International Journal of Mass Spectrometry 313 (2012) 47–57

Contents lists available at SciVerse ScienceDirect

International Journal of Mass Spectrometry

journal homepage: www.elsevier.com/locate/ijms

A theoretical elucidation of coordination properties of histidine and lysine to Mn^{2+}

M. Hassan Khodabandeh, Hamid Reisi, Karim Zare, Mansour Zahedi*

Department of Chemistry, Faculty of Sciences, Shahid Beheshti University, G.C., Evin, 19839-63113 Tehran, Iran

ARTICLE INFO

Article history:
Received 12 November 2011
Received in revised form
29 December 2011
Accepted 30 December 2011
Available online 8 January 2012

Keywords:
Histidine
Lysine
Mn^{2+}
Complexation
Gas phase metal ion chemistry
Ab initio calculations
Density functional theory

ABSTRACT

Present account is an elucidation of interaction between histidine and lysine with Mn^{2+} in the gas phase by quantum chemical calculations. In addition, side chain effects of these amino acids on relative stability of different coordination modes have been considered by theoretical methods. Three types of complexation mode have been considered: (i) three dentate chelation of neutral amino acids; (ii) two dentate chelation of neutral amino acids; (iii) chelation of amino acids to metal ion in zwitterionic forms. Structure and vibrational frequencies have been determined by B3LYP method. Energy calculations are carried out in CCSD(T) level. For both Mn^{2+}–Histidine and Mn^{2+}–Lysine systems, the most stable structure resulted from interaction of neutral amino acids with metal cation via two amino groups and carbonyl oxygen while the complexes ground electronic state is determined as ^6A. This is in contrast to Mn^{2+}–Glycine system in which the most stable structure resulted from interaction of zwitterionic amino acid with metal ion.

1. Introduction

Metallic cations are involved in a wide range of basic processes in living organisms such as their wide presence in some protein structures, generally known as metaloproteins. Most of these metals are transition elements that due to their catalytic and structural properties are very important [1–3]. Accumulation of different transition metal cations such as manganese, cobalt, zinc and/or nickel in cells and tissues has been shown to be toxic [4–10]. Such toxicity will diminish if ions concentration is moderated. One way to achieve the latter goal in plants and mammals is intracellular complexation of toxic metal ions by peptides and amino acid residues [11–13]. Although, metal ions compete in the complexation process, sometimes metals exposure occurs with little or no competition. As an important case of metal ions competition in complexation with a protein, copper and manganese cations interaction with prion protein (PrP) which leads to prion disease have been investigated [5,14]. It has been reported that one of the most important residues, namely histidine is the interaction site for complexation competition [15]. Cylation of manganese ions with histdine in PrP by replacing copper ions has been proposed as the cause of protein abnormal isoform formation leading to prion disease [5]. In a recent investigation on the interaction of manganese ions with a section of the PrP sequence in mouse, GGGTHNQWNKPSKPKTNLKHVAGAAAAGA [15], although the major complexation sites are revealed to be G and A, still the disease causing interaction site has been determined as histidine.

Interactions of amino acid residues with some metal cations, that are often electrostatic and noncovalent in nature, determine the structure of these species. Primary step in understanding the coordination properties of such peptides appear to be dependent upon the exact consideration of the interaction type and determining the relative contribution of each kind in the gas phase. Moreover, the gas phase results are complementary to the mass spectrometry data in analyzing the metal complexes mass spectra generated in an experimental work. Theoretical methods are very useful tools for investigation of intrinsic properties of metal cation-biomolecules. In particular numerous works have been done to investigate the effect of transition metal cations on stability of various amino acids as well as small peptides [4,16–73]. Even though, the interaction of transition metal cations such as copper [17–19,23,24,26–28,34,35,38,39,41–45,48,51–54,56,58,62,64,68–71], zinc [16,19,20,25,27,30–35,50,53,60,62,68,73], cobalt [4,25,34,35,37,39,44,47,53,62,67], nickel [25–27,29,34,35,39,42,44,46,53,59,62,67], with histidine and some other amino acids have been extensively studied, but reports on manganese interaction with amino acids are rare except those with glycine [25,49] and a few more with some small molecules [74–78].

* Corresponding author. Tel.: +98 21 22431667; fax: +98 21 22431663.
E-mail addresses: m-zahedi@sbu.ac.ir, mansourzahedi@yahoo.com (M. Zahedi).

1387-3806/$ – see front matter © 2012 Elsevier B.V. All rights reserved.
doi:10.1016/j.ijms.2011.12.019

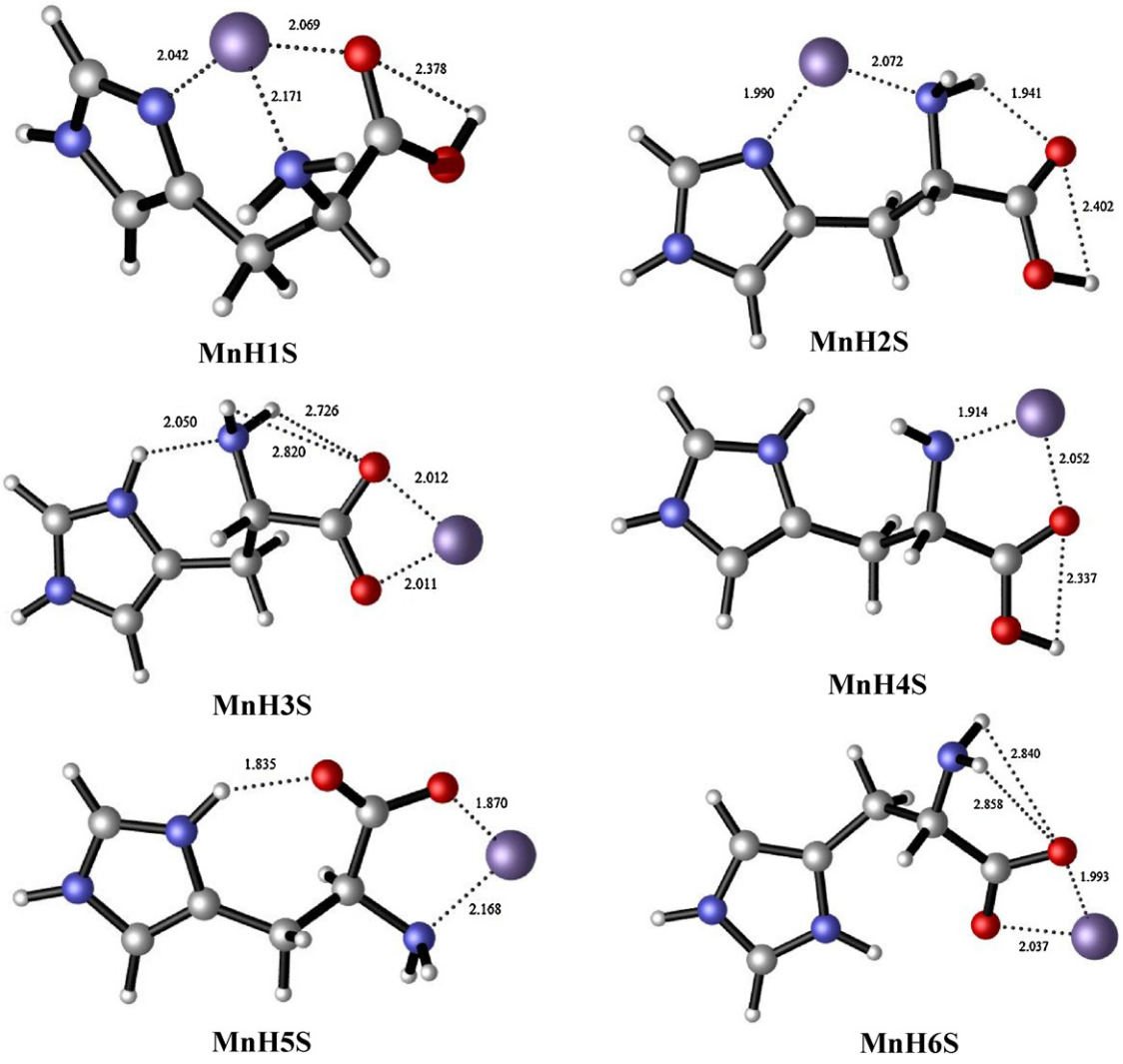

Fig. 1. B3LYP-optimized geometries for different minima of Mn^{2+}–Histidine in the sextet state. Distances are in angstroms.

