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THERMOANALYTICAL INVESTIGATIONS OF 4-METHYLPIPERAZINE-1-CARBODITHIOIC ACID LIGAND AND ITS IRON(III), COBALT(II), COPPER(II) AND ZINC(II) COMPLEXES

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The thermal decomposition studies on 4-methylpiperazine-1-carbodithioic acid ligand (4-MPipzcdtH) and its complexes, viz. $[M(4\text{-MPipzcdtH})_n](ClO_4)_n$ (M=Fe(III) when n=3; M=Co(II), Cu(II) when n=2) and $[Zn(4\text{-MPipzcdtH})_2]Cl_2$ have been carried out using non-isothermal techniques (TG and DTA). Initial decomposition temperatures (IDT), indicate that thermal stability is influenced by the change of central metal ion. Free acid ligand exhibits single stage decomposition with a sharp DTA endotherm. Complexes, $[M(4\text{-MPipzcdtH})_n](ClO_4)_n$ undergo single stage decomposition with detonation and give rise to very sharp exothermic DTA curves while the complex $[Zn(4\text{-MPipzcdtH})_2]Cl_2$ shows three-stage decomposition patterns.

The kinetic and thermodynamic parameters, viz. the energy of activation E, the frequency factor A, entropy of activation S and specific rate constant k, etc. have been evaluated from TG data using Coats and Redfern equation. Based upon the results of the differential thermal analysis study, the $[M(4\text{-MPipzcdtH})_n](ClO_4)_n$ complexes have been found to possess characteristic of high energy materials.

Keywords: *Coats–Redfern method, DTA, metal ions, 4-methylpiperazine-1-carbodithioate, TG*

Introduction

Metal dithiocarbamates constitute an interesting group of compounds pertaining to the stabilization of high oxidation states and existence of spin-crossover behaviour in some of their compounds [1, 2]. However, very few reports regarding their thermal degradation path are available in literature [3–9]. The fact that presence of perchlorate ion in conjunction with organic moiety enhances the explosive nature of the compound [10] and hence leads to the formation of high energy materials has been visualized under present investigation. Though melting points make a hint about the thermal stability of the ligand, 4-MPipzcdtH and its metal carbodithioate complexes, viz. $[M(4\text{-MPipzcdtH})_n](ClO_4)_n$ (M=Fe(III) when n=3; M=Co(II), Cu(II) when n=2) and $[Zn(4\text{-MPipzcdtH})_2]Cl_2$, yet an attempt has been made to further investigate their thermal stability and decomposition behaviour by thermogravimetric measurements under non-isothermal conditions in air atmosphere. This has been done to gain a deep insight as to whether introducing different metal ions into a 4-methylpiperazine-1-carbodithioic acid ligand moiety along with perchlorate as the counter anion, has any effect on the thermal stability of the complexes, the nature and composition of the thermolytic products formed if any, during their decompositions and end-products of thermal decomposition. The measurement of overall kinetic parameters of thermally simulated reactions permit a deeper insight into the mechanism of decomposition of the compounds under study.

Experimental

The preparation of 4-MPipzcdtH ligand and its metal complexes, viz. $[M(4\text{-MPipzcdtH})_n](ClO_4)_n$ (M=Fe(III) when n=3; M=Co(II), Cu(II) when n=2) and $[Zn(4\text{-MPipzcdtH})_2]Cl_2$ has been reported earlier [11].

Thermal analyses of the complexes were carried out on Shimadzu DT-40 (simultaneous TG/DTA module) thermal analyzer. The thermocouple used was Pt/Pt-Rh (10%) with a temperature range of 20–1200°C. Thermal investigations were carried out by heating the sample (5–10 mg) in a Pt crucible in a static air atmosphere and Al_2O_3 was taken as reference. A heating rate of $10°C\ min^{-1}$ was employed. The TG data was analyzed by using Coats and Redfern equation for calculating kinetic and thermodynamic parameters. The instrument calibration was checked periodically with a sample of $CuSO_4{\cdot}5H_2O$.

