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THE THERMOPHOTOMETRY OF SOME COORDINATION COMPOUNDS

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ABSTRACT

The thermophotometry (light emission) of a number of coordination compounds containing vigorous oxidizing groups in the ionization sphere and reducing groups in the coordination sphere was determined. A total of 50 such compounds were studied of which 16 exhibited some light emission during the thermal dissociation reaction. The presence of the light emission peaks and their correlation with composition of the compounds are discussed.

INTRODUCTION

The light emission or thermophotometry [1] of Alathon 1 [2], various other polymers [3], and of miscellaneous substances [4], has been studied by various detection devices in this laboratory since about 1970. It is inferred from the previous investigation of polymers that the initial light emission in all atmospheres is the result of oxyluminescence associated with the formation of hydroperoxide radical intermediates. Subsequent light emission in air and oxygen also manifests oxyluminescence although a weaker phenomenon, noted as chemiluminescence, was observed in nitrogen atmospheres. Except for 66 Nylon, no correlation was observed between light emission and melting. It was noted that there was a clear relationship between the observed light emission of the polymer and its thermal degradation.

The use of light emission techniques to detect ignition temperatures of various substances was investigated by Collins and Wendlandt [4]. Ignition temperature, as used by these authors, referred to the temperature at which the first light emission, due to the combustion of the sample, was detected. It was found that the major instrumental factor which affects the ignition temperature was the sample heating rate. Generally, as the heating rate increased, the ignition temperature increased according to an approximately linear relationship. Some substances were observed to char without ignition if the heating rate was too slow, thus, fast heating rates, usually above 50°C min^{-1}, were recommended.

The light emission or thermophotometry observed during the thermal dissociation of selected coordination compounds is the subject of this investigation. It is well known [5] that transition metal coordination compounds containing vigorous oxidizing groups in the ionization sphere and reducing ligands such as ammonia or amines in the coordination sphere dissociate very rapidly on heating. In certain cases, the thermal dissociation reaction is of explosive violence suggesting their use as detonators or explosives for various applications. In most cases, the rapid thermal dissociation of these compounds has been mainly investigated by the thermal analysis techniques of TG, DTA and DSC. The highly exothermic nature of these reactions results in rather spectacular DTA and DSC curves using small (1 or 2 mg) quantities of samples. With TG, the ensuing rapid dissociation reaction yields an almost vertical displacement of the curve on the mass-loss axis. Since these vigorous thermal dissociation reactions should be accompanied by light emission, the technique of thermophotometry is immediately suggested as another means for their investigation.

EXPERIMENTAL

Thermophotometry apparatus

The construction and use of this apparatus is described elsewhere [6]. In general, the furnace heating rate used was 13°C min^{-1} on samples with a mass of 5—10 mg. An air atmosphere at 1 atm pressure was employed.

Thermobalance

The thermobalance employed was the Perkin-Elmer Model TGS-2. A three-channel recorder (Linear Instruments, Irvine, CA) was used to record the sample mass-loss, first derivative of the sample mass-loss, and the furnace temperature, all as a function of time. Sample mass-loss was recorded as percent mass-loss on samples with a mass of 5—9 mg heated at 10°C min^{-1} in a flowing N_2 atmosphere.

DTA apparatus

The DTA measurements were carried out on a laboratory assembled apparatus. The DTA curve was recorded on an X—Y type plotter. Sample sizes ranged in mass between 5—10 mg and were heated at a rate of 10°C min^{-1} in a flowing N_2 atmosphere.

Coordination compounds

The coordination compounds used were laboratory samples prepared for studies which have previously been described [7—10].

RESULTS AND DISCUSSION

The thermophotometric (light emission) curves of coordination compounds that exhibited this phenomena are illustrated in Figs. 1—4.

