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Synthesis, Characterization and Structural Diversity in Aminoguanidium Salts of Isoelectronic 2-Picolinic Acid N-Oxide and 3-Hydroxypicolinic Acid

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Abstract

Aminoguanidium salts of isoelectronic 2-picolinic acid N-oxide and 3-hydroxypicolinic acid were synthesized and characterized by Infra-Red (IR), Ultra-violet (UV), X-ray diffraction (XRD) and Thermal Analysis. The structure of aminoguanidium salts of isoelectronic 2-picolinate N-oxide and 3-hydroxypicolinate provided in single crystal was determined. The luminescence properties of the parent acids and their salts were studied and compared. The emission spectral results show that the simple salts offer enhanced luminescent activity when compared to the free acids.

Keywords
[AgunH] [2-pico] [AgunH] Aminoguanidium salt 2-picolinic acid N-oxide, [AgunH] [3-hpic] Aminoguanidium salt 3-hydroxypicolinic acid, Infra-Red (IR), Ultra-violet (UV), X-ray diffraction (XRD).

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INTRODUCTION

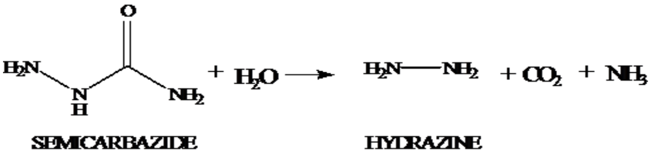
Hydrazine is the simplest diamine and parent of innumerable derivatives. It is a colourless, covalent, oily liquid, which fumes in air and has odour like ammonia. It's melting and boiling points are 2 °C and 113 °C respectively. Hydrogen bonding is responsible for the high boiling point and viscosity of the liquid. Physically it is similar to water but chemically it is a reducing, decomposable, basic and bi-functional monomer. It has a potent N-N bond, two lone pairs of electrons and replaceable hydrogen atoms. It acts as a very good mono or bi-dentate (bridging) ligand due to the presence of two lone pairs of electrons. Hydrazine dissolves in polar solvents like water, alcohols, ammonia and amines but it is slightly soluble in other organic solvent.

SALTS OF HYDRAZINE

Hence, hydrazine is a diacidic base, weaker than ammonia. This may be understood from the fact that hydrazine is regarded as an ammonia derivative in which one of the hydrogen atoms has been replaced by more electronegative NH_2 group[1]. The reaction between hydrazine and water is represented.

HYDROLYTIC REACTIONS

Thiele found that the hydrolysis of aminoguanidine proceeds in two stages; semicarbazide is formed in the first stage and further hydrolysis yields hydrazine, ammonia and carbon dioxide.



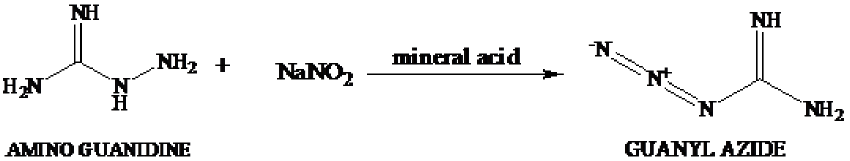
The intermediate, semicarbazide, was obtained in large quantities when the hydrolysis was affected with Na_2CO_3 instead of NaOH. Lieber and Smith[2] studied quantitatively the hydrolysis of aminoguanidine in acid and basic media. They found that contrary to the opinions expressed in literature, aminoguanidine is extremely resistant to acid hydrolysis. Aminoguanidine is slightly hydrolyzed under strong acid concentration.

FORMATION OF 3,6-DIAMINO-1,2-DIHYROTETRAZINE

Ponzio and Gastaldi[3], in 1913, prepared 3,6-diamino-1,2-dihydrotetrazine by the reaction between two molecules of aminoguanidine.

REACTIONS OF AMINOGUANIDINE WITH SODIUM NITRITE

- In general, aminoguanidine reacts with sodium nitrite in the presence of nitrous acid.
- If the reaction carried out in a solution of strong mineral acid, guanylazide is formed.



SCOPE AND OBJECTIVE

- To prepare and characterize aminoguanidinium salts of 2-picolinic acid N-oxide and 3-hydroxypicolinic acids.
- To study the mode of thermal decomposition of parent acids and their aminoguanidinium salts.
- To determine the structures of the aminoguanidinium salts of 2-picolinate N-oxide and 3-hydroxypicolinate provided if single crystals obtained.
- To study and compare the luminescence properties of the parent acids and their salts.

MATERIALS AND METHODS.

ESTIMATION OF HYDRAZINE

The hydrazine content in aminoguanidine salts was determined volumetrically using a standard KIO_3 (0.025 M) solution under Andrew's condition[4].

$$IO_3^- + [(NH_2)_2C{=}N(H)NH_2]^+ + H^+ + Cl^- \longrightarrow ICl + N_2 + 2NH_3 + CO_2 + H_2O$$

One mL of 0.025M KIO_3 = 0.0008013 g of hydrazine.

In a typical experiment about 60 mg of aminoguanidine salt was dissolved in 20 mL of distilled water, and then 10 mL of concentrated HCl and 5 mL of CCl_4 or $CHCl_3$ were added. The mixture contained in a stoppered bottle was titrated against standard KIO_3 solution. The solution was shaken well after the addition of each mL of KIO_3 solution. The end point is the disappearance of pink colour in the organic layer.

