Application of salicylaldehyde based-metal binuclear dithiocarbamate complexes for iron and copper removal from wastewater

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Abstract: This research includes synthesesation and characterization of dinuclear transition metal(II) macrocyclic dithiocarbamate complexes (DTC) of the general formula [M(L)]2, where M(II) could be Mn, Fe, Co, Ni, Cu, and Zn, while L is the potassium mono-dithiocarbamate. Then, these complexes were used to remove iron and copper from wastewater. DTC complexes are prepared via a one-pot reaction by mixing secondary amine, CS2, KOH, and metal chloride. All compounds are characterized by FTIR, UV-visible, mass spectra, magnetic moment, conductance, melting point, mass spectroscopy, and 1H, 13C-NMR spectroscopy. The complexes of divalent metal ions appear to be tetrahedral geometry for Fe(II), Co(II), and Zn(II) complexes, while octahedral geometry is suggested for Mn(II), Ni(II), and Cu(II) complexes. The ligands showed effective Cu and Fe removal efficiency of up to 75.96, 48.9% from wastewater.

1. Introduction
Usually, the use of chemicals in our lifestyle has caused environmental degradation and emissions. Heavy metals are one of the possible contaminants that pose problems and hazards to the environment and living organisms. Therefore, scientists are searching for ways to reduce those risks [1]. Dithiocarbamate ligands are widely used as scavengers for effective heavy metal ions removal owed to their strong binding with metal ions [2]. Dithiocarbamates (DTCs) are a common compound class that is complexed with metal ions due to the existence of CS2 moiety, which may interact with a variety of transition metal ions in a mono- or bidentate manner. Furthermore, dithiocarbamate transition metal complexes, prepared from a variety of new ligands, have been the subject of research groups for more than ten decades. Dithiocarbamates(DTC) are an important species that can be prepared from the reaction of an analogous CS2 molar ratio with an aqueous or alcoholic amine solution with an appropriate base, such as KOH, as in the following equation [3]:

$$RR'NH + CS_2 \xrightarrow{KOH} K^+S_2CNRR' + H_2O$$ (1)

Where R = Alkyl and R' = H or Alkyl

Recently, dithiocarbamates have received growing attention due to their extensive uses in the agricultural, industrial, biomedical, and analytical chemistry fields [4]. The metal pollution in water leads to grave effects on public health as it cause many serious damages to the organs of human beings, such as kidneys and liver damages, along with serious diseases [5, 6], therefore; many studies were done to remove metals from water [7, 8], control the discharged amount of heavy metals with the wastewaters [9-11], or to estimate the
concentration of metals in the sediments and/or waters of rivers [6, 12]. Also, a considerable number of treatment techniques were developed for remediation of water from pollutants; including adsorptions [13-15], natural and artificial coagulants [16-18], electrolyzing of solutions [19-23], and combined methods [24-28]. A considerable number of these methods are either not efficient or unaffordable [29-32], also the extra wastewater loads due to the increase in the inhabitants of the cities [33-36], industrial and agriculture activities [31, 37], or the climate change [38-42] that also resulted from the activities of mankind [43-48].

In this framework, this paper explains the synthesisization and application of ligand and its dinuclear macrocyclic complexes in the removal of heavy metals from water. The efficiency of the ligand in the removal of metals from water has been measured using atomic absorption spectroscopy and IR technology.

2. Experimental

2.1 Materials
All the chemicals used in this research were provided by Aldrich and Fluka Companies. They were of high quality and purity and did not need to be purified.

2.2. Physical measurements
Conductivity measurements of the complexes are conducted for (10^{-3} \text{ mole L}^{-1}) solution of the samples in DMSO using Ohaus, Starter 3100C. FTIR spectra were recorded using IR-Prestige-21 spectrophotometer in range(4000-400 \text{ cm}^{-1}). The spectra are obtained as KBr discs. Magnetic moments were measured at 25°C with the Balance Magnetic Susceptibility Model -M.S.B Auto. The melting points of the compounds are carried out using an Electro-Thermal Stuart melting point DMP-500. ¹H,¹³C NMR spectrum are registered on a Bruker 400.77,400.13MHz. Mass spectra were obtained by Agilent GC-MS. UV-visible for ligands and their complexes are measured in the region (200-900) nm using JASCO-V-650 Spectrophotometer, in DMSO solutions, with (10^{-3} \text{ M}).

