



## INTRODUCTION

We are particularly interested in the study of intramolecular interactions within half-sandwich anticancer organometallic complexes with chelated N,N donor ligands (Figure1).The DFT(Density Functional Theory) model based on B3LYP;B3PW91 and BP86 functionals with a tailoring basic set denoted GEN(Lan12DZ for  $\text{nd}^7$  for transition metals (Co,Ir and Rh) and for halogen atom (Br and Cl) and 6-311+G(d,p) for other atoms has been adopted. we have adopted the differents methods of analysis: the quantum mechanics of atoms in molecules (QMAIN: to analyze the nature of the binding properties) ; the natural bond orbital (NBO) analysis , the analysis of charge decomposition (CDA: to analyze the interactions between different fragments) and the analysis of energy decomposition (EDA: to understand the driving force of the interaction) developed by Morokuma [1] and harmonic oscillator model aromaticity (HOMA: to evaluate the index of chelatoaromatics based on geometric criteria).

## COMPUTATIONAL METHODS

- ✓ The geometry optimizations have have been performed without any symmetrical restrictions using the Gaussian 09 Program [2] ;
- ✓ The complexation thermodynamic energies denoted  $\Delta Y$  have been estimated using the equation (1). The thermodynamic energies studied are total energies ( $Y = E$ ), enthalpies ( $Y = H$ ) and free energies ( $Y = G$ ):

$$\Delta Y = Y_{[\text{MLCpX}]} - (Y_L + Y_{M^{2+}} + Y_{X^-} + Y_{Cp^*}) \quad (1)$$

- ✓ the examination of stability of metal-ligand interaction has been done from the estimation of metal ion affinity (MIA). The MIA is calculated as the negative of the enthalpy variation for the formation of the  $[\text{MLCp}^*X]^-$  complexes .

