Synthesis And Characterization of New Manganese(II), Cobalt(II), Cadmium(II) and Mercury(II) Complexes with ligand [N-(3-acetylphenylcarbamothioyl)-2-chloroacetamide] and their Antibacterial Studies

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Abstract. Addition chloro acetyl isothiocyanate (C₃H₂ClNOS) with 3-Aminoaceto phenone (C₈H₉NO) to prepare a fresh Ligand [N-(3-acetyl phenyl carbamothioyl)-2-chloroacetamide](L). The ligand (L) behaves as bidentate coordinating through O and S donor with metal ions, the general formula of all complexes [M(L)₂(Cl)₂](M⁺₂=Manganese(II), Cobalt(II),Cadmium(II) and Mercury(II)). Compounds were investigation by Proton-1 ,Carbon -13 NMR spectra (ligand (L) only) , Element Microanalysis for C,N,H,O,S , Fourier-transform infrared , UV visible, Conductance , Magnetic susceptibility and Atomic Absorption (A.A). Based on spectral data, complexes appear octahedral geometry. The anti-bacterial activity of the complexes against two type of bacterial was higher than for free ligand.

1.Introduction

3-Aminoacetophenone is one of the most typical aromatic carbonyls which show a wide diversity and an important category of ligands in. chemistry coordination chemistry and the creation of large applications in various fields, such as bio chemistry, nonorganic chemistry and analytical chemistry. Several biological important acetophenone derivatives have been reported in peppers possess, anti-human immunodeficiency virus, antibacterial, antifungal, anti-inflammatory antitumor and antimicrobial [1,2]. Complexes of transition metals were used in different industries such as electro plating, leather tanning ,chemical industry, metal finishing, and others Thus these metals enter in water supply through industrial waste [3].The implication of metal chelation is carried in many important biological processes, where the coordination occurs between different metal ions and a broad range of ligands. As the transition metal complexes contribute a diverse and rich field of research, these complexes received much attention because of their applications in biology, medicine and industry[4]. complexes of Schiff bases and Schiff bases which prepared from reaction primary amines and acetophenone derivatives, have been used as bioreactors to open the door for important research to be consider among chemists to record important factors in solving the recent problems in the living [5].The ligand type [HL], has been prepared from Isatin and 3-aminoacetophenone in the presence of KOH. This ligand has been used to prepare Nickel(II) and Cobalt(II) complexes in the ratio of (1:1)
metal-ligand. All compounds have been characterized by spectroscopic methods FTIR, UV-Vis, C.H.N, thin-layer chromatography, mass spectrum, X-ray diffraction, magnetic moment, conductivity measurements and melting point[6]. Chain of new complexes of Copper(II), Nickel(II) and Zinc(II) are synthesized from the Schiff base ligand derived from 2-amino benzaldehyde with 3-amino acetoephone and investigated by elemental analyzer, cyclic voltammetry(CV), conductivity, and spectroscopic methods,(UV-Vis, IR, NMR and MS) biological efficient of the ligand and its complexes has been studies against various types of bacterial [7]. Synthesis Cobalt(II), Nickel(II) and Copper(II) complexes with ligand Schiff base the reaction between the new derived from Salicylaldehyde, 3-amino acetoephone The compounds were investigation by UV-vis, FT-IR, 1H-NMR spectroscopes, magnetic susceptibility and molar conductivity [8]. The purpose of this work is to synthesis and identification a new ligand [N-(3-acetylphenyl carbamothioyl)-2-chloroacetamide](L), and it's Manganese(II), Cobalt(II), Cadmium(II) and Mercury(II) metal complexes.

2. Experimental

2.1 Materials and reagents

All solvents, reagents, chemical and metal chloride salts from BDH, Merck and Fluka com are commercially available and used as received without purification.

