



DFT/B3LYP AND BP86 EXAMINATION OF MONONUCLEAR HALF-SANDWICH nd^7 METALLO DRUG COMPLEXES BASED ON NNO DENDRITIC SCAFFOLDS.

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1-ABSTRACT

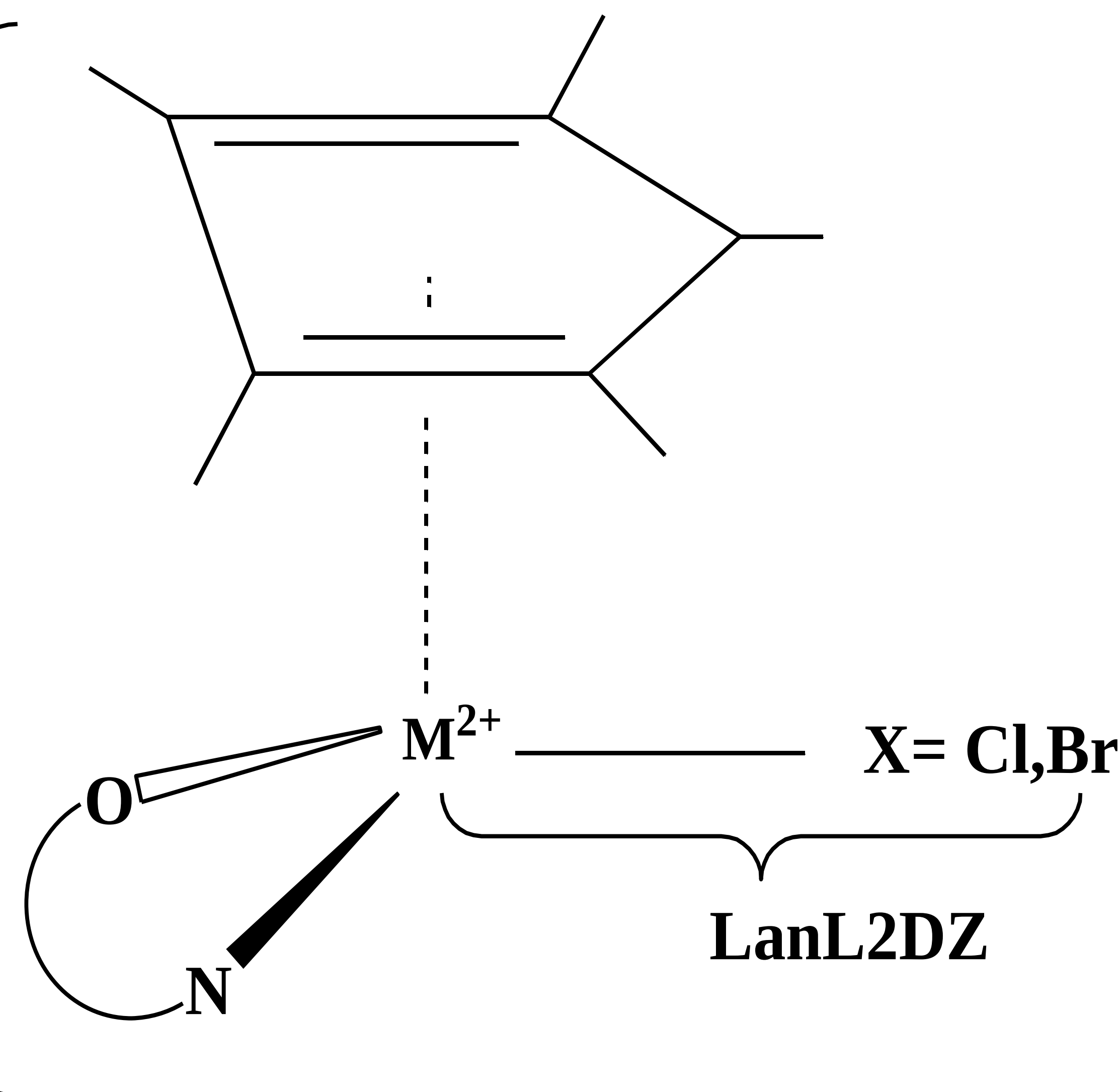
The bonding properties of a series of mononuclear half-sandwich nd^7 anticancer complexes based on NNO dendritic scaffolds (L) were explored using two functionals (B3LYP and BP86) with generic basis set (LanL2DZ for transition metals (as well as halogen atoms) and 6-311+G (d,p) for others atoms. The geometry optimization of structures have led to the adoption of the piano-stool environment and the formation of kings of intermolecular hydrogen bonding. The metal ion affinity (MIA) is increasing in the order: $\text{Ir}^{+2} < \text{Rh}^{+2} < \text{Co}^{+2}$ for both halogen ligands. The metal...oxygen, metal...nitrogen and metal...halogen interactions have shown to be closed-shell interaction. The nature of the $[\text{MLCP}^*]^n$ ($n = 0(\text{A}; \text{B}; \text{C}), n = -2(\text{D}; \text{E})$) ... X^- interaction is mainly dependent on the transition metal and halogen atom involved. The chloride complexes are the least reactive due to the smallest back-donation observed. The possibility of $([\text{LCP}^*]^{-n})^{\delta-} \leftarrow ([\text{MX}]^+)^{\delta+}$ charge separation has been found. B3LYP HOMA indexes are higher than those estimated by PB86 functional for α rings of chloride complexes.

