



Solid State Synthesis, Characterisation and Biological Activity of 4,4'-Bipyridinium Tetrachloronickelate (II) and 4,4'-Bipyridine Dichloronickel (II) Complexes

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ABSTRACT

Complexes of nickel (II) were synthesized by grinding nickel (II) chloride with protonated 4,4'-bipyridiniumchloride. The complexes were characterized by elemental analysis and infrared spectral studies, decomposition temperature determination, conductivity measurement and solubility test. The complexes were found to be very stable and non-electrolyte. Antimicrobial activity of these complexes observed on some bacteria and fungi showed good inhibition zone at highest concentration. The values obtained for molar and electric conductance measurement of the complex are 35.8 and 35.8×10^{-6} respectively, this indicates that the synthesized complexes are non-electrolytes.

Keywords: Hydrogen bond network, Mechanochemistry, Coordination polymers

INTRODUCTION

Solid-state reactivity of molecular crystals has an old history but it was initially restricted to photochemical reactions and acid–base reactions (Kaupp, 1996). Adams *et al.*, (2005) reported the use of a different molecular tecton as a substitute for the square planar $[\text{PtCl}_4]^{2-}$ anion, forming new but analogous synthons and generating a more diverse range of crystal structures. $[\text{Ni}(\text{dtox})_2]^{2-}$ was shown to hydrogen bond effectively (through the use of N-H····O hydrogen bonds) to a variety of pyridinium cations, yielding structures with motifs of planned dimensionality and form (Braga *et al.*, 2003). The planar $[\text{PtCl}_4]^{2-}$ anion has proved to be a particularly useful tecton when coupled with organic dications. Whether based on molecular, supramolecular, aromatic or saturated pyridinium, piperidinium or piperazinium species, and in a similar fashion the dithiooxalate dianion was identified as a ligand offering the suitable combination of good hydrogen bond acceptor ability (through the carbonyl groups), high negative charge, kinetic inertness and the absence of any hydrogen bond donor functionalities. The oxygen atoms of the dithiooxalate ligand bind in chelating fashion to the N-H donor of the pyridinium ions. N-H····O hydrogen bonded ribbon in crystalline $[4,4'\text{-H}_2\text{bipy}][\text{Ni}(\text{S}_2\text{C}_2\text{O}_2)_2]$. In a similar development, Crawford *et al.*, (2004) reported the use of molecular tectons which form cyano-based hydrogen bonded synthons (NH····NC) to synthesize a diverse range of crystal structures. The formation of crystal structures of $[\text{PtCl}_4]^{2-}$ salts of isomeric bipyridinium dications and the mimicry of its ability to bind pyridinium derivatives and

analogues in the salts of 4,4'- bipyridinium ($[4,4'\text{-H}_2\text{bipy}]^{2+}$) and 4,4'-piperidinium ($[4,4'\text{-H}_2\text{bipip}]^{2+}$) through chelating interactions by the square planar $[\text{Ni}(\text{dtox})_2]^{2-}$ led to the preparation of the salts of the $[\text{Pt}(\text{CN})_4]^{2-}$ pseudo-halide analogue with the intention of identifying the consequences of replacing the Cl ligands with CN giving rise to M-CN····HN synthons.

Adams *et al.*, (2007) have established routes to both discrete and network (polymeric) complexes of first row divalent transition metals with pyridine derivatives, which have been prepared by thermal dehydrochlorination of the perchlorometallate salts of the appropriate pyridinium species. The reverse process uses solid – gas reaction (Adams *et al.*, 2007; Takacs, 1996; Burgard *et al.*, 2008 and Gillon *et al.*, 1999). The synthesis of the hydrogen bonded ribbon polymer $[4,4'\text{-H}_2\text{bipy}][\text{MCl}_4]$ (M = Pd or Pt) as a metal-containing synthon for crystal engineering (Markvarsen *et al.*, 2001), while Orpen and Gillon (2005), reported the cation-controlled formation of $[\{\text{MCl}_4\}_n]^{2-}$ chains in $[4,4'\text{-H}_2\text{bipy}][\text{MCl}_4]$ (M = Mn, Cd) (Masciocchi *et al.*, 2005), the exploitation of $\text{MX}\cdots\text{HN}^+$ hydrogen bond synthons in the preparation of crystalline salts, and the structures of the halometallate species of $[4,4'\text{-H}_2\text{bipy}][\text{MX}_4]$ [X = Cl, M = Pd, Pt, Co, Zn, Hg and Cd; X = Br, M = Pd, Zn and Co] (Shirley, 2003). In addition, the exploration of the relationships between the structures formed by $[4,4'\text{-H}_2\text{bipy}][\text{MCl}_4]$ complex salts containing similar molecular components and having closely related hydrogen bond-based synthon networks, and have shown that

