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THERMAL STUDIES OF Zn(II) HYDRAZINE COMPLEXES IN THE SOLID STATE

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ABSTRACT

The synthesis and characterization of $ZnL_nX_2 \cdot mH_2O$, where $L = N_2H_4$; $n = 3$, 2 and 1.5; $X = Cl^-$, Br^- and $\frac{1}{2}SO_4^{2-}$; and $m = 0$ or 1, have been done and their thermal studies have been carried out using a Shimadzu DT-30 Thermal Analyzer. ZnL_3SO_4, $ZnL_{2.75}SO_4$, ZnL_2SO_4, $ZnLCl_2$ and $ZnL_{0.5}Cl_2$ have been synthesized pyrolytically in the solid state from their parent complexes synthesized from solution. Two varieties of ZnL_2Cl_2 synthesized by us are indistinguishable by IR spectroscopy but possess appreciable differences in their thermal profiles. Two forms of ZnL_3SO_4 which are also indistinguishable by IR spectroscopy show noticeable differences in their thermal profiles.

INTRODUCTION

Although the coordination chemistry of hydrazines is widely known [1] the thermal properties of hydrazine complexes have not been extensively investigated [2,3]. Thermal studies of hydrazine complexes of Mn(II), Ni(II), Co(II) and Cd(II) in the solid state have been reported earlier by us [4–7]. In continuation of our investigations on complexes of hydrazine, we report herein complexes of $ZnCl_2$, $ZnBr_2$ and $ZnSO_4$ with hydrazine.

EXPERIMENTAL

Preparation of Zn(II) hydrazine(L) complexes

ZnL_2Cl_2 (1). Hydrazine hydrate (80%, 2 mmol)‡ was added to the concentrated aqueous solution of $ZnCl_2$ (1 mmol) with stirring. Then the mixture was kept for 5–6 h. The white shiny crystals were obtained by

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‡ Excess hydrazine does not alter the composition of the complexes.

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addition of ethanol. The crystals were filtered, washed thoroughly with water–ethanol (1 : 9) and finally with ethanol.

ZnL_2Cl_2(1*). Hydrazine hydrate (2 mmol) was added dropwise with constant stirring to a concentrated solution of $ZnCl_2$ in pyridine medium. The whole mixture was kept for 5–6 h. The crystals were obtained following the procedure as above.

ZnL_2Br_2 (2) and ZnL_3SO_4 (3) have been synthesized by the procedure corresponding to the preparation of complex (1).

$ZnL_{1.5}Br_2$ (2*) and $ZnL_3SO_4 \cdot H_2O$ (3*) have been prepared by applying the procedure adopted for the preparation of complex (1*).

$ZnLCl_2$, $ZnL_{0.5}Cl_2$, $ZnL_{2.75}SO_4$, ZnL_2SO_4, ZnL_3SO_4 have been obtained by applying a temperature-arrest technique to their corresponding parent species in nitrogen atmosphere.

Thermal measurements

Thermal analyses were carried out using a thermal analyzer (Shimadzu, Model DT-30, Japan). A constant flow of dry nitrogen (30 ml min^{-1}) was

