June 2010 ISSN: 0974 - 7516 Volume 6 Issue 2

Trade Science Inc.

Organic CHEMISTRY

An Indian Journal

Full Paper

OCAIJ, 6(2), 2010 [190-199]

Study of interaction between metal halides and sulphur donors by DFT B88-LYP based calculations

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Received: 27th February, 2010 ; Accepted: 9th March, 2010

ABSTRACT

Interaction energy (E_{int}), charge transfer (ΔN) and lowering of energy (ΔE) for 72 interactions between 12 metal halides (A) and 6 sulphur donors (B) have been evaluated with the help of Cache software using DFT B88-LYP method. The halides are chloride, bromide and iodide of tin, zinc, cadmium and mercury. The results indicate that acceptor strength is in the order $SnI_4 > SnBr_4 > CdCl_2 > CdI_2 > SnCl_4 > ZnCl_2 > HgCl_2 > CdBr_2 > HgI_2 > ZnI_2 > HgBr_2 > ZnBr_2$. The acceptor strength of tin halides are in the order iodide > bromide > chloride and halides of zinc, cadmium and mercury are in the order chloride > iodide > bromide. The chemical potential μ_A also supports the above order. Azepane-2-thione ($C_6H_{11}NS$) is the strongest base and thioformamide ($HCSNH_2$) is the weakest base against all the acceptors. The observation also indicates that best interaction is shown when global softness values of acid and base are equal.

KEYWORDS

Interaction energy;
Global softness;
Charge transfer;
Chemical potential;
Energy lowering;
Donor;
Acceptor.

INTRODUCTION

In recent years, density functional theory (DFT) has emerged as a powerful tool through which chemical concepts such as reactivity, selectivity, and reaction path of a system have been studied[1-5]. The concepts of chemical potential (μ), electronegativity, and hardness (η)[6-8],collectively known as global reactivity descriptors, have systematized the study in this area.

The principle of maximum hardness(PMH)[9], relating the relative stability of a system to a larger value of hardness, has been tested using semi-empirical as well as *ab initio* quantum chemical techniques[10]. Local reactivity descriptors, such as Fukui function (FF) and local softness, relating changes in electron density to the number of electrons and chemical potential, respectively, have been used to determine the sitereactivity of a system[11]. Electrophilic and nucleophilic FFs have been used as indicators of reactivity to nucleophilic and electrophilic reagents, respectively[12]. Roy et al.[13] proposed that relative electrophilicity and relative nucleophilicity, based on the ratio of electrophilic and nucleophilic FFs and its inverse, are more reliable descriptors to locate the preferable sites for electrophilic and nucleophilic attack respectively within a molecule. Parr and co-workers have defined a new concept of global philicity[14] using which Chattaraj and co-workers have defined local philicity indices[14b]. The importance of charges and different frontier-controlled descriptors in description of electrostatic interactions in ligand chemistry has been highlighted in the past[14c]. Recently, Tanwar et al. proposed two reactivity descriptors viz. normalized Fukui function (NFF) and bond deformation kernel (BDK)[14d] for comparative studies on the systems with varying number of atoms. A local version of the hard-soft-acid-base (HSAB) principle, proposed by Gazquez and Mendez[15], and pursued by Pal and co-workers[16], as well as, Geerlings and co-workers[17] to a variety of chemical situations, is suited to semiquantitative description of interaction energy.

MATERIAL AND METHOD

Mulliken[18,19] suggested that quantities of ionization potential (I) and electron affinity (A) are of primary importance for processes involving electron transfer reactions. The quantity (I_B-I_A) is an energy cost of transfer of per electron from donor to acceptor to decide which of the two molecules is donor and which is acceptor. The following equations was given,

$$(I_A-I_B)-(I_B-I_A) = 2(\chi^\circ_A-\chi^\circ_B) \qquad (1)$$

DFT[20-24] confirmed this conclusion by identifying the finite difference formula for chemical potential $\mu = (\delta E/\delta N)_v$ with the negative of Mulliken electronegativity. Moreover, using DFT arguments Parr et. al[25,26]. were able to recognize the importance of a second derivative of E vs. N. The finite difference formula for this second derivative,

$$\eta = \tfrac{1}{2}(\delta E/\delta N)_v = \tfrac{1}{2}(\delta\mu/\delta N)_v \approx \tfrac{1}{2}(I-A) \qquad (2)$$

Was identified by them as an operational definition of an absolute hardness[27-29]. Therefore, DFT provided a quantitative measure for a qualitative concept that was so successfully used in a description of Lewis acids and bases[30]. Parr and Pearson also derived simple expressions for the amount of charge transfer ΔN and energy change ΔE which accompany the formation of A:B complex from acid A and base :B. These expressions are,

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

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

Although equations (3) and (4) are incomplete, they have a great value in trying to predict a global change during the reaction with a minimum number of parameters. The shortcomings of equations 3 and 4 are known and were pointed out in original derivation. Thus the dependence of the chemical potential on the changing external field was neglected. Also, stereoselectivity of the reaction is not manifested through these expressions.

The process involving electron transfer reaction, was also described by interaction energy[31, 32] (ΔE_{int}), which is described as follows:

Consider a stable molecule A formed by the bonding of K atoms with a total number of electrons N_A, and a stable molecule B formed by the binding of L atoms with a total number of electrons N_B. The interaction energy between these two chemical species, according to DFT, is given by,

$$\Delta E_{int} = E\,[\rho_{AB}] - [\rho_A] - [\rho_B] \qquad (5)$$

It has been shown by Gazquez[30], that if the interaction energy is divided into two steps and one makes use of the properties of hardness and softness functions, then equation (5) can be written in the following form,

$$\Delta E_{int} = \Delta E_v + \Delta E\mu \qquad (6)$$

Where,

$$\Delta E_v\ -(\mu_A-\mu_B)^2.S_AS_B/\{2(S_A + S_B)\} \qquad (7)$$

And,

$$\Delta E_\mu \approx -\tfrac{1}{2}\,.\,\lambda/(S_A + S_B) \qquad (8)$$

Where μ = Chemical potential,

$$S = 1/\eta,\ \lambda = (N_A + N_B)^2/1000$$

The first term, ΔE_v, corresponds to the charge transfer process between A and B arising from the chemical potential equalization principle at constant external potential. The second term, ΔE_μ, corresponds to a reshuffling of the charge distribution, and it is basically a manifestation of the maximum hardness principle. In the original derivation of Gazquez[30] of equation (8), the proportionality factor was given by the product of a constant times the square of the total number of electrons (N_A + N_B). However, using the hardness functional, and the properties of the hardness and softness kernels, it was shown by Parr and Gazquez[30-33]at the correct proportionality factor is given by the product of a constant times the square of an "effective number of valence electrons". Thus, in equation (8), we have replaced this product by another constant λ.

