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RESEARCH ARTICLE

SYNTHESIS, CHARACTERIZATION, THERMAL AND ANTIMICROBIAL STUDIES OF SCHIFF BASE M(II) COMPLEXES.

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Abstract

The N, O type Schiff base ligand and its five new metal complexes of Co(II), Ni(II), Zn(II), Cd(II) and Cu(II) derivatives of 6-acetyl-7-hydroxy 4,8-dimethyl-2H-chromen-2-one have been synthesized from o-phenylenediamine in alcoholic medium. A series of metal complexes have been characterized quantitatively and qualitatively by using micro elemental analysis, FT-IR, ¹H NMR, Mass, UV-Vis, TGA/DTG, ESR, magnetic susceptibility data and molar conductance studies. From the spectral study, all the complexes obtained were octahedral in nature. Complexes exhibited enhanced anti-microbial activity in comparison to their ligand.

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Introduction:-

Schiff bases are capable of forming coordinate bonds with many metal ions via azomethine group, and so they have been used for the synthesis of metal complexes due to their easy formation and strong metal binding ability. The Schiff base ligands and their corresponding metal complexes have expanded enormously and include a vast area of organometallic compounds and various aspects of bioinorganic chemistry [1-3] and have continued to play the role of one of the most important stereo chemical models in main group and transition-metal coordination chemistry due to their preparative accessibility, diversity and structural variability [4, 5].

Schiff base and its metal complexes attract considerable interest and occupy an important role in the development of chemistry of chelate systems [6, 7] due to the fact that especially these with N₂O₂ tetradentate ligands, such systems closely resemble metallo-proteins. Some Schiff base complexes are also used as model molecules for biological oxygen carrier systems [8] as well as having applications in analytical fields [9] and have been reported to show a variety of biological actions by virtue of the azomethine linkage, which is responsible for various antibacterial, antifungal, antiviral, anti-inflammatory, antioxidant, anticancer, herbicidal, clinical and analytical activities [10-12]. On the other hand, azo compounds are very important molecules and have attracted much attention in both academic and applied research [13]. Azo compounds and their metal complexes are known to be involved in a number of biological reactions, such as inhibition of DNA, RNA, and protein synthesis, nitrogen fixation, and carcinogenesis [14, 15]. Also, the azo compounds and their metal-azo complexes are extremely used in dyes and data storage [16-18].

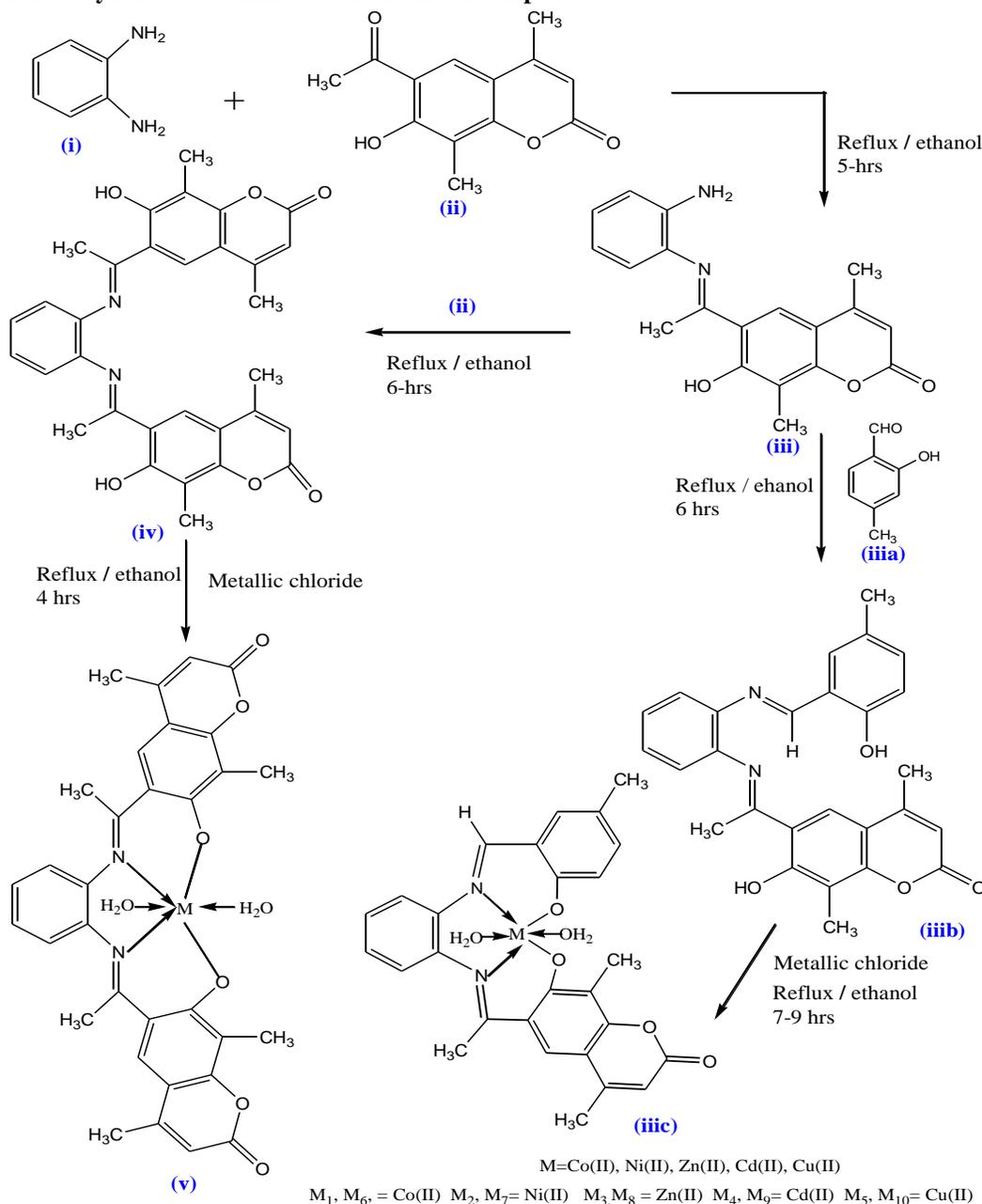
As the continuation interest of our study of transition metal complexes, here we present the synthesis and characterization of new complex derivatives of 6-acetyl-7 hydroxy 4,8-dimethyl-2H-chromen-2-one. The antibacterial screening activities of the complexes obtained are carried out and the results are reported herein.

