

Synthesis and Characterization of Dinuclear Metal Complexes Stabilized by Tetradentate Schiff Base Ligands

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Abstract: Problem statement: The synthesis, spectroscopic properties and theoretical calculations of acetylacetonimine and acetylacetonilidimine Schiff-base ligands, L₁H and L₂H, respectively and their dinuclear complexes of the type [M₂L_nCl₂(H₂O)₂], where n = 1 or 2, M = Co(II), Ni(II), Cu(II), Zn(II) and Cd(II) are described. **Approach:** The new tetradentate dianion Schiff base ligand which was used as stabilizers for the complexes were prepared by condensation of hydrazine with acetylacetone or acetylacetonilide. The dinuclear complexes of these ligands were synthesized by treating an ethanolic solution of the prepared ligand with hydrated metal salts in molar ratio of 1:2 (L:M). **Results:** The ligand and their dinuclear metal complexes were characterized by CHN elemental analysis, FT-IR, UV-Vis, ¹H NMR (for the ligands), conductivity, magnetic susceptibility and theoretical calculation by using MM2 modeling program. **Conclusion:** The reaction of these ligands in a 1:2 (L:M) afford dinuclear M(II) metal complexes with tetrahedral arrangement around Co(II), Zn(II) and Cd(II) and square planar around Ni(II) and Cu(II).

Key words: Schiff base, hydrazine, acetoacetanilide, acetyl acetone, dinuclear complexes

INTRODUCTION

A great deal of work has been reported on the synthesis and characterization of different types of Schiff base complexes with transition and non transition elements (Vigato *et al.*, 2007; De Geest *et al.*, 2007; Knight *et al.*, 2007).

The majority of Schiff bases usually act as multidentate N-N and N-O donors with the formation of mono- or polynuclear complexes (De Geest *et al.*, 2007; Rai and Sharma, 1995; Maurya *et al.*, 1995).

In addition to their interesting ligational properties, both Schiff bases and their complexes have important biological and industrial applications (Al-Razaq *et al.*, 2005; Bedioui, 1995; Brown *et al.*, 1995).

The preparation of anionic and neutral dimeric complexes of the general formula [Ni(phen)₃] [ML₂] were phen = 1,10-phenanthroline, L = 2-mercaptoethylamine-N-salicylaldehyde and 2-mercaptoethylamine-N-acetylacetonimine, M = Ni(II), Cu(II) and Zn(II) and [M₂L₂] were M = Co(II), Ni(II), Cu(II) and Zn(II) and their physico-chemical characterization.

The aim of the present research is the synthesis and physicochemical study of new cobalt(II), nickel(II),

copper(II), zinc(II) and cadmium(II) coordination complexes with new Schiff bases ligands.

MATERIALS AND METHODS

General: [CoCl₂.6H₂O], [NiCl₂.6H₂O], [CuCl₂.2H₂O], [ZnCl₂] and [CdCl₂] the remaining reagents were products from (BDH or Fluka) and used as supplied. The metal content was estimated spectrophotometrically using Shimadzu Atomic Absorption 670 Spectrophotometer. The prepared compounds were analyzed by using the C, H, N elemental analyzer (Carlo Erba). Melting points were determined using Buchi 510 melting point apparatus. Infrared spectra were recorded using Perkin Elmer 580 spectrophotometer in the range 4000-200 cm⁻¹ as KBr pellets. The ¹H NMR spectra were recorded on a Bruker-Avance 300 MHz spectrometer in DMSO-d₆ at room temperature. The electronic spectra were recorded on Shimadzu UV. Visible spectrophotometer UV-160 for 10⁻³ M solution of the complexes in DMSO at 25°C using 1cm quartz conductivity measurements were carried out on 10⁻³ M solution of the complexes in DMSO using (PMC₃ (Jenway) conductivity model) at room temperature. Magnetic measurements were

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carried out on the solids by the Faradys method using Bruker BM6 instrument and AA670 for the determination of metal content.

