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Alkaline-Earth Metal Complexes with Pivaloylacetone

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Abstract—Pivaloylacetonates of alkaline-earth elements with composition $M(Pa)_2 \cdot nH_2O$ ($n = 1$, M = Sr, Ca; $n = 0, 2$, M = Ba) were synthesized and studied by IR and thermal analysis; their solubilities and volatility were estimated. It was found that the volatility changes regularly in the series $M(Acac)_2$–$M(Pa)_2$–$M(Thd)_2$ (HAcac is acetylacetone, HThd is dipivaloylmethane). The replacement of one methyl radical by the *tert*-butyl radical when going from acetylacetonates to pivaloylacetonates was shown to noticeably increase the volatility only for $Sr(Pa)_2 \cdot H_2O$. Complexes of barium pivaloylacetonate with tetraglyme and *o*-phenanthroline were synthesized and characterized.

The volatile compounds of alkaline-earth elements have been intensively studied over the last 15 years due to their use in modern technologies of metalloorganic chemical vapor deposition (MOCVD) of thin films of composite oxide materials. The β-diketonates of alkaline-earth elements and, particularly, dipivaloylmethanates and their mixed-ligand complexes [1, 2] are of special interest, because the alkaline-earth metal complexes with dipivaloylmethane (2,2,6,6-tetramethylheptane-3,5-dione, HThd) whose molecule contains two *tert*-butyl radicals are the most volatile and thermally stable among compounds of these elements. Alkaline-earth metal compounds with another known β-diketone containing two methyl radicals—acetylacetone (pentane-2,4-dione, HAcac)—have also been reported [3]. However, only their calcium complex can be sublimated [4], as their strontium and barium complexes are nonvolatile.

In this work, the alkaline-earth metal complexes with asymmetrical β-diketone—pivaloylacetone (2,2-dimethylhexane-3,5-dione, HPa)—containing methyl and *tert*-butyl radicals were studied. The interest shown in the alkaline-earth metal compounds with pivaloylacetone can be explained by the fact that their comparison with dipivaloylmethanates and acetylacetonates enables one to establish how the volatility changes in the series $M(Acac)_2$–$M(Pa)_2$–$M(Thd)_2$, i.e., upon subsequent replacement of the methyl groups by the *tert*-butyl groups in the ligand molecules. Study of the alkaline-earth metal pivaloylacetonates can also be of practical interest. These complexes are unlikely to be more volatile than dipivaloylmethanates. However, the compounds of asymmetric β-diketones containing two different alkyl radicals are known to be more soluble in organic solvents than the derivatives of their symmetric analogs [5]. In addition, the high solubility in organic solvents together with the volatility, although not very high, will make it possible to use such alkaline-earth metal β-diketonates as precursors in the aerosol variant of the MOCVD method [5].

In this connection, we carried out a synthesis of the alkaline-earth metal pivaloylacetonates $M(Pa)_2 \cdot nH_2O$ and IR and thermal studies, estimated their solubilities and volatility, and prepared and characterized the mixed-ligand complexes on the basis of barium pivaloylacetonate with tetraglyme (Tg) and *o*-phenanthroline (Phen) acting as the additional ligand.

EXPERIMENTAL

Pivaloylacetone (HPa) used in the synthesis was produced by the procedure described in [6] (bp 74–75°C/60 mmHg); high-purity grade metallic barium, the alkaline-earth metal nitrates, Phen · H_2O, and reagent grade tetraglyme were used. The organic solvents (*n*-hexane, acetonitrile, benzene) were purified and dehydrated by standard procedures.

Synthesis of $M(Pa)_2 \cdot nH_2O$ (M = Ba, $n = 2$; M = Ca, Sr, $n = 1$). An aqueous solution of alkaline-earth metal nitrate (7 mmol) was added under stirring to a water–alcohol solution of potassium pivaloylacetone obtained by neutralization of HPa (14 mmol) with an equimolar amount of KOH. The obtained precipitate was filtered off, recrystallized from a mixture of ethyl alcohol and water (2 : 1), and dried in air. The yield was 60–70%.

$Ba(Pa)_2$ was synthesized by reacting metallic barium (5 mmol) with a solution of HPa (10 mmol) in dehydrated *n*-hexane (50 ml). The obtained white amorphous precipitate of $Ba(Pa)_2$ was recrystallized from a mixture of benzene with acetonitrile (1 : 1) and dried in vacuum at room temperature. The yield was 90%.