PREPARATON AND CHARACTERIZATION OF AMINOGUANIDINIUM PICOLINATE N-OXIDE AND 3-HYDROXYPICOLINATE

Aminoguanidine, a bifunctional molecule, is one of the hydrazine derivatives and hence, it is expected to form salts in a similar fashion to that of hydrazine. Aminoguanidine acts as a dibasic and it forms $AmgH^+$ [aminoguanidinium(+1)] and $AmgH_2^+$ [aminoguanidinium(+2)] salts with mineral and/or carboxylic acids. The aminoguanidine and its salts are very interesting from the view point of their preparation and important physical / chemical properties. For example, aminoguanidinium(+1) nitrate[5], aminoguanidinium(+1) dihydrogen phosphate[6]and aminoguanidinium(+1) hydrogen L-tartrate monohydrate[7] have been prepared as a new member of optical materials. The aminoguanidinium(+1) salts of various anions such as Cl$^-$, NO$_3^-$, SO$_4^{2-}$ and H$_2$PO$_4^-$ have been prepared and their crystal structures reported[5, 6, 8,-10]. The crystal structures of aminoguanidinium(+2) dinitrate[11] and sulphate[12] have also been examined.

In contrary, the aminoguanidinium carboxylates are scarcely reported. Only a very few salts viz., aminoguanidinium hemioxalate[13] and hydrogen-L-tartrate monohydrate[7] and squarate[14] have been reported in the literature. The structural study reports that aminoguanidinium ion in these salts exist in its monoprotonated form. Also the structural study has shown that the commercial aminoguanidine bicarbonate was found to be zwitterionic 2-guanidinium-1-amino-carboxylate hydrate.

Similarly, selvakumar et al[15] have reported the salts of malonic and succinic acids. They form only mono-aminoguanidinium salts, whereas oxalic acid mainly forms bis-aminoguanidinium oxalate. In addition to this, interestingly the oxalic acid also forms guanylhydrazido-oxalic acid which is found to exist as zwitter ion. Unlike other acids, the sulfoacetic acid readily forms only the zwitter ionic salts rather than the usual simple salt. This may be due to high acidic nature of sulfonic group which favours the acid catalyzed condensation-cum-internal salt formation. In spite of a number of aminoguanidinium salts with mineral and aliphatic/aromatic mono- and dicarboxylic acids known, there is no report on aminoguanidinium salts of heteroaromatic carboxylic acids, particularly picolinic acids.

Hence, it is considered worthwhile to study these aminoguanidinium carboxylates with respect to their spectral, emission and thermal properties. In this chapter the preparation, spectral and thermal properties of aminoguanidinium salts of 2-picolinic acid N-oxide (**2-Hpico**) and 3-hydroxypicolinic acid (**3-Hhpic**) have been described. Also, the luminescence properties of these acids and their salts have been compared. For clarity, the structures of the isoelectronic acids are detailed below.

2-picolinic acid N-oxide (2-Hpico) **3-hydroxypicolinic acid (3-Hhpic)**

Scheme 1 Structures of isoelectronic picolinic acids

EXPERIMENTAL PREPARATION OF [AGUNH][2-PICO]

Aminoguanidinium picolinate N-oxide was prepared by adding aminoguanidine bicarbonate (0.136 g, 0.001 mol) to an aqueous solution (30 mL) containing picolinic acid N-oxide (0.139 g, 0.001 mol) in equimolar ratio. The resulting mixture was stirred well till the effervescence ceases and was kept over water bath for a few minutes to get a clear solution. This clear solution (pH= 3.6 - 4) was concentrated over water bath to one fourth of its initial volume and kept aside for crystallization at room temperature. The crystalline salts began to appear after a few hours and the crystallization was continued for four days. After four days, the transparent crystals were separated, washed with ethanol and air dried.

Preparation of Preparation of [AgunH][3-hpic]

This salt was prepared by adding aminoguanidine bicarbonate (0.136 g, 0.001 mol) to an aqueous solution (30 mL) of 3-hydroxy picolinic acid (0.139 g, 0.001 mol) in 1:1 ratio. The resulting mixture was heated over water bath till a clear solution was obtained. The resulting clear solution (pH= 2 - 3) was concentrated and crystallized as before. The crystalline solid obtained was separated, washed with absolute alcohol and dried in air. Both the salts are soluble in water.

RESULTS AND DISCUSSION

Treatment of equimolar concentration of respective isoelectronic picolinic acid with aminoguanidine bicarbonate, [AgunH][HCO_3], in water ratio afforded the 1:1 salts, [AgunH][2-pico] and [AgunH][3-hpic]. The results of the chemical and elemental analysis are given in **Table 1**. The analytical data agree well with the proposed formulae for the salts. Both salts are anhydrous. From the analysis, it is clear that the isoelectronic picolinic acids form only mono-aminoguanidinium salts and are structurally characterized. The percentage yield of the salts varies from 60-70.

Table 1 Analytical data

Compound	M.wt	C/% obsd. (calcd.)	H/% obsd. (calcd.)	N/% obsd. (calcd.)	Hydrazine part of AgunH/% obsd. (calcd.)	Melting Point/ °C	Yield/ %
[AgunH][2-pico] **$C_7H_{11}N_5O_3$**	213.21	39.00 **(39.43)**	5.05 **(5.16)**	32.55 **(32.85)**	14.80 **(15.01)**	140-142	67
[AgunH][3-hpic] **$C_7H_{11}N_5O_3$**	213.21	39.50 **(39.43)**	5.30 **(5.16)**	32.60 **(32.85)**	14.50 **(15.01)**	160-161	63

IR SPECTRA

The important infrared absorption bands of the acids, base and their salts are listed in the **Table 2** including the assignments. The broad structured features in the 3,000-3,450 cm^{-1} region, correspond to the stretching vibrations of the NH and OH groups participating in the hydrogen bonds of N-H...O type hydrogen bonds[16]. The broad intense band observed in the region 3310 - 3360 cm^{-1}, is assigned to the O-H vibration of the hydroxyl group in the 3-hydroxypicolinate salt. Both these salts show asymmetric and symmetric stretching's of the carboxylate group in the range 1570 - 1650 and 1350 - 1380 cm^{-1} respectively. The sharp band observed between 1705 and 1701 cm^{-1} for the presence of free acid group in picolinic acids. The presence of $AgunH^+$ cations in crystals is manifested in strong to medium intensity bands in the range 1650-1680 cm^{-1} which can be assigned to δNH and νCN vibrations. The sharp band in the region 1,110-1140 cm^{-1} for theses salts is indicative of N-N stretching of hydrazinic part of aminoguanidine moiety. The infrared spectra of the free acid, base and their salts are given in **Figs. 1 – 5.**

