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Thermal Investigation of Nickel(II) Diamine Complexes in Solid State

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Three tris(ethylenediamine)nickel(II) chloride dihydrate having identical composition, apparently similar in color, magnetic moment and spectral properties showed differences in thermal profile. Thermal investigations of $[Ni(en)_3]Br_2\cdot 2H_2O$, $[Ni(tn)_3]Cl_2\cdot 2H_2O$, and $[Ni(tn)_3]Br_2\cdot H_2O$ where en=ethylenediamine and tn=1,3-propanediamine were carried out. Several bis and mono(diamine) complexes were synthesized in solid state from the corresponding tris complexes. All the bis and mono(diamine) complexes were found to be O_h and T_d symmetry respectively. All tris(diamine) complexes generate *cis* bis(diamine) species upon heating. But only one tris(ethylenediamine)nickel(II) chloride dihydrate generates *cis* bis species by the isomerization from the *trans* species temporarily formed. Monodiamine complexes decomposed through $[Ni_2(diamine)Cl_4]$ species which showed unusually high magnetic moment. The probable mechanistic path for each step of decomposition was also reported.

Thermal investigations of transition metal diamine complexes have been carried out by several workers.[1–4] Solid state kinetics of Cr^{III} complexes of ethylenediamine are well known in literature.[5] Thermal investigations of metal complexes of 1,2-propanediamine are known.[1] But the studies on the complexes of 1,3-propanediamine (tn) are scanty.[4] It is reasonable to expect that the thermal decomposition of $[Ni^{II}(tn)_3]X_2$ (X=Cl or Br) would be a matter of great interest as the complexes may lead to the formation of some new stoichiometric 1,3-propanediamine complexes of nickel(II) in solid state which could not be synthesized even in solution. Previously some work[2] on the thermal decomposition of $[Ni^{II}(en)_3]X_2$ (X=Cl or Br) has been done. Since thermal decomposition pattern is sometimes governed by the instrumental techniques used as also on the experimental conditions, studies on $[Ni^{II}(en)_3]X_2$ are also relevant. The present paper reports the thermal studies of $[Ni^{II}L_3]X_2$, where L=en or tn and X=Cl or Br. It deals with the synthesis and characterization of some new compounds derived in solid state. It also reports the probable mechanistic path for each step of decomposition.

Experimental

Preparation. *$[Ni(en)_3]Cl_2\cdot 2H_2O$ (**1**), $[NiCl_2(en)_2]$(**4**)*: These were prepared following the method described in literature.[6]

*$[Ni(en)_3]Cl_2\cdot 2H_2O$ (**2**)*: Methylhydrazine or *N,N*-dimethylhydrazine or *N,N*-diethylethylenediamine (3 mmol) was added slowly to $[NiCl_2(en)_2]$ (**4**) (1 mmol) dissolved in water–ethanol (1:9) mixture. Shining pinkish crystals separated out. These crystals were collected and purified by washing with ethanol.

*$[Ni(en)_3]Cl_2\cdot 2H_2O$ (**3**)*: Addition of pyridine (3 mmol) to $[NiCl_2(en)_2]$ (**4**) (1 mmol) dissolved in water–ethanol (1:9) mixture, yielded shining pinkish crystals. These crystals were collected and purified by washing with ethanol.

*$[NiCl_2en]$ (**5**)*: This was synthesized by pyrolysis of the complexes **2** or **3** or **4** at 325 °C for 5 min in nitrogen atmosphere.

*$[Ni(en)_3]Br_2\cdot 2H_2O$ (**6**), $[Ni(tn)_3]Cl_2\cdot 2H_2O$ (**3**), and $[Ni(tn)_3]Br_2\cdot H_2O$ (**12**)*: These were prepared by mixing ethanolic solution of diamine (3 mmol) drop by drop to the ethanolic solution of nickel salt (1 mmol). While stirring the mixture, shining crystals separated out slowly. These crystals were collected and purified by washing with ethanol.

*$[NiBr_2(en)_2]$ (**7**)*: This was synthesized by pyrolysis of $[Ni(en)_3]Br_2\cdot 2H_2O$ (**6**) at 275 °C in nitrogen atmosphere.

*$[NiCl_2(tn)_2]$ (**9**)*: This was prepared by pyrolysis of $[Ni(tn)_3]Cl_2\cdot 2H_2O$ at 180 °C for 5 min in nitrogen atmosphere.

*$[NiCl_2tn]$ (**10**)*: This was prepared by pyrolysis of $[Ni(tn)_3]Cl_2\cdot 2H_2O$ (**8**) or $[NiCl_2(tn)_2]\cdot 1.5H_2O$ (**11**) at ≈278 °C in nitrogen atmosphere.

*$[NiCl_2(tn)_2]\cdot 1.5H_2O$ (**11**)*: This was synthesized by the same method adopted for the preparation of $[NiCl_2(en)_2]$ (**4**). This was also synthesized by keeping $[NiCl_2(tn)_2]$ (**9**) in an open air.

