

New Monomeric (Co^{II}, Ni^{II}, Cu^{II} and Zn^{II}) Metal Complexes of a Bidentate Schiff-base Ligand; Synthesis, Characterisation and Biological Studies

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Abstract

The new Co^{II}, Ni^{II}, Cu^{II}, Zn^{II} monomeric complexes with a bidentate Schiff-base ligand [(2-bromo-phenyl)-{3-[(2,4-dinitro-phenyl)-hydrazono]-1-methyl-butylidene}-amine] L are reported. The ligand L was derived from the condensation reaction of 2,4-dinitrophenylhydrazine and acetylacetone, which then reacted with o-bromoaniline. The complexes were prepared from the reaction of the corresponding metal chloride with the ligand. The ligand and its metal complexes were characterised by spectroscopic methods (FTIR, UV-Vis, ¹H NMR, A.A), magnetic measurements, chloride content, conductance and melting point. These studies revealed complexes of the general formulae [M(L)₂]Cl₂ with tetrahedral geometries for Co^{II} and Zn complexes, while square planar geometries have been suggested for Ni^{II} and Cu^{II} complexes. Biological activity of the ligand and its metal complexes against gram positive bacterial strain *Bacillus* (G+) and gram negative bacteria *Pseudomonase* (G-) revealed that the metal complexes become less resistive to the microbial activities as compared to the free ligand.

Keywords: Schiff-base ligand; transition metals; structural and biological studies.

Introduction

Schiff-base compounds have a great importance in coordination chemistry, due to their ability to form a range of stable complexes which have applications in different fields [1]. Schiff-base metal complexes also have application in biomedical [2], biomimetic [3] and catalytic system [4] and in supporting liquid crystalline phase including crystal engineering of coordination polymers, and in the fabrication of potentiometric membrane sensors [5,6]. Schiff-base compounds are reported to show a variety of biological activities including antibacterial, antifungal, anticancer and herbicidal activities [7-9]. Metal complex of Schiff-bases have also been used in oxidation reactions [10], and for binding metal ions *via* the nitrogen atom lone pair, especially when used in combination with one or more donor atoms to form polydentate chelating ligands or macrocycles [11, 12]. In this paper, the synthesis and spectral characterisation of some transition metal complexes with (2-bromo-phenyl)-{3-[(2,4-dinitro-phenyl)-hydrazono]-1-methyl-butylidene}-amine (L) are reported.

Experimental

Materials:

All reagents were commercially available and used without further purification. Solvents were distilled from appropriate drying agents immediately prior to use.

Physical measurements:

Melting points were obtained on a Buchi SMP-20 capillary melting point apparatus and are uncorrected. IR spectra were recorded as (KBr) disc using a Shimadzu 8400 FTIR spectrophotometer in the range 4000-400 cm⁻¹. Electronic spectra of the prepared compounds were measured in the region 250-900 nm for 10⁻³M solutions in EtOH at 25°C using a Shimadzu 160 spectrophotometer with 1.000±0.001 cm⁻¹ matched quartz cell. ¹H NMR spectrum was acquired in DMSO-d₆ solution using a Bruker AMX300 MHz spectrometer with tetramethylsilane (TMS) as an internal standard for ¹H NMR at Al-al-Bayt University, Jordan. Metals were determined using a Shimadzu (A.A) 680 G atomic absorption spectrophotometer. Chloride was determined using potentiometer titration method on a (686-Titro processor-665

Dosimat–Metrohm Swiss). Conductivity measurements were made with EtOH solutions using a PW 9526 digital conductivity meter and room temperature magnetic moments were measured with a magnetic susceptibility balance (Jonson Matthey Catalytic System Division).

Synthesis:

Preparation of the Schiff base ligand:

The Schiff base ligand was prepared in stepwise and in one pot methods. The stepwise was as follows:

Preparation of acetylacetone-2,4-dinitrophenylhydrazine:

To a solution of acetylacetone (0.25g, 2.52 mmole) in methanol (5 mL) was added a solution of 2,4-dinitrophenylhydrazine (0.5 g, 2.52 mmol) in methanol (5 mL), and then 2-4 drops of glacial acetic acid was added to the mixture. The reaction mixture was allowed to reflux for 4 h. The orange solid was collected by filtration and dried in air. Yield (0.55 g, 78%), mp = 205 °C.

