# Differential Thermal Analysis of Some Tervalent Metal Chelates of 1,5-Dialkylpentane-2,4-dionates*

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In connection with the purification of metal chelates by zone refining, thermal properties of the following β-diketone chelates of tervalent cobalt(III), aluminum(III), iron(III), manganese(III), and chromium(III) were investigated by differential thermal analysis (DTA). The β-diketones used in this study were heptane-3,5-dione, nonane-4,6-dione, 2,6-dimethylheptane-3,5-dione, 2,8-dimethylnonane-4,6-dione, 2,2,6,6-tetramethylheptane-3,5-dione, and tridecane-6,8-dione. Metal chelates of the alkyl substituted pentane-2,4-diones showed a lower melting- and higher decomposition temperature in comparison with the pentane-2,4-dionates. Discussion is given on the effects due to the structures of the alkyl substituents upon thermal properties of the hexacoordinate metal chelates.

The criteria for thermal properties of the samples which are to be subjected to zone melting process are the moderate melting temperature convenient for the operation, as well as the thermal durabilty and less volatility under prolonged heating at a molten state. Most of metal chelate compounds, however, decompose prior to melting with a few exceptions:[1,2] Metal oxinates belong to a group of metal chelates of the highest thermal stability; however, they are not found in a stable molten form because of their high melting points.[3,4] Although pentane-2,4-dionates are also regarded as thermally stable and low melting chelates, only the chromium(III),[5] beryllium(II)[6] and aluminum(III)[7] chelates were reported to give melts durable under prolonged heating. Fluoro-substituted pentane-2,4-dionates show lower melting temperatures than the pentane-2,4-dionates,[8,9] but the electron-withdrawing effect of the fluoroalkyl groups decreases the thermal stability of the metal chelates.[10,11] On the other hand, a large number of alkyl-substituted pentane-2,4-dione chelates of copper(II) were reported to melt in a lower temperature region and to be enough stable to melt without decomposition.[12–14]

In the continuation of the previous reports[15,16] on the thermal properties of some bivalent metal chelates of a range of β-diketones, this paper reports on the same aspects of some tervalent metal chelates of the following 1,5-dialkylpentane-2,4-diones.

The β-diketones chosen in this serial study are heptane-3,5-dione(or dipropionylmethane, DNPM), nonane-4,6-dione(or di-*n*-butyrylmethane, DNBM), 2,6-dimethylheptane-3,5-dione(or diisobutyrylmethane, DIBM), 2,8-dimethylnonane-4,6-dione (or diisovalerylmethane, DIVM), 2,2,6,6-tetramethylheptane-3,5-dione(or dipivaloylmethane, DPVM), and tridecane-6,8-dione(or di-*n*-caproylmethane, DNCM), and metal ions are cobalt(III), aluminum(III), iron(III), manganese (III), and chromium(III).

Melting, decomposing and some additional phase transition temperatures were determined by DTA measurements in the air and nitrogen atmosphere. Both melting and pyrolytic degradation reaction gave endothermic DTA peaks. The former peak was characterized as follows: 1) The peak position was reproducible upon repeated DTA runs of a sample. 2) Atmosphere did not affect the position and shape of the peak. 3) IR, UV, and visible spectra were identical on the samples before and after the DTA run. 4) After the endotherm, the base line returned to the same level as before. An endotherm which did not satisfy either of the above qualifications, was regarded as that due to the degradation reactions.[15]

## Experimental

Synthesis of 1,5-dialkylpentane-2,4-diones[17] and their cobalt(III) chelates[18] were reported in our previous papers. Pentane-2,4-dione and all of the inorganic reagents were obtained commercially, and used without any further purifications. Analytical results and solvents used for recrystallization of the following metal chelates are summarized in Table 1.

