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THERMAL BEHAVIOUR OF COMPLEX CATION–COMPLEX ANION-TYPE COORDINATION COMPOUNDS. PART I

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ABSTRACT

This paper contains the results of an investigation concerning the thermal stability of four coordination compounds of the complex cation–complex anion type of the general formula $[M(AA)_3][ZnCl_4]$ ($M \equiv$ Co, Ni; $AA \equiv$ 2,2′-dipyridyl or 1,10-phenanthroline). Unusual chromotropic changes have been observed, which involve the migration of the organic ligand from the coordination sphere of one metal ion to the coordination sphere of the other. The values of the nonisothermal kinetic parameters have been evaluated for the single thermal decomposition steps.

INTRODUCTION

Following research into the thermal stability and nonisothermal kinetics of decomposition of the coordination compounds of nickel(II) and cobalt(II) [1,2], this paper presents the results obtained in the investigation of some coordination compounds of the complex cation–complex anion type. In a previous paper [2], the following chromotropic changes, consisting in irreversible thermochromism, have been noted.

$$\underset{\text{yellow}}{[Co(dipy)_3](SnCl_3)_2} \rightarrow \underset{\text{- green}}{[Co(dipy)Cl_2]} + 2[Sn(dipy)Cl_2]$$

$$\underset{\text{pink}}{[Ni(dipy)_3](SnCl_3)_2} \rightarrow \underset{\text{yellow}}{[Ni(dipy)Cl_2]} + 2[Sn(dipy)Cl_2]$$

In order to illustrate the generality of such phenomena, this paper deals with coordination compounds having the general formulae given in the abstract (dipy = 2,2′-dipyridyl; phen = 1,10-phenanthroline).

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The investigation of chromotropic phenomena represents a recent research direction in coordination chemistry [3].

EXPERIMENTAL

The following powdered coordination compounds have been used: $[Ni(phen)_3][ZnCl_4] \cdot 2H_2O$, $[Co(phen)_3][ZnCl_4] \cdot 2H_2O$, $[Ni(dipy)_3][ZnCl_4]$, and $[Co(dipy)_3][ZnCl_4]$.

The $[M(AA)_3][ZnCl_4]$-type complexes precipitate from alcoholic solutions of $[M(AA)_3]Cl_2$ [4] on adding $ZnCl_2$–hydrochloric acid solution (HCl promotes the formation of the $ZnCl_4^{2-}$ anion). The coordination compounds $[Co(dipy)_3][ZnCl_4]$ (yellow), $[Co(phen)_3][ZnCl_4] \cdot 2H_2O$ (yellow), $[Ni(dipy)_3][ZnCl_4]$ (pink) and $[Ni(phen)_3][ZnCl_4] \cdot 2H_2O$ (pink) were filtered off, washed with ethanol and dried in a desiccator over P_4O_{10}. Elemental chemical analyses gave satisfactory results.

The diffuse reflectance spectra of the complexes were recorded using a Carl Zeiss VSU-2 spectrophotometer with MgO as standard. The heating curves of the samples in air at atmospheric pressure were recorded from ambient temperature to 1000 °C by means of a MOM Budapest Q-1500 type Paulik–Paulik–Erdey derivatograph at heating rates β between 2.5 K min^{-1} and 10 K min^{-1}. In an attempt to confirm some phase transitions, DSC curves at $\beta = 20$ K min^{-1} were recorded by using a DuPont 1090 thermal analyser.

In order to perform a rough initial characterization of the crystalline structure of the coordination compounds, and of some of their intermediates, a Philips PW-1140 X-ray diffractometer was used. The powder diffractograms were recorded with chromium $K\alpha$ source radiation.

The values of the nonisothermal kinetic parameters were obtained using three methods: that of Coats and Redfern [5], based on the equation

$$\ln\frac{F(\alpha)}{T^2} = \ln\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right) - \frac{E}{RT} \tag{1}$$

with

$$F(\alpha) = \begin{cases} \left[1-(1-\alpha)^{1-n}\right]/1-n, & n \neq 1 \\ -\ln(1-\alpha), & n = 1 \end{cases} \tag{2}$$

that of Flynn and Wall for constant heating rate [6], and the Coats–Redfern method as modified by Urbanovici and Segal [7]. The data were automatically processed using programs written in BASIC language by Coseac and Segal [8,9]. In order to generate the TG curve in the (α, t °C) coordinates, a further program written in BASIC was used. The programs were run on a TIM-S computer.