Preparation of the L:

A solution of acetylacetone-2,4-dinitrophenylhydrazine (0.2 g, 0.713 mmol) in methanol (5 mL) was added to a mixture of o-bromoaniline (0.12 g, 0.713 mmol) in methanol (5 mL), and 2-4 drops of glacial acetic acid. The reaction mixture was refluxed for 4 h. The Schiff base was obtained as a yellow solid which was collected by filtration, washed with di ethyl ether (10 mL), and then recrystallised from ethanol and dried at room temperature. Yield (0.25 g, 71%), m.p.=180 °C. The ¹H NMR spectrum of the ligand in DMSO-d₆ showed peaks at; δH(300 MHz, DMSO-d₆): 8.8 (1H, s, Ar-H); 8.4 (3H, m, Ar-H; N-H); 8.0 (1H, d, J_{HH} 8.4 Hz, Ar-H), 7.6 (1H, d, J_{HH} 7.8 Hz, Ar-H); 7.0 (1H, s, N=H); 6.2 (1H, s, =C=H); 2.3 (3H, s, 1 x CH₃); 2.1 (3H, s, 1 x CH₃).

One pot synthesis method of the ligand:

The Schiff base ligand was prepared *via* a one pot reaction. The condensation of 2,4-dinitrophenylhydrazine and o-bromoaniline with acetylacetone was carried out on a mole ratios of 1:1:1 in ethanol (15 mL). The resulting mixture was refluxed for 2 h. The obtained yellow solid precipitate was filtered,

washed with ether (10 mL), recrystallised from ethanol and dried at room temperature to give the title compound as a pale yellow solid. Yield (%73, 0.92 g), m.p = 180 °C.

General synthesis of the complexes:

A methanolic solution (10 mL) of the metal salt (metal (II) salts are hydrated chloride; MCl₂.XH₂O; where: M = Co^{II}, Ni^{II} and Cu^{II}: X = 6, 6 and 2, respectively. Zinc chloride was non hydrated) was stirred into methanolic solution of the Schiff-base ligand (2 mmol) in methanol (15 mL). The reaction mixture was then refluxed around 2 h on a water bath until a coloured precipitate formed which was collected by filtration, washed with cold ethanol (5 mL), ether (10 mL) and dried at room temperature. Elemental analysis data, colours, and yields for the complexes are given in (Table (1)).

Determination of bacteriological activity:

Bioactivities were investigated using agar-well diffusion method [13]. The wells were dug in the media with the help of a sterile metallic borer with centres at least 24 mm. Recommended concentration (100 μL) of the test sample 1 mg/mL in DMSO was introduced in the respective wells. The plates were incubated immediately at 37°C for 20 hours. Activity was determined by measuring the diameter of zones showing complete inhibition (mm). In order to clarify the role of DMSO in the biological screening, separate studies were carried out with the solutions alone of DMSO and they showed no activity against any bacterial strains. Ligand found to be potentially active against these bacterial strains compared with its complexes.

