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**SYNTHESIS, CHARACTERIZATION AND THERMAL BEHAVIOUR
OF MIXED-LIGAND COMPLEXES OF COBALT(III) WITH
DIMETHYLGLYOXIME AND SOME AMINO ACIDS**

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ABSTRACT

Non-electrolyte complexes of the general formula $[\text{Co}(\text{Hdmg})_2(\text{HA})\text{X}]$ where Hdmg = dimethylglyoximato monoanion, HA = alanine, threonine or histidine and X = Cl, Br, I, SCN were synthesized and characterized by elemental analyses, IR, UV-Visible and ¹H NMR spectra. The complexes are pseudo-octahedral with two dimethylglyoximato ligands N-bonded to the metal in the equatorial plane, the two axial sites being occupied by one amino acid molecule and one halogen or pseudo halogen anion. The thermal behaviour of these cobalt(III) complexes, determined by thermogravimetry (TG) and differential thermal analysis (DTA), shows that the dimethylglyoximato ligand is thermally more stable than the two other ligands.

INTRODUCTION

Cobalt complexes based on α,β -dione dioximes as the main ligands and the so called cobaloximes constitute an important class of chemical materials due to their close relationship to vitamin B₁₂^{1,2}. Thus, these materials, especially those based on dimethylglyoxime (H₂dmg), have been a major focus of systematic studies in past decades,

primarily so in search of a sound understanding of factors and mechanisms that control the biological activities of vitamin B₁₂³⁻⁵.

Mixed-ligand complexes of cobalt(III) with dimethylglyoxime as primary ligand, halogens as secondary ligand and various amines as tertiary ligand have been the subject of many structural studies⁶⁻⁸. There are no literature references on the use of amino acids as tertiary ligand in such complexes.

In view of the important biological activity of the amino acids some cobaloximes with alanine, threonine and histidine were synthesized and characterized by microanalyses, conductivity, IR, UV-Visible and ¹H NMR spectrometry. Based on the result obtained, tentative structures are proposed for the complexes. The thermal behaviour of these complexes, determined by thermogravimetry and differential thermal analysis, was discussed on the light of the structure proposed.

EXPERIMENTAL

Materials

All chemical reagents and solvents used in the synthesis of complexes were Flake products and used without further purification. The amino acids used were: L(+) alanine (Ala), L(-) histidine (His) and L(-) threonine (Thr).

Preparation of Complexes

All complexes were prepared using the following general method. To a solution of CoCl₂.6H₂O, (3.57 g, 15 mmoles) in ethanol-water (50% by volume) were added dimethylglyoxime (3.48 g, 30 mmoles), amino acid (15 mmoles) and NaBr, NaI or KSCN (15 mmoles) with constant stirring at room temperature during 2-4 h. In the synthesis of chloro complexes, the Cl come from CoCl₂. After the precipitation of a colored solid, the mixture was kept stirring at room temperature and air was bubbled into the solution for additional 2-4 h to achieve oxidation. The complexes were isolated by filtration, washed once with absolute EtOH and three times with diethyl ether and finally dried in air.

Physical Measurements

The elemental microanalyses were carried out at the Service Central d'Analyse du CNRS (Vernaison, France). Magnetic measurements were made at room temperature by the Gouy method using a Setaram G-70 electrobalance calibrated with Mohr's salt. Conductance values were obtained with a Tacusel CD-810 conductimeter at room temperature of 10⁻³ mol.L⁻¹

solutions of the complexes in DMSO. The IR spectra were recorded with a Shimadzu FTIR-9101M spectrophotometer between 4000 and 400 cm^{-1} (KBr discs). Electronic absorption spectra were recorded with a Shimadzu UV-1601 UV-Visible spectrophotometer in DMSO solutions. The ^1H NMR spectra were obtained with a Jeol GSX 270 MSB (270 MHz) spectrophotometer in DMSO- d_6 solution of the complexes and the dimethylglyoxime ligand, and in D_2O solutions of the amino acids ligands using TMS as internal reference (Service Commun de RMN, Université d'Angers).

RESULTS AND DISCUSSION

The analytical data of the complexes are given in Table I. On the basis of the analytical data, the complexes have the general formula $[\text{Co}(\text{Hdmg})_2(\text{HA})\text{X}]$ showing that dimethylglyoximato group acts as a monoanion. The molar conductance values of all complexes in DMSO at $10^{-3} \text{ mol.L}^{-1}$ are in the range $2\text{-}50 \Omega^{-1}.\text{cm}^2.\text{mol}^{-1}$ and suggest that the complexes are non-electrolytes⁹. Magnetic measurements show that these complexes are diamagnetic and this is due to the presence of cobalt(III) as central ion.

