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**Synthesis ,elemental analysis and spectral studies for
azopyrazolone dyes as chelating agent for divalent metal
(Mn ,Co,Ni,Cu and Zn)**

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هذا البحث بعنوان

Synthesis ,elemental analysis and spectral studies for azopyrazolone dyes as chelating agent for divalent metal (Mn ,Co,Ni,Cu and Zn)

الملخص:

في هذه الورقة تم تقديم نبذة من المراجع عن بعض مركبات البيرازولون ومشتقاتها شملت استخدامها ككواشف في الكيمياء التحليلية وكذلك الفاعلية البيولوجية لهذه المركبات .

وكذلك يتضمن هذا البحث :

1- دراسة السلوك الطيفي للمركب (V) في المذيبات العضوية المختلفة القطبية وذلك في مجال الأشعة تحت الحمراء والمرئية وقد درست العلاقات الخاصة بثابت العزل الكهربائي

$$F(D) = (2D-1)/2(D+1) * \phi (D)$$

مع الرقم الموجي لحزمة الامتصاص الواقعة في مجال الأشعة المرئية في مدى طيف انتقال الشحنة وقد وجد أن العلاقات غير خطية .

2- كما تم دراسة أطيف الكتلة على الليجانادات (I -V) قيد البحث لالقاء المزيد من الضوء على طبيعة انواع التكسير او التجزئة المميزة لكل من الليجانادات مطابقا لوزنه الجزيئي

3- وقد تم كذلك دراسة تركيبات الليجانادات المحضرة بواسطة الأشعة تحت الحمراء والرنين المغناطيسي والتحليل العنصري.

4- أمكن فصل المتراكبات الصلبة لكل من أيونات العناصر الانتقالية (المنجنيز، الكوبلت، النيكل، النحاس والزنك). وقد أجري تحليل كيميائي دقيق لهذه المتراكبات باستخدام التحليل العنصري الذي يشمل تحليل كل من العناصر (الكور، الهيدروجين، الكربون، النيتروجين).

بالإضافة إلى أطيف الامتصاص التذبذبي في مجال الأشعة تحت الحمراء وأطيف الرنين النووي المغناطيسي والتحليل الحراري الوزني والتحليل الحراري التفاضلي .

كذلك تم دراسة العزم المغناطيسي لمتراكبات العناصر الانتقالية المذكورة مع جميع الليجانادات.

5- وقد تم كذلك دراسة الرنين المغزلي الاليكتروني (ESR) لبعض متراكبات النحاس . 6- كما تم دراسة التوصيلية الكهربائية المولارية للتعرف على طبيعة المتراكبات المحضرة من حيث كونها متراكبات متعادلة أو متراكبات أيونية في المذيب DMF، أثبتت الدراسة أن جميع المتراكبات وجدت في الصورة المتعادلة .

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INTRODUCTION

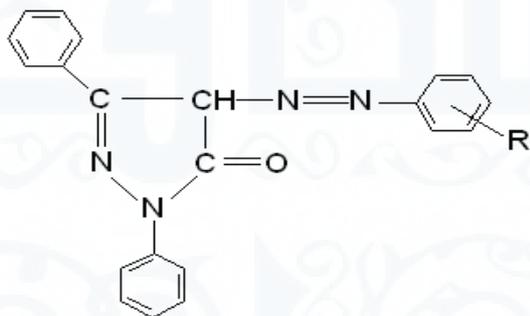
The importance of the pyrazoloneazo dyes in industry as well as their analytical applications and excellent ability to act as ligand attracted the attention of coordination chemists to study their reactions with transition metal ions.

Pyrazolone and pyrazole derivatives such as 5-pyrazolones are formed by the reaction between hydrazines and β -ketonic esters e.g. 3-methyl-1-phenyl-5-pyrazolone was prepared from phenyl hydrazine and ethyl aceto acetate, this on methylation gives antipyrine which is used in medicine as an antipyretic.

Pyrazolone-5-ones have attracted much attention as ligands for a large number of metal ions. The metal chelates produced are well known for their analytical and biological uses. The azo derivatives of 5-pyrazolones, as well as their metal complexes have wide application in the dye industry and as analytical reagents for microdetermination of metals^(1,2).

Aim of Work

The present investigation is concerned with the use of azopyrazolone dyes having the general formula.



(where R = H, p-Cl, p-CH₃, p-OCH₃ or o-COOH).

As chelating agents for divalent Mn, Co, Ni, Cu and Zn. The ligands will thus be synthesized and subjected to elemental analysis and spectral studies (IR, ¹H NMR, Mass spectra and UV-visible) for the purpose of structure elucidation.

The reactions of the above ligands with the metal cations will be prepared in suitable media (ethanol). The solid chelates of the azopyrazolone dyes with divalent Mn, Co, Ni, Cu and Zn will be prepared and subjected to several analytical studies [Elemental analyses, ¹H NMR, IR, TG, DTA, Molar conductivity, Magnetic susceptibility and Electron spin resonance (ESR)] to elucidate the structures. In the light of the previous studies, the metal ligand bond characters will be discussed.

Experimental

Synthesis.

Synthesis of 1,3-diphenyl-5-pyrazolone^[9].

Synthesis of 1,3-diphenyl-4-phenylazo-5-pyrazolone^[8].

Synthesis of 1,3-diphenyl-4-(p-Chlorophenylazo)-5-pyrazolone^[8].

Synthesis of 1,3-diphenyl-4-(p-Methylphenylazo)-5-pyrazolone^[8].

Synthesis of 1,3-diphenyl-4-(p-Methoxyphenylazo)-5-pyrazolone^[8].

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Synthesis of 1,3-diphenyl-4-(o - Carboxyphenylazo)-5-pyrazolone^[8].
Synthesis of solid complexes.

The solid chelates were synthesized by mixing a hot alcoholic saturated solution of (0.001 mole of metal ion dissolved in hot ethanol) with the required amount of ligand under investigation sufficient to form 1:1 or 1:2 (M:L) compounds. The pH of the solution was then maintained at a value of 6.5-7.5 by addition of ammonia solution[7]. The reaction mixture was heated on a steam bath with occasional stirring for 4 hrs, and evaporated till dryness. The produced chelate was then dissolved in ethanol to remove unreacted species. It was then filtered off by suction and rewashed with ethanol till a colorless filtrate was obtained, suction, filtered and then finally kept in a vacuum desiccators⁽⁶⁻⁹⁾.
Determination of metal-content in the complexes¹⁰

The metal content of the prepared solid complexes was determined^[10]

Molar conductivity Measurements.

The molar conductance of the solid complexes in DMF were measured using a conductivity meter type (Philips, PW 9526 digital conductivity meter).

Physical measurements :

Magnetic susceptibility measurements were determined using SHERWOOD scientific magnetic susceptibility balance¹¹.

Elemental analysis was performed in the micro-analytical center of Cairo University, Giza, Egypt.