*Aluminum(III) Chelates.* Tris(acetylacetonato)aluminum(III), $Al(AA)_3$, was prepared according to a standard method.[19] $Al(DIBM)_3$, $Al(DIVM)_3$, and $Al(DPVM)_3$ were prepared according to the modified Jones' method.[20] To a 50 ml of 3M-sodium hydroxide aqueous solution containing 1.25 g (0.003 mol) of aluminum nitrate nonahydrate was added 0.01 mol of each ligands. White precipitate was obtained immediately. These were collected by filtration, and then recrystallized from appropriate solvents which are listed in Table 1. DNPM, DNBM, and DNCM chelates could not be obtained by the above methods.

*Iron(III) Chelates.* To a 10 ml of an aqueous methanol solution containing 1.35 g (0.003 mol) of ferric nitrate hexahydrate was added 0.01 mol of a ligand, and then 6 ml of 2.5M-sodium hydroxide solution was added dropwise under vigorous stirring. AA, DIBM, DIVM, and DPVM gave red-orange solid, while DNPM, DNBM, and DNCM red-orange oil, respectively. Solid chelates were collected by filtration, and then recrystallized from appropriate solvents as listed in Table 1. The oily product was extracted with chloroform, and the chloroform extract was eluted from silica gel and alumina columns, each 10 cm long, successively. The eluate was evaporated, to give an oily liquid chelate.

*Manganese(III) Chelates.*[21] To 20 ml of an aqueous methanol was added 0.54 g of manganese(II) chloride tetrahydrate and 0.11 g of potassium permanganate. The resulting solution was adjusted to pH 6—7 by the addition of 0.8 M ammonium hydroxide. Then 0.01 mol of a ligand was added into the solution with vigorous stirring. Dark brown precipitate was afforded with AA, DIBM, DIVM,

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Table 1. Analytical results of chelates

| Complex | Molecular formula | Found |  | Calcd |  | Recrystallization solvent |
|---|---|---|---|---|---|---|
|  |  | C% | H% | C% | H% |  |
| $Al(AA)_3$ | $C_{15}H_{21}O_6Al$ | 55.46 | 6.59 | 55.55 | 6.48 | Ethanol |
| $Al(DIBM)_3$ | $C_{27}H_{45}O_6Al$ | 65.80 | 9.22 | 65.87 | 9.14 | Ethanol+Water |
| $Al(DIVM)_3$ | $C_{33}H_{57}O_6Al$ | 68.68 | 9.94 | 68.77 | 9.89 | Ethanol+Water |
| $Al(DPVM)_3$ | $C_{33}H_{57}O_6Al$ | 68.81 | 9.93 | 68.77 | 9.89 | Ethanol+Water |
| $Fe(AA)_3$ | $C_{15}H_{21}O_6Fe$ | 51.20 | 6.08 | 51.17 | 5.96 | Methanol+Water |
| $Fe(DNPM)_3$ | $C_{21}H_{33}O_6Fe$ | 57.78 | 7.79 | 57.71 | 7.55 |  |
| $Fe(DNBM)_3$ | $C_{27}H_{45}O_6Fe$ | 61.86 | 8.60 | 62.23 | 8.64 |  |
| $Fe(DIVM)_3$ | $C_{33}H_{57}O_6Fe$ | 65.36 | 9.46 | 65.49 | 9.42 | Methanol+Water |
| $Fe(DNCM)_3$ | $C_{39}H_{69}O_6Fe$ | 68.03 | 10.14 | 67.96 | 10.01 |  |
| $Fe(DIBM)_2(CH_3O)$ | $C_{19}H_{33}O_5Fe$ | 57.14 | 8.31 | 57.41 | 8.31 | Methanol |
| $Fe(DPVM)_2(CH_3O)$ | $C_{23}H_{41}O_5Fe$ | 61.16 | 9.22 | 60.97 | 9.05 | Methanol+Ethyl Acetate |
| $Mn(AA)_3$ | $C_{15}H_{21}O_6Mn$ | 51.20 | 6.08 | 51.17 | 5.96 | Benzene+Petr. Ether |
| $Mn(DNPM)_3$ | $C_{21}H_{33}O_6Mn$ | 56.85 | 7.54 | 57.83 | 7.57 |  |
| $Mn(DNBM)_3$ | $C_{27}H_{45}O_6Mn$ | 62.36 | 8.67 | 62.33 | 8.65 |  |
| $Mn(DIBM)_3$ | $C_{27}H_{45}O_6Mn$ | 61.97 | 8.46 | 62.33 | 8.65 | Methanol+Water |
| $Mn(DIVM)_3$ | $C_{33}H_{57}O_6Mn$ | 65.71 | 9.60 | 65.59 | 9.43 | Methanol+Water |
| $Mn(DPVM)_3$ | $C_{33}H_{57}O_6Mn$ | 65.49 | 9.49 | 65.59 | 9.43 | Methanol |
| $Cr(AA)_3$ | $C_{15}H_{21}O_6Cr$ | 51.63 | 6.15 | 51.62 | 6.01 | Benzene+Petr. Ether |
| $Cr(DNPM)_3$ | $C_{21}H_{33}O_6Cr$ | 57.73 | 7.55 | 58.21 | 7.62 |  |
| $Cr(DIBM)_3$ | $C_{27}H_{45}O_6Cr$ | 62.41 | 8.86 | 62.69 | 8.70 | Acetone+Water |
| $Cr(DPVM)_3$ | $C_{33}H_{57}O_6Cr$ | 65.81 | 9.55 | 65.91 | 9.48 | Acetone+Water |