Results and discussion

4-Methylpiperazine-1-carbodithioic acid (4-MPipzcdtH) ligand obtained by insertion of carbon

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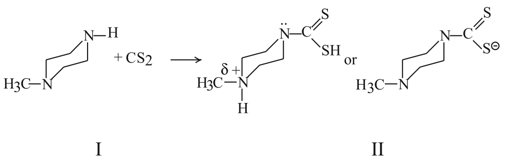
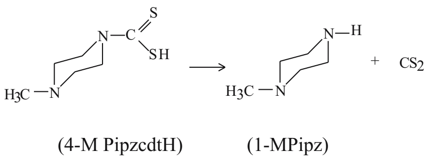
disulfide into the N–H bond of heterocyclic secondary amine, 1-methylpiperazine, 1-MPipz (I), exists as a Zwitterion (II). It acts as a primary ligand with bidentate binding to the metal ion through two sulfur atoms. The positive charge on the nitrogen atom satisfies the *–ve* charge due to counter anions. The ligand (4-MPipzcdtH) exists as a Zwitterion is evident from the fact that in the IR spectra of 4-methylpiperazine-1-carbodithioic acid and its metal complexes, new broad band as compared to the free heterocyclic amine, 1-MPipz, around 3600–3200 cm^{-1} for the acid and 3660–3180 cm^{-1} for the complexes assignable to $\nu_{N\text{–}H}$ was observed. The appearance of this band in the ligand points to the formation of N–H bond indicating the existence of 4-MPipzcdtH ligand as a Zwitterion. The occurrence of this band at higher wave number than the usual values of 3400–3200 cm^{-1} indicates that in the present case the interaction of the lone electron pair on nitrogen with positively charged hydrogen probably is stronger than the normal nitrogen-hydrogen interaction (Scheme 1).



Scheme 1

The thermal data (Table 1) of 4-MPipzcdtH ligand and some of its metal complexes, viz. $[M(4\text{-MPipzcdtH})_n](ClO_4)_n$ (*M*=Fe(III) when *n*=3; *M*-Co(II), Cu(II) when *n*=2) and $[Zn(4\text{-MPipzcdtH})_2]Cl_2$ has been derived from thermogravimetric curves using thermogravimetric (TG) and differential thermal analytical DTA techniques.

A perusal of TG data of free ligand, 4-MPipzcdtH (Fig. 1) reveals that this is stable upto 130°C beyond which it undergoes decomposition in one step without leaving any residue in the crucible. The DTA curve showed a sharp endothermic peak at 156°C. The endothermic degradation nature of the free 4-MPipzcdtH ligand is evident from the fact that synthesis of the carbodithioate ligand in general follows an exothermic pathway. However, the observation of the sharp endothermic peak does not give any evidence of melting since experiment in an open glass tube showed that the ligand sublimates without decomposition. A total mass loss of 100% in temperature range of 130–160°C is in agreement with the decomposition pathway for the free 4-MPipzcdtH ligand as shown in Scheme 2.



Scheme 2

The mass loss of 42.3% in the range 130–152°C corresponds to the theoretical value of 43.18% calculated for the loss of CS_2 molecule and supports the suggested pathway. While the mass loss of 57.69% in the range 152.5–160°C corresponds to the theoretical value of 56.81% calculated for the loss of the amine, 1-methylpiperazine.

TG and DTA curves of $[Fe(4\text{-MPipzcdtH})_3](ClO_4)_3$, $[Co(4\text{-MPipzcdtH})_2](ClO_4)_2$ and $[Cu(4\text{-MPipzcdtH})_2](ClO_4)_2$ have indicated the complexes to be stable upto 151, 115 and 110°C respectively (Figs 2–4). Initial decomposition temperatures (IDT), reveal that thermal stability is influenced by the change of central metal ion. The complexes follow a plateau in the TG curve, and begin to decompose exothermically above these temperatures. The sharp exotherms have been observed at 174.8, 224.9 and 233°C occurring in the temperature range between 170.65–180, 218–229 and 229–240°C (Figs 2–4) for the respective complexes in their DTA curves. The TG curves show that the decomposition is

