

## PREPARATION AND CHARACTERIZATION OF MIXED COMPLEXES FOR SOME TRANSITIONAL ELEMENTS OF THE FLAVONOID LIGAND

Aqeel Amer Hammad<sup>1\*</sup>, Omar Hamad Al-Obaidi<sup>2</sup> and Khalid F. AL-Rawi<sup>3</sup>

<sup>1</sup>Department of Laboratory, Anbar Health Department, Anbar, Iraq.

<sup>2,3</sup>Department of Chemistry, College of Sciences, University of Anbar, Iraq.

\*e-mail : ake19s3019@uoanbar.edu.iq

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**ABSTRACT :** A group of mixed complexes formed by the reaction of simcarbazon and quercetin with chlorides of transition elements was prepared with a ratio of (1:1:1) ligand: metal and the study of some of their physical properties, where the complexes were diagnosed by ultraviolet spectroscopy techniques (Uv. – Vis) and Quantitative Analysis of Elemental Metals (C.H.N.M) These complexes were also identified by infrared radiation Spectra ( FTIR) In addition to the magnetic and molar electrical conductivity measurements, as well as the other mixed complexes were prohibited from the interaction of thiosemicarbazone and quercetin by (1:1:1) ligand: metal. With transitional elements diagnosed in the same ways above. The biological effect of the prepared ligands and their complexes on four genes of pathogenic bacteria was studied *S. aureus*, *Ps. aeruginosa*, *E. coli*, *P. mirabilis*. Measurements were made on the effectiveness of ALP, GPT, GOT and TSB for samples of blood serum of normal people and compared with the inhibition values of the blocked complexes. Most of the complexes showed an inhibitory effect, while the following complexes showed,  $[\text{Ni}(\text{L}_1)(\text{L}_3)\text{Cl}_2\cdot\text{H}_2\text{O}]$ ,  $[\text{Co}(\text{L}1)(\text{L}_3)\text{Cl}_3]$   $[\text{Fe}(\text{L}_1)(\text{L}_2)\text{Cl}]$  tonic effect.

**Key words :** Flavonoid ligand, their biological applications.

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### INTRODUCTION

Simcarbazones are known to form complexes with some transition ions, which were prepared by Jensen, if two types of simcarbazon complexes were attended with the general formula  $[\text{M}(\text{tsc})_2]+2$  and  $[\text{M}(\text{tsc})_2]$  where M = transition metal chlorides and found through Studying the X-ray and infrared spectra of these complexes as having a tetrahedral shape through the formation of a coordination bond with the sulfur atoms and the hydrogen atom (N3) of the hydrazine group (Marder and Paladini, 2002). Cimcarbazon behaves as bivalent ligands, because they contain N and S as donor atoms that play a large role in forming complexes with chlorides of transition metals, and in a few cases it can behave as atomizers of chlorides in  $[\text{Cl}_2] \text{C}_3\text{H}_7\text{NO}(2(\text{C}_8\text{H}_8\text{N}_4\text{O}_2\text{S})_2)$  and by studying the spectrum of infrared and ultraviolet rays and the physical properties of the complex, it was suggested that the shape of the complex is octahedron (Salgueiro *et al*, 1997; Munteanu *et al*, 2020). With other ligands in the preparation of mixed

complexes that are more stable with metallic elements, this type of thiosimcarbazon ligands is prepared in many ways, the most common of which is the direct condensation method between aldehydes, aromatic or aliphatic ketones with the primary amine (Thiosimicarpa Zed), which depends on the reaction conditions and the nature of the reactants (Sanna *et al*, 2014). And for many years, flavonoid complexes have been known by forming complexes with some transitional elements. From the flavonoid ligands, what is known as quercetin, from which mixed ligands were prepared, where the quercetin ligand was mixed with gallic acid (Medina *et al*, 1997; Medina *et al*, 1998). The mixture was reacted with some transition elements, zinc and manganese metal and formed stable complexes and the antioxidants were higher than the free flavonoid ligands. UV, IR, AAS techniques were used, as well as molar conductivity and complex solubility test (Sanna *et al*, 2016; Sanna *et al*, 2015). The flavonoid complexes were much stronger anti-bacterial than the free flavonoid compounds, Thiosimecarbazon derivatives

