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Thermodynamics of Zinc(II) Complexes with N'_1,N'_2-Dihydroxy-N_1,N_2-dipyridin-2-ylethanediamidediimide in the Gas Phase

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Ab initio and density functional calculations were used to study the coordination and thermodynamic properties of mononuclear complexes of dimethylglyoxime (H_2M), diaminoglyoxime (H_2A), and (1*Z*,2*Z*)-N'_1,N'_2-dihydroxy-N_1,N_2-dipyridin-2-ylethanediamidediimide (H_2L) as well as dinuclear complexes of H_2L with zinc(II) at B3LYP/6-31G(d), B3LYP/6-31+G(d), and B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) computational levels. Theoretical calculation shows that unusual O,O-coordination is a stable model for coordination of H_2L to zinc(II) in the gas phase.

Divalent zinc ion plays an important part in the function of numerous enzymes throughout living systems. In the majority of these enzymes, divalent zinc ion is directly involved in the catalytic mechanism. It is an ideal building part for hydrolytic enzymes because of its unique electronic configuration: vacant 4s and filled 3d orbitals mean redox stability and allow coordination number to vary from 4 to 6.[1]

In the past, zinc–ligand interactions have been studied from various points of view. Several studies investigated divalent zinc ion solvation by water and hydroxide anion,[2,3] and binding interactions with small biologically relevant ligands, e.g. acetone, *N*-methylacetamide,[4] imidazole,[5] or ligands used in real or hypothetic inhibitors of metalloenzymes.[6–10] By increasing computational power and the development of new basis sets and methods accurate theoretical calculations of larger complexes have been made possible. Thus, complexes of divalent zinc ion with multidentate ligand molecules, which mimic the surrounding amino residues in enzyme active sites, can be studied.[11–15] The results derived from the calculations of more complex models, bring information of higher quality as they better represent the behavior of zinc in real biological systems.

On the other hand, oximes are widely used for various purposes in organic,[16] inorganic,[17,18] bioinorganic,[19] and analytical chemistry,[20] pigments,[21] and dyes.[22] The *vic*-dioximes are capable of coordinating through N,N or N,O sites of the oxime groups.[23] Recently, metal containing oxime complexes have been utilized in medicine as well.[24,25] Also, synthesis and N,N-coordinated mono and dinuclear complexes of (1*Z*,2*Z*)-N'_1,N'_2-dihydroxy-N_1,N_2-dipyridin-2-ylethanediamidediimide (H_2L) with Zn^{II}, Cd^{II}, and Hg^{II} [26] have been reported. H_2L has six N (N1, N2, N3, N4, N5, and N6, see Figure 1) and two O atoms which through them it can act as a bidentate ligand for a metal ion. Among them coordination through N1–N2 has extensively been considered. Since direct determination of structural and thermodynamic parameters for various kinds of Zn–H_2L interactions is very complicated, the computational chemistry is a good alternative.

The main objective of this study is to investigate structural and electronic parameters for various 1:1 and 2:1 complexes which may occur between $ZnCl_2$ and H_2L. For better illustration of the effect of amine groups on the coordination ability of oximic N atoms, gas-phase thermodynamic parameters for mononuclear complexes of H_2M and H_2A with $ZnCl_2$ have been calculated. Calculation of enthalpies were carried out by combined approach at the B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d) level.

