Chapter 7

Thermal Studies of NiX₄²⁻ Species with Cations of Aromatic Bases in the Solid State; Tetrahedral ↔ Octahedral Structural Transformations
7.1. Introduction

One of the prominent features of Ni(II) complexes is the transformation between the different molecular geometries; the most common one is octahedral = square planar transition.\textsuperscript{1-4} Tetrahedral geometry is less abundant in Ni(II) chemistry owing to the relatively higher CFSEs in other geometries. Thus any transformation involving tetrahedral Ni (II) species is rare.\textsuperscript{5} Isolation of tetrahedral Ni(II) species in the solid state becomes possible usually with large cations, for example NR\textsubscript{4}\textsuperscript{+}, PR\textsubscript{4}\textsuperscript{+} etc.\textsuperscript{6,7} and the bulky halide ions with less CFSE. The tetrahedral NiCl\textsubscript{4}\textsuperscript{2-} anion is also known to exist with pyridinium cation in the solution of NiCl\textsubscript{2} in the molten pyridinium chloride but the pure compound was not isolated in the solid state.\textsuperscript{8} In this chapter the isolation of NiX\textsubscript{4}\textsuperscript{2-} species with the nitrogen containing heterocyclic cations (pyridinium, 2-aminopyridinium, and imidazolium) and solid state (anhydrous) tetrahedral = aquated octahedral transition of Ni(II) effected by aquation-deaquisition have been discussed.

7.2. Result and discussion

7.2. a. Structural transformations

Chloride salts

The chloro complexes, \( (HL)_2[\text{NiCl}_4] \cdot \text{H}_2\text{O} \) (where \( L = \text{Pyridine, 2-aminopyridine, and Imidazole} \) obtained from the solution are all yellow in color. The electronic spectra is typical of an octahedral polymeric, halogen bridged Ni(II) complex.\textsuperscript{7} The magnetic moments (\( \mu = 3.30 \text{ to } 3.42 \text{ BM} \) also supports the proposed octahedral structure.

These yellow complexes, on keeping in a desiccator for long time turn to their corresponding anhydrous green forms, \( (HL)_2[\text{NiCl}_4] \) which can also be obtained by
heating the yellow complexes (Section, 7.2.b). Elemental analyses confirm the composition. The electronic spectra of (HPy)$_2$[NiCl$_4$] are shown in Fig. 7.1. The appearance of the relatively strong doublet with absorption maximum at 662 and 704 nm, suggests the presence of tetrahedral NiCl$_4^{2-}$ ion$^{6,7,9,10}$. The electronic spectra of the other two anhydrous green species, (H2-ampy)$_2$[NiCl$_4$] and (HImd)$_2$[NiCl$_4$] also show very similar doublets at 658, 709 nm, and 665, 700 nm respectively. The higher magnetic moment values of all the three green complexes ($\mu=3.70$ to 3.80 BM) corroborate the tetrahedral geometry of Ni(II) in the anhydrous species. All the green complexes are hygroscopic. On exposure in humid atmosphere, they transform into their respective hydrated yellow forms. These transformations can clearly be observed during the recording of electronic spectra of the green complexes in nujol mull in an open atmosphere (relative humidity ca 60%), as the intensities of the characteristic doublets of tetrahedral NiCl$_4^{2-}$ decrease with time and in ca 20 min they vanish completely to leave the spectra identical to those of the yellow complexes. The change in the electronic spectra of (Hpy)$_2$[NiCl$_4$] in nujol mull are shown in Fig. 7.1.

**Bromide salts**

The bromide salts of Ni(II) with pyridinium, 2-aminopyridinium, and imidazolium cations have also been isolated in the solid state. They are orange-yellow in color and have the composition (HL)$_2$[NiBr$_4$]-H$_2$O. The electronic spectra of all these three compounds are more or less similar in nature and are in fine agreement with those of halogen bridged octahedral Ni (II) complexes. The magnetic moment values ($\mu = 3.25$ BM to 3.35 BM) also support the proposed composition of the compounds. Like the chloro complexes, these bromo complexes also convert to their respective anhydrous
Fig. 7.1: The electronic spectra of green (HPy)$_2$[NiCl$_4$] in nujol mull; upper trace immediately recorded; middle trace and lower trace, recorded after keeping the sample in nujol mull for 5 minutes and 20 minutes respectively in open atmosphere (relative humidity ca 60%).
green forms when they are kept in desiccator for several days. The electronic spectra and magnetic moments suggest the tetrahedral geometry around Ni(II) in the green complexes. The characteristic doublets for green tetrahedral NiBr$_4^{2-}$ appear at ca 670 and 720 nm for all the three complexes.