*$[NiBr_2(tn)_2]$ (**13**)*: This was synthesized by pyrolysis of $[Ni(tn)_3]Br_2\cdot H_2O$ (**12**) at 230 °C in nitrogen atmosphere.

Thermal Measurements. The thermal analysis was carried out using a Shimadzu DT-30 thermal analyzer. A constant flow of nitrogen (30 $cm^3\ min^{-1}$) was maintained. Platinum crucibles were used. Heating rate (10 °C min^{-1}) was maintained. The particle size of the samples was within 150—200 mesh. Aluminum oxide was used as reference. Zinc metal was used as calibrant for evaluation of enthalpy change.

Other Measurements. Infrared spectra in KBr (4000—250 cm^{-1}) and electronic spectra in mull (28570—11111 cm^{-1}) were recorded using a Beckman IR-20A and Pye Unicam SP8-150 spectrophotometers respectively. Cary 17D was also used for mull spectra in some cases. Magnetic moments of the compounds were evaluated at room temperature from the magnetic susceptibilities of the samples, corrected by applying Pascal's constants of the elements involved, using the Gouy technique where $Hg[Co(SCN)_4]$ was taken as standard. EG and G PAR 155 vibrating sample magnetometer was also used for measuring magnetic moment in some cases.

Results

$[Ni(en)_3]Cl_2\cdot 2H_2O$ (**1**) becomes anhydrous at 140 °C (Fig. 1, Table 1). The anhydrous species is thermally stable upto 190 °C. On further heating, it starts to lose en and transforms to metal chloride through bis, mono and hemi(diamine) species. None of the intermediate species and even the metal chloride are isolable. TG curve (Fig. 1) hints the elimination of water taking place in two steps. But the corresponding DTA curve predicts the water elimination occurring

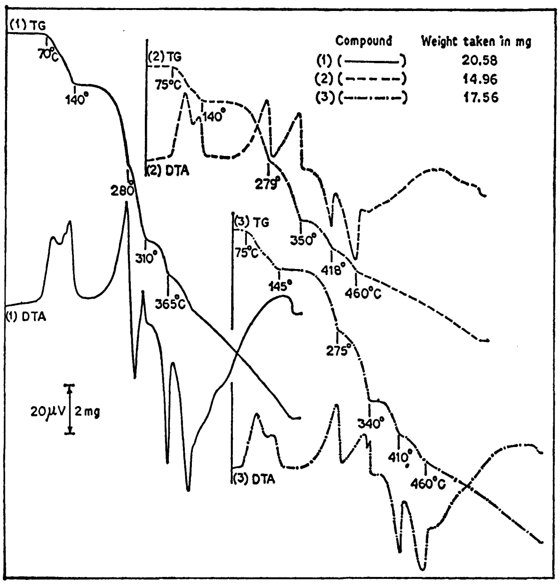


Fig. 1. Thermal curves of $[Ni(en)_3]Cl_2 \cdot 2H_2O$ (**1**) (——), $[Ni(en)_3]Cl_2 \cdot 2H_2O$ (**2**) (— — — —), and $[Ni(en)_3]Cl_2 \cdot 2H_2O$ (**3**) (—·—·—·—).

actually in three steps. DTA profile for the elimination of two molecules of en shows first an endotherm followed by an exotherm followed by an another endotherm. It shows two prominent exotherms for the elimination of last molecule of en. On the other hand, $[Ni(en)_3]Cl_2 \cdot 2H_2O$ (**2**) loses two molecules of water in two steps as evident from its TG as well as DTA curves (Fig. 1). TG curve of the anhydrous species is almost similar to that of the complex **1**. But the DTA curve shows two prominent endotherms for the elimination of first two molecules of en and two exotherms for the elimination of last molecule of en. Thermal profile (Fig. 1) of complex **3** is almost similar to that of complex **2**. The only difference observed in the DTA curve is that endotherm responsible for the elimination of second molecule of en splits here. Thermal behavior of $[NiCl_2(en)_2]$ (**4**) is practically similar to that of the complex **2** in the decomposition from the stage of $[NiCl_2(en)_2]$. The isolation of mono(diamine) species is feasible by temperature arrest technique in nitrogen atmosphere from the complexes **2**, **3**, and **4**.

$[Ni(en)_3]Br_2 \cdot 2H_2O$ (**6**) becomes anhydrous at 100 °C in single step as observed from TG curve (Fig. 2, Table 1). But DTA curve shows elimination of water taking place in two steps. The anhydrous species starts to decompose at 210 °C and generates $[NiBr_2(en)_2]$ (**7**) at 275 °C showing a prominent endotherm in the DTA curve. An exotherm is displayed at the quite early stage of decomposition of the bis species which melts on further heating.

