THERMAL DECOMPOSITION OF THE TRIS-(O-PHEN) COMPLEXES OF SOME FIRST TRANSITION GROUP ELEMENTS

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A series of complexes of transition metals $M(o\text{-}phen)_3X_2$, where $M = Fe^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and $X = Cl^-$, Br^-, has been studied using TG, DTA and spectroscopic methods, to obtain information concerning the decomposition mechanism, the influence of the central metal and halogens on the stability of these complexes and the stereochemical variations caused by heating.

It has been observed from the DTA and TG curves that the complexes decompose, after their dehydration, generally after an endothermic reaction involving the partial substitution of the base in the co-ordination sphere of the metal by the halogen, as can be seen from reflectance spectra. The first base weight loss corresponds generally to one mole of phenanthroline giving the biscomplexes.

In observing the beginning decomposition temperature values one can see that the stability, concerning the central metal as well as the halogen are in the following order: $Ni > Fe \cong Co \cong Cu > Zn$, and $Br^- > Cl^-$.

The purpose of this paper is to discuss the thermal behaviour of a series of complexes of transition metals, $M(o\text{-}phen)_3X_2$, where $M = Fe^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+} and Zn^{2+} and $X = Cl^-$ and Br^-, with a view to finding possible analogies among these complexes, apparently having the same structure. From the values of activation energies and first-decomposition temperatures, information can be obtained as to the stabilities of these complexes and the strengths of the metal-ligand bonds.

All of the complexes studied are of octahedral configuration, except *tris-(o-phen)CuX₂*, which exhibits marked trigonal or tetragonal distortions [1—5].

The complexes with $M = Ni^{2+}$, Co^{2+} and Cu^{2+} are high-spin and paramagnetic; that with $M = Fe^{2+}$ is low-spin and therefore diamagnetic [1, 5].

For a better understanding of the thermal decomposition products, some intermediates were isolated and chemically analyzed.

Experimental

The complexes were prepared by the methods described in the literature, with suitable modifications [1].

TG measurements were made with a Mod. TRO1 Stanton balance, at a heating rate of 2°/min.

DTA measurements were made with a Netzsch apparatus, platinum platinum-rhodium thermocouple, platinum holders, DDK measuring head, and preheated kaolin as inert material, at a heating rate of 5°/min.

The weight of each sample was approx. 100 mg. The activation energies for the first decomposition step were calculated according to the Coats—Redfern and Newkirk methods [6, 7]. The reflectance spectra were measured on a Beckman Model DK2 spectrophotometer.

Results

The thermal decompositions of the complexes $M(phen)_3X_2 \cdot nH_2O$ take place through different reactions, as can be seen from the TG and DTA curves in Figs 1—5. The decomposition can proceed in different ways, according to equations (A) to (H); Table I gives the reactions occurring for each complex.

(A) $M(phen)_3X_2 \cdot nH_2O \rightarrow M(phen)_3X_2 + nH_2O$

(B) endothermic reaction with no weight variation

(C) exothermic reaction with no weight variation

(D) $M(phen)_3X_2 \rightarrow M(phen)_2X_2 + phen$

(E) $M(phen)_2X_2 \rightarrow M(phen)X_2 + phen$

(F) $M(phen)_3X_2 \rightarrow M(phen)_{1.67}X_2 + 1.33\ phen$

(G) $M(phen)_{1.67}X_2 \rightarrow M(phen)X_2 + 0.67\ phen$

(H) $M(phen)X_2 \rightarrow M\ oxides + (M?)$
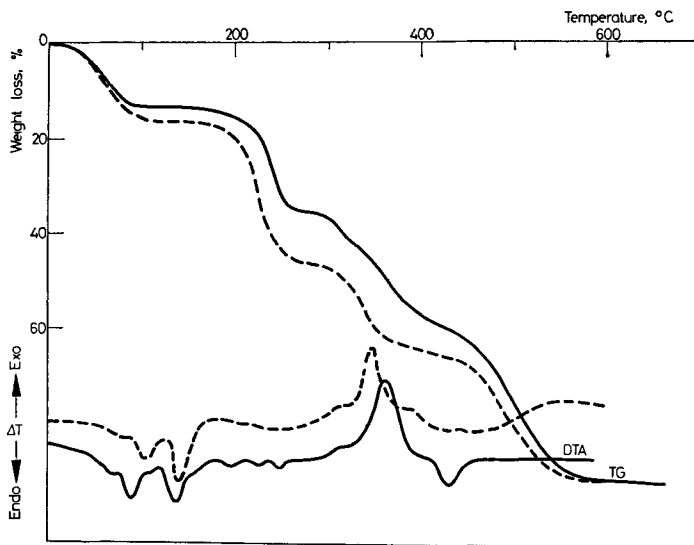
Fig. 1. TG and DTA curves of Fe(phen)$_3$X$_2$ · nH$_2$O, ——— Fe(phen)$_3$Br$_2$ · 5H$_2$O,
— — — Fe(phen)$_3$Cl$_2$ · 7H$_2$O