Theoretical computation was applied on the suggested structures of the prepared complexes using MM2CS ChemOffice version 11.0 by Pentium (IV) computer.

Preparation of the Schiff base compounds: About 0.40 mol of acetylacetone or acetylacetanilide was added to 25 mL of absolute ethanol along with 0.20 mol of hydrazine. After adding a few drops of glacial acetic acid, the mixture was refluxed for 3 h and then cooled to room temperature. Some amount of distilled water was then added to the solution and the whole solution was cooled in ice. A yellow solid gradually appeared which was allowed to stand for nearly 30 min during which a considerable amount of solid was formed and settled down. It was filtered, washed thoroughly with a small amount of distilled water and then dried in air and finally in vacuum.

Preparation of the complexes: Aqueous solution of 0.004 mol of $MCl_2 \cdot nH_2O$, where $M = Co(II), Ni(II), Cu(II), Zn(II)$ and $Cd(II)$ was added to an ethanolic solution of 0.002 mol of the ligand. The mixture was stirred at room temperature for 40 min and warmed on water bath for 4 h. On standing overnight, the precipitated product was obtained which was filtered, washed with water, then with ethanol and recrystallized from hot alcoholic solution. The product was then washed with ethanol, ether and dried in vacuum for 3 h.

Theoretical calculations: The optimized geometry and steric energy of the prepared complexes were done using MM2CS ChemOffice 11.0 molecular modeling program package. These calculations were performed using computer Pentium (IV) with processor operating at 2400 MHz.

RESULTS

The reaction of the Schiff base ligands with metal chloride in (1:2) ligand to metal molar ratio afford the complexes of the general formula $[M_2(L_1)Cl_2(H_2O)_2]$ and $[M_2(L_2)Cl_2(H_2O)_2]$ as shown in Fig. 1 and 2, respectively. The physical properties of the complexes are tabulated in Table 1 and the elemental analysis data which are listed in Table 2 for ligands and complexes assigned to 1: 2 molar ratio of Schiff base ligand: M. They are quite stable in air and melt or decompose above 170°C. They are insoluble in most organic solvent but soluble in DMF and DMSO.

Conductivity measurements: The molar conductivities of 10^{-3} M solution of the complexes listed in Table 1 indicate that all complexes are non electrolyte in DMSO (Geary, 1971).

IR-spectra: The most important IR assignments of the complexes are listed in Table 3. There are some bands appeared in the complex spectra which are attributed to M-O and M-N, this bands confirm the complex formation.

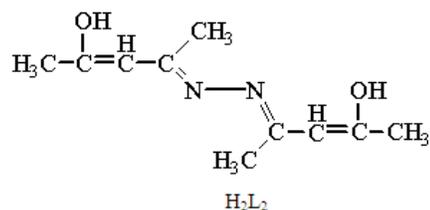
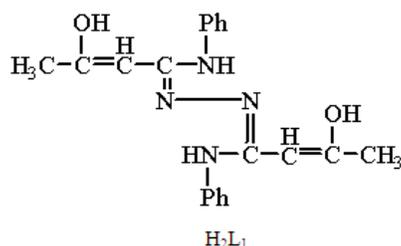


Fig. 1: The suggested structures of the free Schiff bases ligands

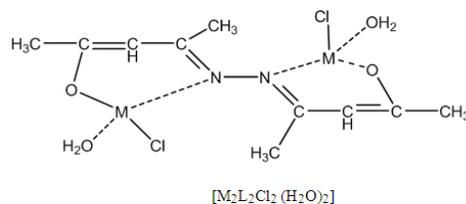
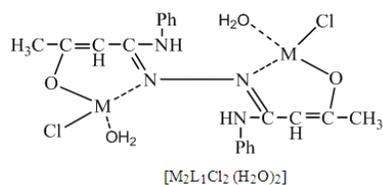


Fig. 2: The suggested structures of the prepared complexes; $M = Co(II), Ni(II), Cu(II), Zn(II), Cd(II)$