have wide applications in medical and biological fields. During its use in the treatment of certain types of diseases and cancers that affect the human body (Munteanu *et al*, 2020). Some compounds containing sulfur and nitrogen have been used as preparatory enzymatic aids, as is the case in nickel, copper and zinc complexes of type (S and N), as the effectiveness of thiosimcarbazine derivatives increases when they form complexes with metal ions (Sandu *et al*, 2021). The scientist Akio used thiosimecarpazone derivatives against some types of bacteria and found them to be effective against some of them, as it showed inhibitory activity against *Staphylococcus aureus*, *E. coli* and *Shigella dysenteriae*, and ineffective against *Pseudomonas aeruginosa* (Yang *et al*, 2021; Arora *et al*, 2020).

### MATERIALS AND METHODS

Chromic Chloride, NICKEL (II) Chloride-6-Hydrate, Manganase Chloride-4-Hydrate, Zink Chloride, Cadmium chloride, Mercuric chloride, Queercetin, Sodium hydroxide, Methanol, Dimethyl sulfoxide, Ethanol absolute, Muller Hinton agar, Nutrient broth, Autoclave, U.V - Visible Spectrophotometer, FT - IR Spectrophotometer, Incubator, Molar Conductivity Sensitive Balance, Water Bath, Spectrophotometer, Magnetic Stirrer with hot plate (Gogoi *et al*, 2020).

#### Preparation of mixed ligand complexes (L1, L2) of type M (L1)(L2)Cln.n H<sub>2</sub>O]

The Cu(L1)(L2)Cln.nH<sub>2</sub>O complex was prepared by adding 1X10<sup>-3</sup> M 0.17048 gm of hydrated copper chloride (CuCl<sub>2</sub>.2H<sub>2</sub>O) dissolved in 10 ml of absolute ethanol to 1 × 10<sup>-3</sup> 0.33823 gm of ligand (L1) and (0.4821 gm) of ligand (L2), respectively, each of them dissolved in 10 ml of absolute ethanol in a ratio (1:1). The mixture was placed in a circular flask with a capacity of 100 ml and it heated up to (50) degrees Celsius with continuous stirring for three hours at the pH: 7, then the reaction mixture was cooled until the appearance of the precipitate, and the formed precipitate was filtered, dried and recrystallized using absolute ethanol. The rest of the other similar complexes were prepared in the same way above, taking into account changing the metal salt each time (Swain *et al*, 2021).

#### Preparation of mixed complexes of lycande L1,L3) of type M (L1)(L3)Cln.n H<sub>2</sub>O]

The Cu(L1)(L3)Cln.nH<sub>2</sub>O complex was prepared by adding 1x10<sup>-3</sup> M 0.17048 gm of hydrated copper chloride (CuCl<sub>2</sub>.2H<sub>2</sub>O) dissolved in 10 ml of absolute ethanol to 1 × 10<sup>-3</sup> 0.33823gm of The ligand (L1) and (0.25633gm) of ligand (L3), respectively, dissolved in 10 ml of absolute ethanol in a ratio of (1:1). The mixture was placed in a

round flask of 100 ml capacity and heated up at a temperature of 50°C with continuous stirring for three hours at PH:7, then the reaction mixture was cooled until the appearance of the precipitate and the formed precipitate was filtered, dried and recrystallized using absolute ethanol. The rest of the other similar complexes were prepared in the same way above, taking into account changing the metal salt each time (Swain *et al*, 2021).

