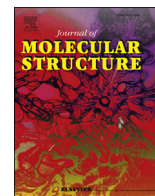




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The molecular structure of tris(dipivaloylmethanato) thulium: Gas-phase electron diffraction and quantum chemical calculations

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Dedicated to Prof. Georgiy V. Girichev on the occasion of his 70th birthday.

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ABSTRACT

The molecular structure of tris-2,2,6,6-tetramethyl-heptane-3,5-dione thulium, or $\text{Tm}(\text{thd})_3$, has been studied by gas-phase electron diffraction monitored by mass spectrometry (GED/MS) and quantum chemical (DFT) calculations. Both the DFT(PBE0) calculations and the GED data collected at 400(8) K indicate that the molecules have D_3 symmetry with a distorted antiprismatic TmO_6 coordination geometry. According to GED refinements the twist angle θ , i.e. the angle of rotation of the upper O_3 triangles relative to their position in regular prism is $\theta = 16.9(2.0)^\circ$. This value is close to both the equilibrium value obtained from the DFT calculations and to the thermal average value at the temperature of the GED experiment obtained by integration over the DFT potential energy surface. The bond distances (r_{hi}) in the chelate ring are $\text{Tm}-\text{O} = 2.214(5)$ Å, $\text{C}-\text{O} = 1.278(4)$ Å, and $\text{C}-\text{C} = 1.404(3)$ Å. The DFT calculations yielded structure parameters in close agreement with those found experimentally. As an alternative to conventional Lewis model which was realized in NBO the topological analysis of $\rho(r)$ in the frame of Bader's quantum theory of atoms in molecule (QTAIM) was performed.

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1. Introduction

The considerable interest to the metal complexes of β -diketones is caused by their properties, which allow to use them for low-temperature gas-phase metal transport (CVD, chemical vapor deposition) in thin film industry [1–4]. The lanthanide complexes with dipivaloylmethane (2,2,6,6-tetramethyl-heptane-3,5-dione, below - thd), $\text{Ln}(\text{thd})_3$, are distinguished by their high volatility and thermal stability as well [5]. Consequently, there has been interest in the structure of $\text{Ln}(\text{thd})_3$ in the gas phase, in which they are used for MOCVD.

The gas-phase molecular structure of several $\text{Ln}(\text{thd})_3$ complexes has been studied experimentally. In earlier gas-phase electron diffraction (GED) research of some $\text{Ln}(\text{thd})_3$ ($\text{Ln} = \text{Er}, \text{Pr}, \text{Sm}, \text{Eu}, \text{Gd}, \text{Tb}, \text{Dy}, \text{Ho}$) by Shibata et al. [6–8] the experimental data for all molecules studied were interpreted in terms of the model of C_3 symmetry with a slightly-twisted triangular prismatic structure of LnO_6 coordination polyhedron and with the chelate rings folded about $\text{O}\cdots\text{O}'$ axis. In contrast, later GED and DFT studies of $\text{La}(\text{thd})_3$

[9], $\text{Er}(\text{thd})_3$ [10], $\text{Lu}(\text{thd})_3$ [11], $\text{Nd}(\text{thd})_3$ [12] and $\text{Yb}(\text{thd})_3$ [12] carried out by G.V. Girichev, N.I. Giricheva and their coworkers, showed that these molecules adopt equilibrium structures with a distorted LnO_6 antiprismatic polyhedra, planar chelate rings and overall D_3 symmetry. The coordination polyhedron LnO_6 configuration (Fig. 1) can be defined by a twist angle θ , which corresponds to the rotation of the upper $\text{O}-\text{O}-\text{O}$ triangle in LnO_6 polyhedron relative to the lower $\text{O}'-\text{O}'-\text{O}'$ triangle starting from triangular prismatic D_{3h} reference configuration. Thus, the available GED data lead to two different conclusions: either the coordination polyhedron LnO_6 is a slightly distorted prism with a twist angle $4.5\text{--}11.8^\circ$ [6–8], or the coordination polyhedron LnO_6 is a distorted antiprism, and θ values are very close in all complexes ($19.1\text{--}22.7^\circ$) [9–12]. Furthermore, the gas-phase electron diffraction study of $\text{Er}(\text{thd})_3$ [10] showed that GED data could be reproduced reasonably well by both models (with C_3 and D_3 symmetry). The authors of [10] have concluded that to solve the problem of planarity or non-planarity of chelate rings and to make a conclusion about the coordination polyhedron structure the additional, data, experimental or theoretical, are needed. It should be noted that the structural analysis for $\text{Lu}(\text{thd})_3$ [11], $\text{Yb}(\text{thd})_3$ [12] and $\text{Nd}(\text{thd})_3$ [12] was accompanied by quantum chemical calculations.