and DPVM. The solid precipitate was collected by filtration, and then recrystallized from an appropriate solvent. DNPM and DNBM gave oily chelates. These were extracted with benzene from the reaction mixture. After the extract was evaporated, the oily residue was dissolved again in an ether–methanol mixture. Then the solution was purified by elution in a similar manner to that for the oily iron(III) chelates. Manganese(II) acetylacetonate was prepared according to a standard method.[22]

*Chromium(III) Chelates.*[23] To 20 ml of an aqueous methanol solution containing 1.3 g (0.003 mol) of chromium nitrate hexahydrate and 7 g of urea was added 0.01 mol of a ligand. Then mixture was maintained at about 95 °C for 10 hr with stirring. AA, DIBM, and DPVM afforded solid precipitate. These were collected by filtration, and then recrystallized from an appropriate solvent. The remaining ligands gave oily products, which were hardly purified except $Cr(DNPM)_3$. The last chelate, $Cr(DNPM)_3$, was purified in a similar manner to those for the manganese(III) chelates.

*Measurements.* DTA curves were recorded on a Rigaku Denki Thermoflex 8001 in the air and nitrogen atmosphere. A hermetic-sealed sample holder was used for volatile and sublimable chelates; otherwise a pressure-capped one was used.** Procedure of the thermoanalysis was the same as described previously.[15]

Evolved ligand vapor upon the pyrolysis of a metal chelate was identified by means of gas-liquid chromatography by direct injection of the metal chelate as a solution into the GC vaporizing port maintained at 300 or 370 °C, or by injection of the solution of a vapor condensate upon the pyrolysis in a sealed tube at 300 °C for 10 min. Some of the vapor condensate were also identified by infrared spectral comparison as a carbon tetrachloride solution. IR spectra were measured on a JASCO-DS-403G spectrophotometer.

## Results and Discussion

*Cobalt(III) Chelates.* Figure 1 shows DTA curves of the cobalt(III) chelates measured in nitrogen atmosphere. $Co(DNPM)_3$, $Co(DIVM)_3$, and $Co(DPVM)_3$ show definite melting points, all of which are assignable to the reversible endotherms (A). The remaining solid

