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Thermal Reactions of *N*,*N*-Dimethyl-1,2-ethanediamine Complexes of Nickel(II) in the Solid State

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Complexes $[NiL_2(H_2O)X]X \cdot nH_2O$ (L=*N*,*N*-dimethyl-1,2-ethanediamine; n=0 when X=BF_4; n=1 when X=Br; n=3 when X= Cl), $[NiL_2(H_2O)Y] \cdot nH_2O$ (n= 2 when Y= SeO_4; n=5 when Y=SO_4), $[NiL_2(H_2O)_2](NO_3)_2 \cdot H_2O$ and $[NiL_2]$ $(ClO_4)_2$ have been synthesized and investigated thermally in the solid state. The complexes $[NiL_2(H_2O)Cl]Cl \cdot 3H_2O$, $[NiL_2(H_2O)Br]Br \cdot H_2O$, $[NiL_2(H_2O)(SO_4)] \cdot 5H_2O$, and $[NiL_2(H_2O(SeO_4)] \cdot 2H_2O$ possess *trans* octahedral geometry and undergo deaquation-anation associated with *trans*→*cis* isomerization upon heating in the solid state whereas on deaquation the complex $[NiL_2(H_2O)_2](NO_3)_2 \cdot H_2O$ retains its *trans* octahedral configuration. The complex $[NiL_2(H_2O)(BF_4)](BF_4)$ possesses *cis* octahedral geometry and on thermal deaquation it transforms to a square planar complex. The complex $[NiL_2](ClO_4)_2$ is square planar and undergoes a yellow→red thermochromic phase transition on heating (203—216 °C; ΔH=6.9 kJ mol^{-1}). The red isomer is also square planar. The species $[NiLCl_2]$, $[NiL(SO_4)]$ and $NiL_{0.33}Cl_2$ have been synthesized pyrolytically in the solid state from their corresponding parent diamine complexes. The complexes $[NiLCl_2]$ and $[NiL(SO_4)]$ possess octahedral geometry. $NiL_{0.33}Cl_2$ possesses an unusually high magnetic moment (4.1 BM at 28 °C).

In the solid state generally the following three types of isomerization occur in the Ni(II)-bis(diamine) complexes on heating; i) octahedral⇄square planar,[1-3] ii) conformational changes of individual diamine chelate rings,[4-9] and iii) geometrical i.e. cis⇄trans.[10,11]

The first kind i.e. octahedral⇄square planar transformations are mostly associated with a change in color and have been investigated by several workers since the historical paper of Lifschitz.[12] The identification of structure can easily and unequivocally be done with the help of electronic spectra and magnetic moment.

The thermally induced conformational changes phenomena in the solid state are associated with the thermochromic behavior of $[Cu(dieten)_2](ClO_4)_2$, (where dieten=*N*,*N*-diethyl-1,2-ethanediamine) first observed by Pfeiffer et al.[13] This phenomenon was originally attributed by Lever et al.[14,15] to a temperature dependent axial interaction between the anion and the CuN_4 plane and later was demonstrated to be due to a weakening of the in-plane ligand field strength as a result of conformational changes of the diamine chelate rings.[16-19] Several Ni(II)-bis(diamine) complexes have been reported to undergo this type of conformational changes.[4-9] Only a few of which are thermochromic, however.[4,5] Several instances of the nonthermochromic conformational changes have been detected by DTA and reported from this laboratory.[5-9]

The literature on cis⇄trans isomerism of Ni(II)-bis(diamine) complexes is scanty[10,11] and their identification by means of the visible and IR spectra were not well-established. Recently, however, it has been found that the electronic spectra in the NIR region are very much useful for characterization of a cis or trans isomer of such complex.[2,20-22] Using this NIR region we characterized a novel cis⇄trans formation phenomenon in $Ni(dmen)_2(NO_3)_2$, where dmen=*N*,*N*′-dimethyl-1,2-ethanediamine.[10]

In continuation of these studies, the thermal behavior of *N*,*N*-dimethyl-1,2-ethanediamine nickel(II) complexes were investigated in the solid state. The result obtained will be reported in the present paper.

Experimental

The metal salts used were all of AR grade and *N*,*N*-dimethyl-1,2-ethanediamine(L) was purchased from Fluka AG, Switzerland and was used without further purification.