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Experimental section:-**Materials and Methods:-**

All the chemicals used in the preparation of the ligand and its metal complexes were of AR grade. The solvents were distilled before use. For the preparation and analyses, distilled water was used. A Perkin-Elmer CHN analyzer (model 2400) was used for C, H and N analyses. The room temperature molar conductance was determined using a Century digital conductivity meter (model cc 601) with a dip type cell and a smooth platinum electrode. The electronic absorption spectra of the complexes were recorded as dilute solutions on a Shimadzu 160A/240A UV-visible spectrophotometer. The ^1H NMR spectra were recorded using Bruker DRX 400 spectrometer at 400 MHz with TMS as the internal standard. Mass spectra were obtained with a VG70-70H spectrophotometer. The infrared spectra of the solid samples were recorded in the range $4000\text{-}500\text{ cm}^{-1}$ on a Perkin-Elmer 597/1650 spectro photometer using KBr pellets. The magnetic moments were measured out using gouy balance. The TG-DTG experiments were carried out in air using a Shimadzu DT-40 thermal analyzer. The heating rate employed was 10°C per minute and platinum cups were used to hold about 5 mg of the samples [19].

Scheme:- Synthesis of Schiff base and its metal complexes.

General procedure for the synthesis of 2-methyl-4-{phenyl-[3-(1-phenyl-ethyldeneamino)-propylimino]-methyl}-phenol (iii):-

The compound (iii) was prepared by a modification of reported method [20]. A mixture of 6-acetyl-7-hydroxy-4,8-dimethyl-2H-chromen-2-one (ii) and o-phenylene diamine in 1:1 molar ratio was refluxed in dry ethanol for about 3 hours. Then it was cooled to room temperature. On cooling, the white coloured intermediate solid compound, mono-Schiff base (iii) was obtained. The solid was washed with distilled water (3×40 ml) and recrystallized from ethanol to achieve pure compound.

Yield 87%; M.p. 152°C; IR (Nujol): (C=N) 1662, (O-H) 3510, (-NH₂) 3296 cm⁻¹. ¹H NMR (DMSO): δ 1.02 (s, 3H, N=C-CH₃), δ 2.35 (s, 3H, Coumarin CH₃), δ 2.57 (s, 3H, Ar-CH₃), 4.27 (bs, 2H, -NH₂), δ 6.25 (s, 1H, Coumarin -H), 7.93 (s, 1H, Coumarin -H), δ 6.57-7.01 (m, 4H, Ar-H), 11.63 (bs, 1H, -OH). MS: m/z 322 (M⁺, 60), 232 (65), relative abundance; 100%. Anal.Calcd. for C₁₉H₁₈N₂O₃ (322): C, 70.79; H, 5.63; N, 8.69. Found: C, 70.50; H, 5.55; N, 8.60 %.

General procedure for the synthesis of ligand 7-hydroxy-6-(1-{2-[(2-hydroxy-5-methyl-benzylidene)-amino]-phenylimino}-ethyl)-4,8-dimethyl-chromen-2-one (iiib):-

Equimolar concentration of 4-methyl-2 hydroxybenzaldehyde (iiia) and intermediate (iii) was refluxed in dry ethanol for 6 hours. The yellow precipitate thus formed (iiib) was filtered, washed with distilled water dried in vacuum over calcium chloride and recrystallized in ethanol.