chlorometallate anions and other metal chloride complexes are good hydrogen bond acceptors. This has enabled the preparation of three classes of tetrachlorometallate $[MCl_4]^{2-}$ anions; square planar when $M = Pt, Pd$; polymerized and zig-zag edge sharing octahedral chains when $M = Pb, Mn$ or Cd ; and tetrahedral when $M = Co, Zn$ or Hg in the solid state (Shirley, 2002).

Recently a number of researchers have shown that a range of coordination compounds can be prepared without recourse to solution methods (James *et al.*, 2012).

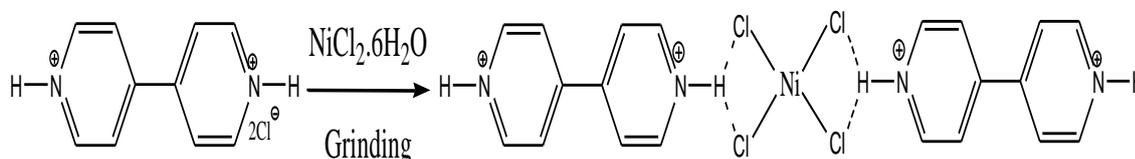
This paper is concerned with the design and synthesis of crystalline solids which are planned to offer chemical reactivity towards dehydrochlorination to yield coordination compounds with novel properties. It is aimed at the exploitation of state of the art techniques in crystal engineering to prepare anionic metal complexes which are hydrogen bonded to 4,4'-bipyridinium cations decorated with NH hydrogen bond donor groups and their subsequent reactions with bases to produce the coordination compounds.

MATERIALS AND METHODS

All the reagents used were of analar grade and were used without further purification; all the glass wares were washed and dried before the start of any experiment. All the complexes were synthesized by grinding with pestle and motor. Characterized using FTIR-8400S Fourier Transform Infrared Spectrophotometer. The elemental analysis of the complexes was carried out using Flash 2000 organic elemental analyzer, at ABU, Zaria, molar conductance was studied using Jenway conductivity meter model 4000 and decomposition temperature were obtained using a Gallenkemp melting apparatus.

Preparation of the Ligand:

5g of 4,4'-bipy was put in a 50ml beaker, the beaker and the content were immersed into a large (1000ml) beaker containing 100ml concentrated hydrochloric acid. The 1000ml beaker was covered so as to allow the escaping HCl gas to enter the 50ml beaker directly. This was allowed to stand for 6hrs to yield $[(4,4'-H_2bipy)]Cl_2$.



Equation 1: Formation of $[\{NiCl_4(4,4'-bipy)\}_n]$

Synthesis of $[\{NiCl_4(4,4'-H_2bipy)\}_n]$

0.229g (1mmole) of $[4,4'-H_2bipy]Cl_2$ and 0.238g (1mmole) of $NiCl_2 \cdot 6H_2O$ were ground in an agate mortar for minutes, after which a light greenish yellow powder was obtained. The complex was then dried in vacuum.

Synthesis of $[\{NiCl_2(4,4'-bipy)\}_n]$

0.4g (1mmole) of $[\{NiCl_4(4,4'-H_2bipy)\}_n]$ was ground with 0.14g (1mmole) of K_2CO_3 for 3 minutes. The light green product obtained was dried in vacuum.

RESULTS AND DISCUSSION:

The infrared Spectrum of the protonated ligand showed a peak at $3429cm^{-1}$ and $3027cm^{-1}$ which are assigned to N-H and H-Cl bonds respectively, these peaks revealed that the original 4,4'-bipyridine was protonated.