Preparation of Complexes. The $[NiL_2(H_2O)Cl]Cl \cdot 3H_2O$ (**1**), $[NiL_2(H_2O)Br]Br \cdot H_2O$ (**2**), and $[NiL_2(H_2O)_2](NO_3)_2 \cdot H_2O$ (**5**) were prepared by the similar methods as reported earlier.[23,24]

The complexes $[NiL_2(H_2O)(SO_4)] \cdot 5H_2O$ (**3**), and $[NiL_2(H_2O)(SeO_4)] \cdot 2H_2O$ (**4**) were prepared by mixing respective metal salts and diamine in 1 : 2 ratio in water and subsequent precipitation by adding ethanol. These complexes were recrystallized from water-ethanol (2 : 1) mixture.

The complex $[NiL_2(H_2O)(BF_4)](BF_4)$ (**6**) was prepared by mixing diamine with metal salts in 1 : 2 ratio in ethanol. The crystals which separated immediately, were filtered and washed with ethanol.

To prepare $[NiL_2](ClO_4)_2$ (**7**), diamine was mixed with $Ni(ClO_4)_2 \cdot 6H_2O$ in 2-propanol in 1 : 2 ratio and the mixture was heated to boiling and the resulting blue-green solution was filtered hot. On cooling the solution, yellow crystals separated out. These were filtered and washed with ether.

The species $[NiLCl_2]$ (**1b**), $NiL_{0.33}Cl_2$ (**1c**) and $[NiL(SO_4)]$ (**3b**) were synthesized thermally by temperature arrest technique from their parent diamine complexes in the solid phase.

Measurements. Simultaneous TG and DTA measurements were carried out with a Shimadzu DT-30 thermal analyzer using a platinum-platinum-rhodium (10%) thermocouple and matched platinum crucible under a constant flow of nitrogen (30 ml min^{-1}). The heating rate and amounts of samples used are given in the figure. Enthalpy change of phase transition was calculated by Perkin Elmer DSC-2 differential scanning calorimeter using indium metal as calibrant.

The IR and electronic spectra (visible and NIR regions) were recorded in nujol mulls with Perkin Elmer 783 infrared spectrophotometer and Hitachi U-3400 spectrophotometer, respectively. Carbon, H and N were estimated by a Perkin Elmer 240C elemental analyzer. The effective magnetic moments were evaluated from magnetic susceptibility measurements with an EG and G PAR 155 vibrating-sample magnetometer at room temperature. The molar conductance data were evaluated with a Philips PR 9500 conductivity bridge using methanol as solvent.

Results and Discussion

Structures of the Original Complexes. All the complexes except $NiL_2(ClO_4)_2$ (**7**) possess octahedral geometry as is evident from their magnetic moment and electronic (mull) spectral data (Tables 1 and 2). However, the species $NiL_2(ClO_4)_2$ (**7**) is diamagnetic and possesses electronic spectrum typical of a square planar Ni(II). The complexes $NiL_2Cl_2 \cdot 4H_2O$ (**1**), $NiL_2Br_2 \cdot 2H_2O$ (**2**), and $NiL_2(BF_4)_2 \cdot H_2O$ (**6**) behave as 1 : 1 electrolyte (Λ_m=70, 85 and 95 $\Omega^{-1}\,mol\,cm^2$ for (**1**), (**2**), and (**6**), respectively) and $NiL_2(NO_3)_2 \cdot 3H_2O$ (**5**) as 1 : 2 electrolyte (Λ_m=170 $\Omega^{-1}\,mol\,cm^2$) whereas the complexes $NiL_2SO_4 \cdot 6H_2O$ (**3**) and $NiL_2SeO_4 \cdot 3H_2O$ (**4**) behave as nonelectrolyte in methanol, suggesting the presence of SO_4, SeO_4, and one of the Cl, Br, and BF_4 ions inside the coordination sphere whereas both the NO_3 ions are noncoordinated. The IR spectra of $NiL_2(NO_3)_2 \cdot 3H_2O$ (**5**) show a sharp single band at ca. 1750 cm^{-1} which indicates the presence of ionic NO_3. IR spectra of these complexes show the presence of

Table 1. Data on the Elemental Analysis and Magnetic Moments of *N*,*N*-Dimethyl-1,2-ethanediamine(L) Complexes of Nickel(II)