We have considered the interaction between metal halides shown in TABLE 1 and sulphur donors shown in TABLE 2.

RESULT AND DISCUSSION

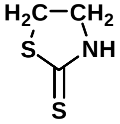
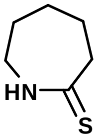
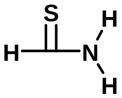
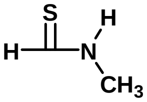
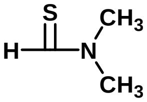
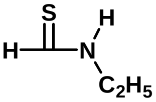
Donor acceptor interaction

The donor acceptor interaction between 6 sulphur

TABLE 1 : A series of twelve lewis acids (A) Acceptor molecules

S.No.	Name of acceptor	Formula of acceptor	S. No.	Name of acceptor	Formula of acceptor
1	Sn(iv) chloride	$SnCl_4$	7	Cd(IIchloride	$CdCl_2$
2	Sn(iv) bromide	$SnBr_4$	8	Cd(II)bromide	$CdBr_2$
3	Sn(iv)iodide	SnI_2	9	Cd(II)iodide	CdI_2
4	Zn(II)chloride	$ZnCl_2$	10	Hg(II)chloride	$HgCl_2$
5	Zn(II)bromide	$ZnBr_2$	11	Hg(II)bromide	$HgBr_2$
6	Zn(II)iodide	ZnI_2	12	Hg(II)iodide	HgI_2

TABLE 2 : Third series of lewis bases (B)- Sulphur donor

S. No.	Lewis bases (B)	Name of lewis bases	Structure of lewis bases
1	$C_3H_5NS_2$	1,3-thiazolidine-2-thione	
2	$C_6H_{11}NS$	azepane-2-thione	
3	$HCSNH_2$	thioformamide	
4	$HCSNHCH_3$	N-methylthioformamide	
5	$HCSN(CH_3)_2$	N,N-dimethylthioformamide	
6	$HCSNHC_2H_5$	N-ethylthioformamide	

donor molecules listed in TABLE 2 and twelve acceptor molecules listed in TABLE 1 has been studied in terms of metal ligand interaction energy (E_{int}). In total there are 72 (6 × 12) interactions between sulphur donors and the acceptor metal halides. The interaction energy of sulphur donors and metal halides are presented in TABLE 3-14.

Interaction of sulphur donors with acceptor metal halide

Stability of complexes formed by increases as the value of interaction energy decreases. Interaction energy of sulphur donors with acceptor metal halide $SnCl_4$ is shown in TABLE 3. The value of interaction energy of interaction of $C_6H_{11}NS$ with metal halide $SnCl_4$ is lowest (-26.490 Electron Volt) which indicates that the $C_6H_{11}NS$ forms most stable complex with $SnCl_4$. The value of interaction energy of interaction of $HCSNH_2$ with metal halide $SnCl_4$ is highest (-11.590 eV) which indicates that the $HCSNH_2$ forms least stable complex with $SnCl_4$. The values of interaction energy indicate that the order of the stability of complexes formed by sulphur donors with $SnCl_4$ is in the following order,

$C_6H_{11}NS > C_3H_5NS_2 > HCSN(CH_3)_2 > HCSNHC_2H_5 > HCSNHCH_3 > HCSNH_2$

Stability of complexes formed with other halides are almost in the same order as indicated by the values presented in TABLE 4-14. Line graph between interaction energy of sulphur donors with the acceptor metal halide $SnCl_4$ is shown in Graph 1.

Chemical potential of metal halides (μ_a)

Acceptor property of metal halides depends on the value of chemical potential (μ_A). The lower is the value of chemical potential (μ_A) better will be the acceptor property. Values of chemical potentials of metal halides are given in the TABLE 15. Among tin (iv) halides the $SnCl_4$ has the lowest value hence best acceptor. The acceptor strength of tin halides can be arranged in the following order,

$SnI_4 < SnBr_4 < SnCl_4$

In the halides of zinc, the value of chemical potential of zinc chloride is lowest indicating its highest acceptor property. The acceptor strength of zinc halides can be arranged in the following order,

$ZnCl_2 < ZnI_2 < ZnBr_2$

In the halides of cadmium, the value of chemical potential of cadmium chloride is lowest indicating its highest acceptor property. The acceptor strength of cadmium halides can be arranged in the following order,

$CdCl_2 < CdI_2 < CdBr_2$

In the halides of mercury the value of chemical potential of mercury chloride is lowest indicating its highest acceptor property. The acceptor strength of mercury halides can be arranged in the following order,

$HgCl_2 < HgI_2 < HgBr_2$

The acceptor strength of all the twelve metal halides can be arranged in the following order depending on the values of chemical potential,

$SnI_4 < SnBr_4 < CdCl_2 < CdI_2 < SnCl_4 < ZnCl_2 < HgCl_2 < CdBr_2 < HgI_2 < ZnI_2 < HgBr_2 < ZnBr_2$

TABLE 3 : Values of interaction energy of sulphur donors (B) with acceptor metal halide $SnCl_4$ (A)

