Synthesis, Characterization and Thermal Studies of Fe(II), Co(II), Ni(II) and Cu(II) Complexes with bis-(4-benzylidenamino-phenyl)-methane Schiff base ligand

Atared F. Hassan, Hiba H. Sabah and Afaq A. Turki

Department of Chemistry, College of Science, University of Basrah

Abstract. A new series of Co(II), Fe(II), Cu(II) and Ni(II) complexes of Bis -(4-benzylidenamino-phenyl)-methane (L) have been prepared and characterized. The complexes conform to general formula [CoL(H₂O)₃]Cl₂, [FeL(H₂O)₅]SO₄.2H₂O, [CuL(H₂O)₅]NO₃ and [NiL(H₂O)₃Cl₂]. Infra red spectra and elemental analysis reveal uni-dentate coordination of Schiff base to metal ions. Molar conductivity measurements show that complexes (I, III) behave as 2:1 electrolyte while complex (II) behave as 1:1 electrolyte. The thermal studies for complexes shows that the complexes are thermal stable.

1. Introduction

Schiff bases are an important organic compounds which carrying imin or azomethane group. Schiff bases are versatile compounds in many fields including biological, analytical, medical and pharmaceutical such as Anti tubercular [1,2], Anti depressant [3], Anticonvulsant [4,5] and anti-inflammatory [6]. Schiff bases easily formed high thermal stability complexes with almost all metal ions were useful for uses as catalysis in highly temperature for both homogeneous and heterogeneous reaction such as polymerization [7,8], For reduction of thionyl chloride [9] and oxidation of organic compounds [10].

These organometallic compounds exhibit larger biological activity than free Schiff base themselves such as anti bacterial [11], Anti fungal [12-14], Anti cancer [15-17] and antiviral activity [18].
The aim of this work, the preparation, spectroscopic studies of Fe(II), Co(II), Ni(II), and Cu(II) complexes with monodentate bis-(4-benzylidenamino-phenyl)-methane ligand and we have study thermal behaviors of these complexes.

2. Material and methods

All chemicals and solvents used in this study were supplied (Merck and Fluka) company. The 'H NMR spectra were recorded with (Bruker DPX-300) Spectrometer (Iran). The elemental analysis was done by using (CE-440) Elemental analyzer (Iran). FT-Infrared spectra were recorded as KBr pellets with (FT-IP 8400S) Shimadzu instrument. Melting point of complexes were determined on (Gallenkamp melting point apparatus). Thermal analysis were carried out under (N₂) atmosphere using α-Al₂O₃ as reference (Iran). The ionic conductivity was measured using (Konduktoskop E 365B Metrohm Herisau) conductivity instrument at room temperature.

2.1. Synthesis:

2.1.1. Preparation of Schiff base complexes:

To a hot solution of CoCl₂.6H₂O, FeSO₄.7H₂O, Cu(NO₃)₂.3H₂O, and NiCl₂.6H₂O in (15 ml) ethyl alcohol (2.5mmol) was added (2.5mmol) solution of Schiff base (L) are mentioned in literature [19] in 25ml ethyl alcohol drop wise with continues stirring and gentle heating for 1hr. The volume of solution reduced to half, colored solid compound was formed were filtered off, washed several times with hot deionized water and then with ethyl alcohol and dried under vacuum.

2.2. Computational methods

The theoretical study in work was performed using the computational methods by Hyper chem. 8.02. Geometry optimization of the studied, compounds by performing the semi-empirical molecular orbital theory at the level PM3[20].

Result and discussion

The C.H.N, molar conductunce data and physical characteristic of new complexes are listed in table (1).

Table (1). Physical properties, molar conductivity and C.H.N data of prepared complexes.

| No. | Empirical formula | Ω⁻¹ cm² mol⁻¹ | % | Color | m.p. °C | Elemental analysis found(calc) |
|-----|------------------|----------------|---|-------|---------|-------------------------------|
|     |                  |                |   |       |         | C    | H    | N    | S    |
| I   | [Co(L(H₂O))₃]Cl₂ | 243.7          | %60 | Dark green | > 320 | 38.61(37.97) | 5.39(5.04) | 3.11(3.01) |
| II  | [Fe(L(H₂O))₃]SO₄·2H₂O | 108.6 | %70 | Golden yellow | 126-128 | 48.89(49.70) | 5.23(5.56) | 4.20(4.29) | 4.33(4.90) |
| III | [Ni(L(H₂O))₃]NO₃·H₂O | 226 | %65 | Dark brown | 260-262 | 48.33(48.29) | 4.80(5.01) | 9.01(8.36) |
| IV  | [Ni(L(H₂O))₃]Cl₂ | - | %62 | Green | 233-235 | 60.60(60.15) | 5.71(4.67) | 5.73(5.19) |
The assignment bands of (IR) spectra of Schiff base ligand and their metal complexes are listed in table(2).

