

Original Research Article

Synthesis and Characterization of Some Coordination Polymalimides

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ABSTRACT

Twelve polymeric complexes were prepared from the polymerization of phenylazo-3-N-(4-hydroxyphenyl) maleimide and Phenylazo-3-N-(3-hydroxyphenyl) maleimide, with salts of Cr^{3+} , Co^{2+} , Ni^{2+} , Mn^{2+} , Cu^{2+} and Fe^{2+} these complexes were characterized by U.V., I.R. spectroscopy, elemental analysis, molar conductivity and magnetic moment, to ensure their geometry, according to these measurements all the complexes have tetrahedral geometry except $[\text{CrL}_2\text{Cl}_3 \cdot \text{H}_2\text{O}]$ and $[\text{NiLCl}_2 \cdot 2\text{H}_2\text{O}]$ which have octahedral one. The biological activity of these complexes showed a moderate inhibition towards some growth bacteria.

Keywords: coordination polymalimdes, biological activity, azo complexes, azo compounds

1. INTRODUCTION

Linking transition metal ions with polymeric ligands has been constantly developed in past years, these are called coordination polymers. Because of their excellent properties in fields such as catalysis [1], nonlinear optics [2], molecular magnetic materials [3,4,5] electrical conductivity [6,7] and molecular recognition [8,9]. Poly-N-Substituted maleimides and their derivatives have excellent heat-resistance property. They can be used in many polymeric applications as heat-resistant additives [10] and as modifying agents for proteins [11]. Azo dyes compounds one of the biggest and most varied groups of synthetic organic dyes in present time [12]. They were highly well-known and widely used chemicals in the paper, textile, coloring agents for foods and cosmetics industries. Other applications in electronic technologies like liquid crystals, organic photoconductors and non-linear optics [13,14]. The pharmacological use of azo compounds came from the discovery of the antibacterial action of Prontosil on streptococcal infections by Dogmagk [15], azo compounds were also show a variety of biological activities including antibacterial [16], antifungal [17], pesticides [18], antiviral [19] and anti-inflammatory [20] activities. In our work we have synthesized azo compounds based on maleimides, polymerized them and prepared complexes with six transition elements.

2. MATERIAL AND METHODS

Maleic anhydride, aniline, *N,N*-dimethylformamide, benzoyl peroxide all from (Merck, Germany), sulfuric acid 98% , hydrochloric acid 37%, chromium(iii) chloride hexahydrate, cobalt(II) chloride dehydrate, nickel(II) chloride dehydrate, manganese(II), sodium nitrite, 2-

propanol, sodium hydroxide also from (Carl Roth, Germany), *p*-aminophenol, *m*-aminophenol (Carlo Erba, Italy), Copper(II) chloride dehydrate, phosphorus pentoxide (Sigma-Aldrich), ferrous(II) chloride trihydrate (Fluka, Switzerland). Aniline was purified by distillation while all the other chemicals were used without purification as received.

Analysis of the ligands and their complexes were carried out using C.H.N.S elemental analyzer model 2400 Perkin Elmer. Metals content from Perkin Elmer (A analyst 200) atomic absorption spectrophotometer. FT-IR spectra were measured at room temperature using a Perkin-Elmer spectrum one B, equipped with potassium bromide (KBr) beam splitter. Conductivity meter JENWAY 4510, were used to measure the conductivity of the complexes, magnetic Susceptibility measurements of all co-ordinate polymers were carried out at room temperature by Farady's method using Bruker BM6 instrument. The electronic spectra of coordination polymers were recorded by Unicam HELIOS β UV-VIS 2000 spectrophotometer using 10⁻³ dimethyl sulphoxide (DMSO) solution at room temperature.

