

A Study on the Development of CVD Precursors VI-Thermal Properties of Co(III) β -Diketonates

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Thermal properties of a series of Co β -diketonates have been systematically investigated and it is found that tris(3,5-heptanedionato) cobalt(III) (Co(hd)₃) with the lowest melting point among them can be a better precursor than tris(2,2,6,6-tetramethyl-3,5-heptanedionato) cobalt(III) (Co(tmhd)₃), one of the most popular precursors to date, under suitable conditions. Isothermal TGA study shows that Co(hd)₃ would work better at higher temperature, while Co(dmhd)₃ would be a better precursor at lower temperature.

Key Words: Thermal properties, Co β -diketonates, CVD precursors, Isothermal TGA

Introduction

Cobalt oxides have attracted much attention due to their unique properties such as high catalytic activity,¹ antiferromagnetism,² and electrochromism.³ These compounds have been extensively investigated for the possible applications⁴ such as thermal solar energy conversion devices, electrochemical capacitors, solid-state gas sensors, magnetic materials and negative electrodes for lithium-ion batteries. For the preparation of cobalt oxide thin films, many synthetic methods including chemical vapor deposition (CVD) or atomic layer deposition (ALD) have been employed⁵ but suitable precursors with high volatility and stability are essential for the success of these processes. Many cobalt (II) and (III) compounds such as salts (CoI₂, Co(OCO-CH₃)₂, Co(NO₃)₃) and complexes (Co₂(CO)₈, Cp₂Co and related derivatives) have been utilized but no successful results have been obtained.⁴ Well-known Co β -diketonates such as Co(acac)₂, Co(acac)₃ (acac = 2,4-pentanedionate) and Co(tmhd)₂ (tmhd = 2,2,6,6-tetramethyl-3,5-heptanedionate)⁶ had been used as CVD/ALD precursors but they suffer some drawbacks such as oligomeric nature⁷ and limited shelf life.⁴ Co(tmhd)₂ and ozone have been successfully utilized to grow thin films of Co₃O₄ [5(c)] or epitaxial growth of cobalt oxide by ALD.⁸ Co(dpm)₂ and oxygen have been used to form various cobalt oxides by CVD.⁹ Co β -diketonates with fluorinated substituents such as hfa (hfa = hexafluoroacetylacetonate) have been utilized and new complexes with coordinated water such as Co(hfa)₂·2H₂O and Co(hfa)₂·2H₂O·L (L = oxygenated base) have drawn much attention but uncontrolled decomposition or premature reactions in CVD/ALD processes limited further application [5(a), (b), 10]. Co(II) β -diketonates with various N-donor Lewis bases such as *N,N,N',N'*-tetramethylethylenediamine (TMEDA) and 1-dimethylamino-2-propanol (DMAPH)^{4,7} have shown favorable properties such as higher chemical stability, longer shelf life, and higher volatility and preliminary CVD experiments proved promising features for cobalt oxide nanosystems.

In this paper, a series of Co(III) β -diketonates have been prepared and their thermal properties have been extensively investigated for the possible application as ALD/CVD precursors.

Experimental

All chemicals including CoCO₃·xH₂O, H₂O₂ solution, 2,4-pentanedione (acetylacetone, acac), 3,5-heptanedione (hd), 2,6-dimethyl-3,5-heptanedione (dmhd), 2,2,6,6-tetramethyl-3,5-heptanedione (tmhd), 1-phenyl-1,3-butanedione (1-benzoylacetone, bzac), and 1,3-diphenyl-1,3-propanedione (dppd; or dbm for dibenzoylmethane), purchased from Aldrich Chemical Co. and Tokyo Chemical Industry Co. (dmhd and dppd), were used as supplied commercially without further purification. Solvents were reagent grade and were distilled under nitrogen over appropriate drying agents prior to use.

A series of Co(III) β -diketonates have been prepared by modified literature method¹¹ and the detailed procedures are described as follows.

General procedure for preparation of Co(III) β -diketonates.

A mixture of 4 mmol of cobalt(II) carbonate (1 equiv.) and 10 mmol of β -diketone (2.5 equiv.) in a 100 mL two-neck round-bottomed-flask was heated to 80 to 100 °C by oil bath. Then the mixture was stirred rapidly while 10 mL of 10% hydrogen peroxide was added dropwise. Care must be taken during the initial minutes of the reaction not to add the hydrogen peroxide too rapidly, since considerable heat is evolved and rapid gas evolution causes frothing. The reaction required 30 minutes. At the end of the reaction the liquid layer was an intense green color, and a quantity of green solid had been deposited. The mixture was cooled at room temperature which was easy to handle. The remnant cobalt carbonate was easily eliminated by filtration. The product was extracted from evolved water during the reaction with a portion of methylene chloride using separate funnel. The product was dried under vacuum and recrystallized by *n*-hexane.

