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Kinetic and Thermal Studies of Zn(II) and Cd(II) Diallyldithiocarbamate Complexes with 2,2'-Bipyridine and 1,10-Phenanthroline

K.A. AL-SOU'OD*, B.F. ALI and M. AL-REFAI
Department of Chemistry, Al al-Bayt University, Mafraq 25113, Jordan
Tel: (962)(795)861350; E-mail: khaldoun@aabu.edu.jo

In present studies, the synthesis and characterization of mixed-ligand complexes of Zn(II) and Cd(II) diallyldithiocarbamate (aldtc) with 2,2'-bipyridine (bipy) and 1,10-phenanthroline (phen) were reported. The new complexes [M(aldtc)$_2$(NN)]; [M = Zn, Cd; NN = bipy and phen] have been characterized by partial elemental analyses and using IR, ^{1}H and ^{13}C NMR spectroscopy. Thermal decomposition of these complexes was investigated using TG and DTG. The decomposition mechanisms were suggested and rationalized based on the structure of complexes and the nature of intermediate products and final residues. The analysis illustrates that the compounds show slightly different pattern of fragmentation leading to M(S$_2$CNR$_2$)SCN which then decomposes to MS residue. Kinetic analysis of the thermogravimetric data using the methods of Kissinger and Flynn-Wall-Ozawa was also made to evaluate the activation energy of the complexes. Both methods gave almost similar results.

Key Words: Zinc, Cadmium, Diallyldithiocarbamate, N-Heterocyclic, Thermal decomposition.

INTRODUCTION

Dithiocarbamate complexes containing substituted dithiocabamato groups along with their thermal decomposition products have attracted much interest from several aspects. These studies explained the role of these compounds in vulcanization, high pressure lubricant agents, fungicides and pesticides[1-5]. The thermochemistry of metal dithiocarbamate has been extensively reported and reviewed[6-10]. Dithiocarbamate complexes considered the most promising species to provide single-source materials for bulk metal sulfides[6,11,12]. They represent a source for MS materials. Barone *et al.*[6] reported the deposition of SnS and SnS$_2$ from (Et$_2$NCS$_2$)$_2$(RS)Sn and (Et$_2$NCS$_2$)$_4$Sn (R = Cy, CH$_2$CF$_3$), respectively. Moreover, MS (M = Zn, Cd) have also been formed thermally[12] from M[S$_2$CN(Me)CH$_2$CH$_2$ CH$_2$NMe$_2$]$_2$.

Less is known about metal diallyldithiocarbamates such as M[S$_2$CN(C$_3$H$_5$)$_2$]$_2$ and their N-heterocyclic adducts of the general formula M[S$_2$CN(C$_3$H$_5$)$_2$]$_2$L; L = bipy and phen.

Recently, the thermal decomposition to MS associated with decomposition mechanisms of $M[S_2CN(C_3H_5)_2]_2$; M = Ni and Cu is also reported[13].

In the present work, the synthesis and characterization of Zn(II) and Cd(II) diallyldithiocarmate complexes containing N-heterocyclic ligands (bipy and phen) and their thermal analysis study associated with thermal decomposition mechanisms along with kinetic study of their decomposition are reported.

EXPERIMENTAL

General method for synthesis of [M(aldtc)$_2$(NN)]; [M = Zn, Cd; NN = bipy and phen][14,15]: To a 1:1 mole ratio (1.0 mmol each) stirred solution of ligands mixture of diallyldithiocarbamate (aldtc) and 2,2'-bipyridine or 1,10-phenanthroline (NN) dissolved in 40 mL EtOH, appropriate $M(NO_3)_2$ salt (1.0 mmol) dissolved in 20 mL EtOH, was added in small portions. The clear resulting mixture was then stirred for 0.5 h, whereupon colourless solid precipitated. The solid was filtered off, washed several times with EtOH and dried under vacuum. The solid was further purified by recrystallization from hot CH_3CN.