3. Synthesis

3.1 Preparation of Schiff-base 2,2’-(butane-1,4-diylbis(azanlylidene)) bis(methaneylidene) diphenol
Salicylaldehyde (1.2ml, 11.34 mmol) are added with stirring to a mixture of 1,4-diaminobutane (0.5g, 5.67mmol) dissolved in MeOH (25ml), and then 3-4 drops of hydrobromic acid is added to the solution. The mixture is permitted to reflux for 2 h, and then filtered off. A yellow solid is formed which is collected by filtration. Yield: 1.344g (80.9%), IR data (cm^{-1}): 3051 ν(C-H); 1631 ν(C-N); 1577 ν(C=C). ¹H NMR (δ, ppm) Figure (1) : 1.7 (C₉,9’–H), 6.86-7.44 (Ar-H), 13.63 (O-H), 8.57 (C₇,7’–H).¹³C NMR Figure (2): 28.5, 58.36, 116.9, 118.8, 119, 132, and 166.34 ppm.
3.2 Preparation of secondary amine 2,2-((butane-1,4-diylbis(asanediyl))bis(methylene)) diphenol

To a solution of Schiff base (0.5g, 1.689mmol) in 20mL of dichloromethane:ethanol (1:9), is added cautiously NaBH₄ (0.322g, 8.446mmol) in small portions. The reaction mixture is stirred at 0°C for 1 h. Add distilled water (200mL) and extract the product into CH₂Cl₂ (4 × 50mL) and dry over CaCO₃. After the filtration and removal of the solvent by evaporation, the resulting was washed with diethylether. The product as a white solid. Yield: 0.698g (68.9%).

IR (KBr, cm⁻¹) 3289 ν(N-H); 1091.7 ν(C-N); 3035.9 ν(C-H); 1604 ν(C=C).

1H NMR (δ, ppm): 1.47 (C₉, 9’–H), 6.66-7.14 (Ar-H), 3.83 (N-H).

13C NMR Figure (2): 28.5, 58.36, 116.9, 118.8, 119, 132, and 166.34 ppm.

3.3 Synthesis of potassium mono((4-(((sulfaneyl)cabonothioyl)2 hydroxybenzyl)amino)butyl)(2-hydroxybenzyldithiocarbamate

To a solution of secondary amine (1) (0.5g, 1.67mmol) dissolved in ethanol (25mL), an excess of KOH 4eq (0.376g, 6.72mmol)dissolved in (5mL) of ethanol is added stirring. The mixture is held for 15 min in an ice bath with stirring, and then a solution of CS₂ 5eq (0.639g, 8.4mmol) was added drop-wise with stirring for 2 h. The potassium dithiocarbamate salt obtained was collected by filtration. Yield: 0.73g , 82.95%). IR (KBr, cm⁻¹) 3389 ν(O-H); 1365 ν(C-N); 3028 ν(C-H); 1581 ν(C=O), 1489 ν(N-CS₂), 1126-1087 νᵥᵥ(C=S). 1H NMR Figure (3) (δ, ppm): 1.47 (C₉, 9’–H), 6.66-7.04 (Ar-H), 3.83 (N-H). 13C NMR Figure (4): 28.5, 58.36, 116.9, 118.8, 119, 132, and 166.34 ppm.

The GC-mass spectra, figure(5) of L exhibited the parent
ion peak at m/z = 529 corresponding to \( C_{20}H_{22}K_2N_2O_2S_4 \). Peaks detected at 490 and 451 corresponding to m/z-K and m/z-K2, respectively.

Figure 3. \(^1\)H NMR spectrum of the ligand of DMSO.

Figure 4. \(^{13}\)C NMR spectrum of the ligand of DMSO.

Figure 5. Mass spectra of the ligand of DMSO.

3.4 **General one-pot synthesis of the complexes**

To a solution of the secondary amine dissolved in ethanol, is added an excess of KOH with stirring. To this reaction mixture, CS2 is added dropwise. The mixture was stirred for 30 min in an icy bath allowing the potassium dithiocarbamate salt to be formed. Then, dropwise, a solution of metal salt in ethanol is added. The reacting mixture is left for 24h with stirring at room temperature overnight. This results in the formation of precipitated that is filtered, collected, washed with profuse of methanol, and dried to give the desired macrocyclic complex. Molar conductivity, color, and yield for the complexes are given in (Table 1).
Table 1. Colour, yield, melting point, and molar conductivity of Complexes.

