

Structure of Trimethyltantalum Difluoride, $(\text{CH}_3)_3\text{TaF}_2$

Johannes Kadel and Heinz Oberhammer*

Institut für Physikalische und Theoretische Chemie,
Universität Tübingen, 72076 Tübingen, Germany

Received February 3, 1994

Introduction

Geometric structures, dynamic stereochemistries, and bonding properties of pentacoordinated main group element compounds have been studied extensively in the past decades.^{1,2} Naturally, the by far largest number of experimental and theoretical investigations deal with P(V) compounds. All phosphoranes studied in the gas phase possess trigonal bipyramidal (TBP) structures, and the bonding is best described by an electron-deficient model with 3c–4e (3-center–4-electron) bonds in the axial direction.³ This model which does not involve the d orbitals is confirmed by ab initio calculations where the contribution of d functions is small.⁴ The similarity of structural properties and substitution effects in pentacoordinated As(V) and Sb(V) compounds suggests that this bonding model can be transferred to these higher row main group elements. So far, very few gas-phase structures or other experimental data of analogous transition metal compounds, such as Nb(V) or Ta(V) derivatives, have been reported which would provide information about the bonding properties of these compounds. NbCl₅ and TaCl₅ are monomeric in the gas phase and have TBP structures with the axial bonds being longer than the equatorial ones by 0.097(9) and 0.142(5) Å, respectively.⁵ Structure determinations for the pentafluorides are more complicated, since the vapor phase of NbF₅ and TaF₅ consists of polymers (mostly tetramers) at lower temperatures (~50 °C)⁶ and investigation of the monomers requires superheating of the vapor above 350 °C. Both monomers possess TBP structures with D_{3h} symmetry. In the Ta compound the difference between axial and equatorial bond lengths is not well determined and two values are reported: +0.044(6) and –0.019(15) Å, depending on the method of analysis (see below).⁷

Recently, gas-phase studies of two Ta(V) derivatives have been reported which possess square pyramidal (SP) structures of C_{4v} symmetry (TaMe₅)⁸ and of C_{2v} symmetry (Ta(NMe₂)₃)⁹. The different geometries of TaF₅ (TBP) and of TaMe₅ (SP) demonstrate that the structure of pentavalent Ta compounds depends on the type of ligands. In this context the structure and geometric parameters of Me₃TaF₂ are of interest. In the present work we describe a gas electron diffraction (GED) study of trimethyltantalum difluoride and compare the results with those for TaF₅ and TaMe₅ and with the analogous main group element compounds, Me₃PF₂ and Me₃AsF₂.

Structure Analysis

The modified molecular intensities for this compound (Figure 1) are extremely weak due to the strong atomic scattering and

- (1) Holmes, R. R. *Pentacoordinated Phosphorus*; ACS Monographs 175 and 176, American Chemical Society: Washington, DC, 1980; Vol. I and II.
- (2) Luckenbach, R. *Dynamic Stereochemistry of Pentacoordinated Phosphorus and Related Elements*; G. Thieme Publishers: Stuttgart, Germany, 1973.
- (3) Rundle, R. E. *J. Am. Chem. Soc.* **1963**, *85*, 112.
- (4) Kutzelnigg, W. *Angew. Chem.* **1984**, *96*, 262 and references cited therein.
- (5) Ischenko, A. A.; Strand, T. G.; Demidov, A. V.; Spiridonov, V. P. *J. Mol. Struct.* **1978**, *43*, 227.
- (6) Romanov, G. V.; Spiridonov, V. P. *Bull. Moscow Univ. Ser. II, Chem. (Engl. Transl.)* **1968**, *63*, 4.
- (7) Petrova, V. N.; Girichev, G. V.; Petrov, V. M. *J. Struct. Chem. (Engl. Transl.)* **1985**, *26*, 192.
- (8) Pulham, C.; Haaland, A.; Hammel, A.; Rypdal, K.; Verne, H. P.; Volden, H. V. *Angew. Chem.* **1992**, *104*, 1534. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1464.
- (9) Hagen, K.; Holwill, C. J.; Rice, D. A.; Runnacles, J. D. *Inorg. Chem.* **1992**, *31*, 4733.