Computational Details

Density functional calculations were carried out by means of the Gaussian 98 package of computer codes.[27] The explicit treatment of all the electrons in these types of complexes constitutes a demanding computational task. Therefore, two ways were used to surmount this difficulty. Geometry optimization was carried out at B3LYP/6-31G(d) and B3LYP/6-31+G(d) then a single point calculation at more sophisticated B3LYP/6-311+G(2d,p) level was done on the optimized geometry of B3LYP/6-31G(d). Starting structures of the free ligands, $ZnCl_2$, and complexes were fully optimized at both levels. Harmonic vibrational frequency calculations confirmed the structures as minima and enabled the evaluation of zero point energies (ZPE). In order to achieve more accurate values of interaction enthalpies for these complexes, calculation with correlated methods possessing more flexible basis sets and diffuse functions is necessary. Thus, energies are calculated with a correlated method on B3LYP/6-31G(d) geometry rather than carrying out the geometry optimization at the correlated level. This is called a single-point calculation, using the B3LYP/6-311+G(2d,p) basis[28–31] on a structure that was optimized with the B3LYP/6-31G(d) basis and designated as B3LYP/6-311+G(2d,p)//B3LYP/6-31G(d). This combination of methods was shown to have acceptable mean absolute deviation ($MAD = 13.4\,kJ\,mol^{-1}$) of interaction energies from experimental results.[32]

In another way, we use the electron core potentials (ECP) or pseudo-potentials,[33] in which only the valence electrons are

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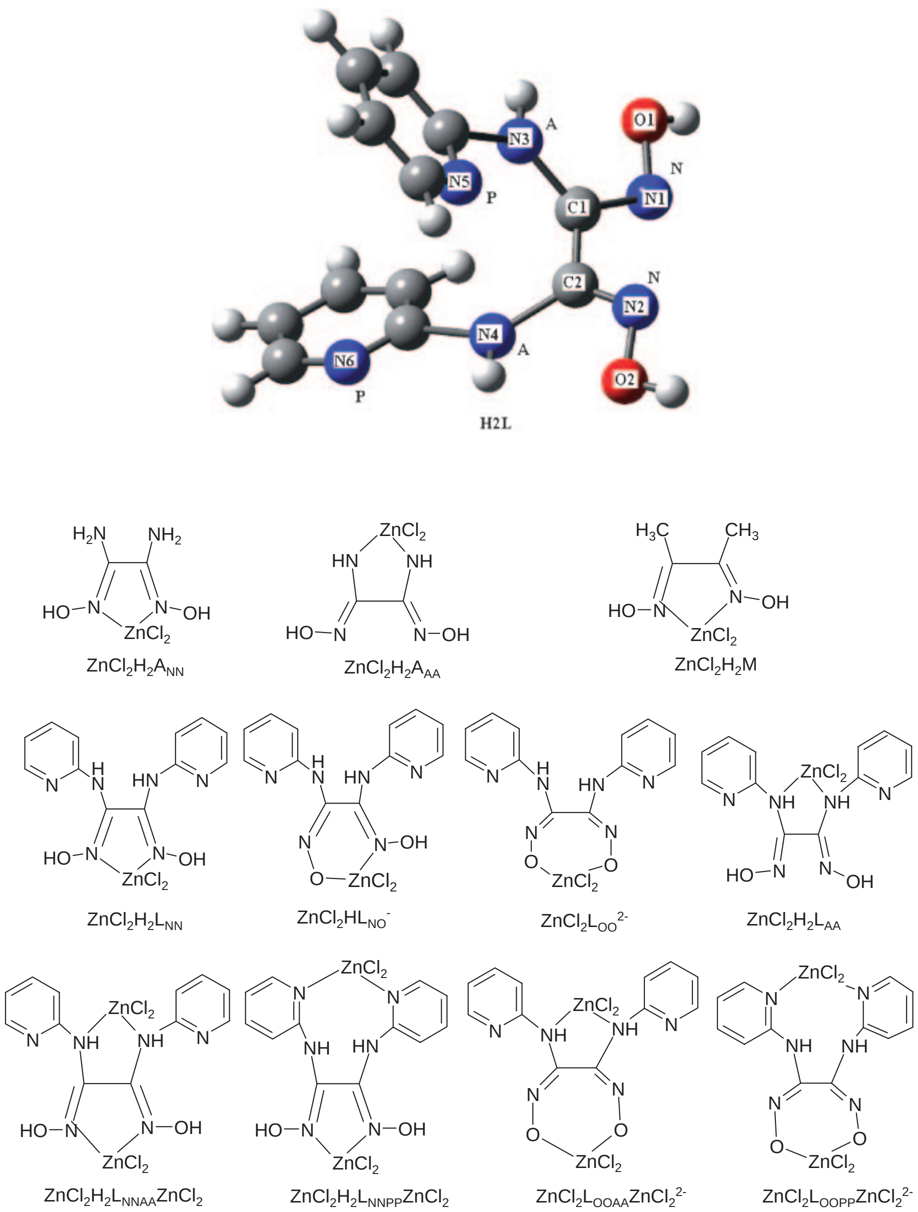