$[Ni(tn)_3]Cl_2 \cdot 2H_2O$ (**8**) becomes anhydrous at 105 °C (Fig. 3, Table 1). The anhydrous species starts to lose tn at 135 °C and transforms to metal chloride through bis (**9**), mono (**10**) and hemi(diamine) species. Bis and mono complexes are isolated in solid state by temperature arrest technique in nitrogen atmosphere. But we could not isolate the hemi species in pure form. The DTA curve shows two distinctly separated endotherms for the elimination of first two molecules of tn and two exotherms for the elimination of rest tn molecule.

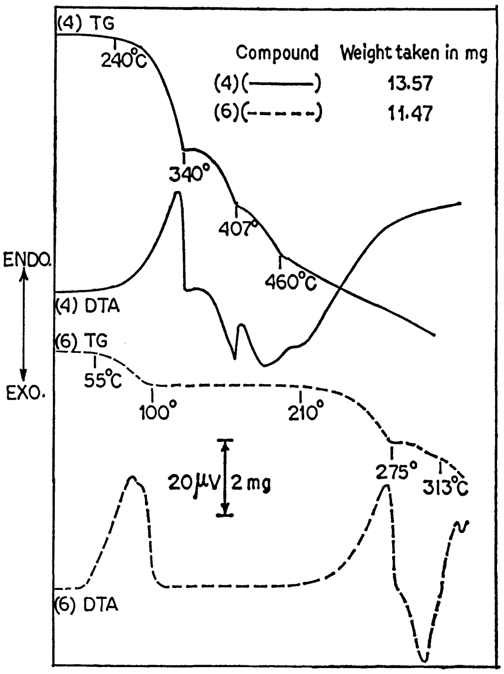


Fig. 2. Thermal curves of $[NiCl_2(en)_2]$ (**4**) (——) and $(Ni(en)_3]Br_2 \cdot 2H_2O$ (**6**) (— — — —).

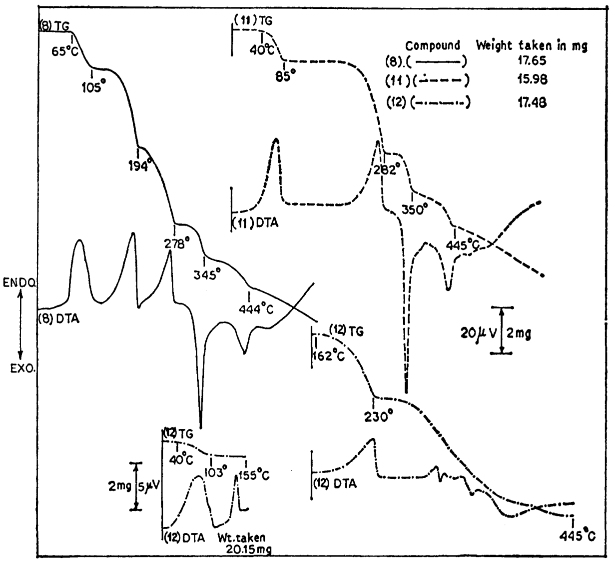


Fig. 3. Thermal curves of $[Ni(tn)_3]Cl_2 \cdot 2H_2O$ (**8**) (——), $[NiCl_2(tn)_2] \cdot 1.5H_2O$ (**11**) (— — — —), and $[Ni(tn)_3]Br_2 \cdot H_2O$ (**12**) (—·—·—·—).

$[Ni(tn)_3]Br_2 \cdot H_2O$ (**12**) starts to lose its water molecule at 40 °C and becomes anhydrous at 103 °C (Fig. 3, Table 1). This anhydrous species shows an endothermic peak in the temperature range 135—155 °C without showing any mass loss. After this change it starts to lose one molecule of tn at 162 °C and becomes $[NiBr_2(tn)_2]$ (**13**) at 230 °C which is isolable in the solid state. On further heating it transforms to metal bromide at 415 °C. But this transformation is found to be very complicated as evident from its TG and

