Thermal Decompositions of Metal Amines Containing Oxo-nitrogen Moieties Either in the Coordination Sphere or as Charge Compensating Anions

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Abstract

This research is a continuation of the study on thermo chemical data of thermal decomposition of metal amines containing NO_x species found both in or out of the coordination sphere. As found previously, these compounds undergo a series of transformations (phase transitions and/or thermally induced chemical reactions) as temperature increases. First, water loss may occur, as documented by TGA and DSC. This often is followed by rapid chemical decomposition of the anhydrous material. Finally, one or more pulses of light of different intensity could be emitted. The light emission process was described as emission thermophotometry (ETP). Neither the mechanism nor the products of the thermally induced chemical reactions were documented previously. This article describes an attempt to do so using a novel apparatus that can do TGA, DSC, and mass spectroscopy.

Introduction

As a follow up of two previous papers published earlier1,2, describing thermochemical data on metal amines (TGA, DSC) containing NOx species in or out of the coordination sphere. Later, we wrote a paper3 in which we described the fact that a metal cluster compound of composition {[(NH3)4Co]3 [m--Co(OH)2](NO3)5}.4H2O(**I**)4 also undergoes a series of transformations (phase transitions and/or thermally induced chemical reactions). First, water loss occurred, as documented by TGA and DSC (range = 40-125 C). This was followed by rapid chemical decomposition of the anhydrous material which begun at ca. 190 C. Finally, two pulses of light were emitted around 217 C (small) and the other one at 223 C (large and sharp). The light emission process was described as emission thermophotometry (ETP). Neither the mechanism nor the products of the thermally induced chemical reactions were documented then. Thermal analysis was performed using a novel apparatus that can do TGA, DSC and mass spectroscopy simultaneously.

Experimental

All compounds were prepared by standard methods available in the literature and were taken from samples prepared here over a number of years and kept in safe storage.

In this experiment samples were heated under helium to 500°C at constant heating rate 10K/min. Three properties were analyzed simultaneously as a function of temperature: mass, energy of transitions, and evolved gas, using STA-MS skimmer system. The instrument combines thermogravimetry (TGA), differential scanning calorimetry (DSC) and quadrupole mass spectrometry (QMS):

TGA recorded sample mass

DSC recorded temperature, heats of thermal transitions and their nature (exotherm vs. endotherm)

QMS analyzed the mass of gaseous products evolving during the heating cycle.

STA-MS skimmer system was produced by Netzsch.

Data

In the course of this project more than fifty chemical compounds were analyzed. TGA, DSC and mass spectra for selected samples are given in Figs. 1-6. Summary of numerical values obtained by thermal analysis is given in Table 1.