2.1 Synthesis of maleimide (I)

p-Aminophenol (11.93 g, 0.11 mol) and maleic anhydride (10.78 g, 0.11 mol) were dissolved separately with dimethyl formamide (DMF) (50 mL) to get solutions A and B, respectively. Solution C obtained by dropping Solution B gradually into solution A. After stirring this solution for 2 hours at 25 °C in a water bath, (10 g) phosphorous pentoxide were dissolved in (10:70) ml H₂SO₄ and DMF mixture respectively. By dropping this mixture into solution C it was stirred at 70 °C for 2 hours and then it was chilled in an ice bath and poured into cold water. The pale orange precipitate was filtered then washed several times with distilled water and recrystallized from isopropyl alcohol and dried overnight in vacuum oven at 60 °C. The yield was 25%; m.p. 183°C.

2.2 Synthesis of maleimide (II)

maleimide II was prepared as the same procedure of I except that *m*-aminophenol was substituted for *p*-aminophenol. The precipitate was yellow and melt at 186 with 35% yield.

2.3 General procedure for preparing azo compounds L1 and L2

Azo compounds L1 and L2 were prepared according to previous work [21,23]. The orange L1 (Phenylazo-3-N-(4-hydroxyphenyl)maleimide) was obtained with 56% yield and the pale yellow L2 (Phenylazo-3-N-(3-hydroxyphenyl)maleimide) L2 with 30% yield.

2.4 General procedure for the polymerization of L1 and L2

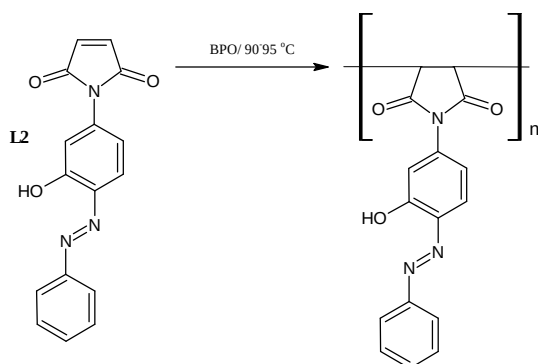
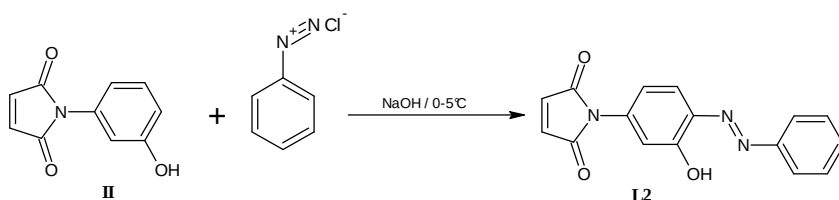
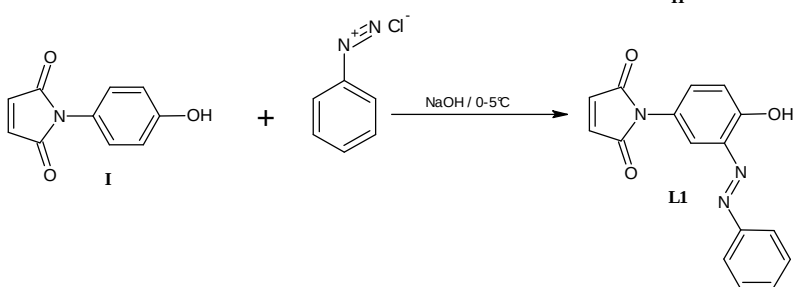
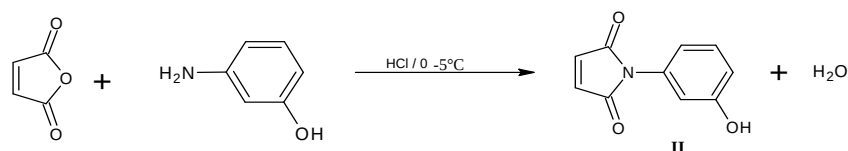
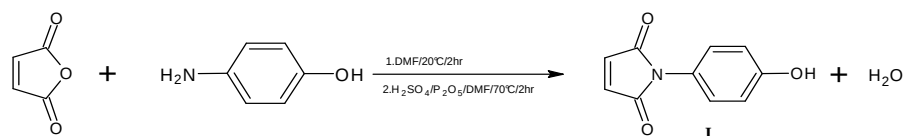
(1.76 g) of L1 or L2 compound was dissolved in (100 ml) toluene with (0.176 g) of benzoyl peroxide (BPO) in a 500ml, three-necked flask. By stirring the reaction mixture at 70. The temperature was raised to 90 °C for 12 hrs. The polymer was precipitated by pouring it into water containing methanol mixture 20% (200 ml). The light brown polymer washed several times with methanol and dried under vacuum at 60 °C overnight.

