

DFT based Study of interaction between Frontier Orbitals of Transition Metal Halides and Thioamides

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Abstract: HOMO and LUMO energies and densities of frontier orbital of M (II) halides (M=Fe, Co, Ni, Cu) and a set of thioamides have been evaluated. The metal-ligand interaction between metal halides and thioamides have been studied on the basis of energies and densities of frontier orbitals. The results of HOMO density of frontier orbitals indicate that among thioamides, the sequence of donor ability is in the order, thiazolidinethione > diethyl thioformamide > ethyl thioformamide > methylthioformamide = thioformamide. In case of transition metal fluorides, the acceptor strength is in order of iron > cobalt > nickel > copper. The magnitude of interaction has been evaluated by lowering of energy and shift in charge, by solving the equation $\Delta E = (\chi_A^0 - \chi_B^0)^2 / 4(\eta_A + \eta_B)$ and $\Delta N = (\chi_A^0 - \chi_B^0) / 2(\eta_A + \eta_B)$ respectively. The results indicate that the magnitude of metal-ligand bond strength in the complexes is $\text{CoCl}_2 \cdot 2\text{ETU} > \text{CoCl}_2 \cdot 2\text{TZT} > \text{CoCl}_2 \cdot 2\text{ATU} > \text{CoCl}_2 \cdot 2\text{TU} > \text{CoCl}_2 \cdot 2\text{EU} > \text{CoI}_2 \cdot 2\text{ATU} > \text{CoI}_2 \cdot 2\text{ETU} > \text{CoI}_2 \cdot 2\text{TZT} > \text{CoI}_2 \cdot 2\text{TU} > \text{CoI}_2 \cdot 2\text{EU} > \text{CoBr}_2 \cdot 2\text{TZT} > \text{CoBr}_2 \cdot 2\text{TU} > \text{CoBr}_2 \cdot 2\text{ATU} > \text{CoBr}_2 \cdot 2\text{ETU} > \text{CoBr}_2 \cdot 2\text{EU}$.

Key words: DFT, energy lowering, charge transfer, thioamides and transition metal halides.

INTRODUCTION

Klopman(1) developed a quantum mechanical equation for calculation of quantitative values of softness of acid and base ions and derived the reactivity by the difference in softness values of acid and base ions. By simple modification of known methods (2-5) Singh et al calculated the values of ionization potential, charge and radius of atom for neutral molecules, and solved the Klopman equation for neutral Lewis acids and bases, and developed matching between them in terms of E_{nm}^{\ddagger} and their relationship to the stability of metal ligand bond. (6) The application of density functional theory (DFT) (7) has given a new concept to chemical system. This concept focuses on the one electron density function instead of wave function (8). For every chemical

system there is a quantity μ called the electronic chemical potential. A chemical system is an atom, molecule, ion or radical or several such unit in a state of interaction. Recent work based on density functional theory has developed the concept of absolute electronegativity, χ , and absolute hardness η (9). The definitions are

$$\chi = -E / N_z = -\mu \quad (1)$$

$$\eta = \frac{1}{2} E / N_z^2 \quad (2)$$

Where E is the electronic energy of a molecule, atom, or ion, N is the number of electrons, and Z is a fixed set of nuclear charges. The absolute electronegativity is also equal to the electronic

chemical potential, μ , with change in sign. The operational (and approximate) definitions are

$$\chi = \frac{1}{2} (I + A) \quad (3)$$

$$\eta = \frac{1}{2} (I - A) \quad (4)$$

Where I is the ionization potential, and A is the electron affinity. The absolute electronegativity is the same as the Mulliken value.

Klopman based his concept on charge and frontier orbital controlled chemical reactions of perturbation theory. Parr and Yang (10) reconciled DFT with the frontier orbital theory of chemical reactivity. Since this theory is very successful, it is important to examine the correlation of this theory with that of the Klopman approach. We in this paper have made DFT calculation and have examined the relationship with the results obtained by Klopman equation.