Lewis bases (B)	μ_B	S_B	N_A	N_B	λ	E_v	E_μ	E_{int}
$C_3H_5NS_2$	-3.157	0.603	32	34	43.560	-1.425	-18.773	-20.198
$C_6H_{11}NS$	-2.934	0.670	32	46	60.840	-1.718	-24.771	-26.490
$HCSNH_2$	-3.303	0.664	32	18	25.000	-1.355	-10.234	-11.590
$HCSNHCH_3$	-3.151	0.660	32	24	31.360	-1.493	-12.875	-14.368
$HCSN(CH_3)_2$	-3.031	0.657	32	30	38.440	-1.605	-15.827	-17.432
$HCSNHC_2H_5$	-3.147	0.676	32	30	38.440	-1.513	-15.579	-17.092

TABLE 4 : Values of interaction energy of sulphur donors (B) with acceptor metal halide $SnBr_4$ (A)

Lewis bases (B)	μ_B	S_B	N_A	N_B	λ	E_v	E_μ	E_{int}
$C_3H_5NS_2$	-3.157	0.603	32	34	43.560	-1.135	-16.885	-18.021
$C_6H_{11}NS$	-2.934	0.670	32	46	60.840	-1.410	-22.405	-23.815
$HCSNH_2$	-3.303	0.664	32	18	25.000	-1.067	-9.252	-10.319
$HCSNHCH_3$	-3.151	0.660	32	24	31.360	-1.196	-11.636	-12.832
$HCSN(CH_3)_2$	-3.031	0.657	32	30	38.440	-1.303	-14.300	-15.602
$HCSNHC_2H_5$	-3.147	0.676	32	30	38.440	-1.214	-14.097	-15.311

TABLE 5 : Values of interaction energy of sulphur donors (B) with acceptor metal halide SnI_4 (A)

Lewis bases (B)	μ_B	S_B	N_A	N_B	λ	E_v	E_μ	E_{int}
$C_3H_5NS_2$	-3.157	0.603	32	34	43.560	-0.947	-14.149	-15.096
$C_6H_{11}NS$	-2.934	0.670	32	46	60.840	-1.217	-18.927	-20.144
$HCSNH_2$	-3.303	0.664	32	18	25.000	-0.879	-7.810	-8.689
$HCSNHCH_3$	-3.151	0.660	32	24	31.360	-1.006	-9.818	-10.824
$HCSN(CH_3)_2$	-3.031	0.657	32	30	38.440	-1.111	-12.061	-13.172
$HCSNHC_2H_5$	-3.147	0.676	32	30	38.440	-1.023	-11.916	-12.939

TABLE 6 : Values of interaction energy of sulphur donors (B) with acceptor metal halide $ZnCl_2$ (A)

Lewis bases (B)	μ_B	S_B	N_A	N_B	λ	E_v	E_μ	E_{int}
$C_3H_5NS_2$	-3.157	0.603	32	16	25.000	-0.819	-15.234	-16.054
$C_6H_{11}NS$	-2.934	0.670	32	16	38.440	-0.964	-21.634	-22.598
$HCSNH_2$	-3.303	0.664	32	16	11.560	-0.765	-6.555	-7.320
$HCSNHCH_3$	-3.151	0.660	32	16	16.000	-0.842	-9.109	-9.951
$HCSN(CH_3)_2$	-3.031	0.657	32	16	21.160	-0.905	-12.095	-13.000
$HCSNHC_2H_5$	-3.147	0.676	32	16	21.160	-0.849	-11.834	-12.682

TABLE 7 : Values of interaction energy of sulphur donors (B) with acceptor metal halide $ZnBr_2$ (A)

Lewis bases (B)	μ_B	S_B	N_A	N_B	λ	E_v	E_μ	E_{int}
$C_3H_5NS_2$	-3.157	0.603	32	16	25.000	-1.594	-15.489	-17.083
$C_6H_{11}NS$	-2.934	0.670	32	16	38.440	-1.800	-21.968	-23.768
$HCSNH_2$	-3.303	0.664	32	16	11.560	-1.530	-6.657	-8.187
$HCSNHCH_3$	-3.151	0.660	32	16	16.000	-1.635	-9.251	-10.886
$HCSN(CH_3)_2$	-3.031	0.657	32	16	21.160	-1.720	-12.284	-14.004
$HCSNHC_2H_5$	-3.147	0.676	32	16	21.160	-1.646	-12.015	-13.661

TABLE 8 : Values of interaction energy of sulphur donors (B) with acceptor metal halide ZnI_2 (A)

Lewis bases (B)	μ_B	S_B	N_A	N_B	λ	E_v	E_μ	E_{int}
$C_3H_5NS_2$	-3.157	0.603	32	16	25.000	-1.336	-13.961	-15.297
$C_6H_{11}NS$	-2.934	0.670	32	16	38.440	-1.554	-19.954	-21.508
$HCSNH_2$	-3.303	0.664	32	16	11.560	-1.270	-6.043	-7.313
$HCSNHCH_3$	-3.151	0.660	32	16	16.000	-1.380	-8.394	-9.774
$HCSN(CH_3)_2$	-3.031	0.657	32	16	21.160	-1.469	-11.142	-12.611
$HCSNHC_2H_5$	-3.147	0.676	32	16	21.160	-1.392	-10.920	-12.312

TABLE 9 : Values of interaction energy of sulphur donors (B) with acceptor metal halide $CdCl_2$ (A)

Lewis bases (B)	μ_B	S_B	N_A	N_B	λ	E_v	E_μ	E_{int}
$C_3H_5NS_2$	-3.157	0.603	32	16	25.000	-0.627	-15.731	-16.358
$C_6H_{11}NS$	-2.934	0.670	32	16	38.440	-0.744	-22.285	-23.028
$HCSNH_2$	-3.303	0.664	32	16	11.560	-0.579	-6.754	-7.333
$HCSNHCH_3$	-3.151	0.660	32	16	16.000	-0.643	-9.386	-10.029
$HCSN(CH_3)_2$	-3.031	0.657	32	16	21.160	-0.695	-12.464	-13.160
$HCSNHC_2H_5$	-3.147	0.676	32	16	21.160	-0.648	-12.187	-12.835