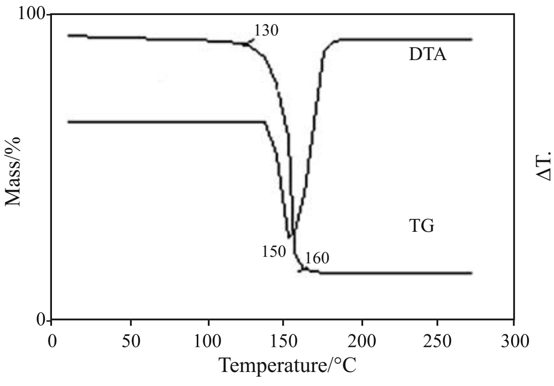


Fig. 1 TG/DTA curves of 4-MPipzcdtH ligand

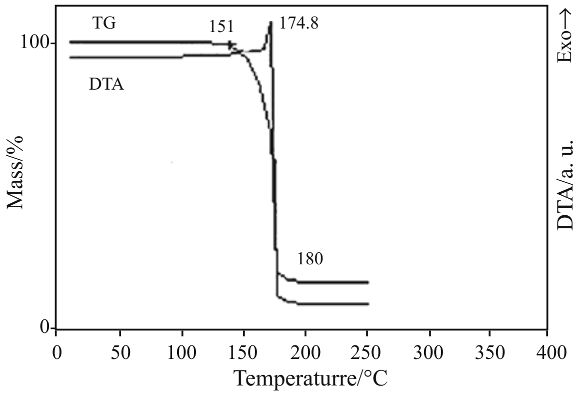


Fig. 2 TG/DTA curves of $[Fe(4\text{-MPipzcdtH})_3](ClO_4)_3$ complex

Table 1 Thermal decomposition data and kinetic parameters for 4-methylpiperazine-1-carbodithioic acid ligand and some of its transition metal complexes computed by Coats–Redfern equation

Compound	Decomposition data							
	Sample mass/mg	*IDT*/ °C	Stage	TG temp. range/°C	Mass loss/ %		DTA peak	
					exp.	theor.	temp./°C	nature
4-MPipzcdtH	2	130	1st	130–160	100	100	156	endo
[Fe(4-MPipzcdtH)$_3$](ClO$_4$)$_3$	3	151	1st	151–180	100	100	175	exo
[Co(4-MPipzcdtH)$_2$](ClO$_4$)$_2$	2.5	115	1st	115–229	100	100	225	exo
[Cu(4-MPipzcdtH)$_2$](ClO$_4$)$_2$	2	110	1st	110–240	100	100	233	exo
[Zn(4-MPipzcdtH)$_2$]Cl$_2$	10.98	120	1st	120–240	36.57		–	–
			2nd	240–360	24.77		–	–
			3rd	380–620	24.13		–	–

Compound	Kinetic parameters					
	Stage	E^*/ kJ mol^{-1}	A/ s^{-1}	S^*/ J K^{-1} mol^{-1}	G^*/ kJ mol^{-1}	H^*/ kJ mol^{-1}
4-MPipzcdtH	1st	116.33	0.01	–574.01	444.72	116.33
[Fe(4-MPipzcdtH)$_3$](ClO$_4$)$_3$	1st	144.51	0.01	–619.83	499.12	144.51
[Co(4-MPipzcdtH)$_2$](ClO$_4$)$_2$	1st	14.70	0.99	–339.62	208.99	14.69
[Cu(4-MPipzcdtH)$_2$](ClO$_4$)$_2$	1st	13.03	2.21	–335.82	205.15	13.02
[Zn(4-MPipzcdtH)$_2$]Cl$_2$	1st	49.51	0.01	–412.04	285.24	49.51
	2nd	89.80	0.01	–458.22	351.95	89.80
	3rd	60.30	0.06	–388.46	282.54	60.30