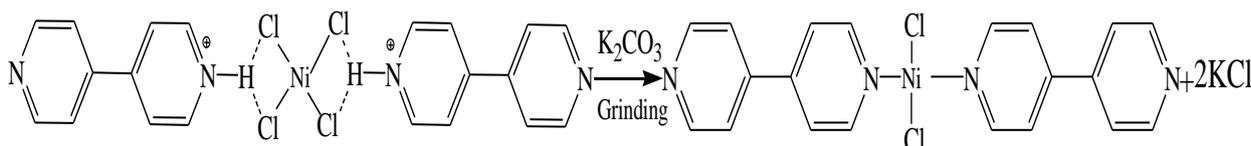
4,4'-bipyridinium tetrachloronickelate (II) $[NiCl_4][(4,4'-H_2bipy)]$

Hydrogen bonded complex $[NiCl_4][(4,4'-H_2bipy)]$ was synthesized by kneading 4,4'-bipyridinium chloride and nickel (II) chloride hexahydrate using pestle and mortar. The infrared spectrum shows N-H, H-Cl and Ni-Cl bonds at $3403cm^{-1}$, $3030cm^{-1}$ and $488cm^{-1}$ respectively, this indicates the formation of the desired complex which contained $[NiCl_4]^{2-}$ anion which chelates via hydrogen bond to the organic cation $[4,4'-H_2bipy]^{2+}$ as shown in equation 1. This assertion was further confirmed by the elemental analysis whose results are very much in agreement between the calculated and experimental values, the elemental analytical data found is 7.03%, 32.99% and 2.63% with respect of nitrogen, carbon and hydrogen while the calculated elemental percentage is 7.18%, 33.47% and 2.81% (Table 2). The value for molar conductivity measurement was found to be $30.0 \Omega^{-1}cm^2 mole^{-1}$ and the electrical conductivity was $30.0 \times 10^{-6} \Omega^{-1}cm^{-1}$ (Table 3), the low value revealed that there is no free ion out of the coordination sphere and the complex is non-electrolyte (Sekhon, *et al.*, 2010). The decomposition temperature is $268^\circ C$, compared with melting temperature of nickel (II) chloride ($\geq 140^\circ C$) and that of protonated 4,4'-bipyridinium chloride ($\geq 112^\circ C$), the absolute raised of the decomposition temperature of the complex is due to the hydrogen bond present and this indicates the stability of the complex.

The solubility test (Table 4) have showed that, the complex is soluble in water, hydrogen peroxide and concentrated hydrochloric acid and slightly soluble in ethanol and acetic acid, this is because covalent complexes are expected to be soluble in covalent solvents (like dissolves like). For the anti-bacterial test, the complex revealed wide inhibition zones at highest concentration on all the bacteria and has no effect on all the fungi. A mixture of green coloured metal salt and white coloured ligand resulted in a light greenish yellow powder after grinding for 1 minute. The infrared spectrum and the elemental analytical data found are shown in appendices 1 and 3 respectively.

4,4'-bipyridine dichloronickel (II) $[\{\text{NiCl}_2(4,4'\text{-bipy})\}_n]$

The complex was synthesized by reacting $[\{\text{NiCl}_4(4,4'\text{-bipy})\}_n]$ with potassium carbonate in 1:1 ratio, a mixture of light greenish yellow and white powder yielded a light green powder. The infrared spectrum of the complex showed peaks assign to Ni-Cl and Ni-N bonds at 491cm^{-1} and 577cm^{-1} . The elemental analytical data found is 6.01%, 27.03% and 1.63% with respect of nitrogen, carbon and hydrogen while the calculated elemental percentage is 6.44%, 27.62% and 1.85% for nitrogen, carbon and hydrogen respectively (Table 2), these analytical data results show the formation of the desired complex equation 2.



Equation 2: Formation of $[\{\text{NiCl}_2(4,4'\text{-bipy})\}_n]$

The molar conductivity measurement (Table 3) was found to be $35.8 \Omega^{-1}\text{cm}^2 \text{mole}^{-1}$ and the electrical conductivity was $35.8 \times 10^{-6} \Omega^{-1}\text{cm}^{-1}$, this showed that the complex is non-electrolyte. The decomposition temperature (Table 3) of the complex is 209°C , comparing with melting temperature of nickel (II) chloride ($\geq 140^\circ\text{C}$) and that of protonated 4,4'-bipyridiniumchloride ($\geq 112^\circ\text{C}$). The solubility test (Table 4) have showed that is soluble in water, hydrogen peroxide and concentrated hydrochloric a

cid and slightly soluble in ethanol and acetic acid, this is because covalent complexes are expected to be soluble in covalent solvents (like dissolves like).