TABLE 10 : Values of interaction energy of sulphur donors (B) with acceptor metal halide $CdBr_2$ (A)

Lewis bases (B)	μ_B	S_B	N_A	N_B	λ	E_v	E_μ	E_{int}
$C_3H_5NS_2$	-3.157	0.603	32	16	25.000	-0.862	-15.780	-16.642
$C_6H_{11}NS$	-2.934	0.670	32	16	38.440	-1.001	-22.349	-23.350
$HCSNH_2$	-3.303	0.664	32	16	11.560	-0.808	-6.773	-7.582
$HCSNHCH_3$	-3.151	0.660	32	16	16.000	-0.883	-9.414	-10.297
$HCSN(CH_3)_2$	-3.031	0.657	32	16	21.160	-0.944	-12.501	-13.445
$HCSNHC_2H_5$	-3.147	0.676	32	16	21.160	-0.890	-12.222	-13.111

TABLE 11 : Values of interaction energy of sulphur donors (B) with acceptor metal halide CdI_2 (A)

Lewis bases (B)	μ_B	S_B	N_A	N_B	λ	E_v	E_μ	E_{int}
$C_3H_5NS_2$	-3.157	0.603	32	16	25.000	-0.856	-14.298	-15.154
$C_6H_{11}NS$	-2.934	0.670	32	16	38.440	-1.019	-20.401	-21.420
$HCSNH_2$	-3.303	0.664	32	16	11.560	-0.799	-6.179	-6.977
$HCSNHCH_3$	-3.151	0.660	32	16	16.000	-0.884	-8.584	-9.468
$HCSN(CH_3)_2$	-3.031	0.657	32	16	21.160	-0.954	-11.395	-12.349
$HCSNHC_2H_5$	-3.147	0.676	32	16	21.160	-0.892	-11.163	-12.055

TABLE 12 : Values of interaction energy of sulphur donors (B) with acceptor metal halide $HgCl_2$ (A)

Lewis bases (B)	μ_B	S_B	N_A	N_B	λ	E_v	E_μ	E_{int}
$C_3H_5NS_2$	-3.157	0.603	32	26	36.000	-0.962	-21.479	-22.441
$C_6H_{11}NS$	-2.934	0.670	32	26	51.840	-1.125	-28.612	-29.738
$HCSNH_2$	-3.303	0.664	32	26	19.360	-0.904	-10.765	-11.669
$HCSNHCH_3$	-3.151	0.660	32	26	25.000	-0.990	-13.955	-14.945
$HCSN(CH_3)_2$	-3.031	0.657	32	26	31.360	-1.060	-17.574	-18.633
$HCSNHC_2H_5$	-3.147	0.676	32	26	31.360	-0.998	-17.201	-18.199

TABLE 13 : Values of interaction energy of sulphur donors (B) with acceptor metal halide $HgBr_2$ (A)

Lewis bases (B)	μ_B	S_B	N_A	N_B	λ	E_v	E_μ	E_{int}
$C_3H_5NS_2$	-3.157	0.603	32	26	36.000	-1.469	-22.694	-24.163
$C_6H_{11}NS$	-2.934	0.670	32	26	51.840	-1.659	-30.103	-31.762
$HCSNH_2$	-3.303	0.664	32	26	19.360	-1.407	-11.330	-12.737
$HCSNHCH_3$	-3.151	0.660	32	26	25.000	-1.505	-14.691	-16.196
$HCSN(CH_3)_2$	-3.031	0.657	32	26	31.360	-1.584	-18.504	-20.088
$HCSNHC_2H_5$	-3.147	0.676	32	26	31.360	-1.515	-18.092	-19.607

TABLE 14 : Values of interaction energy of sulphur donors (B) with acceptor metal halide HgI_2 (A)

Lewis bases (B)	μ_B	S_B	N_A	N_B	λ	E_v	E_μ	E_{int}
$C_3H_5NS_2$	-3.157	0.603	32	26	36.000	-1.341	-20.054	-21.395
$C_6H_{11}NS$	-2.934	0.670	32	26	51.840	-1.561	-26.848	-28.408
$HCSNH_2$	-3.303	0.664	32	26	19.360	-1.276	-10.096	-11.372
$HCSNHCH_3$	-3.151	0.660	32	26	25.000	-1.385	-13.085	-14.471
$HCSN(CH_3)_2$	-3.031	0.657	32	26	31.360	-1.475	-16.474	-17.949
$HCSNHC_2H_5$	-3.147	0.676	32	26	31.360	-1.398	-16.146	-17.545

TABLE 15 : Values of HOMO energy, LUMO energy, electronegativity, chemical potential, electron affinity, absolute hardness and global softness of metal halides

Metal halide	HOMO energy	LUMO energy	Electronegativity	Chemical potential (μ_A)	Ionization potential	Electron affinity	Absolute hardness	Global softness (S_A)
$SnCl_4$	-8.087	-4.500	6.294	-6.294	8.087	4.500	1.794	0.558
$SnBr_4$	-7.271	-4.361	5.816	-5.816	7.271	4.361	1.455	0.687
SnI_4	-6.497	-4.362	5.430	-5.430	6.497	4.362	1.068	0.937
$ZnCl_2$	-10.945	-1.768	6.357	-6.357	10.945	1.768	4.589	0.218
$ZnBr_2$	-12.618	-2.836	7.727	-7.727	12.618	2.836	4.891	0.204
ZnI_2	-10.255	-3.423	6.839	-6.839	10.255	3.423	3.416	0.293
$CdCl_2$	-11.298	-0.882	6.090	-6.090	11.298	0.882	5.208	0.192
$CdBr_2$	-11.890	-1.338	6.614	-6.614	11.890	1.338	5.276	0.190
CdI_2	-9.862	-2.500	6.181	-6.181	9.862	2.500	3.681	0.272
$HgCl_2$	-10.775	-2.280	6.528	-6.528	10.775	2.280	4.248	0.235
$HgBr_2$	-12.909	-2.414	7.662	-7.662	12.909	2.414	5.248	0.191
HgI_2	-10.227	-3.447	6.837	-6.837	10.227	3.447	3.390	0.295

