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THERMALLY INDUCED DECOMPOSITION AND PHASE TRANSITION OF DIAMINE COMPLEXES OF CADMIUM(II) THIOCYANATE

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ABSTRACT

The complexes $[Cd(en)_3](SCN)_2$, $[Cd(deen)_2(NCS)_2]$, $[Cd_2(tn)_4(NCS)_2](SCN)_2$ and $[Cd_2(dmtn)_4(NCS)_2](SCN)_2$ (where en = 1,2-ethanediamine, deen = *N,N*-diethyl-1,2-ethanediamine, tn = 1,3-propanediamine and dmtn = *N,N*-dimethyl-1,3-propanediamine) have been synthesized and their thermal studies carried out. $[Cd_2(tn)_4(NCS)_2](SCN)_2$ undergoes a phase transition (115–130°C; $\Delta H = 11.8$ kJ mol^{-1}) and reverts to the original species (120–90°C; $\Delta H = -12.4$ kJ mol^{-1}) upon cooling. $[Cd_2(tn)_3(NCS)_4]$ has been synthesized from the latter complex in the solid state by the temperature arrest technique, where one of the ligands is found to be bridged. Probable mechanistic paths for the phase transition and decomposition reactions have been proposed.

INTRODUCTION

In earlier communications [1–6], we reported on the thermal behavior of metal(II) [M = Ni(II), Zn(II) and Cd(II)] diamine complexes in the solid state. Recently, we reported on some novel thermally induced structural and conformational change phenomena occurring in the diamine complexes of nickel thiocyanate [7]. This type of phenomenon may take place in complexes other than nickel(II). With this view, the present paper reports the synthesis and characterization of 1,2-ethanediamine (en), *N,N*-diethyl-1,2-ethanediamine (deen), 1,3-propanediamine (tn) and *N,N*-dimethyl-1,3-propanediamine (dmtn) complexes of cadmium thiocyanate and their thermal investigations.

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EXPERIMENTAL

Preparation of [Cd(en)$_3$](SCN)$_2$ (1) and [Cd(deen)$_2$(NCS)$_2$] (2)

Diamine (4–6 mmol) was added slowly to the ethanolic solution of Cd(SCN)$_2$ (1 mmol) with stirring. The resulting turbid solution was filtered off. On standing, colorless crystals separated out from the filtrate. The crystals were filtered, washed with ethanol in the case of complex **1** and with ether in the case of complex **2** and dried over a fused-CaCl$_2$ desiccator.

Preparation of [Cd$_2$(tn)$_4$(NCS)$_2$](SCN)$_2$ (3)

1,3-Propanediamine (2 mmol) was added very slowly to a methanolic solution of Cd(SCN)$_2$ (1 mmol) with stirring. A white crystalline compound immediately separated out from solution which was filtered off and washed with dry ethanol and dried over a fused-CaCl$_2$ desiccator.

Preparation of [Cd$_2$(dmtn)$_4$(NCS)$_2$](SCN)$_2$ (4)

A methanolic (twice distilled) solution (2.5 ml) of freshly distilled diamine (1.10 ml) was very slowly added to Cd(SCN)$_2$ (1 g) dissolved in methanol (10 ml). Colorless crystals of the desired compound separated out from the solution on keeping the mixture overnight. These were filtered, washed with dry ethanol and air dried.

TABLE 1

Analytical and molar conductance data of diamine complexes of cadmium thiocyanate

Compound	Found (calc.) (%)			Molar conductance (mho cm^{-1})
	Metal	Nitrogen	Sulphur	
[Cd(en)$_3$](SCN)$_2$ (**1**)	27.50 (27.52)	27.38 (27.42)	15.27 (15.67)	145 [a]
[Cd(deen)$_2$(NCS)$_2$] (**2**)	24.39 (24.41)	18.16 (18.24)	13.56 (13.90)	5 [b]
[Cd$_2$(tn)$_4$(NCS)$_2$](SCN)$_2$ (**3**)	29.76 (29.86)	22.30 (22.32)	16.71 (17.00)	151 [a]
[Cd$_2$(tn)$_3$(NCS)$_4$] (**3A**)	33.02 (33.12)	20.49 (20.62)	18.70 (18.85)	[c]
[Cd$_2$(dmtn)$_4$(NCS)$_2$](SCN)$_2$ (**4**)	25.81 (25.99)	19.40 (19.43)	14.62 (14.80)	162 [d]

[a] In DMF.
[b] In CHCl$_3$.
[c] Insoluble in all available solvents.
[d] In CH$_3$OH.