Figure 1. Proposed complexes of H_2L with $ZnCl_2$.

treated explicitly. In this way, optimizations were carried out at the DFT level of theory with B3LYP correlation function in conjunction with the LanL2DZ basis sets[29,31,34,35] for the Zn and Cl atoms and with the ordinary 6-31G(d) and 6-31+G(d) basis sets for the C, H, N, and O atoms [DFT-B3LYP/LanL2DZ/6-31G(d) and DFT-B3LYP/LanL2DZ/6-31+G(d)].

Assuming that the complexes are formed according to the following equations, for 1:1 complexes (if $H_2X = H_2L$ then $n = 0$–2; for $H_2X = H_2M$ or H_2A then $n = 0$):

$$\begin{aligned}&\mathrm{ZnCl_2(g)} + \mathrm{H_2X(g)} + n\mathrm{OH^-(g)}\\&\quad\rightarrow \mathrm{ZnCl_2H_{(2-\mathit{n})}X^{\mathit{n}-}(g)} + n\mathrm{H_2O(g)}\end{aligned} \tag{1}$$

In HF and LanL2DZ, the gas-phase interaction enthalpy ΔH is defined by eqs 2–4:

$$\Delta H = \Delta E + \Delta pV \tag{2}$$

$$\begin{aligned}\Delta H = {}&\{E(\mathrm{ZnCl_2H_{(2-\mathit{n})}X^{\mathit{n}-}}) + nE(\mathrm{H_2O})\\&- [E(\mathrm{ZnCl_2}) + E(\mathrm{H_2X}) + nE(\mathrm{OH^-})]\} + \Delta pV\end{aligned} \tag{3}$$

$$\begin{aligned}\Delta H = {}&E(\mathrm{ZnCl_2H_{(2-\mathit{n})}X^{\mathit{n}-}}) + nE(\mathrm{H_2O})\\&- E(\mathrm{ZnCl_2}) - E(\mathrm{H_2X}) - nE(\mathrm{OH^-}) - RT\end{aligned} \tag{4}$$

For 2:1 complexes:

$$\begin{aligned}&2\mathrm{ZnCl_2(g)} + \mathrm{H_2L(g)} + n\mathrm{OH^-(g)}\\&\quad\rightarrow \mathrm{ZnCl_2H_{(2-\mathit{n})}LZnCl_2{}^{\mathit{n}-}(g)} + n\mathrm{H_2O(g)}\end{aligned} \tag{5}$$

ΔH by eqs 6–8:

$$\Delta H = \Delta E + \Delta pV \tag{6}$$

$$\begin{aligned}\Delta H = {}&\{E(\mathrm{ZnCl_2H_{(2-\mathit{n})}LZnCl_2{}^{\mathit{n}-}}) + nE(\mathrm{H_2O})\\&- [(2E(\mathrm{ZnCl_2}) + E(\mathrm{H_2L}) + nE(\mathrm{OH^-})]\} + \Delta pV\end{aligned} \tag{7}$$

Table 1. Calculated Gas-Phase Stabilization Energies SE ($\mathrm{kJ\,mol^{-1}}$) and Interaction Enthalpies ΔH^{298} ($\mathrm{kJ\,mol^{-1}}$) for H_2A and H_2M Complexes with $ZnCl_2$