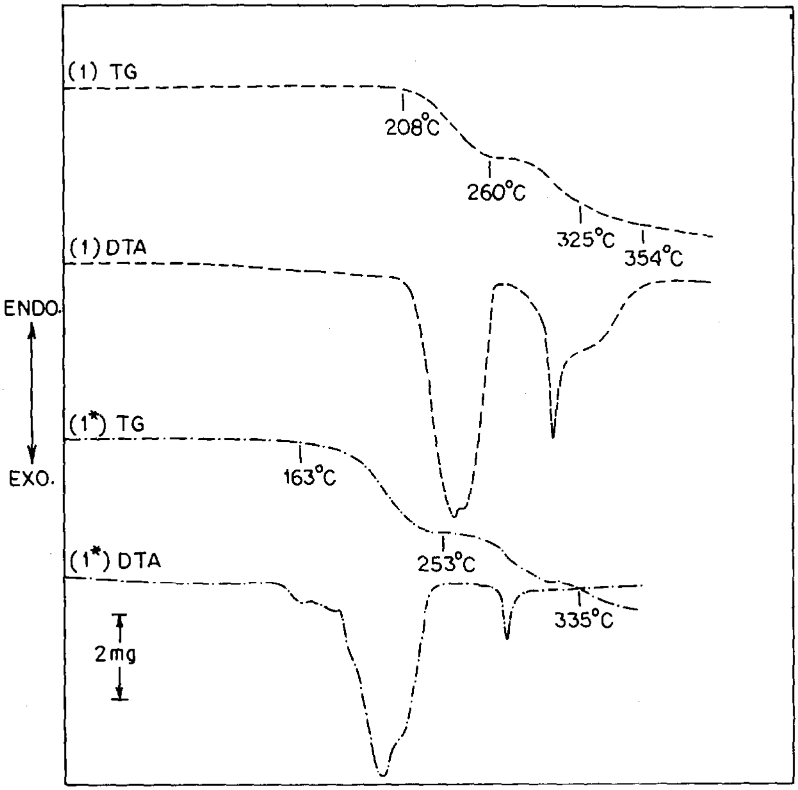


Fig. 1. Thermal curves of ZnL_2Cl_2 (1) (sample mass, 9.68 mg) and ZnL_2Cl_2 (1*) (sample mass, 12.05 mg).

maintained. Platinum crucibles were used. The heating rate was maintained at 5°C $\min^{-1}$. The particle size of the sample was within 150–200 mesh. Aluminum oxide was used as reference.

Elemental analyses and spectral measurements have been done by using instruments as reported earlier [4].

RESULTS

Thermal curves of ZnL_2Cl_2 (1) are shown in Fig. 1. It starts with decomposition at 208°C and transforms to an isolable $ZnLCl_2$ complex at 260°C in a single step, as evident from its TG curve. The corresponding DTA curve shows two overlapping exotherms. The derived $ZnLCl_2$ on further heating decomposes to $ZnCl_2$ in a single step observed from its TG curve but the corresponding DTA curve shows two exotherms overlapping with each other.

ZnL_2Cl_2 (1*) starts decomposition at 163°C (Fig. 1) and transforms to an isolable $ZnL_{0.5}Cl_2$ complex at 245°C in a single step, as evident from its TG curve but its DTA curve shows a number of exothermic peaks overlapping with each other. The derived $ZnL_{0.5}Cl_2$ on further heating decomposes to $ZnCl_2$ in a single step, as evident from its TG and DTA curves.

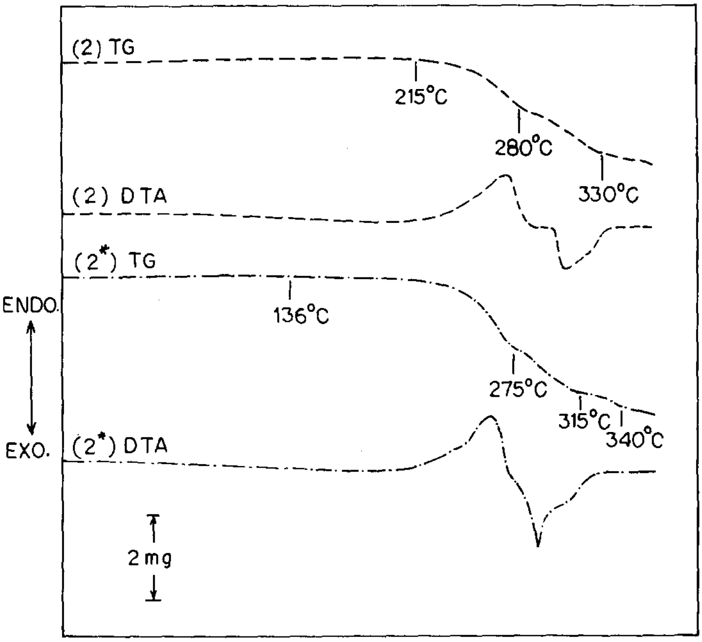


Fig. 2. Thermal curves of ZnL_2Br_2 (2) (sample mass, 8.83 mg) and $ZnL_{1.5}Br_2$ (2*) (sample mass, 15.54 mg).

Figure 2 shows the thermal curves of ZnL_2Br_2 (2). It starts to lose hydrazine at 215°C and transforms to nonisolable $ZnLBr_2$ at 280°C in a single step showing an endothermic peak at 275°C. The derived $ZnLBr_2$ immediately starts decomposition and transforms to the corresponding metal salt at 330°C showing two exothermic peaks overlapping with each other.

The thermal curve of $ZnL_{1.5}Br_2$ (2*) is shown in Fig. 2. It decomposes at 190°C and transforms to $ZnL_{0.5}Br_2$ at 275°C in a single step. The intermediate, $ZnL_{0.5}Br_2$, immediately starts decomposition to $ZnBr_2$ on further heating in a single step, as evident from its TG curve. The corresponding DTA curve shows two exotherms overlapping with each other.

