

SOLID STATE THERMAL PHASE TRANSITION OF CADMIUM(II) DIAMINE COMPLEXES *

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ABSTRACT

Some unusual solid state thermal phase changes phenomena in cadmium(II) diamine complexes have been studied by differential scanning calorimetry. $[\text{CdL}_2\text{SeO}_4]$ and $[\text{CdLSeO}_4]$ (where L = 1,3-propanediamine and *N*-methyl 1,3-propanediamine) have been synthesized. The monodiamine complexes are isolable in the solid state by thermolytic decomposition of their corresponding bisdiamine complexes. Bis and mono-diamine complexes undergo phase transition in solid state upon heating. Infrared spectra of the complexes at ambient temperature and at the temperature where phase transition phenomena is complete were obtained.

INTRODUCTION

This paper is in continuation to our previous reports in which we described some unusual thermal phase transitions and solid state reactions of metal diamine complexes [1–5]. It was believed that these phase transitions occurred because of (i) conformational changes of the diamine chelates [1,2], (ii) formation of hydrogen bonding [3], (iii) formation of the chelated diamine complex from its bridged form [1] and (iv) opening of hydrogen bonding [4,5] etc.

Structurally related phase transitions of coordination complexes are very interesting phenomena [6–9]. In the case of reversible thermal phase transitions, characterization of the high temperature phase becomes difficult unless some physicochemical studies at this temperature are carried out. In this paper we report DSC and IR studies on phase transitions of diamine complexes of CdSeO_4 .

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EXPERIMENTAL

CdSeO_4 in pure form was prepared in the laboratory. 1,3-Propanediamine (tn) and *N*-methyl 1,3-propanediamine (metn) were purified by repeated distillation.

Preparation of $[\text{Cd}(\text{tn})_2\text{SeO}_4]$ (1), $[\text{Cd}(\text{metn})_2\text{SeO}_4]$ (5)

These compounds were prepared by adding diamine (4 mmol) dropwise to CdSeO_4 (1 mmol) dissolved in water (2 ml). To the resulting mixture ethanol (5–6 ml) was added slowly with stirring. The white shiny crystals were separated. These were filtered, washed with ethanol and dried in a desiccator.

Preparation of $[\text{Cd}(\text{tn})\text{SeO}_4]$ (7) and $[\text{Cd}(\text{metn})\text{SeO}_4]$ (9)

These compounds were prepared in the solid state by maintaining the corresponding bis complexes at a constant temperature of 470 and 455 K respectively. Complex (7) was also prepared by adding ethanol (10 ml) to the aqueous solution of its bis species (500 mg in 2 ml water) with stirring. The derived species was filtered, washed with ethanol and dried in a desiccator.

The apparatus employed and experimental procedure for carrying out the thermal analysis are similar to that reported earlier [1]. Infrared spectra were recorded in a KBr matrix (pellets) on a Perkin-Elmer 783 IR spectrophotometer. Temperature of the samples was varied using a variable temperature cell with a temperature controller.

Table 1 lists the thermal data.

TABLE 1

Thermal parameters of the phase transition of diamine complexes of CdSeO_4

Phase transitions	Temperature range (K)	Peak temperature (K)	ΔH (kJ mol ⁻¹)
$[\text{Cd}(\text{tn})_2\text{SeO}_4]$ (1) \rightarrow $[\text{Cd}(\text{tn})_2\text{SeO}_4]$ (2)	362.5–391.0	363.5, 366.0, 368.5, 370.0, 370.5, 372.0, 373.0, 378.5	10.1
$[\text{Cd}(\text{tn})_2\text{SeO}_4]$ (3) \rightarrow $[\text{Cd}(\text{tn})_2\text{SeO}_4]$ (4)	396.0–427.5	398.0, 404.0, 405.0, 419.0	12.3 ^a
$[\text{Cd}(\text{metn})_2\text{SeO}_4]$ (5) \rightarrow $[\text{Cd}(\text{metn})_2\text{SeO}_4]$ (6)	374.0–399.0	392.0	10.6
$[\text{Cd}(\text{tn})\text{SeO}_4]$ (7) \rightarrow $[\text{Cd}(\text{tn})\text{SeO}_4]$ (8)	362.5–377.0	369.6	4.6
$[\text{Cd}(\text{tn})\text{SeO}_4]$ (8) \rightarrow $[\text{Cd}(\text{tn})\text{SeO}_4]$ (7)	366.0–352.0	362.0	4.5

^a Value is approximate owing to partial decomposition (Scheme 2).

