September 2007 Volume 2 Issue 3

Trade Science Inc.

Inorganic CHEMISTRY

An Indian Journal

Full Paper

ICAIJ, 2(3), 2007 [158-167]

DFT Based Study Of Derivatives Of Pyridine And Their Interacton With Metal Halides-Part-II

S.Saxena[2], Abhay Srivastava[2], J.P.Singh[2], P.P.Singh[1]*
[1]Department of Chemistry Bareilly College Bareilly, (INDIA)
[2]Department of Physics Bareilly College Bareilly, (INDIA)
E-mail : dr_ppsingh@sify.com

Received: 2th May, 2007 ; Accepted: 7th May, 2007

ABSTRACT

HOMO and LUMO energies, absolute hardness and electronegativity of 34 derivatives of pyridine and halides of tin, zinc, cadmium and mercury have been evaluated by DFT method using CAChe software. Pyridine derivatives have been considered as base(B) and metal halides as accepters(A). The metal-ligand bond strength has been measured by charge transfer ΔN, and energy lowering ΔE values, derived by solving the equations-$\Delta N=(\chi^o_A - \chi^o_B) / 2(\eta_A+\eta_B)$ and $\Delta E=(\chi^o_A-\chi^o_B)^2/4(\eta_A+\eta_B)$, (where η is absolute hardness and χ is electronegativity). The ΔN and ΔE values indicate that metal-ligand bond strength is strongest in $SnCl_4{\cdot}2L$(L=ortho aminopyridine), and weakest in $SnCl_4{\cdot}2L$(L=para nitropyridine). A comparative stability of metal-ligand bond in 204 complexes has been presented. The effect of ortho, meta, para substitution on metal-ligand bond is also reported.

KEYWORDS

Metal-ligand bond;
Charge transfer;
Energy lowering;
Absolute hardness;
DFT calculation;
Pyridine derivatives.

INTRODUCTION

In our recent communication, we have made DFT based study of frontier orbital of Lewis acids and bases[1]. A theoretical study of metal-ligand interaction has shown to have very close relation with experimental results. In this paper we present a study of HOMO-LUMO energy, absolute hardness and electronegativity of 34 derivatives of pyridine and their interaction with tin (IV) halides and halides of zinc, cadmium and mercury. The magnitude of metal-ligand interaction has mainly been adjudged on the basis of values derived for transfer of charge ΔN, and lowering of energy ΔE on complex formation.

MATERIALS AND METHOD

SnX_4 [X=Cl, Br, I] and MCl_2 [M=Zn, Cd, Hg] have been used as Lewis acids and 34 derivatives of pyridine listed in TABLE 1 have been used as Lewis bases. For metal-ligand interaction study, the 3D modeling, and geometry optimization of all the compounds have been done with the help of CAChe software, using DFT-B88-PW91 method in conjunction with DZVP basis set. The values of absolute hardness and electronegativity of Lewis acid and Lewis bases have been evaluated by solving the equation[2,3] 1 and 2.

$$\chi = \tfrac{1}{2}\ (I+A) \qquad (1)$$

$$\eta = \tfrac{1}{2}\ (I-A) \qquad (2)$$

When Lewis acid reacts with Lewis base there is a shift of electron from the Lewis base to Lewis acid, until the chemical potentials of both becomes equal. The condition of equilibrium is that the chemical potential, μ_A and μ_B, becomes equal. This leads to shift in charge, ΔN, from less electronegative base (B) to more electronegative acid (A), as shown in equation[4,5]

$$\Delta N = (\chi^o_A - \chi^o_B)/2(\eta_A + \eta_B) \qquad (3)$$

Electron transfer leads to an energy lowering given by equation 4.

$$\Delta E = (\chi^o_A - \chi^o_B)^2/4(\eta_A + \eta_B) \qquad (4)$$

In equation 3 and 4 the electronegativity difference derive the electron transfer, and the sum of hardness parameters inhibits it. The hardness is the resistance of the chemical potential to change in the number of electrons. That is,

$$2\eta = (\delta\mu/\delta N)_z \qquad (5)$$

The chemical potential and the absolute electronegativity are molecular properties and not orbital properties. According to Koopman's[5] theorem the I is simply the eigen value of HOMO with change of sign and A is the eigen value of LUMO with change of sign, hence the equation-4 can be written as-

$$\eta = \tfrac{1}{2}(\varepsilon LUMO - \varepsilon HOMO) \qquad (6)$$

RESULTS AND DISCUSSION

Absolute hardness of pyridine derivatives

The HOMO and LUMO energies[7,9] of a series of derivatives of pyridine have been derived with the help of Cache software. The difference in their energies have been evaluated and absolute hardness (η) have been calculated by using the following equation[10,11].

$$\eta = \tfrac{1}{2}(\varepsilon LUMO - \varepsilon HOMO)$$

The values are given in TABLE 1. The values of absolute hardness indicate

(1) The hardness of pyridine increases in its fluoro and bromo derivatives and slightly decreases in chloro and iodo derivatives. The increase in hardness will favour better reaction with harder Lewis acid, and decrease will favour comparatively weaker interaction with hard Lewis acids.

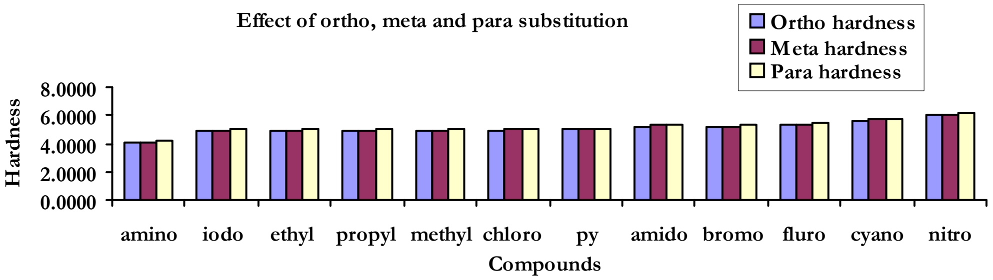
(2) Substitution of methyl, ethyl and propyl at ortho, meta and para position makes the pyridine soft as the values of absolute hardness decrease in all cases.

