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Barium Diketonates as Precursors for HTSC Thin Films: Structure and Properties

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Abstract. Homoligand and mixed ligand barium diketonate complexes have been synthesized and characterized by X-ray structure determination. Homoligand complexes with dipivaloyl-methane hexafluoroacetone and pivaloyltrifluoroacetone have oligigomeric or polymeric structure. The mixed complexes with additional anionic ligands (Cl^- , OH^- , Piv^-) form pentanuclear complexes. The structures of the mixed ligand complexes with Lewis bases contain either mono or dinuclear chelates. Deoligomerization is accompanied by a decrease of the sublimation temperature and improves a storage stability of barium complexes used in MOCVD process for production of HTSC films.

1. INTRODUCTION

One of the problems with the MOCVD of superconducting thin films is the low volatility and thermal stability of the barium chelates used as precursors. Structural investigations revealed that the reason for the poor thermal stability and relatively high sublimation temperatures of the homoligand barium β -diketonates is their oligomeric nature. The low coordination numbers of barium atoms in these compounds (six or seven) make them sensitive to traces of water or carbon dioxide. High chemical reactivity of such complexes is also responsible for a low reproducibility of their volatility at elevated temperatures. One of the ways to decrease a degree of oligomerization and, hence, to improve the volatility, thermal stability and to prolong a storage period, is to prepare mixed ligand complexes containing, in addition to the β -diketonate, different neutral or anionic ligands [1].

2. EXPERIMENTAL

2.1 Synthesis

The preparation of homoligand chelate complexes BaL_2 ($\text{HL} = \text{Hthd}$, 2,2,6,6-tetramethylheptane-3,5-dione [2-4]; Hhfa , 1,1,1,5,5,5-hexafluoroacetylacetone [5]; Hpta , 1,1,1-trifluoro-5,5-dimethylhexanedione, or pivaloyltrifluoroacetone [6]) were carried out using Ba metal and diketone or by vacuum sublimation from the mixed ligand complexes. $\text{BaL}_2 \cdot \text{Q}$.

The mixed ligand diketonates with N- and O-Lewis bases were obtained by dissolving of Ba metal in diketone in the presence of Lewis base or using the reaction between $\text{Ba}(\text{OH})_2$ (or barium salt) and alkali derivative of diketone in the presence of additional ligand [7-10].

2.2 Crystal structure determination

The crystal structure of complexes have been investigated by single crystal X-ray diffraction. The crystals were placed in sealed glass capillaries because the most of compounds were more or less sensitive to air. Diffraction data were collected on Enraf Nonius CAD-4 or Siemens P3/PC diffractometers using $\text{Mo-K}\alpha$ radiation with graphite monochromator.

The crystallographic calculations were performed using SHELXTL PLUS or SDP program packages using direct and Patterson methods. For most structures, all non hydrogen atoms were refined anisotropically to R values in the range of 0.05-0.08. Partial disorder of *tert*-butyl groups around a $\text{C}(\text{CH}_3)_3$ axis has been found in many cases.

3. RESULTS AND DISCUSSION

3.1 Homoligand complexes

Both crystalline forms of $\text{Ba}(\text{thd})_2$ (prepared from solution and from the gas phase) are actually tetranuclear complexes $\text{Ba}_4(\text{thd})_8$ with different packing of molecules (Fig. 1) [2-4]. Other coordination of β -diketonate ligand has been found in the tetranuclear $\text{Ba}_4(\text{pta})_8$ due to additional $\text{Ba}\cdots\text{F}$ interactions at the distances 2.87-3.16 Å (Fig. 2) [6]. Tetranuclear complexes possess relatively high volatility but they are very sensitive to moisture and carbon dioxide due to lower coordination numbers of Ba atoms in respect to oxygen. In contrary, complex $\text{Ba}(\text{hfa})_2$ with fully fluorinated ligand possesses a chain polymeric structure with additional $\text{Ba}\cdots\text{F}$ bonding at 2.76-3.09 Å [5], that results in the low volatility of this substance and in the formation of BaF_2 by its thermal decomposition.

Figure 1: Tetranuclear molecule of $\text{Ba}_4(\text{thd})_8$. *tert*-Butyl groups are omitted for clarity.

Figure 2: Tetranuclear molecule of $\text{Ba}_4(\text{pta})_8$. The dashed lines show the $\text{Ba}\cdots\text{F}$ interactions.

3.2 Mixed ligand complexes

3.2.1 Anionic additional ligand. The use of this type of additional ligands results in increase of the oligomerization degree compared with homoligand complexes. Thus, the mixed ligand complexes containing anionic ligand such as Cl^- , OH^- , and $(\text{CH}_3)_3\text{COO}^-$ (pivalate) consist of pentanuclear species, $\text{Ba}_5(\text{thd})_9\text{Cl}(\text{H}_2\text{O})_7$ (Fig. 3) [7], $\text{Ba}_5(\text{thd})_9(\text{OH})(\text{H}_2\text{O})_3$ [11], and $\text{Ba}_5(\text{thd})_9(\text{piv})$ [3], respectively. As expected, these compounds do not show any increase of volatility or improvement of storage stability compared with corresponding homoligand complexes.

3.2.2 Neutral additional ligand. Barium diketonates with neutral Lewis bases such as H_2O , 2,2'-dipyridyl, diglyme, tetraglyme, 1,10-phenantroline and others have oligomerization degree less than those in homoligand chelates. Their structures contain dinuclear species $[\text{Ba}_2(\text{thd})_4(\text{H}_2\text{O})_4]_2(\text{H}_2\text{O})$ (Fig. 4) [8], $[\text{Ba}_2(\text{thd})_4(\text{dipy})_2]$ [12], $[\text{Ba}(\text{thd})_2(\text{diglyme})]_2(\mu\text{-H}_2\text{O})$ [1], or mononuclear ones $\text{Ba}(\text{thd})_2(\text{tetraglyme})$ [13], $\text{Ba}(\text{thd})_2(\text{Phen})_2$ [12], $\text{Ba}(\text{pta})_2(\text{tetraglyme})$ (Fig. 5) [9]. It is of interest that both $\text{Ba}(\text{hfa})_2(\text{H}_2\text{O})$ [10] and $\text{Ba}(\text{pta})_2$ possess a chain polymeric structure very similar to that of $\text{Ba}(\text{hfa})_2(\text{Et}_2\text{O})_{0.5}$ due to the additional $\text{Ba}\cdots\text{F}$ contacts.

Figure 3: Pentanuclear molecule of $[Ba_5(thd)_9Cl(H_2O)_7]$.

Figure 4: Structure of $[Ba_2(thd)_4(H_2O)_4]_3(H_2O)$.