Solid State Sciences 14 (2012) 495–500

Contents lists available at SciVerse ScienceDirect

Solid State Sciences

journal homepage: www.elsevier.com/locate/ssscie

Preparation, characterization and thermal behaviour of polymeric complex of cadmium hexamethylenetetramine nitrate☆

Dinesh Kumar [a], I.P.S. Kapoor [a], Gurdip Singh [a,*], Nidhi Goel [b], Udai P. Singh [b]

[a] Department of Chemistry, DDU Gorakhpur University, Gorakhpur, 297-Mohaddipur, Uttar Pradesh 273 009, India
[b] Department of Chemistry, Indian Institute of Technology Roorkee, Roorkee – 247 667, India

ARTICLE INFO

Article history:
Received 11 May 2011
Received in revised form
12 November 2011
Accepted 26 January 2012
Available online 9 February 2012

Keywords:
Hexamethylenetetramine
Ignition delay
Isothermal TG
Kinetics
X-ray Crystallography
CHNC (cadmium hexamethylenetetramine nitrate complex)

ABSTRACT

The preparation of cadmium nitrate complex with bridged hexamethylenetetramine-[{Cd(HMTA)(-NO_3)$_2$(H_2O)$_2$}$_n$], CHNC, of polymeric nature has been reported here for the first time. It was characterized by X-ray crystallography, ^{1}H NMR, FT-IR and elemental analysis. The crystal structure is stabilized by hydrogen bonding between the oxygen atom of the nitrate group with the methyl hydrogen of HMTA and hydrogen of the coordinated water molecule via C–H···O and O–H···O interactions. The thermolysis of this complex was investigated by TG-DSC and ignition delay measurements. The model-free isoconversional and model-fitting kinetic approaches have been applied to isothermal TG data for kinetics investigation of thermal decomposition of the complex. At higher temperatures, the complex gets ignited to produce highly thermally stable residue most closely resembles CdO proved by XRD.

1. Introduction

Chemically and thermally stable explosive compounds are needed for military applications. Many complexes of transition metals having hexamethylenetetramine (HMTA) [1–4] and NO_3^- or ClO_4^- ions are well known for their exothermic autocatalytic thermal decomposition. Thus, they are of interest as rocket propellants [5,6] and explosives [7,8]. In addition, these complexes are good source of ultra-fine metal oxides. Frazer and Hicks [9,10] proposed the thermal ignition model where heat of reaction is taken to be a function of temperature. The heat liberated due to exothermic reaction leads to deflagration. It is well known that when a solid material deflagrates, a steep temperature gradient is produced at the surface [11]. The surface region can be thought of as a thin film of material where heat and mass transfer are driven by physico-chemical changes. The reaction zone in the condensed phase (which may be a solid phase) is thin, transient and non-isothermal. Reactions in the condensed phase liberate gaseous products for ignition. In our earlier publications [12–14], it has been possible to gain insight into the mechanism of pre-ignition reactions by using tube furnace (TF) and thermogravimetric (TG) technique where deflagration conditions are simulated.

Hexamethylenetetramine (HMTA) known as urotropine or tetraazaadamantane (taad) having four nitrogen atoms at corners of a tetrahedron, is a ligand of polycyclicpolydentate type. In many complexes, it acts as a monodentate [15] or bidentate ligand [1] and shows nonchelating behavior [16] (in low valent organometallic complexes). In addition, it is useful in the production of antibacterial agents, adhesives, coatings, dye fixatives, anticorrosive agents as well as powerful explosives, e.g., 1,3,5,7-tetranitro-1,3,5,7-tetraazacyclooctane(HMX), 1,3,5-trinitro-1,3,5-triazacyclohexane(RDX) and dinitropentamethylenetetramine (DPT) [17,18]. The mechanism of nitration of HMTA was also studied in detail [17]. Synthesis of two new 1D and 3D networks of Cu(II) and Co(II) using malonate and HMTA as bridging ligands has also been reported by S. Konar et al. [3]. The crystal structure of a novel copper (I) cyanide complex with HMTA of the molecular formula $(CuCN)_3(C_6H_{12}N_4)_2$ was reported by F.B. Stocker [19]. Simultaneous determination of Pt and Rh by catalytic adsorptive stripping voltametry, using HMTA as a complexing agent was investigated by A.A. Dalvi et al. [4].

There is growing interest in understanding the thermolysis of some transition metal nitrate and perchlorate complexes of HMTA

☆ Part 80.

* Corresponding author. Tel.: +91 551 2200745 (R), +91 551 2202856 (O); fax: +91 551 2340459.
E-mail address: gsingh4us@yahoo.com (G. Singh).

