Synthesis, characterization and theoretical study of some transition metal complexes with N-(4-(dimethyl amino benzylidene)benzo[d]thiozal-2-amine)

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Abstract. In this paper, the cobalt(II), nickel(II), copper(II) and zinc(II) complexes were prepared with a new Schiff bases ligand and the three complexities were identified using infrared spectroscopy, UV and UV spectroscopy and atomic absorption spectrometry to diagnose the ratio of prepared elements and accurate diagnosis of carbon elements Hydrogen and nitrogen The physical properties of the record and its complexities such as color, temperature, electrical conductivity and magnetic properties were also studied. The ligand preparation was 2: 1 and all the prepared complexes were eight distorted surfaces. A theoretical study was also carried out to calculate the physical energies of the transitions.

1. Introduction
Schiff bases are compounds that contain a (C=N) bond where product from condensation primary amines with carbonyl compounds (aldehyde or ketone), Schiff bases reported by Hugo Schiff et.al. (1864). The most structural of these compounds is the azomethine group with a general formula RN=CH-R1, where R and R1 are alkyl, aryl, cyclo alkyl or heterocyclic groups. Azomethaine compounds have different names such as imine, ketimines when it is derived from ketone or aldimeine when it is derived from aldehyde, Benzylidene aniline, benzanil, and anil [1,2]. Schiff bases metal complexes play important rule in coordination chemistry as ligands because of their excellent donor abilities. There metal complexes have wide applications such as antibacterial, antifungal and other biological as well as clinical, industrial uses especially in catalysis, dying, and analytical chemistry [3,4]. Because of prefect selectivity, sensitivity and stability of Schiff bases for specific metal ions.

2. Preparation of The Ligand
A mixture of equimolar amount (0.09) mol of 2-amino benzothiazole and Dimethyl amino benzaldehyde in absolute ethanol (15 ml) with (3) drops of glacial acetic acid was refluxed in water bath for (3) hours. The reaction mixture was then allowed to cool room temperature, and the precipitate was filtered and dried, recrystallized from ethanol to give yellow crystals [5].

3. Preparation of Complexes
An amount of (0.321 g of CoCl2.6H2O, 0.277 g of NiCl2.6H2O, 0.122 g CuCl2.2H2O and 0.234 g ZnCl2 were dissolved in 10 ml of ethanol for each one and mixed with (0.93 g of ligand dissolved in 15 ml ethanol) in a molar ratio 1:2 refluxed for 3 hrs. The colored precipitates were filtered then washed with hot ethanol and dried by using desiccator at 60 °C. Elemental micro analysis data, color and yield for the complexes are given in Table (1).
4. Results and Discussion

Some physical properties of the ligand and new complexes are listed in Table (1), elemental microanalysis (C.H.N.), were in a good agreement with the calculated values.

Table 1. Elemental microanalysis and some physical properties of the complexes.

| Comp.        | Color    | Melting point (°C) | Yield % | C   | H   | N   | M   |
|--------------|----------|--------------------|---------|-----|-----|-----|-----|
| L (C6H12N3S) | Deep yellow | 160-163            | 84%     | 52.33| 3.44| 9.78| ----|
| L-Co         | Deep     | 210                | 73%     | 44.62| 3.32| 7.55| 8.70|
| (C32H32O2N3S2Co) | Brown | 222                | 65%     | 43.89| 2.34| 6.82| 8.86|
| L-Ni         | Brown    | 211                | 73%     | 44.78| 3.57| 7.44| 9.61|
| (C32H31O2N3S2Ni) | Yellow |                  | 70%     | 42.66| 3.88| 6.96| 9.25|
| L-Cu         | Dark     | 230                | 70%     | 41.55| 4.00| 7.11| 9.67|

4.1 The FTIR Spectrum of Ligand [L] and Complexes

The ligand [L] exhibited a strong high intensity bands appeared at 1662 and 1122.57 cm⁻¹ which were ascribed to the stretching mode of υ(C=N) and υ(C-N) groups. The weak absorption bands appeared at 3047.53cm⁻¹ assigned to υ(C=H) aromatic and 2904.80-2819 υ(C-H) aliphatic, Table (2) shows the FTIR of ligand. Schiff base behaved as a tetra- dentate ligand, which was been coordinating with the metal via nitrogen of azomethane group. FTIR spectra of the complexes.

