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Magnesium hydrate complexes of nucleotides 5'-monophosphates (CMP, UMP, dTMP, AMP, GMP, IMP): Ab initio, SCRF

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ABSTRACT

The interaction of magnesium hydrates at the phosphate oxygen atoms of the nucleotides (CMP, UMP, dTMP, AMP, GMP, IMP) were studied at the Hartree-Fock level of Theory. We used LANL2DZ basis set for Mg and 6-31g* basis set for other atoms. The basis set superposition error (BSSE) begins to converge for used Method/basis set. SCRF calculations have been performed at HF/6-31G* level and has proved useful in describing the effects of the solvent and the variations in zero point energies were considered in the calculations together with thermo chemical analysis at 298°K in order to obtain the entropic and free energy variation for the nucleotides and Magnesium Hydrate complexes of nucleotide 5'-monophosphates.

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KEYWORDS

Ab initio calculation;
Nucleotide
5'-monophosphates;
Magnesium complexes;
Solvent effects.

INTRODUCTION

Metal ions are known to have an effect on the stability of both DNA and RNA in vivo. Physiologically, the important complexes are those involving Mg²⁺. Metal complexes of mononucleotides involve phosphate monoesters that carry two negative charges per phosphate group, in the normal protonation state. Consequently the role of the phosphate groups either through direct metal binding or through electrostatic interaction with the metal^[1,2].

The latter kind of structure was also described for the Mg(II)-hydrate complexes of the 5'-monophosphates interaction with the phosphate group was suggested to be either a direct one or mediated through water of molecule, depending on the conditions in which the complexes were prepared^[3,4]. A nucleotide con-

sists of three main subunits, the nucleobase residue (purine or pyrimidine), the sugar part and the phosphate group(s)^[5-8].

The solvent effect is taken into account via the Self-Consistent Reaction field (SCRF) method. This method is based on Onsager reaction field theory of electrostatic solvation. In this model, the solvent is considered as a uniform dielectric with a given dielectric constant. The solute is placed into a cavity within the solvent. SCRF approaches differ in how they define the cavity and the reaction field.

We describe in detail the structures of magnesium hydrate complexes of nucleotide 5'-monophosphates using Ab initio quantum-chemical calculation made at the Hartree-Fock (HF) theoretical level with 6-31g* basis set predicted effects of the Magnesium hydrate on the phosphate coordination. Lanl2DZ for Mg and

