

Synthesis, Characterization and Theoretical Studies of a New Macroacyclic Schiff-Base Ligand Containing Piperazine Moiety and Related Mn(II), Cu(II), Ni(II) and Cd(II) Complexes

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Four new $[\text{MnL}](\text{ClO}_4)_2$ (1), $[\text{CuL}](\text{ClO}_4)_2$ (2), $[\text{NiL}](\text{ClO}_4)_2$ (3) and $[\text{CdL}](\text{ClO}_4)_2$ (4), complexes were prepared by the reaction of a new Schiff base ligand and Cu(II), Ni(II), Mn(II) and Zn(II) metal ions in equimolar ratios. The ligand, L was synthesized by the reaction of 1,4-bis(2-formylphenyl)piperazine and ethanolamine and characterized by IR and ^1H , ^{13}C NMR spectroscopies. All complexes were characterized by IR, EI-Mass and elemental analysis. Theoretical studies on structures, molecular orbital and nature of bond in these complexes were also carried out with NBO analysis at DFT (BP86) method using Def-2/SVP basis set. The results of WBI and charge transfer confirm that the covalent character in bonding interactions between the L and metal ions in $[\text{MnL}]^{2+}$ and $[\text{CuL}]^{2+}$ complexes is minimum and maximum, respectively.

Keywords: Schiff base, Metal complexes, Piperazine, Ethanolamine, Theoretical study

INTRODUCTION

Schiff base ligands have played an important role in the development of coordination chemistry. Metal complexes of these ligands are ubiquitous due to their facile synthesis, wide applications and the possibility of diverse structural modifications [1]. Schiff base complexes are considered to be among the most important stereochemical models in main group and transition metal coordination chemistry due to their preparative accessibility and structural variety [2]. The chemistry of Schiff base ligands and their metal complexes has expanded enormously and encompasses a vast area of organometallic compounds and various aspects of bioinorganic chemistry [3], and have various applications in catalysis [4-6], and as antibacterial agents [7-9] or chemosensors [10-13].

In previous works, we have reported some macrocyclic and macroacyclic Schiff base complexes containing piperazine moiety [14-22]. In other works, several mono