TABLE 1. THERMAL PARAMETERS OF NICKEL(II) DIAMINE COMPLEXES

Decomposition reactions	Temperature range/°C	DTA peak temperature/°C		ΔH/kJ mol^{-1}
		Endo	Exo	
$[Ni(en)_3]Cl_2 \cdot 2H_2O$ (**1**) → $[Ni(en)_3]Cl_2$	70—140	98, 115, 135		153
$[Ni(en)_3]Cl_2$ → $[NiCl_2(en)_2]$	190—280	277		b)
$[NiCl_2(en)_2]$ → $[NiCl_2en]$	280—310	308	290	b)
$[NiCl_2en]$ → $[Ni_2Cl_4en]$	310—365		360	b)
$[Ni_2Cl_4en]$ → $NiCl_2$	365—416		398	b)
$[Ni(en)_3]Cl_2 \cdot 2H_2O$ (**2**) → $[Ni(en)_3]Cl_2$	75—140	100, 135		141
$[Ni(en)_3]Cl_2$ → $[NiCl_2(en)_2]$	195—279	275		104
$[NiCl_2(en)_2]$ → $[NiCl_2en]$	279—350	347		100
$[NiCl_2en]$ → $[Ni_2Cl_4en]$	362—418		417	36
$[Ni_2Cl_4en]$ → $NiCl_2$	418—460		460	79
$[Ni(en)_3]Cl_2 \cdot 2H_2O$ (**3**) → $[Ni(en)_3]Cl_2$	75—145	100, 136		144
$[Ni(en)_3]Cl_2$ → $[NiCl_2(en)_2]$	200—275	270		105
$[NiCl_2(en)_2]$ → $[NiCl_2en]$	275—340	330, 340		70
$[NiCl_2en]$ → $[Ni_2Cl_4en]$	350—410		406	52
$[Ni_2Cl_4en]$ → $NiCl_2$	410—460		450	69
$[NiCl_2(en)_2]$ (**4**) → $[NiCl_2en]$ (**5**)	240—340	335		116
$[NiCl_2en]$ → $[Ni_2Cl_4en]$	345—407		399	b)
$[Ni_2Cl_4en]$ → $NiCl_2$	407—460		440	b)
$[Ni(en)_3]Br_2 \cdot 2H_2O$ (**6**) → $[Ni(en)_3]Br_2$	55—100	80, 90		130
$[Ni(en)_3]Br_2$ → $[NiBr_2(en)_2]$ (**7**)	210—275	271		124
$[NiBr_2(en)_2]$ → $[NiBr_2(en)_2]^{d)}$	280—313		300	b)
$[Ni(tn)_3]Cl_2 \cdot 2H_2O$ (**8**) → $[Ni(tn)_3]Cl_2$	65—105	88		135
$[Ni(tn)_3]Cl_2$ → $[NiCl_2(tn)_2]$ (**9**)	135—195	190		129
$[NiCl_2(tn)_2]$ → $[NiCl_2tn]$ (**10**)	200—278	274		83
$[NiCl_2tn]$ → $[Ni_2Cl_4tn]$	305—345		343	104
$[Ni_2Cl_4tn]$ → $NiCl_2$	345—444		440	41
$[NiCl_2(tn)_2] \cdot 1.5H_2O$ (**11**) → $[NiCl_2(tn)_2]$ (**9**)	40— 85	72		92
$[NiCl_2(tn)_2]$ → $[NiCl_2tn]$ (**10**)	205—282	278		102
$[NiCl_2tn]$ → $[Ni_2Cl_4tn]$	310—350		348	134
$[Ni_2Cl_4tn]$ → $NiCl_2$	350—445		442	51
$[Ni(tn)_3]Br_2 \cdot H_2O$ (**12**) → $[Ni(tn)_3]Br_2$	40—103	75, 98		37
$[Ni(tn)_3]Br_2$ → $[Ni(tn)_3]Br_2$	135—155	153		8
$[Ni(tn)_3]Br_2$ → $[NiBr_2tn_2]$ (**13**)	161—230	228		121
$[NiBr_2(tn)_2]$ → $NiBr_2$	250—400	c)	c)	b)

a) en=$NH_2CH_2CH_2NH_2$; tn=$NH_2CH_2CH_2CH_2NH_2$. b) Value of enthalpy change could not be evaluated. c) Very weakly resolved peaks. d) Thermal decomposition of $[NiBr_2(en)_2]$ (**7**) could not be done.

TABLE 2. ANALYTICAL AND MAGNETIC DATA OF NICKEL(II) DIAMINE COMPLEXES

Compound		Color	Found (Calcd) (%)			$\frac{\mu_{eff}}{BM}$
			Metal	Nitrogen	Halogen	
$[Ni(en)_3]Cl_2 \cdot 2H_2O$	(**1**)	Pink	16.82 (16.98)	24.25 (24.29)	20.51 (20.53)	3.06
$[Ni(en)_3]Cl_2 \cdot 2H_2O$	(**2**)	Pink	16.90 (16.98)	24.24 (24.29)	20.50 (20.53)	3.07
$[Ni(en)_3]Cl_2 \cdot 2H_2O$	(**3**)	Pink	16.92 (16.98)	24.26 (24.29)	20.50 (20.53)	3.07
$[NiCl_2(en)_2]$	(**4**)	Blue	23.47 (23.51)	22.39 (22.42)	28.40 (28.43)	3.18
$[NiCl_2en]$	(**5**)	Green	30.98 (30.94)	14.72 (14.76)	37.45 (37.42)	3.55
$[Ni(en)_3]Br_2 \cdot 2H_2O$	(**6**)	Pink	13.52 (13.51)	19.30 (19.32)	36.80 (36.77)	3.09
$[NiBr_2(en)_2]$	(**7**)	Blue	17.38 (17.34)	16.50 (16.54)	47.22 (47.20)	3.28
$[Ni(tn)_3]Cl_2 \cdot 2H_2O$	(**8**)	Bluish pink	15.09 (15.14)	21.61 (21.66)	18.29 (18.31)	3.01
$[NiCl_2(tn)_2]$	(**9**)	Blue	21.10 (21.14)	20.14 (20.16)	25.54 (25.56)	3.17
$[NiCl_2tn]$	(**10**)	Green	28.79 (28.82)	13.76 (13.74)	34.86 (34.85)	3.54
$[NiCl_2(tn)_2] \cdot 1.5H_2O$	(**11**)	Blue	19.20 (19.27)	18.34 (18.37)	23.26 (23.30)	3.15
$[Ni(tn)_3]Br_2 \cdot H_2O$	(**12**)	Bluish pink	12.78 (12.80)	18.35 (18.31)	34.87 (34.85)	3.10
$[Ni(tn)_2Br_2]$	(**13**)	Blue	16.03 (16.01)	15.26 (15.27)	43.62 (43.60)	3.20