Table 1: Physical properties of the free ligands and complexes

| Seq. | Compound | Color | m.p. (°C) | A_M (ohm ⁻¹ . cm ² mol ⁻¹) | μ_{eff} B.M. |
|------|-----------------------------------------------------------------------------------|--------------|-----------|----------------------------------------------------------------|-------------------------|
| | H ₂ L ₁ | Yellow | 122 | - | - |
| | H ₂ L ₂ | Pale yellow | 135 | - | - |
| 1 | [Co ₂ L ₁ Cl ₂ (H ₂ O) ₂] | Dark brown | 138 | 15.3 | 4.22** |
| 2 | [Ni ₂ L ₁ Cl ₂ (H ₂ O) ₂] | Green | 149 | 10.8 | Dia |
| 3 | [Cu ₂ L ₁ Cl ₂ (H ₂ O) ₂] | Yellow-green | 172* | 18.1 | 1.61** |
| 4 | [Zn ₂ L ₁ Cl ₂ (H ₂ O) ₂] | White | 166 | 19.6 | - |
| 5 | [Cd ₂ L ₁ Cl ₂ (H ₂ O) ₂] | White | 151 | 12.6 | - |
| 6 | [Co ₂ L ₂ Cl ₂ (H ₂ O) ₂] | Red-brown | 160 | 14.2 | 4.01** |
| 7 | [Ni ₂ L ₂ Cl ₂ (H ₂ O) ₂] | Blue | 142 | 6.3 | Dia |
| 8 | [Cu ₂ L ₂ Cl ₂ (H ₂ O) ₂] | Pink | 196* | 9.2 | 1.80** |
| 9 | [Zn ₂ L ₂ Cl ₂ (H ₂ O) ₂] | White | 190 | 21.0 | - |
| 10 | [Cd ₂ L ₂ Cl ₂ (H ₂ O) ₂] | white | 203* | 11.7 | - |

*: Decomposition; **: Per metal atom

Table 2: elemental analysis of the ligands and complexes

| Compound | Yield (%) | Elemental analysis: Percentage of found (Clac.) | | | |
|-------------------------------|-----------|-------------------------------------------------|---------------|-------------|---------------|
| | | M (%) | C (%) | H (%) | N (%) |
| H ₂ L ₁ | 72.10 | - | 68.20 (68.57) | 6.19 (6.29) | 15.70 (16.00) |
| H ₂ L ₂ | 69.65 | - | 61.00 (61.22) | 8.03 (8.16) | 13.90 (14.29) |
| 1 | 54.02 | 20.22(20.57) | 41.40 (41.90) | 4.02 (4.54) | 9.82 (9.78) |
| 2 | 63.70 | - | 41.00 (41.93) | 4.02 (4.54) | 9.57 (9.78) |
| 3 | 71.31 | 21.66(21.84) | 41.60 (41.23) | 4.16 (4.47) | 9.63 (9.62) |
| 4 | 68.91 | - | 40.70 (40.98) | 4.06 (4.44) | 9.45 (9.56) |
| 5 | 79.22 | 32.96(33.07) | 35.10 (35.31) | 3.32 (3.83) | 8.01 (8.24) |
| 6 | 66.83 | - | 28.50 (28.66) | 4.25 (4.78) | 6.49 (6.69) |
| 7 | 65.68 | 27.90(28.07) | 27.60 (28.69) | 4.15 (4.78) | 6.34 (6.69) |
| 8 | 70.11 | - | 28.80 (28.04) | 4.19 (4.67) | 6.23 (6.54) |
| 9 | 76.40 | 29.88(30.29) | 27.60 (27.80) | 4.19 (4.63) | 6.30 (6.48) |
| 10 | 62.32 | - | 22.70 (22.83) | 3.20 (3.80) | 5.00 (3.35) |

