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Comparative study of semi empirical calculations of energies and densities of frontier orbitals of Lewis acids and bases

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ABSTRACT

Energies and densities of certain Lewis acids and bases have been evaluated by semi empirical methods. AM1, PM3 and PM5, on CACHE Software. The energy values have been mainly used to prepare the scale of hardness, and density values for identifying sites in different compounds. The metal-ligand interaction and the stability of metal-ligand bond have been studied with the help of LUMO density values of acceptor molecules and HOMO density values of donor molecules. The stability of metal ligand bond has also been related with transfer of charge ΔN and lowering of energy ΔE on complex formation.

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KEYWORDS

Energies of frontier orbital;
Densities of frontier orbital;
Semi empirical calculations;
Metal ligand bonding;
Charge transfer;
Energy lowering.

INTRODUCTION

In our recent communication we have made a DFT based study of energies and densities of frontier orbital of Lewis acids and bases and their interaction^[1]. In this paper we present semiempirical-based study.

Semi empirical quantum chemical method can be used for the calculation of the molecular parameters. These methods have been developed within the mathematical frame work of the molecular orbital theory (SCFMO) but based on simplifications and approximations introduced into the computational procedure, which dramatically reduced the computational time^[2-3] Various semi empirical methods like extended Huckel theory (EHT), complete neglect of differential overlap (CNDO)^[4-5], intermediate neglect of differential overlap (INDO)^[6], modified INDO (MINDO)^[7], modified neglect of diatomic overlap (MNDO)^[8], autism model

1-(AMI)^[9], and parametric models (PM3)^[10], and PM5, have been developed over the last few decades .In this papers we have evaluated energy and density of HOMO and LUMO, absolute hardness electronegativity, chemical potential, ionization potential and electron affinity of certain lewis acids and bases with the help of AM-1, PM-3 and PM5 methods. The parameters have been used to draw the scale of hardness of Lewis acids and bases, to identify the site of activity, and to study the stability of metal-ligand bond. The results if semi empirical calculations have been compared with our earlier work based on Klopman equation^[11-12] and also with the values calculated by DFT methods.

MATERIAL AND METHODS

Metal halides of transition and non transition metal have been used as lewis acids and various organic com-

pounds as Lewis bases. The acids and bases have been used as study material of this paper.

The 3D modeling and geometry optimization of all the compounds have been done with the help of Cache software, using PM3Hamiltonian^[10]. The values of various descriptors such as ionization potential, electron affinity, charge, electron density, eigen values of frontier orbital, of Lewis acid and Lewis bases have been taken from semi empirical-AM1, PM3, PM5 calculations. The values of various parameters have been used for solving the equations 1-6.

Recent work based on density functional theory has developed the concept of absolute electro negativity, χ° and absolute hardness η ^[13]. The operation (and approximate) definitions are: -

$$\chi = \frac{1}{2}(I+A) = -\mu \quad (1)$$

$$\eta = \frac{1}{2}(I-A) \quad (2)$$

Where I is the ionization potential A is the electron affinity and μ is chemical potential. The absolute electronegativity is the same as the Mulliken value. When acid and base, are allowed to react, there will be a shift of electrons from the less electronegative base (B), to the more electronegative acid (A). The condition of equilibrium is that the chemical potential, μ_A and μ_B , become equal, this leads to a shift in charge ΔN and is given by the equation.

$$\Delta N = (\chi_A^{\circ} - \chi_B^{\circ}) / [2(\eta_A - \eta_B)] \quad (3)$$

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

$$\Delta E = (\chi_A^{\circ} - \chi_B^{\circ})^2 / [4(\eta_A - \eta_B)] \quad (4)$$

In eqn 3 and 4 the electronegativity difference drive 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 or shift in charge. The chemical potential and the absolute electronegativity are molecular properties and not orbital properties. According to Koopman's 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-2 can be written as:

$$\eta = \frac{1}{2}(\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}}) \quad (5)$$

$$\chi = \frac{1}{2}(\epsilon_{\text{LUMO}} + \epsilon_{\text{HOMO}}) \quad (6)$$

RESULTS AND DISCUSSION

Frontier molecular orbital energies

Energies of HOMO and LUMO are very popular

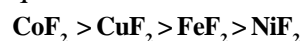
quantum mechanical descriptors. It has been shown^[14] that these orbitals play a major role in governing many chemical reactions, and are also responsible for charge transfer complexes. The treatment of the frontier molecular orbitals separately from the other orbitals is based on the general principles governing the nature of chemical reactions^[15]. The energy of the HOMO is directly related to the ionization potential and characterizes the susceptibility of the molecule towards attack of electrophile. The energy of LUMO is directly related to the electron affinity and characterizes the susceptibility of the molecule towards attack of nucleophile. The concept of hard and soft nucleophiles and electrophiles has been also directly related to the relative energies of the HOMO and LUMO orbitals. Hard nucleophiles have a low energy HOMO, soft nucleophiles have a high energy HOMO, hard electrophiles have a high energy LUMO and soft electrophiles have a low energy LUMO^[16]. HOMO-LUMO gap, that is the difference in energy between the HOMO and LUMO is an important stability index^[13].

$\epsilon_{\text{LUMO}} - \epsilon_{\text{HOMO}} = \text{energy gap}$

Absolute hardness η is equal to half the value of the difference in energy of the LUMO and HOMO^[17] as shown in equation 5.

