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SIMULTANEOUS LIGHT EMISSION—DIFFERENTIAL THERMAL ANALYSIS OF SELECTED COORDINATION COMPOUNDS *

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ABSTRACT

A new apparatus which permits the simultaneous determination of both the light emission (LE) and differential thermal analysis (DTA) curves of a compound is described. LE—DTA curves are reported for a selected number of coordination compounds, each containing vigorous reducing—oxidizing ligands or ions. New LE curve peaks are reported for $[Co(NH_3)_6](NO_3)_3$, $[Ni(en)_3](NO_3)_2$, and $[Rh(NH_3)_5X](NO_3)_2$ (X = Cl, Br on NO_3) complexes. Multiple LE peaks were found for [Co dien $(NO_3)_3$], *cis*-$[Co(en)_2(NO_2)_2]$ NO_2 and [Co dien $NH_3(NO_2)_2$]Cl. The presence of carbon-containing reducing ligand is not necessary in order to obtain a LE peak during the thermal dissociation process.

INTRODUCTION

The thermally stimulated light emission (LE) or thermophotometry [1] of a group of selected coordination compounds has previously been reported [2,3]. All of the compounds that exhibited light emission contained vigorous oxidizing and reducing ligands or ions and were of the general formula, $[ML_x]A_y$, where L is the reducing group and A the oxidizing group. These compounds dissociated very rapidly at some elevated temperature during which time visible light was emitted. The light emission process, compared with the total enthalpic effect, was quite rapid, of the order of several seconds at the most.

Of fifty coordination compounds investigated, only sixteen exhibited light emission under the experimental conditions employed. Some of these compounds gave sharp pronounced curve peaks, which often went off the recorder chart scale, while others, using identical conditions, gave only a small curve peak. Of the cobalt(III) compounds studied, light emission during thermal dissociation was linked with the presence of carbon-containing ligands such as en, dien, trien, etc. Complexes that contained only ammonia ligands, such as $[Co(NH_3)_6](NO_3)_3$, $NH_4[Co(NH_3)_2NO_2$ oxalate], $[Co(NH_3)_4(NO_3)_2]NO_3$, etc., did not exhibit light emission. Also, several nickel(II), rhodium(III), and platinum(II) compounds did not exhibit light

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emission during their thermal dissociation reactions, irrespective of the fact that they contained en or NH_3 ligands.

Using a newly constructed simultaneous LE—DTA apparatus, it was found that light emission did indeed occur in certain complexes although they did not contain carbon-containing reducing ligands. Using this apparatus, not only could the LE curves be recorded but also the DTA curves of the dissociation reactions. The DTA curves of these compounds, as expected, were all highly exothermic in nature.

EXPERIMENTAL

Apparatus

The LE—DTA apparatus, which is similar to that previously described [3], is schematically illustrated in Fig. 1.

The aluminum furnace block was replaced by a quartz tube, F, 25 mm in diameter by 50 mm in length, on which was wound a Nichrome wire heating element. The sample and reference containers, G and H, were placed on a nickel thermoelectric plate, I, to which three thermocouple wires, two Alumel and one Chromel, were attached. The two Alumel wires were used for the differential temperature measurement, $T_s - T_r$, while the Chromel wire, along with one of the Alumel wires, was used as the sample temperature, T_s, detector. The other parts of the furnace and sample holder were identical to the previous apparatus [3].