Detailed experimental studies have been carried out on histidine interaction with Ag^+ and $Cu^{+/2+}$ [36,48]. Three dentate chelation of neutral histidine to Ag^+ and Cu^{2+} and chelation of zwitterionic form of histidine to Cu^+ have been determined as the most stable structures. Some of the most detailed studies done for lysine interaction with Ag^+, and Co^{2+} [4,21] have shown that such interaction occurs between the non-zwitterionic form of lysine with the mentioned cations. As was mentioned above, since manganese and copper competitive interaction with histidine in prion is crucial in understanding the prion disease, investigating the nature of manganese interaction with histidine is of priority. As can be seen from the aforementioned PrP sequence, lysine lies in the vicinity of histidine. Since lysine has one active amino group although being linear compared to that in histidine, Mn^{2+}–Lysine interaction seems advisable.

Current account is a manifestation of detailed theoretical analysis of gas phase chemical interaction between Mn^{2+} cation and two important amino acids histidine and lysine. Ground electronic state in Mn^{2+} is $^6S(3d^5)$. Since manganese ion has an open shell electronic configuration, its various electronic states could be considered. In addition, depending on the extent of the metal complexation, relative stability of various spin electronic states could vary. In our previous study [49] it was shown that complexes resulted from interaction of doublet and quartet electronic spin state of Mn^{2+} with glycine are very unstable relative to those of sextet electronic spin state. For this reason, although the former two spin states are of low importance, the most stable complex in quartet state has been considered for comparison.

2. Computational details

Optimized molecular geometries and corresponding harmonic vibrational frequencies have been obtained by employing nonlocal hybrid three-parameter B3LYP density functional method [79–81]. Previous theoretical calculations on analogue systems including various metal complexes of amino acids [82–85] as well as a recent study on Mn^{2+}–Glycine complexation [49], have revealed that B3LYP serves as a very effective method for studying transition metal–ligand systems. In the present work which electron delocalization is assumed to be important, a comparative study of B3LYP with the high correlated CCSD(T) method again proved the fruitfulness of former method. Moreover, in order to justify results that have been achieved for the desired systems by DFT method, calibration calculations have been carried out on the most stable conformers by employing the single and double couple cluster method with a perturbational estimate of the triple excitation CCSD(T) [86]. All valence electrons are correlated by such calculation method. 6-31G(d,p) basis set [87,88], has been used for all

Table 1
Relative energies (kcal/mol) of Mn^{2+}–Histidine and population analysis at B3LYP/basis level.

Structure	Coordination	State	ΔE	Mn natural population			q(Mn)	Spin(Mn)
				4s	3d	4p		
MnH1S	N_t, N_1, O_C	^6A	0.0	0.18	5.17	0.13	1.52	4.82
MnH2S	N_t, N_1	^6A	25.0	0.21	5.14	0.07	1.58	4.85
MnH3S	O, O^-	^6A	16.1	0.17	5.18	0.05	1.60	4.84
MnH4S	N_t, O_C	^6A	22.9	0.17	5.24	0.09	1.50	4.72
MnH5S	N_t, O^-	^6A	15.0	0.15	5.20	0.07	1.57	4.79
MnH6S	O, O^-	^6A	27.0	0.18	5.18	0.05	1.59	4.84
MnH1Q	N_t, N_1, O_C	^4A	38.6	0.17	5.41	0.11	1.31	2.99

atoms in geometry optimizations as well as vibrational frequency calculations. Results obtained by utilizing this basis set show close correspondence with larger ones as such claim has also been validated elsewhere [49]. In order to calculate energies and molecular wavefunctions, Wachters [14s11p6d3f/8s6p4d1f] basis set for Mn [89,90] and 6-31++G(d,p) basis set for other existing atoms have been employed [91,92].

Thermodynamical corrections assuming ideal gas, unscaled harmonic vibrational frequencies, and rigid rotor approximation resulting from a standard statistical method have been obtained [93]. Average atomic charges and spin densities have been achieved by benefiting Weinhold et al. [94,95] natural population analysis method. In addition, open shell calculations have been carried out by employing unrestricted formalism. All computations have been performed using Gaussian 98 suite of programs [96].

3. Results and discussion

3.1. Mn–Histidine system

As was stated earlier, Mn^{2+} ions ^6S spin state interaction with histidine ^1A state leads to the most stable complex. Thus their interaction resulting in the formation of Mn^{2+}–Histidine complex in ^6A state has been investigated. Since, there are more basic interaction sites in histidine (four basic centers) relative to those of glycine, as well as the presence of an aromatic ring in the former, a more complicated metal ion–amino acid coordination chemistry is expected. Existence of more functional groups relative to glycine introduces three new possible rotations in histidine (namely, rotations about C—C and C—N) while brings about six new rotations in lysine (such as C—C, C—N) which translates to a more complicated conformational space for the latter two amino acids. This fact leads to locating up to 8 and 12 stable conformers in a 2.5 kcal/mol range for histidine and lysine, respectively at PM3 level [97,98]. Besides, at a still higher computational level and in a 4 kcal/mol compass, more than 30 conformers can be situated for both aforementioned amino acids. Thus, due to the large number of conformers in the complexation process, a good guide for choosing the starting structures can be obtained from the results of $[gly–Mn]^{2+}$ [49]. So, the first clue for an appropriate start is going after polydentate linkages. Therefore, no attempt to generate monodentate minimum structures has been made. However, as stated above all stable conformers in the 2.5 kcal/mol range have been utilized in present study. Moreover, since some chemically important conformers were not present in above search results, they were also included to have a complete set. Final geometry optimizations were carried out using these conformers. Fig. 1 summarizes the most important optimized minima for the sextet state of Mn^{2+}–Histidine conformers.

Due to a large energy gap between the remaining species and those in Fig. 1, they are excluded from further consideration. Besides, the most stable optimized structure in the quartet electronic state has been also included in Fig. 2 for comparison.

Table 1 summarizes relative energies as well as metal ions natural population analysis data of all investigated moieties.

It should be mentioned that in the coordination environment for the most stable structures, N_1 denotes active amine's nitrogen atom in the side chain, N_t terminal amine's nitrogen, O_C carbonyl oxygen and O^- is the carboxylate oxygen of the zwitterionic amino acid. C_1 symmetry is obtained for all optimized structures. Based on the metal's interaction environment with regard to the amino acid's side chain, two structural categories can be recognized. In the first group, namely **MnH1S** and **MnH2S** complexes, the basic section of the side chain is directly involved in the amino acid–metal ion interaction. In the second group however, only the main part of amino acid, meaning similar sites that are present in glycine as the simplest amino acid, have interaction with metal ion. These include **MnH3S**, **MnH4S**, **MnH5S** and **MnH6S** of Fig. 1. Coordination of former set with metal ion results in six and seven member ring formation. In the second set however, coordination environment of metal cation is such that four and five member ring, such as those in glycine coordination environment [44], are arrived. Taking a close look at Table 1, it is revealed that the most stable quartet spin state structure **MnH1Q** is higher in energy relative to the most and least stable sextet state structures by about 38.6 and 11.6 kcal/mol, respectively. This is while in the Mn^{2+}–Glycine complex case, quartet state was less stable relative to the most stable sextet state by about 43.5 kcal/mol and more stable relative to the least stable sextet moiety by about 0.5 kcal/mol [49]. It is noteworthy that for the most stable structures of both quartet and sextet states, namely **MnH1Q** and **MnH1S**, according to the metal cation interaction, both amino nitrogens and carbonyl oxygen sites of neutral histidine are involved. Such an interaction model has been proposed for some other metal ions such as Ag^+ [36] and Cu^{2+} [48]. Whereas, for singly charged copper ion Cu^+, in which the effect of nuclear charge is lower, the preferred structure has been determined as a charge solvated species [28,48]. Realizing the fact that except for the sextet spin state structures, other states namely doublet and

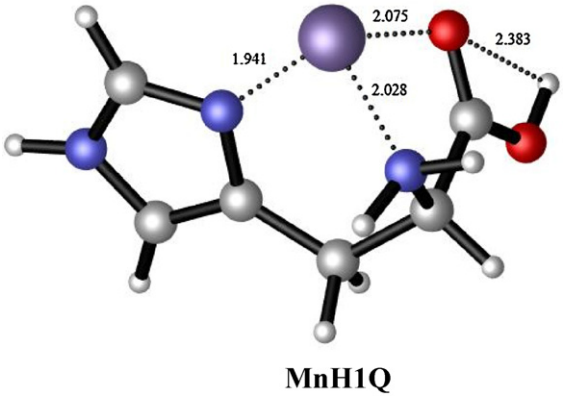

Fig. 2. B3LYP-optimized geometries for the low-lying conformer of Mn^{2+}–Histidine in quartet state. Distances are in angstroms.