2.5 Preparation of the polymeric complexes

All the complexes were prepared by 1:1 molar ratio polymer to metal respectively. A solution of salts (0.001 mol) in ethanol was added drop wise to an ethanolic of polymer I' and II' (0.001 mol) with stirring. The mixture was reflux for 6 hrs. The resultant complex was collected by filtration and washed with methanol, then acetone. The coordination polymer was dried in vacuum oven for 24 hrs at 40 °C.

The synthesis, characterization and chelating properties of polymer I' and II' and its coordination complexes are shown in Scheme 1.

Scheme1: synthesis of Phenylazo-3-N-(4-hydroxyphenyl)maleimide (L1), Phenylazo-3-N-(3-hydroxyphenyl)maleimide (L2) and their polymeric complexes.



2.6 Antibacterial activity

The bioactivity for all polymeric complexes was tested against five species according to Standards methods with slight modifications[34]. The Gram-positive (*Staphylococcus aureus*) and Gram-negative (*Klebsiella pneumonia*, *Escherichia coli*, *Enterococcus faecalis* and *Pseudomonas aeruginosa*) were isolates in (Azadi hospital-duhok). (10^{-3}M) of polymeric complex solution in dimethyl sulphoxide was placed on Muller-Hinton agar plates with tested

organisms and incubated for 24 hs at 37 °C. The inhibition zone were measured in mm depending upon diameter and clarity.

3. RESULTS AND DISCUSSION

3.1 Infrared spectra

The two ligands were synthesized according to scheme 1, they characterized by FTIR, UV-VS spectra and elemental analysis. The infrared spectra (table 2) of I' and II' compounds showed the ν -stretching of (C=O) carbonyls at 1702-1697 cm^{-1} , and the presence of aromatic rings indicated by bands at 1585, 1604 and 1,522 cm^{-1} , ν -stretching frequencies of alkene group (HC=CH) at 3170 cm^{-1} , and, also -OH hydroxyl group at 3482-3440 cm^{-1} for I and II, respectively. All the above peaks confirm the formation of I and II. These peaks maintained at their positions in compounds I' and II' accompanied by the ν -stretching of (N=N) azo group band at 1605–1578 cm^{-1} range which confirm the synthesis. Another absorption at 763–776 cm^{-1} confirm that azo groups was attached at ortho position of benzene ring. The two polymers showed the same peaks as the monomers except the absence of the alkene group (HC=CH) bands which indicate the formation of the polymers.[21,22]

The reaction of polymer ligands with Co(II), Ni(II), Cu(II), Fe(II), Mn(II) and Cr(III) in (1:1) ratio gives the $[\text{MLCl}_2 \cdot 2\text{H}_2\text{O}]$ and $[\text{MLCl}_2]$ complexes. The elemental analysis are confirmed with the proposed molecular formula (Table1).

Table 1. elemental analysis, magnetic moment value and physical properties of the prepared ligands and their complexes.

