



INFLUENCE OF MULTIPLICITY ON nd^x ($x=6, 7$ AND 8) TRANSITION METAL CHELATING PROPERTIES OF GLYOXIME DERIVATIVES IN AQUEOUS SOLUTION: DFT, QTAIM, NBO, EDA AND CDA ASSESSMENT

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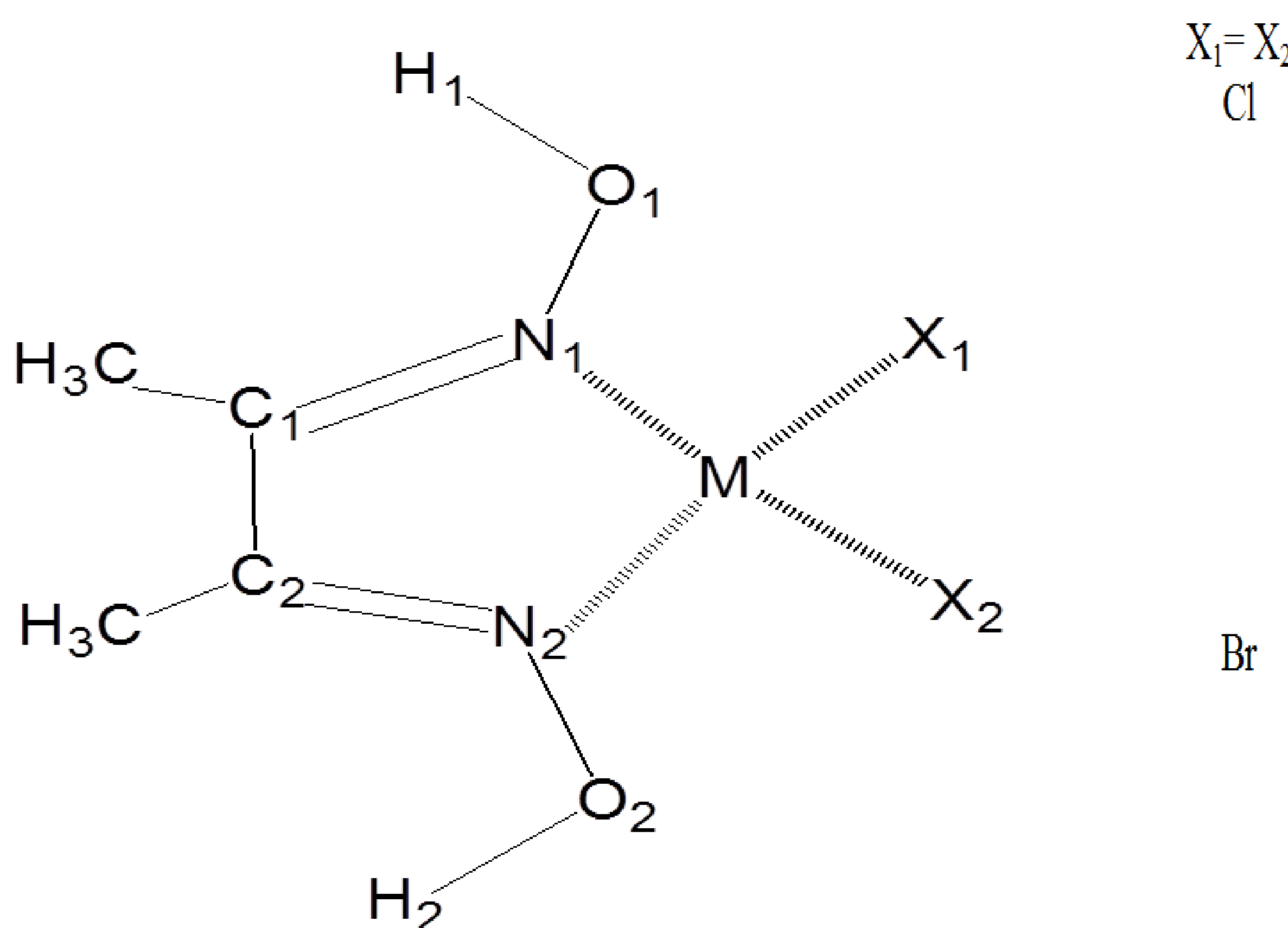
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1-ABSTRACT