[Zn(aldtc)$_2$(bipy)][15] (m.p. 249-251 °C; Yield = 83 %). IR (KBr, ν_{max}, cm^{-1}): 2940 (CH), 1495 (CN), 1088 (CS). Analysis, calculated for $ZnC_{22}H_{28}N_4S_4$: C 50.92, H 4.92, N 9.33 %; found: C 51.03, H 4.92, N 9.33 %.

[Zn(aldtc)$_2$(phen)] (m.p. 265-268 °C; Yield = 87 %). IR (KBr, ν_{max}, cm^{-1}): 2941 (CH), 1499 (CN), 1090 (CS); ^{1}H NMR (δ ppm): allylic protons (δ ppm): 4.438 (d, 4H, H_2C-N), 5.153 (d, 4H, H_2C=CH-), 5.841 (m, 2H, H_2C=CH-); phen protons (δ ppm): 8.846 (d, 2H, H_4, H_4'), 8.07 (dd, 2H, H_4, H_4'), 9.297 (d, 2H, H_6, H_6'), 8.245 (d, 2H, H_7, H_7'); ^{13}C (δ ppm): allylic carbons (δ ppm): 56.140 (CH_2=CH-CH_2N), 118.564 (CH_2=CH-CH_2N), 132.41 (CH_2=CH-CH_2N), 207.801 (N-CS_2); phen carbons (δ ppm): 140.88 (C_2), 129.21 (C_3), 139.61 (C_4), 125.75 (C_5), 149.1 (C_6), 127.55 (C_7). Analysis, calculated for $ZnC_{24}H_{28}N_4S_4$: C 52.92, H 4.78, N 9.49 %; found: C 52.77, H 4.71, N 9.42 %.

[Cd(aldtc)$_2$(bipy)] (m.p. 289-291 °C; Yield = 91 %). IR (KBr, ν_{max}, cm^{-1}): 2945 (CH), 1495 (CN), 1095 (CS); Analysis, calculated for $CdC_{22}H_{28}N_4S_4$: C 47.01, H 4.60, N 9.14 %; found: C 47.12, H 4.63, N 9.22 %.

[Cd(aldtc)$_2$(phen)] (m.p. 253-255 °C; Yield = 89 %). IR (KBr, ν_{max}, cm^{-1}): 2941 (CH), 1499 (CN), 1090 (CS). Analysis, calculated for $CdC_{24}H_{28}N_4S_4$: C 49.01, H 4.43, N 8.79 %; found: C 48.89, H 4.23, N 8.50 %.

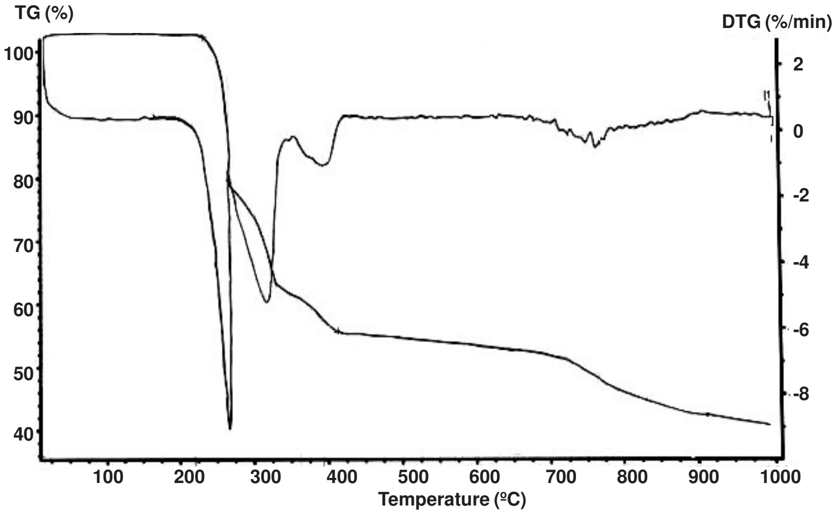
RESULTS AND DISCUSSION

The reaction of zinc(II) or cadmium(II) nitrate metal salt, with a mixture of ligands (2:1; diallyldithicarbamate:N-heterocyclic base) yielded colourless complexes of general formula [M(aldtc)$_2$(NN)] (M = Zn, Cd; aldtc = $S_2CN(C_3H_5)_2$; NN = bipy and phenanthroline). The quantitative yield and various physical measurements are commensurate with the formulation of all the named complexes (Table-1). All complexes are stable in air, soluble in most organic solvents and were isolated in good yields.