abroad bands were observed a round (3353, 3435, 3322, 3455) cm⁻¹ in each of Co(II), Ni(II),Cu(II) and Zn(II) complexes spectra, which are assigned to the υ(O-H) (H2O), results led to a suggestion for the presence of coordinated water molecules[6]. New bands at (513.7,509.5, 543and 555) cm⁻¹ for metal complexes Co(II), Ni(II),Cu(II) and Zn(II) respectively. Refer to the coordination of the ligand to the central metal ion through nitrogen atom of imine group (M-N).

Table 2. Infrared data of Ligand and metal complexes (cm⁻¹).

| Comp. | υ(C=N) | υ(C-N) | υ(C-H) Ar | υ (C-H) Al | υ (O-H) H2O | υ(M-N) |
|-------|--------|--------|-----------|------------|-------------|--------|
| L     | 1662   | 1122.57| 3047.53   | 2904.8     | ----        | ----   |
| L-Co  | 1658.7 | 1126.4 | 3080      | 2912.5     | 3353        | 513.7  |
| L-Ni  | 1597.06| 1130.3 | 3089.9    | 2980       | 3435        | 509.5  |
| L-Cu  | 1658.9 | 1122.9 | 3090      | 2908       | 3322        | 543    |
| L-Zn  | 1654   | 1127   | 3088      | 2907       | 3455        | 555    |

4.2 Electronic Spectra of Ligand [L] and Complexes

The ultraviolet visible electronic spectrum of the ligand and complexes are given in Table (3). Electronic spectra of the all compounds were recorded in the range 190-1100 nm. The absorption spectrum of the one ligand observes absorption at 240 nm, which can be attributed to π→π* transitions of the Schiff base ligand [7]. The electronic spectra of Co(II) complexes show bands at 780,650 , 430 and 320 nm, which may be attributed to 4T1g(F)→4T2g(F),4T1g(F)→4A2g(f), 4T1g(F) → 4T1g (p), and charge transfer transitions, respectively.[8]

The electronic spectrum of the Ni(II) complex shows four absorption bands at 920,570,370 and 460nm which ascribed to the transitions 3A2g→3T2g(f) , 3A2g(f)→3T1g(f) , 3A2g(f)→3T1g(p) and charge transfer transitions respectively. The electronic spectra of Cu(II)ion complexes showed two
transitions at 750 and 450 nm, which are attributed to the electronic transition of 2B1g → 2B2g and because the distorted in octahedral geometry [9], Zn (II) ion complex showed one transitions at 320 nm to charge transfer, all complexes are octahedral geometry.

| Compounds | Absorption bands (cm⁻¹) | Assigned transition |
|-----------|-------------------------|---------------------|
| L         | 41,666                  | π-π*                |
|           | 27,027                  | n- π*               |
|           | 12,820                  | ⁴T₁g(F)→⁴T₂g(F)     |
|           | 15,384                  | ⁴T₁g(F)→⁴A₂g(f)     |
| L-Co      | 23,255                  | ⁴T₁g(F)→⁴T₁g(p)     |
|           | 31,250                  | Charge Transfer     |
| L-Ni      | 10,869                  | ³A₂g→³T₂g(f)        |
|           | 17,543                  | ³A₂g(f)→³T₁g(f)     |
|           | 27,027                  | ³A₂g(f)→³T₁g(p)     |
|           | 21,739                  | Charge Transfer     |
| L-Cu      | 13,333                  | ²B₁g → ²B₂g         |
|           | 22,222                  | Charge Transfer     |
| L-Zn      | 31,250                  | Charge Transfer     |