Metal halides

The absolute hardness (η) and electronegativity (χ) values of transition and non transition metal halides have been evaluated by solving the eqn-5-6 from HOMO and LUMO energies and are presented in TABLE 1A and 1B in three columns separately for AM1, PM3, PM5 and DFT methods. TABLE 1A indicates that in case of transition metal halides, none of the methods provide any logical trends. In case of Fe (II) halides the highest value of hardness is of Fe (II) chloride in all the three method. In case of cobalt the highest value is of fluoride in AM1 and PM3, whereas in case of PM5 the highest value of chloride. In case of nickel the highest value is of iodide in AM1 and fluoride in PM3 and PM5. If all the fluorides of AM1 series are compared the sequence is as:



PM3 and PM5, calculations also provide irregular trends. Scale of hardness if drawn by the value of IP and EA of our previous work^[11] or if the softness val-

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TABLE 1A: Absolute hardness(η) and electronegativity(χ) values of transition metal halide derived by semi empirical method-AM1, PM3, and PM5 method

Compounds	AM1				PM3				PM5			
	Energy				Energy				Energy			
	HOMO	LUMO	η	χ	HOMO	LUMO	η	χ	HOMO	LUMO	η	χ
FeF ₂	-14.421	-9.471	2.475	11.946	-13.071	-8.415	2.328	10.743	-13.388	-8.789	2.2995	
FeCl ₂	-11.714	-1.242	5.236	6.478	-10.733	-1.208	4.7625	5.9705	-10.424	-0.616	4.904	
FeBr ₂	-13.655	-8.109	2.773	10.882	-13.492	-8.088	2.702	10.79	-12.284	-60.651	2.3165	
FeI ₂	-12.732	-7.73	2.501	10.231	-11.914	-7.205	2.3545	9.5595	-10.754	-7.137	1.8085	
Fe(NCS) ₂	-9.196	-5.716	1.74	7.456	-9.227	-6.154	1.5365	7.6905	-9.067	-5.99	1.5385	
Fe(NCSe) ₂	-8.452	-4.642	1.905	6.547	-9.506	-6.43	1.538	7.968	-9.064	-6.134	1.465	
CoCl ₂	-15.092	-7.801	3.6455	11.4465	-14.811	-7.609	3.601	11.21	-16.241	-8.69	3.7755	
CoF ₂	-13.389	-5.338	4.255	9.3635	-15.159	-6.401	4.374	10.775	-16.305	-9.207	3.549	
CoBr ₂	-13.388	-6.769	3.3095	10.0785	-15.678	-8.915	3.3815	12.2965	-15.735	-8.565	3.585	
CoI ₂	-12.788	-6.239	3.2745	9.5153	-13.639	-7.185	3.227	10.412	-15.194	-7.759	3.7175	
Co(NCS) ₂	-11.11	-6.212	2.449	8.661	-12.224	-6.98	2.622	9.602	-11.951	-6.551	2.7	
Co(NCSe) ₂	-9.829	-5.909	1.96	7.869	-12.398	-7.603	2.3975	10.0005	-11.91	-6.69	2.61	
NiF ₂	-9.146	-6.248	1.449	7.697	-10.983	-8.168	1.4075	9.5755	-16.334	-11.638	2.348	
NiCl ₂	-11.171	-8.364	1.4035	9.7675	-12.329	-9.571	1.379	10.95	-15.046	-10.379	2.3335	
NiBr ₂	-11.507	-8.734	1.3865	10.1205	-12.484	-9.732	1.376	11.108	-14.381	-10.237	2.072	
NiI ₂	-10.998	-6.972	2.013	8.985	-11.959	-9.176	1.3915	10.5675	-12.202	-9.07	1.566	
Ni(NCS) ₂	-9.078	-6.536	1.271	7.807	-9.743	-7.802	0.9705	8.7725	-10.798	-7.598	1.6	
Ni(NCSe) ₂	-12.461	-8.982	1.7395	10.7215	-12.015	-10.029	0.993	11.022	-11.22	-7.907	1.6565	
CuF ₂	-20.867	-13.743	3.562	17.305	-23.176	-14.226	4.475	18.701	-25.018	-15.082	4.968	
CuCl ₂	-18.235	-12.511	2.862	15.373	-17.216	-11.378	2.919	14.297	-8.026	-2.176	2.925	
CuBr ₂	-16.392	-11.866	2.263	14.129	-18.153	-11.167	3.493	14.66	-6.382	-0.026	3.178	
CuI ₂	-15.019	-11.165	1.927	13.092	-12.512	-10.591	0.9605	11.5515	-15.232	-11.155	2.0385	
Cu(NCS) ₂	-13.08	-9.387	1.8465	11.2335	-13.977	-7.353	3.312	10.665	13.634	-7.724	2.955	
Cu(NCSe) ₂	-10.392	-8.472	0.96	9.432	-13.964	-7.986	2.989	10.975	-14.391	-7.807	3.292	

TABLE 1B: Absolute hardness (η) and electronegativity (χ) values of non transition metal halide derived by semi empirical method-AM1, PM3, and PM5 method

