August, 1983] © *1983 The Chemical Society of Japan* *Bull. Chem. Soc. Jpn., 56, 2509—2517 (1983)* 2509

Thermal Studies of Nickel(II) Hydrazine Complexes in Solid State[†]

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(Received July 13, 1982)

Two bis(hydrazine)nickel(II) fluoro complexes of the type $[NiL_2F_2]\cdot H_2O$, where $L=NH_2NH_2$ have been synthesized. Besides these, $[NiL_{2.5}(H_2O)_2]F_2\cdot 0.5H_2O$ and $[NiL_{2.5}F_2]\cdot 2H_2O$ have also been synthesized. Thermal investigations of these complexes have been carried out. Four tris(hydrazine)nickel(II) chloride and four tris(hydrazine)nickel(II) bromide complexes have been prepared and their thermal investigations have been done. Two bis(hydrazine) thiocyanato complexes have also been prepared and their thermal studies have also been carried out. These nickel(II) hydrazine complexes have been found to decompose through several complex species as intermediates. All these intermediates as well as the parent complexes have been characterized by elemental analyses, color, magnetic moment, electronic spectra (mull), and IR spectra. X-Ray powder diffraction pattern of two tris(hydrazine)nickel(II) bromide complexes have been obtained. The probable mechanistic paths for each step of decomposition have been proposed.

The formation of many inorganic compounds is generally dependent upon the conditions employed. Slight alteration in a described procedure sometimes results in an apparently identical but rather different compounds. This type of difference exhibited in the apparently similar compounds is very difficult to detect unless we characterize the compounds with X-ray crystal structure determinations. On the other hand, identification by thermal techniques may differentiate the compounds qualitatively. With this idea we have synthesized several hydrazine complexes of NiX_2, where $X=F^-$, Cl^-, Br^-, or SCN^-, considering the versatile character of hydrazine as complexing ligand[1–4] and tried to utilize the thermal techniques in differentiating apparently similar type of compounds. We wish to report the thermal investigation of hydrazine complexes of nickel(II) salts.

Experimental

Preparation of Nickel(II) Hydrazine Complexes. $[NiL_2F_2]\cdot H_2O$ $(L=NH_2NH_2)$ *(1)*: 2 mmol[††] of hydrazine hydrate (80%) was added to the 1 mmol of green hydrated nickel(II) fluoride crystals. While stirring the green crystals turned bluish pink crystals **1**. The crystals were filtered, washed thoroughly with ethanol–water mixture (1 : 1) and finally with dry ethanol.

$[NiL_2F_2]\cdot H_2O$ *(2)*: Hydrazine hydrate (2 mmol) was added dropwise with constant stirring to the concentrated ammoniacal solution of nickel(II) fluoride crystals. Fine bluish pink shining crystals **2** separated out slowly from the solution. These shining crystals were collected and washed as mentioned in the preparation of complex **1**.

$[NiL_{2.5}(H_2O)_2]F_2\cdot 0.5H_2O$ *(3)*: This compound was synthesized following the method adopted for the preparation of complex **1**. Here aqueous solution of nickel(II) fluoride was used instead of crystals.

$[NiL_{2.5}F_2]\cdot 2H_2O$ *(4)*: Aqueous solution of nickel(II) fluoride afforded this compound following the method described for the preparation of complex **2**.

$[NiL_3]Cl_2$ *(5)*: This was prepared following the method described for complex **1**.

$[NiL_3]Cl_2$ *(6)*: This was prepared following the method described for complex **2**.

$[NiLCl_2]$ *(7)*: This was prepared by pyrolysis of $[NiL_3]Cl_2$ (**5**) at ≈176 °C.

$[NiLCl_2]$ *(8)*: This was synthesized by pyrolysis of $[NiL_3]Cl_2$ (**6**) at ≈170 °C.

$[NiL_3]Cl_2\cdot H_2O$ *(9)*: This was synthesized by addition of hydrazine hydrate to the $[NiLCl_2]$ (**7**).

$[NiL_3]Cl_2\cdot H_2O$ *(10)*: This was prepared by addition of hydrazine hydrate to the $[NiLCl_2]$ (**8**).

$[NiL_3]Br_2$ *(11)*: This was synthesized by the corresponding procedure to the preparation of complex **1**.

$[NiL_3]Br_2$ *(12)*: This was prepared by the corresponding procedure to the preparation of complex **2**.

$[NiL_2Br_2]$ *(13)*: This was obtained on keeping the complex **11** in vacuum at ambient temperature. This was also prepared similarly from the complex **12**. The preparation from complex **11** required comparatively high vacuum relative to that from complex **12**.

$[NiL_2Br_2]$ *(14)*: This was obtained from complex **11** by pyrolytic technique at ≈176 °C in nitrogen atmosphere.

$[NiL_3]Br_2$ *(15)*: This was prepared by treatment of hydrazine hydrate on complex **13**.

$[NiL_3]Br_2$ *(16)*: This was synthesized by treating complex **14** with hydrazine hydrate.

$[NiL_2(SCN)_2]$ *(17)*: This was prepared by treating hydrazine hydrate (2—3 mmol) with ethanolic solution of nickel(II) thiocyanate (1 mmol).

$[NiL_2(SCN)_2]$ *(18)*: This was prepared by the treatment of hydrazine hydrate (2—3 mmol) with ethanolic ammoniacal nickel(II) thiocyanate solution.

Thermal Measurements. The thermal analysis was carried out using a thermal analyzer (Shimadzu, Model DT-30, Japan). A constant flow of dry nitrogen (30 ml min^{-1}) was maintained. Platinum crucibles were used. Heating rate was maintained 5 °C min^{-1}. The particle size of the samples was within 150—200 mesh. Aluminium oxide was used as reference.

Elemental Analyses. Elemental analyses were carried out in the microanalytical section of the Australian Mineral Development Laboratories as well as in the microanalytical laboratory of our institute.

Spectral Measurements. Infrared spectra (KBr disk, 4000—400 cm^{-1}) and electronic spectra in mull (28570—11111 cm^{-1}) were recorded using a Beckman IR spectrophotometer, Model IR-20A and a Pye Unicam spectrophotometer, model SP8-150, respectively. Cary 17D was also used for mull

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[†] Part of the work was presented at the third national symposium of Indian Thermal Analysis Society held at VSSC, Trivandrum, India.

[††] Similar experiment was performed by using 3 mmol of hydrazine hydrate but we obtained complex $[NiL_2F_2]\cdot H_2O$.

spectra in some cases.

Magnetic Measurement. Magnetic moments of the compounds were evaluated from the magnetic susceptibilities of the samples at room temperature, corrected by applying Pascal's constants of the elements involved, using the Gouy technique where $Hg[Co(SCN)_4]$ was taken as standard.

