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Molecular Structures of Gaseous $(NbF_5)_3$ and $(SbF_5)_3$ by Electron Diffraction

J. BRUNVOLL,[a] A. A. ISCHENKO,[b] I. N. MIAKSHIN,[b] G. V. ROMANOV,[b] V. P. SPIRIDONOV,[b] T. G. STRAND[c] and V. F. SUKHOVERKHOV[b]

[a] Institute of Physical Chemistry, Technical University of Norway, N-7034 Trondheim-NTH, Norway, [b] Department of Chemistry, Moscow State University, Moscow 117234, USSR and [c] Chemistry Department, University of Oslo, Oslo 3, Norway

At the applied nozzle temperatures the gaseous pentafluorides of niobium and antimony are mostly trimeric with each of the three metal atoms surrounded by six fluorine atoms in a distorted octahedral arrangement. The data of niobium pentafluoride agree with a D_{3h} symmetric molecule while the six-membered ring of trimeric antimony pentafluoride is nonplanar.

A boatlike conformation of C_s symmetry agrees insignificantly better with the data than a C_{3v} chair conformation and the parameters of the two models are practically the same. The structure parameters and standard deviations are for $(NbF_5)_3$ and for the boatlike conformation of $(SbF_5)_3$, respectively, $M-F_a$ (axial) $= M-F_t$ (terminal) $= 1.810(2)$ and $1.811(2)$ Å, $M-F_b$ (bridged) $= 2.046(4)$ and $2.044(4)$ Å, $\angle(F_a-M-F_a) = 162.5(1.4)$ and $161.6(1.7)$, $\angle(F_t-M-F_t) = 102.9(1.2)$ and $98.2(1.9)$, $\angle(F_b-M-F_b) = 82.0(1.0)$ and $81.5(1.5)$, and $\angle(M-F_b-M) = 158.0(1.0)$ and $149.7(1.0)$°.

An earlier electron diffraction investigation of gaseous tantalum pentafluoride at a lower nozzle temperature resulted in a trimeric molecule of D_{3h} symmetry.[1] In the present paper the results of a corresponding investigation of the niobium and antimony pentafluorides are reported.

ESTIMATES OF *u*- AND *D*-VALUES

The root mean-square amplitudes of vibration, *u*, and the correction terms between the electron diffraction distance parameters and the distances between the thermal average atomic positions, the *D*-values, were estimated from the same simple valence force field as for $(TaF_5)_3$.[1] The molecules were assumed to possess D_{3h} symmetry. The valence force field gave the symmetry force field.[2] From this symmetry force field the transformation between symmetry coordinates and normal coordinates, the **L** matrix, was obtained. The computed normal frequencies were then replaced by experimental ones[3] wherever possible and the *u*- and *D*-values were computed by means of these frequencies and the **L** matrix of the approximate force field. In Tab. 1 computed *u*- and *D*-values for some of the distances of $(NbF_5)_3$ are listed.

ELECTRON DIFFRACTION INVESTIGATION

The compounds were synthesized[4] and purified by vacuum distillation. Diffraction patterns were obtained using the improved apparatus[5] of the Moscow State University. The experimental conditions are summarized in Tab. 2.

The data were treated in the usual way[6] applying $sM(s)$ molecular intensities. The scattering factor of fluorine was computed[7] from an analytical representation of the potential[8] while the scattering factors of Nb and Sb were obtained by interpolation of numerical tables.[9]

The results of final least-squares refinements are given in Tab. 3 and the corresponding *u*-values in Tab. 1. The intensities from the two camera distances were kept separate in the refinements and nondiagonal weight matrices were applied.[10]

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Table 1. Root mean-sguare amplitudes of vibration u (Å) and correction terms D (Å).