TABLE 16 : Values of HOMO energy, LUMO energy, electronegativity, chemical potential, electron affinity, absolute hardness and global softness of sulphur donors (B)

Lewis bases (B)	HOMO energy (eV)	LUMO energy (eV)	Electronegativity	Chemical potential	Ionization potential	Electron affinity	Absolute hardness	Global softness (S_B)
$C_3H_5NS_2$	-4.816	-1.497	3.157	-3.157	4.816	1.497	1.660	0.603
$C_6H_{11}NS$	-4.425	-1.442	2.934	-2.934	4.425	1.442	1.492	0.670
$HCSNH_2$	-4.809	-1.796	3.303	-3.303	4.809	1.796	1.507	0.664
$HCSNHCH_3$	-4.665	-1.636	3.151	-3.151	4.665	1.636	1.515	0.660
$HCSN(CH_3)_2$	-4.553	-1.508	3.031	-3.031	4.553	1.508	1.523	0.657
$HCSNHC_2H_5$	-4.626	-1.668	3.147	-3.147	4.626	1.668	1.479	0.676

Graph between chemical potential of metal halides is shown in the Graph 2.

Recently the order of acceptor strength in respect of interaction with nitrogen donors has been shown as below[3c],

$\mathbf{SnCl_4 > HgCl_2 > SnBr_4 > HgBr_2 > SnI_4 > CdCl_2 > HgI_2 > ZnCl_2 > CdBr_2 > ZnBr_2 > CdI_2 > ZnI_2}$

This order differs with the present work which is on account of change in donor atom from nitrogen to sulphur. This is in consonance with the HSAB principle.

Chemical potential of sulphur donors (μ_b)

Donor ability of sulphur donors (B) depends on the value of their chemical potential. As the value of chemical potential increases, the donor ability decreases i.e. the having lowest value of chemical potential can be treated as the best donor. Values of chemical potentials of sulphur donors are given in the Table-16. The value of chemical potential of $C_6H_{11}NS$ is lowest and the value of $HCSNH_2$ is highest. Thus the best sulphur donor is $C_6H_{11}NS$ and least donor is $HCSNH_2$. Order of

TABLE 16(a) : Values of S_A, S_B and their differences in ascending order

S.No.	Chem. For.	S_B	Metal halide	S_A	Difference between S_A and S_B
1	$HCSNHC_2H_5$	0.676	$SnBr_4$	0.687	0.011
2	$C_6H_{11}NS$	0.670	$SnBr_4$	0.687	0.017
3	$HCSNH_2$	0.664	$SnBr_4$	0.687	0.023
4	$HCSNHCH_3$	0.660	$SnBr_4$	0.687	0.027
5	$HCSN(CH_3)_2$	0.657	$SnBr_4$	0.687	0.030
6	$C_3H_5NS_2$	0.603	$SnCl_4$	0.558	0.045
7	$C_3H_5NS_2$	0.603	$SnBr_4$	0.687	0.084
8	$HCSN(CH_3)_2$	0.657	$SnCl_4$	0.558	0.099
9	$HCSNHCH_3$	0.660	$SnCl_4$	0.558	0.102
10	$HCSNH_2$	0.664	$SnCl_4$	0.558	0.106
11	$C_6H_{11}NS$	0.670	$SnCl_4$	0.558	0.112
12	$HCSNHC_2H_5$	0.676	$SnCl_4$	0.558	0.118
13	$HCSNHC_2H_5$	0.676	SnI_4	0.937	0.261
14	$C_6H_{11}NS$	0.670	SnI_4	0.937	0.267
15	$HCSNH_2$	0.664	SnI_4	0.937	0.273
16	$HCSNHCH_3$	0.660	SnI_4	0.937	0.277
17	$HCSN(CH_3)_2$	0.657	SnI_4	0.937	0.280
18	$C_3H_5NS_2$	0.603	HgI_2	0.295	0.308
19	$C_3H_5NS_2$	0.603	ZnI_2	0.293	0.310
20	$C_3H_5NS_2$	0.603	CdI_2	0.272	0.331
21	$C_3H_5NS_2$	0.603	SnI_4	0.937	0.334
22	$HCSN(CH_3)_2$	0.657	HgI_2	0.295	0.362
23	$HCSN(CH_3)_2$	0.657	ZnI_2	0.293	0.364
24	$HCSNHCH_3$	0.660	HgI_2	0.295	0.365
25	$HCSNHCH_3$	0.660	ZnI_2	0.293	0.367
26	$C_3H_5NS_2$	0.603	$HgCl_2$	0.235	0.368
27	$HCSNH_2$	0.664	HgI_2	0.295	0.369
28	$HCSNH_2$	0.664	ZnI_2	0.293	0.371
29	$C_6H_{11}NS$	0.670	HgI_2	0.295	0.375
30	$C_6H_{11}NS$	0.670	ZnI_2	0.293	0.377
31	$HCSNHC_2H_5$	0.676	HgI_2	0.295	0.381
32	$HCSNHC_2H_5$	0.676	ZnI_2	0.293	0.383
33	$C_3H_5NS_2$	0.603	$ZnCl_2$	0.218	0.385
34	$HCSN(CH_3)_2$	0.657	CdI_2	0.272	0.385
35	$HCSNHCH_3$	0.660	CdI_2	0.272	0.388
36	$HCSNH_2$	0.664	CdI_2	0.272	0.392
37	$C_6H_{11}NS$	0.670	CdI_2	0.272	0.398
38	$C_3H_5NS_2$	0.603	$ZnBr_2$	0.204	0.399
39	$HCSNHC_2H_5$	0.676	CdI_2	0.272	0.404
40	$C_3H_5NS_2$	0.603	$CdCl_2$	0.192	0.411
41	$C_3H_5NS_2$	0.603	$HgBr_2$	0.191	0.412
42	$C_3H_5NS_2$	0.603	$CdBr_2$	0.190	0.413
43	$HCSN(CH_3)_2$	0.657	$HgCl_2$	0.235	0.422
44	$HCSNHCH_3$	0.660	$HgCl_2$	0.235	0.425
45	$HCSNH_2$	0.664	$HgCl_2$	0.235	0.429
46	$C_6H_{11}NS$	0.670	$HgCl_2$	0.235	0.435
47	$HCSN(CH_3)_2$	0.657	$ZnCl_2$	0.218	0.439
48	$HCSNHC_2H_5$	0.676	$HgCl_2$	0.235	0.441
49	$HCSNHCH_3$	0.660	$ZnCl_2$	0.218	0.442
50	$HCSNH_2$	0.664	$ZnCl_2$	0.218	0.446
51	$C_6H_{11}NS$	0.670	$ZnCl_2$	0.218	0.452
52	$HCSN(CH_3)_2$	0.657	$ZnBr_2$	0.204	0.453
53	$HCSNHCH_3$	0.660	$ZnBr_2$	0.204	0.456
54	$HCSNHC_2H_5$	0.676	$ZnCl_2$	0.218	0.458
55	$HCSNH_2$	0.664	$ZnBr_2$	0.204	0.460
56	$HCSN(CH_3)_2$	0.657	$CdCl_2$	0.192	0.465
57	$HCSN(CH_3)_2$	0.657	$HgBr_2$	0.191	0.466
58	$C_6H_{11}NS$	0.670	$ZnBr_2$	0.204	0.466
59	$HCSN(CH_3)_2$	0.657	$CdBr_2$	0.190	0.467
60	$HCSNHCH_3$	0.660	$CdCl_2$	0.192	0.468
61	$HCSNHCH_3$	0.660	$HgBr_2$	0.191	0.469
62	$HCSNHCH_3$	0.660	$CdBr_2$	0.190	0.470
63	$HCSNH_2$	0.664	$CdCl_2$	0.192	0.472
64	$HCSNHC_2H_5$	0.676	$ZnBr_2$	0.204	0.472
65	$HCSNH_2$	0.664	$HgBr_2$	0.191	0.473
66	$HCSNH_2$	0.664	$CdBr_2$	0.190	0.474
67	$C_6H_{11}NS$	0.670	$CdCl_2$	0.192	0.478
68	$C_6H_{11}NS$	0.670	$HgBr_2$	0.191	0.479
69	$C_6H_{11}NS$	0.670	$CdBr_2$	0.190	0.480
70	$HCSNHC_2H_5$	0.676	$CdCl_2$	0.192	0.484
71	$HCSNHC_2H_5$	0.676	$HgBr_2$	0.191	0.485
72	$HCSNHC_2H_5$	0.676	$CdBr_2$	0.190	0.486