Compound	AM1				PM3				PM5			
	HOMO energy	LUMO energy	χ	η	HOMO energy	LUMO energy	χ	η	HOMO energy	LUMO energy	χ	η
	ZnF ₂	-13.325	-0.057	6.691	6.634	-15.318	-0.974	8.146	7.172	-14.081	0.004	7.039
ZnCl ₂	-12.197	-1.065	6.631	5.566	-10.945	-1.768	6.357	4.589	-11.714	-0.260	5.987	5.727
ZnBr ₂	-11.365	-1.089	6.227	5.138	-12.619	-2.835	7.727	4.892	-11.175	-0.700	5.938	5.238
ZnI ₂	-10.492	-1.679	6.086	4.407	-10.255	-3.422	6.839	3.417	-10.031	-1.753	5.892	4.139
Zn(NCS) ₂	-9.393	-1.029	5.211	4.182	-9.406	-2.497	5.952	3.455	-9.501	-1.024	5.263	4.239
Zn(NCSe) ₂	-8.139	-1.389	4.764	3.375	-9.226	-2.696	5.961	3.265	-9.040	-1.248	5.144	3.896
CdF ₂	Error	Error	Error	Error	-12.851	0.096	6.378	6.474	-13.403	-3.506	8.455	4.949
CdCl ₂	Error	Error	Error	Error	-11.297	-0.882	6.090	5.208	-12.290	-2.636	7.463	4.827
CdBr ₂	Error	Error	Error	Error	-11.890	-1.338	6.614	5.276	-11.480	-2.653	7.067	4.414
CdI ₂	Error	Error	Error	Error	-9.862	-2.499	6.181	3.682	-10.225	-2.515	6.370	3.855
Cd(NCS) ₂	Error	Error	Error	Error	-9.037	-1.413	5.225	3.812	-9.634	-3.343	6.489	3.146
Cd(NCSe) ₂	Error	Error	Error	Error	-8.864	-1.880	5.372	3.492	-9.193	-3.465	6.329	2.864
HgF ₂	-12.684	-1.386	7.035	5.649	-13.784	-1.541	7.663	6.122	-14.062	-2.708	8.385	5.677
HgCl ₂	-11.929	-2.323	7.126	4.803	-10.775	-2.280	6.528	4.248	-11.331	-2.530	6.931	4.401
HgBr ₂	-11.164	-2.276	6.720	4.444	-12.909	-2.414	7.662	5.248	-10.713	-2.537	6.625	4.088
HgI ₂	-10.383	-2.591	6.487	3.896	-10.227	-3.447	6.837	3.390	-10.123	-3.280	6.702	3.422
Hg(NCS) ₂	-9.219	-2.697	5.958	3.261	-9.029	-2.805	5.917	3.112	-9.433	-3.299	6.366	3.067
Hg(NCSe) ₂	-8.032	-3.076	5.554	2.478	-8.891	-3.273	6.082	2.809	-8.969	-3.508	6.239	2.731
SnCl ₄	Error	Error	Error	Error	-11.722	-3.962	7.842	3.880	-12.131	-3.422	7.777	4.355
SnBr ₄	Error	Error	Error	Error	-13.023	-5.393	9.208	3.815	-11.525	-3.766	7.646	3.880
SnI ₄	Error	Error	Error	Error	-10.323	-4.574	7.449	2.875	-10.226	-4.218	7.222	3.004
PhSnCl ₃	Error	Error	Error	Error	-10.507	-3.170	6.839	3.669	-9.935	-2.514	6.225	3.711
Ph ₂ SnCl ₂	Error	Error	Error	Error	-10.255	-2.183	6.219	4.036	-9.641	-1.733	5.687	3.954
Ph ₃ SnCl	Error	Error	Error	Error	-9.918	-1.228	5.573	4.345	-9.310	-1.087	5.199	4.112
CH ₃ SnCl ₃	Error	Error	Error	Error	-11.381	-3.141	7.261	4.120	-10.818	-2.492	6.655	4.163
(CH ₃) ₂ SnCl ₂	Error	Error	Error	Error	-10.984	-2.172	6.578	4.406	-9.985	-1.600	5.793	4.193
(CH ₃) ₃ SnCl	Error	Error	Error	Error	-10.543	-1.091	5.817	4.726	-9.539	-0.781	5.160	4.379

TABLE 2: Absolute hardness(η) and electronegativity(χ) values of organic bases derived by semi empirical method-AM1, PM3, and PM5 method