Table 2 Infrared spectral data (cm^{-1})

Compound	O-H Str.	N-H Str.	C=N Str.	$\nu_{C=O}$ of COOH	COO Asym.Str.	COO Sym.Str.	N-N Str.
2-Hpico	3452-3100	…	…	1705	…	…	…
AgunH.HCO_3	3478	3038	1668	…	…	1353	1113
[AgunH][2-pico]	3359	3172	1670	...	1571	1380	1140
3-Hhpic	3356	2899	…	1701	…	…	…
[AgunH][3-hpic]	3348	3089	1680	...	1650	1361	1138

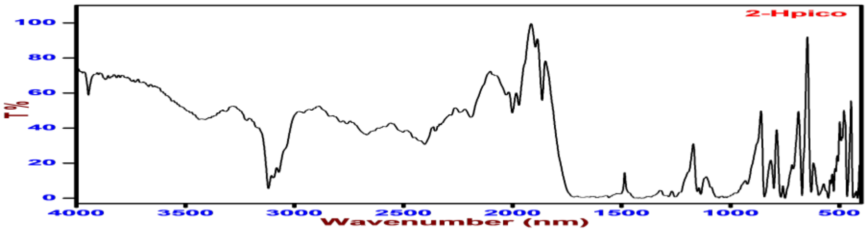


Fig. 1. IR spectra of 2-picolinic acid N-oxide

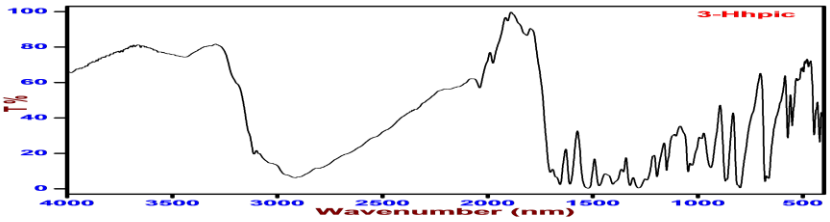


Fig. 2. IR spectra of 3-hydroxypicolinic acid

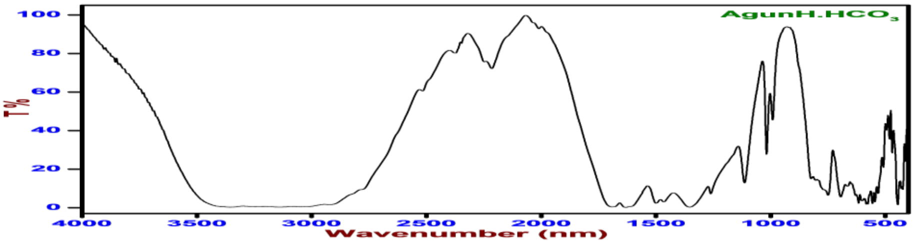


Fig. 3. IR spectra of aminoguanidine bicarbonate

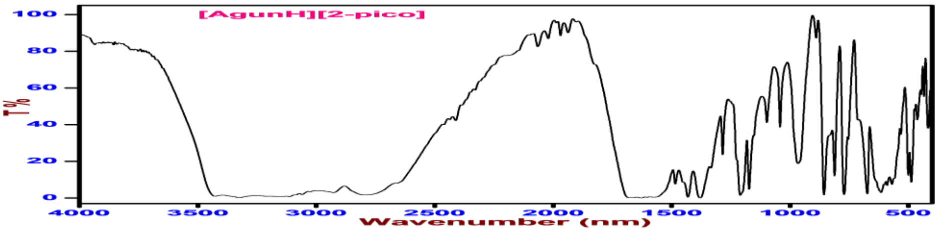


Fig. 4. IR spectra of [AgunH][2-pico]

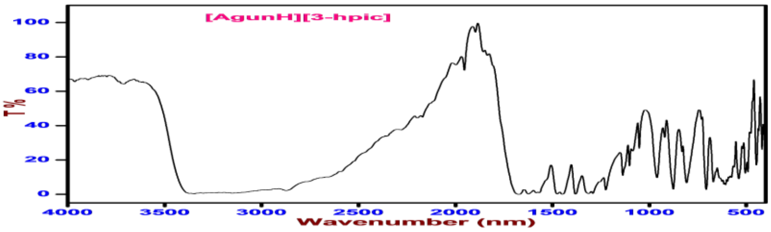


Fig. 5. IR spectrum of [AgunH][3-hpic]

THERMAL STUDIES

The thermal data of the compounds are listed in **Table.3.** The composition of intermediates and final products are those, which best fit with observed mass losses in the TG curve. The thermogravimetric results are in good agreement with the DTA data. The thermograms of the salts are given in **Figs. 6 – 10.** From the thermal data it is clear observed that both the salts undergo melting with decomposition. The free acids decompose in a single step to give gaseous products.

Unlike the parent acids, the both aminoguanidinium-picolinate N-oxide and 3-hydroxypicolinate salts show clear melting with endothermic decomposition, in DTA. After melting, the aminoguanidinium picolinate N-oxide decompose endothermically around 280 °C to give NH=C=NH as intermediate. Further, the intermediate decomposes into gaseous products, exothermically around 500 °C. Whereas, the aminoguanidinium3-hydroxypicolinate salt in a single step decomposition is exothermically around 500 °C to give gaseous product.

As expected, the aminoguanidine bicarbonate undergoes dehydration with decomposition to give gaseous products via HN=C=NH intermediate (**Fig 8**).