### RESULTS AND DISCUSSION

The study included the preparation of complexes by reacting the ligands (L2) and (L1) with elemental chlorides in a ratio of (1:1:1) mol, using pure ethanol as the reaction medium and sodium hydroxide as a strong base by the process of heat escalation. Various solvents, as well as other complexes were prepared by the reaction of the ligands (L3) and (L1) with the chlorides of the elements and in the same way above. Metallic complexes have appeared to us with remarkable thermal stability at room temperature and in the air, and they were of different colors, as well as they had a solubility in different solvents. As I mentioned in the practical part, and through the results of these techniques, the structural formulas of the prepared complexes were reached. It was found in this study that the molar electrical conductivity measurements

**Table 1 :** Electronic spectra of the prepared complexes (L2), (L1).

No.	Complexes	Wave number (cm <sup>-1</sup> )	Electronic transition type
1	[Cr(L <sub>1</sub> )(L <sub>2</sub> )Cl <sub>2</sub> ]	47619 33898 30769	<sup>4</sup> A <sub>2g</sub> → <sup>4</sup> T <sub>1g</sub> (p) <sup>4</sup> A <sub>2g</sub> → <sup>4</sup> T <sub>1g</sub> (F) <sup>4</sup> A <sub>2g</sub> → <sup>4</sup> T <sub>1g</sub>
2	[Mn (L <sub>1</sub> )(L <sub>2</sub> )Cl H <sub>2</sub> O]	39370 34483 21739	<sup>6</sup> A <sub>1g</sub> → <sup>4</sup> A <sub>1g</sub> + <sup>4</sup> E <sub>g</sub> (G) <sup>6</sup> A <sub>1g</sub> → <sup>4</sup> T <sub>2g</sub> (G) <sup>6</sup> A <sub>1g</sub> → <sup>4</sup> A <sub>1g</sub> (G)
3	[Fe(L <sub>1</sub> )(L <sub>2</sub> )Cl <sub>2</sub> ]	41666 33898 20408	<sup>2</sup> A <sub>2g</sub> → <sup>4</sup> T <sub>1g</sub> <sup>2</sup> A <sub>2g</sub> → <sup>4</sup> E <sub>g</sub> <sup>2</sup> A <sub>2g</sub> → <sup>4</sup> T <sub>1g</sub>
4	[Co(L <sub>1</sub> )(L <sub>2</sub> )Cl H <sub>2</sub> O]	38461 26315 17543 15625	<sup>4</sup> T <sub>1</sub> → <sup>4</sup> A <sub>2</sub> <sup>4</sup> T <sub>1</sub> → <sup>4</sup> T <sub>1</sub> (p) <sup>4</sup> T <sub>1</sub> → <sup>4</sup> T <sub>2</sub> <sup>4</sup> T <sub>1</sub> → <sup>2</sup> E
5	[Ni(L <sub>1</sub> )(L <sub>2</sub> )Cl H <sub>2</sub> O]	32051 15576 10245	<sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>2g</sub> <sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub> <sup>3</sup> A <sub>2g</sub> → <sup>3</sup> T <sub>1g</sub>
6	[Cu(L <sub>1</sub> )(L <sub>2</sub> )Cl H <sub>2</sub> O]	33898 25974 14925	C. T. <sup>3</sup> A <sub>1</sub> (g) → <sup>1</sup> (g) <sup>2</sup> B <sup>2</sup> B <sub>2(g)</sub> → <sup>1</sup> (g) <sup>2</sup> B
7	[Zn(L <sub>1</sub> )(L <sub>2</sub> )Cl H <sub>2</sub> O]	41666 33898	C. T. C. T.
8	[Cd(L <sub>1</sub> )(L <sub>2</sub> )Cl H <sub>2</sub> O]	48780 35714	C. T. C. T.
9	[Hg(L <sub>1</sub> )(L <sub>2</sub> )Cl H <sub>2</sub> O]	42553 35714	C. T. C. T.