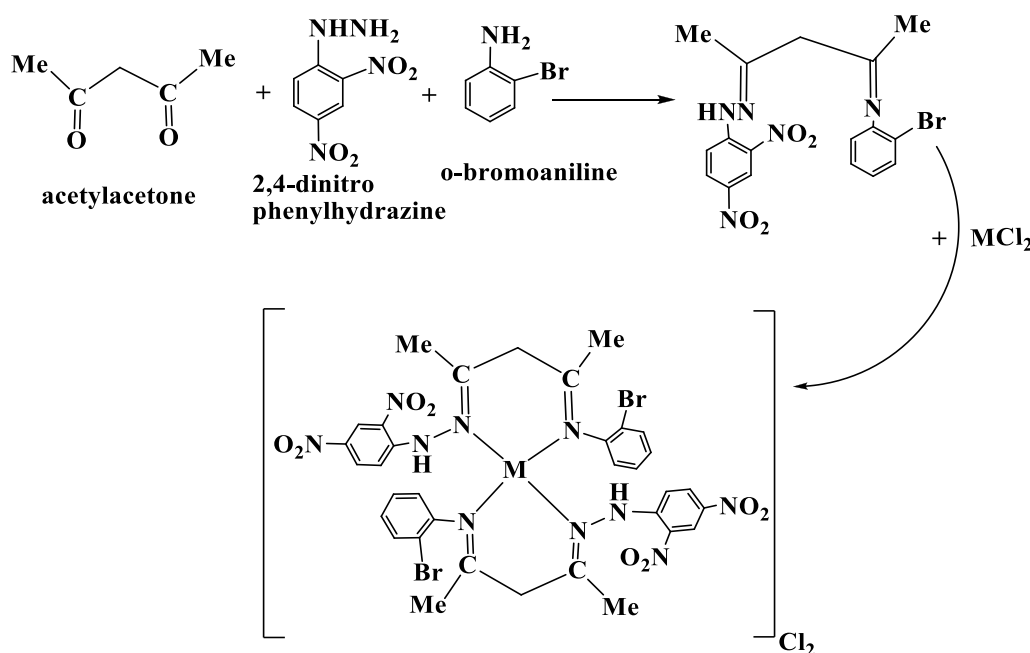
Results and Discussion

Chemistry:

The condensation reaction of 2,4-dinitrophenylhydrazine and acetylacetone in mole ratios of 1:1 gave the derivative acetylacetone-2,4-dinitrophenylhydrazine in good yield. The reaction of this derivative with o-bromoaniline in mole ratios of 1:1 resulted in the formation of the Schiff-base ligand L in good yield (Scheme (1)). The Schiff-base ligand was characterised by elemental analysis (Table (1)), IR (Table (2)), UV–Vis (Table (3)) spectroscopy and ¹H NMR spectrum. The di-electrolyte metal-

complexes were synthesised by mixing at reflux 2 mmole of the Schiff-base ligand with 1 mmole of the appropriate metal chloride. Monomeric complexes of the general formulae $[M(L)_2]^{+2}$ (where $M = Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}$) was obtained (Scheme 1). The complexes are air-stable solids, soluble in EtOH, DMSO and DMF. The complexes are sparingly soluble in MeOH and not soluble in other common

organic solvents. The coordination geometries of the complexes were deduced from their spectra. The analytical data (Table (1)) agree well with the suggested formulae. Conductivity measurements of the complexes in EtOH solutions lie in the 65.8-76 $cm^2\Omega^{-1}mol^{-1}$ range, indicating their 2:1 electrolytic behavior (Table (1)) [14].



Scheme (1) Synthesis diagram of the Schiff-base Ligand L and it's complexes.

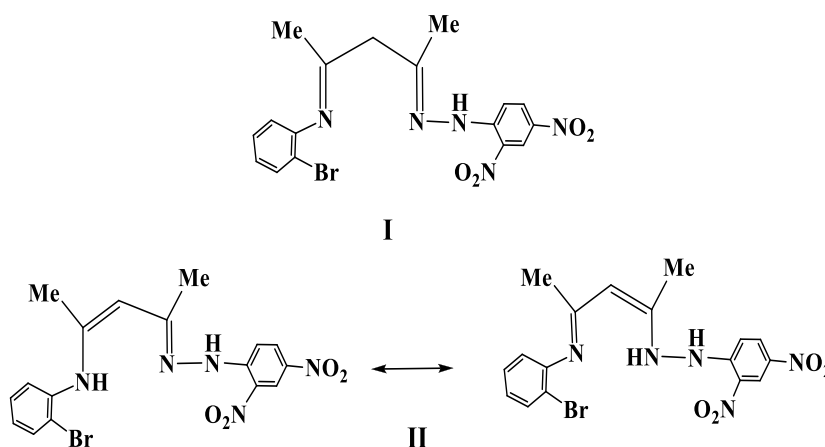
IR and NMR Spectra:

The important infrared bands for the ligand and its metal complexes together with their assignments are listed in Table (2). The IR spectra of the ligand shows characteristic bands at 3315; 1618, 1595, and 1311, 1268 cm^{-1} due to the $\nu(N-H)$, and $\nu(C=N)$ imine and $\nu(C-N)$ functional groups, respectively. The IR spectrum shows the azomethins groups are non equivalent [11, 15, 16]. The Schiff-base can exist in two tautomeric forms, the acetylacetone Schiff-base form I and the allyl Schiff base form II (Scheme 2). In the solid state, L exists in the the acetylacetone Schiff-base form was confirmed by the IR spectrum, which shows two distinct imine bands at 1618 and 1595 cm^{-1} . The IR spectra of the complexes exhibited ligand bands with the appropriate shifts due to complex formation (Table 2). The $\nu(C=N)$ imine at 1618, 1595 cm^{-1} in the free

Schiff-base ligands is shifted to lower frequency and observed in the range 1607-1610, 1586-1591 cm^{-1} for the complexes. The bands are assigned to a $\nu(C=N)$ stretch of reduced bond order. This can be attributed to delocalisation of metal electron density (t_{2g}) to the π -system of the ligand [17, 18], indicating coordination of nitrogen of the C=N moieties to the metal atoms [19]. Fig.(1) represents the IR of the ligand and it's Co-complex. Upon complex formation, The $\nu(N-H)$ band at 3315 cm^{-1} in the free ligand is shifted to lower wave number and appeared 3116-3128 cm^{-1} for the complexes [19]. At lower frequency the complexes exhibited bands around 470-497 and 538-557 cm^{-1} which could be assigned to $\nu(M-N)$ vibration mode [11, 17]. These bands indicated that the imine nitrogens of the ligand is involved in coordination with metal ion. The present of two characteristic bands indicated

that the M–N bonds are non equivalents. This can be related to the steric effect generated upon complexation and/or the two azomethine groups in the ligand are non equivalents. The main peaks of ^1H NMR of L in DMSO are collected in the experimental section “preparation of L” and presented in Fig.(3). The ^1H NMR of free ligand showed the resonance of CH_3 protons at 2.1 and 2.2 ppm, indicating the two methyl groups are non equivalents. The resonance peaks associated with the aromatic groups are observed in the

range 7.6–8.8 ppm. The ^1H NMR spectrum does not display any signal at approximately 4.00 ppm that is related to CH_2 proton, for acetylacetone moiety, in DMSO solution. A resonance around 6.2 ppm equivalent to one proton supported that the ligand exists in solution as the allyl Schiff-base form II (Scheme (2)). This is in accord with the appearance of the two methyl groups in different environments; acetylacetone Schiff base form will show one chemical shift for both methyl groups.



Scheme (2) The two tautomeric forms of Schiff-base, the acetylacetone Schiff-base form I and the allyl Schiff-base form II.

Electronic spectra and magnetic moment measurements:

The electronic spectra and magnetic moment data of the ligand and its complexes are summarised in (Table (3)). The UV-Vis spectrum of L exhibits a high intense absorption peaks at 261 and 287nm, assigned to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$, transition respectively. The electronic spectra of the complexes Co(II), Ni(II) and Cu(II) exhibit a high intensity peak around 242–300 nm related to the intra-ligand field transition. Bands exhibit around 316–360 nm assigned to the charge transfer (CT). The spectrum of the Co(II) complex exhibited two bands characteristic of tetrahedral Co(II) complexes [20–23]. The magnetic moment of this complex is typical for tetrahedral structure complexes [20–23]. The electronic spectrum of the Cu(II) complex shows a broad band which can be attributed to $^2\text{B}_{1g} \rightarrow ^2\text{E}_g$ transition, corresponding to square planar geometry [20, 24]. Ni-complex

exhibits band at 674 nm attributed to $^1\text{A}_{1g} \rightarrow ^1\text{A}_{2g}$ transition, indicating square planar geometry about Ni(II). The diamagnetic behavior is consistent with the square planar geometry [25]. The spectrum of the Zn(II) complex exhibited bands assigned to ligand $\pi \rightarrow \pi^*$ and L \rightarrow M charge transfer [20, 26]. This complex is diamagnetic as expected. The metal normally prefers tetrahedral coordination.

