.1563 (10)	5.3 (4)
C(3)	0.4917 (12)	−0.311 (2)	0.2011 (10)	6.0 (4)
C(4)	0.1186 (9)	0.228 (2)	−0.0379 (7)	3.4 (3)
C(5)	−0.0499 (13)	0.214 (3)	−0.0752 (11)	6.7 (4)
C(6)	0.0253 (14)	0.473 (3)	−0.0997 (11)	6.7 (4)
C(7)	0.2148 (8)	0.202 (2)	0.1584 (7)	3.3 (2)
C(8)	0.2724 (11)	−0.034 (2)	0.2527 (9)	5.1 (3)
C(9)	0.1343 (13)	0.130 (2)	0.2457 (11)	5.9 (4)
C(10)	0.4830 (13)	0.202 (3)	0.0542 (11)	6.6 (4)
C(11)	0.3688 (14)	0.408 (2)	−0.0140 (11)	5.7 (4)
C(12)	0.1831 (15)	−0.146 (3)	−0.1153 (12)	7.1 (5)
C(13)	0.3011 (13)	0.032 (2)	−0.1376 (10)	5.9 (4)

[a] For Ta: $\beta_{11} = 0.00244$ (2), $\beta_{22} = 0.01013$ (9), $\beta_{33} = 0.00348$ (2), $\beta_{12} = 0.00106$ (7), $\beta_{13} = 0.00282$ (3), $\beta_{23} = 0.00093$ (6). The form of the anisotropic thermal parameter is $\exp[-(\beta_{11}h^2 + \beta_{22}k^2 + \beta_{33}l^2 + \beta_{12}hk + \beta_{13}hl + \beta_{23}kl)]$.

but poorly understood class of compounds. Theoretical studies imply that the three frequently found geometries [D_{5h} (pentagonal bipyramid), C_{2v} (monocapped trigonal prism), C_{3v} (monocapped octahedron)] are close in energy.[5] Seven-coordination is by no means uncommon in the chemistry of tantalum, and examples of molecules or ions corresponding to, or at least approaching closely to, each of the above idealized geometries are known.[6] Although it is not obvious why $Ta(NMe_2)_2(O_2CNMe_2)_3$ should adopt a pentagonal-bipyramidal structure, a simple analysis of the types of orbitals required to form the bonds and a consideration of the symmetry properties of the metal valence shell orbitals lead to the following qualitative formulation of the electronic structure of the molecule.

The axial σ bonds, that is, those involving Ta–N(5) and Ta–O(5), may use tantalum p_z and d_{z^2} orbitals. The five quasi-coplanar bonds involving Ta, O(1), O(2), O(3), O(4), and N(4) may then use metal s, p_x, p_y, d_{xy}, and $d_{x^2-y^2}$ orbitals. As a result of forming seven σ bonds, tantalum attains only a 14-valence shell electronic configuration. There remain vacant and available π-bonding metal d_{xz} and d_{yz} atomic orbitals. These have the appropriate symmetry to interact with the lone pairs on the NMe_2 ligands. [There is now considerable structural evidence to support the notion that the NMe_2 ligand is capable of significant nitrogen-to-metal π bonding in early transition metal dimethylamido compounds.[7]] In the present case, the short Ta–N bond distances, the planarity of the Ta–NC_2 moieties, and *the fact that the dihedral angle between the two Ta–NC_2 planes 88.9°* all indicate that N-to-Ta π bonding is important in $Ta(NMe_2)_2(O_2CNMe_2)_3$. Thus, in forming seven σ bonds and with both metal d_{xz} and d_{yz} atomic orbitals involved in π bonding, tantalum attains an 18-valence shell electronic configuration.

Quite probably, the satisfactory attainment of a saturated valence shell configuration accounts for (1) the observed geometry and (2) the fact that $Ta(NMe_2)_2(O_2CNMe_2)_3$ appears to be the most thermodynamically and kinetically stable intermediate in the reaction between $Ta(NMe_2)_5$ and CO_2.

NMR Studies. ^1H and $^{13}C[^1H]$ NMR spectra have been obtained for $Ta(NMe_2)_2(O_2CNMe_2)_3$ in toluene-d_8 in the temperature range −90 to +60 °C. NMR data are given in the Experimental Section.

