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Physico-Chemical Study of Barium (II) Dipivaloylmethanate Nature

N.E. Fedotova, I.K. Igumenov, V.I. Mamatyuk and G.V. Sidorenko

Institute of Inorganic Chemistry, Lavrentieva 3, Novosibirsk 630090, Russia

Abstract. A physico-chemical research of bis-(dipivaloylmethanato)barium(II) ($\text{Ba}(\text{thd})_2$) has been carried out from the point of its use in CVD processes as a precursor (thermal stability, immunity to external effects and etc.). The optimal conditions for synthesis, purification and storage have been found. It has been shown, that the sublimated product presents a mixture of several modifications with the main phase of a composition $\text{Ba}_4(\text{thd})_8$. At a lowered pressure the sublimated product is preserved without decomposition for a long time. In the air it is a monomer of a composition $\text{Ba}(\text{thd})_2 \cdot 2\text{H}_2\text{O}$, decomposing in the course of time with forming a free ligand or a diketone ($\text{C}_8\text{H}_{10}\text{O}_2$) depending on the way of purification of the initial compound.

1. INTRODUCTION

The synthesis of the HTSC $\text{YBa}_2\text{Cu}_3\text{O}_{7-x}$ films by the chemical vapour deposition (CVD) is based on the possibility to obtain the Y_2O_3 , BaO and CuO films from volatile chelates of these metals [1-7]. As the dipivaloylmethanates of Y(III), Ba(II) and Cu(II) have a substantial vapour pressure already at 150-250°C [1], it is these complexes that are used as precursors in CVD processes. The main problem, arising at the preparation of oxide barium films, is a low reproducibility of the experiments. Peculiar of the complexes of the alkaline-earth metals is the ion nature of the metal-ligand coordination bond, as a consequence, the latter are highly susceptible to polymerization [8-15]. In the case of $\text{Ba}(\text{thd})_2$ the propensity to polymerization makes conditions for existence of this complex in several modifications of similar, or close-to-similar compositions [11-16], which in its turn influences on stability of this compound to external effects. Traditionally the introduction of additional donor molecules, such as the H_2O , CH_3OH , 1,10-phenantroline (Phen) and etc. [12], as well as the use of fluorocontaining ligands [3, 4, 6] leads to the formation of more stable monomeric compounds. But, firstly, for barium complexes the introduction of H_2O results in oligomeric complexes, such as $[\text{Ba}_5(\text{thd})_9\text{OH}(\text{H}_2\text{O})_3]$ [11], $[\text{Ba}_6(\text{thd})_{12}(\text{H}_2\text{O})_{13}]$ [17], secondly, only few mixed-ligand complexes can be transferred into the gas phase with preserving the structural unit and, thirdly, as is shown in refs. [3,6], the vapour mixture of three precursors is accompanied by undesirable side chemical reactions in the gas phase. In order to simplify the HTSC film growing process it is expedient to use complexes with the same ligand. As far as Hthd is the most widely used ligand, it seems impossible, at least for the time being, to refuse the use barium (II) dipivaloylmethanate as the precursor in the CVD processes. The wide circle of papers devoted to the synthesis and research of physico-chemical properties of $\text{Ba}(\text{thd})_2$ and its derivatives contains a number of inconsistent data [7, 11-20]. On the one hand, the structures of two modifications of water-free $\text{Ba}_4(\text{thd})_8$ [12-15] and number of mixed-ligand complexes [11, 12, 16, 17] isolated at recrystallization from donor solvents have been

established. On the other hand, there are essential discrepancies in the melting temperatures (142-172°C, 185-192°C [7, 8], 160-165°C, 158-165°C [16] depending on the method of synthesis) and also in the information on the capability of Ba(thd)₂ to sublimate (Ba(thd)₂ is described as a nonvolatile product [20]; $T_{\text{sub.}} = 220\text{-}240^\circ\text{C}$ [1-3, 5, 6], $T_{\text{sub.}} = 280^\circ\text{C}$ [21], $T_{\text{sub.}} = 190\text{-}240^\circ\text{C}$ [22]). Having analyzed the data from publications and based on the results of alkaline-earth metal β -diketonates studies carried out at our laboratory [23], we have come to a conclusion that the reason of the discrepancies and insufficient reproducibility of the results in the experiments with Ba(thd)₂ is a probable existence of the complex several modifications, the formation of mixed-ligand complexes, the hydrolysis of the compounds and sensitivity of Ba(thd)₂ to external effects.