X-Ray Powder Diffraction. X-Ray powder diffraction patterns of the compounds were obtained on a Philips powder diagram camera, using Cu *Ka* radiation.

Results

The thermal curves of two bis(hydrazine)nickel(II) fluoro complexes **1** and **2** are shown in Fig. 1. Both the species become anhydrous first and then lose hydrazine on heating. But the thermal profiles of them are distinctly different from each other.

$[NiL_{2.5}(H_2O)_2]F_2\cdot 0.5H_2O$ (**3**) loses first its lattice water and then two molecules of coordinated water. The derived $NiL_{2.5}F_2$ is very much unstable and loses immediately hydrazine molecules in two steps as observed in TG curve (Fig. 2). The first step corresponds roughly to elimination of 0.5 molecule of hydrazine and the second corresponds to that of two molecules. But its DTA curve indicates that the elimination of hydrazine occurs in more than two steps. On the other hand, thermal curve of $[NiL_{2.5}F_2]\cdot 2H_2O$ (**4**) shown in Fig. 2 indicates that hydrazine elimination occurs here also in two steps. The first step corresponds to the elimination of one hydrazine and the second corresponds to that of the rest of hydrazine.

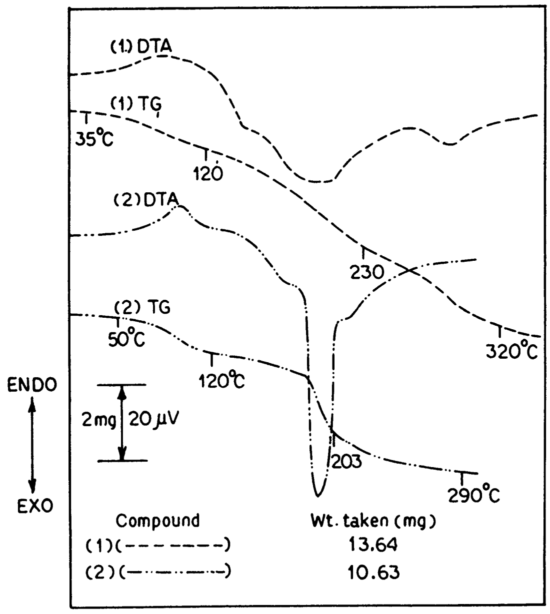


Fig. 1. Thermal curves of $[NiL_2F_2]\cdot H_2O$ (**1**) and $[NiL_2F_2]\cdot H_2O$ (**2**).

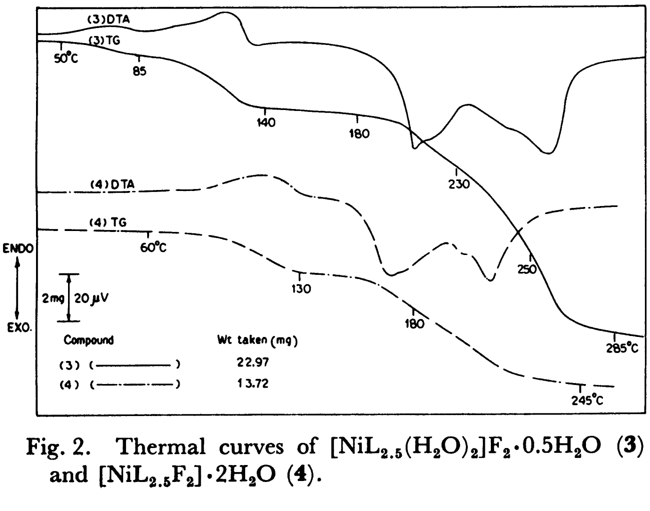


Fig. 2. Thermal curves of $[NiL_{2.5}(H_2O)_2]F_2\cdot 0.5H_2O$ (**3**) and $[NiL_{2.5}F_2]\cdot 2H_2O$ (**4**).

Thermal curve of tris(hydrazine)nickel(II) chloride (**6**) is shown in Fig. 3. It transforms straightly to $NiLCl_2$ on heating and then to nickel(II) chloride *via* an unstable intermediate compound $NiL_{0.5}Cl_2$. Thermal curve of tris(hydrazine)nickel(II) chloride (**5**) is almost identical to that of complex **6**. Here the TG curve does not support the formation of hemi(hydrazine) species (Fig. 3).

The TG curve of $[NiL_3]Cl_2\cdot H_2O$ (**9**) (Fig. 3) shows that it decomposes stepwise with the formation of bis as well as unis(hydrazine) chloro complex on heating. Its DTA curve hints the formation of another intermediate species in between $NiLCl_2$ and $NiCl_2$. The thermal profile of $[NiL_3]Cl_2\cdot H_2O$ (**10**) does not differ much from that of complex **9**. In complex **10** formation of hemi(hydrazine) species, though not isolable, is evident from the TG and DTA profile (Fig. 3).

The TG curve of tris(hydrazine)nickel(II) bromide (**11**) (Fig. 4) shows that it transforms to NiL_2Br_2 in single step. But its DTA curve shows an exotherm followed by a prominent hump which indicates that the formation of isolable NiL_2Br_2 takes place *via* an unstable intermediate $[NiL_{2.5}Br]Br$. The TG curve of derived bis species shows elimination of two hydrazine molecules taking place in one step, but its DTA curve indicates the elimination taking place *via* an another unstable intermediate complex. On the other hand, tris(hydrazine)nickel(II) bromide (**12**) transforms straightly to $NiLBr_2$ in a single step as evident from its thermal curves (Fig. 4). This uni species is not isolable in pure form even by arresting temperature rising. $NiLBr_2$ on further heating transforms to $NiBr_2$ *via* probably an unstable hemi(hydrazine) complex $NiL_{0.5}Br_2$.

The TG curve of $[NiL_2Br_2]$ (**13**) (Fig. 5) shows elimination of two hydrazine molecules taking place in a single step but its DTA profile hints the elimination in two steps probably through a uni (hydrazine)species. The thermal behavior of $[NiL_2Br_2]$ (**14**) is almost identical to that of **13**.

$[NiL_3]Br_2$ (**15**) transforms straightly to $NiBr_2$ in a single step as evident from its sharp TG and DTA curves, but $[NiL_3]Br_2$ (**16**) transforms to $NiLBr_2$ in a single step (Fig. 5). The unis(hydrazine) species derived from complex **16** is not isolable in pure state even by temperature arrest technique, but transforms to $NiBr_2$ in a single step (Fig. 5).