Compound	AM1				PM3				PM5			
	HOMO energy	LUMO energy	χ	η	HOMO energy	LUMO energy	χ	η	HOMO energy	LUMO energy	χ	η
NH ₃	-10.418	4.223	3.098	7.321	-9.695	3.333	3.181	6.514	-10.160	2.842	3.659	6.501
CH ₃ NH ₂	-9.756	3.813	2.972	6.785	-9.404	3.109	3.148	6.257	-9.468	2.500	3.484	5.984
(CH ₃) ₂ NH	-9.386	3.480	2.953	6.433	-9.219	2.909	3.155	6.064	-9.089	2.286	3.402	5.688
(CH ₃) ₃ N	-9.117	3.192	2.963	6.155	-9.070	2.730	3.170	5.900	-8.867	2.122	3.373	5.495
PhNH ₂	-8.214	0.758	3.728	4.486	-8.067	0.615	3.726	4.341	-7.978	0.870	3.554	4.424
Ph ₃ N	-7.957	0.180	3.889	4.069	-8.345	0.093	4.126	4.219	-8.037	0.393	3.822	4.215
HCONH ₂	-10.667	1.569	4.549	6.118	-9.846	1.361	4.243	5.604	-10.519	0.607	4.956	5.563
CH ₃ CONH ₂	-10.542	1.513	4.515	6.028	-9.751	1.294	4.229	5.523	-10.386	0.690	4.848	5.538
C ₂ H ₅ CONH ₂	-10.517	1.550	4.484	6.034	-9.728	1.323	4.203	5.526	-10.348	0.732	4.808	5.540
PhCONH ₂	-9.941	-0.214	5.078	4.864	-9.719	-0.357	5.038	4.681	-9.883	-0.366	5.125	4.759
NH ₂ CONH ₂	-10.468	1.898	4.285	6.183	-9.618	1.061	4.279	5.340	-10.309	0.175	5.067	5.242
CH ₃ NHCONH ₂	-10.121	1.585	4.268	5.853	-9.938	1.027	4.456	5.483	-10.022	0.325	4.849	5.174
(CH ₃) ₂ NCONH ₂	-9.694	1.611	4.042	5.653	-9.695	0.982	4.357	5.339	-9.619	0.362	4.629	4.991
PhNHCONH ₂	-8.721	0.451	4.135	4.586	-8.670	0.280	4.195	4.475	-8.706	-0.176	4.441	4.265
Ph ₂ NCONH ₂	-8.743	-0.069	4.406	4.337	-9.206	-0.132	4.669	4.537	-8.862	-0.005	4.434	4.429
Ph ₂ NCSNHPH	-8.215	-0.378	4.297	3.919	-8.454	-0.905	4.680	3.775	-8.461	-0.324	4.393	4.069
(CH ₃) ₂ NCONH ₂	-9.694	1.611	4.042	5.653	-9.695	0.982	4.357	5.339	-9.619	0.362	4.629	4.991
HCSNHCH ₃	-8.563	-0.097	4.330	4.233	-8.733	-0.706	4.720	4.014	-8.843	-0.290	4.567	4.277
HCSNH ₂	-8.603	-0.105	4.354	4.249	-8.777	-0.733	4.755	4.022	-8.938	-0.367	4.653	4.286
HCSNHC ₂ H ₅	-8.516	-0.043	4.280	4.237	-8.686	-0.656	4.671	4.015	-8.781	-0.225	4.503	4.278
HCSN(C ₂ H ₅) ₂	-8.383	0.006	4.189	4.195	-8.578	-0.646	4.612	3.966	-8.581	-0.100	4.341	4.241
HCSNHPh	-8.754	-0.715	4.735	4.020	-8.821	-1.174	4.998	3.824	-8.804	-0.835	4.820	3.985
HCSNPh ₂	-8.457	-0.539	4.498	3.959	-8.545	-0.873	4.709	3.836	-8.568	-0.552	4.560	4.008
NH ₂ CSNH ₂	-8.525	0.365	4.080	4.445	-8.618	-0.270	4.444	4.174	-8.915	-0.195	4.555	4.360
(CH ₃) ₂ NCSNH ₂	-8.350	0.386	3.982	4.368	-8.618	-0.627	4.623	3.996	-8.703	-0.109	4.406	4.297
(C ₂ H ₅) ₂ NCSNH ₂	-8.291	0.344	3.974	4.318	-8.553	-0.551	4.552	4.001	-8.603	-0.049	4.326	4.277
Ph ₂ NCSNHPH	-8.215	-0.378	4.297	3.919	-8.454	-0.905	4.680	3.775	-8.461	-0.324	4.393	4.069
CH ₃ NHCSNH ₂	-7.466	-0.199	3.833	3.634	-8.186	-0.759	4.473	3.714	-8.228	-0.281	4.255	3.974
(CH ₃) ₂ NCSNH ₂	-7.430	-0.172	3.801	3.629	-8.096	-0.670	4.383	3.713	-8.147	-0.244	4.196	3.952
(C ₂ H ₅) ₂ NCSNH ₂	-7.410	-0.176	3.793	3.617	-8.034	-0.629	4.332	3.703	-8.064	-0.195	4.130	3.935
PhNHCSNH ₂	-7.429	-0.281	3.855	3.574	-8.033	-0.984	4.509	3.525	-8.153	-0.358	4.256	3.898

ues reported there are examined a clear trend of hardness is demonstrated. The fluorides of all the transition metal reported there are harder than other halides. The softest in all case is iodide. The trend in hardness values among the metals is Fe > Co > Ni > Cu which is almost as per reported trend [18]. In case of halides other than transition metal halides (TABLE 1B) the semiempirical methods provide very good trends which are compatible with established trends. In all these cases the fluorides have the highest value of hardness and the iodides have the lowest. All the zinc halides have higher values of hardness, as compared to their cadmium and mercury counterparts. The Sn(IV) halides have very high

values of hardness, which is consistent with their higher oxidation state, PM5 method provides better results than AM1 and PM3 methods.

Nucleophiles

The absolute hardness and electronegativity values of organic bases have similarly been calculated by all the semi empirical methods and the results are included in TABLE 2. The scale of hardness of various bases is according to the established trends and also similar to our earlier work [11].