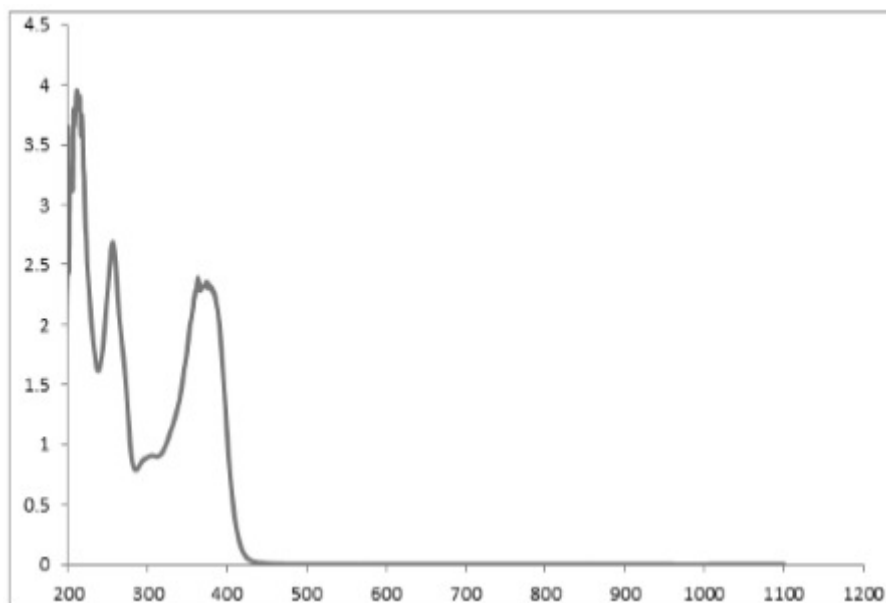


Fig. 1 : UV-Visible Spectrum of Quercetin . Lycand.

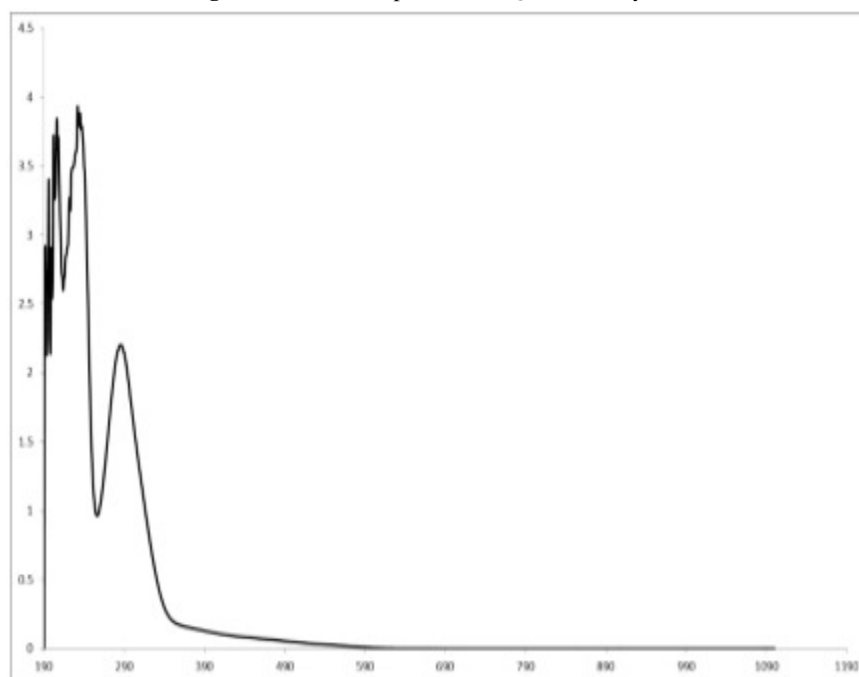


Fig. 2 : UV-visible spectrum of 1,5diphenyl carbazone ligand.

agree with the proposed structural formulas for the complexes and Table 1 shows that, and all the prepared complexes behaved as neutral compounds non-electrolytic or very weakly conductive. The magnetic susceptibility of the forbidden complexes was also measured, which showed that the proposed octahedral shape was found, as it was found that the values of the magnetic moment of the manganese complex ( $^{22}$ ) are equal to (5.85B.M) and this value agrees with the magnetic values of the manganese ( $^{22}$ ) complexes of highly twisted octahedral shape. As for the prepared iron ( $^{22}$ ) complex, it showed a magnetic moment (5.25B.M) and this value is similar

to the magnetic moments of the highly twisted octahedral iron ( $^{22}$ ) complexes, and these measurements apply to the rest of the complexes. The UV spectrum was measured in a solvent dimethyl sulfoxide (DMSO) using a cell with a diameter of (1 cm). At room temperature, the ligands showed two main absorption bands

- 1- A band appeared in the region between (212 - 286 nm), which represents electronic transitions of the type ( $p \rightarrow p^*$ ), which belong to the aromatic ring, as well as the double bond transitions for the two groups C=N and (C=S).