$[Ba(Pa)_2Tg]$ was prepared as a yellow precipitate forming in the reaction between metallic barium

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Table 1. The elemental analysis data

Compound	Empirical formula	Content (calcd/found), %		
		C	H	M
$Ba(Pa)_2 \cdot 2H_2O$	$C_{16}H_{30}O_6Ba$	42.20/42.35	6.59/6.42	30.1/30.0
$Sr(Pa)_2 \cdot H_2O$	$C_{16}H_{28}O_5Sr$	49.48/49.65	7.22/7.34	22.7/22.4
$Ca(Pa)_2 \cdot H_2O$	$C_{16}H_{28}O_5Ca$	56.47/56.24	8.24/8.11	11.8/11.7
$Ba(Pa)_2$	$C_{16}H_{26}O_4Ba$	45.82/45.75	6.21/6.32	32.7/32.4
$[Ba(Pa)_2Tg]$	$C_{24}H_{44}O_8Ba$	48.67/48.45	7.49/7.54	21.4/21.2

(8 mmol) and HPa (16 mmol) and tetraglyme (8 mmol) in *n*-hexane (30 ml). The yield was 80%.

$[Ba(Pa)_2(Phen)_2]$ was obtained by reacting $Ba(Pa)_2$ (5 mmol) with Phen (10 mmol) in a mixture of benzene–MeCN (1 : 1, 100 ml) upon boiling with a reflux condenser for 1 h. The transparent solution formed was evaporated under reduced pressure in order to decrease the reaction mixture volume by 80%. However, no precipitate was formed. The evaporation of the reaction mixture to dryness yielded a yellow oily viscous product that was further analyzed. The change of the solvent, as well as the drying in vacuum, did not result in the formation of crystalline products.

Dipivaloylmethanates and acetylacetonates $M(Thd)_2 \cdot 2H_2O$ and $M(Acac)_2 \cdot 2H_2O$ (M = Ba, Sr, Ca) were synthesized by the procedures described in [7, 8]. The anhydrous complex $Ba(Thd)_2$ was obtained by vacuum sublimation of the dihydrate (220°C/0.01 mmHg).

The contents of C, H, and N in the synthesized complexes were determined by elemental microanalysis, while Ba was determined gravimetrically and Sr and Ca were found by direct complexometric titration (Table 1).

The IR spectra were recorded on a UR-20 spectrometer at 400–4000 cm^{-1} with samples represented as hexachlorobutadiene and nujol mulls.

The thermal analysis was performed on a Q-1500D derivatograph in a nitrogen atmosphere at a heating rate of 5 K/min and with a sample weight of 50 mg.

The thermal analysis in vacuum (10^{-2} mmHg) was carried out on a TGD-700 Thermogravimetric Analyzer (SinkuRiko Co.) at a heating rate of 10K/min in the temperature interval of 25–500°C with a sample weight of 6–9 mg.

The solubility was estimated from the saturated solutions of the barium and strontium complexes in benzene at 20°C. The metal content in the samples was determined gravimetrically.

The ^1H NMR spectra of HPa and $[Ba(Pa)_2Tg]$ were recorded on a Varian VXR-400 spectrometer with $CDCl_3$/TMS solvent. HPa (δ, ppm): 1.25, 1.20, 1.17 (9H *t*-Bu); 2.20, 2.06 (3h Me); 2.57 (0.28H CH_2); 5.54 (0.86H CH); 15.79 (0.86H OH). $[Ba(Pa)_2Tg]$ (δ, ppm): 1.05 (18H *t*-Bu); 1.86 (6H Me); 3.70–3.36 (22H Tg); 5.30 (2H CH).

The vacuum sublimation was carried out in a glass tube placed in a tube furnace without temperature gradient under 0.5 mmHg. The content of the alkaline-earth metals in the obtained sublimates was determined gravimetrically, and then, the extent of transfer of the alkaline-earth metals to the gas phase was calculated as $\alpha_M = n_{subl}/n_{in} \cdot 100\%$, where n_{subl}, n_{in} are the molar contents of the alkaline-earth metals in the sublimate and initial sample, respectively.