The anti-bacterial test (Table 5) showed no effect on all the bacteria with the exception of *Klebsiella Specie* which shows effect at highest concentration, on the other hand, *Aspergillus Specie* shown effect at highest concentration, while the remaining fungi revealed no activity (Table 6).

Table 1: IR Spectral Analysis of the Metal (II) Complexes

FITR Value/ Samples	$\nu(\text{M-Cl})$	$\nu(\text{M-N})$	$\nu(\text{N-H})$	$\nu(\text{H-Cl})$	$\nu(\text{C-H})$	$\nu(\text{C=N})$	$\nu(\text{C-C})$
	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}	cm^{-1}
$[\{\text{NiCl}_4(4,4'\text{-H}_2\text{bipy})\}_n]$	488		3403	3030	1406	1406	1220
$[\{\text{NiCl}_2(4,4'\text{-bipy})\}_n]$	491	577			1397	1488	1220

Keys: ν = Wave number; M = Metal

Table 2: Elemental Analysis of the Metal (II) Complexes

Complexes	Elements	Percentage (%)		
		Nitrogen	Carbon	Hydrogen
$[\{\text{NiCl}_4(4,4'\text{-H}_2\text{bipy})\}_n]$	Calculated	7.18	33.47	2.81
	Found	7.03	32.99	2.63
$[\{\text{NiCl}_2(4,4'\text{-bipy})\}_n]$	Calculated	6.44	27.62	1.85
	Found	6.01	27.03	1.63

Table 3: Decomposition Temperature, Molar and the Electrical conductivity

Complexes	Decomposition Temp. (°C)	Electrical conductivity ($\Omega^{-1}\text{cm}^{-1}$)	Molar Conductivity ($\Omega^{-1}\text{cm}^2\text{mole}^{-1}$)
[{NiCl ₄ (4,4'-H ₂ bipy)} _n]	268	30.0 x 10 ⁻⁶	30.0
[{NiCl ₂ (4,4'-bipy)} _n]	209	35.8 x 10 ⁻⁶	35.8

Table 4: Solubility Test Results

Solvents/ Complexes	Water	Ethanol	Hydrogen Peroxide	Acetic Acid	Conc. HCl
[{NiCl ₄ (4,4'-H ₂ bipy)} _n]	S	SS	S	SS	S
[{NiCl ₂ (4,4'-bipy)} _n]	S	SS	S	SS	S

Key: S = Soluble; SS = Slightly Soluble

Table 5: Anti-Bacterial Activity Inhibition Zones

Complexes	Concentrations ($\mu\text{g}/\text{disk}$)	<i>E. coli</i> (mm)	<i>Ps.</i> (mm)	<i>Strep.</i> (mm)	<i>Staph.</i> (mm)	<i>Kleb.</i> (mm)
[NiCl ₄ (4,4'-H ₂ bipy)] _n	50	6	6	6	6	6
	500	15	15	6	11	13
	1000	16	40	10	15	15
[NiCl ₂ (4,4'-bipy)] _n	50	6	6	6	6	6
	500	6	6	6	6	6
	1000	6	6	6	6	13
CONTROL (Gentemecyn)	10	45	31	38	37	46

Key: *E. coli* = *Escherichia Coli*
Ps = *Psuedomona aeruginosa*
Strep = *Streptococcus pneumoniae*
Stap = *Staphylococcus aureus*
Kleb = *Klebsiella Specie*

Table 6: Anti-fungal Activity Inhibition Zones

Complexes	Concentrations ($\mu\text{g}/\text{disk}$)	<i>Pen</i> (mm)	<i>Met</i> (mm)	<i>Asp</i> (mm)
[NiCl ₄ (4,4'-H ₂ bipy)] _n	50	6	6	6
	500	6	6	6
	1000	6	6	6
[NiCl ₂ (4,4'-bipy)] _n	50	6	6	6
	500	6	6	6
	1000	6	6	13
CONTROL (Apron plus)	10	38	28	20