Metal-ligand interaction

We have applied the results of semiempirical cal-

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TABLE 3A: HOMO-LUMO density values of transition metal halide derived by semi empirical method-AM1, PM3, and PM5 and DFT-PW91 method

Compounds	Metal atom	AM1		PM3		PM5		DFT	
		Density		Density		Density		Density	
		HOMO	LUMO	HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
FeF ₂	Fe	0.9420	0.8260	0.9360	0.8380	0.9430	0.8150	0.9990	0.0600
FeCl ₂	Fe	0.8760	0.8800	0.7790	0.8610	0.9930	0.0930	0.7250	0.0390
FeBr ₂	Fe	0.0030	0.8750	0.6800	0.9170	0.9090	0.8620	0.2550	0.0400
FeI ₂	Fe	-0.0050	0.8770	0.1800	0.9500	-0.0550	0.7480	0.1290	0.0470
Fe(NCS) ₂	Fe	0.1480	0.4060	0.2200	0.3330	0.9600	0.2320	0.0520	0.0060
Fe(NCSe) ₂	Fe	0.0520	0.4360	0.0670	0.9950	0.9620	0.2660	0.0010	0.0170
CoCl ₂	Co	0.4870	0.5610	0.6370	0.9790	0.5920	0.6970	0.9990	0.8150
CoF ₂	Co	0.5770	0.6030	0.5600	0.9270	0.6510	1.5660	0.5680	0.8160
CoBr ₂	Co	0.4590	0.5510	0.5810	0.8650	0.5860	1.1500	0.9830	0.0550
CoI ₂	Co	0.8580	0.5150	0.5320	0.9770	1.1710	0.5320	0.9280	0.0720
Co(NCS) ₂	Co	0.2480	0.2410	0.3310	0.4130	0.2500	0.1590	0.3670	0.1550
Co(NCSe) ₂	Co	0.1810	0.1820	0.2890	0.0620	0.1110	0.2930	-0.0810	0.4270
NiF ₂	Ni	0.8640	0.8440	0.9130	0.9010	0.9220	0.8410	0.8780	0.9660
NiCl ₂	Ni	0.8720	0.8720	1.0000	0.9340	0.0500	0.9740	0.6040	0.6860
NiBr ₂	Ni	0.8000	0.8130	0.9980	0.9200	0.1200	0.7750	0.5520	0.9930
NiI ₂	Ni	0.0716	0.7270	0.9180	0.8980	0.0510	0.6990	0.5090	0.9990
Ni(NCS) ₂	Ni	0.7970	0.9100	0.7820	1.0000	0.1340	0.4060	-110.0000	0.0300
Ni(NCSe) ₂	Ni	0.2880	0.7120	0.5480	0.0210	0.5850	0.4750	0.2720	0.6480
CuF ₂	Cu	0.6900	0.6400	1.0000	0.6370	1.0000	0.6310	0.5250	0.4740
CuCl ₂	Cu	0.0301	0.6970	0.3280	0.8970	0.3520	0.7350	0.3680	0.3140
CuBr ₂	Cu	0.1860	0.7200	0.5400	0.7790	0.2280	0.7500	0.3070	0.2550
CuI ₂	Cu	0.1120	0.7400	0.0000	0.9680	0.0400	0.8480	0.2360	0.1860
Cu(NCS) ₂	Cu	0.8900	0.1950	0.3700	0.0000	0.3290	0.0000	0.0000	0.1580
Cu(NCSe) ₂	Cu	0.0190	0.0910	0.0040	0.0010	0.2650	0.0230	0.1220	0.1140

TABLE 3B: HOMO-LUMO density values of non transition metal halide derived by semi empirical method-AM1, PM3, and PM5

Compounds	Metal atom	AM1		PM3		PM5	
		Density		Density		Density	
		HOMO	LUMO	HOMO	LUMO	HOMO	LUMO
ZnF ₂	Zn	0.0000	0.7290	0.0000	0.6840	0.0000	0.9280
ZnCl ₂	Zn	0.7000	0.9660	0.6740	0.9580	0.7990	0.9800
ZnBr ₂	Zn	0.0000	0.6740	0.0000	0.6770	0.0000	0.8120
ZnI ₂	Zn	0.0000	0.5970	0.0000	0.5840	0.0000	0.7000
Zn(NCS) ₂	Zn	0.0000	0.7150	0.0000	0.5940	0.0000	0.5330
Zn(NCSe) ₂	Zn	0.0000	0.6420	0.0000	0.6340	0.0000	0.5420
CdCl ₂	Cd	Error	Error	0.0000	0.6340	0.0000	0.5420
CdI ₂	Cd	Error	Error	Error	0.7510	Error	0.6430
CdF ₂	Cd	Error	Error	0.0000	0.6890	0.0000	0.6020
CdBr ₂	Cd	Error	Error	Error	0.6540	Error	0.4890
Cd(NCS) ₂	Cd	Error	Error	0.0000	0.7250	0.0010	0.5860
Cd(NCSe) ₂	Cd	0.0000	0.6850	0.0000	0.7220	0.0000	0.6340
HgCl ₂	Hg	Error	0.5780	0.0550	0.7500	0.6700	0.7260
HgBr ₂	Hg	0.0000	0.4480	Error	0.7370	Error	0.6390
HgI ₂	Hg	Error	0.5610	0.1280	0.5180	0.0000	0.5660
HgF ₂	Hg	0.0000	0.7240	Error	0.7210	Error	0.5660
Hg(NCS) ₂	Hg	0.7840	0.0100	0.0000	0.7750	0.0000	0.7010
Hg(NCSe) ₂	Hg	Error	Error	0.8870	0.0150	0.7210	0.0220
SnCl ₄	Sn	Error	Error	0.0190	0.3800	0.0000	0.5030
SnBr ₄	Sn	Error	Error	0.0090	0.4170	0.0020	0.4050
SnI ₄	Sn	Error	Error	0.0000	0.3320	0.0290	0.2250
PhSnCl ₃	Ph	Error	Error	0.0000	0.4390	0.0000	0.5100
Ph ₂ SnCl ₂	Ph	Error	Error	0.0000	0.4860	0.0000	0.5230
Ph ₃ SnCl	Ph	Error	Error	0.0000	0.5280	0.0130	0.5950
Ph ₃ SnCl ₃	Ch	Error	Error	0.0270	0.4200	0.0900	0.5020
(CH ₃) ₂ SnCl ₂	Ch	Error	Error	0.0290	0.4560	0.1090	0.5260
(CH ₃) ₃ SnCl	Ch	Error	Error	0.0290	0.4880	0.1400	0.6010

culations to metal ligand interaction. The electron transfer between donor acceptor reaction involves definite filled orbitals on the donor and definite empty orbital on the acceptor. The important donor orbital will usually be the HOMO and the most important acceptor orbital will be the LUMO. The normalized electron densities of these frontier orbital are called the fukui function^[13].

