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المملكة العربية السعودية

جامعة الامام محمد بن سعود
الإسلامية

كلية العلوم

قسم الكيمياء

Synthesis and Characterization of Ni(II) , Co(II) and Cu(II) Complexes with Dimethylglyoxime Ligand

A graduation research project

submitted to the Department of Chemistry in partial fulfillment of the requirement for completing a degree of science in chemistry.

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1446

Table of Content

Table of Figures:

Table of schematics:

Table of Equations:

Table of Tables :

Acknowledgment:

We are immensely grateful to Dr. Hanan Alhussain for her outstanding supervision and guidance during this project. She was a constant source of inspiration and support throughout our research. She provided us with invaluable insights and feedback that significantly improved the quality of our work. This work was conducted as graduation research under the College of Sciences chemistry department at Imam Muhammad ibn Saud Islamic University. This study revealed the potential of synthesizing complexes of Ni(II), Co(II), and Cu(II) with dimethylglyoxime (DMG) ligand.

Abstract:

The Ni(II), Co(II), and Cu(II) complexes with Dimethylglyoxime (DMG) ligand were synthesized by a direct combination of reactants (metal salt and DMG) method in stoichiometric ratios. The resulting complexes have been characterized using UV-visible spectroscopy, and FT-IR spectroscopy data, and by comparing their melting points. The spectral data, and the differences in melting points between the starting salt materials and the synthesized complexes, indicate the successful formation of these metal-DMG complexes.

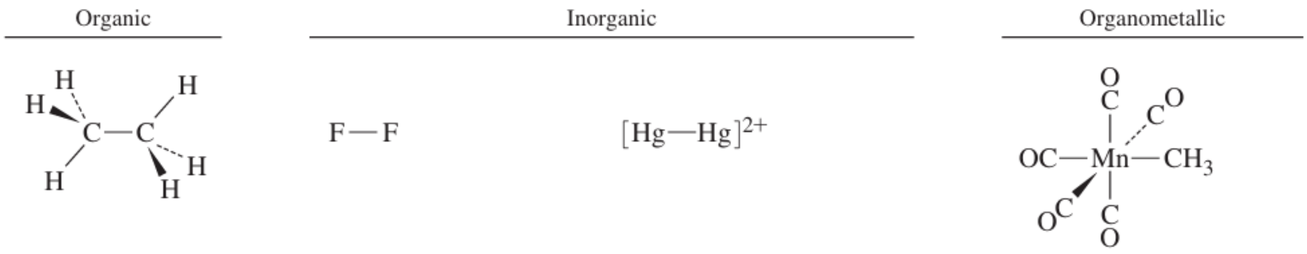
الملخص:

تم تحضير معقدات النيكل والكوبالت والنحاس مع ثنائي ميثيل غليوكسيم باستخدام طريقة التفاعل المباشر بين مكونات المعقد (ملح المعدن والليغند) باستخدام نسب وزنية محسوبة. وتم توصيف المعقدات الناتجة باستخدام مطيافية الأشعة فوق البنفسجية-المرئية، وبيانات مطيافية الأشعة تحت الحمراء، بالإضافة إلى مقارنة نقطة الانصهار. تشير البيانات الطيفية والاختلافات في نقاط الانصهار بين مواد الملحية الأولية والمعقدات المُحضّرة إلى التكوين الناجح لهذه المعقدات المعدنية مع ثنائي ميثيل غليوكسيم.

1. INTRODUCTION:

1.1 What Is Inorganic Chemistry?

If organic chemistry is defined as the chemistry of hydrocarbon compounds and their derivatives, inorganic chemistry can be described as the chemistry of “everything else.” This includes all the remaining elements in the periodic table, including carbon. Inorganic chemistry as a field of study was essential during the early years of the exploration and development of mineral resources. Early in the twentieth century, Werner and Jørgensen made considerable progress in understanding the coordination chemistry of transition metals and discovered several organometallic compounds. Inorganic chemistry is not simply the study of elements and compounds; it is also the study of physical principles; for example, In the solid state, X-ray diffraction methods are routinely used to obtain pictures of the spatial arrangements of atoms in a complex and to interpret the behavior of molecules in solution, we use physical techniques such as nuclear magnetic resonance (NMR) spectroscopy. (1)



Figure**(1.1**)For inorganic chemistry

1.2 Coordination Chemistry:

Coordination compounds comprise a metal atom or ion and one or more ligands (atoms, ions, or molecules) that donate electrons to the metal. In coordination compounds, the donors are usually the ligands, and the acceptors are the metals. Coordination compounds are frequently called complexes or, if charged, complex ions. (1)

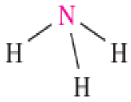
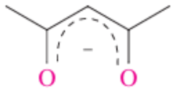
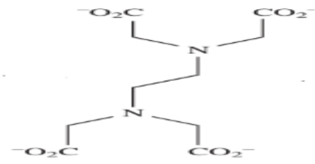
Ligand with:

One donor atom (monodentate) such as NH_3

Two donor atoms (bidentate) such as $[acac]^-$

More than one donor atom (polydentate), such as EDTA (2)