Table II. Bond Distances (Å) and Angles (Deg) in $Ta(NMe_2)_2(O_2CNMe_2)_3$[a]

	Distances		
Ta–O(1)	2.144 (6)	C(4)–O(3)	1.29 (1)
–O(2)	2.176 (7)	–O(4)	1.28 (1)
–O(3)	2.141 (7)	–N(2)	1.35 (1)
–O(4)	2.172 (8)	N(1)–C(5)	1.45 (2)
–O(5)	2.052 (6)	–C(6)	1.48 (2)
–N(4)	1.964 (8)	C(7)–O(5)	1.30 (1)
–N(5)	1.977 (9)	–O(6)	1.22 (1)
O(1)–O(2)	2.16 (1)	–N(3)	1.35 (1)
O(3)–O(4)	2.19 (1)	N(3)–C(8)	1.46 (1)
O(5)–O(6)	2.22 (1)	–C(9)	1.46 (2)
C(1)–O(1)	1.30 (1)	N(4)–C(10)	1.46 (2)
–O(2)	1.27 (1)	–C(11)	1.50 (1)
–N(1)	1.33 (1)	N(5)–C(12)	1.52 (2)
N(1)–C(2)	1.44 (2)	–C(13)	1.47 (2)
–C(3)	1.47 (2)		
	Angles		
N(5)–Ta–N(4)	94.5 (3)	O(2)–C(1)–N(1)	122.1 (8)
–O(1)	97.9 (3)	C(1)–N(1)–C(2)	122 (1)
–O(2)	84.6 (3)	–C(3)	120 (1)
–O(3)	95.2 (3)	C(2)–N(1)–C(3)	118 (1)
–O(4)	86.8 (3)	Ta–O(3)–O(4)	91.4 (6)
–O(5)	165.3 (3)	Ta–O(4)–C(4)	90.3 (6)
O(5)–Ta–O(4)	100.2 (3)	O(3)–C(4)–O(4)	117.3 (9)
–O(1)	83.4 (2)	–N(2)	120.4 (9)
–O(2)	83.4 (2)	O(4)–C(4)–N(2)	122.3 (9)
–O(3)	88.0 (2)	C(4)–N(2)–C(5)	119 (1)
–O(4)	82.1 (3)	–C(6)	120 (1)
O(1)–Ta–O(2)	60.0 (2)	C(5)–N(2)–C(6)	121 (1)
–O(3)	160.0 (3)	Ta–O(5)–C(7)	133.8 (6)
–O(4)	135.3 (3)	O(5)–C(7)–O(6)	123.3 (9)
–N(4)	81.8 (3)	–N(3)	115.6 (8)
O(2)–Ta–O(3)	137.3 (3)	O(6)–C(7)–N(3)	121.1 (9)
–O(4)	76.4 (3)	C(7)–N(3)–C(8)	122.6 (9)
–N(4)	141.1 (3)	–C(9)	120.9 (9)
O(3)–Ta–O(4)	61.0 (3)	C(8)–N(3)–C(9)	116.5 (9)
–N(4)	81.6 (3)	Ta–N(4)–C(10)	126.2 (8)
O(4)–Ta–N(4)	142.5 (3)	–C(11)	127.5 (7)
Ta–O(1)–C(1)	92.7 (5)	C(10)–N(4)–C(11)	106.4 (9)
Ta–O(2)–C(1)	92.1 (6)	Ta–N(5)–C(12)	120.5 (8)
O(1)–C(1)–O(2)	115.1 (8)	–C(13)	125.5 (8)
–N(1)	122.7 (8)	C(12)–N(5)–C(13)	113.9 (9)

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

Table III. Weighted Least-Squares Planes[a]