MATERIALS AND METHOD:

Metal (II) halides of iron, cobalt, nickel and copper have been used as Lewis acids and compounds 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 method in conjunction with DZVP basis set. The values of charge, electron density, eigenvalues of frontier orbital, and absolute hardness and electronegativity of Lewis acid and Lewis bases have been evaluated by solving the equation 1-8. 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 become equal. The condition of equilibrium is that the chemical potential, μ_A and μ_B , become equal. This leads to shift in charge, ΔN , from less electronegative base (B) to more electronegative acid (A).

$$\Delta N = (\chi^{\circ}_A - \chi^{\circ}_B) / 2(\eta_A + \eta_B) \quad (5)$$

Electron transfer leads to an energy lowering given by equation 6.

$$\Delta E = (\chi^{\circ}_A - \chi^{\circ}_B)^2 / 4(\eta_A + \eta_B) \quad (6)$$

In equation 5 and 6 the electronegativity difference drives 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,

$$2\eta = (\delta\mu / \delta N)_z \quad (7)$$

The chemical potential and the absolute electronegativity are molecular properties and not orbital properties. According to Koopman's (7) theorem the I is simply the eigenvalue of HOMO with change of sign and A is the eigenvalue of LUMO with change of sign, hence the equation-4 can be written as-

$$\eta = \frac{1}{2} (\epsilon \text{ LUMO} - \epsilon \text{ HOMO}) \quad (8)$$

RESULTS AND DISCUSSION:

Frontier Molecular Orbital Energies as obtained by DFT method:

Energies of HOMO and LUMO are popular quantum mechanical descriptors. It has been shown (11) that these orbitals play a major role in governing many chemical reactions, and are also responsible for charge transfer complexes (12). The treatment of the frontier molecular orbitals separately from the other orbitals is based on the general principles governing the nature of chemical reactions (13). The energy of the HOMO is directly related to the ionization potential and characterizes the susceptibility of the molecule towards attack of electrophiles. The energy of LUMO is directly related to the electron affinity and characterizes the susceptibility of the molecule towards attack of nucleophiles. 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 (14). HOMO-LUMO gap is an important stability index (15).

$$\epsilon \text{ LUMO} - \epsilon \text{ HOMO} = \text{energy gap} \quad (9)$$

Absolute hardness η is equal to half the value of the difference in energy of the LUMO and HOMO (11,16).

$$\eta = (\epsilon \text{ LUMO} - \epsilon \text{ HOMO}) / 2.$$

The energies of the LUMO and HOMO have been evaluated for thiazolidinethione and also a set of organic nucleophiles having thioamides as donor site by DFT method. The difference in energies of HOMO-LUMO, and value of absolute hardness η , derived from the energy values are presented in Table-1.

Table 1 : Absolute hardness values of nucleophiles drawn from eigen values of HOMO and LUMO by DFT method.

Chemical sample	ϵ HOMO	ϵ LUMO	LUMO-HOMO	η
HCSNH ₂	-4.813	-1.805	3.008	1.5040
HCSNHCH ₃	-4.662	-1.626	3.036	1.5180
HCSNHC ₂ H ₅	-5.270	-2.504	2.766	1.3830
HCSN(C ₂ H ₅) ₂	-4.772	-2.887	1.885	0.9425
HCSNHPH	-4.992	-2.796	2.196	1.0980
HCSNPh ₂	-4.800	-2.863	1.937	0.9685
NH ₂ CSNH ₂	-4.999	-1.199	3.800	1.9000
(CH ₃) ₂ NCSN(CH ₃) ₂	-4.352	-0.849	3.503	1.7515
(C ₂ H ₅) ₂ NCSN(C ₂ H ₅) ₂	-4.048	-0.799	3.249	1.6245
H ₂ CSCSNHCH ₂ (TZT)	-4.815	-1.496	3.319	1.6595

ϵ HOMO is eigen values of highest occupied molecular orbital, ϵ LUMO is eigen values of lowest unoccupied molecular orbital, LUMO-HOMO is the energy gap, and η is the absolute hardness calculated from equation 7.