	$(NbF_5)_3$		$(SbF_5)_3$			
Distance[a]	D[b]	u[b]	A[c]	B[c]	C[c]	Group[d]
M1–F4	−0.0154	0.0396				
M1–F2	−0.0177	0.0392				
M1–F6	−0.0038	0.0576				
M1···M7	0.0003	0.0749	0.101(3)	0.096(4)	0.097(4)	
F2···F3	−0.0187	0.1272	0.103(7)	0.071(11)	0.065(11)	1
M1···F8	−0.0034	0.0962	0.189(15)	0.140(9)	0.128(9)	2
M1···F9	0.0002	0.1587	0.263(67)	0.200(9)	0.189(9)	2
M1···F10	0.0032	0.1831	0.257(37)	0.231(58)	0.345(74)	3
M1···F11				0.505(183)	0.479(123)	4

[a] For numbering of the atoms see Fig. 2. [b] Computed for 20 °C from the force field of Ref. 1 modified by experimental frequencies. [c] Experimental u-values and standard deviations from the corresponding refinements of Tab. 3. [d] Some of the u-values were refined in groups, see text.

Table 2. Experimental conditions for the electron diffraction diagrams of NbF_5 and SbF_5 at about 40 keV.

	NbF_5		SbF_5	
Camera distance (mm)	519.59	269.84	519.29	269.75
Wavelength (Å)[a]	0.06169	0.06162	0.06134	0.06143
Beam current (μA)	1.2	1.2	1.4	1.4
Nozzle temperature (°C)	60(3)	60(3)	20(2)	20(2)
Exposure time (s)	18–20	30–32	18–20	30–32
Blackness interval	0.2–0.4	0.2–0.4	0.2–0.4	0.2–0.4
Applied s-range	2.0–12.5[b]	4.5–23.5[c]	2.5–13.0[b]	7.0–18.0[c]
Applied number of plates	6	6	4	4

[a] Determined from zinc oxide diffraction patterns. [b] Intervals of $s = 0.125$ Å^{-1} were applied. [c] Intervals of $s = 0.25$ Å^{-1} were applied.

Table 3. Final least-squares results for the distances (Å) and angles (°) of the thermal average atomic positions according to the D-values of Tab. 1. F_a, F_t and F_b denote the axial, terminal and bridged fluorine atoms. K_1 and K_2 are the scale factors for the data of the long and short camera distances and R_f is a weighted agreement factor in percent according to egn. 16 of Ref. 10. Standard deviations using a nondiagonal weighting matrix are given.

Parameters	$(NbF_5)_3$ A[a]	$(SbF_5)_3$ B[b]	C[c]
$R(M-F_a)=R(M-F_t)$	1.810(2)	1.811(2)	1.812(2)
$R(M-F_b)$	2.046(4)	2.044(4)	2.045(4)
$\angle(F_a-M-F_a)$	162.5(1.4)	161.6(1.7)	160.5(1.2)
$\angle(F_t-M-F_t)$	102.9(1.2)	98.2(1.9)	96.7(1.7)
$\angle(F_b-M-F_b)$	82.0(1.0)	81.5(1.5)	80.9(1.1)
$\angle(M-F_b-M)$	158.0(1.0)	149.7(1.0)	149.7(1.0)
K_1	0.584(15)	0.703(12)	0.705(12)
K_2	0.636(15)	0.568(17)	0.570(17)
R_f	10.18	6.20	6.42

[a] Results for a D_{3h} symmetric model. $\angle(M-F_b-M)$ is here a dependent parameter. [b] Results for a boatlike model of C_s symmetry. [c] Results for a chairlike model of C_{3v} symmetry.

Contributions from triatomic intramolecular scattering were included in the theoretical intensities according to Ref. 11 by modifying eqn. 23 of this reference by $s/I_T^B(s)$, where $I_T^B(s)$ is the theoretical background.

The models were satisfied by the thermal average atomic positions by correcting the distances according to the D-values computed for the D_{3h} symmetric models.

In the refinements, the u-values of the M–F bonded distances were fixed on the computed values and the u-value of the M···M distance was an independent parameter. Some of the other u-values were varied in groups where all the values in one group were regarded as one independent parameter getting the same shifts and standard deviations and starting the refinements from the computed values. Group 1 of Tab, 1 included the values of the five shortest F···F distances, the u-values of the other distances of this type were fixed on the computed values. For refinement B group 2 included the u-values of the distances 1···8, 1···9, 1···12, 2···7, 2···13 and 6···13, group 3 1···10 and 5···7, and group 4 1···11 and 4···7. For refinement C group 2 included the values of the distances 1···8, 1···9 and 1···12, the u-values of the other two Sb···F distances were independent variables. For refinement A the u-value of distance 1···8 and 1···12 were refined in the same group, the other Nb···F u-values were independent variables.