In The Infrared spectra of Schiff base ligand (L), The νC=N stretching frequency for azomethane group is observed at 1625 cm⁻¹. The value of these band was shifted to lower wave number in the spectra of all metal complexes in the range (1589-1618) cm⁻¹ which due to coordination the nitrogen of azomethane with the central metal ions [21,22]. On the other hand all complexes exhibit a broad bands at (3315-3454) and bands at (910-960) cm⁻¹ which due to stretching modes of O-H group and rocking mode of coordinated water to metal ion respectively [23,24]. The ν(C=N) stretching modes appeared around (1172-1244) cm⁻¹ and the ν(C=C) stretching frequency of aromatic ring appears a round (1508-1591) cm⁻¹. While the bands in the (3020-3059) cm⁻¹ and (2860-2924) cm⁻¹ attributed to ν(C-H) stretching of aromatic rings and ν(C-H) aliphatic respectively. The new bands appears in the spectral of all metal complexes a round (509-580) and (428-518) cm⁻¹ due to Metal-Oxygen (M-O) and Metal-Nitrogen (M-N) stretching mode[25]

Table 2. The assignment IR bands of schiff base ligand and their complexes:

| Com | νC=N (cm⁻¹) | νO-H (cm⁻¹) | νC-H ar. (cm⁻¹) | νC-H ali. (cm⁻¹) | νC-N (cm⁻¹) | νM-N (cm⁻¹) | νM-O (cm⁻¹) |
|-----|-------------|-------------|----------------|----------------|-------------|-------------|-------------|
| L   | 1625        | 3030        | 2950           | 1192           |             |             |             |
| Co(II) | 1589      | 3348-3444   | 3036           | 2924           | 1222        | 428         | 516         |
| Fe(II) | 1599      | 3358-3454   | 3020           | 2916           | 1244        | 456         | 520         |
| Cu(II) | 1600      | 3352-3444   | 3059           | 2920           | 1172        | 432         | 509         |
| Ni(II) | 1618      | 3315-3446   | 3030           | 2860           | 1234        | 518         | 580         |

Figures 1 and 2 show the typical ¹H NMR spectrum of compound(I) and (III) respectively. The ¹H NMR data for all complexes are summarized in the table(3). All the ¹H NMR spectrum of new complexes were studied[26,27] by the presence of singlet signals in the range (7.73-8.56) ppm which due to proton of azomethane group in (I) position. The aromatic protons showed multiplet signals in the range (6.18-8.22) ppm due to the protons in (4,5,6,7 and 8) positions in the aromatic rings. While the aliphatic proton of CH₂ group (proton in 2 position) showed singlet signals within the range (1.19-2.08) ppm. The OH protons showed singlet signal in the region (3.81-4.68) ppm which appeared to coordinated water with metals. While the peak of solvent (DMSO) showed singlet signal within the range 2.50 ppm and 3.30 ppm

Table 3. The ¹H NMR spectral data of new complexes

| Complex | δ ppm | δ ppm | δ ppm | δ ppm |
|---------|-------|-------|-------|-------|
|         | CH=N  | aromatic protons | -CH₂- | O-H   |
| Co(II)  | 8.56  | (6.35-6.92) | 2.04  | 4.68  |
| Fe(II)  | 7.73  | (7.01-7.20) | 2.08  | 3.81  |
| Cu(II)  | 8.23  | (6.25-7.52) | 1.20  | 4.14  |
| Ni(IV)  | 8.56  | (6.87-8.22) | 1.19  | 3.92  |
Scheme (1)

Figure (1) $^1$HNMR spectrum of (I)
TG/DTA analysis of synthesized complexes was done from ambient temperature to 817 °C under (N\textsubscript{2}) atmosphere. The TG/DTA data for prepared complexes are listed in table (4), and the thermo grams are given in figures (3-6). The TG/DTA curve of Co(II) complex (I) exhibit one exothermic decomposition step occur in the range 334-360 °C with weight loss 36.17% calc.(36.60 21% found) indicate to removal the three coordinated water, chlorine and non-coordinated ligand moiety [29-30].The mass residue at 801°C is 29.12%(30.44%) may be attributed to formation C\textsubscript{7}H\textsubscript{6}NCo.

The TG/DTA curve of Fe (II) complex (II) exhibit three exothermic decomposition step . The first step occur in the range 116-140 °C with mass loss of 5.517%(5.14%) due to removal the two crystalline water molecules. A small peak at 126°C indicate to melting point .The second step occur between 280 -340 °C with weight loss of 20.23%(20.23%) due to removal sulfate ions . In the third step which occur in the range 480-510 °C a peak exhibit at 498°C with mass loss of 54.88% (54.31%) attributed to loss the five coordinated water and non-coordinated part of Schiff base ligand [29,30]. The mass residue at 750°C is 35.48% (35.51%) may be attributed to formation Fe\textsubscript{3}O\textsubscript{4}.