$[NiL_2(SCN)_2]$ (**17**) begins to lose hydrazine at ≈160 °C and becomes $Ni(SCN)_2$ at ≈225 °C in a single step observed from its TG curve (Fig. 6). But the presence of two peaks overlapping with each other in the corresponding DTA curve indicates elimination of hydrazine taking place in two steps. The metal thiocyanate is not

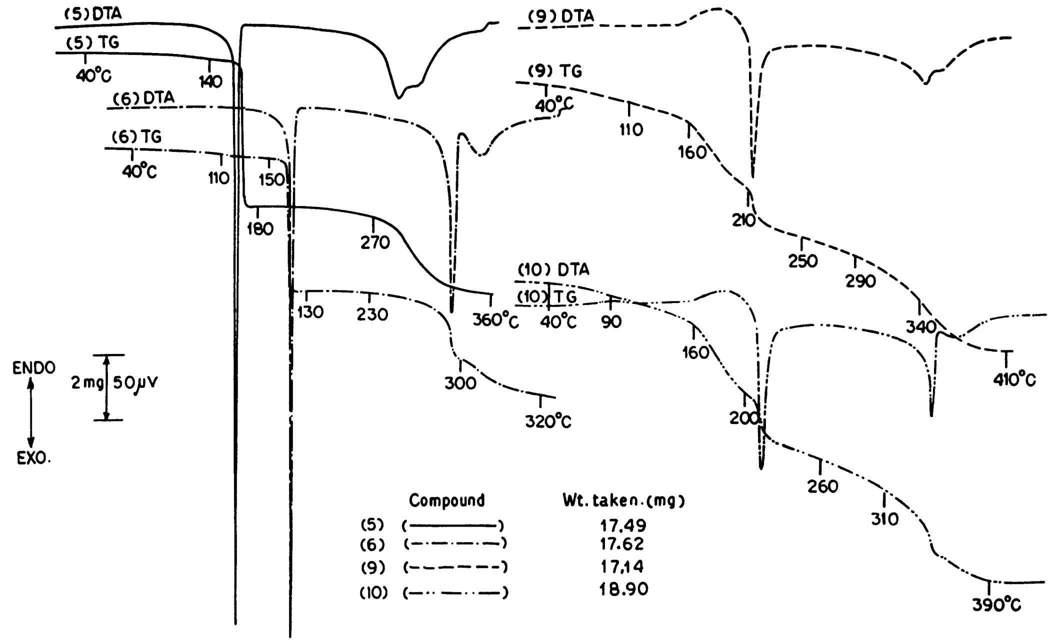


Fig. 3. Thermal curves of $[NiL_3]Cl_2$ (**5**), $[NiL_3]Cl_2$ (**6**), $[NiL_3]Cl_2 \cdot H_2O$ (**9**), and $[NiL_3]Cl_2 \cdot H_2O$ (**10**).

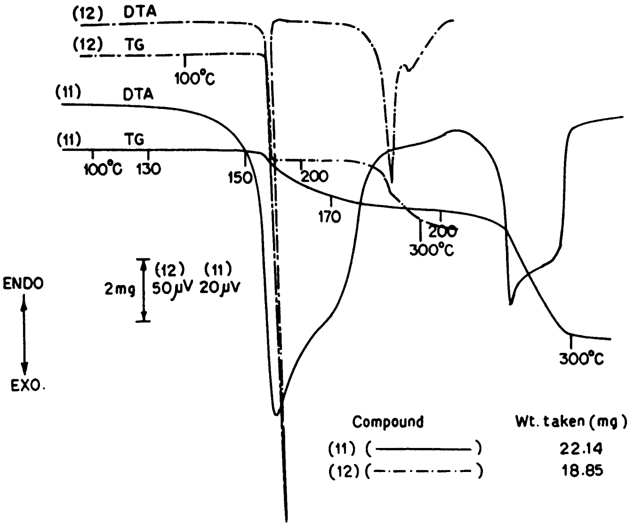


Fig. 4. Thermal curves of $[NiL_3]Br_2$ (**11**) and $[NiL_3]Br_2$ (**12**).

isolable. It immediately decomposes to metal sulfide and sulfur in two steps. On the other hand, in case of $[NiL_2(SCN)_2]$ (**18**) elimination of hydrazine and decomposition of metal thiocyanate occur simultaneously (Fig. 6).

Table 1 shows the thermal decomposition reaction in details along with temperature range and DTA peak temperature for each step of decomposition. Table 2 shows the analytical data of the hydrazine complexes and intermediate hydrazine complex species isolated by temperature arrest technique along with the color and magnetic data. IR spectra of all the hydrazine complexes are taken. Electronic mull spectra of the complexes are taken and corresponding data are shown in Table 3. X-Ray data of two complexes are shown in Table 4.

Discussion

The Complexes Derived from NiF_2 and Hydrazine Hydrate. $NiL_xF_y \cdot zH_2O$ (x=2, 2.5, y=2, z=1, 2, 2.5): Treatment of NiF_2 crystal with hydrazine hydrate afforded bluish pink $[NiL_2F_2] \cdot H_2O$ (**1**), whilst the samely formulated complex **2** was synthesized by reaction of hydrazine hydrate with NiF_2 crystals in concentrated ammoniacal solution. Electronic spectra (Table 3) in mull of both **1** and **2** complexes suggest O_h symmetry[5] existing in the system which is also supported by the magnetic moment (Table 2). The thermal profile for the water elimination shows existence of water molecule[6,7] as noncoordinated in both the cases. IR data also collaborate with the inference[8] drawn from thermal profile regarding the play of water molecule (Fig. 7). The medium broad band at $\approx 580\ cm^{-1}$ in IR is expected to be assigned to $\nu(Ni-F)$.[8] The bridging character of NH_2NH_2 exists in both species as $\nu(N-N)$[9,10] appearing at $\approx 980\ cm^{-1}$. The weak intensity of this band seems to be due to the fact that the vibrational mode of N–N stretching frequency tends to be IR inactive for the strong hydrogen bonding between F and hydrogen of NH_2 group. On the other hand, the thermal decomposition patterns of both species are different which implies that they are structurally somewhat different. It is rather difficult to comment on the mechanism of decomposition pattern as no intermediate species are isolable. However, for **1** the decomposition probably follows O_h $Ni^{II} \rightarrow T_d$ Ni^{II} which ultimately affords NiF_2.