Co(acac)₃ (1): Yield: 59.4%; mp 210 °C; IR (KBr pellet) $\nu(\text{CO}) = 1573 \text{ cm}^{-1}$; Anal. Calc. for C₁₅H₂₁O₆Co: C, 50.57; H, 5.94. Found: C, 50.64; H, 5.89.

Co(hd)₃ (2): Yield: 49.8%; mp 53.5 °C; IR (KBr pellet) $\nu(\text{CO}) = 1573 \text{ cm}^{-1}$; Anal. Calc. for C₂₁H₃₃O₆Co: C, 57.27; H, 7.55. Found: C, 57.15; H, 7.51.

Co(dmhd)₃ (3): Yield: 60.4%; mp 157 °C; IR (KBr pellet) $\nu(\text{CO}) = 1577 \text{ cm}^{-1}$; Anal. Calc. for C₂₇H₄₅O₆Co: C, 61.82; H,

8.65. Found: C, 61.71; H, 8.66.

Co(tmhd)₃ (4): Yield: 15.0%; mp 247 °C; IR (KBr pellet) $\nu(\text{CO}) = 1574 \text{ cm}^{-1}$; Anal. Calc. for $\text{C}_{33}\text{H}_{57}\text{O}_6\text{Co}$: C, 65.11; H, 9.44. Found: C, 65.39; H, 9.71.

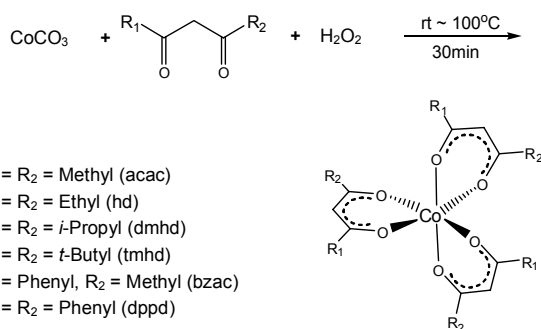
Co(bzac)₃ (5): Yield: 40.1%; mp 197 °C (193 - 194 °C¹²); IR (KBr pellet) $\nu(\text{CO}) = 1554 \text{ cm}^{-1}$; Anal. Calc. for $\text{C}_{30}\text{H}_{27}\text{O}_6\text{Co}$: C, 66.42; H, 5.02. Found: C, 66.01; H, 5.25.

Co(dppd)₃ (6): Yield: 54.9%; mp 237 °C; IR (KBr pellet) $\nu(\text{CO}) = 1545 \text{ cm}^{-1}$; Anal. Calc. for $\text{C}_{45}\text{H}_{33}\text{O}_6\text{Co}$: C, 74.17; H, 4.56. Found: C, 74.27; H, 4.57.

Elemental analysis and thermal analysis have been done with elemental analyzer (model EA1110, CE Instruments) and TGA/DTA instrument (model STA409PC; temperature elevation rate is 10 °C/min up to 990 °C under nitrogen atmosphere.), respectively in the Inha University. IR analysis has been done with IR spectroscopy (model NICOLET 6700 FT-IR, Thermo electron corporation) with KBr pellet. Melting points were determined on a melting point apparatus (OptiMelt, Stanford Research System) and are uncorrected.

Results and Discussion

As shown in Scheme 1, a series of Co(III) β -diketonates have been successfully synthesized. As Drinkard¹³ pointed out, basic conditions in general increase the sensitivity of the ligand to oxidation, allow CO₂ absorption by the ligand and increase volatility problem. Since β -diketonates are stable toward oxidation, conventional preparative method has been used as reported in the literature. All complexes are already known and melting points of these complexes are relatively high for the possible precursors. However, Co(hd)₃ as first reported by Yoshimura¹⁴ showed the melting point is unusually low (53.5 °C (this work), 55.7 ~ 56.1 °C¹⁴) for the Co precursors and this could be used as a potential CVD/ALD precursor even though this has not been used so far. Even though the melting point determined in this work is lower than that in the literature, elemental analysis shows high purity of the compound prepared in this work. Further characterization has been done with FT/IR spectroscopy and $\nu(\text{CO})$ less than 1600 cm⁻¹ confirms six-membered resonance structure of M β -diketonates.¹⁵ It has been known that sterically bulky substituents of the ligand prevent the complex from aggregation and they helped the complex to adopt a mononuclear structure.¹⁶ This strategy to lower the mp and to increase the volatility has been successful and many complexes with bulky