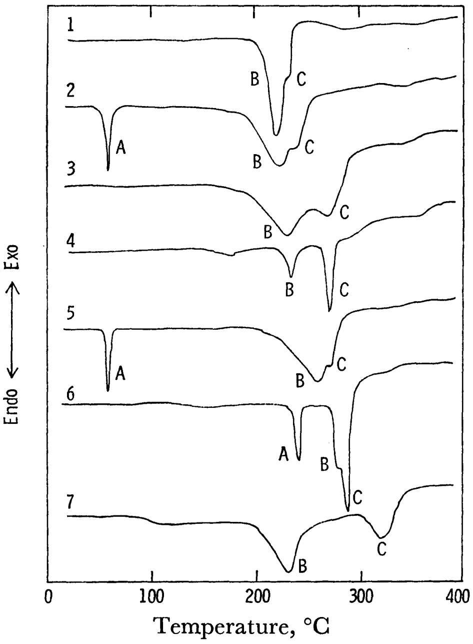

Fig. 1. DTA curves of the cobalt(III) chelates obtained in nitrogen atmosphere at heating rate of 10 °C/min. 1, $Co(AA)_3$; 2, $Co(DNPM)_3$; 3, $Co(DNBM)_3$; 4, $Co(DIBM)_3$; 5, $Co(DIVM)_3$; 6, $Co(DPVM)_3$; 7, $Co(DNCM)_3$.

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** Details of the two types of sample holders were given in the previous paper.[15]

chelates, $Co(AA)_3$ and $Co(DIBM)_3$, decompose without showing any melting peak. All the chelates show two irreversible endotherms (B) and (C) above 200 °C.

Green tris-$\beta$-diketonato cobalt(III) chelates turn to blood-red or pink solid after DTA scanning up to the temperature of the first irreversible endotherm (B). Figure 2 shows, as an example, IR spectra of the cobalt–DNPM chelates before and after the above transition. The latter, differing from the former, rather resembles that of the cobalt(II) chelate of the same ligand, $Co(DNPM)_2 \cdot H_2O$.[18] When the present cobalt(III) chelate was heated above the peak (B) temperature, the evolution of the free ligand was confirmed. The irreversible endotherm (B) is, therefore, considered due to a thermal degradation accompanied by the reduction of the central metal ion, to give an anhydrous cobalt(II) $\beta$-diketonate, which may become hydrated subsequently by atmospheric moisture.

The last peak (C) is presumably due to the decomposition of the resulting bis($\beta$-diketonato)cobalt(II).

*Aluminum(III) Chelates.* The aluminum(III) chelates are highly volatile, and DTA curves were, therefore, obtained by use of a hermetic-sealed sample holder in nitrogen atmosphere. The results are shown in Fig. 3.

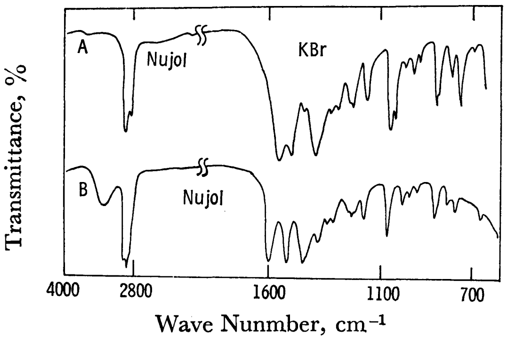

Fig. 2. IR spectrum of $Co(DNPM)_3$, A, and of the product from pyrolysis of the above chelate at 230 °C, B.

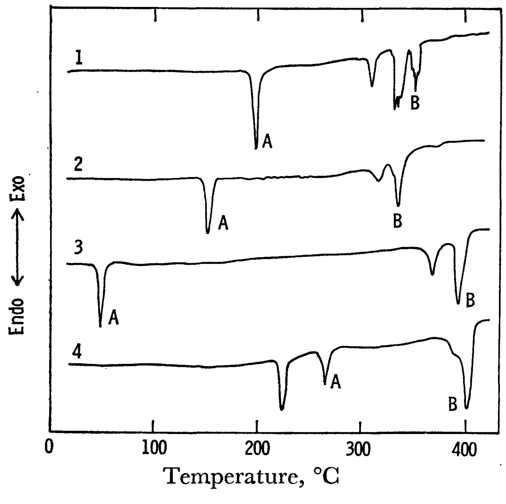

Fig. 3. DTA curves of the aluminum(III) chelates obtained in nitrogen atmosphere at heating rate of 10 °C/min.
1, $Al(AA)_3$; 2, $Al(DIBM)_3$; 3, $Al(DIVM)_3$; 4, $Al(DPVM)_3$.