To reveal the chemical nature and properties of Ba(thd)₂ as the precursor depending on the synthesis, purification and storage conditions, we have carried out NMR-, IR-, and Raman-spectroscopy, chromatography, thermoanalytical and X-ray diffraction studies of the complex.

2. EXPERIMENTAL

General Nomenclature: 2,2,6,6-tetramethylheptane-3,5-dione (dipivaloylmethane, Hthd).

2.1 Synthesis of Ba(thd)₂*2H₂O

Ba(thd)₂*2H₂O was prepared when reacting a freshly prepared barium hydroxide (aqueous solution) and Hthd (alcohol solution) (4:1). The water-alcohol solution was stirred without heating for about 30 min. Ba(thd)₂*2H₂O was precipitated by a five-fold amount of water and collected by filtration on a glass filter. To optimize the synthesis conditions, we have found a relationship between the yield of Ba(thd)₂*xH₂O, the amount of barium hydroxide and the temperature of the reaction mixture. The yield of Ba(thd)₂ was shown to be maximal at a 4-fold excess of barium hydroxide, whereas a heating of the reaction mixture to 80°C gives rise to the formation of considerable amounts of a barium carbonate.

2.2 Recrystallization

The crude product was solved in a minimal volume of alcohol, filtered and precipitated by adding a 10-fold excess of water with stirring. The precipitate was collected on a glass filter and then dried. The results of elemental analysis correspond to a dihydrate of barium dipivaloylmethanate Ba(thd)₂*2H₂O:

found: C 48.81%, H 7.60%; calculated: C 48.95%, H 7.79%.

To find the Hthd-ligand content in the recrystallized product, a gas-liquid chromatographic technique was applied. (A weight of the product was decomposed by 20% H₂SO₄ and the released Hthd was extracted with isooctane. Hexachloroethane served as a standard and 19% dinonylphthalate on dinochrome II served as a stationary phase). The Hthd-ligand content in the recrystallized and air-dried samples corresponds to that in a dihydrate Ba(thd)₂*2H₂O. The quantities are as follows: 67.7% (found) and 69.7% (calculated) for Ba(thd)₂*2H₂O.

2.3 Sublimation

Ba(thd)₂*2H₂O was sublimated in a horizontal gradient furnace in special ampoules. The design of the ampoule allows the precursor to be sublimated twice. The compound was sublimated at $P=3\text{-}5 \cdot 10^{-2}$ Torr and $T = 210\text{-}230^\circ\text{C}$. After the sublimation was finished, a cooled ampoule was

unsoldered at $P=5 \cdot 10^{-2}$ Torr.

Chromatographic studies of sublimated samples have confirmed that it is anhydrous. The found amount of Hthd corresponds to $\text{Ba}(\text{thd})_2$. The found and calculated amounts are 73.1% and 72.7%, respectively (for $\text{Ba}(\text{thd})_2$).

2.4 The procedure of handling the sublimated $\text{Ba}(\text{thd})_2$

The work with sublimated $\text{Ba}(\text{thd})_2$: unsoldering of the ampoule, preparation of solution for the NMR experiments, gas-liquid chromatographic experiments were performed in a dry chamber. P_2O_5 and NaOH served as dryers and absorbers of CO_2 , respectively; the chamber was cleaned with dry argon for 24 hours before the work started. The residual pressure of water vapour was estimated to be $2 \cdot 10^{-5}$ Torr.

3. RESULTS AND DISCUSSION

3.1 Definition of forms of barium dipivaloylmethanate

It is worth mentioning that the information derived by means of this or that physico-chemical research technique is not sufficient to identify an exact composition of the complex. Only a comprehensive study has enabled definite conclusions on the properties and composition of the complex to be drawn.