Table 3 Thermal data

Compound	DTA Peak Temp./ °C	Thermogravimetry			Decomposition products
		Temp. range/ °C	Mass loss/%		
			Obsd.	Calcd.	
2-Hpico	(+) 180	-	-	-	Melting
	(+) 200	150 – 220	100	100	Complete decomposition
3-Hhpic	(+) 215	120-220	100	100	Complete decomposition
AgunH.HCO_3	(+) 135	90-180	69.00	69.12	Formation of NH=C=NH
	(+) 175				
	(-) 595	180-600	100	100	Complete decomposition
[AgunH][2-pico]	(+) 180	-	-	-	Melting
	(+) 275	200-290	80.00	80.30	Formation of NH=C=NH
	(-) 500	290-550	100	100	Complete decomposition
[AgunH][3-hpic]	(+) 180	-	-	-	Melting
	(+) 260				
	(-) 455	190-500	100	100	Complete decomposition
	(-) 490				

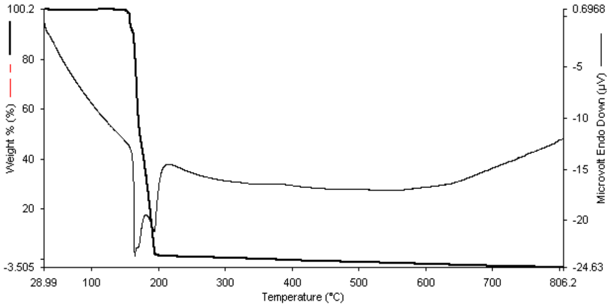


Fig. 6. Simultaneous TG-DTA of 2-picolinic acid N-oxide

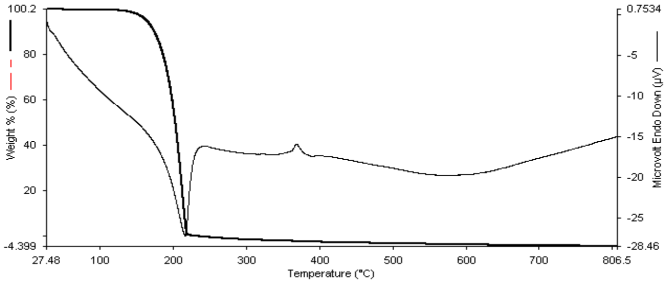


Fig. 7. Simultaneous TG-DTA of 3-hydroxypicolinic acid

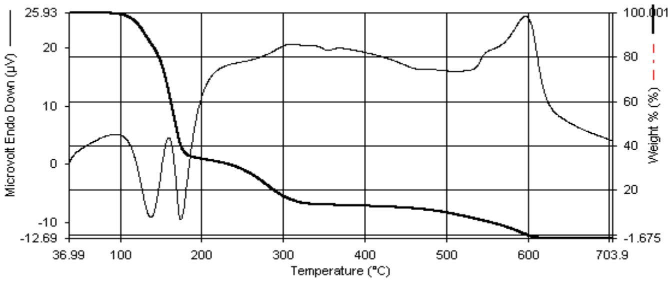


Fig. 8. Simultaneous TG-DTA of aminoguanidine bicarbonate

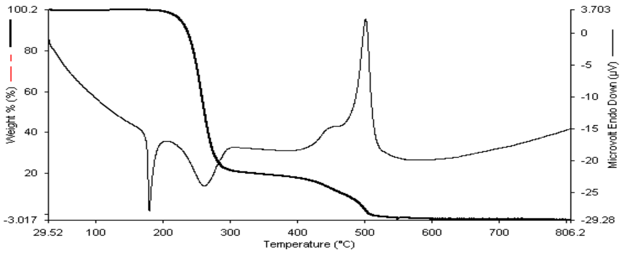


Fig. 9. Simultaneous TG-DTA of [AgunH][2-pico]

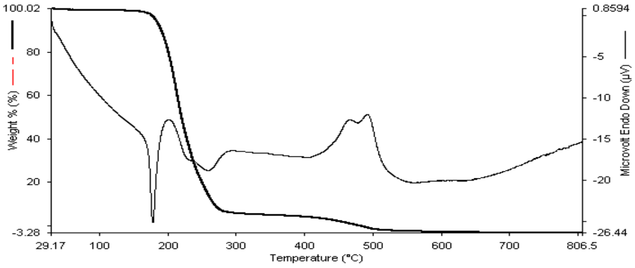


Fig. 10. Simultaneous TG-DTA of [AgunH][3-hpic]

CRYSTALLOGRAPHIC STUDIES ON [AGUNH][2-PICO] 1 AND [AGUNH][3-HPIC] 2

During crystallisation, both [AgunH][2-pico] and [AgunH][3-hpic] provided crystals suitable for X-ray diffraction. Crystal data including experimental details, bond parameters and hydrogen bonding are given in **Tables 4-8**. In both cases, H atoms were located in the difference maps and their positions refined with appropriate restraints. **[AgunH][2-pico]** crystallizes in the monoclinic space group ***$P2_1/n$*** with four molecules in the unit cell. The asymmetric unit with atom numbering scheme is presented in **Fig 11a**. The structure of [AgunH][2-pico] consists of one aminoguanidinium cation and picolinate N-oxide anion. The N(2), N(3), and N(4) N atoms of the aminoguanidinium cation appear to exhibit C-N bond lengths (1.312(19)-1.319(2) Å) consistent with some degree of delocalization over the CN_3 frawork (cf standard C-N and C=N bond lengths at 1.469 Å (amine) and 1.279 Å (imine))[16]. The shortest C-N bond length in the $AgunH^+$ cation is C(7)-N(4) at 1.312(19) Å. The fourth N atom appears *sp^3*-like in nature is out-of molecular plane and N(2)-N(5) bond length of 1.405(17) Å consistent with the perspective that it is not involved in π-conjugation to the rest of the CN_3 framework.

