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Synthesis, crystal structure and thermolysis kinetics of $[Co(H_2O)_6](ClO_4)_2.(HMTA)_2.2H_2O$ (HMTA = hexamethylenetetramine)

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A new compound, $[Co(H_2O)_6](ClO_4)_2.(HMTA)_2.2H_2O$; HMTA = hexamethylenetetramine) has been synthesized and characterized with the assistance of X-ray crystallography, elemental analysis, FT-IR spectroscopy, TG-DTA and DSC (N_2 atmosphere). Both TG data model-fitting method as well as method of model free isoconversional have been employed to observe the kinetics of thermolysis of the compound. In order to understand the effect of sudden high heat, measurements of explosion delay are undertaken at regular five unique temperatures and the kinetics of explosion has also been explored using Arrhenius equation.

Keywords: Cobalt compound, Crystal structure, Thermolysis, Kinetics of explosion

Coordination compounds find exclusive place as energetic compounds for explosive and propellant compositions[1]. When these coordination compounds possess anyhow oxidizing group like NO_3^- and ClO_4^- in their structure, undergo combustion phenomenon[2]. In these energetic compounds organic ligand acts as fuel. Recent past years energetic compounds have been attracted great attention of chemists[3-9]. Energetic compounds of transition metal find application like a burn rate changer for composite solid propellants[10-14]. It is established that these compounds result metal oxide/oxides as end product of their decomposition and these oxides may find several uses such as in photo inorganic electrochromic films,[15] composite solid propellants as burning rate modifier,[16,17] anodic material for lithium-ion battery[18], gas sensors, self cleaning and photocatalysis[19].

Hexamethylenetetramine (HMTA) generally known as urotropine, is a polycyclic polydentate ligand and exhibits the behaviour of mono or bidentate ligand[20,21]. Non-chelating nature of HMTS has also been reported[22]. Dalvi *et al.*[23] have proven that it acts as a strong complexing agent and they used it for simultaneous determination of Pt and Rh by catalytic adsorptive stripping voltametry. Singh *et al.* have prepared and studied the thermal properties of Mn, Ni, and Zn perchlorates[24] and Co, Ni and Zn nitrates[25] containing HMTA. Thermal nature of polymeric compound of cadmium HMTA nitrate compound was also reported by Kumar *et al.*[6] HMTA nitrate compound of iron (III) can be used for the synthesis of nanoparticles of α-Fe_2O_3[26]. Zn(II) and Co(II) compounds of HMTA have been employed as source precursors of nanoparticles of their metal oxide[27]. A compound of Ni(II) with HMTA and SCN^- ion as co-ligand[28] has been synthesized, characterized and screened for activity against resistant strains of certain bacteria and fungi. HMTA copper (II) sulphate complex is detected as active against certain bacteria for which HMTA is inactive[29-31]. Increase in CO_2 adsorption has been reported with hexamethylenetetramine-doped Cu-BDC framework of metal-organic[32]. A novel 2-D Coordination compound, $[Cd(hmt)_2(hbz)_2(H_2O)]$ has been studied[33]. Zinc-HMTA compound has been reported as sulphur reservoir for high performance Li-S batteries[34]. 2D and 3D metal organic framework of copper(I) halides and HMTA has been prepared and analysed for their properties[35]. $Co(HMTA)_2Cl_2{\cdot}6H_2O$ has a remarkable influence on the poly(L-lactic acid) thermal characteristics[36].

The present study deals with the preparation, structural determination and thermal performance of a new compound, $[Co(H_2O)_6](ClO_4)_2.(HMTA)_2.2H_2O$ (compound **1**). Thermal characterization of the compound **1** was investigated by measurements of DSC, TG, and DTA. Kinetic of isothermal decomposition and explosion have also been detailed.

Materials and Methods

Materials

Cobalt carbonate (S.D. Fine; impurity limit 0.65%), perchloric acid (S.D. Fine; 60%), hexamethyl–enetetramine (Merck 99%), all of AR grade have been utilized as taken without any type of purification.

Synthesis

Two-steps synthesis for the compound **1** was followed. In the first step, cobalt(II) perchlorate hexahydrate[#] was obtained by reacting the metal carbonate (2.0 g) with 60% $HClO_4$, followed by recrystallization. In second step, aqueous solution of cobalt perchlorate[#] and HMTA was mixed together in stoichiometric ratio (2.0 g and 1.5 g, respectively) at room temperature. The solution has been filtered and the rest was kept in vacuum to afford pink colored crystals which were washed with distilled water and dried in desiccator on fused calcium chloride. Elementary analysis (%), calculated (found): C, 20.10 (20.53); N, 16.41 (16.17); H, 5.86 (6.50); IR (ν, cm^{-1}): 621 (ionic perchlorate), 511 (M-O), 776 ($CH_{2\ rocking}$), 1466 ($C\text{-}H_{def}$), 1007 ($C\text{-}N_{str}$), 1089 (ClO_4), 3417 $(C - H_{H_2O})$, 1668 ($O\text{-}H_{str,}H_2O$), 2974 ($C\text{-}H_{str}$).