Antimicrobial activity:

The free Schiff-base ligand and its metal complexes were screened against *Bacillus* (G+) and *Pseudomonase* (G-) to assess their potential as an antimicrobial agent by disc diffusion method. The measured zone of inhibition against the growth of various microorganisms is listed in Table 4. It is found that the ligand has higher antimicrobial activity than its metal complexes. This can be explained as follows: The biological activity of the Schiff-base ligand is related to the imine

moiety, which plays a key role in the inhibition of the tested bacteria. The lower antimicrobial activity of the metal complexes compared with that in the ligand may be due to the strong interaction between the imine moieties and the metal ions. Such interaction will reduce the activity of the imine moiety in the inhibition.

Conclusion

In this paper, the synthesis and coordination chemistry of some monomeric complexes derived from the Schiff-base (2-bromo - phenyl) - {3 - [(2,4 - dinitro - phenyl)-

hydrazono]-1-methyl-butylidene}-amine are investigated. The complexes were prepared by mixing at reflux 2 mmole of the Schiff-base ligand with 1 mmole of the appropriate metal chloride. Monomeric complexes of the general formulae $[M(L)_2]^{+2}$ (where $M = Co^{II}, Ni^{II}, Cu^{II}, Zn^{II}$) was obtained. Physico-chemical analysis indicated the formation of four coordinate dicationic metal complexes. Biological activities revealed that the ligand has higher antimicrobial activity than its metal complexes.

Table (1)
Colours, yields, elemental analyses, and molar conductance values.

| Compound | Colour | Yield (%) | m.p °C | Metal content | Chloride content | $\Lambda_M(cm^2\Omega^{-1}mol^{-1})$ |
|----------------------|-------------|-----------|--------|----------------|------------------|--------------------------------------|
| | | | | Found(Calc.) | Found(Calc.) | |
| L | Yellow | 71 | 180 | – | – | – |
| $[Co^{II}(L)_2]Cl_2$ | Dark green | 72 | 300 | 5.19 (5.30) | 6.03 (6.28) | 69.7 |
| $[Ni^{II}(L)_2]Cl_2$ | Pale green | 59 | 160 | 5.33 (5.38) | 5.17 (6.28) | 76.5 |
| $[Cu^{II}(L)_2]Cl_2$ | Red brown | 54 | 210 | 4.46 (5.31) | 4.46 (6.26) | 65.8 |
| $[Zn^{II}(L)_2]Cl_2$ | Pale yellow | 68 | 240 | 4.08 (5.76) | 5.15 (6.25) | 65.8 |

Table (2)
FTIR frequencies (cm^{-1}) of the compounds.

| Compound | $\nu(N-H)$ | $\nu(C=N)_{imin}$ | $\nu(NO_2)$ | $\nu(C-N)$ | $\nu(N-N)$ | $\nu(M-N)$ |
|----------------------|------------|-------------------|-------------|------------|------------|------------|
| L | 3315 | 1618, 1595 | 1533, 1340 | 1311, 1268 | 987 | – |
| $[Co^{II}(L)_2]Cl_2$ | 3128 | 1607, 1586 | 1527, 1315 | 1290, 1247 | 914 | 541,470 |
| $[Ni^{II}(L)_2]Cl_2$ | 3116 | 1608, 1585 | 1521, 1334 | 1295, 1271 | 906 | 557,488 |
| $[Cu^{II}(L)_2]Cl_2$ | 3126 | 1610, 1591 | 1525, 1386 | 1301, 1280 | 910 | 545,457 |
| $[Zn^{II}(L)_2]Cl_2$ | 3118 | 1605, 1587 | 1515, 1375 | 1323, 1265 | 930 | 538,497 |

Table (3)
Magnetic moment and u.v-vis spectral data in EtOH solutions.

