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Preparation, Characterization, and Solid State Thermal Studies of Nickel(II) Iodide Complexes of Ethane-1,2-diamine and Its Derivatives

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$[NiL_3]I_2 \cdot 2H_2O$ [L = *N*-methylethane-1,2-diamine (meen) and 2-methylpropane-1,2-diamine (ibn)], $[NiL_3]I_2$ [L = ethane-1,2-diamine (en), *N*-ethylethane-1,2-diamine (eten), *N*-propylethane-1,2-diamine (pren), and propane-1,2-diamine (pn)], $[NiL_2(H_2O)_2]I_2$ (L = meen and eten), and $[Ni_2L_2]I_2$ [L = *N*-isopropylethane-1,2-diamine (ipren) and ibn] have been synthesized from solution and characterized. $[NiL_2I_2]$ (L = en, meen, eten, and pren] and $[Ni(ibn)_2]I_2$ have been isolated in the solid state from their corresponding parent tris(diamine) complex by temperature arrest technique. $[NiL_2(H_2O)_2]I_2$ (L=meen and eten) upon heating undergo deaquation-anation reaction. All the diamine species excepting $[Ni(ipren)_2]I_2$ and $[Ni(ibn)_2]I_2$ which possess square-planar geometry, are octahedral and both the diaqua and diiodobis(diamine) species possess *trans*-octahedral geometry showing variation only in $[Ni(en)_2I_2]$, which is having *cis*-octahedral geometry. $[Ni(meen)_2I_2]$ and $[Ni(eten)_2I_2]$ show irreversible endothermic phase transitions (160—190 °C; $\Delta H = 5.65\ \mathrm{kJ\,mol^{-1}}$ and 204—225 °C; $\Delta H = 4.23\ \mathrm{kJ\,mol^{-1}}$, respectively) without any visual color change with retention of *trans*-octahedral configuration. In case of $[Ni(eten)_2I_2]$ the post phase species reverts to the original diaqua species, $[Ni(eten)_2(H_2O)_2]I_2$ on keeping in open atmosphere whereas the rehydrated species of its meen analogue, $[Ni(meen)_2(H_2O)_2]I_2$ after deaquation does not show the phase transition. On the other hand, corresponding pren analogue shows reversible endothermic phase transition (68—111 °C; $\Delta H = 2.42\ \mathrm{kJ\,mol^{-1}}$ for heating and 98—77 °C; $\Delta H = -1.4\ \mathrm{kJ\,mol^{-1}}$ for cooling). The occurrence of this type of phase transition is due to the conformational changes in the diamine chelate rings. The square-planar $[Ni(ibn)_2]I_2$ undergoes time dependent reversible phase transition (232—248 °C; $\Delta H = 5.99\ \mathrm{kJ\,mol^{-1}}$) without any visual color change retaining the original geometry. Here also conformational changes in chelate rings are assumed to be responsible for this transition.

Diamine complexes of nickel(II) upon heating in the solid state undergo several interesting phase transformation phenomena e.g. (i) octahedral ⇄ square-planar structural transformation,[1—3] (ii) cis ⇄ trans-geometrical isomerization,[4] (iii) on set of dynamic disorder of the diamine chelate rings,[5—7] and (iv) conformational isomerism.[8—11] Almost all the transitions of (i) and (iii) are associated with prominent thermochromism whereas (ii) and (iv) scarcely show any drastic color change. The phenomena (i), (ii), and (iii) have also been observed along with deaquation in several complexes.[1,12—15]

On the basis of results reported so far one can conclude that in general the C-substituted diamines are suitable for structural transformation (i) whereas unsubstituted and N-substituted diamines are prone to conformational change (iv). On the other hand, the dynamic disorder of the chelate rings (iii) has been found to occur both in C- and N-substituted diamines provided the counter anion (e.g. NO_3, ClO_4, and BF_4) can undergo rotational reorientation.[5,6,16] The geometrical isomerisms (ii) among the nickel(II) diamine complexes are scanty.[4] However, there are several complexes where this type of transformation takes place as a consequence of deaquation-anation reaction.[12—14] Ihara et al.[13] reported that the diaqua complexes are usually trans and on deaquation-anation the original trans configuration is retained in the symmetric (*N*,*N*′-dialkylsubstituted)-diamines. While in the complexes with asymmetric (*N*,*N*′-dialkylsubstituted)-diamine trans→cis configurational change takes place.