Yield 89%; M.p. 167°C; IR (Nujol): (C-O) 1236, (C-N) 1384, (C=N) 1676, (C=O) 1746, (O-H) 3512 cm⁻¹. ¹H NMR (DMSO): δ 1.03 (s, 3H, N=C-CH₃), δ 2.34 (s, 3H, coumarin CH₃), δ 2.56 (s, 6H, Ar-CH₃), 6.38 (s, 1H, coumarin -H), δ 6.96 (d, 2H, Ar-H), δ 7.07 (s, H, Ar-H), δ 7.3-7.4 (m, 4H, Ar-H), 7.95 (s, H, coumarin H), δ 8.67 (s, H, N=C-H), δ 11.27 (bs, 2H, -OH). MS: m/z 440 (M⁺, 60), 336 (10), 216 (60), 104 (70), relative abundance; 92%. Anal.Calcd. for C₂₇H₂₄N₂O₄ (440): C, 73.62; H, 5.49; N, 6.36. Found: C, 73.52; H, 5.38; N, 6.25%.

General procedure for the synthesis of complexes (iiic M₁-M₅):-

For a solution of ligand (iiib), metal chloride in 1:1 molar ratio in ethanol was added under constant stirring. The pH of the reaction mixture was adjusted to 7-8 by adding 10% alcoholic ammonia solution and refluxed for about 6-9 hours. The colored precipitate (iiic M₁-M₅) of metal complex was filtered off in hot condition and washed with hot ethanol, and dried over calcium chloride in vacuum desiccators.

Co(II): Yield 75%; M.p. >250°C; IR (Nujol): (M-O) 430, (M-N) 510, (C-O) 1263, (C-N) 1392, (C=N) 1665, (C=O) 1766, (H₂O) 3263 cm⁻¹. MS: m/z 534 (M⁺, 80), 438 (60), 215 (10), 103 (55), relative abundance; 83%. Anal.Calcd. for C₂₇H₂₆N₂O₆Co (534): C, 60.52; H, 4.32; N, 5.01. Found: C, 60.67; H, 4.86; N, 5.24%. Molar conductance: 21.0, Magnetic moment: 4.68 B M.

Ni(II): Yield 72%; M.p. >250°C; IR (Nujol): (M-O) 440, (M-N) 520, (C-O) 1269, (C-N) 1402, (C=N) 1659, (C=O) 1756, (H₂O) 3280 cm⁻¹. MS: m/z 534 (M⁺, 80), 439 (15), 199 (20), 103 (50), relative abundance; 89%. Anal.Calcd. for C₂₇H₂₆N₂O₆Ni (534): C, 60.35; H, 4.54; N, 5.01. Found: C, 60.42; H, 4.45; N, 5.25%. Molar conductance: 15.5, Magnetic moment: 3.45 B M.

Zn(II): Yield 78%; M.p. >250°C; IR (Nujol): (M-O) 420, (M-N) 527, (C-O) 1272, (C-N) 1412, (C=N) 1657, (C=O) 1764, (H₂O) 3320 cm⁻¹. MS: m/z 540 (M⁺, 80), 439 (10), 341 (65), 199 (25), relative abundance; 88%. Anal.Calcd. for C₂₇H₂₆N₂O₆Zn (540): C, 60.02; H, 4.81; N, 5.18. Found: C, 60.15; H, 4.35; N, 5.05%. Molar conductance: 19.7.
Cd(II): Yield 71%; M.p. >250°C; IR (Nujol): (M-O) 445, (M-N) 530, (C-O) 1275, (C-N) 1410, (C=N) 1663, (C=O) 1762, (H₂O) 3375 cm⁻¹. MS: m/z 588 (M⁺, 100), 438 (05), 389 (25), 199 (10), 103 (30), relative abundance; 67%. Anal.Calcd. for C₂₇H₂₆N₂O₆Cd (588): C, 55.25; H, 4.12; N, 4.35. Found: C, 55.10; H, 4.42; N, 4.76%. Molar conductance: 14.2.

Cu(II): Yield 75%; M.p. >250°C; IR (Nujol): (M-O) 425, (M-N) 532, (C-O) 1273, (C-N) 1407, (C=N) 1664, (C=O) 1765, (H₂O) 3403 cm⁻¹. MS: m/z 538 (M⁺, 45), 439 (35), 339 (65), 103 (15), relative abundance; 82%. Anal.Calcd. For C₂₇H₂₆N₂O₆Cu (538): C, 60.22; H, 4.83; N, 5.20. Found: C, 60.35; H, 4.53; N, 5.15%. Molar conductance: 18.8, Magnetic moment: 1.91 B M.

General Procedure for the synthesis of ligand di[1,2-7-Hydroxy-6-(1-imino-ethyl)]-4,8-dimethyl-chromen-2-one]benzene(iv):-

A mixture of 6-acetyl-7hydroxy4,8-dimethyl-2H-chromen-2-one (ii) and intermediate (iii) in 1:1 molar ratio was refluxed in dry ethanol for about 4 hours. The yellow precipitate thus formed (iv) was filtered, washed with distilled water (3×30 ml) dried in vacuum over Calcium chloride and recrystallized in ethanol.