DTA curves (Fig. 3).

Discussion

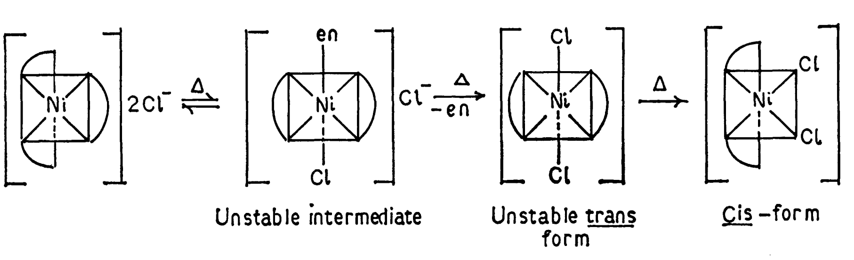
Ethylenediamine Complexes of Nickel(II) Chloride. It is interesting to note that complexes **1**, **2**, and **3** seem apparently identical (Table 2) but they are basically different in structures as evident from their DTA profiles. These structural differences may be due to the changes in conformation of the individual chelate ring as may be expected for these complexes. But the possession of similar IR bands by these three tris complexes rules out the possibility of conformational changes. Structural changes observed against these three complexes are not due to the changes in microsymmetry (D_3) as evident from their identical electronic spectra (Table 3). It is expected that the differences as observed during the decomposition appear to be due to the existence of different crystal symmetries belonged to them or due to some other factors (*vide supra*). It is difficult to understand what mechanism plays while synthesizing complexes **2** and **3** by adding pyridine, methylhydrazine *etc.* to the bis complex **4**. However, it is expected that non-bridging of halide ion in $[NiCl_2(en)_2]$ resulting in bond stretching phenomenon as reported by Benson and Haim[7] is responsible for the transformation of $[NiCl_2(en)_2]$ to $[Ni(en)_3]Cl_2$. It is observed that dehydration pattern of complex **1** is different (Fig. 1) from the complexes **2** and **3**. One interesting observation is that these three anhydrous tris complexes take two molecules of water while keeping them in air. The difference exhibited in the dehydration process does not exist in the dehydration of the rehydrated complexes in solid state. This is probably due to different attachment of H_2O molecules between **1** and the rehydrated compounds of anhydrous **1**. DTA profile for the transformation of bis→mono species in complex **1** is an exotherm followed by an endotherm (Fig. 1) which suggests that the decomposition takes place after geometrical isomerization. In complex **1** three chelated en are arranged in such a manner that during tris→bis transformation, a square pyramidal intermediate[8] is expected to be formed by chelate opening followed by the instantaneous axial coordination by chloride ion to the unstable intermediate (Scheme 1). The further heating develops unstable *trans*-$[NiCl_2(en)_2]$ which transforms to *cis* variety as Cl^- acts as reasonably good *cis* directing product.[5] As a consequence, the exotherm at the beginning of the decomposition of bis species is responsible for the *trans*→*cis* isomerization as evident from literature[9] that such isomerization would generally cause exotherm in the system. Moreover, a weakly resolved plateau in TG curve for tris→bis formation in **1**, unlike the cases of **2** and **3** (Fig. 1) is probably due to the formation of unstable *trans* intermediate (Scheme 1). On the other hand, during the isomerization process complexes **2** and **3** exhibit simply endotherms for bis→mono transformation. Occurrence of splitting in endotherm in complex **3** suggests that complexes **2** and **3** are possibly structurally different, which would indicate that bis→mono transformation occurs in two steps though the corresponding TG curve shows no inflexion due to the extreme instability of the intermediate complex species. The above observation indicates that the complex **2** possesses more simple structure in comparison to that of complex **3**. $[NiCl_2(en)_2]$ (**4**) is undoubtedly *cis* as evident from IR assignments[10–13] and X-ray crystallographic studies.[14] TG curves (Fig. 1) of the decomposition of **1**, **2**, and **3** do not permit the isolation of bis$[NiCl_2(en)_2]$ in very pure state. However, we have isolated the bis species from complexes **2** and **3**. The IR spectral data of these two bis species support the configuration as that (Table 4) of complex *cis*-$[NiCl_2(en)_2]$ (**4**). This shows that basic *cis* form of complex **4** is not disturbed at all while synthesizing the complexes **2** and **3**.