Preparation of $[Cd_2(tn)_3(NCS)_4]$ *(3A)*

This complex was synthesized by keeping complex **3** at 170°C in a (di)nitrogen (gas) atmosphere. The thermolysis was stopped when no more diamine was lost, as is evident by a constancy of weight.

Analytical and molar conductance data of the above complexes are presented in Table 1.

The apparatus employed for recording the spectral and thermal data are the same as reported earlier [1–7]. The molar conductance data in solution were evaluated using a Philips PR 9500 conductivity bridge.

RESULTS AND DISCUSSION

The literature shows the synthesis of the $[Cd(en)_3]^{2+}$ complex [8–10]. The similar IR data of complex **1** with the reported data indicate that the three en molecules are chelated in the complex. The decomposition of complex **1**

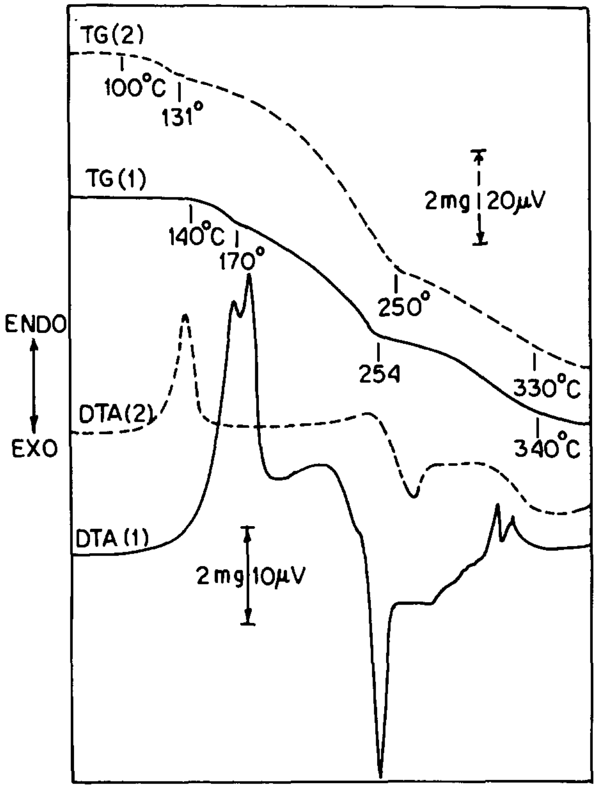
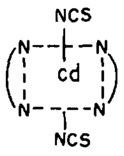


Fig. 1. Thermal curves of $[Cd(en)_3](SCN)_2$ (**1**), sample mass 10.24 mg (———) and $[Cd(deen)_2(NCS)_2]$ (**2**), sample mass 11.76 mg (- - - - -).

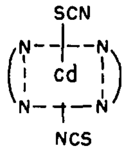
(Fig. 1) is different from that of the decomposition patterns of $[Cd(en)_3]X_2$ ($X = Cl^-$, Br^- and $0.5SO_4^{2-}$) reported earlier [5]. Complex **1** starts deamination at 140°C and becomes $[Cd(en)(NCS)_2]$ at 250°C (Fig. 1) through the formation of an unstable intermediate $Cd(en)_{2.75}(SCN)_2$ (calculated from the TG curve). The DTA curve shows three endothermic and one exothermic peaks for the elimination of two molecules of en. The intermediate species $[Cd(en)(NCS)_2]$ isolated at 250°C is orange in color. Although the analytical composition of the isolated complex is quite satisfactory, the color of the complex indicates the presence of some impurities as a similar type of complex, white in color, was reported in the literature [8]. The orange color of the complex is probably due to the presence of a small amount of CdS which is formed during the exothermic reaction of the complex occurring at 254°C, causing some decomposition of $[Cd(en)(NCS)_2]$ to CdS. The presence of broad band at ~ 270 cm^{-1} in the IR spectrum may be due to the CdS vibration [11]. The appearance of ν_{CN} at 2062 and 2048 cm^{-1} in the IR suggests the presence of an N-bonded thiocyanate group in $[Cd(en)(NCS)_2]$ [12,13]. The broadening of $\nu_{(NH_2)}$, the weakening of $\nu_{(CH_2)}$, the presence of very strong bands in the region of ~ 1670–1590 cm^{-1} due to $\nu_{(NH_2)}$ (which is shifted surprisingly towards a longer wavenumber) and various other unusual weak multiple bands [1–5] due to some other vibration of diamine, in the IR spectrum indicate that the coordination character of the diamine is complicated and thereby any prediction of the structure of this isolated complex from IR is difficult. $[Cd(en)(NCS)_2]$ starts decomposition at 254°C and becomes $Cd(SCN)_2 + CdS$ at 340°C. The DTA curve shows one exothermic peak and two endothermic peaks for this decomposition.