Compounds	Color	%Calculated(found)				Meff B.M.	Cond. $\mu\text{S}/\text{cm}^{-1}$	geometry
		C	H	N	M			
Polymer L1	orange	65.53(65.51)	3.78(372)	14.33(14.30)	-	-	-	
Polymer L2	Pale yellow	65.53(65.50)	3.78(3.76)	14.33(14.30)	-	-	-	
$[\text{CrL1Cl}_3 \cdot \text{H}_2\text{O}]$	beige	46.18(46.14)	2.66(2.63)	10.10(10.98)	12.49(12.45)	3.9	19.5	Tetragonal
$[\text{CrL2Cl}_3 \cdot \text{H}_2\text{O}]$	Pale yellow	40.92(40.89)	2.79(2.75)	8.95(8.92)	11.07(11.03)	4	17.5	Octahedral
$[\text{NiL1Cl}_2 \cdot 2\text{H}_2\text{O}]$	pink	43.39(43.35)	3.41(3.40)	9.49(9.47)	13.25(13.21)	3.1	18.7	Octahedral
$[\text{NiL2Cl}_2]$	Dark yellow	45.44(45.41)	2.62(2.60)	9.94(9.91)	13.88(13.85)	3.9	15	Tetrahedral
$[\text{CuL1Cl}_2 \cdot 2\text{H}_2\text{O}]$	brown	44.93(44.90)	2.59(2.57)	9.82(9.80)	14.86(14.84)	2.9	18	tetrahedral
$[\text{CuL2Cl}_2 \cdot 2\text{H}_2\text{O}]$	Pale yellow	44.93(44.89)	2.59(2.58)	9.82(9.80)	14.86(14.81)	2.8	19	tetrahedral
$[\text{MnL1Cl}_2]$	beige	45.85(45.83)	2.65(2.63)	10.03(10.01)	13.11(13.09)	6	21.4	Tetrahedral
$[\text{MnL2Cl}_2]$	yellow	45.85(45.82)	2.65(2.63)	10.03(10.00)	13.11(13.08)	5.9	23	Tetrahedral
$[\text{CoL1Cl}_2]$	Pale pink	45.42(45.40)	2.62(2.61)	9.93(9.91)	13.93(13.90)	3.9	18.7	Tetrahedral
$[\text{CoL2Cl}_2]$	green	43.37(43.33)	3.41(3.39)	9.48(9.46)	13.30(13.00)	4.25	14.8	tetrahedral
$[\text{FeL1Cl}_2]$	Pale brown	45.75(45.73)	2.64(2.61)	10.00(9.98)	13.30(13.37)	5.4	13.9	Tetrahedral
$[\text{FeL2Cl}_2]$	yellow	45.75(45.72)	2.64(2.62)	10.00(9.99)	13.30(13.10)	5.3	18.1	Tetrahedral

The molar conductivity of the complexes illustrate that all are non-electrolyte[23] except for Cr(III) which 1:1 as in (table1). The IR spectra for the metal complexes in (table 2) showed that there are many shifts for the absorption bands, ν (-N=N-) vibrational stretching bands in the ligands appears at (1522-1511 cm^{-1}) are shifted in their complexes to lower frequencies to (1511-1402 cm^{-1}) which indicate the coordination through the -N=N-group[23]. The ligand spectrum shows an absorption band at (1217-1223 cm^{-1}) due to ν (C-O). it is remarks with a change in shape and shifted to higher frequencies at (1221-1242 cm^{-1})

¹) in metal chelates. These shifts suggest the linkage of metal ion with oxygene[24]. The most important conclusion from the above suggest that the polymeric azo malimides ligands is coordinated to the central metal ion as N,O bidentate ligand. The free bonding positions are the central azo nitrogen atom and the oxygen of the hydroxyl group.