The TG/DTA curve of Cu(II) complex(II) exhibit three endothermic decomposition step .The mass loss 2.69% (2.63%) in the first step occur at 100°C due to loss crystalline water molecules . The second step between 165-260 °C with mass loss of 16.12% (16.12%) attributed to loss coordinated water molecules. In the third stage which occur in the range 430-500 °C with mass loss of 34.62% (34. 63%) due to loss tow nitrate ions .At 817°C the mass loss 46.128% (46.52%) due to loss the non-coordinated part of Schiff base ligand .

In the TG/DTA curve of Ni(II) complex (IV)exhibit two exothermic decomposition step . The first step consist of two peaks at 128 and 198°C with mass loss of 3.33% (3.35%) due to elimination of one water molecule . A small peak at 235 °C indicate to its melting point . Next stage occur in the
range 341 to 428 °C with mass loss of 54.82% (54.42) attributed to loss coordinated water, two chloride ions and non-coordinated ligand moiety.

**Table (4).** TG/DTA of synthesis complexes:

| Complex | Step | Type of molecule loss | Temp. of TGA (°C) | Temp. of DTA°C | Mass residuel% | Mass loss% | Temp. of 50% Mass loss°C |
|---------|------|-----------------------|-------------------|----------------|---------------|------------|-------------------------|
| Co (II) | I    | 3H₂O+2Cl⁻ +C₆H₅     | 334-360           | 801            | 36.17         | 36.21      | 387                    |
|         | Last | Formation C₆H₁₅NCo   |                   |                |               |            |                         |
| Fe (II) | I    | 2H₂O                 | 116-140           | 119            | 5.547         | 5.136      | 489                    |
|         | m.p  |                      |                   | 126            |               |            |                         |
|         | II   | SO₄²⁻                 | 280-340           | 298            | 20.23         | 20.19      | 20.19                  |
|         | III  | 5H₂O +                | 480-510           | 498            |               |            |                         |
|         | Last | 2C₆H₅                 | 750               | 35.48          | 35.51         | 19.24      |                         |
|         |      | Formation of F₃O₄     |                   |                |               | 54.88      | 54.31                  |
|         |      |                      |                   |                |               | 54.31      |                         |
| Cu (II) | I    | H₂O                  | 100               | 100            | 2.69          | >          |                         |
|         | II   | 5H₂O                 | 165-260           | 255            | 2.63          | 2.63       | 700                    |
|         | III  | 2NO₃⁻¹                | 430-500           | 450            | 16.12         | 16.12      | 34.62                  |
|         | Last | C₆H₅                 | 817               |                | 34.63         | 46.128     | 46.52                  |
| Ni (II) | I    | H₂O                  | 123-265           | 128.198        | 3.22          | 3.35       | 403                    |
|         | m.p  |                      |                   | 235            |               |            |                         |
|         | II   | 2H₂O +2Cl⁻ +C₁₀H₁₁N  | 341-428           | 411            | 54.82         | 54.42      |                         |

Concerning the computational Study, All optimised structure of this study molecules are shown in Figures (7) and (8). The (PM3) geometry optimizations yields planar structure for the new compounds. The generals geometry of molecules all this compounds are very similar. The [the dipole moment, μ (in Debyes), highest occupied and the lowest unoccupied molecular orbital (HOMO and LUMO, respectively) energies, total energy, and the energy band gap (LUMO–HOMO energy difference) and for the studied molecules are given in Table (5)]. The dipole moment calculated indicates the molecules are pole. This means that these molecules may, especially other polar molecules. The spatial distributions of (HOMO LUMO) are shown in Figure. (9). In general the all molecules gave similar (HOMO) and (LUMO) orbitals.

**Conclusion:**

Co(II), Fe(II), Cu(II) and Ni(II) complexes with bis-(4-benzyldenamino-phenyl)-methane have been prepared and characterized by different physical and chemical methods. The analysis confirmed the
structures of complexes. All synthesized complexes are thermally stable. Based on the thermal studies and most of the complexes in this study show similar behaviors and the Cu(II) complexes are more stable. Molar conductivity measurements show that complexes (I, III) behave as 2:1 electrolyte while complex (II) behave as 1:1 electrolyte.