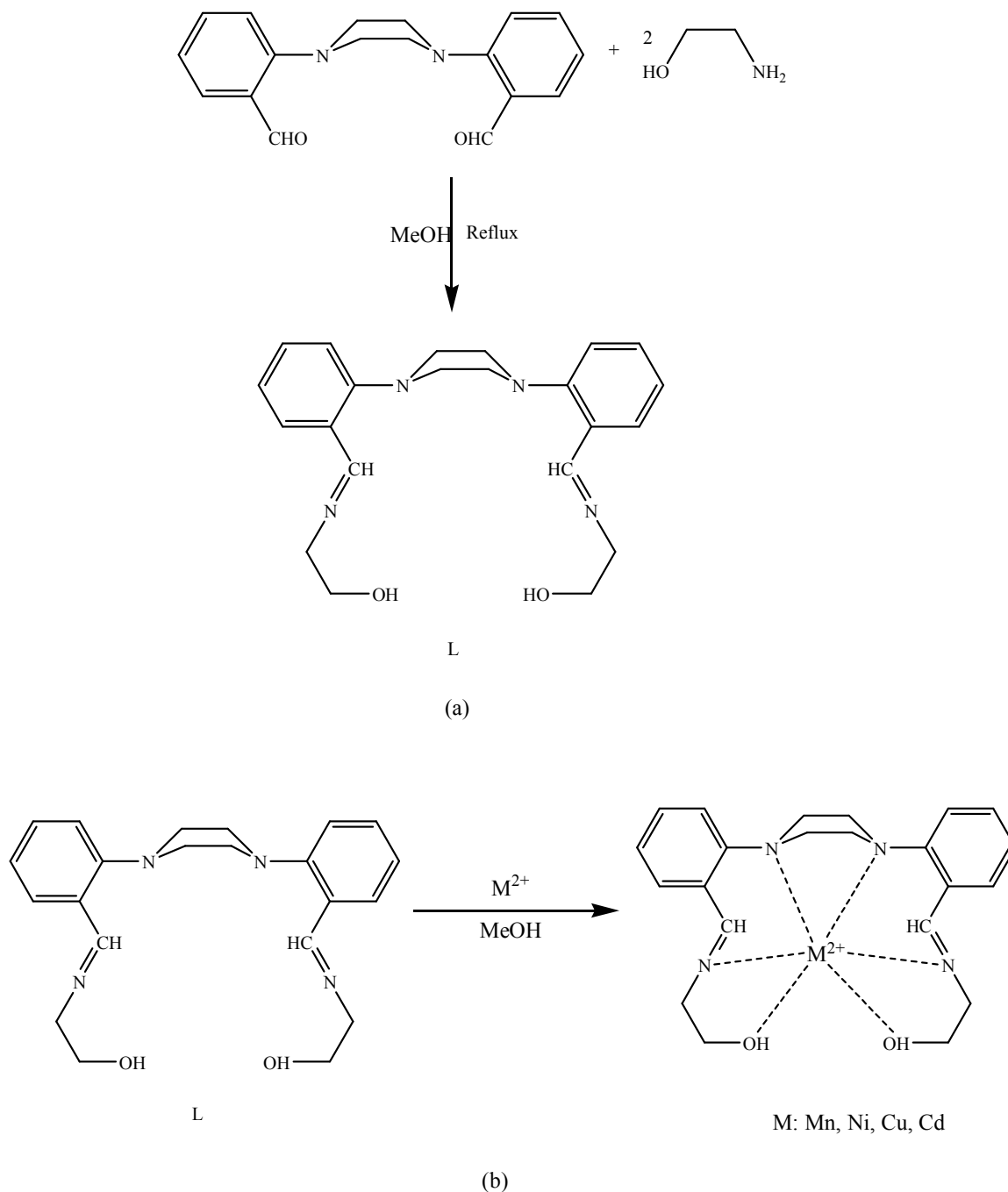
and dinuclear macrocyclic and macroacyclic metal complexes of tripodal tetraamine Schiff base ligands with N_xO_y donor sets (x and y include different numbers) have been reported [23,24], which show characteristic architecture and properties depending on the conformation of the Schiff base ligand. Herein, we report the synthesis and characterization of Mn(II), Ni(II), Cu(II) and Cd(II) complexes with a new linear Schiff base ligand derived from the 1,4-bis(2-formylphenyl)piperazine and ethanolamine (Scheme 1). The resulting complexes were characterized by elemental analysis, EI-Mass and IR spectroscopy. Theoretical studies on structures, molecular orbital and nature of bond in the aforementioned complexes were also carried out with NBO analysis at DFT (BP86) method using Def-2/SVP basis set.

EXPERIMENTAL

General Information

Hydrated metal salts and ethanolamine were obtained from Aldrich and used without further purification. 1,4-

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Scheme 1. Synthesis of the Schiff base ligand, L (a) and related complexes (b)

Bis(2-formylphenyl)piperazine was prepared according to the literature method [19]. IR and NMR spectra were measured on a Perkin-Elmer FT-IRGX and a Bruker DPX 300 spectrometer, respectively. Mass spectra were

measured on a Bruker micro TOFQ.

