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THERMALLY-INDUCED PHASE TRANSITION OF ZINC(II) DIAMINE COMPLEXES IN THE SOLID STATE

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ABSTRACT

$ZnLCl_2 \cdot 0.5H_2O$ and $ZnL_2X_2 \cdot nH_2O$ (L = *N*-2(hydroxyethyl)-1,2-ethanediamine; X = Br, $0.5SO_4$, $0.5SeO_4$ and $n = 0.5–2$) have been synthesized and thermal investigations have been carried out in the solid state. $ZnLCl_2 \cdot 0.5H_2O$ and $ZnL_2Br_2 \cdot 0.5H_2O$ show endothermic reversible phase transitions (135.0–152.0 °C, $\Delta H = 1.6$ kJ mol^{-1} and 127.0–144.5 °C, $\Delta H = 10.4$ kJ mol^{-1}, respectively) after dehydration. $ZnL_2SO_4 \cdot 2H_2O$ becomes dehydrated at 100 °C and on further heating undergoes an exothermic irreversible phase transition (109.5–146.0 °C, $\Delta H = -9.5$ kJ mol^{-1}), whereas $ZnL_2SeO_4 \cdot H_2O$ first undergoes dehydration at 134 °C and then an endothermic irreversible phase transition occurs (141.5–171.5 °C, $\Delta H = 14.2$ kJ mol^{-1}).

INTRODUCTION

Thermally-induced phase transitions and decomposition of metal diamine complexes have been reported by us [1–9]. The phase transitions were reported to be due to either (i) conformational changes in the diamine chelate ring [1–4] or (ii) formation/breaking of hydrogen bonds [5,6]. We report here thermal studies of zinc(II) complexes of *N*-2(hydroxyethyl)-1,2-ethanediamine (L) in the solid state. This study is likely to be meaningful considering the coordination through protonated oxygen [10,11], which seems to be very weak. This bond may be dissociated upon heating causing another type of phase transition. Besides this, it is expected that generation of monodiamine species through pyrolysis is likely to be possible as literature shows formation of MLC_2O_4 [M = Mn(II), Cu(II), Zn(II) and Cd(II)] from its corresponding bis analogue [12].

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EXPERIMENTAL

Preparation of $ZnLCl_2$ 0 $5H_2O$ *(1),* ZnL_2Br_2 0 $5H_2O$ *(2),* ZnL_2SO_4 $2H_2O$ *(3) and* ZnL_2SeO_4 H_2O *(4)*

Diamine (2–3 mmol) were added slowly with continuous stirring to the aqueous solutions of the corresponding zinc salts (1 mmol) The resulting mixture was filtered and to the filtrate ether–ethanol (1 1) was added dropwise till the separation of the complex started The desired complex was filtered, washed with dry ethanol and dried over a fused calcium chloride desiccator Analytical data of the above complexes are presented in Table 1

The apparatus employed for recording thermal and IR spectral data (ambient and above ambient temperature) are the same as reported earlier [1–9] The molar conductance data in solution were taken using a Philips PR 9500 conductivity bridge

RESULTS AND DISCUSSION

The ligand yields complexes with a ligand to metal ratio of 2 1 with zinc bromide, sulphate and selenate whereas with zinc chloride the mono complex results under similar experimental condition The attempts to isolate ZnL_2Cl_2 remained unsuccessful even on increasing the ligand–metal ratio up to ten-fold in every case we obtained the mono complex The isolation of mono complex in solid state from the corresponding bis species is not possible here by the temperature arrest technique as there is no such indication of the stable intermediate in their respective TG and DTA profile This behaviour is in contrast to that of the oxalato complexes reported by Rao and Murthy [12] where the mono complexes were obtained easily by controlled thermal decomposition of the bis complexes This difference in