1293-2558/$ – see front matter © 2012 Elsevier Masson SAS. All rights reserved.
doi:10.1016/j.solidstatesciences.2012.01.021

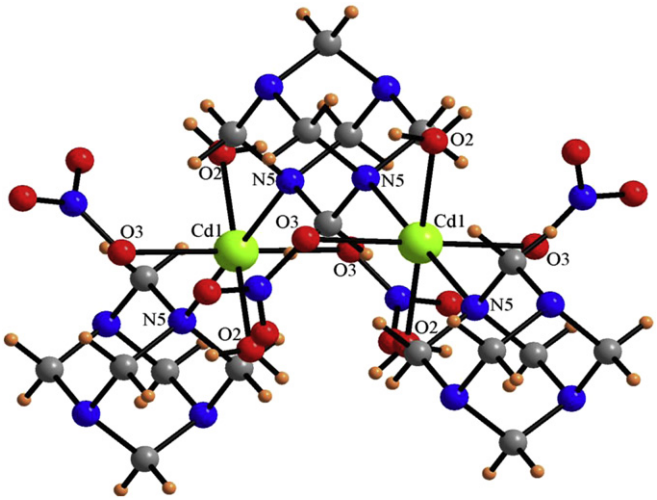

Fig. 1. Crystal structure of CHNC.

with H-bonding network [1,2]. This paper describes for the first time, preparation, characterization and thermal behaviour of energetic polymeric complex of cadmium nitrate with bridged HMTA (CHNC).

2. Materials and method

2.1. Materials

Cadmium nitrate was obtained from s.d.fine and HMTA from Lancaster and these were used without any further purification.

2.2. Preparation and characterization

Solid cadmium nitrate and solid HMTA into 2:1 weight ratio were mixed together at room temperature. After mixing thoroughly few drops of water were added into the solid content. During addition of water reaction between cadmium nitrate and HMTA starts which results slight increase in the temperature of reaction container. Then more water was added with constant stirring to dissolve the contents. The solution was filtered, and the filtrate was kept in vacuum for about 4 h to afford crystals. Recrystallization from water yielded colorless crystals. Different data obtained from various techniques are listed as; [^{1}H NMR (δ ppm) (300 MHz, DMSO) (s, $\delta = 3.4$, t, $\delta = 4.5$); FT-IR cm^{-1} (403, 504, 1006, 1234, 1373, 1466 & 2941) and elemental analysis Calculated: C, 17.5; H, 3.8; N, 20.3. Found; C, 17.9; H, 3.9; N, 20.4%]. Caution! The complex ignites when heated rapidly at higher temperatures. Therefore, due care was taken in handling the sample.

2.3. X-ray structural determination

A crystal of [{Cd(HMTA)$(NO_3)_2(H_2O)_2$}$_n$] of size 0.27 × 0.23 × 0.19 mm was grown at room temperature over a period of 10 h in evaporation from the mother liquor water . The X-ray data collection was performed on Brucker Kappa Apex-CCD diffractometer by using graphite monochromated Mo-Kα radiation ($\lambda = 0.71073$ Å) at 296 K. The structure was straightforwardly solved by direct methods. SHELXTL software [20,21] was used for structure solutions, refinement and data output. Hydrogen atoms were placed in geometrically calculated positions by using a rigid model. Image was created with the DIAMOND and MERCURY program [22,23]. Refinement with anisotropic thermal parameters for non-hydrogen atoms led to Final *R* indices value of 0.0313. Part of the zig-zag coordination network and various hydrogen bonding interactions between the adjacent layers are depicted in Figs. 1 and 2 respectively. The crystallographic data, structure refinement parameters, bond length, and bond angles are given, respectively, in Tables 1 and 2 [CCDC number 765844]. The selected hydrogen bonding parameters are summarized in Table 3.

NMR spectroscopy studies conducted with high resolution NMR spectrometer (Bruker, 300 MHz); FTIR on Nicolet Impact I-410 spectrophotometer and elemental analysis on Analytic Gena.

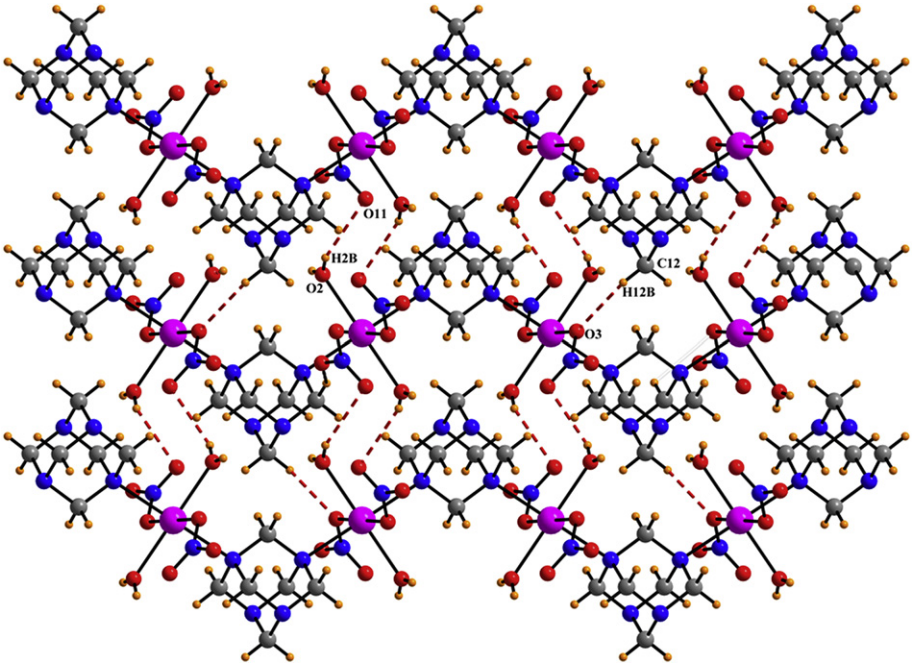

Fig. 2. C-H···O and O-H···O intermolecular interactions in CHNC.