With a view to test the validity of above mentioned generalization we report here thermal investigations of nickel(II) iodide complexes of some unsubstituted and C- and N-alkylsubstituted diamines. The complexes of these diamines with several other counter anions have already been reported.[17] The iodide ion being poorer coordinating anion, has been found to be very useful[18] for the study of square-planar ⇄ octahedral transformations. The larger size of it should have steric influence on chelate ring conformations and thus increases the possibility of conformational isomerism which mostly occurs with another larger counter anion e.g. thiocyanate.[8—11]

Experimental

Reagents. High purity ethane-1,2-diamine (en), *N*-methylethane-1,2-diamine (meen), *N*-ethylethane-1,2-diamine (eten), *N*-propylethane-1,2-diamine (pren), *N*-isopropylethane-1,2-diamine (ipren), propane-1,2-diamine (pn), and 2-methylpropane-1,2-diamine (ibn) were purchased from Aldrich Chemical Company Inc. and used as received. Commercial anhydrous nickel(II) iodide was found to be practically insoluble in ethanol. Accordingly, an ethanolic solution of nickel(II) iodide was prepared by mixing solutions of nickel(II) nitrate hexahydrate and sodium iodide in ethanol in 1:2 molar ratio and filtering off sodium nitrate as described by Goodgame and Venanzi.[19] All other chemicals used were of analytical reagent grade.

Preparation of Complexes. The $[Ni(en)_3]I_2$ (**1**) and $[Ni(pn)_3]I_2$ (**5**) were prepared by slow addition of the respective diamine (3 mmol) to an ethanolic solution (5 cm^3) of nickel(II) iodide (1 mmol) with constant stirring. Both were separated immediately as fine pink colored crystals. They were filtered off, washed with ethanol and dried in a $CaCl_2$ desiccator.

The complexes $[Ni(meen)_3]I_2 \cdot 2H_2O$ (**2**), $[Ni(eten)_3]I_2$ (**3**), $[Ni(pren)_3]I_2$ (**4**), and $[Ni(ibn)_3]I_2 \cdot 2H_2O$ (**7**) were synthesized by adopting the above procedure. These complexes were not separated immediately but obtained on keeping the mixture overnight in $CaCl_2$ desiccator.

The complexes $[Ni(en)_2I_2]$ (**1a**), $[Ni(meen)_2(H_2O)_2]I_2$ (**2a**), $[Ni(eten)_2(H_2O)_2]I_2$ (**3a**), $[Ni(pren)_2I_2]$ (**4a**), $[Ni(ipren)_2]I_2$ (**6**), and $[Ni(ibn)_2]I_2$ (**7a**) were prepared by following the above procedure only by changing metal–diamine ratio to 1 : 2.

The complexes $[Ni(meen)_2I_2]$ (**2b**) and $[Ni(eten)_2I_2]$ (**3b**) were synthesized from their respective tris complexes as well as from diaquabis complexes in solid state by temperature arrest technique. These two **2b** and **3b** transform to their diaqua species on keeping them in humid atmosphere.

The complexes $[Ni(pren)_2I_2]$ (**4a**) and $[Ni(ibn)_2]I_2$ (**7a**) were also prepared from their corresponding tris complexes in the solid state by adopting temperature arrest technique.

Measurements. The instruments used for thermal investigation, magnetic susceptibility, elemental analysis, X-ray powder diffraction, and for IR and electronic spectra (mull) were as reported earlier.[4,20]