donor ability of sulphur donors based on the value of chemical potential is as follows,

$C_6H_{11}NS > HCSN(CH_3)_2 > CSNHC_2H_5 > HCSNHCH_3 > C_3H_5NS_2 > HCSNH_2$

Global softness (S_A and S_B)

Acidic strength of metal halide depends on the value of global softness (S_A). As the value of global softness increases, the acidic strength decreases. The global softness (S_A) values are lowest in chlorides and highest in iodides, in other words chlorides are harder acids as

TABLE 17 : ΔN and ΔE of interaction of sulphur donors with $SnCl_4$

Lewis bases (B)	χ_A	χ_B	η_A	η_B	ΔN	ΔE
$C_3H_5NS_2$	6.293	3.157	1.793	1.660	0.454	-0.712
$C_6H_{11}NS$	6.293	2.934	1.793	1.492	0.511	-0.859
$HCSNH_2$	6.293	3.303	1.793	1.507	0.453	-0.678
$HCSNHCH_3$	6.293	3.151	1.793	1.515	0.475	-0.746
$HCSN(CH_3)_2$	6.293	3.031	1.793	1.523	0.492	-0.803
$HCSNHC_2H_5$	6.293	3.147	1.793	1.479	0.481	-0.756

TABLE 18 : ΔN and ΔE of interaction of sulphur donors with $SnBr_4$

Lewis bases (B)	χ_A	χ_B	η_A	η_B	ΔN	ΔE
$C_3H_5NS_2$	5.806	3.157	1.464	1.660	0.424	-0.562
$C_6H_{11}NS$	5.806	2.934	1.464	1.492	0.486	-0.698
$HCSNH_2$	5.806	3.303	1.464	1.507	0.421	-0.527
$HCSNHCH_3$	5.806	3.151	1.464	1.515	0.446	-0.592
$HCSN(CH_3)_2$	5.806	3.031	1.464	1.523	0.465	-0.645
$HCSNHC_2H_5$	5.806	3.147	1.464	1.479	0.452	-0.601

TABLE 19 : ΔN and ΔE of interaction of sulphur donors with SnI_4

Lewis bases (B)	χ_A	χ_B	η_A	η_B	ΔN	ΔE
$C_3H_5NS_2$	5.428	3.157	1.069	1.660	0.416	-0.473
$C_6H_{11}NS$	5.428	2.934	1.069	1.492	0.487	-0.608
$HCSNH_2$	5.428	3.303	1.069	1.507	0.413	-0.439
$HCSNHCH_3$	5.428	3.151	1.069	1.515	0.441	-0.502
$HCSN(CH_3)_2$	5.428	3.031	1.069	1.523	0.463	-0.555
$HCSNHC_2H_5$	5.428	3.147	1.069	1.479	0.448	-0.510

TABLE 20 : ΔN and ΔE of interaction of sulphur donors with $ZnCl_2$

Lewis bases (B)	χ_A	χ_B	η_A	η_B	ΔN	ΔE
$C_3H_5NS_2$	-2.829	3.157	1.949	1.660	-0.829	-2.482
$C_6H_{11}NS$	-2.829	2.934	1.949	1.492	-0.837	-2.413
$HCSNH_2$	-2.829	3.303	1.949	1.507	-0.887	-2.720
$HCSNHCH_3$	-2.829	3.151	1.949	1.515	-0.863	-2.581
$HCSN(CH_3)_2$	-2.829	3.031	1.949	1.523	-0.844	-2.473
$HCSNHC_2H_5$	-2.829	3.147	1.949	1.479	-0.872	-2.604