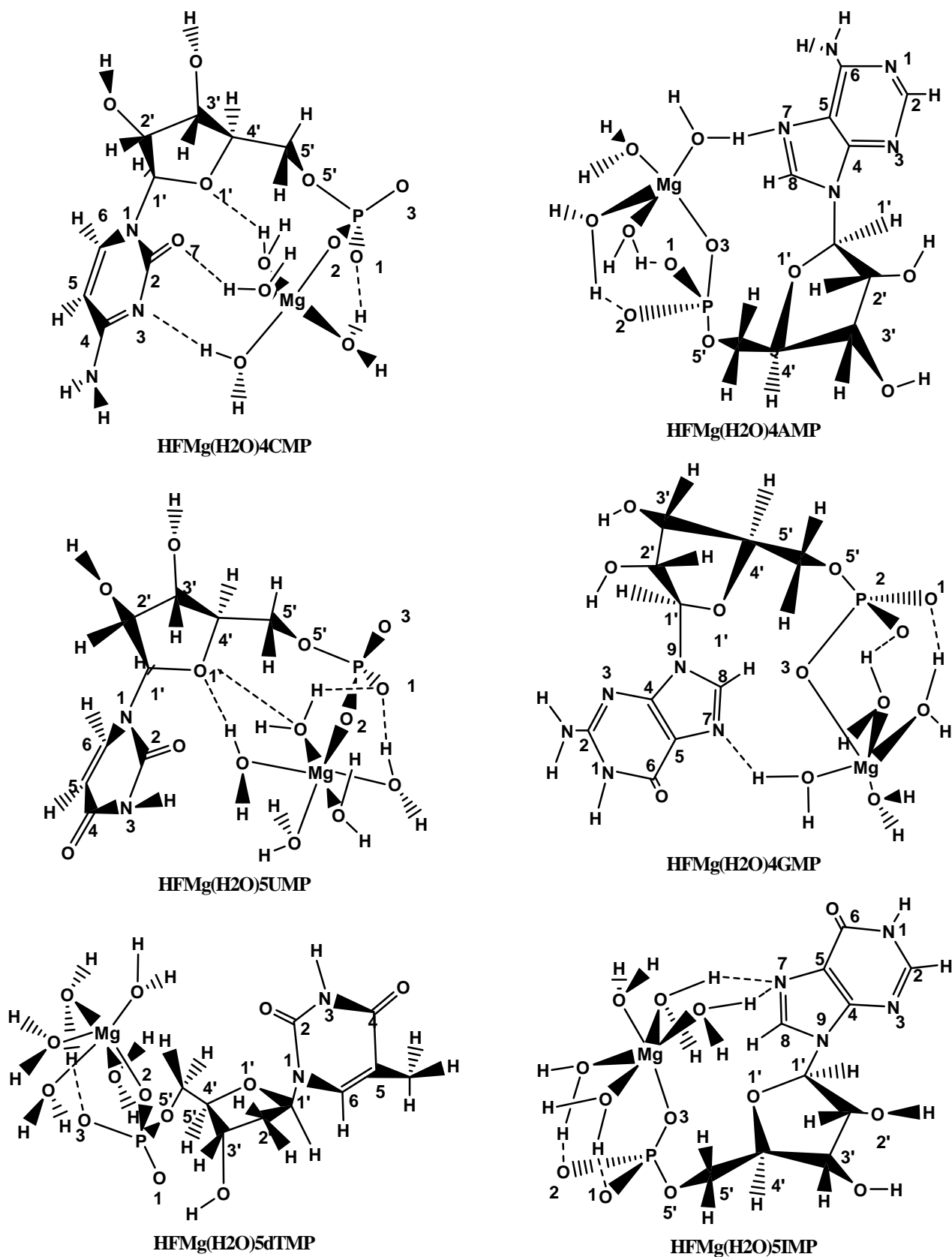


Figure 1 : Optimized structures of Mg-nucleotide complexes in the HF/6- 1g*:LANL2DZ Indirect (outer-sphere) phosphate coordination probably occur between atoms oxygen phosphate and water molecules of Mg-coordination

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TABLE 1 : Stability energies(Hartree) for metalated and non-metalated nucleotides in gas phase with HF/6-31g* level

Complexes	HF/6-31g*
CMP	-1450.764
UMP	-1470.623
dTMP	-1434.751
AMP	-1522.592
GMP	-1597.553
IMP	-1542.523
Mg(H2O)4CMP	-1954.752
Mg(H2O)5UMP	-2050.633
Mg(H2O)5dTMP	-2014.823
Mg(H2O)4AMP	-2026.665
Mg(H2O)5GMP	-2101.543
Mg(H2O)5IMP	-2122.534

TABLE 2 : E_I (Interaction energies), BSSE and E_{I+BSSE} (Hartree) for complexes in HF/6-31g* level

Complexes	E_I	BSSE	E_{I+BSSE}
Mg(H2O)4CMP	-0.36075	-0.0188594	-0.3796106
Mg(H2O)5UMP	-0.36299	0.0282317	-0.3347583
Mg(H2O)5dTMP	-0.37151	-0.0111472	-0.3826603
Mg(H2O)4AMP	-0.36437	-0.01306	-0.3774
Mg(H2O)5GMP	-0.3757	-0.01422	-0.3899
Mg(H2O)5IMP	-0.3896	-0.01774	-0.3896