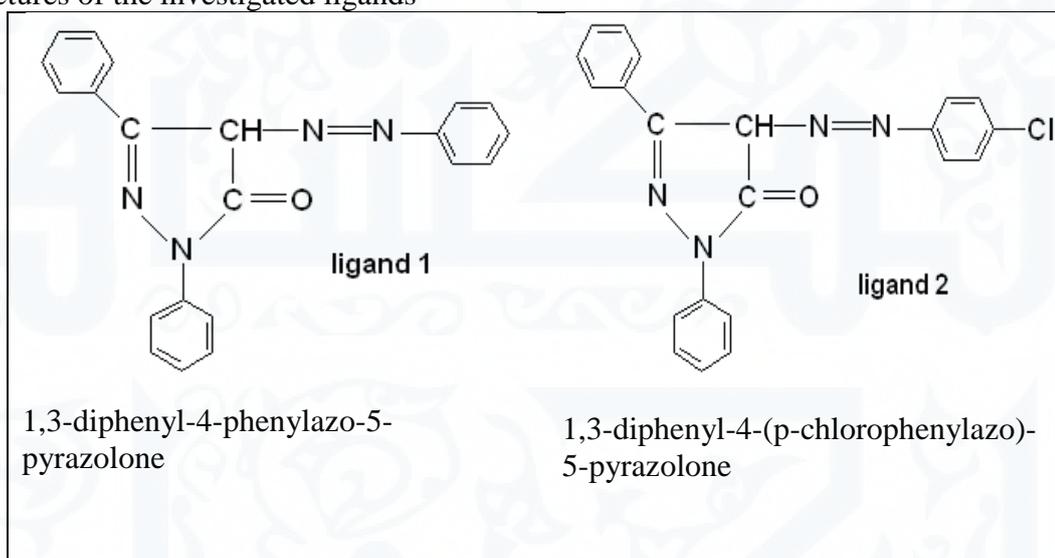
The IR spectra were recorded on SHIMADZU FTIR-8201 PC spectrophotometer applying the KBr disc technique.

The NMR spectra were measured by using a VARIAN Gemini 200 MHz spectrophotometer.

Mass spectra were done on GC-Mass 2b 1000 Ex mass spectrophotometer

Thermal analysis (TG and DTA) were done using SHIMADZU, Type TG-50 and DTA-50 thermal analyzer

The structures of the investigated ligands



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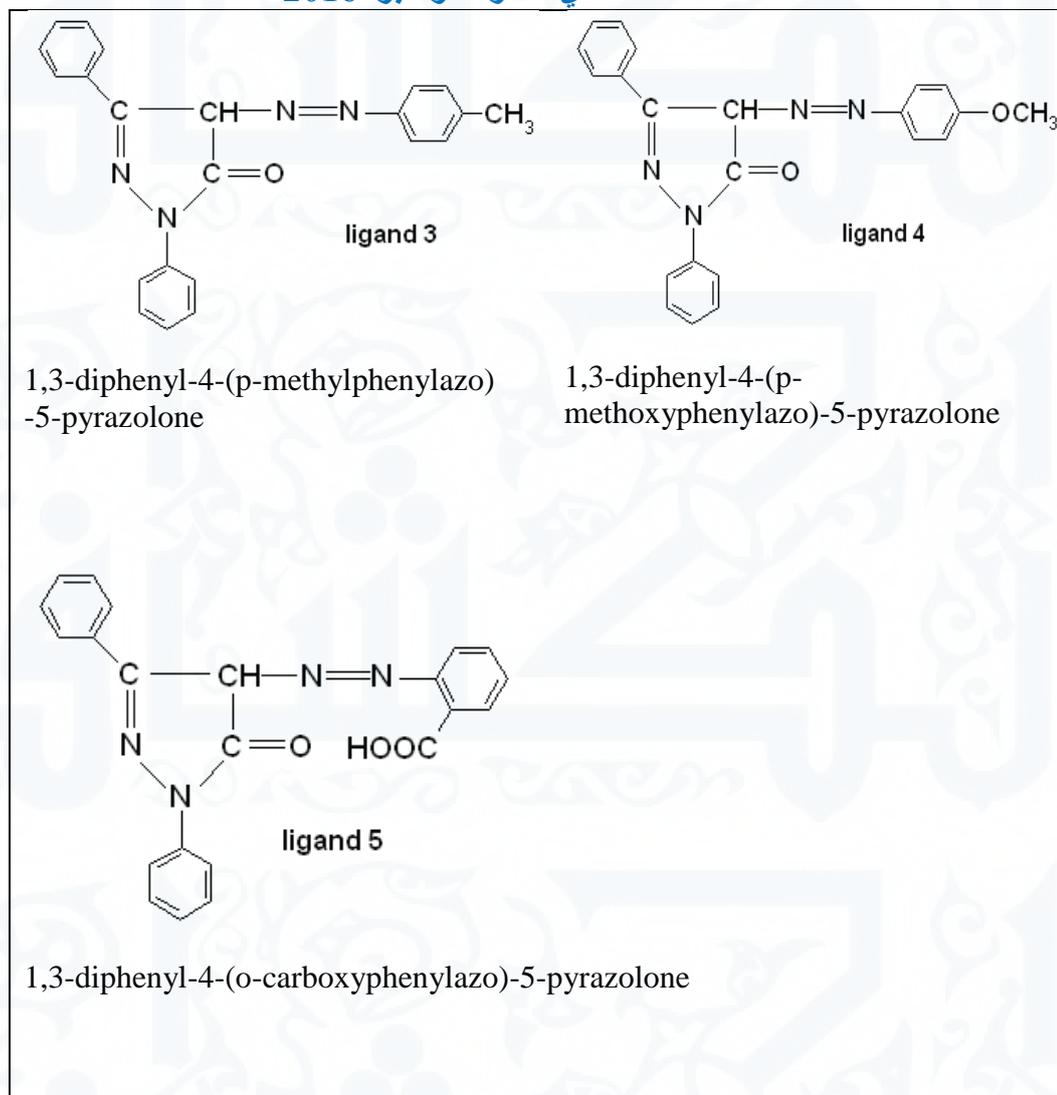


Figure (1) : Structures and names of the investigated ligands.

Results

Interpretation of IR spectra of the free ligands

Table (1): The most significant bands in IR spectra of the investigated ligands (I-V).

| Band Assignment | Ligand | | | | |
|-----------------|--------|------|------|------|------|
| | I | II | III | IV | V |
| ν_{OH} | 3429 | 3406 | 3421 | 3440 | 3429 |
| ν_{NH} | 3294 | 3058 | 3298 | 3031 | 3058 |
| $\nu_{C=O}$ | 1654 | 1651 | 1651 | 1654 | 1651 |
| ν_{C-C} | 1593 | 1593 | 1593 | 1593 | 1593 |
| $\nu_{C=C}$ | 1550 | 1550 | 1550 | 1550 | 1550 |
| $\nu_{N=N}$ | 1496 | 1492 | 1492 | 1496 | 1497 |
| ν_{C-H} | 1338 | 1338 | 1338 | 1338 | 1338 |
| δ_{OH} | 1230 | 1226 | 1226 | 1230 | 1226 |

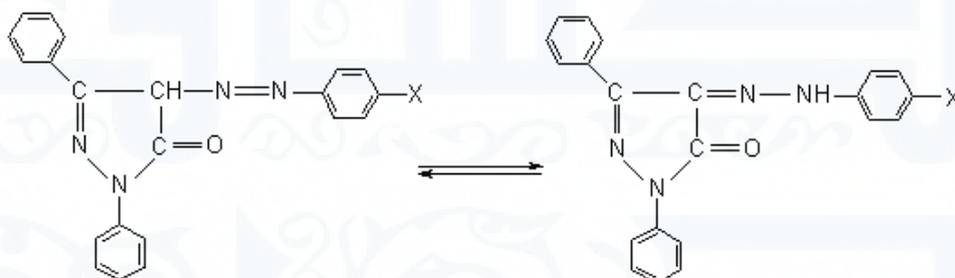
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^1H NMR spectral studies.