In order to obtain more information about the stereochemical changes induced by heat in the complexes, reflectance spectra were taken on products calcined at different temperatures. The choice of these temperatures was related to the weight and energy changes deduced from the TG and DTA curves.
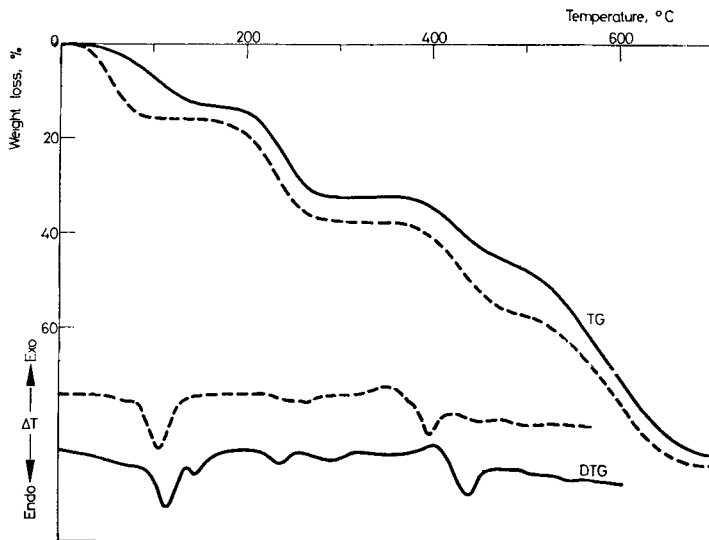

Fig. 2. TG and DTA curves of Co(phen)$_3$X$_2$ · nH$_2$O, ——— Co(phen)$_3$Br$_2$ · 6H$_2$O, — — — Co(phen)$_3$Cl$_2$ · 7H$_2$O
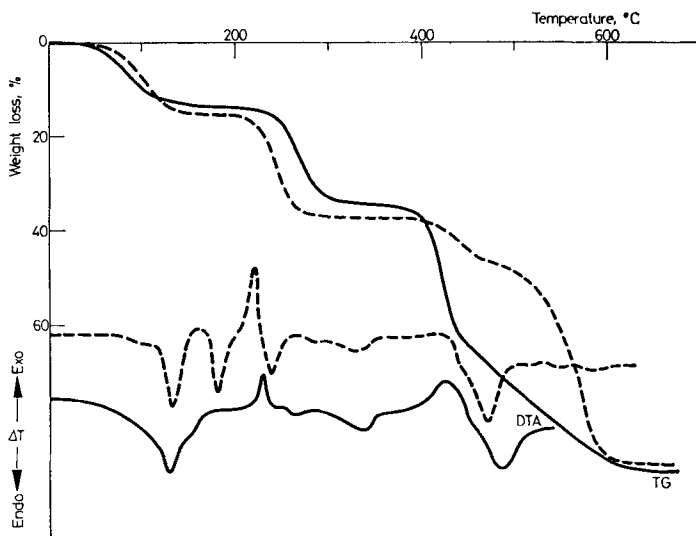
Fig. 3. TG and DTA, curves of Cu(phen)$_3$X$_2$ · nH$_2$O, ——— Ni(phen)$_3$Br$_2$ · 7H$_2$O, — — — Ni(phen)$_3$Cl$_2$ · 7H$_2$O

The activation energies corresponding to the elimination of the first mole of phen are reported in Table 2.