Scheme 1. Synthesis of Co(III) β -diketonates

substituents such as *iso*-propyl and *t*-butyl groups have been prepared to show higher volatility. However, Co(III) β -diketonates do not follow this trend and Co(tmhd)₃ and Co(dmhd)₃ do not melt at much lower temperatures than Co(acac)₃. From the literature survey, it is found that Co(tmhd)₃ has been used as a precursor of CVD /ALD but Co(hd)₃ has never been used

Table 1. Expected residual masses of cobalt oxides of Co(III) β -diketonates.

	CoO	Co ₂ O ₃	Co ₃ O ₄	Δ^*
1	21.03	23.28	22.53	1.58 ~ -0.67
2	17.01	18.83	18.23	-6.21 ~ -8.03
3	14.28	15.81	15.30	-12.83 ~ -14.36
4	12.31	13.62	13.19	-12.31 ~ -13.62
5	13.81	15.29	14.80	13.62 ~ 12.14
6	10.28	11.38	11.02	16.53 ~ 15.43

*Actual residual mass - expected residual mass

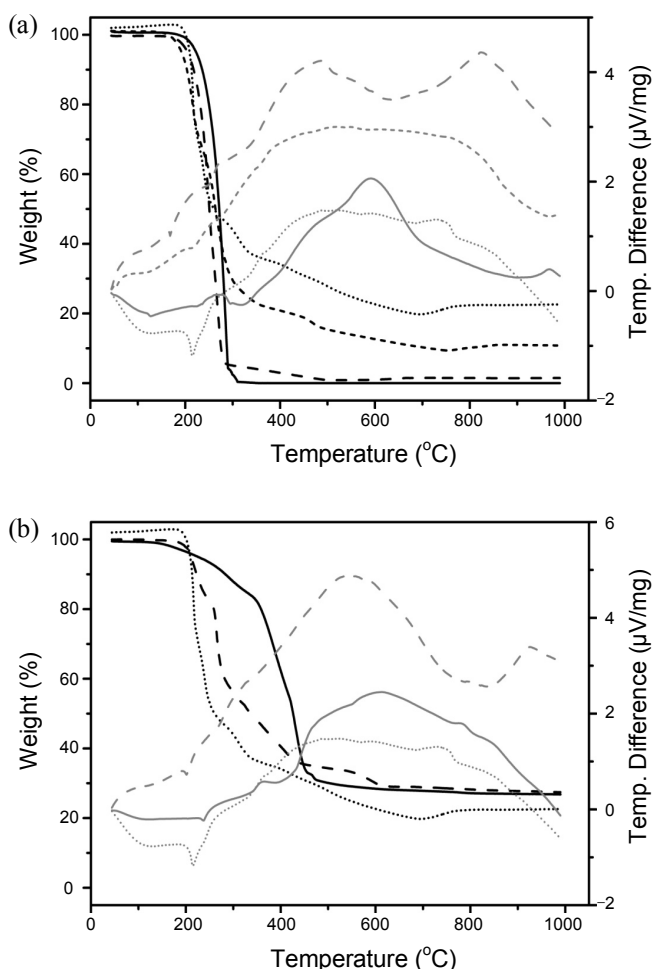


Figure 1. (a) TG(black line) and DTA(gray line) diagrams of Co (β -diketonates)₃ which have alkyl substituents at backbone. Each residual masses are **Co(acac)₃** (dot) 22.61%, **Co(hd)₃** (short dash) 10.80%, **Co(dmhd)₃** (dash) 1.45% and **Co(tmhd)₃** (solid) 0%. (b) TG(black line) and DTA(gray line) diagrams of Co(β -diketonates)₃ which have aryl substituents at backbone. Each residual masses are **Co(acac)₃** (dot) 22.61%, **Co(bzac)₃** (dash) 27.43% and **Co(dppd)₃** (solid) 26.81%.