It is a matter of great interest that mono species, $[NiCl_2en]$ (**5**), green in color, has been isolated in pure form in solid state, whilst attempt for the preparation of this compound in solution has been unsuccessful. The IR spectrum (Table 4) of this compound suggests that en is chelated. Moreover, the medium broad band at ≈330 cm^{-1} in IR spectrum is well

Table 3. Electronic spectra of nickel(II) diamine complexes in mull

Compound		Absorbance[a)] maxima λ/nm
$[Ni(en)_3]Cl_2\cdot 2H_2O$	(**1**)	(625sh, 575sh, 540, 500sh, 465sh, 345)[b)]
$[Ni(en)_3]Cl_2\cdot 2H_2O$	(**2**)	(625sh, 575sh, 540, 500sh, 465sh, 345)[b)]
$[Ni(en)_3]Cl_2\cdot 2H_2O$	(**3**)	(625sh, 575sh, 540, 500sh, 465sh, 345)[b)]
$[NiBr_2(en)_2]$[c)]	(**7**)	580, 366
$[NiCl_2en]$	(**5**)	672, 398
$[NiCl_2(tn)_2]$[c)]	(**9**)	570, 352
$[NiCl_2tn]$[c)]	(**10**)	664, 408
$[NiBr_2(tn)_2]$[c)]	(**13**)	564, 364

a) Arbitrary absorbance. b) Spectral data of the crystals of the corresponding complexes. c) Compound synthesized in solid state.



Scheme 1.

Table 4. IR spectral data of nickel(II) diamine complexes in KBr

Compound		Assignments							
		$\nu_{(NH_2)}$	$\nu_{(CH_2)}$	$\delta_{(NH_2)}$	$\delta_{(CH_2)}$	$\rho_{w(CH_2)}$	$\tau_{(NH_2)}+\rho_{w(NH_2)}+\tau_{(CH_2)}$	Stretching vibrations of skeleton $\nu_{C-N}+\nu_{C-C}$	$\rho_{r(CH_2)}+\nu_{(MN)}$
[NiCl$_2$(en)$_2$]$^{a)}$	(**4**)	3330 w, 3280 s, 3235 m, 2195 m, 3145 m, 3120 m	2960 m, 2940 m, 2880 m	1580 sh, 1570 s	1445 m, 1435 m	1385 w, 1360 vw	1330 m, 1320 w, 1280 w, 1265 m, 1135 m, 1100 sh	1090 s, 1020 vs, 1010 sh, 970 w, 960 sh	870 vw, 855 w, 665 m, 650 sh, 500 m,
[NiBr$_2$(en)$_2$]$^{b)}$	(**7**)	3335 w, 3290 s, 3250 m, 3200 m, 3160 m, 3127 m	2962 w, 2950 m, 2886 m	1590 sh, 1580 s	1455 m, 1445 m	1392 w, 1370 vw	1330 m, 1320 w, 1290 w, 1275 m, 1142 m, 1105 sh	1100 s, 1030 vs, 1020 sh, 980 w	860 vw, 675 m, 660 m, 515 m
[NiCl$_2$(tn)$_2$]$^{b)}$	(**9**)	3340 w, 3300 s, 3230 m	2970 m, 2930 m, 2880 m	1628 m, 1580 s, 1560 m, 1555 w	1468 w, 1452 w, 1440 w	1404 w, 1390 w, 1352 vw	1325 w, 1315 w, 1280 m, 1165 s	1090 vw, 1070 m, 1020 s	908 s, 879 vw, 730 sh, 690 br, 630 m, 585 m
[NiBr$_2$(tn)$_2$]$^{b)}$	(**13**)	3358 m, 3303 s, 3235 m	2970 m, 2928 m, 2880 m	1622 m, 1576 s, 1550 m, 1555 m	1460 w, 1450 vw, 1442 w	1400 w, 1385 m, 1350 vw	1320 w, 1310 w, 1275 m, 1152 s	1085 w, 1060 m, 1012 s	900 s, 870 w, 720 sh, 680 br, 621 m, 585 m
[NiCl$_2$en]$^{b)}$	(**5**)	3260 sbr	2960 w, 2940 w, 2880 w	1640 m, 1600 m, 1570 s, 1565 sh	1462 w, 1455 w	1400 vw, 1375 vw	1330 m, 1335 sh, 1285 m, 1155 w, 1145 w, 1112 m, 1105 sh	1050 sh, 1035 vs, 1015 sh, 1000 sh, 970 m	875 vw, 685 s, 665 sh, 620 sh, 515 m
[NiCl$_2$tn]$^{b)}$	(**10**)	3340 m, 3315 m, 3260 m, 3040 m	2970 sh, 2900 m, 2800 w	1590 sh, 1580 s	1470 s, 1460 s, 1450 sh	1405 m	1315 vw, 1265 m, 1245 vw, 1212 m, 1185 w, 1140 s, 1120 m	1100 m, 1070 sh, 1052 w, 1010 sh, 1000 s	942 s, 918 m, 870 vw, 642 br, 595 vw, 550 sh

s=strong, vs=very strong, m=medium, w=weak, br=broad, sh=shoulder, vw=very weak, sbr=strong broad. a) IR spectral data of two bis species from complexes **2** and **3** are similar to that of complex **4**. b) Synthesized in solid state.