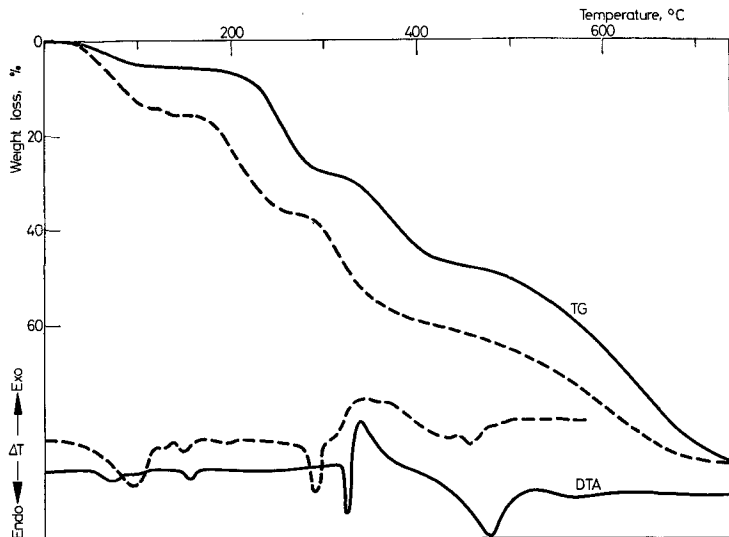Fig. 4. TG and DTA curves of $Cu(phen)_3X_2 \cdot nH_2O$, ——— $Cu(phen)_3Br_2 \cdot 2H_2O$, — — — $Cu(phen)_3Cl_2 \cdot 7H_2O$
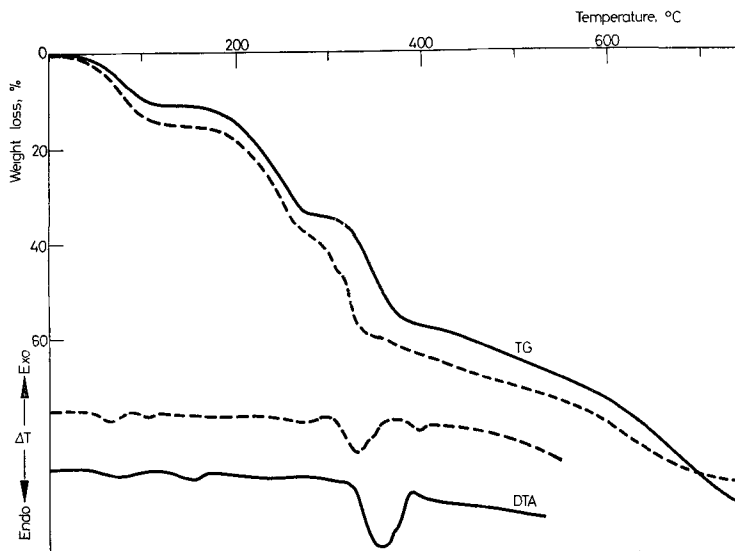
Fig. 5. TG and DTA curves of $Zn(phen)_3X_2 \cdot nH_2O$, ——— $Zn(phen)_3Br_2 \cdot 5H_2O$, — — — $Zn(phen)_3Cl_2 \cdot 7H_2O$

The results for all complexes are reported in Table 3 and Figs 6 and 7. It can be seen that a sharp variation of the reflectance spectra is observed for $Fe(phen)_3Cl_2$ at as low as 160°, i.e. even before the reaction through which the first mole of phenanthroline is lost. The spectrum is similar to that of the initial complex,

Fig. 6. Reflectance spectra of $Ni(phen)_3X_2 \cdot nH_2O$ at different temperatures.
——— $Ni(phen)_3 \cdot Cl_2$, — — — $Ni(phen)_3 \cdot Br_2$

and therefore still indicates an octahedral configuration, but there is a shift of the maxima towards lower frequencies. Partial substitution of phenanthroline by chlorine in the co-ordination sphere is evident, in agreement with the sequence of such ligands in the spectrochemical series.

Thus, the endothermal reaction between 130° and 170° is associated with this partial internal ligand substitution, and only after this rearrangement is the beginning of the loss of the first mole of base noticeable.

For *Fe(phen)₃Br₂* only a slight change in the spectrum is observed at 170° after the endothermal reaction, in contrast to what was observed in the case of the chloride compound, where the change is much more marked. It must be inferred that in this case the substitution of the phenanthroline by halogen is more hindered, possibly due to the larger dimensions of bromine.
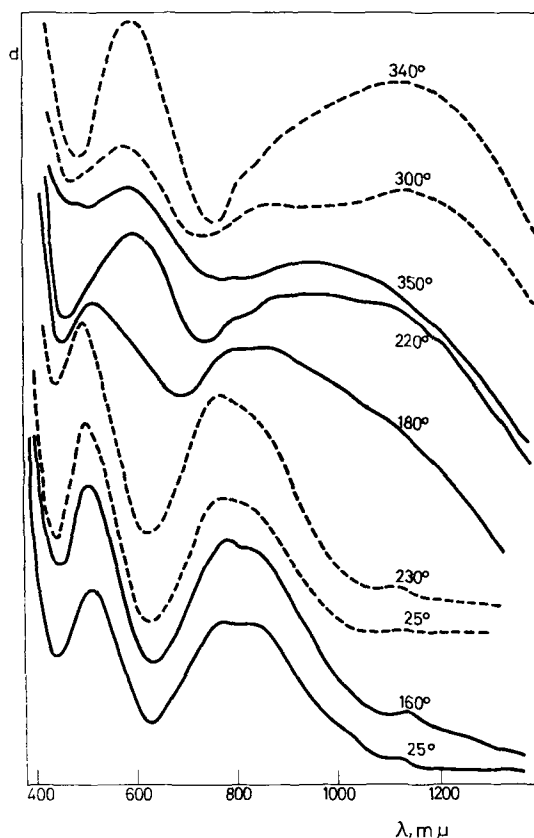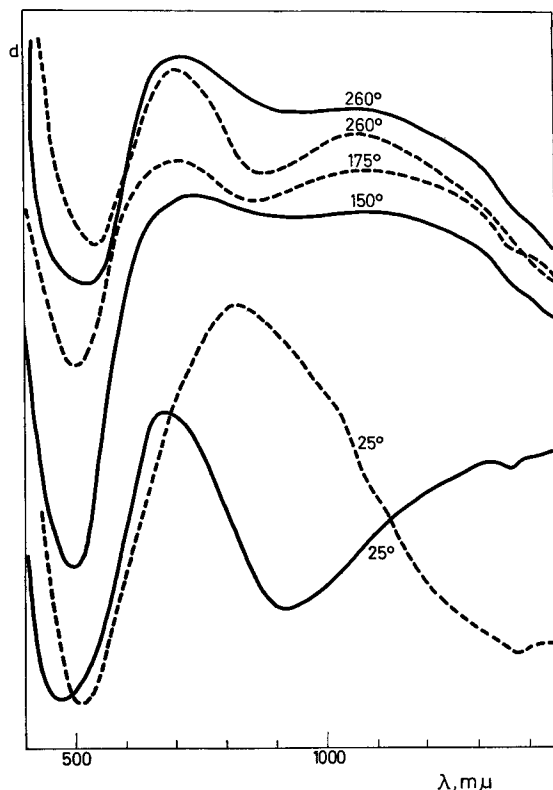