Atom	Dist, Å	Atom	Dist, Å
	Plane 1		
	Atoms in Plane		
Ta	0.00 (0)	O(4)	−0.08 (1)
O(1)	−0.24 (1)	N(4)	0.06 (1)
O(2)	0.03 (1)		
O(3)	−0.18 (1)		
	Other Atoms		
O(5)	−2.03 (1)	N(5)	1.97 (1)
	Plane 2		
	Atoms in Plane		
O(1)	0.00 (1)	C(2)	−0.01 (2)
O(2)	0.00 (1)	C(3)	−0.02 (2)
C(1)	0.00 (1)		
N(1)	0.02 (1)		
	Other Atoms		
Ta	−0.09 (0)		
	Plane 3		
	Atoms in Plane		
O(3)	−0.01 (1)	C(5)	−0.04 (2)
O(4)	0.00 (1)	C(6)	0.00 (2)
C(4)	0.00 (1)		
N(2)	0.02 (1)		
	Other Atoms		
Ta	−0.03 (0)		
	Plane 4		
	Atoms in Plane		
O(5)	0.01 (1)	C(3)	−0.01 (1)
O(6)	0.00 (1)	C(8)	−0.01 (2)
C(7)	−0.01 (1)	C(9)	0.03 (2)
	Other Atoms		
Ta	1.32 (0)		
	Plane 5		
	Atoms in Plane		
Ta	0.00 (0)	C(10)	0.00 (2)
N(4)	0.00 (1)	C(11)	0.00 (2)
	Plane 6		
	Atoms in Plane		
Ta	0.00 (0)	C(12)	0.02 (2)
N(5)	−0.02 (1)	C(13)	0.02 (2)

[a] Weighted least-squares planes were calculated using the atomic positional parameters and uncertainties shown in Table I. Figures in parentheses are the estimated standard deviations in the least significant digits.

The ^{13}C[^{1}H] NMR spectrum recorded at −80 °C is shown in Figure 2. The low-field resonances marked A and B are assigned to the carboxylic carbons of bidentate and monodentate carbamato ligands, respectively. The resonances marked C, D, E, and F correspond to *N*-methyl carbons; all the other signals shown in Figure 2 arise from toluene-d_8. We assign the resonances C and D to the Ta–NMe$_2$ ligands and E and F to the monodentate and bidentate O_2CNMe_2 groups, respectively.

Since the six nonhydrogen atoms of each O_2CNMe_2 group lie in a plane and the energy of activation for rotation about the central C–N bond is quite high,[8] the methyl groups may be viewed as NMR spectroscopic probes for the oxygen atoms, at least at temperatures below 0 °C. In the ground state (Figure 1) all the carbamato methyl groups are inequivalent and so we are forced to conclude that at −80 °C either there is considerable fortuitous accidental magnetic degeneracy or that the molecule is still fluxional on the NMR time scale. We are inclined toward the latter view and note that the observed spectrum at −80 °C can be reconciled with the adoption of pentagonal-bipyramidal coordination of tantalum. (i) There are two types of Ta–NMe$_2$ groups. These may be assigned to axial and equatorial positions. (ii) Two types of carbamato methyl carbons may be accounted for by the presence of monodentate and bidentate ligands. The observation of only a single methyl carbon signal for the monodentate ligand at −80 °C is paralleled by previous observations of M(O_2CNMe_2)$_5$ compounds (M = Nb and Ta).[3] The latter contain eight-coordinate metal atoms, having three bidentate and two monodentate O_2CNMe_2 ligands, but even at −120 °C only a single methyl carbon signal is observed for the monodentate ligands. This we attributed[3] to a facile site exchange between the coordinated and noncoordinated oxygen atoms of monodentate ligands. In the present case a facile exchange of O(5) and O(6) would similarly account for the observed equivalence of the C(8) and C(9) methyl carbons. Such a motion would also create an apparent plane of symmetry containing the axial bonds Ta–O(5)/O(6), Ta–N(5) and the equatorial nitrogen N(4), thereby making the bidentate carbamato groups equivalent.

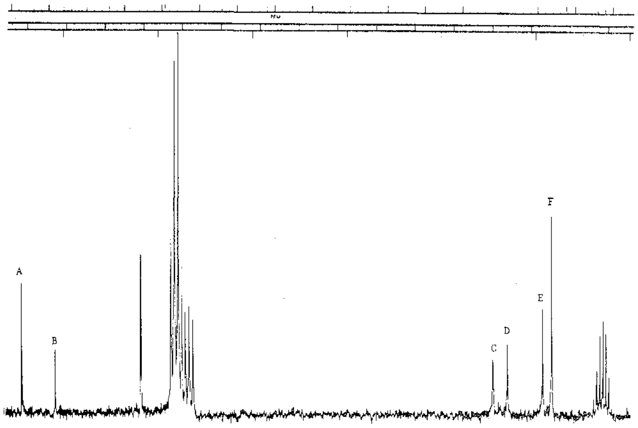

Figure 2. ^{13}C[^{1}H] NMR spectrum of Ta(NMe$_2$)$_2$(O_2CNMe_2)$_3$ obtained in toluene-d_8 solution at −80 °C. Signals A and B correspond to carboxylic carbons, C and D to Ta–NMe$_2$ carbons, and E and F to the carbamato methyl carbons. See text for detailed assignments.