Key:
Pen = *Penicillium Specie*
Met = *Meterhizium Specie*
Asp = *Aspergillus Specie*

CONCLUSION

The results discussed in this work clearly revealed that mechanochemical synthetic methods can be exploited in the syntheses of hydrogen bonded complex $[4,4'\text{-H}_2\text{bipy}][\text{NiCl}_4]$ via the mechanochemical grinding of $[4,4'\text{-H}_2\text{bipy}]\text{Cl}_2$ and NiCl_2 . Similarly polymeric nickel (II) complexes $[\text{NiCl}_2(4,4'\text{-bipy})]$ can also be synthesized by grinding of NiCl_2 and neutral 4,4'-bipy in the solid state, which can also be afforded via mechanochemical dehydrochlorination of $[4,4'\text{-H}_2\text{bipy}][\text{NiCl}_4]$ with K_2CO_3 . Furthermore, the complexes do not show any appreciable biological activity as they are not found to be active against any organism at concentration lower than 1000 $\mu\text{g}/\text{disk}$.

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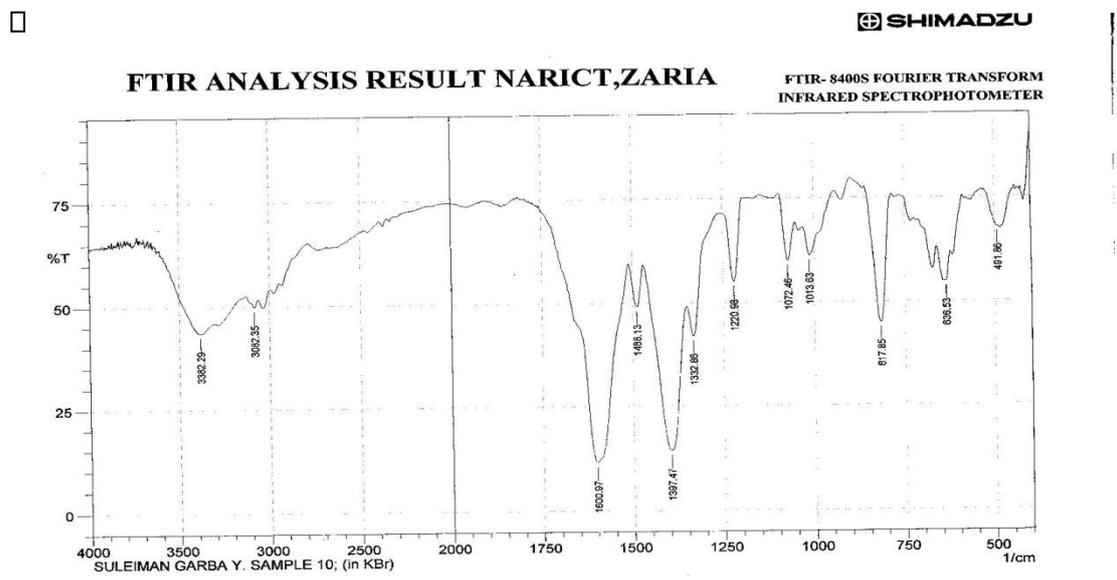
REFERENCES