Thus it can be concluded that the tetrahedral NiX$_4^{2-}$ anions (X = Cl and Br) are stabilized with pyridinium, 2-aminopyridinium, and imidazolium cations in dry atmosphere in the solid state. In open atmosphere, they absorb one molecule of water and the geometry changes to a halogen bridged octahedral one.

7.2. b. Thermal analyses

Results of thermal analyses for all the complexes along with the calculated and observed weight losses for the respective thermally induced reactions were presented in Table 7.1.

**Compound 1.**

The simultaneous TG-DTA curves (Fig.2) for the complex 1 show that upon heating, first it undergoes dehydration at ca. 85°C producing complex 1a and then loses two molecules of HCl to produce NiPy$_2$Cl$_2$ at ca. 135°C, color of which is yellow. The electronic spectra and magnetic moment of NiPy$_2$Cl$_2$ are typical of octahedral Ni(II)$^{15}$. On further heating, it decomposes to NiCl$_2$ at ca 500°C via an isolable intermediate NiPyCl$_2$ at ca. 210°C. Electronic spectra and magnetic moment suggest that NiPyCl$_2$ also possess octahedral geometry.$^{11}$

**Compound 2.**

(HPy)$_2$[NiBr$_4$]$\cdot$H$_2$O loses the water molecule at 100°C. Then it loses two HBr molecules at 200°C to produce a compound of composition NiPy$_2$Br$_2$ and finally
Fig. 7.2: TG – DTA curve for (HPy)$_2$[NiCl$_4$] · H$_2$O
decomposes to NiBr₂ at 580°C without any thermally stable intermediate. The electronic 
spectra and magnetic moment of are typical of distorted octahedral Ni(II) as reported 
earlier for this compound.¹¹

**Compound 3.**

(H-2ampy)₂[NiCl₄]·H₂O upon heating first undergoes dehydration at ca.100°C to 
produce its anhydrous green form and then undergoes dehydrohalogenation to yield a 
yellow compound of composition Ni(2-ampy)₂Cl₂ at 130°C. The electronic spectra and 
magnetic moment value of the compound are in very close resemblance with the typical 
octahedral Ni(II). On further heating, it decomposes to NiCl₂ at 400°C by losing the two 
2-aminopyridine molecules in multiple overlapping steps.

**Compound 4.**

(H-2ampy)₂[NiBr₄]·H₂O becomes dehydrated at 80°C. The anhydrous green form 
on heating decomposes to NiBr₂ in multiple steps. Unlike the other complexes isolation 
of Ni(2-ampy)₂ was not possible as no plateau was found in the TG curve during 
decomposition.

**Compound 5.**

(HImd)₂[NiCl₄]·H₂O becomes dehydrated at 120°C to yield its tetrahedral 
anhydrous form. Like the Py and 2-ampy analogous it also produce the yellow octahedral 
compound Ni(Imd)₂Cl₂, as is evident from the elemental analysis, electronic spectra and 
magnetic moment. On further heating the compound decomposes to NiCl₂ at 590°C.

**Compound 6.**

(HImd)₂[NiBr₄]·H₂O undergoes dehydration at 110°C to produce tetrahedral 
(HImd)₂[NiBr₄], which upon further heating loses two HBr molecules to produce
Ni(Imd)\textsubscript{2}Br\textsubscript{2}, the composition of which is confirmed by elemental analyses. The compound also possesses distorted octahedral geometry. It finally decomposes to NiBr\textsubscript{2} at 560°C.