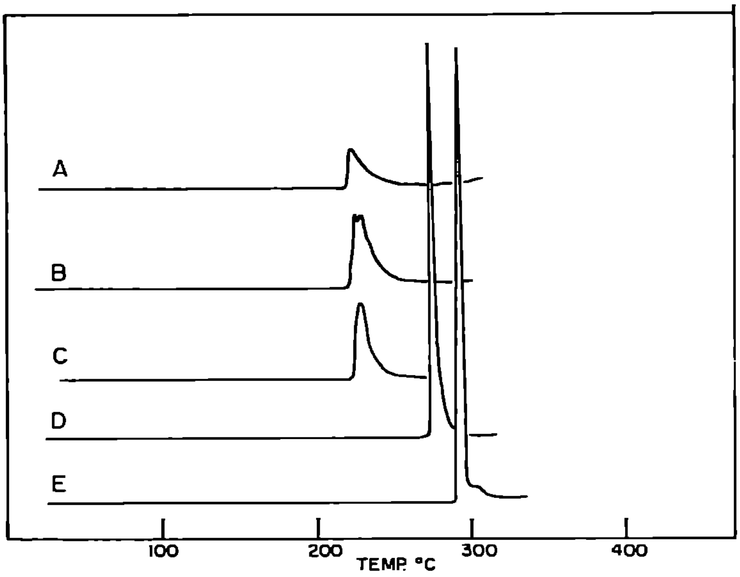

Fig. 1. Light emission curves of some coordination compounds. A, α-*cis*[Co(trien)-$(NO_2)_2$]Cl; B, [Co(dien)$(NO_3)_3$]; C, [Co(dien)$NH_3(NO_2)_2$]Cl; D, *cis*-[Co$(en)_2(NO_2)_2$]-NO_3; E, [Co$(NH_3)_4$en]$(NO_3)_3$.

Preliminary studies of about 50 compounds, all containing reducing and oxidizing ligands, showed that 16 of them exhibited some light emission during their decomposition reaction. These 16 compounds, as listed in Table 1, produced various amounts of light emission. Some compounds gave pronounced peaks in the curve, which often went off the recorder chart scale, while others, using the identical photometric sensitivity, gave only a small peak. The peaks in the curves, with the exception of [Cr$(NH_3)_5NO_2$]

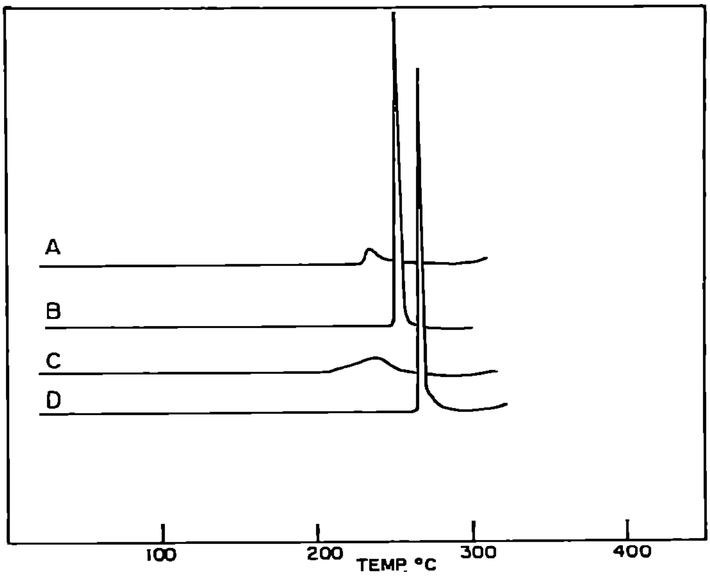

Fig. 2. Light emission curves of some coordination compounds. A, [Co(dien)Cl$(NO_2)_2$]; B, *trans*-[Co$(en)_2(NO_3)_2$]NO_3; C, *trans*-[Co$(en)_2Cl_2$]NO_3; D, *cis*-[Co$(en)_2(NO_3)_2$]NO_3.

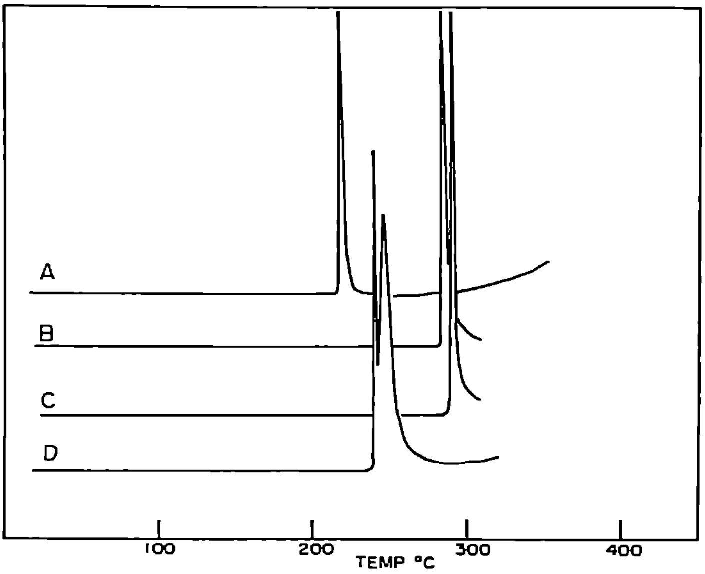

Fig. 3. Light emission curves of some coordination compounds. A, $\mathrm{Na[Co(acac)_2(NO_2)_2]}$; B, $\mathrm{[Co(en)_3](ClO_4)_3}$; C, $\mathrm{[Co(en)_3](NO_3)_3}$; D, $\mathrm{[Co({}^{OH}_{OH}{>}Co(en)_2]_3(NO_3)_6}$.