TABLE 1

Analytical data of zinc(II) diamine (L) complexes

Compound	Found (calc) (%)			
	Metal	Nitrogen	Carbon	Hydrogen
$ZnLCl_2$ 0 $5H_2O$ (1)	26 18 (26 20)	11 20 (11 22)	19 21 (19 24)	5 21 (5 21)
$ZnLCl_2$ (1a)	27 15 (27 18)	11 61 (11 64)	19 93 (19 96)	4 98 (4 99)
ZnL_2Br_2 0 $5H_2O$ (2)	14 75 (14 77)	12 63 (12 65)	21 66 (21 69)	5 63 (5 65)
ZnL_2Br_2 (2a)	15 05 (15 08)	12 88 (12 91)	22 11 (22 14)	5 52 (5 54)
ZnL_2SO_4 $2H_2O$ (3)	16 07 (16 11)	13 75 (13 80)	23 62 (23 66)	6 94 (6 90)
ZnL_2SeO_4 H_2O (4)	15 01 (15 04)	12 85 (12 88)	22 06 (22 09)	6 00 (5 98)
ZnL_2SeO_4 (4a)	15 64 (15 69)	13 41 (13 44)	23 01 (23 04)	5 78 (5 76)

TABLE 2

Thermal parameters of zinc(II) diamine (L) complexes

Reactions	Temperature range (° C)	DTA peak temperature (° C)	
		Endothermic	Exothermic
$ZnLCl_2$ 0 $5H_2O$ (1) → $ZnLCl_2$ (1a)	75 0–126 0	86 0, 115 0	–
$ZnLCl_2$ (1a) → $ZnLCl_2$ (1b)	135 0–152 0	149 0	–
$ZnLCl_2$ (1b) → $ZnLCl_2$ (1a)	148 0–131 0	–	145 0
$ZnLCl_2$ (1b) → $ZnCl_2$	246 0–475 0	322 0	338 0
ZnL_2Br_2 0 $5H_2O$ (2) → ZnL_2Br_2 (2a)	65 0–98 0	80 0	–
ZnL_2Br_2 (2a) → ZnL_2Br_2 (2b)	127 0–144 5	137 5	–
ZnL_2Br_2 (2b) → ZnL_2Br_2 (2a)	141 5–124 0	–	134 5
ZnL_2Br_2 (2b) → $ZnBr_2$	269 0–470 0	319 0	333 0
ZnL_2SO_4 $2H_2O$ (3) → ZnL_2SO_4 (3a)	35 0–100 0	82 0, 98 0	–
ZnL_2SO_4 (3a) → ZnL_2SO_4 (3b)	109 5–146 0		132 0
ZnL_2SO_4 (3b) → $ZnSO_4$	174 0–514 0	186 0, 200 0	306 0, 322 0
ZnL_2SeO_4 H_2O (4) → ZnL_2SeO_4 (4a)	86 0–134 0	126 0	–
ZnL_2SeO_4 (4a) → ZnL_2SeO_4 (4b)	141 5–171 5	159 5	–
ZnL_2SeO_4 (4b) → $ZnSeO_4$	182 0–340 0	204 0	225 0

behaviour of the oxalato complex is probably due to the greater coordinating power of the oxalate than the bromide, sulphate and selenate group. All the four complexes reported here undergo solid-state thermal phase transition Their probable structures and the nature of phase transitions are described below

$ZnLCl_2$ (1a) shows 1 1 electrolytic behaviour in methanol ($\Lambda_m = 75$ mho) It was reported earlier [10] that the noncoordinated hydroxyethyl group showed a strong sharp $\nu_{(OH)}$ in the IR spectrum at ~ 3370 cm^{-1} However, in the IR spectrum of (1a), no corresponding OH frequency was recorded. Therefore, the OH group should be coordinated to Zn(II) and consequently the $\nu_{(OH)}$ band must have shifted to a lower frequency due to the metal–oxygen bond in the region 3300–3100 cm^{-1}, overlapping the NH frequencies [10] These observations along with its composition (Table 1) lead us to suggest that in the complex (1a), Zn(II) possesses tetrahedral configuration with the ZnN_2OCl chromophore. This complex (1a) on crystallization from water yields its hydrated species $ZnLCl_2$ 0 $5H_2O$ (1) The species (1) can also be synthesized directly by mixing ligand and metal salt as described in the experimental section Complex (1) starts to lose water at 75 °C and transforms to (1a) at 126 °C (Table 2) The complex (1a) on heating undergoes an endothermic phase transition (135 0–152 0 °C, $\Delta H =$ 1 6 kJ mol^{-1}) yielding (1b), which reverts to (1a) on cooling, showing an exothermic transition in the corresponding DTA and DSC curves (Table 2, Fig 1) Complex (1b), on further heating, melts (melting peak temp = 167 °C) and then starts to decompose at 246 °C