As expected, the crystal structure is dominated by hydrogen bonding between cation and anionic molecules. The $AgunH^+$ cation offers an extensive array of N-H hydrogen bond donors, and the amine groups form a web of N-H…O contacts close to the cation molecular plane; H(4A) forms a bifurcated contact to O(2) [carboxylate oxygen] and O(3) [N-oxide] [$d_{O…H}$ = 2.629 and 2.273 Å, respectively] whereas H(4B) does not form any hydrogen bond to the anionic molecule. The second amine group also implements both N-H groups in hydrogen bonding H(3A)…O(2) [2.132 Å] and H(3B) to the adjacent carboxyl group of oxygen atom O(1) [$d_{O…H}$ = 2.139 Å]. The third N atom of the cation also bonds to the another entity of N-oxide (N O) H(2)…O(3) [$d_{O…H}$ = 1.849 Å]. All these contacts lie close to the $AgunH^+$ molecular plane. Conversely, the H atoms attached to N(5) are involved in out-of-plane hydrogen bonding to the two adjacent picolinate N-oxide anion [H(5A)…O(2) and H(5B)…O(1) at 2.238 and 2.167 Å, respectively] as shown in **Fig. 11b**.

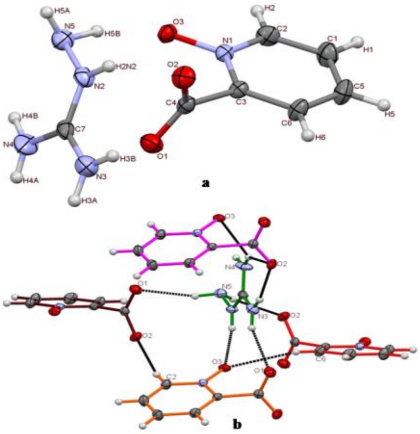


Fig. 11a-b. Ortep diagram of the [AgunH][2-pico$^-$] with 40% thermal ellipsoid; (b) various types of hydrogen bonding through AgunH$^+$ cation.

Table 4 Bond Lengths for [AgunH][2-pico] 1 and [AgunH][3-hpic]

Compounds		**1**		**2**	
Atom	**Atom**	**Length/Å**	**Atom**	**Atom**	**Length/Å**
C1	C2	1.359(2)	C1	C2	1.409(5)
C1	C5	1.375(2)	C1	N1	1.343(12)
C2	N1	1.3439(17)	C1	C6	1.504(8)
C3	C4	1.5093(17)	C2	C3	1.398(13)
C3	C6	1.3730(17)	C2	O1	1.35(2)
C3	N1	1.3442(15)	C3	C4	1.372(12)
C4	O1	1.2335(17)	C4	C5	1.393(11)
C4	O2	1.2409(15)	C5	N1	1.336(14)
C5	C6	1.372(2)	C6	O2	1.259(5)
C7	N2	1.3127(18)	C6	O3	1.266(16)
C7	N3	1.319(2)	C7	N2	1.323(3)
C7	N4	1.3121(19)	C7	N3	1.325(11)
N1	O3	1.3228(13)	C7	N4	1.338(12)
N2	N5	1.4054(17)	N4	N5	1.407(2)

Table 5 Crystal data and structure refinement for [AgunH][2-pico]1 and [AgunH][3-hpic]2

Compounds Name	**[AgunH][2-pico] 1**	**[AgunH][3-hpic] 2**
Empirical formula	$C_7H_{11}N_5O_3$	$C_7H_{11}N_5O_3$
Formula weight	213.21	213.21
Temperature/K	296(2)	296(2)
Crystal system	monoclinic	orthorhombic
Space group	$P2_1/n$	$Pca2_1$
a/Å	7.4194(7)	19.003(7)
b/Å	10.3401(12)	6.357(2)
c/Å	12.9840(16)	7.943(3)
α/°	90	90
β/°	103.280(4)	90
γ/°	90	90
Volume/Å^3	969.46(19)	959.531
Z	4	1
ρ_{calc}g/cm^3	1.461	1.462
μ/mm^1	0.117	0.138

Compounds Name	**[AgunH][2-pico] 1**	**[AgunH][3-hpic] 2**
F(000)	448	252
Crystal size/mm^3	0.5 × 0.35 × 0.3	0.35 × 0.25 × 0.25
2Θ range for data collection/°	5.1 to 56.96	3.48 to 56.44o
Index ranges	$-9 \le h \le 9$, $-13 \le k \le 13$, $-17 \le l \le 17$	$-8 \le h \le 9$, $-9 \le k \le 9$, $-10 \le l \le 15$
Reflections collected	11394	3024
Independent reflections	2394 [R_{int} = 0.0300, R_{sigma} = 0.0213]	2392 [R_{int} = 0.0132, R_{sigma} = 0.0215]
Data/restraints/parameters	2394/3/153	2392/8/140
Goodness-of-fit on F^2	1.039	1.043
Final R indexes [$I>=2\sigma(I)$]	R_1 = 0.0358, wR_2 = 0.0951	R_1 = 0.0379, wR_2 = 0.1123
Final R indexes [all data]	R_1 = 0.0487, wR_2 = 0.1037	R_1 = 0.0477, wR_2 = 0.1187
Largest diff. peak/hole / e Å^{-3}	0.26/-0.20	0.30/-0.22

Table 6 Hydrogen bonding for [AgunH][2-pico]/Å

D-H...A	**D-H**	**H...A**	**D-H...A/dist.**	**D-H...A/°**
N3-H3A...O2^{i}	0.860	2.132	2.958	160.70
N4-H4A...O2^{i}	0.811	2.629	3.301	141.31
N4-H4A...O3^{i}	0.811	2.273	2.864	130.15
N5-H5A...O2^{ii}	0.837	2.238	3.014	163.70
N5-H5B...O1^{iii}	0.936	2.167	3.076	154.09
C2-H2...O2^{ii}	0.930	2.321	3.216	161.42
C6-H6...O3^{iii}	0.930	2.686	3.527	150.73
N2-H2N2...O3^{iv}	0.860	1.849	2.699	169.63
N3-H3B...O1^{iv}	0.860	2.139	2.959	159.25