Results and Discussion

Structure of the Complexes. All the tris complexes i.e. $[Ni(en)_3]I_2$ (**1**), $[Ni(meen)_3]I_2 \cdot 2H_2O$ (**2**), $[Ni(eten)_3]I_2$ (**3**), $[Ni(pren)_3]I_2$ (**4**), $[Ni(pn)_3]I_2$ (**5**), and $[Ni(ibn)_3]I_2 \cdot 2H_2O$ (**7**) possess octahedral geometry as is evident from their electronic spectra and magnetic moment (Table 1). Among the bis complexes, $[Ni(ipren)_2]I_2$ (**6**) and $[Ni(ibn)_2]I_2$ (**7a**) show relatively strong absorption band at ca. 438 and ca. 426 nm, respectively in their corresponding electronic spectra and are diamagnetic (Table 1), indicating a square-planar geometry around nickel(II).[3] All the other bis complexes are paramagnetic and their electronic spectra are characteristics of octahedral nickel(II) (Table 1). The electronic spectra in the NIR region have been used for the identification of cis or trans geometry of both the diaqua and diiodo bis(diamine) complexes.[3,4] It is evident from the spectral pattern that only $[Ni(en)_2I_2]$ (**1a**) possesses a *cis*-configuration as its d–d band in the NIR region does not show any splitting (Fig. 1) whereas, the appearance of two bands in the NIR region (Fig. 1) of the rest bis complexes (three diaqua and diiodo) indicates that they possess *trans*-octahedral geometry.[21]

Thermal Decomposition. The simultaneous TG-DTA analyses of $[Ni(en)_3]I_2$ (**1**) $Ni(meen)_3]I_2 \cdot 2H_2O$ (**2**), $[Ni(eten)_3]I_2$ (**3**), $[Ni(pren)_3]I_2$ (**4**), and $[Ni(ibn)_3]I_2 \cdot 2H_2O$ (**7**) reveal that all of them on heating decompose to produce the corresponding bis(diamine) complexes whereas, $[Ni(pn)_3]I_2$ (**5**) does not yield any intermediate during the course of decomposition (Figs. 2 and 3; Scheme 1). The bis complexes can also be prepared by direct stoichiometric addition of the ligand to nickel(II) iodide as described in experimental section (Scheme 1). The complexes $[Ni(meen)_2(H_2O)_2]I_2$ (**2a**) and $[Ni(eten)_2(H_2O)_2]I_2$ (**3a**) obtained by the latter procedure are found to be aquated and on heating yield the anhydrous diiodo complexes (Fig. 4; Scheme 1). The magnetic moment and electronic spectral data of the aquated [**2a** and **3a**] and deaquated [**2b** and **3b**] (Table 1) species indicate that both of them possess *trans*-octahedral geometry. The red shift of the band maxima on deaquation is due to the lower ligand field strength of iodide compared with that of water molecule. Thus any kind of structural transformation (octahedral ⇄ square-planar)/cis ⇄ trans) on deaquation is excluded.

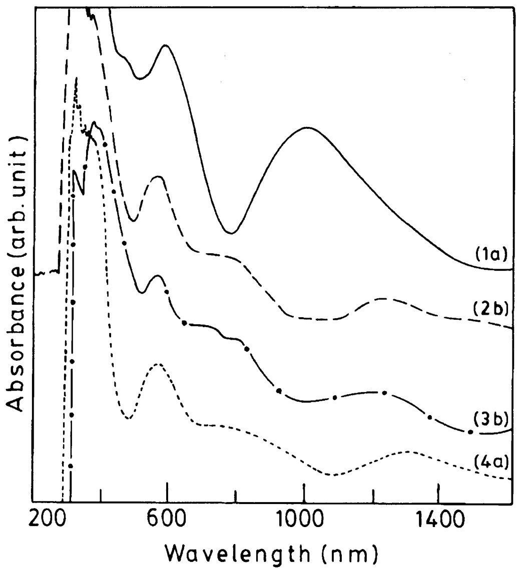


Fig. 1. Electronic spectra (Nujol) of *cis*-$[Ni(en)_2I_2]$ (**1a**) (—), *trans*-$[Ni(meen)_2I_2]$ (**2b**) (---), *trans*-$[Ni(eten)_2I_2]$ (**3b**) (-•-), and *trans*-$[Ni(pren)_2I_2]$ (**4a**) (---).