RESULTS AND DISCUSSION

Data on the alkaline-earth metal complexes with pivaloylacetone are not available in the literature. Therefore, pivaloylacetonates of alkaline-earth metals were synthesized by the standard procedures commonly used for other β-diketonates of alkaline-earth metals [7, 8].

The reaction of equimolar amounts of alkaline-earth metal nitrates with the potassium salt of pivaloylacetone in a water-alcohol mixture gives complexes $M(Pa)_2 \cdot nH_2O$ (M = Ba, $n = 2$; M = Ca, Sr, $n = 1$). In the case of Ba, which is the most active among the alkaline-earth metals, the reaction of the metal with pivaloylacetone in the dehydrated solvent also gave anhydrous pivaloylacetonate. The hydrate nature of the complexes thus obtained was confirmed by the results of thermal analysis in a nitrogen atmosphere. In the temperature range 60–150°C, these complexes become dehydrated and the weight loss corresponds to the elimination of one H_2O molecule (~5%) for the calcium and strontium complexes and of two H_2O molecules (~8%) for $Ba(Pa)_2 \cdot 2H_2O$. The $Ba(Pa)_2$ thermogram does not contain the stage corresponding to the elimination of the water molecule.

IR spectra of the isolated complexes $M(Pa)_2 \cdot nH_2O$ (Table 2) exhibit bands due to characteristic vibrations of the β-diketonate ligands $\nu(C \mathbin{\dot{=}} O)$, $\nu(C \mathbin{\dot{=}} C)$ [9]. When going from M = Ca to M = Ba, the position of these bands in the $M(Pa)_2 \cdot nH_2O$ spectra remains almost unchanged, whereas the frequencies of these vibrations are close to those in the IR spectra of alkaline-earth metal dipivaloyomethanates and acetylacetonates [2, 3, 7]. The differences in the $Ba(Pa)_2 \cdot 2H_2O$ and $Ba(Pa)_2$ spectra only consist in that the latter spec-

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Table 2. Selected vibration frequencies (cm^{-1}) in IR spectra of the investigated complexes

Compound	$\nu(C\overset{\cdots}{-}O)$	$\nu(C\overset{\cdots}{-}C)$	$\nu(C–H)$	$\delta(C–(CH_3)_3)$	$\delta(C–CH_3)$	$\nu(H_2O)$	$\delta(H_2O)$
$Ca(Pa)_2 \cdot H_2O$	1605	1520	2880, 2930sh, 2980	890	960	3200–3600	1660
$Sr(Pa)_2 \cdot H_2O$	1605	1520	2880, 2910sh, 2940sh, 2980	890	960	3200–3600	1660
$Ba(Pa)_2 \cdot 2H_2O$	1600	1525	2880, 2920sh, 2980	890	960	3200–3600	1660
$Ba(Pa)_2$	1605	1520	2880, 2920sh, 2980	880	960		
$[Ba(Pa)_2Tg]$*	1605	1510	2880sh, 2900–2970	880	960		

* $\nu(C–O)_{Tg} \approx 1100$ cm^{-1}.

trum lacks the bands from the stretching and deformation modes of the water molecules (Table 2).

Thus, as we expected, the alkaline-earth metal pivaloylacetonates are formed by standard procedures in sufficiently high yield. The subsequent replacement of the methyl radical by the *tert*-butyl radical in the series HAcac–HPa–HThd has almost no effect on the composition and IR spectra of the complexes.

The question as to how the volatility and solubility of alkaline-earth metal complexes in organic solvents change in the indicated series is of much greater interest. The anhydrous alkaline-earth metal β-diketonates $M(Dik)_2$ are known to be coordination-unsaturated compounds that can form stable intermolecular bridging bonds and oligomers (polymers). The introduction of the branched alkyl radicals into the molecules of the β-diketonate ligands makes these intermolecular bonds weaker. However, even in the case of dipivaloylmethanates, whose ligand contains two *tert*-butyl radicals, the anhydrous $M(Thd)_2$ complexes retain their oligomeric structure [10]. Nevertheless, alkaline-earth metal dipivaloylmethanates are volatile compounds. The strontium and barium acetylacetonates with polymeric structure are nonvolatile and insoluble in organic solvents [11]. Only $Ca(Acac)_2$ was found to be volatile [4, 12].

