

Note

THE THERMAL LIGHT EMISSION OF [TRIS(TETRAAMMINE-BIS- μ -HYDROXOCOBALT(III))COBALT(III)](NO₃)₅(OH) · 4H₂O

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(Received 3 January 1989)

INTRODUCTION

It is well known [1] that transition metal coordination compounds containing vigorous oxidizing groups in the ionization sphere (or coordination 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. The highly exothermic nature of these reactions results in rather spectacular DTA or DSC curves, even with very small samples (1–2 mg).

It was observed by Wendlandt [2,3] that these vigorous thermal dissociation reactions were accompanied by light emission. Using the new technique of emission thermophotometry (ETP), 60 compounds were investigated of which 25 were shown to exhibit light emission. The light emission occurred during the thermal dissociation reaction in the 200–300 °C temperature range.

In a continuation of these investigations, the thermal properties (DTA and TG) as well as the light emission of [tris(tetraammine-bis- μ -hydroxocobalt(III)cobalt(III))](NO₃)₅(OH) · 4H₂O, hereafter, referred to as **I**, were studied. New information concerning the light emission process mechanism is provided using recent crystallographic data for **I** [4].

EXPERIMENTAL

ETP apparatus

The emission thermophotometry apparatus has previously been described [5]. Sample sizes ranged from 5–10 mg. A furnace heating rate of 20 °C

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min^{-1} was employed in a static air atmosphere. No corrections were necessary for background radiation, even at high photometric sensitivity.

TG and DTA instruments

A Deltatherm V System Model D8100 DTA instrument was used for the DTA studies and ΔH_f determinations [6]. Sample sizes ranged from 5–10 mg, using a furnace heating rate of $10^\circ\text{C min}^{-1}$. A static air atmosphere was present in the furnace chamber for all DTA and ΔH_f determinations. The instrument was calibrated for the ΔH_f determinations using the fusion enthalpies of In, Sn and Pb, as previously described.

A Perkin–Elmer TGS-2 thermobalance was employed for the TG studies, using sample masses of 1–4 mg in a flowing nitrogen (40 ml min^{-1}) furnace atmosphere. All TG curves were obtained using a heating rate of $10^\circ\text{C min}^{-1}$.

Preparation of compound I

Ten grams of $[\text{Co}(\text{NH}_3)_5(\text{NO}_2)]\text{NO}_3$ were dissolved in a minimum of water previously heated to 80°C , whereupon the red color of the original

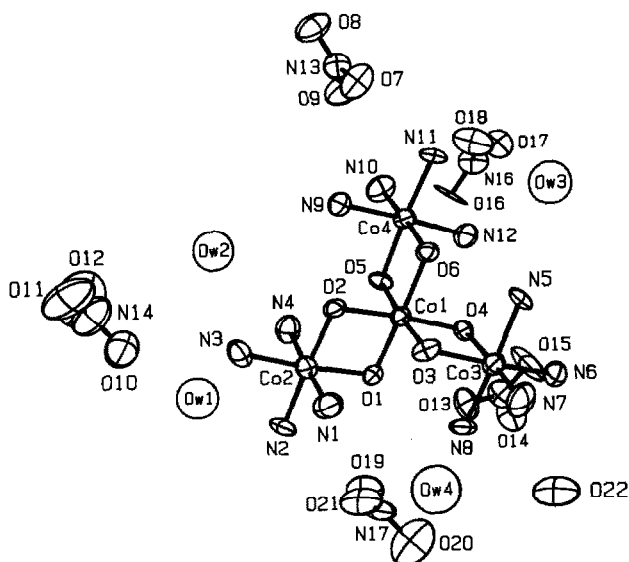


Fig. 1. A labeled drawing showing the contents of the asymmetric unit of I. The location of the hydroxide anion is marked by a partially shaded ellipsoid, whereas the water of hydration are shown as unshaded circles. Note that the nitrates, the hydroxide, and the waters completely surround the cation indicating extensive hydrogen bonding between their oxygens and the amine hydrogens. Hydrogens on the various species are not shown because those found in the crystallographic study were not a complete set or well positioned. See ref. 4 for details.

compound immediately changed to brown-black. The solution was stirred for approximately five minutes at 80 °C and then allowed to slowly cool to room temperature. The cold solution was filtered to remove the small amount of brown-black solid that had deposited. The mother liquor was placed in a clean beaker, covered with a watch glass and allowed to crystallize overnight at room temperature (ca. 21 °C). Shiny black crystals of the compound were thus obtained.