5. Theoretical study

5.1 Electrostatic potential

It designates the interaction of energy of the molecular system with a positive charge point, in order to find the most reactive sites of reaction in molecule positive charge species. They tend to attack a molecule wherever the E.P is powerfully negative electrophilic attach. The E.P of the free ligand is measured and plotted as 2D and 3D contour to inspect the reactive sites of the molecules and can be shown in Figure (1). The results of calculation illustrate that the LUMO of transition metal ion choose to react with the HOMO of donor atoms in ligand [10, 11], as represented in Figure (2) via adopting Hyperchem-8.07 program.
5.2 Optimized geometries and energy of ligand its Metal Complexes:
The program HyperChem-8.7 is used for the semi-empirical calculation at optimized geometries energies. The results of PM3 methods of calculation in gas phase for heat of formation (ΔH°f), binding energy (ΔEb) and total energy (ΔET) for the ligand and its complexes are calculated and tabulated in Table (4) [12,13,14]. Theoretically probable structures of metal complexes with ligand have been calculated to find the most possible model building stable structure [15]. The shapes appearing in Figure (3) indicate the calculation optima geometries for the imines and its complexes.

| Compound | ΔH°f (KJ.mol⁻¹) | ΔEb (KJ.mol⁻¹) | ΔET (KJ.mol⁻¹) |
|----------|----------------|----------------|----------------|
| L        | 347.27         | -16506.16      | -273161.78     |
| L-Co     | -1131.33       | -36201.94      | -682988.88     |
| L-Ni     | -635.46        | -35707.74      | -707052.15     |
| L-Cu     | -137.47        | -35117.22      | -720740.19     |
| L-Zn     | 482.12         | -34290.25      | -608643.17     |

Table 4. Conformation Energetic in (KJ.mol⁻¹) and for the Ligand and its Metal Complexes.
5.3 Optimized vibrational spectra for the Ligand and its Metal Complexes

Theoretically calculated wave numbers for the molecular show some deviations from the experimental values [16, 17, 18]. These deviations are generally acceptable in theoretical calculation and are described in (Table 5).

**Table 5. A Comparison between Experimental and Theoretical Vibrational Frequencies**

data for the Ligand and its Metal Complexes (cm⁻¹).

| Compound | \( \nu \text{C=N} \) | \( \nu \text{C-H} \) Aliph. | \( \nu \text{C-H} \) Arom. | \( \nu \text{C-N} \) | \( \nu \text{(O-H)} \) H₂O | \( \nu \text{M-N} \) |
|----------|----------------|----------------|----------------|----------------|----------------|------------------|
| L        | 1662           | 2904.80        | 3047.53        | 1122.57        | ----           | ----             |
|          | 1892\(^a\)    | 3067\(^a\)     | 3081.46\(^a\) | 1140\(^a\)     | ----           | ----             |
|          | 12.156\(^b\)  | 5.288\(^b\)    | 1.101\(^b\)    | 1.528\(^b\)    | ----           | ----             |
| L-Co     | 1658.7         | 2912.5         | 3080           | 1126.4         | 3353           | 513.7            |
|          | -1.387\(^b\)  | -0.085\(^b\)   | -0.162         | 0.845\(^b\)    | 7.298\(^b\)    | 0.638\(^b\)      |
|          | 1597.06        | 2980           | 3089.9         | 1130.3         | 3435           | 509.5            |
| L-Ni     | 1618\(^a\)    | 2973\(^a\)     | 3078\(^a\)     | 1125\(^a\)     | 3683\(^a\)     | 504\(^a\)        |
|          | 1.294\(^b\)   | -0.235\(^b\)   | -6.884         | -0.471\(^b\)   | 6.733\(^b\)    | -1.091\(^b\)     |
|          | 1658.9         | 2908           | 3090           | 1122.9         | 3322           | 543              |
| L-Cu     | 1684\(^a\)    | 3030\(^a\)     | 3078\(^a\)     | 1126\(^a\)     | 3721\(^a\)     | 561\(^a\)        |
|          | 1.490\(^b\)   | 4.026          | -0.389\(^b\)   | 0.275\(^b\)    | 10.722\(^b\)  | 3.208\(^b\)      |
|          | 1654           | 2907           | 3088           | 1127           | 3455           | 555              |
| L-Zn     | 1621\(^a\)    | 2825\(^a\)     | 3080\(^a\)     | 1123\(^a\)     | 3804\(^a\)     | 577\(^a\)        |
|          | -2.035\(^b\)  | -2.902\(^b\)   | -2.599         | -0.356         | 9.174\(^b\)   | 3.812\(^b\)      |

Experimental frequencies:
\(^a\) Theoretical frequencies
\(^b\) Error %

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