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New Barium Volatile Complexes Useful in CVD

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Abstract. New volatile barium precursors based on pivaloyl-trifluoroacetone are obtained and studied. The results of X-ray structure determination of two compounds are given.

1. INTRODUCTION

The major problem with the MOCVD of superconducting thin films is the low thermal stability and unsufficient volatility of barium chelates used. Among them barium 2,2,6,6-tetramethylheptanedionate-3,5 $\text{Ba}(\text{thd})_2$ and 1,1,1,5,5,5-hexafluoropentanedionate-2,4 $\text{Ba}(\text{hfa})_2$ are the main ones. These compounds possess quite different structure and properties. Thus, the former is a tetranuclear complex [1-4], one of its hydrates consists of a dimeric fragments combined into hexanuclear species [5], while the latter (in form of hydrate [6], or ether solvate [7]) has a chain structure. Due to its molecular structure $\text{Ba}_4(\text{thd})_8$ can be quantitatively sublimed at temperature range 220-240°C, whereas the volatility of polymeric $[\text{Ba}(\text{hfa})_2]_n$ is by far less. Nevertheless, mononuclear mixed ligand diketonates with hfa-ligand are much more volatile than those with thd. We decided to study barium complexes with 1,1,1-trifluoro-5,5-dimethylhexanedione-2,4 (pivaloyltrifluoroacetone, Hpta), which contains both tert-butyl (as in Hthd) and trifluoro-methyl (as in Hhfa) terminal groups. We succeeded to obtain sublimed product and also its water, tetraglyme and 2,2'-dipyridyl (dipy) derivatives.

2. EXPERIMENTAL

2.1 General proceedings

IR spectra were recorded on a Perkin-Elmer PEFTIER spectrometer as

Nujol mulls. Thermogravimetric analysis was performed by using Paulik-Paulik thermogravimetric system under a dry nitrogen flow; the furnace was heated at $5^{\circ}\text{C min}^{-1}$ from ambient temperature up to 500°C . The X-ray powder patterns were obtained with a DRON-2 powder diffractometer (Co K_{α} -radiation).

2.2 Synthesis

$\text{Ba}_2(\text{pta})_4(\text{H}_2\text{O})_2$ (I). 4.09 g of Hpta was added with stirring to 100 ml of saturated (15°C) freshly prepared solution of recrystallized $\text{Ba}(\text{OH})_2 \cdot 8\text{H}_2\text{O}$. The white precipitate formed was extracted by ether. Extract was evaporated for dryness. The substance was recrystallized from water ethanol. Complex is a white solid substance, soluble in ether, benzene and ethanol. IR (cm^{-1}): 3400, 1630, 1520, 2880-2980, 1260, 1250-1360, 525, 400.

$\text{Ba}_4(\text{pta})_8$ (II) was obtained by heating $\text{Ba}_2(\text{pta})_4(\text{H}_2\text{O})_2$ in vacuo 0.01 torr at $200\text{-}220^{\circ}\text{C}$. It is a white powder, air sensitive. It dissolves in ether and benzene. IR (cm^{-1}): 2880-2980, 1635, 1590, 1520, 1260, 1180, 1120, 565, 520, 480.

The adduct with overall composition $\text{Ba}(\text{pta})_2(\text{dipy})_{1.5}$ (III) was prepared dissolving Ba in benzene solution of Hpta and dipy ($\text{Ba:Hpta:dipy} = 1:2:2$). The white precipitate formed was recrystallized from toluene. IR (cm^{-1}): 1625, 1590, 1560, 1540, 1455, 1180, 1120, 765, 595, 520, 480.

$\text{Ba}(\text{pta})_2(\text{tetraglyme})$ (IV) [8] was synthesized as a previous compound using tetraglyme instead of dipy ($\text{Ba:Hpta:tetraglyme} = 1:2:1$) in a mixture of pentane and ethylacetate. A white solid substance unsoluble in pentane, soluble in ether. IR (cm^{-1}): 1510, 1620, 1640.

2.3 Crystal structure determination

Diffraction data were collected on Siemens P3/PC diffractometer using Mo-K_{α} radiation with a graphite monochromator. Crystals were placed in glass capillaries for the measurements of intensities. To record the intensities of reflections θ - 2θ scan method was used. The calculations were performed using the SHELXTL PLUS program package [9]. The positions of barium atoms were found by direct methods. Successive difference Fourier syntheses gave the coordinates of other non-hydrogen atoms. Structures were anisotropically refined by full-matrix least-squares for all non-hydrogen atoms to $R = 0.054$ (structure I) and 0.056 (structure II).

Crystal data for I: $\text{BaC}_{16}\text{H}_{20}\text{F}_6\text{O}_4$, $\text{P}\bar{1}$, $a=14.382(7)$, $b=15.777(8)$, $c=20.613(9)$ Å, $\alpha=95.21(2)$, $\beta=108.03(2)$, $\gamma=96.25(2)^\circ$; $V=4383$ Å³, $z=8$.

Crystal data for II: $\text{BaC}_{16}\text{H}_{22}\text{F}_6\text{O}_5$, $\text{P}\bar{1}$, $a=8.641(3)$, $b=15.737(4)$, $c=16.372(5)$ Å, $\alpha=79.43(2)$, $\beta=82.21(2)$, $\gamma=82.34(2)^\circ$; $V=2155$ Å³, $z=4$.