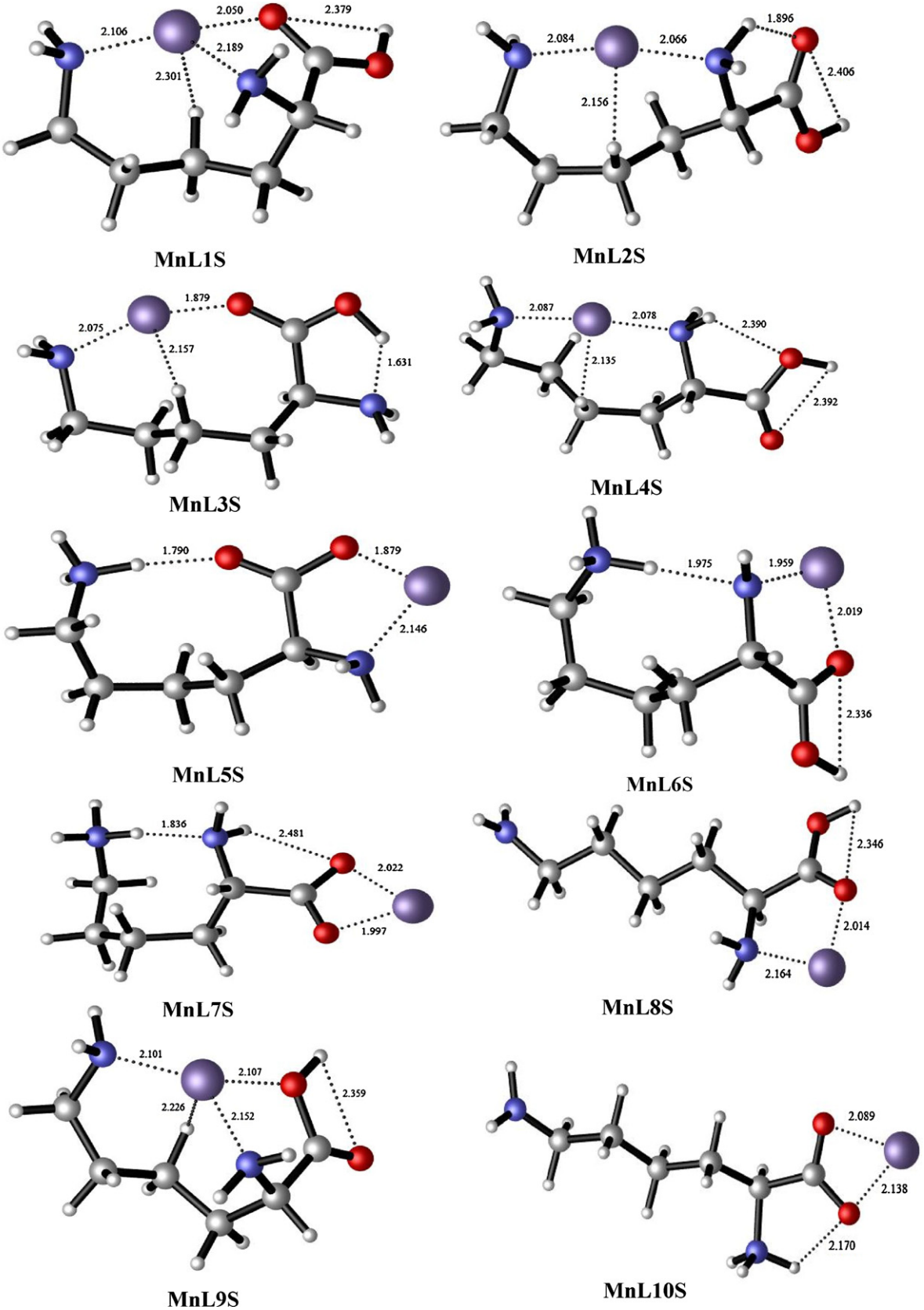

Fig. 3. B3LYP-optimized geometries for different minima of Mn^{2+}–Lysine in the sextet state. Distances are in angstroms.

quartet are of little importance, henceforth our main focus will be directed at the former case. Considering sextet moieties structures and energies of Table 1 and Fig. 1, with regard to their stability order, **MnH1S** of the first category mentioned earlier is the most stable, after which come some of the species of second category namely **MnH5S**, **MnH3S**, and **MnH4S**, respectively. In all three latter structures, the side chain amino nitrogen atom has been protonated and therefore is unable to interact with the metal ion. An important feature to note on two of the mentioned three moieties, namely **MnH5S** and **MnH3S**, is the existence of a relatively strong interamolecular hydrogen bond which has been formed between the side chain amino hydrogen atom and the amino acid's back bone amino nitrogen atom. Such bonding can lend support as being the main factor of these two complexes stability. Even though **MnH2S** moiety includes two interaction sites with metal ion, one due to back bone amino nitrogen site while the other from the side chain, but it assumes fifth rank with respect to stability. In all structures but **MnH1S**, metal ion only interacts with two amino acid's basic sites. A curious point to be noted here is that except for structures **MnH1S** and **MnH2S**, in all other four species the interaction occurs between metal ion and zwitterion from of amino acid. In this four zwitterionic species, the side chain's amino group which is also a member of imidazol ring is the protonated site. However there is a slight difference among the deprotonated sites. In **MnH5S**, **MnH3S** and **MnH6S** moieties, deprotonation site is the hydrocylic oxygen atom of the neutral amino acid, whereas in **MnH4S** case, this is the amino acid's back bone amino group which has lost its hydrogen atom. Justifying the relative sextet moieties stabilities, one encounters with the fact that although **MnH5S** and **MnH3S** complexes both contain carboxylate group in their ligand structure but they show different coordination sites. In **MnH3S** structure, metal ion–ligand interaction has occurred via two carboxylate oxygen sites. Such type of coordination has led to the formation of two intermolecular hydrogen bonds between one of the carboxylate oxygen with two of the amino hydrogen of the main chain. Existence of these two hydrogen bondings has caused higher stability in one hand while, due to decreasing of carboxylate oxygen basicity, has lowered the metal ion level of interaction. In the **MnH5S** moiety however, only one of the two carboxylate oxygens along with nitrogen atom of the back bone amino group plays the role of interaction site with metallic ion. Contrary to the **MnH3S** structure where two hydrogen bondings have been created, in **MnH5S** case, intramolecular hydrogen bonding has been formed by imidazol's N—H interaction with carboxylic oxygen which latter plays no role in coordination with metal ion. The small difference in stability of 1.1 kcal/mol of **MnH5S** relative to **MnH3S** complex may be attributed to the difference in coordinations centers and the fact that five member ring formation in former structure compared to four member ring in latter one, suggests higher stability than the number of interamolecular hydrogen bonding. **MnH3S** moiety is more stable than **MnH4S** by about 4.8 kcal/mol. In the latter complex, coordination with metal ion has occurred via carbonyl oxygen atom as well as the back bone amino group's deprotonated nitrogen atom. It appears as if the difference in coordination sites and lower number of intramolecular hydrogen bonds in **MnH4S** moiety can be held responsible for its lower stability in comparison to **MnH3S** complex. Loss of a hydrogen atom by the back bone amino nitrogen in **MnH4S** leads to higher basicity strength as well as more negative charge on the mentioned nitrogen atom. Such effects cause a higher electrostatic interaction with metal ion which can explain higher stability of **MnH4S** over **MnH6S** species. Furthermore it should be mentioned that transfer of one hydrogen from the interacting nitrogen atom with metal ion can be regarded as the result of the fact that by coordination to Mn^{2+}, NH_2 group's acidity is raised.

Similar to Mn^{2+}–Glycine complex [49], interaction of Mn^{2+} in sextet state with histidine results in a more stable complex than

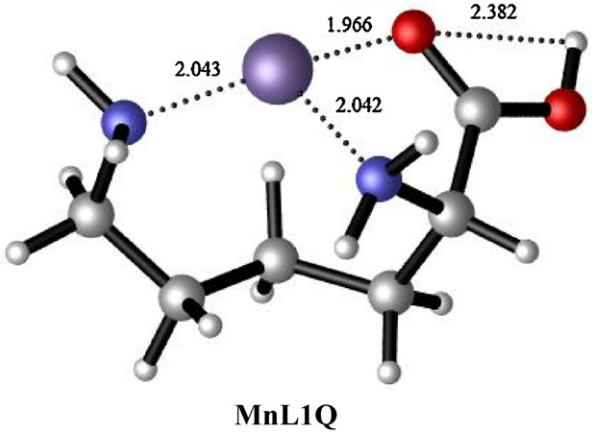

Fig. 4. B3LYP-optimized geometries for the low-lying conformer of Mn^{2+}–Lysine in quartet state. Distances are in angstroms.