(3) The nitro, cyano and amido substituents at ortho, meta and para positions increase the hardness of pyridine considerably. The highest values are indicated by nitro substituent and lowest by

TABLE 1 : Absolute hardness values of pyridine derivatives drawn from eigen values of HOMO and LUMO

Com. No.	Compound	εHOMO	εLUMO	LUMO-HOMO	η
1	C_5H_4FN-o	-10.2114	-0.3707	-10.5821	-5.2910
2	C_5H_4FN-m	-10.1855	-0.3761	-10.5616	-5.2808
3	C_5H_4FN-p	-10.4678	-0.3616	-10.8294	-5.4147
4	C_5H_5N	-10.1031	-0.0053	-10.1084	-5.0542
5	C_5H_4ClN-o	-9.6498	-0.3008	-9.9506	-4.9753
6	C_5H_4ClN-m	-9.6692	-0.3173	-9.9864	-4.9932
7	C_5H_4ClN-p	-9.9228	-0.3116	-10.2344	-5.1172
8	C_5H_4BrN-o	-10.1047	-0.3403	-10.4450	-5.2225
9	C_5H_4BrN-m	-10.1158	-0.3350	-10.4508	-5.2254
10	C_5H_4BrN-p	-10.3694	-0.3752	-10.7446	-5.3723
11	C_5H_4IN-o	-9.1118	-0.5932	-9.7050	-4.8525
12	C_5H_4IN-m	-9.2212	-0.6802	-9.9014	-4.9507
13	C_5H_4IN-p	-9.3583	-0.7304	-10.0887	-5.0443
14	$C_5H_4NO_2N$-o	-10.0051	-2.0778	-12.0829	-6.0414
15	$C_5H_4NO_2N$-m	-9.9793	-2.1334	-12.1127	-6.0563
16	$C_5H_4NO_2N$-p	-10.1962	-2.2061	-12.4023	-6.2012
17	$C_5H_4CONH_2N$-o	-9.7525	-0.6802	-10.4327	-5.2163
18	$C_5H_4CONH_2N$-m	-9.8949	-0.7105	-10.6054	-5.3027
19	$C_5H_4CONH_2N$-p	-9.9618	-0.7182	-10.6800	-5.3400
20	$C_5H_4CH_3N$-o	-9.8024	0.0034	-9.7991	-4.8995
21	$C_5H_4CH_3N$-m	-9.8114	-0.0090	-9.8204	-4.9102
22	$C_5H_4CH_3N$-p	-10.0597	0.0006	-10.0591	-5.0296
23	$C_5H_4C_2H_5N$-o	-9.7612	0.0261	-9.7352	-4.8676
24	$C_5H_4C_2H_5N$-m	-9.7730	0.0141	-9.7590	-4.8795
25	$C_5H_4C_2H_5N$-p	-10.0367	0.0212	-10.0155	-5.0077
26	$C_5H_4C_3H_7N$-o	-9.7631	0.0227	-9.7404	-4.8702
27	$C_5H_4C_3H_7N$-m	-9.7750	0.0110	-9.7639	-4.8820
28	$C_5H_4C_3H_7N$-p	-10.0397	0.0183	-10.0214	-5.0107
29	$C_5H_4NH_2N$-o	-8.3566	0.2962	-8.0604	-4.0302
30	$C_5H_4NH_2N$-m	-8.3507	0.2592	-8.0914	-4.0457
31	$C_5H_4NH_2N$-p	-8.5852	0.2840	-8.3012	-4.1506
32	C_5H_4CNN-o	-10.4355	-0.9075	-11.3430	-5.6715
33	C_5H_4CNN-m	-10.4414	-0.9400	-11.3814	-5.6907
34	C_5H_4CNN-p	-10.6269	-0.9477	-11.5745	-5.7873

o=ortho, m=meta, p=para.



G-1

amido. The sequence is as below.

nitro>cyano>amido

(4) The amino substitution at ortho, meta and para positions, decreases the absolute hardness values and makes the pyridine favorable for soft interaction.

(5) The of effect of ortho, meta and para substitution on absolute hardness shows the following trend.

i. With one exception of chloro derivative where ortho and meta substituents decrease the hardness of pyridine and para substituent increases the hardness, in all other cases ortho meta and para substituents have similar effect on hardness of pyridine, that is if ortho of one substituent increase the hardness, the meta and para substituents will also increase the hardness.

ii. In case of fluro derivative the para substituent increases the hardness by 0.36, ortho by 0.24 and meta by 0.23. In other words the para has greater effect and meta has lesser effect. In case of bromo derivative the effect has the same sequence that is para>meta>ortho

iii. The chloro and iodo derivatives decrease the hardness of pyridine, the maximum decrease is shown by ortho followed by meta in both the cases. The para substituent has negligible effect.

iv. The nitro substituent at para position increases the hardness of pyridine by 1.2, the substituent at ortho and meta position increase the hardness by 1.05, and 1.04 respectively. This shows that para substituent has greater effect.

v. In case of amino substituents, the effect of para substituent is greater than meta and ortho. The next is meta. The sequence is para>meta>ortho

vi. The alkyl substituents decrease the hardness of pyridine. The value of hardness in all cases are in the following order para>meta>ortho

vii. The amino substituents at ortho, meta and para positions also have a sequence similar to alkyl substituents, i.e. para>meta>ortho

viii. The cyano substituents considerably increase the hardness value. The para has the highest value, and the sequence is para>meta>ortho

The variation in absolute hardness values in ortho meta and para positions, in various derivatives is shown in the graph. Figure G-1

(6) The important results derived from the above discussion are presented below.

i. The energy of HOMO reflects the relative reactivity of different molecule, thus molecules with small ionization potential(-εHOMO) are reported to be more reactive as nucleophile[12]. The lowest value of HOMO is 8.35 which is shown by ortho amino pyridine and the highest is shown by cyano pyridine, the value being 10.62. In other words the ortho amino pyridine is most reactive out of all the derivatives of pyridine.

ii. The activity has also been examined in between ortho, meta and para substituents. In case of fluro derivatives the meta is most reactive, where is in other halogen derivatives the ortho substituents are more reactive. In case of nitro derivatives, meta is most reactive.

iii. The absolute hardness is a measure of hardness, where as the HOMO energy is a measure of reactivity. The para substituents have higher value of hardness, whereas the reactivity is more either in ortho or in meta substituents.

