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THE THERMAL LIGHT EMISSION OF *cis*-$[Co(en)_2(NO_2)_2]NO_2$ and *cis*- and *trans*-$[Co(en)_2(NO_2)_2]NO_3$

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ABSTRACT

The TG, DTA and light emission (LE) curves of *cis*- and *trans*-$[Co(en)_2(NO_2)_2]NO_3$ and the LE curve of *cis*-$[Co(en)_2(NO_2)_2]NO_2$ were determined. The TG and DTA curves indicated very rapid, highly exothermic thermal dissociation reactions, as expected. Short duration (2–3 s) bursts of radiation, as seen in the LE curves, accompanied the dissociation reactions. The light emission is highly dependent upon the ease with which electron transfer can occur between species in the redox process. Examination of structural information for these compounds indicates the presence of significant hydrogen bonds between oxidizing and reducing groups, which may facilitate this reaction by providing a convenient pathway for electron transfer.

INTRODUCTION

Previous studies in this laboratory have shown that some transition metal amine coordination compounds containing oxidizing and reducing ligands or ions exhibit short duration light emission on thermal decomposition [1–4]. The dissociation reaction is highly exothermic (about 100 kJ mol^{-1}), which suggests their use as detonators or explosives for military application. The thermal light emission is of short duration (about 2–3 s) at a heating rate of 20 °C min^{-1} and is found mainly in the 200–300 °C temperature range and, occasionally, at temperatures above 300 °C. In most cases, only a single light emission peak is observed; however, certain compounds exhibit two or more such peaks.

We have previously suggested that the occurrence of thermal light emission might be linked to the ease of electron transfer in a redox process, and that the extensive hydrogen bonding present in some transition metal amine complexes might facilitate this process [4]. In an attempt to discover more about the light emission mechanism of these compounds, a series of

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cobalt(III) ethylenediamine complexes containing nitrite (NO_2^-) and nitrate (NO_3^-) groups in the coordination and/or ionization spheres was studied. The crystal structures of *cis*-$[Co(en)_2(NO_2)_2]NO_2$ and *cis*- and *trans*-$[Co(en)_2(NO_2)_2]NO_3$ are known [5–7] and perhaps, from the positions and interactions of neighboring groups, a more thorough understanding of the light emission mechanism can be obtained.

EXPERIMENTAL

Emission thermophotometry apparatus

The emission thermophotometry (ETP) apparatus has been described previously [8]. A furnace heating rate of 20 °C min^{-1} was employed on samples ranging in mass from 5 to 10 mg. A static air atmosphere was present in the furnace chamber. No corrections were necessary for background radiation, even at high photometric sensitivities.

TG and DTA instruments

A Deltatherm V system Model D8100 DTA instrument was used for the DTA studies and ΔH_t determinations [9]. Samples sizes employed were 5–10 mg, and samples were studied at a furnace heating rate of 10 °C min^{-1}. A static air atmosphere was present in the furnace chamber for all DTA studies, while a dynamic nitrogen atmosphere (flow rate 40 mL min^{-1}) was used for the ΔH_t determinations. The instrument was calibrated for the ΔH_t determinations using the fusion enthalpies of indium, tin and lead, as previously described [9].

A Perkin–Elmer TGS-2 thermobalance was used for the TG studies. Sample ranging in mass from 1 to 4 mg were heated in a dynamic nitrogen furnace atmosphere (flow rate 40 ml min^{-1}). All TG curves were obtained using a furnace heating rate of 10 °C min^{-1}.

Syntheses of complexes

The samples of both *cis*- and *trans*-$[Co(en)_2(NO_2)_2]NO_3$ (**I** and **II**, respectively) used in these studies were prepared as described in the literature [10]. The nitrite compounds was prepared from *trans*-$[Co(en)_2(NO_2)_2]Cl \cdot HCl$ [11(a)], which, using the procedure of Bailar [11(b)], was transformed into *cis*-$[Co(en)_2Cl_2]Cl$ and, finally, converted to *cis*-$[Co(en)_2(NO_2)_2]NO_2$ (**III**) by reacting with a large excess of sodium nitrite.