3.1.1 Infrared spectroscopic analysis

The spectrum of recrystallized and air-dried $\text{Ba}(\text{thd})_2 \cdot 2\text{H}_2\text{O}$ is in accord with the data of [20, 22]. The lines of valent vibrations (cm^{-1}) lie in the regions usual for metal β -diketonates: $\text{C}=\text{O}$ (1590, 1575, 1560); $\text{C}=\text{C}$ (1505, 1450); $\text{C}-\text{C}(\text{CH}_3)_3$ (1415, 1355); $\text{C}-\text{CH}_3$ (1220, 1240); $\text{M}=\text{O}$ (475). The presence of bound water is confirmed by the absorption in the 3400 cm^{-1} range.

3.1.2 Raman spectroscopic spectra

In the spectrum of the recrystallized sample at a minimum intensity (I , mV) of exciting radiation, among recorded are the following characteristic lines in the metal-ligand vibration region: 387 and 472 cm^{-1} , and a weak structureless band ($500\text{--}580 \text{ cm}^{-1}$) which frequency range correlates with vibrations of coordinated oxygen.

A comparison of the IR and Raman spectra with the results of alternative investigations [12, 16, 17, 24] makes it possible to assume the formation of a mixture of water adducts under $\text{Ba}(\text{thd})_2 \cdot 2\text{H}_2\text{O}$ recrystallization from a water-alcohol solution. This accounts for both considerable errors in chemical analysis and a broadened interval of melting temperatures. The Raman spectrum of a sample, prepared in dry atmosphere, has the characteristic lines in the 387 and 472 cm^{-1} metal-ligand vibration ranges.

3.1.3 Thermal analysis

TG, DTG and DTA curves of $\text{Ba}(\text{thd})_2 \cdot 2\text{H}_2\text{O}$ are shown in Fig. 1. We assign the endoeffect, minimal at 60°C , to the dehydration of the complex (loss in the mass within $40\text{--}80^\circ\text{C}$: calculated 6.7%, found 8.5%). A gradual weight loss also occurs over this temperature, probably, due to a simultaneous process of Hthd withdrawal (minimum on DTG and DTA curves at 140°C). Based on literary data [25] this process is attributable to hydrolysis: $\text{Ba}(\text{thd})_2 \cdot 2\text{H}_2\text{O} \rightarrow \text{Ba}(\text{OH})_n(\text{thd})_n + (2-n)\text{Hthd} + \text{H}_2\text{O}$.

In [26] the endoeffect at 140°C is assigned to melting. At $175\text{--}180^\circ\text{C}$ the endoeffect corresponds to melting of the complex, while an intense transition to the gas phase, accompanying by the decomposition, starts at 300°C . The decrease in the sample weight amounts to 83%, thereby corresponding to the evaporation of about 53% of $\text{Ba}(\text{thd})_2$ and does not contradict to the results of refs. [8, 26]. If the complexes were decomposed entirely to BaO without sublimation the % weight loss would be accounted for 72%. According to the thermal analysis data of the double sublimated sample of anhydrous $\text{Ba}(\text{thd})_2$ is sufficiently thermal stable ($T_{\text{sub.}} = 216^\circ\text{C}$, $P = 3 \cdot 10^{-3}$ Torr). The decrease in the sample weight amounts to 88%, thereby corresponding to the evaporation of about 70% of $\text{Ba}(\text{thd})_2$ (Fig. 1).

Figure 1: a) Thermal curves at linear heating ($10^\circ/\text{min}$) of $\text{Ba}(\text{thd})_2 \cdot 2\text{H}_2\text{O}$ in helium atmosphere; b) Thermograms of $\text{Ba}(\text{thd})_2 \cdot 2\text{H}_2\text{O}$ (1); $\text{Ba}(\text{thd})_2$ sublimated in vacuum at $P = 3 \cdot 10^{-3}$ Torr (2).