$(NO_3)_2$, all appeared in the temperature range 200—300°C. Although not investigated, the position of the light emission with respect to the temperature axis is probably dependent on the furnace heating rate, as are other thermal analysis data.

For the cobalt(III) compounds investigated, light emission during dissociation is linked with the presence of a carbon-containing ligand such as en, dien, trien, etc. Compounds that contained only ammonia ligands, such as

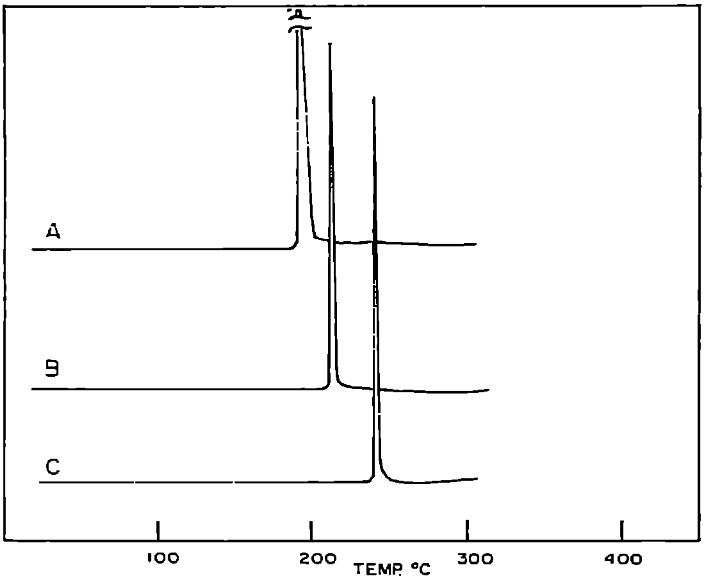

Fig. 4. Light emission curves of some coordination compounds. A, $\mathrm{[Cr(NH_3)_5NO_2](NO_3)_2}$; B, $\mathrm{[Cr(NH_3)_5NO_3](NO_3)_2 \cdot NH_4NO_3}$; C, $\mathrm{[Co(mal)(NH_3)_4]NO_3 \cdot 6\ H_2O}$.

TABLE 1

Light emission of some coordination compounds

Compound [a]	Temp. (°C)	Light emission peak		
		Small	Medium	Large
1 $[Co(NH_3)_4en](NO_3)_3$	290			X
2 $[Co(dien)(NH_3)(NO_3)_2]Cl$	225	X		
3 *cis*-$[Co(en)_2(NO_2)_2]NO_3$	272			X
4 α-*cis*-$[Co(trien)(NO_2)_2]Cl$	220	X		
5 $[Co(dien)(NO_3)_3]$	222	X		
6 *cis*-$[Co(en)_2(NO_3)_2]NO_3$	265			X
7 *trans*-$[Co(en)_2Cl_2]NO_3$	205	X		
8 $[Co(dien)Cl(NO_2)_2]$	230	X		
9 *trans*-$[Co(en)_2(NO_3)_2]NO_3$	250			X
10  $[Co(\overset{OH}{\underset{OH}{>}}Co(en)_2)_3](NO_3)_6$	240		X	
11 $[Co(en)_3](NO_3)_3$	290			X
12 $[Co(mal)(NH_3)_4]NO_3 \cdot 6\ H_2O$	240			X
13 $Na[Co(acac)_2(NO_2)_2]$	215			X
14 $[Co(en)_3](ClO_4)_3$	282			X
15 $[Cr(NH_3)_5NO_2](NO_3)_2$	190			X
16 $[Cr(NH_3)_5NO_3](NO_3)_2 \cdot NH_4NO_3$	210			X

[a] Abbreviations employed: en = ethylenediamine; trien = triaminotriethylamine; dien = diethylenetriamine; acac = acetylacetone; mal = malonate.

$[Co(NH_3)_6](NO_3)_3$, $NH_4[Co(NH_3)_2NO_2$ oxalate], $[Co(NH_3)_4(NO_3)_2]NO_3$, $[Co(NH_3)_4CO_3]NO_3$, etc. did not exhibit light emission. However, compounds containing ammonia and one or more of the carbon-containing ligands mentioned previously generally did exhibit light emission, such as $[Co(mal)(NH_3)_4]NO_3 \cdot 6\ H_2O$, $[Co(dien)NH_3(NO_2)_2]Cl$, $[Co(NH_3)_4en](NO_3)_3$, etc. The oxidizing group in most cases was either the nitrate (NO_3^-) or nitrite (NO_2^-) ion. Several nickel(II), rhodium(III) and platinum(II) compounds investigated did not exhibit light emission during their dissociation reactions, although neither did their en analogs, $[Ni(en)_3](NO_3)_2$ and $[Rh(en)_2Cl_2]NO_3$, for example. On the other hand, the chromium(III) ammine compounds, $[Cr(NH_3)_5NO_2](NO_3)_2$ and $[Cr(NH_3)_5NO_3](NO_3)_2 \cdot NH_4NO_3$, did emit light. No en compounds were investigated, so the presence of a carbon-containing compound on the light emission properties could not be ascertained.