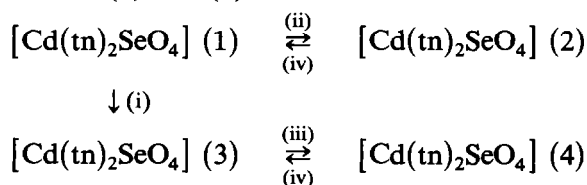
RESULTS AND DISCUSSION

Earlier, we reported the thermal behavior of Cd(II) diamine complexes [10]. It is interesting to note that the diamine complexes of CdSO₄ [10] showed no thermal phase transition but the CdSeO₄ complexes undergo solid state thermal phase transitions upon heating. The occurrence of phase changes in selenato complexes but not in sulfato complexes, is probably due to the intramolecular interaction of the SeO₄ group (the ionic size of which is larger than that of SO₄) with the hydrogen atoms of the six-membered chelate ring owing to its unfavorable internal entropy effect [11] resulting in lower symmetry.

We have studied the complexes [Cd(tn)₂SeO₄] (1), [Cd(metn)₂SeO₄] (5), [Cd(tn)SeO₄] (7) and [Cd(metn)SeO₄] (9). Among these [Cd(metn)SeO₄] shows no phase transition upon heating. [Cd(tn)₂SeO₄] has similar IR spectra to those of octahedral *cis*-[Cd(tn)₂X₂] (X = Cl and Br) [10] which suggests that it also possesses *cis* octahedral geometry. Similarly by analogy with the IR spectra of *cis*-[Cd(metn)₂(SCN)₂] (prepared in the laboratory for comparison), we infer that [Cd(metn)₂SeO₄] also possesses a *cis* octahedral configuration. Cd(II) attains a coordination of six in [CdLX₂] (L = tn and 2,2-dimethyl tn) (known from their crystal structures [12,13]). Therefore, if Cd(II) attains a coordination of six in [CdLSeO₄] then the SeO₄ anion should function as a tetracoordinated ligand. This is corroborated by the splitting seen in the IR bands of the monodiamine species in the region 800–900 cm⁻¹ (ν_3 of SeO₄). Diamine vibrations of [CdLSeO₄] (L = tn and metn) are very much split, specially in the $\nu(\text{NH}_2)$, $\nu(\text{C-N})$ region unlike those of [CdtnX₂] (X = Cl, Br or 0.5SO₄) [10] which suggests a lower symmetry of the six-membered chelate rings in monodiamineselenato-cadmium complexes.

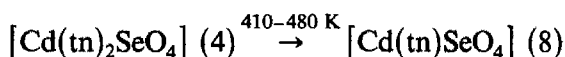
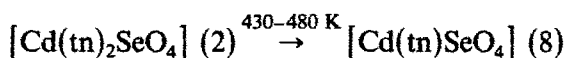
Phase transition of bisdiamine complexes

[Cd(tn)₂SeO₄] (1) shows multistep reversible phase transition in the temperature range 362.5 to 391.0 K upon heating and transforms to (2) (Scheme 1; Fig. 1). The species (1) isomerizes to (3) on grinding. The complex (3) on heating also isomerizes to (4) (Scheme 1; Fig. 1) showing two endothermic phase transitions (Fig. 1; Table 1) in the DSC curves. Species (1) probably does not convert totally to (3) on grinding, and thus a very weak peak at 372 K is observed (Fig. 1). The species (4) and (2) revert to their original forms (i.e. (3) and (1)) on keeping in a humid atmosphere. The isomers (4) and (2) are stable in a desiccator with anhydrous CaCl₂.



(i) Grinding; (ii) 362.5–391.0 K; (iii) 396.0–427.5 K; (iv) 24 h in humid atmosphere (relative humidity 60–70%) at ambient temperature.

This type of reversibility in a humid atmosphere has been reported by us [1]. Moisture in some way catalyzes the reversion of the after-phase species to their respective original species. The transformation of (1) → (3) is very interesting, since grinding the crystalline form of any compound should not change its species. However, it seems that on the evidence of Fig. 1, Table 1 and Scheme 1 that species (1) and (3) are different. This suggests that this irreversible (1) → (3) transformation takes place due to pressure while grinding. DSC traces of (1) → (2) and (3) → (4) transformations show multiple steps, suggesting that the phase transformation goes through several crystalline modifications of $[\text{Cd}(\text{tn})_2\text{SeO}_4]$. Because of technical limitation we are unable to record the IR spectra of (1) and (2), as grinding and pressure to make pellets are necessary. As a result, while recording the IR spectra of (1) or (2) we have always obtained that of the (3) form. In addition recording the IR spectrum of (4) at 433 K causes some decomposition. Hence it is not possible to infer any conclusion about the phase transition from the IR spectra. Species (2) and (4) decompose to $[\text{Cd}(\text{tn})\text{SeO}_4]$. Decomposition temperatures of (2) and (4) appear different (Scheme 2). This observation also implies



that isomers (1) and (3) are different and monodiamine species derived from (2) and (4) are identical.