Synthesis

Preparation of the ligand L. 1,4-Bis(2-

formylphenyl)piperazine (0.294 g, 1 mmol) and ethanolamine (0.122 g, 2 mmol) were mixed in ethanol (30 ml) and heated under reflux at 40 °C for 30 min. The solution was filtered and the filtrate volume was reduced to *ca.* 10 ml. The obtained yellow crystalline compound was washed with cooled ethanol and dried. Yield: 65%. For C₂₂H₂₈N₄O₂: Anal. Calcd. (%), C:69.45; H, 7.42; N, 14.73. Found, (%): C, 69.86; H, 7.40; N, 14.90. EI-MS (m/z): found (calcd.): 380.00 (380.22) [L]⁺. IR (ν, cm⁻¹): 3218 (OH), 1645 (C=N Schiff base), 1486 (C=C). ¹H NMR (δ, ppm, 300 MHz): δ 3.137 (s, 8H), 3.653 (t, 4H), 3.853 (t, 4H), 7.09-7.32 (m, 6H) 7.96 (m, 2H), 7.93 (m, 2H), 8.71 (s, 2H), ¹³C NMR (δ, ppm, 75 MHz): δ 49.50 (piperazine rings), 58.6 (-CH₂CH₂OH), 63.90 (=NCH₂CH₂), 114.4, 118.38, 130.1, 132, 150.8 (aromatic rings), 160.87 (Schiff base).

Synthesis of complexes-general procedure. The appropriate metal salts MX₂ (M = Cu(II), Ni(II), Mn(II) or Cd(II) with X = ClO₄⁻) (1 mmol) was dissolved in methanol (5 ml) and added to a solution of L (1 mmol) in methanol (10 ml). The mixture was stirred at 50-69 °C for 24 h. The solution was filtered and filtrate volume was reduced to 10 ml. A crystalline compound was obtained by slow diffusion of Et₂O vapor into this solution.

[MnL](ClO₄)₂ (1). Yield: 67%. Anal. Calcd., (%): C, 41.66; H, 4.45; N, 8.83. Found, (%): C, 41.86; H, 4.36; N, 8.93%. EI-MS (m/z), found (calcd.): 634.0 (634.3) {[MnL](ClO₄)₂]⁺, 534.3 (534.1) {[MnL](ClO₄)]⁺. IR (ν, cm⁻¹): 3406 ν (OH), 1630 ν (C=N Schiff base), 1487 ν (C=C), 1097, 623 ν (ClO₄).

[NiL]ClO₄ (2). Yield: 75%. Anal. Calcd., (%): C, 41.41; H, 4.42; N, 8.78. Found, (%): C, 41.82; H, 4.32; N, 8.88. EI-MS (m/z), found (calcd.): 636.1(636.0) {[NiL](ClO₄)₂]⁺, 536.1 (537.1), {[NiL](ClO₄)]⁺. IR (ν, cm⁻¹): 3435 ν (OH), 1634 ν (C=N Schiff base), 1486 ν (C=C), 1096, 624 ν (ClO₄).

[CuL](ClO₄)₂ (3). Yield: 67%. Anal. Calcd., (%): C, 41.10; H, 4.39; N, 8.71. Found: C, 41.21; H, 4.21; N, 8.62. EI-MS (m/z), found (calcd.): 641.1 (641.0) {[CuL](ClO₄)₂]⁺, 542.6 (542.1) {[CuL](ClO₄)]⁺. IR (ν, cm⁻¹): 3440 ν (OH), 1637 ν (C=N Schiff base), 1486 ν (C=C), 1099, 623 ν (ClO₄),

[CdL](ClO₄)₂ (4). Yield: 75%. Anal. Calcd., (%): C, 38.20; H, 4.08; N, 8.10. Found, (%): C, 38.30; H, 4.00; N,

8.20. EI-MS (m/z), found (calcd.): 691.8 (692.0) {[CdL](ClO₄)₂]⁺, 592.8 (593.1) {[CdL](ClO₄)]⁺. IR (ν, cm⁻¹): 3445 ν (OH), 1638 ν (C=N Schiff base), 1483 ν (C=C), 1089, 624 ν (ClO₄).

Computational Methods

We used the DFT (BP86 [25,26]) method using Def-2/SVP basis set to study the structure and nature of bond in [MnL]²⁺, [NiL]²⁺, [CuL]²⁺ and [CdL]²⁺ complexes. All calculations were performed using Gaussian 03 [27] set of programs. In all cases, the vibrational frequency analyses, calculated at the same level of theory indicated that optimized structures are at the stationary points corresponding to local minima without any imaginary frequency. The NBO [28] analyses were carried out with the internal module GAUSSIAN 03 at the same level of theory. A starting molecular-mechanics structure for the DFT calculations was obtained using the HYPERCHEM 5.02 program. It should be noted that we have considered a 2, 3 and 6 spin states for Cu(II), Ni(II) and Mn(II) complexes investigated here, respectively.