Complexes		Color	Analytical data[a)]			μ_{eff}
			C/%	H/%	N/%	BM
trans-$[NiL_2(H_2O)Cl]Cl \cdot 3H_2O$	(**1**)	Blue-Violet	25.1(25.4)	8.1(8.5)	14.8(14.8)	3.2
cis-$[NiL_2Cl_2]$	(**1a**)	Bluish-Green	31.1(31.4)	7.8(7.8)	18.0(18.3)	3.2
$[NiLCl_2]$	(**1b**)	Greenish-Yellow	22.0(22.0)	5.4(5.5)	12.7(12.8)	3.2
$NiL_{0.33}Cl_2$	(**1c**)	Brownish-Grey	10.3(10.1)	2.7(2.5)	6.0(5.8)	4.1
trans-$[NiL_2(H_2O)Br]Br \cdot H_2O$	(**2**)	Blue-Violet	22.6(22.3)	6.6(6.5)	13.1(13.0)	3.3
cis-$[NiL_2Br_2]$	(**2a**)	Bluish-Green	24.1(24.3)	6.2(6.1)	14.3(14.2)	3.2
trans-$[NiL_2(H_2O)(SO_4)] \cdot 5H_2O$	(**3**)	Blue-Violet	21.7(21.9)	8.1(8.2)	12.8(12.8)	3.2
cis-$[NiL_2(SO_4)]$	(**3a**)	Greenish-Blue	28.9(29.0)	7.4(7.3)	16.7(16.9)	3.3
$[NiL(SO_4)]$	(**3b**)	Greenish-Yellow	20.0(19.8)	4.7(4.9)	11.3(11.5)	3.3
trans-$[NiL_2(H_2O)(SeO_4)] \cdot 2H_2O$	(**4**)	Blue-Violet	22.0(22.2)	6.7(6.9)	12.9(13.0)	3.2
cis-$[NiL_2(SeO_4)]$	(**4a**)	Bluish-Green	25.1(25.4)	6.5(6.3)	14.6(14.8)	3.2
trans-$[NiL_2(H_2O)_2](NO_3)_2 \cdot H_2O$	(**5**)	Blue-Violet	23.4(23.2)	7.1(7.3)	19.9(20.3)	3.3
trans-$[NiL_2(NO_3)_2]$	(**5a**)	Blue-Violet	27.0(26.7)	6.4(6.7)	23.6(23.4)	3.3
cis-$[NiL_2(H_2O)(BF_4)](BF_4)$	(**6**)	Greenish-Blue	22.7(22.5)	6.4(6.1)	12.8(13.1)	3.3
$[NiL_2](BF_4)_2$	(**6a**)	Yellow	23.2(23.5)	5.7(5.9)	13.9(13.7)	Diamagnetic
$[NiL_2](ClO_4)_2$	(**7**)	Yellow	21.9(22.1)	5.7(5.5)	12.6(12.9)	Diamagnetic
$[NiL_2](ClO_4)_2$	(**7a**)	Red	21.9(22.1)	5.9(5.5)	12.7(12.9)	Diamagnetic

a) Calculated values are in parentheses.

Table 2. Data on Some Selective Bands of Electronic and Infrared Spectra of *N*,*N*-Dimethyl-1,2-ethanediamine(L) Complexes of Nickel(II)

Complexes		Electronic spectra λ_{max}/nm	IR spectra[a)] $\rho_r(CH_2)$ bands/cm^{-1}
trans-$[NiL_2(H_2O)Cl]Cl \cdot 3H_2O$	(**1**)	1176, 775, 605	930, 880
cis-$[NiL_2Cl_2]$	(**1a**)	1020, 625	940, 920, 882
trans-$[NiL_2(H_2O)Br]Br \cdot H_2O$	(**2**)	1174, 825, 620	925, 878
cis-$[NiL_2Br_2]$	(**2a**)	1025, 602	942, 925, 885
trans-$[NiL_2(H_2O)(SO_4)] \cdot 5H_2O$	(**3**)	1158, 817, 612	930, 881
cis-$[NiL_2(SO_4)]$	(**3a**)	1038, 630	960, 925, 885
trans-$[NiL_2(H_2O)(SeO_4)] \cdot 2H_2O$	(**4**)	1142, 821, 590	b)
cis-$[NiL_2(SeO_4)]$	(**4a**)	1030, 631	b)
trans-$[NiL_2(H_2O)_2](NO_3)_2 \cdot H_2O$	(**5**)	1162, 815, 610	930, 885
trans-$[NiL_2(NO_3)_2]$	(**5a**)	1142, 805, 602	940, 892
cis-$[NiL_2(H_2O)(BF_4)](BF_4)$	(**6**)	1065, 612	965, 938, 892
$[NiL_2](BF_4)_2$	(**6a**)	465	—
$[NiL_2](ClO_4)_2$	(**7**)	455	—
$[NiL_2](ClO_4)_2$	(**7a**)	478	—