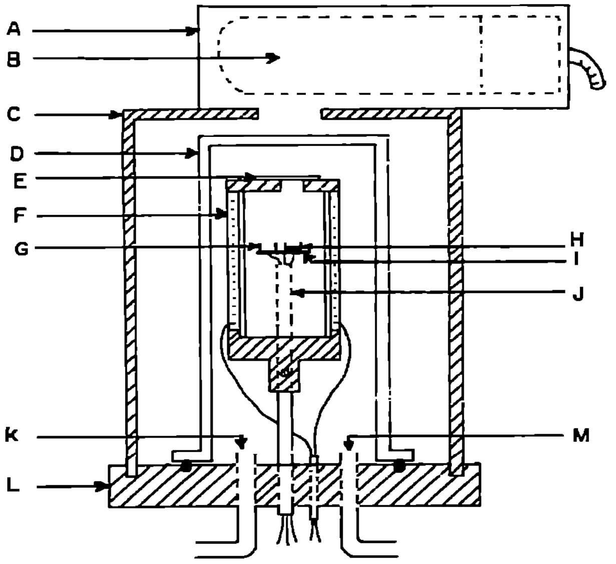

Fig. 1. Schematic diagram of furnace, sample holder and enclosure. A, photomultiplier tube housing; B, 1P28 photomultiplier tube; C, aluminum enclosure (light-tight); D, glass enclosure; E, cover glass; F, furnace; G, reference container; H, sample and sample container; I, nickel thermoelectric plate; J, ceramic tube for thermocouple wires; K, gas inlet port; L, aluminum base; and M, gas outlet port.

The external equipment such as the photometer, X—Y plotter and furnace temperature programmer was the same as previously described [3]. A microvolt amplifier and X—Y plotter were added to process the $T_s - T_r$ signal and record it as the DTA curve of the sample.

Procedure

The procedure employed is similar to that of the earlier apparatus [2,3]. The sample is weighed out into the aluminum container (usually 5—10 mg) and placed on the nickel thermoelectric plate located in the furnace chamber. The furnace chamber is then flushed with nitrogen gas at atmospheric pressure. A furnace heating rate of 20°C min^{-1} was employed for all of the runs. Although capable of higher maximum temperatures, all runs were carried out to maximum temperatures of less than 400°C.

Coordination compounds

The compounds used were all laboratory samples prepared for previously reported investigations [2].

RESULTS AND DISCUSSION

Using the simultaneous LE—DTA technique, it was possible to correlate the dissociation reaction enthalpic effect with the light emission process. Such data are shown in Fig. 2, where the simultaneous LE—DTA curves of

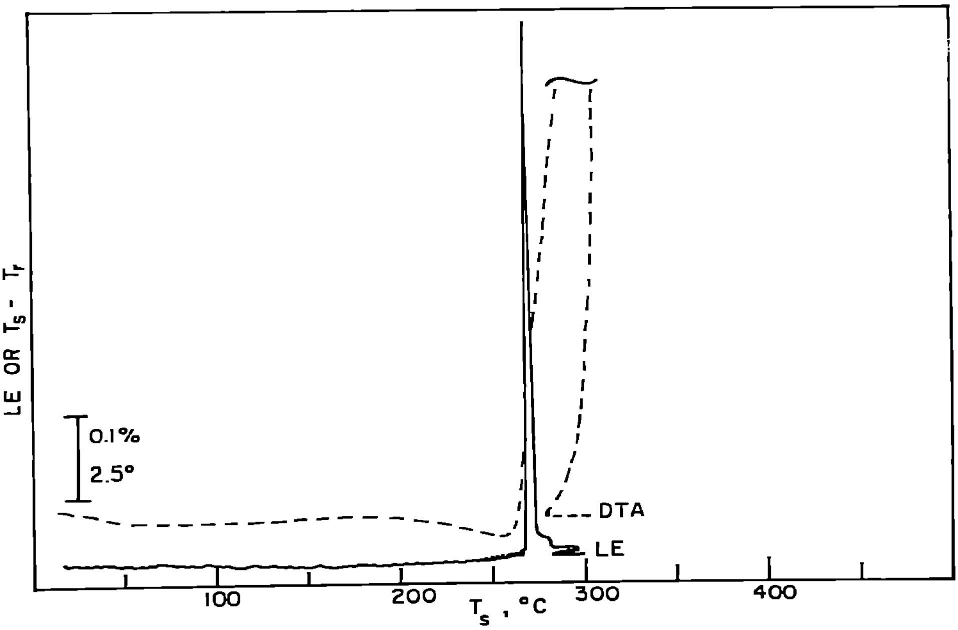

Fig. 2. LE—DTA curves of $[Co(NH_3)_6](NO_3)_3$.