The structural features and regularities in the series of $\text{Ln}(\text{thd})_3$

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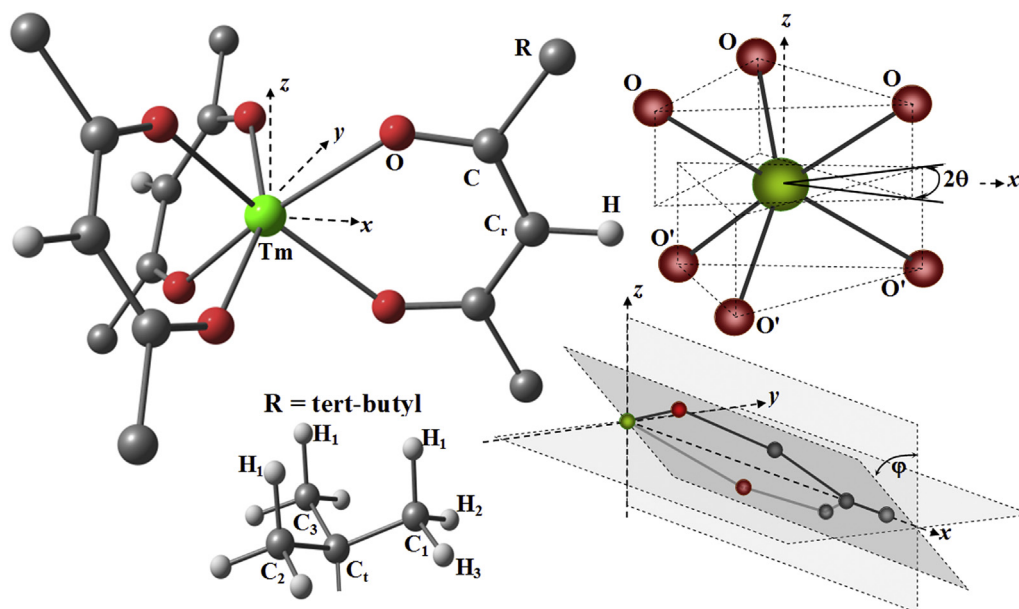


Fig. 1. Equilibrium D_3 structure of $\text{Tm}(\text{thd})_3$ complex and atom notations.

complexes have been studied by quantum chemical calculations [13]. It was concluded that the structure of $\text{Ln}(\text{thd})_3$ complexes of overall D_3 symmetry with planar chelate rings is an equilibrium structure for all series from $\text{La}(\text{thd})_3$ to $\text{Lu}(\text{thd})_3$. The model of C_3 symmetry with folded chelate rings should be considered as an artifact since it does not represent a minimum on the potential energy surface [14,15].

According to our recent research [13] the largest discrepancies in the experimental and theoretical parameters of $\text{Ln}(\text{thd})_3$ concern the values, which connected with the internal rotation of $\text{C}(\text{CH}_3)_3$ groups and with the intramolecular rearrangements in LnO_6 polyhedron. Both types of intramolecular movement are non-rigid and possess rather low potential barrier [13].