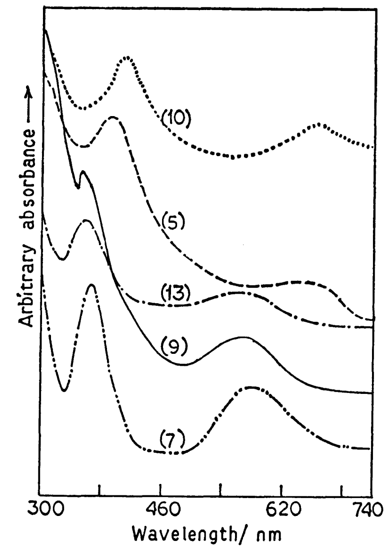
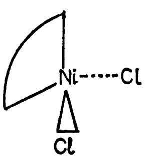
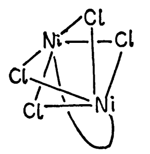


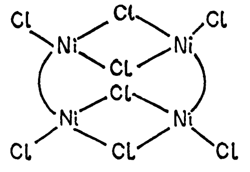
Fig. 4. Electronic spectra of [$NiBr_2(en)_2$] (**7**) (—··——··—), [$NiCl_2(tn)_2$] (**9**) (——), [$NiBr_2(tn)_2$] (**13**) (—·—·—·—), [$NiCl_2en$] (**5**) (— — — —), and [$NiCl_2tn$] (**10**) (······) in mull).



Structure 1



Structure 2



Structure 3

significant for Ni–Cl terminal coordination in T_d symmetry.[15] Magnetic moment (Table 2) is higher than those of the complexes **2**, **3**, and **4** which suggests that the symmetry is lowered in [$NiCl_2en$] causing greater orbital contribution. The electronic spectra in mull (Fig. 4) display the characteristic band of the T_d Ni^{II} system (Structure 1) at ≈650 nm which is tentatively assignable to the $^3T_1 \rightarrow ^3T_1(P)$ transition (ν_3).[16,17]

We could not isolate [Ni_2Cl_4en] in pure form as TG curve (Fig. 1) does not indicate stable step. But we have measured magnetic moment of this species isolated by temperature arrest technique at the temperature (410 °C) where the desired composition corresponds to the TG curve. The compound possesses unusually high magnetic moment (μ_{eff}=10.0 BM using the formula, [Ni_2Cl_4en]). This may be due to the ferromagnetic behavior which is possibly developed from the Cl^- bridging[18—20] and metal-metal interaction.[21] These phenomena and the stoichiometry of the compound would require either pentacoordinated species (Structure 2) developed from monomeric [Ni_2Cl_4en] or tetracoordinated tetrahedral species (Structure 3) formed from dimeric [Ni_2Cl_4en] *i.e.*, [$Ni_4Cl_8(en)_2$]. In this type of geometry two Ni^{II} ions probably come closer with each other to satisfy the proposed interaction. Since the compound is hygroscopic (in nature) its IR spectrum is not well resolved. However, comparing the complicated IR spectrum of [$NiCl_2en$] (**5**) with the simpler IR of [Ni_2Cl_4en] it is expected that en is possibly bridged and *trans*. Electronic spectrum in mull of [Ni_2Cl_4en] is not also well resolved. As a result it would not be prudent to support the structures from electronic spectrum.

Ethylenediamine Complexes of Nickel(II) Bromide. Dehydration of [$Ni(en)_3$]$Br_2 \cdot 2H_2O$ (**6**) occurs in two steps like complexes **2** and **3**. Isolation of [$NiBr_2(en)_2$] (**7**) in pure state from complex **6** is possible unlike the corresponding chloro complexes. This bis complex (**7**) is expected to possess *cis* configuration as the IR spectrum of it closely resembles that of *cis* variety of [$NiCl_2(en)_2$] (**4**). Though the method or preparation of complexes **4** and **7** are different the complexes are having *cis* configuration. As the intermediate bis species obtained from the complexes **2** and **3** are exhibiting almost similar IR spectra with those of **4** and **7** the possession of similar *cis* configuration like that of complexes **4** and **7** is also supported here for the bis species isolated from **2** and **3**. It is interesting to note that an exotherm appears in DTA profile (Fig. 2) at the threshold of decomposition of *cis*-[$NiBr_2(en)_2$]. This exotherm is probably due to the isomerization process. However, it is difficult to say which configuration is being formed here. On the contrary, it is expected that melting process generally happens to more symmetric species. As *trans* species is more symmetric than *cis*, *trans* configuration is possibly formed before melting. As a consequence, it seems that the initial configurations of the bis products obtained from the decomposition of **1** and **6** are not similar. Such differences are possibly due to the different polarizability of halide ions. It is reasonable to expect that, Br^- has stronger bridging character owing to its higher polarizability and larger size than Cl^- which prefers *cis* configuration as evident from the isolable *cis* complex **7**. On the other hand, the less polarizability and smaller size of Cl^- possibly hinders bridging character, and so the *cis* form (Scheme 1) generated is less stable (Fig. 1, Table 1).