## RESULTS

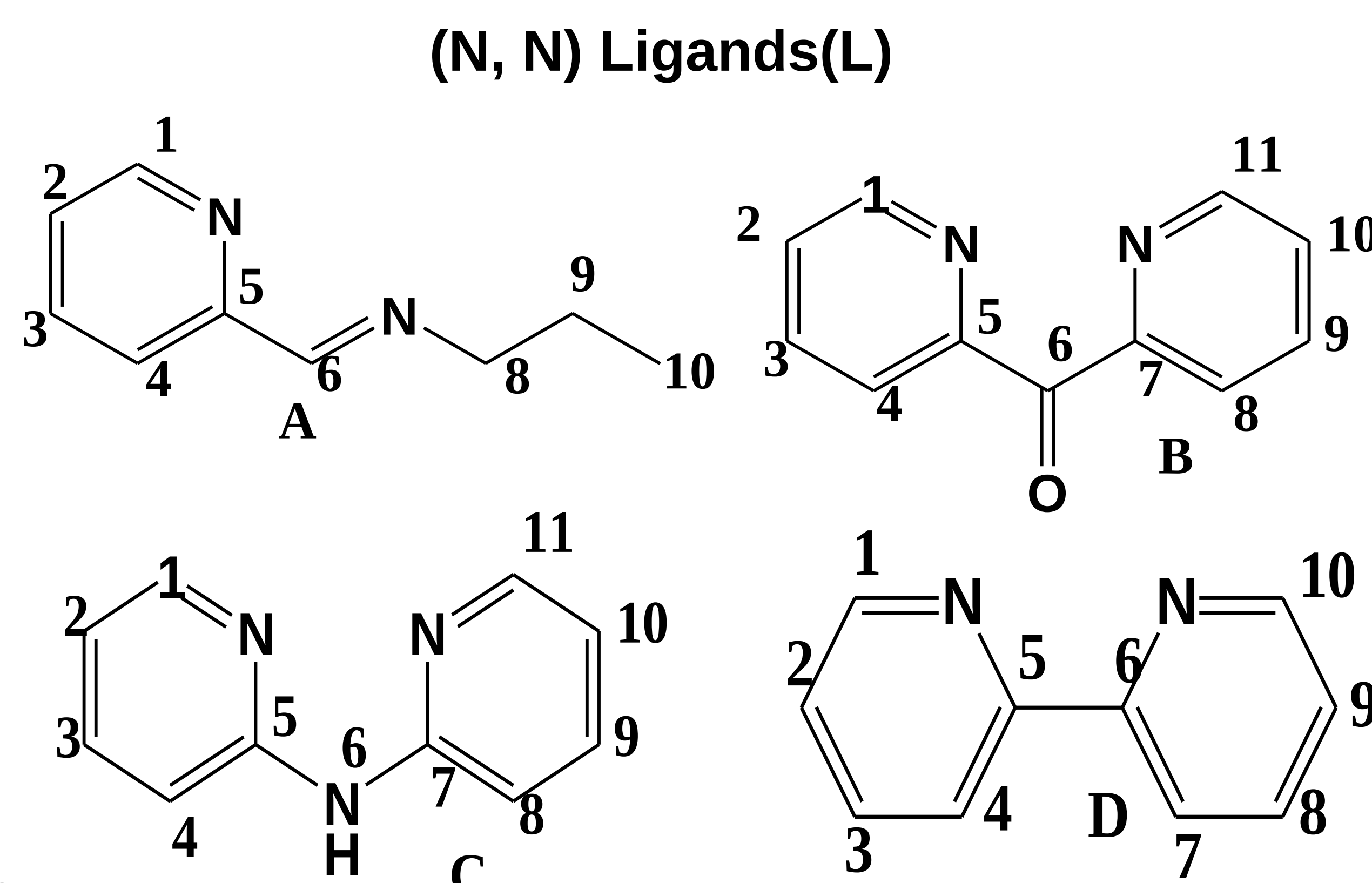
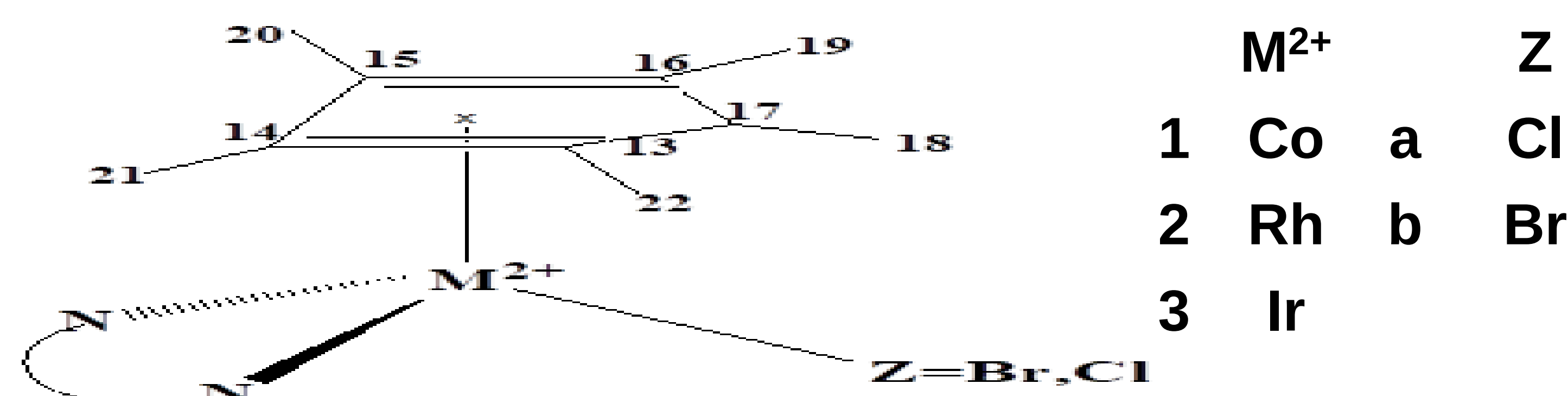


Figure 1: Schematic representation of molecular system used to identify complexes and (N, N) Ligands involved.