Absolute hardness of metal halides

The energies of LUMO and HOMO of metal

TABLE 2 : Absolute hardness values of metal halides drawn from eigen values of HOMO and LUMO

Chemical sample	εHOMO	εLUMO	LUMO-HOMO	η
$ZnCl_2$	0.88	4.778	3.8980	1.9490
$CdCl_2$	-7.902	-3.253	4.6490	2.3245
$HgCl_2$	-8.489	-4.533	3.9560	1.9780
$SnCl_4$	-8.086	-4.5	3.5860	1.7930
$SnBr_4$	-7.27	-4.342	2.9280	1.4640
SnI_4	-6.497	-4.359	2.1380	1.0690

halides, the values of difference between the two energies, and the values of absolute hardness are included in TABLE 2. A reference to the TABLE indicates that

i. The values of hardness are highest in case of zinc halides and lowest in case of mercury halides. The hardness value for $ZnCl_2$, is 2.752, that of $CdCl_2$ and $HgCl_2$ are 2.324 and 1.978 respectively.

ii. In case of Sn(IV) halides, the iodide derivative is softer than its bromide and chloride derivatives.

Charge transfer ΔN and energy lowering ΔE

There have been a number of molecular orbital treatments of Lewis acid-base reaction. The Mulliken[13] treatment has been recognized as best for donor acceptor interaction in charge transfer complexes. This theory uses only electron affinity A_A for acceptor and only ionization potential I_B for the electron donor. The quantity(I_B-A_A) is an energy cost of transfer of per electron for donor to acceptor to decide which of the two molecules is donor and which is acceptor, we have the following equation-

$$(I_A-A_B)-(I_B-A_A)=2(\chi_A^o-\chi_B^o) \qquad (7)$$

where is in other halogen derivatives the ortho substituents are more reactive. In case of nitro derivatives, meta is most reactive.

In amino, amido and alkyl derivatives, the ortho substituents are most reactive, whereas in case of cyano derivatives the meta substituent is most reactive.

A positive value indicates that it cost less energy to transfer an electron from B to A. Thus the direction of electron transfer is determined by the absolute electronegativity and the magnitude is the deriving force for electron transfer. The absolute electronegativity of acceptor(A) and donors(B) are included in TABLE 3. A lower value of electronegativity is indicative of a better donor character whereas a higher value of electronegativity is indicative of a better acceptor character[4]. A reference to the table indicates that electronegativity values of donor molecules are less than that of acceptor molecules hence the equation-7 has a positive value. The values indicated that the acceptor strength of Sn(IV) halides will be $SnCl_4$>$SnBr_4$>SnI_4 and in case of Zn, Cd and Hg halides, the Hg halides will be the best acceptor when react with donor molecules.

The electronegativity(χ) difference derives the electron transfer and the sum of hardness parameters(η) inhibits it. The net result of shift in charge ΔN and lowering in energy ΔE due to electron transfer is given by the equation 3 and 4. The values of ΔN and E of 204 complexes formed between derivatives of pyridine and halides of tin, zinc, cadmium and mercury have been evaluated and are reported in TABLE 3. A reference to these tables provides the following valuables information about the stability of metal ligand bond.

(1) The electronegativity values of ortho, meta and para fluoro pyridine are 5.29, 5.28, 5.41, respectively. The lower is the value; the better is the donor ability. The sequence of donor ability is accordingly meta>ortho>para. In all other halogen derivatives the highest value is shown by para substituents and lowest by ortho substituent, hence the best donors are ortho derivatives. The values of electronegativity of different halogen substituents are in the following order, being 5.29, 5.22, 4.97 and 4.88. fluoro>bromo>chloro>iodo.

(2) The donor ability will therefore be in reverse order. The electronegativity value of pyridine is 5.05, which indicates that iodo and chloro substitution at ortho position increase the donor ability of pyridine whereas fluoro and bromo substituents at ortho position decrease the donor ability. The meta substituents have almost the same effect. The substituents at para position have negligible effect on donor ability of pyridine.

(3) Nitro substitution at ortho, meta and para position increase the electronegativity considerably. The value goes high and becomes more

TABLE 3 : The Absolute hardness and electronegativity of acid (A) and base (B) and ΔN and ΔE derived from them