Fig. 7. Reflectance spectra of $Cu(phen)_3X_2 \cdot nH_2O$ at different temperatures.
———— $Cu(phen)_3 \cdot Cl_2$, — — — $Cu(phen)_3Br_2$

For *Co(phen)₃Cl₂* the reflectance spectrum changes noticeably at as low as 160°, before the loss of the first mole of phenanthroline, with a systematic shift of the maxima towards the red. The shape of the spectrum, however, appears similar to that of the initial complex. As in the case of the analogous complex with iron, it should be recognized that a partial substitution of halogen into the inner co-ordination sphere precedes the decomposition of the complex, with the formation of *Co(phen)₂Cl₂*. The DTA curve, however, shows no evidence of any connected endothermal reaction.

Table 1

Reactions and corresponding temperature ranges observed in thermal decomposition of $M(II)(phen)_3X_2 \cdot nH_2O$

$M(phen)_3X_2 \cdot nH_2O$	A) nH_2O	B) endothermic, with exothermic	C) exothermic, with no weight loss	D) -1 phen	E) -1 phen	F) -1.33 phen	G) -0.67 phen	H) $-$ phen $\rightarrow -X_2 + O \rightarrow$ oxides
$Fe(phen)_3Cl_2 \cdot 7H_2O$	$<120°$	$120-160°$		$170°-270°$	$280°-410°$	$160°-270°$	$280°-375°$	$380°-600°$
$Fe(phen)_3Br_2 \cdot 5H_2O$	$<120°$	$120-160°$		$160°-250°$	$330°-420°$			$420°-600°$
$Co(phen)_3Cl_2 \cdot 7H_2O$	$<120°$			$195°-250°$			$360°-450°$	$450°-650°$
$Co(phen)_3Br_2 \cdot 6H_2O$	$<140°$	$130°-170°$						$450°-650°$
$Ni(phen)_3Cl_2 \cdot 7H_2O$	$<140°$	$150°-190°$		$200°-280°$	$370°-$			$470°-600°$
$Ni(phen)_3Br_2 \cdot 7H_2O$	$<140°$	$140-170°$	$210-230°$	$230°-300°$	$370°-420°$			$440°-600°$
$Cu(phen)_3Cl_2 \cdot 7H_2O$	$<140°$	$140-160°$		$180°-290°$	$275°-375°$			$400°-700°$
$Cu(phen)_3Br_2 \cdot 2H_2O$	$<140°$	$150°-170°$		$145°-270°$	$300°-440°$			$440°-700°$
$Zn(phen)_3Cl_2 \cdot 7H_2O$	$<120°$			$160°-300°$	$280°-350°$			$380°-700°$
$Zn(phen)_3Br_2 \cdot 5H_2O$	$<100°$	$140°-170°$			$310°-400°$			$420°-700°$

Table 2

Activation energy values observed during the elimination of the first mole of phen from $M(II)(phen)_3X_2 \cdot nH_2O$

