



**SYNTHESIS, CHARACTERIZATION, THEORETICAL STUDIES AND
BIOLOGICAL ACTIVITIES OF MIXED LIGAND COMPLEXES OF
Cr(III), Mn(II), Fe(III), Co(II), Ni(II) AND Cu(II) WITH
2-HYDROXYBENZALDEHYDE AND OXALIC ACID**

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ABSTRACT

The new mix ligand complexes of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), or Cu(II) with 2-hydroxybenzaldehyde, and oxalic acid were synthesized and characterized by FT-IR, and Uv-Vis spectroscopy, elemental analysis, and flame atomic absorption techniques as well as magnetic susceptibility, and conductivity measurements. The antibacterial activity of the mix ligand metal complexes was studied against two types of pathogenic bacteria micro-organisms (*Escherichia coli*) and (*Staphylococcus aureus*). Furthermore, the antifungal activity against two fungi micro-organisms (*Candida albicans*) and (*Aspergillus flavus*) was studied too. The work also includes a theoretical treatment of the formed complexes in the gas phase; this was done using the (hyperchem-8) program for the molecular mechanics and semi-empirical calculations. The heat of formation (ΔH_f°), binding energy (ΔE_b), and total energy (ΔET) of the ligand and its complexes were calculated using (PM3) method at 298 K°. PM3 was used to evaluate the bond length, vibrational spectra, and electronic spectra of the mix ligand metal complexes, also the experimental values were compared. The theoretical results agree with those found experimentally.

Key words: 2-Hydroxybenzaldehyde, Oxalic acid, Mix ligand complexes, Antimicrobial studies, Theoretical studies.

INTRODUCTION

Oxalic acid is naturally contained as potassium or calcium salt in plants, vegetables, human urine, animal urine, and kidney stones and it is also product of the metabolism of many molds¹. It can be released to the environment by tobacco smoke, automobile exhaust, rendering, waste streams from pulp bleaching and by photochemical oxidations of anthropogenic compounds during long range transport^{1,2}. When it released to soil, oxalic acid under environmental conditions (pH 5-9) will be in the oxalate ion form (pKa1, pKa2 of 1.25, and 4.28, respectively) and is expected to leach in soil². Oxalic acid at three concentrations (2, 4, and 6 mM) was applied by dipping to pomegranate fruits of cv. Mollar de Elche, which was then stored for 84 days at 2°C, pomegranate is a chilling-sensitive fruit and, thus, controls fruits exhibited chilling injury (CI) symptoms after long-term storage at 2°C that were accompanied by increased respiration rate, weight loss, and electrolyte leakage (EL)³. The CI symptoms were significantly reduced by oxalic acid treatment, especially for the 6 mM concentration. In addition, controlling pomegranates showed significant

reduction in the content of total phenolics and ascorbic acid, and in total antioxidant activity (TAA) as well, in both hydrophilic (H-TAA) and lipophilic (L-TAA) fractions. Applying oxalic acid leads to lower losses of total phenolics and it leads to significant increase in both ascorbic acid content and H-TAA, whereas L-TAA remains unaffected. Thus, oxalic acid could be a promising postharvest treatment to alleviate CI and increase antioxidant potential⁴.

In the literature survey, there is little attention concerning the mode of coordination of 2-hydroxybenzaldehyde and oxalic acid with d-block metal ions. Prasad et al.⁵ studied the alkaline earth metals with [5-chloro salicylaldehyde and salicylaldehyde, 2-hydroxy acetophenone or 2-hydroxy propiophenone] have been carried out in 1:1:1 mole ratio and the mixed ligand complexes of the type $[MLL^-(H_2O)_2]$, where M=Mg(II), Co(II), Sr(II), and Ba(II), which were isolated in 2003⁶. The same metal ions formed complexes of the type $[MLL^-(H_2O)_2]$, where L = bromosalicylaldehyde and HL⁻ = pentane-2,4-dione, 1-phenylbutane-1,3-dione or 1,3-diphenyl propane dione, which have been synthesized by 1:1:1 molar reactions of metal chlorides with 5-bromo salicylaldehydediketones. For continuity, we have employed in this study the coordination mode of oxalic acid and 2-hydroxy benzaldehyde via some of d-block such as Cr(III), Mn(II), Fe(III), Co(II), Ni(II), and Cu(II). The solid products were isolated, and characterized, and then the mixligand complexes were screened for their biological potent against a variety of pathogenic fungal and bacterial strains. Furthermore, the theoretical studies of the mixligand complexes were also studied and compared with the experimental results.

EXPERIMENTAL

Chemicals

Reagent grade 2-hydroxybenzaldehyde, oxalic acid dehydrate, chromium chloride hydrate, manganese chloride hydrate, ferric chloride hydrate, cobalt chloride hydrate, copper chloride hydrate salts (Aldrich).

Solvent was purified using standard methods.