Figure 3 shows the thermal curves of ZnL_3SO_4 (3). It starts to lose hydrazine at 175°C and transforms to an isolable intermediate, $ZnL_{2.75}SO_4$, in a single step showing an endotherm. The derived $ZnL_{2.75}SO_4$ starts decomposition at 255°C and transforms to ZnL_2SO_4 at 320°C in a single step showing an endothermic peak at 290°C. The derived ZnL_2SO_4 on further heating transforms to $ZnSO_4$ at 425°C showing two endotherms and one exotherm overlapping with each other.

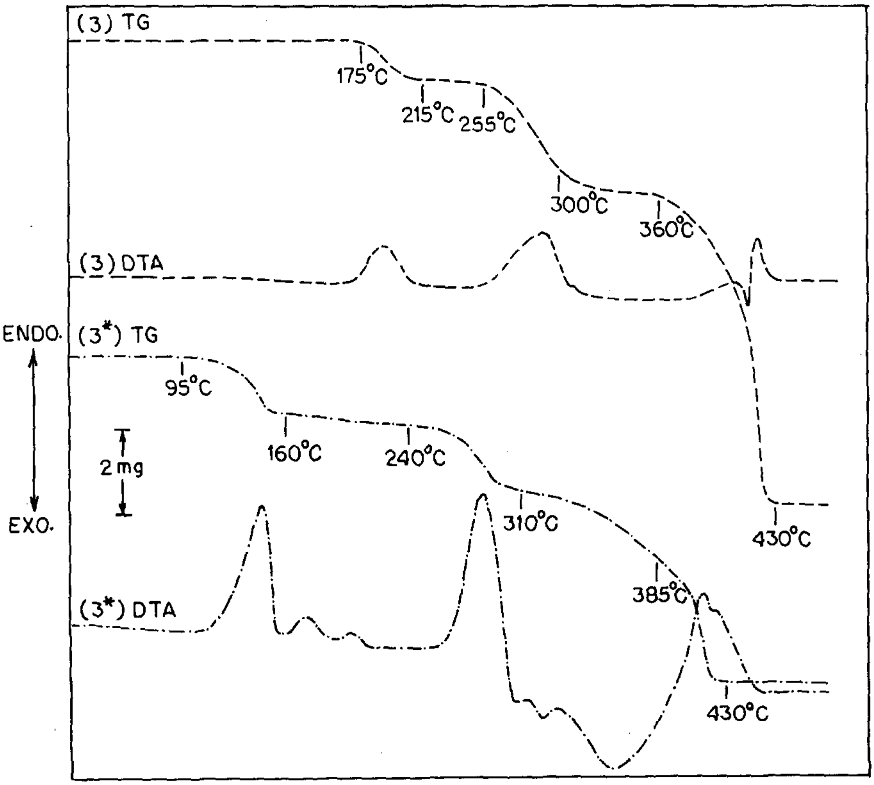


Fig. 3. Thermal curves of ZnL_3SO_4 (3) (sample mass, 27.29 mg) and $ZnL_3SO_4 \cdot H_2O$ (3*) (sample mass, 19.65 mg).

$ZnL_3SO_4 \cdot H_2O$ (3*) starts decomposition at 100°C (Fig. 3) and transforms to an anhydrous species at 145°C in a single step. The anhydrous species starts decomposition at 160°C and transforms to ZnL_2SO_4 at 325°C

TABLE 1

Thermoanalytical data of Zn(II) hydrazine(L) complexes

Decomposition reaction	Temperature range (°C)	DTA peak temperature (°C)	
		Exothermic	Endothermic
ZnL_2Cl_2 (1) → $ZnLCl_2$	208–260	238, 248	
$ZnLCl_2$ → $ZnCl_2$	275–354	310, 335	
ZnL_2Cl_2 (1*) → $ZnL_{0.5}Cl_2$	163–245	165, 180, 200, 216, 230	
$ZnL_{0.5}Cl_2$ → $ZnCl_2$	255–320	293	
ZnL_2Br_2 (2) → $ZnLBr_2$	215–280		275
$ZnLBr_2$ → $ZnBr_2$	280–330	315, 325	
$ZnL_{1.5}Br_2$ (2*) → $ZnL_{0.5}Br_2$	190–275		263
$ZnL_{0.5}Br_2$ → $ZnBr_2$	275–315	293, 310	
ZnL_3SO_4 (3) → $ZnL_{2.75}SO_4$	175–215		190
$ZnL_{2.75}SO_4$ → ZnL_2SO_4	255–320		290
ZnL_2SO_4 → $ZnSO_4$	360–425	415	407, 420
$ZnL_3SO_4 \cdot H_2O$ (3*) → ZnL_3SO_4	100–145		140
ZnL_3SO_4 → ZnL_2SO_4	160–325		170, 200, 285
ZnL_2SO_4 → $ZnLSO_4$	325–403	330, 360	
$ZnLSO_4$ → $ZnSO_4$	403–418		410, 418