One of the crystals was mounted in a computer-controlled Enraf-Nonius CAD4 diffractometer and the space group and cell constants determined. It was found that the compound crystallizes in the monoclinic space group $P2_1/c$ with cell constants of $a = 11.789(2)$, $b = 13.855(2)$, $c = 21.534(3)$ Å, $\beta = 91.94(1)^\circ$, and $V = 3515.44$ Å³. Details of data collection, solution and refinement of the structure are given elsewhere [4]. A drawing of the contents of the asymmetric unit is depicted in Fig. 1.

RESULTS AND DISCUSSION

The TG and DTA curves are shown in Fig. 2.

The thermal dissociation curves indicated that two reactions occurred: the dehydration of compound **I** in two well defined steps and the dissociation of **I** to a cobalt oxide, probably Co_3O_4 . The TG curve showed that the dehydration occurred in the temperature range of about 40 to 125 °C. Rapid decomposition of the anhydrous **I** then began at about 190 °C.

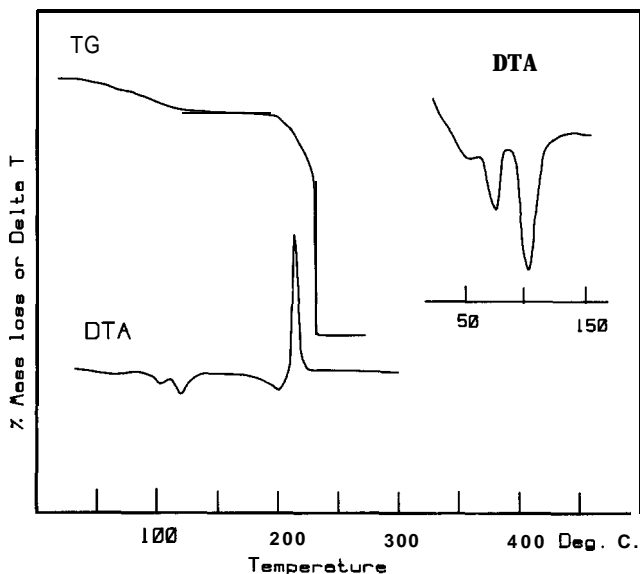


Fig. 2. TG and DTA curves for **I**. The DTA curve of the dehydration is shown in the inset.

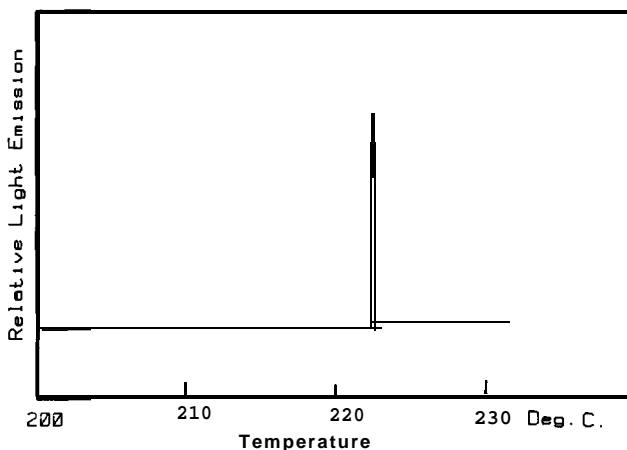


Fig. 3. Light emission curve for I.

The DTA curves showed that the dehydration reaction occurred in two stages, each resulting in the evolution of about two moles of H_2O per mole of **I**. From the DTA curves, the second dehydration reaction where the final two moles of H_2O were lost to produce the anhydrous compound **I** required a much larger heat input. From the ΔH_{dehydr} measurements, the evolution of the first two moles of water requires about 18.2 kJ, while the latter two moles enthalpy change is about 35.7 kJ. The thermal dissociation of anhydrous compound **I** begins at about 175°C; the reaction is endothermic in the initial stages and then becomes highly exothermic, with a ΔT , of about 215°C. It was not possible to determine the ΔH , of the decomposition reaction because of the overlapping endothermic and exothermic peaks.