It is interesting to note that the treatment of hydrazine hydrate with concentrated solution of NiF_2 yields $[NiL_{2.5}(H_2O)_2]F_2 \cdot 0.5H_2O$ (**3**). The electronic spectrum in mull as well as magnetic moment suggests it to exist as O_h symmetry. As water molecules evolve in two steps, it seems that two types of water *i.e.* lattice water

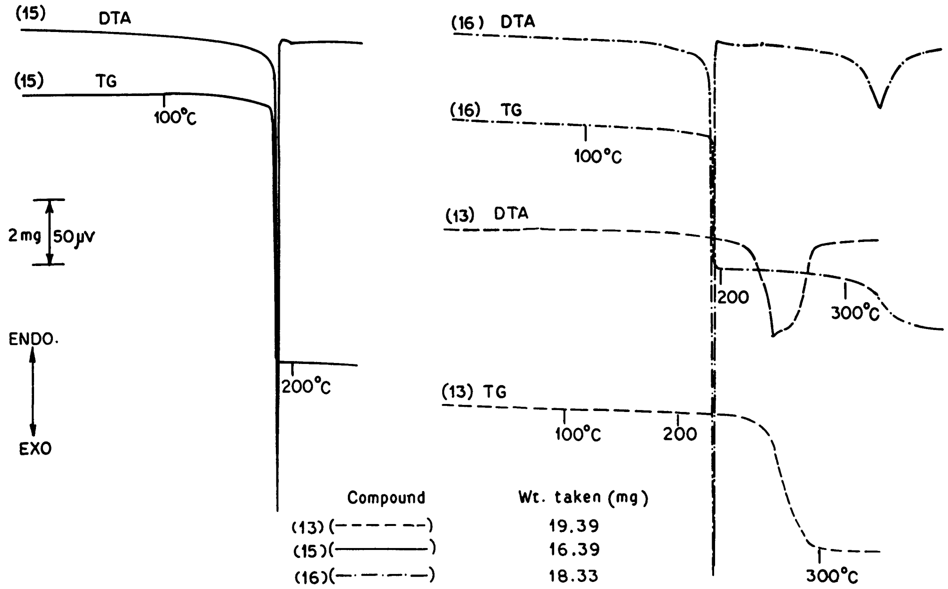


Fig. 5. Thermal curves of [NiL_3]Br_2 (**15**), [NiL_3]Br_2 (**16**), and [NiL_2Br_2] (**13**).

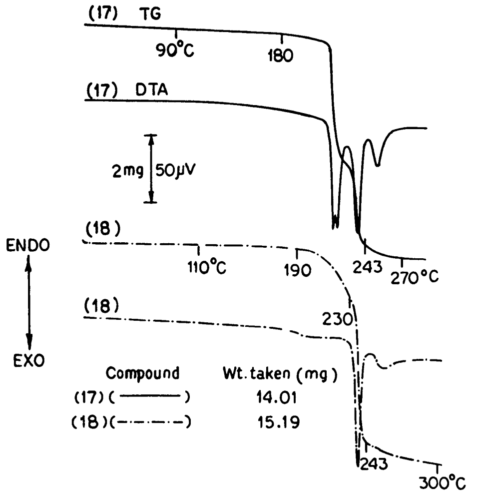


Fig. 6. Thermal curves of [$NiL_2(SCN)_2$] (**17**) and [NiL_2-$(SCN)_2$] (**18**).

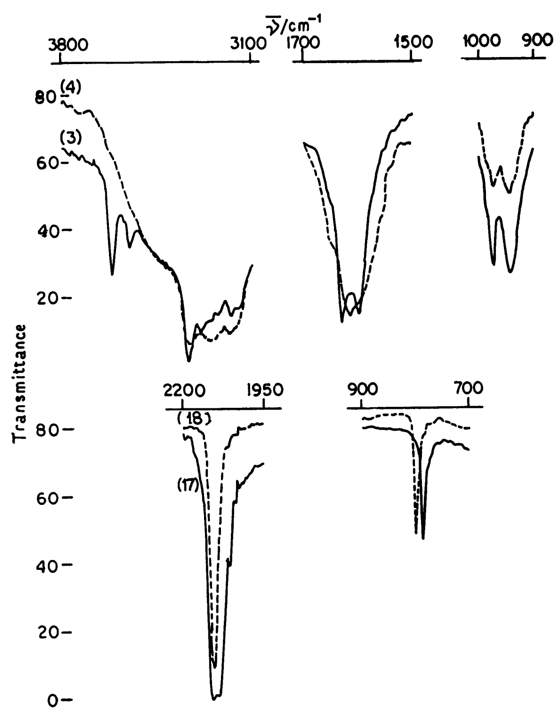


Fig. 7. IR spectra (3800—3100, 1700—1500, and 1000—900 cm^{-1}) of [$NiL_{2.5}(H_2O)_2$]F_2·$0.5H_2O$ (**3**)and [$NiL_{2.5}$-F_2]·$2H_2O$ (**4**); IR spectra (2200—1950, 900—700cm^{-1}) of [$NiL_2(SCN)_2$] (**17**) and [$NiL_2(SCN)_2$] (**18**).

and coordinated water exist in the system. However, the IR spectrum suggests that the two molecules of water are coordinated[11,12] to Ni^{II} as evident from the sharp bands at $\approx$3500 cm^{-1} [ν(OH)] (Fig. 7) and δ(HOH) at $\approx$1630 cm^{-1}, ρw(HOH) at 625 cm^{-1}, and [ν(MO)] at $\approx$465 cm^{-1}. The coordination of F^- to Ni^{II} is nullified by the absence of ν(MF) at $\approx$590 cm^{-1} as observed in the case of complexes **1** and **2**. Hydrazine molecules are existing in the system as both unidentate and bidentate as evident[2,4] from the presence of ν(N–N) vibrations at $\approx$935 and $\approx$975 cm^{-1} respectively (Fig. 7). The tentative structure of complex **3** is shown in Fig. 8. The elimination of water and hydrazine is complicated as the decomposition follows a number of intermediates as evident from DTA profile (Fig. 2). On the other hand, the treatment of hydrazine hydrate with concentrated solution of NiF_2 in ammoniacal medium yields [$NiL_{2.5}F_2$]·$2H_2O$ (**4**). O_h symmetry also exists here and the existence of hydrazine in the species is similar to complex **3**. Moreover, Ni–F bonding is also suggested by the presence of ν(MF) at $\approx$590 cm^{-1} as observed in complexes **1** and **2**. Water molecules in the complex **4** exist outside the coordination sphere as evident from its IR spectrum (Fig. 7) though temperature range for the elimination of water shown in Table 1 differs from that of complex **3**. The tentative structure of complex **4** is shown in Fig. 8. The decomposition of complex **4** appears also complicated (Fig. 2).