Table (2): ^1H NMR spectral data of the azopyrazolones.

| Ligand | Chemical Shift | Assignment |
|------------|----------------|-----------------------------------|
| Ligand I | 13.7 | NH hydrazone |
| | 8.19-7.23 | Aromatic C-H protons |
| | 3.33 | H ₂ O solvent protons |
| | 2.5 | DMSO protons |
| Ligand II | 8.2-7.25 | Aromatic C-H protons |
| | 3.35 | H ₂ O solvent protons |
| | 2.51 | DMSO protons |
| Ligand III | 13.8 | NH hydrazone |
| | 8.16-7.23 | Aromatic protons |
| | 3.32 | H ₂ O solvent protons |
| | 2.5 | DMSO protons |
| | 2.30 | CH ₃ protons |
| Ligand IV | 8.18-7.03 | Aromatic protons |
| | 3.79 | OCH ₃ protons |
| | 3.38 | H ₂ O solvent protons |
| | 2.52 | DMSO protons |
| Ligand V | 15.04 | COOH proton |
| | 8.21-7.23 | Aromatic protons |
| | 3.37 | H ₂ O solvents protons |
| | 2.50 | DMSO protons |

The ^1H NMR spectra of all ligands exhibit a singlet signal at (2.5-2.52) ppm which is assigned to the CH₃ protons of the solvent, also the aliphatic protons of the methyl groups appeared 2.30 ppm for ligand III. The signals observed at (7.03-8.21) ppm are assigned to the protons of the aromatic ring^[15]. The signals observed at (13.7-13.8) ppm are assigned to the proton of the NH group for ligands (I) and (III), table (2). The appearance of these signals indicates the involvement of these ligands in azo-hydrazotautomerism and has the following structure:



X = H or CH₃.

The signals observed at 15.04 ppm for ligand (V) are assigned to the proton of the carboxylic group (-COOH).

Mass spectral studies:

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The mass spectral pattern of ligand I shows a peak of 339 (calcd. M.wt = 340). The fragmentation pattern of this ligand can be regarded as general scheme showing the main fragmentation paths involved. the differences in other ligands (II-V) result from the effect of electronegativities of the substituents attached to the aromatic ring.

For ligand II, the main peak is observed at 374 (calcd. M.wt = 374).

For ligand III, the main peak is observed at 354 (calcd. M.wt = 354).

For ligand IV, the main peak is observed at 370 (calcd. M.wt = 370)

For ligand V, the main peak is observed at 384 (calcd. M.wt = 384) .From the data obtained we concluded that the molecular weights are in good agreement with the calculated values.

Elemental analysis for the investigated ligand:

Table (3): Elemental analysis data of the investigated ligands (I-V)

| Ligand | R | C% (Calcd) found | H% (Calcd) found | N% (Calcd) found | Cl% (Calcd) Found |
|--------|--------------------|------------------------|------------------------|------------------------|-------------------------|
| I | H | (74.12) 74.84 | (4.71) 5.03 | (16.47) 16.64 | ----- |
| II | p-Cl | (67.29) 67.24 | (4.02) 4.52 | (14.95) 15.17 | (9.48) 9.64 |
| III | p-CH ₃ | (74.57) 73.47 | (5.08) 5.37 | (15.82) 15.85 | ----- |
| IV | p-OCH ₃ | (71.35) 71.31 | (4.86) 5.03 | (15.13) 13.51 | ----- |
| V | o-COOH | (68.75) 68.08 | (4.17) 4.54 | (14.58) 14.91 | ----- |

The absorption of ligand V in organic solvents of different polarities:

Table (4) : Some solvent parameters

| solvent | D | (D-1)/(D+1) | f(D) | φ(D) |
|---------------|-------|-------------|-------|-------|
| Ethanol | 25.00 | 0.923 | 0.941 | 0.889 |
| methanol | 32.70 | 0.941 | 0.955 | 0.913 |
| isopropanol | 18.60 | 0.898 | 0.922 | 0.854 |
| 1,4 - dioxane | 3.30 | 0.500 | 0.571 | 0.400 |
| cyclohexane | 2.00 | 0.333 | 0.400 | 0.250 |
| chloroform | 5.10 | 0.672 | 0.732 | 0.577 |

Stoichiometry and structure of the solid complexes:

The solid complexes of the metal ions (Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) with the investigated ligands (I-V) were prepared as described in the experimental section. The resulting complexes were subjected to elemental analysis for (C, H, N, Cl) and metal content^[10],

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infrared spectral studies (IR), magnetic susceptibility, thermogravimetric analysis (TG), differential thermal analysis (DTA) and electron spin resonance (ESR).

Infrared spectra of the solid complexes:

The infrared spectra of the solid complexes display interesting changes which may give a reasonable idea about the structure of these complexes.

The main IR bands of the solid complexes are given in tables (5-9)

Table (5): The most significant bands in IR spectra of the complexes of ligand I with the metal ions (Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}).

| Complex | Band Assignment | | | | | | |
|------------|-----------------|-------------|-------------|-------------|-------------|-------------|-------------|
| | ν_{OH} | $\nu_{C=N}$ | $\nu_{C=C}$ | $\nu_{N=N}$ | ν_{C-O} | ν_{M-N} | ν_{M-O} |
| Mn-I (2:2) | 3413 | 1596 | 1550 | 1488 | 1265 | 590 | 489 |
| Mn-I (2:3) | 3444 | 1596 | 1550 | 1488 | 1265 | 590 | 489 |
| Co-I (2:2) | 3448 | 1593 | 1593-1550 | 1492 | 1218 | 520 | 416 |
| Co-I (2:3) | 3494 | 1554 | 1554 | 1492 | 1218 | 513 | 474 |
| Ni-I (2:2) | 3425 | 1658 | 1596-1550 | 1488 | 1265 | 510 | 424 |
| Ni-I (2:3) | 3363 | 1658 | 1600-1581 | 1488 | 1211 | 528 | 416 |
| Cu-I (2:2) | 3355 | 1654 | 1558 | 1488 | 1222 | 567 | 428 |
| Cu-I (2:3) | 3440 | 1654 | 1593-1558 | 1488 | 1218 | 509 | 424 |
| Zn-I (2:2) | 3386 | 1666 | 1596 | 1485 | 1242 | 532 | 424 |

Table (6): The most significant bands in IR spectra of the complexes of ligand II with the metal ions (Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}).