2.2 Physical measurements.

1H and 13C–NMR spectra were registered by using Ultra Shield 300 MHz Switzerland at University of Al al-Bayt, Jordan. Melting point was recorded by using Stuart melting point apparatus. FT-IR spectra have been registered at (4000-400) cm\(^{-1}\) range and(4000-200)cm\(^{-1}\) range of ligand and metal complexes on a Shimadzu IR-470 spectrum used KBr and CsI pellets. UV-160 Shimadzu spectrophotometer at 25 C for 10\(^{-3}\)M solution DMSO with 1.000 ± 0.001 cm matched quartz cell was used to obtain electronic spectra Philips PW. Digital was used to measure the molar conductivity at 25 C for 10\(^{-3}\)M solution of DMSO Micro elemental analysis(C,H,N,S) were performed using AcrolErba 1106 elemental analyzer. Magnetic susceptibility measurements were obtained by balance magnetic susceptibility model MSB-MKI. Metal contents of the complexes were determined by atomic absorption technique by using Shimadzu (AA680G ).

2.3 Method for the preparation of ligand.

The ligand was prepared by two steps(Scheme-1)

![Scheme 1. Preparation way for the ligand (L)](image)
2.3.1 Preparation of the (Chloro acetyl isothiocyanate) [9]

Mixture of chloro acetyl chloride(C₂H₂Cl₂O) (2.07ml, 26mmol) and ammonium thiocyanate(CH₄N₂S) (2g, 26mmol) in (25 ml) of acetone was stirred under refluxed for 3 hrs and then filtered, the filtrate was used in the subsequent step.

2.3.2 Preparation of [N-(3-acetylphenylcarbamothioyl)-2-chloroacetamide] (L)

(3.6g, 26mmol) of 3-aminoacetophenone(C₈H₉NO) in (20ml) acetone was quickly added to chloro acetyl isothiocyanate(C₃H₂ClNOS) and left under reflux for 6 hours, after which the solid precipitate back was collected, washed with acetone and re-crystallized from ethanol, yield (85.3%), (m.p=120-122°C). C% found (48.82) calc.(48.80), H% found (4.16) calc.(4.10), N% found (10.22) calc.(10.35), S% found (11.55) calc.(11.84).

2.4 Method for the synthesis of metal complexes

2.4.1 Synthesis of the [Mn(L)₂Cl₂] complex.

Add the ethanol solution (10ml) of MnCl₂.4H₂O (4.42g, 26mmol) to the ethanol solution (10ml) of the ligand (6.50g, 26mmol)(L). The mixture was stirred for 6 hours at room temperature, and the dark green precipitate back was collected, washed with H₂O and C₂H₅OH mixture (1:1) and re-crystallized with C₂H₅OH and placed in an oven at 50°C to dry.

2.4.2 Synthesis of [Co(L)₂Cl₂], [Cd(L)₂Cl₂], [Hg(L)₂Cl₂] complexes.

The complexes of [Co(II), Cd(II) and Hg(II)] ions with(L) were prepared in the same way as the manganese complex. Most of the physical data of all complexes are listed in the Table (1)

| Compound | M.wt (gm/mole) | Color | M.P(°C) or dec. | M% Calculation (Found) | Molar Cond. Ohm⁻¹cm²mol⁻¹ in DMSO | µeff (B.M) |
|----------|----------------|-------|-----------------|------------------------|-----------------------------------|------------|
| C₁₁H₁₁N₂O₂SCl \( (L) \) | 270.5 | Yellow | 120-122 C | - | 2.2 | - |
| [Mn(L)₂Cl₂] | 727.45 | green | 280-282 C | 7.55 (7.53) | 17 | 5.95 |
| [Co(L)₂Cl₂] | 731.45 | green | 272-274 C | 8.06 (8.02) | 16 | 4.82 |
| [Cd(L)₂Cl₂] | 784.93 | Yellow | 236-238 C | 14.32 (14.96) | 12 | 0 |
| [Hg(L)₂Cl₂] | 873.10 | Yellow | 296 (dec) | 22.97 (22.85) | 15 | 0 |

Dec.=decomposition
3. Results and Discussion

3.1 Ligand (L)

Proton-1 Nuclear magnetic resonance spectra of free ligand (L), Fig. (1) which was recorded in CD$_3$-CS-CD$_3$ solvent display the signals: single peak at (1.63) ppm of (3H, CH$_3$CO), single peak at (2.42) ppm of (Dimethyl sulfoxide), single peak at (3.78) ppm of (2H, CH$_2$Cl), single peak at (3.92) ppm of (1H, N-Hsec.NH$_2$), multiple peaks at (6.42-8.68) ppm of aromatic protons, single peak at (10.5) ppm of (1H, N-Hsec amide).