Spectral characterization

Characterization of compound **1** was done by elemental analysis (C, H, N; Elementar Vario EL III), infrared (IR)[37-39] (Thermo Nicolet, Avatar 370 FT-IR spectrometer; KBr beam splitter, resolution 4.0 cm^{-1}) and thermal analysis techinques.

X-Ray crystallographic study

Crystal of (0.25 X 0.20 X 0.05) mm of compound **1** was kept on a Nonius Kappa CCD diffractrometer, equipped with rotating anode generator Nonius FR591 and used for data collection at low temperature 223(2) K. The programmes used were data collects (B.V. Nonius, 1998) data reduction[40] and correction of absorption DENZO-SMN[41]. By direct methods (SHELXS-97),[42] the structure has been obtained and all atoms other than H-atoms are refined anisotropically applying least-squares method and full matrix on F^2. For data collection, the theta range was selected from 4.34 to 67.22º. For all except H-atoms, refinement with anisotropic thermal scale lead to the value of R (0.036). The crystal structure (graphic done with SCHAKAL, made in XP with 30% probability)[43] of the synthesized compound is established.

Thermal analysis

Using an indigenously fabricated thermogravimetry (TG) apparatus[44] with sample mass of 20 mg, TG in static air with heating rate 10 ºC min^{-1} was recorded. Simultaneous TG- differential thermal analysis (DTA) traces were obtained in flowing N_2-atmosphere (rate of flow 100 mL min^{-1} and sample mass 3.605 mg) at a rate of heating 10 ºC min^{-1} (on Perkin Elmer, Diamond). DSC trace was also recorded in flowing N_2 atmosphere (flow rate 100 mL min^{-1}) with sample mass 8.962 mg at a heating rate of 10 ºC min^{-1}. At various five temperatures (240 ºC, 230 ºC, 220 ºC, 210 ºC and 200 ºC), isothermal TG traces were recorded, in static air atmosphere using the original fabricated TG equipment as described previously[44]. In all isothermal TG experiments conducted, 20 mg of sample was taken and data have been captured for decomposition (30%). Kinetics of isothermal decomposition was investigated using isothermal TG data by applying model-fitting[45] and isoconversional methods[46,47]. Explosion delay experiment was performed using tube furnace technique[48] (sample mass of 10 mg), at temperatures 280, 300, 320, 340 and 360 ºC within experimental limit of ±1 ºC. Equal size of ignition tubes (4.0 cm long and 0.4 cm diameter) were used. Time has been recorded between insertion of ignition tube into furnace and explosion of sample. Explosion delay (D_E) data were fitted in Arrhenius equation shown in Eqn. (1),

$$D_E = A \exp^{E^* / RT} \qquad \ldots(1)$$

Where, D_E = explosion delay, A = Arrhenius factor, E* = activation energy for explosion, T = absolute temperature and R = universal gas constant.

Results and Discussion

Spectroscopic characterization

Elemental data of compound **1** furnishes a good concurrence between calculated and observed mass percent of C, H and N. IR peak at 511 cm^{-1} was

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[#] ***Caution !:*** *Perchlorate compounds are known to be explosive. In view of this, it is necessary to observe appropriate safety regulations in the handling, storage and disposal of perchlorate compounds.*

designated for ν(M-O)[37] which confirms metal to ligand (H_2O) bond formation. Peaks at 621 and 1089 cm^{-1} are caused by existence of ionic perchlorate[39].