TABLE 3a : Thermochemistry analysis of the complexes at HF/6-31g* level

Complexes	Zero point energies (Hartree)	Thermal energies (Hartree)	Thermal enthalpies (Hartree)	Thermal free energies (Hartree)
CMP	-1450.508035	-1450.488797	-1450.487853	-1450.559426
UMP	-1470.379717	1470.360829	-1470.359885	-1470.431209
dTMP	-1434.481262	-1434.462658	-1434.461713	-1434.531543
AMP	-1522.324416	-1522.304661	-1522.303717	-1522.374898
GMP	-1597.27171	-1597.252077	-1597.251133	-1597.321293
IMP	-1542.091738	-1542.076630	-1542.075686	-1542.135978
Mg(H2O)4CMP	-1954.374938	-1954.347274	-1954.346330	-1954.431938
Mg(H2O)5UMP	-2050.242326	-2050.211466	-2050.210522	-2050.303913
Mg(H2O)5dTMP	-2014.408897	-2014.377170	-2014.376225	-2014.474458
Mg(H2O)4AMP	-2026.277343	-2026.248395	-2026.247451	-2026.33704
Mg(H2O)5GMP	-2101.149735	-2101.119737	-2101.118793	-2101.210341
Mg(H2O)5IMP	-2122.129950	-2122.098536	-2122.097592	-2122.191895

nucleotide 5'-monophosphates have been carried out. Hydrogen bonding will be discussed in term of observable properties such as geometry. The basis set superposition error (BSSE) was computed, through the counterpoise method^[11] implemented in the Gaussian 98

TABLE 3b : Thermochemistry analysis of the complexes at HF/6-31g* level

Complexes	Total thermal	E(Kcal/mol) electronic	Translation	Rotational	Vibrational
CMP	172.637	0.000	0.889	0.889	170.860
UMP	164.726	0.000	0.889	0.889	162.949
dTMP	180.680	0.000	0.889	0.889	178.902
AMP	180.435	0.000	0.889	0.889	178.657
GMP	188.322	0.000	0.889	0.889	186.545
IMP	170.613	0.000	0.889	0.889	168.836
Mg(H2O)4CMP	253.952	0.000	0.889	0.889	252.174
Mg(H2O)5UMP	262.205	0.000	0.889	0.889	262.427
Mg(H2O)5dTMP	279.742	0.000	0.889	0.889	277.965
Mg(H2O)4AMP	261.568	0.000	0.889	0.889	259.791
Mg(H2O)5GMP	265.563	0.000	0.889	0.889	263.786
Mg(H2O)5IMP	273.039	0.000	0.889	0.889	271.261

TABLE 3c : Thermochemistry analysis of the complexes at HF/6-31g* level

Complexes	Total thermal	Electronic	Translational	Rotational	Vibrational
Cal/mol-kelvin)					
CMP	70.791	0.000	2.981	2.981	64.830
UMP	69.053	0.000	2.981	2.981	63.091
dTMP	68.556	0.000	2.981	2.981	62.594
AMP	74.512	0.000	2.981	2.981	68.551
GMP	74.698	0.000	2.981	2.981	68.736
IMP	61.292	0.000	2.981	2.981	55.330
Mg(H2O)4CMP	104.357	0.000	2.981	2.981	98.396
Mg(H2O)5UMP	113.659	0.000	2.981	2.981	107.697
Mg(H2O)5dTMP	115.502	0.000	2.981	2.981	109.541
Mg(H2O)4AMP	108.271	0.000	2.981	2.981	102.309
Mg(H2O)5GMP	112.465	0.000	2.981	2.981	106.504
Mg(H2O)5IMP	116.346	0.000	2.981	2.981	110.385

code, for the most stable complexes. PCM calculations in this report have been performed at the HF/6-31g* level in GAUSSIAN 98^[13].

COMPUTATIONAL DETAILS

The structures of all the systems were optimized using the framework of the Hartree-Fock and LANL2DZ basis set for Magnesium and 6-31g* basis set^[10,11] for other atoms. The interaction energies of the counterparts estimated as the energy difference between the complex and the isolated components and were corrected for the basis set superposition error (BSSE).