Physical measurement

Melting points were recorded using Gallenkamp MF B600 melting point apparatus. Elemental analyses (C, H, N) were obtained using EA-034 mth. for metal complexes of naringin (L). Metal contents of complexes were spectrophotometrically estimated using flame atomic absorption Shimadzu-670 AA Spectrophotometer. Infrared spectra were recorded using FT-IR-8300 Shimadzu in the range of (4000-350) cm^{-1} ; samples were measured as (CsI) disc. Magnetic susceptibilities of samples in the solid state were measured using Bruker BM6 magnetic balance. Molar conductivity was measured using electrolytic conductivity measuring set Model MC-1-Mark V, using platinum electrode (EDC 304) with cell constant (1 cm^{-1}), concentration (10^{-3} M) in dimethylformide as a solvent at room temperature. Electronic spectra were obtained using UV-1650PC-Shimadzu spectrophotometer at room temperature; the measurements were recorded using (10^{-3} M) concentration of the metal complexes in dichloro-methane as a solvent.

Synthesis of the metal complexes [M = Cr(II), Mn(II), Fe(II), Co(II), Ni(II), and Cu(II)] with 2-hydroxybenzaldehyde (HD) and oxalic (OX)

Ethanol solution of $\text{CrCl}_3 \cdot 6\text{H}_2\text{O}$ (0.26 g/1 mmol), $\text{MnCl}_2 \cdot 4\text{H}_2\text{O}$ (0.197 g/1 mmol), $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ (0.237 g/1 mmol), $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$ (0.237 g/1 mmol), $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ (0.237 g/1 mmol), and $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ (0.12 g/1 mmol) mixed with ethanol solution of (0.1 g/1 mmol) of 2-hydroxy benzaldehyde and (0.1 g/1 mmol) of oxalic acid in 1:1:1 (HD:OX:M) followed by the gradual addition of sodium hydroxide (2 mL, 5% M). The resulted homogeneous solution was refluxed for 1 hr. at 50°C during this period the products formed, and

then they were filtered, washed with hot ethanol, washed with cold water and dried in Vacuo anhydrous CaCl_2 . The physical properties and analytical data of these complexes are shown in Table 1.

Table 1: The physical data of complexes (1-6)

| Compd. No. | Color | Melting point ($^{\circ}\text{C}$) | Yield (%) | Metal analysis found calc. | | | Suggested formula |
|------------|------------|--------------------------------------|-----------|----------------------------|------|-------|--|
| | | | | C% | H% | M% | |
| 1 | Dark green | >250 | 80 | 36.44 | 3.76 | 18.43 | [Cr(C ₉ H ₆ O ₆)(H ₂ O) ₂] |
| | | | | 36.24 | 3.36 | 17.45 | |
| 2 | Yellow | >238 | 73 | 41.12 | 5.04 | 15.22 | Na[Mn (C ₉ H ₆ O ₆)(C ₂ H ₅ OH) ₂] |
| | | | | 41.06 | 4.74 | 14.49 | |
| 3 | Dark brown | >258 | 85 | 43.90 | 5.22 | 15.18 | [Fe (C ₉ H ₆ O ₆)(C ₂ H ₅ OH) ₂] |
| | | | | 43.59 | 5.03 | 15.61 | |
| 4 | Pink | >212 | 89 | 33.06 | 2.97 | 18.39 | Na[Co (C ₉ H ₆ O ₆)(H ₂ O) ₂] |
| | | | | 32.83 | 2.74 | 18.24 | |
| 5 | Red | >240 | 80 | 41.00 | 4.80 | 15.34 | Na[Ni (C ₉ H ₆ O ₆)(C ₂ H ₅ OH) ₂] |
| | | | | 40.66 | 4.69 | 15.30 | |
| 6 | Green | >249 | 83 | 36.66 | 2.11 | 22.26 | Na[Cu (C ₉ H ₆ O ₆)] |
| | | | | 36.42 | 2.02 | 21.43 | |

Programs used in theoretical calculation

Hyperchem is a sophisticated molecular modeler, editor and powerful computational package, that is known for its quality, flexibility and ease of use^{7,8}. It can plot orbital wave functions resulting from semi-empirical quantum mechanical calculations, as well as the electrostatic potential, the total charge density or the total spin density can also be determined during semi-empirical calculation, this information is useful in determining reactivity and correlating calculation results with experimental data.

Computational methods

- (i) Semi-empirical quantum mechanical
- (ii) Molecular mechanics
- (iii) Mopac 2000

Types of calculations

Types of possible prediction of molecules are^{9,10}:

- (i) Geometry optimization calculations employ energy minimization algorithms to locate stable structures.
- (ii) Bond distances.
- (iii) Molecular dynamics which provide the thermodynamic calculations and dynamic behavior of molecules.
- (iv) Plot the electrostatic potential field (HOMO and LUMO).
- (v) Vibrational spectrum (I.R and Raman spectra).

RESULTS AND DISCUSSION

Part (I) Study complexes in solid state

Elemental analyses

The physical and analytical data of the mixligand complexes (1-6) are given in Table 1. The results obtained from elemental analysis agree with the calculated value. The suggested molecular formula was also supported by spectral measurement as well as magnetic moment. The new (1-6) complexes colored crystalline solid were soluble in (CH₂Cl₂, CHCl₃, DMF, and DMSO). They are thermally stable and unaffected by atmospheric oxygen and moisture.