Table(**1.1**) Type of Ligand

Name of ligand	Abbreviation (if any)	Denticity	Structure with donor atoms marked in red
Ammonia		Monodentate	
Acetylacetonate ion	$[acac]^-$	Didentate	
N,*N*,*N'*,*N'*-Ethylenediaminetetraacetate ion*	$[EDTA]^{4-}$	Hexadentate	

1.2.1 History of Coordination Chemistry:

Werner’s theory required so-called primary bonding, in which the positive charge of the metal ion is balanced by negative ions, and secondary bonding, in which molecules or ions (ligands) are attached directly to the metal ion. The secondary bonded unit is called the complex ion or the coordination sphere; modern formulas are written with this part in brackets, and the ions outside the coordination sphere are sometimes called counterions. (1)

1.2.2 Coordination Numbers:

The coordination Number is the number of donor atoms surrounding the central metal atom in a complex ion. In coordination compounds, the arrangement of these ligands around the metal center defines the compound's geometry, and the most common coordination numbers are:

Octahedral: Common for coordination number 6, with ligands positioned at the vertices of an octahedron. (1)

Tetrahedral: Occurs with coordination number 4, where ligands are at the corners of a tetrahedron.

Square Planar: For coordination number 4, ligands are arranged around the metal in a flat square plane.

Trigonal Bipyramidal: For coordination number 5, with three ligands in a plane and two above and below. (1)

1.2.3 Bonding in coordination chemistry:

In coordination chemistry, bonding involves interacting between a central metal atom or ion and surrounding ligands, molecules, or ions that donate electron pairs. The bonding can be described using theories such as Crystal Field Theory, an electrostatic approach to explain the split in metal d-orbital energies within an octahedral environment. It provides an approximate description of the electronic energy levels often responsible for the ultraviolet and visible spectra of coordination complexes, but it does not describe metal-ligand bonding. Another theory is Ligand Field Theory, which describes bonding in terms of the interactions between metal and ligand frontier orbitals to form molecular orbitals. It uses crystal field theory terminology but focuses on orbital interactions rather than attractions between ions. Lastly, the Angular Overlap Method estimates the relative magnitudes of molecular orbital energies within coordination complexes. It explicitly considers the orbitals responsible for ligand binding as well as the relative orientation of the frontier orbitals. (1)

1.3 Reactions of coordination complexes:

It can be divided into:

(1) substitution at the metal center.

(2) oxidation-reduction.

(3) reactions of the ligands that do not change the attachments to the metal center.

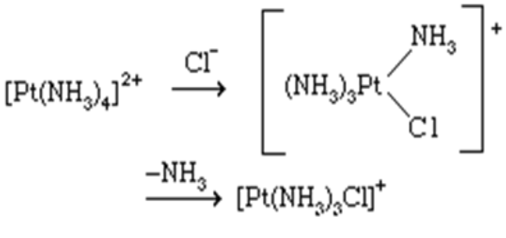
1.3.1 Substitution reaction:

One of the most general reactions of coordination compounds is substituting, or replacing, one ligand with another. This process is depicted in LnMX+Y→LnMY+X. There are two limiting mechanisms (or pathways) through which substitution may occur—namely, dissociative and associative mechanisms. In the dissociative mechanism, a ligand is lost from the complex to give an intermediate compound of a lower coordination number. This type of reaction path is typical of octahedral complexes, many aqua complexes, and metal carbonyls such as tetracarbonyl nickel (3). An example of a dissociative reaction pathway for an octahedral complex of cobalt is as follows:

$$[Co(CN)_5(H_2O)]^{2-} \xrightarrow{-H_2O} [Co(CN)_5]^{2-} \xrightarrow{+I^-} [Co(CN)_5I]^{3-}.$$

Equation**(1.1)** For dissociative reaction

On the other hand, the associative mechanism for substitution reactions involves the association of an extra ligand with the complex to give an intermediate of higher coordination number; one of the original ligands is then lost to restore the initial coordination number. Substitution reactions of square planar complexes, such as those of the nickel (2+), palladium (2+), and platinum (2+) ions, usually proceed through associative pathways involving intermediates with coordination number five (3). An example of a reaction following such a pathway is:



$$[Pt(NH_3)_4]^{2+} \xrightarrow{Cl^-} \left[(NH_3)_3Pt\begin{matrix}NH_3\\Cl\end{matrix}\right]^+ \xrightarrow{-NH_3} [Pt(NH_3)_3Cl]^+$$

Equation (1. 2) for Associative reaction

1.3.2 Oxidation–Reduction Reactions:

Transition metals commonly exhibit two or more stable oxidation states, and their complexes thus undergo oxidation-reduction reactions. The simplest such reactions involve electron transfer between two complexes, with little, if any, accompanying rearrangement or chemical change. (4). An example is shown below.

$$[Fe(CN)_6]^{4-} + [IrCl_6]^{2-} \longrightarrow [Fe(CN)_6]^{3-} + [IrCl_6]^{3-}.$$

Equation **(1.3)** for Oxidation-reduction reaction

Two limiting electron transfer mechanisms have been recognized: the outer-sphere and inner-sphere. Outer-sphere electron transfer occurs without dissociation or disruption of the coordination sphere of either complex, i.e., through both intact coordination spheres. The reaction above is of this type. On the other hand, inner-sphere electron transfer proceeds by forming a binuclear complex in which the two metal ions are joined by a common bridging ligand through which the electron is transferred (4).