Symmetry code: (i) 1+x, y, z (ii) 1/2+x, 1/2-y, 1/2+z (iii) 1.5-x, 1/2+y, 1/2-z (iv) x, y, z

Table 7 Bond Angles for [AgunH][2-pico] 1 and [AgunH][3-hpic] 2

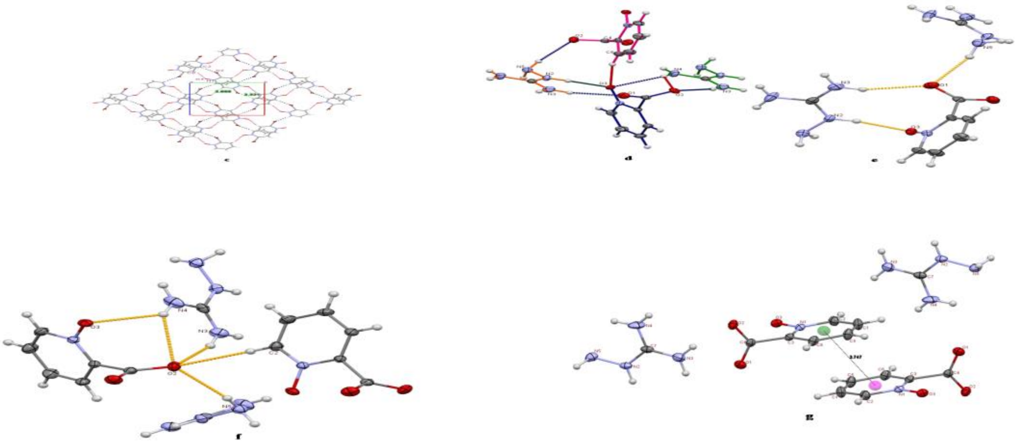
Compounds			**1**		**2**		
Atom	**Atom**	**Atom**	**Angle/˚**	**Atom**	**Atom**	**Atom**	**Angle/˚**
C2	C1	C5	120.25(14)	N1	C1	C2	121.79(11)
N1	C2	C1	120.14(13)	C1	C2	C3	119.43(10)
C6	C3	C4	124.46(11)	C2	C3	C4	118.05(9)
N1	C3	C4	115.98(10)	C5	C4	C3	119.21(13)
N1	C3	C6	119.56(11)	C4	C5	N1	123.67(15)
O1	C4	C3	117.21(11)	N1	C1	C6	117.05(10)
O1	C4	O2	127.58(12)	C6	C1	C2	121.16(12)
O2	C4	C3	115.20(11)	C1	C2	O1	121.89(12)
C6	C5	C1	118.64(13)	O1	C2	C3	118.68(14)
C5	C6	C3	120.22(13)	O2	C6	O3	123.84(16)
N2	C7	N3	119.95(12)	C5	N1	C1	117.82(13)
N4	C7	N2	119.22(15)	N2	C7	N3	120.68(14)
N4	C7	N3	120.83(15)	N3	C7	N4	121.47(15)
C2	N1	C3	121.18(11)	N2	C7	N4	117.82(11)
O3	N1	C2	119.86(10)	C6	N4	N5	118.17(13)
O3	N1	C3	118.96(10)	C1	C6	O2	119.82(10)
C7	N2	N5	118.34(11)	C1	C6	O3	116.34(11)

Table 8 Hydrogen bonding for [AgunH][3-hpic]/Å

D-H...A	D-H	H...A	D-H...A/dist.	D-H...A/°
O1-H1...O3^{i}	0.907	1.648	2.529	162.94
N2-H2A...O2^{i}	0.871	1.988	2.843	166.58
N4-H4A…N1^{i}	0.887	2.094	2.977	173.58
C4-H4...N3^{ii}	0.950	2.742	3.476	134.67
N2-H2B…O2^{iii}	0.882	2.030	2.889	164.19
N3-H3A…O3^{iii}	0.889	2.088	2.958	165.81
N3-H3B...O2^{iv}	0.793	2.382	3.128	157.27
N5-H5A...O2^{v}	0.895	2.396	3.208	150.86
N5-H5B…O1^{vi}	0.975	2.190	3.155	170.25

Symmetry code: (i) x, y, z (ii) 1/2+x, -y, z (iii) -x, 1-y, 1/2+z (iv) -x, -y, 1/2+z (v) 1/2-x, 1+y, 1/2+z (vi) x, -1+y, z

Further, the C-H…O hydrogen bonding creates the 2D sheet via C(2)-H(2)…O(2) and C(6)-H(6)…O(3); [d$_{O…H}$ = 2.321 and 2.686 Å, respectively] as shown in **Fig. 11c**. The deprotonated carboxylate group is twisted out of the molecular plane (angle between CO$_2$ and pyridyl ring planes = 84. 44 Å) in order to form hydrogen bonds to AgunH$^+$ cation. Interestingly, the pyridyl ring of N O oxide forms a trifurcated acceptor to two aminoguanidinium molecules and one 2-pico anion (**Fig. 11d**.) [O(3)…H(4A) = 2.273, O(3)…H(2N2) = 1.849 and O(3)…H(6) = 2.686 Å, respectively]. Additionally, the carboxylate oxygen atom O(1) and O(2) form bifurcated and tetrafurcated hydrogen bonding via AgunH$^+$ cation and 2-pico$^-$ anionic molecules (**Fig. 11e-f**). The structure therefore satisfies all the hydrogen bonding requirements of both cation and anion entity. The 2-pico anion is extensively involved in hydrogen bonding and π-π interactions (**Fig. 11g**).



Figs. 11c-g. (c-e) different types of hydrogen bonding through cation as well as anionic moiety; (g) the π-π stacking interactions between two aromatic rings of [AgunH][2-pico].