a) IR spectra are taken in Nujol. b) Ligand bands are not distinguishable due to overlapping with selenate bands.

$\rho_w(H_2O)$[25] at ca. 700 cm^{-1} and from which it is suggested that the water molecules are probably coordinated with the Ni atom.[26]

The number of observed bands in electronic spectra and mode of splitting in the NIR region (Table 2, Fig. 1) clearly suggest that the complexes (**1**), (**2**), (**3**), (**4**), and (**5**) possess *trans* octahedral structure.[20–22] Moreover, the $\rho_r(CH_2)$ bands of the complexes (**1**), (**2**), (**3**), and (**5**) appearing in the IR region at ca. 1000—750 cm^{-1} are characteristic of trans isomer.[27] But the complex $NiL_2(BF_4)_2 \cdot H_2O$ (**6**) possesses cis configuration as is evident from IR and electronic spectra (Table 2, Fig. 1). It is interesting to note that the complex (**6**) is different from the other hydrated complexes in geometrical arrangement. Very probably it is due to the intramolecular hydrogen bonding between the aquo ligand and the tetrafluoroborate ion. The formulas of the complexes corroborating the above facts are shown in Table 1. However, the IR bands for coordinated SO_4, SeO_4 or BF_4 are not distinguishable due to the overlapping with diamine bands. The complex $NiL_2(ClO_4)_2$ (**7**) is diamagnetic and shows only one strong band in its electronic spectrum at 455 nm. Therefore it is square planar.

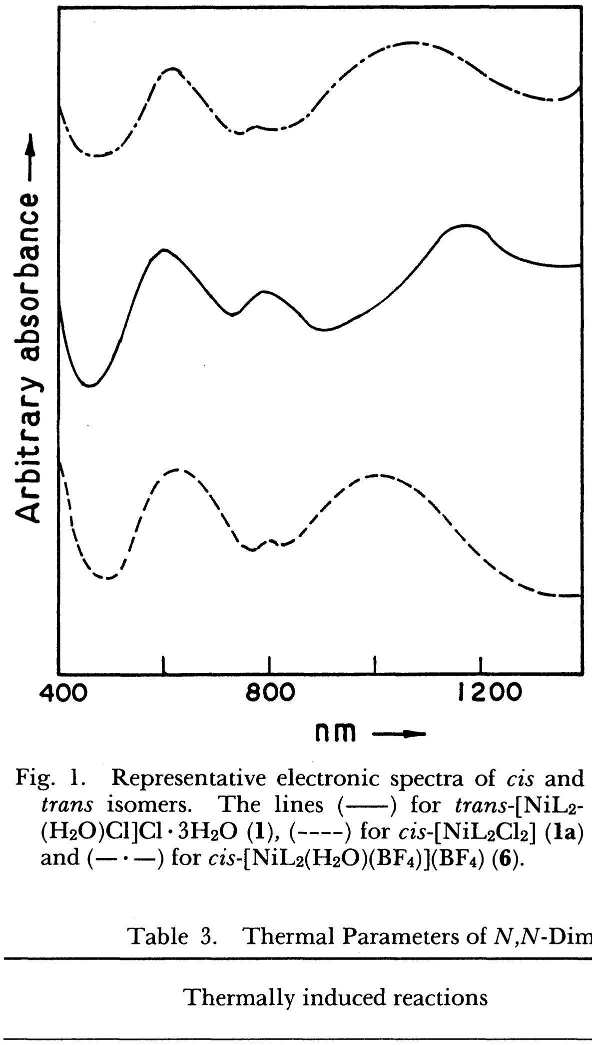

Fig. 1. Representative electronic spectra of *cis* and *trans* isomers. The lines (——) for *trans*-$[NiL_2(H_2O)Cl]Cl \cdot 3H_2O$ (**1**), (----) for *cis*-$[NiL_2Cl_2]$ (**1a**) and (—•—) for *cis*-$[NiL_2(H_2O)(BF_4)](BF_4)$ (**6**).