Infrared spectroscopic study

The characteristic vibrations of the important groups are described in Table 2. The strong band at 1679 cm⁻¹, which is attributed to [ν_{C=O}] group¹², was shifted to lower frequency cm⁻¹ in the all mix ligand complexes as compared to (2-hydroxybenzaldehyd) (HD), Table 2. A broad band is observed at 3700 cm⁻¹ in IR spectra of (HD) that assigned to ν_{OH}, which disappeared in all their respective complexes¹⁻⁶ that means its bonding with metal ions through deprotonating^{12,13}.

Table 2: Stretching vibrational frequencies (cm⁻¹) located in the FT-IR spectra of (HD and OX) and their complexes

| Compd. No. | ν _{C=O} | ν _{OH} (hydroxyl group) | ν _{C-O} (phenolic) | ν _{COO-asy. sym.} | ν _{M-O} | ν _{O-H} (of C ₂ H ₅ OH) | ρ _{O-H} of H ₂ O |
|------------|------------------|-------------------------------------|--------------------------------|----------------------------|------------------|---|---|
| (HD) | 1679 | 3700 | 1275 | - | - | - | - |
| (OX) | - | - | - | 1665 1410 | - | - | - |
| 1 | 1666 | - | 1255 | 1593 1410 | 522 | - | 840 |
| 2 | 1662 | - | 1253 | 1620 1408 | 516 | 3525 | - |
| 3 | 1660 | - | 1260 | 1626 1410 | 508 | 3530 | - |
| 4 | 1666 | - | 1265 | 1622 1409 | 513 | - | 830 |
| 5 | 1668 | - | 1257 | 1593 1410 | 505 | 3500 | - |
| 6 | 1660 | - | 1261 | 1593 1410 | 511 | - | - |

Another important band occurs at 1275 cm⁻¹ due to phenolic ν_{C-O} shifts to lower frequency by (22-10) cm⁻¹ in the complexes, Table 2. As well as, FT-IR spectra show strong evidence supporting the involvement of carboxylate group (COO⁻) in coordination, in comparison with free ligand Oxalic acid (OA), a band observed at 1665 cm⁻¹ due to ν_{(COO⁻)asy.} In (OA) spectra, it was shifted to lower wave number in the spectra of mixed ligand complexes, representing coordination of carboxylic group with metal ions through the oxygen atom, which confirms the monodenticity of the carboxylate group¹². These observations were

further indicated by the appearance of ν_{M-O}^{14} . The complexes (1, and 4) show additional bands at 840 and 830 cm^{-1} , respectively, indicating the presence of coordinated water^{14,15}. Broad bands were observed around (3500-3530) cm^{-1} in spectra of some mixed ligand complexes (2, 3, and 5), assigned to ν_{OH} , which suggested the presence of ethanol molecule in the complexes¹⁵.

Electronic absorption spectra of the free ligands (HD and OX) and their complexes (1-6)

Electronic spectra of the free ligands (HD and OX)

The electronic spectra of the free ligands (HD, and OX) and their complexes (1-6) were recorded in DMF solution.

The spectrum of (HD) shows a strong band at 42194 cm^{-1} , which is attributed to $\pi \rightarrow \pi^*$ and another one at 31545, 29411 cm^{-1} due to $n \rightarrow \pi^*$ ^{12,13,15}.

The (OX) spectrum shows absorption bands at 34246, 32573 cm^{-1} , respectively, due to $\pi \rightarrow \pi^*$ and another bands at 26881, 25380 cm^{-1} belong to $n \rightarrow \pi^*$.

Electronic spectra of the complexes (1-6)

1. The spectra of Cr(III) complex exhibit three absorption bands at (12364, 16493, and 29881) cm^{-1} . The spectrum was typical of octahedral Cr(III) complexes¹⁶⁻¹⁸. The (ν_2/ν_1) ratio is (1.33), which is very close to the value of obtained for pure octahedral Cr(III) complexes^{17,18}, Table 3.
2. The electronic spectra of Mn(II) complex showed a series of very weak and some narrow bands, which is expected because of the only sextet term of the d^5 configuration in octahedral stereo chemistry is the ${}^6A_{1g}$, consequently, there can be no spin-allowed transitions^{16,19}, and were assigned to ${}^6A_{1g} \rightarrow {}^4T_{1g}(G)$, ${}^6A_{1g} \rightarrow {}^4T_{2g}(G)$ and ${}^6A_{1g} \rightarrow {}^4A_{1g} + {}^4E_g(G)$, respectively¹⁶. The values of ligand field parameters (10Dq, \bar{B} and β) have been calculated, Table 3.
3. The prepared dark brown Fe(III) complex showed three bands at (15018, 17803, and 33214) cm^{-1} , which are assigned to the transitions: ${}^6A_{1g} \rightarrow {}^4T_{1g}$, ${}^6A_{1g} \rightarrow {}^4T_{2g}$ and (L) \rightarrow Fe (C.T), respectively^{16,20,21}. The values of 10 Dq obtained by $Dq/B = 1.2$, as well as B and β come out to (6818, 611, and 0.5), respectively^{16,20} (Table 3).
4. The electronic spectra of (HD), and (OX) Co(II) complex showed two spin-allowed transitions at 15337, and 18450 cm^{-1} assigned to ${}^4T_{1g} \rightarrow {}^4A_{2g(F)}(\nu_2)$ and ${}^4T_{1g} \rightarrow {}^4T_{1g(P)}(\nu_3)$ transitions, respectively, which indicate an octahedral stereo-chemistry¹⁶⁻¹⁸. The ν_1 transition is expected to appear at larger (λ) below 10000 cm^{-1} and hence it could not be observed. The values of ligand field parameters (ν_1 , 10Dq, \bar{B} , and β) have been calculated to be (8151, 9509, 715, and 0.74), respectively (Table 2).
5. The electronic spectrum of the mixed Ni(II) complex displayed three bands at 10996, 14662, and 24570 cm^{-1} , these transitions have tentatively been assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g(F)}(\nu_1)$, ${}^3A_{2g} \rightarrow {}^3T_{1g(F)}(\nu_2)$, and ${}^3A_{2g} \rightarrow {}^3T_{1g(P)}(\nu_3)$ transitions, respectively^{16,20,21}. The 10 Dq value of the complex equals 10923 cm^{-1} , and \bar{B} value found to be 733.1 cm^{-1} , while β equals 0.65 (Table 3). These assignments correspond to Ni(II) octahedral complexes^{16,18,20,21}.
6. The solution spectrum of the dark green copper complex (4), displays a broad band at 11286 cm^{-1} and a well-defined shoulder around 22727 cm^{-1} , attributable to ${}^2B_{1g} \rightarrow {}^2E_g$ and ${}^2B_{1g} \rightarrow {}^2A_{1g}$ transitions, which strongly favour square planar geometry around the central metal ion^{16,18-21}. The broadness of the band can be taken as an indication of distortion from perfect planar symmetry.

