Vaporization of Molecular Strontium and Barium \(\beta\)-Diketonates

[\text{Sr}(15C5)(C\text{\textsubscript{5}}O\text{\textsubscript{2}}F\text{\textsubscript{6}}H\text{\textsubscript{2}})] and [\text{Ba}(18C6)(C\text{\textsubscript{5}}O\text{\textsubscript{2}}F\text{\textsubscript{6}}H\text{\textsubscript{2}})].

Structure-Thermochemical Approach

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Abstract—Vaporization of the barium molecular complex [\text{Ba}(18C6)(C\text{\textsubscript{5}}O\text{\textsubscript{2}}F\text{\textsubscript{6}}H\text{\textsubscript{2}})] and the newly prepared strontium complex [\text{Sr}(15C5)(C\text{\textsubscript{5}}O\text{\textsubscript{2}}F\text{\textsubscript{6}}H\text{\textsubscript{2}})] was studied using a semiempirical structure-thermochemical approach. The studies of intermolecular steric shielding of individual atoms and analysis of the possible intermolecular contacts in these complexes made it possible to identify the atoms and atom groups with significant contributions to the vaporization enthalpy. The hypothetical vaporization enthalpies were calculated by summing the contributions of groups. The melting and sublimation enthalpies were determined experimentally.

Chemical vapor deposition of organometallic compounds used for the production of functional barium and strontium titanate coatings is quite attractive. The success of this procedure depends on the volatility and stability of the precursors. The structure- thermochemical approach we suggest would be helpful in selection of these compounds. Previously [1, 2], titanium coordination compounds (binuclear alkoxides) have been studied and their vaporization enthalpies have been determined and analyzed. In order to prepare strontium and barium titanates by MOCVD, the conformational analysis of the molecular design of strontium- and barium-containing compounds with potentially small numbers of intermolecular interactions (IMI) was preliminary carried out. \(\beta\)-Diketonate complexes with crown ligands represent such a class of compounds. The structural data available from the literature are inadequate for detailed analysis of the steric restrictions or the number and the types of thermodynamically significant intermolecular contacts. Nevertheless, substantial volatility of [\text{Ba}(18C6)(C\text{\textsubscript{5}}O\text{\textsubscript{2}}F\text{\textsubscript{6}}H\text{\textsubscript{2}})] has been noted in [3], but thermochemical parameters for its melting, vaporization, or sublimation have not been reported. The purpose of this work is to synthesize and to study vaporization of molecular \(\beta\)-diketonates of strontium [\text{Sr}(15C5)(C\text{\textsubscript{5}}O\text{\textsubscript{2}}F\text{\textsubscript{6}}H\text{\textsubscript{2}})] (I) and barium [\text{Ba}(18C6)(C\text{\textsubscript{5}}O\text{\textsubscript{2}}F\text{\textsubscript{6}}H\text{\textsubscript{2}})] (II) using the structure- thermochemical approach.

EXPERIMENTAL

Compounds I and II were prepared by a procedure similar to that described previously [3] in water–alcohol solutions of barium or strontium nitrate with successive addition of stoichiometric amounts of the crown ligand, hexafluoroacetylacetone, and an excess of a 5% solution of ammonia hydrate \(\text{NH}_3 \cdot \text{H}_2\text{O}\). The product yield was \(\sim 70\%\).

The conditions of preparative sublimation of compounds I and II are similar to those described previously [4] (above 200°C, 10\(^{-3}\) mmHg). Compound I sublimes at a higher temperature than does II.

X-ray powder diffraction showed that [\text{Ba}(18C6)(C\text{\textsubscript{5}}O\text{\textsubscript{2}}F\text{\textsubscript{6}}H\text{\textsubscript{2}})] crystallizes in the tetragonal system, its unit cell parameters \((a = 14.413(1) \text{ Å}, c = 15.494(2) \text{ Å}, V = 3219 \text{ Å}^3)\) being closely similar to those of the compound studied previously in [4] \((a = 14.4210 \text{ Å}, c = 15.4940 \text{ Å}, V = 3222.21 \text{ Å}^3)\). Like the compound prepared previously [4] from barium hydride in non-aqueous media, complex II has a \textit{trans}-configuration, one hexafluoroacetylacetone (HFA) ligand being located above the plane of the coordinated polyether and the other ligand being below this plane. It should be noted that previously [3], a different modification of compound II has been prepared under similar conditions. In the latter modification, the two bidentate HFA ligands occupy \textit{cis}-positions with respect to each other.