Thermal Analysis. The results of simultaneous TG-DTA measurements of the complexes are shown in Table 3. The weight losses observed in all the complexes except $[NiL_2](ClO_4)_2$ (**7**) within the temperature range 40—150 °C correspond to the liberation of water molecules (obsd 19.1%, calcd 19.0% for (**1**); 8.2%, 8.4% for (**2**); 24.5%, 24.7% for (**3**); 9.2%, 9.4% for (**4**); 12.8%, 13.1% for (**5**); 3.9%, 4.2% for (**6**), respectively). All the complexes except (**5**) change their color on deaquation (Table 1). A distinct color change from violet-blue to greenish blue is observed for the complexes (**1**), (**2**), (**3**), and (**4**) whereas the color of complex (**6**) changes drastically from greenish blue to yellow. The complexes (**1**) and (**3**) on further heating decompose to their respective metal salts via several isolable intermediates (Table 3, Fig. 2). The complex (**2**) after dehydration decomposes to metal salt upon heating without showing any break in the TG curve for the formation of any intermediate. The counter anions of the complexes (**4**), (**5**), and (**6**) (SeO_4, NO_3, and BF_4, respectively) start to decompose along with

Table 3. Thermal Parameters of *N*,*N*-Dimethyl-1,2-ethanediamine(L) Complexes of Nickel(II)

Thermally induced reactions	Temperature range/ °C	DTA peak temperature/ °C	
		Endo.	Exo.
trans-$[NiL_2(H_2O)Cl]Cl \cdot 3H_2O$ (**1**)⟶*cis*-$[NiL_2Cl_2]$ (**1a**)	50—130	74, 120	—
cis-$[NiL_2Cl_2]$ (**1a**)⟶$[NiLCl_2]$ (**1b**)	174—260	251	—
$[NiLCl_2]$ (**1b**)⟶$NiL_{0.33}Cl_2$ (**1c**)	286—361	345	355
$NiL_{0.33}Cl_2$ (**1c**)⟶$NiCl_2+C$	371—425	—	418
trans-$[NiL_2(H_2O)Br]Br \cdot H_2O$ (**2**)⟶*cis*-$[NiL_2Br_2]$ (**2a**)	60—120	97, 117	—
cis-$[NiL_2Br_2]$ (**2a**)⟶$NiBr_2+C$	212—410	276, 290	330, 365
trans-$[NiL_2(H_2O)(SO_4)] \cdot 5H_2O$ (**3**)⟶*cis*-$[NiL_2(SO_4)]$ (**3a**)	40—145	70, 121	—
cis-$[NiL_2(SO_4)]$ (**3a**)⟶$[NiL(SO_4)]$ (**3b**)	220—268	256	—
$[NiL(SO_4)]$ (**3b**)⟶ $NiL_{0.33}(SO_4)$	321—422	392	—
$NiL_{0.33}(SO_4)$⟶$NiSO_4+C$	422—490	—	428, 442
trans-$[NiL_2(H_2O)(SeO_4)] \cdot 2H_2O$ (**4**)⟶*cis*-$[NiL_2(SeO_4)]$ (**4a**)	70—130	112, 120	—
cis-$[NiL_2(SeO_4)]$ (**4a**)⟶a)	202[b)]	271	310
trans-$[NiL_2(H_2O)_2](NO_3)_2 \cdot H_2O$ (**5**)⟶*trans*-$[NiL_2(NO_3)_2]$ (**5a**)	40—70	65	—
trans-$[NiL_2(NO_3)_2]$ (**5a**)⟶a)	220[b)]	—	230
cis-$[NiL_2(H_2O)(BF_4)](BF_4)$ (**6**)⟶$[NiL_2](BF_4)_2$ (**6a**)	101—150	135,	—
$[NiL_2](BF_4)_2$ (**6a**)⟶a)	165[b)]	188, 208	290,315
$[NiL_2](ClO_4)_2$ (**7**)⟶$[NiL_2](ClO_4)_2$ (**7a**)	203—216	209	—

a) Decompositions are complicated. b) Temperature at which decomposition starts.

