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Theoretical Structural Investigation of Some New Zinc Complexes

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Introduction

Schiff bases are considered as an important class of ligands in coordination chemistry and have extensive applications in different fields. They readily coordinate with a wide range of transition metal ions, yielding stable and intensely colored metal complexes, which exhibit interesting physical, chemical, biological and catalytic properties [1,2]. In this research, some new zinc complexes of a symmetric bidentate Schiff base (L) were synthesized and characterized by IR, ^{1}H and ^{13}C NMR spectroscopies. Moreover, optimized structures, molecular parameters and vibrational frequencies were calculated at the B3LYP/LANL2DZ level of theory. Some important parameters such as bond lengths, bond angles, dihedral angles, ΔH, ΔG, total energy were extracted for optimized structures.

Preparation of Schiff base ligand (L) and its Zn(II) complexes

Schiff base ligand titled as N,N-bis((E)3-(2-nitrophenyl)acrylaldehydene)-2,2- dimethyl-1,3–diaminopropane (L) was synthesized by condensation reaction of 2,2-dimethyl-1,3-diaminopropane and (E)-3-(2-nitrophenyl)acrylaldehyde in absolute ethanol. The Zn(II) complexes were prepared as cream precipitate via stepwise addition of ethanolic solution of ligand to zinc salts (Cl^-, Br^-, I^-) under vigorous stirring for 2–3 h at room temperature.

Computational details

The quantum chemical calculations were performed with the Gaussian 03 program package (running under Linux openSUSE) [3] using density functional theory (DFT) [4] at B3LYP/ LanL2DZ level of theory [5]. All geometries were optimized without any symmetry restrictions and C1 symmetry was assumed for all compounds. Zero point energies (ZPVE) and IR frequencies obtained from FREQ calculations have been used after correcting with the appropriate scaling factor.

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Results and Discussion

The results of optimization show that the geometry of complexes is pseudo-tetrahedral as it would expect for d^{10} group metal ions in four coordinated complexes. The optimized structure of $ZnLI_2$ is seen in Fig. 1. Some important bond lengths, bond angles and totional angles are summarized in Tables 1, 2 and 3, respectively.

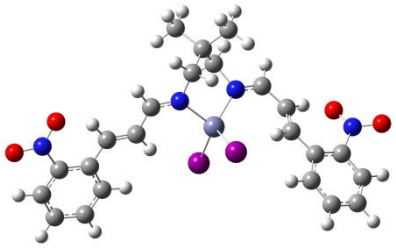

Fig. 1. Optimized structure of $ZnLI_2$

Table 1. Some important bond lengths (Å)

molecule	$ZnLCl_2$	$ZnLBr_2$	$ZnLI_2$	Ligand
M-N	2.08658	2.08299	2.08053	-
M-N'	2.08448	2.08103	2.07585	-
M-X	2.45276	2.66141	2.90536	-
M-X'	2.42745	2.63209	2.86875	-
C_4=N	1.33125	1.33262	1.33483	1.32367
$C_{4'}$=N'	1.32935	1.33029	1.33119	1.32408

Table 2. Some important bond angles (˚)

molecule	$ZnLCl_2$	$ZnLBr_2$	$ZnLI_2$
N'-M-N	91.55067	92.13583	92.81965
N'-M-X	100.13592	98.74382	97.38902
N'-M-X'	112.96516	114.62624	116.46331
N-M-X	113.38960	115.58886	118.44711
N-M-X'	108.76817	107.00326	105.24097
X-M-X'	124.70344	124.02195	122.66703

Table 3. Some important tortion angles (˚)

molecule	$ZnLCl_2$	$ZnLBr_2$	$ZnLI_2$	Ligand
N-C_4-C_5-C_6	-30.67724	-28.93061	-23.34489	1.94120
N'-$C_{4'}$-$C_{5'}$-$C_{6'}$	179.13963	179.11979	178.84535	179.92693
C_5-C_6-C_7-C_8	16.66126	16.54770	15.59856	17.33725
$C_{5'}$-$C_{6'}$-$C_{7'}$-$C_{8'}$	179.40044	179.12858	178.60762	-179.60480

Various energies of complexes after optimization at the mentioned level of theoretical method are summarized in Table 4. The results show the values HF-energy, ΔH, ΔG and total energy of complexes are being more positive from zinc chloride complexes to zinc iodide one.

Table 4. HF-energy, ΔH, ΔG and total energy of ligand and its complexes (a.u.)

Molecule	$ZnLCl_2$	$ZnLBr_2$	$ZnLI_2$	ligand
HF energy	-1488.298413	-1484.737539	-1481.174971	-1392.599697
Corrected ZPE	0.448341096	0.447728939	0.447219609	0.442768257
Corrected total energy	-1487.850072	-1484.28981	-1480.727751	-1392.156929
Corrected Gibs Free energy	-1487.92262	-1484.364702	-1480.804813	-1392.22394
Total elect. En	-1487.797605	-1484.236875	-1480.67451	-1392.109458
Corrected Enthalpy	-1487.814856	-1484.254101	-1480.691715	-1392.126483

Conclusions

The results of optimization show that the geometry of complexes is pseudo-tetrahedral. Thermodynamic parameters are being more positive from $ZnLCl_2$ to $ZnLI_2$.

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