The crystal structure of *cis*-$[Co(en)_2(NO_2)_2]NO_2$ was determined in our laboratory and is reported elsewhere [5]. The structural information included in this paper for *cis*- and *trans*-$[Co(en)_2(NO_2)_2]NO_3$ was obtained from the crystal structure reports of Bortin [6,7].

DISCUSSION

The TG curves of *cis*- and *trans*-$[Co(en)_2(NO_2)_2]NO_3$ are shown in Fig. 1. The *cis* compound was more stable than the *trans* form; the former began to lose mass at about 225°, while the latter first lost mass at about 200°C. As expected for this class of compounds, the first mass loss was very rapid, indicating an explosive type of reaction. No attempt was made to determine the composition of the residue, but it is expected to be an oxide of composition Co_3O_4. The *trans* compound forms an intermediate species which subsequently began to lose mass, starting slowly at ca. 210°C and becoming much more rapid at 250°C.

The DTA curves of *cis*- and *trans*-$[Co(en)_2(NO_2)_2]NO_3$ are shown in Fig. 2. Only a single exothermic peak was observed for both compounds, indicating a very rapid decomposition process. The $\Delta T_{\max}$ for the *trans* compound (≈ 235 °C) was observed at a higher temperature than for the *cis* compound (≈ 220 °C). An approximate determination was made for the enthalpy of the exothermic reaction using standard DTA procedures. For the *cis* compound, the ΔH_{reac} observed was -290 J g^{-1} or -96.5 kJ mol^{-1}; for the *trans* compound, the ΔH_{reac} observed was -427 J g^{-1} or -142 kJ mol^{-1}.

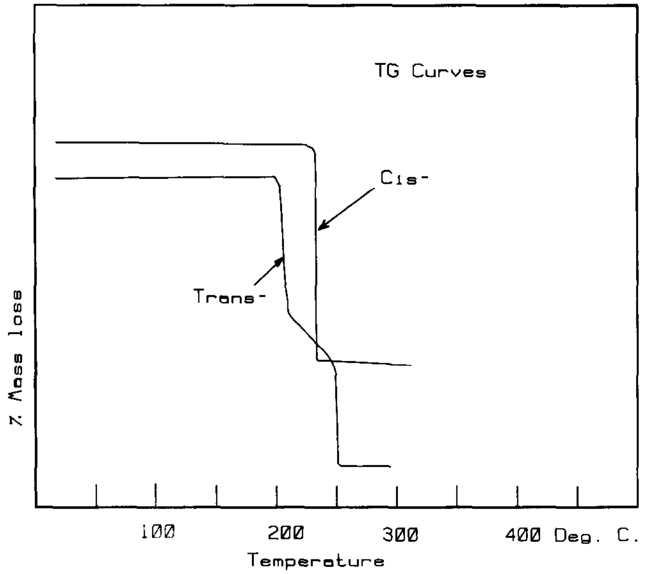

Fig. 1. TG curves of *cis*-$[Co(en)_2(NO_2)_2]NO_3$ and *trans*-$[CO(en)_2(NO_2)_2]NO_3$.