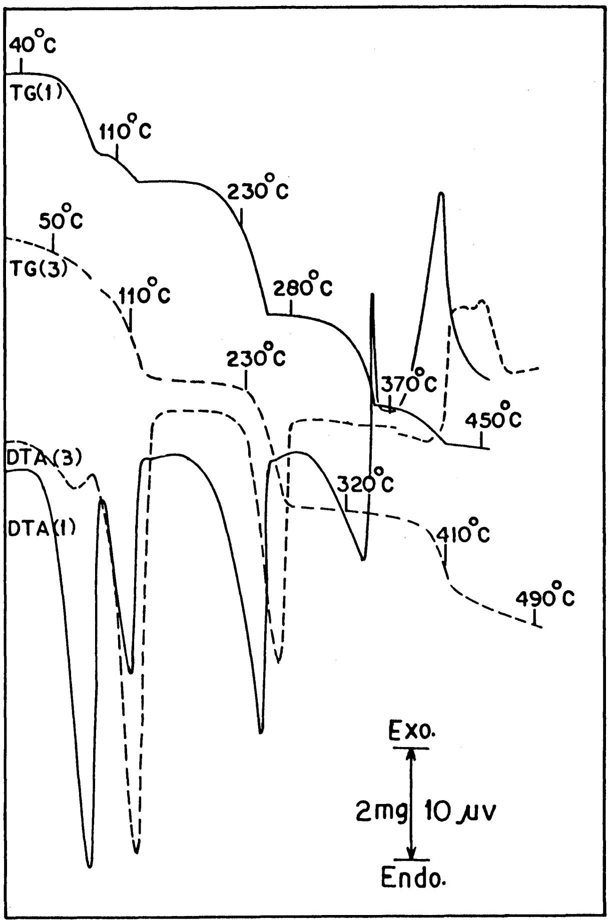

Fig. 2. TG-DTA patterns of *trans*-$[NiL_2(H_2O)Cl]Cl \cdot 3H_2O$ (**1**) (——) and *trans*-$[NiL_2(H_2O)(SO_4)] \cdot 5H_2O$ (**3**) (----). Heating rate: 10 °C min^{-1} for both the complexes. Amount of sample used: 10.20 mg for (**1**) and 11.35 mg for (**3**).

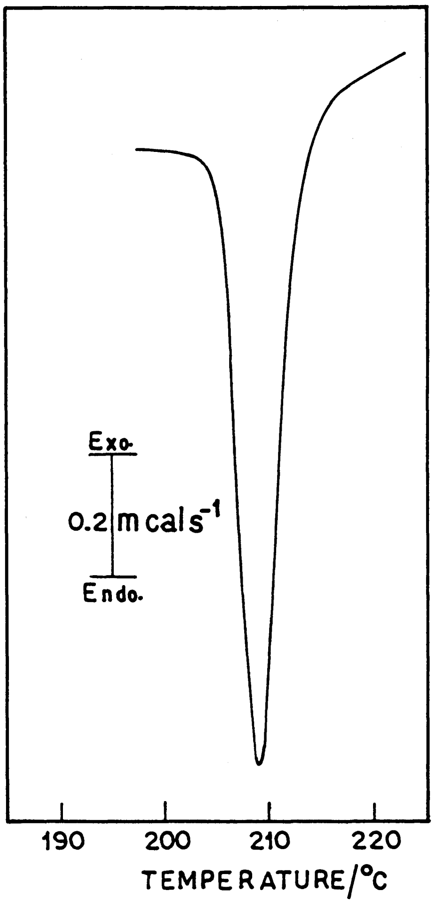

Fig. 3. DSC curve showing transformation of $[NiL_2](ClO_4)_2$ (**7**) (wt taken=7.65 mg) into (**7a**). Heating rate: 10 °C min^{-1}.

the elimination of the diamine at higher temperature. Thus the decomposition patterns of these complexes are very complicated. The species $[NiLCl_2]$ (**1b**), $[NiL(SO_4)]$ (**3b**), and $NiL_{0.33}Cl_2$ (**1c**) are synthesized by temperature arrest technique and characterized (vide infra).

The TG-DTA study shows that the complex $[NiL_2](ClO_4)_2$ (**7**) undergoes an endothermic phase transition associated with thermochromism from yellow to red at ca. 203 °C (Fig. 3). Enthalpy change for this transformation is calculated with the help of DSC (ΔH=6.9 kJ mol^{-1}). The transformation is irreversible and the red species can be stored in a desiccator but not in open atmosphere due to its extreme hygroscopic nature.