| Compound       | Metal salt (g) | Weight of complexes | M.Wt | Yield (%) | Colour | m.p. °C | (Ω⁻¹ cm² mol⁻¹) |
|----------------|----------------|---------------------|------|-----------|--------|---------|-----------------|
| L              | 0.73           | 529                 | 82.9 | Beige     | 190-193| -       |                 |
| [MnL(H₂O)]₂    | 0.197          | 1082                | 68.6 | Brown     | 220-224| 0.18    |                 |
| [FeL]₂         | 0.27           | 1012                | 65.2 | Dark red  | Over300| 19.68   |                 |
| [CoL]₂         | 0.237          | 1018                | 61.4 | Green     | 250-252| 14.1    |                 |
| [NiL(H₂O)]₂    | 0.237          | 1090                | 62.6 | Light green | Over300| 9.48    |                 |
| [CuL(H₂O)]₂    | 0.24           | 1099                | 72.8 | Green     | Over300| 204*    | 27.5            |
| [ZnL]₂         | 0.244          | 1031                | 54.6 | Whit      | 223-226| 25.3    |                 |

*Decomposed

3.5 Removal of the heavy metals from aquatic solution

The wastewater is treated by adding 0.04gm of Potassium dithiocarbamate. The mixture is allowed stirred for 20 minutes at 25 °C. The metal complexes are extracted by filter paper. The absorbance of the heavy metal in the aqueous phase is measured by atomic absorption and is contrasted with the mother's absorbance solution (Cu²⁺(5.5472 ppm) and Fe²⁺(30.344 ppm)) [49].

4. Results and Discussion

The synthesis of the ligand is based on the use of the secondary diamine as starting materials for the preparation of the dithiocarbamate compounds (DTC). The secondary diamine was prepared in two steps; (i) condensation of dialdehyde with a primary diamine in methanol, resulting in the formation of the Schiff base, and (ii) reduction of the Schiff base using NaBH₄ in methanol. (Scheme 1), were prepared by mixing Schiff base, CS₂ and KOH in ethanol. The resulting bis secondary amine is reacted with KOH, CS₂, and metal(II) salt to produce the bis-metallic macrocyclic complexes. The dinuclear DCT based macrocyclic complexes are air-stable solid, completely soluble in DMSO, and not soluble in other organic solvents. The molar conductance of solutions of the complexes in DMSO is indicative of their non-electrolytic nature [50].

4.1 FTIR

The FTIR spectra of L and its complexes [ML]₂; (when M=Mn²⁺, Fe²⁺, Co²⁺, Ni²⁺, Cu²⁺, Zn²⁺) are collected together in Figure (6, 7) respectively. The spectrum exhibited a band at 3367.71 cm⁻¹ corresponds to ν(O-H) [10]. The spectrum shows the peak at 1581 cm⁻¹ ascribed to ν(C=C) of the aromatic ring. Moreover, the new peak at 1489 cm⁻¹ is assigned to ν(C-N) stretching of

Scheme 1. Synthesis route of the ligand.
(N-CS$_2$) [51]. The FTIR spectra expose two new bands at 1126 and 1087 cm$^{-1}$ ascribed to $\nu$(C-S) and $\nu$(N-C$_2$S), respectively of carbon disulfide. The assignment of bands is collected in Table (2). The important regions in the FTIR spectra of the dinuclear macrocycles are based on checking bands in the range 350–400, 950–1050, and 1450–1550 cm$^{-1}$. The bands around 350–400 cm$^{-1}$ are associated with $\nu$(M-S), while, the bands around 950–1050 cm$^{-1}$ are related to the $\nu$(C-S) stretching frequency. The third region is connected to the (C-N) of the (NC$_2$S$_2$) band, about 1450-1550 cm$^{-1}$. As a consequence of a polar structure such as (N=CSS), the existence of a band about 1500 cm$^{-1}$ is expected [51]. This structure would be stabilized by increasing the electron-donating character in the alkyl group and the $\nu$(C-N) wavenumber would increase [52].

| Compound   | $\nu$(O-H) | $\nu$(C-H) | $\nu$(C=H) | $\nu$(C=O) | $\nu$(N-C$_2$S$_2$) | $\nu$(CH$_2$) | $\nu$(C=N) | $\nu$(CS$_2$) |
|------------|------------|------------|------------|------------|---------------------|--------------|------------|--------------|
| L$_1$      | 3367       | 3028       | 2939       | 1581       | 1489                | 1404         | 1365       | 1126, 968    |
| [Mn(L)(H$_2$O)$_2$]$_2$' | 3321       | 3078       | 2939       | 1593       | 1454                | 1427         | 1354       | 1103, 956    |
| [Fe(L)]$_2$ | 3325       | 3097       | 2939       | 1593       | 1477                | 1427         | 1350       | 1099, 960    |
| [Co(L)]$_2$ | 3336       | 3066       | 2939       | 1593       | 1489                | 1427         | 1354       | 1099, 956    |
| [Ni(L)(H$_2$O)$_2$]$_2$' | 3360       | 3035       | 2927       | 1593       | 1496                | 1431         | 1357       | 1095, 960    |
| [Cu(L)(H$_2$O)$_2$]$_2$ | 3240       | 3083       | 2939       | 1597       | 1496                | 1454         | 1354       | 1099, 960    |
| [Zn(L)]$_2$ | 3356       | 3048       | 2939       | 1585       | 1492                | 1427         | 1365       | 1095, 960    |