![Figure 1. $^1$H-NMR spectrum of ligand (L)](image)

Carbon-13 Nuclear magnetic resonance spectrum of the free ligand (L) Fig. (2) which was recorded in CD$_3$-CS-CD$_3$ solvent display the signals: single peak at (26.25) ppm of (CH$_3$CO), signal peak at (40.00) ppm of (Dimethyl sulfoxide), single peak at (54.75) ppm of (CH$_2$Cl), signals at (110.99-132.07) ppm of aromatic carbons, signal peak at (166.25) ppm of (CONH), signal peak at (172.50) ppm of (CS), signal peak at (197.50) ppm of (COCH$_3$) [10,11].

![Figure 2. $^{13}$C-NMR spectrum of ligand (L)](image)
The Fourier-transform infrared spectrum of the free ligand (L), Fig (3), displays bands at (1685) cm⁻¹ and (1168) cm⁻¹ to (CO amide) and (CS) respectively. While the other absorption band appears at (3138) cm⁻¹ could be explained as NH[12-14]. The Fourier-transform infrared spectral data of the free ligand were recorded in Table (2).

![](image)

**Figure 3. Infrared spectrum of ligand (L)**

| Compound          | υ(N-H)  | υ(C=O) Amide | υ(C=S) | υ(M-O) | υ(M-S) | υ(M-Cl) |
|-------------------|---------|-------------|--------|--------|--------|--------|
| Ligand (L)        | 3138(s) | 1685(s)     | 1168(m)|        |        |        |
| [Mn(L₂Cl₂)]      | 3135(s) | 1616(s)     | 1205(s)| 455(m) | 418(w) | 253(w) |
| [Co(L₂Cl₂)]      | 3137(m) | 1620(m)     | 1230(s)| 453(m) | 416(m) | 279(m) |
| [Cd(L₂Cl₂)]      | 3140(m) | 1611(s)     | 1238(m)| 450(m) | 424(m) | 261(w) |
| [Hg(L₂Cl₂)]      | 3135(s) | 1625(m)     | 1215(s)| 445(s) | 422(w) | 260(w) |

s=strong         m=medium     w=wee
The Ultraviolet–visible spectrum of (L). Fig. (4) shows strong absorption peak at (33898) cm\(^{-1}\) which can return to the electronic transition class \(^*\) [15]. In the Table (3), the electronic spectrum data for the (L) were developed.

![Figure 4. U.V. spectrum of ligand (L)](image)