In the refinements only the average of the axial and terminal M–F distances was determined. Trying to split these distances by adding the independent parameter $\Delta R = [R(M-F_a) - R(M-F_t)]$ resulted in the values $\Delta R = 0.001(14)$ for $(NbF_5)_3$ and $\Delta R = -0.022(22)$ Å for the boat form of $(SbF_5)_3$, in both cases without improving the agreement significantly.

Attempts to fit the nonplanar C_s geometry to the $(NbF_5)_3$ data converged very closely to the planar form before the refinement broke down, and the $(SbF_5)_3$ data disagreed significantly with a D_{3h} symmetric model.

The parameters of refinement B of Tab. 3 for the C_s model correspond to an angle of 34.2° between the planes through atoms 6, 12, 18 and 1, 6, 18. The angles between the planes 6, 12, 18 and 6, 7, 12 are 13.2° for the C_s model (B) and 13,5° for the C_{3v} model (C).

The molecular intensities are shown in Fig. 1 and the radial distribution functions are illustrated in Fig. 2. Correlation coefficients for the final refinements are given in Tab. 4.

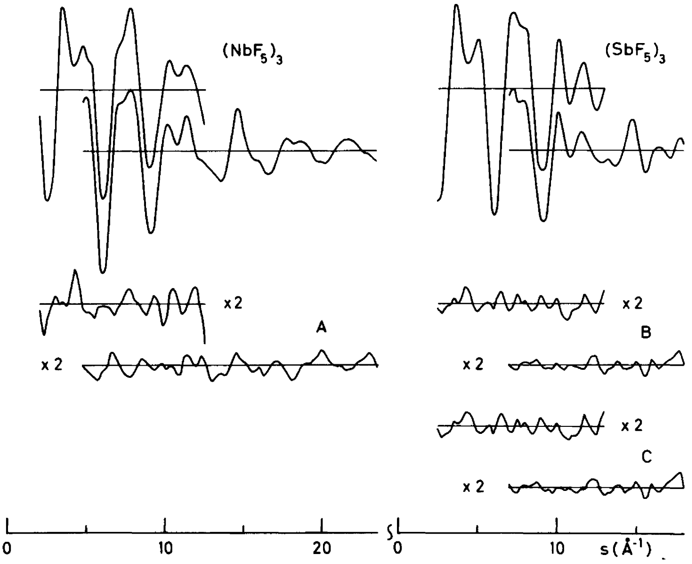

Fig. 1. $sM(s)$ average experimental intensities of $(NbF_5)_3$ and $(SbF_5)_3$. The curves A, B and C give the differences between the experimental intensities and the intensities computed from the parameters of Tab. 3, A, B and C.

Table 4. Correlation coefficients with absolute values greater than 0.5 for the three least-squares refinements.

Parameter[a]	$R(M-F_b)$	$\angle(F_a-M-F_a)$	$\angle(F_t-M-F_t)$	$\angle(F_b-M-F_b)$	$\angle(M-F_b-M)$
No.	1	2	3	4	5
Parameter	$u(M1\cdots M7)$	$u(1)$		$u(M1\cdots F9)$	$u(3)$ $u(4)$ K_2
No.	6	7		8	9 10 11
Refinement	Correlation	coefficients[b]			
A	0.617(1,3)	0.831(1,4)	0.574(1,8)	0.744(1,9)	
	0.729(2,7)	−0.567(2,8)	0.542(3,8)	0.582(3,9)	
	0.881(8,9)				
B	−0.789(1,5)	0.770(2,7)	0.658(3,9)	0.527(4,9)	
	0.568(6,11)				
C	−0.945(1,5)	0.701(2,7)	0.562(6,11)	0.723(9,10)	

[a] Parameters of Tab. 1 or Tab. 3. [b] Correlation coefficients for the three refinements of Tab. 3. Numbers in parenthesis after each coefficient refer to the parameters above.