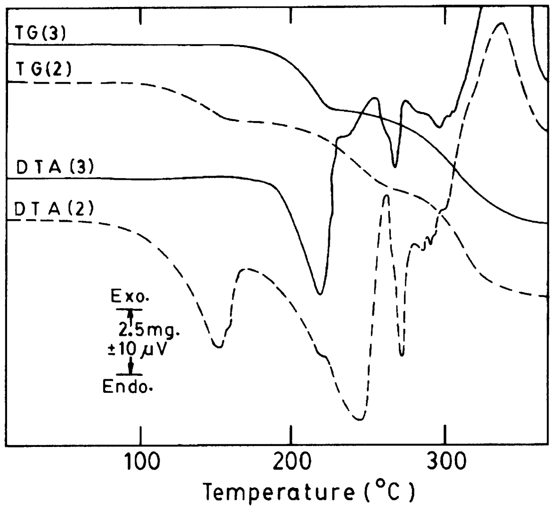


Fig. 2. TG-DTA curves for $[Ni(meen)_3]I_2 \cdot 2H_2O$ (**2**) (wt taken=14.70 mg) (---) and $[Ni(eten)_3]I_2$ (**3**) (wt taken=13.15 mg) (—).

Table 1. Data of the Elemental Analyses, Magnetic Moments, and Some Selective Bands of Electronic Spectra of Nickel(II) Iodide Complexes with Diamines

Compound		Color	Analyses/% a)			μ_{eff}	Electronic Spectra
			C	H	N	BM	λ_{max}/nm
$[Ni(en)_3]I_2$	**(1)**	Pink	14.6 (14.6)	4.9 (4.9)	17.0 (17.0)	3.1	865, 545, 360
cis-$[Ni(en)_2I_2]$	**(1a)**	Blue	11.1 (11.1)	3.7 (3.7)	12.8 (12.9)	3.2	990, 575, 380
$[Ni(meen)_3]I_2 \cdot 2H_2O$	**(2)**	Pink	18.8 (18.9)	6.0 (5.9)	14.5 (14.7)	3.2	874, 526, 345
trans-$[Ni(meen)_2(H_2O)_2]I_2$	**(2a)**	Bluish-pink	14.3 (14.5)	4.6 (4.8)	11.4 (11.3)	3.2	1215, 780, 565, 355
trans-$[Ni(meen)_2I_2]$	**(2b)**	Bluish-pink	15.5 (15.6)	4.3 (4.3)	12.1 (12.1)	3.2	1225, 795, 570, 375
$[Ni(eten)_3]I_2$	**(3)**	Blue-violet	24.8 (24.9)	6.3 (6.2)	14.5 (14.5)	3.2	882, 559, 359
trans-$[Ni(eten)_2(H_2O)_2]I_2$	**(3a)**	Light-violet	18.2 (18.3)	5.2 (5.3)	10.6 (10.7)	3.0	1200, 770, 565, 345
trans-$[Ni(eten)_2I_2]$	**(3b)**	Light-violet	19.5 (19.6)	4.90 (4.91)	11.5 (11.5)	3.0	1220, 790, 570, 365
$[Ni(pren)_3]I_2$	**(4)**	Blue-violet	29.0 (29.1)	6.7 (6.8)	13.4 (13.6)	3.2	890, 554, 387
trans-$[Ni(pren)_2I_2]$	**(4a)**	Sky-blue	23.2 (23.2)	5.6 (5.4)	10.9 (10.8)	3.2	1300, 785, 570, 365
$[Ni(pn)_3]I_2$	**(5)**	Pink	20.3 (20.2)	5.8 (5.6)	15.8 (15.7)	3.1	885, 550, 354
$[Ni(ipren)_2]I_2$	**(6)**	Reddish-yellow	23.1 (23.2)	5.4 (5.4)	10.8 (10.8)	Diamagnetic	438
$[Ni(ibn)_3]I_2 \cdot 2H_2O$	**(7)**	Light-violet	23.5 (23.5)	6.4 (6.5)	13.6 (13.7)	3.2	895, 550, 355
$[Ni(ibn)_2]I_2$	**(7a)**	Yellow	19.6 (19.6)	4.9 (4.9)	11.5 (11.5)	Diamagnetic	426