2-NEWTON RAPHTON GEOMETRY OPTIMIZATION

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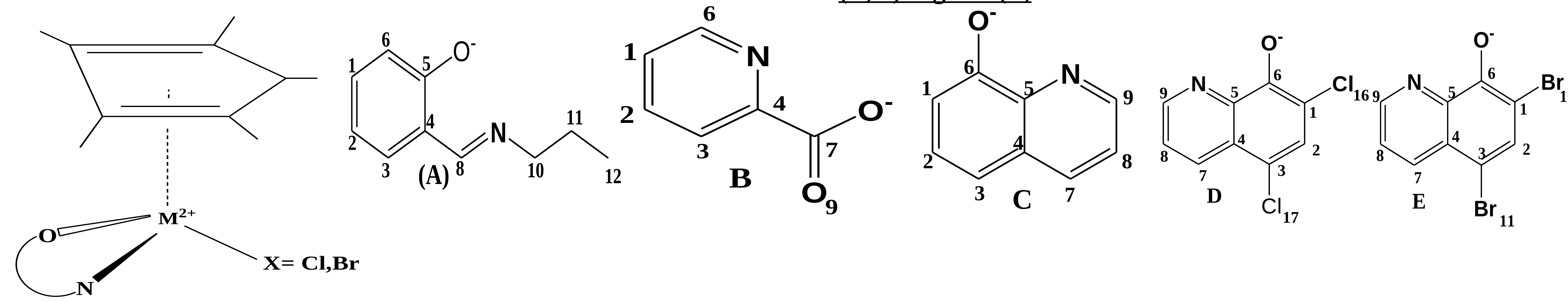
B3LYP and BP86 functionals

6-311+G(d,p)



3- RESULTS

Molecular library examined



Cardiotonic activity (Each value represents the mean + or - SEM (n = 6). ****P < 0.0001: statistically significant when compared to the normal.)