Acid	Base	Complex No.	η acid	χ acid	η base	χ base	ΔN	ΔE
$SnCl_4$	C_5H_4FN-o	1	1.793	6.293	4.92037	5.29103	0.0746	0.0374
$SnBr_4$	C_5H_4FN-o	2	1.464	5.806	4.92037	5.29103	0.0403	0.0104
SnI_4	C_5H_4FN-o	3	1.069	5.428	4.92037	5.29103	0.0114	0.0008
$ZnCl_2$	C_5H_4FN-o	4	1.949	2.829	4.92037	5.29103	-0.1792	0.2206
$CdCl_2$	C_5H_4FN-o	5	2.3247	5.577	4.92037	5.29103	0.0197	0.0028
$HgCl_2$	C_5H_4FN-o	6	1.9779	6.5107	4.92037	5.29103	0.0884	0.0539
$SnCl_4$	C_5H_4FN-m	7	1.793	6.293	4.90471	5.28079	0.0756	0.0382
$SnBr_4$	C_5H_4FN-m	8	1.464	5.806	4.90471	5.28079	0.0412	0.0108
SnI_4	C_5H_4FN-m	9	1.069	5.428	4.90471	5.28079	0.0123	0.0009
$ZnCl_2$	C_5H_4FN-m	10	1.949	2.829	4.90471	5.28079	-0.1789	0.2193
$CdCl_2$	C_5H_4FN-m	11	2.3247	5.577	4.90471	5.28079	0.0205	0.003
$HgCl_2$	C_5H_4FN-m	12	1.9779	6.5107	4.90471	5.28079	0.0893	0.0549
$SnCl_4$	C_5H_4FN-p	13	1.793	6.293	5.05311	5.41469	0.0641	0.0282
$SnBr_4$	C_5H_4FN-p	14	1.464	5.806	5.05311	5.41469	0.03	0.0059
SnI_4	C_5H_4FN-p	15	1.069	5.428	5.05311	5.41469	0.0011	0
$ZnCl_2$	C_5H_4FN-p	16	1.949	2.829	5.05311	5.41469	-0.1846	0.2387
$CdCl_2$	C_5H_4FN-p	17	2.3247	5.577	5.05311	5.41469	0.011	0.0009
$HgCl_2$	C_5H_4FN-p	18	1.9779	6.5107	5.05311	5.41469	0.0779	0.0427
$SnCl_4$	C_5H_5N	19	1.793	6.293	5.04891	5.05419	0.0905	0.0561
$SnBr_4$	C_5H_5N	20	1.464	5.806	5.04891	5.05419	0.0577	0.0217
SnI_4	C_5H_5N	21	1.069	5.428	5.04891	5.05419	0.0306	0.0057
$ZnCl_2$	C_5H_5N	22	1.949	2.829	5.04891	5.05419	-0.159	0.1769
$CdCl_2$	C_5H_5N	23	2.3247	5.577	5.04891	5.05419	0.0355	0.0093
$HgCl_2$	C_5H_5N	24	1.9779	6.5107	5.04891	5.05419	0.1036	0.0755
$SnCl_4$	C_5H_4ClN-o	25	1.793	6.293	4.6745	4.97531	0.1019	0.0671
$SnBr_4$	C_5H_4ClN-o	26	1.464	5.806	4.6745	4.97531	0.0677	0.0281
SnI_4	C_5H_4ClN-o	27	1.069	5.428	4.6745	4.97531	0.0394	0.0089
$ZnCl_2$	C_5H_4ClN-o	28	1.949	2.829	4.6745	4.97531	-0.162	0.1739
$CdCl_2$	C_5H_4ClN-o	29	2.3247	5.577	4.6745	4.97531	0.043	0.0129
$HgCl_2$	C_5H_4ClN-o	30	1.9779	6.5107	4.6745	4.97531	0.1154	0.0886
$SnCl_4$	C_5H_4ClN-m	31	1.793	6.293	4.67595	4.9932	0.1005	0.0653
$SnBr_4$	C_5H_4ClN-m	32	1.464	5.806	4.67595	4.9932	0.0662	0.0269
SnI_4	C_5H_4ClN-m	33	1.069	5.428	4.67595	4.9932	0.0378	0.0082
$ZnCl_2$	C_5H_4ClN-m	34	1.949	2.829	4.67595	4.9932	-0.1633	0.1767
$CdCl_2$	C_5H_4ClN-m	35	2.3247	5.577	4.67595	4.9932	0.0417	0.0122
$HgCl_2$	C_5H_4ClN-m	36	1.9779	6.5107	4.67595	4.9932	0.114	0.0865
$SnCl_4$	C_5H_4ClN-p	37	1.793	6.293	4.80557	5.11721	0.0891	0.0524
$SnBr_4$	C_5H_4ClN-p	38	1.464	5.806	4.80557	5.11721	0.0549	0.0189
SnI_4	C_5H_4ClN-p	39	1.069	5.428	4.80557	5.11721	0.0265	0.0041
$ZnCl_2$	C_5H_4ClN-p	40	1.949	2.829	4.80557	5.11721	-0.1694	0.1938
$CdCl_2$	C_5H_4ClN-p	41	2.3247	5.577	4.80557	5.11721	0.0322	0.0074
$HgCl_2$	C_5H_4ClN-p	42	1.9779	6.5107	4.80557	5.11721	0.1027	0.0716
$SnCl_4$	C_5H_4BrN-o	43	1.793	6.293	4.88224	5.22249	0.0802	0.0429
$SnBr_4$	C_5H_4BrN-o	44	1.464	5.806	4.88224	5.22249	0.046	0.0134
SnI_4	C_5H_4BrN-o	45	1.069	5.428	4.88224	5.22249	0.0173	0.0018
$ZnCl_2$	C_5H_4BrN-o	46	1.949	2.829	4.88224	5.22249	-0.1752	0.2097
$CdCl_2$	C_5H_4BrN-o	47	2.3247	5.577	4.88224	5.22249	0.0246	0.0044
$HgCl_2$	C_5H_4BrN-o	48	1.9779	6.5107	4.88224	5.22249	0.0939	0.0605
$SnCl_4$	C_5H_4BrN-m	49	1.793	6.293	4.89039	5.22538	0.0799	0.0426
$SnBr_4$	C_5H_4BrN-m	50	1.464	5.806	4.89039	5.22538	0.0457	0.0133
SnI_4	C_5H_4BrN-m	51	1.069	5.428	4.89039	5.22538	0.017	0.0017
$ZnCl_2$	C_5H_4BrN-m	52	1.949	2.829	4.89039	5.22538	-0.1752	0.2099
$CdCl_2$	C_5H_4BrN-m	53	2.3247	5.577	4.89039	5.22538	0.0244	0.0043
$HgCl_2$	C_5H_4BrN-m	54	1.9779	6.5107	4.89039	5.22538	0.0936	0.0601
$SnCl_4$	C_5H_4BrN-p	55	1.793	6.293	4.99709	5.37229	0.0678	0.0312