$[Co(NH_3)_6](NO_3)_3$ are presented. The thermal dissociation of this compound has previously been reported by Wendlandt [4] who found that the complex reaction followed the stoichiometry

$$12\ [Co(NH_3)_6](NO_3)_3 \rightarrow 4\ Co_3O_4 + 18\ NH_3 + 7\ N_2 + 73\ H_2O + 4\ NH_4NO_3 + 32\ N_2$$

The thermal dissociation reaction, as expected, was highly exothermic in nature, as indicated by the DTA curve peak.

The data shown here indicate that light emission does occur during the thermal reaction, a result which was not previously indicated [2]. The reason for this discrepancy is probably twofold: (a) increased photometric sensitivity, and (b) geometry of the furnace chamber and sample holder. The latter may contribute to the ignition of the rapidly evolved dissociation products, hence, the presence of a light emission curve peak. Also, it should be noted that the DTA curve peak is very asymmetric due to the plotting of $(T_s - T_r)$ versus the sample temperature, T_s. The vigorous exothermic reaction results in a large temperature increase of the nickel thermoelectric plate, which on termination of the reaction, cools slowly due to the time constant of the system. All of the DTA curves presented here exhibit this behavior. The LE curves are more symmetrical due to the shorter reaction time period.

The LE—DTA curves of $[Co(en)_3](NO_3)_3$ are given in Fig. 3. The thermal dissociation of this compound has previously been reported by Collins et al. [5] in 1973. They reported that the reaction takes place in two steps (not

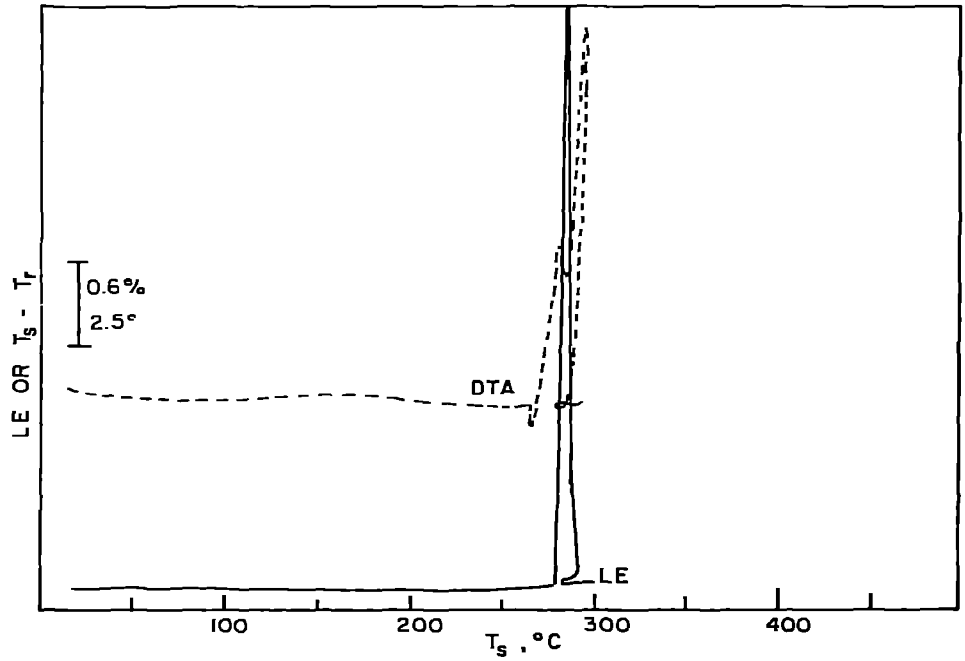

Fig. 3. LE—DTA curves of $[Co(en)_3](NO_3)_3$.

balanced)

$[Co(en)_3](NO_3)_3 \rightarrow Co(NO_3)_2 + NH_4NO_3 + en + \text{organic products}$

$Co(NO_3)_2 \rightarrow Co_3O_4 + Co + N_2O + N_2 + \text{nitrogen oxides}$

Wendlandt [2] found that the compound exhibited light emission during the thermal dissociation reaction and this behavior is confirmed here.

The LE curve peak is very large compared with that found for $[Co(NH_3)_6](NO_3)_3$ previously discussed. As indicated by the highly exothermic DTA curve peaks, the reaction starts out endothermically and then becomes highly exothermic, involving perhaps several reactions.