| Complex | Band Assignment | | | | | | |
|-------------|-----------------|-------------|-------------|-------------|-------------|-------------|-------------|
| | ν_{OH} | $\nu_{C=N}$ | $\nu_{C=C}$ | $\nu_{N=N}$ | ν_{C-O} | ν_{M-N} | ν_{M-O} |
| Mn-II (2:2) | 3433 | 1589 | 1554 | 1488 | 1261 | 505 | 420 |
| Mn-II (2:3) | 3398 | 1589 | 1554 | 1488 | 1261 | 505 | 443 |
| Co-II (2:2) | 3436 | 1651 | 1554 | 1488 | 1261 | 509 | 474 |
| Co-II (2:3) | 3436 | 1589 | 1554 | 1488 | 1261 | 505 | 416 |
| Ni-II (2:2) | 3340 | 1581 | 1488 | 1454 | 1215 | 532 | 424 |
| Ni-II (2:3) | 3348 | 1581 | 1488 | 1454 | 1211 | 536 | 420 |
| Cu-II (2:2) | 3344 | 1647 | 1593-1566 | 1458 | 1222 | 617 | 416 |
| Cu-II (2:3) | 3363 | 1647 | 1593-1566 | 1458 | 1222 | 493 | 416 |
| Zn-II (2:2) | 3433 | 1651 | 1589 | 1454 | 1261 | 478 | 410 |
| Zn-II (2:3) | 3417 | 1651 | 1589 | 1454 | 1261 | 505 | 482 |

Table (7): The most significant bands in IR spectra of the complexes of ligand III with the metals (Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}).

| Complex | Band Assignment | | | | | | |
|--------------|-----------------|-------------|-------------|-------------|-------------|-------------|-------------|
| | ν_{OH} | $\nu_{C=N}$ | $\nu_{C=C}$ | $\nu_{N=N}$ | ν_{C-O} | ν_{M-N} | ν_{M-O} |
| Mn-III (2:2) | 3421 | 1593 | 1554 | 1488 | 1269 | 509 | 443 |
| Mn-III (2:3) | 3375 | 1593 | 1554 | 1488 | 1272 | 509 | 439 |
| Co-III (2:2) | 3444 | 1596 | 1550 | 1488 | 1288 | 520 | 416 |
| Co-III (2:3) | 3448 | 1596 | 1550 | 1488 | 1288 | 520 | 466 |

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|--------------|------|------|-----------|------|------|-----|-----|
| Ni-III (2:2) | 3436 | 1651 | 1593-1550 | 1488 | 1269 | 516 | 428 |
| Ni-III (2:3) | 3440 | 1651 | 1593-1550 | 1488 | 1269 | 513 | 428 |
| Cu-III (2:2) | 3352 | 1647 | 1596-1562 | 1488 | 1296 | 559 | 416 |
| Cu-III (2:3) | 3355 | 1651 | 1596-1562 | 1488 | 1296 | 509 | 416 |
| Zn-III (2:2) | 3440 | 1651 | 1593-1550 | 1488 | 1269 | 543 | 486 |
| Zn-III (2:3) | 3433 | 1651 | 1593-1554 | 1488 | 1269 | 547 | 489 |

Table (8): The most significant bands in IR spectra of the complexes of ligand IV with the metal ions (Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}).

| Complex | Band Assignment | | | | | | |
|-------------|-----------------|-------------|-------------|-------------|-------------|-------------|-------------|
| | ν_{OH} | $\nu_{C=N}$ | $\nu_{C=C}$ | $\nu_{N=N}$ | ν_{C-O} | ν_{M-N} | ν_{M-O} |
| Mn-IV (2:2) | 3444 | 2693 | 1550-1523 | 1492 | 1245 | 520 | 412 |
| Mn-IV (2:3) | 3398 | 1593 | 1550-1523 | 1492 | 1245 | 516 | 412 |
| Co-IV (2:2) | 3440 | 1596 | 1596-1550 | 1492 | 1245 | 516 | 420 |
| Co-IV (2:3) | 3421 | 1596 | 1596-1550 | 1492 | 1245 | 520 | 424 |
| Ni-IV (2:2) | 3425 | 1654 | 1589-1550 | 1492 | 1245 | 516 | 428 |
| Ni-IV (2:3) | 3386 | 1654 | 1589-1550 | 1492 | 1245 | 516 | 424 |
| Cu-IV (2:2) | 3244 | 1647 | 1596-1554 | 1492 | 1249 | 567 | 470 |
| Cu-IV (2:3) | 3440 | 1647 | 1554-1488 | 1454 | 1249 | 567 | 505 |
| Zn-IV (2:2) | 3433 | 1654 | 1593-1550 | 1492 | 1254 | 567 | 470 |
| Zn-IV (2:3) | 3390 | 1654 | 1593-1550 | 1492 | 1245 | 520 | 493 |

Table (9): The most significant bands in IR spectra of the complexes of ligand V with the metal ions (Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}).

| Complex | Band Assignment | | | | | | |
|------------|-----------------|-------------|-------------|-------------|-------------|-------------|-------------|
| | ν_{OH} | $\nu_{C=N}$ | $\nu_{C=C}$ | $\nu_{N=N}$ | ν_{C-O} | ν_{M-N} | ν_{M-O} |
| Mn-V (1:1) | 3379 | 1585 | 1485 | 1427 | 1296 | 489 | 420 |
| Mn-V (1:2) | 3375 | 1585 | 1485 | 1427 | 1296 | 489 | 420 |
| Co-V (1:1) | 3394 | 1600 | 1554 | 1488 | 1222 | 532 | 451 |
| Co-V (1:2) | 3390 | 1589 | 1488 | 1423 | 1296 | 482 | 420 |
| Ni-V (1:1) | 3379 | 1596 | 1581 | 1450 | 1253 | 520 | 432 |
| Ni-V (1:2) | 3394 | 1658 | 1593 | 1485 | 1249 | 520 | 447 |
| Cu-V (1:1) | 3390 | 1643 | 1585 | 1435 | 1249 | 524 | 428 |
| Cu-V (1:2) | 3425 | 1658 | 1585 | 1435 | 1245 | 520 | 424 |
| Zn-V (1:1) | 3325 | 1627 | 1596 | 1485 | 1242 | 470 | 451 |
| Zn-V (1:2) | 3386 | 1662 | 1596 | 1485 | 1245 | 489 | 439 |

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^1H NMR spectra of the complexes:

^1H NMR spectra of Zn complexes with the investigated ligands (I-V), ^1H NMR spectral data of Zn complexes with the investigated ligands (I-V) are illustrated in tables(10-11).

Table (10): ^1H NMR spectral data of Zn complexes with the investigated ligand (I-III).

| complex M:L | Chemical shift | Assignment |
|-----------------|----------------|-----------------------------------|
| Zn-I (2:2) | 16.6 | OH bridge |
| | 8.19-6.71 | Aromatic C-H protons |
| | 3.32 | H ₂ O solvent protons |
| | 2.5 | DMSO protons |
| Zn-II (2:2) | 8.00-7.48 | Aromatic C-H protons |
| | 3.35 | H ₂ O solvents protons |
| | 2.51 | DMSO protons |
| Zn-II (2:3) | 13.6 | NH hydrazone |
| | 8.14-7.27 | Aromatic protons |
| | 3.30 | H ₂ O solvent protons |
| | 2.50 | DMSO protons |
| Zn-III (2:2) | 13.8 | NH hydrazone |
| | 8.18-7.13 | Aromatic protons |
| | 3.35 | H ₂ O solvent protons |
| | 2.52 | DMSO protons |
| Zn-III (2:3) | 13.8 | NH proton |
| | 8.20-7.28 | Aromatic protons |
| | 3.35 | H ₂ O protons |
| | 2.51 | DMSO protons |
| | 2.33 | CH ₃ protons |

Table (11): ^1H NMR spectral data of Zn complexes with the investigated ligands (IV and V).