RESULT AND DISCUSSION

Synthesis and Characterization

All complexes 1-4 were synthesized by the reaction of Schiff base ligand, L and Mn(II), Ni(II), Cu(II) and Cd(II) metal ions, respectively (Scheme 1). These compounds are quite stable in air and can be stored in a desiccator for long periods of time without decomposition. The resulting compounds were characterized by IR, EI-Mass and elemental analysis. Condensation of all the primary amino group is confirmed by the lack of N-H stretching bands in the IR region (3150-3450 cm⁻¹) [29] and the presence of strong C=N (Schiff base) stretching bands at 1645 cm⁻¹ for Schiff base ligand L. Also the stretching bands of C=N (imine) complexes 1-4 have been observed at 1630, 1634, 1631 and 1638 cm⁻¹, respectively. It is evident that the bands related to the imine groups in Schiff bases have been shifted to the lower frequencies in the IR spectra of all complexes and it shows that the donor atoms in ligands have been coordinated to the metal ions and the complexes have been formed. A intense broad band at *ca.* 1100 cm⁻¹ due to ClO₄⁻ shows no splitting [30,31], indicating the absence

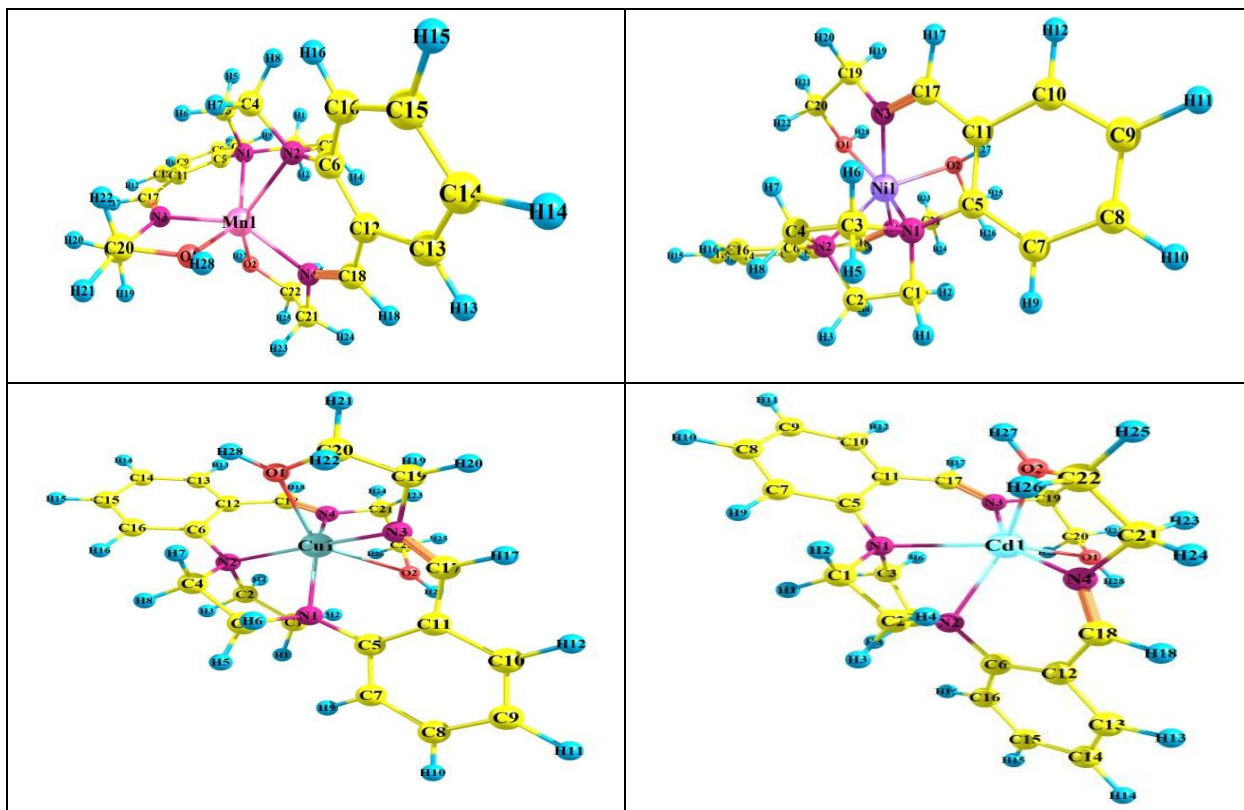


Fig. 1. Optimized geometries of $[\text{MnL}]^{2+}$, $[\text{NiL}]^{2+}$, $[\text{CuL}]^{2+}$ and $[\text{CdL}]^{2+}$.

of coordinated of ClO_4^- for all complexes. According to similar works, the hydrogen of OH groups is not deprotonated and all of donor atoms are coordinated to metal ions. The structure of all complexes can be described as distorted octahedral geometry [32,33].

Theoretical Studies