Several of the compounds investigated here exhibited two stages of dissociation which resulted in LE—DTA curve peaks in two temperature ranges, 200—300°C and 300—400°C, respectively. The two compounds, $[Co\ dien\ NH_3(NO_2)_2]Cl$ and $[Co\ dien\ (NO_3)_3]$, are shown in Figs. 4 and 5, respectively.

For $[Co\ dien\ NH_3(NO_2)_2]Cl$, light emission was found to occur beginning at 240°C and 325°C; a fairly broad peak was found during the former temperature, which, according to the DTA curve, was the main dissociation reaction. The second LE curve peak was quite narrow and was found to occur during the second, smaller dissociation reaction (as indicated by the DTA curve).

Contrary to the compound previously discussed, $[Co\ dien\ (NO_3)_3]$ appears to dissociate according to two equal reactions, both of which are accompanied by LE curve peaks. The LE peaks are about equal in magnitude, one begins at 215°C, the other at 305°C. According to the TG curve (not

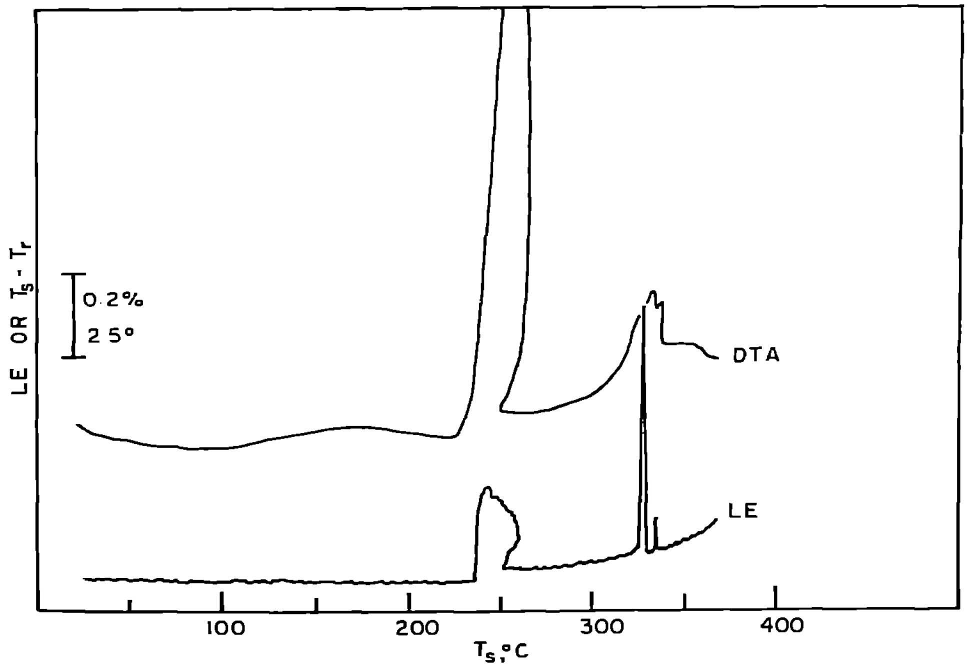

Fig. 4. LE—DTA curves of $[Co\ dien\ NH_3(NO_2)_2]Cl$.