On lowering the temperature to −95 °C, no change in the O_2CNMe_2 carbon resonances was observed, but the TaNMe$_2$ resonance A broadened significantly. This we attribute to hindered rotation about the Ta–N bond[9] which leads us to a tentative assignment of the Ta–NMe$_2$ resonances A and B. The methyl carbons C(10) and C(11) are contained in the pentagonal plane (Ta, O(1), O(2), O(3), O(4), N(4)) and are equivalent if the molecule achieves an apparent plane of symmetry containing Ta, N(5), N(4), and O(5)/O(6) by the rapid O(5)–O(6) exchange discussed previously. On the other hand, the methyl carbons C(12) and C(13), which are contained in this apparent plane of symmetry, occupy what are expected to be magnetically very different positions in space. C(13) is directed directly over the NMe$_2$ lone pair of N(4) while C(12) lies below and directly between O(2) and O(4). Thus, as rotation about Ta–N bonds becomes slow on the NMR time scale, we anticipate that the C(12) and C(13) (but not C(10) and C(11)) carbons will become magnetically inequivalent. We tentatively assign the resonances A and B to the dimethylamido groups containing N(5) and N(4), respectively.

On raising the temperature the resonances A and B, C and D, and E and F collapse giving, at room temperature, a simple three-line spectrum. Although a detailed line-shape analysis has not been performed, it is evident that the processes which make equivalent the Ta–NMe$_2$ groups and interchange the O_2CNMe_2 ligands have very similar, if not the same, energies of activation. Thus it is likely, but not proven, that the exchange of monodentate and bidentate O_2CNMe_2 ligands occurs with simultaneous site exchange of Ta–NMe_2 ligands. Speculation about the detailed mechanism is fruitless. It should be noted, however, that the previous work, involving extensive labeling of $Ta(NMe_2)_2(O_2CNMe_2)_3$ and related compounds, precludes that site exchange occur by an intermolecular or amine-catalyzed mechanism.[4]

A Comparison with Other PBP Structures

An interesting comparison can be made between the structure of $Ta(NMe_2)_2(O_2CNMe_2)_3$ and a large class of compounds of general formula $M(chel)_3X$[10–17] which are known to adopt pentagonal-bipyramidal structures. In the latter, two bidentate ligands occupy four of the coordination sites of the pentagonal plane, the monodentate X ligand is axial, and the remaining bidentate ligand spans the fifth position of the pentagonal plane and the axial position trans to X. The structure of $Ta(NMe_2)_2(O_2CNMe_2)_3$ may be considered to be derived from this type of structure by the substitution of an X ligand at the equatorial position of the unique bidentate ligand which then becomes monodentate and occupies an axial position. The preference for the two NMe_2 ligands to occupy axial and equatorial sites rather than two axial or two equatorial sites is readily understood in terms of N-to-Ta π bonding.

Experimental Section

General procedures and the synthesis of $Ta(NMe_2)_2(O_2CNMe_2)_3$ have been described.[4]

NMR spectra were obtained using a Varian XL-100 spectrometer.

^{1}H NMR data obtained from toluene-d_8 solutions with δ in ppm relative to Me_4Si: $T = +30$ °C, $\delta(NMe_2) = 3.82$, $\delta(O_2CNMe_2) = 2.63$; $T = -63$ °C, $\delta(NMe_2) = 3.87$ and 3.77 (relative intensity 1:1), $\delta(O_2CNMe_2) = 2.73$ and 2.58 (relative intensity 1:2); $T_c(NMe_2) = -40$ °C, $T_c(O_2CNMe_2) = -25$ °C.

^{13}C[^{1}H] NMR data obtained from toluene-d_8 solutions with δ in ppm relative to Me_4Si: $T = -62$ °C, $\delta(A) = 167.5$, $\delta(B) = 159.1$, $\delta(C) = 48.7$, $\delta(D) = 45.0$, $\delta(E) = 36.1$, $\delta(F) = 33.8$; $T = +35$ °C, $\delta(A,B) = 163.4$, $\delta(C,D) = 46.8$, $\delta(E,F) = 34.8$.