The hardness value in case of thioamide and thioureas are in the range of 0.942 for diethyl thioamide, and 1.752 for tetramethyl thiourea. It is also evident that phenyl substitution makes them softer. The value in tetra methyl thiourea is 1.752. It is quite clear that absolute hardness value of thiazolidinethione is in the range of sulphur donors. The nitrogen donors have higher values and are in the range 2.50-3.45.

Transition Metal Halides:

The energies of HOMO and LUMO, the differences in their energies, and absolute hardness values of cobalt (II) halides and the halides of other transition metals as derived by DFT method are included in Table-2. Following observations are made from different values of this table.

Unlike non transition metal halides, they do not furnish any trend. The highest value of hardness in case of manganese (II) halides is shown by MnCl₂ and lowest by MnF₂. In case of iron (II) halides and cobalt (II) halides, the hardness value is highest in their bromides and lowest in their iodides. The highest value of hardness in case of nickel (II) halides are shown by NiCl₂ and in copper (II) halides by CuF₂. The lowest value in these two cases are respectively shown by NiF₂ and CuI₂. It is prominently demonstrated that absolute hardness values do not furnish any trend which may be compatible with established trend of hardness or softness. Scale of hardness if drawn by the value of IP and EA of previous work (6) or if the softness values E_n^\ddagger 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 among the metal is as below which is almost as per reported trend (17).

Fe > Co > Ni > Cu.

Frontier Molecular Orbital Densities:

Molecular orbital energies are molecular properties whereas orbital densities are atomic properties, and provide useful information about donor acceptor interaction (18). According to frontier electron reactivity theory, the chemical reaction takes place at a position where overlap of the HOMO and LUMO are the maximum (13). In the case of donor molecule the HOMO density and in case of acceptor molecule the LUMO density are important for any reaction. Frontier orbital densities can strictly be used to describe the reactivity of different atoms in the same molecule (12,13). The electron density of the HOMO at an atom is a measure of relative reactivity of the HOMO at that atom within a single molecule while the energy level of the HOMO reflects the reactivity of different molecule, thus molecules with smaller ionization potential ($-\epsilon$ HOMO) are expected to be more reactive as nucleophiles (19).

The HOMO densities of a number of donor molecules have been evaluated by DFT method at different sites that is at sulphur and nitrogen in thiazolidinethione and results are tabulated in the Table-3 along with value of other nucleophiles which too have sulphur and nitrogen as possible reactive site for example thioamide and thioureas. The atom having highest density has been identified. It is evident that in all case the HOMO density is highest at thioamide sulphur.

The thioamide generally coordinate through thioamide sulphur (20a, 20b), but in some cases, nitrogen has been shown as coordinating site (21). The values of HOMO densities at various thioamide and thioureas are highest at sulphur as compared to other atoms. The highest value 0.891 is shown by thiazolidinethione and lowest value 0.009 by thioformamide. This supports the coordination through sulphur in thioamides. In thiazolidinethione the HOMO density at thioamide sulphur is higher as

compared to HOMO density at nitrogen. The value of thioamide sulphur is 0.891. On the basis of the HOMO density values at thioamide sulphur, the donor ability (reactivity) of various thioamides can be arranged as follows.

Thiazolidinethione > diethyl thioformamide > ethyl thioformamide > methyl thioformamide > thioformamide.

Table-2 : Absolute hardness value of metal (II) halides derived from HOMO and LUMO energy by DFT method.

Chemical sample	ϵ HOMO	ϵ LUMO	LUMO - HOMO	η
FeF ₂	3.271	-1.572	4.843	2.4215
FeCl ₂	5.382	0.835	4.547	2.2735
FeBr ₂	4.641	-0.230	4.871	2.4355
FeI ₂	4.262	-0.212	4.474	2.2370
CoF ₂	-7.275	-6.327	-0.948	0.4740
CoCl ₂	-6.894	-6.703	-0.191	0.0955
CoBr ₂	2.539	0.392	2.147	1.0735
CoI ₂	-5.185	-5.168	-0.017	0.0085
NiF ₂	-7.227	-7.108	0.119	0.0595
NiCl ₂	-6.386	-6.911	0.525	0.2625
NiBr ₂	-5.955	-6.347	0.392	0.1960
NiI ₂	-5.559	-5.946	0.387	0.1935
CuF ₂	-8.229	-2.414	-5.815	2.9075
CuCl ₂	-7.295	-1.847	-5.448	2.7240
CuBr ₂	-6.798	-1.789	-5.009	2.5045
CuI ₂	-6.307	-1.737	-4.570	2.2850

ϵ HOMO is eigen values of highest occupied molecular orbital, ϵ LUMO is eigen values of lowest unoccupied molecular orbital, LUMO-HOMO is the energy gap, and η is the absolute hardness calculated from equation 1.