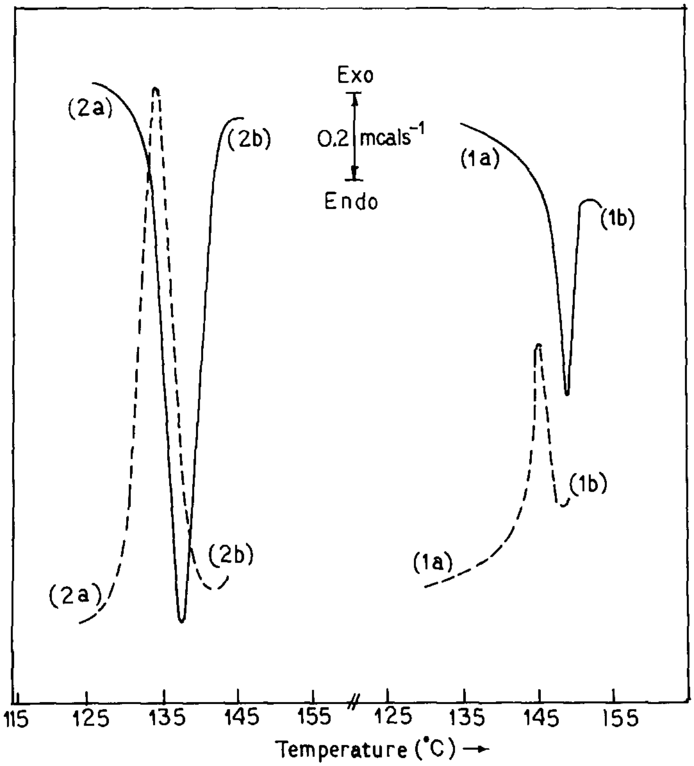

Fig 1 DSC curves of $ZnLCl_2$ (1a) (heating) (wt taken = 6 65 mg) (———), $ZnLCl_2$ (1b) (cooling) (wt taken = 6 65 mg) (— — —), ZnL_2Br_2 (2a) (heating) (wt taken = 6 91 mg) (———), ZnL_2Br_2 (2b) (cooling) (wt taken = 6 91 mg) (— — —)