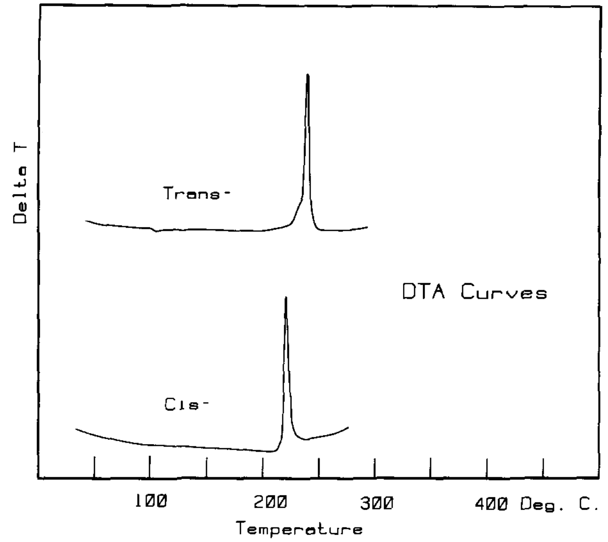

Fig. 2. DTA curves for *cis*-$[Co(en)_2(NO_2)_2]NO_3$ and *trans*-$[Co(en)_2(NO_2)_2]NO_3$.

The light emission (LE) curves of these compounds are given in Figs. 3–5. For the complexes *cis*-$[Co(en)_2(NO_2)_2]NO_2$ and *cis*-$[Co(en)_2(NO_2)_2]NO_3$, the LE curves indicated a short duration (several seconds) burst of radiation indicative of a single step reaction. The LE peak occurred in the temperature range 220–230 °C. There appeared to be little difference in the peaks caused by the substitution of NO_3^- for NO_2^- in the ionization sphere of the complex. No further LE peaks were found in the curves up to a maximum temperature of 350 °C.

For the *trans*-$[Co(en)_2(NO_2)_2]NO_3$ complex, the LE peak appeared to be broader and consisted of several maxima, indicative, perhaps, of multiple

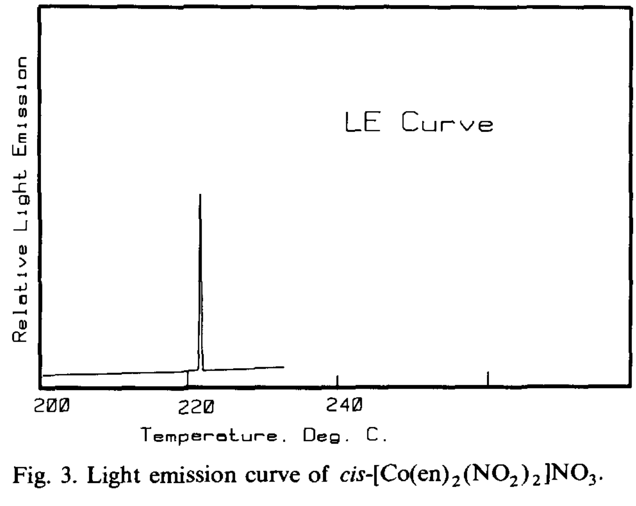

Fig. 3. Light emission curve of *cis*-$[Co(en)_2(NO_2)_2]NO_3$.

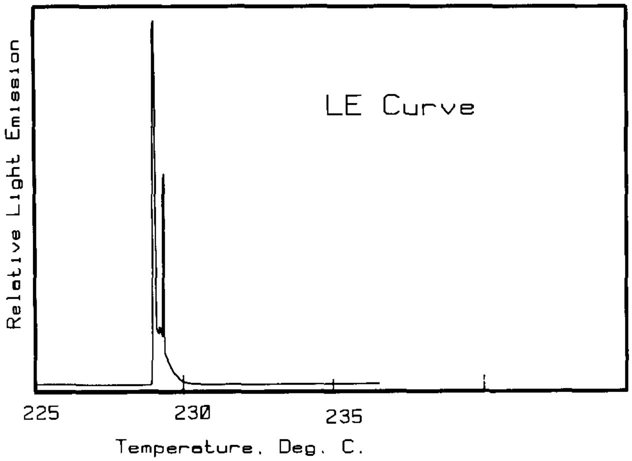

Fig. 4. Light emission curve of *trans*-$[Co(en)_2(NO_2)_2]NO_3$.

reactions, each of which produced a burst of light radiation. No further LE peaks were observed up to a maximum temperature of 350 °C.