Continue on next page

Acid	Base	Complex No.	η acid	χ acid	η base	χ base	ΔN	ΔE
$SnBr_4$	C_5H_4BrN-p	56	1.464	5.806	4.99709	5.37229	0.0336	0.0073
SnI_4	C_5H_4BrN-p	57	1.069	5.428	4.99709	5.37229	0.0046	0.0001
$ZnCl_2$	C_5H_4BrN-p	58	1.949	2.829	4.99709	5.37229	-0.1831	0.2328
$CdCl_2$	C_5H_4BrN-p	59	2.3247	5.577	4.99709	5.37229	0.014	0.0014
$HgCl_2$	C_5H_4BrN-p	60	1.9779	6.5107	4.99709	5.37229	0.0816	0.0465
$SnCl_4$	C_5H_4IN-o	61	1.793	6.293	4.25934	4.85251	0.119	0.0857
$SnBr_4$	C_5H_4IN-o	62	1.464	5.806	4.25934	4.85251	0.0833	0.0397
SnI_4	C_5H_4IN-o	63	1.069	5.428	4.25934	4.85251	0.054	0.0155
$ZnCl_2$	C_5H_4IN-o	64	1.949	2.829	4.25934	4.85251	-0.163	0.1649
$CdCl_2$	C_5H_4IN-o	65	2.3247	5.577	4.25934	4.85251	0.055	0.0199
$HgCl_2$	C_5H_4IN-o	66	1.9779	6.5107	4.25934	4.85251	0.1329	0.1102
$SnCl_4$	C_5H_4IN-m	67	1.793	6.293	4.27052	4.95071	0.1107	0.0743
$SnBr_4$	C_5H_4IN-m	68	1.464	5.806	4.27052	4.95071	0.0746	0.0319
SnI_4	C_5H_4IN-m	69	1.069	5.428	4.27052	4.95071	0.0447	0.0107
$ZnCl_2$	C_5H_4IN-m	70	1.949	2.829	4.27052	4.95071	-0.1706	0.1809
$CdCl_2$	C_5H_4IN-m	71	2.3247	5.577	4.27052	4.95071	0.0475	0.0149
$HgCl_2$	C_5H_4IN-m	72	1.9779	6.5107	4.27052	4.95071	0.1248	0.0974
$SnCl_4$	C_5H_4IN-p	73	1.793	6.293	4.31399	5.04434	0.1022	0.0638
$SnBr_4$	C_5H_4IN-p	74	1.464	5.806	4.31399	5.04434	0.0659	0.0251
SnI_4	C_5H_4IN-p	75	1.069	5.428	4.31399	5.04434	0.0356	0.0068
$ZnCl_2$	C_5H_4IN-p	76	1.949	2.829	4.31399	5.04434	-0.1769	0.1959
$CdCl_2$	C_5H_4IN-p	77	2.3247	5.577	4.31399	5.04434	0.0401	0.0107
$HgCl_2$	C_5H_4IN-p	78	1.9779	6.5107	4.31399	5.04434	0.1165	0.0854
$SnCl_4$	$C_5H_4NO_2N$-o	79	1.793	6.293	3.96365	6.04144	0.0218	0.0027
$SnBr_4$	$C_5H_4NO_2N$-o	80	1.464	5.806	3.96365	6.04144	-0.0217	0.0026
SnI_4	$C_5H_4NO_2N$-o	81	1.069	5.428	3.96365	6.04144	-0.0609	0.0187
$ZnCl_2$	$C_5H_4NO_2N$-o	82	1.949	2.829	3.96365	6.04144	-0.2717	0.4363
$CdCl_2$	$C_5H_4NO_2N$-o	83	2.3247	5.577	3.96365	6.04144	-0.0369	0.0086
$HgCl_2$	$C_5H_4NO_2N$-o	84	1.9779	6.5107	3.96365	6.04144	0.0395	0.0093
$SnCl_4$	$C_5H_4NO_2N$-m	85	1.793	6.293	3.92296	6.05634	0.0207	0.0024
$SnBr_4$	$C_5H_4NO_2N$-m	86	1.464	5.806	3.92296	6.05634	-0.0232	0.0029
SnI_4	$C_5H_4NO_2N$-m	87	1.069	5.428	3.92296	6.05634	-0.0629	0.0198
$ZnCl_2$	$C_5H_4NO_2N$-m	88	1.949	2.829	3.92296	6.05634	-0.2748	0.4435
$CdCl_2$	$C_5H_4NO_2N$-m	89	2.3247	5.577	3.92296	6.05634	-0.0384	0.0092
$HgCl_2$	$C_5H_4NO_2N$-m	90	1.9779	6.5107	3.92296	6.05634	0.0385	0.0087
$SnCl_4$	$C_5H_4NO_2N$-p	91	1.793	6.293	3.99505	6.20115	0.0079	0.0004
$SnBr_4$	$C_5H_4NO_2N$-p	92	1.464	5.806	3.99505	6.20115	-0.0362	0.0072
SnI_4	$C_5H_4NO_2N$-p	93	1.069	5.428	3.99505	6.20115	-0.0763	0.0295
$ZnCl_2$	$C_5H_4NO_2N$-p	94	1.949	2.829	3.99505	6.20115	-0.2837	0.4783
$CdCl_2$	$C_5H_4NO_2N$-p	95	2.3247	5.577	3.99505	6.20115	-0.0494	0.0154
$HgCl_2$	$C_5H_4NO_2N$-p	96	1.9779	6.5107	3.99505	6.20115	0.0259	0.004
$SnCl_4$	$C_5H_4CONH_2N$-o	97	1.793	6.293	4.536	5.216	0.085	0.046
$SnBr_4$	$C_5H_4CONH_2N$-o	98	1.464	5.806	4.536	5.216	0.049	0.014
SnI_4	$C_5H_4CONH_2N$-o	99	1.069	5.428	4.536	5.216	0.019	0.002
$ZnCl_2$	$C_5H_4CONH_2N$-o	100	1.949	2.829	4.536	5.216	-0.184	0.22
$CdCl_2$	$C_5H_4CONH_2N$-o	101	2.325	5.577	4.536	5.216	0.026	0.005
$HgCl_2$	$C_5H_4CONH_2N$-o	102	1.978	6.511	4.536	5.216	0.099	0.064
$SnCl_4$	$C_5H_4CONH_2N$-m	103	1.793	6.293	4.592	5.303	0.078	0.038
$SnBr_4$	$C_5H_4CONH_2N$-m	104	1.464	5.806	4.592	5.303	0.042	0.01
SnI_4	$C_5H_4CONH_2N$-m	105	1.069	5.428	4.592	5.303	0.011	0.001
$ZnCl_2$	$C_5H_4CONH_2N$-m	106	1.949	2.829	4.592	5.303	-0.189	0.234
$CdCl_2$	$C_5H_4CONH_2N$-m	107	2.325	5.577	4.592	5.303	0.02	0.003
$HgCl_2$	$C_5H_4CONH_2N$-m	108	1.978	6.511	4.592	5.303	0.092	0.056
$SnCl_4$	$C_5H_4CONH_2N$-p	109	1.793	6.293	4.622	5.34	0.074	0.035
$SnBr_4$	$C_5H_4CONH_2N$-p	110	1.464	5.806	4.622	5.34	0.038	0.009
SnI_4	$C_5H_4CONH_2N$-p	111	1.069	5.428	4.622	5.34	0.008	0