Magnetic moments

The magnetic moment values were measured at room temperature for all the studied complexes (1-6), and they are given in Table 3.

Table 3: Electronic spectra, molar conductivity and magnetic moment of mixligand complexes

| Comp. No. | Wave number (cm ⁻¹) | Assignment | \bar{B} | 10Dq | β | μ_{eff} B.M | Molar cond. (Ohm ⁻¹ .cm ² . mol ⁻¹) | Structure |
|-----------|---------------------------------|---|-----------|-------|---------|------------------------|---|---------------|
| 1 | 12364 | ${}^4A_{2g} \rightarrow {}^4T_{2g}$ | - | - | - | 3.89 | 22.43 | Octahedral |
| | 16493 | ${}^4A_{2g} \rightarrow {}^4T_{1g}$ | | | | | | |
| | 29881 | ${}^4A_{2g} \rightarrow {}^4T_{1g} (P)$ | | | | | | |
| 2 | 11822 | ${}^6A_{1g(S)} \rightarrow {}^4T_{1g(G)}$ | 848 | 12720 | 0.99 | 5.22 | 13.07 | Octahedral |
| | 2080 | ${}^6A_{1g(S)} \rightarrow {}^4T_{2g(G)}$ | | | | | | |
| | 29851 | ${}^6A_{1g(S)} \rightarrow {}^4A_{1g} +$ | | | | | | |
| | 36364 | ${}^4E_{g(G)}$ C.T | | | | | | |
| 3 | 15018 | ${}^6A_{1g} \rightarrow {}^4T_{1g(G)}$ | 611 | 0.5 | 6818 | 5.86 | 15.98 | Octahedral |
| | 17803 | ${}^6A_{1g(S)} \rightarrow {}^4T_{2g(G)}$ | | | | | | |
| | 33214 | C.T | | | | | | |
| 4 | 8151 (cal.) | ${}^4T_{1g} \rightarrow {}^4T_{2g(F)}$ | 715 | 9509 | 0.74 | 4.98 | 10.36 | Octahedral |
| | 15337 | ${}^4T_{1g} \rightarrow {}^4A_{2g(F)}$ | | | | | | |
| | 18450 | ${}^4T_{1g} \rightarrow {}^4T_{1g(P)}$ | | | | | | |
| 5 | 10996 | ${}^3A_{2g} \rightarrow {}^3T_{2g(F)}$ | 733.1 | 10923 | 0.65 | 3.25 | 14.51 | Octahedral |
| | 14662 | ${}^3A_{2g} \rightarrow {}^3T_{1g(F)}$ | | | | | | |
| | 24570 | ${}^3A_{2g} \rightarrow {}^3T_{1g(P)}$ | | | | | | |
| 6 | 11286 | ${}^2B_{1g} \rightarrow {}^2E_g$ | - | - | - | 1.80 | 18.33 | Square Planer |
| | 22727 | ${}^2B_{1g} \rightarrow {}^2A_{1g}$ | | | | | | |