RESULTS AND DISCUSSION

The X-ray diffractograms of $[Ni(phen)_3][ZnCl_4] \cdot 2H_2O$ and $[Co(phen)_3][ZnCl_4] \cdot 2H_2O$ showed that these compounds are amorphous. As far as the compounds $[Co(dipy)_3][ZnCl_4]$ and $[Ni(dipy)_3][ZnCl_4]$ are concerned, according to the X-ray diffractograms, these are in the crystalline state. The relative intensities of the diffraction lines, the interplanar distances, d (Å), and the crystallite mean size L for the most intense diffraction line calculated using Scherrer's formula [11] are given in Table 1.

Thermal behaviour of the coordination compound $[Ni(phen)_3][ZnCl_4] \cdot 2H_2O$

According to the derivatogram of this compound, after loss of water by the reaction

$$[Ni(phen)_3][ZnCl_4] \cdot 2H_2O(s) \rightarrow [Ni(phen)_3][ZnCl_4](s) + 2H_2O(g) \qquad (I)$$

which occurs with maximum rate at 60 °C *, the DTA curve exhibits a weak endothermic effect located at 315 °C, without change of weight, corresponding to the migration of the organic ligand from the coordination sphere of Ni^{II} to the coordination sphere of Zn^{II}

$$[Ni(phen)_3][ZnCl_4](s) \rightarrow [Ni(phen)_2Cl_2](s) + [Zn(phen)Cl_2](s) \qquad (II)$$

This phenomenon is accompanied by a change in colour from pink to green (thermochromism). The electronic spectrum of the green intermediate mixture similar to the electronic spectra of *cis*-$[Ni(dipy)_2Cl_2]$ and *cis*-$[Ni(phen)_2Cl_2]$ [12–14] (Fig. 1), proving clearly the migration of a phenanthroline molecule from the coordination sphere of Ni^{II} to that of Zn^{II}.

TABLE 1

Relative diffraction line intensities, interplanar distances and crystallite mean sizes for $[Co(dipy)_3][ZnCl_4]$ and $[Ni(dipy)_3][ZnCl_4]$

Compound	Relative intensity	d (Å)	L (Å)
$[Co(dipy)_3][ZnCl_4]$	100	6.02	215
	60	3.95	
$[Ni(dipy)_3][ZnCl_4]$	100	4.69	318
	60	4.48	
	40	3.89	

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* The temperatures corresponding to the maximum decomposition rates, as well as the temperature intervals, are given for $\beta = 10$ K min^{-1}.

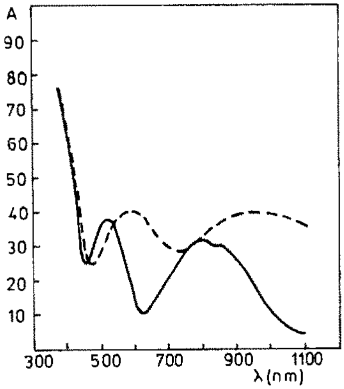

Fig. 1. Diffuse reflectance spectra of (a) [Ni(phen)$_3$][ZnCl$_4$]·2H$_2$O (———) and (b) [Ni(phen)$_2$Cl$_2$]+[Zn(phen)Cl$_2$] (— — —).

At higher temperatures, a first step of ligand loss occurs according to the equation

$$[\mathrm{Ni(phen)_2Cl_2}](s) + [\mathrm{Zn(phen)Cl_2}](s) \rightarrow \mathrm{Ni(phen)_{1.33}Cl_2}(s) + [\mathrm{Zn(phen)Cl_2}](s) + 0.67\mathrm{phen}(g) \qquad \text{(III)}$$

with its maximum rate at 440 ° C.