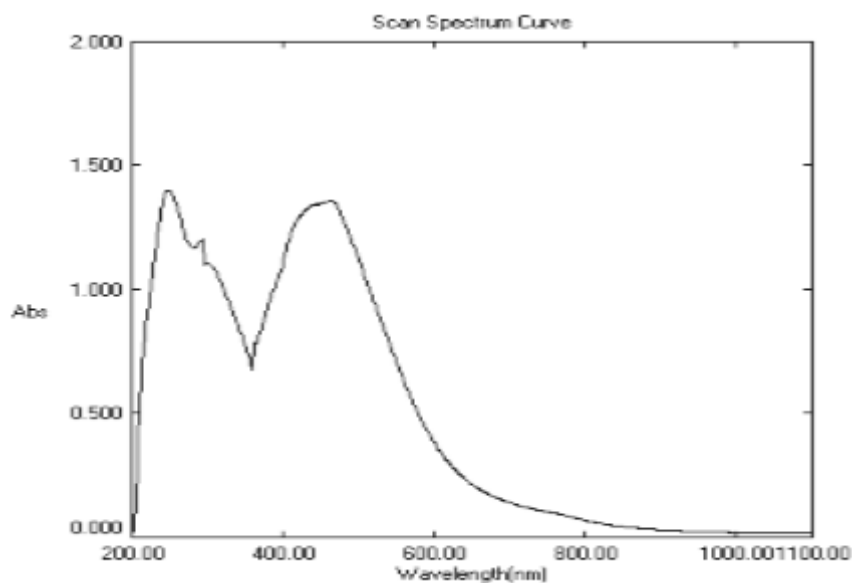


Fig. 3 : UV-visible spectrum of the complex  $[Mn(L1)(L2) Cl H_2O]$ .

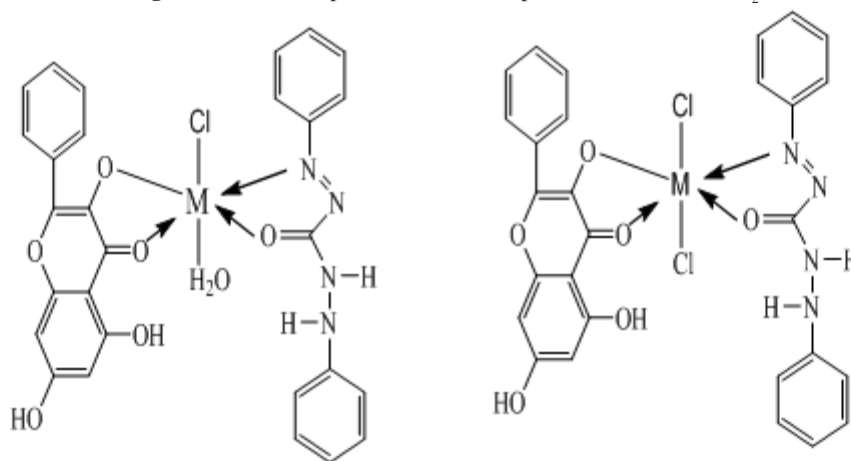


Fig. 4 : Structure of the prepared complex of type L1 and (L2).

- 2- A band that appeared in the region between (255-357 nm), which represents electronic transitions of the type ( $n \rightarrow p^*$ ), which belong to the two groups C=S and C=N, and these also appeared in the ligands and the Tables 1, 2 and Figs. 3 and 4 shows that, in the case of the prepared complexes.