The **aminoguanidinium-3-hydroxypicolinate, [AgunH][3-hpic]**, crystallizes in the non-centrosymmetric (orthorhombic) space group ***Pca2₁*** with one cation and anion in the asymmetric unit but no water of crystallization (**Fig.12a.**). Like [AgunH][2-pico], the aminoguanidinium cation is essentially planar, with the cation exhibiting an extensive hydrogen bonding network of the N-H atoms to the carboxylate group of the 3-hpic anions in the crystal lattice. Unlike 2-pico$^-$, the 3-hpic$^-$ anion has intra-molecular hydrogen bonding formed between the deprotonated carboxylate and hydroxyl groups of pyridyl ring [d$_{O…H}$ = 1.648 Å].The AgunH$^+$ cation suggest an extensive array of N-H hydrogen bond donors, and the amine groups form a net of N-H…O contacts close to the cation molecular plane; three amines (NH_2) are present in the cation, and each amine group hydrogen bonded to two anionic unit via N-H…O hydrogen bonds [N(2)-H(2A)…O(2) = 2.843 Å, N(2)-H(2B)…O(2) = 2.889 Å, N(3)-H(3A)…O(3) = 2.088 Å, N(3)-H(3B)…O(2) = 2.382 Å, N(5)-H(5A)…O(2) = 2.396 Å, N(5)-H(5B)…O(1) = 2.190 Å, respectively]. Additionally, one of the amine groups acting as both donor as well as acceptor and they the range from $d_{O…H}$ = 2.088 – 2.382 Å and [C(4)-H(4)…N(3)] $d_{N…H}$ = 2.742 Å as shown **Figs. 12b-d**. Also the pyridyl-ring N atom forms a contact to the $AgunH^+$ cation [N(1)…H(4A) at 2.094 Å].

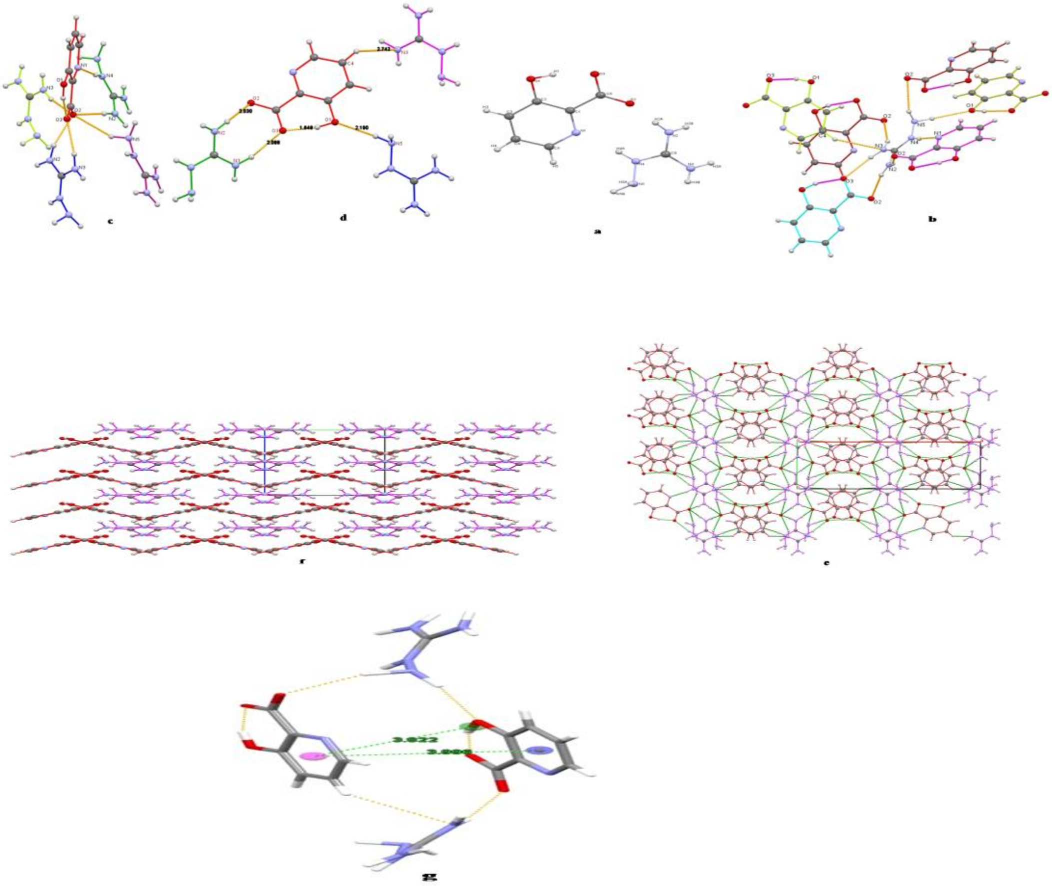


Fig. 12a-g. (a) Molecular structure of [AgunH][3-hpic$^-$]; (b-e) various type of hydrogen bonding between cation and anion molecules; (g) π-π- Interaction between anionic moiety.

Furthermore, the cations and anions are interlinked via N-H…O, C-H…N and N-H…N network of hydrogen bonds to create 2D-wave like structure as shown in **Figs. 12e-f**. Interestingly, one of the carboxylate oxygen atoms O(2) to form tetrafurcated hydrogen bonding to four $AgunH^+$ cations (**Fig. 12c**). The other non-covalent forces stabilizing the salt (3-hpic) are π-π stacking interaction between the two planar 3-hydroxypicolinate of hpic$^-$ (centroid – centroid & O-H…π distance are 3.996 & 3.822 Å) molecule as shown in **Fig. 12g**.