other states. In addition, latter complexation doesn't alter relative energies of quartet–sextet or doublet–sextet. However, the most stable Mn^{2+}–Histidine structure namely **MnH1S**, is different from Mn^{2+}–Glycine and many other reported doubly charged ions–amino acid species as far as the type of coordination is concerned. In most cases, it has been reported that interaction with a doubly charged ion can stabilize a zwitterionic type structure of amino acids more than that of their neutral case [18,22,29,33]. In our example of histidine however, interaction with three basic centers as well as indirect presence of aromatic ring during interaction, can compensate for large electrostatic interaction between carboxylate group and doubly charged metal cation moiety. Such fact enlightens the significant role of side group basicity which it plays in stabilizing the neutral form of amino acid during interaction with metal cation. Besides, taking a close look at data of Table 1 and noting the manganese atom charge within complex reveals some charge transfer from ligand to metal cation which is to some extent larger than that of Mn^{2+}–Glycine case [49]. However the spin density is largely located on the metal cation. The aforementioned charge transfer has been approximately occurred in the same range for all of the desired complexes considered here. Such transfer of charge that has been occurred in **MnH4S** structure has been to some extent more than all other species (by about 0.5). Above observation can be ascribed to hydrogen atom transfer from amino group nitrogen atom thereby giving higher flexibility to charge to transfer. Charge transfer in **MnH1Q** complex has been determined considerably higher than all stable sextet states moieties. This fact can be attributed to a vacant metal ion d orbital. Thus due to charge transfer from ligand to metal ion, Pauli repulsion diminishes relative to other mentioned cases. A direct consequence of this reduction in repulsion can be seen as the reduction in coordination site to metal ion distance in **MnH1Q** relative to that of **MnH1S**.

3.2. Mn^{2+}–Lysine system

Similar to Mn^{2+}–Histidine complex, since doublet and quartet spin state lysine complexes are higher in energy than those of sextet, here our main attention has been paid to the latter ones only. In order to search for the most stable structure in coordination environments, same procedure has been applied as that explained for Mn^{2+}–Histidine case earlier. Figs. 3 and 4 include the stable minimum energy structures while Table 2 summarizes their relative energies as well as the metal natural population analysis data.

Due to commonality of minima structures obtained in lysine and histidine complexes, one can come to the conclusion that the most stable Mn^{2+}–Lysine complex can be the one formed by amino

Table 2
Relative energies (kcal/mol) of Mn^{2+}–Lysine and population analysis at B3LYP/basis level.

Structure	Coordination	State	ΔE	Mn natural population			q(Mn)	Spin(Mn)
				4s	3d	4p		
MnL1S	N_t, N_1, O_C	^6A	0.0	0.25	5.13	0.17	1.43	4.85
MnL2S	N_t, N_1	^6A	26.1	0.30	5.09	0.13	1.46	4.91
MnL3S	N_1, O_C	^6A	19.0	0.25	5.12	0.12	1.51	4.85
MnL4S	N_t, N_1	^6A	31.8	0.30	5.10	0.14	1.45	4.91
MnL5S	N_t, O^-	^6A	9.3	0.15	5.20	0.07	1.57	4.79
MnL6S	N_t^-, O_C	^6A	29.4	0.18	5.21	0.08	1.52	4.76
MnL7S	O, O^-	^6A	15.7	0.17	5.18	0.05	1.60	4.83
MnL8S	N_t, O_C	^6A	48.3	0.26	5.36	0.05	1.32	4.51
MnL9S	N_t, N_1, O_{OH}	^6A	17.0	0.26	5.13	0.18	1.42	4.85
MnL10S	O, O^-	^6A	43.6	0.47	5.10	0.09	1.34	5.25
MnL1Q	N_t, N_1, O_C	^4A	39.2	0.21	5.43	0.15	1.19	3.03

acid three dentate coordination at N_t, N_1 and O_C sites to Mn^{2+}, namely **MnL1S** of Fig. 3. Another point worth mentioning is the fact that, similar to histidine moiety, the second most stable lysine structure, namely **MnL5S** is generated via zwitterionic amino acid interaction at O^- and N_t sites with metal ion in which a relatively strong intramolecular hydrogen bond has been formed between O^- and $H—H_2N^+$. Next stable Mn^{2+}–Lysine complex namely **MnL7S** resembles that of histidine **MnH3S** but with a slight difference. This species is the result of interaction of carboxylate oxygen atoms of zwitterionic amino acid with metal ion which also includes a strong hydrogen bonding interaction of $^+NH_2—H\cdots N_tH_2$ type. A closer look at Fig. 3 and Table 2 suggests that location of active nitrogen in the side group has not affected the formation of three most stable structures of both Mn^{2+}–Histidine and Mn^{2+}–Lysine complexes. But, since the side chain in lysine is linear with no cyclic group, various structures with possible coordinations with metal ion which are presumably different from those of histidine are plausible. Thus more minimum energy structures are achieved of which, some with higher importance are considered here. Regarding the type of coordination sites, **MnL6S** resembles **MnH4S**. In the former complex, zwitterionic form of lysine has been coordination to manganese ion. Moreover, due to strong coordination of back bone amino nitrogen site with Mn^{2+}, existing amino hydrogens become more acidic and one H atom gets transferred to the side group nitrogen atom. Among stable Mn^{2+}–Lysine moieties, no structure similar to **MnH6S** exists. However, **MnL10S** complex can be referred to as one which is created via direct coordination of both carboxylate oxygen atoms of zwitterionic form of amino acid to Mn^{2+} cation. Such structure underlines the fact that by coordination of hydroxyl group to metal ion, its hydrogen assumes more acidic character and detaches. **MnL2S** and **MnL4S** are among complexes with no resemblance to Mn^{2+}–Histidine structure considered earlier. The former two moieties are generated by neutral lysine molecule coordination to manganese ion. The major difference between the two results from CO_2H rotation causing interamolecular hydrogen bonding $N_tH_2\cdots O_C$ and $N_tH_2\cdots O_{OH}$ formation in **MnL2S** and **MnL4S**, respectively. Aforementioned rotation and resulting difference in hydrogen bonding can be accounted for higher stability of **MnL2S** by 5.7 kcal/mol than **MnL4S** (see Table 2). Both **MnL8S** and **MnL9S** are also created by complexation of neutral lysine, with the former very much resembling the most stable neutral form in Mn^{2+}–Glycine case [49]. **MnL9S** too, in its appearance looks very much alike the most stable Mn^{2+}–Lysine moiety with the difference that instead of O_C, O_{OH} has been coordinated to Mn^{2+} ion. Such change in coordination site can be accounted for lower stability of **MnL9S** relative to **MnL1S** by about 17.0 kcal/mol.

Similar to histidine case, the most stable quartet spin state has been considered here (Fig. 4) with the relevant data summarized

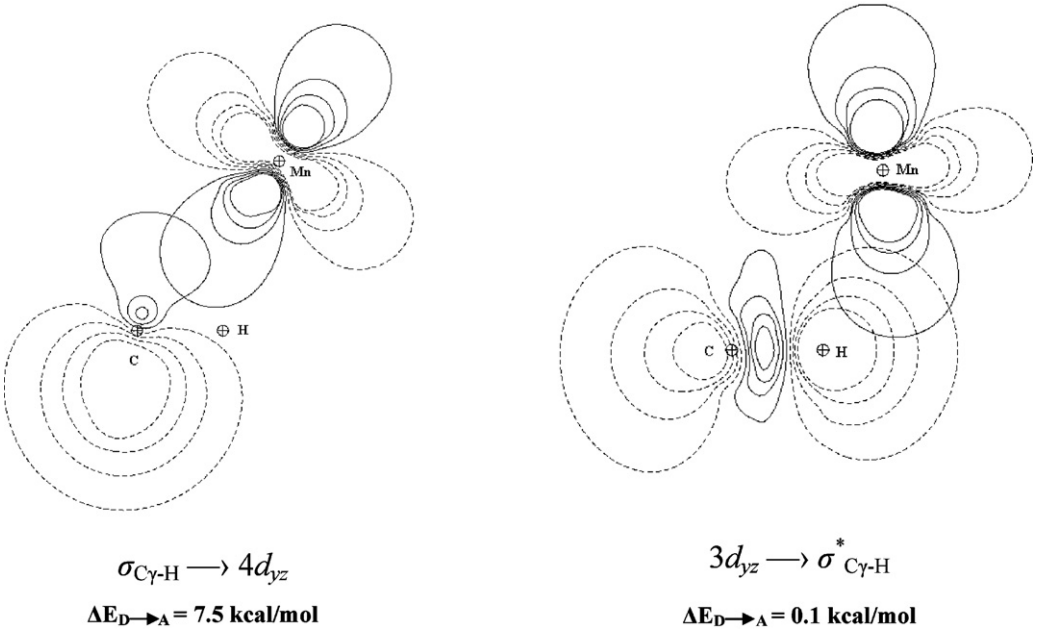

Fig. 5. NBO Donor–Acceptor interaction analysis with their corresponding energies (kcal/mol) for the agostic interaction in **MnL1S** (2-D Contour Images).