Table 3: IR spectra (cm⁻¹) and electronic spectra of the ligands and complexes

| Seq. | $\nu(\text{C}=\text{N})$ | $\nu(\text{C}-\text{O})$ | $\nu(\text{M}-\text{N})$ | $\nu(\text{M}-\text{O})$ | $\nu(\text{M}-\text{Cl})$ | $\nu(\text{M}-\text{OH}_2)$ | M_{max} (UV) |
|-------------------------------|--------------------------|--------------------------|--------------------------|--------------------------|---------------------------|-----------------------------|-----------------------------------|
| H ₂ L ₁ | 1642 (m) | 1243 (m) | - | - | - | - | - |
| H ₂ L ₂ | 1638 (m) | 1236 (w) | - | - | - | - | - |
| 1 | 1632 (w) | 1213 (m) | 366 (w) | 496 (w) | 272 (m) | 418 (m) | 13800 |
| 2 | 1621 (w) | 1210 (m) | 416 (w) | 486 (w) | 286 (m) | 491 (w) | 15386, 15396, 16000, 20820, 21146 |
| 3 | 1618 (s) | 1218 (m) | 422 (s) | 512 (s) | 293 (m) | 476 (s) | 13403, 14612, 15860 |
| 4 | 1628 (s) | 1232 (s) | 373 (s) | 504 (m) | 315 (m) | 510 (w) | - |
| 5 | 1612 (m) | 1226 (w) | 395 (w) | 520 (m) | 320 (m) | 466 (w) | - |
| 6 | 1622 (m) | 1203 (w) | 406 (m) | 492 (m) | 296 (w) | 446 (m) | 13815 |
| 7 | 1625 (s) | 1200 (w) | 432 (m) | 488 (w) | 332 (w) | 482 (s) | 15390, 16000, 20835, 21210 |
| 8 | 1615 (s) | 1222 (w) | 382 (w) | 510 (w) | 346 (m) | 500 (m) | 13338, 14612, 15788 |
| 9 | 1623 (m) | 1209 (w) | 412 (m) | 490 (w) | 316 (s) | 504 (m) | - |
| 10 | 1610 (m) | 1218 (m) | 426 (s) | 519 (w) | 321 (s) | 432 (m) | - |

¹H NMR spectra: The ¹H NMR spectra were recorded on a Bruker- Avence 300 MHz spectrometer in DMSO-d₆ at room temperature which confirms the suggested structures of the ligands (Fig. 1) (Tas *et al.*, 2009). The ¹H NMR spectra of the L₁ and L₂ do not give any signal corresponding to acetylacetone or acetylacetanilide and hydrazine protons.

Electronic spectra and magnetic moments: The values of magnetic moment of Co (II) complexes (No. 1 and 6) is (4.22 and 4.01) B.M. respectively. The Ni(II) complexes (No. 2 and 7) show a diamagnetic moment and the electronic spectra of these complexes show bands at (15386-16000 cm⁻¹) and (20835-21146 cm⁻¹).

The Cu (II) complexes (No. 3 and 8) show a magnetic moment (1.61 and 1.80) B.M. respectively and the electronic spectrum showed broad band at (14612 cm⁻¹).

The Zn(II) and Cd(II) complexes (No. 4, 5, 9 and 10) show a diamagnetic properties and do not display any d-d transition.

Theoretical calculations: theoretical studies have been carried out to investigate the optimized geometries by calculating the steric energies (Table 4) and to investigate the bonding sites in addition to presence (or not) of M-M bonding in all complexes.