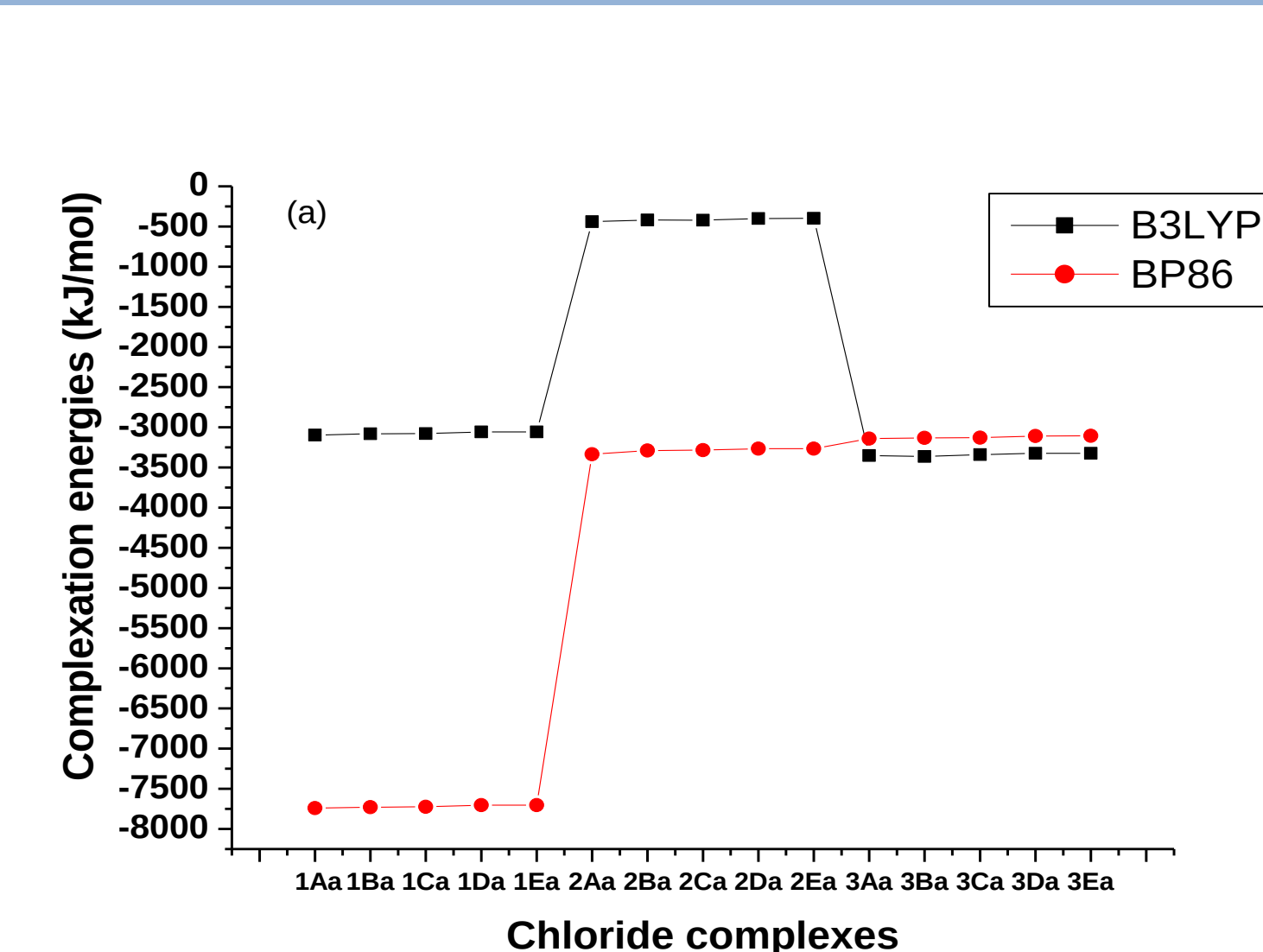