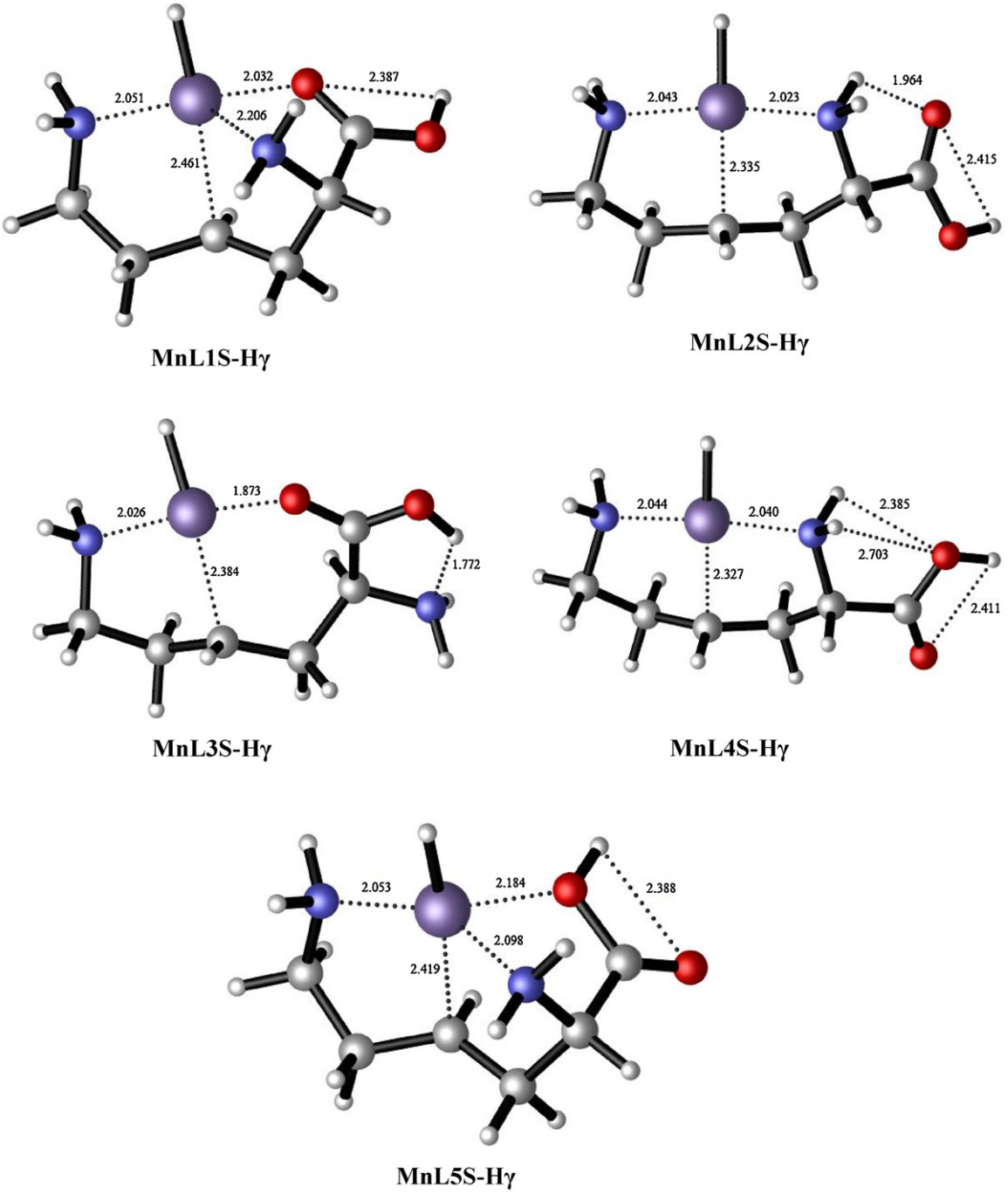

Fig. 6. B3LYP-optimized geometries for the different minima of the sextet states of HMn^{2+}(lysine-H). Distances are in angstroms.

in Table 2. As it is revealed, the concerned **MnL1Q** structure is less stable by about 39 kcal/mol than the most stable sextet counterpart. Due to such observation, quartet spin state investigation proves fruitless and is ignored.

A closer look at the Mn^{2+}–Lysine complexes formed, agostic interactions become evident. Such fact is due to interaction between H_γ or H_δ with manganese ion which are illustrated in Fig. 3. This observation underlines the high significance of the amino acid's side group in stabilizing its neutral forms while interacting with metal cations. Such agostic interactions have been also reported in some earlier works [4,99–102]. At the present case the latter interaction is caused by Cγ–H σ donor bonding orbitals with vacant metal ion orbitals. As an example second order NBO interaction analysis of the most stable structure, **MnL1S** reveals a charge transfer from Cγ–H σ donor bonding orbital to manganese ion empty orbital d_{yz} with an interaction energy amounting 7.5 kcal/mol. In addition, a weak back donation with 0.1 kcal/mol interaction energy from half filled d_{yz} orbital to Cγ–H σ* antibonding orbital is evident (see Fig. 5).

3.3. HMn^{2+}(lysine-H) system

Presence of agostic interactions persuaded us to consider those structures in which hydrogen atom transfer from σ bond interacting with metal cation is plausible. Fig. 6 and Table 3 include all optimized structures along with relative energies as well as metal

Table 3
Relative energies (kcal/mol) of HMn^{2+}(lysine-H) and population analysis at B3LYP/basis level, with respect to the most stable, **MnL1S**, structure.

Structure	Coordination	State	ΔE	Mn natural population			q(Mn)	Spin(Mn)
				4s	3d	4p		
MnL1S-Hγ	N_t, N_1, O_C, C, H	^{6}A	62.0	0.39	5.22	0.35	1.01	4.29
MnL2S-Hγ	N_t, N_1, C, H	^{6}A	79.8	0.42	5.16	0.25	1.16	4.32
MnL3S-Hγ	N_1, O_C, C, H	^{6}A	80.1	0.39	5.17	0.26	1.16	4.23
MnL4S-Hγ	N_t, N_1, C, H	^{6}A	83.2	0.41	5.16	0.25	1.15	4.33
MnL5S-Hγ	N_t, N_1, O_{OH}, C, H	^{6}A	77.0	0.39	5.22	0.35	1.01	4.30
MnL1Q-Hγ	N_t, N_1, O_C, C, H	^{4}A	84.4	0.34	5.21	0.43	0.99	4.35

ion charge and spin resulting from natural population analysis. For comparison, the most stable quartet spin state and its relevant data are illustrated in Fig. 7 and Table 3, respectively. As it is indicated in Table 3, relative energies of species in which an H atom from lysine has been transferred to metal cation are larger than their counterparts that show just agostic interaction with no H atom transfer. Comparison of the most stable similar type structures in quartet state **MnL1Q-H$_\gamma$** with sextet state indicate the point that even with transfer of a H atom to metal ion, no spin change has occurred, thereby still sextet moieties are more stable than quartet complexes.

3.4. Interaction energies

Tables 4 and 5 summarize interaction energies for the most stable structures of Mn^{2+}–Histidine and Mn^{2+}–Lysine moieties, respectively.

In both complexes, coordination of side chain with basic character leads to an increase in interaction with metal cation. Due to same reason, histidine and lysine affinities (ΔH°_{298}) to Mn^{2+} are 95 and 91.4 kcal/mol greater than that of glycine ΔH°_{298} (Mn^{2+}–Glycine) = 155.3 kcal/mol [49], respectively (see Tables 4 and 5). Comparison of interaction energies (D_e) of histidine with Cu^{2+} and Mn^{2+} ions reveal a large difference in stability of the corresponding complexes, the former being more stable by about 36 kcal/mol, Table 4. Also, comparing dissociation energies of lysine complexes with Co^{2+} and Mn^{2+} metal ions, Table 5 indicates lower dissociation energy for latter species. Lower stability of two aforementioned Mn^{2+} complexes relative to Cu^{2+} and Co^{2+} cases can be mostly attributed to an increase in effective nuclear charge of Cu^{2+} and Co^{2+} compared to that of Mn^{2+}. This fact causes a greater metal cation–amino acid electrostatic interaction which leads to higher stability. Paying a closer attention to Tables 4 and 5 data, it can be seen that values obtained by employing B3LYP method with basis sets lacking diffuse functions are to some extent smaller than the corresponding values while such functions are included. In addition, even though B3LYP results for manganese ion interaction with amino acid includes a small percentage of exact exchange, mentioned results corroborate well with those of CCSD(T) method. Such conclusion has not been common for interactions of other metals with amino acids in recent studies [103,104]. Regarding Mn^{2+}–Histidine and Mn^{2}–Lysine complexes it can be concluded that spin delocalization is small (Tables 1 and 2). This fact can be accounted as the main reason for very satisfactory correspondence between B3LYP data and those of CCSD(T). Same conclusion has been arrived by Constantino et al. for Co^{2+}–Lysine case [4].