3.1.4 NMR spectra

According to the NMR data (NMR spectra for $\text{Ba}(\text{thd})_2$ were recorded on AC 200 Bruker spectrometer. Dry chloroform, D_2 -dichloromethane, carbon tetrachloride and D_8 -toluene were used as solvents. Chemical shifts are given in ppm relative to TMS.), the product, which was precipitated from the reaction mixture, is a dihydrate of barium dipivaloylmethanate. In the NMR spectra there are lines which are assigned to the complex, free ligand (as an impurity) and bound water. The complex (solvent CD_2Cl_2 , $\delta[\text{CH}_2\text{Cl}_2] = 5.3$ ppm) is: CH_3 - 1.008, CH - 5.56 and H_2O - 5.0 ppm. The free ligand contains enol: CH_3 - 1.14, CH - 5.74, OH - 16.0 ppm and ketone: CH_2 - 3.72 ppm (Fig. 2).

The mole share of the free ligand decreases in going from crud product to recrystallized sample.

Figure 2: The PMR spectrum of crude product.

The NMR spectrum of ^{13}C shows the complex: CH_3 - 28.9, $-\text{C}-$ 41.3, CH - 90.6 and $\text{C}=\text{O}$ - 199.7 ppm; the free ligand: there are bands of only CH_3 - group at 27.7 ppm; the other signals are not seen because of a low signal-to-noise ratio (low concentration) (Fig. 3). The mole water-ligand ratio in the complex is about 1:1, which corresponds to a dihydrate. As it has been noted, the dissolution in some solvents contributes to the destruction of the complex accompanied by the formation of the barium carbonate. As the NMR data show, the complex can be regenerated from CCl_4 , C_6H_6 and CHCl_3 , but the amount of bound water approximately halves thus indicating $\text{Ba}(\text{thd})_2 \cdot \text{H}_2\text{O}$. The extraction of the complex from heptane has failed. Only the signals of unidentified compounds have been found in the spectra of the samples extracted from the heptane.

Figure 3: The NMR spectrum of crude product.

The studies performed on the sublimated samples have shown that the NMR spectra of the samples prepared in unpolar solvents (CCl_4 , toluene) are much different from the NMR spectra of the initial complex (Fig. 4). (^1H spectrum, solvent CCl_4 : CH_3 - 1.20, 1.28; CH - 5.72, 5.80 ppm). Passing from CCl_4 to CHCl_3 and also with the use of pyridine or water as donors the spectrum returns to the initial shape (Fig. 2). Such behaviour of the compound can be unambiguously interpreted as the

polymerization-depolymerization effect. If one works with the sublimated sample in air, the NMR spectra show only $\text{Ba}(\text{thd})_2 \cdot x\text{H}_2\text{O}$.

Figure 4: The PMR spectrum of sublimated $\text{Ba}(\text{thd})_2$.

The low-temperature NMR studies (Fig. 5) have not made it possible to identify the structure of the complex in a solution without ambiguity. Despite our precautions, we have not succeeded in obtaining a $\text{Ba}(\text{thd})_2$ solution in D_8 -toluene, not containing the traces of H_2O and, therefore, some signals can be assigned to hydrated forms of $\text{Ba}(\text{thd})_2 \cdot x\text{H}_2\text{O}$. A considerable complication of the NMR spectrum at decreased temperatures, in particular the signal broadening and splitting, indicates the existence of a number of chemical forms and/or nonequivalent sites of thd and also of a rapid exchange at a room temperature. A variety of lines within the CH and CH_3 resonance is an attribute of the formation of coordinate polymers.

Figure 5: The PMR spectrum of sublimated $\text{Ba}(\text{thd})_2$ at different temperatures.

3.1.5 X-ray diffraction analysis

According to XRD data, the main phase of sublimated product is a rhombic modification of $\text{Ba}_4(\text{thd})_8$ [13]. Relative intensities of doped phase do not exceed 15-20%. Measurements carried out in a twenty four hours have disclosed that the new phase arises. We suggest that it may be $\text{Ba}(\text{thd})_2 \cdot x\text{H}_2\text{O}$. The following change of this phase was not detected.