X-ray powder diffraction of [\text{Sr}(15C5)(C\text{\textsubscript{5}}O\text{\textsubscript{2}}F\text{\textsubscript{6}}H\text{\textsubscript{2}})] was measured in a FR-552 chamber (Cu\(\kappa\)-\(\text{II}\) radiation). The unit cell parameters are \(a = 10.455(2) \text{ Å}, b = 13.025(2) \text{ Å}, c = 11.485(2) \text{ Å}, \beta = 112.59(1)^\circ, V = 1443.9(3) \text{ Å}^3\). The results of autoindexing of lines show that compound I is isotypical to the monoclinic modification of the barium-containing complex [3].

The thermal studies of the obtained coordination compounds were carried out on a DUPONT 1090 deri-
vatograph (heating rate 10 K/min, indium in sealed aluminum tubes as the reference).

For strontium-containing complex I, the melting range was 210–214°C. The average value for the melting enthalpy (Δ_melt H°_exp) is 14.7(1.0) J/g (10.6(7) kJ/mol). A typical curve of a differential scanning calorimetry experiment (DSC) is shown in Fig. 1a. The melting of complex I is followed by an exotherm related, apparently, to thermal decomposition.

The melting range of compound II is 181–188°C. The average melting enthalpy is 23.1(5) J/g (18.8(4) kJ/mol). In the DSC experiment (Fig. 1b) for [Ba(18C6)(C5O2F6H)2], a nonreproducible endotherm in the temperature range from 50 to 90°C was noted. As the effect increases, the melting enthalpy of compound II somewhat decreases down to 20.1 J/g (16.4 kJ/mol). In connection with this, we additionally investigated complex II on an STA 1500H instrument in an atmosphere of oxygen-free nitrogen (heating rate 5 K/min). In this case, the melting enthalpy was 25.3 J/g (20.6 kJ/mol) and the melting range was 173–183°C.

In our opinion, the effects preceding melting are due, most likely, to the reaction of this compound with atmospheric oxygen, which decreases the melting enthalpy. The highest Δ_melt H°_exp value for compound II under oxygen-free nitrogen (the minimum preceding effect) amounts to 20.6 kJ/mol; this was taken as a calculated value. The loss of mass corresponding to the destruction of the compound is observed almost immediately after melting (~200°C). The maximum heating rate corresponds to a temperature of 265.34°C.

Proceeding from the foregoing, we take the melting enthalpy for compound I to be 10.6(7) kJ/mol and that for II, 20.6 kJ/mol.

High-temperature mass spectrometry. The experimental data were obtained by the Knudsen effusion method with MS analysis of the gas phase on an MS-1301 mass spectrometer. A standard nickel effusion cell with an evaporation/effusion surface ratio of ~600 served as the molecular beam source. The temperature was measured by a platinum/platinum–rhodium thermocouple and maintained constant with an accuracy of ±1 K.

The recommended values of the sublimation enthalpy for compounds I and II are 141.7(4.6) kJ/mol (T = 436 K; temperature range, 402–470 K) and 135.2(8.8) kJ/mol (T = 378 K; temperature range, 347–409 K), respectively.

Detection of the possible intermolecular contacts of identical molecules. Due to the lack of reliable experimental structural data for II and any data for compound I, we modeled their molecules (Figs. 2a, 2b) with fixed Ba(Sr)–O crown distances, which were estimated on the basis of published data for the structures of barium- and strontium-containing monomeric compounds incorporating the corresponding crown ligands [3–7].

Using the original CONTACT program [1, 2], the possible types and numbers of intermolecular interactions between the identical molecules of I or II were revealed and the molecular structures were determined by MM2 calculations.

The calculation revealed the contacts for all CF3 groups in the HFA ligand and the Cl2 groups in the crown rings.

RESULTS AND DISCUSSION

Experimental and theoretical vaporization enthalpies of compounds I and II calculated by the additive method are given in the table.

To determine the thermochemical contribution of the HFA groups to the vaporization enthalpy (Δ_vap H°_calc), we used the averaged values for coordina-