| complex M:L | Chemical shift | Assignment |
|----------------|----------------|-----------------------------------|
| Zn-IV (2:2) | 13.1 | NH proton |
| | 8.14-7.01 | Aromatic protons |
| | 3.77 | OCH ₃ protons |
| | 3.3 | H ₂ O solvents protons |
| | 2.52 | DMSO protons |
| Zn-IV (2:3) | 13.8 | NH proton |
| | 8.18-7.03 | Aromatic protons |
| | 3.79 | OCH ₃ protons |
| | 3.33 | H ₂ O solvent protons |
| Zn-V (1:1) | 16.4 | OH proton |
| | 8.18-7.05 | Aromatic protons |
| | 3.37 | H ₂ O solvent protons |

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|---------------|-----------|----------------------------------|
| | 2.50 | DMSO protons |
| Zn-V (1:2) | 16.2 | OH proton |
| | 8.21-7.23 | Aromatic protons |
| | 3.43 | H ₂ O solvent protons |
| | 2.51 | DMSO protons |

Elemental analysis for the complexes:

Table (12): Elemental analysis, molar conductance (Λ_m) and μ_{eff} for the complexes of the divalent metal ions (Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) with ligand I

| Complex | C% (Calcd) found | H% (Calcd) found | N% (Calcd) found | M% (Calcd) found | Λ_m | μ_{eff} |
|------------|------------------------|------------------------|------------------------|------------------------|-------------|-------------|
| Mn-I (2:2) | (61.17) 61.87 | (4.12) 3.89 | (13.59) 14.54 | (6.66) 6.21 | 6.66 | 5.13 |
| Mn-I (2:3) | (65.91) 66.03 | (4.01) 4.01 | (14.64) 15.55 | (4.78) 4.23 | 4.78 | 4.75 |
| Co-I (2:2) | (60.58) 58.78 | (4.08) 4.76 | (13.46) 14.08 | (7.08) 7.12 | 7.08 | 3.99 |
| Co-I (2:3) | (65.46) 65.99 | (3.98) 3.88 | (14.54) 16.08 | (5.10) 5.08 | 5.10 | 2.79 |
| Ni-I (2:2) | (60.58) 60.14 | (4.08) 4.14 | (13.47) 14.08 | (7.06) 7.01 | 7.06 | 3.89 |
| Ni-I (2:3) | (65.48) 66.26 | (3.98) 4.20 | (14.55) 14.59 | (5.03) 5.22 | 5.03 | 2.67 |
| Cu-I (2:2) | (59.92) 60.93 | (4.04) 4.41 | (13.31) 13.96 | (7.55) 7.63 | 7.55 | 1.31 |
| Cu-I (2:3) | (64.94) 65.13 | (3.95) 4.08 | (14.43) 14.53 | (5.37) 6.02 | 5.37 | 1.26 |
| Zn-I (2:2) | (59.66) 58.99 | (4.02) 4.47 | (13.2) 13.36 | (7.73) 7.54 | 7.73 | 0.91 |

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| | | | | | | |
|------------|------------------|----------------|------------------|----------------|------|------|
| Zn-I (2:3) | (64.73) 64.76 | (3.93) 4.07 | (14.38) 14.50 | (5.51) 5.59 | 5.51 | 0.54 |
|------------|------------------|----------------|------------------|----------------|------|------|

Table (13): Elemental analysis, molar conductance (Λ_m) and μ_{eff} for the complexes of the divalent metals (Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) with ligand II

| Complex | C% (Calcd) found | H% (Calcd) found | N% (Calcd) found | Cl% (calcd) found | M% (Calcd) found | (Λ_m) | μ_{eff} |
|-------------|------------------------|------------------------|------------------------|-------------------------|------------------------|-----------------|--------------------|
| Mn-II (2:2) | (56.44) 56.35 | (3.36) 3.55 | (12.55) 12.88 | (7.83) 8.41 | (6.15) 6.78 | 49.16 | 5.80 |
| Mn-II (2:3) | (60.46) 60.99 | (3.43) 3.20 | (13.43) 15.44 | (8.51) 7.83 | (4.39) 4.54 | 13.44 | 4.06 |
| Co-II (2:2) | (56.00) 56.92 | (3.33) 3.38 | (12.44) 12.62 | (7.77) 8.03 | (6.54) 6.69 | 44.25 | 3.42 |
| Co-II (2:3) | (60.05) 58.69 | (3.41) 3.34 | (13.35) 13.18 | (8.46) 8.36 | (4.68) 5.21 | 15.22 | 3.81 |
| Ni-II (2:2) | (56.03) 56.10 | (3.29) 3.43 | (12.45) 13.05 | (7.78) 8.00 | (6.52) 7.03 | 35.18 | 2.70 |
| Ni-II (2:3) | (60.10) 61.08 | (3.41) 3.55 | (13.35) 12.91 | (8.40) 8.43 | (4.66) 4.59 | 9.11 | 2.28 |
| Cu-II (2:2) | (55.04) 54.85 | (3.52) 3.37 | (12.30) 11.91 | (7.70) 7.31 | (6.98) 7.25 | 25.13 | 1.75 |
| Cu-II (2:3) | (59.64) 58.26 | (3.39) 3.46 | (13.25) 12.85 | (8.29) 9.04 | (5.00) 5.02 | 17.25 | 1.76 |
| Zn-II (2:2) | (55.21) 58.83 | (3.28) 3.96 | (12.27) 13.48 | (7.66) 7.37 | (7.16) 7.55 | 37.35 | 0.73 |
| Zn-II (2:3) | (59.46) 65.55 | (3.38) 3.13 | (13.21) 13.67 | (8.37) 8.15 | (5.14) 4.93 | 11.50 | 0.97 |

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Table (14): Elemental analysis, molar conductance (Λ_m) and μ_{eff} for the complexes of the divalent metals (Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) with ligand III.

| Complex | C% (Calcd) found | H% (Calcd) found | N% (Calcd) found | M% (Calcd) found | (Λ_m) | μ_{eff} |
|--------------|------------------------|------------------------|------------------------|------------------------|-----------------|--------------------|
| Mn-III (2:2) | (61.98) 59.16 | (4.46) 4.45 | (13.14) 13.23 | (5.06) 5.35 | 32.77 | 6.44 |
| Mn-III (2:3) | (69.23) 68.93 | (4.54) 4.45 | (14.68) 14.55 | (5.93) 5.81 | 13.62 | 4.80 |
| Co-III (2:2) | (61.40) 60.59 | (4.41) 4.47 | (13.02) 13.63 | (2.98) 2.79 | 13.18 | 6.85 |
| Co-III (2:3) | (66.17) 66.78 | (4.34) 4.98 | (12.95) 15.20 | (2.90) 2.69 | 7.70 | 4.58 |
| Ni-III (2:2) | (63.66) 64.21 | (4.58) 5.04 | (13.50) 13.79 | (3.40) 3.17 | 13.14 | 7.07 |
| Ni-III (2:3) | (66.19) 67.30 | (4.34) 4.44 | (14.04) 14.53 | (2.91) 2.99 | 6.67 | 4.90 |
| Cu-III (2:2) | (60.75) 60.84 | (4.37) 4.50 | (12.88) 12.50 | (1.55) 1.31 | 14.06 | 7.30 |
| Cu-III (2:3) | (65.19) 65.19 | (4.31) 4.15 | (13.93) 14.23 | (1.29) 1.11 | 8.25 | 5.26 |
| Zn-III (2:2) | (60.49) 59.27 | (4.35) 3.96 | (12.83) 12.35 | (0.59) 0.52 | 14.42 | 7.49 |
| Zn-III (2:3) | (65.46) 66.64 | (4.29) 4.38 | (13.88) 13.74 | (0.57) 0.49 | 8.47 | 5.40 |