The starting temperature for the light emissions of the compounds shown in Figs. 1—4 are given in Table 1. Most of the light-emission curve peaks were quite narrow, except for those compounds containing the dien ligand.

Typical TG and DTG curves for one of the coordination compounds are given in Fig. 5. Due to the rapid dissociation reaction, the TG curve of *cis*-$[Co(en)_2(NO_2)_2]NO_3$ exhibited a practically vertical decrease in mass at about 260°C. The DTG curve indicated this rapid change by the presence of a narrow curve peak.

Rapid exothermic dissociation reactions are also revealed by the DTA

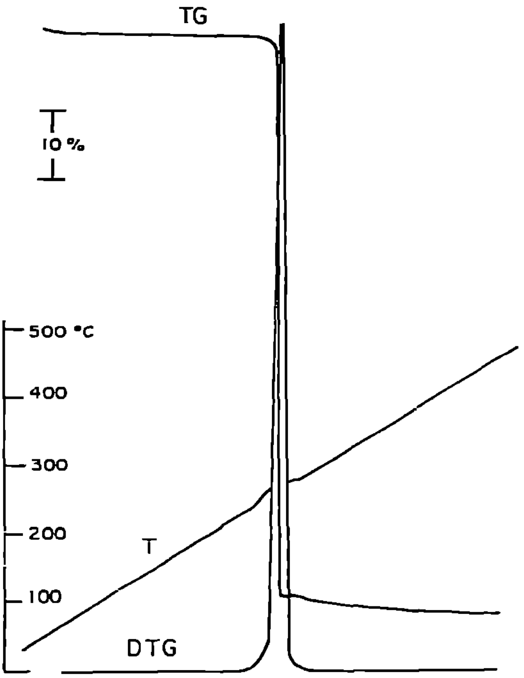

Fig. 5. TG and DTG curves of *cis*-$[\mathrm{Co(en)_2(NO_2)_2}]\mathrm{NO_3}$.

curves for four of the compounds in Fig. 6. Except for the small endothermic peak in the DTA curve of $[\mathrm{Co}(^{\mathrm{OH}}_{\mathrm{OH}}{>}\mathrm{Co(en)_2})_3](\mathrm{NO_3})_6$ caused by the olation reaction [11,12], all of the curves contained large exothermic peaks in the 200—300°C temperature range. This is to be expected due to the presence of the oxidizing and reducing groups in the compounds.

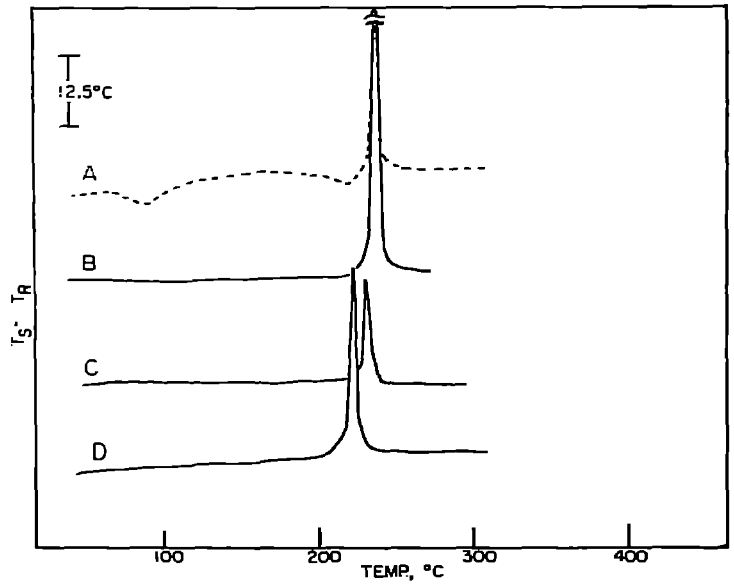

Fig. 6. DTA curves of some coordination compounds. A, $[\mathrm{Co}(^{\mathrm{OH}}_{\mathrm{OH}}{>}\mathrm{Co(en)_2})_3](\mathrm{NO_3})_6$; B, $[\mathrm{Co(dien)NH_3(NO_2)_2}]\mathrm{Cl}$; C, $[\mathrm{Co(dien)Cl(NO_2)_2}]$; D, $[\mathrm{Co(dien)(NO_3)_3}]$.

ACKNOWLEDGEMENT

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