Structure of the Complexes Obtained by Heating. The dehydrated species (**1a**), (**2a**), (**3a**), (**4a**), and (**5a**) possess octahedral geometry as is evident from magnetic moment and electronic spectra (mull) (Tables 1 and 2, Fig. 1). The complexes (**1a**), (**2a**), (**3a**), and (**4a**) show one band in the NIR region in their electronic spectra (Table 2, Fig. 1) which clearly suggest their cis configuration.[20-22] Moreover, the IR spectra of (**1a**), (**2a**), and (**3a**) show three bands in the region 1000—850 cm^{-1} where generally $\rho_r(CH_2)$ vibrations appear corroborating the cis geometry of the complexes.[27] On the other hand the electronic spectra of (**5a**) are identical with that of the original trans-$[NiL_2(H_2O)_2](NO_3)_2 \cdot H_2O$ (**5**) except for a slight shift of the band positions which indicate a partial exchange of ligands. The IR spectra of (**5a**) reveal that the $\rho_r(CH_2)$ vibrations at 1000—750 cm^{-1} remain the same as in (**5**) but the combination band of NO_3 in the region 1700—1800 cm^{-1} splits into two weaker peaks characteristic of monodentate nitrate group in contrast to the single sharp peak of ionic nitrate in (**5**).[2,28] This indicates that in complex (**5a**) the two nitrate ions coordinate in the axial position as monodentate ligand to form the trans octahedral structure. From the foregoing discussion it is, therefore, concluded that on deaquation the complexes (**1**), (**2**), (**3**), and (**4**) change their geometry from trans→cis but the complex (**5**) retains its trans octahedral geometry.

The yellow anhydrous product (**6a**) is diamagnetic and its electronic spectrum is characteristic of a square planar nickel(II) complex having a broad and strong absorption band in the blue part of the spectrum

(Table 2). Therefore, it is clear that the dehydration of the complex (**6**) is accompanied with an octahedral→square planar structural transformation.

The electronic spectrum of red isomer i.e. post-phase species of yellow $[NiL_2](ClO_4)_2$ (**7**) is very similar to that of its pre-phase species except for a shift of the peak to the longer wave length region (Table 2). This spectral patterns and diamagnetism of the isomers clearly suggest that both the yellow and the red isomers are square planar. The IR spectra of yellow and red form differ appreciably in the regions 3350—3100, 1600, 1400—1350, and 950—850 cm^{-1} where the νNH_2, δNH_2, $\rho_w(CH_2)$ and skeletal vibrations appear (Table 4). This difference in the spectral pattern suggests that the conformation of the chelate ring are different in the two isomers.$^{7-9)}$ The vibrational mode of ClO_4 in the region 1200—900 cm^{-1} has been examined carefully and it is found that the ClO_4 is not involved in partial covalent bonding in either form. This observation is consistent with the square planar geometry of both the forms. Consequently, a sudden change of in-plane ligand field strength caused by conformational changes in the diamine ring system is assumed to be responsible for the observed thermochromic phase transformation. The same mechanism has been established for the thermochromism of $[M(dieten)_2]$ $(ClO_4)_2$ (where M=Cu(II) and Ni(II)) with the help of X-ray single crystal analysis of both phases of $[Cu(dieten)_2]$ $(ClO_4)_2$.$^{16-19)}$ It is interesting to note that the color change, enthalpy change (ΔH in kJ mol^{-1}) and spectral shift for transition of $[NiL_2](ClO_4)_2$ resemble closely to those of $[Ni(dieten)_2](ClO_4)_2$ (Table 5). These observations strengthen the proposed conformational change mechanism for the phase transition of $[NiL_2](ClO_4)_2$.

The electronic spectra (mull) of $[NiLCl_2]$ (**1b**) and $[NiLSO_4]$ (**3b**) show two bands in the visible region which is typical of the octahedral nickel(II). The magnetic moment data also support the octahedral geometry (Table 1). The IR spectra suggest that chelating character of diamine is retained. Therefore, to satisfy the octahedral geometry both the chloride and sulfate ions should act as bridging ligands as reported earlier by us.$^{29)}$

The complex $NiL_{0.33}Cl_2$ (**1c**) possesses unusually high magnetic moment (μ_{eff}=4.1 BM at 28 °C) considering the formula $NiL_{0.33}Cl_2$. This type of high magnetic moment probably arises due to the ferromagnetic behavior developed from chloride bridging$^{30-32)}$ and metal-metal interaction.$^{33)}$ But, as the compound is very much hygroscopic, its IR and electronic spectrum are not well resolved. Therefore, it is very difficult to comment on the structure of this species.