The common feature of thermal analyses of these compounds is that the compounds of composition NiL\textsubscript{2}X\textsubscript{2} can be isolated in the solid state by heating the respective tetrahalo Ni(II) salt in all cases excepting (H2-ampy)\textsubscript{2}[NiBr\textsubscript{4}]. It is interesting to note that in all the cases the aromatic cations after losing its proton as HX (X = Cl and Br) entered into the coordination sphere of the central metal ion, Ni(II). Thus it can be concluded that thermogravimetric analysis can be used for synthesizing NiL\textsubscript{2}X\textsubscript{2} type of complexes from their respective tetrahalo salts (table 7.1).

7.3. Experimental

7.3. a. Materials and measurements

High purity (98%) pyridine, 2-aminopyridine, imidazole, nickel(II) chloride, hexahydrate, and nickel(II) bromide, hexahydrate were purchased from Lancaster England and used as received. Elemental analyses (carbon, hydrogen and nitrogen) were performed using a Perkin-Elmer 240C elemental analyzer and the nickel contents in all the complexes were estimated gravimetrically.\textsuperscript{12} IR spectra in KBr (4500-500 cm\textsuperscript{-1}) were recorded using a Perkin-Elmer RXI FT-IR spectrophotometer. Electronic spectra of mulls (1200-350nm) were recorded with a Hitachi U-3501 spectrophotometer where nujol was used as a medium as well as a reference. The effective magnetic moments were calculated from magnetic susceptibility measurements with an EG \& G PAR vibrating sample magnetometer model 155 at room temperature and diamagnetic corrections were made using Pascal's constants.\textsuperscript{13} The thermal analyses (TG-DTA) were carried out on a
Metler Toledo TGA/SDTA 851 thermal analyzer in a dynamic atmosphere of dinitrogen (flow rate: 30 cm³ min⁻¹). The sample was heated in an alumina crucible at a rate of 5°C min⁻¹.

7.3. b. Preparations

(HPy)₂NiCl₄·H₂O (yellow), 1.

5 mmols. NiCl₂·6H₂O was taken in a beaker and it was dissolved in minimum volume of water. To this 10 mmols. of pyridine along with 4 ml. of concentrated HCl were added. The resulting solution was concentrated and then cooled in a desiccator. The yellow compounds obtained were then filtered. (Found: C, 31.5; H, 3.9; N, 7.3; Ni, 15.6; Cl, 37.2; requires C, 31.7; H, 3.7; N, 7.4; Ni, 15.5; Cl, 37.5%), μeff=3.76 BM, λmax 468, 798, 882 nm.

(HPy)₂[NiCl₄] (green), 1a:

The complex was isolated thermally by heating the complex 1 at 85°C for ca 15 minutes. (Found: C, 33.2; H, 3.3; N, 7.8; Ni, 16.2; Cl, 39.4; requires C, 33.3; H, 3.3; N, 7.8; Ni, 16.3; Cl, 39.4%), μeff=3.70 BM, λmax 662 and 704 nm.

NiPy₂Cl₂, 1b, and NiPyCl₂, 1c.

The complexes were isolated thermally by heating the complex 1a at ca. 135°C for 20 minutes and at 210°C for 30 minutes respectively. For compound 1b, found: C, 41.5; H, 3.7; N, 9.5; Ni, 20.6; Cl, 24.5; requires C, 41.7; H, 3.5; N, 9.7; Ni, 20.4; Cl, 24.7% and μeff=3.38 BM, λmax 462 and 800 nm and for 1c, found: C, 28.5; H, 3.2; N, 6.8; Ni, 28.3; Cl, 34.1; requires C, 28.7; H, 2.4; N, 6.7; Ni, 28.1; Cl, 34.0% and μeff=3.41 BM, λmax 460 and 805 nm.
5 mmol of NiBr2·6H2O was dissolved in minimum volume of water. To this solution was mixed pyridine (10 mmol) dissolved in 5 ml. of 10(M) HBr. The resulting solution was concentrated in a water bath to ca 3ml and kept in a desiccator. After a few days orange compounds were obtained. (Found: C, 21.4; H, 2.7; N, 5.1; Ni, 10.6; Br, 57.2; requires C, 21.6; H, 2.5; N, 5.0; Ni, 10.5; Br, 57.5%), μ\text{eff} = 3.35 BM, λ\text{max} 478, 668, and 853 nm.