Description of crystal structure

The compound **1** crystallizes in triclinic crystal system with space group P-1 (No.2) (Z=1). Its crystal structure (Fig. 1) turns out that cobalt ion is six fold coordinated by O-atom of water molecule. Out of two HMTA molecules, none of the HMTA is directly bonded to the cobalt atom. Two H_2O lies in between $[Co(H_2O)_6]^{++}$ and HMTA molecule. Table 1 represents refinement parameters and crystal data. Specific bond angles and bond length are also presented in Table 2. All O-Co-O bond angles are very close to 90º (adjacent O-Co-O angle) or 180º (Trans O-Co-O angle). Thus, we can say that the $[Co(H_2O)_6]^{++}$ is geometrically very close to an octahedron. However, Co-O bond length data speaks that it is slightly elongated on $H_2O(2)$-Co-($H_2O(2^*)$ (bond length 2.118 Å). Co-O(1) and Co-O(1*) lengths are 2.0783 Å whereas Co-O(3) and Co-O(3*) lengths are 2.0710 Å. *Trans* O-Co-O bond angles exhibit ideal value of 180 while the *cis* O-Co-O angles deviate from right angles (in addition to Co-O bond lengths varying from 2.0710(18) to 2.1181(18) which indicates a slight deviation of the $\{CoO_6\}$ octahedron. Although HMTA molecules are not directly coordinated to Co^{++} yet it is strongly held in the crystal lattice. Coordinated water, uncoordinated water, ClO_4^- and HMTA all might be connected to each other by a network of hydrogen bonding. Indirect attachment of HMTA and metal through hydrogen bonding has also been reported earlier[25,37]. CheckCIF report of the compound 1 and some of the other important bond angles and bond lengths are shown in Supplementary Data, Table S1.

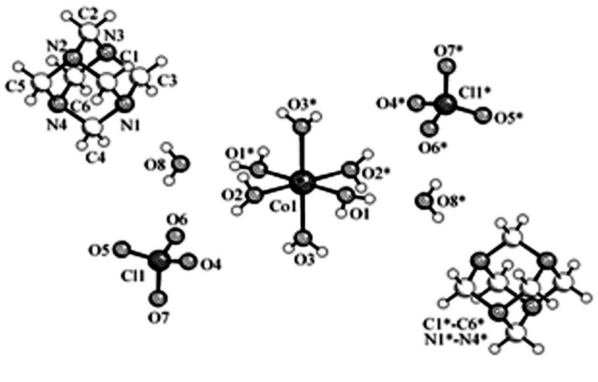

Fig. 1 — Crystal structure of the compound **1**

Thermal decomposition and kinetics

TG, DTA and differential scanning calorimetry (DSC) curves elaborate the thermal decomposition behaviour of compound **1**. TG curve of compound in static air (Fig. 2) as well as in flowing nitrogen

Table 1 — Refinement parameters and crystal parameters for cobalt hexamethylenetetramine perchlorate compound

Empirical formula	$C_{12}H_{40}Cl_2CoN_8O_{16}$
Formula weight	682.35
Temperature	223(2) K
Wavelength	1.54178 Å
Crystal system, space group	triclinic, P-1 (No. 2)
Unit cell dimensions	a = 8.2273(1) Å ..α = 93.816(1)° b = 9.1409(1) Å β = 104.484(1)° c = 10.7089(1) Å γ = 114.119(1)°
Volume	698.593(13) Å^3
Z, Calculated density	1, 1.622 g/m^3
Absorption coefficient	7.334 mm^{-1}
F(000)	357
Crystal size	0.25 x 0.20 x 0.05 mm
Theta range for data collection	4.34 to 67.22°
Limiting indices	0<=h<=9, -10<=k<=9, -12<=l<=12
Reflections collected / unique	8128 / 2369 [R(int) = 0.039]
Completeness to theta = 67.22 94.7 %	94.7 %
Absorption correction	Semi-empirical from equivalents
Max. and min. transmission	0.7106 and 0.2614
Refinement method	Full-matrix least-squares on F^2
Data / restraints / parameters	2369 / 89 / 247
Goodness-of-fit on F^2	1.095
Final R indices [I>2σ(I)]	R1 = 0.0357, wR^2 = 0.0971
R indices (all data)	R1 = 0.0358, wR^2 = 0.0972
Largest diff. peak and hole	0.363 and -0.399 e.Å^{-3}

Table 2 — Selected bond lengths (Å) and bond angles (º) of the compound **1**

Bond length	Bond	Bond angle	Bond
2.0710(18)	Co1-O3*1	180.0	O3#1-Co1-O3
2.0710(18)	Co1-O3	89.67(7)	O3#1-Co1-O1#1
2.0783(17)	Co1-O1*1	90.33(7)	O3-Co1-O1#1
2.0783(17)	Co1-O1	90.33(7)	O3#1-Co1-O1
2.1181(18)	Co1-O2	89.67(7)	O3-Co1-O1
2.1181(18)	Co1-O2*1	180.00(1)	O1#1-Co1-O1
		89.93(8)	O3#1-Co1-O2
		90.07(8)	O3-Co1-O2
		89.30(7)	O1#1-Co1-O2
		90.70(7)	O1-Co1-O2
		90.07(8)	O3#1-Co1-O2#1
		89.93(8)	O3-Co1-O2#1
		90.70(7)	O1#1-Co1-O2#1
		89.30(7)	O1-Co1-O2#1
		180.000(1)	O2-Co1-O2#1