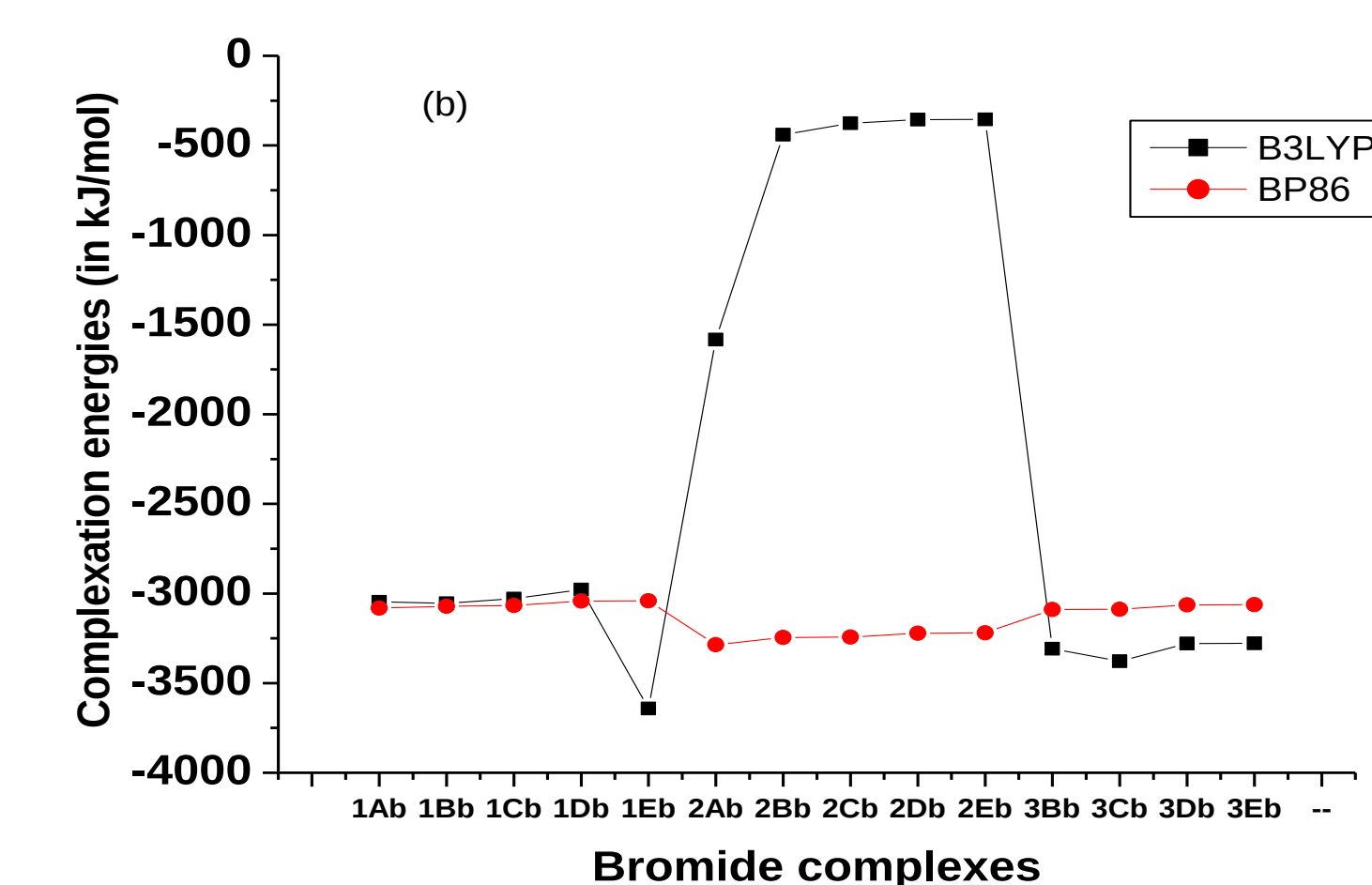