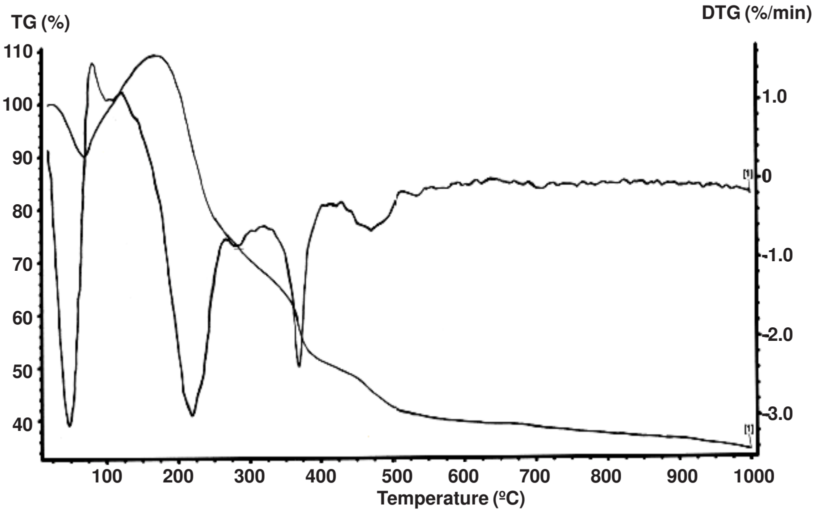
TABLE-1
ACTIVATION ENERGIES OBTAINED WITH THE KISSINGER METHOD FOR [M(aldtc)$_2$(NN)] COMPLEXES

Complex	E_a (kJ/mol)	r
Cd(aldtc)$_2$(phen)	320.4	0.9819
Cd(aldtc)$_2$(bipy)	242.9	0.9905
Zn(aldtc)$_2$(phen)	356.1	0.9918
Zn (aldtc)$_2$(bipy)	279.4	0.9848

Thermal decomposition of diallyldithiocarbamato complexes: Thermogravemetric curves in Fig. 1, suggest that the decomposition of Cd(II) complexes occurs in four stages with the formation of cadmium sulfide as an end product. The first stage starts at about 279 °C and is completed upto *ca.* 300 °C. The mass loss during this stage is 27.9 % (calculated 28.3 %) in case of phen, while 25.89 % (calculated 25.47 %) in case of bipy derivative. This loss corresponds to the separation of NN ligand. After this stage, the decomposition proceeds upto 326.7 % where one aldtc ligand is lost. The observed mass loss is 55.0 % (calculated 55.3 %) for phen and 53.29 % (calculated 53.57 %) in bipy derivative. The third stage starts at 326.7 and ends at 422.1 where further decomposition occurs by the loss of 2(C_3H_5) species, which is evident by the 67.5 % mass loss (calculated 68.2 %) in case of phen while 66.46 % (calculated 67.00 %) in bipy complex. In the final stage (> 425 °C) the metal sulfide is formed, where loss of SCN group occurs and this is confirmed by the mass percentage of the residue (found 23.4 %; calculated 22.7 %) which is consistent with CdS.