Continue on next page

Acid	Base	Complex No.	η acid	χ acid	η base	χ base	ΔN	ΔE
$ZnCl_2$	$C_5H_4CONH_2N$-p	112	1.949	2.829	4.622	5.34	-0.191	0.24
$CdCl_2$	$C_5H_4CONH_2N$-p	113	2.325	5.577	4.622	5.34	0.017	0.002
$HgCl_2$	$C_5H_4CONH_2N$-p	114	1.978	6.511	4.622	5.34	0.089	0.052
$SnCl_4$	$C_5H_4CH_3N$-o	115	1.793	6.293	4.903	4.9	0.104	0.072
$SnBr_4$	$C_5H_4CH_3N$-o	116	1.464	5.806	4.903	4.9	0.071	0.032
SnI_4	$C_5H_4CH_3N$-o	117	1.069	5.428	4.903	4.9	0.044	0.012
$ZnCl_2$	$C_5H_4CH_3N$-o	118	1.949	2.829	4.903	4.9	-0.151	0.156
$CdCl_2$	$C_5H_4CH_3N$-o	119	2.325	5.577	4.903	4.9	0.047	0.016
$HgCl_2$	$C_5H_4CH_3N$-o	120	1.978	6.511	4.903	4.9	0.117	0.094
$SnCl_4$	$C_5H_4CH_3N$-m	121	1.793	6.293	4.901	4.91	0.103	0.071
$SnBr_4$	$C_5H_4CH_3N$-m	122	1.464	5.806	4.901	4.91	0.07	0.032
SnI_4	$C_5H_4CH_3N$-m	123	1.069	5.428	4.901	4.91	0.043	0.011
$ZnCl_2$	$C_5H_4CH_3N$-m	124	1.949	2.829	4.901	4.91	-0.152	0.158
$CdCl_2$	$C_5H_4CH_3N$-m	125	2.325	5.577	4.901	4.91	0.046	0.015
$HgCl_2$	$C_5H_4CH_3N$-m	126	1.978	6.511	4.901	4.91	0.116	0.093
$SnCl_4$	$C_5H_4CH_3N$-p	127	1.793	6.293	5.03	5.03	0.093	0.058
$SnBr_4$	$C_5H_4CH_3N$-p	128	1.464	5.806	5.03	5.03	0.06	0.023
SnI_4	$C_5H_4CH_3N$-p	129	1.069	5.428	5.03	5.03	0.033	0.007
$ZnCl_2$	$C_5H_4CH_3N$-p	130	1.949	2.829	5.03	5.03	-0.158	0.173
$CdCl_2$	$C_5H_4CH_3N$-p	131	2.325	5.577	5.03	5.03	0.037	0.01
$HgCl_2$	$C_5H_4CH_3N$-p	132	1.978	6.511	5.03	5.03	0.106	0.078
$SnCl_4$	$C_5H_4C_2H_5N$-o	133	1.793	6.293	4.894	4.868	0.107	0.076
$SnBr_4$	$C_5H_4C_2H_5N$-o	134	1.464	5.806	4.894	4.868	0.074	0.035
SnI_4	$C_5H_4C_2H_5N$-o	135	1.069	5.428	4.894	4.868	0.047	0.013
$ZnCl_2$	$C_5H_4C_2H_5N$-o	136	1.949	2.829	4.894	4.868	-0.149	0.152
$CdCl_2$	$C_5H_4C_2H_5N$-o	137	2.325	5.577	4.894	4.868	0.049	0.017
$HgCl_2$	$C_5H_4C_2H_5N$-o	138	1.978	6.511	4.894	4.868	0.12	0.098
$SnCl_4$	$C_5H_4C_2H_5N$-m	139	1.793	6.293	4.894	4.879	0.106	0.075
$SnBr_4$	$C_5H_4C_2H_5N$-m	140	1.464	5.806	4.894	4.879	0.073	0.034
SnI_4	$C_5H_4C_2H_5N$-m	141	1.069	5.428	4.894	4.879	0.046	0.013
$ZnCl_2$	$C_5H_4C_2H_5N$-m	142	1.949	2.829	4.894	4.879	-0.15	0.154
$CdCl_2$	$C_5H_4C_2H_5N$-m	143	2.325	5.577	4.894	4.879	0.048	0.017
$HgCl_2$	$C_5H_4C_2H_5N$-m	144	1.978	6.511	4.894	4.879	0.119	0.097
$SnCl_4$	C_5H_4CNN-m	193	1.793	6.293	4.751	5.691	0.046	0.014
$SnBr_4$	C_5H_4CNN-m	194	1.464	5.806	4.751	5.691	0.009	0.001
SnI_4	C_5H_4CNN-m	195	1.069	5.428	4.751	5.691	-0.023	0.003
$ZnCl_2$	C_5H_4CNN-m	196	1.949	2.829	4.751	5.691	-0.214	0.306
$CdCl_2$	C_5H_4CNN-m	197	2.325	5.577	4.751	5.691	-0.008	0
$HgCl_2$	C_5H_4CNN-m	198	1.978	6.511	4.751	5.691	0.061	0.025
$SnCl_4$	C_5H_4CNN-p	199	1.793	6.293	4.84	5.787	0.038	0.01
$SnBr_4$	C_5H_4CNN-p	200	1.464	5.806	4.84	5.787	0.001	0
SnI_4	C_5H_4CNN-p	201	1.069	5.428	4.84	5.787	-0.03	0.005
$ZnCl_2$	C_5H_4CNN-p	201	1.949	2.829	4.84	5.787	-0.218	0.322
$CdCl_2$	C_5H_4CNN-p	203	2.325	5.577	4.84	5.787	-0.015	0.002
$HgCl_2$	C_5H_4CNN-p	204	1.978	6.511	4.84	5.787	0.053	0.019

B=base- pyridine derivatives, χ=electronegativity, η=absolute hardness ΔN=charge transfer, ΔE=energy lowering

than 6.04. This shows that donor ability of pyridine decreases, in all cases. On change of position at ortho, meta, and para the value changes to 6.04, 6.05 and 6.20 respectively. Since the value is lowest at ortho position, the ortho derivative will be a better donor.

(4) The amido derivative shows a trend similar to nitro derivative, but the value of electronegativity is lower than nitro derivative. The amido derivatives will be better donors as compared to nitro derivatives as their electronegativity values are 5.21 in ortho derivatives and 5.30 in meta and 5.34 in para derivative.