**Table (5).** The Total energy, MO energy of the lowest, highest, (HOMO), (LUMO), levels, and the dipole moment, \( \mu \) (in Debyes) for the studied molecules

| Mol. | Method | Total energy (Kcal/mol) | HOMO (ev) | LUMO (ev) | \( \mu \) (D) |
|------|--------|-------------------------|-----------|-----------|-------------|
| II   | PM3    | -1.38871                | -6.503585 | -0.4283036| 6.287       |
| IV   | PM3    | -1.50249                | -9.076046 | -1.378737 | 8.481       |

Figure (3) TG Curve of (I)

Figure (4) TG curve of (II)
Figure (5) TG curve of (III)

Figure (6) TG curve of (IV)
Figure (7) Balls and cylinders model of (II)

Figure (8) Balls and cylinders model of (IV)
HOMO (II)

LUMO (II)
The optimized structure of the studied molecules optimization has been performed by PM3 method.

References:

[1] T. Aboul-Fadl, F A S Bin-Jubair and O. Aboul-Wafa 2010 European Journal of Medicinal Chemistry. 45 4578-4586.

[2] M D I Ferreira, T R A Vasconcelos and E M. de Carvalho 2009 Carbohydrate Research. 334 2042-2047.
[3] A B Thomas, R K Nanda, L P Kothapalli and S C Hamane 2011 Arabian Journal of Chemistry.

[4] M A Bhat and M A Al-Omar 2011 Acta Polonica Pharmaceutica 68 375-380.

[5] A A Kulkarni, S B Wankhed, N D Dhawale, P B Yadav, V V Deore and I D Gonjar 2012 Arabian Journal of Chemistry.

[6] Nithinchandra, B Kalluraya, S Aamir, and A R Shabaraya 2012 European Journal of Medicinal Chemistry 54 597-604.

[7] Gupta K G, Sutar AK 2008 Catalytic activity of Schiff base complexes coord. Chem. Rev 25a 1420-1450.

[8] M S Alam, J Choi and D Lee 2012 Bioorganic Medical Chemistry 20 4103-4108.

[9] Lin Che T, Chang Gao Q, She zhao J and Zhang G 2008 Chin. Journal Chem. 26 1079-1084.

[10] MM Tamizh, K Mereiter, K Kurchner and R Karvembu 2012 J Organomet Chem 700 194-201.

[11] AS Gaballa, MS Asker, AS Barakat and SM Teleb 2007 J Spectrochim Acta 67 A 114-121.

[12] N Raman, A Kulaindaisham, A Shanmugasundaram and K Jeyasubramanian 2001 J Trans Met Chem 26.

[13] Y Prashanthi, K Kiranmai, Subhashini NJP and Shivaraj S 2008 J Spectrochim Acta 70 A 30-35.

[14] S. Santhi and CG. Radhakrishnan Namboori 2013 Int J Chem Tech Res 4 1750-1755.

[15] M. Hajrezaie, M. Paydar, SZ. Moghadamtous, P. Hassan Darvish and M. Zahedifard 2014 Sci World J 1.

[16] Li YF, Liu ZQ 2011 Eur J Pharm Sci 44 158-163.

[17] TS. Kamatchi, N. Chitrapriya, H. Lee, CF. Fronczek, FR. Fronczek and K. Natrajian 2012 Dalton Trans J 2066-2077.

[18] KS. Kumar, S. Gangly, R. Veerasamy and E. De Clercq 2010 Eur J Med Chem col. 45 5474-5479.

[19] H. Heba -Sabah 2014 J Derpharma Chemical, 6 38-41.

[20] M. Yoko, M. Mai, T. Yuri, S. Mitsuaki, W. Hidetsugu and T. Hiroyuki 2010 J Tetrahydro, 66 605-611.

[21] D. Fatih, U. Mahmut, F. Omar and Ozturk 2009 J Therm Anal Calorim 98 785-792.

[22] P. Yokeswari Nithya, P. Ananthi and D. Shanmugapriya 2019 International J of Advanced Scientific Research and Management, Special ISSU 4 77-81.

[23] W.J Geary 1971 The use of conductivity measurements inorganic solvent for the characterization of coordination compounds Coot. Chem. Rev. 7 81.

[24] Atared F Hassan, H. Hayat Abass and A. Nadhim Abul-Hussein 2016 International Research Journal of Natural Sciences 4.
[25] JR. Ferraro (1971) *Low Frequency Vibrations of inorganic and coordination compounds* 2nd. Edn. (Wiley, New York).

[26] R M Silverstien, F X Webster and D J Kiemle 2005 *Spectrometric Identification of Organic Compounds* 6th ed (John Wiley and Sons, New York, USA).

[27] R L Shriner and C K Hermann 2004 *Spectroscopic Techniques for Organic Chemistry* (John Wiley and Sons, New York, USA).

[28] J.W. Cooper 1980 *Spectroscopic Techniques for Organic Chemistry* (John Wiley and Sons, New York, USA).

[29] N Kavitha, P V Anatha Lakshmi 2017 *Journal of Saudi chemical Society* 21 S456-S466.

[30] S M. Abdalah, M. Zayed and G. Gehad 2010 *Arabian J Chem*. 3 103-113.