On the basis of our investigation it may be concluded that the sublimation of a dihydrate of barium (II) dipivaloylmethanate results in the formation of an anhydrous complex with the $[\text{Ba}(\text{thd})_2]_4$ oligomer structure of several modifications. It is confirmed by literary data [8-10, 12, 14, 15, 18] and the results of mass spectrometric studies of $\text{Ba}(\text{thd})_2$ in the gas phase carried out at our laboratory [27].

3.2 Analysis of the decomposition products of $\text{Ba}(\text{thd})_2 \cdot 2\text{H}_2\text{O}$

Analyzing the reasons of the irreproducibility of experiments in the case of Ba oxide films, we have paid attention to the fact that the outlook of the complex changes with time. It has turned out that depending on the storage conditions, the complex decomposes with the formation of either a free ligand or the lower diketone. For example, upon heating of sublimated $\text{Ba}(\text{thd})_2$ in the vacuum after its prolonged storage (in darkness, over a drier) a volatile crystalline substance was extracted. Using the NMR technique, it was identified as $(\text{CH}_3)_3\text{C}-\text{CO}-\text{CH}=\text{CH}-\text{CO}-\text{C}(\text{CH}_3)_3$. The JHH for 14.5 Hz double-bond protons (found from satellites of ^{13}C in the PMR spectrum) allows to identify it as a trans-product. In PMR spectra the shifts are $(\text{CH}_3)_3$ - 1.16 and $\text{CH}=$ 7.42 ppm. In the spectrum of ^{13}C the shifts are as follows: CH_3 - 25.92, $-\text{C}-$ 43.90, $\text{CH}=$ 133.46 and $\text{C}=\text{O}$ 205.2 ppm. The data are consistent with the results of the elemental analysis (found: % H 10.15, % C 73.4, % O 16.4; calculated: % H 10.26, % C 73.43, % O 16.30), infrared (νCO , cm^{-1} : 1670st, 1650m) and Raman spectroscopic (νCO , cm^{-1} : 1699m; νCC , cm^{-1} : 1612st) experiments. According to our assumption, the formation of this unsaturated diketone is caused by the condensation reaction between the probable products of oxidizing and hydrolytic splitting of a thd anion: trimethylpyrroacemic aldehyde and pinacolone. After a three-month storage of the sublimated $\text{Ba}(\text{thd})_2$, in the NMR spectrum the unsaturated diketone mentioned above, free ligand, water and other unidentified products were found. Three months after the synthesis of the non sublimated $\text{Ba}(\text{thd})_2 \cdot 2\text{H}_2\text{O}$, only a free ligand was recorded in the NMR spectrum of this compound, i.e. the complex is practically not found. The sublimated $\text{Ba}_4(\text{thd})_8$ is conserved in vacuum-soldered ampoules for a long time without changes. Practically, there are no changes in the NMR spectra of $\text{Ba}_4(\text{thd})_8$ after its 3-month storage in a soldered ampoule. It is apparent that one of the factors responsible for the decomposition of the complex is its contact with CO_2 or O_2 , because such precautions as darkness, low ambient temperature and drying have no noticeable effect on the behaviour of the substance. It is interesting to note that the diketone is formed upon storage of only a sublimated product.

4. CONCLUSION

The results of the present work show that the sublimated product presents a mixture of several modifications of composition $\text{Ba}(\text{thd})_2$. The main phase of this mixture is $\text{Ba}_4(\text{thd})_8$ having a rhombic modification. The sublimated product is stored at a lowered pressure for a long time without changes. In the air it is a dihydrate of barium (II) dipivaloylmethanate gradually decomposing.

Thus, when satisfying all the synthesis, purification and storage conditions (relationship between reagents, temperature condition, choice of solvents, etc.) it is possible to avoid the problems connected with specific peculiarities of $\text{Ba}(\text{thd})_2$ and increase the stability of the CVD process results. Since the work with $\text{Ba}(\text{thd})_2$ is rather complicated, a search for new, more stable Ba-containing compounds suitable for obtaining oxide coatings seems to be evidently important.

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