Thermal Reactions. Considering the discussions in the preceeding sections it may be concluded that six types of thermochemical changes are occurring which are represented by the following equations:

(i) Deaquation-anation associated with geometrical isomerization:$^{34)}$

$$\underset{\text{Oh}}{trans\text{-}[NiL_2(H_2O)X]\cdot nH_2O} \xrightarrow[-(n+1)H_2O]{\Delta} \underset{\text{Oh}'}{cis\text{-}[NiL_2X_2]}$$

(X=Cl and Br).

(ii) Deaquation associated with geometrical isomerization:

$$\underset{\text{Oh}}{trans\text{-}[NiL_2(H_2O)Y]\cdot nH_2O} \xrightarrow[-(n+1)H_2O]{\Delta} \underset{\text{Oh}'}{cis\text{-}[NiL_2Y]}$$

($Y=SO_4$ and SeO_4).

Table 4. IR Spectral Data for the Isomers (**7**) and (**7a**) in Nujol

Isomer $[NiL_2](ClO_4)_2$	$\nu(NH_2)$	$\delta(NH_2)$	$\rho_w(CH_2)$	$\tau(NH)+\rho_w(NH)+\tau(CH_2)^{a)}$ +stretching vibrations of skeleton$+\nu(C\text{-}N)+\nu(C\text{-}C)$	$\rho_r(CH_2)$
(**7**)	3265 s, 3220 sbr, 3245 s(sp), 3238 sh	1588 s(sp)	1470 sbr, 1460 sh, 1452 sh	1315 s, 1287 s, 1240 s, 1205 vs, 1177 vs	945 s(sp) 931 s, 925 m, 912 s
(**7a**)	3320 wbr, 3280 sbr, 3230 s, 3140 mbr	1580 sbr	1390 w, 1380 m, 1360 s	1318 s, 1291 vs, 1245 m, 1205 s	935 sbr, 915 m, 892 w

a) These band are partially overlapped by ClO_4 bands.

Table 5. Comparative Statement of Color Change, Enthalpy Change (ΔH) and Spectral Shift of Thermochromic Transition of *N*,*N*-Diethyl-1,2-ethanediamine(L′) and *N*,*N*-Dimethyl-1,2-ethanediamine(L) Complexes of Nickel(II) Perchlorate

Complexes	Color change	Enthalpy change /kJ mol^{-1}	Spectral shift /nm
$[NiL'_2](ClO_4)_2{}^{a)}$	Orange→red	6.7	465→488
$[NiL_2](ClO_4)_2$	Yellow→red	6.9	455→478

a) Data taken from Ref. 4.

(iii) Deaquation-anation without any structural change:

$$\underset{\text{Oh}}{\textit{trans}\text{-}[NiL_2(H_2O)_2](NO_3)_2\cdot H_2O} \xrightarrow[-3H_2O]{\Delta} \underset{\text{Oh}'}{\textit{trans}\text{-}[NiL_2(NO_3)_2]}.$$

(iv) Deaquation-deanation associated with configurational changes:

$$\underset{\text{Oh}}{\textit{cis}\text{-}[NiL_2(H_2O)(BF_4)](BF_4)} \xrightarrow[-H_2O]{\Delta} \underset{\text{Sp}}{[NiL_2](BF_4)_2}.$$

(v) Thermally induced conformational changes:

$$\underset{\text{Sp}}{[NiL_2](ClO_4)_2} \xrightarrow{\Delta} \underset{\text{Sp}}{[NiL_2](ClO_4)_2}.$$

(vi) Thermally induced decompositions:

$$\textit{cis}\text{-}[NiL_2Cl_2] \xrightarrow[-L]{\Delta} [NiLCl_2] \xrightarrow[-0.66L]{\Delta} NiL_{0.33}Cl_2.$$

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34) Here, Oh (or Oh′) and Sp represent an octahedral mono or di-aqua (or aniono) and a square planar species, respectively.