ZnL_2Br_2 0 $5H_2O$ (2) starts to lose water at 65 °C to generate the anhydrous species ZnL_2Br_2 (2a) at 98 °C (Table 2) The species (2a) shows 1 2 electrolytic behaviour in methanol ($\Lambda_m = 154$ mho) The IR spectra of (2a) show a band at 3340 cm^{-1}, probably due to the $\nu_{(OH)}$ which is in lower frequency region in comparison to the free $\nu_{(OH)}$, but not as low as the coordinated hydroxyl group in $ZnLCl_2$ (1a) Consequently, the hydroxyl groups are considered to be weakly coordinated to Zn(II) to form a pseudo-octahedral configuration with the ZnN_4O_2 chromophore The complex (2a), upon heating, undergoes an endothermic phase transition (127 0–144 5 °C, $\Delta H = 10\ 4$ kJ mol^{-1}) transforming into (2b) which, on cooling, reverts to (2a) (141.5–124 0 °C, $\Delta H = -10\ 6$ kJ mol^{-1}) as is evident from the TG, DTA and DSC curves (Table 2, Fig 1) On further heating, it first melts (melting peak temp = 166 °C) and then starts to decompose at 269 °C It was reported earlier [13,14] that several diamine complexes of Cu(II) and Ni(II) undergo a similar type of endothermic reversible phase transition due to the conformational changes of diamine chelate rings, and such transitions are associated with IR spectral changes in the regions ~ 1600 cm^{-1} and 1400–800 cm^{-1} [1–4,14] To explain the nature of these reversible phase transitions we have recorded the IR spectra of both complexes [(1a) and (2a)] at room temperature and at the temperatures where the phase transitions complete but where spectral changes in these regions are minimal Again, on increasing the temperature, the thermal vibration of the chelate ring increases, thereby the weakly coordinated O–Zn bond may dissociate causing either a geometrical change from octahedral to tetrahedral (in the case of ZnL_2Br_2) or chromophoric changes retaining the respective configurations (tetrahedral in the case of $ZnLCl_2$ and octahedral in the case of ZnL_2Br_2) However, these types of changes must be associated with the IR spectral changes of the $\nu_{(OH)}$ vibration, and as no such changes were observed in the IR spectra of room temperature and higher temperature phases of the complexes, the cause for the phase transition is probably not due to the change of the coordination behaviour of the -OH group For the solid-state phase transition the opening/formation of the H-bonds and/or change in the crystalline state may also be responsible It is thus very difficult to characterize the phase transition prevailing here

The complex, ZnL_2SO_4 $2H_2O$ (3) is highly hygroscopic It shows nonelectrolytic behaviour in methanol ($\Lambda_m = 37$ mho) Coordination of hydroxyl group is not interpretable from the IR spectra due to the presence of water molecules Although the coordination of sulphate groups are also not interpretable from the IR-active sulphate bands due to overlapping with diamine bands, the composition and the nonelectrolytic behaviour suggest that the diamine should be coordinated here only through the nitrogen and, to satisfy the hexa coordination around the Zn(II), the sulphate group should act as a chelating bidentate species Complex (3) starts dehydration at 35 °C and becomes ZnL_2SO_4 (3a) at 100 °C which, on further heating, shows an irreversible exothermic phase transition (109 5–146 0 °C, $\Delta H = -9\ 5$ kJ mol^{-1}) yielding (3b) (Table 2, Fig 2) This phase transition takes place only with freshly prepared complex The ΔH values of the transition gradually decrease on aging and, ultimately, after ~ 72 h, this transition disappears completely The post-phase species (3b) is also hygroscopic However, the rehydrated species, on heating, does not undergo any phase transition phenomena after loss of water

ZnL_2SeO_4 H_2O (4) shows nonelectrolytic behaviour in methanol ($\Lambda_m =$ 42 mho) It is not as hygroscopic as its sulphato analogue This complex, after dehydration, undergoes an irreversible endothermic phase transition (141 5–171 5 °C, $\Delta H = 14\ 2$ kJ mol^{-1}) yielding (4b), which does not revert to (4) even on rehydration from the atmospheric moisture like sulphato complex (3b) (Table 2, Fig 2) This is the most notable difference in behaviour of these post-phase species [(3b) and (4b)] from some of the Ni(II) diamine complexes [1,2,9] where a similar type of phase transition occurred