3.2 Electronic spectra and magnetic susceptibility

According to molar conductivity measurements all the complexes are non-electrolyte in their nature (table 1)[25, 26]. The electronic spectra of ligands and their complexes tabulated in table (table2), the free azo ligand shows high intensity peaks at 420 nm and 371 nm respectively these peaks belongs to the chromospheres of -N=N- and -OH groups. The magnetic moment value of Cr (III) complexes were (3.9, 4) B.M, this suggest an octahedral geometry with terms of triplet 4F that means there are three d-d bands spectrum $^4A_2g \rightarrow ^4T_2g$, $^4A_2g \rightarrow ^4T_1g$, $^4A_2g_{(F)} \rightarrow ^4T_1g_{(P)}$, with very low intensity because the transitions are forbidden and we found a very high band of LMCT at 304 nm in L1 cover some bands of (d-d) transitions, while in L2 the following bands (421,367,325,304) nm[23]. Ni (II) complex in L1 show an octahedral geometry as it gave 3.1 B.M value of magnetic moment this means there is no orbital contribution with three transitions $^3A_2g \rightarrow ^3T_2g$, $^3A_2g \rightarrow ^3T_1g$, $^3A_2g_{(F)} \rightarrow ^3T_1g_{(P)}$, these transition are forbidden (d-d) or (gerade – grade) 402,368,288 transitioned with low intensity, the band observed with high intensity attributed to LMCT and MLCT at (371,282,401) nm respectfully[27], while the Ni(II) complex with L2 ligand gave 3.9 B.M value of magnetic moment this means the complex is tetrahedral with orbital contribution and gave electronic transitions $^3T_1g \rightarrow ^3T_2g$, $^3T_1g \rightarrow ^3A_2g$, $^3T_1g_{(F)} \rightarrow ^3T_1g_{(P)}$ with MLCT And LMCT, the color of tetrahedral is more dark than octahedral with peaks at (414,364,293) nm[28]. The magnetic moments values of Cu(II) complexes are (2.8, 2.9)B.M. this means that both of them are tetrahedral with orbital contribution and gave one band low intensity of (d-d) transition $^2T_2 \rightarrow ^2E$, the other bands contribute to LMCT and MLCT with high intensity at (381,360,313,281) nm and (377,342,300,246) nm respectly[29,30]. The complexes of Mn(II) with (6, 5.9) B.M. value have strong field ligand with tetrahedral geometry and the transition is $^6S \rightarrow ^6A_1g$ only MLCT and LMCT at (344,300,296) nm and (405,363,293) nm[31]. Co(II) both have tetrahedral geometry with (3.9, 4.2) B.M. respectively and this geometry observed with three (d-d) bands $^4A_2g \rightarrow ^4T_2g$, $^4A_2g \rightarrow ^4T_1g$, $^4A_2g_{(F)} \rightarrow ^4T_1g_{(P)}$ with LMCT and MLCT at (353,306,293) nm and (402,368,288) nm, the different between these complexes are there colors repeatedly[32]. Fe(II) have (5.4, 5.3) B.M. in both complexes and tetrahedral is the predominant geometry with orbital contribution and the observed (d-d) spectra is one (d-d) band $^5E \rightarrow ^5T_2$ with high intensity bands of charge transfere[33].

Table 2. infrared spectra (cm⁻¹)for the ligands and their polymeric complexes.

Compounds	ν (-OH)	ν (C-H) arom.	ν (-C=C-) arom.	ν (-N=N-)	ν (C-O)	δ (C-H) arom.	UV-VIS abs. λ (nm)
Polymer L1	3421	3109	1604	1522	1217	831	327,302,230
Polymer L2	3328	3090	1599	1511	1223	825	325,302,230
[CrL1Cl ₂]Cl	3413	-	1513	1420	1221	832	304,246
[CrL2Cl ₃ .H ₂ O]	3412	-	1561	1446	1225	830	421,367,325,304
[NiL1Cl ₂ .2H ₂ O]	3411	-	1533	1512	1232	827	371,282,401
[NiL2Cl ₂]	3398	-	1537	1456	1239	823	414,364,293
[CuL1Cl ₂]	3416	-	1512	1404	1225	835	381,360,313,281
[CuL2Cl ₂]	3414	-	1544	1449	1232	767	377,342,300,246
[MnL1Cl ₂]	3435	-	1512	1402	1233	837	344,300,296
[MnL2Cl ₂]	3400	-	1544	1454	1242	865	405,363,293
[CoL1Cl ₂]	3411	-	1512	1402	1233	835	353,306,293
[CoL2Cl ₂ .2H ₂ O]	3409	-	1537	1407	1239	816	402,368,288
[FeL1Cl ₂]	3412	-	1526	1407	1236	854	401,362,297
[FeL2Cl ₂]	3399	-	1547	1411	1230	833	395,367,293