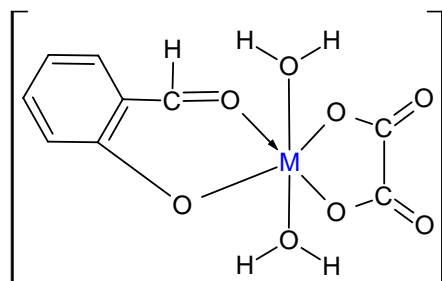
Magnetic moment of Cr(III) solid complex (**1**) was found to be (3.89 B.M). Mn(II) complex (**2**) have μ_{eff} value (5.22 B.M.) corresponding to five unpaired electrons. The magnetic moment of Fe(III) complex (**3**) is (5.86 B.M), with five unpaired electrons and an octahedral configuration^{22,23}. The magnetic susceptibility of Co(II) complex (**4**) shows magnetic moment value (4.98 B.M.), and suggests high spin octahedral geometry with three unpaired electrons^{18,22,23}, which is further supported by electronic spectral data in this complex. Ni(II) of mixed ligand complex (**5**) shows μ_{eff} value (3.25 B.M.) corresponding to two unpaired electrons in an octahedral environment²²⁻²⁴. The magnetic moments of Cu(II) complex (**6**) in the present study, corresponds to μ_{eff} value for one unpaired electron (1.80 B.M.)^{18,23,24}.

Molar conductivity

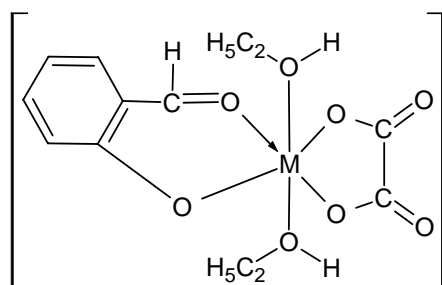
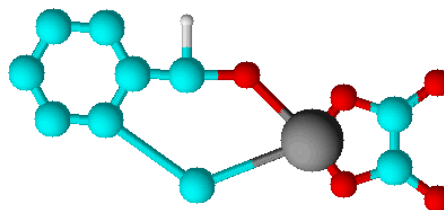
The molar conductivity of mixed ligands complexes (**1-6**) with the mentioned metal ions were measured using 10⁻³ M DMF solvent at room temperature (Table 3). The obtained data indicate that all the synthesized mix ligand complexes have non-electrolytic nature.

Stereo chemistry structure of metal complexes (1-6)

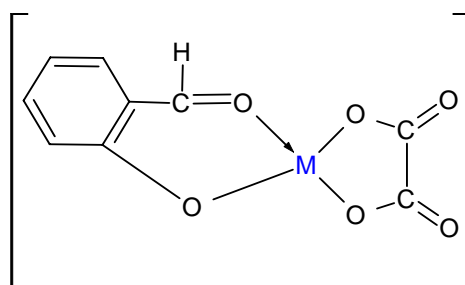
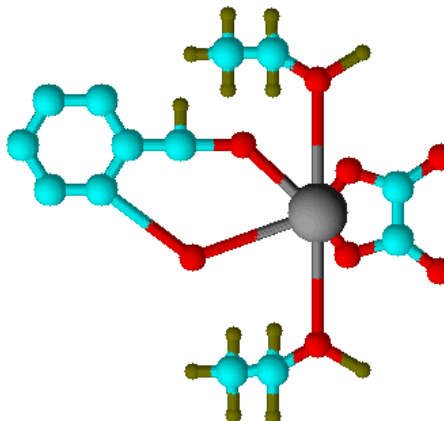
According to the results obtained from elemental and spectral analysis, as well as magnetic moment and conductivity measurements, the structure of the above mentioned compounds can be illustrated as follows, Figure (2).



Where M = Cr(III) and Co(II)



Where M = Mn(II), Fe(III) and Ni(II)



Where M = Cu(II)

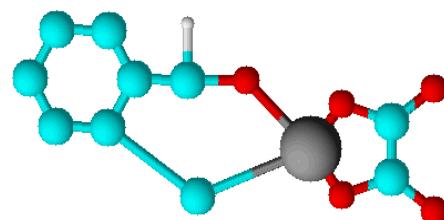


Fig. 1: The suggested structure of complexes (1-6)

Part (II) study complexes in gas stat (Theoretical studies)

Optimized energies

Program hyperchem-8 was used for the semi-empirical and molecular mechanics calculations. The heat of formation (ΔH_f°) and binding energy (ΔE_b) for Mix ligand complexes (1-6) were calculated (Table 4).

Table 4: Conformation energetic (in KJ. mol⁻¹) for mix ligand complexes

| Compd. No. | ΔE_{tot} | ΔH°_f | ΔE_b |
|------------|-------------------------|----------------------|--------------|
| 1 | -185054.96 | -84.88 | -10681.47 |
| 2 | -113605.75 | -266.77 | -5662.60 |
| 3 | -119290.09 | -85.25 | -5481.49 |
| 4 | -122833.58 | -98.94 | -5607.85 |
| 5 | -96003.98 | -36.79 | -5361.40 |
| 6 | -137008.36 | -15.17 | -8153.68 |

Optimized vibrational spectra for mix ligand complexes

The vibrational spectra of the mix ligand complexes (**1-6**) has been calculated and the results shown at Table 5. The theoretically calculated wave numbers for these mix ligand complexes (**1-6**) showed that some deviations from the experimental values, these deviations are generally accepted in theoretical calculations^{25,26}. The most diagnostic calculated vibrational frequencies were chosen for the assignment of mix ligand complexes (**1-6**), which are included in Table 5 and their respective experimental vibrational modes are shown in the same table.

The results obtained for the theoretical calculations of the frequencies agreed well with those obtained from the experimental values (Table 2).