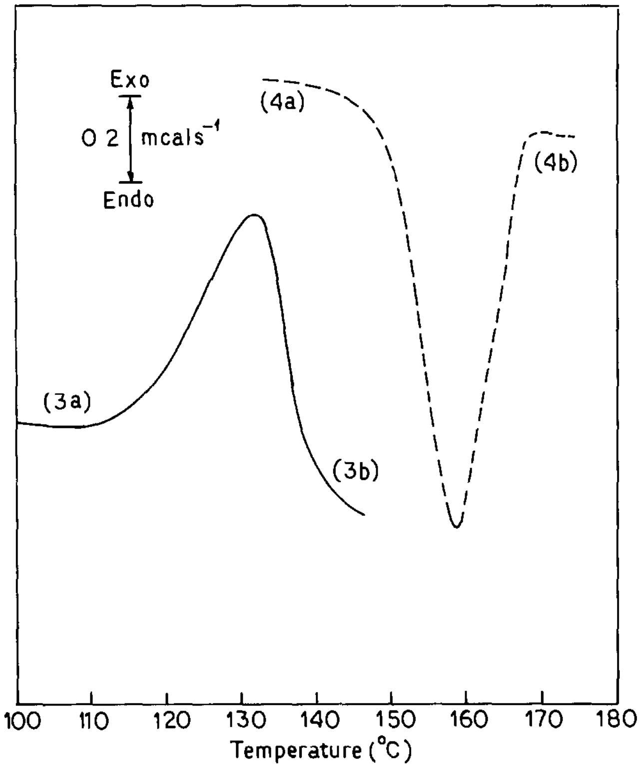

Fig 2 DSC curves of ZnL_2SO_4 (3a) (heating) (wt taken = 9 31 mg) (———), ZnL_2SeO_4 (4a) (heating) (wt taken = 7 60 mg) (— — —)

and the reversion of the post-phase species took place on exposure to a humid atmosphere

It is interesting to note here that, though the complexes (3) and (4) possess similar IR spectra due to the diamine vibration (and consequently they are considered to possess similar structure), the nature of the phase transitions which occur just after dehydration is completely different, i e in (3) the phase transition is exothermic whereas in (4) it is endothermic This difference may be due to the larger ionic size of SeO_4^{2-} compared with SO_4^{2-} In the case of complexes (3) and (4) there is also no noticeable difference in the IR spectra of the post-phase species from their corresponding pre-phase species, such as (1) and (2) Therefore, the exact nature of the phase transition could not be characterized here, though any one of the causes that was described above may be responsible It should be mentioned here that in our earlier works [1,8] with several diamine complexes of Zn(II), we did not find any similar types of phase transition phenomena Therefore, it is reasonable to infer that the hydroxyethyl group plays an important role in these phase transitions However, from the IR spectra it can be seen that the coordination behaviour of the –OH group most likely does not change after the phase transition, and thus the H-bonding phenomena may be taken as the probable cause for the transition

REFERENCES

1 G De, P K Biswas and N Ray Chaudhuri, J Chem Soc Dalton Trans , (1984) 2509
2 G De and N Ray Chaudhuri, Transition Met Chem , 10 (1985) 476
3 A K Mukherjee, M Mukherjee, A J Welch, A Ghosh, G De and N Ray Chaudhuri, J Chem Soc Dalton Trans , (1987) 997
4 A Ghosh, G De and N Ray Chaudhuri, J Chem Res , (1987) 104
5 A Ghosh, G De and N Ray Chaudhuri, Transition Met Chem , 11 (1986) 81
6 A Ghosh, G De and N Ray Chaudhuri, J Therm Anal , 30 (1985) 447
7 A Ghosh, G De and N Ray Chaudhuri, Bull Chem Soc Jpn , 58 (1985) 715
8 G De and N Ray Chaudhuri, Thermochim Acta, 69 (1983) 349
9 A Ghosh, G De and N Ray Chaudhuri, Thermochim Acta, 105 (1986) 35
10 B Das Sharma and John C Bailar, Jr , J Am Chem Soc , 91 (1969) 5958
11 J Bassett, R Grzeskowiok and B L O'Leary, J Inorg Nucl Chem , 32 (1970) 3861
12 G N Rao and C S R Murthy, Thermochim Acta, 48 (1981) 375
13 D R Bloomquist and R D Willet, Coord Chem Rev , 47 (1982) 125
14 L Menabue, G C Pellacani, L P Battagila, A B Corradi, F Sandrolini, A Motori, R J Pylkki and R D Willet, J Chem Soc Dalton Trans , (1984) 2187