DISCUSSION

As argued in the discussion of $(TaF_5)_3$,[1] an incorrect degree of association of NbF_5 and SbF_5 should show up as systematic discrepancies between the calculated and experimental radial distribution functions in the areas of the bonded M−F peaks relatively to the area(s) of the non-bonded M···M peak(s). The agreement for the trimeric models is satisfactory and the amount of other species present must be relatively small.

The six-membered rings of $(NbF_5)_3$ and $(TaF_5)_3$ are planar or close to planar while the ring of $(SbF_5)_3$ deviates significantly from planarity. The Sb···Sb distance of the latter molecule of 3.95 Å is sufficiently long to expect that internuclear repulsion[12] would be unimportant. A possible explanation is that *d* orbitals on Nb and Ta take part in π type delocalized molecular orbitals therby favouring a planar ring.[13] With the filled 4d orbitals of the Sb atom such molecular orbitals would be less favourable in $(SbF_5)_3$.

The chair and boat conformations of $(SbF_5)_3$ fit the data about equally well according to the R_f factors, and the difference curves for the two models are very similar. Accordingly, a refinement on a mixture of the two conformers would be expected neither to improve the agreement nor to

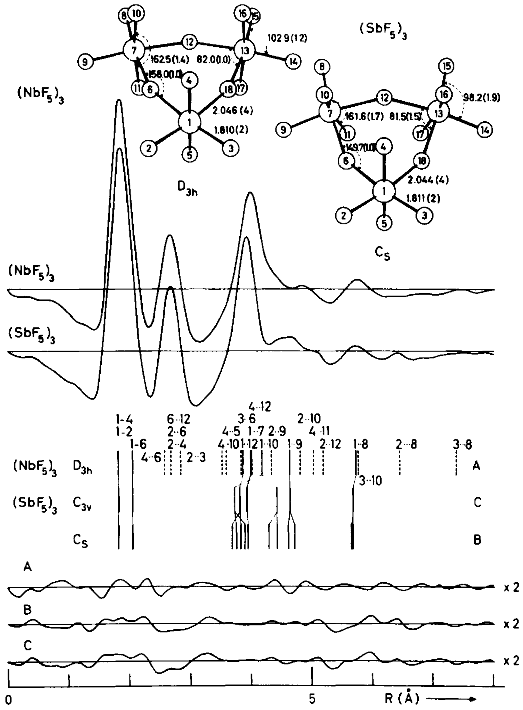

Fig. 2. Experimental radial distribution functions of $(NbF_5)_3$ and $(SbF_5)_3$ for damping functions of $\exp(-0.005s^2)$. Computed intensities were added inside $s=4.5$ Å^{-1} for $(NbF_5)_3$ and inside $s=2.5$ Å^{-1} for $(SbF_5)_3$. The different distances of the D_{3h} symmetric model of $(NbF_5)_3$ according to the parameters of Tab. 3, A are given with the F···F distances as broken lines. The Sb···Sb and Sb···F distances of the chair, C, and the boat conformation, B, of $(SbF_5)_3$ are also indicated. The curves A, B and C give the differences between the experimental radial distribution functions and the functions computed for the parameters and models of Tab. 3, A, B and C, respectively.

give any meaningful result for their relative abundance. For the same energy and entropy of the two forms one would expect 75 % of the boat conformation due to its higher symmetry number.

The structure parameters obtained for the chair and for the boat conformations of $(SbF_5)_3$ are practically the same, and comparing the parameters of $(NbF_5)_3$ to $(SbF_5)_3$, only the $M-F_b-M$ angles differ really significantly.

Finally, comparing the two D_{3h} symmetric molecules $(NbF_5)_3$ and $(TaF_6)_3$,[1] the bonds are longer and the angles (F_a-M-F_a) and (F_t-M-F_t) are closer to the octahedral angles in the latter molecule.

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