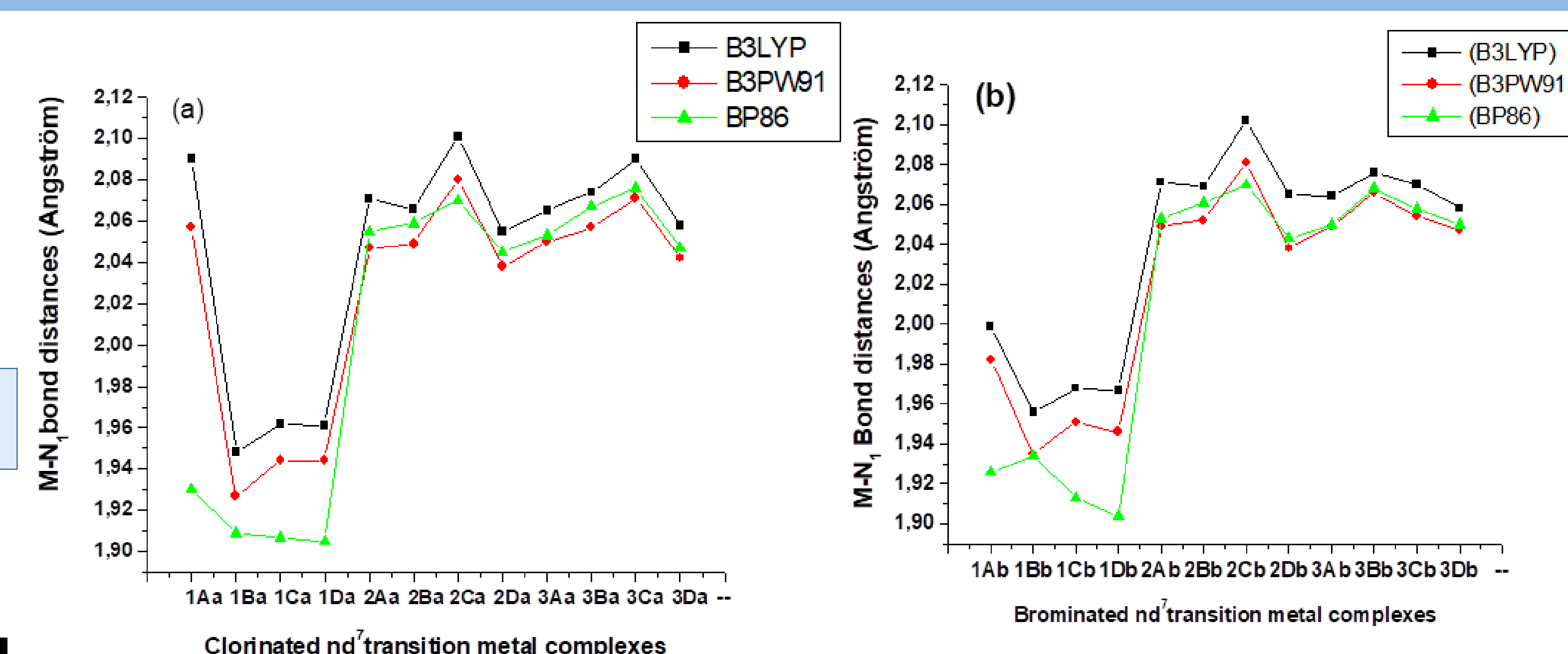


Figure 2: M-N<sub>1</sub> bond of optimized chlorinated (a) and brominated complexes at X(Mixed) level (X = B3LYP, B3PW91 and BP86)