The volatility of the alkaline-earth metal pivaloylacetonates was estimated from the data of thermal analysis in a vacuum and of isothermal vacuum sublimation. For comparison, vacuum sublimation of the alkaline-earth metal acetylacetonates and dipivaloylmethanates was performed (Table 3).

Two stages can be distinguished in the curve of the $Ca(Pa)_2 \cdot H_2O$ weight loss (see figure). At the first stage, in the temperature interval 60–165°C, the water molecule is eliminated (weight loss of ~5%), while at the second stage (200–400°C), the weight loss is ~65%, which is somewhat less than the value calculated for the transformation of $Ca(Pa)_2$ into $CaCO_3$ (69%). The $Sr(Pa)_2 \cdot H_2O$ thermogram shown in the figure also represents a two-stage curve. The main portion of the weight is lost in the temperature range 135–430°C and is equal to ~48%, which is noticeably less than the value calculated for the decomposition to carbonate (60%). The data obtained suggest the low thermal stability of the $M(Pa)_2$ complexes (M = Ca, Sr).

However, when $M(Pa)_2 \cdot H_2O$ (M = Ca, Sr) was isothermally heated in a vacuum (220°C), 80% of $Ca(Pa)_2$ and 65% of $Sr(Pa)_2$ were found to transform into the sublimate (Table 3, nos. 1 and 2), while the remaining part of the initial samples resinified. This implies that upon heating in a vacuum, the sublimation and decomposition of $M(Pa)_2$ (M = Ca, Sr) occur simultaneously and the volatilities and thermal stabilities of these complexes are comparable with those of $Ca(Acac)_2 \cdot 2H_2O$ (Table 3, no. 6). Like barium acetylacetonate, barium pivaloylacetonate is almost nonvolatile under these conditions (Table 3, nos. 3 and 10, respectively).

Thus, the replacement of one methyl radical by the *tert*-butyl radical when going from acetylacetonates to pivaloylacetonates resulted in a significant volatility increase only for strontium, whereas its acetylacetonate is nonvolatile (Table 3, no. 8). However, pivaloylacetonates of calcium and strontium are less volatile and thermally less stable than the alkaline-earth metal dipivaloylmethanates, which sublime quantitatively at 220°C and at higher rates (Table 3, nos. 1, 2, 7, 9).

The estimated solubilities of strontium and barium pivaloylacetonates agree with the results of the vacuum

Table 3. Results of vacuum sublimation of $M(Dik)_2 \cdot nH_2O$ (Dik = Acac, Pa, Thd), $Ba(Pa)_2Tg$, and $Ba(Pa)_2(Phen)_2$ (0.5 mmHg, 220°C, 60 min)

No.	Compound	α_M, % (±2)
1	$Ca(Pa)_2 \cdot H_2O$	80
2	$Sr(Pa)_2 \cdot H_2O$	65
3	$Ba(Pa)_2$	7
4	$[Ba(Pa)_2Tg]$	5
5	$[Ba(Pa)_2(Phen)_2]$	5
6	$Ca(Acac)_2 \cdot 2H_2O$	85
7	$Ca(Thd)_2^*$	100
8	$Sr(Acac)_2 \cdot 2H_2O$	0
9	$Sr(Thd)_2^*$	100
10	$Ba(Acac)_2 \cdot 2H_2O$	0
11	$Ba(Thd)_2^*$	100

* The sublimation time was 30 min.

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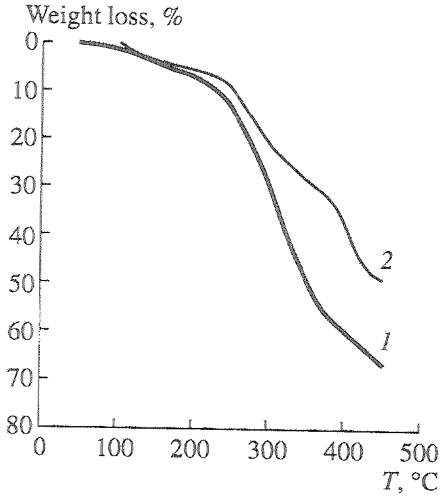
Table 4. Solubilities of $M(Dik)_2 \cdot nH_2O$ and $[Ba(Pa)_2Tg]$ in dehydrated benzene at 20°C

Compound	Solubility, mol/l
$Sr(Thd)_2 \cdot 2H_2O$	0.0132
$Sr(Pa)_2 \cdot H_2O$	0.0048
$Ba(Thd)_2$	0.008
$Ba(Pa)_2$	>0.0001
$[Ba(Pa)_2Tg]$	~0.05

sublimation: the $Sr(Pa)_2 \cdot H_2O$ solubility is substantially lower that that of $Sr(Thd)_2 \cdot 2H_2O$, whereas $Ba(Pa)_2$ is nearly insoluble in benzene (Table 4).