1.3.3 reactions of the ligands that do not change the attachments to the metal center:

Coordination to the metal changes ligand properties sufficiently to make possible reactions at the ligands that either (a) could not happen with the unbound ligand or (b) could occur without the metal but much more slowly. (1)

1.4 Transition Metals:

Transition metal is any of various chemical elements with valence electrons, i.e., electrons that can form chemical bonds in two shells instead of only one. While the term *transition* has no particular chemical significance, it is a convenient name to distinguish the similarity of the atomic structures and resulting properties of the designated elements. They occupy the middle portions of the long periods of the periodic table of elements between the groups on the left-hand side and the groups on the right. Specifically, they form Groups 3 through 12 (5). The chemistry of the first-row transition metals is highly diverse, with many different reactivity and property patterns. This richness results from a wide range of ligands and coordination flexibility around the metal. Still, most of all, it results from the partial occupation of the d-orbitals shell, leading to different oxidation and spin states (6) . This research was focused on the three elements: Nickel (Ni), Cobalt (Co), and Copper (Cu) (5) .Nickel (Ni): Atomic number 28, nickel is a silvery-white metal known for its corrosion resistance and ability to form alloys, particularly with iron and copper. It is widely used in batteries, coins, and as a catalyst in chemical reactions. (7)

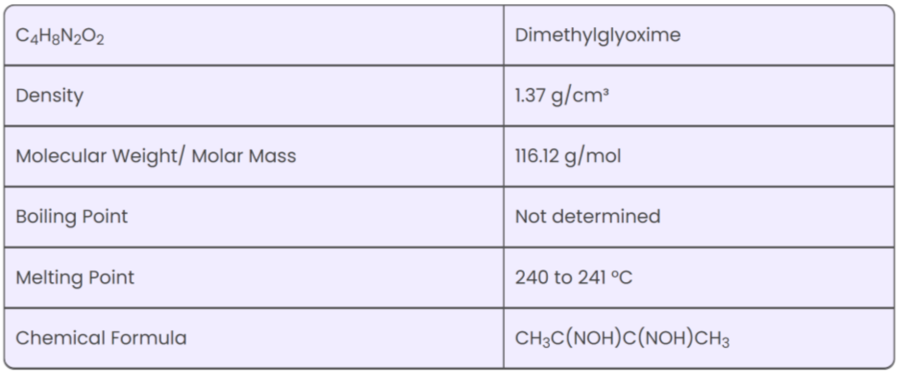
Cobalt (Co): Atomic number 27, cobalt is a hard, lustrous metal primarily used in high-strength alloys and batteries, especially lithium-ion batteries. It is also essential in producing cobalt blue pigments and has applications in the medical field for specific treatments. (8)

Copper (Cu): Atomic number 29, copper is a reddish-brown metal known for its excellent electrical and thermal conductivity. It is extensively used in electrical wiring plumbing and as a critical component in various alloys, such as bronze and brass. Copper also plays a vital role in biological systems as a trace element. The chemistry of the first-row transition metals is highly diverse, with many different reactivity and property patterns. (9)

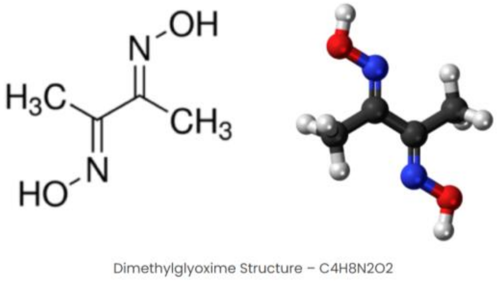
1.5 What is (DMG)?

DMG is a white powder with the molecular formula $C_4H_8N_2O_2$. It is an extraordinarily sensitive and specific reagent for nickel. Many derivatives of DMG have been synthesized and proposed. Although commonly used as a reagent specific to nickel, DMG allows the detection of other metal ions. (10)

Table (1.2) General information about DMG



$C_4H_8N_2O_2$	Dimethylglyoxime
Density	1.37 g/cm³
Molecular Weight/ Molar Mass	116.12 g/mol
Boiling Point	Not determined
Melting Point	240 to 241 °C
Chemical Formula	$CH_3C(NOH)C(NOH)CH_3$



Figure(**1.2**)For DMG

1.5.1 (DMG) Ligand:

DMG is an example of an asymmetric ligand. The charge of DMG is -1, which is an anionic ligand. The number of donor atoms in the DMG ligand is 2. It is a bidentate ligand. It coordinates through 2 N atoms. (10)

1.5.2 Physical and Chemical Properties of (DMG):

Physical Properties:

Odor: Odorless

Appearance: Off White Powder

Complexity: 112

Dipole moment: 0

Hydrogen Bond Donor: 2

Solubility: Insoluble in water, soluble in alcohol (10)

Chemical Properties:

Dmg is a white crystalline powder. Soluble in alcohol, ether, acetone, and pyridine. Solubility in water 0.5g/l, insoluble in tolerate chloroform, toluene, and xylene. It is one of the first selective organic reagents applied in analytical chemistry. It is an extraordinarily sensitive and specific reagent for nickel. under appropriate conditions DMG is specific for nickel(II) and palladium(II), but it also forms colored water-soluble complexes with iron(II), cobalt(II) and copper(II). (11)

1.5.3 Applications of Co-DMG complex:

Electrochemical analysis: To determine cobalt concentration in solutions using volumetric and polarographic techniques. (12)

Enhancing detection sensitivity: The presence of nitrite significantly improves the volumetric response and lowers the detection limit of the complex. (12)

Studying reaction mechanisms: To investigate the cobalt-DMG complex's electrochemical behavior and reaction mechanisms in various electrolyte media. (12)

1.5.4 Applications of Ni-DMG complex:

1- Nickel is an essential constituent of several steel alloys, and DMG is widely used for the spectrophotometric determination of nickel. It has also been used for the separation and preconcentration of Ni by liquid-liquid extraction or solid-phase extraction. The complex was separated, and Ni was determined spectrophotometrically by DMG after the addition of an oxidizing agent (13).

2- Determination of nickel in steel by extraction of Ni (II)- DMG complex in an aqueous polyethylene glycol (PEG)–(NH4)2SO4 system and applied the proposed system to the spectrophotometric (14).

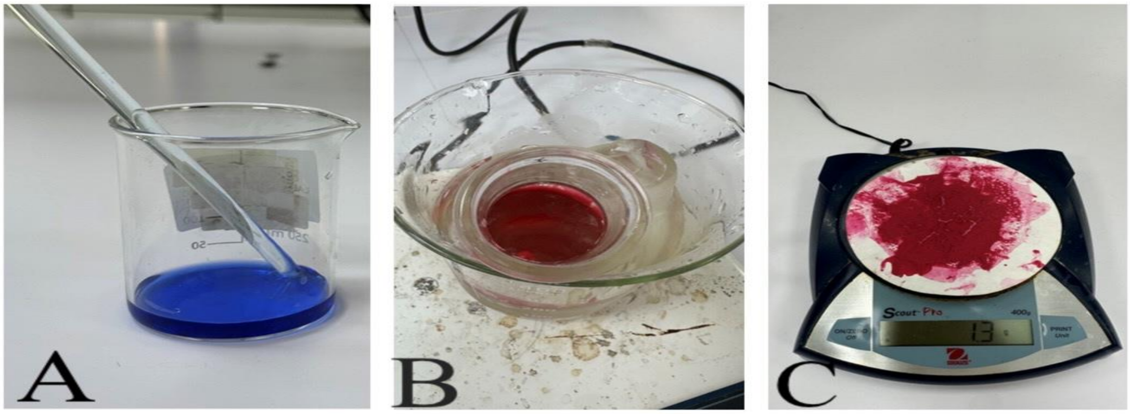
1.5.5 Applications of Cu-DMG complex:

The adsorptive properties of the Cu-DMG complex can be utilized for sensitive determination of Cu traces (from 1 × 10−7 M to ca. 1 × 10−5M Cu) or for simultaneous determination of Cu, Ni and Co by differential pulse polarography or linear fast sweep polarography (15).

2. EXPERIMENTAL:

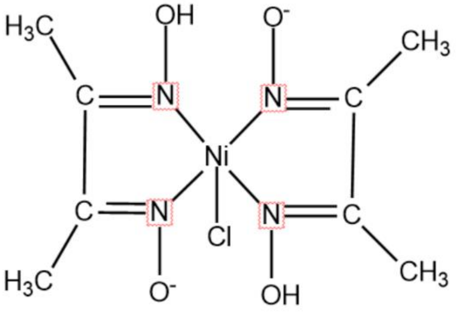
2.1 Synthesis of Ni-DMG Complex:

1.18g of Ni chloride salt was added to 20 ml of ammonia, as shown in Figure (2.1A). Then, 5ml of the solution was obtained and added to 5ml of DMG solution, as shown in Figure (2.1B). The solution was placed in an ice bath and mixed for 10 minutes until a red precipitate formed. The resulting precipitate was filtered and washed with ammonia. Figure (2.1C) shows the red powder produced.



Figure**(2.1)**Synthesis of Ni-DMG complex

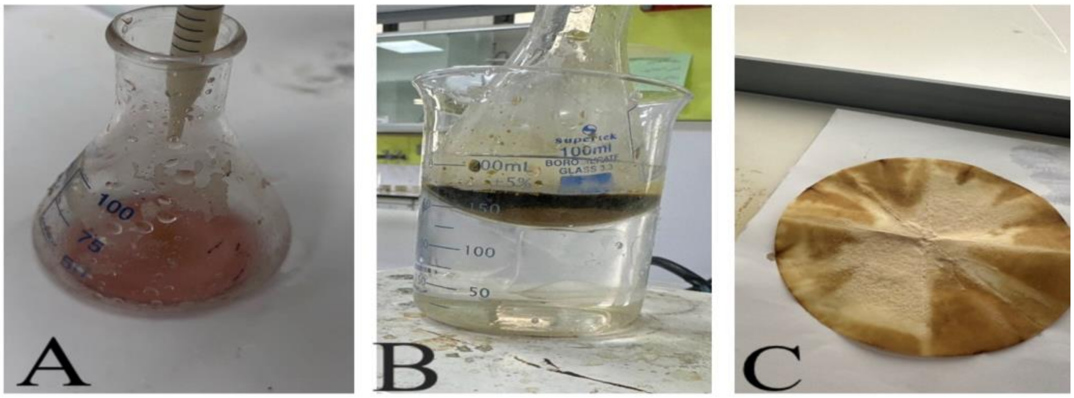
2.1.1 Schematic drawings for the expected complex Ni-DMG:



Schematic **(2.1)**drawing for the expected complex Ni-DMG

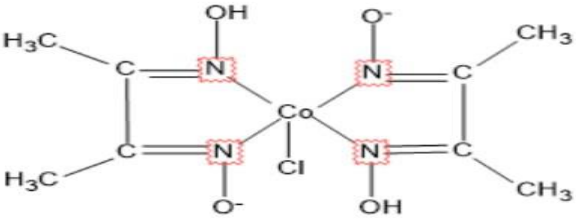
2.2 Synthesis of Co-DMG Complex:

0.6g of Co chloride salt was added to 10 ml of H_2O, as shown in Figure (2.2A). Then, 5ml of the solution was obtained and added to 5ml of DMG solution, as shown in Figure (2.2B). The solution was placed in an ice bath and mixed for 10 minutes until a brown precipitate formed. The resulting precipitate was filtered and washed with H_2O. The brown powder produced is shown in Figure (2.2C).



Figure(**2.2**)Synthesis of Co-DMG

2.2.1 Schematic drawings for the expected complex Co-DMG:

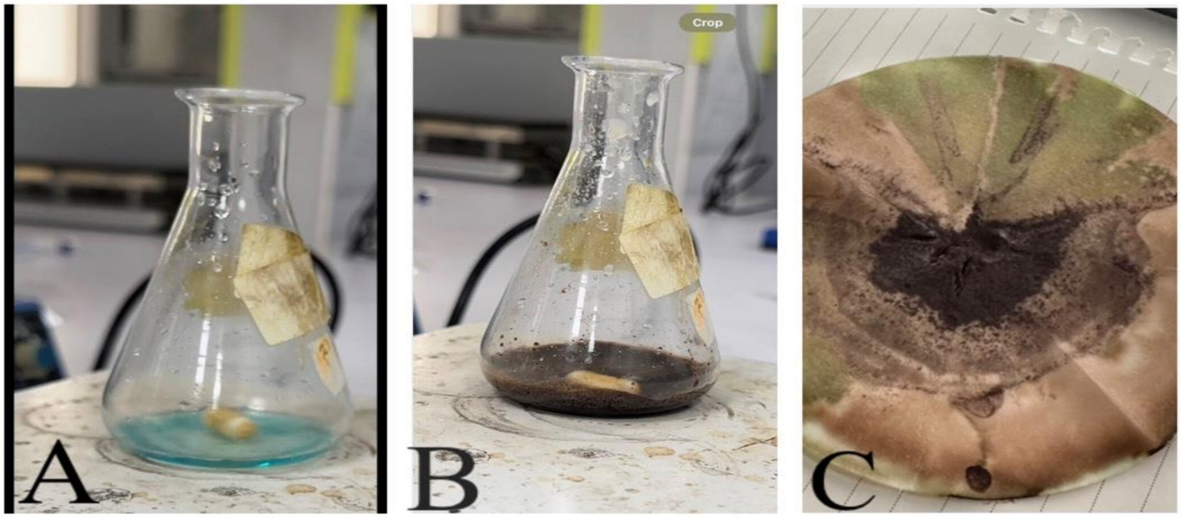


Schematic**(2.2)** drawing for the expected complex Co-DMG

2.3 Synthesis of Cu-DMG Complex:

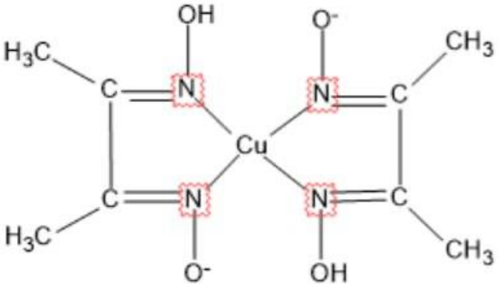
0.43 grams of Cu chloride salt was added to 10 ml of H_2O, as depicted in Figure(2.3A) . Subsequently, 5 ml of the resulting solution was mixed with 5 ml of DMG solution, as illustrated in

Figure (2.3B). The mixture was then placed in an ice bath and stirred for 10 minutes until a dark brown precipitate formed. The resulting precipitate was filtered and washed with H_2O. The amount of dark brown powder produced is shown in Figure (2.3C).