IR Studies

The main IR bands of both ligands and the complexes are given in Table II. The spectra of the amino acids exhibit the $\nu(\text{NH}_3^+)$ band in the 3030-3130 cm^{-1} range¹⁰. In alanine, threonine and histidine this band is located at 3080, 3030 and 3090 cm^{-1} , respectively. The $\delta(\text{NH}_3^+)$ vibration leads to a band in the 1610-1640 cm^{-1} region. In the complexes, $\nu(\text{NH}_3^+)$ is shifted to higher wave numbers. The bands of medium intensity appearing at 1578-1593 cm^{-1} are due to the asymmetric stretching vibration of the COO^- moiety^{10,11}. The broad bands which occur in the 1625 cm^{-1} region may be attributed to the asymmetric vibration of threonine. In the spectra of the complexes the broad bands of medium intensity appearing between 1547 and 1578 cm^{-1} are assigned to the asymmetric stretching vibration of the COO^- group. The $\nu(\text{C}=\text{N})$ band appearing at 1447 cm^{-1} in dimethylglyoxime is slightly shifted to 1444 cm^{-1} , this suggests that dimethylglyoxime is coordinated to the metal ion through the nitrogen atom of the oxime. The only new feature in the IR spectra of the complexes is a strong and sharp absorption around 510 cm^{-1} which is assigned to the $\nu(\text{Co-N})$ vibration, these bands are not found in the spectrum of the ligand. These determinations are in good agreement with those described in the literature¹²⁻¹⁴.

The sharp and weak band occurring around 1020 cm^{-1} and 1145 cm^{-1} in all the complexes is assigned to the N-O stretching vibration of the oxime moieties. All of the IR spectra of the

Table I. Analytical Data of the Complexes^a

Compound Formula	F.Wt	Colour	Yield (%)	Anal. Found (calc.) (%)				X ^b
				C	H	N	Co	
[Co(Hdmg) ₂ (Ala)Cl] CoC ₁₁ H ₂₁ N ₅ O ₆ Cl	413.5	Brown-Greyish	45	30.6 (31.0)	4.7 (5.0)	16.5 (16.9)	14.3 (14.2)	8.2 (8.6)
[Co(Hdmg) ₂ (Ala)Br] CoC ₁₁ H ₂₁ N ₅ O ₆ Br	453.5	Brown-Green	37	28.3 (28.8)	4.7 (4.6)	15.8 (15.3)	13.0 (12.9)	16.9 (17.4)
[Co(Hdmg) ₂ (Ala)I] CoC ₁₁ H ₂₁ N ₅ O ₆ I	505	Brown	45	25.6 (26.1)	3.8 (4.1)	13.3 (13.8)	12.3 (11.7)	25.6 (25.1)
[Co(Hdmg) ₂ (Ala)SCN] CoC ₁₁ H ₂₁ N ₅ O ₆ S	436	Brown	69	32.5 (33.0)	4.7 (4.8)	19.8 (19.3)	13.0 (13.5)	7.9 (7.3)
[Co(Hdmg) ₂ (Thr)Cl]2H ₂ O CoC ₁₂ H ₂₇ N ₅ O ₉ Cl	479.5	Brown-Greyish	34	29.8 (30.0)	5.5 (5.8)	15.1 (14.6)	12.0 (12.3)	7.4 (7.4)
[Co(Hdmg) ₂ (Thr)Br] CoC ₁₂ H ₂₃ N ₅ O ₇ Br	488	Brown-Greyish	27	29.0 (29.5)	4.7 (4.7)	14.1 (14.3)	12.3 (12.1)	16.9 (16.4)
[Co(Hdmg) ₂ (Thr)I] CoC ₁₂ H ₂₃ N ₅ O ₇ I	535	Brown-Dark	35	26.4 (26.9)	3.8 (4.3)	12.9 (13.1)	10.9 (11.0)	24.2 (23.7)
[Co(Hdmg) ₂ (Thr)SCN] CoC ₁₃ H ₂₃ N ₆ O ₇ S	446	Brown-Red	27	32.9 (33.4)	4.5 (4.9)	18.6 (18.1)	13.2 (12.7)	7.1 (6.9)
[Co(Hdmg) ₂ (His)Cl]3H ₂ O CoC ₁₄ H ₃₀ N ₇ O ₉ Cl	533.5	Tan	15	31.2 (31.5)	5.6 (5.6)	17.9 (18.4)	10.8 (11.0)	7.0 (6.6)
[Co(Hdmg) ₂ (His)Br]8H ₂ O CoC ₁₄ H ₃₉ N ₇ O ₁₄ Br	668	Brown-Rousse	40	25.1 (25.2)	5.2 (5.3)	14.7 (14.7)	8.5 (8.6)	11.8 (12.0)
[Co(Hdmg) ₂ (His)I]3H ₂ O CoC ₁₄ H ₃₀ N ₇ O ₉ I	625	Brown-Rousse	34	27.4 (27.9)	4.8 (4.6)	16.2 (15.7)	8.7 (9.4)	19.8 (20.3)
[Co(Hdmg) ₂ (His)SCN]3H ₂ O CoC ₁₅ H ₃₀ N ₈ O ₉ S	556	Brown-Rousse	19	31.8 (32.2)	4.9 (5.2)	20.0 (20.1)	11.0 (10.6)	5.7 (5.7)