- Adams C. J., Kurawa M. A. and Orpen G. A. (2010). Coordination Chemistry in the Solid State: Synthesis and Interconversion of Pyrazolium Salts Complexes and Pyrazolate MOFs. *Dalton Trans*, 39, 6974-6984
- Adams C. J., Colquhoun H. M., Crawford P. C., Lusi M. and Orpen A. G. (2007). Solid-state Methods for the Preparation of Crystalline Metal Complexes $[4,4'\text{-H}_2\text{bipy}][\text{MCl}_4]$ and $[\text{MCl}_2(4,4'\text{-bipy})]$ (M = Co, Zn or Pt). *Angew.Chem. Int. Ed.* **46**:1124-1128.
- Adams C. J., Crawford P. C., Orpen A. G., Podesta T. J. and Salt B. (2005). Solid-State Dehydrochlorination of 4-picolinium Salts of Crystalline $[\text{PdCl}_4]^{2-}$ and $[\text{PtCl}_4]^{2-}$. *Chem. Commun.* **6**: 2457-2458.
- Atkins P. W. (1996). Elemental Physical Chemistry. Oxford University Press. 2nd Edition. Pp 430-432.
- Braga D., Desiraju G. R., Miller J. S., Orpen A. G. and Price S. L. (2003). The Oxygen Atoms of the Dithiooxalate Ligand bind in Chelating Fashion to the N-H Donor of the Pyridinium ions. *CrystEngComm.* **4**: 500-509.
- Burgard M. D., Rath N. P., Brunelli M. and Brammer L. (2008). The Reverse Process uses Solid – gas Reaction. *Angew.Chem. Int. Ed.* **47**: 1693-1697.
- Cheesbrough M. (2000). District Laboratory Practice in Tropical Countries. Press Syndicate Publishers, University of Cambridge, Edinburgh, Cambridge United Kingdom. Pp 194-204.
- Crawford, P. C., Adams, C. J., Lusi M. and Orpen A. G. (2004). The Use of Molecular Tectons which Form Cyano-Based Hydrogen Bonded Synthons ($\text{NH}\cdots\text{NC}$) to Synthesize a Diverse Range of Crystal Structures. *Angew. Chem. Int. Ed.* **24**: 1224-1230.
- Gillon A. L., Orpen A. G., Starbuck J., Wang X.-M., Rodriguez-Martin Y. and Ruiz-Perez C. (1999). The Thermal Dehydrochlorination of the Perchlorometallate Salts of the Appropriate Pyridinium Species. *Chem. Commun.* **12**: 2287-2288.
- James S. L., Adams C. J., Bolm C., Braga D., Collier P., Friscic T., Grepioni F., Harris K. D. M., Hyett G., Jones W., Krebs A., Mack J., Maini L., Orpen A. G., Parkin I. P., Shearouse W. C., Steed J. W. and Waddelli D. C., *Chem. Soc. Rev.*, 2012, **41**, 413-447.
- Kaupp G. (1996). Supermicroscopy in Supramolecular Chemistry: AFM, SNOM, and SXM, in Comprehensive Supramolecular Chemistry, ed. J. E. D. Davies, Elsevier, Oxford. **8**: 381-423.
- Markvardsen A. J., David W. I. F., Johnson J. C. and Shankland K. (2001). The Synthesis of the Hydrogen Bonded Ribbon Polymer $[4,4'\text{-H}_2\text{bipy}][\text{MCl}_4]$ (M = Pd or Pt) as a Metal-containing Synthons for Crystal Engineering. *Acta Cryst.* **A57**: 47-54.
- Masciocchi N., Galli S. and Sironi A. (2005). The Cation-controlled Formation of $\{[\text{MCl}_4]_n\}^{2-}$ Chains in $[4,4'\text{-H}_2\text{bipy}][\text{MCl}_4]$ (M = Mn, Cd). *CommentsInorgChem.* **26**:1-37.
- Matthews P. (1996). Advanced Chemistry. Cambridge University Press. Pp 149-153.
- Mukhtar M. D. and Okafor M. C. (2002). Antibacterial Activity of *Guera Senegalensis*. *Journal Empiric Research.* **1**(2): 166-173.
- Sekhona B.S. and Leena G. (2010). Synthesis and Characterization of Metal Complexes of Some Antimicrobial Drugs, *International Journal of Chemitech Research.* **2**(1): 286-288.
- Shriver D. F., Atkins P. W. and Langford C. H. (1996). *Inorganic Chemistry*. Oxford University Press. 2nd Edition. Pp 136-141.
- Shirley R. (2003). The Exploitation of $\text{MX}\cdots\text{HN}^+$ Hydrogen Bond Synthons in the Preparation of Crystalline Salts, and the Structures of the Halometallate Species of $[4,4'\text{-H}_2\text{bipy}][\text{MX}_4]$ [X = Cl, M = Pd, Pt, Co, Zn, Hg and Cd; X = Br, M = Pd, Zn and Co]. *Crysfire.* **9**: 46