Table 4: Computational steric energies of the ligands and their complexes

| No. | Steric energy (Kcal mol ⁻¹) | No. | Steric energy (Kcal mol ⁻¹) |
|----------------|--------------------------------------------|-----|--------------------------------------------|
| L ₁ | 15.4373 | 5 | 20.4352 |
| L ₂ | 13.1292 | 6 | 69.3639 |
| 1 | 82.7444 | 7 | 44.6007 |
| 2 | 119.6799 | 8 | 192.1933 |
| 3 | 213.6190 | 9 | 27.9856 |
| 4 | 17.2006 | 10 | 18.5688 |

DISSCUSION

IR-spectra: The most important band which appeared at 1642 and 1636 cm⁻¹ due to $\nu(\text{C}=\text{N})$ stretching in the free ligand is shifted to the lower field in the prepared complexes. This is usually indicates that the (C=N) groups of the ligands are involved in coordination with metal atom through the azomethine nitrogen atom (Sallomi and Al-Shaheen, 1994). Another important band which appeared at 1243 and 1236 cm⁻¹ due to $\nu(\text{C}-\text{O})$ stretching in the free ligand is shifted to the lower field in the prepared complexes. This is usually indicates that the (C-O) groups of the ligands are involved in coordination with metal atom through deprotonation of the alcoholic groups (Patton and Taylor, 1974).

In addition to these changes, in the spectra of all complexes, new bands were observed at about (440-454 cm⁻¹) and (80-510 cm⁻¹) attributed to $\nu(\text{M}-\text{N})$ and $\nu(\text{M}-\text{O})$ stretching vibration, respectively. This represents a further evidence for the coordination of the ligands through both azomethine nitrogen and oxygen atoms (Nakamoto, 1997).

Furthermore, the IR spectra of the all complexes showed another bands were observed at about (272-346 cm⁻¹) and (418-510 cm⁻¹) which may be due to $\nu(\text{M}-\text{Cl})$ and $\nu(\text{M}-\text{OH}_2)$ stretching vibration, respectively (Bayoumi *et al.*, 2001).

¹HNMR-Spectra: The ¹HNR of the hydroxyl part in the ligands possesses one type of protons and will show two doublets. The spectra of the ligands show broad peak as singlet at 14.71 ppm for L₁H and at 13.93 ppm for L₂H, characteristic of intermolecular hydrogen bonded OH proton. In the ¹H NMR spectra of the ligands, the chemical shifts observed at δ 3.81 ppm for L₁H, characteristic also of intermolecular hydrogen bonded NH proton, but the peak at δ 3.12 ppm in L₂H spectra is assigned to the proton of N=C-CH₃. The peaks at 1.96 ppm and at 2.12 ppm are assignable to the protons of C=C-CH₃ for L₁H and L₂H, respectively. The protons of C-CH=C for L₂H and L₂H arises at 3.63 and 4.84 ppm, respectively.

Table 5: Some selected calculated parameters of the complex (5), [Cd₂L₁Cl₂(H₂O)₂]

| | Selected calculated parameters | Value |
|------------------|--------------------------------------------------|----------|
| Bond angles (°) | N ₁ -Cd ₁ -Cl ₁ | 83.0000 |
| | N ₁ -Cd ₁ -O ₁ | 82.0000 |
| | O ₁ -Cd ₁ -Cl ₁ | 87.0000 |
| | O ₃ -Cd ₂ -O ₄ | 98.0000 |
| | N ₂ -Cd ₂ -O ₄ | 102.0000 |
| | N ₂ -Cd ₂ -Cl ₂ | 85.0000 |
| Bond lengths (Å) | Cd ₁ -N ₁ | 1.9085 |
| | Cd ₁ -O ₁ | 1.8394 |
| | Cd ₂ -O ₃ | 1.8000 |
| | Cd ₂ -N ₂ | 1.8513 |
| | N ₁ -N ₂ | 1.4250 |

Electronic-spectra: The electronic spectrum (Table 3) of Co(II) complexes shows a strong band in the visible region at 13800 and 13815 cm⁻¹ respectively corresponding to transition ⁴A₂(F)→⁴T₁(P) (ν_3) in tetrahedral environment for Co(II) while (ν_1), (ν_2) was not observant due to instrumental limit (Wilkinson, 1987).

The bands in the electronic spectra of Ni(II) complexes (No. 2 and 7) were attributed to ¹A_{1g}→¹A_{2g} and ¹A_{1g}→¹B_{1g}, which is consistent with square planar geometry for Ni(II) complexes (Singh *et al.*, 1989).