In a temperature range below 300 °C, $Al(AA)_3$, $Al(DIBM)_3$, and $Al(DIVM)_3$ show single endothermic peaks (A), which agree well with their melting points. The peaks (A) were reproducible in the repeated DTA runs, being ascribable to the melting process. On the other hand, $Al(DPVM)_3$ shows two endothermic peaks in the same temperature region and that at the higher temperature is related to the melting points.[19] Irreversible endotherms (B) above 300 °C were probably due to the thermal degradation of the chelates, except $Al(AA)_3$. Endotherms (B) due to thermal degradation of $Al(AA)_3$ was probably accompanied by different kind of endotherms such as due to vaporization of the molten chelate.

*Iron(III) Chelates.* Analytical and IR data show that the DIBM and DPVM chelates of iron(III) have the composition of $FeL_2(CH_3O)$,[24] where L denotes the anionic ligand. Thermal behaviors of the two chelates are, therefore, not comparable to those of the other chelates of $ML_3$ form.

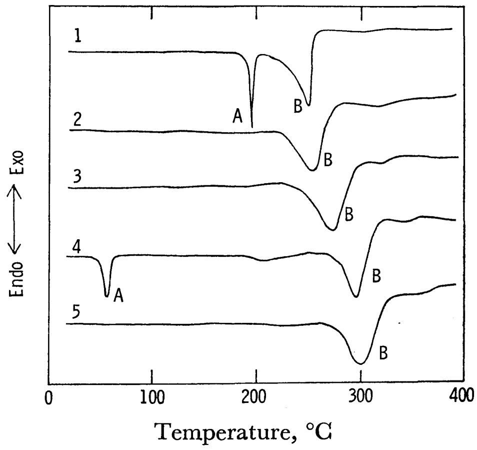

Fig. 4. DTA curves of the iron(III) chelates obtained in nitrogen atmosphere at heating rate of 10 °C/min. 1, $Fe(AA)_3$; 2, $Fe(DNPM)_3$; 3, $Fe(DNBM)_3$; 4, $Fe(DIVM)_3$; 5, $Fe(DNCM)_3$.

Figure 4 shows the DTA curves of the $ML_3$-type iron(III) chelates obtained in nitrogen atmosphere. $Fe(DIVM)_3$ and $Fe(AA)_3$ show reversible endotherms at 57 and 199 °C, respectively, which are related to their melting points. The corresponding endotherms of $Fe(DNCM)_3$ and $Fe(DNBM)_3$ occur below room temperature, which can not be detected on our DTA apparatus. The irreversible broad endotherms (B) at a higher temperature region are related to thermal decomposition. The melting process of $Fe(AA)_3$ chelate is immediately followed by a thermal degradation, indicating its poor thermal stability in a molten state. The decomposition temperature of the iron(III) chelates seemed to increase with the increasing size of alkyl substituents as observed in the case of cobalt(III) chelates.

*Manganese(III) Chelates.* DTA curves of manganese(III) chelates measured in nitrogen atmosphere are shown in Fig. 5. Reversible endotherms (A) of the $Mn(DIBM)_3$, $Mn(DIVM)_3$, and $Mn(DPVM)_3$ are ascribable to their melting processes. $Mn(AA)_3$ shows