The structures and volatilities of the $Cu(Acac)_2$, $Cu(Pa)_2$, and $Cu(Thd)_2$ complexes were compared in [13], and it was shown that the latter two complexes have close volatilities. Different behavior of the copper and alkaline-earth metal complexes upon variation of the ligands in the series HAcac–HPa–HThd can be explained by the structures being different in the copper and alkaline-earth metal β-diketonates. The introduction of even one *tert*-butyl radical into the copper complexes with monomeric square-planar structures results in a significant loosening of the structure and in a noticeable increase in volatility as compared to acetylacetonates. In the case of the oligomeric alkaline-earth metal diketonates with large CNs of the central ions, this type of introduction was efficient only for strontium.

We made an attempt to obtain volatile forms of barium pivaloylacetonate by converting pivaloylacetonates with homogeneous ligands into mixed-ligand complexes containing neutral donor ligands (tetraglyme and *o*-phenanthroline).



Curves of the weight loss for $M(Pa)_2 \cdot H_2O$: M = (*1*) Ca and (*2*) Sr in a vacuum (10^{-2} mmHg).

The reaction of barium β-diketonates with tetraglyme or *o*-phenanthroline is known to give the mixed-ligand complexes $[Ba(Dik)_2Tg]$ and $[Ba(Dik)_2(Phen)_2]$, in which the central barium atom is coordinated to all five oxygen atoms of the tetraglyme [14] or to the nitrogen atoms of two *o*-phenanthroline molecules [2]. However, similar complexes of barium acetylacetonate are not formed, since the equilibrium of the reaction $Ba(Acac)_2 + nQ \rightleftharpoons [Ba(Acac)_2Q_n]$ ($n = 1$, Q = Tg; $n = 2$, Q = Phen) is shifted to the right due to the negligible solubility of $Ba(Acac)_2$ in the organic solvents.

The $[Ba(Pa)_2Tg]$ complex was obtained by interacting metallic barium with HPa and tetraglyme. Its composition was confirmed by elemental analysis and IR data. It has sufficiently high solubility in benzene (Table 4). The ^1H NMR spectrum of this complex exhibits only one signal from the methyl protons (5.30 ppm), indicating that this complex does not contain bridging pivaloylacetonate ligands and, therefore, has a monomeric structure in solution.

However, the transformation of $Ba(Pa)_2$ into $[Ba(Pa)_2Tg]$ did not induce volatility: heating in a vacuum caused the elemination of tetraglyme, while barium pivaloylacetonate practically did not sublime (Table 3, no. 4).

The product of the $Ba(Pa)_2$ interaction with *o*-phenanthroline (taken at a molar ratio of 1 : 2) looks like an oily substance with an excess content of carbon and hydrogen as compared to the values calculated for $[Ba(Pa)_2(Phen)_2]$. Its IR spectrum contains, in addition to the bands ν(C$\cdots$O) and ν(C$\cdots$C) of the β-diketonate ligand, bands due to stretching vibrations of the Phen molecule. However, this fact cannot serve as a convincing argument in favor of the complex formation, since the product was obtained by evaporation of the reaction mixture to dryness. The substance formed crystallizes very poorly and is readily soluble in organic solvents. An increase in the solubility of the product of evaporation of the solution containing $Ba(Pa)_2$ and Phen, as compared with the solubility of each component in the mixture, provides indirect evidence of the mixed-ligand complex formation.

Unfortunately, the mixed-ligand complex formation with *o*-phenanthroline, as with tetraglyme, did not result in the appearance of volatility: heating in a vacuum caused the elimination of Phen, while the sublimation of barium pivaloylacetonate was effectively not observed (Table 3, no. 5).

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