$[\text{Cd}(\text{metn})_2\text{SeO}_4]$ (5) shows an endothermic phase transition in the temperature range 374–399 K (Fig. 2; Table 1) and transforms to species (6) which like complex (1) reverts to (5) on keeping in a humid atmosphere. However the reversal is much quicker; the complex starts decomposition at 413 K and has transformed to $[\text{Cd}(\text{metn})\text{SeO}_4]$ completely at 463 K. IR spectra of $[\text{Cd}(\text{metn})_2\text{SeO}_4]$ at ambient temperature and at 400 K were recorded. We noticed no spectral change in the 800–950 cm^{-1} and 400–450 cm^{-1} regions where SeO_4 (ν_3 and ν_4) vibration occurs, although some spectral change is observed in the $\nu(\text{CH}_2)$, $\delta(\text{NH}_2)$, $\rho_w(\text{CH}_2)$ and $\nu(\text{MN})$ vibrational region. Most of these vibrations in compound (6) appear broad compared with those of compound (5). From these data, it is clear that if a phase transition such as *cis* → *trans* or any change relating to the SeO_4 group occurs some change in selenate vibrations should have been seen. Therefore this phase transition is probably due to orientation of six-membered chelate rings or some change in crystallinity. We observed [1] some

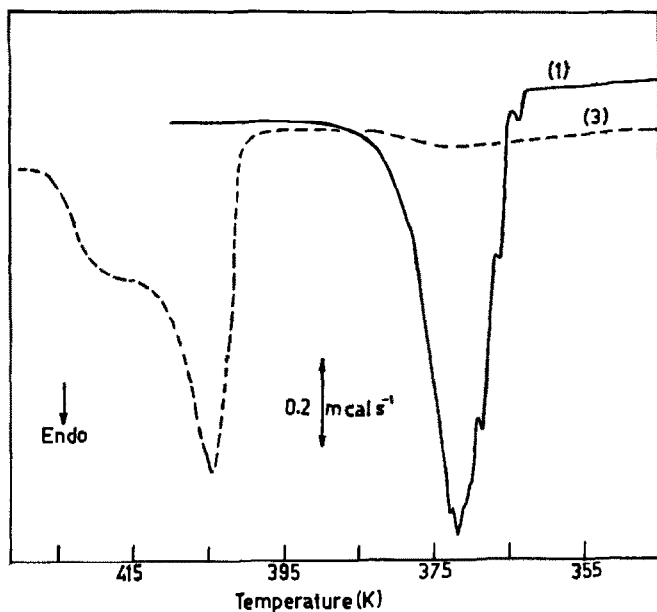


Fig. 1. DSC curves of $[\text{Cd}(\text{tn})_2\text{SeO}_4]$ (1) (wt. taken = 8.10 mg (—)) and $[\text{Cd}(\text{tn})_2\text{SeO}_4]$ (3) (wt. taken = 7.42 mg) (---).

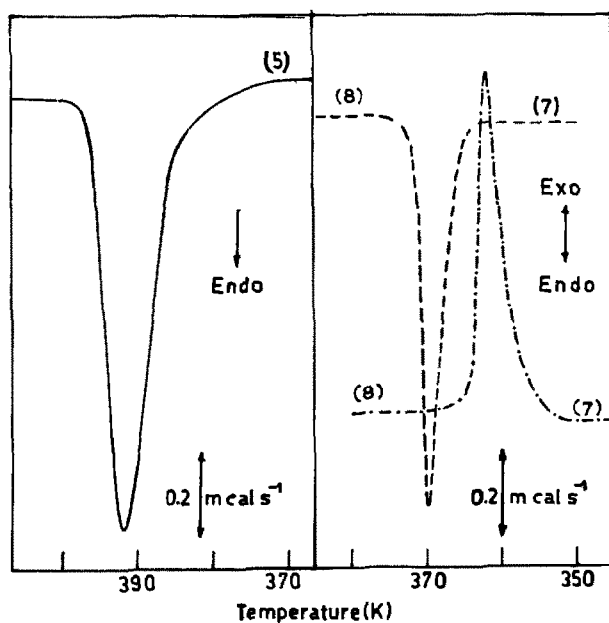


Fig. 2. DSC curves of $[\text{Cd}(\text{metn})_2\text{SeO}_4]$ (5) (wt. taken = 7.42 mg) (—); $[\text{Cd}(\text{tn})\text{SeO}_4]$ (7) (wt. taken = 5.88 mg) heating curve (---) and cooling curve (-·-·-).

phase transitions of Ni(II) diamine complexes where conformational changes occurred during heating and these phase changes were found reversible when the after-phase species was exposed to a humid atmosphere. Here also, we observed that the reversibility of this phase transition was catalyzed by a humid atmosphere.

Phase transition of monodiamine complex

[Cd(tn)SeO₄] (7) has been synthesized from the decomposition of its parent bis complex and also has been prepared from solution. The species (7) undergoes a phase transition on heating and transforms to (8) which reverts to (7) upon cooling (Fig. 2; Table 1). Infrared spectra of both the room temperature and high temperature forms of [Cd(tn)SeO₄] have been recorded and no noticeable spectral changes are observed. It is thus very difficult to characterize the phase transition prevailing here.

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