Complex	Temperature range °C	E Kcal/mole	Temperature range °C	E Kcal/mole	Temperature range °C	E Kcal/mole	Moles of phen lost overall
$Fe(phen)_3Cl_2 \cdot 7H_2O$	$170-205$	11.0	$210-250$	17.7			1.33
$Fe(phen)_3Br_2 \cdot 5H_2O$	$180-1205$	60.0	$205-240$	31			1
$Co(phen)_3Cl_2 \cdot 7H_2O$	$160-280$	27.0					1
$Co(phen)_3Br_2 \cdot 6H_2O$	$195-280$	19.3					1
$Ni(phen)_3Cl_2 \cdot 7H_2O$	$200-260$	35.3					1
$Ni(phen)_3Br_2 \cdot 7H_2O$	$230-250$	62	$265-300$	29			1
$Cu(phen)_3Cl_2 \cdot 7H_2O$	$170-190$	25.3	$190-210$	15.8	$210-270$	22.1	1
$Cu(phen)_3Br_2 \cdot 2H_2O$	$190-230$	14	$230-240$	23	$240-275$	15	1
$Zn(phen)_3Cl_2 \cdot 7H_2O$	$160-180$	18.7	$180-200$	10.3	$200-270$	21.7	1
$Zn(phen)_3Br_2 \cdot 5H_2O$	$170-270$	17.95					1

Table 3

Reflectance spectra

Complex	Temp. (°C)	Reflectance spectra λ(mμ)						
$Fe(phen)_3Cl_2 \cdot 7H_2O$	25	460	(490)	(550)	815		1110	
$Fe(phen)_3Cl_2$	160	540				930		
$Fe(phen)_{1.67}Cl_2$	270	540		(600)		930	1200	
$Fe(phen)_3Br_2 \cdot 5H_2O$	25	475			800		1120	
$Fe(phen)_3Br_2$	140	470		(550)	815		1110	
$Fe(phen)_3Br_2$	175	470			830		1110	
$Fe(phen)_2Br_2$	260	500		(600)		900	1200	
$Co(phen)_3Cl_2 \cdot 7H_2O$	25	(460)		635		925	1115	
$Co(phen)_3Cl_2$	160	510					1090	
$Co(phen)_2Cl_2$	260	515				(1060)	1135	
$Co(phen)_3Br_2 \cdot 6H_2O$	25	(440)		610		900		
$Co(phen)_3Br_2$	160	520				1025	1230	
$Co(phen)_2Br_2$	260	525				1050	1250	
$Ni(phen)_3Cl_2 \cdot 7H_2O$	25	525			790	850	1115	
$Ni(phen)_3Cl_2$	160	520			780	850	1140	
$Ni(phen)_3Cl_2$	220	(520)	600		790		1110	
$Ni(phen)_2Cl_2$	280		610	(660)	810	1000	1140	
$Ni(phen)Cl_2$	350	500	600		800	980	1150	
$Ni(phen)Cl_2$	380		595		800	980	1120	
$Ni(phen)_3Br_2 \cdot 7H_2O$	25	515			775	855	1120	
$Ni(phen)_3Br_2$	230	510			770	850	1120	
$Ni(phen)_2Br_2$	300		600			870	1130	1200
$Ni(phen)_2Br_2$	340		600		(825)	(950)	1125	1250
$Cu(phen)_3Cl_2 \cdot 7H_2O$	25		680	(750)			(1330)	1500
$Cu(phen)_3Cl_2$	150		725			1100	1250	
$Cu(phen)_2Cl_2$	260		730	(750)		1050		
$Cu(phen)_3Br_2 \cdot 2H_2O$	25		820			(1025)	1420	
$Cu(phen)_3Br_2$	175		710			1090	(1270)	
$Cu(phen)_2Br_2$	260		700	(760)		1070	1315	

Changes regarding the position of the maxima in the spectra have been observed for $Co(phen)_3Br_2$ at 160° for $Ni(phen)_3Cl_2$ above 180° and for $Ni(phen)_3Br_2$ at 300°, as shown in Fig. 6. Thus for the first two complexes the partial substitution of the halogen by phenanthroline takes place before the elimination of the base. For $Ni(phen)_3Br_2$ the similarity of the spectra for samples uncalcined or treated at 230° shows that even after the exothermic reaction at 225° there are no changes in the metal co-ordination sphere. At 300°, with the elimination of the first mole of base, the maxima appear shifted towards lower frequencies, due to the inclusion of bromine into the nickel co-ordination sphere. At 340°, after an endothermal reaction with no weight changes, the spectrum appears more sharply defined, unlike that at 300°, which includes other bands of intermediate frequencies. Similarly to what was observed for the iron complexes, the substitution of phenanthroline by Br is much more difficult than that by Cl.