TABLE 2

Analytical (calculated values in parentheses) data of Zn(II) hydrazine complexes

Compounds	Analysis %		
	Metal	Nitrogen	Halogen/sulfur
ZnL_2Cl_2 (1)	32.58(32.62)	27.87(27.94)	35.37(35.43)
ZnL_2Cl_2 (1*)	32.57(32.62)	27.88(27.94)	35.39(35.43)
ZnL_2Br_2 (2)	22.53(22.60)	19.31(19.36)	55.20(55.26)
$ZnL_{1.5}Br_2$ (2*)	23.88(23.93)	15.31(15.37)	58.47(58.49)
ZnL_3SO_4 (3)	25.37(25.40)	32.58(32.63)	12.37(12.43)
$ZnL_3SO_4 \cdot H_2O$ (3*)	23.68(23.74)	30.45(30.50)	11.61(11.62)
$ZnLCl_2$ [a]	38.80(38.82)	16.59(16.62)	42.11(42.16)
$ZnL_{0.5}Cl_2$ [b]	42.83(42.90)	9.16(9.18)	46.52(46.59)
$ZnL_{2.75}SO_4$ [c]	26.16(26.21)	30.81(30.87)	12.81(12.83)
ZnL_2SO_4 [c]	28.70(29.00)	24.76(24.84)	14.16(14.19)
ZnL_3SO_4 [d]	25.36(25.40)	32.57(32.63)	12.39(12.43)

[a] Derived from complex (1).
[b] Derived from complex (1*).
[c] Derived from complex (3).
[d] Derived from complex (3*).

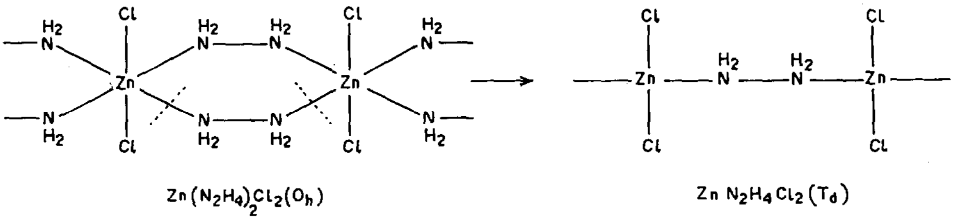
in a single step observed from its TG curve. The corresponding DTA curve shows three distinct endotherms. The derived ZnL_2SO_4 on further heating transforms to $ZnSO_4$ through the formation of nonisolable $ZnLSO_4$. The corresponding DTA curve shows two overlapping exotherms for the formation of $ZnLSO_4$ and two overlapping endotherms for the elimination of residual hydrazine.

Thermoanalytical data are shown in Table 1 and analytical data are shown in Table 2.

DISCUSSION

Complexes derived from $ZnCl_2$ and hydrazine

Treatment of a saturated aqueous solution of $ZnCl_2$ with hydrazine results in ZnL_2Cl_2 (1) while the treatment of $ZnCl_2$ in pyridine medium with hydrazine generates ZnL_2Cl_2 (1*). Both complexes are perfectly white in color. The appearance of bands in the IR spectra between 960–980 cm^{-1} ν(N–N) indicates the bridging bidentate character of hydrazine [8] in both cases. The physicochemical investigations of complex (1) synthesized by us suggest no difference in geometry from the complex reported earlier [9,10]. $Zn(N_2H_4)_2Cl_2$ shows infinite-chain structure with *cis*-bridging hydrazine and *trans*-Cl ions as evident from its crystal structure determination [10]. We have been able to isolate $ZnLCl_2$ as an intermediate species. IR spectral data show the bridging character of hydrazine. The monohydrazine species may attain O_h geometry where halogens act as bridging bidentate ligands and T_d geometry where chloride ion behaves as a monodentate ligand. A tetrahedral arrangement of the ligands around Zn is assumed in this compound since coordination number 4 is more characteristic for Zn^{2+} [11]. The thermal decomposition pattern of ZnL_2Cl_2 (1) shows that one molecule of hydrazine is evolved from one molecule of the complex in the first step. Since one hydrazine molecule is linked by two Zn^{2+} ions, one of the two bridged hydrazines in ZnL_2Cl_2 (1) is evolved when decomposition starts, as shown below.