Table-3 Highest HOMO density values of various donor molecules.

Compound	Atom	ρ_{HOMO}
HCSNH ₂	S	0.009
HCSNHCH ₃	S	0.009
HCSNHC ₂ H ₅	S	0.257
HCSN(C ₂ H ₅) ₂	S	0.568
H ₂ CSCSNHCH ₂ (TZT)	S	0.891

ρ_{HOMO} is the HOMO density calculated from DFT method, in conjunction with DZVP basis set.

Table - 4 HOMO and LUMO densities on metal atoms of metal (II) halides

Metal halide	Atom	ρ_{LUMO}	ρ_{HOMO}
FeF ₂	Fe	0.999	0.060
FeCl ₂	Fe	0.725	0.039
FeBr ₂	Fe	0.255	0.040
FeI ₂	Fe	0.129	0.047
Fe(CNS) ₂	Fe	0.052	0.006
Fe(CNSE) ₂	Fe	0.001	0.017
CoF ₂	Co	0.999	0.815
CoCl ₂	Co	0.568	0.816
CoBr ₂	Co	0.983	0.055
CoI ₂	Co	0.928	0.072
Co(CNS) ₂	Co	0.367	0.155
Co(CNSE) ₂	Co	0.081	0.427
NiF ₂	Ni	0.878	0.966
NiCl ₂	Ni	0.604	0.686
NiBr ₂	Ni	0.552	0.993
NiI ₂	Ni	0.509	0.999
Ni(CNS) ₂	Ni	0.011	0.030
Ni(CNSE) ₂	Ni	0.272	0.648
CuF ₂	Cu	0.525	0.474
CuCl ₂	Cu	0.368	0.314
CuBr ₂	Cu	0.307	0.255
CuI ₂	Cu	0.236	0.186
Cu(CNS) ₂	Cu	0.000	0.158
Cu(CNSE) ₂	Cu	0.122	0.144

ρ_{LUMO} is the LUMO density, ρ_{HOMO} is the HOMO density calculated from DFT method, in conjunction with DZVP basis set.

Transition Metal Halides:

HOMO-LUMO densities of metal atom in cobalt halides have been evaluated by DFT method and difference between them has been evaluated and is presented in Table-4, along with values of other transition metal halide.

The highest LUMO density is observed in the fluorides, the next is chloride in all the cases except cobalt where it is bromide. The lowest value is thiocyanates in the case of iron and cobalt, and selenocyanate in the case of nickel and copper. It is evident that fluorides will be the best acceptor. The acceptor strength in the case of different fluorides is Fe-Co > Ni > Cu, whereas in other case it changes from halide to halide. Whereas HOMO-LUMO density difference does not indicate any worthwhile trend.

Metal-Ligand Interaction:

Parr and Yang (10) reconciled DFT with the frontier orbital theory of chemical reactivity. Since this theory is very successful we have applied the result of DFT calculations to cobalt halide and

thiazolidinethione interaction. The electron transfer between donor acceptor reactions involve definite filled orbitals on the donor and definite empty orbitals on the acceptors. The most 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 orbitals are called the fukui function- f (15).

$$\begin{array}{ll}
 f = \rho_{HOMO} & \text{donor molecule} \\
 f = \rho_{LUMO} & \text{acceptor molecule} \\
 f = \frac{1}{2} (\rho_{HOMO} + \rho_{LUMO}) & \text{both donor and} \\
 & \text{acceptor.}
 \end{array}$$

The last equation is for the case where as electron transfers in both directions as in $\sigma + \pi$ bonding. The difference in energies of the HOMO of nucleophiles and LUMO of electrophiles has also been used to describe the stability of the bond formed between them (1,15,22). 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 (23).