The synthesis of $[Cd(deen)_2(NCS)_2]$ (**2**) is not found in the literature. The IR spectrum of complex **2** indicates the chelation character of the ligand. Again, the appearance of bands at 2042 and 2062 cm^{-1} due to ν_{CN} clearly indicate the N-bonded terminal coordination mode of the thiocyanato groups [12,13]. Molar conductance data (taken in $CHCl_3$) prove the absence of ionic thiocyanato groups in the complex, i.e., the complex is neutral where both the thiocyanato groups are bonded to Cd(II). The DTA and TG curves of complex **2** (Fig. 1) indicate the complicated nature of its decomposition. This complex starts decomposition at 102°C and becomes $Cd(SCN)_2 + CdS$ at 330°C through the formation of unstable intermediates $Cd(deen)_{1.85}(NCS)_2$ and $Cd(deen)_{0.5}(NCS)_2$ (calculated from the TG curve). The DTA curve shows two endothermic and two exothermic peaks for the said decompositions.

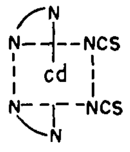
The synthesis of the complex **3** is not known. Regarding the structure of this complex, the probable structures (**i**–**v**) may be assumed on the basis of its composition. It shows ν_{CN} bands at 2094 and 2062 cm^{-1} and ν_{CS} at 815 and 770 cm^{-1}. The absence of any band in the region 690–720 cm^{-1} indicates that there is no terminal S-bonded thiocyanato group [14,15] in the complex. Again, strong splitting of ν_{CN} discards the possibility of **i**. The IR



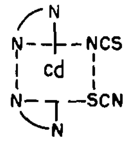
(i)



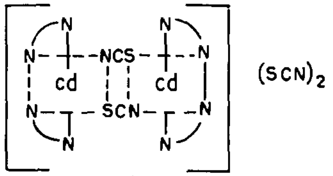
(ii)



(iii)



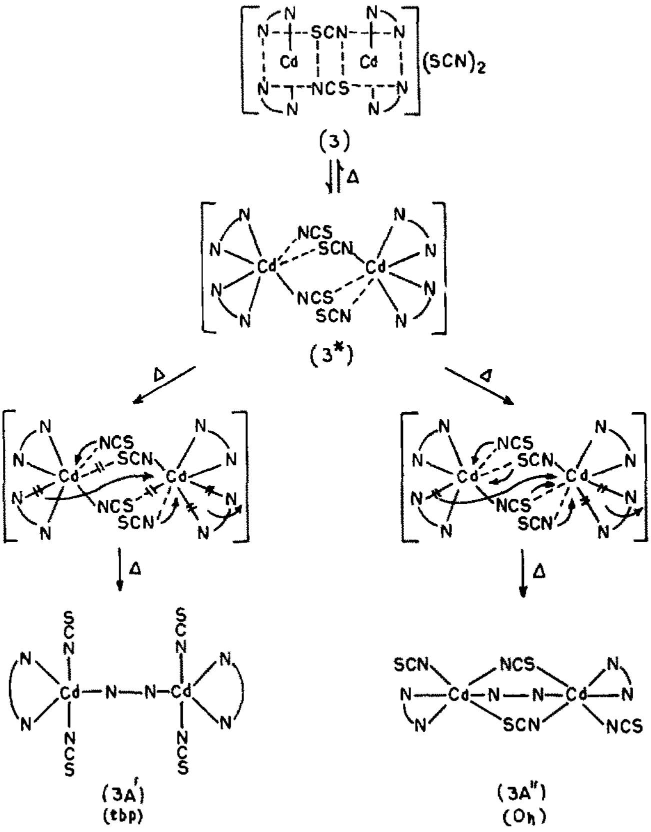
(iv)