(A)

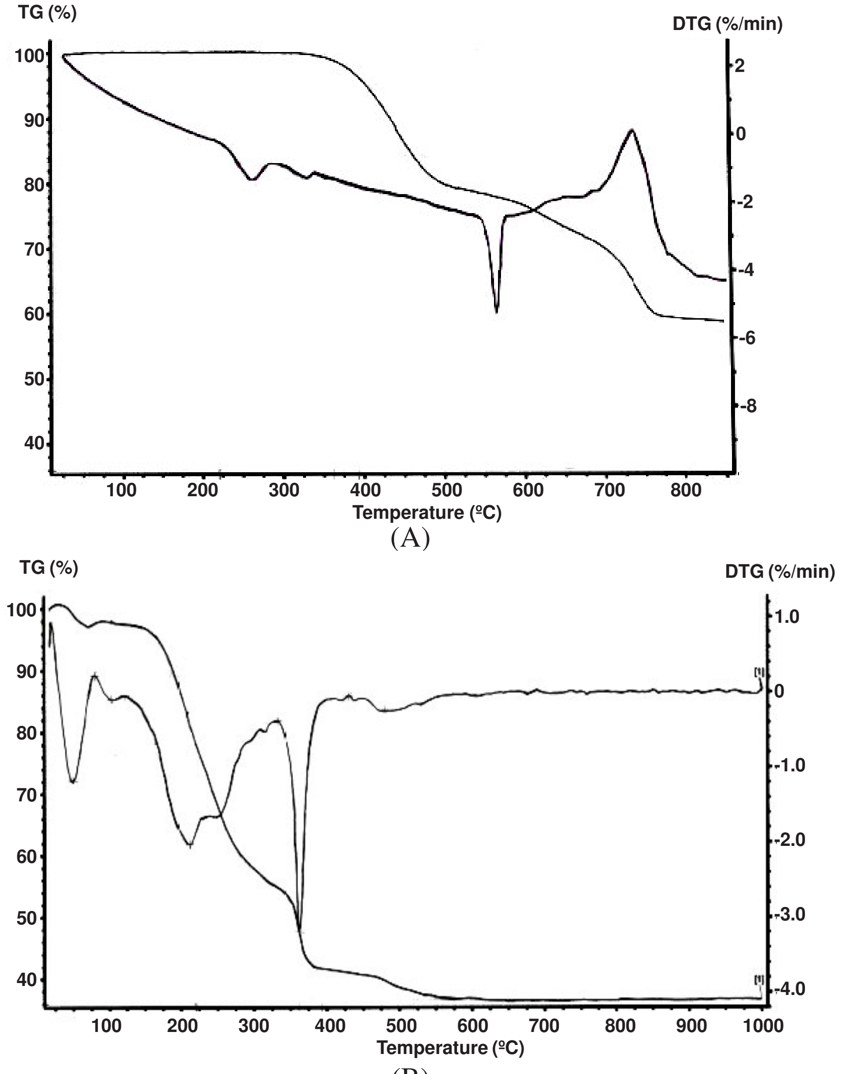


(B)

Fig. 1. Thermogravemetric curves of the thermal decomposition of Cd(II) derivatives: (A) phen; (B) bipy.

The case of Zn complexes, the decomposition occurs (Fig. 2) in three stages with the formation of ZnS as an end product, **Scheme-II**. A careful look of the TG curves shows some mass loss (2.6 %) before the first stage which might be attributed to the loss of a water molecule (calculated 3.1 %) associated with the complex. The first step decomposition for the bipy derivative starts at 122.7 °C and ends up to 219.6 °C, whereupon loss of SR_2 occurs with a mass % loss of 20.9 % (calculated 22.6 %). After this stage, the second stage proceeds up to 393.6 °C where the bipy ligand is lost. The observed mass loss is 50.8 % (calculated 49.4 %). The last stage (> 394 °C) ends up by the formation of ZnS (observed residual mass: 16.1 %; calculated 16.7 %), *via* loss of SCN and then $SCNR_2$ species. Similar pattern is observed for the phen derivative (Fig. 2).