Fig. 7 shows the reflectance spectra for the hydrated and anhydrous copper complexes. The spectrum of $Cu(phen)_3Cl_2 \cdot 7H_2O$ is somewhat different from that of $Cu(phen)_3Br_2 \cdot 2H_2O$, as regards both the frequencies and intensities of the maxima, unlike the analogous Fe, Co and Ni complexes, which yield similar spectra with $X = Cl$ or Br. The spectrum of $Cu(phen)_3Cl_2 \cdot 7H_2O$ exhibits two bands, at 14.6 and 6.7 kK, characteristic of a trigonal configuration, as observed for other similar complexes by Faye [2] and Palmer [3]. $Cu(phen)_3Br_2 \cdot 2H_2O$ shows instead, a very strong band with maxima at 12.5 kK and a shoulder at ca. 10 kK, characteristic of a distorted octahedral configuration [2, 4]. When these compounds are heated to 150 and 175°, respectively, i.e. after their total dehydration and after the occurrence of the endothermal reaction involving no base loss at $140 - 160°$ and $150 - 170°$, respectively, the reflectance spectra of the two compounds are fairly similar, with two main bands at $13.8 - 9.2$ kK and $14.2 - 9.3$ kK, respectively. According to Faye [2], these spectra are characteristic of trigonal bipyramidal configurations, while according to Jørgensen [4] the configuration is a strongly tetragonally distorted octahedral one. Without going into considerations not within the scope of our investigation, however, we can infer from the change in the spectra that for these complexes too substitution of a ligand molecule by halogen takes place even before the loss of the first base molecule, which occurs at only 160° and 175°, respectively, for the chloride and bromide complexes.

Discussion

From a study of the TG, DTA and spectroscopic data obtained for complexes of the type $M(phen)_3X_2 \cdot nH_2O$, where $M = Fe$, Co, Ni, Cu and Zn, and $X = Cl$ and Br, some information can be inferred concerning the process of thermal decomposition, of the individual complexes and the influence of the central metal and halogens on their stability.

As observed by several authors [1, 3, 5, 8] all the complexes studied have octahedral configurations except $Cu(phen)_3X_2$ which exhibits marked trigonal or tetragonal distortions [2 − 4]. The complexes lose their crystallization water in one or two stages, usually in the range $40 - 140°$.

The anhydrous complexes begin to decompose, producing the bis derivatives by the reaction: $M(phen)_3X_2 \rightarrow M(phen)_2X_2$ at temperatures ranging between 145 and 200° for the complexes with $X = Cl$, and between 160 and 230° for the complexes with $X = Br$. This reaction, however, does not occur in the case of $Fe(phen)_3Cl_2$, which exhibits as a first stage the elimination of 1.3 moles of phenanthroline.

The temperature at which the tris complexes begin decomposing varies with the central metal: for $M = Fe$, Co, Ni, Cu and Zn the values are 160, 160, 200, 160 and 145°, respectively, when $X = Cl$, and 170, 195, 230, 190 and 160° when $X = Br$. It is evident that the nickel and cobalt complexes have higher thermal stabilities than the complexes with the other metals, and the bromide complexes than the chloride ones.

With many complexes, the occurrence of an endothermal reaction was observed at temperatures $20-30°$ below the beginning of the decomposition of the tris complexes to bis complexes, but not connected with any weight loss. After such a reaction, however, a marked change was generally observed in the reflectance spectra, which differ both from those of the initial hydrated complexes, which are similar to each other.

It is evident, therefore, that dehydration reactions do not involve changes in the co-ordination sphere of the tris complexes, as proved by the reflectance spectra. The endothermal reactions observed prior to the beginning of the decomposition of the tris complexes to bis complexes rather seem to be connected with substitution of the ligand by halogen around the central metal.

The shift of the band maxima takes place, in most cases, towards lower frequencies; considering the respective positions of these ligands in the spectrochemical series, the partial substitution of phenanthroline by halogen in the metal co-ordination sphere can account for the observed band shifts.

There are no changes in the reflectance spectrum prior to the beginning of decomposition to bis complexes in the case of $Ni(phen)_3Br_2$, for which the endothermal reaction shortly prior to the decomposition is not even evident. With $Fe(phen)_3Br_2$ too the spectral change is minimal at $170°$; it should be mentioned only that for these two complexes fairly high values of the activation energy relating to the first base loss were found.

No endothermal reactions are observed with $Co(phen)_3Cl_2$ after dehydration and prior to the loss of phenanthroline, but the reflectance spectrum of the complex at $160°$ differs from that at room temperature. This observation, which agrees with the low value of the activation energy relating to the decomposition of the tris complex, and the fact that generally the transformations for the chlorine compounds always take place at lower temperatures than for the bromine compounds, suggest that the lack of evidence for the endothermal reactions relating to the substitution of the ligand by halogen may be due to the low temperature at which it takes place: the dehydration reaction could mask this reaction.

Only with $Ni(phen)_3X_2$ is a clear exothermal reaction noted at around $210-225°$, irreversible by cooling, and involving no change in the reflectance spectrum: this must be attributed to a recrystallization of the complexes that are stable at these temperatures.

The decomposition of tris complexes to bis complexes + phen generally takes place in several stages, as indicated by the series of endothermal reactions observed in the temperature range in which the TG curves show the loss of 1 base mole. The reactions are fairly slow, and therefore the heights of the peaks and their differentiation are not very marked, chiefly in the Zn, Cu and Co complexes, which begin decomposing at low temperatures with fairly wide thermal intervals. More evident are those for the Ni and Fe complexes, for which the decomposition range is narrower. That the loss of the first mole does not always take place through a single process is also confirmed by the values of E, obtained from the TG curves, which in several cases do not remain constant during this loss.