Yield 85%; M.p. 152°C; IR (Nujol): (C-O) 1222, (C-N) 1398, (C=N) 1658, (C=O) 1756, (O-H) 3519 cm⁻¹. MS: m/z 536 (M⁺, 80), 320 (60), 216 (25), 104 (100), relative abundance; 88%. Anal. Calcd. for C₃₂H₂₈N₂O₆ (536): C, 71.63; H, 5.26; N, 5.22. Found: C, 71.33; H, 5.58; N, 5.90%.

General procedure for the synthesis of complexes (v M₆-M₁₀):-

For a solution of ligand (iv), metal chloride in 1:1 molar ratio in ethanol was added under constant stirring. The pH of the reaction mixture was adjusted to 7-8 by adding 10% alcoholic ammonia solution and refluxed for about 4 hours. The colored precipitate (v M₆-M₁₀) of metal complex was filtered off in hot condition and washed with hot ethanol, and dried over calcium chloride in vacuum desiccator.

Co(II): Yield 75%; M.p. >250°C; IR (Nujol): (M-O) 415, (M-N) 510, (C-O) 1256, (C-N) 1410, (C=N) 1645, (C=O) 1766, (H₂O) 3230 cm⁻¹. MS: m/z 630 (M⁺, 80), 534 (10), 431 (25), relative abundance; 86%. Anal. Calcd. for C₃₂H₃₀N₂O₈Co (630): C, 60.95; H, 4.76; N, 4.44. Found: C, 60.58; H, 4.30; N, 4.21%. Molar conductance: 20.8. Magnetic moment: 4.87 B M.

Ni(II): Yield 72%; M.p. >250°C; IR (Nujol): (M-O) 424, (M-N) 516, (C-O) 1265, (C-N) 1420, (C=N) 1638, (C=O) 1768, (H₂O) 3300 cm⁻¹. MS: m/z 630 (M⁺, 80), 534 (55), 432 (15), 199 (60), 124 (90), relative abundance; 83%. Anal. Calcd. for C₃₂H₃₀N₂O₈Ni (630): C, 61.05; H, 4.82; N, 4.56. Found: C, 61.25; H, 4.62; N, 4.31%. Molar conductance: 16.7, Magnetic moment: 3.39 B M.

Zn(II): Yield 78%; M.p. >250°C; IR (Nujol): (M-O) 425, (M-N) 520, (C-O) 1267, (C-N) 1422, (C=N) 1642, (C=O) 1770, (H₂O) 3310 cm⁻¹. MS: m/z 636 (M⁺, 95), 534 (25), 422 (15), 104 (55), relative abundance; 88%. Anal. Calcd. for C₃₂H₃₀N₂O₈Zn (636): C, 60.37; H, 4.71; N, 4.40. Found: C, 60.98; H, 4.90; N, 4.15%. Molar conductance: 20.2 B M.

Cd(II): Yield 74%; M.p. >250°C; IR (Nujol): (M-O) 421, (M-N) 515, (C-O) 1260, (C-N) 1415, (C=N) 1647, (C=O) 1775, (H₂O) 3350 cm⁻¹. MS: m/z 682 (M⁺, 90), 534 (15), 216 (55), 104 (95), relative abundance; 71%. Anal. Calcd. for C₃₂H₃₀N₂O₈Cd (682): C, 56.30; H, 4.39; N, 4.10. Found: C, 56.75; H, 4.50; N, 4.72%. Molar conductance: 14.8.

Cu(II): Yield 78%; M.p. >250°C; IR (Nujol): (M-O) 429, (M-N) 525, (C-O) 1273, (C-N) 1437, (C=N) 1637, (C=O) 1776, (H₂O) 3382 cm⁻¹. MS: m/z 634 (M⁺, 98), 534 (20), 418 (35), relative abundance; 81%. Anal. Calcd. for C₃₂H₃₀N₂O₈Cu (634): C, 60.56; H, 4.75; N, 4.41. Found: C, 60.15; H, 4.89; N, 4.79%. Molar conductance: 19.5, Magnetic moment: 1.98 B M.

Biology:-**Tested microbes for antimicrobial activity:-**

Streptomycin and ciprofloxacin (Sigma) were used as positive controls against bacteria. fluconazole and ketoconazole (Himedia, Mumbai) were used as positive controls against fungi. The following gram positive bacteria were used for the experiments; *Micrococcus luteus* (MTCC 1538), *Staphylococcus aureus* (MRSA), *Staphylococcus aureus* (MTCC 7443), (MTCC 84), *Enterobacter aerogenes* (MTCC 111). The gram negative bacteria included *Salmonella typhimurium* (MTCC 2488), *Salmonella paratyphi-B* (MTCC 733), *Proteus vulgaris* (MTCC 321) and *Klebsiella pneumoniae* (MTCC 109). In addition, fungi *Botrytis cinerea* (MTCC 2880), *Candida albicans* (MTCC 227), *M. pachydermatis* and *Candida krusei* (MTCC 231) were also used for the experiments.