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Table (15): Elemental analysis, molar conductance (Λ_m) and μ_{eff} for the complexes of the divalent metals (Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) with ligand IV.

| Complex | C% (Calcd) found | H% (Calcd) found | N% (Calcd) found | M% (Calcd) Found | (Λ_m) | μ_{eff} |
|-------------|------------------------|------------------------|------------------------|------------------------|-----------------|--------------------|
| Mn-IV (2:2) | (59.73) 58.44 | (4.29) 4.36 | (12.67) 12.69 | (6.21) 6.52 | 38.15 | 5.91 |
| Mn-IV (2:3) | (64.03) 64.02 | (4.20) 4.28 | (13.58) 13.35 | (4.44) 4.33 | 10.40 | 5.07 |
| Co-IV (2:2) | (59.20) 58.57 | (4.26) 4.41 | (12.55) 10.62 | (6.60) 6.45 | 32.20 | 3.62 |
| Co-IV (2:3) | (63.62) 64.49 | (4.17) 4.98 | (13.39) 13.45 | (4.73) 4.79 | 9.30 | 2.55 |
| Ni-IV (2:2) | (59.23) 59.65 | (4.26) 4.14 | (12.56) 12.38 | (6.58) 6.83 | 35.70 | 2.88 |
| Ni-IV (2:3) | (64.64) 65.63 | (4.17) 4.28 | (13.50) 13.98 | (4.71) 4.23 | 7.58 | 3.29 |
| Cu-IV (2:2) | (58.02) 57.79 | (4.17) 4.25 | (12.30) 12.96 | (6.97) 6.58 | 29.13 | 1.59 |
| Cu-IV (2:3) | (63.15) 63.59 | (4.14) 4.60 | (13.39) 13.72 | (5.09) 5.05 | 7.16 | 1.31 |
| Zn-IV (2:2) | (58.35) 59.82 | (4.20) 4.99 | (12.37) 12.81 | (7.91) 7.34 | 9.17 | 0.005 |
| Zn-IV (2:3) | (62.96) 63.62 | (4.13) 4.57 | (13.35) 13.82 | (5.19) 4.91 | 8.59 | 0.79 |

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Table (16): Elemental analysis, molar conductance (Λ_m) and μ_{eff} for the complexes of the divalent metals (Mn^{2+} , Co^{2+} , Ni^{2+} , Cu^{2+} and Zn^{2+}) with ligand V.

| Complex | C% (Calcd) found | H% (Calcd) found | N% (Calcd) found | M% (Calcd) Found | (Λ_m) | μ_{eff} |
|------------|------------------------|------------------------|------------------------|------------------------|-----------------|--------------------|
| Mn-V (1:1) | (55.39) 56.29 | (3.73) 3.84 | (12.30) 12.97 | (12.07) 11.79 | 38.17 | 6.17 |
| Mn-V (1:2) | (64.31) 63.86 | (3.65) 3.99 | (13.64) 13.54 | (6.69) 6.15 | 14.24 | 6.61 |
| Co-V (1:1) | (54.91) 54.74 | (3.70) 3.11 | (12.20) 12.10 | (12.84) 12.16 | 25.58 | 4.18 |
| Co-V (1:2) | (64.00) 64.04 | (3.63) 3.44 | (13.57) 13.32 | (7.14) 7.33 | 8.16 | 4.35 |
| Ni-V (1:1) | (54.93) 54.99 | (4.14) 4.61 | (12.20) 12.10 | (12.70) 12.52 | 45.78 | 2.31 |
| Ni-V (1:2) | (64.02) 63.86 | (3.63) 4.21 | (13.58) 13.91 | (7.11) 6.81 | 12.44 | 2.07 |
| Cu-V (1:1) | (54.36) 54.22 | (3.88) 3.37 | (12.08) 12.63 | (13.70) 13.31 | 29.92 | 1.30 |
| Cu-V (1:2) | (63.65) 63.51 | (3.61) 3.66 | (13.50) 13.70 | (7.65) 7.89 | 7.35 | 1.24 |
| Zn-V (1:1) | (54.14) 55.04 | (3.65) 3.78 | (12.03) 12.41 | (14.04) 14.89 | 24.15 | 0.75 |
| Zn-V (1:2) | (63.50) 62.26 | (3.60) 4.00 | (13.47) 13.48 | (7.86) 7.93 | 10.24 | 0.59 |

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Thermogravimetric analysis (TG):

These methods of analysis open up new possibilities for the investigation of metal complexes^[4,5]. The aim of this study is to obtain information concerning the thermal stability of the divalent transition metal-azopyrazolone complexes, establish whether the water molecules are inner or outersphere if present and suggest a general scheme for the thermal decomposition of these complexes. The thermogram follows the decrease in sample weight with the linear increase in temperatures.

Differential thermal analysis (DTA):

The differential thermal analysis curves (DTA) are characterized by the presence of a large and sharp exothermic peak on the DTA curves at the temperature range (426-549), figures (31-40). For [Mn-I (2:2)] and [Mn-I (2:3)] are 437 and 438. For [Ni-II (2:2)] and [Ni-II (2:3)] are 461 and 526. For [Co-III (2:2)] and [Co-III (2:3)] are 500 and 426. For [Cu-IV (2:2)] and [Cu-IV (2:3)] are 476 and 443. For [Zn-V (1:1)] and [Zn-V (1:2)] are 549 and 542, respectively. At these temperatures a phase change is liable to occur due to the change in crystal structure of the complex. i.e. crystallographic phase transition. Rising the temperature than these temperature results in the decomposition and combustion, and at the end there would be the metallic residue as oxide.

Table (17): Molecular weight, temperatures of decomposition, loss percent and the corresponding ps in thermogravimetry (TG).