Complex	B3LYP/LanL2DZ/6-31+G(d) (corrected for ZPE)		B3LYP/LanL2DZ/6-31G(d) (corrected for ZPE)		B3LYP/6-311+G(2d,p)//LanL2DZ/6-31G(d)	
	SE	ΔH^{298}	SE	ΔH^{298}	SE	ΔH^{298}
$ZnCl_2H_2A_{AA}$	−88.7	−91.2	−113.0	−115.1	−39.3	−32.2
$ZnCl_2H_2M$	−278.7	−281.2	−158.2	−160.7	−100.4	−93.7
$ZnCl_2H_2A_{NN}$	−165.7	−168.2	−193.7	−196.2	−132.6	−124.7

$$\Delta H = E(\mathrm{ZnCl_2H_{(2-\mathit{n})}LZnCl_2}^{n-}) + nE(\mathrm{H_2O}) - 2E(\mathrm{ZnCl_2}) - E(\mathrm{H_2L}) - nE(\mathrm{OH^-}) - RT \qquad (8)$$

In eqs 3 and 7 the term ΔpV is substituted with $-RT$, as one mole of gas is lost by reaction 1 or 5. To define gas-phase interaction enthalpy at 298.15 K, thermal correction to energy, *therm*, at 298.15 K from vibrational analysis at B3LYP/LanL2DZ/6-31G(d) level must be added to single point energy E calculated at B3LYP/6-311+G(2d,p) level of each energy term in eqs 4 and 8. The final eqs 9 and 10 were derived for calculation of gas-phase interaction enthalpy of 1:1 and 2:1 complexes at 298.15 K.

$$\begin{aligned}\Delta H^{298} = {} & [E(\mathrm{ZnCl_2H_{(2-\mathit{n})}L}^{n-}) + \mathit{therm}(\mathrm{ZnCl_2H_{(2-\mathit{n})}L}^{n-})] \\ & + n[E(\mathrm{H_2O}) + \mathit{therm}(\mathrm{H_2O})] - [E(\mathrm{ZnCl_2}) \\ & + \mathit{therm}(\mathrm{ZnCl_2})] - [E(\mathrm{H_2L}) + \mathit{therm}(\mathrm{H_2L})] \\ & - n[E(\mathrm{OH^-}) + \mathit{therm}(\mathrm{OH^-})] - RT \end{aligned} \qquad (9)$$

$$\begin{aligned}\Delta H^{298} = {} & [E(\mathrm{ZnCl_2H_{(2-\mathit{n})}LZnCl_2}^{n-}) \\ & + \mathit{therm}(\mathrm{ZnCl_2H_{(2-\mathit{n})}LZnCl_2}^{n-})] + n[E(\mathrm{H_2O}) \\ & + \mathit{therm}(\mathrm{H_2O})] - 2[E(\mathrm{ZnCl_2}) + \mathit{therm}(\mathrm{ZnCl_2})] \\ & - [E(\mathrm{H_2L}) + \mathit{therm}(\mathrm{H_2L})] - n[E(\mathrm{OH^-}) \\ & + \mathit{therm}(\mathrm{OH^-})] - RT \end{aligned} \qquad (10)$$

where $E(\mathrm{ZnCl_2H_{(2-\mathit{n})}L}^{n-})$, $E(\mathrm{ZnCl_2H_{(2-\mathit{n})}LZnCl_2}^{n-})$, $E(\mathrm{ZnCl_2})$, $E(\mathrm{H_2O})$, $E(\mathrm{OH^-})$, and $E(\mathrm{H_2L})$ are single point energies calculated at the B3LYP/6-311+G(2d,p) level, *therm* for various species are thermal corrections to energies from vibrational analysis performed at B3LYP/LanL2DZ/6-31G(d) level.

Results and Discussion

Coordination Compounds of H_2M and H_2A with $ZnCl_2$. For reaction of H_2M with $ZnCl_2$ a 1:1 complex [$ZnCl_2H_2M$], and for H_2A with $ZnCl_2$ two 1:1 complexes as $ZnCl_2H_2A_{NN}$ (coordination through oximic N atoms), $ZnCl_2H_2A_{AA}$ (coordination through amines N atom) were considered.