TABLE 21 : ΔN and ΔE of interaction of sulphur donors with $ZnBr_2$

Lewis bases (B)	χ_A	χ_B	η_A	η_B	ΔN	ΔE
$C_3H_5NS_2$	5.003	3.157	2.218	1.660	0.238	-0.220
$C_6H_{11}NS$	5.003	2.934	2.218	1.492	0.279	-0.289
$HCSNH_2$	5.003	3.303	2.218	1.507	0.228	-0.194
$HCSNHCH_3$	5.003	3.151	2.218	1.515	0.248	-0.230
$HCSN(CH_3)_2$	5.003	3.031	2.218	1.523	0.264	-0.260
$HCSNHC_2H_5$	5.003	3.147	2.218	1.479	0.251	-0.233

TABLE 22 : ΔN and ΔE of interaction of sulphur donors with ZnI_2

Lewis bases (B)	χ_A	χ_B	η_A	η_B	ΔN	ΔE
$C_3H_5NS_2$	4.789	3.157	1.921	1.660	0.228	-0.186
$C_6H_{11}NS$	4.789	2.934	1.921	1.492	0.272	-0.252
$HCSNH_2$	4.789	3.303	1.921	1.507	0.217	-0.161
$HCSNHCH_3$	4.789	3.151	1.921	1.515	0.238	-0.195
$HCSN(CH_3)_2$	4.789	3.031	1.921	1.523	0.255	-0.225
$HCSNHC_2H_5$	4.789	3.147	1.921	1.479	0.241	-0.198

TABLE 23 : ΔN and ΔE of interaction of sulphur donors with $CdCl_2$

Lewis bases (B)	χ_A	χ_B	η_A	η_B	ΔN	ΔE
$C_3H_5NS_2$	5.354	3.157	2.112	1.660	0.291	-0.320
$C_6H_{11}NS$	5.354	2.934	2.112	1.492	0.336	-0.406
$HCSNH_2$	5.354	3.303	2.112	1.507	0.283	-0.291
$HCSNHCH_3$	5.354	3.151	2.112	1.515	0.304	-0.335
$HCSN(CH_3)_2$	5.354	3.031	2.112	1.523	0.320	-0.371
$HCSNHC_2H_5$	5.354	3.147	2.112	1.479	0.307	-0.339

TABLE 24 : ΔN and ΔE of interaction of sulphur donors with $CdBr_2$

Lewis bases (B)	χ_A	χ_B	η_A	η_B	ΔN	ΔE
$C_3H_5NS_2$	5.057	3.157	1.954	1.660	0.263	-0.250
$C_6H_{11}NS$	5.057	2.934	1.954	1.492	0.308	-0.327
$HCSNH_2$	5.057	3.303	1.954	1.507	0.254	-0.222
$HCSNHCH_3$	5.057	3.151	1.954	1.515	0.275	-0.262
$HCSN(CH_3)_2$	5.057	3.031	1.954	1.523	0.291	-0.295
$HCSNHC_2H_5$	5.057	3.147	1.954	1.479	0.278	-0.266

TABLE 25 : ΔN and ΔE of interaction of sulphur donors with CdI_2

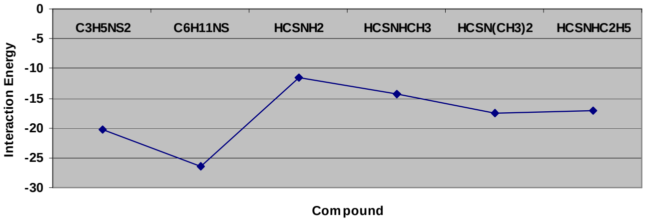
Lewis bases (B)	χ_A	χ_B	η_A	η_B	ΔN	ΔE
$C_3H_5NS_2$	5.059	3.157	1.953	1.660	0.263	-0.250
$C_6H_{11}NS$	5.059	2.934	1.953	1.492	0.309	-0.328
$HCSNH_2$	5.059	3.303	1.953	1.507	0.254	-0.223
$HCSNHCH_3$	5.059	3.151	1.953	1.515	0.275	-0.263
$HCSN(CH_3)_2$	5.059	3.031	1.953	1.523	0.292	-0.296
$HCSNHC_2H_5$	5.059	3.147	1.953	1.479	0.279	-0.266

TABLE 26 : ΔN and ΔE of interaction of sulphur donors with $HgCl_2$

Lewis bases (B)	χ_A	χ_B	η_A	η_B	ΔN	ΔE
$C_3H_5NS_2$	6.083	3.157	1.739	1.660	0.431	-0.630
$C_6H_{11}NS$	6.083	2.934	1.739	1.492	0.487	-0.768
$HCSNH_2$	6.083	3.303	1.739	1.507	0.428	-0.596
$HCSNHCH_3$	6.083	3.151	1.739	1.515	0.451	-0.661
$HCSN(CH_3)_2$	6.083	3.031	1.739	1.523	0.468	-0.714
$HCSNHC_2H_5$	6.083	3.147	1.739	1.479	0.456	-0.670

TABLE 27 : ΔN and ΔE of interaction of sulphur donors with $HgBr_2$

Lewis bases (B)	χ_A	χ_B	η_A	η_B	ΔN	ΔE
$C_3H_5NS_2$	5.667	3.157	1.611	1.660	0.384	-0.482
$C_6H_{11}NS$	5.667	2.934	1.611	1.492	0.441	-0.602
$HCSNH_2$	5.667	3.303	1.611	1.507	0.379	-0.448
$HCSNHCH_3$	5.667	3.151	1.611	1.515	0.403	-0.506
$HCSN(CH_3)_2$	5.667	3.031	1.611	1.523	0.421	-0.554
$HCSNHC_2H_5$	5.667	3.147	1.611	1.479	0.408	-0.514