Table 5: Comparison between the experimental and theoretical vibrational frequencies (cm⁻¹) of the mix ligand complexes

| Compd. No. | $\nu_{\text{C=O}}$ | $\nu_{\text{C-O}}$ (phenolic) | $\nu_{\text{COO-}}$ asy./sym. | $\nu_{\text{M-O}}$ | $\nu_{\text{O-H}}$ (of C ₂ H ₅ OH) | $\rho_{\text{O-H}}$ of H ₂ O |
|------------|--------------------|----------------------------------|----------------------------------|--------------------|---|--|
| 1 | 1666* | 1255* | 1593* (1590)** | 522* | - | 840* |
| | 1660** | 1250** | 1410* (1412)** | 520** | | 833** |
| 2 | 1662* | 1253* | 1620* (1622)** | 516* | 3525* | - |
| | 1665** | 1255** | 1408* (1406)** | 511** | 3522** | |
| 3 | 1660* | 1260* | 1626* (1620)** | 508* | 3530* | - |
| | 1658** | 1258** | 1410* (1413)** | 500** | 3528** | |
| 4 | 1666* | 1265* | 1622* (1628)** | 513* | - | 830* |
| | 1660** | 1260** | 1409* (1411)** | 511** | | 833** |
| 5 | 1668* | 1257* | 1593* (1599)** | 505* | 3500* | - |
| | 1669** | 1260** | 1410* (1415)** | 503** | 3498** | |
| 6 | 1660* | 1261* | 1593* (1589)** | 511* | - | - |
| | 1658** | 1258** | 1410* (1418)** | 508** | | |

*Theoretical frequency

**Experimental frequency

Bond length measurements for the mix ligand complexes:

Calculation of parameters has been optimized bond lengths of the mix ligand complexes by applying the semi-empirical (PM3) at geometry optimization (0.001 K.Cal.mol⁻¹), which give excellent agreement with the experimental data^{27,28}, as shown in Table 6.

Table 6: Selected bond lengths (Å) of Mix ligand complexes (1-6)

| Compd. No. | C=O | C-O | COO ⁻ | M-O |
|------------|------|------|------------------|------|
| 1 | 1.67 | 1.55 | 2.28 | 2.28 |
| 2 | 1.71 | 1.58 | 2.25 | 2.25 |
| 3 | 1.69 | 1.55 | 2.22 | 2.22 |
| 4 | 1.65 | 1.53 | 2.28 | 2.28 |
| 5 | 1.70 | 1.56 | 2.14 | 2.14 |
| 6 | 1.63 | 1.54 | 2.19 | 2.19 |

Theoretical electronic spectra for the metal complexes (1-6)

The electronic spectra of the mix ligand complexes have been calculated and the wave number for these compounds showed some deviations from the experimental values, as shown in Table 7. These deviations in theoretical calculation are generally accepted due to couplings between the electronic spectra modes and the approximation that each normal mode of the electronic spectra inter acts independently electronic spectra beam^{28,29}. The most diagnostic calculated electronic spectra were chosen for the assignment of the metal complexes (1-6). Experimental electronic modes are shown in Table 3. All the theoretical electronic spectra of all compounds were calculated using the semi-empirical (PM3) method at geometry optimization (0.01 K.Cal. Mol⁻¹), and the comparison between of the experimental data and theoretical data of the electronic spectra for [1-6] metal complexes was carried out, Table 8.

Table 7: Comparison between experimental and theoretical electronic spectra of (1-6) complexes

| Comp. No. | Maximum absorption ν_{\max} (cm ⁻¹) | Band assignment | Suggested geometry |
|-----------|---|---|--------------------|
| 1 | 12364* (12360)** | ⁴ A _{2g} → ⁴ T _{2g} | Octahedral |
| | 16493* (16490)** | ⁴ A _{2g} → ⁴ T _{1g} | |
| | 29881* (29879)** | ⁴ A _{2g} → ⁴ T _{1g} (P) | |
| 2 | 11822* (11830)** | ⁶ A _{1g(S)} → ⁴ T _{1g(G)} | Octahedral |
| | 2080* (2077)** | ⁶ A _{1g(S)} → ⁴ T _{2g(G)} | |
| | 29851* (29844)** | ⁶ A _{1g(S)} → ⁴ A _{1g} + ⁴ E _{g(G)} | |
| | 36364* (36360)** | C.T | |
| 3 | 15018* (15020)** | ⁶ A _{1g} → ⁴ T _{1g(G)} | Octahedral |
| | 17803* (17800)** | ⁶ A _{1g(S)} → ⁴ T _{2g(G)} | |
| | 33214* (33211)** | C.T | |

Cont...