At still higher temperatures, the following decomposition steps have been recorded

$$\mathrm{Ni(phen)_{1.33}Cl_2}(s) + [\mathrm{Zn(phen)Cl_2}](s) \rightarrow \mathrm{Ni(phen)Cl_2}(s) + [\mathrm{Zn(phen)Cl_2}](s) + 0.33\mathrm{phen}(g) \qquad \text{(IV)}$$

the maximum rate occurring at 530 ° C, and

$$\mathrm{Ni(phen)Cl_2}(s) + [\mathrm{Zn(phen)Cl_2}](s) \rightarrow \mathrm{NiCl_2}(s) + \mathrm{ZnCl_2}(s) + 2\mathrm{phen}(g) \qquad \text{(V)}$$

which is overlapped by the oxidation of the mixture of Ni^{II} and Zn^{II} chlorides. Reaction (V) and the oxidation occur in the temperature range 550–660 ° C.

The values of the nonisothermal kinetic parameters for reaction (III), the only one workable kinetically, are listed in Table 2.

Thermal behaviour of the coordination compound [Co(phen)$_3$][ZnCl$_4$] · 2H$_2$O

As in the preceding case, the first decomposition step, which occurs with maximum rate at 76 ° C, is dehydration

$$[\mathrm{Co(phen)_3}][\mathrm{ZnCl_4}] \cdot 2\mathrm{H_2O}(s) \rightarrow [\mathrm{Co(phen)_3}][\mathrm{ZnCl_4}](s) + 2\mathrm{H_2O}(g) \qquad \text{(VI)}$$

The DSC curve recorded for the sample (sealed pan) exhibits, before the endothermic effect corresponding to dehydration and located at 344.1 ° C, an exothermic effect at 235 ° C, corresponding probably to the crystallization of

TABLE 2

Nonisothermal kinetic parameter values for reaction (III) at $\beta = 2.5$ K min^{-1}

Coats–Redfern method				Flynn–Wall method				Modified Coats–Redfern method			
n	E (cal mol^{-1})	A (s^{-1})	r [a]	n	E (cal mol^{-1})	A (s^{-1})	r [a]	n	E (cal mol^{-1})	A (s^{-1})	r [a]
0	23500	1.33×10^{4}	−0.970	0	24000	9.05×10^{4}	−0.975	0	24500	4.68×10^{4}	−0.976

[a] Correlation coefficient of the linear regression.

TABLE 3

Nonisothermal kinetic parameter values for reaction (VIII) at $\beta = 2.5$ K min^{-1}

Coats–Redfern method				Flynn–Wall method				Modified Coats–Redfern method			
n	E (cal mol^{-1})	A (s^{-1})	r	n	E (cal mol^{-1})	A (s^{-1})	r	n	E (cal mol^{-1})	A (s^{-1})	r
2.3	42800	2.96×10^{12}	−0.998	2.3	43000	3.77×10^{12}	−0.998	2	40000	2.82×10^{11}	−0.998

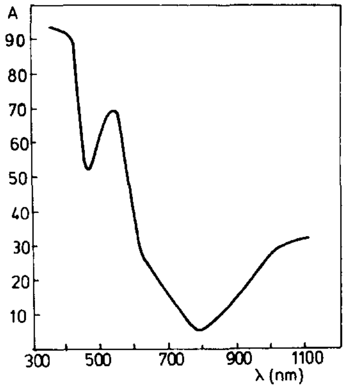

Fig. 2. Electronic spectrum of the mixture $[Co(phen)_2Cl_2]+[Zn(phen)Cl_2]$.

the hydrated coordination compound. Between 280 ° C and 320 ° C, the DTA curve exhibits two weak endothermic effects without change in weight, corresponding to the migration of the organic ligand according to the equation

$$[Co(phen)_3][ZnCl_4](s) \rightarrow [Co(phen)_2Cl_2](s) + [Zn(phen)Cl_2](s) \qquad (VII)$$

In this case also a change in colour is evident, from yellow to red. The latter colour is due to the compound $[Co(phen)_2Cl_2]$, whose electronic spectrum, given in Fig. 2, is identical with the electronic spectrum of the mixture obtained after the migration reaction.