| Compound | μ_{eff} (BM) | Band position (λnm) | Extinction coefficient $\epsilon_{\text{max}}(\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1})$ | Assignments |
|--|-------------------------|--------------------------------------|--|---|
| L | | 261 | 3577 | $\pi \rightarrow \pi^*$ |
| | | 287 | 2273 | $n \rightarrow \pi^*$ |
| $[\text{Co}^{\text{II}}(\text{L})_2]\text{Cl}_2$ | 4.1 | 242 | 779 | $\pi \rightarrow \pi^*$ |
| | | 307 | 401 | CT |
| | | 455 | 75 | ${}^4\text{T}_{1\text{g}}^{(\text{F})} \rightarrow {}^4\text{T}_{1\text{g}}^{(\text{P})}$ |
| | | 686 | 225 | ${}^4\text{T}_{1\text{g}}^{(\text{F})} \rightarrow {}^4\text{A}_{2\text{g}}^{(\text{F})}$ |
| $[\text{Ni}^{\text{II}}(\text{L})_2]\text{Cl}_2$ | diamagnetic | 265 | 675 | $\pi \rightarrow \pi^*$ |
| | | 300 | 485 | $n \rightarrow \pi^*$ |
| | | 316 | 450 | CT |
| | | 360 | 779 | CT |
| | | 674 | 24 | ${}^1\text{A}_{1\text{g}} \rightarrow {}^1\text{A}_{2\text{g}}$ |
| $[\text{Cu}^{\text{II}}(\text{L})_2]\text{Cl}_2$ | 1.7 | 271 | 357 | $\pi \rightarrow \pi^*$ |
| | | 344 | 232 | CT |
| | | 448 | 156 | ${}^2\text{B}_{1\text{g}} \rightarrow {}^2\text{E}_{\text{g}}$ |
| $[\text{Zn}^{\text{II}}(\text{L})_2]\text{Cl}_2$ | diamagnetic | 269 | 888 | $\pi \rightarrow \pi^*$ |
| | | 302 | 601 | CT |

Table (4)
Antibacterial activities of the synthesised Schiff-base and metal complexes.

| Compounds | <i>Baeillus</i> (G+) | <i>Pseudomonase</i> (G-) |
|--|----------------------|--------------------------|
| L | +++ | ++++ |
| $[\text{Co}^{\text{II}}(\text{L})_2]\text{Cl}_2$ | ++ | +++ |
| $[\text{Ni}^{\text{II}}(\text{L})_2]\text{Cl}_2$ | +++ | +++ |
| $[\text{Cu}^{\text{II}}(\text{L})_2]\text{Cl}_2$ | +++ | +++ |
| $[\text{Zn}^{\text{II}}(\text{L})_2]\text{Cl}_2$ | + | +++ |

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الخلاصة

تضمن البحث تحضير الليكاند الجديد قاعدة شف [(2-Bromo-phenyl)-{3-[(2,4-dinitro-phenyl)-hydrazono]-1-methyl-butylidene}-amine] المشتق من 2,4-dinitrophenylhydrazine and المشتق مع acetylacetone with o-bromoaniline ثم مفاعلة مع بعض العناصر الفلزية باستخدام الميثانول وسطا للتفاعل وبنسبة (1:2) حيث تكونت معقدات جديدة ذات الصيغ العامة: $[M(L)_2] Cl_2$ حيث: $M = Co^{(II)}, Ni^{(II)}, Cu^{(II)}$ and $Zn^{(II)}$ وشخصت جميع المركبات بالطرق الطيفية التالية (الأشعة تحت الحمراء والأشعة فوق البنفسجية - المرئية ومطيافية الامتصاص الذري للعناصر، 1H NMR، ومحتوى الكلور ودرجات الانصهار)، مع قياس التوصيلية المولارية الكهربائية والفعالية البايولوجية، من النتائج أعلاه كان الشكل الفراغي المقترح لمعقدات الكوبالت والزنك هو رباعي السطوح بينما النحاس والنيكل تتخذ شكل المربع المستوي.