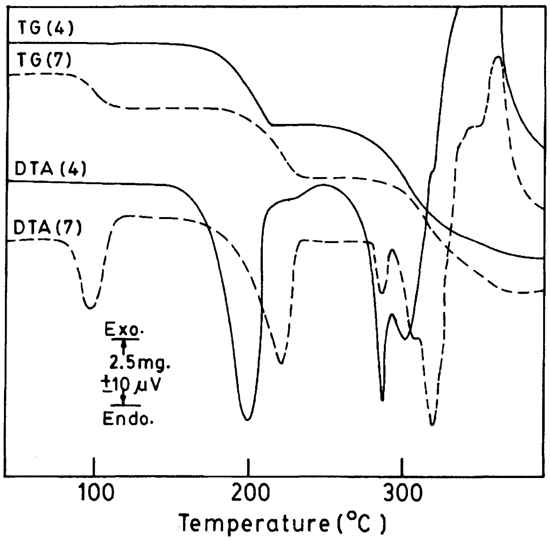


Fig. 3. TG-DTA curves for $[Ni(pren)_3]I_2$ (**4**) (wt taken = 14.30 mg) (—) and $[Ni(eten)_3]I_2$ (**7**) (wt taken = 14.00 mg) (- - -).

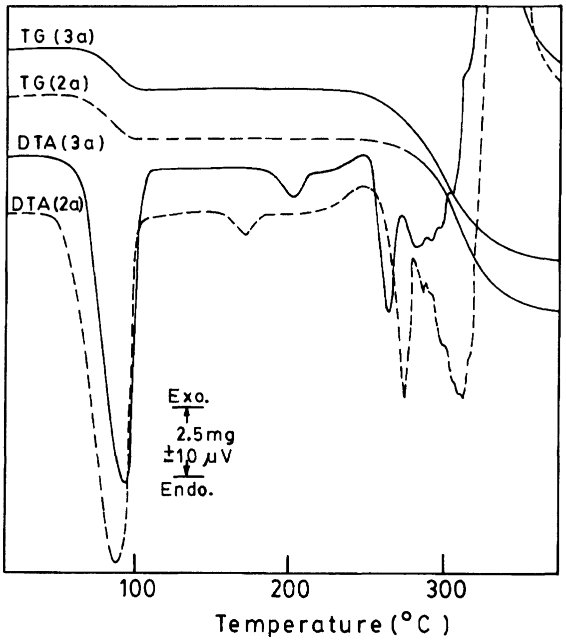
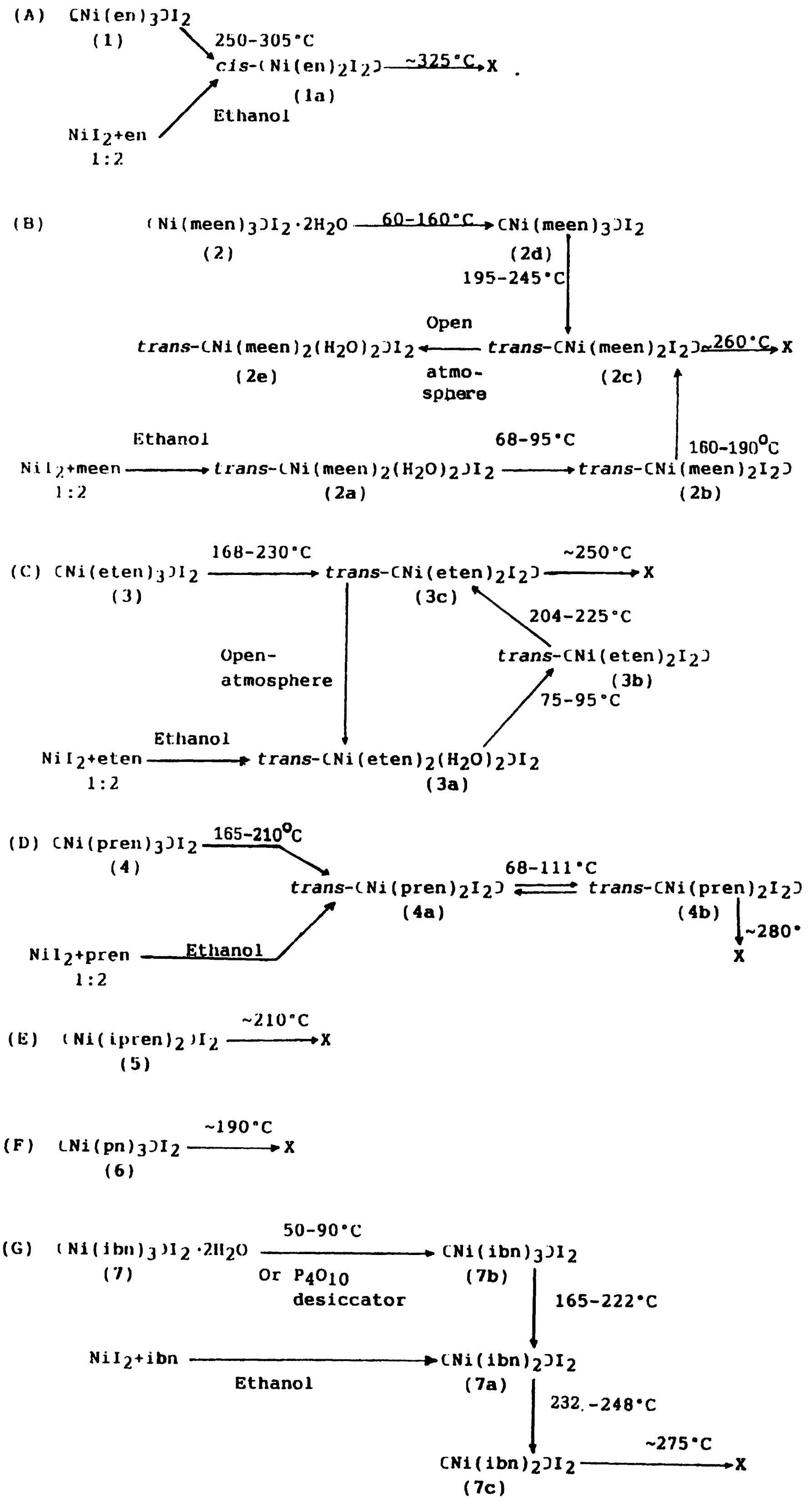