**Table 3. The peaks electronic transitions and structure geometries of the ligand (L) and its complexes**

| Compounds    | \( \lambda_{\text{max}} \) nm | Wave number \( \text{cm}^{-1} \) | ABS \( \epsilon_{\text{max}} \) molar\(^{-1}\)cm\(^{-1} \) | Transitions |
|--------------|-------------------------------|----------------------------------|-----------------------------------|-------------|
| Ligand (L)   | 295                           | 33898                           | 2.246                             | 2246 \( \rightarrow \) * |
| \([\text{Mn}(L)_2\text{Cl}_2]\) | 294                           | 34013                           | 2.212                             | 2212 \( \text{Intra ligand} \) |
|              | 893                           | 11198                           | 0.018                             | 18 \( ^6\text{A}_{1g} \rightarrow ^4\text{T}_{2g(G)} \) |
|              | 932                           | 10729                           | 0.011                             | 11 \( ^6\text{A}_{1g} \rightarrow ^4\text{T}_{1g(G)} \) |
| \([\text{Co}(L)_2\text{Cl}_2]\) | 295                           | 33898                           | 2.258                             | 2258 \( \text{Intra ligand} \) |
|              | 365                           | 27397                           | 0.424                             | 424 \( \text{C.T mixed with} ^4\text{T}_{1g(F)} \rightarrow ^4\text{T}_{1g(P)} \) |
|              | 673                           | 14858                           | 0.019                             | 19 \( ^4\text{T}_{1g(F)} \rightarrow ^4\text{A}_{2g} \) |
|              | 839                           | 11918                           | 0.011                             | 11 \( ^4\text{T}_{1g(F)} \rightarrow ^4\text{T}_{2g(F)} \) |
| \([\text{Cd}(L)_2\text{Cl}_2]\) | 291                           | 34364                           | 2.273                             | 2273 \( \text{Intra ligand} \) |
| \([\text{Hg}(L)_2\text{Cl}_2]\) | 289                           | 34602                           | 2.321                             | 2321 \( \text{Intra ligand} \) |
|              | 365                           | 27397                           | 1.728                             | 1728 \( \text{Intra ligand} \) |
4. The ligand complexes

By studying the prepared complexes, it was found to be thermally stable and dissolve in some solvents such as DMF, DMSO. From the data listed in the table (1), each the prepared complexes have the non-electrolytic nature of DMSO solvent in $10^{-3}$M at $25^\circ$C [16]. The theoretical and practical results of atomic absorption measurements for all prepared complexes were approximated.

5. FT-IR Spectra of complexes

The FT-IR spectra showed various bands, Fig.(5) relationship to the stretch vibration of (CO amide) limit between (1625-1611) cm$^{-1}$ shifted low frequencies by (74-60) cm$^{-1}$ proposed the coordination of ligand by the (O atom) at the (CO group) [17]. While the band give rise to by (CS) showed between (1238-1205) cm$^{-1}$ shift to high frequencies by (70-37) cm$^{-1}$ which due to the co-ordination of ligand by the (S atom) at the (thiol group) to the centric ion [18]. The stretching vibration band (NH) display no or very small shifting in their frequencies (3140-3135) cm$^{-1}$. There for indicating do no co-ordination with the metal ion. M-O, M-S and M-Cl bonds shows around (455-445) cm$^{-1}$, (424-416) cm$^{-1}$ and (279-253) cm$^{-1}$ respectively [19]. Table (2) describes the bands of all prepared complexes.

![Figure 5. Infrared spectrum of complex [Co(L)$_2$Cl$_2$]](image-url)
6. Electronic spectra of complexes

The spectrum of Manganese (II) display band at (34013) cm⁻¹ of intra-ligand and other bands at 11198 cm⁻¹ and 10729 cm⁻¹ which are display the electronic transfer $^6A_1g \longrightarrow ^4T_2g(G)$ and $^6A_1g \longrightarrow ^4T_1g(G)$ respectively, proposed octahedral around Manganese (II) ion.[20]. The Cobalt (II) complex gave four bands at 33898, 27397, 14858 and 11918 cm⁻¹ attributed to intra-ligand, C.T mixed with $^4T_{1g}(F)$, $^4T_{1g}(P)$, $^4A_{2g}$ and $^4T_{2g}(F)$ respectively, proposed octahedral around Cobalt (II) ion [21]. The Cadmium(II) and Mercury(II) complexes show only C.T of M→L in range 34602-27397cm⁻¹[22,23]. All transitions included in Table 3.

![Figure 6. U.V. spectrum of complex [Cd(L)2Cl2]](image)

7. Magnetic moment of complexes

On the basis of effective magnetic moment(μeff) values of the manganese and cobalt complexes (5.95and4.82)B.M listed in the Table (1), It was found to be high spin octahedral complexes.[24]

8. Biological Activity of the ligand (L) and its Complexes

The biological activity for the ligand(L) and its complexes were studied using inhibition method[25-26],two types of bacteria (+) (Staphylococcus aureu) and (-) (Escherichia coli). In concentrations prepared, ligand (L) and its complexes display high efficacy to inhibit the spread of bacteria. The data obtained are found in the table(4),Fig.(7)
Table 4. Showed the inhibition circle diameter for the bacteria after 24 hrs in cubation paid and 37 (°C).

