The Asian Journal of Experimental Chemistry, **Vol. 4 No. 1&2 (June & December, 2009) : 26-27**

Research Paper :

Theoritical relationship between softness parameters and the stability of thiocyanate bridge in bimetallic tetrathio cyanate complexes

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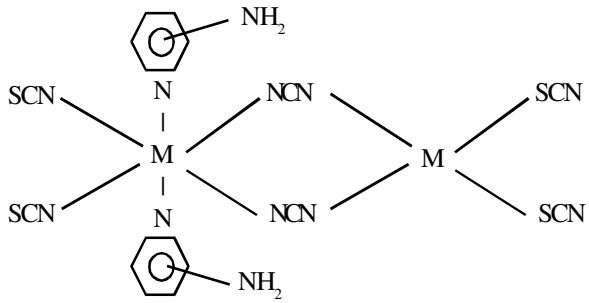
Accepted : ***February, 2009***

ABSTRACT

The softness parameters of M and M' in respect of the O/m/p-amino pyridine of MM'$(NCS)_4$ type of complexes, have been evaluated.



MNDO calculations were made to get precise values of softness of M and M'. Therefore stability of thiocyanate bridge in M and M' $(NCS)_4$ (M=Co, M' = Hg, Cd, Zn) is given below :

Co/Hg > Co/Cd > Co/Zn

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Key words : Stability, Thiocyanates, Bimetallic complexes

Complexes of metal thocyanates and selenocyanates have the subject of interest, and different workers have studies their different aspects. Burmeister (1966) described the effects of a large number of ligands on the change of M-SCN bonding to M-NCS and also reviewed linkage isomerism (1968) which included thiocyate ions. Bailey *et al.* (1971) discussed the infrared spectra of bimetallic tetrathio cyanates and selenocynates and described the effect of change of metal on the infrared active bands associated with the thiocyanate and selenocyanate ions. The Lewis-acid character of bimetallic tetra thiocyanate and selenocyanate of $CoHg(XCN)_4$ (X=S,Sc) type have been described in a review article by Singh. The corresponding selenocyanates have also been studied but comparatively less is reported in the literature.

Both bimetallic tetra thiocyanates and selenocyanates of general formula MM' $(XCN)_4$, M=Mn(II), Fe(II), Co(II), Ni(II), M'= Zn(II), Cd(II), Hg(II), Pd(II), X=S, Se can be used as Lewis acids because the co-ordination numbers of M and M' in MM' $(XCN)_4$ are four rather than their maximum of six.

Singh *et al.* extended the work to other bimetallic tetrathiocyanates and also studied the corresponding tetra selenocyanated (1979). They observed that the nature of these tetra thoicyanates and selenocyanates depends mainly upon the nature of M and M' in MM' $(NCS)_4$ (X=S, Se) and also upon the base strength of the lignads.

MATERIALS AND METHODS

The quantum mechanical equation which has been used for quantitative evaluation of softness values of metal and base ions is given below:-

$$E_n^{\#} = IP_n - b_2 (IP_n - EA_n) - (X_s(C_s^n)^2 / R_s) (1-1/\epsilon) + q_s - 2b^2 X_s (C_s^n)^2 \quad .....(I)$$

$$E_m^{\#} = IP_m - a^2 (IP_m - EA_m) - (X_r(C_r^m)^2 / R_r) (1-1/\epsilon) + q_r - 2b^2 X_s(C_s^m)^2 \quad .....(II)$$

The ionisation potential (IP), charge (q), radius (R), electron affinity (EA), desolvation energy (DE) are the essential requirements for the solution of the above equation. These values are available for ions, but in neutral molecules these values are not available.

The original equation is modified, for evaluation of softness values in neutal Lewis acids and bases. With the help of modified equation the softness of a large number of neutral Lewis acids and neutral Lewis bases were calculated. The values so calculated are termed as

Table 1 : Values of $E_n^{\#}M$, $E_n^{\#}M'$ and $\Delta E_n^{\#}$ (M–M') when o/m/p-amino phyridine is used as Lewis base

M/M'	Earlier values			Values after MNDO calculation		
	$E_n^{\#}M$	$E_n^{\#}M'$	$\Delta E_n^{\#}(M - M')$	$E_n^{\#}M$	$E_n^{\#}M'$	$\Delta E_n^{\#}(M - M')$
Co/Hg	-0.22	-4.86	-4.64	-5.22	-11.64	6.42
Ni/Hg	-0.28	-4.86	-4.58	-3.58	-11.64	8.06
Co/Cd	-0.22	-2.27	-2.05	-5.25	-14.51	9.26
Ni/Cd	-0.28	-2.27	-1.09	-3.61	-14.51	10.90
Co/Zn	-0.22	-1.29	-1.07	-5.23	-16.62	11.39
Ni/Zn	-0.28	-1.29	-1.01	-3.84	-16.62	13.04

effective softness.

RESULTS AND DISCUSSION

We have accordingly evaluated the values of ionisation potential, electron affinities and orbital energy from the Molecular orbital package (MOPAC) development by Dewar and Co-workers (1978). The derivation of these values is based upon MNDO calculation using the values q., IP, EA, etc.

We have calculated the softness parameters of M and M' in a number of combinations of M and M' in MM' $(NCX)_4$ type of complexes, when o/m/p - amino pyridine is used as Lewis base.

The softness values $E_n^{\#}$ of M and M' were calculated by using Klopman's equation (1968) and difference evaluated. The difference was designated $\Delta E_n^{\#}$(M-M') $(SCN)_4$ and subsequently the nature of the complexes.

A reference to table indicates that the values of softness of M and M' differ much as compared to the values obtained earlier. The $\Delta E_n^{\#}$ values follow a reverse trend as compared to the values reportd earlier. The earlier value of $\Delta E_n^{\#}$ when M=Co and M' =Hg is 4.65 and that of Co/Zn pair was 1.07. These values have been changed to 11.39 and 6.42, respectively, after MNDO calculation. In other words the bridge is more stable when the value is low that is Co/Hg bridge is more stable than Co/Zn in tetrathiocyanate. The sequence of stability of thiocyanate bridge in MM' $(NCS)_4$ {M=Co, M'=Hg, Cd, Zn} is given below :

Co/Hg > Co/Cd > Co/Zn

Acknowledgement:

The authors are thankful to the Principal M.L.K. (P.G.) College, Balrampur and Dr. Priti Singh, Department of Chemistry, K.S.S.(P.G.) College, Ayodhya, Faizabad for providing necessary facilities.

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