From a study of the reflectance spectra of the various hydrated or partly calcined compounds it was observed that the octahedral configurations of the tris complexes, partially distorted in some, are retained by the bis complexes. The $M(phen)_2X_2$ complexes, with $M = Fe^{2+}$, Co^{2+} and Ni^{2+}, have an octahedral configuration, characteristic also of the tris complexes. This conclusion was reached by consideration of our reflectance spectra taken after the loss of the first base molecule (or immediately before, when the halogen had already replaced the base, and from the corresponding spectra taken by other authors.

As regards the iron compounds, the spectra obtained are entirely similar to those described by Madeja and König [9] which for $Fe(phen)_2Cl$ show bands with maxima at 535, (600), 950 and 1,180 mμ; for $Fe(phen)_2Br_2$, the maxima are slightly shifted towards higher frequencies compared to those of the chloride complex except for the last one which remains unchanged: 530, (590), 930 and 1,180 mμ. The spectra obtained after calcining at 160° and 270° in the case of the Fe complex with chlorine show a pattern quite similar to those described by Madeja in both number of bands and wavelengths of the maxima: at as low as 160°, i.e. prior to the first base loss, the spectrum shows (because of its resemblance to that of $Fe(phen)_2Cl_2$) that halogen has already partially replaced the base. In the case of this complex, however, unlike what happens with all other complexes studied by us, the first base loss corresponds to 1.3 moles of phenanthroline, with the formation of a complex, $Fe(phen)_{1.7}Cl_2$ in which the octahedral configuration is retained, however, as shown by the reflectance spectra. This configuration may occur with the Fe/phen ratio observed only if we assume the formation of partially polymeric compounds, with some halogen atoms bridging two metal atoms.

Further, for the complex of Fe with Br the spectra obtained after calcining at 175° and 270° show that the complex still displays an octahedral configuration. At 175° the spectrum more closely resembles that of the uncalcined complex, but a certain variation of the maxima is undeniable. At 270° the spectrum bands are similar to those reported by Madeja et al., i.e. 530, (590), 930 and 1,180 mμ. It can therefore be stated that with this complex too the partial substitution of phenanthroline by bromine may start at as low as 170°, prior to the elimination of the base, but this substitution takes place with greater difficulty compared to the corresponding complex with chlorine.

As regards the Ni complexes, it was observed that the initial spectrum of the typical octahedral tris complexes does not change with the loss of the first mole of base, but only shows systematic shifts towards lower frequencies. Our spectrum of $Ni(phen)_2Cl_2$ exhibits a band with maximum at $600-610$ mμ and a broad band with maximum at about 1,000 mμ.

Harris and McKenzie [10], and Leet et al. [11] studied a similar complex, $Ni(bipy)_2Cl_2$, which has a very similar absorption spectrum: a band with maximum at $605-622$ mμ and a broad band with maximum at 1,050 mμ, and on the basis of magnetic measurements attributed a cis octahedral configuration to such complexes.

The $Ni(phen)_2Br_2$ spectrum is very similar, but is obtained, unlike the chlorine

product, only after the loss of the first mole of base and after the subsequent endothermal reaction unconnected with weight losses at between 300 and 340°.

For $Co(phen)_2Cl_2$ we have a reflectance spectrum showing a pattern similar to that of the corresponding Ni bis complex: a band with maximum at 510 mμ and a broad band with maximum at approx. 1,100 mμ very similar to the spectrum reported by [8].

The analogous complex, $Co(bipy)_2Cl_2$, has been studied by several authors [5, 11]; it exhibits a spectrum with maxima at 510 mμ and approx. 1,150 mμ according to [11], or at 610 mμ and 1,280 mμ according to [5]. In the case of Co complexes too, both the chloride and the bromide derivatives, the absorption spectra are typical of an octahedral configuration.

Concerning the configuration of the copper tris complexes, it has already been pointed out that in the respective reflectance spectra the compounds with $X = Cl^-$ or Br^- display rather different situations, with octahedral symmetries, distorted perhaps less strongly in the case of the bromide complex, but with strong trigonal distortion in the chloride complex. At between 140 and 160°, concurrently with the endothermal relation involving no weight change, the two complexes show a sharp change in their initial spectrum and at such temperatures give rise to similar configurations, regardless of the halogen replacing the base. The configuration of the complexes under such conditions is still controversial, as some authors mention a strongly tetragonally distorted configuration [4], while others [2, 3] consider the spectra to correspond to trigonal bipyramidal configurations.

As regards the thermal stabilities of these complexes, some indication may be obtained by considering the temperatures at which the thermal decompositions of the anhydrous tris complexes to bis complexes begin; the values of the activation energies for this process are not very informative, however, possibly because the mechanisms through which the first base fraction is eliminated differ widely from complex to complex.

