MOLECULAR STRUCTURE OF TmCl₃ BY SYNCHRONOUS ELECTRON DIFFRACTION AND MASS SPECTROMETRIC EXPERIMENT

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The molecular structure of lanthanide trihalides has been discussed since 1959, when the first electron diffraction data were obtained for LaHal₃ and NdHal₃ [1]. The diffraction pattern was initially interpreted [1] with the assumption that the molecules have a planar structure. Later, more elaborate procedures for recording and interpreting electron diffractograms led to structure determination for three lanthanide trifluorides (PrF₃, GdF₃, HoF₃) [2], six trichlorides (LaCl₃, PrCl₃, GdCl₃, TbCl₃, HoCl₃, LuCl₃) [3-7], three tribromides (LaBr₃, GdBr₃, LuBr₃) [8, 9], and five triiodides (PrI₃, NdI₃, GdI₃, LuI₃ [10], CeI₃ [11]). It was found that all of these molecules have an effective nonplanar configuration. An attempt was made to trace the tendencies of bond angle variation for the equilibrium configuration in the series LaHal₃-LuHal₃ and LnF₃-LnI₃ [12].

This molecular structure study performed on TmCl₃ is aimed to clarify details of molecular structure variation in the second half of the LnCl₃ series.

EXPERIMENTAL

The experiment was run on an ÉMR-100/APDM-1 instrument complex [13]. A reagent-grade sample of TmCl₃ was evaporated from a molybdenum ampule at T = 1123 ± 20 K. The temperature of the ampule was measured with a tungsten-rhenium thermocouple VR5/20. Electron wavelength was determined from the diffraction pattern of the crystalline standard ZnO. Accelerating voltage was 73 kV. Electron diffractograms were recorded for two nozzle-to-plate distances: L₁ = 598 mm and L₂ = 338 mm. The total molecular intensity functions were obtained within s = 1.8-14.2 Å⁻¹ and s = 4.8-25.2 Å⁻¹. Simultaneously, mass spectra of the vapors were recorded. Ionizing voltage was 50 V. The following ions were recorded in the mass spectrum: Tm⁺ (10), TmCl⁺ (20), TmCl₂⁺ (100), and TmCl₃⁺ (12). The values in parentheses are the relative intensities of ion currents including isotope distribution. No ions with a mass exceeding that of TmCl₃ were detected, which indicates that the saturated vapor of thulium trichloride does not contain any dimeric molecules Tm₂Cl₆ in the stated conditions of electron diffraction experiment. According to a preliminary mass spectrometric study on an MI 1201 instrument [20], no other volatile compounds of lanthanides were found in the vapors.*

The molecular intensity function was determined by the relation sM(s) = ʃ(s) - G(s)/G(s) • s.

STRUCTURAL ANALYSIS

In accordance with mass spectrometric control data, the structural analysis was performed with the assumption that the vapor contains a single molecular form, TmCl₃.

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TABLE 1. Results of the Least-Squares Analysis of the Function \( sM(s) \) for Thulium Trichloride

<table>
<thead>
<tr>
<th>( s_{\text{min}} - s_{\text{max}} ) Å(^{-1})</th>
<th>( r_\text{ex}(\text{Tm-Cl}) ), Å</th>
<th>( l(\text{Tm-Cl}) ), Å</th>
<th>( k(\text{Tm-Cl}) ), Å(^3)</th>
<th>( r_\text{ex}(\text{Cl-Cl}) ), Å</th>
<th>( l(\text{Cl-Cl}) ), Å</th>
<th>( R_f^{**} ), %</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.6-14.6</td>
<td>2.4201(9)*</td>
<td>0.0880(9)</td>
<td>3.82(90) ( \cdot 10^{-5} )</td>
<td>4.0951(72)</td>
<td>0.2955(60)</td>
<td>2.48</td>
</tr>
<tr>
<td>4.2-25.2</td>
<td>2.4155(11)</td>
<td>0.0905(10)</td>
<td>2.9(8) ( \cdot 10^{-5} )</td>
<td>4.0610(220)</td>
<td>0.3316(111)</td>
<td>14.7</td>
</tr>
<tr>
<td>1.6-14.6</td>
<td>2.4185(16)***</td>
<td>0.0913(15)</td>
<td>4.65(12) ( \cdot 10^{-5} )</td>
<td>—</td>
<td>—</td>
<td>4.60</td>
</tr>
<tr>
<td>4.2-25.2</td>
<td>2.4185(8)</td>
<td>0.0894(7)</td>
<td>3.8(6) ( \cdot 10^{-5} )</td>
<td>4.0896(79)</td>
<td>0.3081(59)</td>
<td>6.78</td>
</tr>
</tbody>
</table>

* \( \sigma_{\text{LS}} \).  
** The \( R_f \) value was calculated by the formula 
\[
R_f = \frac{\sum_i \omega(s_i)[s_i M_{\text{exp}}(s_i) - \text{scale} \cdot s_i M_{\text{theor}}(s_i)]^2}{\sum_i \omega(s_i)[s_i M_{\text{exp}}(s_i)]^2}.
\]  
*** The calculations demonstrating the Cl-Cl contribution to different sections of the function \( sM(s) \) and the reliability of determination for the corresponding parameters.

When solving the diffraction pattern we postulated that the TmCl\(_3\) molecule has a threefold symmetry axis and that its geometrical configuration may be attributed to either \( D_{3h} \) (planar symmetrical model) or \( C_{3v} \) (pyramidal symmetrical model) point group.

In the course of the least-squares analysis of the function \( sM(s) \), the internuclear distances \( r_\text{ex}(\text{Tm-Cl}) \) and \( r_\text{ex}(\text{Cl-Cl}) \), the vibration amplitudes \( l(\text{Tm-Cl}) \) and \( l(\text{Cl-Cl}) \), and the asymmetry constant \( k \) of Tm-Cl were varied independently. Table 1 lists the results of simultaneous or sequential processing for two sections of the function \( sM(s) \).

Table 1 also gives the results of the least-squares analysis of the function \( sM(s) \) neglecting the Cl-Cl contribution. The high \( R_f \) value points to a significant contribution of this atomic pair to the initial section of the function \( sM(s) \).

Figure 1 compares the experimental and theoretical functions \( sM(s) \). Figure 2 compares the radial distribution functions \( f(r) \) and demonstrates that they are in good agreement.

![Fig. 1. Experimental (dots) and theoretical (solid line) molecular intensity functions \( sM(s) \) for different nozzle-to-plate distances and the difference curves.](image-url)