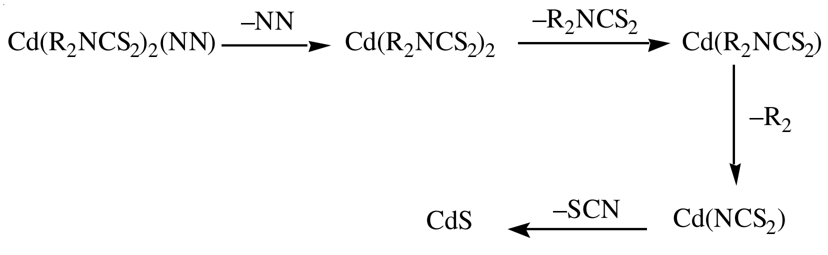
In all complexes small endotherms are observed at temperatures just before the end of the first stage of decomposition. These may correspond to melting of the complexes followed by the decomposition. Much sharper endotherms and exotherms are also observed in the range 300-500 °C and this may correspond to structural changes during decomposition[16]. On the basis of initial thermal decomposition temperatures in all complexes, it is observed that Cd bipy derivative starts decomposition at 180 °C, while the phen derivative starts at 190 °C. On the other hand, Zn phen shows the highest starting decomposition temperature (200 °C) whereas for bipy derivative it is 185 °C. Thus stability of complexes can be arranged accordingly as Cd bipy < Zn bipy < Cd phen < Zn phen. Based on the above discussion the decomposition of the complexes might be considered to occur by the given mechanism which is consistent to reported path[13].



(A)

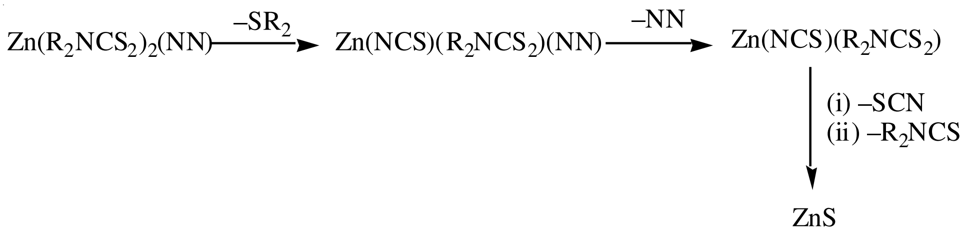
(B)

Fig. 2. Thermogravemetric curves of the thermal decomposition of Zn(II) derivatives: (A) phen; (B) bipy.



$$\begin{tikzcd}
Cd(R_2NCS_2)_2(NN) \arrow[r, "-NN"] & Cd(R_2NCS_2)_2 \arrow[r, "-R_2NCS_2"] & Cd(R_2NCS_2) \arrow[d, "-R_2"] \\
 & CdS & Cd(NCS_2) \arrow[l, "-SCN"']
\end{tikzcd}$$

(A)



(B)

Scheme

It is clear that decomposition of these complexes depends on the metal ion, alkyl group as well as N-heterocyclic ligands bonded to metal.

Decomposition kinetics and activation energies: Decomposition kinetics, were done using the methods of Kissenger and Flynn-Wall-Ozawa (FWO). Activation energies (E_a) for all complexes were calculated as listed in Tables 1 and 2.

TABLE-2
ACTIVATION ENERGIES OBTAINED WITH THE FLYNN-WALL-OZAWA METHOD FOR $Cd(aldtc)_2(phen)$

a (%)	E_a (kJ/mol)	r
7	242.0	0.9943
10	340.9	0.9935
15	336.8	0.9897
20	296.5	0.9966
25	311.8	0.9723
Average	305.6	

TABLE-3
AVERAGE ACTIVATION ENERGIES OBTAINED WITH THE FLYNN-WALL-OZAWA METHOD FOR OTHER COMPLEXES

Complex	E_a (kJ/mol)
$Cd(aldtc)_2(bipy)$	225.6
$Zn(aldtc)_2(phen)$	369.3
$Zn(aldtc)_2(bipy)$	284.1