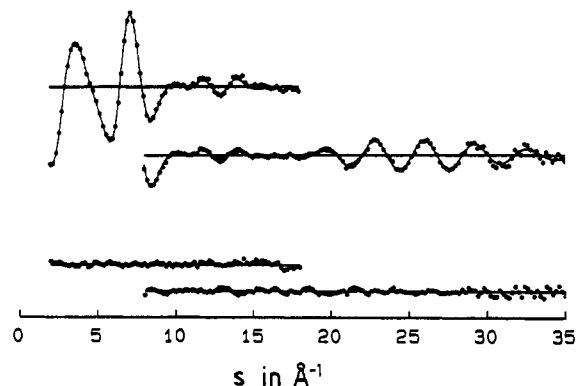


Figure 1. Experimental (dots) and calculated (full line) molecular intensities and differences.

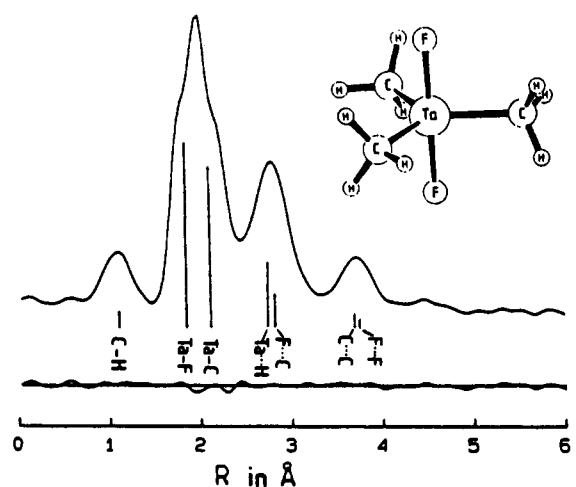


Figure 2. Experimental radial distribution function and difference curve.

the large phase shift η of Ta (atomic number $Z = 73$). Because of this large phase shift, the terms $\cos[\eta_{\text{Ta}}(s) - \eta_{\text{C}}(s)]$ and $\cos[\eta_{\text{Ta}}(s) - \eta_{\text{F}}(s)]$ in the expression for the molecular intensities¹⁰ cause additional damping. The phase-shift differences become $\pi/2$ around $s = 15\text{--}17 \text{ \AA}^{-1}$, which makes the contributions of the Ta–C and Ta–F distances to the molecular intensities zero. For $s > 17 \text{ \AA}^{-1}$ these contributions increase again but the cosine terms reverse their sign. The large Ta phase shift is also evident from the radial distribution curve (Figure 2) where it causes the peculiar shape of the strongest peak near 2 Å. Preliminary analysis of the radial distribution function clearly results in a TBP structure with the methyl groups occupying the three equatorial positions, in agreement with the VSEPR theory. In the following least-squares analyses the molecular intensities were modified with a diagonal weight matrix and scattering amplitudes and phases of Haase¹¹ were used. Assuming C_{3h} overall symmetry, i.e. one hydrogen atom of each methyl group lies in the equatorial plane, the geometry of this compound is determined by four parameters, C–H, Ta–C, Ta–F, and $\angle\text{TaCH}$. Refinements with the methyl groups rotated around the Ta–C bonds (C_3 symmetry) or with freely rotating methyl groups did not improve the fit of the experimental intensities. Vibrational amplitudes for all non-bonded C–H and F–H distances were collected in one group. With these assumptions four geometric parameters and six vibrational amplitudes were refined simultaneously. Only one correlation coefficient had a value larger than $|0.6|$: $l_4/l_5 = -0.67$. The results of this analysis are collected in Table 1, which gives also the numbering of the vibrational amplitudes l_i .

(10) Hargittai, I.; Hargittai, M. *Stereochemical Applications of Gas-Phase Electron Diffraction, Part A*; VCH Publishers: New York, 1988.

(11) Haase, J. Z. *Naturforsch., A* **1970**, *25*, 936.