Based on the above principles we have made studies on metal-ligand interaction between cobalt halides and thiazolidinethione and have compared it with other metal and ligand interaction as below.

The LUMO densities of M (II) halides (M=Fe,Co,Ni,Cu) and HOMO densities of thiazolidinethione are included in Table-5. The difference in their energies (LH) does not provide any sequence, which may be well related with the experimental results or the established trend. The $f = \frac{1}{2} (\rho_{\text{HOMO}} + \rho_{\text{LUMO}})$, also does not provide any trend. The E_{nm} values derived by Klopman equation also did not provide any such sequence in earlier work, (6) and a good relationship 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 rather more important (24,25). In the light of the above we tried other parameters which in combination with ΔLH could provide a proper trend in studying the transition metal reactions. Ionization potential evaluated by the method described else where (26) provided the solution. If values of IP of the Lewis acids are added to the 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 (17).

$\text{Cu} > \text{Ni} > \text{Co} > \text{Fe}$.

It is clear from Table-5, that chlorides are the best acceptors, and the sequence in all cases is $\text{MCl}_2 > \text{MBr}_2 > \text{MI}_2$ (M = Fe, Co, Ni, Cu). It is concluded that cobalt halides have acceptor strength more than iron (II) halides, and less than nickel and copper halides.

Table-5: LUMO densities and IP of transition metal halides and HOMO densities of thiazolidinethione

Compounds	ρ_{LUMO}	ρ_{HOMO}	IP	ΔLH	$\Delta\text{LH} + \text{IP}$
Fe (TZT) ₂ Cl ₂	0.725	0.891	20.11	0.166	20.276
Fe (TZT) ₂ Br ₂	0.255	0.891	19.28	0.636	19.916
Fe (TZT) ₂ I ₂	0.129	0.891	17.84	0.762	18.602
Co (TZT) ₂ Cl ₂	0.568	0.891	21.23	0.323	21.553
Co (TZT) ₂ Br ₂	0.983	0.891	20.20	0.092	20.292
Co (TZT) ₂ I ₂	0.928	0.891	18.65	0.037	18.687
Ni (TZT) ₂ Cl ₂	0.604	0.891	22.27	0.287	22.557
Ni (TZT) ₂ Br ₂	0.552	0.891	21.29	0.339	21.629
Ni (TZT) ₂ I ₂	0.509	0.891	19.57	0.382	19.952
Cu (TZT) ₂ Cl ₂	0.368	0.891	27.34	0.523	27.863
Cu (TZT) ₂ Br ₂	0.307	0.891	26.27	0.584	26.854
Cu (TZT) ₂ I ₂	0.236	0.891	24.36	0.655	25.015

ρ_{LUMO} is LUMO density, ρ_{HOMO} is HOMO density and ΔLH is their difference calculated from DFT method on CAChe Pro Software. IP is the ionization potential of an atom in molecule. The TZT is thiazolidinethione.

Table-6 : The absolute hardness and electronegativity of acid (A) and base (B) and ΔN and ΔE derived from them

Acid	Base	η_A	χ_A	η_B	χ_B	ΔE	ΔN
CoCl ₂	2 TZT	0.0955	6.7985	1.6500	3.1555	1.9008	1.0435
CoBr ₂	2 TZT	1.0735	1.4655	1.6500	3.1555	0.2622	0.3103
CoI ₂	2 TZT	0.0085	5.1765	1.6500	3.1555	0.6157	0.6093
CoCl ₂	2 ETU	0.0955	6.7985	1.8720	2.6280	2.2100	1.0598
CoBr ₂	2 ETU	1.0735	1.4655	1.8720	2.6280	0.1147	0.1973
CoI ₂	2 ETU	0.0085	5.1765	1.8720	2.6280	0.8634	0.6776
CoCl ₂	2 ATU	0.0955	6.7985	1.6905	2.8625	2.1685	1.1019
CoBr ₂	2 ATU	1.0735	1.4655	1.6905	2.8625	0.1765	0.2527
CoI ₂	2 ATU	0.0085	5.1765	1.6905	2.8625	0.7879	0.6810
CoCl ₂	2 TU	0.0955	6.7985	1.9000	3.0990	1.7146	0.9270
CoBr ₂	2 TU	1.0735	1.4655	1.9000	3.0990	0.2243	0.2747
CoI ₂	2 TU	0.0085	5.1765	1.9000	3.0990	0.5654	0.5443
CoCl ₂	2 EU	0.0955	6.7985	2.9665	2.6265	1.4211	0.6813
CoBr ₂	2 EU	1.0735	1.4655	2.9665	2.6265	0.0834	0.1437
CoI ₂	2 EU	0.0085	5.1765	2.9665	2.6265	0.5464	0.4286