Ultimately, IR gas phase spectra of most stable histidine and lysine complexes with manganese are depicted in details in Fig. 8.

Table 4
Interaction energies (D_e, D_0, ΔH°_{298}, and ΔG°_{298}), (kcal/mol) of Mn^{2+}–Histidine.

Interaction energies	Method	Mn^{2+}, ^{6}A	Ag^+ [e]	Cu^{2+} [f]
D_e	B3LYP[c]	250.2		
	B3LYP[d]	254.8		
	MP2[d]	249.4		
	CCSD(T)[d]	253.5		289.8[g]
D_0		250.6[a]		286.0[h]
ΔH°_{298}		250.3[b]	68.0	287.1[h]
ΔG°_{298}		251.6[b]	59.6	276.9[h]

[a] Determined using CCSD(T)/basis values and the B3LYP/6-31G(d,p) unscaled harmonic frequencies.
[b] After taking into consideration thermal corrections determined at the B3LYP/6-31G(d,p).
[c] Determined by B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p) level.
[d] Determined by method/basis//B3LYP/6-31G(d,p) level.
[e] Ref. [36]. Experimental data.
[f] Ref. [48].
[g] Determined at CCSD(T) level.
[h] Determined at B3LYP level.

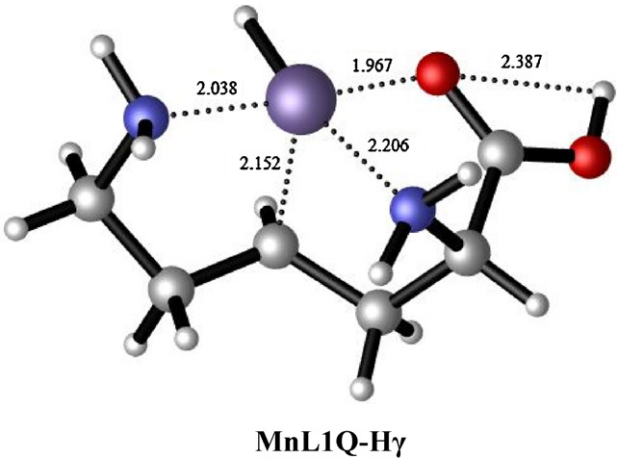

Fig. 7. B3LYP-optimized geometries for the quartet state of HMn^{2+}(lysine-H). Distances are in angstroms.

Table 5
Interaction energies (D_e, D_0, ΔH°_{298}, and ΔG°_{298}), (kcal/mol) of Mn^{2+}–Lysine.

Interaction energies	Method	Mn^{2+}, ^{6}A	Ag^+ [e]	Co^{2+} [f]
D_e	B3LYP[c]	248.6		
	B3LYP[d]	250.8		278.8[g]
	MP2[d]	246.4		
	CCSD(T)[d]	250.1		
D_0		246.4[a]		267.6[h]
ΔH°_{298}		246.7[b]	71.0	269.6[h]
ΔG°_{298}		246.4[b]	62.4	256.0[h]

[a] Determined using CCSD(T)/basis values and the B3LYP/6-31G(d,p) unscaled harmonic frequencies.
[b] After taking into consideration thermal corrections determined at the B3LYP/6-31G(d,p).
[c] Determined by B3LYP/6-31G(d,p)//B3LYP/6-31G(d,p) level.
[d] Determined by method/'basis'//B3LYP/6-31G(d,p) level.
[e] Ref. [36]. Experimental data.
[f] Ref. [4].
[g] Determined at B3LYP level.
[h] Determined at CCSD(T) level.

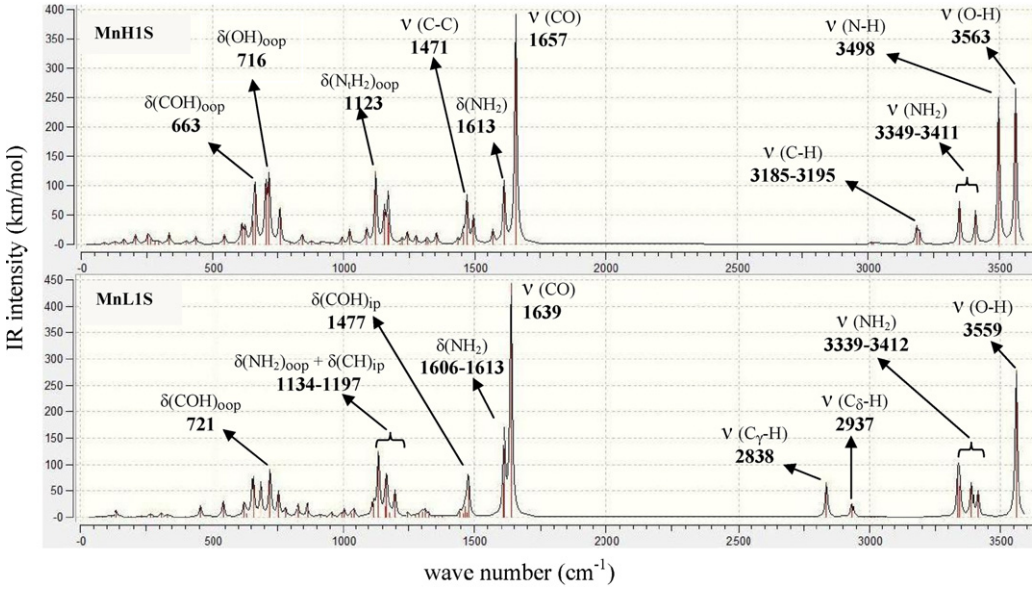

Fig. 8. Computed spectra of the most stable structures of Mn^{2+}–Histidine (**MnH1S**) and Mn^{2+}–Lysine (**MnL1S**) complexes at the B3LYP/6-31G(d,p) level. The frequencies have been scaled by 0.96.

All vibrational frequencies obtained are scaled by a factor of 0.96 to arrive at the real values [105].

Some of the outstanding features encountered in these spectra are as follows. Carbonyl oxygen coordination which has induced a red shift in ligand (shift values relative to free histidine and lysine are 132 and 143 cm^{-1}) shows a sharp C=O stretching feature that has occurred at 1657 and 1639 cm^{-1} for Mn^{2+}–Histidine and Mn^{2+}–Lysine, respectively. Out of plane bending mode of COH for Mn^{2+}–Histidine and Mn^{2+}–Lysine has appeared at 716 and 721 cm^{-1}, respectively. The latter features show 37 and 10 cm^{-1} red shifts relative to those of free amino acid. Such shifts can be attributed to the loss of interamolecular hydrogen bonding $OH\cdots NH_2$ after formation of complex with metal ion. Symmetric and asymmetric stretching vibrations of amino groups for Mn^{2+}–Histidine and Mn^{2+}–Lysine moieties have been appeared in the range 3349–3411 cm^{-1}, respectively. Again a red shift of about 45 and 51 cm^{-1}, relative to same two ranges for the free amino acid, has occurred, respectively. Red shifts caused by complexation of lysine with Mn^{2+} are less than the corresponding shifts for their Co^{2+}–Lysine analogues [4]. This point again reveals the significance of electrostatic interaction effect. Imidazole ring N—H stretching vibration in histidine has experienced a 62 cm^{-1} red shift after complexation and has been appeared at 3498 cm^{-1}. Finally the sharp band at 2838 cm^{-1} in Mn^{2+}–Lysine spectrum merits special attention. A 169 cm^{-1} red shift relative to that of free lysine emphasizes the significance of agoastinc interaction between C_γ—H and metal ion.

4. Conclusions

Several coordination modes as the result of interaction of sextet spin electronic state of Mn^{2+} ($3d^5$) with histidine and lysine have been investigated. For the purpose of comparison, the most stable coordination mode arising from Mn^{2+} ($3d^5$) quartet spin state interaction has also been considered. For Mn^{2+}–Histidine complex, ground electronic state has a three dentate configuration stemming from amino and carbonyl oxygen groups of neutral histidine coordination. In this case, ground electronic state of the system is determined as ^6A. Although histidine has one more basic site that glycine which leads to higher coordination level with metal atom, but the most stable histidine complexes in sextet and quartet spin states are not much lower in energy than those found for Mn^{2+}–Glycine counterparts. Such observation may suggest the low influence of ligand coordination in causing metal ion spin state alteration. In addition, energy considerations of sextet electronic state conformers reveals that the zwitterion configuration is higher than the ground state structure by about 15–27 kcal/mol. In all structures studied for Mn^{2+}–Histidine case, metal ion d orbital show a large overlap with the interaction site orbital of histidine. While the complex is in sextet electronic state, all metal's d orbitals are singly occupied whereas in quartet spin state one d orbital is left vacant. This fact can be regarded as the cause for lower repulsion in quartet state leading to smaller metal–ligand distances.