Table 1. Results of the Electron Diffraction Analysis^a

Geometric Parameters					
C-H	1.098(16)	\angle Ta-C-H	112.1(16)		
Ta-F	1.863(4)	τ (CH ₃) ^b	0.0 ^c		
Ta-C	2.125(5)				
Interatomic Distances and Vibrational Amplitudes (without H-H Distances)					
C-H	1.10	0.101(18) (<i>I</i> ₁)	F-C	2.83	0.13(2) (<i>I</i> ₅)
Ta-F	1.86	0.051(4) (<i>I</i> ₂)	C-C	3.68	0.11(4) (<i>I</i> ₆)
Ta-C	2.13	0.064(5) (<i>I</i> ₃)	F-F	3.73	0.08 ^c
Ta-H	2.73	0.15(3) (<i>I</i> ₄)	X-H ^d	2.77-4.60	0.20 ^c

^a *r*_s distances in Å and \angle angles in deg. Error limits refer to the last digit and are 3 σ values. ^b Torsional angle of CH₃ groups. $\tau = 0$ corresponds to C_{3v} overall symmetry with one hydrogen atom of each CH₃ group in the equatorial plane. ^c Not refined. ^d X = C or F.

Comparison of experimental and calculated radial distribution functions (see difference curve in Figure 2) shows a small discrepancy for the strongest peak around 2 Å. Several attempts were made to improve the fit in this region. (1) The use of scattering phases of Schäfer et al.¹² instead of Haase's values does not remove this discrepancy and has a marginal effect on geometric parameters and vibrational amplitudes. (2) If multiple scattering is included in the calculated molecular intensities,¹³ the fit of the radial distribution curve does not improve either. The Ta-C and Ta-F bond lengths change by less than 0.001 Å, and the vibrational amplitudes, by ca. 0.003 Å. This finding is in accordance with that for TeF₆,¹⁵ where inclusion of multiple scattering also affects only the Te-F amplitude. Thus, both attempts to improve the agreement of the radial distribution curves for Me₃TaF₂ near 2 Å were unsuccessful and we have no explanation for this discrepancy. It is pleasing, however, that even for molecules which contain atoms as heavy as Ta, the geometric parameters depend very little on the scattering phases and on the inclusion of multiple scattering. In contrast to this, a very large effect of multiple scattering on bond lengths has been reported for TaF₅.⁷ The electron energy in this experiment (57 keV) was similar to that in the present study (ca. 60 keV). Whereas the mean Ta-F bond length increases only by 0.003 Å, the bond length difference TaF_{ax} - TaF_{eq} changes from -0.019(14) Å to +0.044(6) Å upon inclusion of multiple scattering. This implies a big change of the individual Ta-F bond lengths. On the other hand, the vibrational amplitudes which have been shown to be more sensitive in TeF₆ and Me₃TaF₂, were fixed in the TaF₅ analyses. Since these amplitudes correlate strongly with the closely spaced Ta-F distances, we suspect that constraining the vibrational amplitudes magnifies in this case artificially the effect of multiple scattering on the individual bond lengths.

Discussion

Me₃TaF₂ possesses a trigonal bipyramidal structure, in contrast to the pentamethyl derivative, but in agreement with TaF₅. Theoretical considerations using the MO picture show that the relative stability of TBP and SP structures of d⁰ complexes depends on the electronegativity of the five ligands.¹⁶ Electropositive ligands stabilize the SP structure, and ab initio calculations for TaMe₅ indeed reproduce the experimentally determined SP structure of TaMe₅. The present result demonstrates that the

two electronegative fluorines in Me₃TaF₂ lead to a TBP ground-state structure. In this context, a structural study of the intermediate member, Me₄TaF, would be of high interest.

