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Synthesis of Mixed-Ligand Alkali Earth Element Dipivaloylmethanates with *o*-Phenanthroline

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Abstract—A one-step method for the synthesis of volatile barium and strontium complexes $[M(Thd)_2(Phen)_2]$ (M = Ba, Sr; Thd is the dipivaloylmethane anion) was developed. The method is based on the reaction of metal hydroxide octahydrates with dipivaloylmethane (HThd) and *o*-phenanthroline (Phen) accompanied by removal of water from the reaction mixture as a solvent–water azeotrope. In the case of calcium hydroxide monohydrate, a similar interaction causes destruction of the dipivaloylmethanate ligand to give a mixed-ligand calcium complex with the pivalate anion and *o*-phenanthroline.

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Most metals are complexed with β-diketones to give volatile chelates. Therefore, metal β-diketonates find use in metal-organic chemical vapor deposition (MOCVD) of oxide films and coatings [1]. The interest in volatile alkaline earth metal β-diketonates was enhanced in the late 1980s–early 1990s when methods for deposition of oxide films of high-temperature superconductors, ferroelectrics, and manganites with colossal magnetoresistance were vigorously developed [2].

The studies [3-5] devoted to the preparation of volatile alkaline earth metal β-diketonates focused attention on barium compounds as barium has the greatest radius and the least pronounced complexation ability among this group of elements [6]. As a rule, if it is possible to prepare a volatile barium β-diketonate whose composition does not change during storage and evaporation, then similar strontium and calcium compounds also have these properties.

The specific character of volatile barium β-diketonates is due to specific features of barium complexation, in particular, predominantly ionic bonding, large radius and, as a consequence, large and variable coordination numbers (C.N.) up to 12, and relatively low stability of coordination compounds, especially those with ligands of medium denticity such as β-diketonate anions [3, 6]. The formation of a crystal structure composed of isolated $Ba(Dik)_2$ molecules (HDik is β-diketone) in which the ligands Dik^- would be bidentate is impossible. Two single-charged Dik^- ligands can neither shield the central barium ion from intermolecular contacts nor saturate its coordination sphere without performing bridging function.

Among known non-fluorinated barium β-diketonates, dipivaloylmethanate $Ba(Thd)_2$ (HThd is 2,2,6,6-tetramethylheptane-3,5-dione or dipivaloylmethane) containing branched *tert*-butyl substituents is most volatile and thermodynamically stable [3, 7]. Barium dipivaloylmethanate is the tetramer $[Ba_4(Thd)_8]$ [8, 9] whose structure comprises ligands with different denticity (2 to 4) and barium ions with C.N.s of 6 and 7. These C.N.s are insufficient to saturate the large barium ion, therefore, $[Ba_4(Thd)_8]$ is very sensitive to the action of water and atmospheric CO_2 and is unstable during vaporization due to oligomerization in the melt [10, 11]. This complicates its use in the MOCVD technique.

Modification of properties of coordinatively unsaturated alkaline earth metal β-diketonates is often accomplished using the mixed-ligand complexation technique [3, 4], which is also based on the specific nature of these elements as complexing agents and on their ability to incorporate, in the coordination sphere, together with the anionic β-diketonate ligands, also neutral mono- or polydentate donor ligands (**Q**) to give mononuclear complexes $[M(Dik)_2Q_n]$. More than a dozen mixed-ligand complexes $[Ba(Thd)_2Q_n]$ are known [3] but the complex $[Ba(Thd)_2(Phen)_2]$ (Phen is *o*-phenanthroline) is one of most promising compounds as regards the use for MOCVD. This compound as well as its calcium and strontium analogues have been studied in detail [11–15] and have been successfully used to obtain alkaline earth metal-containing oxide films [16].

The known methods for the synthesis of $[M(Thd)_2(Phen)_2]$ (M = Ba, Sr, Ca) comprise two key steps [3, 4]. The first step is preparation of the dihydrate $M(Thd)_2(H_2O)_2$ from a water–ethanol solution, while the essence of the second step is replacement of water molecules by Phen molecules and it is this step that faces with difficulties caused by the specific complex-

ing properties of alkaline earth metal ions and the nature of the $M(Dik)_2$–Q ions in mixed-ligand complexes $[M(Dik)_2Q_n]$. The strength of this bond and, hence, the ease of water replacement by a neutral donor ligand Q depends on the Lewis acidity and basicity of $M(Dik)_2$ and Q, respectively. Among β-diketonates of various metals, alkaline earth metal complexes ($M(Thd)_2$) have the lowest Lewis acidity, which decreases on going from calcium to barium. Hence, during the synthesis of mixed-ligand complexes $[M(Thd)_2(Phen)_2]$ (M = Ba, Sr, Ca) from $M(Thd)_2(H_2O)_2$, it is necessary to remove water from the reaction area, this requirement being most vital for the synthesis of barium compounds.