(HPy)\textsubscript{2}NiBr\textsubscript{4} (green), 2a.

The complex was isolated thermally by heating the complex 2 at 100°C for ca 30 minutes. (Found: C, 22.2; H, 3.0; N, 5.8; Ni, 10.2; Br, 59.0; requires C, 22.3; H, 2.2; N, 5.2; Ni, 10.9; Br, 59.4%), μ\text{eff} = 3.75 BM, λ\text{max} 662 and 704 nm.

NiPy\textsubscript{2}Br\textsubscript{2}, 2b.

The complex was isolated thermally by heating the complex 2 at ca. 200°C for 20 minutes. For compound 2b, found: C, 31.5; H, 3.0; N, 7.5; Ni, 16.0; Br, 42.0; requires C, 31.9; H, 2.7; N, 7.4; Ni, 15.6; Br, 42.5% and μ\text{eff} = 3.39 BM, λ\text{max} 475 and 810 nm.

(H-2ampy)\textsubscript{2}[NiCl\textsubscript{4}]-H\textsubscript{2}O (yellow), 3.

5 mmol of NiCl\textsubscript{2}-6H\textsubscript{2}O was dissolved in minimum volume of water. To this solution was mixed 2-aminopyridine (10 mmol) dissolved in 5 ml. of 10(M) HCl. The resulting solution was concentrated in a water bath to ca 3ml and kept in a desiccator. After a few days yellow compounds obtained were filtered. (Found: C, 29.5; H, 3.7; N, 13.6; Ni, 14.6; Cl, 34.2; requires C, 29.4; H, 3.9; N, 13.7; Ni, 14.4; Cl, 34.7%), μ\text{eff} = 3.40 BM, λ\text{max} 475, 805, and 890 nm.
The complex was isolated thermally by heating the complex 3 at 100°C for ca 15 minutes. (Found: C, 30.2; H, 4.3; N, 14.8; Ni, 15.2; Cl, 36.9; requires C, 30.1; H, 3.6; N, 14.3; Ni, 15.0; Cl, 36.3%), \( \mu_{\text{eff}} = 3.77 \) BM, \( \lambda_{\text{max}} \) 670 and 714 nm.

**Ni(2-ampy)\(_2\)Cl\(_2\), 3b.**

The complex was isolated thermally by heating the complex 3 at ca. 130°C for 30 minutes. For compound 3b, found: C, 41.5; H, 3.7; N, 9.5; Ni, 20.6; Cl, 24.5; requires C, 37.8; H, 3.8; N, 17.6; Ni, 18.5; Cl, 22.3% and \( \mu_{\text{eff}} = 3.34 \) BM, \( \lambda_{\text{max}} \) 450 and 780 nm.

**Ni(2-ampy)\(_2\)Br\(_4\)-H\(_2\)O (orange), 4.**

5 mmol of NiBr\(_2\)-6H\(_2\)O was dissolved in minimum volume of water. To this solution was mixed 2-aminopyridine (10 mmol) dissolved in 5 ml. of 10(M) HBr. The resulting solution was concentrated in a water bath to ca 3ml and kept in a desiccator. After a few days orange compounds were obtained. (Found: C, 20.2; H, 2.9; N, 9.3; Ni, 10.6; Br, 54.2; requires C, 20.5; H, 2.7; N, 9.5; Ni, 10.0; Br, 54.5%), \( \mu_{\text{eff}} = 3.27 \) BM, \( \lambda_{\text{max}} \) 480, and 895 nm.

**Ni(2-ampy)\(_2\)[NiBr\(_4\)] (green), 4a.**

The complex was isolated thermally by heating the complex 4 at 70°C for ca 30 minutes. (Found: C, 21.5; H, 3.0; N, 10.4; Ni, 10.9; Br, 56.0; requires C, 21.1; H, 2.5; N, 9.8; Ni, 10.3; Br, 56.3%), \( \mu_{\text{eff}} = 3.79 \) BM, \( \lambda_{\text{max}} \) 462 and 794 nm.