Fig. 4. TG-DTA curves for $[Ni(meen)_2(H_2O)_2]I_2$ (**2a**) (wt taken = 17.75 mg) (- - -) and $[Ni(eten)_2(H_2O)_2]I_2$ (**3a**) (wt taken = 17.65 mg) (—).

Phase Transitions. The $[Ni(meen)_2I_2]$ (**2b**) and $[Ni(eten)_2I_2]$ (**3b**) on further heating undergo an irreversible endothermic phase transition (160—190 °C; $\Delta H = 5.65$ kJ mol^{-1} and 204—225 °C; $\Delta H = 4.23$ kJ mol^{-1}, respectively) without any mass loss (Fig. 5; Scheme 1). The magnetic moment and electronic spec-



X Products were not identified

Scheme 1.

tra of the pre-phase [**2b** and **3b**] and the post-phase [**2c** and **3c**] species are very similar and typical of *trans*-octahedral geometry.[3,4] The IR spectra of the post-phase species, however, show some differences in the

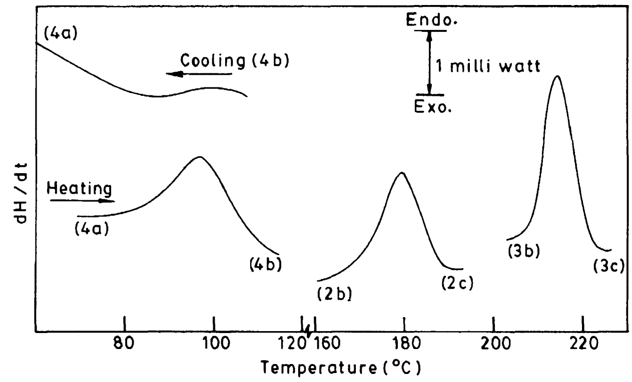


Fig. 5. DSC curves for [Ni(meen)$_2$I$_2$] (**2b**) (wt taken=7.8 mg), [Ni(eten)$_2$I$_2$] (**3b**) (wt taken=8.1 mg), and [Ni(pren)$_2$I$_2$] (**4a**) (wt taken=8.5 mg).