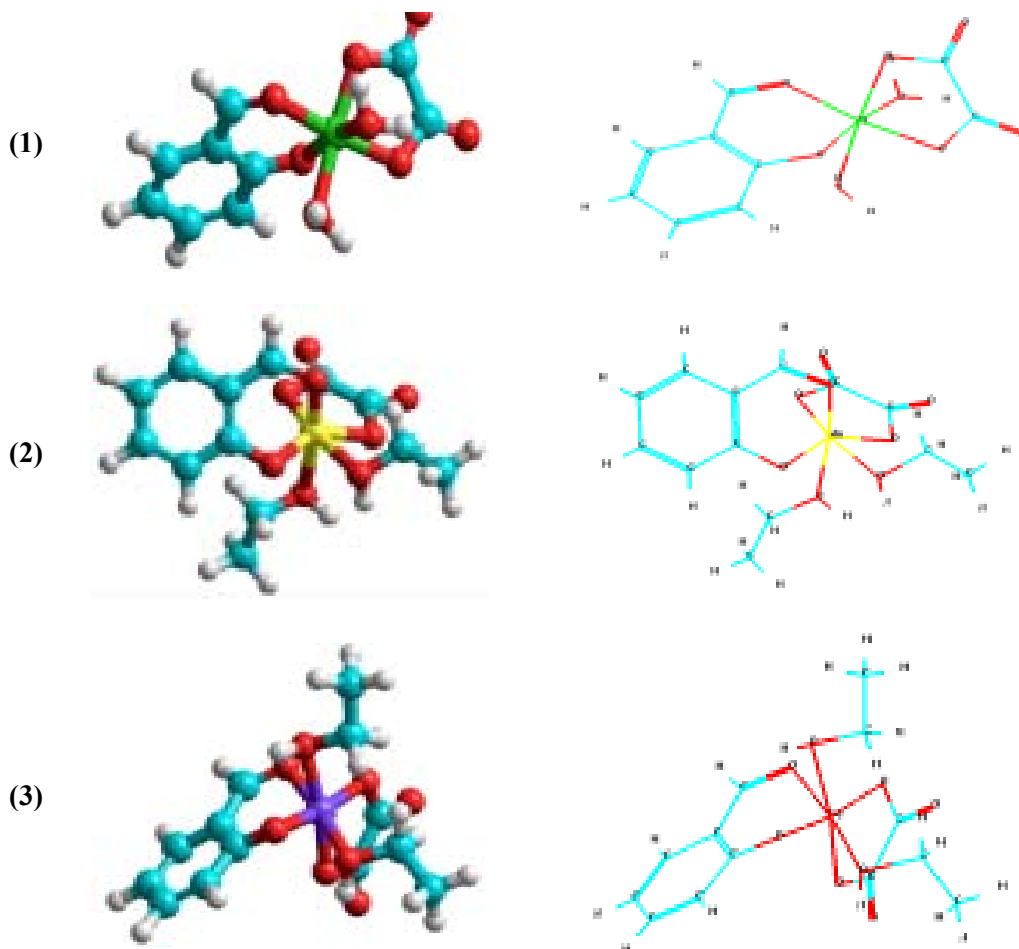
| Comp. No. | Maximum absorption ν_{\max} (cm ⁻¹) | Band assignment | Suggested geometry |
|-----------|---|--|--------------------|
| 4 | 8151 (cal.)* (8144)** | ${}^4T_{1g} \rightarrow {}^4T_{2g(F)}$ | Octahedral |
| | 15337* (15330)** | ${}^4T_{1g} \rightarrow {}^4A_{2g(F)}$ | |
| | 18450* (18455)** | ${}^4T_{1g} \rightarrow {}^4T_{1g(P)}$ | |
| 5 | 10996* (10999)** | ${}^3A_{2g} \rightarrow {}^3T_{2g(F)}$ | Octahedral |
| | 14662* (14660)** | ${}^3A_{2g} \rightarrow {}^3T_{1g(F)}$ | |
| | 24570* (24566)** | ${}^3A_{2g} \rightarrow {}^3T_{1g(P)}$ | |
| 6 | 11286* (11280)** | ${}^2B_{1g} \rightarrow {}^2E_g$ | Square planer |
| | 22727* (22722)** | ${}^2B_{1g} \rightarrow {}^2A_{1g}$ | |

*Theoretical frequency,

**Experimental frequency

Optimized geometries of mix ligand complexes (1-6)

All theoretically probable structures of mix ligand complexes have been calculated using (PM3) method in gas phase to search for the most probable model building stable structure (Fig. 2).



Cont...