^aThe complexes decompose and did not melt up to 300° C^bX = Cl, Br, I or SCN.

Table II. Main IR Spectral Data

Complexes	$\nu(\text{NH})^a$	$\delta(\text{NH}_2)^a$	$\nu_{\text{as}}(\text{COO}^-)$	$\nu_{\text{s}}(\text{COO}^-)$	$\nu(\text{CN})$	$\nu(\text{NO})$	$\nu'(\text{NO})$	$\delta(\text{NO})$	$\nu(\text{Co-N})$	$\nu(\text{NCS})$
Ala	3080 w	1618 w	1593 b	1410 s	-	-	-	-	-	-
Thr	3030 w	1618 w	1625 s	1414 w	-	-	-	-	-	-
His	3090 w	1638 w	1578 sh	1417 s	-	-	-	-	-	-
H ₂ dmg	-	-	-	-	1447 b	1144 s	1025 w	750 b	-	-
[Co(Hdmg) ₂ (Ala)Cl]	3375 b	1630 sh	1574 s	1375 s	1445 s	1150 w	1022 w	760 b	510 s	-
[Co(Hdmg) ₂ (Ala)Br]	3250 w	1630 s	1572 b	1370 s	1443 w	1150 w	-	758 b	507 s	-
[Co(Hdmg) ₂ (Ala)I]	3250 w	1630 s	1572 b	1370 s	1443 w	1144 w	1018 w	756 b	509 s	-
[Co(Hdmg) ₂ (Ala)SCN]	3250 w	1630 s	1542 b	1364 w	1438 b	1144 w	1030 w	738 w	511 s	2178, 2145 s
[Co(Hdmg) ₂ (Thr)Cl]2H ₂ O	3220 w	1615 w	1574 b	1365 w	1443 b	1144 w	-	758 w	511 m	-
[Co(Hdmg) ₂ (Thr)Br]	3230 w	1618 w	1574 b	1367 s	1445 m	1144 w	1020 w	759 b	509 m	-
[Co(Hdmg) ₂ (Thr)I]	3430 b	1630 sh	1574 s	1385 s	1445 w	1150 w	1020 w	754 b	511 s	-
[Co(Hdmg) ₂ (Thr)SCN]	3230 w	1618 w	1547 b	1383 w	1443 b	1144 w	1006 w	737 w	511 m	2180, 2145 s
[Co(Hdmg) ₂ (His)Cl]3H ₂ O	3150 w	1641 s	1578 s	1364 w	1444 w	1158 m	1007 w	741 s	517 s	-
[Co(Hdmg) ₂ (His)Br]8H ₂ O	3140 w	1630 w	1570 b	1375 w	1437 w	1144 w	1005 w	741 s	513 s	-
[Co(Hdmg) ₂ (His)I]3H ₂ O	3140 w	1645 w	1575 w	1368 w	1444 w	1146 w	1003 w	739 m	517 s	-
[Co(Hdmg) ₂ (His)SCN]3H ₂ O	3150 w	1630 w	1547 b	1385 w	1405 sh	1120 w	1005 w	745 b	513 m	2178, 2118 s

^a(NH₃⁺) in ligand

s = strong; m = medium; w = weak; b = broad; sh = shoulder

complexes exhibit a sharp band at 750 cm^{-1} , attributed to the C=N-OH deformation vibration¹². In the three isothiocyanato complexes the very strong sharp bands at 2145 (Ala, Thr) and 2178 cm^{-1} (His) are due to $\nu(\text{C}=\text{N})$ vibrations of the coordinated isothiocyanato group¹¹