We carried out DFT calculations at the BP86 [24, 25]/def2-SVP level of theory using the GAUSSIAN 03 optimizer on $[\text{MnL}]^{2+}$, $[\text{NiL}]^{2+}$, $[\text{CuL}]^{2+}$ and $[\text{CdL}]^{2+}$ complexes (Fig. 1). A starting molecular-mechanics structure for the DFT calculations was obtained. The calculated bond lengths and bond angles of the aforementioned complexes are given in Table 1. As it can be seen all M–N and M–O bond lengths in $[\text{MnL}]^{2+}$ are greater than $[\text{NiL}]^{2+}$ complex and both are greater than $[\text{CuL}]^{2+}$ (See Table 1). Also, the result show that the

$[\text{CdL}]^{2+}$ complex has a greatest M–N and M–O bond lengths between all compounds studied here (Table 1). On the other hand, all $\text{N}_x\text{--M--N}_y$ bond angles expected for $[\text{CuL}]^{2+}$ complex are greater than $[\text{NiL}]^{2+}$ and both are greater than $[\text{MnL}]^{2+}$ complex. Also the $[\text{CdL}]^{2+}$ complex has a smallest $\text{N}_x\text{--M--N}_y$ bond angles between all compounds studied here (Table 1). In continuation of this computational study, we begin the analysis of the bonding situation in M–N and M–O bond lengths in these complexes with a discussion on the conventional indices that are frequently used to characterize the bonding situation in the molecules, *i.e.* bond orders and atomic charges. Table 2 gives the Wiberg bond indices (WBI) and the natural charges on Mn^{2+} , Ni^{2+} , Cu^{2+} and Cd^{2+} in these complexes and the value of charge transfer from L to metal ions. The results of the natural bond orbital (NBO) analysis in M–N and M–O for latter complexes are given

Table 1. The Calculated Important Bond Lengths (Å) and Bond Angles for [MnL]²⁺, [NiL]²⁺, [CuL]²⁺ and [CdL]²⁺