Kissinger method: This method has been used to determine the activation energy of solid state reactions from plots the logarithm of the heating rate *versus* the inverse of temperature at the maximum reaction rate in a constant heating rate experiments. The advantage of this method that E_a can be estimated without a precise knowledge of the reaction mechanism, using the following equation:

$$\ln\frac{\beta}{T_p^2} = \ln\frac{AR}{E_a} + \ln\left[n(1-\alpha_p)^{n-1}\right] - \frac{E_a}{RT_p}$$

where β is the heating rate, T_p and α_p are the absolute temperature and weight loss at the maximum weight loss rate at $(da/dt)_p$. A is the pre-exponential factor and n is the reaction order. The plot of ln (β/T_p^2) *vs.* $(1/T_p)$ and fitting to a straight line, yields E_a as it is calculated from the slope as listed in Table-1.

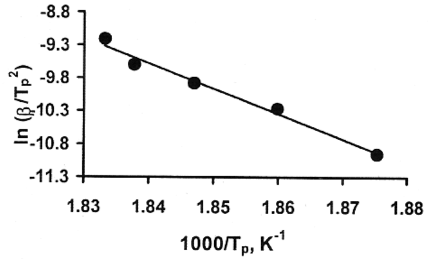


Fig. 3. Plots of ln (β/Tp₂) *vs.* 1000/T_p at different heating rates for complex Cd(aldtc)$_2$(phen) according to Kissinger method

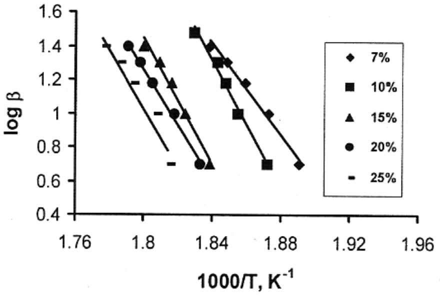


Fig. 4. Plot of log β *vs.* 1000/T with weight loss from 7 to 25 % according to Flynn-Wall-Ozawa method for complex Cd(aldtc)$_2$(phen)

Flynn-Wall-Ozawa (FWO) method: The Flynn-Wall-Ozawa determines the activation energy directly from weight loss *versus* temperature data obtained at several heating rates. The Flynn-Wall-Ozawa treatment uses eqn. 1, which was derived using the Doyle approximation, with only conversion values in the low range can be used (7, 10, 15, 20 and 25% have been used in this study).

$$\log\beta = \log\frac{AE_a}{g(\alpha)R} - 2.315 - \frac{0.457E_a}{RT}$$

where β, A, E_a and T have known meanings. Using this method the reaction order need not to be known inorder to calculate E_a, which can be calculated from log β *vs.* 1000/T plot. From the thermal analysis of the complexes studied and from a linear fitting of log β *vs.* 1000/T at different conversions, E_a were calculated and found to be as listed in Table-2. It is noteworthy that nearly parallel fitted straight lines, indicate the applicability of this method to our system in the conversion range studied. The results of Flynn-Wall-Ozawa method is in good agreement with those obtained using Kissinger method.

The E_a from both methods varies in the range 242.9-348.3 kJ mol^{-1}, being larger for the zinc complexes. This may be due to the smaller size of zinc ions which permits a closer approach of the ligands.

Conclusion

The complexes are octahedral with the two dithicarbamate ligands *cis* to each others. Metal dithiocarbamate complexes containing N-heterocyclic ligand represent a good source of metal sulfide materials. 1,10-Phenanthroline complexes decompose by loss of phen ligand followed by evaporation of metal diallydithiocarbamates and the residue at 600 ºC corresponds to MS. On the other hand, the decomposition process of 2,2'-bipyridyl complexes proceeds by the loss of SR_2 group followed by loss of bipy ligand and the residue was also metal sulfide.

The activation energy of zinc complexes is higher than cadmium complexes that have the same geometry. The smaller the size of the ions permits a closer approach of the ligand.

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