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| Complex (ligand-metal) | M.wt | Temp (°C) | Caltd loss% | Found loss% | Assignment |
|------------------------|---------|-----------|-------------|-------------|--|
| Mn-I (2:2) | 823.86 | 150-378 | 53.04 | 53.51 | 4C ₆ H ₅ , 8N, OH |
| | | 378-459 | 29.73 | 30.23 | 2C ₆ H ₄ , 6C, 2H, OH |
| | | 459-800 | 8.60 | 6.78 | MnO |
| Mn-I (2:3) | 1146.86 | 223-319 | 27.11 | 27.26 | 3C ₆ H ₅ , 4N, 2C |
| | | 319-557 | 61.64 | 62.66 | 6C ₆ H ₅ , 8N, 7C, OH, 2O |
| | | 557-800 | 12.36 | 11.04 | 2MnO |
| Ni-II (2:2) | 900.4 | 126-242 | 6.21 | 5.92 | 4N |
| | | 242-365 | 22.43 | 21.91 | 2C ₆ H ₄ , 4C, 2H |
| | | 365-553 | 54.75 | 56.70 | 4C ₆ H ₅ , 2Cl, 2OH, 4N, 2C, OH |
| | | 553-800 | 16.61 | 15.85 | 2NiO |
| Ni-II (2:3) | 1257.9 | 165-357 | 2.86 | 2.61 | 3C |
| | | 357-465 | 17.13 | 17.74 | 2C ₆ H ₄ , 2N, Cl |
| | | 465-642 | 50.95 | 50.15 | 6C ₆ H ₅ , 2Cl, 2C, 6N |
| | | 642-800 | 11.64 | 12.44 | 2NiO |
| Co-III (2:2) | 859.86 | 200-362 | 27.67 | 26.4 | 2CH ₃ , 2C ₆ H ₄ , 4N |
| | | 362-435 | 14.65 | 15.6 | 2OH, 4N, 3C |
| | | 435-519 | 40.00 | 39.25 | 4C ₆ H ₅ , 3C |
| | | 519-800 | 17.42 | 16.87 | 2CoO |
| Co-III (2:3) | 1196.86 | 200-357 | 34.17 | 34.51 | 3CH ₃ , 4C ₆ H ₄ , 4N |
| | | 357-508 | 58.56 | 59.23 | 5C ₆ H ₅ , 2C ₆ H ₄ , 4N, 9C |
| | | 508-800 | 6.26 | 5.83 | CoO |
| Cu-IV (2:2) | 901 | 135-393 | 36.62 | 36.22 | 2OH, 4N, 2C ₆ H ₅ , 2OCH ₃ , |

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| | | | | | |
|-------------|--------|---------|-------|-------|--|
| | | 393-464 | 14.65 | 14.93 | 2C |
| | | 464-557 | 29.52 | 29.44 | C ₆ H ₄ , 4N |
| | | 557-800 | 17.64 | 17.55 | 2C ₆ H ₅ , C ₆ H ₄ , 3C 2CuO |
| Cu-IV (2:3) | 1254 | 137-230 | 4.94 | 4.87 | 2OCH ₃ |
| | | 230-340 | 17.94 | 18.11 | 2C ₆ H ₄ , 4N, OH |
| | | 340-483 | 64.19 | 66.31 | 6C ₆ H ₅ , C ₆ H ₄ , 8N, 9C, OCH ₃ , O |
| | | 483-800 | 12.67 | 10.62 | 2CuO |
| Zn-V (1:1) | 465.38 | 196-342 | 22.56 | 23.87 | C ₆ H ₄ , 2N, H |
| | | 342-457 | 28.79 | 28.63 | C ₆ H ₅ , COOH, C |
| | | 457-715 | 34.59 | 34.91 | C ₆ H ₅ , 2C, 2N, 2O |
| | | 715-800 | 17.48 | 17.56 | ZnO |
| Zn-V (1:2) | 831.38 | 192-261 | 2.88 | 2.75 | 2C |
| | | 261-357 | 23.33 | 24.88 | C ₆ H ₅ , 2N, C, H, C ₆ H ₄ |
| | | 357-457 | 31.15 | 30.65 | 3C ₆ H ₅ , 2N |
| | | 457-642 | 29.58 | 29.86 | C ₆ H ₄ , 4N, 2COOH, 2C |
| | | 642-800 | 9.78 | 9.70 | ZnO |

Molar conductivity measurements:

The molar conductivities of the solid complexes were measured for the solutions of the complexes of 2:2 and 2:3 are in the range 7.16-49.26 ohm⁻¹ cm² mol⁻¹. These values were measurably small for the ionic complexes of the divalent metal ions. These low conductivity values may be attributed to the absence of chloride ions rather than ionic association to the metal ions during complex formation. This directly support the fact that all of the investigated complexes are non-ionic in nature. The conductivity values for all of the investigated complexes are listed in tables (12-16).

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Magnetic susceptibility measurements:

The magnetic moment (μ) of a transition metal can give important information about the number of unpaired electrons in the metal ion, and in some special cases help to indicate the structure of the complex

All of the meta ions (Mn^{2+} , Co^{2+} , Ni^{2+} and Cu^{2+}) complexes show paramagnetism, which means that the ligands have little effects on the metal ions field i.e. the ligands exhibit a weak field effect.

Zn^{2+} complexes show diamagnetic behavior since the d-orbitals are completely filled and Zn^{2+} considered as non-transition metal ion.

Electronic spin resonance (ESR):

The X-band ESR spectra of Cu^{2+} - azopyrazolone complexes at room temperature generally show one or two broad signals depending on the nature of the ligands used and the type of the complexes formed

Table (18): ESR spectral data of Cu^{2+} complexes with ligands I, IV&V

| Complex | $g_z = g_{//}$ | $g_x = g_{\perp}$ |
|-------------|----------------|-------------------|
| Cu-I (2:2) | 2.0559 | |
| Cu-I (2:3) | 2.03806 | |
| Cu-IV (2:2) | 2.05616 | 2.06776 |
| Cu-IV (2:3) | 2.06037 | 2.07141 |
| Cu-V (1:1) | 2.12941 | 2.18337 |
| Cu-V (1:2) | 2.11293 | 2.17279 |

General structures of the complexes:

Based on the results of elemental analysis, IR, 1H NMR, thermal analysis, Electron spin resonance (ESR) and magnetic moments calculations, the Mn, Co, Ni, Cu and Zn complexes with the investigated ligands (I-IV) 2:2 and 2:3, and are illustrated in figures (2). For ligand V, 1:1 and 1:2 complexes are isolated, their structures may be formulated as seen in figures (3). The proposed stereochemical structure for the investigated metal complexes suggest tetrahedral geometry with respect to Mn, Co, Ni, Cu and Zn 2:2 and 2:3.

For ligand V, the proposed stereochemical structures for the investigated metal complexes suggest tetrahedral geometry for 1:1 complexes and suggest octahedral geometry for 1:2 complexes and all of the formed complexes are without coordinated water molecules.