Where the results showed that the UV-visible spectrum of the complex (L2) L1 manganese (II) three absorption peaks were the first ( $11822 \text{ cm}^{-1}$ ) and the second ( $20080 \text{ cm}^{-1}$ ) and the third ( $29851 \text{ cm}^{-1}$ ) to the electron transitions  $6A1g \rightarrow 4T1g$ ,  $6A1g \rightarrow 4A1g$  and  $6A1g \rightarrow 4A1g$ , respectively. It has a shift towards a higher wavelength (red shift) of approximately (10-30 nm). This is due to the change in the electron structure and the energy level in the ligands when they are coordinated with the metal ions if the second and third bands return to the electron transition  $n \rightarrow p^*$ ,  $p \rightarrow p^*$ . The emergence of a new band with a limit of ( $11822 \text{ cm}^{-1}$ ) is due to the

spectrum of the charge transfer from the ligands to the metal.

#### Group stretching vibrations $\nu$ (C=N)

Stretching vibrations of the group (C=N) appeared in the ligands with a range of ( $1620 \text{ cm}^{-1}$ ) and this region of the spectrum suffered from changes in the spectra of the metal complexes under study in terms of the shape, strength and positions of the bands that appeared to us and were in the complexes that were prepared within the range ( $1429\text{-}1593 \text{ cm}^{-1}$ ). The shift of the values of this group was observed in those ligands, which was about 15% and the reason for these changes was the size of the coordination of the ligands with the ions of the metal elements, as they were shifted to lower frequencies for the spectrum of the metal complexes, as shown in Table 1 and this shift in the bond stretching (C = N) of the ligands indicates that the metal is attached to the nitrogen atom

**Table 2** : Frequencies of the infrared spectra in cm<sup>-1</sup> for metal complexes (L<sub>2</sub>) (L<sub>1</sub>).

No	Complexes	$\nu$ N-H	$\nu$ C=N	$\nu$ O-H	$\nu$ C=O	$\nu$ M-O	$\nu$ M-N	$\nu$ M-Cl
1	[Cr(L <sub>1</sub> )(L <sub>2</sub> ) Cl <sub>2</sub> ]	3236	1490	3560	1683	518	470	284
2	[Mn(L <sub>1</sub> )(L <sub>2</sub> ) Cl H <sub>2</sub> O]	3224	1429	3566	1635	523	453	288
3	[Fe(L <sub>1</sub> )(L <sub>2</sub> ) Cl <sub>2</sub> ]	3101	1429	3481	1622	528	463	345
4	[Co(L <sub>1</sub> )(L <sub>2</sub> ) Cl H <sub>2</sub> O]	3086	1436	3446	1616	516	443	360
5	[Ni (L <sub>1</sub> )(L <sub>2</sub> ) Cl H <sub>2</sub> O]	3076	1489	3421	1660	532	445	379
6	[Cu(L <sub>1</sub> )(L <sub>2</sub> ) Cl H <sub>2</sub> O]	2997	1490	3446	1622	510	480	280
7	[Zn(L <sub>1</sub> )(L <sub>2</sub> )Cl H <sub>2</sub> O]	2922	1490	3446	1616	535	478	298
8	[Cd(L <sub>1</sub> )(L <sub>2</sub> ) Cl H <sub>2</sub> O]	3072	1487	3439	1598	532	465	390
9	[Hg(L <sub>1</sub> )(L <sub>2</sub> ) Cl H <sub>2</sub> O]	3068	1456	3549	1627	520	472	387

### Group stretching vibrations $\nu$ (C=O)

Stretching vibrations of the group (C=O) appeared in the ligands with a range of (1700cm<sup>-1</sup>) and this region of the spectrum suffered from changes in the spectra of the metal complexes under study in terms of the shape, strength and positions of the bundles that appeared to us and were in the complexes that were prepared within the range (1519-1625cm<sup>-1</sup>) and the shift of most of the values of this group in those ligands, which was about 12% and the reason for these changes was the size of the coordination of the ligands with the ions of the metal elements as they were shifted to lower frequencies for the spectrum of the metal complexes, as shown in the Table 1 and this shift in the bond stretching (C=O) of the ligands indicates the bonding of the metal to the oxygen atom.

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