At higher temperatures, the derivatogram exhibits the following decomposition steps

$$[Co(phen)_2Cl_2](s) + [Zn(phen)Cl_2](s)$$
$$\rightarrow Co(phen)_{1.33}Cl_2(s) + [Zn(phen)Cl_2](s) + 0.67phen(g) \qquad (VIII)$$

with maximum decomposition rate at 370 ° C, and

$$Co(phen)_{1.33}Cl_2(s) + [Zn(phen)Cl_2](s)$$
$$\rightarrow Co(phen)Cl_2(s) + [Zn(phen)Cl_2](s) + 0.33phen(g) \qquad (IX)$$

The decomposition of the resulting mixture, as well as the oxidation of Co^{II} and Zn^{II} chlorides, occur in the temperature range 500–680 ° C. For reaction (VIII), the only one workable kinetically, the values of the nonisothermal kinetic parameters are given in Table 3.

Thermal behaviour of the coordination compound $[Co(dipy)_3][ZnCl_4]$

The derivatograms recorded at various heating rates between 160 ° C and 200 ° C exhibit endothermic effects, without changes of weight, corresponding to the migration of the organic ligand, according to the equation

$$[Co(dipy)_3][ZnCl_4](s) \rightarrow [Co(dipy)_2Cl_2](s) + [Zn(dipy)Cl_2](s) \qquad (X)$$

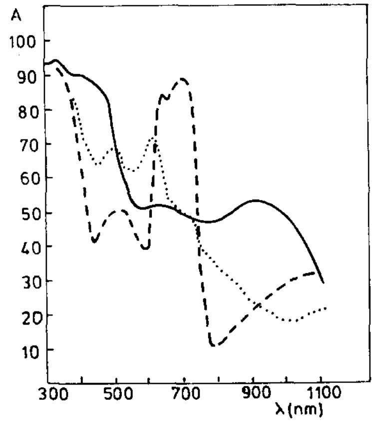

Fig. 3. Diffuse reflectance spectra of (a) $[\mathrm{Co(dipy)_3}][\mathrm{ZnCl_4}]$ (———), (b) $\mathrm{Co(dipy)_{1.5}Cl_2}$ + $[\mathrm{Zn(dipy)Cl_2}]$ (– – –) and (c) α-$[\mathrm{Co(dipy)Cl_2}]+[\mathrm{Zn(dipy)Cl_2}]$ (······).

On the DSC curve, the migration effect is shifted toward higher temperatures (322.2 °C) due to the particular working conditions (sealed pan). At higher temperatures, the derivatogram exhibits the following decomposition step

$$[\mathrm{Co(dipy)_2Cl_2}](\mathrm{s}) + [\mathrm{Zn(dipy)Cl_2}](\mathrm{s})$$

$$\rightarrow \mathrm{Co(dipy)_{1.5}Cl_2(s)} + [\mathrm{Zn(dipy)Cl_2}](\mathrm{s}) + 0.5\mathrm{dipy(g)} \qquad \text{(XI)}$$

which occurs with maximum rate at 280 °C. The electronic spectrum of the coordination compound $\mathrm{Co(dipy)_{1.5}Cl_2}$, given in Fig. 3, shows the stereochemical non-equivalency of the $\mathrm{Co^{II}}$ ions; the absorption band at ~ 680 nm is characteristic of tetracoordinated $\mathrm{Co^{II}}$ ions, while the band located at ~ 500 nm is characteristic of hexacoordinated $\mathrm{Co^{II}}$ ions. Thus, the compound $\mathrm{Co(dipy)_{1.5}Cl_2}$ could be represented as a binuclear coordination compound with stereochemically non-equivalent $\mathrm{cobalt^{II}}$ ions, i.e. $[(\mathrm{dipy})_2\mathrm{Co}\!<\!\begin{smallmatrix}\mathrm{Cl}\\ \mathrm{Cl}\end{smallmatrix}\!>\!\mathrm{Co(dipy)}]\mathrm{Cl_2}$; the formulation $[\mathrm{Co(dipy)_3}][\mathrm{CoCl_4}]$ seems to be less probable, taking into account the precursor as well as the next decomposition product, α-$[\mathrm{Co(dipy)Cl_2}]$.