Fig.1:Complexation energies of chloride complexes (a) and Bromide complexes (b) from

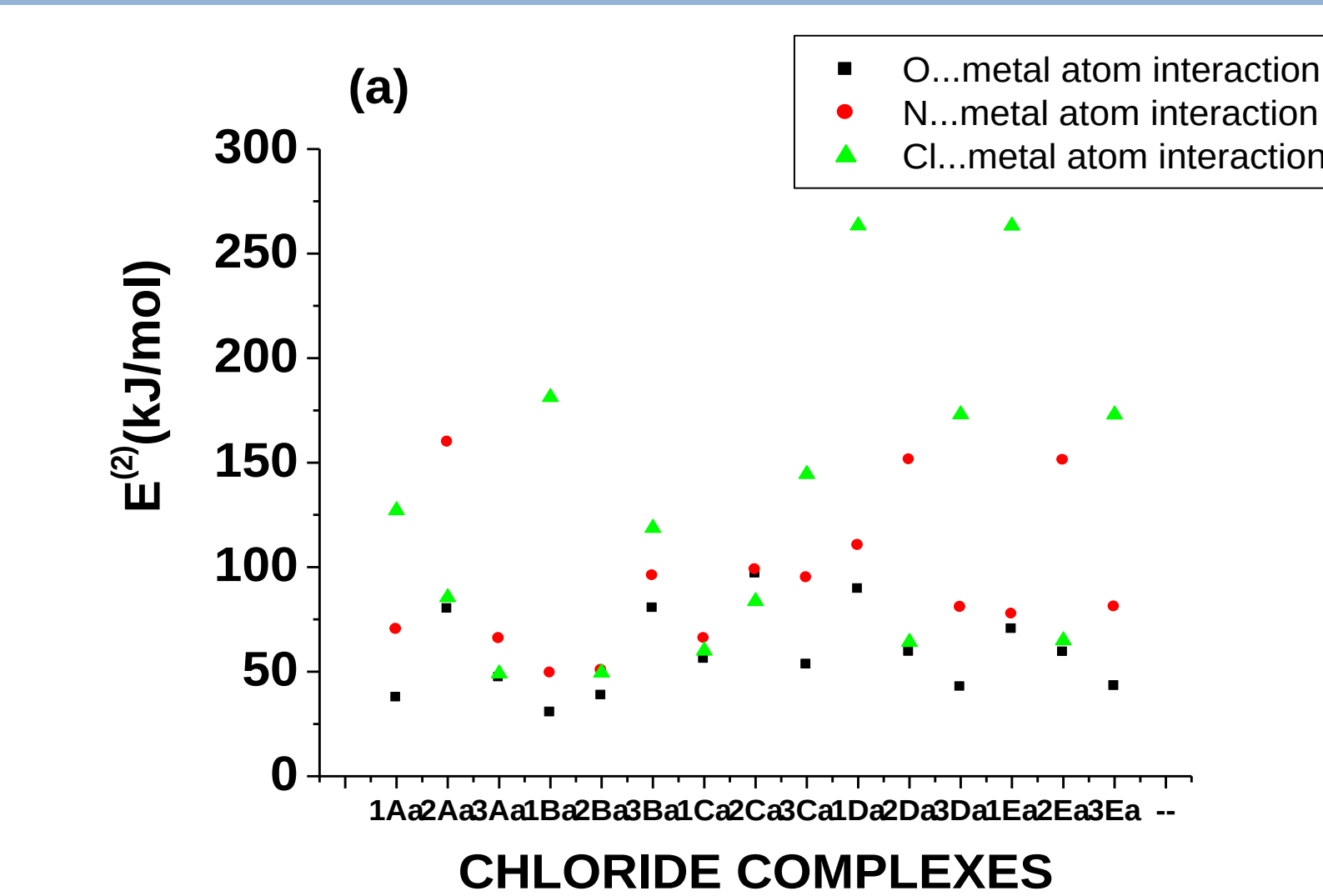
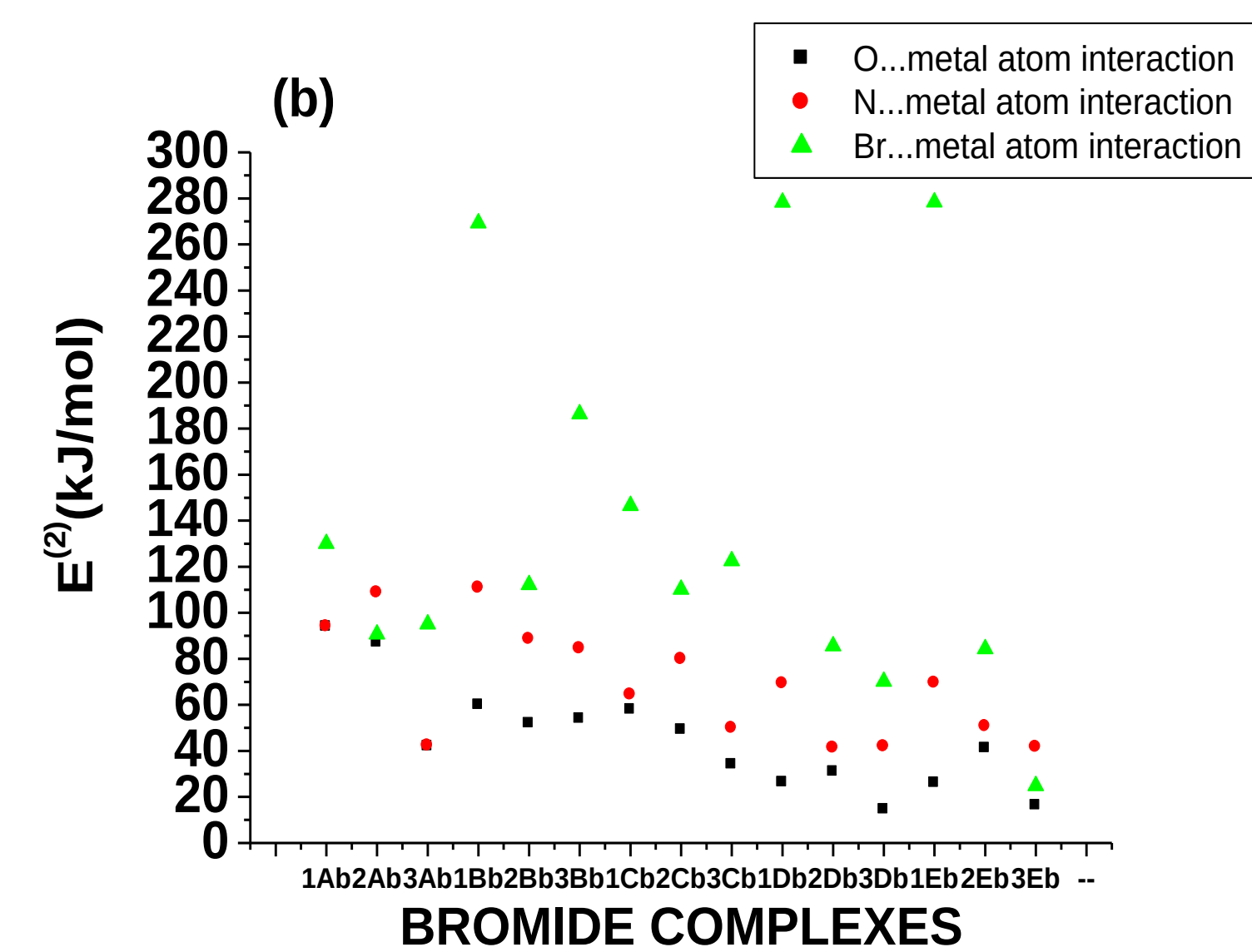