regions of 3350—3100, 1600, 1400—1350, and 950—850 cm^{-1} where the ν_{NH_2}, δ_{NH_2}, $\rho\omega_{CH_2}$, and skeletal vibrations appear. The conformational change[8—11,15] of the diamine chelate rings have been usually found to be responsible for this type of changes in the IR spectra, with no change (or a very little) in the electronic spectra and magnetic moments. Both the post-phase species [**2c** and **3c**] on keeping in humid atmosphere absorb two molecules of water and thereby (**3c**) reverts to **3a** (Scheme 1). But the rehydrated species **2e** (Scheme 1) is not identical to **2a** as its X-ray powder patterns[22] is considerably different from those of **2a** and after deaquation it transforms straightway to **2c** without showing any phase transition.

The [Ni(pren)$_2$I$_2$] (**4a**) on heating undergoes a reversible endothermic phase transition (68–111 °C; ΔH=2.42 kJ mol^{-1}) without showing any visual color change transforming to its isomer **4b** (Fig. 5; Scheme 1). On cooling **4b** reverts to **4a** showing an exotherm (98—77 °C; ΔH=−1.4 kJ mol^{-1}) (Scheme 1). The magnetic moment, IR and electronic spectra of **4a** and **4b** have been recorded at room temperature and at ca. 120 °C, respectively. It is evident from those data that both **4a** and **4b** possess *trans*-octahedral geometry but the chelate ring conformations[8—11,15] are probably different in the two forms as in the case of [**2b**/**2c** and **3b**/**3c**].

The yellow, diamagnetic complex [Ni(ibn)$_2$]I$_2$ (**7a**) synthesized from solution shows an endothermic phase transition (232—248 °C; ΔH=5.99 kJ mol^{-1}) (Scheme 1). The post-phase species on cooling upto room temperature does not show any exotherm. On immediate reheating it shows the endothermic phase transition at the same temperature range but with smaller enthalpy change. However, the post-phase species on exposure to ambient temperature for several hours shows the same enthalpy value as the initial one (**7a**). The color of the post-phase species (**7c**) is also yellow and the magnetic and electronic spectra recorded immediately after isolation are identical to those of **7a**. The IR spectra of **7c** could not be recorded as the addition of pressure for making pellet probably enhances the rate of reversion [**7c** →**7a**]. Anyway, the enthalpy change, temperature range of transition and the square-planar structure of both (**7a**) and (**7c**) lead us to assume that conformational[8—11,15] change of the diamine chelate rings may be responsible for this phase transition also.

It is interesting to note the bis complex **7a** obtained by pyrolysis of the corresponding tris complex **7** undergoes endothermic phase transition at higher temperature range (Fig. 3) and just before the decomposition starts. As a result, the post-phase species could not be isolated in pure form from **7**.

Conclusions

The results presented in the report strengthen the conclusion that bis complexes of N-substituted diamines are prone to conformational changes on heating as [Ni(meen)$_2$]I$_2$ (**2b**), [Ni(eten)$_2$]I$_2$ (**3b**), and [Ni(pren)$_2$]I$_2$ (**4a**) show this phenomenon. However, unlike the *N*,*N*-dialkyl substituted diamines,[13] deaquation-anation is not found to be associated with trans → cis-geometrical isomerism in N-alkyl substituted diamines. The only cis-complex is formed with ethane-1,2-diamine. On the other hand, the bulky and poorly coordinating iodide ion in [Ni(ibn)$_2$]I$_2$ (**7a**) cannot coordinate to the metal ion at higher temperature unlike its chloro and bromo analogue. As a result no square-planar → octahedral transition is observed; instead conformational changes of chelate rings occur.

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21) As the diaqua and diiodo species of any of the three diamines possess quite similar electronic spectral pattern, only the spectral positions of diaqua species are given in Table 1.

22) X-Ray powder diffraction data of **2a** and **2e** are deposited as Document No. 67071 at the Office of the Editor of Bull. Chem. Soc. Jpn.