η and χ are the absolute hardness and electronegativity of acid A and base B. ΔN is the shift in charge calculated from equation 4 and ΔE is energy lowering calculated from equation 5 by using DFT method. The TZT is thiazolidinethione, ETU is ethylene thiourea, ATU is allyl thiourea, TU is thiourea and EU is ethylene urea.

Charge Transfer ΔN and Energy Lowering ΔE :

There has been number of molecular orbital treatments of Lewis acid-base reaction. The Mulliken (27) 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-

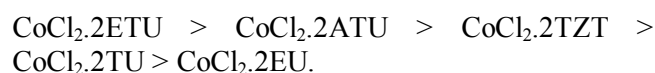
$$(I_A - A_B) - (I_B - A_A) = 2(\chi_A^0 - \chi_B^0) \quad (10)$$

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 cobalt halides (A) and thiazolidinethione (B) are included in Table-6. 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 (28). A reference to the table indicates that electronegativity value of thiazolidinethione is less than that of acceptor cobalt halides hence the equation-10 has a positive value. The χ values indicated that the acceptor strength of cobalt (II) halides is in the order $\text{CoCl}_2 > \text{CoBr}_2 > \text{CoI}_2$. On the

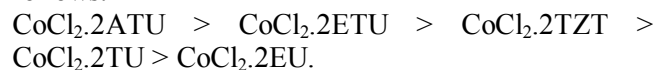
basis of χ values the base strength of donor molecules can be arranged as below.



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 5 and 6. The values of ΔN and ΔE have been evaluated and are reported in Table-6. The ΔN values clearly indicate that maximum charge transfer is in CoCl_2 complexes and minimum in case of CoBr_2 complexes. Similarly the maximum energy lowering ΔE is exhibited by $\text{CoCl}_2 \cdot 2\text{ETU}$ complexes. The stability of the complexes as derived from ΔE values indicate that CoCl_2 forms most stable complex with ETU, and the order with other ligands is as below.



The stability order derived from ΔN values is as follows.



It is clear that both ΔE and ΔN provide almost the same sequence of stability of metal-ligand bond.

Table-7 Difference ($\square E_{nm}^\ddagger$) derived from E_n^\ddagger of M and E_m^\ddagger of ligand(TZT)

Compound	E_n^\ddagger of M	E_m^\ddagger of TZT at S	$\square E_{nm}^\ddagger$
Fe (TZT) ₂ Cl ₂	329.8281	-6.7049	336.5330
Fe (TZT) ₂ Br ₂	310.1027	-6.7049	316.8076
Fe (TZT) ₂ I ₂	314.8305	-6.7049	321.5354
Co (TZT) ₂ Cl ₂	537.7105	-6.7049	544.4154
Co (TZT) ₂ Br ₂	534.3908	-6.7049	541.0957
Co (TZT) ₂ I ₂	536.9348	-6.7049	543.6397
Ni (TZT) ₂ Cl ₂	751.0237	-6.7049	757.7286
Ni (TZT) ₂ Br ₂	785.8024	-6.7049	792.5073
Ni (TZT) ₂ I ₂	763.3953	-6.7049	770.1002
Cu (TZT) ₂ Cl ₂	1368.001	-6.7049	1374.7059
Cu (TZT) ₂ Br ₂	1324.288	-6.7049	1330.9929
Cu (TZT) ₂ I ₂	1297.293	-6.7049	1303.9979

M = Fe (II), Co (II), Ni (II) and Cu (II). TZT = Thiazolidinethione.