Considering Mn^{2+}–Lysine moiety, the most stable structure shows a coordination environment about metal resembling that of Mn^{2+}–Histidine complex. In both cases, Mn^{2+} ion interacts with neutral amino acid via amino and carbonyl oxygen groups. Such observation is contrary to what has been found for glycine in which zwitterionic form of amino acid comes into interaction with manganese ion. Agostic interactions between metal ion and a C_γ—H σ bond from ligand have been evident at the instances when amino side group is coordinated to metal center. Mn^{2+} interaction with the side chain as well as agostic interaction in neutral lysine are some reasons for the difference found with that of stable glycine structure.

Letting migration of H atom involved in agostic interaction has led to structures with H located on metal center. Such species show energies which are higher than that of the most stable sextet state complex, **MnL1S**. Moreover, with above migration, no spin state change occurs and thus, the most stable conformer of these species namely **MnL1S-H$_\gamma$** assumes sextet electronic spin state. For both complexes studied in this account, Mn^{2+}–Histidine and Mn^{2+}–Lysine, calculated bond dissociation energies are higher than that previously reported for glycine. Such difference can be accounted for by presence of amino acid side change which includes three basic coordination sites.

Supplementary data

Optimized structures and total energies as well as zero point corrections of all considered complexes.

Acknowledgments

We are grateful to Prof. S.W. Ng for providing us the software (G98W suite of programs) and hardware (machine time) facilities and also making us available the opportunity to access some new features of Gaussian products. The authors would like to acknowledge financial support from the Research Council of Shahid Beheshti University. Also technical support of the Chemistry Computational Center at Shahid Beheshti University is greatly acknowledged.

Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.ijms.2011.12.019.