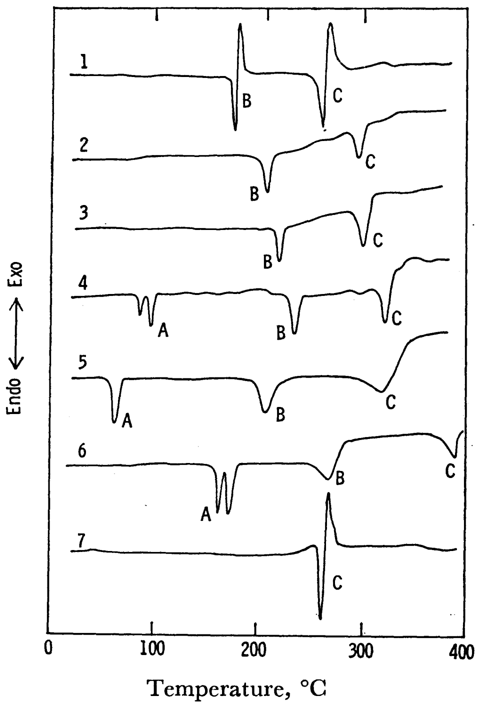

Fig. 5. DTA curves of the manganese(III) and manganese(II) chelates obtained in nitrogen atmosphere at heating rate of 10 °C/min. 1, $Mn(AA)_3$; 2, $Mn(DNPM)_3$; 3, $Mn(DNBM)_3$; 4, $Mn(DIBM)_3$; 5, $Mn(DIVM)_3$; 6, $Mn(DPVM)_3$; 7, $Mn(AA)_2$.

two irreversible endotherms immediately followed by exotherms. DTA characteristics of the second inflection (C) at 250—260 °C[22] seems quite similar to those observed on manganese(II) acetylacetonate, $Mn(AA)_2$, DTA curve of which was obtained separately, as shown in Fig. 5. When the $Mn(AA)_3$ was heated slightly above the first inflection (B) temperature, the resulting product showed an IR spectrum quite resembled that of $Mn(AA)_2$, and the evolution of acetylacetone was also confirmed upon the above thermal process.

The remaining manganese(III) chelates also liberate the ligand molecules when heated up to the peak (B) temperature. Thus the endotherms (B) can be ascribed to the reductive degradation from the tris($\beta$-diketonato)manganese(III) to the bis($\beta$-diketonato)manganese(II), just so as observed in the cobalt(III) chelates.

The irreversible endotherms (C) at a higher temperature region may be due to the pyrolytic decomposition of the manganese(II) chelates which resulted at the endotherms (B).

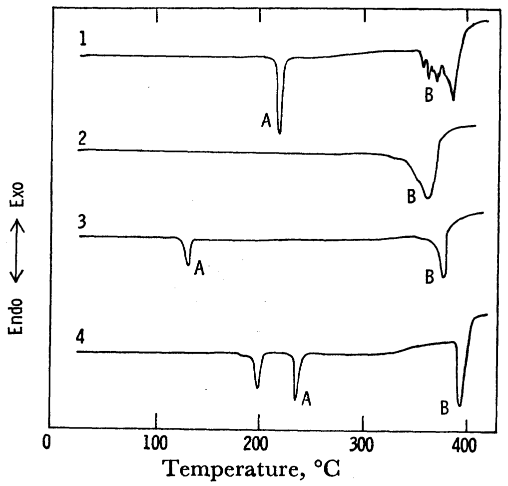

Fig. 6. DTA curves of the chromium(III) chelates obtained in nitrogen atmosphere at heating rate of 10 °C/min. 1, $Cr(AA)_3$; 2, $Cr(DNPM)_3$; 3, $Cr(DIBM)_3$; 4, $Cr(DPVM)_3$.

*Chromium(III) Chelates.* Figure 6 shows the DTA curves of the chromium(III) chelates measured with a hermetic-sealed sample holder in nitrogen atmosphere. $Cr(AA)_3$ and $Cr(DIBM)_3$ show reversible endotherms (A), which are related to their melting process. On the other hand, $Cr(DPVM)_3$ shows two reversible endotherms at about 200 °C, of which an endotherm at the higher temperature is ascribed to its melting process.[19]

In a higher temperature region, each chromium(III) chelate shows an irreversible endotherm (B). This was due to their decomposition process.

Table 2 summarizes the melting- and decomposition temperatures of the present chelates determined by DTA method. $Al(AA)_3$, $Cr(AA)_3$, and $Fe(AA)_3$ show characteristic melting points, respectively. The last acetylacetonate is, however, not very durable in the molten form. $Co(AA)_3$ and $Mn(AA)_3$ decompose prior to melting.