Coordination Compounds of H_2L with $ZnCl_2$. For reaction of H_2L with $ZnCl_2$ five 1:1 complexes [$ZnCl_2H_2L_{AA}$] (coordination through N3,N4), [$ZnCl_2H_2L_{NN}$] (N1,N2), [$ZnCl_2H_2L_{PP}$] (N6,N5), $[ZnCl_2HL_{NO}]^-$ (N1,O2), and $[ZnCl_2L_{OO}]^{2-}$ (O1,O2) as well as six 2:1 complexes [$ZnCl_2H_2L_{NNAA}ZnCl_2$] (N1,N2,N3,N4), [$ZnCl_2H_2L_{NNPP}ZnCl_2$] (N1,N2,N5,N6), $[ZnCl_2HL_{NOPP}ZnCl_2]^-$ (N1,O2,N5,N6), $[ZnCl_2HL_{NOAA}ZnCl_2]^-$ (N1,O2,N3,N4), $[ZnCl_2L_{OOAA}ZnCl_2]^{2-}$ (O1,O2,N3,N4), and $[ZnCl_2L_{OOPP}ZnCl_2]^{2-}$ (O1,O2,N5,N6) were considered, Figure 1. It should be mentioned that the starting configurations $[ZnCl_2HL_{NOPP}ZnCl_2]^-$ and $[ZnCl_2HL_{NOAA}ZnCl_2]^-$ go to their corresponding $[ZnCl_2L_{OOPP}ZnCl_2]^{2-}$ and $[ZnCl_2L_{OOAA}ZnCl_2]^{2-}$ structures upon optimization in which H_2L_{NN} represents coordination of oximic N atoms to Zn was carried out. Similarly H_2L_{AA}, H_2L_{PP}, and L_{OO} indicate coordination through amines N, pyridines N, and oximes O atoms of H_2L to Zn, respectively. In HL_{NO} coordination through an oximic N and an O atom to Zn was carried out. Also, similar notations were used for 2:1 complexes. For example, in [$ZnCl_2H_2L_{NNAA}ZnCl_2$] the H_2L as a bidentate bridging ligand coordinated to two $ZnCl_2$ through its oxime and amine N atoms.

Table 2. Selected Bond Lengths (Å) of H_2L and Its Proposed Complexes with $ZnCl_2$ Optimized at B3LYP/LanL2DZ/6-31+G(d)

Compound	C1–N1	C2–N2	C1–N3	C2–N4
H_2L	1.292	1.294	1.381	1.377
$ZnCl_2H_2L_{PP}$	1.291	1.291	1.380	1.380
$ZnCl_2H_2L_{AA}$	1.281	1.283	1.454	1.436
$ZnCl_2H_2L_{NN}$	1.303	1.303	1.363	1.357
$ZnCl_2L_{OO}{}^{2-}$	1.301	1.304	1.432	1.429
$ZnCl_2L_{OOPP}ZnCl_2{}^{2-}$	1.302	1.303	1.453	1.445
$ZnCl_2L_{OOAA}ZnCl_2{}^{2-}$	1.294	1.300	1.477	1.466
$ZnCl_2H_2L_{NNPP}ZnCl_2$	1.294	1.298	1.391	1.364
$ZnCl_2H_2L_{NNAA}ZnCl_2$	1.283	1.283	1.436	1.426
H_2M	1.285	1.285	—	—
$ZnCl_2H_2M$	1.290	1.290	—	—
H_2A	1.293	1.288	1.408	1.386
$ZnCl_2H_2A_{AA}$	1.280	1.278	1.432	1.423
$ZnCl_2H_2A_{NN}$	1.295	1.295	1.364	1.364

Theoretical calculations predicted the following order of stability for complexes of H_2M and H_2A with $ZnCl_2$ in all methods of calculations, Table 1. $ZnCl_2H_2A_{NN} > ZnCl_2H_2M > ZnCl_2H_2A_{AA}$