atmosphere (Fig. 3) clearly indicates that the compound decomposes in four steps. The decomposition regions and nature of peaks are given in Supplementary Data, Table S2. In the first step six ligated and two unligated water molecules release (~19% mass loss) in between temperature 95-140 ºC. This is observed as an endothermic process as indicated by an endothermic peak each in DTA at 103 ºC and in DSC at 113 ºC (Fig. 4). In the second and third steps (although not well separated in TG) reducing (fuel) HMTA and oxidizer ClO_4^- undergo rapid redox reactions giving sudden mass loss (~48%) and two exothermic peaks in DTA (at 233 and 286 ºC) and DSC (at 226 and 292 ºC). Finally in fourth stage remaining residue undergo gradual mass loss (~15%) leaving a mass in the crucible comparable to cobalt oxide. In air atmosphere (Fig. 2) this fourth step is not clear because of presence of oxygen in air which supports the oxidation of HMTA during second and third step. However in N_2 atmosphere, due to unavailability of extra oxygen other than which is in the complex itself, oxidation in second and third step suppress and show mass loss in fourth step at elevated temperatures. In the light of above discussions, decomposition pattern of the compound can be summarized in which second reaction comprises of last three step of decomposition.

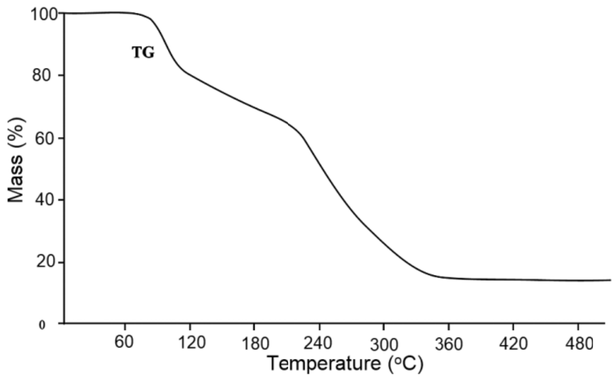

Fig. 2 — TG curve of compound **1** in static air atmosphere

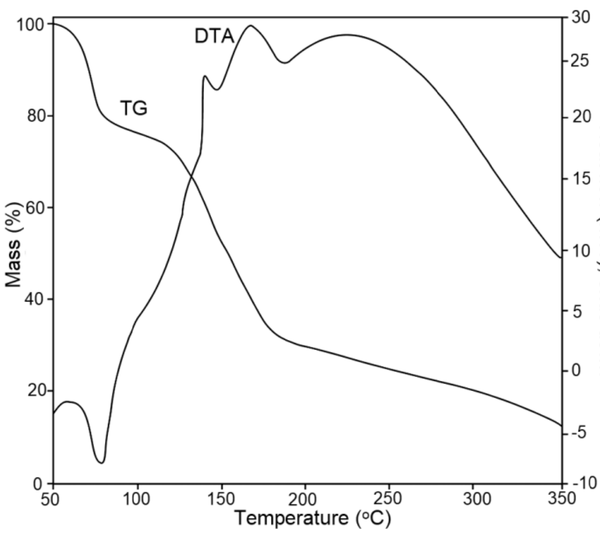

Fig. 3 — TG-DTA curve of compound **1** in flowing nitrogen atmosphere

$$[Co(H_2O)]_6(ClO_4)_2(H_2O)_2(HMTA)_2 \xrightarrow{65-140\ ℃} Co(HMTA)_2(ClO)_4 + 8H_2O$$

$$[Co(HMTA)_2(ClO_4)_2 \xrightarrow{141-650\ ℃} CoO + Gases$$

Activation energy for early decomposition (~30% mass loss) has been calculated using isothermal TG data by applying model-fitting[46, 47] (Table 3) as well as isoconversional method[41]. In model-fitting each method has given a single value of E_a in between 50.1 and 54.6 kJ mol^{-1}. However, isoconversional method has resulted different E_a values corresponding to each extent of conversion, α. Isothermal TG of the compound in static air atmosphere at different temperature and the plot of E_a values *vs*. α are given in Supplementary Data as Fig. S1 and S2, respectively. Thus, isoconversional method is a better approach to explore kinetics of such a complex solid state thermolysis.