The analogous main group element compounds, Me₃PF₂ and Me₃AsF₂, also possess TBP structures with the methyl groups in the equatorial plane. Available experimental gas-phase data for compounds of the type EF₅ and L₃EF₂ demonstrate that the axial bond lengths E-F_{ax} increase with decreasing electronegativity of the equatorial substituents. Naturally, this effect is most strongly pronounced for L = Me. The P-F_{ax} bond length increases by 0.105(3) Å (from 1.580(2) Å in PF₃¹⁷ to 1.685(1) Å in Me₃PF₂¹⁸), and the As-F_{ax} bond lengthens by 0.109(8) Å (from 1.711(5) Å in AsF₃¹⁹ to 1.820(6) Å in Me₃AsF₂²⁰). In Me₃TaF₂, however, the axial Ta-F bond (1.863(4) Å) is shorter by 0.021(7) Å or only slightly longer by 0.018(13) Å than that in TaF₅, depending on whether the value with (1.886(5) Å) or without (1.845(12) Å) inclusion of multiple scattering is used for comparison. These rather different substitution effects in P(V) and As(V) compounds on one side and in Ta(V) derivatives on the other side indicate a different bonding scheme in the transition metal compound compared to that in the main group element derivatives. The concept of the 3c-4e bonds in the axial direction implies a high polarity of such bonds (F^{-0.5}-E^{+1.0}-F^{-0.5}) and provides a straightforward rationalization of the above substitution effects in P(V) and As(V) compounds. The electropositive substituents in the equatorial plane decrease the positive net charge of the central atom and thus also the attractive polarity of the axial bonds. In tantalum compounds the 5d orbitals are within the valence shell and thus readily available for bonding. There is no need for electron-difficent bonds. Regular 2e-2c bonds can be formed in axial direction, and such bonds are less affected by the electronegativity of the equatorial substituents, as is demonstrated by the above results for Me₃TaF₂. The equatorial Ta-C bonds in Me₃TaF₂ (2.125(5) Å) are shorter than these bonds in TaMe₅, where the mean length of basal (2.180(5) Å) and apical bonds (2.11(2) Å) is 2.166(6) Å.

Experimental Section

Me₃TaF₂ was synthesized by G. Rüntger and S. Elbel,²¹ who provided us with a sample of this compound. The GED intensities were recorded with a Gasediffraktograph KD-G2²² at two camera distances (25 and 50 cm) and with an accelerating voltage of ca. 60 kV. The electron wavelength was determined from ZnO diffraction patterns. The sample was kept at 7 °C, and the stainless steel inlet system and nozzle were at room temperature. The camera pressure was 5 × 10⁻⁶ Torr during the experiment. Two plates for each camera distances were analyzed with the usual methods,²³ and the averaged molecular intensities in the s-ranges 2-18 and 8-35 Å⁻¹ in steps of $\Delta s = 0.2$ Å⁻¹ are presented in Figure 2.

Acknowledgment. We thank Prof. Dr. S. Elbel for the sample of Me₃TaF₂. We are very grateful to Ing. Snefrid Gundersen and to Dr. Tor Strand, Department of Chemistry, University of Oslo, for the calculation of the three-atomic scattering contribution in Me₃TaF₂. Furthermore, we acknowledge financial support by the Fonds der Chemischen Industrie.

- (12) Schäfer, L.; Yates, A. C.; Bonham, R. A. *J. Chem. Phys.* **1971**, *55*, 3055.
 (13) The contribution of three-atomic scattering has been calculated by Snefrid Gundersen and Tor Strand, University of Oslo, using the geometry of Table 1 and the method described in Ref 14.
 (14) Bartell, L. S. *J. Chem. Phys.* **1975**, *63*, 3750.
 (15) Gundersen, G.; Hedberg, K.; Strand, T. G. *J. Chem. Phys.* **1978**, *68*, 3548.
 (16) Albright, T. A.; Tang, H. *Angew. Chem.* **1992**, *104*, 1532. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1462. Kang, S. K.; Tang, H.; Albright, T. A. *J. Am. Chem. Soc.* **1993**, *115*, 1971.

- (17) Kurimura, H.; Yamamoto, S.; Egawa, T.; Kuchitsu, K. *J. Mol. Struct.* **1986**, *140*, 79.
 (18) Yow, H.; Bartell, L. S. *J. Mol. Struct.* **1973**, *15*, 209.
 (19) Clippard, F. B.; Bartell, L. S. *Inorg. Chem.* **1970**, *9*, 805.
 (20) Downs, A. J.; Goode, M. J.; McGrady, G. S.; Steer, I. A.; Rankin, D. W. H.; Robertson, H. E. *J. Chem. Soc., Dalton Trans.* **1988**, 451.
 (21) Rüntger, G. Ph.D. Thesis; University of Hamburg, 1989.
 (22) Oberhammer, H. *Molecular Structures by Diffraction Methods*; The Chemical Society, Burlington House: London, 1976; Vol. 4, p 24.
 (23) Oberhammer, H.; Gombler, W.; Willner, H. *J. Mol. Struct.* **1981**, *70*, 273.