Figure**(2.3)**Synthesis of Cu-DMG complex

2.3.1 Schematic drawings for the expected complex Cu-DMG:



schematic **(2.3)**drawing for the expected complex Cu-DMG

3. RESULT AND DISCUSSION:

3.1 Melting Point Testing:

The table below shows the measured melting point for complexes of Ni(II), Cu(II), and Co(II) with DMG ligand and starting salt materials:

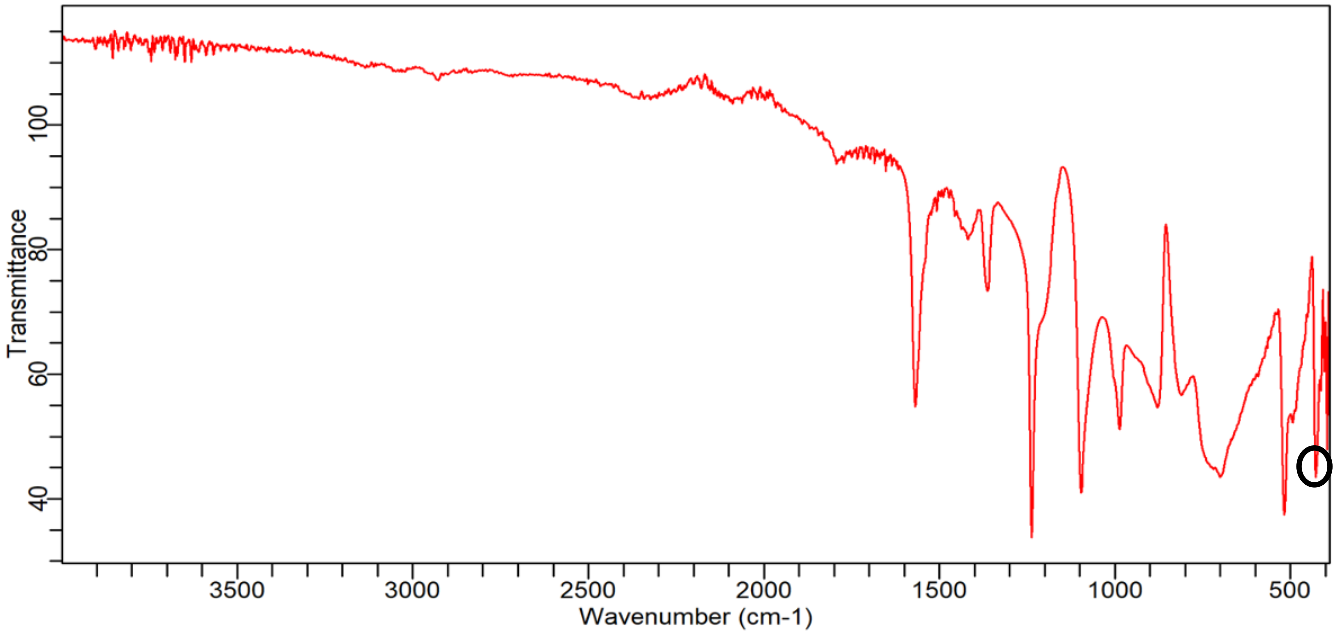
Table(3.1) for melting point

Complexes	Melting point	Metal salt	Melting point
$[Ni(DMG)_2Cl]$	>246 °C	$NiCl_2.6H_2O$	140 °C
$[Co(DMG)_2C]$	243 °C	$CoCl_2.6H_2O$	86 °C
$[Cu(DMG)_2]$	224 °C	$CuCl_2.2H_2O$	100 °C

Based on the information presented in the table, it can be inferred that complexation has taken place between nickel (Ni), cobalt (Co), and copper (Cu) with the (DMG) ligand, as evidenced by the significantly higher melting points of the complexes compared to their respective starting salt materials.