¹H NMR Spectra

The chemical shift of the dimethylglyoxime methyl resonance (0.95 ppm) shifts considerably downfield in the complexes (around 2.50 ppm) indicating that this ligand is bound by the nitrogen atoms. The dimethylglyoximato methyl group resonances are almost invariant across the series¹⁵ excepted for the thiocyanato complexes (2.23-2.40 ppm). The presence of one alanine or threonine ligand and two dimethylglyoximato ligands was confirmed by the 1:4 ratio of the corresponding methyl resonances. The signal at 10.4 ppm in the spectra of the dimethylglyoxime attributed to the hydroxyl group is shifted downfield to 11.4 ppm in the threonine and alanine complexes and is absent in the histidine complex spectra. This is probably due to the strong hydrogen bonding present in the histidine complex.

Electronic Spectra

In DMSO solutions (around $10^{-3}\text{ mol.L}^{-1}$ for Visible and $5.10^{-5}\text{ mol.L}^{-1}$ for UV spectra), the spectra of the complexes show two d-d transitions and one band due to ligand to metal charge transfer in the UV range. The position of these bands and the molar absorption coefficient ϵ are given in Table III. The values are in good agreement with those already observed in pseudo octahedral cobalt(III) complexes¹⁶. The variation in the position of the transition bands allows us to obtain two spectrochemical series: $\text{I} < \text{Br} < \text{Cl} < \text{NCS}$ and $\text{Thr} < \text{His} < \text{Ala}$ for the amino acids. In addition, we observe that the charge transfer bands are shifted to higher energies and this order follows the increasing electronegativities of the halogens.

Thus, on the basis of the analytical and spectroscopic data, all of the complexes of cobalt(III) have a pseudo-octahedral structure (see Fig. 1) where the two dimethylglyoxime monoanions are in the equatorial plane, and the monodentate ligands HA (amino acid) and X (halogen) occupy the two axial coordination sites.

Thermal Analysis

The TG and DTA curves show unambiguously that the loss of the crystallization water molecules occurs between 25 and 189°C , particularly for the complexes containing histidine the temperature varies with the nature of the ligands. This process occurs mainly in one step but in two or even three steps in some cases. Stoichiometric calculations show that the weight

Table III. Electronic Spectral Data of Cobalt(III) Complexes

Compound	Electronic transitions ^a (ε) ^b		
	${}^1A_{1g} \rightarrow {}^1T_{1g}$	${}^1A_{1g} \rightarrow {}^1T_{2g}$	$\pi \rightarrow e_g$
[Co(Hdmg) ₂ (Ala)Cl]	17545 (260)	-	33670 (720)
[Co(Hdmg) ₂ (Ala)Br]	17390 (250)	16660 (275)	-
[Co(Hdmg) ₂ (Ala)I]	12285 (560)	22470 (1900)	25315 (2300)
[Co(Hdmg) ₂ (Ala)SCN]	20620 (1240)	27030 (4400)	-
[Co(Hdmg) ₂ (Thr)Cl]2H ₂ O	15150 (60)	18180 (350)	27390 (1460)
[Co(Hdmg) ₂ (Thr)Br]	14490 (110)	17700 (460)	27030(1840)
[Co(Hdmg) ₂ (Thr)I]	10834 (130)	22370 (1914)	17390 (1600)
[Co(Hdmg) ₂ (Thr)SCN]	20200 (1066)	-	-
[Co(Hdmg) ₂ (His)Cl]3H ₂ O	17390 (55)	20200 (112)	27400 (1440)
[Co(Hdmg) ₂ (His)Br]8H ₂ O	15455 (45)	20200 (312)	26650 (1300)
[Co(Hdmg) ₂ (His)I]3H ₂ O	13500 (150)	18700 (484)	24690 (2440)
[Co(Hdmg) ₂ (His)SCN]3H ₂ O	21050 (1400)	27050 (220)	33300 (700)