Preparation of inoculums:-

Bacterial inoculums were prepared by growing cells in Mueller Hinton Broth (MHA) (Himedia) for 24 h at 37°C. These cell suspensions were diluted with sterile MHA to provide initial cell counts of about 10⁴ CFU/ml. The filamentous fungi were grown on sabouraud dextrose agar (SDA) slants at 28°C for 10 days and the spores were collected using sterile doubled distilled water and homogenized.

Disc diffusion assay:-

Antibacterial activity was carried out using a disc diffusion method [21]. Petri plates were prepared with 20 ml of sterile Mueller Hinton Agar (MHA) (Himedia, Mumbai). The test cultures were swabbed on the top of the solidified media and allowed to dry for 10 mins. The tests were conducted at 1000 µg/disc. The loaded discs were placed on the surface of the medium and left for 30 min at room temperature for compound diffusion. Negative control was prepared using respective solvent. Streptomycin (10 µg/disc) was used as positive control. The plates were incubated for 24 h at 37°C for bacteria and 48 h at 27°C for fungi. A zone of inhibition was recorded in millimeters and the experiment was repeated twice.

Minimum inhibitory concentration (MIC):-

Minimum inhibitory concentration studies of synthesized compounds were performed according to the standard reference method for bacteria [22] and filamentous fungi [23] (CLSI 2008). Required concentrations (1000 µg/ml, 500 µg/ml, 250 µg/ml, 125 µg/ml, 62.5 µg/ml, 31.25 µg/ml and 15.62 µg/ml) of the compounds were dissolved in DMSO (2%), and diluted to give serial two fold dilutions that were added to each medium in 96 well plates. An inoculum of 100 µl from each well was inoculated. The antifungal agent's ketoconazole, fluconazole for fungi and streptomycin, ciprofloxacin for bacteria were included in the assays as positive controls. For fungi, the plates were incubated for 48-72 h at 28°C and for bacteria the plates were incubated for 24 h at 37°C. The MIC for fungi was defined as the lowest extract concentration, showing no visible fungal growth after incubation time. 5 ml of tested broth was placed on the sterile MHA plates for bacteria and incubated at respective temperatures. The MIC for bacteria was determined as the lowest concentration of the compound inhibiting the visual growth of the test cultures on the agar plate.

Results and Discussion:-**Chemistry:-**

2-methyl-4-{phenyl-[3-(-1-phenyl-ethylenediamino)-propylimino]-methyl}-phenol (**iii**) was synthesized by the condensation of o-phenylenediamine (**i**) and 6-Acetyl-7 hydroxy 4, 8-dimethyl-2H-chromen-2-one (**ii**) (1: 1 molar ratio), dissolved in dry ethanol. The reaction mixture was stirred for 3hrs. On cooling white coloured intermediate solid compound, mono-Schiff base of 2-methyl-4-{phenyl-[3-(-1-phenyl-ethylenediamino)-propylimino]-methyl}-phenol (**iii**) was obtained. The product is confirmed by NMR and mass spectra.

The product (**iii**) obtained was treated with an equimolar volume of 4- methyl -2 hydroxybenzaldehyde (**iiia**) in dry ethanol and stirred for 6 hours with a few drops of glacial acetic acid. The white solid precipitate of Schiff base (**iiib**) obtained was recrystallized from ethanol. Formation of Schiff base is confirmed by IR, ¹H NMR and mass.

Aqueous ethanolic solution of metal chloride of Co(II), Ni(II), Zn(II), Cd(II) and Cu(II) were added to the hot ethanolic solution of the ligand (**iiib**) in 1:1 molar ratio. The pH of the reaction mixture was adjusted to 7-8 by adding 10% alcoholic ammonia solution and refluxed for about 7-9 hrs which resulted in the precipitation of metal derivatives in all the cases (**iiic M₁-M₅**).

The ligand di[1,2-7-Hydroxy-6-(1-imino-ethyl)-4,8-dimethyl-chromen-2-one]benzene (**iv**) was synthesized by the condensation of 2-methyl-4-{phenyl-[3-(-1-phenyl-ethylenediamino)-propylimino]-methyl}-phenol (**iii**) and 6-acetyl-7 hydroxy 4,8-dimethyl-2H-chromen-2-one (**ii**) (1:1 molar ratio), dissolved in dry ethanol. The reaction mixture was stirred for 6 hours with a few drops of glacial acetic acid. The yellow solid precipitate of Schiff base (**iiib**) obtained was recrystallized from ethanol. Formation of Schiff base is confirmed by IR, ¹H NMR, and mass.