The synthesis of $[M(Thd)_2(Phen)_2]$ was first carried out in five steps: (1) preparation of the sodium salt of dipivaloylmethane; (2) preparation of $M(Thd)_2(H_2O)_2$; (3) preparation of $[M(Thd)_2]_x$ by dehydration and sublimation of $M(Thd)_2(H_2O)_2$; (4) preparation of Phen by dehydration and sublimation of Phen · H_2O; (5) reaction of stoichiometric amounts of $[M(Thd)_2]_x$ and Phen in a benzene–acetonitrile mixture [11, 12].

For the synthesis of $[Ba(Thd)_2(Phen)_2]$, it is necessary to use anhydrous Phen, because the presence of even a slight amount of water in the reaction mixture results in the formation of a mixed-ligand complex $[Ba(Thd)_2(Phen)(H_2O)]$ [12]. However, in the case of calcium and strontium complexes, anhydrous mixed-ligand complexes $[M(Thd)_2(Phen)_2]$ are formed even when hydrated Phen · H_2O is used [13]. This change in the composition of complexes depending on the conditions of synthesis of mixed-ligand complexes is consistent with the fact that the stability constants of $[M(Phen)]^{2+}$ increase in the series Ba–Sr–Ca [17].

More recently it was shown [14] that $[M(Thd)_2(Phen)_2]$ can be prepared by the reaction of $[M(Thd)_2(H_2O)_2]$ and anhydrous Phen in benzene with subsequent distilling off water as the benzene–water azeotropic mixture. This method is faster as it does not include the rather labor-consuming dehydration and sublimation steps but the risk of obtaining partially hydrolyzed product or a $M(Thd)_2(Phen)(H_2O)$ impurity is higher in this case. Note that this synthetic approach has been also used previously in coordination chemistry. In particular, it is used in the synthesis of various metal carboxylates, fatty acid derivatives by reactions of appropriate carboxylic acetates and acids followed by distilling off azeotrope with acetic acid [18].

All the above suggests that $[M(Thd)_2(Phen)_2]$ can be synthesized by a simple one-step procedure the key point of which is the removal of water from the reaction area. This is conveniently attained by distilling off the azeotropic mixture of water with an organic solvent. The possibility of this synthesis is indicated also by the fact that barium hydroxide reacts with HThd to give dipivaloylmethanate even in the presence of water [19]. Here we describe the synthesis of $[Ba(Thd)_2(Phen)_2]$ by the proposed method and discuss its use for the preparation of analogous calcium and strontium derivatives.

EXPERIMENTAL

The following reagents and solvents were used: $Ba(OH)_2 \cdot 8H_2O$ (high-purity grade) was recrystallized from water; $Sr(NO_3)_2 \cdot 4H_2O$, $Ca(NO_3)_2 \cdot 4H_2O$, and NaOH (reagent grade); HThd (>99%), *o*-phenanthroline monohydrate (ChemPur); and *m*-xylene, toluene, and benzene (Aldrich) were used as received.

Analysis for C, H, and N was carried out by microanalysis technique on a C,H,N analyzer at the Center for Drug Chemistry of the All-Russia Research Chemico-Pharmaceutical Institute. The barium content in the products was determined by the gravimetric method, the strontium and calcium contents were found by complexometric titration.

The frustrated total internal reflection IR spectra of the solid samples were recorded on a SpectrumOne spectrophotometer (Perkin-Elmer) in the region of 650-4000 cm^{-1}. The ^1H and ^{13}C NMR spectra were measured on an Avance-400 Bruker instrument (400 MHz) at 25°C in $CDCl_3$/TMS.

Powder X-ray diffraction analysis of the complexes was carried out on a STADI/IP diffractometer (CuK_α radiation). The theoretical X-ray diffraction pattern was simulated and the reflections were indexed using the STOE WinXPOW 1.04 program package.