In this work, we have examined the ability of the glyoxime ligand [glyoxime ligand] to chelate to the $[MX_2]$ inorganic moieties in which M describes the nd^x ($x=6, 7$ and 8) transition metals associated with a halogenated ligand X ($X=Br$ or Cl). By altering the multiplicity in gas phase and water, we have performed geometry optimizations using a functional hybrid B3LYP coupled to a generic base: LanL2DZ and 6-311+G (d,p) respectively for nd^x transition metals (as well as halogen atoms) and for others atoms. Our findings display an enhancement of the reactivity of the complexes obtained during the passage from the fourth period transition metals to the sixth period ones regardless of the adopted halogen atom in gas phase. The negligible $T\Delta S^0$ values attached to large ΔH^0 values highlight the fact that enthalpy is the main driving force for complex formation in solution. Topological examinations indicate that the metal-nitrogen bonds are found to be the most unstable in both media for the higher multiplicity nd^7 and nd^8 metal complexes. In both series regardless of the environment, the [glyoxime ligand].... $[MX_2]$ interaction strength has been found to grow in the following order: $Fe^{2+} < Co^{2+} < Ni^{2+}$ (3d); $Pd^{2+} < Rh^{2+} < Ru^{2+}$ (4d) and $Pt^{2+} < Ir^{2+} < Os^{2+}$ (5d). For lower multiplicity bromide complexes exclusively, the enhancement of the donor character of the organic glyoxime ligand is promoted by their solvations except for nd^6 transition metal complexes.

2-NEWTON RAPHTON GEOMETRY OPTIMIZATION :

B3LYGEN: LanL2DZ for nd^x ($x=6, 7$ and 8) transition metals, Br and Cl and (6-311+G(d,p)) for other atoms



$X_1 = X_2$	M	
Cl	Fe	3a
	Co	3b
	Ni	3c
	Ru	4a
	Rh	4b
	Pd	4c
	Os	5a
	Ir	5b
	Pt	5c
Br	Fe	3A
	Co	3B
	Ni	3C
	Ru	4A
	Rh	4B
	Pd	4C
	Os	5A
	Ir	5B
	Pt	5C

3- RESULTS

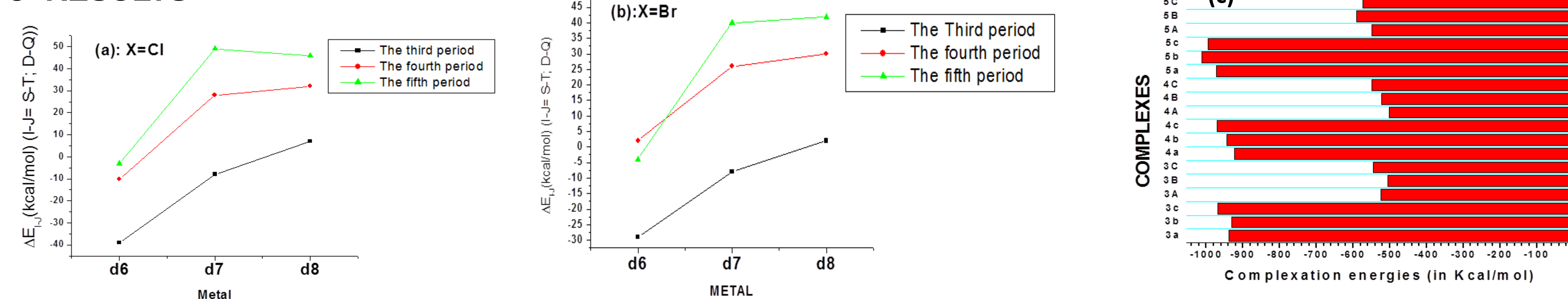


Figure 1: Predicted ΔE_{I-J} ($I-J=S-T, D-Q$) values of nd^x ($n=3-5; x=6-8$) chloride ((a) bromide (b) complexes and complexation energies (in kcal/mol) of nd^x ($n=3-5; x=6-8$) halide (c).