It is important to note that, of all the transition metal complexes studied in this laboratory thus far, those containing oxidizing and reducing ligands or ions in different ionization spheres are predominantly the ones that exhibit light emission during thermal decomposition. The majority of complexes containing both oxidizing and reducing ligands only in the same coordination sphere have not exhibited light emission [1–3]. Also, note that the types of ligands both in the complexes that exhibit light emission and those that do not are the same. The examination of crystallographic data [4–7] for several complexes that produce light emissions, {tris[tetraammine-bis-μ-hydroxocobalt(III)]cobalt(III)}$(NO_3)_5(OH) \cdot 4H_2O$, *cis*- and *trans*-$[Co(en)_2(NO_2)_2]NO_3$, and *cis*-$[Co(en)_2(NO_2)_2]NO_2$, has yielded an interest-

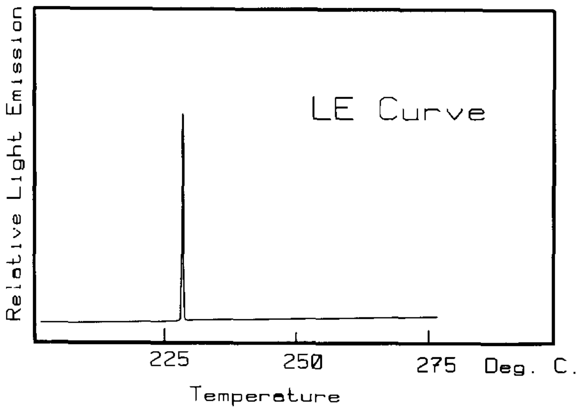

Fig. 5. Light emission curve of *cis*-$[Co(en)_2(NO_2)_2]NO_2$.

TABLE 1

Hydrogen bonding present in **I**, **II** and **III**; distances in Å, angles in degrees

O–H distance		N–H...O angle	
Hydrogen bonds for *cis*-$[Co(en)_2(NO_2)_2]NO_3$ [a]			
O5–H7	1.96	N2–H7...O5	166
O5–H16	2.07	N4–H16...O5	170
O7–H8	2.15	N2–H8...O7	156
O2–H1	2.23	N1–H1...O2	155
O3–H15	2.29	N4–H15...O3	158
O3–H10	2.32	N3–H10...O3	166
Hydrogen bonds for *trans*-$[Co(en)_2(NO_2)_2]NO_3$ [b]			
O7–H10	2.03	N3–H10...O7	166
O5–H7	2.24	N2–H7...O5	143
O5–H15	2.27	N4–H15...O5	139
O7–H2	2.33	N1–H2...O7	152
Hydrogen bonds for *cis*-$[Co(en)_2(NO_2)_2]NO_2$ [c]			
O5–H8	1.90	N2–H8...O5	158.3
O5–H2	2.06	N1–H2...O5	150.7
O3–H10	2.21	N3–H10...O3	151.2
O6–H15	2.31	N4–H15...O6	138.4
O1–H7	2.32	N2–H7...O1	157.2

[a] Idealized hydrogens calculated from the non-hydrogen atom positional parameters given in ref. 6, so that hydrogen bonding interactions could be determined.

[b] Data from list of hydrogen bonds given in ref. 7.

[c] Data from list of hydrogen bonds given in ref. 5.

ing observation. Many of the oxidizing and reducing ligands or anions in these complexes are in very close contact with one another through the presence of very strong hydrogen bonding.