Attempt to prepare [$Ni(en)_3$]Br_2 by the treatment of complex [$NiBr_2(en)_2$] with pyridine, methylhydrazine *etc.* has been unsuccessful unlike the cases of complexes **2** and **3**. It is not unlikely to expect that bond stretching phenomenon of Ni–Br in [$NiBr_2(en)_2$] is not pronounced here since the Br^- has greater tendency to form bridge.

1,3-Propanediamine Complexes of Nickel(II) Chloride. [$Ni(tn)_3$]$Cl_2 \cdot 2H_2O$ (**8**) shows almost similar thermal behavior as observed by the complex **2**. We have synthesized [$NiCl_2(tn)_2$]$\cdot 1.5H_2O$ in two ways. We thought initially that two types of [$NiCl_2(tn)_2$]$\cdot 1.5H_2O$ would be generated due to the difference in synthetic procedure. But we find no difference in structure between the two bis species owing to their similar spectral and thermal behavior. This bis species is also suggested to possess *cis* configuration like [$NiCl_2(en)_2$] (**4**) as evident from a number of bands in the region 1550—1650 cm^{-1} (Table 4) which are mainly contributed due to $\delta_{(NH_2)}$ vibration. Here also, this bis species did not yield tris species at all by the reaction with pyridine, methylhydrazine *etc.* unlike the complex **4**. The reason is probably due to the longer chain of chelate ring in the complex than en, whose effect is pronounced for Br^- rather than Cl^- ion. Another intermediate complex, $[NiCl_2tn]$ (**10**) synthesized in solid state from complex **8** is much hygroscopic in nature, and green in color like **5**. IR, electronic spectra (in mull) as well as magnetic moment of $[NiCl_2tn]$ suggests its T_d symmetry similar to the corresponding en complex. Here also, we could not isolate $[Ni_2Cl_4tn]$ in pure form. It is interesting to note that $[Ni_2Cl_4tn]$ is also ferromagnetic like $[Ni_2Cl_4en]$.

1,3-Propanediamine Complexes of Nickel(II) Bromide. $[Ni(tn)_3]Br_2 \cdot H_2O$ (**11**) after dehydration, exhibits an endotherm with no weight loss. The detail studies of the observed phase change is to be reported separately[22] along with the other phase transition phenomena occurring in diamine complexes. Decomposition of this dehydrated complex species (**12**) to bis complex follows the path similar to that of complex **2** (Fig. 3). The $[NiBr_2(tn)_2]$ (**13**) is O_h suggested by its magnetic moment (Table 2) and electronic spectra in mull (Table 3). IR spectrum of $[NiBr_2(tn)_2]$ also shows more bands than *trans* chelated $[Ni(NCS)_2(tn)_2]$[23] which indicate that two tn molecules are chelated (Table 4). The decomposition of $[NiBr_2(tn)_2]$ to $NiBr_2$ follows in multiple steps, unlike $[NiCl_2(tn)_2]$.

It is clear from the decomposition patterns of the complexes that change of halide ion in the system causes remarkably different decomposition, whilst the increase in chain length in the diamines does not affect it much.

Water elimination in tris(diamine) complexes of nickel(II) bromide takes place at lower temperature (Table 1) in comparison to those of the corresponding chloride. This is probably due to anion variation in the complexes. The value of enthalpy change for water elimination appears very low in $[Ni(tn)_3]Br_2 \cdot H_2O$ (**12**) which indicates that attraction of water molecule towards nickel(II) is less here in comparison of enthalpy changes among **1**, **2**, **3**, **6**, and **8** complexes (Table 1). It is reasonable to expect that the water molecule in **12** is attached by van der Waals force only. On the other hand, water molecules in the **1**, **2**, **3**, **6**, and **8** complexes are probably attached by hydrogen bonding as well as van der Waals force causing more attraction of the water molecules in the species.

It is interesting to note that the ΔH value for the decomposition of $[NiCl_2tn]$ to $[Ni_2Cl_4tn]$ is considerably high (Table 1) in comparison to that for $[NiCl_2en]$ to $[Ni_2Cl_4en]$ transformation. Here the ΔH values involve the metal ligand bond energies, polarization energies of the ligands and other contributions. However, it is rather difficult to say which factor is predominant to cause such difference in the ΔH values of the two transformations.

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