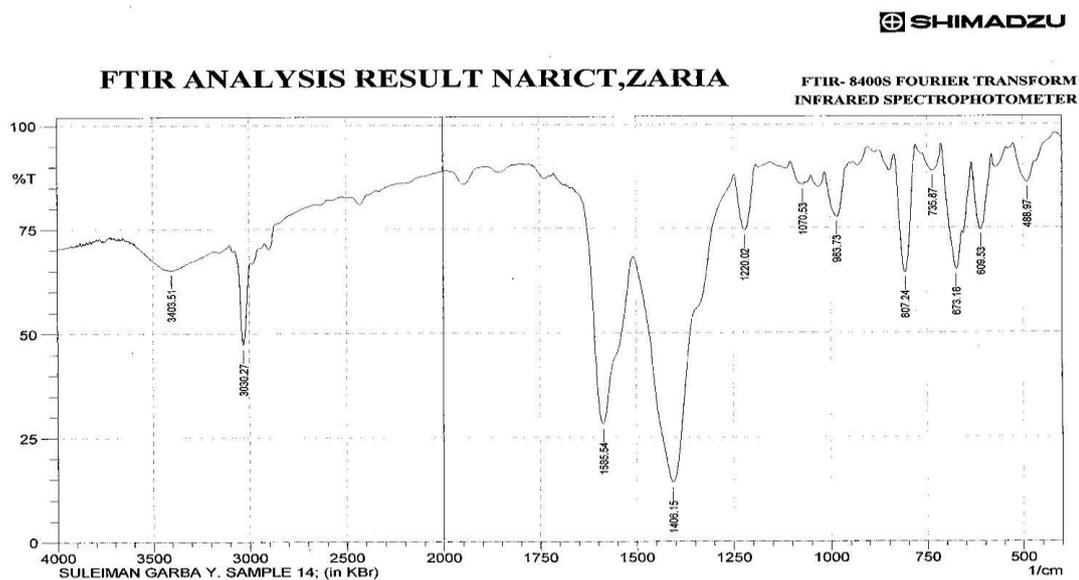
Shirley R. (2002). The Structures Formed by [4,4'-H₂bipy][MCl₄] Complex Salts Containing Similar Molecular Components. *XF2Crys.* **1**: 7.

Takacs L. (1996). The Successful Application of Trifurcated N-H·····Cl₃M and Bifurcated N-H·····Cl₂M Hydrogen Bonds (M = Pt) as Inorganic Synthons in the Construction of Linear and Zig-zag Self-assembled 1-D Chains in the Solid-state. *J. Solid State Chem.* **125**: 75-84.

Appendix 1: Infrared Spectrum of 4,4'-bipyridiniumtetrachloronickelate (II)



Appendix 2: Infrared Spectrum of 4,4'-bipyridinedichloronickel (II)



Appendix 3: Elemental analysis result of 4,4'-bipyridiniumtetrachloronickelate (II)**Eager 300 Report**

Page: 1 Sample: Ni/Complex (File001)

Method Name : MUSRL/ABU Zaria
 Method File : C:\Eager for FLASH\data\Sys_data_example\Multi user Science F
 Chromatogram : File001
 Operator ID : Company Name :
 Analysed : 13/03/2013 10:40 Printed : 13/03/2013 10:40
 Sample ID : Ni/Complex (#001)
 Instrument N. : 2011F0138
 Analysis Type : UnkNown (Area) Sample weight : .004439

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	7.0281	47	2035768	RS	5.009486	.132683E+1
Carbon	32.9862	62	6494226	RS	1.000000	.463970E+1
Hydrogen	2.6250	186	2428263	RS	3.126548	.173407E+1

Appendix 4: Elemental analysis result of 4,4'-bipyridinedichloronickel (II)**Eager 300 Report**

Page: 1 Sample: Ni/Complex (File002)

Method Name : MUSRL/ABU Zaria
 Method File : C:\Eager for FLASH\data\Sys_data_example\Multi user Science F
 Chromatogram : File002
 Operator ID : Company Name :
 Analysed : 13/03/2013 10:55 Printed : 13/03/2013 10:55
 Sample ID : Ni/Complex (#002)
 Instrument N. : 2011F0138
 Analysis Type : UnkNown (Area) Sample weight : .002489

Calib. method : using 'K Factors'

!!! Warning missing one or more peaks.

Element Name	%	Ret.Time	Area	BC	Area ratio	K factor
Nitrogen	6.0111	45	4822180	RS	1.128837	.132683E+1
Carbon	27.0289	71	6214426	RS	1.000000	.463970E+1
Hydrogen	1.6288	172	1246777	RS	1.632197	.173407E+1