Aqueous ethanolic solution of metal chloride of Co(II), Ni(II), Zn(II), Cd(II) and Cu(II) were added to the hot ethanolic solution of the ligand (**iv**) in 1:1 molar ratio. The pH of the reaction mixture was adjusted to 7-8 by adding 10% alcoholic ammonia solution and refluxed for about 7-9 hrs which resulted in the precipitation of metal derivatives in all the cases (**v M₆-M₁₀**).

The yield, elemental analysis and molar conductance data of metal complexes are presented in **Table 1 and 2**.

Table 1:-Elemental and molar conductance data.

Compound (Colour)	M.p. (°C)	Yield (%)	Found (Calc.) %			Λ_{m2} (ohm ⁻¹ cm ² mol ⁻¹)
			C	H	N	
C₂₇H₂₄N₂O₄ (iiib) White	167	89	73.62 (73.52)	5.49 (5.38)	6.36 (6.25)	–
C₂₇H₂₂N₂O₄Co(H₂O)₂ (iiic M₁) Light brown	>250	75	60.52 (60.67)	4.32 (4.86)	5.01 (5.24)	21.0
C₂₇H₂₂N₂O₄Ni(H₂O)₂ (iiic M₂) Light Yellow	>250	72	60.42 (60.35)	4.45 (4.54)	5.25 (5.01)	15.5
C₂₇H₂₂N₂O₄Zn(H₂O)₂ (iiic M₃) White	>250	78	60.02 (60.15)	4.81 (4.35)	5.18 (5.05)	19.7
C₂₇H₂₂N₂O₄Cd(H₂O)₂ (iiic M₄) White	>250	71	55.10 (55.25)	4.42 (4.12)	4.76 (4.35)	14.2
C₂₇H₂₂N₂O₄Cu(H₂O)₂ (iiic M₅) Dark green	>250	75	60.22 (60.35)	4.83 (4.53)	5.20 (5.15)	18.8

Table 2:-Elemental and molar conductance data.

Compound (Colour)	M.p. (°C)	Yield (%)	Found (Calc.) %			Λ_{m2} (ohm ⁻¹ cm ² mol ⁻¹)
			C	H	N	
C₃₂H₂₈N₂O₆ (iv) Yellow	152	85	71.63 (71.33)	5.26 (5.58)	5.22 (5.90)	–
C₃₂H₃₀N₂O₈Co(H₂O)₂ (v M₆) Dark brown	>250	75	60.95 (60.58)	4.76 (4.30)	4.44 (4.21)	20.8
C₃₂H₃₀N₂O₈Ni(H₂O)₂ (v M₇) Light brown	>250	72	61.05 (61.25)	4.85 (4.62)	4.56 (4.31)	16.7
C₃₂H₃₀N₂O₈Zn(H₂O)₂ (v M₈) White	>250	78	60.37 (60.98)	4.71 (4.90)	4.40 (4.15)	20.2
C₃₂H₃₀N₂O₈Cd(H₂O)₂ (v M₉) White	>250	74	56.30 (56.75)	4.39 (4.50)	4.10 (4.72)	14.8
C₃₂H₃₀N₂O₈Cu(H₂O)₂ (v M₁₀) Dark brown	>250	78	60.56 (60.15)	4.75 (4.89)	4.41 (4.79)	19.5

IR Spectra:-

The IR spectra of the complexes were compared with those of the free ligands in order to determine the coordination sites that may be involved in chelation. There were some guide peaks in the spectra of the ligands, which were helpful in achieving this goal. The IR spectral bands of metal(II) complexes are listed in **Table 3**.

Table 3:-The important diagnostic IR absorption bands (in cm⁻¹) of ligands and their complexes:

Compound	ν (H ₂ O)	ν (O-H)	ν (C=O)	ν (C=N)	ν (C-N)	ν (C-O)	ν (M-N)	ν (M-O)
C₂₇H₂₄N₂O₄ (iiib)	-	3512	1746	1676	1384	1236	---	----
C₂₇H₂₂N₂O₄Co(H₂O)₂ (iiic M₁)	3493	-	1766	1665	1392	1263	515	460
C₂₇H₂₂N₂O₄Ni(H₂O)₂ (iiic M₂)	3503	-	1756	1659	1402	1269	595	498
C₂₇H₂₂N₂O₄Zn(H₂O)₂ (iiic M₃)	3498	-	1764	1657	1412	1272	575	505
C₂₇H₂₂N₂O₄Cd(H₂O)₂ (iiic M₄)	3490	-	1762	1663	1410	1275	592	480
C₂₇H₂₂N₂O₄Cu(H₂O)₂ (iiic M₅)	3497	-	1765	1664	1407	1273	525	458
C₃₂H₂₈N₂O₆ (iv)	-	3519	1756	1658	1398	1222	---	----
C₃₂H₃₀N₂O₈Co(H₂O)₂	3496	-	1766	1645	1410	1256	512	458