3. RESULTS AND DISCUSSION

According to X-ray structural study of sublimed $\text{Ba}(\text{pta})_2$, it consists of tetranuclear units $\text{Ba}_4(\text{pta})_8$, Ba atoms form rhombus (Fig.1). In the cell there are two types of crystallographically independent $\text{Ba}_4(\text{pta})_8$ molecules with similar interatomic distances and coordination modes. Ba...Ba distances in each tetranuclear species are : 4.184 Å (4.199 Å in the other tetramer) for Ba(1)Ba(2) and 4.073 Å (4.078 Å) for Ba(1)Ba(2'). In this compound there are weak contacts between fluorine atoms of CF_3 -groups and metal ion ($\text{Ba}\cdots\text{F}$ 2.87 - 3.29 Å). Similar interactions have been also found in barium chelates with hfa [6,7]. Due to coordination of the fluorine atoms, coordination modes of ligands differ from those found in $\text{Ba}_4(\text{thd})_8$ (see Fig. 1 in the paper of A.Drosdov and S.Troyanov in the Conference Proceedings). Each Ba atom has CN=9 (7 O + 2 F), Ba-O distances ranging from 2.59 to 2.92 Å. The ligands

Figure 1. Tetranuclear $\text{Ba}_4(\text{pta})_8$ molecule.

O(3)O(4), O(5)O(6), O(7)O(8) in both tetranuclear molecules belong to chelating bridging coordination mode (signed 1b in [2]). The Ba...O distances in chelate rings (ranging from 2.60 to 2.78 Å) are shorter than bridging ones (Ba-O 2.79 - 2.82 Å). The ligand O(1)O(2) in both tetramers unites all the four barium atoms in a tetranuclear molecule. O(1) atom is three-dentate being connected with Ba(1), Ba(1') and Ba(2) atoms. O(2) is coordinated by Ba(1) and Ba(2') atoms. We don't know any other example of such coordination mode in metal diketonates. It includes one chelate ring with Ba(1) and three bridging Ba-O bonds. The different coordination number of O(1) and O(2) results in a strong distortion of the chelate ring (the difference of two Ba-O bond distances in the first tetramer is 0.15 Å, and 0.19 Å in the second). The average O(1)-Ba distance in both tetramers is 2.86 Å, while O(2)-Ba is 2.74 Å in the first tetramer and 2.72 Å in the second. The larger is the coordination number of the oxygen, the larger Ba-O distance is.

The structure of $\text{Ba(pta)}_2(\text{H}_2\text{O})$ (Fig.2) consists of infinite chains: Ba atoms are linked by chelating bridging pta-ligands and $\mu\text{-H}_2\text{O}$ molecules. Distances Ba...Ba (4.345 Å) are slightly longer

Figure 2. Chain structure of $[\text{Ba(pta)}_2(\text{H}_2\text{O})]$

than in $\text{Ba}_2(\text{hfa})_4(\text{Et}_2\text{O})$ [7] (4.213 Å and 4.229 Å) due to bulky tert-Bu groups. Each of two Ba atoms have CN=10 (8O + 2F; Ba-O(pta) 2.69 - 2.88 Å, Ba-O(H_2O) 2.77 - 3.10 Å, Ba...F 2.97 - 3.03 Å). All the pta ligands in the structure are chelate bridging (one chelate ring and one bridging O-atom). The Ba-O distances in chelate ring are in range 2.69 - 2.78 Å, whereas the bridging ones are longer 2.86- 2.88 Å. This structure is very similar to $\text{Ba}(\text{hfa})_2(\text{H}_2\text{O})$ studied by Bradley et al [6], in which Ba is also ten-coordinated.

Complex $\text{Ba}(\text{pta})_2(\text{tetraglyme})$ [8] was found to be mononuclear with the structure very similar to other tetraglyme adducts known (CN Ba = 9) [10 ,11]. In the molecule of adducts there are no Ba...F contacts (see Fig.5 in the the paper of A. Drozdov and S. Troyanov).

Being heated under nitrogen flow $\text{Ba}(\text{pta})_2(\text{H}_2\text{O})$ first loses water (80-90°C) and then decomposes and partly sublimes (160-220°C). In vacuo 0.01 torr this compound loses water (40-50°C) and then sublimes in the form of $\text{Ba}_4(\text{pta})_8$. The latter compound can be resublimed in vacuo at 180-200°C, that is slightly lower in comparison with those for $\text{Ba}_4(\text{thd})_8$. Being heated in inert atmosphere $\text{Ba}(\text{pta})_2 \cdot (\text{dipy})_{1.5}$ evolves dipy (250°C) and then $\text{Ba}_4(\text{pta})_8$ remained decomposes with partial sublimation (300°C). The residue is barium fluoride. Being heated in vacuo 0.01 torr adduct with dipy first loses the additional ligand (120-140°C); remaining $\text{Ba}(\text{pta})_2$ can be sublimed at 180 - 200°C as $\text{Ba}_4(\text{thd})_8$. Under vacuo 0.01 torr at 150°C in the case of $\text{Ba}(\text{pta})_2(\text{tetraglyme})$, both thermal decomposition to dipy and $\text{Ba}_4(\text{pta})_8$ and sublimation of adduct take place. $\text{Ba}_4(\text{pta})_8$ remained can be sublimed at 220°C.

The complexes with pta mentioned are suggested as precursors for MO CVD process of thin films production. In comparison with water barium thd-chelates (usually a mixture of different unstable products formes during storage) in $\text{H}_2\text{O}-\text{Ba}(\text{pta})_2$ system only one stable compound is formed - monohydrate. This substance was kept for 6 months in a closed vessel without any changes and without decrease of volatility. The use of $\text{Ba}_4(\text{pta})_8$ instead of $\text{Ba}_4(\text{thd})_8$ allows to diminish the sublimation temperature for 10°C. Adduct with dipy is the best form to store a precursor for a long time.

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