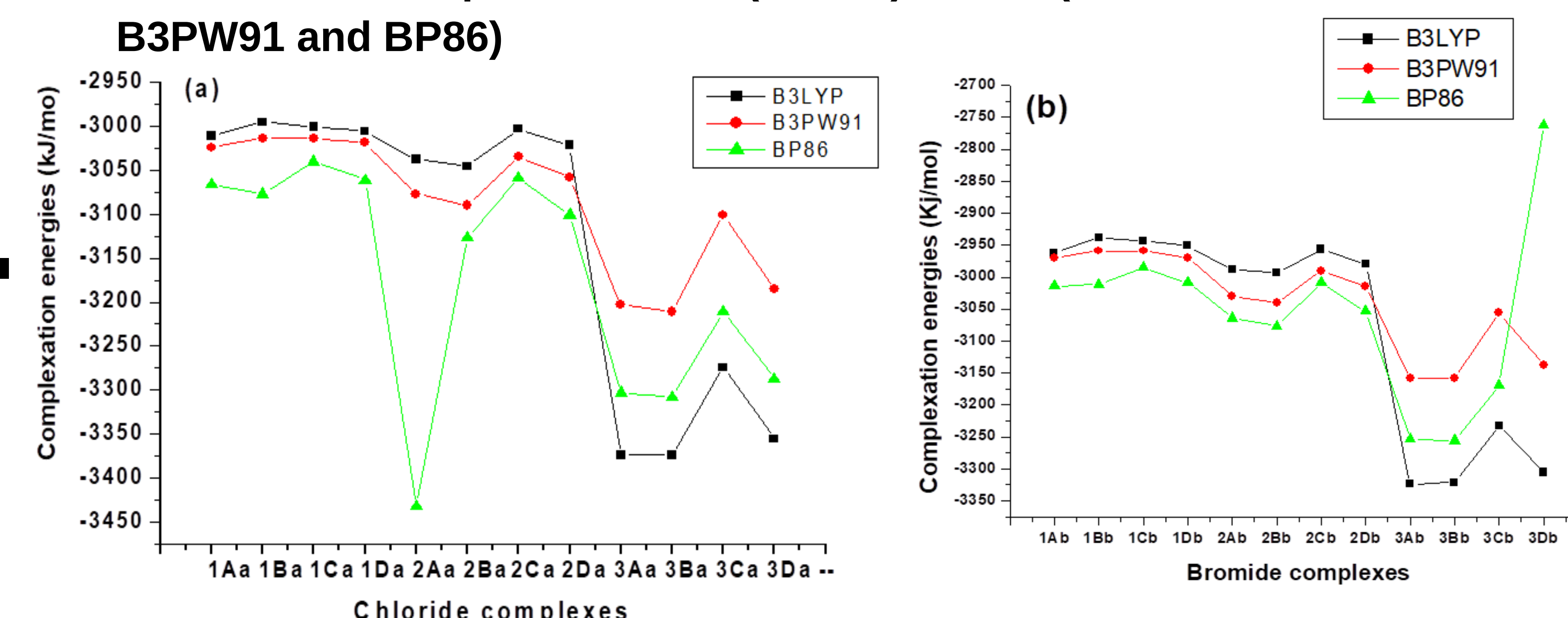


Figure 3: Comparative performance to estimate the complexation energy (by functional: B3LYP, B3PW91 and BP86) in chloride (a) and bromide complexes.