(ν M_6)								
$C_{32}H_{30}N_2O_8Ni(H_2O)_2$	3450	-	1768	1638	1420	1265	550	462
(ν M_7)								
$C_{32}H_{30}N_2O_8Zn(H_2O)_2$	3460	-	1770	1642	1422	1267	575	484
(ν M_8)								
$C_{32}H_{30}N_2O_8Cd(H_2O)_2$	3480	-	1775	1647	1415	1260	575	496
(ν M_9)								
$C_{32}H_{30}N_2O_8Cu(H_2O)_2$	3450	-	1776	1637	1437	1273	632	505
(ν M_{10})								

In the IR spectrum of o-phenylenediamine, a pair of bands corresponding to ν (NH_2) was present at 3210 and 3270 cm^{-1} but was absent in the IR spectra of all the complexes [24]. A single broad medium band at 3157 and 3134 cm^{-1} was observed in the spectra of ligand **iiib** and **iv** respectively, which may be assigned to intramolecular hydrogen bonded ν (OH). The absence of (O-H) stretching and ν (O-H) vibration in the spectra of the complexes indicated deprotonation of the -OH groups [25, 26].

The phenolic ν (O-H) band is shifted from 3512 (**iiib**) and 3519 (**iv**) to 1263–1275 (**iiic** M_1 - M_5) and 1256-1273 cm^{-1} (ν M_6 - M_{10}) as a consequence of the delocalization of double bond in chelate rings that has increased the bond order of the phenolic C-O. The phenolic oxygen, after the loss of O-H proton gets coordinated to the metal. This is supported by a shift in the stretching frequency of ν (C-O) to the lower wave number of its position in the free ligand [27]. A strong peak at 1746 and 1756 cm^{-1} in the IR spectrum of Schiff base **iiib** and **iv** respectively was assigned to the ν (>C=O) stretching moiety. This band was shifted to a higher frequency by ~ 10-20 cm^{-1} in the IR spectrum of metal complexes at 1756-1766 (**iiic**, M_1 - M_5) and 1766-1776 cm^{-1} (ν , M_6 - M_{10}) as compared to the corresponding ligands [28, 29, 30]. The strong band observed in the region 1676 and 1658 cm^{-1} in the ligands **iiib** and **iv** assigned to C=N stretching. The complexes show a strong band at 1657-1665 cm^{-1} (**iiic**, M_1 - M_5) and 1637-1647 cm^{-1} (ν , M_6 - M_{10}) band at region, representing the C=N stretching moiety. This band is shifted to a lower frequency by ~ 11-21 cm^{-1} , as compared to the corresponding ligands indicating that the azomethine nitrogen of the C=N group has participated in the coordination [31]. This can be ascribed to the withdrawn of electron density from the nitrogen atom owing to coordination. The bands present at 1384, 1398 cm^{-1} and 1392–1412 and 1410-1437 cm^{-1} were assigned to ν (C-N) vibrations. The IR spectra showed bands in the region 510-532 and 510-525 cm^{-1} corresponding to ν (M-N) vibrations in all the complexes [32]. The presence of this band supports the fact concerning the coordination of the azomethine nitrogen with the metal [33]. The bands present at 420-445 and 415-429 cm^{-1} in all complexes were due to ν (M-O) [34]. The IR spectra showed a strong band in 3450-3503 cm^{-1} region (**iiic** M_1 - M_5 and ν , M_6 - M_{10}) suggesting the presence of coordinated water.

Magnetic susceptibility, electronic and ESR spectral studies:-

The electronic absorption spectra of the Schiff base ligand and its Co(II), Ni(II), Zn(II), Cd(II) and Cu(II) complexes were recorded in DMF solution in the range of 200 to 800 nm regions and data are presented in **Table 4**.

The electronic transitions due to the organic ligand in the metal complexes, showed the absorption bands of the $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions results from the C=N and O-H groups and appeared at 273-295 nm and 360-389 nm regions, respectively. These values are lower than the corresponding absorption bands for the ligand, which were observed at 390- 394 nm, respectively. This may be due to the coordination of the nitrogen and oxygen atoms of the ligand to the metal ions.

The magnetic moment of the complexes were measured at room temperature. The electronic spectra of the Schiff base ligands and their Co(II), Ni(II), Zn(II) Co(II) and Cu(II), complexes have been measured in DMF solution between 200-800 nm at room temperature. The electronic absorption spectra are often very helpful for structural investigation. The electronic spectral measurements were used for assigning the geometry of metal ions in the complexes based on the positions and number of d-d transition peaks. Magnetic properties arise from the spin and orbital angular momentum of the electrons contained in a compound.

The magnetic moment of the complexes were measured at room temperature. The magnetic moment of the cobalt (II) lay in the range 4.68 and 4.87 B M (**iiic** M_1 and ν M_6) which corresponds to 3 unpaired electrons. The solution spectra of the cobalt (II) complexes exhibited absorption in the region 290, 350, 440 (**iiic** M_1) and 280, 360, 450 nm

(v M_6). The spectra resemble that reported for octahedral complex [35]. Thus the various bands can be assigned to: ${}^4T_{1g} \rightarrow {}^4T_{2g}$, ${}^4T_{1g} \rightarrow {}^4A_{2g}$, ${}^4T_{1g} \rightarrow {}^4T_{1g}$.