TABLE 4: HOMO density values of organic donors derived by semi empirical method-AM1, PM3, and PM5.

Compounds	Metal atom	AM1	PM3	PM5
		Density	Density	Density
CH ₃ NH ₂	N	0.715	0.816	0.711
(CH ₃) ₂ NH	N	0.654	0.764	0.649
(CH ₃) ₃ N	N	0.622	0.737	0.617
PhNH ₂	N	0.29	0.439	0.338
Ph ₂ NH	N	0.283	0.389	0.294
Ph ₃ N	N	0.291	0.398	0.304
HCONH ₂	O	0.319	0.237	0.351
CH ₃ CONH ₂	O	0.315	0.226	0.336
C ₂ H ₅ CONH ₂	O	0.308	0.232	0.36
PhCONH ₂	O	0.21	0.185	0.023
NH ₂ CONH ₂	O	0.483	0	0
CH ₃ NHCONH ₂	O	0.174	0.092	0.133
PhNHCONH ₂	O	0.029	0.034	0.37
Ph ₂ NCONH ₂	O	0.032	0.04	0.033
HCSNHCH ₃	S	0.03	0.037	0.03
HCSNH ₂	S	0.029	0.032	0.03
HCSNHC ₂ H ₅	S	0.0163	0.361	0.352
HCSN(C ₂ H ₅) ₂	S	0.163	0.355	0.378
C ₅ H ₄ FN	N	0.018	0.019	0.013
C ₅ H ₄ CIN	N	0.012	0.039	0.017
C ₅ H ₄ BrN	N	0.009	0.014	0.012
C ₅ H ₄ IN	N	0.006	0.025	0.012

$f = \rho$ HOMO donor molecule

$f = \rho$ LUMO acceptor molecule

$f = 1/2 (\rho \text{HOMO} + \rho \text{LUMO})$ both donor and acceptor

The last equation is for the case where electron transfer is in both directions as in $\sigma + \pi$ bonding. The difference in energy of the HOMO of nucleophiles and LUMO of electrophiles has also been used to describe the stability of the bond formed between them^[24,13,26]. In our recent communication we have shown that lower is the value of difference between the energy of HOMO and LUMO greater is the stability of the bond^[26]. Based on the above principles we have made studies of various types of metal-ligand interaction as below.

Frontier molecular orbital densities

The LUMO densities at metals of metal halides [Metals=Sn(IV),Zn(II), Cd(II),Hg(II)], and HOMO densities at sulphur in ethylenethiourea ally thioiourea and ring nitrogen in nicotinamide, at oxygen in pyridine oxide and at phosphorus in triphenyl phosphine have been derived and the results are included in TABLE 3A, 3B, and 4. The difference in LUMO densities of metals and HOMO densities of donor atom has been obtained by the equation:-

$$\Delta LH = [\text{HOMO-LUMO}]$$

and are presented in TABLE 5 The PM3 calculation shows that Sn(Br)₄ is better acceptor than SnCl₄ and SnI₄ and HgCl₂ is better acceptor as compared to CdCl₂ and ZnCl₂. PM5 calculation however shows that SnCl₄ and HgCl₂ are the best acceptor. The results of

TABLE 5: Difference DLH = (HOMO-LUMO), between LUMO density of metal halides and HOMO density of donor molecules

Compounds	ΔE_{nm}^{++}	PM3			PM5			DFT-PW91		
		LUMO	HOMO	ΔLH	LUMO	HOMO	ΔLH	LUMO	HOMO	ΔLH
SnCl ₄ .2ETU	25.740	0.380	0.933	0.553	0.503	0.892	0.389	0.487	0.909	0.422
SnBr ₄ .2ETU	24.070	0.417	0.933	0.516	0.405	0.892	0.487	0.411	0.909	0.498
SnI ₄ .2ETU	21.970	0.332	0.933	0.601	0.225	0.892	0.667	0.293	0.909	0.616
SnCl ₄ .2ATU	26.040	0.380	0.916	0.536	0.503	0.887	0.384	0.487	0.890	0.403
SnBr ₄ .2ATU	24.290	0.417	0.916	0.499	0.405	0.887	0.482	0.411	0.890	0.479
SnI ₄ .2ATU	22.250	0.332	0.916	0.584	0.225	0.887	0.662	0.293	0.890	0.597
ZnCl ₂ .2NIA	7.030	0.958	0.208	0.750	0.980	0.002	0.987	0.702	0.570	0.132
CdCl ₂ .2NIA	6.050	0.751	0.208	0.543	0.643	0.002	0.641	0.752	0.570	0.182
HgCl ₂ .NIA	5.180	0.737	0.208	0.529	0.639	0.002	0.637	0.539	0.570	0.031
ZnCl ₂ .2PPh ₃	0	0.958	0.547	0.411	0.980	0.491	0.489	0.702	0.525	0.177
CdCl ₂ .2PPh ₃	0.980	0.751	0.547	0.204	0.643	0.491	0.152	0.752	0.525	0.227
HgCl ₂ .PPh ₃	1.850	0.737	0.547	0.190	0.639	0.491	0.148	0.539	0.525	0.014
ZnCl ₂ .2PYO	6.210	0.958	0.315	0.643	0.980	0.462	0.518	0.702	0.537	0.165
CdCl ₂ .2PYO	5.230	0.751	0.315	0.436	0.643	0.462	0.181	0.752	0.537	0.215
HgCl ₂ .2PYO	4.360	0.737	0.315	0.422	0.639	0.462	0.177	0.539	0.537	0.002