A, B, C, D, E, and F are defined in the text.

X-ray Crystallography. Crystal Selection and Data Collection. Crystals of $Ta(NMe_2)_2(O_2CNMe_2)_3$ which had been recrystallized from hexane were immersed in Nujol and examined under a microscope. A nearly transparent crystal measuring 0.22 × 0.25 × 0.44 mm was cleaved from a longer needle and wedged in a thin-walled glass capillary under Nujol. The crystal was mounted with the longest dimension along ϕ. The crystal was judged to be of good quality by examination of θ–2θ scans of several intense reflections. Lattice constants showed the crystal to be monoclinic. Final values of the lattice constants and the orientation matrix used for data collection were calculated from the setting angles of 25 intense reflections having $11° < 2\theta(\text{Mo K}\alpha) < 31°$. The refined lattice constants ($\lambda_{\text{Mo K}\alpha}$ 0.71073 Å) are $a = 15.488$ (3) Å, $b = 8.214$ (1) Å, $c = 17.808$ (3) Å, $\beta = 115.25$ (1)°, and $V = 2049$ (1) Å^3. The observed volume was consistent with that anticipated for $Z = 4$.

The data were collected at room temperature, 22 ± 1 °C, using an Enraf-Nonius CAD-4 autodiffractometer equipped with a graphite-crystal monochromator, using Mo Kα radiation. Variable scan rates ranging from 4.0 to 20.0°/min were used for θ–2θ scans, 0.9° in width, with a background to scan ratio of 0.5. A total of 3011 reflections having $0° < 2\theta(\text{Mo K}\alpha) < 45°$ were recorded. The intensities of three standard reflections were monitored throughout data collection and showed a 12% decrease in intensity; a correction for crystal decay was applied to the data. Since the crystal was colorless and immersed in Nujol, it was nearly invisible. This made morphological measurements difficult and the data were not corrected for absorption ($\mu = 57.0$ cm^{-1}). The data were corrected for Lorentz and polarization effects and reduced to a set of relative $|F_o|^2$. Non-unique and systematically absent data were rejected leaving 2367 reflections. The 2247 reflections having $I > 3\sigma(I)$ were used for structure solution and least-squares refinement.

The $0k0$ ($k = 2n + 1$) and $h0l$ ($l = 2n + 1$) reflections were systematically absent, indicating the uniquely determined space group $P2_1/c$. The observed volume and space group require that the assymmetric unit consist of one $Ta(NMe_2)_2(O_2CNMe_2)_3$ molecule.

Structure Solution and Refinement.[18] The position of the Ta atom was determined from the solution of the three-dimensional Patterson function. Positional parameters of the Ta atom were refined in two cycles of least-squares refinement to yield discrepancy indices

$$R_1 = \Sigma||F_o| - |F_c||/|F_o| = 0.227$$

$$R_2 = (\Sigma||F_o| - |F_c||^2/\Sigma|F_o|^2)^{1/2} = 0.333$$

The least-squares refinement minimized the quantity $\sum w(|F_o| - |F_c|)^2$ where w was the weight of the observation. The positions of the remaining 24 nonhydrogen atoms were determined from a difference Fourier function. Two cycles of least-squares refinement of positional and isotropic thermal parameters for all atoms yielded discrepancy indices $R_1 = 0.112$ and $R_2 = 0.131$. The structure was refined to convergence in three cycles of least-squares refinement utilizing anisotropic thermal parameters for the Ta atom and isotropic thermal parameters for the remaining atoms. During the final refinement cycle no parameter shifted by more than 0.36 times its estimated standard deviation. The estimated standard deviation of an observation of unit weight was 2.23. Final discrepancy indices were $R_1 = 0.070$ and $R_2 = 0.088$. A final difference map showed no peaks of structural significance. The two largest peaks were in the vicinity of the Ta atom and are ascribed to the lack of an absorption correction.

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Registry No. $Ta(NMe_2)_2(O_2CNMe_2)_3$, 62292-30-2.

Supplementary Material Available: Table of observed and calculated structure factors (10 pages). Ordering information is given on any current masthead page.

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