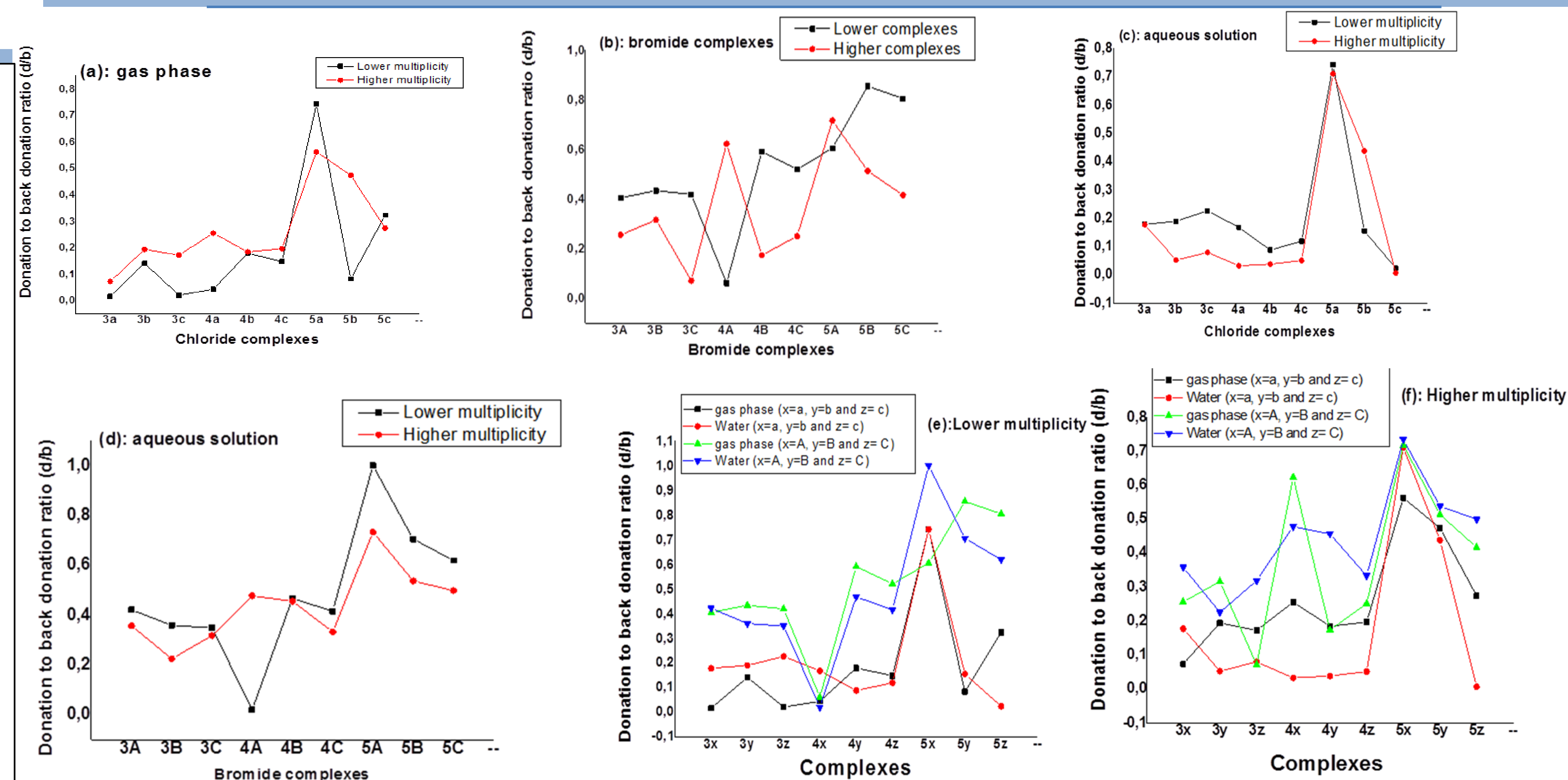


Fig.2: Graphical display of parameters influencing donation to back donation ratio d/b: (i) multiplicity state: in gas phase (chloride complexes (a) and bromide complexes (b)) and aqueous solution (chloride complexes (c) and bromide complexes (d)) (ii): study environment and halogen nature of complexes: lower multiplicity (e) and higher multiplicity (f).

4-Conclusion

The square planar configuration has been preferred by the lower multiplicity optimized structures in their majority. The sensitive augmentation of the M-X bond distances induced by solvation highlighting its higher lability in aqueous solution may be the polarization effect of halide ligands. The solvation of the complexes makes the retained charge on the central metal is inversely proportional to and the value of MIA for both nd^8 transition metal complexes. It demonstrates that that these interaction strengths in a column of the periodic table tends to increase from the top to the bottom in both series regardless of the environment. From general NBO observation, the hybridizations of the metal cation in M-N

5- References

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6-Aknowledgements

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