3.3 Biological activity study

The antimicrobial activity examination of the polymeric complexes was carried out by disk diffusion method[35,36]. The test solutions prepared in dimethyl sulfoxide. The zone of inhibition was measured in mm and the values was summarized in (table 3). These values indicate that all the complexes have moderate activity (14-19mm moderate, ≥ 20 susceptible, ≤ 14 resistant) towards the tested organisms on the basis of overtone's concept and chelating theory[27,28].

Table 3. Antibacterial activity (inhibition zone/mm) of chemicals complex (10^{-3} M) Against Gram positive and Gram negative pathogen isolates.

Complex	<i>E. coli</i>	<i>P. aeruginosa</i>	<i>S. aureus</i>	<i>K. pneumonia</i>	<i>E. faecalis</i>
[MnL1Cl ₂]	18 mm	18 mm	15 mm	14 mm	19 mm
[MnL2Cl ₂]	-----	14 mm	18 mm	-----	14 mm
[FeL2Cl ₂]	-----	-----	-----	14mm	17 mm
[FeL1Cl ₂]	-----	14 mm	-----	17 mm	14 mm
[NiL2Cl ₂]	-----	15 mm	12 mm	18 mm	18 mm
[NiL1Cl ₂ .2H ₂ O]	-----	14 mm	17 mm	18 mm	-----
[CoL2Cl ₂ .2H ₂ O]	-----	18 mm	-----	-----	18 mm
[CrL1Cl ₂]Cl	-----	11 mm	-----	13 mm	15 mm
[CrL2Cl ₃ .H ₂ O]	18 mm	13 mm	13 mm	20 mm	17 mm
[CuL1Cl ₂]	-----	18 mm	14 mm	-----	18 mm
[CuL2Cl ₂]	12 mm	12 mm	13 mm	12mm	17 mm

4. CONCLUSION

The ligands Phenylazo-3-N-(4-hydroxyphenyl)maleimide I' and Phenylazo-3-N-(3-hydroxyphenyl)maleimide (II') were polymerized free radically, these polymers were coordinated successfully with some transition elements through azo ($-N=N-$) and hydroxyl ($-OH$) with tetrahedral metal (II) complexes except [CrL2Cl₃.H₂O] and [NiL1Cl₂.2H₂O] which were octahedral in (1:1 metal to ligand ratio) were synthesized and characterized. . All the complexes have a well considerable activity against different organisms.

REFERENCES

1. Maruoka K, Murase N and Yamamoto H. Chiral helical Lewis acids for asymmetric Diels-Alder catalysts. 1993 *J. Org. Chem.* **58** 2938.
2. Chen C. and Suslick K S. One dimensional coordination polymers: application to material science. 1993 *Coord. Chem. Rev.* **128** 293.
3. Stumpf H O, Ouahab L, Pei Y, Grandjean D and Kahn O. A Molecular-Based Magnet with a Fully Interlocked Three-Dimensional Structure. 1993 *Science* **261** 447.
4. Lloret F, Munno G D, Cano M J, Ruiz R and Caneschi A. Spin Polarization and Ferromagnetism in Two-Dimensional Sheetlike Cobalt(II) Polymers: [Co(L)₂(NCS)₂] (L=Pyrimidine or Pyrazine) 1998 *Angew. Chem. Int. Ed. Engl.* **37** 135.
5. Real J A, Andre E, Munoz M C, Julve M, Granier T, Bousseksou A and Varret F. Spin Crossover in a Catenane Supramolecular System. 1995 *Science* **268** 265.
6. Hoskins B F and Robson R. Design and construction of a new class of scaffolding-like materials comprising infinite polymeric frameworks of 3D-linked molecular rods. A reappraisal of the zinc cyanide and cadmium cyanide structures and the synthesis and structure of the diamond-related frameworks [N(CH₃)₄][CuI ZnII(CN)₄] and