If one considers the thermal stability of a compound in terms of its pyrolytic decomposition temperature, the thermal stability of the pentane-2,4-dionates decreases in the order of Cr(III)>Al(III)>Fe(III)>Co(III)>Mn(III) so far as studied. A similar tendency in the thermal stability of pentane-2,4-dionates of the same tervalent metal ions was also observed by a different

TABLE 2. MELTING- AND DECOMPOSITION TEMPERATURE (°C) OF CHELATES

| Ligand | Co(III) | | Al(III) | | Fe(III) | | Mn(III) | | Cr(III) | |
|---|---|---|---|---|---|---|---|---|---|---|
| | mp | dp | mp | dp | mp | dp | mp | dp | mp | dp |
| AA | a | 222 | 197 | 330—350 | 191 | 250 | a | 174 | 216 | 360—380 |
| DNPM | 59 | 224 | b, c | | b | 254 | b | 209 | b | 370 |
| DNBM | b | 230 | b, c | | b | 272 | b | 220 | b, c | |
| DIBM | a | 232 | 154 | 330 | d | | 85—96 | 234 | 132 | 376 |
| DIVM | 58 | 259 | 50 | 393 | 57 | 295 | 63 | 237 | b, c | |
| DPVM | 240 | 286 | 266 | 402 | d | | 163—171 | 269 | 236 | 400 |
| DNCM | b | 232 | b, c | | b | 300 | b, c | | b, c | |

a) Decomposed prior to melting. b) Oily liquid at room temperature. c) Not obtained as pure chelates. d) Not obtained as $ML_3$ composition.

method.[25] The present 1,5-dialkylpentane-2,4-dione chelates gave the same order of the thermal stability in respect to the kind of the central metal ion.

Regarding to the structures of $\beta$-diketones, one can see a general trend that the branched-alkyl derivatives afford metal chelates of higher melting temperatures than that of the linear-alkyl substituted ligands: DNPM, DNBM, and DNCM give liquid chelates with an exception of Co(DNPM)$_3$, while DIBM, DIVM, and DPVM solid chelates at room temperature.

For the cobalt(III) chelates, thermal stability increased in the order of AA$<$DNPM$<$DNBM$<$DIBM$<$DNCM$<$DIVM$<$DPVM, which agreed with the order of bulkiness of alkyl substituents. Similar tendencies were also obtained for the other tervalent metal chelates. The thermal stabilities of the present chelates are, therefore, considered to be partly due to the electron releasing effect of the alkyl groups. Such effect increases the basicity of the ligand oxygen atoms to form increasingly stable metal-oxygen bonding,[18] and this kind of thermodynamic stabilization effect was also observed with some bivalent metal chelates.[15] On the other hand, kinetic destabilization effect by the alkyl substituents such as observed in the copper(II) and palladium(II) chelate[15] was unlikely to operate on the present octahedral hexacoordinate chelates.

As described before, the pyrolytic degradation of the manganese(III) and cobalt(III) chelates is accompanied by the reduction of the central metal ion from tervalent to bivalent and the liberation of the free ligand.[26,27] Although the stoichiometry of the whole scheme of the reaction is unknown at this moment, it is most likely that the metal-oxygen bonding in the tervalent metal chelates may be homolytically cleaved at the endotherm (B) to form the bivalent metal chelates, meanwhile the liberated ligand radical regenerates as the ligand molecule through hydrogenation processes such as hydrogen-abstraction from neighboring matrix or disproportionation with other radical.

Such radical termination processes are usually exothermic, and the exothermic branch of the inflection (B) on the DTA curve of Mn(III)(AA)$_3$ might be an indication of such a kind of process. The other DTA curves lack apparent exotherms subsequent to the endotherms (B), and this might possibly result from that the exotherms overlaps on the endotherms or diffuse widely.

Similar pyrolytic reduction reaction was observed also in Fe(III)(AA)$_3$,[28] and these facts seem to suggest that the pyrolytic reduction occurs in the chelate of such a metal ion that in the bivalent state can also form a stable chelate of the same ligand. Although an LCAO–MO calculation on the tervalent metal pentane-2,4-dionates[29] might provide an explanation for the ease with which Mn(III)(AA)$_3$ could be reduced to Mn(II)(AA)$_2$, a consistent understanding is not attained for the reason why these particular metal ions are labile to be reduced in the tris($\beta$-diketonato)metal chelates.

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