The calculated values of the angles of *tert*-butyl groups internal rotation relative to a chelate ring plane (γ - torsion angle $\text{C}_1\text{C}_t\text{CC}_r$) are about 0° [13], whereas the experimental values of γ are in a wide range: from 9.1° to 22.1° [13], and there is not any trend in the changing of this parameter. For $\text{Tm}(\text{thd})_3$ molecule the potential energy surface of *tert*-butyl groups internal rotation was scanned and two conformers were found. The most stable configuration (CONF1) corresponds to the orientation of $\text{C}(\text{CH}_3)_3$ groups where one of $\text{C}_t\text{--C}_1$ bond eclipses C--C_r bond in a chelate ring ($\gamma = 0^\circ$). For local minimum (CONF2) $\gamma = 60^\circ$ ($\text{C}_t\text{--C}_1$ bond eclipses C--O bond in a chelate ring). The question of substitutes internal rotation in the β -diketonates was studied in Ref. [16]. The authors described the internal rotation of different substitutes CX_3 ($\text{X} = \text{H}, \text{F}, \text{CH}_3$) and established the presence of local minimum on the PES only for $\text{C}(\text{CH}_3)_3$ groups. It has been noted also that the standard procedure of GED structural analysis does not take into account the hindered rotation of the *tert*-butyl groups, and, as the result, the value of experimental γ_{exp} angle is different from an equilibrium one [16]. Moreover, the value of torsion γ_{exp} angle can depend on a structural analysis scheme. Using the method developed in Ref. [16] the values of thermal average angles γ_{av} for different temperatures were calculated for thulium complex $\text{Tm}(\text{thd})_3$. It is interesting to note that the γ_{av} value for $\text{Tm}(\text{thd})_3$ [13] is close to γ_{av} obtained for $\text{Ca}(\text{thd})_2$ and $\text{Sr}(\text{thd})_2$ [16].

The position of the oxygen atoms surrounding the central atom Ln in coordination polyhedron LnO_6 can be defined by twist angle,

θ , mentioned above. The twist angle can be expressed as a function of the pitch angle, φ , which describes the rotation of each of three chelate ring planes around C_2 axis starting from regular triangular prism configuration of the polyhedron (see Fig. 1):

$$\tan \theta = b \sin \varphi / (4 - b^2)^{1/2}, \quad b = r(\text{O}\cdots\text{O}')/r(\text{Ln} - \text{O})$$

According to the quantum chemical results [13] the values of θ as well as φ angles increase in the series $\text{Ln}(\text{thd})_3$ from La to Lu, that corresponds to the increase of the distortion of LnO_6 from a triangular prismatic structure configuration in the series from $\text{La}(\text{thd})_3$ to $\text{Lu}(\text{thd})_3$ [13]. Thus, PBE0 calculations result in the values of twist angle θ equal to 1.1° for $\text{La}(\text{thd})_3$ and 17.1° for $\text{Lu}(\text{thd})_3$ [13]. On the other hand, the experimental GED values of the twist angle for all $\text{Ln}(\text{thd})_3$ studied (with D_3 symmetry) are in a small range of $19.1\text{--}22.7^\circ$ [9–12].

The intramolecular $D_3 \rightarrow C_{2v} \rightarrow D_3$ rearrangement, which includes the rotation of one ligand respectively to its C_2 axis, have been studied for $\text{La}(\text{thd})_3$ and $\text{Tm}(\text{thd})_3$ [13]. Using the method developed in Ref. [16] and based on the calculated potential energy curves the average values of the pitch angle, φ_{av} , were obtained for $\text{La}(\text{thd})_3$ and $\text{Tm}(\text{thd})_3$. For $\text{La}(\text{thd})_3$ the average angle is $\varphi_{\text{av}} = 21.5^\circ$ at the temperature of GED experiment. This value is closer to the experimental $\varphi_{\text{exp}} = 35.6^\circ$ than the equilibrium $\varphi_e = 1.5^\circ$.

The comparison of the results of quantum chemical calculations and of GED study show that the equilibrium structure can differ from the experimental structure considerably, it is especially noticeable in the presence of the non-rigid rearrangements [13]. Obviously, in such case one should not restrain the parameters during structural analysis of GED data guided by the optimized structure. In that case the thermal average values of non-rigid parameters obtained from the PES can closely reproduce the experimental values.

Besides the geometrical structure the information about electron density distribution can help to understand the nature of chemical bonds into $\text{Tm}(\text{thd})_3$ molecule, in particularly the thulium–oxygen chemical interaction. In the article [13] the analysis of natural bond orbitals (NBO) for $\text{Ln}(\text{thd})_3$ molecules was carried out and data are given about atomic charges and Wiberg bond indexes.

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