Graph 1 : Interaction energy of sulphur donors with the acceptor $SnCl_4$

compared to their bromide and iodide counterparts in terms of HSAB principle. The scale of softness of various halides is as given in TABLE 15. Order of global softness of metal halides is given below,

$CdBr_2 > HgBr_2 > CdCl_2 > ZnBr_2 > ZnCl_2 > HgCl_2 > CdI_2 > ZnI_2 > HgI_2 > SnCl_4 > SnBr_4 > SnI_4$

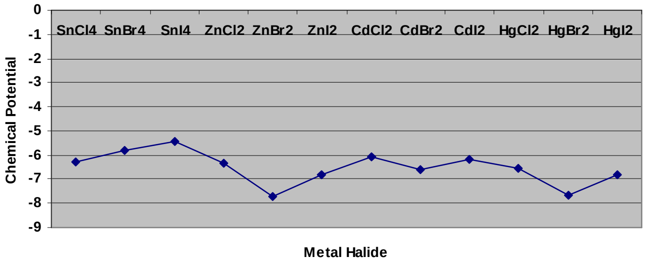
Analysis of the equation (3) indicates that for a given values of S_A the larger the value of S_B, the better, while equation (4) indicates that for the same values of S_A the smaller value of S_B the better. Since the total energy is given by the summation of these two terms, it seems that the best situation corresponds to the average between the two extreme situations that is $S_A \approx S_B$, which is precisely the global HSAB principle. A similar analysis, based on the two opposing tendencies, was first given by Chattaraj et al. The S_A value of $SnBr_4$ is 0.687 and S_B value of $HCSNHC_2H_5$ is 0.676. Since the two values are almost equal the best interaction is shown between them. This observation is in conformity with the global HSAB principle. TABLE 16(a) shows the values of S_A, S_B and their differences arranged in ascending order. As we move down to this Table the strength of interaction decreases. The weakest interaction is between the $HCSNHC_2H_5$ and the metal halide $CdBr_2$ because the difference between S_A and S_B is highest in this case.

Eμ

For a molecule μ measures the ability to attract electrons to itself. If two molecules (A and B) are brought together electrons will flow from the one, which has lower value of μ to that which has higher value. At equilibrium a single value of μ will exist through out. ΔEμ is the energy transfer on account of this reshuffling.

TABLE 28 : ΔN and ΔE of interaction of sulphur donors with HgI_2

Lewis bases (B)	χ_A	χ_B	η_A	η_B	ΔN	ΔE
$C_3H_5NS_2$	5.321	3.157	1.391	1.660	0.355	-0.384
$C_6H_{11}NS$	5.321	2.934	1.391	1.492	0.414	-0.494
$HCSNH_2$	5.321	3.303	1.391	1.507	0.348	-0.351
$HCSNHCH_3$	5.321	3.151	1.391	1.515	0.373	-0.405
$HCSN(CH_3)_2$	5.321	3.031	1.391	1.523	0.393	-0.450
$HCSNHC_2H_5$	5.321	3.147	1.391	1.479	0.379	-0.412



Graph 2 : Graph between chemical potential of metal halides

The ΔEμ shows that chlorides have higher value than bromide and iodide. The sequence is chloride > bromide > iodide. The values do not demonstrate the order of acceptor or base strength.

Comparison with ΔN

Metal ligand bond strength between interaction of acceptor (A) and ligand (B) has also been calculated by solving the following equations for shift in charge or charge transfer ΔN and lowering of energy ΔE[23] on formation of A-B.

$$\Delta N = (\chi^\circ_A - \chi^\circ_B) / 2(\eta_A + \eta_B) \qquad (12)$$

$$\Delta E = -(\chi^\circ_A - \chi^\circ_B)^2 / 4(\eta_A + \eta_B) \qquad (13)$$

Metal ligand bond strength between interaction of acceptor (A) and ligand (B) increases as the lowering in energy increases. Further this bond strength decreases as the charge transfer increases. The values of ΔN, ΔE (calculated in eV) are included in TABLE 17 to TABLE 28. All the energies calculated in this chapter e.g. HOMO energy, LUMO energy etc. are in electron volts (eV).

A reference to the TABLE 17 to TABLE 28, indicates that all the three parameters viz interaction energy (E_{int}), shift in charge (ΔN), and lowering of energy (ΔE) provide results which are in consonance to each other, all of them have reliable predictive power.

CONCLUSIONS

The acceptor strength of all the twelve metal halides can be arranged in the following order depending on the values of chemical potential (μ_B)

$SnI_4 < SnBr_4 < CdCl_2 < CdI_2 < SnCl_4 < ZnCl_2 < HgCl_2 < CdBr_2 < HgI_2 < ZnI_2 < HgBr_2 < ZnBr_2$

The chemical potential (μ_B) values of indicate the same order of base strength as is indicated by interaction energy.

The $C_6H_{11}NS$ is the strongest base against all the acceptors (A). $HCSNH_2$ is the weakest base against all the acceptors (A).

$E\mu$ is the energy transfer on account of flow of electrons from lower value of μ to high value of μ. The $E\mu$ does not demonstrate the order of acid or base strength.

The best interaction is when global softness values of acid and base are equal i.e. $S_A \approx S_B$.

The interaction energy (E_{int}) for interaction between $HgBr_2$ and $C_6H_{11}NS$ is lowest and is equal to -31.762; the next is for interaction of $HgCl_2$ with the base $C_6H_{11}NS$, the value being -29.738.

Order of metal-ligand bond strength for all the 72 interactions between sulphur donors and metal halides are shown in the decreasing order in the TABLE 29.

The values of interaction energy (E_{int}) above -14.945 indicate weak interaction between metal halide and sulphur donors.

The least interaction is between CdI_2 and $HCSNH_2$ as the value of interaction energy is highest and equal to -6.977 eV.

Order of stable complex formation of sulphur donors (B) is same with all the halides of tin, zinc, cadmium and mercury.

All the results of ΔN and ΔE show almost the same sequence as predicted by interaction energy.

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