Considering the temperatures at which decomposition begins, it may be said that the greatest stability is displayed by the Ni complexes (220 — 230° for $X = Cl^-$ or Br^-) and the lowest by the Zn complexes (145 — 160°). The values for Fe, Co and Cu are roughly similar (160 — 190°).

A certain similarity exists with the stabilities observed by Banks and Bystoff [12] for such complexes in solution; $Ni(phen)_3^{++}$ has a $\log \beta_3$ value of 23.9 and $Zn(phen)_3^{++}$ of 17; the other ions (Fe, Co, Cu) $(phen)_3^{++}$ exhibit values that are not much different: 21.5, 20.1 and 20.4 respectively.

An explanation for the observed pattern of thermal stabilities can also be acquired by considering at the same time the effect of the CFSE (greatest for Fe and decreasing to Zn) and the electrostatic attraction, which increases as the ionic radius decreases from Fe(II) to Cu(II). We can therefore account for the maximum stability in the Ni complexes by considering that the rigidity of the ligand molecule contributes for its part to the lower stability of the Cu complexes because of the lack of the tetragonal distortion required by the Jahn — Teller stabilization of the d^9 system.

A further investigation with other types of less rigid ligands is now in progress, with a view to obtaining a better understanding of the effect of the nature of the ligand on the thermal stabilities of the complexes containing metals of the first transition series.

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RÉSUMÉ. On a étudié, par TG, ATD et par spectroscopie, une série de complexes des métaux de transition de formule $[M(o\text{-phén})_3]X_2$, où $M = Fe^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} et $X = Cl^-$, Br^-, dans le but de connaître le mécanisme de la décomposition thermique, l'influence du métal M et des halogènes sur la stabilité de ces complexes et les modifications stéréochimiques provoquées par le chauffage.

Par ATD et par TG, on a observé que les complexes, après déshydratation, se décomposent généralement après une réaction endothermique qui met en jeu la substitution partielle de la base dans la sphère de coordination du métal avec l'halogène, comme l'indiquent les spectres de réflexion. La première perte de poids correspond généralement au départ d'une mole de phénanthroline et conduit aux complexes bis.

En comparant les températures initiales de décomposition, il apparaît que la stabilité dépend de la nature du métal central et de l'halogène, suivant l'ordre: Ni > Fe = Co = Cu > < Zn et Br⁻ < Cl⁻.

ZUSAMMENFASSUNG — Eine Reihe von Übergangsmetallkomplexen mit $[Me(o\text{-phen})_3]X_2$, $M = Fe^{2+}$, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+} und $X = Cl^-$, Br^-, wurden durch TG, DTA und spektroskopische Methoden untersucht um Informationen über den thermischen Zersetzungsmechanismus, den Einschuß des zentralen Metalls, sowie der Halogene auf die Stabilität dieser Komplexe und die erhitzungsbedingten stereochemischen Änderungen zu erhalten.

An Hand der DTA und TG wurde beobachtet, daß die Zersetzung der Komplexe nach ihrer Dehydrierung gewöhnlich nach einer endothermen Reaktion erfolgt, in welcher die teilweise Substituierung der Base in der Koordinationssphäre des Metalls durch das Halogen mit inbegriffen ist, wie dies aus den Reflexionsspektra ersichtlich ist. Der erste Basengewichtsverlust entspricht im allgemeinen einem Mol Phenantrolin, welches die Bis-Komplexe ergibt.

Durch Beobachtung der Anfangstemperaturen der Zersetzungsprozesse ist ersichtlich, daß die Stabilität hinsichtlich des zentralen Metalls in folgender Reihenfolge abnimmt: $Ni > Fe \cong Co \cong Cu > Zn$ und hinsichtlich des Halogens in folgender Ordnung: $Br^- > Cl^-$.

Резюме — Методами ТГ, ДТА и спектроскопии изучен ряд комплексов переходных металлов [M (о-фен.)$_3$] X$_2$, где M = Fe^{2+}, Co^{2+}, Ni^{2+}, Zn^{2+} и X = Cl^-, Br^-, с целью получения информации о механизме термораспада, влиянии центрального металла и галогенов на стабильность этих комплексов и о стереохимических изменения, вызванных нагреванием. Из данных ДТА и ТГ установлено, что комплексы распадаются после их дегидратации, обычно после эндотермической реакции, включающей частичное замещение основания в координационной сфере металла галогеном, как это видно из спектра отражения. Первая основная потеря веса соответствует одному молю фенантролина, дающего бискомплексы.

На основании начальной температуры распада можно сделать вывод, что стабильность в зависимости от центрального металла изменяется в следующем порядке: $Ni > Fe \cong Co \cong Cu > Zn$, а в зависимости от галогена в следующем: $Br^- > Cl^-$.