Although, the compound is stable at room temperatures, it explodes releasing a large volume of gases when exposed to sudden to high temperatures. Kinetic parameters are summarized in Table 4. Activation energy of explosion (E*) has been calculated using explosion delay data recorded at five

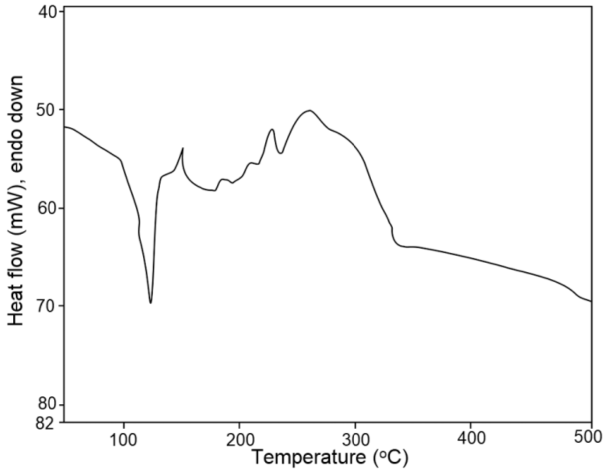

Fig. 4 — DSC curve of compound **1** in flowing nitrogen atmosphere

Table 3 — Arrhenius factor, activation energy *(E_a)* and correlation coefficients (*r*) for the isothermal decomposition of compound **1**

S. No.	Model	*r*	E (kJ mol^{-1})	Mean dev.	Std. dev.
1	Power law [$\alpha^{1/2}$]	0.9873	53.8	1.947	2.072
2	Power law [$\alpha^{1/4}$]	0.9867	54.6	2.188	2.324
3	Power law [$\alpha^{2/3}$]	0.9869	54.3	2.080	2.211
4	Power law [$\alpha^{3/2}$]	0.9894	51.4	1.730	1.843
5	Parabolic law [α^2]	0.9905	50.6	1.714	1.826
6	Mampel [$-\ln(1-\alpha)$]	0.9965	51.0	1.164	1.255
7	Avrami-Erofeev [$-\ln(1-\alpha)]^{1/2}$	0.9965	53.4	1.488	1.594
8	Avrami-Erofeev [$-\ln(1-\alpha)]^{1/3}$	0.9964	54.3	1.669	1.782
9	Avrami-Erofeev [$-\ln(1-\alpha)]^{1/4}$	0.9858	52.6	2.036	2.165
10	Contracting cylinder [$1(1-\alpha)^{1/2}$]	0.9927	51.4	1.799	1.915
11	Contracting sphere [$1(1-\alpha)^{1/3}$]	0.9951	51.2	1.834	1.952
12	Three-dimensional diffusion	0.9978	50.6	1.890	2.010
13	Prout-Tompkins [$\ln(\alpha/1-\alpha)$]	0.9965	54.5	0.854	0.945
14	Ginstling-Brounshtein	0.9949	50.1	2.335	2.476

Table 4 — Explosion delay (D_E), activation energy for thermal explosion (E*) and correlation coefficient (*r*) of compound **1**

D_E (s) at temperature (ºC)					*r*	E* (kJ mol^{-1})	ln*k*	Mean Dev.	Std. Dev.
360±1	340±1	320±1	300±1	280±1					
41	45	60	74	99	0.9930	33.1	-2.609	2.050	2.174

different temperatures. E* value was found to be 33.1 kJ mol^{-1} and a graph of ln D_E *vs*. 1/T is presented in Supplementary data, Fig. S3.

Conclusions

In conclusion, the X-ray crystallographic analysis of a new compound, $[Co(H_2O)_6](ClO_4)_2.(HMTA)_2.2H_2O$ (HMTA = hexamethylenetetramine) reveals the formation of a hexacoordinated cationic species with Co atom surrounded with six H_2O molecules, while the HMTA ligands remain uncoordinated in outer coordination sphere. Thermal studies reveal that the compound remains thermally stable upto 100 ºC in static air, whereas it gradually decomposes in four steps in inert N_2 atmosphere involving removal of eight water molecules. HMTA and perchlorate ion undergo redox reaction to give two exothermic peaks in DSC and DTA. The energy of activation for isothermal decomposition varies with extent of conversion whereas, energy of activation for explosion has been found to be 33.1 kJ mol^{-1}. The study thus compiled in the work will give impetus to a detailed study of the kinetics of energetic products in future.

Supplementary Data

The related crstallographic data with CCDC 1026396 is deposited in Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge CB2 1EZ, UK; fax: (+44-1223-336-033; or e-mail: deposit@ccdc.cam.ac.uk) and can also be accessed free of cost at http://www.ccdc.cam.ac.uk. Supplementary data associated with this article are available in the electronic form at http://nopr.niscair.res.in/jinfo/ijca/IJCA_60A(05)676-681_SupplData.pdf.

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