An interesting feature is that alternation of the preparative procedure yields ZnL_2Cl_2 (1*), which is indistinguishable by IR spectroscopy. A major difference in the thermal profile is observed between complexes (1) and (1*) (Table 1). The difference in the thermal profile observed between complexes (1) and (1*) also indicates the difference in their geometries. Complex (1) appears more stable in comparison to that of complex (1*). This shows more regular geometry in complex (1) in comparison to complex (1*). We have isolated a hemihydrazine complex as an intermediate from the parent (1*). In the complex $ZnL_{0.5}Cl_2$, the chloride ligands are possibly bridged, considering the composition and the preferential stereochemistry (T_d symmetry) of the Zn^{2+} ion.

Complexes derived from $ZnBr_2$ and hydrazine

Treatment of hydrazine hydrate with the concentrated aqueous solution of $ZnBr_2$ affords ZnL_2Br_2 (2) whilst on treatment of hydrazine hydrate with $ZnBr_2$ in pyridine medium results in $ZnL_{1.5}Br_2$ (2*). Both the species are white in color. IR spectra show the bridging character of hydrazine in both complexes. The geometry of ZnL_2Br_2 appears similar to that of ZnL_2Cl_2 reported earlier. We found similarity in the TG profile of complexes (1) and (2) though their DTA profiles have appreciable differences (Table 1). We could not isolate $ZnLBr_2$ as shown by complex (2) (Table 1). We have failed also to isolate the intermediate $ZnL_{0.5}Br_2$, which appears upon heating of $ZnL_{1.5}Br_2$ (2*) (Fig. 2). The composition of $ZnL_{1.5}Br_2$ (2*) suggests the bridging bidentate character of the bromide ligand existing in it, considering its preferential stereochemistry.

The complexes derived from $ZnSO_4$ and hydrazine

A concentrated aqueous solution of $ZnSO_4$ reacting with hydrazine hydrate results in ZnL_3SO_4 (3) while on treatment of hydrazine hydrate with $ZnSO_4$ in pyridine medium affords $ZnL_3SO_4 \cdot H_2O$ (3*). The IR spectral data of both complexes show the bridging character of hydrazine. The literature shows that Zn^{2+} ion is coordinated octahedrally by six nitrogen atoms of three N_2H_4 groups in $ZnL_3(NO_3)_2$ reported earlier [3]. We have isolated two intermediates, $ZnL_{2.75}SO_4$ and ZnL_2SO_4 derived from complex (3). The $ZnL_{2.75}SO_4$ appears very interesting as it is very difficult to suggest how it exists from the bridging bidentate character of hydrazine and noncoordinated character of the SO_4 group, indicated by its IR spectra. The geometry of ZnL_2SO_4 is likely to exist as that of ZnL_2Cl_2. The interesting thermal behavior of ZnL_2SO_4 is that it does not generate any intermediates, either $ZnLSO_4$ or $ZnL_{0.5}SO_4$, like those of ZnL_2Cl_2 complexes. The alteration of preparative procedure also yields a tris species with one molecule of water. The water present in complex (3*) is not coordinated to the zinc ion, as evident from its IR spectral data though it requires a comparatively high temperature for its dehydration. The anhydrous tris species derived from the parent complex (3*) shows practically no difference from the IR spectra of ZnL_3SO_4 (3). In complex (3), three NH_2 stretching frequencies at 3260 cm^{-1}, 3220 cm^{-1} and 3170 cm^{-1} are observed whereas only one band at 3260 cm^{-1} is observed in the tris complex derived from the parent (3*). The decomposition pattern of complex (3*) appears simple with respect to that of complex (3) though we could not isolate the intermediates, ZnL_2SO_4 and $ZnLSO_4$, pyrolytically from complex (3*). These observations definitely indicate that the geometry attained by complex (3) is not identical to the geometry attained by the anhydrous species of complex (3*).

The thermal stability of ZnL_2X_2 ($X = Cl^-$ or Br^- or SO_4^{2-}) shows the order $Cl \leqslant Br < SO_4$. This order also prevails in monohydrazine complexes. The interesting observation is that we noticed some kind of rearrangement taking place in the freshly prepared hydrazine complexes of Cd^{2+} ion on keeping them in a desiccator for a month [7]. This type of rearrangement does not take place here. Another interesting feature is that zinc hydrazine complexes generate a smaller number of complexes as intermediates in comparison to that of Cd complexes reported by us.

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