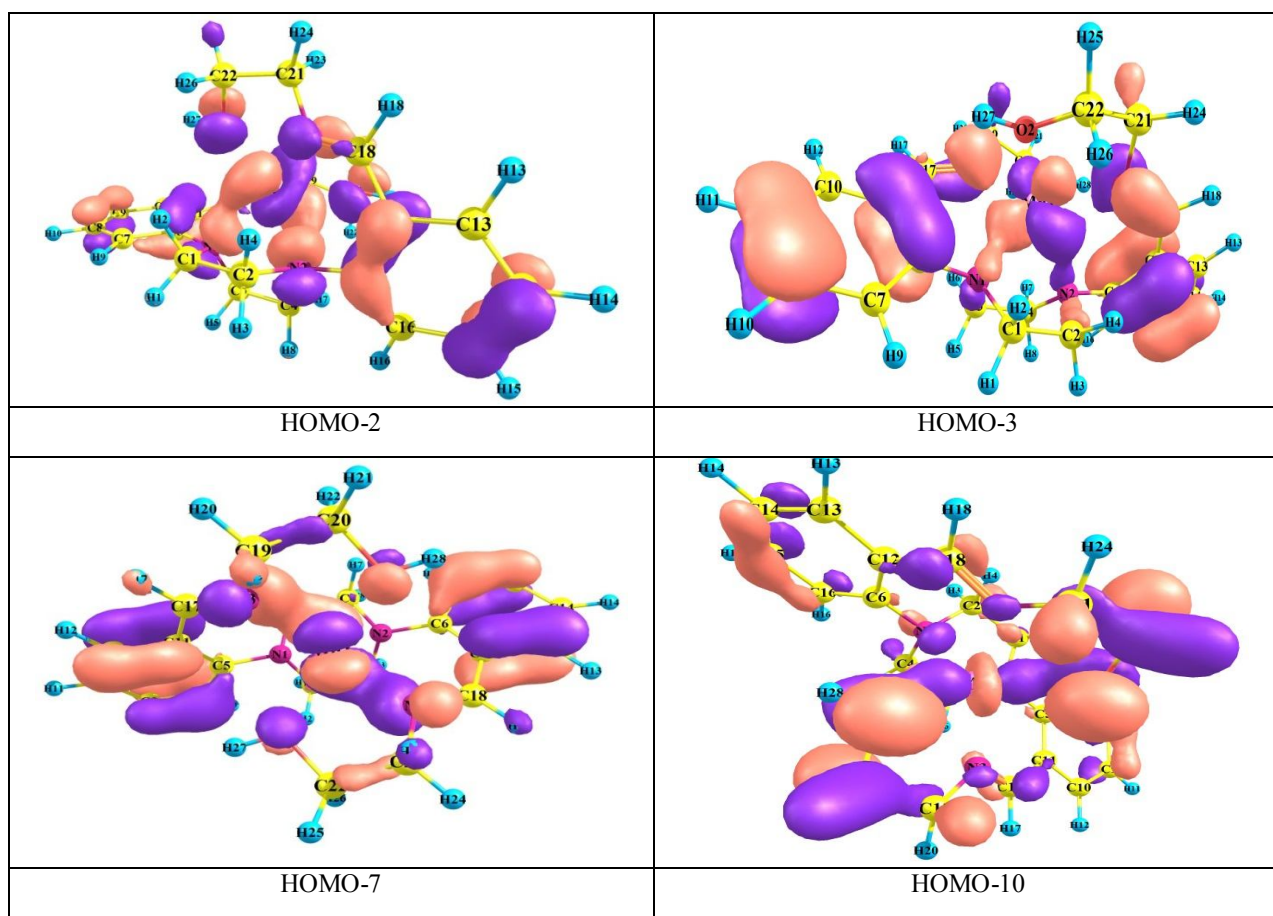
Bond lengths (Å)	[MnL] ²⁺	[NiL] ²⁺	[CuL] ²⁺	[CdL] ²⁺
M–N1	2.288	2.172	2.017	2.475
M–N2	2.288	2.169	2.027	2.476
M–N3	2.154	2.055	1.904	2.253
M–N4	2.154	2.045	1.894	2.253
M–O1	2.278	2.182	2.041	2.457
M–O2	2.278	2.176	2.039	2.457
Bond angles (°)				
N1–M–N2	68.14	70.45	74.83	63.87
N1–M–N3	84.13	84.25	87.29	81.58
N1–M–N4	124.51	114.02	113.88	123.97
N1–M–O1	135.48	155.91	161.50	135.22
N1–M–O2	92.82	84.25	103.99	102.45
N2–M–N3	124.50	113.67	114.18	123.93
N2–M–N4	84.13	84.43	86.88	81.58
N2–M–O1	92.82	100.05	98.82	102.38
N2–M–O2	135.47	155.19	163.16	135.26
N3–M–O4	147.45	158.44	154.08	151.90
N3–M–O1	74.18	79.48	79.46	71.87
N3–M–O2	90.85	87.37	82.33	92.68
N4–M–O1	90.84	86.07	82.59	92.63
N4–M–O2	74.18	78.41	78.21	71.88
O1–M–O2	125.22	96.53	87.09	113.94