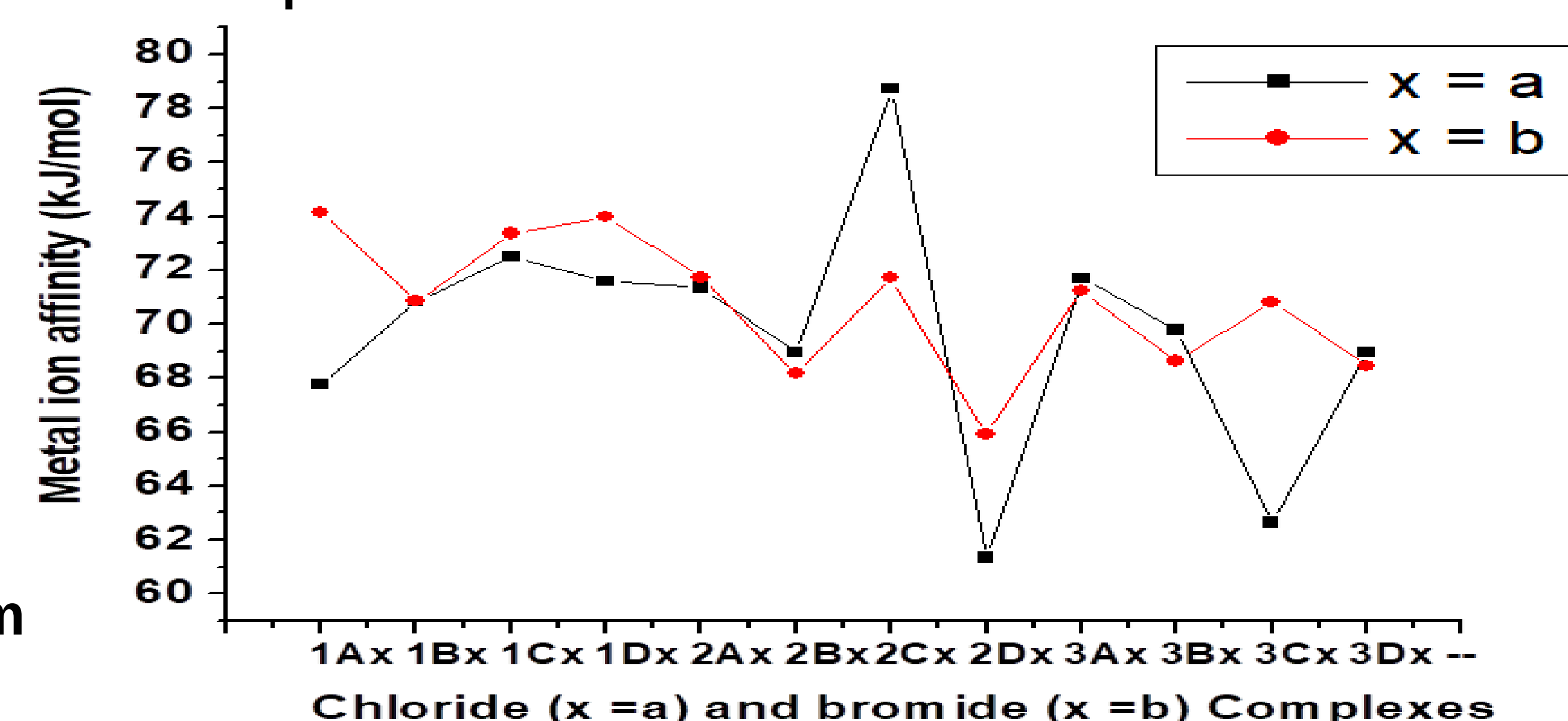


Figure 4: Metal ion affinity from optimized chloride and bromide complexes at B3LYP/GEN

## CONCLUSION

The optimized structures obtained at X/GEN level (X = B3LYP; B3PW91 and BP86) adopt a piano stool environment. Overall, the B3LYP functional shows a high performance of each functional well beyond the geometrical requirements.

The charge retained on the transition metal is inversely proportional to the metal ionic affinity to ligands. Except for one chloride structure resulting chelation of  $\text{Rh}^{2+}$  to (E)-N-(Pyridin-2-ylmethylene) propan-1-amine ligand and two brominated complexes resulting from the combination of the same ligand or the 2, 2'-bipyridyl ligand to the same metal .

## REFERENCES

1. F.M. Bickelhaupt, E.J. Baerends, Rev Comp Chem Kohn-Sham Density Functional Theory: Predicting and Understanding Chemistry, 15, 2000, pp. 1–86.
2. M.J.Frisch, C.Y. Peng, A. Nanayakkara, M. Challacombe, P.M.W. Gill, J.A. Pople, Gaussian 09 Revision B.04 Gaussian Inc Pittsburgh: PA (Licence G09), 2009.