Fig. 2: Second perturbative interaction energies E_2 (in kJ/mol) between nd^7 transition metal and lone pair electron ligand atoms (oxygen atom (O),

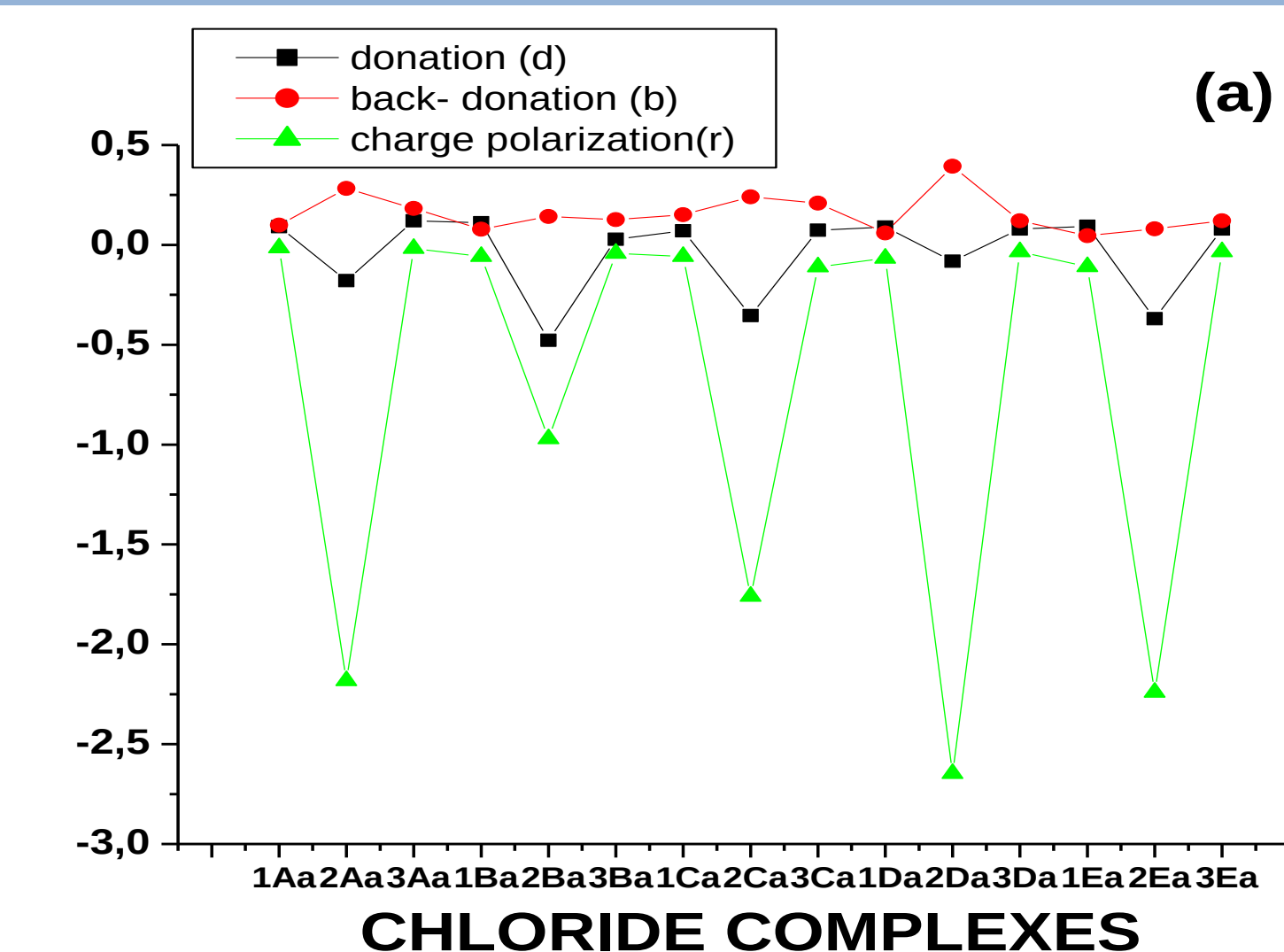
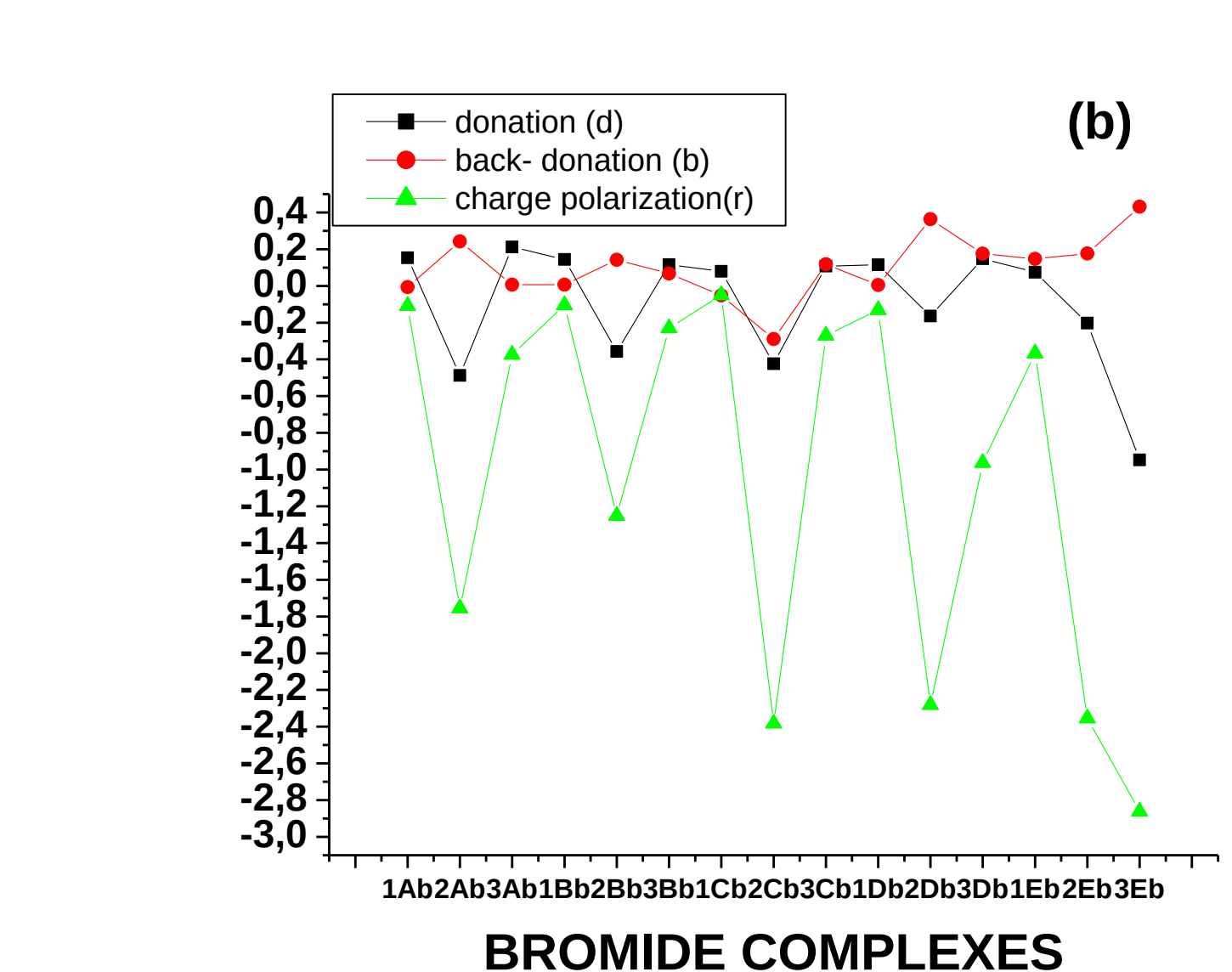


Fig. 3: Charge donation (d), back donation (b), and term charge polarization for chloride (a)

4-Conclusion

In this work, nd^7 metal atoms are bound to the pentamethylcyclopentadienyl ligand (CP^*), one halogen atom (Cl or Br) and N^{NO} chelating ligands (L) in the piano-stool environment. From $[\text{MLCP}^*] \leftarrow \text{X}^-$.back donation, the reactivity is very versatile . For $[\text{LCP}^*]^{-n} \rightarrow [\text{MX}]^+$ interactions, many cases negative contribution of donating and back-donating components have been yielded. This results from the inclusion of polarization effect in (d) and (b).

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5- References

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