Because of the higher quality of Lanl2dz and B3LYP/6-311+G(2d,p) it seems their results are more reliable than the B3LYP/LanL2DZ/6-31G(d) method. The results show that the H_2A_{NN} complexes are more stable than H_2M. This might be due to contribution of amine N lone pairs in a tight resonance with the C=N bond of oximic functions in H_2A. This resonance increases the bond order of C1–N3 bond directly, in contrast it decreases the bond order of C1–N1 through $n_{\text{(amines lone pair)}}$ to $\pi^*{}_{(\mathrm{C1=N1\ or\ C2=N2})}$ transition. Also, such discussion can be given for C2–N2 and C2–N4 bonds. The C1–N1 and C1–N3 bond lengths are 1.293 and 1.408 Å in free H_2A. They change to 1.280 and 1.432 in $ZnCl_2H_2A_{AA}$ or 1.295 and 1.364 in $ZnCl_2H_2A_{NN}$, Table 2. These results show that coordination of amine lone pairs to Zn prohibit their con-

Table 3. Calculated Gas-Phase Stabilization Energies SE ($\mathrm{kJ\,mol^{-1}}$) and Interaction Enthalpies ΔH^{298} ($\mathrm{kJ\,mol^{-1}}$) for H_2L Complexes with $ZnCl_2$

Complex	B3LYP/LanL2DZ/ 6-31+G(d) (corrected for ZPE)		B3LYP/LanL2DZ/ 6-31G(d) (corrected for ZPE)		B3LYP/6-311+G (2d,p)//LanL2DZ/ 6-31G(d)	
	SE	ΔH^{298}	SE	ΔH^{298}	SE	ΔH^{298}
$ZnCl_2H_2L_{AA}$	−40.6	−43.1	−29.7	−32.2	−18.0	−12.1
$ZnCl_2H_2L_{NN}$	−132.6	−135.1	−130.5	−133.1	−112.1	−104.6
$ZnCl_2H_2L_{PP}$	−143.9	−146.4	−134.3	−136.8	−116.3	−108.8
$ZnCl_2HL_{NO}{}^-$	−400.4	−402.9	−543.9	−546.4	−373.2	−364.0
$ZnCl_2L_{OO}{}^{2-}$	−407.1	−409.6	−674.5	−677.0	−375.3	−362.3
$ZnCl_2H_2L_{NNAA}ZnCl_2$	−193.3	−195.8	−179.1	−181.6	−106.3	−91.6
$ZnCl_2H_2L_{NNPP}ZnCl_2$	−277.0	−279.5	−268.6	−271.1	−187.9	−172.0
$ZnCl_2L_{OOAA}ZnCl_2{}^{2-}$	−639.3	−641.8	−911.3	−913.8	−530.5	−550.6
$ZnCl_2L_{OOPP}ZnCl_2{}^{2-}$	−703.3	−705.8	−976.5	−979.1	−590.0	−566.1

tribution in resonance with C=N bonds. Elongation of C1–N3 (C2–N4) and shortening of C1–N1 (C2–N2) bonds could be predicted from this phenomena. Clearly, this resonance inhances the donation ability of oximic N atoms, and diminishes the tendency of amines N atom for coordination to $ZnCl_2$. Thus, $ZnCl_2H_2A_{AA}$ shows the least stability between these complexes. In $ZnCl_2H_2A_{NN}$ coordination of oximic N atoms to Zn enhances the resonance between N3 and C1, similarly for C2 and N4. Therefore, changes of bond lengths in $ZnCl_2H_2A_{NN}$ are in contrast to $ZnCl_2H_2A_{AA}$.