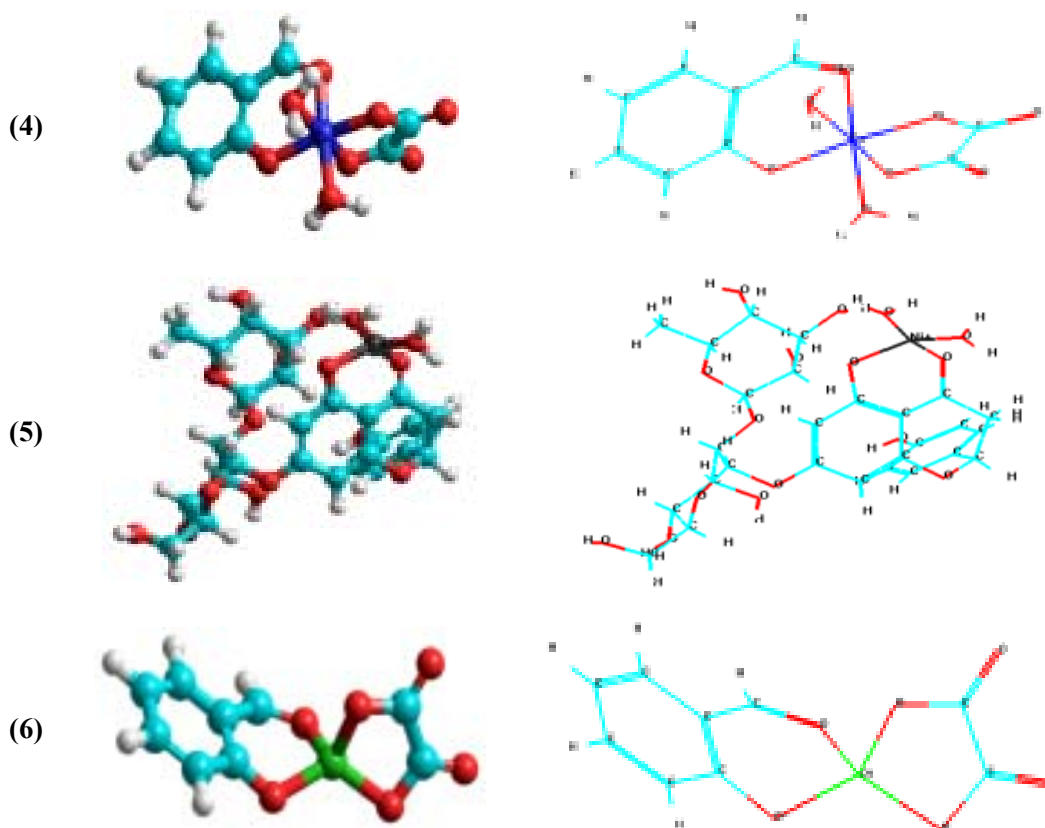


Fig. 2: Conformational structure of mix ligand complexes (1-6)

Part (III) study the biological activities of mixligand complexes (1-6)

The biological activities of the mixligand complexes (**1-6**) were studied against selected types of bacteria which include (*Escherichia coli*) and (*Staphylococcus aureus*) cultivated in Nutrient agar medium, DMSO was used as a solvent and as a control, the concentration of the compounds in this solvent were (10^{-3} M).

The new mixligand complexes (**1-6**) were tested for their *in vitro* growth inhibitory activity against further pathogenic fungi, i.e., (*Candida albicans* and *Aspergillus flavus*) on potato dextrose agar medium and incubated at 30°C for 72 hrs. DMSO was used as a solvent and as a control for both techniques. The concentrations of the compounds in this solvent were (10^{-3} M). The inhibition of fungal growth expressed in percentage terms, were determined on the growth in test plates compared to the respective control plates, as given by Vincent equation¹¹. Furthermore, the antifungal activity against two micro-organisms was tested too.

$$\text{Inhibition \%} = 100 (C - T)/C$$

Where: C = Diameter of fungal growth on the control plate, T = Diameter of fungal growth on the test plate

Biological studies

The free ligands (HD, and OX) and their mix ligand complexes (**1-6**) were screened *in vitro* for their ability to inhibit the growth of representative [*E. coli*] as gram negative and [*Staph. aureus*] as gram

positive] are shown in Table 8. Also, the study was done against (*Aspergillus flavus* and *Penicillium Spp.*) fungus, in DMSO as a solvent, Table 8. According to the results from the above mentioned studies, the following points were concluded:

- (HD, and OX) was non active against *Staph.* and *E. coli* (Table 8).
- All complexes (**1-6**) were highly active against the two types of bacteria, in comparison to the ligands (HD, and OX) which used to prepare them (Table 8).
- Results of the antifungal activity of the new compounds shown in Table 8, which shows that the metal ion chelates (**1-6**) were more toxic in comparison to their parent ligands (HD, and OX) toward the same micro-organisms and under the identical experimental conditions. The increase in the antifungal activity of metal chelates may be due to the effect of the metal ion on the normal cell process. These activities may be explained by Tweedy's Chelation theory³⁰, according to which chelation reduces the polarity of the metal atom mainly, because of the partial sharing of its positive charge with the donor groups of the ligand, which favours permeation of the complexes through the lipid layer of cell membrane³¹.

Table 8: Antibacterial and antifungal activities for ligand (HD and OX) and their metal complexes (1-6) (10^{-3} mgm.ml⁻¹)

| Comp. No. | <i>E. coli</i> | <i>Staph. Aureus</i> | <i>Asp. Flavus</i> | <i>Penci. SPP.</i> |
|--------------|----------------|----------------------|--------------------|--------------------|
| Control DMSO | - | - | - | - |
| (HD) | - | - | 44 | 36 |
| (OX) | - | - | - | - |
| 1 | 8 | 6 | 22 | 30 |
| 2 | 6 | 10 | 17 | 19 |
| 3 | 6 | - | 28 | 30 |
| 4 | 6 | 6 | 28 | 30 |
| 5 | - | 6 | 26 | 20 |
| 6 | 10 | 6 | 18 | 15 |

| | |
|----------------|---------------------|
| Where:- (+)6-8 | Where:- (+++) 30-40 |
| (++)8-10 | (+++++)20-30 |
| (+++) $10 >$ | (+++++)10-20 |

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