Calcium and strontium hydroxides were synthesized by the reactions of aqueous solutions of the appropriate metal nitrate and sodium hydroxide by previously described procedures [19].

For	Sr found/anal. calcd, %
$Sr(OH)_2 \cdot H_2O$	62.4/62.6
$Sr(OH)_2 \cdot 8H_2O$	32.5/32.8
	Ca found/anal. calcd, %
$Ca(OH)_2$	54.1/54.1
$Ca(OH)_2 \cdot H_2O$	44.8/43.5

Synthesis of $[Ba(Thd)_2(Phen)_2]$. A mixture of stoichiometric amounts of $Ba(OH)_2 \cdot 8H_2O$ (4.85 mmol), HThd (9.70 mmol), and Phen · H_2O (9.70 mmol) in the specified solvent were heated in a round-bottom flask with a reflux condenser until the components completely dissolved and then the solvent–water azeotrope mixture was distilled off. After cooling the reaction mixture, a solid precipitated, which was recrystallized from the same solvent. The syntheses were carried out in three solvents: *m*-xylene (15 ml), toluene (25 ml), and benzene (50 ml). The yields were 98, 92, and 90%, respectively. The products obtained in different solvents were identical regarding elemental composition, powder X-ray diffraction data, and IR and NMR spectroscopy data

For $C_{46}H_{54}N_4O_4Ba$ (M = 863)

anal. calcd, %:	C, 63.9;	H, 6.3;	N, 6.5;	Ba, 15.9.
Found, %:	C, 63.7;	H, 6.5;	N, 6.4;	Ba, 15.8.

IR (ν, cm^{-1}): 1595 ν(C–O); 1515 ν(C=C); 2880, 2910, 2930, 2970 ν(C–H); 740, 870, 3060, 3090 (Phen).

NMR ^1H ($CDCl_3$/TMS; δ, ppm): 9.25 (4 H), 8.22 (4 H), 7.77 (4 H), 7.59 (4 H), 5.42 (2 H), 0.94 (36 H).

^{13}C NMR ($CDCl_3$/TMS; δ, ppm): 197.63 (CO), 150.50, 146.12, 135.05, 128.56, 126.40, 123.02 (Phen), 89.05 (CH), 40.57 (CMe_3), 28.52 (Me).

The strontium and calcium complexes were synthesized by a similar procedure using $Sr(OH)_2 \cdot 8H_2O$, 12.30 (6.15 mmol), HThd (12.30 mmol), Phen · H_2O (12.30 mmol), and toluene (40 ml). Yield 92%.

For $C_{46}H_{54}N_4O_4Sr$ (M = 813)

anal. calcd, %:	C, 67.8;	H, 6.6;	N, 6.9;	Sr, 10.7.
Found, %:	C, 67.8;	H, 7.0;	N, 6.8;	Sr, 10.6.

IR (ν, cm^{-1}): 1586 ν(C–O); 1510 ν(C=C); 2861, 2900, 2920, 2960 ν(C–H); 750, 870, 3060, 3090 (Phen).

NMR ^1H ($CDCl_3$/TMS; δ, ppm): 9.28 (4 H), 8.25 (4 H), 7.79 (4 H), 7.64 (4 H), 5.41 (2 H), 0.98 (36 H).

NMR ^{13}C ($CDCl_3$/TMS; δ, ppm): 196.15 (CO), 150.60, 146.07, 136.09, 128.56, 126.37, 123.05 (Phen), 89.04 (CH), 40.57 (CMe_3), 28.63 (Me).

One more synthesis was carried out using strontium hydroxide monohydrate: $Sr(OH)_2 \cdot H_2O$ (3.74 mmol), HThd (7.48 mmol), Phen · H_2O (7.48 mmol), and *m*-xylene (25 ml). Yield 90%.

For $C_{6.9}H_{9.8}N_{0.6}O_{2.3}Sr[Sr(Thd)_{0.3}(OH)_{1.7}(Phen)_{0.3}]$, ($M$ = 225)

anal. calcd, %:	C, 36.8;	H, 4.4;	N, 3.7;	Sr, 38.7.
Found, %:	C, 37.6;	H, 4.3;	N, 3.2;	Sr, 36.8.