(v)

bands appearing due to the diamine vibration are quite similar with the complexes *cis*-$[Cd(tn)_2X_2]$ ($X = Cl^-$ and Br^-) [5]. Therefore, the probable structure of the complex is either **iii** or **v**. Molar conductance data (in DMF) of complex **3** show a 1 : 1 electrolyte, if we consider the molecular weight of the monomeric form of **3**, i.e., $Cd(tn)_2(NCS)_2$ and a 1 : 2 electrolyte if we consider the molecular weight of the dimeric form of **3**, i.e., $[Cd_2(tn)_4(NCS)_2](SCN)_2$. As pentacoordination is very much unfavorable in this case, structure **v** should be the most probable for the representation of complex **3**. Although bridging thiocyanato groups [M–NCS–M] have been claimed to give a band well above 2100 cm^{-1} in IR [16,17], a number of examples are cited in the literature where ν_{CN} of a bridged SCN group appears in the 2090 cm^{-1} region [18–20]. Here, the two ν_{CN} and two ν_{CS} bands in IR are assigned to the bridging and anionic thiocyanato groups, respectively.

Complex **3** undergoes a phase change (Fig. 2) without having any mass loss upon heating (115–130°C; $\Delta H = 11.8$ kJ mol^{-1}) and reverts to the original species (120–90°C; $\Delta H = -12.4$ kJ mol^{-1}) on cooling, showing hysteresis in the system. This phase change phenomenon may be due to some kind of conformational changes of individual chelate rings like *trans*-$[Ni(tn)_2(NCS)_2]$ [7]. However, as the structure of the cadmium and nickel complexes are distinctly different, a similar type of phase change probably does not occur here. The probable reason for the phase change is shown in Scheme 1. At 130°C the complex probably exists in such a way that each cadmium ion attains an unstable heptacoordinated chromophore (produced by lengthening of the Cd–S linkage of the bridged SCN from the S-bonded side) and simultaneous anation of the non-coordinated SCN group (**3***) (Scheme 1). Complex **3** starts deamination at 138°C (Fig. 3) and becomes $Cd(SCN)_2 + CdS$ at 375°C through the formation of two stable intermediates, $[Cd_2(tn)_3(NCS)_4]$ (**3A**) and $[Cd(tn)(NCS)_2]$, at 185 and 250°C, respectively. The DTA curve (Fig. 3) altogether shows two endotherms and



Scheme 1

three exotherms for the elimination of two molecules of tn. The complex $[Cd_2(tn)_3(NCS)_4]$ (**3A**) isolated at 185°C is very pale yellow in color. The mechanism of its formation is shown in Scheme 1. The IR spectrum of complex **3A** shows all the bands of complex **3** (considering diamine vibrations only) and some extra bands in the region of $\nu_{(NH_2)}$, $\nu_{(CH_2)}$, $\delta_{w(CH_2)}$ and $\delta_{w(NH_2)}$ which indicate the existence of chelated as well as bridged diamines * in complex **3A**. This complex may attain either structure **3A′** or **3A″** (Scheme 1). However, the extensive splitting of ν_{CN} and ν_{CS} bands in the IR spectrum supports structure **3A″**. The complex $[Cd(tn)(NCS)_2]$ isolated at 250°C is also orange in color like the corresponding en complex. This also shows a complicated IR spectrum like its corresponding en analogue.

Complex **4** shows ν_{CN} at 2118, 2085 and 2050 cm^{-1} which is consistent with the bridging thiocyanato group [16,17]. Molar conductance data (in

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* The literature shows different IR-active vibrations for the chelated and bridged diamine metal complexes [8–10].