- 214 Cul[4,4',4'',4'''-tetracyanotetraphenylmethane]BF₄.xH₂O. 1990 *J. Am. Chem.*
215 *Soc.* **112** 1546.
- 216 7. C.L. Bowes and Ogini G A. Self-Assembling Frameworks: Beyond microporous
217 oxides.1996 *Adv. Mater.*, **8** 13.
- 218 8. Kondo M, Yoshitomi T, Seki K, Matsuzaka H and Kitagawa S. Three-Dimensional
219 Framework with Channeling Cavities for Small Molecules: {[M₂(4, 4'-
220 bpy)₃(NO₃)₄·xH₂O]}_n (M [DOUBLE BOND] Co, Ni, Zn). 1997 *Angew. Chem. Int.*
221 *Ed. Engl.* **36** 1725-1727.
- 222 9. Venkataraman D., Gardner G F, Lee S and Moore J.S. Zeolite-like Behavior of a
223 Coordination Network 1995. *J. Am.Chem. Soc.* **117** 11600-11601.
- 224 10. Wu H H and Chu P P. Structure characteristics contributing to flame retardancy in
225 diaz modified novolac resins. 2009 *Polym. Degrad. Stab.* **94** 987-995.
- 226 11. SIPPEL T O. The histochemistry of thiols and disulphides. I. The use of N-(4-
227 aminophenyl)maleimide for demonstrating thiol groups. 1973 *Histochemical Journal*
228 **5** 413-423.
- 229 12. Zollinger H *Color Chemistry*, 2nd Ed. VCH, Weinheim 1991.
- 230 13. Hamon F , Djedaini-Pilard F , Barbot F and Len C. Azobenzenes—synthesis and
231 carbohydrate applications. 2009 *Tetrahedron* **65** 10105-10123.
- 232 14. Gordon P F. The Chemistry and Applications of Dyes (Topics in Applied
233 Chemistry)(Warning, D. R.; Hallas, G. Eds.) New York, Plenum Press. 1990.
- 234 15. Carey F A. Organic Chemistry, 4th Ed, New York, McGraw)Hill. 2000.
- 235 16. Pathak P, Jolly V S and Sharma K P. Synthesis and biological activities of some
236 new substituted arylazo Schiff bases. 2000 *Orient. J. Chem.* **16** 161-162.
- 237 17. Xu H and Zeng X. Synthesis of diaryl-azo derivatives as potential antifungal agents.
238 2010 *Bioorg. Med. Chem. Lett.* **20** 4193-4195.
- 239 18. Samadhiya S and Halve A. Synthetic utility of Schiff bases as potential herbicidal
240 agents. 2001 *Orient. J. Chem.* **17** 119-122.
- 241 19. Tonelli M, Vazzana I, Tasso B, Boido V, Sparatore F, Fermeglia M, Paneni M S,
242 Posocco P, Pricl S, Colla P, Ibba C, Secci B, Collu G and Loddo R. Antiviral and
243 cytotoxic activities of aminoarylazo compounds and aryltriazene derivatives. 2009
244 *Bioorg. Med. Chem.* **17** 4425-4440.
- 245 20. Rani P, Srivastava V K and Kumar A. Synthesis and antiinflammatory activity of
246 heterocyclic indole derivatives. 2004 *Eur. J. Med. Chem.* **39** 449-452.
- 247 21. Issam A and Asniza M. Synthesis of New Azo Compounds Based on N-(4-
248 Hydroxyphenyl)maleimide and N-(4-Methylphenyl)maleimide. 2010 *Molecules* **15**
249 7498-7508.
- 250 22. Xing-Rong Z, Bing-Tao T and Shu-Fen Z. A Simple and Practical Solvent-Free
251 Preparation of Polymaleimide. 2011 *Molecules* **16** 1981-1986.
- 252 23. Mahmoud N Al-Jibouri. Synthesis AND Characterization of transition Metal
253 Complexes With Azo Ligand Derived from 4-Hydroxy-6-Methyl-2-Pyranone. 2014
254 *Eur. Chem. Bull.* **3(5)**, 447-451.
- 255 24. Williams D H and Fleming I. Spectroscopic methods in organic chemistry,5th. Ed.,
256 London; 1995.
- 257 25. Murty N M, Dash R N and Rao D V R 1984 *J. Indian chem. Soc.* **61** 943.