For $C_{7.1}H_{10}N_{0.6}O_{2.7}Sr[Sr(Piv)_{0.7}(OH)_{1.3}(Phen)_{0.3}]$, ($M$ = 234)

anal. calcd, %:	C, 36.4;	H, 4.3;	N, 3.6;	Sr, 37.2.

IR (ν, cm^{-1}): 3340 ν(OH); 2865, 2957, 2974 ν(C–H); 1543 ν_{as}(COO); 1421 ν_s(COO); 731. 839, 1560, 1630, 3050 (Phen).

On heating of a mixture of $Ca(OH)_2$ (4.2 mmol), HThd (8.4 mmol), and Phen · H_2O (8.4 mmol) in *m*-xylene (50 ml) followed with distilling off the azeotrope, no reaction took place. The insoluble precipitate was the initial $Ca(OH)_2$.

The reaction of $Ca(OH)_2 \cdot H_2O$ (11.5 mmol) mixed with H_2O (1 ml, 55.5 mmol), HThd (23.0 mmol), and Phen · H_2O (23.0 mmol) in *m*-xylene (100 ml) carried out by a similar procedure did not result in complete dissolution of the reactants. After distilling off the azeotrope, a white precipitate was separated from the hot reaction mixture. Yield 10%.

For $C_{13.8}H_{12.6}N_2O_{2.7}Ca[Ca(OH)_{1.8}(Piv)_{0.2}(Phen)(H_2O)_{0.5}]$, ($M$ = 289)

anal. calcd, %:	C, 57.2;	H, 4.6;	N, 9.4;	Ca, 13.8.
Found, %:	C, 57.0;	H, 4.7;	N, 8.3;	Ca, 11.3.

IR (ν, cm^{-1}): 3742 ν(OH); 2868, 2905, 2937, 2963 ν(C–H); 1572 ν_{as}(COO); 1408 ν_s(COO); 731, 847, 1560, 1630, 3050 (Phen).

NMR ^1H ($CDCl_3$/TMS; δ, ppm): 9.23 (2 H), 8.28 (2 H), 7.83 (2 H), 7.67 (2 H), 1.67 (1.8 H), 1.20 (0.4 H).

NMR ^{13}C ($CDCl_3$/TMS; δ, ppm): 194.86, 188.84, 185.91 (COO); 150.37, 136.03, 128.65, 126.53, 123.11 (Phen); 39.53 (CMe_3); 27.95 (Me).

The white finely crystalline product isolated from the filtrate was recrystallized from benzene. Yield 65%.

For $C_{34}H_{34}N_4O_4Ca[Ca(Piv)_2(Phen)_2]$, ($M$ = 602)

anal. calcd, %:	C, 67.8;	H, 5.6;	N, 9.3;	Ca, 6.5.
Found, %:	C, 67.2;	H, 6.3;	N, 9.3;	Ca, 6.8.

IR (ν, cm^{-1}): 2857, 2910, 2951 ν(C–H); 1552 ν_{as}(COO); 1415 ν_s(COO); 732, 845, 3052 (Phen).

NMR ^1H ($CDCl_3$/TMS; δ, ppm): 9.23 (4 H), 8.25 (4 H), 7.78 (4 H), 7.64 (2 H), 1.07 (18 H).

NMR ^{13}C ($CDCl_3$/TMS; δ, ppm): 188.90 (COO); 150.37, 145.93, 136.38, 128.69, 126.51, 123.25 (Phen); 39.20 (CMe_3); 27.99 (Me).

RESULTS AND DISCUSSION

The method of synthesis $[Ba(Thd)_2(Phen)_2]$ is based on the reaction

$$Ba(OH)_2 \cdot 8H_2O + 2HThd + 2Phen \cdot H_2O \longrightarrow [Ba(Thd)_2(Phen)_2] + 10H_2O. \quad (1)$$

It is expedient to use high-boiling solvents with high contents of water in the azeotropic mixture similarly to the approach used for the synthesis of carboxylates [18, 21]. Analysis of the published data showed [22] that *m*-xylene, toluene, and benzene can be used as such solvents. The azeoptope boiling points and compositions are given below:

Solvent	$[H_2O]$, wt %	Bp(azeotrope), °C	Bp(solvent), °C
Benzene	9	69.25	80.2
Toluene	20	85	110.6
m-Xylene	40	94.5	139.1

Reaction (1) was successfully carried out in *m*-xylene: the target product $[Ba(Thd)_2(Phen)_2]$ was obtained in a high yield; the product composition was

confirmed by elemental analysis, powder X-ray diffraction analysis, and IR and NMR spectroscopy. On heating the reaction mixture, $Ba(OH)_2 \cdot 8H_2O$ completely dissolved at ~70°C, which is indicative of reaction (1). This suggests that this reaction could occur in solvent with lower boiling points, toluene and benzene. Indeed, the complex $[Ba(Thd)_2(Phen)_2]$ was obtained by reaction (1) also in these solvents in high yields and with high degrees of purity.