The Complexes Derived from $NiCl_2$ and Hydrazine Hydrate. Treatment of hydrazine hydrate with $NiCl_2$ affords

Table 1. Thermal parameters of the nickel(II) complexes of hydrazine

Decomposition reactions	Temp range / °C	DTA peak temp/°C
$[NiL_2F_2]\cdot H_2O$ (**1**)$\rightarrow NiL_2F_2$	40—140	85
$NiL_2F_2\rightarrow NiF_2$	140—340	150, 195, 290
$[NiL_2F_2]\cdot H_2O$ (**2**)$\rightarrow NiL_2F_2$	40—120	95
$NiL_2F_2\rightarrow NiL_{1.66}F_2$	120—188	175
$NiL_{1.66}F_2\rightarrow NiL_{0.66}F_2$	188—207	197
$NiL_{0.66}F_2\rightarrow NiF_2$	207—280	210
$[NiL_{2.5}(H_2O)_2]F_2\cdot 0.5H_2O$(**3**)$\rightarrow NiL_{2.5}(H_2O)_2F_2$	54—86	68
$NiL_{2.5}(H_2O)_2F_2\rightarrow NiL_{2.5}F_2$	87—137	125
$NiL_{2.5}F_2\rightarrow NiL_2F_2$	138—212	208
$NiL_2F_2\rightarrow NiF_2$	212—290	242, 255
$[NiL_{2.5}F_2]\cdot 2H_2O$(**4**)$\rightarrow NiL_{2.5}F_2$	86—134	114
$NiL_{2.5}F_2\rightarrow NiL_{1.5}F_2$	135—178	169
$NiL_{1.5}F_2\rightarrow NiF_2$	178—247	194, 208
$[NiL_3]Cl_2$(**5**)$\rightarrow NiLCl_2$	120—176	160
$NiLCl_2\rightarrow NiCl_2$	240—350	290, 305
$[NiL_3]Cl_2$(**6**)$\rightarrow NiLCl_2$	115—170	158
$NiLCl_2\rightarrow NiL_{0.5}Cl_2$	220—295	285
$NiL_{0.5}Cl_2\rightarrow NiCl_2$	295—360	305
$[NiL_3]Cl_2\cdot H_2O$(**9**)$\rightarrow NiL_2Cl_2$	40—215	158
$NiL_2Cl_2\rightarrow NiLCl_2$	215—320	220
$NiLCl_2\rightarrow NiCl_2$	320—400	340, 360
$[NiL_3]Cl_2\cdot H_2O$(**10**)$\rightarrow NiL_2Cl_2$	40—218	180
$NiL_2Cl_2\rightarrow NiLCl_2$	218—295	220
$NiLCl_2\rightarrow NiL_{0.5}Cl_2$	295—345	342
$NiL_{0.5}Cl_2\rightarrow NiCl_2$	345—410	364
$[NiL_3]Br_2$(**11**)$\rightarrow NiL_2Br_2$	140—176	155, 170
$NiL_2Br_2\rightarrow NiBr_2$	195—280	250, 270
$[NiL_3]Br_2$(**12**)$\rightarrow NiLBr_2$	170—180	172
$NiLBr_2\rightarrow NiL_{0.5}Br_2$	185—280	257
$NiL_{0.5}Br_2\rightarrow NiBr_2$	280—320	300
$[NiL_2Br_2]$(**13**)$\rightarrow NiBr_2$	200—310	250, 270
$[NiL_3]Br_2$(**15**)$\rightarrow NiBr_2$	130—190	175
$[NiL_3]Br_2$(**16**)$\rightarrow NiLBr_2$	160—200	185
$NiLBr_2\rightarrow NiBr_2$	205—350	320
$[NiL_2(SCN)_2]$(**17**)$\rightarrow Ni(SCN)_2$	160—225	210, 215
$Ni(SCN)_2\rightarrow NiS+S$	225—255	235, 250
$[NiL_2(SCN)_2]$(**18**)$\rightarrow NiS+S$	190—290	235, 268

$[NiL_3]Cl_2$ (**5**), while with ammoniacal medium another $[NiL_3]Cl_2$ (**6**) is formed. These two show similarity in color, magnetic moment as well as in other physical properties *e.g.*, IR and electronic spectra (mull). The spectral behavior suggests them to exist as O_h symmetry with the bridging characteristic of hydrazine. Thermal curves suggest that unis(hydrazine)nickel(II) chloride complexes $[NiLCl_2]$ (**7** and **8**), derived from the complexes **5** and **6** are slightly structurally different.

Treatment of hydrazine with complex **7** results in $[NiL_3]Cl_2\cdot H_2O$ (**9**). Similar treatment with complex **8** results in $[NiL_3]Cl_2\cdot H_2O$ (**10**). These two tris(hydrazine) species also show similarity in color, magnetic moment and other physical properties. We expected that these two hydrated tris species, on heating, will generate anhydrous tris species, identical to complexes **5** and **6**, but the thermal behaviors of complexes **9** and **10** show that synthesis of anhydrous tris species is not feasible by pyrolytic treatment. This hints the presence of water within the coordination sphere, but both IR and electronic (mull) spectra indicate noncoordination of water molecule. No significant DTA curve is obtained (Fig. 3) at the time of evolution of first hydrazine molecule, which probably due to the simultaneous elimination of H_2O and NH_2NH_2. The exotherm for NH_2NH_2 evolution and the endotherm of H_2O probably nullify the energy with each other. This also suggests that tris species **9** and **10** are quite different

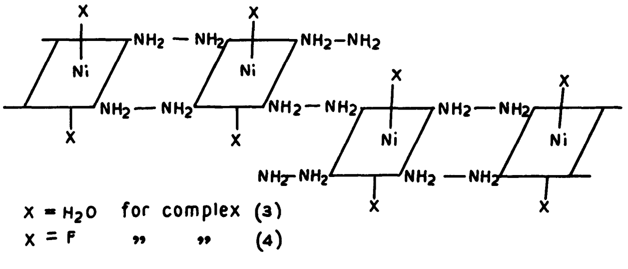


Fig. 8. Structures of $[NiL_{2.5}(H_2O)_2]F_2\cdot 0.5H_2O$ (**3**) and $[NiL_{2.5}F_2]\cdot 2H_2O$ (**4**).