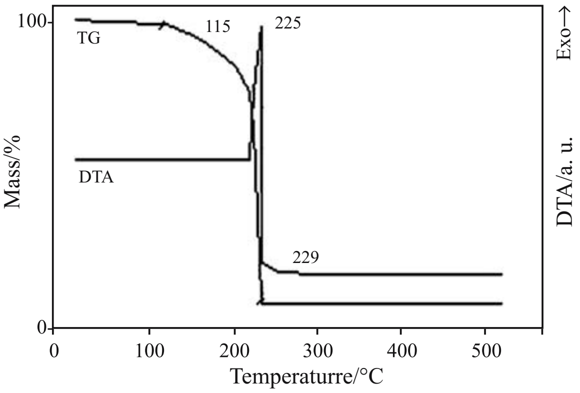


Fig. 3 TG/DTA curves of [Co(4-MPipzcdtH)$_2$](ClO$_4$)$_2$ complex

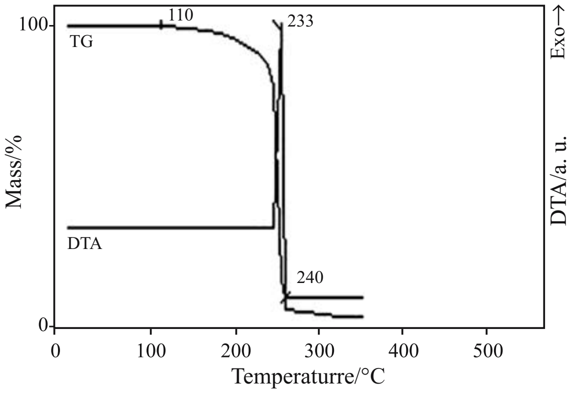


Fig. 4 TG/DTA curves of [Cu(4-MPipzcdtH)$_2$](ClO$_4$)$_2$ complex

a continuous single stage process. A peculiar feature of decomposition of the complexes is that nearly 100% mass loss has occurred within a small temperature range of 9.35–11°C accompanied by a cracking sound. An incubation period of ~2 min for the exothermic change is most plausibly suggestive of the complexes displaying a characteristic of high-energy materials [12]. However, it is pertinent to mention here, that no such exothermic effect has been observed in free 4-MPipzcdtH ligand. The free ligand 4-MPipzcdtH decomposes endothermically while the complexes exhibit exothermic decomposition pathway. The overall effect of decomposition in the complexes follows the counter effect due to the ligand and the effect of perchlorate as the counter part as well as the effect of the metal ion, too. It is of interest to note that the behaviour of the carbodithioate complexes under study is contrary to the previous reports wherein metal oxides or metal sulfides [13] have resulted as end-products from these thermal decomposition processes. In view of the earlier reports of explosive nature of the perchlorates [10] in conjunction with organic group, the present results of TG/DTA data for the carbodithioate complexes under study, are quite meaningful because they leave no residue in the crucible upon decomposition.

Furthermore, the thermal decomposition reactions have been observed to terminate at 180.39, 228.9 and 240°C in Fe(III), Co(II) and Cu(II) carbodithioate complexes, respectively. It has been observed that of all the complexes violent decomposition was more pronounced with the Fe(III) carbodithioate complex. It is worth mentioning here that the present observations of DTA have a close resemblance with the characteristic features of high energy materials and have provided a straight forward means for determining the utility of these complexes as high energy materials in future and it is reasonable to conclude that thermal decomposition processes are energetically favourable.

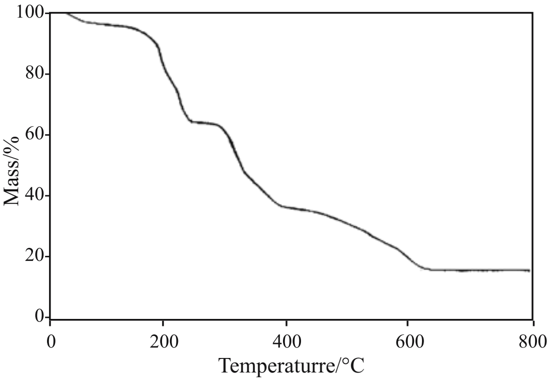


Fig. 5 TG curve of [Zn(4-MPipzcdtH)$_2$]Cl$_2$ complex

TG and DTA curves of [Zn(4-MPipzcdtH)$_2$]Cl$_2$ has shown it to be stable upto 120°C (Fig. 5). Interestingly this complex having chloride as the counter anion in place of perchlorate anion exhibits a three-step decomposition pattern. The nature of the intermediate species as well as that of the lost moiety corresponding to 36.57% mass loss upto 240°C for the first decomposition stage could not be defined. Then mass loss of 24.77% in second stage of decomposition upto 360°C corresponds to the proposition of Zn(SCN)$_2$ as the probable intermediate. The subsequent mass loss of 24.13% in third step of decomposition upto 620°C of this complex has been found to correspond well with the oxidative decomposition of the intermediate to yield ZnO as the ultimate product of decomposition.