3.2 IR spectrum:

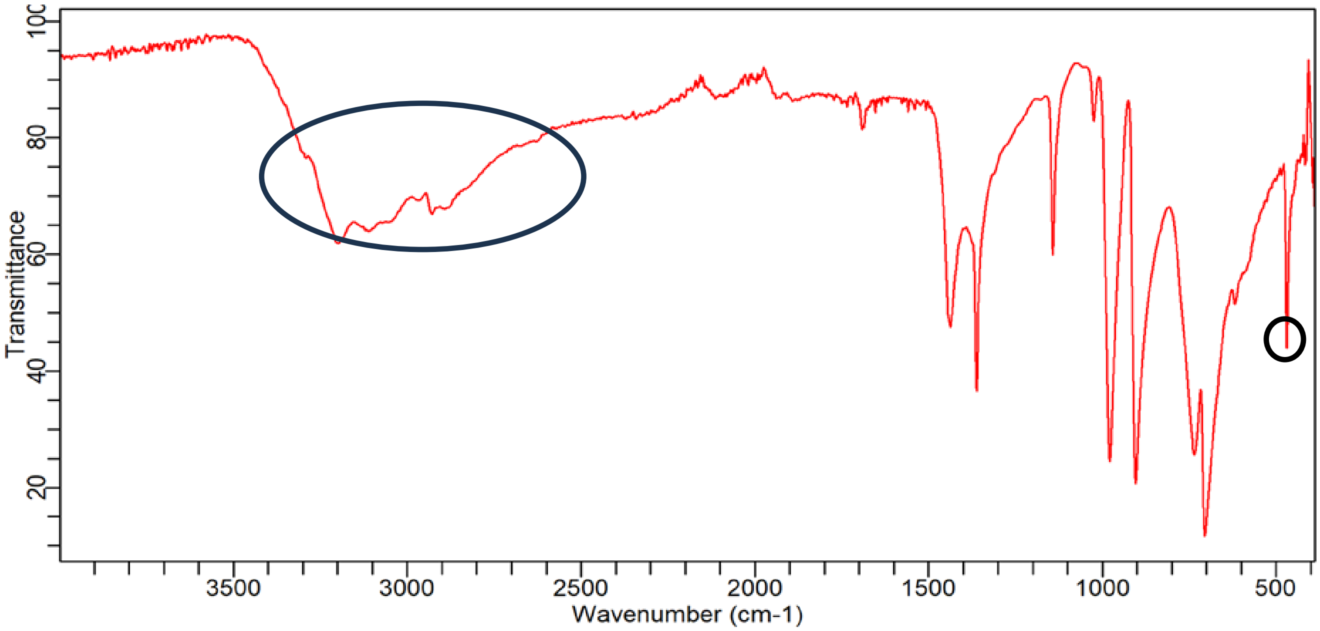
3.2.1 Complex1: Ni-DMG



Figure(**3.1**)IR spectra of Ni-DMG complex

In the FT-IR spectra of the Ni-DMG complex, the characteristic stretching band of the (Ni—N) at 520 cm^{-1} has been detected, which indicates the formation of the complex. We predict that the fifth coordination bond of Ni is with chlorine (Ni—Cl), which should appear at a wavelength between 200-260 cm$^{-1.}$ However, this falls outside the detectable range of the FT-IR spectra.

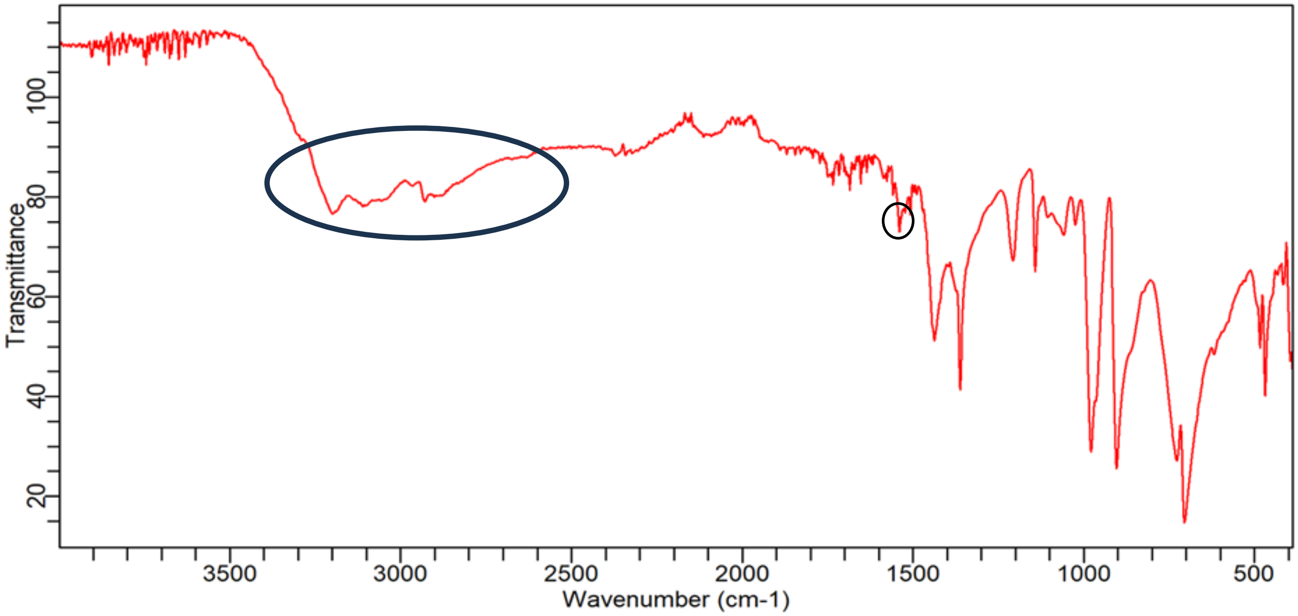
3.2.2 Complex 2: Co-DMG



Figure**(3.2)** IR spectra of Co-DMG complex

In the FT-IR spectra of the Co-DMG complex, the characteristic stretching band of the (Co—N) at 446 cm^{-1} has been detected, which indicates the formation of the complex. We predict that the fifth coordination bond of Co is with a Cl ligand (Co—Cl), which should appear at a wavelength of 166 cm$^{-1.}$ This wavelength falls outside the detectable range of FT-IR spectra. The presence of a stretching band at ≈3000 cm^{-1} may be caused by the residue water solvent used in the experiment.