According to the derivatogram, in the temperature range 300–480 °C, the decomposition steps described by the following equations occur

$$\mathrm{Co(dipy)_{1.5}Cl_2(s)} + [\mathrm{Zn(dipy)Cl_2}](\mathrm{s})$$

$$\rightarrow \alpha\text{-}[\mathrm{Co(dipy)Cl_2}](\mathrm{s}) + [\mathrm{Zn(dipy)Cl_2}](\mathrm{s}) + 0.5\mathrm{dipy(g)} \qquad \text{(XII)}$$

$$\alpha\text{-}[\mathrm{Co(dipy)Cl_2}](\mathrm{s}) + [\mathrm{Zn(dipy)Cl_2}](\mathrm{s})$$

$$\rightarrow \mathrm{CoCl_2(s)} + [\mathrm{Zn(dipy)Cl_2}](\mathrm{s}) + \mathrm{dipy(g)} \quad \text{(XIII)}$$

$$\mathrm{CoCl_2(s)} + [\mathrm{Zn(dipy)Cl_2}](\mathrm{s}) \rightarrow \mathrm{CoCl_2(s)} + \mathrm{ZnCl_2(s)} + \mathrm{dipy(g)} \qquad \text{(XIV)}$$

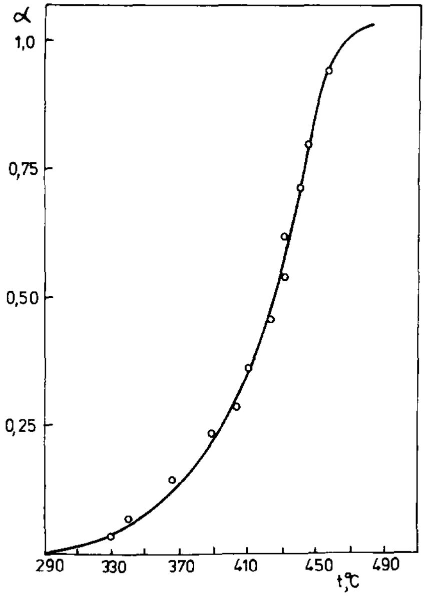

Fig. 4. TG curve in coordinates (α, t °C) for reaction (XV): ———, calculated curve; o; experimental points.

The electronic spectrum of the powder formed as the product of reaction (XII) (Fig. 3c) shows the formation of α-[Co(dipy)Cl_2], in which the cobalt(II) ion is tetracoordinated (C_{2v} symmetry) [12]. The pronounced overlap of the reactions (XII), (XIII) and (XIV), even at $\beta = 2.5$ K min^{-1}, demonstrates the impossibility of performing a nonisothermal kinetic analysis. For $\beta = 10$ K min^{-1} the summation of reactions (XIII) and (XIV) gives essentially the following single reaction

$$[\text{Co(dipy)Cl}_2](\text{s}) + [\text{Zn(dipy)Cl}_2](\text{s}) \rightarrow \text{CoCl}_2(\text{s}) + \text{ZnCl}_2(\text{s}) + 2\text{dipy}(\text{g}) \qquad \text{(XV)}$$

The values of the nonisothermal kinetic parameters of reactions (XI) and (XV) are listed in Table 4. Inspection of these results shows, in this case also, a satisfactory agreement between the values of the nonisothermal kinetic parameters obtained by means of the three mentioned methods. Figure 4 shows the regenerated TG curve in (α, t °C) coordinates for reaction (XV). The experimental points lie practically on the curve, thus justifying the treatment of reaction (XV) as a single step.

Thermal behaviour of the coordination compound [Ni(dipy)$_3$][ZnCl$_4$]

The inspection of the derivatogram corresponding to this compound shows: (i) a slight humidity loss between room temperature and 100 °C; (ii) a weak endothermic effect on the DTA curve, without change of weight,

TABLE 4

Nonisothermal kinetic parameter values for reactions (XI) and (XV) at $\beta = 2.5$ K min^{-1} and $\beta = 10$ K min^{-1}, respectively

Reaction	Coats–Redfern method				Flynn–Wall method				Modified Coats–Redfern method			
	n	E (cal mol^{-1})	A (s^{-1})	r	n	E (cal mol^{-1})	A (s^{-1})	r	n	E (cal mol^{-1})	A (s^{-1})	r
XI	0.9	30300	2.68×10^9	−0.999	0.9	30900	4.99×10^9	−0.999	0.8	30200	2.41×10^9	−0.999
XV	0.3	22000	1.01×10^4	−0.989	0.2	22100	0.74×10^4	−0.992	0.3	21700	1.69×10^4	−0.991