Kinetic parameters

Kinetic parameters of the TG data were computed using Coats–Redfern equation [14]. The parameters like entropy S^* [15], free energy G^* [16] and enthalpy of activation H were obtained from their standard relations and results are being presented in Table 1. A perusal of the values of energy of activation (‘E^*’) of the ligand and its complexes (Table 1) under study is indicative of the following decreasing order of the thermal stability wherein all the species follow the single step decomposition:

[Fe(4-MPipzcdtH)$_3$](ClO$_4$)$_3$ (144.51 kJ mol^{-1})>
4-MPipzcdtH (116.33 kJ mol^{-1})>
[Co(4-MPipzcdtH)$_2$](ClO$_4$)$_2$ (14.70 kJ mol^{-1})>
[Cu(4MPipzcdtH)$_2$](ClO$_4$)$_2$ (13.03 kJ mol^{-1})

The trend in activation energies has revealed a compatibility with the order of thermal stability suggesting that higher the value of E^*, the more stable is the complex. However, the Fe(III) complex and the free ligand have exceptionally high values of activation energy indicating their very high stability. This might arise because of the strongest interactions of a trivalent metal ion as compared to divalent metal ion with the ligand. Amongst cobalt(II) and copper(II) complexes, higher activation energy amounting to higher stability of cobalt complex may be because of its relatively larger size compared to the smaller size of copper(II) ion in first transition metal ion series, and hence result in larger accumulation of charge density on the latter ion. Also larger ‘E^*’ and *IDT* values hence higher stability of the free 4-MPipzcdtH ligand may be attributed to its Zwitterionic nature resulting into stronger lattice forces of interaction. Moderate ‘E^*’ and *IDT* values for [Zn(4-MPipzcdtH)$_2$]Cl$_2$ complex and hence its moderate stability may arise because of the relatively stronger lattice forces of interaction as a result of the presence of different counter anion (Cl$^-$) in comparison to that of the ClO$_4^-$ in cobalt and copper complexes. The kinetic data for thermal decomposition of [Zn(4-MPipzcdtH)$_2$]Cl$_2$ complex indicates that the magnitude of activation energy for its second stage of decomposition is larger than that for the first and third stages of decomposition and is suggestive of higher thermal stability of the intermediates, i.e. undefined products of the first stage decomposition step. The ‘E^*’ for the first stage decomposition is the smallest, while ‘E^*’ for the third stage decomposition of Zn(SCN)$_2$, intermediate species, lies in between that for second and first stages of decomposition. It has been attributed to the oxidative decomposition of Zn(SCN)$_2$ (2nd stage intermediate) to yield ZnO.

In general, the value of frequency factor ‘A’ is known to be inversely proportional to ‘E^*’ i.e. higher the ‘E^*’ lower is the ‘A’ or vice-versa. However, it is not always true. The contributions of some more inherent physical and chemical factors, viz. thermodynamic, kinetic and stereospecific etc. have been described for the deviations in this trend [17]. The inverse relationship between ‘E^*’ and frequency factor ‘A’ has been observed for all the compounds under study (Table 1). The magnitude of frequency factor ‘A’ for [Cu(4-MPipzcdtH)$_2$](ClO$_4$)$_2$ has been found to be the highest, for which activation energy is the least. The negative values of entropy of activation ‘S^*’ for all the complexes suggest that the complexes are more ordered [18] in the activated state than the reactants (decomposition products) and that the reactions are slower than normal. It is also noteworthy that the complexes with larger negative values of entropy ‘S^*’ have low values of frequency factor, ‘A’. The large and positive values of free energy of activation ‘G^*’ (205.15–499.13 kJ mol^{-1}) are suggestive of the stability of the complexes. The magnitude of ‘E^*’ and ‘H^*’ are equivalent. The *–ve* value of ‘S^*’ and *+ve* value of ‘G^*’ follow the trend as that of ‘E^*’, giving a highly satisfactory relationship in consonance with the stability factor of the complexes. All the other kinetic parameters are within the range usually observed for a first order reaction.

The thermal decomposition and kinetic parameters, for the metal-4-methylpiperazine-1-carbodithioic acid complexes and the ligand, 4-MPipzcdtH, derived under present investigation are influential in drawing conclusions about the role of the metal ion as well as of perchlorate anion, since dramatic change in the kinetic parameters has been noticed upon the change of the metal ion when perchlorate anion is the counter ion in conjunction with 4-methylpiperazine-1-carbodithioic acid ligand as organic moiety.

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