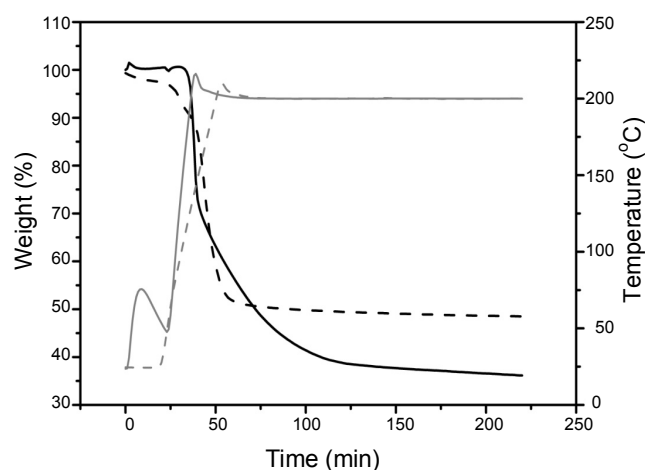


Figure 2. Isothermal weight losses for $\text{Co}(\text{hd})_3$ (solid line) and $\text{Co}(\text{dmhd})_3$ (dash line) at $200\text{ }^\circ\text{C}$.

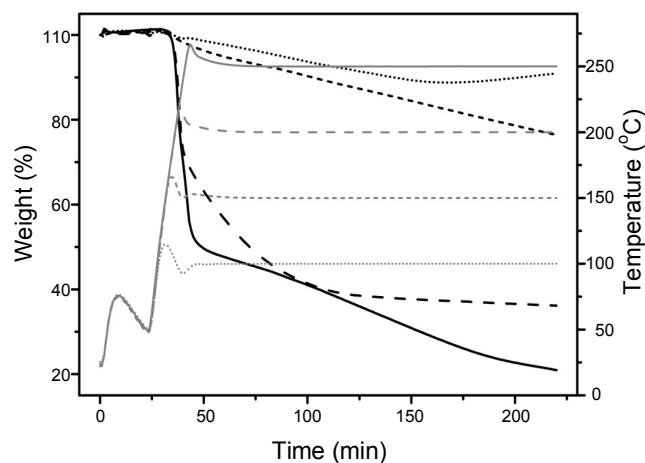


Figure 3. Isothermal weight loss studies for $\text{Co}(\text{hd})_3$ carried out at different temperatures. TG(black line) and DTA(gray line); $100\text{ }^\circ\text{C}$ (dot), $150\text{ }^\circ\text{C}$ (short dash), $200\text{ }^\circ\text{C}$ (dash), $250\text{ }^\circ\text{C}$ (solid)

as a precursor. It is also interesting that $\text{Co}(\text{dmhd})_3$ has not been used in the CVD/ALD process for its much lower melting point and higher yield than $\text{Co}(\text{tmhd})_3$. Even though thermal properties of some Co β -diketonates have been reported,¹⁷ systematic and extensive investigation on the thermal properties of Co β -diketonates has not reported yet. Therefore, comparison of thermal properties of $\text{Co}(\text{hd})_3$ and other Co β -diketonates was tried in this work.

For the application of CVD/ALD, characterization of thermal properties is very important and extensive TGA/DTA study has been done. As shown in Figure 1(a) and 1(b), TGA and DTA diagrams of Co β -diketonates support the melting points determined by a melting point apparatus again and the reason why $\text{Co}(\text{tmhd})_3$ has been extensively used as precursor of CVD/ALD. The residual masses of Co β -diketonates after heating up to $990\text{ }^\circ\text{C}$ were 22.61%, 10.80%, 1.45%, 0%, 27.43%, and 26.81%, respectively. This data clearly shows the compounds with bulky substituents such as *iso*-propyl and *t*-butyl groups are much more volatile than others. However, much lower melting point of

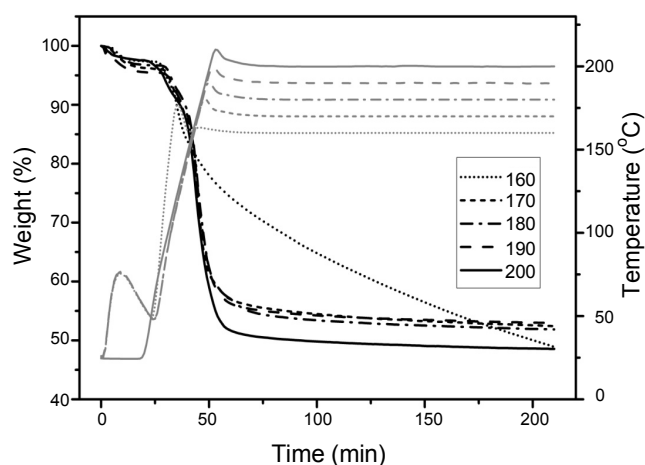


Figure 4. Isothermal weight loss studies for $\text{Co}(\text{dmhd})_3$ carried out at different temperatures. (160 , 170 , 180 , 190 and $200\text{ }^\circ\text{C}$)