PHOTO LUMINESCENCE PROPERTIES

Recently, the photo luminescent properties of many metal complexes and organic ligands have been studied and the studies reveal that their luminescence behaviour is closely associated with the different metal ions and the ligand coordinated around them[17]. The photo luminescent properties of free isoelectronic picolinic acids and their salts have been investigated in aqueous medium at room temperature. The emission spectra of free 2-picolinic acid N-oxide, 3-hydroxypicolinic acids and their salts are illustrated in **Fig. 13a**. The free acids display luminescence with an emission maximum at 412 nm (excitation λ = 330 nm), which is attributed to the intra-ligand π* – n transition. The simple salts give an intense sharp emission band between 390-410 nm with maximum at 403 nm upon excitation at 330 nm which are shown in **Fig. 13b.**

Notably no emission spectrum for aminoguanidine bicarbonate was observed and it would appear that protonation on the iminidine (C=N) nitrogen disfavours emission characteristics of AgunH$^+$ ion. The contribution of photoluminescent properties is therefore mainly due to picolinate and not due to aminoguanidinium cation.

The origin of the increase in emission intensity for simple salts compared with those of the free acid is currently uncertain but may be associated with change in molecular conformation or change in hydrogen bonding characteristics in solution affecting emission performance. Nevertheless, these preliminary emission spectral results show that the simple salts exhibit enhanced luminescent activity as compared to the free acids.

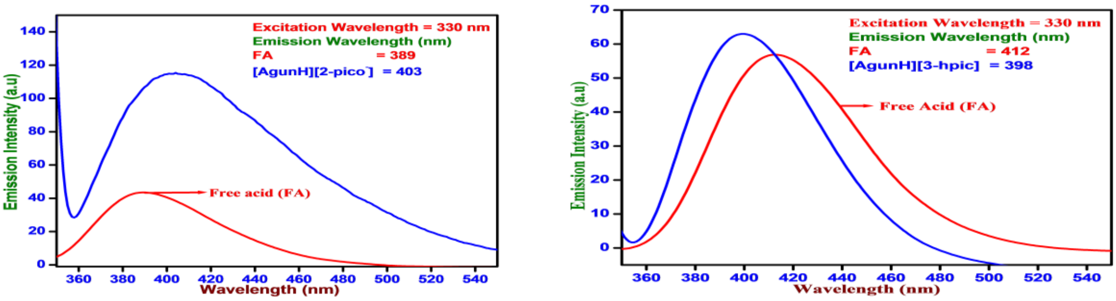


Fig. 13a-b. Emission spectra of free 2-picolinic acid N-oxide & 3-hydroxypicolinic acid (FA) and their salts

SUMMARY AND CONCLUSIONS

The reaction of isoelectronic picolinic acids, 2-picolinic acid N-oxide and 3-hydroxypicolinic acid with aminoguanidine bicarbonate in 1:1 mole ratio has yielded mono salts of [AgunH][2-pico] and [AgunH][3-hpic] respectively. The crystal structures of aminoguanidinium-picolinate N oxide and 3-hydroxypicolinate salts have been determined and exhibit more number of hydrogen bonded networks between cations and anions. Interestingly, the aminoguanidinium2-picolinate N-oxide crystallizes in centric space group (***$P2_1/n$***), whereas aminoguanidinium3-hydroxypicolinate crystallizes in non-centric space group (***$Pca2_1$***). Further, both the structures are stabilized through N-H….O, C-H….O, N-H…N and C-H…N hydrogen bonding network and different type of π- interactions. As a whole, the structural arrangements of picolinate N-oxide and 3-hydroxypicolinate are totally different, is due to position of the carboxylic group in pyridine ring.

These salts have been characterized by infrared spectra and thermal analysis. All the prepared salts undergo melting (180 °C) with endothermic decomposition to give gaseous products.It is observed that the aminoguanidinium salts are crystalline in nature compared to the corresponding hydrazinium salts. This may be due to better hydrogen bonding ability of aminoguanidine than hydrazine. The emission spectra of the parent acids and their salts have been recorded, and the emission spectral results show that the simple salts offer enhanced luminescent activity when compared to the free acids.

REFERENCES

1. G.H.Hudson, R.C.H.Spencer, J.P.Stern, "Hydrazine", "Mellor's Comprehensive Treatise on Inorganic and Theoretical chemistry", Vol.VIII, Suppl.II, Nitrogen (part II), Longmans, London, 1967.
2. M. Bujak, P. Osadczuk, J. Zaleski, Acta. Crystals C57, 2001, 388-391.
3. J.Thiele, J.Ann; 273, 1893, 133.
4. A.Akella, D.A.Keszler, Acta. Crystals, C50, 1994, 1974.
5. A. W. Bauer, W. M. M. Kirby, J. C. Sherries and M. Truck, Am. J. Clin. Pathol. 45 1996 493.
6. C. H. Collins and P. M. Zyne, “Microbial methods” University Park Press, Bultimore, 1970.
7. I. Nemec, Z. Machackova, K. Teubner, I. Cisarova, P. Vanek and Z. Micka, Journal of Solid State Chemistry,177 2004, 4655.
8. Z. Machackova, I. Nemec, K. Teubner P. Nemec, P. Vanek and Z. Micka, Journal of Molecular Structures, 832 (2007) 101.
9. John H. Bryd, Acta. Crystals, 10 1957, 677.
10. C. H. -Yan, Z. T. –Lai, Q. X. – Jing, Y. Li and S. F. -Lei, J. Beijing. Inst. Tech., 15, 2006, 473.
11. M. Koskinen and I. Mutikainen, H. Elo, Z. Naturforsh., 49b, 1994, 556.

12. Kolev, Z. Glavcheva, R. Stahl, H. Preut, P. Bleckmann and V. Radomirska, Acta Crystals, C53, 1997.
13. R.Selvakumar, "Studies on Simple Salts and Metal complexes of Oxalic, Malonic and Sulfoacetic acids with hydrazine/guanylhydrazine'', Ph.D., Thesis, Bharathiar University, Coimbatore, India 2011.