For the complexes in this study, the strongest hydrogen bonding can occur between the amine hydrogens and nitrate or nitrite oxygens because these anions are better able to position themselves into a location favorable for interacting with an amine hydrogen than, for example, an NO_2 ligand bound to the same metal center. This is readily demonstrated by the data presented in Table 1, which lists the strongest hydrogen bonding interactions present in compounds **I**, **II**, and **III**. The most favorable hydrogen bonds (those with the shortest O–H distances and with N–H...O angles nearest 180°) in all three complexes are between amine hydrogens and the anion oxygens (see Figs. 6 and 7 for labelling schemes). Note that in the *cis* complexes there also exist significant hydrogen bonding interactions between amine hydrogens and the oxygens of nitro groups which are bound to an adjacent cobalt center. The total of these effects results in a complex network of cation–anion and cation–cation interactions in the solid state that is providing some very close contacts between oxidizing and reducing groups.

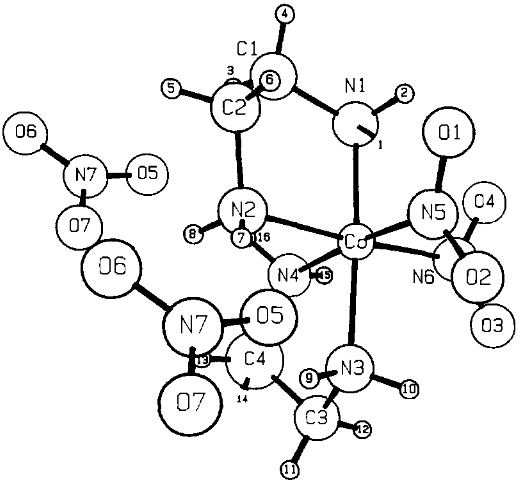

Fig. 6. ORTEP drawing of *cis*-$[Co(en)_2(NO_2)_2]NO_3$ (redrawn from the coordinates of Bortin [6]) showing the nitrate anions engaged in the strongest hydrogen bonds with the cation and showing the atom labelling scheme. The labelling scheme for *trans*-$[Co(en)_2(NO_2)_2]NO_3$ is the same as for the *cis* compound.

The observations discussed above add weight to the proposition that the mechanism for producing a light emission is highly dependent upon the ease with which electron transfer between species in a redox process can occur,

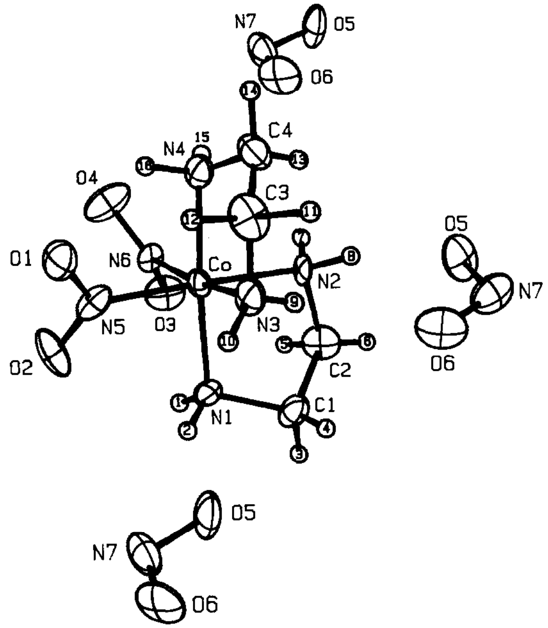

Fig. 7. ORTEP drawing of *cis*-$[Co(en)_2(NO_2)_2]NO_2$ showing the nitrite anions engaged in the strongest hydrogen bonds with the cation and showing the atom labelling scheme.

and that the presence of significant hydrogen bonds between oxidizing and reducing groups facilitates this process by providing a convenient pathway. It is not difficult to visualize that, at some relatively specific, high temperature, when a complex begins to decompose, the small distances between fairly reactive species would tend to encourage a vigorous redox reaction, resulting in the substantial light emissions that have been recorded. At this time we are unable to report on the specific reaction which is producing the light emission. Further investigations of light emission upon thermal decomposition that allow us to determine exactly under what conditions it occurs, in addition to the present data, will provide insight into the origin of the process.

ACKNOWLEDGMENT

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