$\text{Co}(\text{hd})_3$ prevents it from being excluded as a possible precursor and we want to find the window of application of this underestimated complex. In Table 1, the expected masses of possible cobalt oxides from each compound are listed assuming their non-volatility. From these data, the less (the more-absolute value) is the differences between actual residual mass and expected ones summarized in Table 1, the better volatility is expected. Therefore, it can be concluded that the volatility of Co β -diketonates decreases in the order as follows; $\text{Co}(\text{dmhd})_3 \sim \text{Co}(\text{tmhd})_3 > \text{Co}(\text{hd})_3$. Considering the preparative yields of Co β -diketonates, $\text{Co}(\text{dmhd})_3$ can be utilized instead of $\text{Co}(\text{tmhd})_3$ from the economic point of view.

However, investigation of isothermal weight losses of $\text{Co}(\text{hd})_3$ and $\text{Co}(\text{dmhd})_3$ at $200\text{ }^\circ\text{C}$ (Figure 2) reveals that $\text{Co}(\text{hd})_3$ is more volatile than $\text{Co}(\text{dmhd})_3$ at this temperature. Even though complete evaporation cannot be achieved, around 15% more compounds can be vaporized. Initial evaporation rate of $\text{Co}(\text{dmhd})_3$ appears to be more than that of $\text{Co}(\text{hd})_3$ but very little evaporation occurs after rapid initial evaporation. The behavior of $\text{Co}(\text{hd})_3$ is similar to that of $\text{Co}(\text{dmhd})_3$ except retardation of evaporation occurs much later. Even though characterization of the residue cannot be done, appearance of the residues of both $\text{Co}(\text{hd})_3$ and $\text{Co}(\text{dmhd})_3$ is similar, which indicates the formation of similar nonvolatile polymeric compounds or cobalt oxides from Co β -diketonates after longer exposure to heat. Isotherm TGA experiments with $\text{Co}(\text{hd})_3$ at different temperatures (Figure 3) show that slow evaporation occurs at 100 and $150\text{ }^\circ\text{C}$ but much faster evaporations are observed at 200 and $250\text{ }^\circ\text{C}$. At $250\text{ }^\circ\text{C}$, less amount of residue is found than that at $200\text{ }^\circ\text{C}$. Moreover, no flat region (no more evaporation in this region) is found at this temperature, indicating that no nonvolatile compound is formed. In other words, evaporation rate of $\text{Co}(\text{hd})_3$ is faster than formation rate of nonvolatile polymeric-compounds or cobalt oxides or it is thermally stable enough to vaporize at this temperature. From these data, it may be concluded that $\text{Co}(\text{hd})_3$ can be a better precursor with higher deposition rate than $\text{Co}(\text{tmhd})_3$ under suitable conditions such as high temperature ($250\text{ }^\circ\text{C}$). Therefore, when the heating the precursor up to around $250\text{ }^\circ\text{C}$ is allowed for the CVD/ALD process, $\text{Co}(\text{hd})_3$ can be a good

candidate for the faster process.

On the other hand, $\text{Co}(\text{dmhd})_3$ showed different thermal behavior (Figure 4). Continuous weight loss with time is observed at 160 °C but higher initial weight loss rate and no weight loss after some time are common characteristics over 170 °C. This can be interpreted that $\text{Co}(\text{dmhd})_3$ is not thermally stable over 170 °C. Therefore, it can be concluded that $\text{Co}(\text{dmhd})_3$ is a better precursor at lower temperature (160 °C) while $\text{Co}(\text{hd})_3$ is a better precursor at high temperature (around 250 °C).

As reported earlier,^{16,18} the presence of phenyl substituents enhances the thermal stability of Co β -diketonates. As shown in Figure 1 and Table 1, residual masses of $\text{Co}(\text{bzac})_3$ and $\text{Co}(\text{dppd})_3$ are more than any other Co β -diketonates. The more phenyl substituents result in higher mp but similar residual mass.

Conclusion

A series of Co β -diketonates have been prepared from CoCO_3 . Conventional variable temperature thermal analysis of these Co β -diketonates proves that $\text{Co}(\text{tmhd})_3$ and $\text{Co}(\text{dmhd})_3$ are the most volatile. As reported earlier, the presence of bulky substituents enhances the volatility but introduction of phenyl groups increases the thermal stability.

However, isothermal TGA indicates that $\text{Co}(\text{hd})_3$ can be a better precursor with faster deposition rate than $\text{Co}(\text{dmhd})_3$ under higher temperature but $\text{Co}(\text{dmhd})_3$ can be an alternative for $\text{Co}(\text{tmhd})_3$ at the lower temperature.

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