(5) The alkyl derivatives cause a decrease in electronegativity values, hence are supposed to be better donors. The values in ortho, meta and para substituent in methyl derivatives are 4.90, 4.91 and 5.03 respectively. In ethyl derivatives the corresponding values are 4.86, 4.87 and 5.00. The propyl derivatives have 4.87, 4.88 and 5.01 values in their ortho, meta and para derivatives. The above values indicate that donor ability of alkyl derivatives of pyridine is in the following order meta>para>ortho.

(6) It is also noticeable that para substituents in all the alkyl derivatives have higher electronegativity value, hence are comparatively weaker donor than their ortho and meta counterpart. The ortho derivatives have lowest values hence are better donors.

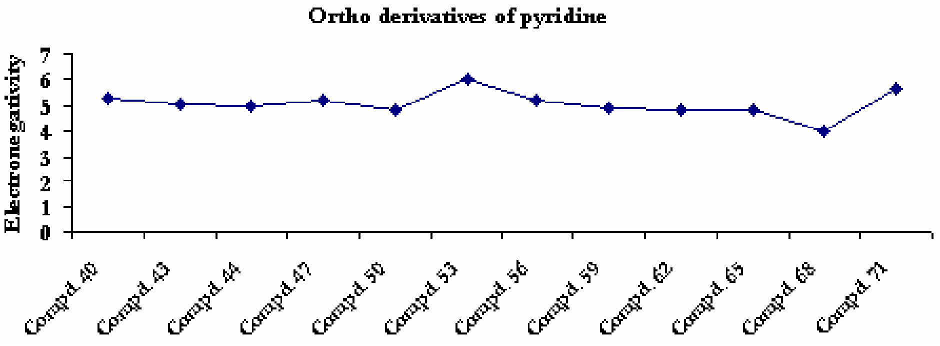
(7) The amino derivatives have the lowest values of electronegativity as compared to other derivatives studied here. The values are 4.03 for ortho, 4.04 for meta and 4.15 for para substituents. The lower value indicates that they are best donors. The trends in between ortho meta and para is similar to amido and alkyl derivatives. The ortho substituents are better donor than meta and para. The sequence is ortho>meta>para.

(8) The cyano derivatives have higher values of electronegativity as compared to pyridine. The values of ortho, meta and para derivatives are 5.67, 5.69 and 5.78 respectively. The sequence of donor ability will accordingly be ortho > meta>para. This sequence is similar to amido, alkyl and amino derivatives. The values of electronegativity of all the derivatives of pyridine studied here are represented in the form of graph, presented in figure G2, G3, G4.

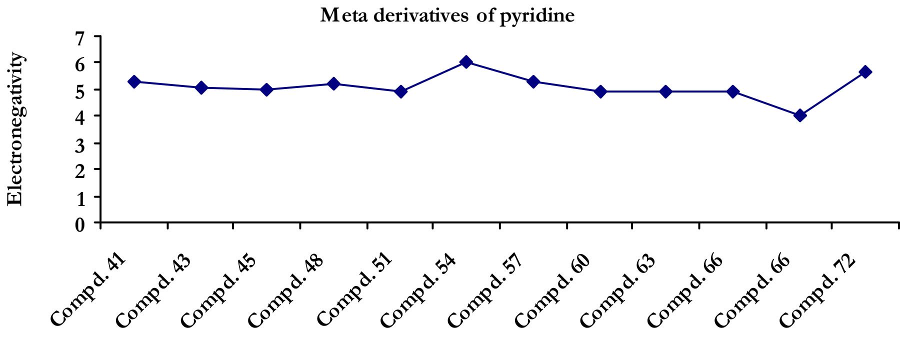
On the basis of electronegativity values of ortho substituents of various derivatives of pyridine, the sequence of donor ability will be as below-amino (4.03)>iodo (4.85)C_2H_5(4.86)>propyl (4.87)>methyl (4.90)>chloro(4.97)>Py(5.04)>amido(5.21)>Br (5.22)>F(5.29)>cyano (5.67)>nitro(6.04)

The examination of ΔN and ΔE values of complexes formed between various derivatives of pyridine and $SnCl_4$, $SnBr_4$ and SnI_4 indicates the following noticeable trends.

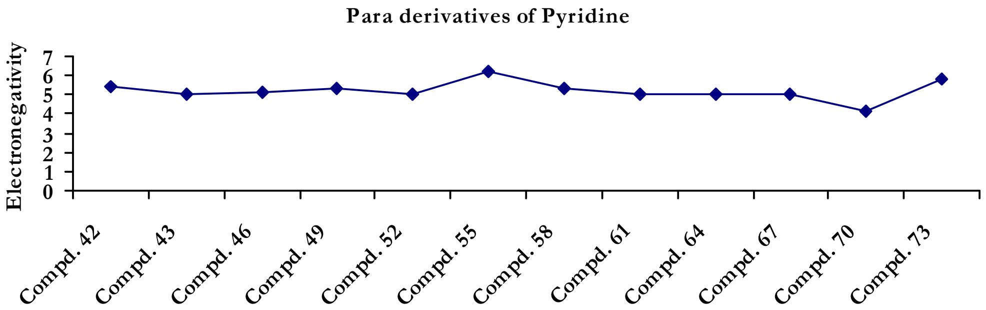
i. On reaction of ortho, meta and para derivatives of fluoro pyridine, the complexes formed by $SnCl_4$ are more stable, as ΔN and ΔE values are highest. The sequence is $SnCl_4$>$SnBr_4$>SnI_4. The values arte highest in meta substituents followed