- 258 26. Preti C., Tosi G., De Filippo D and Verani G. Group IIB metal complexes with
259 thiazolidine-2-selenone and thiazolidine-2-one as ligands. 1974 *J. Inorg. Nucl.*
260 *Chem.* **36** 3725-3729.
- 261 27. Mamdouh S M, Sawsan S H, Alaa E A and Nessma M N. Synthesis and
262 spectroscopic characterization of gallic acid and some of its azo complexes. 2012
263 *Journal of Molecular Structure* **1014** 17-25.
- 264 28. Alaghaz A M A, Bayoumi H A, Ammar Y A and Aldhlmani S A. Synthesis,
265 characterization, and antipathogenic studies of some transition metal complexes
266 with N,O-chelating Schiff's base ligand incorporating azo and sulfonamide Moieties.
267 2013 *J. Molec. Struct.* **1035** 383-399.
- 268 29. Mishra L and Singh V K . Synthesis and structural and antifungal studies of Co(II),
269 Ni(II), Cu(II) and Zn(II) complexes with new Schiff bases bearing benzimidazoles.
270 1993 *Indian J. Chem.* **32A** 446-449.
- 271 30. Thakara A S, Friedricha H B, and Joshib K T. Synthesis and structural analogs of
272 novel Schiff bases derived from sulfadoxine with 4-acetyl/benzoyl-1-(4'-nitrophenyl)-
273 3-methyl-2-pyrazolin-5 one their metal complexes and antibacterial activity. 2013 *J.*
274 *Chem. Pharm. Res.* **5(4)** 319-325.
- 275 31. Mohamed AA, Buttrus N H and Younis M K. New Complexes of Polyurea with
276 Copper (II), Manganese (II) and Chromium (III) (Synthesis and Characterization)
277 2010 *National J.Chem.* **38**, 333-348.
- 278 32. Cotton F A, Wilkinson G, Murillo C A and Bochmann M Advance inorganic
279 chemistry, 6th Ed., John Wiley and Sons NewYork 1999.
- 280 33. Steffen M, Claudia M O, Serhiy D, Sebastian D and Franc M. Synthesis and
281 Characterization of Di- and Tetracarbene Iron(II) Complexes with Chelating N-
282 Heterocyclic Carbene Ligands and Their Application in Aryl Grignard-Alkyl Halide
283 Cross-Coupling. 2011 *Organometallics* **30** 6692-6702.
- 284 34. Franklin R C, Matthew A W, Jeff A, Michael N D, George M E, Mary J F, Dwight J H,
285 David W H, Janet A H, Jean B P, Mair P, Jana M S, Richard B T, Maria M T, John D
286 T, Melvin P W and Barbara L Z. Performance Standards for Antimicrobial Disk
287 Susceptibility Tests; Approved Standard. 2012 *National Committee for Clinical*
288 *Laboratory Standards*, **32(1)** 45.
- 289 35. Bodeis B G S, Walker R D , White D G , Zhao S, Mcdermott P F and J Meng,
290 Comparison of the Etest and agar dilution for in vitro antimicrobial susceptibility
291 testing of *Campylobacter*. 2002 *J. Antimicrob. Chemother.* **50** 487-494.
- 292 36. Kaya E M and Gur S. Synthesis, Characterization of Some Co(III) Complexes with
293 vic-Dioxime Ligands and Their Antimicrobial Properties. 2004 *Tur. J. Chem.* **28** 235-
294 242.