| Compound   | Diameter of inhibition zone (mm) |
|------------|----------------------------------|
|            | Staphylococcus Aureus (gram positive) | Escherichia Coli (gram negative) |
| L          | 6                                 | 5                                 |
| [Mn(L)₂Cl₂] | 8                                 | 12                                |
| [Co(L)₂Cl₂] | 14                                | 15                                |
| [Cd(L)₂Cl₂] | 24                                | 25                                |
| [Hg(L)₂Cl₂] | 31                                | 32                                |

Figure 7. Effect of Staphylococcus Aureus(+) Escherichia Coli(−) on ligand (L) and their complexes

9. Conclusion

The octahedral geometry of the prepared complexes was proposed on the basis of the spectral studies (¹H-¹³C NMR for ligand(L)only), conductance and magnetic moment for the compounds. It is also found the ligand(L) exhibit as a bi dentate on co-ordination with Manganese(II), Cobalt(II), Cadmium(II) and Mercury(II) ions by(O atom) of (CO amide) and (S atom) of(CS thiol), Fig.(8).
10. References

[1] Rasheed, R.T.; (2012) “Synthesis of new metal complexes derived from 5-nitroso 8- hydroxyl quinoline and salicylidene P-imino acetophenone with Fe(II), Co(II), Ni(II) and Cu(II) ions", Journal of Al-Nahrain University; 15(4): 68-73.

[2] Alam, M.A.; Hossain, M.N. and Nazimuiddin, M.(2013) “Synthesis, Characterization and Antimicrobial Activity of Metal Complexes of Schiff’s Base Derived from S-benzyl thiocarbazate with 2-hydroxyacetophenone” Chemistry Journal, 3(1) :13-19.

[3] Praveen, K.T. and Sulekh, C.; (2011) “Chromium(III) ion selective PVC membrane electrode based on a Schiff base ligand, 3-aminoacetophenonethiosemicarbazone ”,Anal. Bioanal. Electro Chem.; 3(2): 119-133.

[4] Momle, R. G.; Vedpathak, S.G. and Kakade, G. K.;(2018) “antimicrobial potential of schiff base metal complexes: an overview”, ejpmr; 5(3): 225-235.

[5] Maihub, A.A.; El-ajaily,M.M.; (2018) “Synthesis, Characterization and Biological Applications of Schiff Base Complexes Containing Acetophenone or Resemblance Compounds”, To Chemistry Journal; 1(1): 19-37.

[6] Alsalihi, E. I. and Al-Fahdawi, A.S. ; (2018) “Synthesis and Antibacterial Activity of Isatin Schiff Base Derivative with 3-Aminoacetophenone and its NiII, CoI Transition Metals Complexes", The Scientific Journal of Koya University ; VI(1) : 38-45.

[7] Geetha, S. and Sumathi, N; (2017)“Synthesis, Spectral Characterization and Biological Activity of Cu(II), Ni(II) and Zn(II) Schiff Base Complexes derived from 3-Aminoacetophenone”, JCHPS , 1: 6-11.

[8] Kadhim, S.H;Abd-Alla, I.Q. and Hashim, T.J.;(2017)“Synthesis and Characteristic Study of Co(II), Ni(II) and Cu(II) Complexes of New Schiff Base Derived from 4-Amino Antipyrine”, International journal of chemical sciences,15(1):1-9.

[9] Kabbani, A.; Ramadan, H. and Hanuom, A.; (2005) “Synthesis of some metal complexes of N-[(benzoyl amino)-thioxomethyl] amino acid (HL)”; Journal of the University of Chemical Technology and Metallurgy,40(4): 339-344.