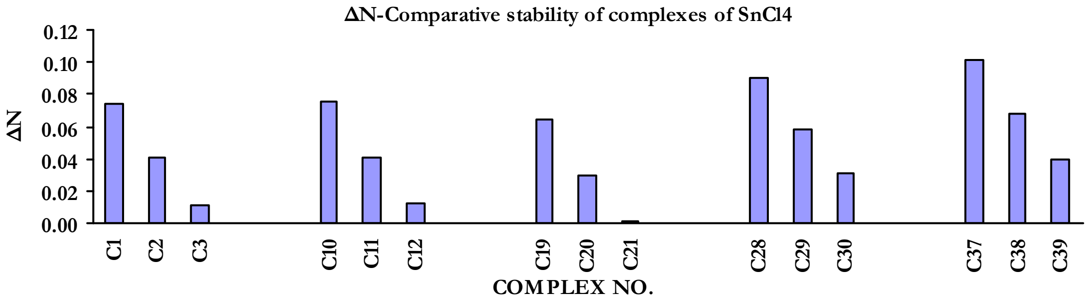
G-2



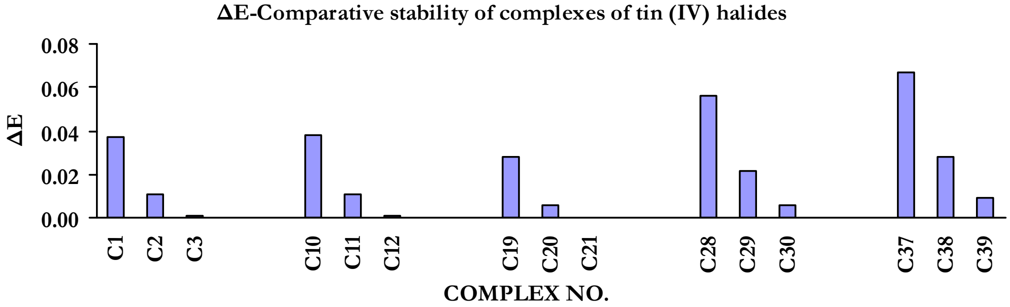
G-3



G-4



G-5



G-6

by ortho and the lowest is in para substituents.

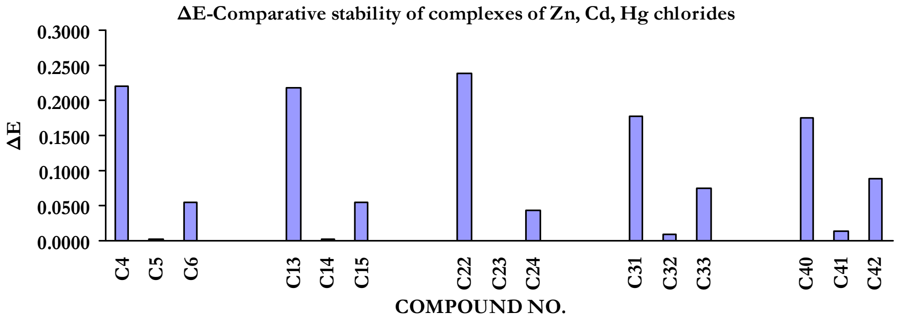
ii. Pyridine and its chloro, bromo, iodo, amido, methyl, ethyl, propyl, nitro and amino derivatives show the same trend as is shown by ortho, meta and para derivatives of fluro pyridine.

iii. The cyano derivative is the only exception where the sequence is $SnCl_4$>SnI_4> $SnBr_4$ in ortho, meta and para derivatives. This may be considered as outliers.

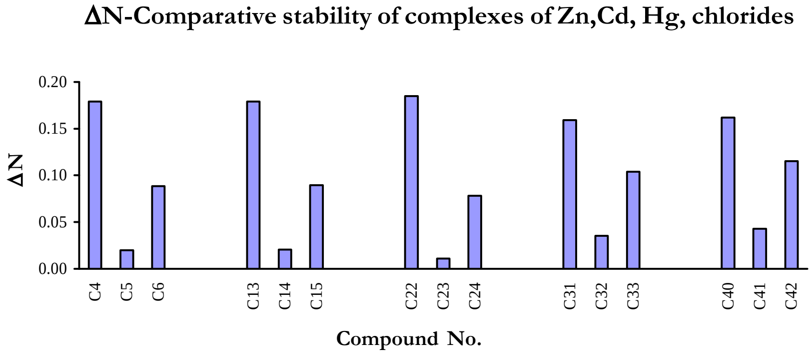
iv. In case of zinc, cadmium and mercury halides, the zinc forms the most stable complex with fluoro derivative of pyridine irrespective of the position of substituents at ortho, meta and para positions. The zinc halides have highest values of ΔN and ΔE, in the complexes formed by all the derivatives of pyridine studied here. The position of cadmium and mercury halide complexes changes. Sometimes the ΔN and ΔE values are higher for cadmium complexes and sometimes for mercury complexes.

v. The DN and DE values are highest for the complexes formed between $SnCl_4$, and ortho amino pyridine. The values are 0.185 and 0.209 respectively. The lowest values are for the complex formed between $SnCl_4$ and para nitro pyridine. The values are 0.0079 for DN and 0.0004 for ΔE.

vi. The comparative stability of complexes of $SnCl_4$ on the basis of ΔN and ΔE values are shown in the graph, figure G5 and figure G6 respectively and of $ZnCl_2$, $CdCl_2$ and $HgCl_2$ are shown in G7 A and G8.



G-7



G-8

REFERENCES

[1] S.Saxena, Abhay Srivastava, J.P.Singh, P.P.Singh; Inorg.Chem.(AI.J), **2**, 93, **(2007)**.

[2] P.Hohenberg, W.Kohn; Phys.Rev., **B136**, 864, **(1964)**.

[3] R.G.Parr, R.G.Pearson; J.Am.Chem.Soc., **105**, 7512, **(1983)**.

[4] R.G.Pearson; J.Am.Chem.Soc., **107**, 6806, **(1985)**.

[5] R.G.Parr, W.Yang; J.Am.Chem.Soc., **106**, 4049, **(1987)**.

[6] R.G.Parr, R.A.Donnelly, W.E.Palke, M.Levy; J.Chem.Phys., **69**, 3801, **(1978)**.

[7] R.Franke; Theoretical Drug Design Method, **123**, **(1984)**.

[8] K.Fukui; Theory of Orientation and Stereoselection. Springer Verlag-New York, 39 **(1975)**.

[9] I.Fleming; Frontier Orbital and Organic Chemical Reactions, John Wiley and Sons New York, **(1976)**.

[10] R.G.Pearson; Coord.Chem.Rev., **24**, 401, **(1994)**.

[11] A.C.Gaudio, A.Korolkovas; J.Pharma Sci., **83**, 1110, **(1994)**.

[12] A.Nakayama.K.Hagiwara, S.Hashimoto, S.Shimoda; Quant.Struct.Act.Relat., **12**, 251, **(1993)**.

[13] R.S.Mulliken, W.B.Pearson; Annu.Rev.Phys.Chem., **13**, 107, **(1962)**.