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TABLE 6: Difference between the HOMO density value of donors and LUMO density value of metal ion- $\Delta LH = \text{HOMO} - \text{LUMO}$

HOMO density of donor			LUMO density of metal ions				
Donors	Site	Density	Li	Be	Sr	Ca	Mg
			1	0.92	0.918	0.918	1.015
			$\Delta LH = \text{HOMO} - \text{LUMO}$				
Ethylenediamine	N	0.314	0.686	0.606	0.604	0.604	0.701
Nicotinamide	O	0.002	0.998	0.918	0.916	0.916	1.013
Tetrahydrofuran	O	0.539	0.461	0.381	0.379	0.379	0.476
Diethylformamide	O	0.219	0.781	0.701	0.699	0.699	0.796
Triphenylphospine	O	0.491	0.509	0.429	0.427	0.427	0.524

PM5 calculations are also supported by DFT calculation results, and by ΔE_{nm} values^[11]. The ΔLH values are also in agreement with the results derived by ΔN and ΔE values, (TABLE 8). AM1 calculations indicate error in number of cases hence have not been included in the table or in discussion. The HOMO densities of certain metal ions are presented in TABLE 6. The ΔLH value indicate highest value for magnesium and lowest for calcium for strontium. The same sequence of stability is exhibited by $\log K$ values^[27].

Transition metal halide complexes

Since semi empirical methods do not provide a reliable information about transition metal halides we made DFT calculation for their study. The LUMO densities of M (II) halides (M=Fe, Co, Ni, Cu) and HOMO densities of pyridine and isoquinoline at their nitrogen ends, have been evaluated by DFT method and are included in TABLE 7. The Difference in their energies does not provide any sequence, which may be well related with the experimental results or the established trend. The $f=1/2(\text{HOMO}+\text{LUMO})$, also does not provide any trend. The ΔE_{nm} ^[11] values also did not provide any good relationship and a good relation with experimental results could only be obtained after addition of CFSE values to ΔE_{nm} values. Similarly one more parameter will have to be added to ΔLH to obtain the required trend. Density functional theory or electron density alone could not describe all the chemical phenomena its sensitivities of structural perturbation and responses to changes in external condition are more important^[28]. In the light of the above we tried other parameters, in combination with ΔLH values, which could provide a proper trend in studying the transition metal reactions. Ionization potential evaluated by the method described elsewhere^[29] provided the solution. If values of IP of the Lewis acids are added to the

TABLE 7 : LUMO densities and IP of transition metal halides and HOMO densities of pyridine (Py) and isoquinoline (IQ) by DFT-PW 91 method

Compounds	ρLUMO	ρHOMO	IP	ΔLH	$\Delta LH+IP$
Fe(py) ₄ .Cl ₂	0.725	0.693	20.11	0.032	20.142
Fe(Ppy) ₄ Br ₂	0.255	0.693	19.28	0.438	19.718
Fe(IQ) ₄ Cl ₂	0.725	0.032	20.11	0.693	20.803
Fe(IQ) ₄ Br ₂	0.255	0.032	19.28	0.223	19.503
Fe(IQ) ₄ I ₂	0.129	0.032	17.84	0.097	17.937
Co(py) ₄ .Cl ₂	0.568	0.693	21.23	0.125	21.355
Co(Ppy) ₄ Br ₂	0.983	0.693	20.2	0.29	20.49
Co(IQ) ₄ Cl ₂	0.568	0.032	21.23	0.536	21.766
Co(IQ) ₄ Br ₂	0.983	0.032	20.2	0.951	21.151
Co(IQ) ₄ I ₂	0.928	0.032	18.65	0.896	19.546
Ni(py) ₄ .Cl ₂	0.604	0.693	22.27	0.089	22.359
Ni(IQ) ₄ Cl ₂	0.604	0.032	22.27	0.572	22.842
Ni(IQ) ₄ Br ₂	0.552	0.032	21.29	0.52	21.81
Ni(IQ) ₄ I ₂	0.509	0.032	19.57	0.477	20.047
C(py) ₄ .Cl ₂	0.368	0.693	27.24	0.325	27.565
C(py) ₄ Br ₂	0.307	0.693	26.27	0.386	26.656
C(py) ₄ I ₂	0.236	0.693	24.36	0.457	24.817
Co(IQ) ₄ Cl ₂	0.368	0.032	27.34	0.336	27.676
Co(IQ) ₄ Br ₂	0.307	0.032	26.27	0.275	26.545
Co(IQ) ₄ I ₂	0.236	0.032	24.36	0.204	24.564

value of ΔLH , the following trend in stability of metal ligand bond is obtained which is similar to the order reported on the basis of thermodynamic stability ($\log K$) of transition metal complexes^[30].