TABLE 3d : Thermochemistry analysis of the complexes at HF/6-31g* level

Complexes	Total thermal	Electronic	Translational	Rotational	Vibrational
S(Cal/mol-kelvin)					
CMP	150.638	2.183	43.195	35.024	70.236
UMP	150.113	2.183	43.204	35.021	69.705
dTMP	146.968	2.183	43.186	34.636	66.963
AMP	149.813	2.183	43.410	35.077	69.143
GMP	147.664	0.000	43.545	35.334	68.784
IMP	126.896	2.183	43.419	35.437	45.857
Mg(H2O)4CMP	180.178	0.000	43.975	35.611	100.592
Mg(H2O)5UMP	196.558	0.000	44.108	36.103	116.348
Mg(H2O)5dTMP	206.749	0.000	44.094	36.613	126.042
Mg(H2O)4AMP	188.515	0.000	44.142	36.372	108.001
Mg(H2O)5GMP	192.680	0.000	44.248	36.582	11.850
Mg(H2O)5IMP	198.478	0.000	44.267	36.510	117.701

TABLE 4 : Dipole moment (debye) for structures Mg-nucleotides and nucleotides in gas phase and various solvent in HF/6-31g* level

Complexes	Gas phase	Solvent					
		Cyclohexane	Dichloroethane	Acetone	Acetonitrile	DMSO	H2O
Mg(H2O)4CMP	20.2892	21.5076	22.84444	23.0436	23.1347	23.154823.8075	
Mg(H2O)5UMP	12.4763	13.1976	14.1154	14.2510	14.3709	14.332714.9005	
Mg(H2O)5dTMP	13.4593	13.9561	14.5832	14.6339	14.7004	14.6828	
Mg(H2O)4AMP	14.2439	15.0850	16.0740	16.2290	16.3016	16.317616.7538	
Mg(H2O)4GMP	14.2372	15.1980	16.4538	16.6735	16.7778	16.797417.2613	
Mg(H2O)5IMP	11.6008	12.3542	13.3680	13.5235	13.6197	13.636414.1926	
CMP	11.7544	12.3581	13.0954	13.2464	13.3078	13.325513.8794	
UMP	44.3789	46.3420	48.3312	48.6335	48.7726	48.812649.5936	
dTMP	32.8183	34.4562	36.0694	36.2926	36.3945	36.419637.1032	
AMP	26.2045	27.8922	29.7839	30.0692	30.1984	30.239830.8400	
GMP	35.7554	38.1199	40.8177	41.2240	41.4123	41.460642.8616	
IMP	46.5329	48.5499	50.6131	50.9110	51.0454	51.083651.6352	

The Boys-Bernardi counterpoise method^[12], applied at the Magnesium hydrate nucleotide complexes geometry, is used to account for BSSE According to this method:

$$E_{\text{Corr}} = E_{\text{Interaction}} + \Delta E_{\text{BSSE}}$$

where E_{Corr} is corrected-interaction energies and:

$$\Delta E_{\text{BSSE}} = [E^*_{\text{Magnesium Hydrate}} - E_{\text{Magnesium Hydrate}}(\text{complex})] + [E^*_{\text{Pyrimidine nucleotide}} - E_{\text{Pyrimidine nucleotide}}(\text{complex})]$$

where E^* indicates that the energy of components at complex geometry calculated of Methods/Basis set of complex geometry.

Tomasi's Polarized Continuum Model (PCM)^[14] de-

TABLE 5 : Free energy (Kcal mol⁻¹) for structures Mg-nucleotides and nucleotides in various solvent in HF/6-31g* level

