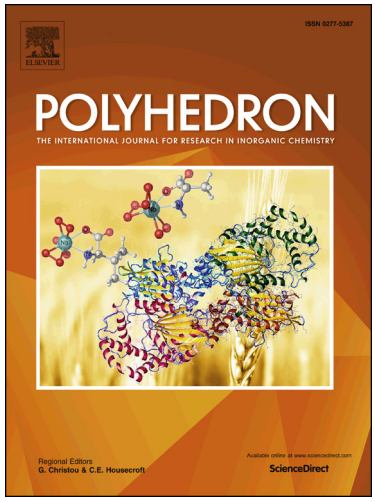

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Structural diversity of volatile mixed ligand complexes of alkaline earth element hexafluoroacetylacetonates with triglyme and related polyglymes

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The crystal structures were determined for four novel and two earlier reported mixed ligand complexes of Ca, Sr and Ba hexafluoroacetylacetonates with two tetradentate polyglymes – triethyleneglycol dimethyl and monomethyl ethers (triglyme and trigmo respectively). The new compounds $[M(hfa)_2(trigmo)]_2$ have identical compositions and similar dimeric structures for M = Ca, Sr and Ba, while the volatile mixed ligand complexes with triglyme demonstrate a variety of compositions and structures depending on central ion. Among the Ba complexes, the novel volatile ionic supramolecular extraordinary crystal $[Ba(hfa)(triglyme)_2]_2[Ba(hfa)_4]$ was revealed. The thermal behavior in the gas phase for the full set of mixed ligand AEE hexafluoroacetylacetonates with tetraglyme, triglyme, trigmo and diglyme was discussed on the base of mass spectrometry and DFT calculations.

Keywords: volatile precursors; X-ray crystal structure; mixed-ligand complexes; alkaline earth elements; beta-diketonates

1. Introduction

Interest in Alkaline Earth Element (AEE) β-diketonate complexes arose in the 1990's from strong requirements for volatile precursors for Metal Organic Chemical Vapor Deposition (MOCVD) of thin films containing AEEs [1-6]. Many AEE β-diketonates were synthesized and their crystal structures and volatility were determined. Different approaches to improve their characteristics as volatile AEE precursors for MOCVD were suggested taking into account both structural and volatility data. Results of these efforts were presented in numerous publications and comprehensive reviews, for example [7-9].

Mixed ligand complexes of AEE hexafluoroacetylacetonates with tetraglyme $[M(hfa)_2(tetraglyme)]$ (Hhfa = hexafluoroacetylaceton, M = Ca, Sr, Ba) have been recognized as the most popular volatile precursors for MOCVD [4]. Even the barium and strontium complexes have molecular structures, sublime intact in the temperature range 100-200 ^oC at low pressure or 200-300 ^oC under an inert atmosphere and have good stability during storage and exploitation [4,7,10,11].