in Table 2. As presented in Table 2, the value of WBI for M–N (imine) are about 0.071, 0.3207, 0.3340 and 0.2614 and for M–O bond lengths are about 0.0422, 0.2067, 0.1334, 0.1663 in the case of [MnL]²⁺, [NiL]²⁺, [CuL]²⁺ and [CdL]²⁺ complexes, respectively. These values are in good

agreement with the trend of M–N and M–O bond length of [MnL]²⁺, [NiL]²⁺, [CuL]²⁺, while greatest values of bond lengths in [MnL]²⁺ illustrate the smallest value of WBI. The natural charges of the atoms involved in the bonding interactions between the L and metal ions evaluated through

Table 2. Natural Charges of Metal ions, Wiberg Bond Indices, the Values of Charge Transfer from L to Metal Ions(ΔQ) and Total Spin Density [MnL]²⁺, [NiL]²⁺, [CuL]²⁺ and [CdL]²⁺

WBI	Mn	Ni	Cu	Cd
M-N1	0.0350	0.2137	0.2342	0.1362
M-N2	0.0350	0.2177	0.2328	0.1361
M-N3 (imine)	0.0710	0.3207	0.3340	0.2614
M-N4 (imine)	0.0710	0.3227	0.3160	0.2615
M-O1	0.0422	0.2067	0.1334	0.1663
M-O2	0.0422	0.2121	0.0401	0.1664
Q _M	1.1745	0.929	0.395	0.653
ΔQ	0.8255	1.071	1.605	1.347
Total Spin density	4.761	1.490	0.453	0

**Fig. 2.** Shape of the energetically highest-lying orbitals HOMO-2, HOMO-3, HOMO-7 and HOMO-10 for [MnL]²⁺.

natural population analysis, are given in Table 2. As can be seen, in all the cases, upon the interaction of the L and Cu^{2+} and Mn^{2+} metal ions the charges of both metal ions are changed. The maximum value of charge transfer from L derived for Cu^{2+} metal ion and is about 1.347e and minimum value derived for Mn^{2+} and is about 0.8255. The above data suggest that the covalent character in bonding interactions between the L and metal ions in $[\text{MnL}]^{2+}$ and $[\text{CuL}]^{2+}$ complexes is minimum and maximum, respectively. Figure 2 shows the shape of the energetically highest-lying orbitals, HOMO-2, HOMO-3, HOMO-7 and HOMO-10. The shape of HOMO-2 can be associated with the interaction of Mn^{2+} with the secondary nitrogen atoms of L, HOMO-3 and HOMO-7 associated with the interaction of Mn^{2+} with the imines and secondary nitrogen atoms of L, and HOMO-10 associated with the interaction of Mn^{2+} with the oxygen atoms of L.

CONCLUSIONS

The synthesis and characterization of a new Schiff base ligand and related Mn(II), Ni(II), Cu(II) and Cd(II) complexes are reported. The ligand and related complexes were characterized by elemental analysis, IR, EI-Mass in all cases and ^1H and ^{13}C NMR for the ligand. Also, theoretical studies on structures, molecular orbital and nature of bond in these complexes were carried out with NBO analysis at DFT (BP86) method using Def-2/SVP basis set. The results of WBI and Charge transfer confirm that the covalent character in bonding interactions between the L and metal ions in $[\text{MnL}]^{2+}$ and $[\text{CuL}]^{2+}$ complexes is minimum and maximum, respectively.

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