Complexes	Solvent					
	Cyclohexane	Dichloroethane	Acetone	Acetonitrile	DMSO	H2O
Mg(H2O)4CMP	-10.43	-22.79	-27.11	-18.91	-24.99	-48.07
Mg(H2O)5UMP	-8.33	-19.13	-23.54	-14.72	-20.82	-46.81
Mg(H2O)5dTMP	-9.15	-17.92	-22.34	-13.04	-19.93	
Mg(H2O)4AMP	-9.18	-19.40	-23.70	-14.84	-21.57	-44.55
Mg(H2O)4GMP	-10.86	-23.39	-28.06	-19.24	-26.04	-52.87
Mg(H2O)5IMP	-7.72	-18.24	-22.75	-13.60	-20.21	-44.32
CMP	-71.88	-129.43	-138.55	-134.33	-140.83	-165.71
UMP	-99.92	-184.20	-197.06	-194.54	-201.34	-241.11
dTMP	-85.02	-152.95	-163.28	-159.54	-166.40	-192.75
AMP	-83.33	-152.06	-162.71	-158.94	-165.89	-194.76
GMP	-87.96	-163.02	-174.93	-171.38	-178.46	-212.81
IMP	-94.4	-172.65	-184.56	-181.26	-188.32	-224.81

TABLE 6 : Polar solute – Solvent (A) and solute polarization (B) for structures Mg-nucleotides and nucleotides in various solvent in HF/6-31g* level

Complexes		Solvent					
		Cyclohexane	Dichloroethane	Acetone	Acetonitrile	DMSO	H2O
Mg(H2O)4CMP	A	-14.90	-33.33	-36.19	-37.50	-37.92	-67.72
	B	0.59	2.69	3.13	3.34	-3.41	7.04
Mg(H2O)5UMP	A	-13.88	-30.82	-33.40	-34.67	-35.03	-68.02
	B	0.49	2.32	2.72	2.97	2.98	6.91
Mg(H2O)5dTMP	A	-12.07	-26.96	-29.49	-30.60	-30.91	
	B	0.37	1.81	2.13	2.30	2.33	
Mg(H2O)4AMP	A	-12.24	-28.51	-31.20	-32.47	-32.79	-62.80
	B	0.42	2.10	2.49	2.69	2.74	6.57
Mg(H2O)4GMP	A	-14.38	-33.69	-36.82	-38.48	-38.78	-73.77
	B	0.55	2.85	3.39	3.69	3.74	8.67
Mg(H2O)5IMP	A	-12.83	-29.64	-32.34	-33.72	-34.20	-65.80
	B	0.43	2.24	2.67	2.90	2.97	7.16
CMP	A	-72.54	-135.46	-143.75	-147.46	-148.51	180.16
	B	0.47	2.47	2.96	3.21	3.29	7.56
UMP	A	-102.09	-194.92	-207.59	-231.28	-214.89	-263.42
	B	1.55	6.75	7.93	8.52	8.69	15.01
dTMP	A	-85.51	-159.68	-169.23	-173.37	-174.74	-206.99
	B	0.92	3.75	4.28	4.51	4.64	8.06
AMP	A	-84.42	-160.23	-170.39	-174.90	-176.24	-212.30
	B	1.03	4.71	5.51	5.89	6.02	10.54
GMP	A	-90.09	-174.73	-186.50	-191.85	-193.27	-237.67
	B	1.59	7.56	8.89	9.55	9.27	17.12
IMP	A	-95.92	-181.70	-193.16	-198.25	-199.69	-243.43
	B	1.27	5.44	6.32	6.74	6.86	11.46

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finest the cavity as a union of a series of interlocking atomic spheres.

RESULT AND DISCUSSION

Theoretical results of the calculated optimized geometries for structures of nucleotide complexes obtained in the HF/6-31g*:LANL2DZ are shown in figure 1^[15].

Figure 1 show the Hydrogen-bonds between other phosphate oxygen atoms and N3,O7 atoms of Mg(H₂O)₄CMP and N7 atom of Mg-Purin nucleotides with water molecules around Magnesium that the calculated at the HF/6-31g*:LANL2DZ.

The results of these calculations at the HF/6-31g* level showed that Metal-nucleotide sugar conformations in pyrimidine nucleotide complexes fall into categories, C3' endo, syn and in the purine nucleotide complexes are C3' endo, anti^[15].

