


Lanthanides | Hot Paper |

 Gas-Phase Structures of Potassium Tetrakis(hexafluoroacetylacetonato) Lanthanide(III) Complexes $[\text{KLn}(\text{C}_5\text{HF}_6\text{O}_2)_4]$ (Ln = La, Gd, Lu)Georgiy V. Girichev,^{*[a]} Nina I. Giricheva,^[b] Alexey E. Khochenkov,^[a] Valery V. Sliznev,^[a] Natalya V. Belova,^[a] and Norbert W. Mitzel^{*[c]}

Abstract: The molecular structures of potassium tetrakis(hexafluoroacetylacetonato)lanthanide(III) complexes $[\text{KLn}(\text{hfa})_4]$ (Ln = La, Gd, Lu; $\text{hfa} = \text{C}_5\text{HF}_6\text{O}_2$) were studied by synchronous gas-phase electron diffraction/mass spectrometry (GED/MS) supported by quantum-chemical (DFT/PBE0) calculations. The compounds sublime congruently and the vapors contain a single molecular species: the heterobinuclear complex $[\text{KLn}(\text{hfa})_4]$. All molecules are of C_1 symmetry with the lanthanide atom in the center of an LnO_8 coordination polyhedron, while the potassium atom is coordinated

by three ligands with formation of three K–O and three K–F bonds. One hfa ligand is not bonded to the potassium atom. Topological analysis of the electron-density distributions confirmed the existence of ionic-type K–O and K–F bonding. The structures of the free $[\text{KLn}(\text{hfa})_4]$ molecules are compared with those of the related compounds $[\text{KDy}(\text{hfa})_4]$ and $[\text{KEr}(\text{hfa})_4]$ in their crystalline state. The complex nature of the chemical bonding is discussed on the basis of electron-density topology analyses.

Introduction

Metal complexes with β -diketonate ligands have attracted considerable interest due to their stabilities under normal conditions and their exceptionally high volatilities. These properties allow their use for low-temperature gas-phase metal transport (metal–organic chemical vapor deposition: MOCVD, plasma-enhanced CVD: PECVD) in the thin-film, semiconductor, and superconductor industries.^[1–4]

Polyfluorinated complexes, in particular those containing the hexafluoroacetylacetonato ligand $[\text{M}(\text{hfa})_n]$ ($\text{hfa} = 1,1,1,5,5,5$ -hexafluoropentane-2,4-dionate) have considerably higher vola-

tilities than the nonfluorinated β -diketonate counterparts.^[5] However, a drawback of using the hexafluoroacetylacetonato complexes of the lanthanides for gas-phase technologies is the frequently observed complicated composition of their saturated vapors. According to mass spectrometry studies,^[6–8] the vapors generally consist of monomeric, dimeric, and trimeric forms of $[\text{Ln}(\text{hfa})_3]$. The reason for oligomerization is the tendency of the central lanthanide atom to form a coordinatively saturated coordination polyhedron with eight or nine ligating oxygen atoms.^[9]


In the monomeric $[\text{Ln}(\text{hfa})_3]$ complexes, the lanthanide atom has a coordination number of six. Saturation of the Ln^{III} coordination sphere can be used to prevent polymerization in the gas and solid phases as well as during hydrolysis processes. Making use of binuclear alkali metal–lanthanate complexes as volatile lanthanide-containing species is one of the strategies to solve this problem.^[7] Saturation of the coordination sphere of the central Ln^{3+} ion can in this case be achieved by addition of a fourth hexafluoroacetylacetonate chelating ligand, which results in complexes of the composition $[\text{MLn}(\text{hfa})_4]$. Such heterobinuclear β -diketonates remain poorly studied up to now, despite their high potential for creating new materials with specified properties.^[10,11]


Detailed information not only on the volatility of such precursors, but also on the types and molecular structures of species present in the gas phase, is necessary for rational design, prediction, and control of CVD processes as well as for other practical perspectives of this class of compounds. However, up to now there is no information available in the literature on the molecular structures of $[\text{MLn}(\text{hfa})_4]$ compounds in the gas

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