For 1:1 complexes of H_2L with $ZnCl_2$ the following order of stability has been predicted (Table 3),

$$ZnCl_2HL_{NO}{}^- \approx ZnCl_2L_{OO}{}^{2-} > ZnCl_2H_2L_{PP} > ZnCl_2H_2L_{NN} > ZnCl_2H_2L_{AA} \tag{11}$$

The interaction enthalpy of negatively charged monoanion and dianion ligands are significantly greater than those of neutral H_2L, which is obviously due to the negative charge of ionic ligand that leads to stronger interaction. But interestingly fewer reports were found for such O,O-coordinated Zn–oxime complexes in the literature.[26] However, our results indicate that these complexes could potentially be prepared.

On the other hand, in $ZnCl_2H_2L_{AA}$ a situation like $ZnCl_2H_2A_{AA}$ was observed which arises from contribution of amine N lone pairs in resonance with C1=N1 (or C2=N2) bonds. The predicted bond lengths 1.292 and 1.381 Å for C1–N1 and C1–N3 in H_2L compared to 1.281 and 1.454 in $ZnCl_2H_2L_{AA}$ or 1.303 and 1.363 in $ZnCl_2H_2L_{NN}$ indicate this fact, Table 2. The changes of C1–N1 and C1–N3 bond lengths in $ZnCl_2H_2L_{AA}$ and $ZnCl_2H_2L_{NN}$ are similar to $ZnCl_2H_2A_{AA}$ and $ZnCl_2H_2A_{NN}$. Data in Table 2 shows that coordination of pyridine N atoms to Zn was not accompanied by considerable changes in C1–N1 and C1–N3 bond length. A similar explanation could be given for C2–N2 and C2–N4 bonds.

Theoretical calculation predicts diminished tendency of amine N atoms for coordination to Zn. Thus among uncharged 1:1 complexes of $ZnCl_2$ with H_2L, $ZnCl_2H_2L_{AA}$ has the least stability while the stabilities of $ZnCl_2H_2L_{PP}$ and $ZnCl_2H_2L_{NN}$ are comparable (Table 3).

The geometry of $ZnCl_2H_2L_{NN}$ in 1:1 and 2:1 complexes is distorted from an ideal tetrahedral arrangement. It seems this distortion helps hydrogen-bond formation between H atoms of hydroxy groups of oxime function and Cl atoms of $ZnCl_2$. In other cases tetrahedral arrangements of ligands has been predicted around the Zn atom.

Stability of 2:1 complexes is in the order: $ZnCl_2L_{OOPP}ZnCl_2{}^{2-} > ZnCl_2L_{OOAA}ZnCl_2{}^{2-} > ZnCl_2H_2L_{NNPP}ZnCl_2 > ZnCl_2H_2L_{NNAA}ZnCl_2$. So, it was discussed in the last paragraph, complexes with negatively charged ionic ligand L^{2-} have significantly more negative interaction enthalpies than those of neutral ligand H_2L (Table 3).

Interaction enthalpies ΔH^{298} between ligands and $ZnCl_2$ systems calculated at B3LYP/LanL2DZ/6-31G(d), B3LYP/LanL2DZ/6-31+G(d), and B3LYP/6-311+G(2d,p) levels are summarized in Tables 1 and 3.

Calculations at B3LYP/6-311+G(2d,p) level give a more realistic view of the interaction thermodynamics.

Natural Population Analysis. The natural atomic charges computed using NBO program[36] for zinc atoms and atoms binding directly to it, are summarized in Table 4. The electron population on zinc is more increased (positive charge of zinc ion is decreased) when less electronegative N atom (with sp^3 hybrid orbitals) charged ligands bind to it, e.g. the natural charge of zinc is 1.589 e^- for $ZnCl_2H_2A_{AA}$ (sp^3 lone pair electron) and 1.614 e^- for $ZnCl_2H_2A_{NN}$ (sp^2 lone pair electron). Similarly, for H_2L complexes, the greatest electron population was found on Zn coordinating to amine N atoms of ligand (natural charge 1.596 e^-). In contrast very low electron population was found for Zn coordinating to pyridine N atoms of H_2L (natural charge 1.619 e^- in 1:1 and 1.627 e^- in 2:1 complexes) due to the high electronegativity of sp^2 N atoms. It seems that the presence of a resonance between lone pair electrons of amines N atoms with oximic N atoms enhances the polarizability of later atoms. Therefore, it might be concluded that binding of ligands through softer (more polarizable) and less electronegative sp^3 N atoms to zinc cause the highest increase in electron population on zinc, when compared to hard (less polarizable) sp^2 N, e.g. the natural charge of zinc atom is 1.601 e^- for $ZnCl_2H_2L_{AA}$ and 1.619 e^- for $ZnCl_2H_2L_{PP}$.