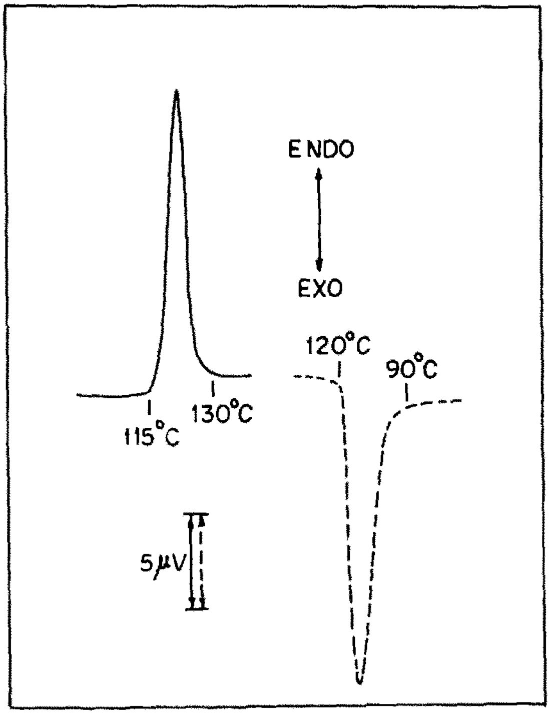

Fig. 2. Heating (———) and cooling (- - - - -) DTA curves of $[Cd_2(tn)_4(NCS)_2](SCN)_2$ (**3**), sample mass 29.81 mg.

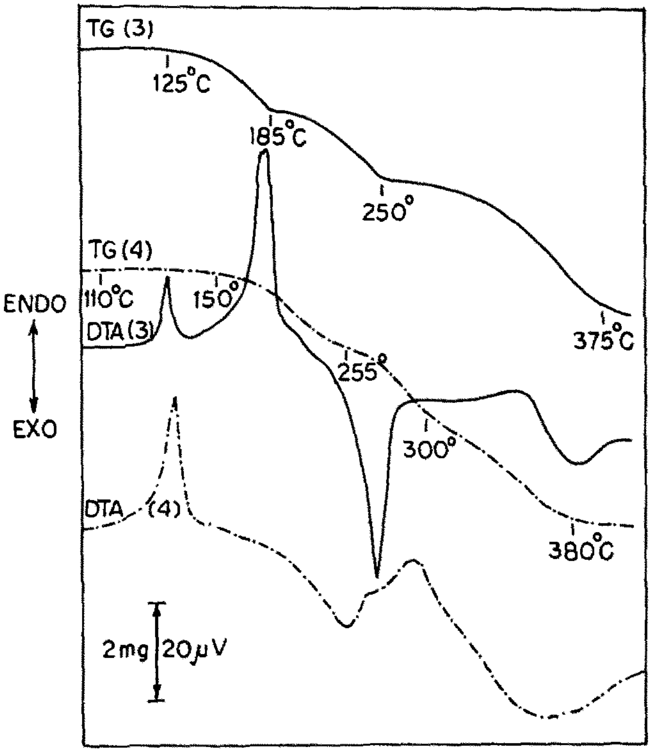

Fig. 3. Thermal curves of $[Cd_2(tn)_4(NCS)_2](SCN)_2$ (**3**), sample mass 12.78 mg (———) and

CH_3OH) indicate a 1 : 2 complex with a dimeric bridged structure. Thus, the structure of complex **4** is probably identical to that of complex **3**. $[Cd_2(dmtn)_4(NCS)_2](SCN)_2$ shows an endothermic peak at 154°C without any mass loss. This is probably due to some structural change phenomena like complex **3**, but the complex melts at that temperature. Therefore, it would not be prudent to suggest anything about this. This complex starts deamination at 180°C (Fig. 3) and transforms to $Cd(SCN)_2$ + CdS at 380°C through the formation of unstable intermediates, $[Cd_2(dmtn)_3(NCS)_4]$ and $[Cd(dmtn)(NCS)_2]$ (calculated from the TG curve). Unlike complex **3** here the DTA curve shows only exothermic peaks for the elimination of diamines.

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