TABLE 5

Nonisothermal kinetic parameter values for reaction (XVII)

β (K min^{-1})	Coats–Redfern method				Flynn–Wall method				Modified Coats–Redfern method			
	n	E (cal mol^{-1})	A (s^{-1})	r	n	E (cal mol^{-1})	A (s^{-1})	r	n	E (cal mol^{-1})	A (s^{-1})	r
5	0.7	27400	2.89×10^6	−0.998	0.7	28400	9.11×10^6	−0.998	0.7	27700	4.20×10^6	−0.999
2.5	0.7	27500	4.17×10^6	−0.994	–	–	–	–	1	30000	4.28×10^7	−0.991

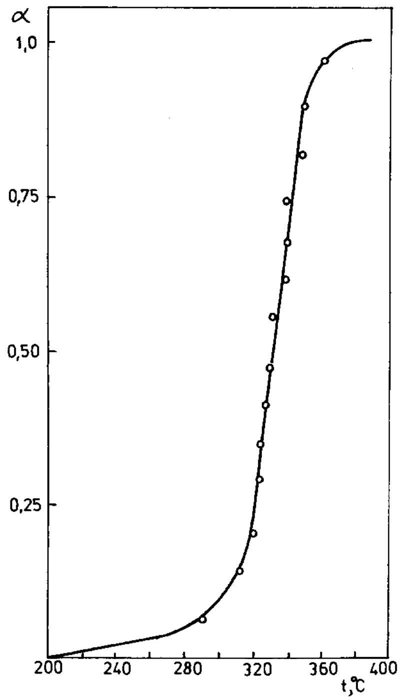

Fig. 5. TG curve in coordinates (α, t °C) for reaction (XVII) at 2.5 K $\min^{-1}$: ——, calculated curve; ○, experimental points.

located at 235 °C, corresponding to the migration of the organic ligand between the two coordination spheres according to the equation

$$[Ni(dipy)_3][ZnCl_4](s) \rightarrow [Ni(dipy)_2Cl_2](s) + [Zn(dipy)Cl_2](s) \qquad \text{(XVI)}$$

(iii) the loss of the organic ligand, according to the equation

$$[Ni(dipy)_2Cl_2](s) + [Zn(dipy)Cl_2](s)$$
$$\rightarrow NiCl_2(s) + ZnCl_2(s) + 3dipy(g) \qquad \text{(XVII)}$$

with the maximum rate at 380 °C; and (iv) the oxidation of the mixture of Ni^{II} and Zn^{II} halides, which occurs with maximum rate at 590 °C.

The values of the nonisothermal kinetic parameters of reaction (XVII) for heating rates $\beta = 5$ K $\min^{-1}$ and 2.5 K $\min^{-1}$ are listed in Table 5.

Inspection of the results given in Table 5 shows that the values of the nonisothermal kinetic parameters obtained by means of the three methods are in satisfactory agreement. It may also be noted, from the same table, that the values of the nonisothermal kinetic parameters do not depend on the heating rate, thus showing no heat transfer limitation at heating rates lower than 5 K $\min^{-1}$.

In Fig. 5 the regenerated TG curve for $\beta = 2.5$ K $\min^{-1}$, in coordinates (α, t °C) calculated using the values of the nonisothermal kinetic parameters according to the Coats–Redfern method, is given. In processing the data using this method, the term $2RT/E$ from the right side of eqn. (1) was neglected. As shown in Fig. 5, the experimental points fit well to the calculated curve, so confirming the validity of the approximation.

The values of reaction order lower than unity could be assigned, as shown previously, to the occurrence of the decomposition in a mixed regime, kinetic and diffusional [15]. As far as the values of reaction order higher than unity are concerned, these are probably due to the decomposition of some structural units with low or variable numbers of molecules.

CONCLUSIONS

(1) A derivatographic study of the thermal stability of some coordination compounds of cobalt(II) and nickel(II) was performed.

(2) For the decomposition steps that are workable kinetically, values of the nonisothermal kinetic parameters have been determined.

(3) The values of the kinetic parameters obtained by means of three methods are in satisfactory agreement.

(4) Migration phenomena of the organic ligand between coordination spheres have been identified from DTA curves and confirmed by spectral data.

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