For negatively charged 2:1 complexes, the electron population on zinc attached to ionized O atoms is higher than Zn attached to neutral N atoms, e.g. the natural charge of Zn1 (attached to O atoms) is 1.605 e^- for $ZnCl_2L_{OOPP}ZnCl_2{}^{2-}$ and 1.627 e^- for Zn2 (attached to pyridine N atoms).

Table 4. Natural Charges in Respective Complexes from Natural Bond Orbital Analysis Atoms Attached to Zinc Have Been Denoted as the Bold-Face

Complex	Zn1	N1	N2	N3	N4	N5	N6	O1	O2	Zn2
$ZnCl_2H_2A_{AA}$	1.59	**−1.05**	**−1.04**							
$ZnCl_2H_2A_{NN}$	1.61			**−0.46**	**−0.46**					
$ZnCl_2H_2M$	1.61			**−0.34**	**−0.34**					
$ZnCl_2H_2L_{AA}$	1.60	−0.12	−0.11	**−0.90**	**−0.88**	−0.52	−0.51	−0.59	−0.58	
$ZnCl_2H_2L_{NN}$	1.61	**−0.44**	**−0.47**	−0.71	−0.70	−0.52	−0.55	−0.58	−0.57	
$ZnCl_2H_2L_{PP}$	1.62	−0.24	−0.24	−0.74	−0.74	**−0.72**	**−0.72**	−0.60	−0.60	
$ZnCl_2HL_{NO}{}^-$	1.62	**−0.45**	−0.03	−0.74	−0.73	−0.53	−0.51	−0.61	**−0.77**	
$ZnCl_2L_{OO}{}^{2-}$	1.60	−0.22	−0.10	−0.69	−0.72	−0.61	−0.58	**−0.79**	**−0.79**	
$ZnCl_2H_2L_{NNAA}ZnCl_2$	1.61	**−0.31**	**−0.30**	**−0.89**	**−0.88**	−0.55	−0.52	−0.53	−0.53	1.60
$ZnCl_2H_2L_{NNPP}ZnCl_2$	1.61	**−0.37**	**−0.42**	−0.78	−0.77	**−0.67**	**−0.66**	−0.56	−0.54	1.62
$ZnCl_2L_{OOAA}ZnCl_2{}^{2-}$	1.61	−0.09	−0.12	**−0.88**	**−0.88**	−0.49	−0.53	**−0.77**	**−0.76**	1.62
$ZnCl_2L_{OOPP}ZnCl_2{}^{2-}$	1.61	−0.08	−0.17	−0.76	−0.75	**−0.77**	**−0.78**	**−0.78**	**−0.77**	1.63

Conclusion

The basis sets B3LYP/LanL2DZ/6-31G(d), B3LYP/LanL2DZ/6-31+G(d), and B3LYP/6-311+G(2d,p)//B3LYP/LanL2DZ/6-31G(d) have been used for eluciding interaction enthalpy and stability of complexes. The results of this study showed that H_2L ligand is able to bind with $ZnCl_2$ through its oximic, amine, and pyridine N atoms as well as O atoms and form stable tetra-coordinated neutral and anionic complexes. Results indicate that anionic O,O complex is more stable than neutral complexes. Also coordination of pyridine N atoms is preferred on other N atoms in neutral complexes. In the case of 2:1 complexes the same conclusion might be reached.

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