**Imd\(_2\)NiCl\(_4\)-H\(_2\)O (yellow), 5.**

5 mmol of NiCl\(_2\)-6H\(_2\)O was dissolved in minimum volume of water. To this solution was mixed imidazole (10 mmol) dissolved in 5 ml. of 10(M) HCl. The resulting solution was concentrated in a water bath to ca 3ml and kept in a desiccator. After a few
days orange compounds were obtained. (Found: C, 27.5; H, 3.0; N, 7.8; Ni, 16.3; Cl, 40.0; requires C, 27.2; H, 3.4; N, 7.9; Ni, 16.6; Cl, 40.3%), μ_eff = 3.32 BM, λ_max 500, 800, and 860 nm.

(HImd)_2[NiCl_4] (green), 5a.

The complex was isolated thermally by heating the complex 5 at 110°C for ca 15 minutes. (Found: C, 30.2; H, 4.3; N, 14.8; Ni, 15.2; Cl, 36.9; requires C, 28.7; H, 3.0; N, 8.4; Ni, 17.5; Cl, 42.4%), μ_eff = 3.79 BM, λ_max 656 and 710 nm.

Ni(Imd)_2Cl_2, 5b.

The complex was isolated thermally by heating the complex 5 at ca 200°C for 30 minutes. For compound 5b, found: C, 36.5; H, 3.7; N, 10.5; Ni, 22.6; Cl, 27.5; requires C, 36.7; H, 3.1; N, 10.7; Ni, 22.4; Cl, 27.1% and μ_eff = 3.34 BM, λ_max 455 and 790 nm.

(HImd)_2[NiBr_4]·H_2O (yellow), 6.

5 mmol of NiBr_2·6H_2O was dissolved in minimum volume of water. To this solution was mixed imidazole (10 mmol) dissolved in 5 ml. of 10(M) HBr. The resulting solution was concentrated in a water bath to ca 3ml and kept in a desiccator. After a few days orange compounds were obtained. (Found: C, 18.5; H, 2.9; N, 5.0; Ni, 11.6; Br, 60.0; requires C, 18.1; H, 2.3; N, 5.3; Ni, 11.1; Br, 60.3%), μ_eff = 3.39 BM, λ_max 513, 820, and 882 nm.

(HImd)_2[NiBr_4] (green), 6a.

The complex was isolated thermally by heating the complex 6 at 100°C for ca 15 minutes. (Found: C, 18.2; H, 3.0; N, 5.8; Ni, 11.2; Br, 62.9; requires C, 18.7; H, 2.0; N, 5.5; Ni, 11.4; Br, 62.4%), μ_eff = 3.83 BM, λ_max 665 and 725 nm.
Ni(Imd)_{2}Br_{2}, \textit{6b}.

The complex was isolated thermally by heating the complex 3 at ca. 230°C for 30 minutes. For compound \textit{6b}, found: C, 27.0; H, 3.0; N, 8.5; Ni, 16.6; Br, 45.9; requires C, 27.4; H, 2.3; N, 8.0; Ni, 16.7; Br, 45.6% and μ\textit{eff}=3.48 BM, λ\textit{max} 473 and 815 nm.
Table 7.1.
Results of thermal analysis of compounds 1, 2, 3, 4, 5, and 6

<table>
<thead>
<tr>
<th>Thermal Reactions</th>
<th>Temperature Range (°C)</th>
<th>Weight Loss (%)</th>
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<tr>
<td></td>
<td>Obs.</td>
<td>Calc.</td>
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<tr>
<td>(HPy)$_2$[NiCl$_4$]·H$_2$O $\rightarrow$ (HPy)$_2$[NiCl$_4$]</td>
<td>60 - 88</td>
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<td>130 - 140</td>
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<td>21.30</td>
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<tr>
<td></td>
<td>60 - 170</td>
<td>3.40</td>
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<td>29.50</td>
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<tr>
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<td>340 - 590</td>
<td>29.00</td>
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<td>26.80</td>
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<td>(H-2ampy)$_2$[NiCl$_4$] $\rightarrow$ Ni(2ampy)$_2$Cl$_2$</td>
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<td>45 - 85</td>
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<td></td>
<td>95 - 570</td>
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<td>(H-2ampy)$_2$[NiBr$_4$]·H$_2$O $\rightarrow$ (H-2ampy)$_2$[NiBr$_4$]</td>
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