It was of particular interest to verify the possibility of one-step synthesis of $[Sr(Thd)_2(Phen)_2]$ and $[Ca(Thd)_2(Phen)_2]$, because it is known that, unlike barium hydroxide, reactions of strontium and calcium hydroxides with HThd do not give the corresponding hydrated dipivaloyl methanates [4]. Apparently, this is due to the change in the basicity of alkaline earth metal hydroxides on going from barium to calcium [6].

Strontium hydroxide exists in two hydrate forms, as octa- and monohydrate, and their use in reaction (1) produced different results. The reaction of HThd, $Phen \cdot H_2O$, and $Sr(OH)_2 \cdot 8H_2O$ in toluene resulted in quantitative formation of $[Sr(Thd)_2(Phen)_2]$. As in the synthesis of $[Ba(Thd)_2(Phen)_2]$, the reaction was accompanied by complete dissolution of strontium hydroxide. Upon replacement of the octahydrate by monohydrate, the dissolution was incomplete but the reaction partly proceeded. This is indicated by data of elemental analysis of the precipitate isolated from the reaction mixture, which can be represented by two formulas: $[Sr(Thd)_{0.3}(OH)_{1.7}(Phen)_{0.3}]$ (**A**) and $[Sr(Piv)_{0.7}(OH)_{1.3}(Phen)_{0.3}]$ (**B**). However, the results of IR spectroscopic analysis corresponds to a larger extent to formula (B), because the spectrum did not exhibit ν(C–O) or ν(C=C) bands of the dipivaloylmethanate ligands. The IR spectrum of the product in the 1600–1300 cm^{-1} region coincides almost entirely with the spectrum of strontium pivalate [23]; therefore, the bands at 1543 and 1421 cm^{-1} were assigned to asymmetric and symmetric (respectively) stretching vibrations of the pivalate (carboxyl) group. The ^1H and ^{13}C NMR could not be used for identification of this product, because it was almost insoluble in organic solvents, in particular, in dimethyl sulfoxide. Thus, the reaction with strontium monohydrate proceeds as alkaline hydrolysis of dipivaloylmethane to give a hydroxy pivalate complex instead of $[Sr(Thd)_2(Phen)_2]$.

The destruction of dipivaloylmethane giving pivalic acid anions was detected in the synthesis involving calcium hydroxide (anhydrous or as monohydrate). With anhydrous $Ca(OH)_2$, reaction (1) does not proceed; when the monohydrate is used and water is added, a greater part of the hydroxide precipitate (~80%) is dissolved, the insoluble part being the hydroxy complex $[Ca(OH)_{1.8}(Piv)_{0.2}(Phen)(H_2O)_{0.5}]$. The product isolated from the solution is a mixed-ligand complex of calcium pivalate with *o*-phenanthroline $[Ca(Piv)_2(Phen)_2]$. The IR and NMR spectra exhibit no bands or signals typical of the β-diketonate ligand but contain bands and signals for the carboxyl (pivalate) group.

Thus, in this work we propose a simple one-step method for the synthesis of volatile alkaline earth metal complexes $[M(Thd)_2(Phen)_2]$. The method is based on the reaction of alkaline earth metal hydroxides with dipivaloylmethane and *o*-phenanthroline accompanied by distillation of water–organic solvent azeotrope mixture from the reaction area. The product composition depends on the hydration degree and basicity of the alkaline earth metal hydroxide. An important condition for the reaction to occur is obtaining a homogeneous reaction mixture and removal of water from it. The composition of the products is determined by the nature of the alkaline earth metal, and water can also be removed by other methods (e.g., using drying agents).

The proposed synthesis of $[M(Thd)_2(Phen)_2]$ (M = Ba, Sr) differs from the previously reported methods by simplicity and high product yield and can be recommended for producing large amounts of volatile precursors for gas phase deposition of thin films.

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