3.2.3 Complex 3: Cu-DMG

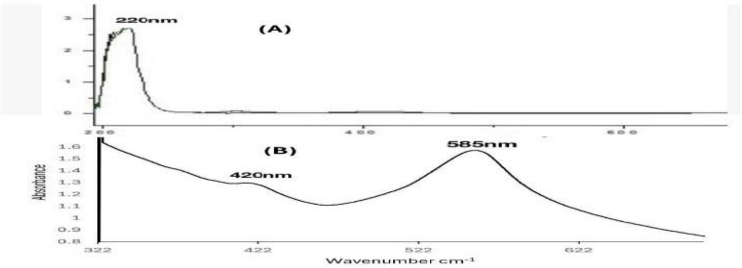


Figure(**3.3**)IR spectra of Cu-DMG complex

In the FT-IR spectra of the Cu-DMG complex, the characteristic stretching band of the (Cu—N) at 1580 cm^{-1} has been detected, which indicates the formation of the complex. The presence of a stretching band at ≈3000 cm^{-1} may be caused by the residue water solvent used in the experiment.

3.3 Electronic spectrum:

3.3.1 Complex 1: Ni-DMG



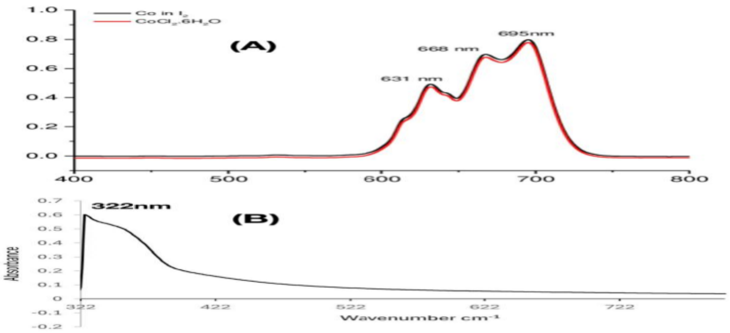
(16)

Figure(**3.4**) UV-Vis spectrum of NiCl26H2O of (A)VS Ni-DMG complex of (B)

The UV-visible spectrum of the $NiCl_2.6H_2O$ (fig. 3.4A) shows a band at 220 nm. It is also observed in the spectra of the complex Ni-DMG (fig. 3.4B) with a shift to a higher wavelength (585 nm).

There is also a new band at 420 nm in the spectra of the complex Ni-DMG (fig. 3.4B). This indicates the formation of new bonds and, thus, the formation of the complex.

3.3.2 Complex 2: Co-DMG

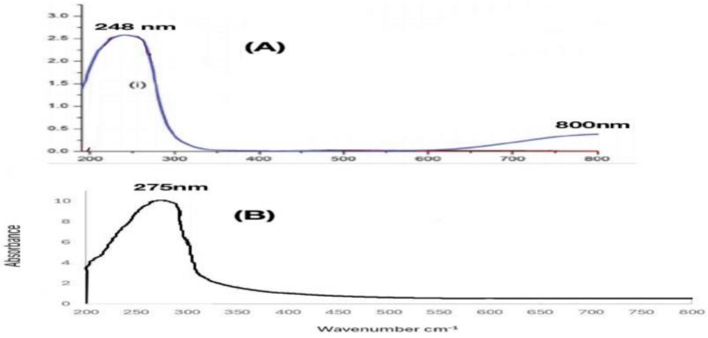


(17)

Figure **(3.5**) UV-Vis spectrum of CoCl26H2O Of (A)VS Co-DMG complex of (B)

The UV-visible spectrum of the CoCl2.6H2O(fig3.5A) showed the band at 695nm. It is also observed in the spectra of the complex (fig 3.5B) with a shift to a lower wavelength (322nm). This indicates the formation of new bonds and, thus, the formation of the complex.

3.3.3 Complex 3: Cu-DMG



Figure(**3.6**)UV-Vis spectrum of CuCl26H2O Of (A)(18), VS Cu-DMG complex of (B)

The UV-visible spectrum of $CuCl_2.2H_2O$ (fig 3.6A) displayed a band at 248 nm. In the spectrum of the complex (fig 3.6B), this band shifts to a higher wavelength at 275 nm. This shift indicates the formation of new bonds and suggests that the complex has been formed. Additionally, a band was present at 800 nm in the spectrum of $CuCl_2.2H_2O$ (fig 3.6A), but it is absent in the spectrum of the complex (fig 3.6B). This disappearance further supports the conclusion that new bonds have formed and confirms the creation of the complex.

4. CONCLUSION AND RECOMMENDATIONS:

4.1 Conclusion:

In this study, the metal complexes were synthesized by direct reacting of metal salts with (DMG) as the ligand with utilizing of specific solvents. $NiCl_2 \cdot 6H_2O$ salt and the DMG ligand were solved in ammonia, while $CoCl_2 \cdot 6H_2O$ and $CuCl_2 \cdot 2H_2O$ salts were solved in water. UV-vis spectroscopy, FT-IR analysis, and melting point calculations were utilized to characterize the synthesized complexes.

4.2 Recommendations:

We suggest that these complexes can be prepared by substitution reaction or by grinding technique as well and we recommend that they be used to determine the concentration of some elements.

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