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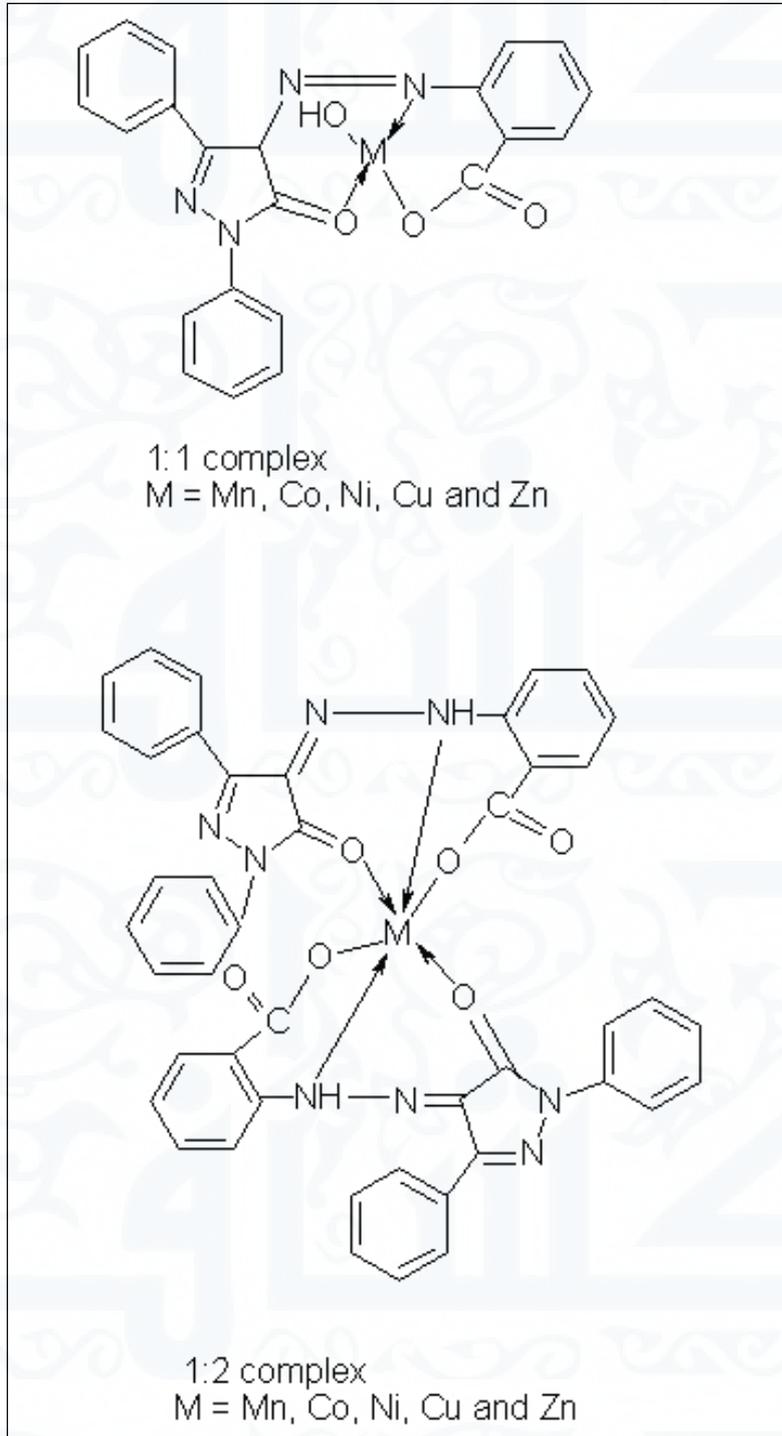


Figure (2): structures of 1:1 and 1:2 complexes.

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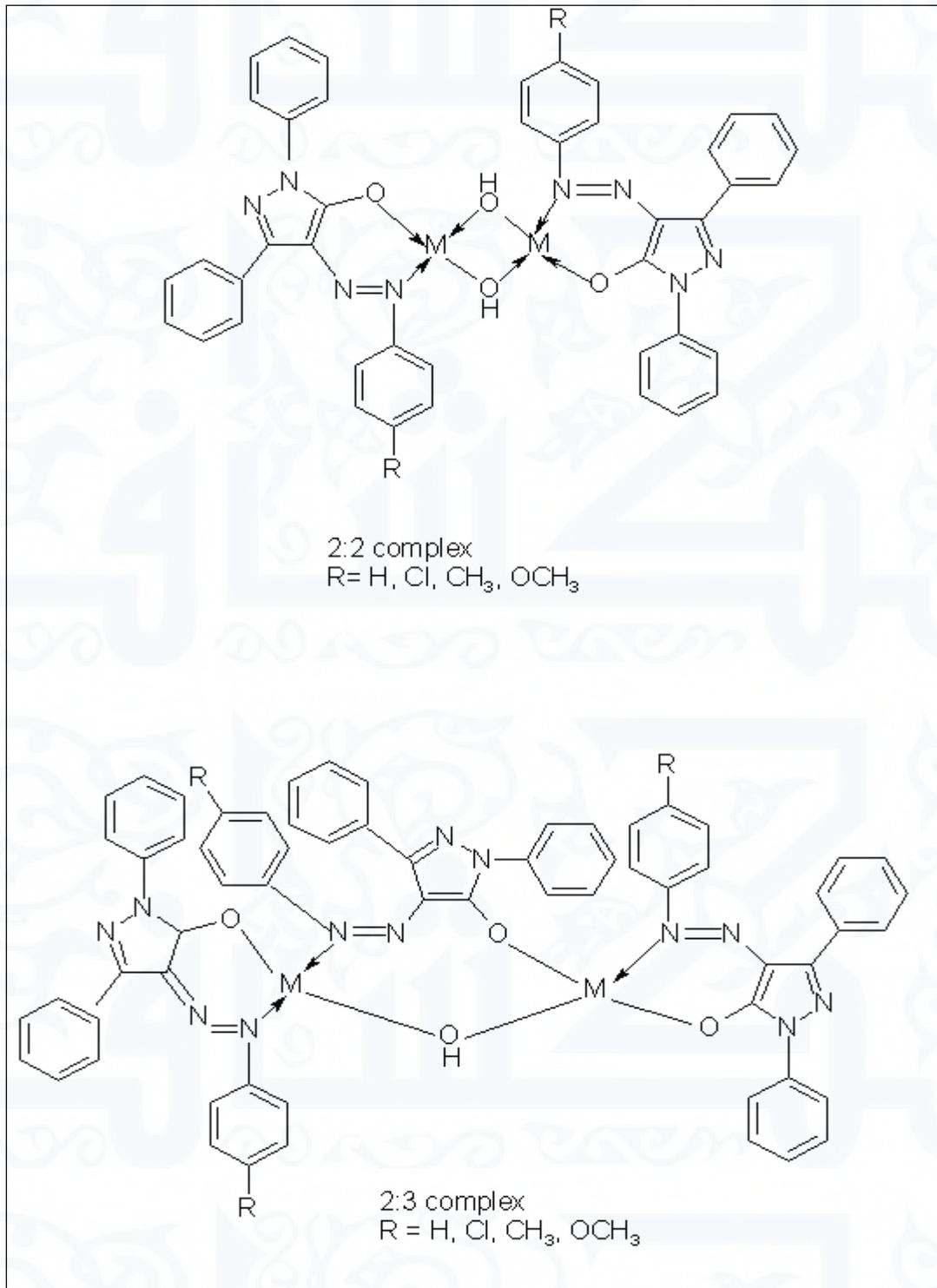


Figure (3): Structures of 2:2 and 2:3 complexes.

Conclusion

The electronic absorption spectra of the investigated ligand (V) was investigated in some Organic solvents of different polarities . the solvent effect on absorption bonds was studied . The plots of dielectric constant $D, (D-1), (D+1), F(D)$ and $\Phi (D)$ against of the bond observed in the C.T bond are not linear relations.

The mass spectra of all ligands (I-V) were studied to get further insight as the nature and different fragmentations which are characteristic for every compound . The mass spectra of each compound showed the molecular ion M^+ at m/z value corresponding to its molecular weight.

The infrared spectra , 1H NMR and elemental analysis were also obtained and studied for the investigated ligands (I-V) .

The solid complexes of the transition metal ions with the investigated ligands (I-V) were prepared and the precipitated complexes were chemically analyzed .The results of analysis suggested chemical composition for each of the solid complexes obtained . IR , 1H NMR , thermal analysis ,magnetic susceptibility , mass spectra , electron spin resonance (ESR) and molar conductance confirmed the compositions and structure of the separated solid complexes for ligand (I- IV) , 1:1 and 1:2 (M:L) complexes for ligand V .

The complexes were formed through coordination with the oxygen of the pyrazolone ring , N of the azo-hydrato group and covalent bond with the oxygen of the hydroxyl group.

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