TABLE 2. ANALYTICAL AND MAGNETIC DATA OF NICKEL(II) COMPLEXES DERIVED FROM THEM BY PYROLYSIS

Compound		Color	Found (Calcd) (%) Metal	Nitrogen	Halogen	μ_{eff} / BM
$[NiL_2F_2]\cdot H_2O$	(**1**)	Bluish pink	32.80(32.85)	31.28(31.33)	21.21(21.26)	2.95
$[NiL_2F_2]\cdot H_2O$	(**2**)	Bluish pink	32.82(32.85)	31.30(31.33)	21.23(21.26)	2.93
$[NiL_{2.5}(H_2O)_2]F_2\cdot 0.5H_2O$	(**3**)	Bluish pink	26.47(26.48)	31.54(31.57)	17.09(17.13)	2.89
$[NiL_{2.5}F_2]\cdot 2H_2O$	(**4**)	Bluish pink	27.57(27.60)	32.87(32.90)	17.81(17.86)	2.88
$[NiL_3]Cl_2$	(**5**)	Pink	25.09(26.01)	37.20(37.21)	31.43(31.45)	2.99
$[NiL_3]Cl_2$	(**6**)	Pink	26.00(26.01)	37.19(37.21)	31.41(31.45)	2.99
$[NiLCl_2]$	(**7**)	Sky blue	36.19(36.30)	17.27(17.31)	43.77(43.90)	3.38
$[NiLCl_2]$	(**8**)	Sky blue	36.21(36.30)	17.26(17.31)	43.89(43.90)	3.39
$[NiL_3]Cl_2\cdot H_2O$	(**9**)	Pink	24.01(24.09)	34.43(34.46)	29.11(29.13)	2.98
$[NiL_3]Cl_2\cdot H_2O$	(**10**)	Pink	24.05(24.09)	34.42(34.46)	29.09(29.13)	2.95
$[NiL_3]Br_2$	(**11**)	Pink	18.64(18.66)	26.62(26.70)	50.76(50.80)	3.02
$[NiL_3]Br_2$	(**12**)	Pink	18.63(18.66)	26.64(26.70)	50.74(50.80)	3.00
$[NiL_2Br_2]$	(**13**)	Sky blue	20.75(20.78)	19.76(19.82)	56.50(56.56)	3.00
$[NiL_2Br_2]$	(**14**)	Sky blue	20.74(20.78)	19.73(19.82)	56.52(56.56)	3.02
$[NiL_3]Br_2$	(**15**)	Pink	18.63(18.66)	26.64(26.70)	50.81(50.80)	3.02
$[NiL_3]Br_2$	(**16**)	Pink	18.63(18.66)	26.61(26.70)	50.78(50.80)	3.03
$[NiL_2(SCN)_2]$	(**17**)	Pink	24.55(24.59)	35.14(35.18)	26.79(26.81)*	3.10
$[NiL_2(SCN)_2]$	(**18**)	Pink	24.57(24.59)	35.13(35.18)	26.80(26.81)*	3.06

*denotes sulfur.

TABLE 3. ELECTRONIC (MULL) SPECTRA OF NICKEL(II) COMPLEXES OF HYDRAZINE (L)

Compound		Absorbance[a] maxima λ/nm	Compound		Absorbance[a] maxima λ/nm
$[NiL_2F_2]\cdot H_2O$	(**1**)	870, 550, 345, 305	$[NiL_3]Cl_2\cdot H_2O$	(**10**)	860, 525, 330, 290
$[NiL_2F_2]\cdot H_2O$	(**2**)	850, 530, 335(sh), 305	$[NiL_3]Br_2$	(**11**)	850, 780, 560, 500(sh), 375, 295
$[NiL_{2.5}(H_2O)_2]F_2\cdot 0.5H_2O$	(**3**)	850, 545, 345, 320	$[NiL_3]Br_2$	(**12**)	850, 780(sh), 540, 375, 300
$[NiL_{2.5}F_2]\cdot 2H_2O$	(**4**)	850, 560, 355, 320	$[NiL_2Br_2]$	(**13**)	590, 375
$[NiL_3]Cl_2$	(**5**)	845, 780(sh), 530, 340, 295	$[NiL_3]Br_2$	(**15**)	830, 530, 340(sh), 310
$[NiL_3]Cl_2$	(**6**)	860, 780(sh), 530, 335, 295	$[NiL_3]Br_2$	(**16**)	870, 545, 340(sh), 290
$[NiLCl_2]$	(**7**)	850, 570, 370, 295	$[NiL_2(SCN)_2]$	(**17**)	840, 550, 350(sh), 295
$[NiLCl_2]$	(**8**)	850, 530(sh), 410(sh),340(sh),310	$[NiL_2(SCN)_2]$	(**18**)	890, 555, 345, 300
$[NiL_3]Cl_2\cdot H_2O$	(**9**)	850, 520, 330, 295			

sh=shoulder. a) Arbitrary absorbance.

TABLE 4. X-RAY DIFFRACTION DATA OF $Ni(NH_2–NH_2)_3Br_2$ (**11**) AND $Ni(NH_2NH_2)_3Br_2$ (**12**)

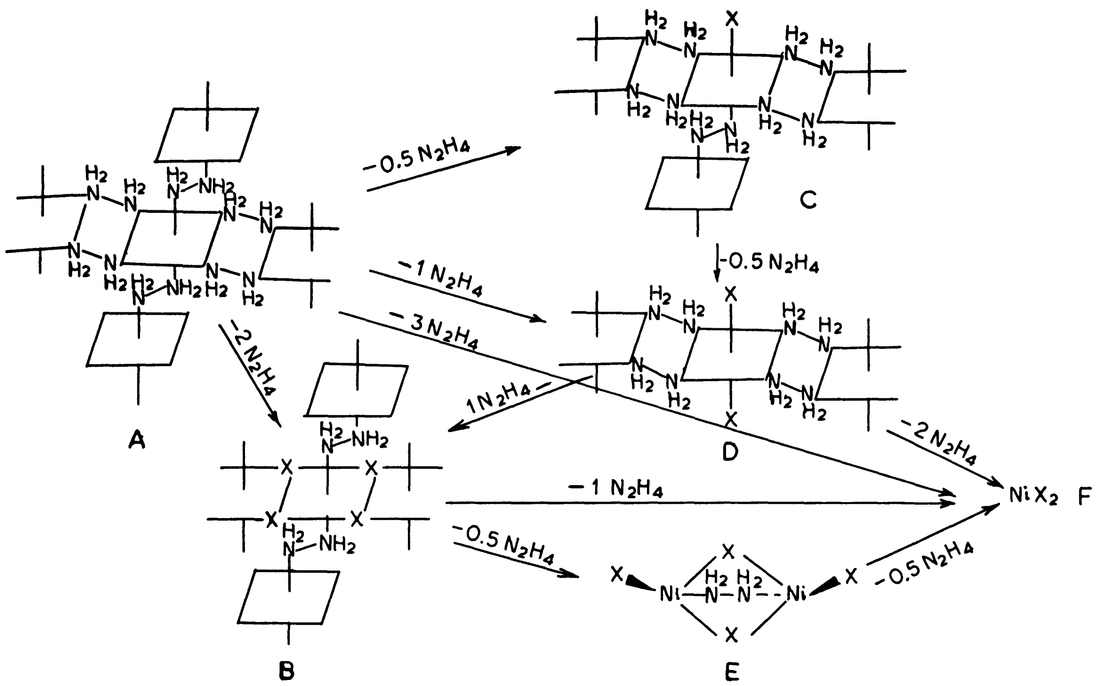
$Ni(NH_2NH_2)_3Br_2$ (**11**)	$Ni(NH_2NH_2)_3Br_2$ (**12**)	
4.33(vs)	4.66(w)	2.28(m)
4.06(s)	4.41(w)	2.21(m)
3.46(w)	4.13(w)	2.17(s)
3.13(s)	3.97(vs)	1.99(m)
3.00(s)	3.77(w)	1.98(m)
2.90(vs)	3.38(vs)	1.94(m)
2.65(vw)	3.20(w)	1.87(s)
2.36(w)	3.06(vs)	1.75(s)
2.12(w)	2.93(s)	1.68(s)
	2.84(w)	1.64(w)
	2.77(w)	1.56(s)
	2.59(vs)	1.48(w)
	2.50(s)	1.38(w)
	2.36(m)	1.35(w)