References

[1] L.A. Finney, T.V. O'Halloran, Science 300 (2003) 931.
[2] S.J. Lippard, J.M. Berg, Principles of Bioinorganic Chemistry, University Science Books, Mill Valley, CA, 1994.
[3] A. Sigel, H. Sigel (Eds.), Metal Ions in Biological Systems, vol. 38, Marcel Dekker, New York, 2001.
[4] E. Constantino, J. Tortajada, M. Sodupe, L. Rodríguez-Santiago, J. Phys. Chem. A 112 (2008) 12385.
[5] D.R. Brown, F. Hafiz, L.L. Glasssmith, B.S. Wong, I.M. Jones, C. Clive, S.J. Haswell, EMBO J. 19 (2000) 1180.
[6] G.S. Jackson, I. Murray, L.L. Hosszu, N. Gibbs, J.P. Waltho, A.R. Clarke, J. Collinge, Proc. Natl. Acad. Sci. U.S.A. 98 (2001) 8531.
[7] E. Gaggelli, F. Bernardi, E. Molteni, R. Pogni, D. Valensin, G. Valensin, M. Remelli, M. Luczkowski, H. Kozlowski, J. Am. Chem. Soc. 127 (2005) 996.
[8] C.E. Jones, M. Klewpatinond, S.R. Abdelraheim, D.R. Brown, J.H. Viles, J. Mol. Biol. 346 (2005) 1393.
[9] W.S. Perera, N.M. Hooper, Curr. Biol. 11 (2001) 519.
[10] R.N. Tsenkova, I.K. Iordinova, K. Toyoda, D.R. Brown, Biochem. Biophys. Res. Commun. 325 (2004) 1005.
[11] C.S. Cobbett, Plant Physiol. 123 (2000) 825.
[12] A.A. Bliznyuk, H.F. Schaefer III, I.J. Amster, J. Am. Chem. Soc. 115 (1993) 5149.
[13] Z.B. Maksic, B. Kovacevic, Chem. Phys. Lett. 307 (1999) 497.
[14] S.R. Abdelraheim, S. Kralovicova, D.R. Brown, Int. J. Biochem. Cell Biol. 38 (2006) 1429.
[15] M.W. Brazier, P. Davies, E. Player, F. Marken, J.H. Viles, D.R. Brown, J. Biol. Chem. 283 (2008) 12831.
[16] H. Ai, Y. Bu, K. Han, J. Chem. Phys. 118 (2003) 10973.
[17] C.K. Barlow, D. Moran, L. Radom, W.D. McFadyen, R.A.J. O'Hair, J. Phys. Chem. A 110 (2006) 8304.
[18] J. Bertran, L. Rodríguez-Santiago, M. Sodupe, J. Phys. Chem. B 103 (1999) 2310.
[19] S. Bouchonnet, Y. Hoppilliard, G. Ohanessian, J. Mass Spectrom. 30 (1995) 172.
[20] Y. Hoppilliard, F. Rogalewicz, G. Ohanessian, Int. J. Mass Spectrom. 204 (2000) 267.
[21] S. Hoyau, G. Ohanessian, J. Am. Chem. Soc. 119 (1997) 2016.
[22] S. Hoyau, J.P. Pelicier, F. Rogalewicz, Y. Hoppilliard, G. Ohanessian, Eur. J. Mass Spectrom. 7 (2001) 303.
[23] T. Marino, N. Russo, M. Toscano, J. Inorg. Biochem. 79 (2000) 179.
[24] T. Marino, N. Russo, M. Toscano, J. Mass Spectrom. 37 (2002) 786.
[25] T. Marino, M. Toscano, N. Russo, A. Grand, J. Phys. Chem. B 110 (2006) 24666.
[26] S. Pulkkinen, M. Noguera, L. Rodríguez-Santiago, M. Sodupe, J. Bertran, Chem. Eur. J. 6 (2000) 4393.
[27] M. Remko, B.M. Rode, J. Phys. Chem. A 110 (2006) 1960.
[28] A. Rimola, M. Sodupe, J. Tortajada, L. Rodríguez-Santiago, Int. J. Mass Spectrom. 257 (2006) 60.
[29] L. Rodríguez-Santiago, M. Sodupe, J. Tortajada, J. Phys. Chem. A 105 (2001) 5340.
[30] F. Rogalewicz, Y. Hoppilliard, G. Ohanessian, Int. J. Mass Spectrom. 201 (2000) 307.
[31] F. Rogalewicz, Y. Hoppilliard, G. Ohanessian, Int. J. Mass Spectrom. 206 (2001) 45.
[32] F. Rogalewicz, Y. Hoppilliard, G. Ohanessian, Int. J. Mass Spectrom. 227 (2003) 439.
[33] F. Rogalewicz, G. Ohanessian, N. Gresh, J. Comput. Chem. 21 (2000) 963.
[34] L. Rulísek, Z. Havlas, J. Am. Chem. Soc. 122 (2000) 10428.
[35] L. Rulísek, Z. Havlas, J. Phys. Chem. B 107 (2003) 2376.
[36] T. Shoeib, K.W.M. Siu, A.C. Hopkinson, J. Phys. Chem. A 106 (2002) 6121.
[37] R. Spezia, G. Tournois, T. Cartailler, J. Tortajada, Y. Jeanvoine, J. Phys. Chem. A 110 (2006) 9727.
[38] B.K. Bluhm, S.J. Shields, C.A. Bayse, M.B. Hall, D.H. Russell, Int. J. Mass Spectrom. 204 (2001) 31.
[39] E. Constantino, A. Rimola, L. Rodríguez-Santiago, M. Sodupe, New J. Chem. 29 (2005) 1585.
[40] T.N. Parac, G.M. Ullmann, N.M. Kostic, J. Am. Chem. Soc. 121 (1999) 3127.
[41] D.F. Raffa, R. Gómez-Balderas, P. Brunelle, G.A. Rickard, A. Rauk, J. Biol. Inorg. Chem. 10 (2005) 887.
[42] M. Remko, B.M. Rode, Chem. Phys. Lett. 316 (2000) 489.
[43] M. Remko, B. Rode, Mol. Struct. Chem. 15 (2004) 223.
[44] L. Rulíšek, Z. Havlas, J. Phys. Chem. A 106 (2002) 3855.
[45] T. Shoeib, C.F. Rodríguez, K.W.M. Siu, A.C. Hopkinson, Phys. Chem. Chem. Phys. 3 (2001) 853.
[46] J.H. Xu, C.W. Hu, Acta Chim. Sinica 64 (2006) 1622.
[47] E. Constantino, L. Rodríguez-Santiago, M. Sodupe, J. Tortajada, J. Phys. Chem. A 109 (2005) 224.
[48] A. Rimola, L. Rodríguez-Santiago, M. Sodupe, J. Phys. Chem. B 110 (2006) 24189.
[49] M.H. Khodabandeh, M.D. Davaria, M. Zahedi, G. Ohanessian, Int. J. Mass Spectrom. 291 (2010) 73.
[50] B.A. Cerda, C. Wesdemiotis, J. Am. Chem. Soc. 117 (1995) 9734.
[51] B.A. Cerda, C. Wesdemiotis, Int. J. Mass Spectrom. 107 (1999) 185.
[52] C.L. Gatlin, K. Turecek, T. Vaisar, J. Am. Chem. Soc. 117 (1995) 3637.
[53] H. Lavanant, E. Hecquet, Y. Hoppilliard, Int. J. Mass Spectrom. 11 (1999) 185.
[54] H. Lavanant, Y. Hoppilliard, J. Mass Spectrom. 32 (1997) 1037.
[55] V.W.M. Lee, H. Li, T.C. Lau, R. Guevremont, K.W.M. Siu, J. Am. Soc. Mass Spectrom. 9 (1998) 760.
[56] Q.P. Lei, I.J. Amster, J. Am. Soc. Mass Spectrom. 7 (1996) 722.
[57] D. Wen, T. Yalcin, A.G. Harrison, Rapid Commun. Mass Spectrom. 9 (1995) 1155.
[58] Y. Xu, X. Zhang, A.L. Yergey, J. Am. Soc. Mass Spectrom. 7 (1996) 25.
[59] T. Yalcin, J. Wang, D. Wen, A.G. Harrison, J. Am. Soc. Mass Spectrom. 8 (1997) 749.
[60] S. Yu, S. Lee, G. Chung, H. Oh, Bull. Korean Chem. Soc. 25 (2004) 1477.
[61] I.K. Chu, X. Guo, T.C. Lau, K.W.M. Siu, Anal. Chem. 71 (1999) 2364.
[62] P. Hu, J.A. Loo, J. Am. Chem. Soc. 117 (1995) 11314.
[63] M.M. Kish, C. Wesdemiotis, Int. J. Mass Spectrom. 227 (2003) 191.
[64] M. Lagarrigue, A. Bossée, C. Afonso, F. Fournier, B. Bellier, J.C. Tabet, J. Mass Spectrom. 41 (2006) 1073.
[65] V.W.M. Lee, H. Li, T.C. Lau, K.W.M. Siu, J. Am. Chem. Soc. 120 (1998) 7302.
[66] A.H. Payne, G.L. Glish, Int. J. Mass Spectrom. 204 (2001) 47.
[67] A. Reiter, J. Adams, H. Zhao, J. Am. Chem. Soc. 116 (1994) 7827.
[68] A.C. Schmidt, J. Koppelt, M. Neustadt, M. Otto, Rapid Commun. Mass Spectrom. 21 (2007) 153.
[69] C. Seto, J.A. Stone, Int. J. Mass Spectrom. 192 (1999) 289.
[70] S.J. Shields, B.K. Bluhm, D.H. Russell, J. Am. Soc. Mass Spectrom. 11 (2000) 626.
[71] T. Vaisar, C. Gatlin, R.D. Rao, J.L. Seymour, F. Turecek, J. Mass Spectrom. 36 (2001) 306.
[72] I.K. Chu, T. Shoeib, X. Guo, C.F. Rodríguez, T.C. Lau, A.C. Hopkinson, M.K.W. Siu, J. Am. Soc. Mass Spectrom. 12 (2001) 163.
[73] T. Dudev, C. Lim, Chem. Rev. 103 (2003) 773.
[74] B.J. Duncombe, J.O.S. Ryden, L. Puskar, H. Cox, A.J. Stace, J. Am. Soc. Mass Spectrom. 19 (2008) 520.
[75] M. Trachtman, C.W. Bock, J. Mol. Struct. (Theochem.) 672 (2004) 75.
[76] A.T. Blades, P. Jayaweera, M.G. Ikonomou, P. Kebarle, J. Chem. Phys. 92 (1990) 5900.
[77] U.N. Andersen, G. Bojesen, Int. J. Mass Spectrom. 153 (1996) 1.
[78] A.T. Blades, P. Kebarle, J. Phys. Chem. A 110 (2006) 12055.
[79] A.D. Becke, J. Chem. Phys. 98 (1993) 5648.
[80] C. Lee, W. Yang, R.G. Parr, Phys. Rev. B 37 (1988) 785.
[81] P.J. Stephens, F.J. Devlin, C.F. Chabalowski, M.J. Frisch, J. Phys. Chem. 98 (1994) 11623.
[82] C.W. Bauschlicher, A. Ricca, H. Partridge, S.R. Langhoff, Recent Advances in Density Functional Theory, Part II, World Scientific, Singapore, 1997.
[83] M.R.A. Blomberg, P.E.M. Siegbahn, M. Svensson, J. Chem. Phys. 104 (1996) 9546.
[84] M.C. Holthausen, M. Mohr, W. Koch, Chem. Phys. Lett. 240 (1995) 245.
[85] A. Luna, M. Alcamí, O. Mó, M. Yáñez, Chem. Phys. Lett. 320 (2000) 129.
[86] K. Raghavachari, G.W. Trucks, J.A. Pople, M. Head-Gordon, Chem. Phys. Lett. 157 (1989) 479.
[87] E.R. Davidson, D. Feller, Chem. Rev. 86 (4) (1986) 681.
[88] W.J. Hehre, L. Radom, P.V. Schleyer, J. Pople, Ab initio Molecular Orbital Theory, Wiley, New York, 1998.
[89] A.J.H. Wachters, J. Chem. Phys. 52 (1970) 1033.
[90] K. Raghavachari, G.W. Trucks, J. Chem. Phys. 91 (1989) 1062.
[91] P.C. Hariharan, J.A. Pople, Theor. Chim. Acta 28 (1973) 213.
[92] T. Clark, J. Chandrasekhar, G.W. Spitznagel, P.V.R. Schleyer, J. Comput. Chem. 4 (1983) 294.
[93] D.A. McQuarrie, Statistical Mechanics, Harper & Row, New York, 1986.
[94] A.E. Reed, L.A. Curtiss, F. Weinhold, Chem. Rev. 88 (1988) 899.
[95] F. Weinhold, J.E. Carpenter, The Structure of Small Molecules and Ions, Plenum, New York, 1988.
[96] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, V.G. Zakrzewski, J.A. Montgomery, R.E. Stratmann, J.C. Burant, S. Dapprich, J.M. Millam, A.D. Daniels, K.N. Kudin, M.C. Strain, O. Farkas, J. Tomasi, V. Barone, M. Cossi, R. Cammi, B. Mennucci, C. Pomelli, C. Adamo, S. Clifford, J. Ochterski, G.A. Petersson, P.Y. Ayala, Q. Cui, K. Morokuma, D.K. Malick, A.D. Rabuck, K. Raghavachari, J.B. Foresman, J. Cioslowski, J.V. Ortiz, B.B. Stefanov, G. Liu, A. Liashenko, P. Piskorz, I. Komaromi, R. Gomperts, R.L. Martin, D.J. Fox, T. Keith, M.A. Al-Laham, C.Y. Peng, A. Nanayakkara, C. Gonzalez, M. Challacombe, P.M.W. Gill, B.G. Johnson, W. Chen, M.W. Wong, J.L. Andres,

M.R.E.S. Head-Gordon, J.A. Pople, Gaussian 98, Gaussian, Inc., Pittsburgh, PA, 1998.
[97] J.J.P. Stewart, J. Comput. Chem. 10 (1989) 209.
[98] J.J.P. Stewart, J. Comput. Chem. 10 (1989) 221.
[99] I. Corral, O. Mó, M. Yáñez, J. Phys. Chem. A 107 (2003) 1370.
[100] I. Corral, O. Mó, M. Yáñez, New J. Chem. 27 (2003) 1657.
[101] I. Corral, O. Mó, M. Yáñez, Theor. Chem. Acc. 112 (2004) 298.
[102] I. Corral, O. Mó, M. Yáñez, Int. J. Mass Spectrom. 227 (2003) 401.
[103] J. Poater, M. Sola', A. Rimola, L. Rodríguez-Santiago, M. Sodupe, J. Phys. Chem. A 108 (2004) 6072.
[104] I. Georgieva, N. Trendafilova, L. Rodríguez-Santiago, M. Sodupe, J. Phys. Chem. A 109 (2005) 5668.
[105] A.P. Scott, L. Radom, J. Phys. Chem. 100 (1996) 16502.