[10] Seenniah, D.; Venkatesh, B.C.; Padmaja, A.and Padmavathi, V.; (2013)“Synthesis of some new oxazolinyl/thiazolinyl/imidazolinyl- benzoxazoles, benzothiazoles and benzimidazoles” ,Indian Journal of Chemistry , 52B : 942-948.
[11] Ahmad, S. and Amr,M.;(2018)“Preparation, Characterization and Antimicrobial Activity of Schiff Base of (E)-N-(4-(Thiophen-2-ylmethyleneamino) Phenylsulfonfyl) Acetamide Metal Complexes”; The Open Bioactive Compounds Journal, 6: 1-10.

[12] Sarhan, B.M.; Lateef, S.M.; Waheed, E.J., (2015) “Synthesis and Characterization of Some Metal Complexes of [N-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylcarbamothioyl) acetamide]”; Ibn Al-Haitham J. for Pure & Appl. Sci, 28 (2) :102-115.

[13] Silverstein, R.M. ; Bassler, G.C. and Morrill, T.C;(1981) “Spectroscopic identification of organic compounds”, 4th Ed., John Wiley and Sons, New York.

[14] Sarhan, B.M.; Lateef, S.M.; Waheed, E.J.,(2016) “Synthesis and characterization of some new metal complexes of [N-(3-acetylphenylcarbamothioyl)-4-methoxybenzamide]’; DJPS, 12(1): 28-42.

[15] Dyes, R.J; (1996) “Application of absorption spectroscopy of organic compounds”, Prentice – Hall, Inc., Englewood cliffs,N.J.London.

[16] Yu-Ye, Y. and Jian-Feng, L.; (2009)“Synthesis, Characterization, Crystal Structure and Antibacterial Activities of Metal ion(II) Complexes of the Schiff Base 2-[4-Methylphenylimino)methyl]-6-methoxyphenol” ; Molecules, 14: 1747-1754.

[17] Nakamoto, K; (1996) “Infrared spectra of inorganic and coordination compounds”, 4th Ed., John Wiley and Sons, New York.

[18] Sarhan, B.M.; Waheed, E.J.; Kadhim, N.J.;(2016)“Synthesis and Characterization of Some Metal Complexes of[2-chloro-N-(1,5-dimethyl-3-oxo-2-phenyl-2,3-dihydro-1H-pyrazol-4-ylcarbamothioyl)acetamide] Journal University of Karbala, 14(3):91-101.

[19] Nawar, N.; El-swah, I., Hosny, N.M. and Mostafa, M.M., (2011) “Novel mono-and binuclear complexes derived from N-benzoyl-N-glycylthiourea(BGH)with some transition metal ions”, Arabian Journal of chemistry,17(1):434–438.

[20] Sarhan, B .M.; Abed, A.H. and Rumez, R.M. (2013) “Synthesis and characterization of some mixed ligand complexes of quinaldic acid and -picoline with some metal salts”; AL-Mustansiriyah Journal of science,24(4): 65-74.

[21] Lever, A.B.P.; (1968) “Inorganic electronic spectroscopy”, Elsevier publishing company Amsterdam, London, New York.

[22] Arjmamd,F.; Parveen,S. and Mohapatra,D.K. (2012) “Synthesis, characterization of Cu(II) and Zn(II) complexes of proline-glycine and proline-leucine tetrpeptides:in vitro DNA binding and cleavage studies”, Inorg.Chem.Acta,388(15): 1-10.

[23] Naik,A.D.; Beck,J.; Dirtu,M.N. and Bebrone,C. (2011) “Zinc complexes with 1,2,4-triazole functionalized amino acid derivatives, synthesis, structure and -lactamasessay”, Inorg.Chem.Acta,368: 21-28.

[24] Mulay,L., (1977) “Magnetic Susceptibility”, John wiley and sons; New York;part1,vol(4).

[25] Tauber, S. and Nau, R. (2008) “Immunomodulatory properties of antibiotics”, Current molecular pharmacology, 1: 68-75.

[26] Neha, M.; Imran, A. and Ashok, K., (2014)“Biological Activities of Some New Environmentally Safe 2- Amino benzothiazole Complexes of Copper (II) Derived Under Microwave Irradiation”, International Archive of Applied Sciences and Technology, 5 : 37-42.