vw=very weak, w=weak, m=medium, s=strong, vs=very strong.

from **5** and **6** complex species. It is observed that unis(hydrazine) complex could not be isolated from complexes **9** and **10** but it is true that the structure of unis(hydrazine) complexes **7** and **8** remains intact on hydrazine treatment as evident from the comparison of the nature of decomposition of either complexes **5** and **9** or **6** and **10**. Color, magnetic moment, IR and electronic (mull) spectra of complexes **9** and **10** apparently show no difference between them, suggesting O_h symmetry and bridging characteristic of hydrazine as observed in complexes **5** and **6**.

Tsuchiya *et al.*[2] investigated the thermal behaviors of $[Ni(NH_2NH_2)_6]X_2$. They noticed that hexakis(hydrazine) species becomes nickel(II) chloride *via* tris, bis and unis(hydrazine) complexes. It seems that much differences existing between the decomposition pattern of the complexes being to be reported by us and of the species reported by Tsuchiya *et al.*[2] will be due to the basic differences playing in the preparative procedures. The tentative decomposition mode of complexes **5** and **6** is probably A→B→E→F (Scheme 1), whilst the complexes **9** and **10** form $NiCl_2$ through A→D→B→E→F (Scheme 1).

The unis(hydrazine)nickel(II) chloro complexes **7** and **8** are characterized. The magnetic moments appear to be higher than those of the tris complexes (Table 2). The mull spectra suggest its O_h symmetry but the shift



(X=Cl/Br)

Scheme 1.

of the bands (Table 3) towards lower energy region is probably due to the displacement of hydrazine molecules by chloride ions as evident from the fact that halide ions are in the lower position of the spectrochemical series. The color change, pink (tris) to sky blue (unis), also supports the halide substitution.[2,13] Moreover, this unis(hydrazine) complex further decomposes to nickel(II) chloride through unstable hemi(hydrazine) complex as evident from DTA and TG profiles (Fig. 3).

The Complexes Derived from $NiBr_2$ and Hydrazine Hydrate. Treatment of nickel(II) bromide with hydrazine hydrate yields $[NiL_3]Br_2$ (**11**) while with ammoniacal medium another tris species **12** is generated. Both of the species show no difference in color, magnetic moment and IR spectra. Electronic spectra in mull suggest O_h symmetry in them. IR spectra suggest bridging characteristics of hydrazine. But the thermal characteristics of these two species (Fig. 4, Table 1) are distinctly different from each other. It is interesting to note that both the tris species, **11** and **12** yield $[NiL_2Br_2]$ (**13**) while keeping in vacuum though the preparation from the species **11** requires high vacuum in comparison with that from the species **12**. On the contrary, complex **13** is not obtained (Table 1) as an intermediate product upon heating the complex **12**.

Treatment of hydrazine with bis(hydrazine) bromo complex **13** yields tris species **15**. Bis species **14** also yields another tris species **16** with hydrazine hydrate. These two tris species **15** and **16** possess the same color as those of complexes **11** and **12**. IR and electronic mull spectra of these two species imply here also the O_h symmetry as well as bridging characteristic of hydrazine like those of complexes **11** and **12**. But thermal profile of complex **16** is distinctly different from that of complex **15** (Fig. 5, Table 1). These observations indicate that bis species **13** is structurally different from the bis species **14** although the thermal behaviors of these two bis species **13** and **14** apparently show no difference amongst them. Moreover, these two bis complexes **13** and **14** are identical in color, magnetic moments, electronic (mull) and IR spectra suggesting here also O_h symmetry and bridging characteristic of hydrazine. DTA profile of thermal curves of complex **11** exhibits that the stable (D*** of Scheme 1) bis(hydrazine) bromo complex is formed *via* an intermediate $[NiL_{2.5}Br]Br$ (C of Scheme 1). This bis(hydrazine) bromo complex again passes through a nonisolable$[NiLBr_2]$ (B** of Scheme 1) which ultimately transforms straightly to nickel(II) bromide unlike complexes **5**, **6**, **9**, and **10**. On the other hand, the thermal curves of complex **12** suggest the decomposition to follow A→B→E→F in which B is not well characterized like complexes **5** and **6**. Moreover, the thermal curves of complex **16** suggest its decomposition pattern to follow A→B→F where B is not isolable in pure form. However, it is interesting to note that thermal curves distinctly suggest the structural differences existing in complexes **12** and **16** as an intermediate species (E) found in complex **12** is not observed in complex **16**.

The Complexes Derived from $Ni(SCN)_2$ and Hydrazine Hydrate. Treatment of nickel(II) thiocyanate in ethanol with hydrazine hydrate yields $[NiL_2(SCN)_2]$ (**17**). On the other hand, hydrazine hydrate treatment with ammoniacal nickel(II) thiocyanate in ethanolic

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** B form in the general scheme is well characterized for **5** and **6**. This form is also expected for **12** as Cl/Br belongs to halide group.

*** D form is well characterised by **11**. This suggests to follow the general scheme for the other complexes such as **9** and **10**.