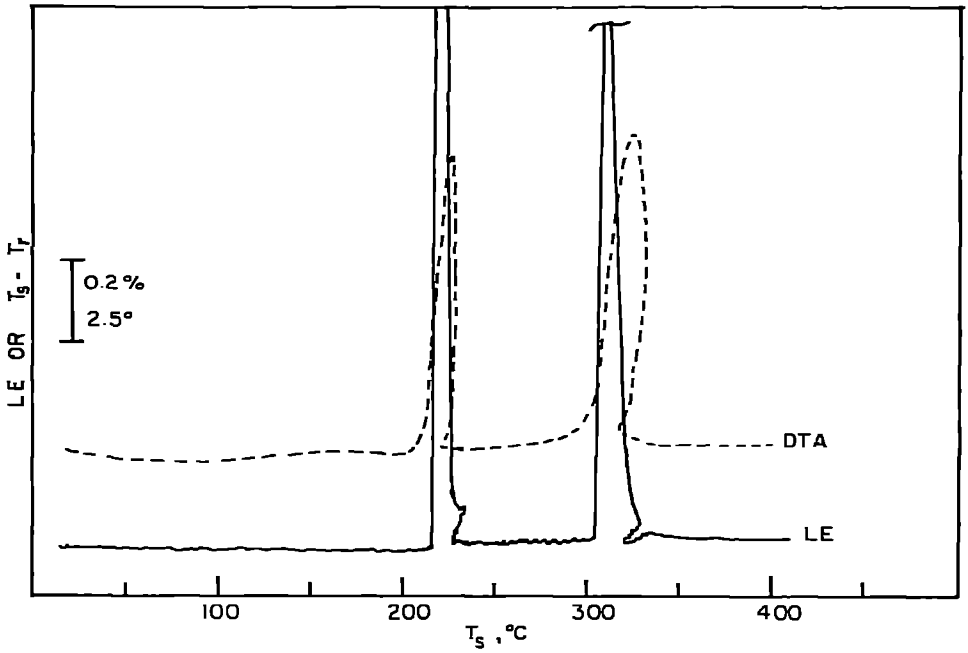

Fig. 5. LE—DTA curves of [Co dien $(NO_3)_3$].

shown), most of the mass loss occurs during the first step (about 59%) compared with the second step (about 15%). However, the DTA curve peak for the second reaction appears to be somewhat larger than the first peak.

Contrary to the previous report [2], light emission was found to occur

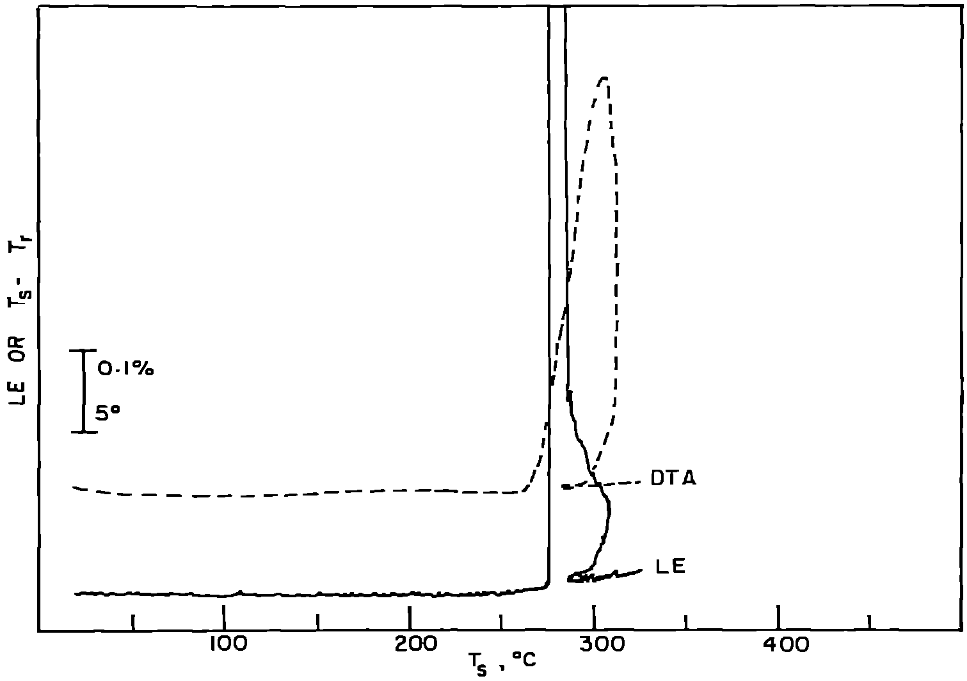

Fig. 6. LE—DTA curves of $[Ni(en)_3](NO_3)_2$.