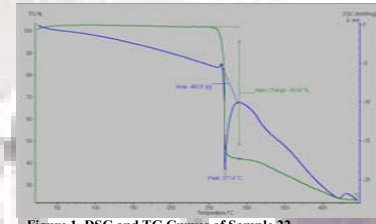

Figure 1. DSC and TG Curves of Sample 22

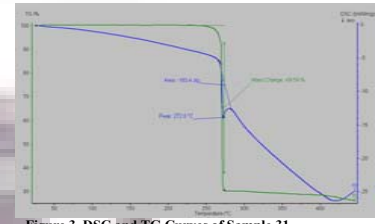

Figure 3. DSC and TG Curves of Sample 31

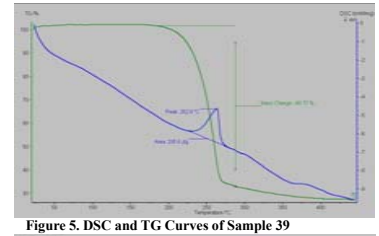

Figure 5. DSC and TG Curves of Sample 39

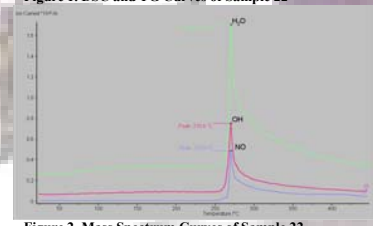

Figure 2. Mass Spectrum Curves of Sample 22

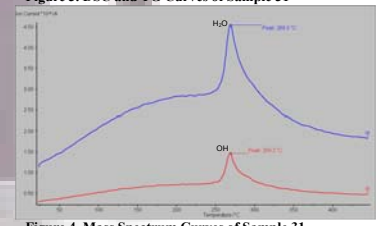

Figure 4. Mass Spectrum Curves of Sample 31

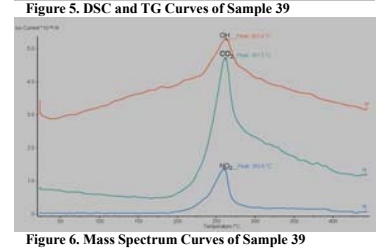

Figure 6. Mass Spectrum Curves of Sample 39

Melting and Thermal Decomposition of Compounds

Sample	Molecular Formula	DSC		TG	Mass Spectrum
		Tp(°C)	ΔH(J/g)*	% Mass Loss	Most Causal to Least Causal
18	$Co(NH_3)_6(NO_2)_3$	253.0	-225.5	72.1	H_2O, O_2, OH, NO
21	$[Cr(NH_3)](NO_3)_2$	193.0	-218.3	58.5	H_2O, OH, NO
22	$[Co(en)_3](NO_3)_3$	271.4	-462.4	60.0	H_2O, OH, NO
24	$[Co(NH_3)_4Ox]NO$	227.3	214.1	40.8	OH, CO_2
29	$[Co(trien)(NO_2)_2]Br$	143.4	11.9	5.0	H_2O, OH, CO_2,NO
		207.3	-182.3	25.0	
30	Mer-$[Co(dien)(NO_2)_3]$	225.5	-267.3	58.9	H_2O, CO_2, OH, NO
		402.6	-1156.0		
31	$Cu(1,2\text{-}PN)_2(NO_3)_2$	272.8	-183.4	69.6	H_2O, OH
35	Trans-$Co(4NH_3{\cdot}2NO_2){\cdot}NO_3$	189.9	-149.4	81.6	H_2O, OH, NO
38	$Co[(NH_3)_2NO_3](NO_3)_2$	245.1	-379.7	78.85	H_2O, OH, NO_2
39	$Co[(oxamide)(gly)(NO_2)_2]$	262.9	205.8	68.77	OH, CO_2, NO_2
40	$Co[(tetraen)(NO_2)]Cr_2O$	209.6	113.1	35.05	NH_2, OH
42	$Cu(en)_2(NO_3)_2$	238.6	-258.2	27.24	H_2O, OH, NO
		256.8	-194.4	37.4	

Table 1. Thermal Analysis Data for Selected Compounds

Results

- Figures 1, 3, and 5 depict DSC and TG curves for three of the nitrogenous samples as a function of temperature.
- Figures 2, 4, and 6 display the mass spectrum curves for the corresponding samples, and the relative ratios of the corresponding gases that were liberated at the respective points of transition.
- The table outlines the main characteristics of each compound including the identity of the sample, specific temperatures of the transition points, percent mass loss as well, as the energy released at each transition. The compounds that are released are indicated in order of most contributive to mass loss first, followed by the least contributive.

Discussion

The DSC and TG curves demonstrated repetitive patterns with some compounds. In Figure 1 and 2, the exothermic nature of the thermal transitions may have been essential to the higher contribution of H_2O as opposed to OH, often in a ratio of 2:1. In figure 3, however, the endothermic thermal transition may have been the reason that OH liberation played a more pronounced role in the sample's mass loss. This phenomenon will be further investigated. In some of the studied samples, the release of a few other gases were slightly influential to the mass loss of the sample, therefore these minimal effects were ignored. In Figures 2,4, and 6, the temperatures at which the individual gases were released tended to be exactly the same. In other samples, however, slight variations were observed, possibly due to the structure of the sample. The need be a more thorough study of the known structures of the samples that exhibited this behavior.

Many of the analyzed samples underwent thermal transitions at only one point, and displayed definitive mass loss at specific temperatures. There were samples, also, that had multiple transition peaks, accompanied with definitive or broad ranges for mass loss. Table 1. outlines all significant occurrences.

References

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3. Cetrullo, I. Bernal and W. W. Wendlandt, Thermochim. Acta, 150, 193 (1989).
4. I. Bernal, J. Cetrullo and S. Berhane, J. Coord. Chem., 52, 185 (2000).

Acknowledgements

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