The light emission curve of **I** is shown in Fig. 3. It consists of a very small peak at 217 °C followed by a much larger one at about 223° C. This, of course, is in the temperature range found with the other thermal techniques.

While the exothermic thermal decomposition reactions that transition metal complexes undergo are not uncommon, the occurrence of light emission accompanying a decomposition, as in the case of compound **I**, appears to be more specific in its origin. The simple presence of both an oxidizing ligand (nitrate, nitrite, etc.) and a reducing ligand (ammonia, ethylenediamine, etc.) in the compound is not sufficient to observe a light pulse upon thermal decomposition. Of the compounds investigated so far using ETP, those with oxidizing groups in one ionization sphere and reducing groups in a second ionization sphere are those which predominantly exhibit this light emission. These oxidizing and reducing ligands may be both bonded to a metal center or one of them could be a simple charge compensating cation or anion, as long as there is at least one oxidizing or reducing ligand in a different ionization sphere from another reducing or oxidizing group, respectively.

TABLE 1

Close N(NH₃)-O(NO₃) contacts in I ^a

Contact	Distance
O7...N11	2.98 Å
O15...N6	3.04 Å
O16...N10	3.01 Å
O21...N1	3.07 Å
O10...N3	3.06 Å

^a Hydrogen positions could not be accurately determined in the structural analysis; therefore, nitrogen-oxygen distances are given to demonstrate the presence of hydrogen bonding in I. These N-O distances realistically depict the presence of hydrogen bonding given that a typical N-H distance is 0.95 Å.

The amine ligands of the compounds studied thus far [2,3] are all fairly good hydrogen bonding species, and the oxidizing species (nitrite, nitrate) are good hydrogen bond acceptors. Figure 1 shows how tightly the nitrates surround the ammonia ligands of the cobalt cluster in compound **I**. Examination of some amine nitrogen-nitrate oxygen distances listed in Table 1 reveals that there are substantial hydrogen bonding interactions occurring between the amine hydrogens and nitrate oxygens.

Based on the information presented in Table 1 we postulate that the mechanism for producing a light emission is highly dependent upon the ease with which electron transfer between species in a redox reaction can occur and that the presence of hydrogen bonding facilitates this process by providing a convenient pathway. By having hydrogen bonding species (amines) in one ionization sphere and hydrogen bond accepting species (nitrates, nitrites) in a second ionization sphere, the tendency to form hydrogen bonds is enhanced due to the increased ability of the interacting species to orient themselves into positions more favorable for hydrogen bond formation. Ligands bound to the same metal center encounter greater constraints if they attempt to orient themselves into positions that would lead to an intramolecular hydrogen bonding situation. Thus, they form weaker interactions and are less able to facilitate the light emission process.

However, a few coordination compounds having both oxidizing and reducing ligands only in the same ionization sphere, such as [*cis-α*-Co(triethylenetetramine)(NO₂)₂]Cl, [Co(diethylenetriamine)(NO.)], and [Co(diethylenetriamine)(NH₃)(NO₂)₂]Cl, have been reported to give off a very weak light pulse during thermal decomposition [2]. This fact does not necessarily contradict our proposal that hydrogen bonding interactions facilitate the light emission process. In fact, it may lend more credence to the proposal, in that, a crystallographic study of [*cis-α*-Co(trien)(NO₂)₂]Cl [7] demonstrated that there are strong intramolecular hydrogen bonds between amine hydrogens and nitro group oxygens whose ligating atoms are bound to the same

metal center. Therefore, there still exists, to some extent, the pathway for electron transfer that was discussed previously. The extent of hydrogen bonding by way of intramolecular interactions is not as great as that seen in interionic interactions; but, neither is the intensity of the light pulse generated.

ACKNOWLEDGMENT

The financial support of this work by the Robert A. Welch Foundation, Houston, Texas, through Grants No. D-184 and E-594, is gratefully acknowledged.

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