The computed energies of the complexes for non metalated and metalated nucleotides are compared by HF/6-31g* method (TABLE 1). On the other hand metalation of nucleotides have been found more stable than in nonmetalated molecules.

TABLE 2 shows the value of BSSE and $E_{\text{I-BSSE}}$ for the structures. Clearly for the all complexes, values of BSSE are rather small. Therefore, for these cases BSSE is negligible.

Zero point energy (Hartree) for the CMP nucleotide and Mg(H₂O)₄CMP are -1450.508 and -1954.375, respectively. These results and thermo chemistry analysis are shown that Mg nucleotide complexes are stable than the nucleotides (TABLE 3). The data of TABLE 3 is accepted into following equation:

$$E_{\text{Total}} - E_0 = E_{\text{Rot}} + E_{\text{Trans}}$$

Solvent effects

The effect of solvent on the nucleotides and Magnesium hydrate complexes of nucleotides show that the nonmetalated and metalated nucleotides with the increase of dielectric constants of solvent the dipole moment and free energy and Polar solute-solvent and Solute Polarization have been increased.

CONCLUSION

The results of calculations were carried out at the

Hartree-Fock level with LANL2DZ basis set were agreement with the similar complexes systems of experimental data show that phosphate oxygen atoms of nucleotides are suitable site for magnesium coordination.

SCRF calculations on complexes show that the polar solute-solvent interaction in different solvent have been increased with the increase of dielectric constants and the stability of the Magnesium complexes decrease with the increasing polarity of solvent.

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REFERENCES

- [1] S.K.Miller, D.G.Van Derveer, L.G.Marzilli; *J.Am.Chem.Soc.*, **107**, 1048 (1985).
- [2] L.G.Marzilli, P.Chalilpoyil, C.C.Chiang, T.J.Kistenmacher; *J.Am.Chem.Soc.*, **102**, 2480 (1980).
- [3] (a) H.Brintzinger; *Helv.Chim.Acta*, **48**, 47-54 (1965); (b) H.Brintzing, G.Hammes; *Inorganic.Chem.*, **5**, 1286-1287 (1966).
- [4] (a) eophanides, H.A.Tajmir-Riahi; *NATOASI Ser., Ser.C*, **139**, 137-152 (1984); (b) P.Bour, V.Sychrovsky, P.Malon, J.Hanzlikova, V.Baumruk, J.Pospisek, M.Budesinsky; *J.Phys.Chem.A*, **106**, 7321-7327 (2002).
- [5] K.Aoki; *Met.Ions Biol.Syst.*, **32**, 91-134 (1996).
- [6] D.B.Davies, P.Rajani, H.Sadikot; *J.Chem.Soc. Perkin Trans*, **2**, 279-285 (1985).
- [7] R.B.Martin, Y.H.Mariam; *Met.Ions Biol.Syst.*, **8**, 57-124 (1979).
- [8] R.Tribolet, H.Sigel; *Eur.J.Biochem.*, **163**, 353-363 (1987).
- [9] M.J.Frisch, J.E.DelBene, J.S.Binkley, H.F.Schaefer; *J.Chem.Phys.*, **84**, 2279 (1986).
- [10] P.C.Hariharan, J.A.Pople; *Theor.Chim.*, **28**, 213 (1973).
- [11] B.A.Hathaway, G.Day, M.Lewis, R.Glaser; *J.Chem.Soc.Perkin Trans*, **2**, 2713-2719 (1998).
- [12] F.S.Boys, F.Bernardi; *Mol.Phys.*, **19**, 553 (1970).
- [13] R.C.Cambie, P.S.Rutledge, D.W.Scatt, P.D.Woodgate; *J.Chem.*, **32**, 695 (1979).
- [14] J.R.Hanson, M.D.Liman, C.Uyanik; *J.Chem.Research(s)*, 126 (1998).
- [15] M.Monajjemi, M.A.Seyed Sajadi, R.Sayyadi, M.Kia, G.Ghasemi; *Main Group Metal Chemistry*, **28(2)**, 71-83 (2005).