* $\nu$(Ni-S) observed at 462 and 435 cm$^{-1}$

* $\nu$(Mn-S) observed at 474 and 459 cm$^{-1}$

Figure 6. FTIR Spectra of the ligand.
4.2. UV-visible spectrum and magnetic moments
The UV-vis spectrum showed a wide peak at the range (257-282) and (341-471) nm apportioned to intra-ligand and charge transfer (CT) transitions, respectively in the complexes. The spectrum of the visible region of the Mn-( L) complex showed peaks at 583 - 750 nm due to (d-d) transitions of type $^6A_g^{(F)}\rightarrow^2T_{2g}^{(G)}$ and $^6A_g^{(F)}\rightarrow^4T_{1g}^{(G)}$ indicating an octahedral geometry [53]. The magnetic moments' value of $\mu_{\text{eff}}$ 2.06 B.M also the other analytical data agree with octahedral geometry around Mn atoms. The electron spectrum of the Fe-( L) complex showed an absorption peak at 505 nm, which followed the electron transitions $^3E_{1g}^{(D)}\rightarrow^5T_{2g}^{(D)}$, indicating a tetrahedral geometry. The magnetic moments' value of $\mu_{\text{eff}}$ 3.21 B.M, attributed to tetrahedral geometry around the Fe atom. The electronic spectrum of the Co-( L) complexes showed peaks around 632-741 nm consigned to $^4T_{1g}^{(F)}\rightarrow^4T_{1g}^{(P)}$ and $^4T_{1g}^{(F)}\rightarrow^4A_{2g}^{(F)}$, indicating a tetrahedral geometry [53]. The data agree with the magnetic moment values of $\mu_{\text{eff}}$ 4.2 B.M, for tetrahedral geometry around Co atom. The spectrum of the Ni-( L) complex showed peaks at 617 nm due to (d-d) transitions of type $^1A_{2g}\rightarrow^3T_{2g}$, indicating an octahedral geometry about Ni atom. The magnetic moments' value of $\mu_{\text{eff}}$ 3.15 B.M, attributed to octahedral geometry around the Ni atom. The Cu-complex of ( L) showed a peak around 423 nm, related to $^2B_{1g}\rightarrow^2E_g$ confirming an octahedral geometry about the metal center [54]. The magnetic moments' value of $\mu_{\text{eff}}$ 1.77 B.M, attributed to octahedral geometry around the Cu atom. The spectrum of the Zn-( L) complex revealed beaks 262 and 280 apportioned to ligand $\pi\rightarrow\pi^*$, $\pi\rightarrow\pi^*$, and CT. The complex is diamagnetic as expected and I usually favor tetrahedral geometry [54].
Table 3. UV-Vis Spectral data of L1 complexes in DMSO solutions x 10-5 mol/L.