According to the band in Cu(II) complexes electronic spectrum which is assigned to ²B_{1g}→²E_g transition, is consistent with square planner geometry around Cu(II) complexes (Wilkinson, 1987).

The Zn(II) and Cd(II) complexes due to their diamagnetic properties and no d-d transitions and based on stoichiometry of these complexes and elemental analysis, they are four coordinated, which could be either tetrahedral or square planer, however, tetrahedral geometry is the more preferred stereochemistry for this Zn(II) and Cd(II).

Theoretical studies: Theoretical calculations (Geary, 1971; Allen *et al.*, 1991; Rappe and Casewit, 1997) have paid a considerable attention to the characterization and inferences of geometrical optimization of the prepared complexes, therefore we could obtain the optimized geometry for each complex by computing the minimum steric energy and the theoretical physical parameters, such as, bond length and bond angles using MM2CS ChemOffice version 9.0 molecular modeling program. The steric energies of the prepared complexes are listed in Table 4; according to these values we could determine the bonding via imine and hydroxyl groups also there is no M-M bonding mode. The optimized structures of complex 5 and 7 (Fig. 3 and 4, respectively) were drawn here, as an example, with some selected calculated parameters in coordination sphere (Table 5 and 6 respectively).



Fig. 3: Configuration of complexes (5) $Cd_2(L_1)Cl_2(H_2O)_2$, optimized by MM2 CS molecular modeling program package

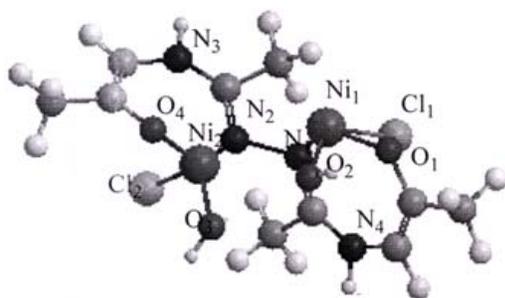


Fig. 4: Configuration of complexes (7) $[Ni_2(L_2)Cl_2(H_2O)_2]$, optimized by MM2 CS molecular modeling program package

Table 6: Some selected calculated parameters of the complex (7), $[Ni_2L_2Cl_2(H_2O)_2]$

| | Selected calculated parameters | Value |
|-------------------|--------------------------------------------------|---------|
| Bond angles (°) | N ₁ -Ni ₁ -Cl ₁ | 93.0000 |
| | O ₁ -Ni ₁ -O ₂ | 78.0000 |
| | Cl ₁ -Ni ₁ -O ₂ | 84.0000 |
| | N ₂ -Ni ₂ -Cl ₂ | 98.0000 |
| | O ₃ -Ni ₂ -O ₄ | 95.0000 |
| | N ₂ -Ni ₂ -O ₄ | 87.0000 |
| Bond lengths (Å°) | N ₁ -Ni ₁ | 1.1103 |
| | O ₁ -Ni ₁ | 1.8211 |
| | N ₂ -Ni ₂ | 1.0362 |
| | O ₄ -Ni ₂ | 1.7498 |
| | N ₁ -N ₂ | 1.5562 |

CONCLUSION

New hydrazine Schiff-base ligands, LnH, (n = 1 or 2) with their dinuclear metal complexes of the type $[M_2(L_n)Cl_2(H_2O)_2]$ were synthesized. The structure of

the ligands and their complexes were determined by several methods such as FT-IR, UV-Vis, ¹H NMR, elemental analysis, molar conductivities, magnetic susceptibility, in addition to theoretical calculation using MM2 modeling program. The tetradentate Schiff-base ligands are used as stabilizer ligands for dinuclear metal complexes and according to the measurements and theoretical calculations, the Co(II), Zn(II) and Cd(II) complexes have tetrahedral geometries while Ni(II) and Cu(II) complexes have square planar geometries around the central metal atom.

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