Table-8 Matching constant values derived from $\square E_{nm}^\ddagger$ + CFSE values

Lewis Acid	Lewis Base	E_n^\ddagger	E_m^\ddagger	$\square E_{nm}^\ddagger$	CFSE	$\square E_{nm}^\ddagger$ + CFSE Matching Constant
CoCl ₂	2 TZT	537.7105	-6.7049	544.4154	1.5413	545.9567
CoBr ₂	2 TZT	534.3908	-6.7049	541.0957	1.5443	542.6400
CoI ₂	2 TZT	536.9348	-6.7049	543.6397	1.5711	545.2108
CoCl ₂	2 ETU	537.7105	-8.4495	546.1600	1.5384	547.6984
CoBr ₂	2 ETU	534.3908	-8.4495	542.8403	1.5473	544.3876
CoI ₂	2 ETU	536.9348	-8.4495	545.3843	1.5666	546.9509
CoCl ₂	2 ATU	537.7105	-9.7268	547.4373	1.5622	548.9995
CoBr ₂	2 ATU	534.3908	-9.7268	544.1176	1.5770	545.6946
CoI ₂	2 ATU	536.9348	-9.7268	546.6616	1.5860	548.2476
CoCl ₂	2 TU	537.7105	-9.5769	547.2874	-	-
CoBr ₂	2 TU	534.3908	-9.5769	543.9677	-	-
CoI ₂	2 TU	536.9348	-9.5769	546.5117	-	-
CoCl ₂	2 EU	537.7105	-23.2760	560.9865	-	-
CoBr ₂	2 EU	534.3908	-23.2760	557.6668	-	-
CoI ₂	2 EU	536.9348	-23.2760	560.2108	-	-

ΔE_n^\ddagger is softness of Lewis acid (metal halide), $\square E_m^\ddagger$ is softness of Lewis base (ligand) and ΔE_{nm}^\ddagger is difference in softness values of metal halides and donor molecules.

Softness and Stability of Metal-Ligand Bond:

It is well established that the stability of the compound formed between metal halide and ligand, depends upon the value of difference between softness values E_n^\ddagger of metal halide, and softness values E_m^\ddagger of ligand, E_{nm}^\ddagger represents the difference. The higher is the value of E_{nm}^\ddagger greater is the stability of the compound. (1,23,25-32)

$$E_{nm}^\ddagger = |E_n^\ddagger - E_m^\ddagger| \quad (11)$$

The softness E_n^\ddagger of metal (Fe, Co, Ni, Cu) in their halides and the softness E_m^\ddagger at thioamide sulphur in TZT are presented in Table-7. The E_{nm}^\ddagger values

derived as per equation-11 have also been derived and are included in the same. The E_{nm}^\ddagger values clearly indicate the following order of stability in respect of metal ions.

Cu > Ni > Co > Fe.

This sequence is consistent with the established trend, derived from thermodynamic stability (log k) (33). The E_{nm}^\ddagger values compared for different halides also indicates that chlorides form most stable complexes as compared to bromide and iodide counterparts.

The ligands have often been compared for their donor ability on the basis of their position in

spectrochemical series (21). The spectrochemical series is prepared on the basis of Dq values. A new method was proposed by us (6) for deriving the comparative donor ability on the basis of softness values, with the help of the following equation.

$$\text{Matching Constant} = \text{CFSE} + E_{\text{nm}}^{\ddagger} \quad (12)$$

On the basis of above equation we have derived the donor ability of a set of ligand having sulphur as donor site, and the results are presented in Table-8. A reference to Table-8, shows

that CoCl_2 forms most stable complex with ATU, and the order with other ligands is as below.
 $\text{CoCl}_2 \cdot 2\text{ATU} > \text{CoCl}_2 \cdot 2\text{ETU} > \text{CoCl}_2 \cdot 2\text{TZT}$.

This sequence is similar to the sequence of stability of metal-ligand bond as derived from ΔN values.

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