| Comp. | Band Position \( \lambda nm \) | Wave number (cm\(^{-1}\)) | Extinction coefficient \( \epsilon_{\text{max}} \) (dm\(^3\)mol\(^{-1}\)cm\(^{-1}\)) | Assignment | Suggested geometry |
|-------|-----------------|-----------------|---------------------------------|-----------------|-----------------|
| L     | 265             | 37735           | 1.076                           | Intra-ligand \( \pi \rightarrow \pi^* \) |      |
|       | 298             | 33557           | 1.015                           | \( n \rightarrow \pi^* \) |      |
| Mn    | 265             | 37735           | 1.703                           | \( \pi \rightarrow \pi^* \) | a distorted |
|       | 583             | 17152           | 0.029                           | \( 6A_1g(P) \rightarrow 4T_2g(G) \) | octahedral |
|       | 750             | 13333           | 0.004                           | \( 6A_1g(P) \rightarrow 4T_1g(G) \) |          |
| Fe    | 266             | 37593           | 1.102                           | \( \pi \rightarrow \pi^* \) | Tetrahedral |
|       | 471             | 21231           | 0.005                           | C.T |      |
|       | 505             | 19801           | 0.0016                          | \( ^5E_1(D) \rightarrow ^3T_2(D) \) |      |
| Co    | 257             | 38910           | 0.558                           | Intra-ligand | Tetrahedral |
|       | 277             | 36101           | 0.641                           | \( \pi \rightarrow \pi^* \) |      |
|       | 632             | 15822           | 0.020                           | \( 4T_{1g}(P) \rightarrow 2T_{1g}(P) \) |          |
|       | 741             | 13495           | 0.0119                          | \( 4T_{1g}(P) \rightarrow 2A_{2g}(F) \) |          |
| Ni    | 257             | 38910           | 0.6                             | \( \pi \rightarrow \pi^* \) | Octahedral |
|       | 282             | 35460           | 0.330                           | \( n \rightarrow \pi^* \) |      |
|       | 386             | 25906           | 0.136                           | C.T |      |
|       | 617             | 16207           | 0.002                           | \( 3A_{2g} \rightarrow 3T_{2g} \) |      |
| Cu    | 257             | 38910           | 0.722                           | Intra-ligand | Octahedral |
|       | 272             | 36764           | 0.678                           | \( \pi \rightarrow \pi^* \) |      |
|       | 341             | 29325           | 0.154                           | C.T |      |
|       | 423             | 23640           | 0.125                           | \( ^2B_{1g} \rightarrow ^2E_g \) |      |
| Zn    | 262             | 38167           | 1.055                           | \( \pi \rightarrow \pi^* \) | Tetrahedral |
|       | 280             | 35714           | 1.039                           | \( n \rightarrow \pi^* \) |      |

4.3. Heavy metal removal study
The research was carried out to determine the efficiency of ligand chelating to remove heavy metals (Cu\(^{2+}\) and Fe\(^{2+}\)). Aqueous solution, the permissible limit value for Cu\(^{2+}\) and Fe\(^{2+}\) in drinking water according to WHO are 1, 0.3ppm, respectively [5]. Industrial wastewater was obtained from the General Company for Copper and Mechanical Industries in Ameriyat al-Fallujah. The water contained Cu\(^{2+}\) (5.5472)ppm and Fe\(^{2+}\) (30.344)ppm. The process of removing heavy metals from water using ligand is studied by adding a ligand to the solution to be precipitated, where the filtration complex is separated by filtration, then the metal ratio in the aqueous solution is measured by the atomic absorption of the metal. The percentage of removed heavy metals were calculated under experimental conditions using the formula as followed [29]:

\[
\text{Removed efficiency (\%)} = \frac{C_0 - C_f}{C_0} \times 100
\]  \hspace{1cm} (2)

Where: \( (C_0) \) and \( (C_f) \) are the initial and final concentrations of metals. The precipitation was characterized by FTIR that showed prominent bands related to the formation of the complex. The bands at 1492, 1138-991, and 474-424 cm\(^{-1}\) attributed to \( \nu (N-CS_2) \), \( \nu_{as}(CS_2) \) and \( \nu_{s}(M-S) \), respectively. The removal efficiency is observed as 75.9% and 48.99% for Cu\(^{2+}\) and Fe\(^{2+}\), respectively.

Finally, the performance of the complex in the removal of iron and copper could be monitored in a precise way by embedding sensors in the treatment space to monitor the residual concentrations of iron and copper; this suggestion is based on the successful uses of the sensors in the monitoring of different parameters [55-58].
5. Conclusions
This study involved the synthesis and characterization of DCT ligand and its metal(II) dithiocarbamate macrocyclic complexes. A one-pot synthetic route reaction is used to isolate complexes. the complexes are characterized by FTIR, UV-Vis, magnetic susceptibility, $^1$H, $^{13}$C-NMR spectroscopy melting points, and conductance. These results obtained, the synthetic formulas for the complexes, the general formula $[M(L_2)_2]_2$ (where $M(II)$= Fe, Co, Zn), and the second general formula $[M(L_2)(H_2O)_2]_2$ (where $M(II)$= Mn, Cu, and Ni). This ligand, using its S-donors could effectively and, remove the selected heavy metals (such as Cu$^{2+}$ and Fe$^{2+}$) through chemical precipitation from an aqueous solution. The formed metal precipitates are characterized by FT-IR, it showed prominent bands related to the formation of the complex. The atomic absorption of water is measured after removing the precipitation, and it is found that the efficiency of ligand to remove metals is 75.9% and 48.99% for Cu$^{2+}$ and Fe$^{2+}$, respectively.

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