^aWave number in cm⁻¹

^bAbsorption molar coefficient in mol⁻¹ L cm⁻¹

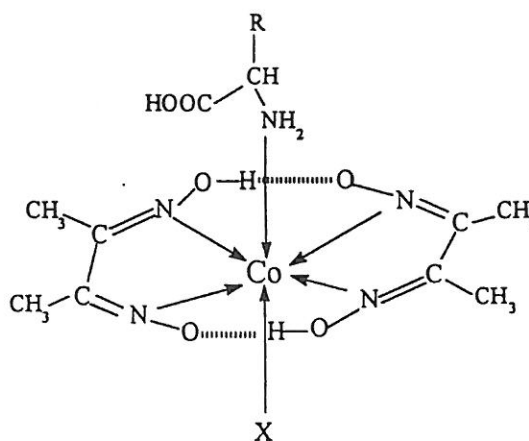
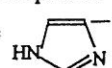


Fig. 1. Suggested Structure of the Complexes

R = CH₃ : (Ala) ; R = CH₃CH(OH) : (Thr) ; R =  : (His)

losses correspond approximately to the elimination of HX (X = Cl, Br, I, or SCN), HA (Ala, Thr or His) and H₂dmg.

Complexes [Co(Hdmg)₂(Ala)X]. In this series we note that HCl, HBr and HSCN are eliminated between 125 and 210° C and, as it will be demonstrate below, a higher temperature is observed for HI compound. The elimination of Ala and Thr is faster than that of His and occurs at lower temperature. For the chloro complex, a simultaneous departure of Ala and HCl is observed. On one hand, we observed in the DTA curves, that the elimination of at least one molecule of dimethylglyoxime is characterized by an exothermic peak. On the other hand, we note that in the case of the iodo complex, the loss of H₂dmg occurs at higher temperature via an endothermic process.

Complexes [Co(Hdmg)₂(Thr)X]. The observation of TG curves and the experimental data show that no molecules of water are involved here, except for the chloro derivative. In this series the loss of HCl, HSCN and HBr is observed at 91-136, 126-190 and 139-196° C, respectively, whereas for HI the range is 204-265° C. In addition, we observed that in the bromo derivative the molecules of HBr and Thr are lost simultaneously. The pyrolysis of the whole series reveals a fast and important mass loss corresponding to the elimination of two molecules of H₂dmg.

Complexes [Co(Hdmg)₂(His)X]nH₂O. It is seen that [Co(Hdmg)₂(His)Br]8H₂O first loses crystallization water in three stages and the analogous SCN and I compounds in two steps. The DTA curves of the isothiocyanato and bromo complexes show that the elimination of HSCN and HBr occurs between 95-230° C and 189-244° C, respectively. The loss of HI from the iodide complexes follows a more complicated pattern, the complete elimination of hydriodic acid needs higher temperature. The calculations show that this acid begins to decompose after the stepwise degradation of histidine which proceeds by successive breaking of the hydrocarbon chain. We may point out that the temperatures of elimination of HSCN, HBr and HI (95-230; 189-244 and 250-422° C) are in the same order as the bonding strength as established by Varehlyi¹⁷ et al: SCN < Br < I.

The TG and DTA curves of the thiocyanato and bromo complexes show an important endothermic peak followed by a large weight loss between 400-500° C. This phenomenon is due to the elimination of at least one H₂dmg molecule. The pyrolysis of H₂dmg occurs at higher temperature for the iodo compound. We observed that the pyrolysis of the thiocyanato and bromo complexes produces mainly endothermic reactions. For the iodo complexes both endothermic and exothermic steps are observed.

The study of the temperatures at which HX molecules are lost from the complexes indicates that in the three series the stability of these species increases in the order: Ala < Thr < His. This