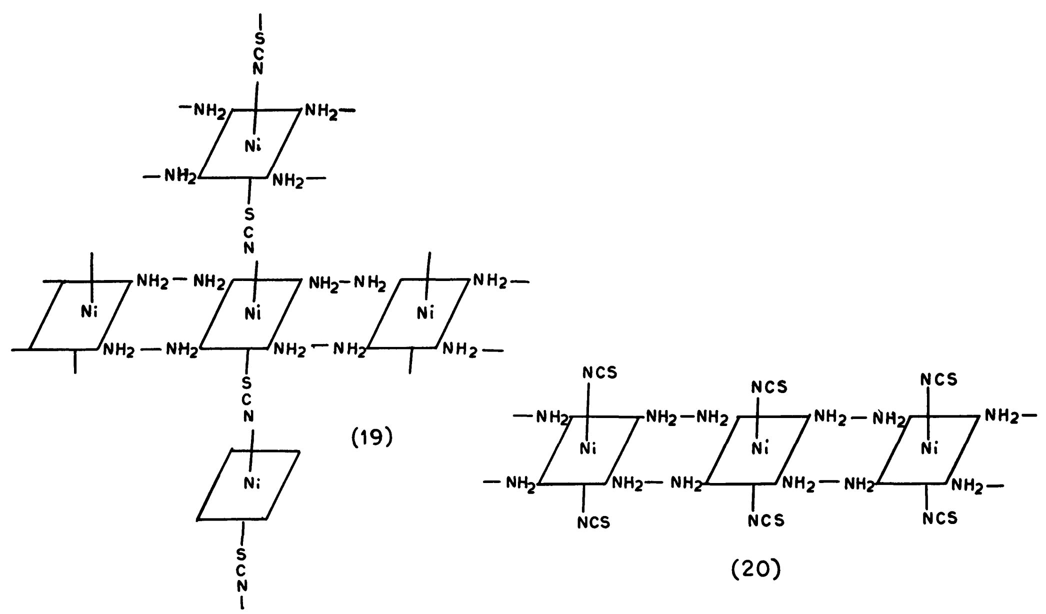

Fig. 9. Structures of $[NiL_2(SCN)_2]$ (**17**) and $[NiL_2(SCN)_2]$ (**18**).

medium yields $[NiL_2(SCN)_2]$ (**18**) which is similar in color to the species (**17**). Electronic mull spectra and magnetic data of these two thiocyanato complexes having identical chemical composition show O_h symmetry in each case. IR spectra indicate the bridging character of the hydrazine. But the thermal behaviors of these two species **17** and **18** are distinctly different from each other, indicating some structural differences. Their structural differences are evident from IR spectra of complexes **17** and **18**. The sharp band at 2085 cm^{-1} [$\nu(CN)$] corresponds to Ni–N bonding[8] which is further supported by the sharp medium band at 800 cm^{-1} $\nu(CS)$, whilst the splitting of $\nu(CN)$ at 2085 cm^{-1} in complex **17** (Fig. 7) collaborates the bridging of SCN group.[14,15] Moreover, the negative shift of $\nu(CS)$ to 785 cm^{-1} [17] (Fig. 7) for complex **17** indicates also Ni–S bonding. The structure for compound **17** should be either $Ni(N_5S)$ or $[Ni(N_4S_2)+Ni(N_6)]$ type. However, the present limited data cannot exclusively comment on the exact chromophores of the system. Thermal data support the higher stability of compound **18** than the compound **17** as compound **18** possesses more symmetric system *i.e.*, NiN_6 chromophores whilst complex **17** possesses less symmetric system as shown in Fig. 9. Nature of the DTA curve of compound **17** suggests that the hydrazine molecules evolve successively through an unstable hydrazine complex as intermediate. On the other hand, the DTA profile for thiocyanate decomposition displays two exotherms suggesting a complicated pattern shown below:

$$\left.\begin{array}{l} Ni(SCN)_2 \longrightarrow Ni^{2+} + 2(SCN)^- \\ 2(SCN)^- \longrightarrow S^{2-} + 1/2(CN)_2 + 1/2(SCN)_2 \end{array}\right\}$$

responsible for 1st DTA peak

$$\left.\begin{array}{l} Ni^{2+} + S^{2-} \longrightarrow NiS \\ 1/2(SCN)_2 \longrightarrow S + 1/2(CN)_2 \end{array}\right\}$$

responsible for 2nd DTA peak

On continuation of heating it is evident that sulfur is evolved first as SO_2 followed by the decomposition of NiS which ultimately transforms to NiO.

Conclusion

In the foregoing discussion, it was observed that the presence of ammonia during the preparation of complexes **2**, **4**, **6**, **12**, and **18** probably plays an important role to form the apparently identical but structurally different complexes as explored by thermal techniques. The structural differences existing in the apparently identical compounds do not involve the change of microsymmetry (O_h) as evident from their absorption spectra taken in mull. However, this is not true for the apparently identical compounds **11** and **12** in which the spectra (Fig. 10) appearing at 540 nm as a maximum in complex **12** is split to 560 and 600 nm in complex **11**.

The X-ray diffraction patterns (Table 4) of complexes **11** and **12** are absolutely different from each other which would indicate the difference in crystal symmetry implying the bond distances being different from each

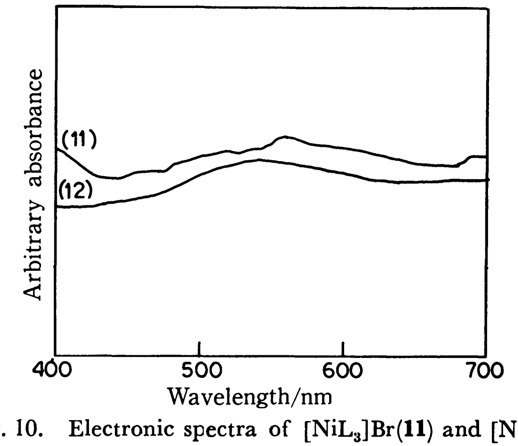

Fig. 10. Electronic spectra of $[NiL_3]Br$(**11**) and $[NiL_3]Br_2$(**12**) in mull.

other. Such concept about the structures of complexes **11** and **12** also supports the differences exhibited (high vacuum for **11** and low vacuum for **12**) in vacuum treatment. In the case of chloride, the vacuum treatment does not alter the tris variety. Since the Br^- is more labile than Cl^- in the complexes, however, the different varieties of Br^- complexes are obtained by the change of the physical and chemical environments. On the other hand, nickel fluoro complexes of hydrazine take up water molecule as F^- and H_2O possess almost similar coordinating ability.[19] Among the tested halide ions (F^-, Cl^-, Br^-)Cl^- is the most preferable one for bridging between two metal ions provided the condition for the bridging should be filled in. Br^- behaves as both bridging and unidentate ligand since the coordinating as well as briding capacity of Br^- and hydrazine may be the same. Therefore, the degree of variation in the case of bromo complexes is more than that of chloro complexes.

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