

s13.m35.p34 **Synthesis, Structure and Thermal Properties of Volatile Hafnium(IV) β -diketonates.** Ksenia V. Zherikova^a, Iraida A. Baydina^b, Sergey V. Sysyov^b, Natalia B. Morozova^b and Igor K. Igumenov^b, ^aNikolaev Institute of Inorganic Chemistry SBRAS, Russia, and ^bNikolaev Institute of Inorganic Chemistry SBRAS, Russia. E-mail: kseniya@ngs.ru

Keywords: Complexes; Hafnium(IV); β -diketonates

Synthesis and X-ray analysis of volatile Hf(IV) β -diketonates: hafnium(IV) dipivaloylmethanate Hf(thd)₄, hafnium(IV) pivaloyltrifluoroacetate Hf(ptan)₄, hafnium(IV) trifluoroacetylacetonate Hf(tfan)₄, hafnium(IV) hexafluoroacetylacetonate [HfO(hfan)₃]₂ - were carried out, and the thermodynamic properties of vaporization processes of the mentioned complexes were determined. Hf(thd)₄ and Hf(ptan)₄ were synthesized by the method of the direct interaction of aqueous alcoholic solutions of inorganic salt HfCl₄ with the appropriate β -diketone under heating with the subsequent addition of NaOH up to δ 5-6. Hf(tfan)₄ and [HfO(hfan)₃]₂ were prepared under heating with reverse cooling of anhydrous HfCl₄ with trifluoroacetylacetonate and hexafluoroacetylacetonate, respectively. Absolute ethyl ether was used as solvent for preparing Hf(tfac)₄, and carbon tetrachloride - for [HfO(hfan)₃]₂. The obtained compounds (white crystals) were purified by zone sublimation in vacuum gradient furnace at O = 200⁰N (Hf(thd)₄), O = 150⁰N (Hf(ptan)₄), O = 110⁰N ([HfO(hfan)₃]₂) and D = 5*10⁻² torr and O = 120⁰N and D = 1*10⁻² torr (Hf(tfan)₄). The substances were identified by IR spectroscopy, chemical analyses for C, H, and F and melting point determination. X-ray analysis for all the substances was carried out. The crystallographic data were obtained for Hf(ptan)₄ and [HfO(hfan)₃]₂. The single crystals Hf(ptan)₄ (transparent colourless polyhedra) were obtained by sublimation in helium stream at 120⁰N. The crystallographic data for C₃₂H₄₀F₁₂HfO₈: a = 20.046(2) Å, b = 11.9460(8) Å, c = 16.901(2) Å, β = 95.52 (1)°, s.g. Nc. The single crystals [HfO(hfan)₃]₂ for X-ray structure research were prepared by vacuum sublimation at 170⁰N and pressure 5*10⁻² torr. They represent transparent colourless polyhedra, belonging to monoclinic system, unstable in air. The crystallographic data for C₃₀H₆F₃₆Hf₂O₁₄: a = 12.957(3) Å, b = 16.687(3) Å, c = 12.398(3) Å, β = 108.970, s.g. P2(1)/c, Z = 2, $d_{\text{calculated}}$ = 2.137 g/cm³. The structure of the investigated compound is molecular, it consists of discrete centrosymmetrical dimers [HfO(hfan)₃]₂. The Hf atom has the eight-fold coordination formed by six oxygen atoms of three bidentately co-ordinated hfac-ligands and two oxy-oxygens. The Hf-O distances range in 2.116-2.230 Å, a small bond lengthening in trans-position to O(oxy) is observed. The chelate valent O-Hf-O angles have the average value of 74.90. The dioxydihafniumcyclobutane skeleton represents a planar rhomb with Hf-O_{average} distances of 2.128 Å, Hf...Hf 3.533 Å and O-Hf-O angles of 67.80. The Hf...Hf distance in binuclear molecule is 3.533 Å, the dimers are connected Van der Waals interactions. The crystallographic analysis of the volatile Hf(IV) complexes with β -diketonates known in the literature is carried out. The density of saturated vapour pressure above Hf(IV) complexes are studied by a flow method. The standard thermodynamic parameters DH⁰_O and DS⁰_O for the processes of sublimation and evaporation are calculated from the temperature dependences of saturated vapour pressure for the investigated complexes.

s13.m36.p1 **A study of the structure-anti-HIV activity relationship using a new topological index and the CSD.** S. García-Granda, A. Menéndez-Velázquez and L. Torre-Fernández. Dpto. Química Física y Analítica, c/ Julián Clavería 8, 33006 Oviedo, Spain. E-mail: sgg@fq.uniovi.es

Keywords: Topological-index; HIV-inhibitors; CSD

A single number that can be used to characterize the graph of a molecule is called a topological index[1]. A topological index, thus, appears to be a convenient device for converting chemical constitution into a number. It should also be pointed that topological indices do not generally allow the reconstruction of the molecular graph, implying that a certain loss of information has occurred during their creation. The interest in the topological indices is in the main related to their use in nonempirical[2] quantitative structure-property relationships (QSPR) and quantitative structure-activity relationships (QSAR). Topological indices are intensively used in such areas as pharmacology, toxicology, environmental chemistry and drug design.

Most of the proposed topological indices are related to either a vertex adjacency relationship (connectivity) in the molecular graph G or to graph-theoretical (topological) distances in G. Therefore, the origin of topological indices can be traced either to the adjacency matrix of a molecular graph or to the distance matrix of a molecular graph. Furthermore, since the distance matrix can be generated from the adjacency matrix, most of the topological indices are really related to the latter matrix.

Based in the topological properties derived from the analysis of conventional electron density maps[3] we introduced a new Shannon-type topological index [4]. The new Topological Index reflects the heterogeneity by means of the number and type of the critical points of the electron density function.

$$S^t = S_{\text{atom}} + S_{\text{bond}} + S_{\text{ring}} + S_{\text{cage}}$$

This index shows low degeneration and good correlation to biological activity anti-HIV of the most common used inhibitors. We have found a reasonable correlation between molecular variety and the biological activity anti-HIV[5].

In this work we will show the effectivity of our topological index over a group of molecules, with activity anti-HIV, extracted from the Cambridge Structural Database.

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