Cu > Ni > Co > Fe

Charge transfer N and energy lowering ΔE

There has been number of molecular orbital treatments of Lewis acid-base reactions. The Mulliken^[31] 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,

TABLE 8: The absolute hardness and electronegativity of acid (A) and bases(B) and ΔE and ΔN derived from them

Compounds		A		B		ΔE	ΔN
A	B	η	χ	η	χ		
ZnF ₂	NH ₃	7.0430	7.0390	6.5010	3.6590	0.2109	0.1248
ZnCl ₂	CH ₃ NH ₂	5.7270	5.9870	5.9840	3.4840	0.1337	0.1069
ZnBr ₂	(CH ₃) ₂ NH	5.2380	5.9380	5.6880	3.4020	0.1472	0.1161
ZnI ₂	(CH ₃) ₃ N	4.1390	5.8920	5.4950	3.3730	0.1647	0.1307
Zn(NCS) ₂	PhNH ₂	4.2390	5.2630	4.4240	3.5540	0.0843	0.0986
Zn(NCSe) ₂	Ph ₃ N	3.8960	5.1440	4.2150	3.8220	0.0539	0.0815
CdCl ₂	HCONH ₂	4.9490	8.4550	5.5630	4.9560	0.2912	0.1664
CdI ₂	CH ₃ CONH ₂	4.8270	7.4630	5.5380	4.8480	0.1649	0.1261
CdF ₂	C ₂ H ₅ CONH ₂	4.4140	7.0670	5.5400	4.8080	0.1282	0.1135
CdBr ₂	PhCONH ₂	3.8550	6.3700	4.7590	5.1250	0.0450	0.0723
Cd(NCS) ₂	NH ₂ CONH ₂	3.1460	6.4890	5.2420	5.0670	0.0603	0.0848
Cd(NCSe) ₂	CH ₃ NHCONH ₂	2.8640	6.3290	5.1740	4.8490	0.0681	0.0921
HgCl ₂	(CH ₃) ₂ NCONH ₂	5.6770	8.3850	4.9910	4.6290	0.3306	0.1760
HgBr ₂	PhNHCONH ₂	4.4010	6.9310	4.2650	4.4410	0.1789	0.1437
HgI ₂	Ph ₂ NCONH ₂	4.0880	6.6250	4.4290	4.4340	0.1409	0.1286
HgF ₂	Ph ₂ NCONHPh	3.4220	6.7020	4.0690	4.3930	0.1779	0.1541
Hg(NCS) ₂	(CH ₃) ₂ NCONH ₂	3.0670	6.3660	4.9910	4.6290	0.0936	0.1078
Hg(NCSe) ₂	HCSNHCH ₃	2.7310	6.2390	4.2770	4.5670	0.0997	0.1193
SnCl ₄	HCSNH ₂	4.3550	7.7770	4.2860	4.6530	0.2824	0.1808
SnBr ₄	HCSNHC ₂ H ₅	3.8800	7.6460	4.2780	4.5030	0.3027	0.1926
SnI ₄	HCSN(C ₂ H ₅) ₂	3.0040	7.2220	4.2410	4.3410	0.2864	0.1988
PhSnCl ₃	HCSNHPh	3.7110	6.2250	3.9850	4.8200	0.0641	0.0913
Ph ₂ SnCl ₂	.HCSNPh ₂	3.9540	5.6870	4.0080	4.5600	0.0399	0.0708
Ph ₃ SnCl	NH ₂ C ₂ SNH ₂	4.1120	5.1990	4.3600	4.5550	0.0122	0.0380
CH ₃ SnCl ₃	(CH ₃) ₂ .NCSNH ₂	4.1630	6.6550	4.2970	4.4060	0.1495	0.1329
(CH ₃) ₂ SnCl ₂	(C ₂ H ₅) ₂ .NCSNH ₂	4.1930	5.7930	4.2770	4.3260	0.0635	0.0866
(CH ₃) ₃ SnCl	Ph ₂ NCSNHPh	4.3790	5.1600	4.0690	4.3930	0.0174	0.0454

we have the following equation:

$$(A_A - A_B) - (I_B - A_A) = 2(\chi_A^\circ - \chi_B^\circ) \quad (7)$$

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 driving force for electron transfer. The absolute electronegativity of acceptor A and donor B calculated by PM5 method are included in TABLE 8. A lower value of electronegativity is indicative of a better donor character whereas a higher value of electronegativity is indicative of better acceptor character^[13]. A reference to the table indicates that electronegativity values of donor molecules are less than of acceptor molecules, hence the equation-8 has a positive value. The χ values indicate that the acceptor strength of Sn (IV) halides will be $\text{SnCl}_4 > \text{SnBr}_4 > \text{SnI}_4$ and in case of Zn, Cd and Hg thiocyanates, the mer-

cury thiocyanate will be best acceptor. On the basis of χ values the base strength of donor molecules can be examined.

The electronegativity (χ) difference derives the electron transfer and the sum of hardness parameter (η) inhibits it. The net result of shift in charge ΔN and lowering in energy ΔE due to electron transfer is given by the equations-3 and 4. The value of ΔN and ΔE have been evaluated and are included in Table 8. The ΔN values clearly indicate that maximum charge transfer is in SnCl_4 complexes and minimum in case Ph_3SnCl complexes. In case of Zn, Cd and Hg complexes the maximum values of ΔN and ΔE are observed in case of mercury thiocyanate complexes. All the results are in conformity with the result obtained by ΔL_H values and ΔE_{nm} values^[11].

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