Table IV. Thermal Decomposition Data of the Co(III) Complexes

Compound (M.W.)	Temperature Range (°C)	Weight Obs	Loss (%) Calc	Species formed	DTA peak
[Co(Hdmg) ₂ (Ala)Cl] (413.5)	106-149	8.70	8.60	Co(Hdmg) ₂ Ala	End
	149-197	40.70	41.20	Co(Hdmg) _{1.6}	Exo
	197-306	53.00	52.40	Co(Hdmg) _{1.2}	Exo
	306-500	68.83	69.00	Co(Hdmg) _{0.6}	Exo
[Co(Hdmg) ₂ (Ala)Br] (458)	123-168	17.50	17.46	Co(Hdmg)Ala	End
	168-200	37.20	37.00	Co(Hdmg) ₂	Exo
	200-285	56.60	56.90	Co(Hdmg) _{1.2}	Exo
	285-500	67.18	66.88	Co(Hdmg) _{0.85}	Exo
[Co(Hdmg) ₂ (Ala)I] (505)	120-149	11.11	11.10	Co(Hdmg) ₂ Ala _{0.51} I	Exo
	149-262	33.93	33.86	Co(Hdmg) ₂ Ala _{0.51}	End
	262-444	43.28	42.80	Co(Hdmg) ₂	End
[Co(Hdmg) ₂ (Ala)SCN] (436)	147-200	13.75	13.34	Co(Hdmg) ₂ Ala	End
	200-222	24.00	23.60	Co(Hdmg) ₂ Ala _{0.5}	Exo
	222-293	43.10	43.80	Co(Hdmg) _{1.6}	Exo
	293-550	67.60	68.10	Co(Hdmg) _{0.70}	Exo
[Co(Hdmg) ₂ (Thr)Cl]2H ₂ O (479.5)	91-136	14.5	14.90	Co(Hdmg) ₂ Thr	Exo
	136-195	24.36	24.08	Co(Hdmg) ₂ Thr _{0.63}	End
	195-276	51.88	52.20	Co(Hdmg) _{1.48}	End
	276-493	63.18	63.30	Co(Hdmg)	End
	493-550	82.00	81.40	Co(Hdmg) _{0.26}	End
[Co(Hdmg) ₂ (Thr)Br] (488)	139-196	52.68	52.86	Co(Hdmg) _{1.5}	Exo
	196-292	59.27	58.88	Co(Hdmg) _{1.24}	Exo
	292-500	71.49	71.51	Co(Hdmg) _{0.68}	Exo
[Co(Hdmg) ₂ (Thr)I] (535)	24-185	6.30	6.35	Co(Hdmg) ₂ Thr _{0.71} I	End
	185-204	11.39	11.58	Co(Hdmg) ₂ Thr _{0.48} I	Exo
	204-265	51.69	52.52	Co(Hdmg) _{1.70}	Exo
	265-455	73.80	74.00	Co(Hdmg) _{0.70}	End
[Co(Hdmg) ₂ (Thr)SCN] (466)	126-190	12.62	12.44	Co(Hdmg) ₂ Thr	End
	190-230	59.57	59.23	Co(Hdmg) _{1.4}	Exo
	230-500	72.34	71.50	Co(Hdmg) _{0.36}	Exo
[Co(Hdmg) ₂ (His)Br]8H ₂ O (668)	25-92	5.40	5.39	[Co(Hdmg) ₂ HisBr]6 H ₂ O	End
	92-110	13.33	13.47	[Co(Hdmg) ₂ His Br]3H ₂ O	End
	189-244	40.40	40.56	Co(Hdmg) ₂ His _{0.70}	End
	244-397	57.08	56.90	Co(Hdmg) ₂	End
	397-550	78.87	78.74	Co(Hdmg) _{0.73}	End
[Co(Hdmg) ₂ (His)I]3H ₂ O (625)	26-54	5.30	5.76	[Co(Hdmg) ₂ His I]1.5H ₂ O	Exo
	54-90	11.43	10.06	Co(Hdmg) ₂ His I	Exo
	90-159	21.22	20.96	Co(Hdmg) ₂ His _{0.56} I	Exo
	159-250	27.80	28.00	Co(Hdmg) ₂ His _{0.28} I	Exo
	250-422	40.00	40.32	Co(Hdmg) ₂ His _{0.19} I _{0.5}	End
	422-480	53.06	53.90	Co(Hdmg) ₂ His _{0.11}	End
[Co(Hdmg) ₂ (His)SCN]3H ₂ O (556)	25-95	6.20	6.47	[Co(Hdmg) ₂ HisSCN]H ₂ O	Exo
	95-230	31.00	31.00	Co(Hdmg) ₂ His _{0.52}	End
	230-294	41.00	42.60	Co(Hdmg) ₂ His _{0.19}	End
	294-460	61.15	61.50	Co(Hdmg) _{1.39}	End
	460-550	78.50	79.10	Co(Hdmg) _{0.5}	End

order may be explained by the presence of stronger hydrogen bonding with Thr and His, because of the presence of OH (Thr) and nitrogen atoms (His).

Considering a series containing the same amino acid, thermal analyses show that in all cases the strengths of the Co(III)-X bond is greater with iodide than with Cl, Br and SCN; for these three ions the order varies with the nature of the amino acid.

The stoichiometric calculation of the weight loss indicates that the pyrolysis of His and Thr proceeds by successive degradation while Ala mainly decomposes in one step. In the three series, the elimination of two molecules of dimethylglyoxime occurs after the elimination of HX (X = Cl, Br or SCN) and the amino acid. When X = I, we note that around 500-550° C, only one molecule of H₂dmg is eliminated.

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