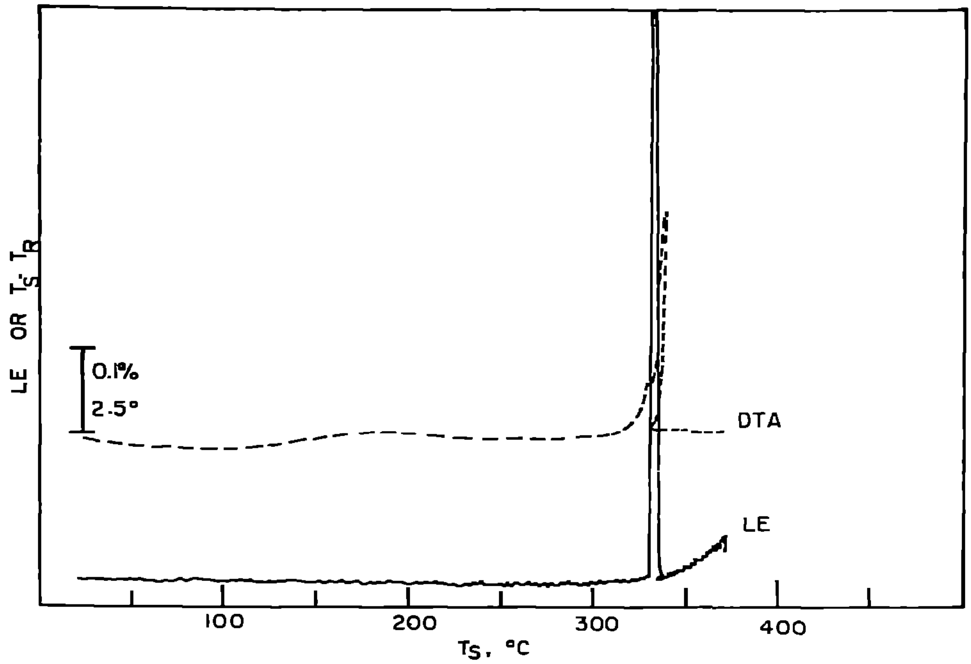

Fig. 7. LE—DTA curves of $[Rh(NH_3)_5NO_3](NO_3)_2$.

during the thermal dissociation of $[Ni(en)_3](NO_3)_2$, as shown by the curves in Fig. 6.

A rather large LE curve, beginning at about 275°C, was found during the thermal dissociation of $[Ni(en)_3](NO_3)_2$. However, light emission was not found during the thermal dissociation of the ammonia analog, $[Ni(NH_3)_6](NO_3)_2$ (not shown). In the case of $[Ni(en)_3](NO_3)_2$, this is the first time that light emission has been reported for any nickel(II) compound.

It was also found in this investigation that selected rhodium(III) com-

TABLE 1

Light emission of some coordination compounds

Compound	Approx. beginning temp. (°C)
$[Co(NH_3)_6](NO_3)_3$ *	265
$[Ni(en)_3](NO_3)_2$ *	275
$[Co\text{-}dien(NO_3)_3]$	215, 305 **
cis-$[Co(en)_2(NO_2)_2]NO_2$	245, 345 **
$[Co\text{-}dien\text{-}NH_3(NO_2)_2]Cl$	235, 325 **
$[Rh(NH_3)_5Br](NO_3)_2$ *	350
$[Rh(NH_3)_5Cl](NO_3)_2$ *	345
$[Rh(NH_3)_5NO_3](NO_3)_2$ *	330

* Compound not previously reported [2].
** Multiple LE peaks.

plexes exhibited LE, as shown by $[Rh(NH_3)_5NO_3](NO_3)_2$ in Fig. 7.

Although higher temperatures are involved, $[Rh(NH_3)_5NO_3](NO_3)_2$ had a sharp LE peak beginning at about 330°C. Similar results were found for $[Rh(NH_3)_5Br](NO_3)_2$ and $[Rh(NH_3)_5Cl](NO_3)_2$.

The results obtained here using the simultaneous LE—DTA technique indicates that the presence of a carbon-containing ligand is not necessary in order to obtain a LE peak during the thermal dissociation reaction. New LE curve peaks for the various compounds are shown in Table 1. Multiple LE curve peaks are reported also for compounds which previously had only a single LE peak. These compounds, however, still contain a reducing ligand with carbon—carbon or carbon—nitrogen bonds.

ACKNOWLEDGEMENT

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