The magnetic moment of the nickel (II) lay in the range 3.45 and 3.39 BM (iiic M_1 and v M_6) which corresponds to 2 unpaired electrons. The solution spectra of the nickel (II) complexes exhibited absorption in the region 370, 390, 470, 440 (iiic M_1) and 360, 380, 460, 480 nm (v M_6). The spectra resemble that reported for octahedral complex. Thus the various bands can be assigned to: ${}^4T_{1g} \rightarrow {}^4T_{2g}$, ${}^4T_{1g} \rightarrow {}^4A_{2g}$, ${}^4T_{1g} \rightarrow {}^4T_{1g}$ and L→M charge transfer respectively.

The electronic spectrum of the copper(II) complex shows broad band absorption in the region 675 nm, 647 nm and 515 nm (iiic M_5), 678 nm, 642 nm and 519 nm (v M_{10}), which may be assign to ${}^2B_{1g} \rightarrow {}^2A_{1g}$, ($dx^2 - y^2 \rightarrow dz^2$)(v_1), ${}^2B_{1g} \rightarrow {}^2B_{2g}$, ($dx^2 - y^2 \rightarrow dxy$) (v_2), and ${}^2B_{1g} \rightarrow {}^2E_g$, ($dx^2 - y^2 \rightarrow dxy, dyz$) (v_3) transition and it is in conformity with octahedral geometry [36]. The broadness of the band which are similar in energy give rise to only one broad absorption band, and the broadness of the band is due to dynamic Jahn-Teller distortion. These data suggest that the Cu(II) complex have distorted octahedral geometry [37].

An indication of the most probable geometric configuration of the synthesized metal complexes is their magnetic moment values. So, it has been further confirmed by the magnetic moment measurements, room temperature values lie at 1.91(iiic M_5) and 1.98 B M (v M_6) corresponding to the presence of one unpaired electron and it supports a distorted octahedral geometry [38, 39].

The ESR spectrum of Cu(II) complex has been recorded on X-band at frequency 9.1GHz at low temperature. The spectrum of Cu(II) (viiM₉ and viiiM₁₀) complex is characteristic of axial symmetry with g_{\parallel} , g_{\perp} , and Δg values of 2.40, 2.07, (viiM₉) and 2.48, 2.07 (viiM₁₀) 0.37 (viiM₉) and 0.39 (viiM₁₀). Anisotropy of the g-tensor is due to the Jahn-Teller effect, which reduces the symmetry from octahedral to distorted octahedral. The fact that $g_{\parallel} > g_{\perp} > 2.0023$ (g_e) and $G = 5.06$, > 4 indicates octahedral geometry of the Cu(II) ion of $d_x^2 - y^2$ ground state with negligible exchange interaction in the complex [39].

Table 4:-Magnetic susceptibility and electronic spectral data:

Ligand/ complexes	Electronic absorption bands and their assignments (nm)			Magnetic Moment μ_{eff} , BM
	$\pi \rightarrow \pi^*$	$n \rightarrow \pi^*$	d→d transition	
$C_{27}H_{24}N_2O_4$ (iiib)	292	390	----	----
$C_{27}H_{22}N_2O_4Co(H_2O)_2$ (iiic M_1)	285	376	490	4.68
$C_{27}H_{22}N_2O_4Ni(H_2O)_2$ (iiic M_2)	273	382	485	3.45
$C_{27}H_{22}N_2O_4Zn(H_2O)_2$ (iiic M_3)	288	387	----	----
$C_{27}H_{22}N_2O_4Cd(H_2O)_2$ (iiic M_4)	285	389	----	----
$C_{27}H_{22}N_2O_4Cu(H_2O)_2$ (iiic M_5)	287	377	479	1.91
$C_{32}H_{28}N_2O_6$ (iv)	299	394	----	----
$C_{32}H_{30}N_2O_8Co(H_2O)_2$ (v M_6)	295	386	518	4.87
$C_{32}H_{30}N_2O_8Ni(H_2O)_2$ (v M_7)	288	372	510	3.39
$C_{32}H_{30}N_2O_8Zn(H_2O)_2$ (v M_8)	293	360	----	----
$C_{32}H_{30}N_2O_8Cd(H_2O)_2$ (v M_9)	278	374	----	----

$C_{32}H_{30}N_2O_8Cu(H_2O)_2$ (v M_{10})	286	380	517	1.98
-------------------------------------------------	-----	-----	-----	------

Zn and Cd(II) ion with d^{10} electronic configuration permits a wide range of symmetries and coordination numbers. Since d^{10} configuration affords no crystal field stabilization, the stereochemistry of a particular compound depends on the size and polarizing power of the M(II) cation and the steric requirement of the ligands and have no $d-d$ transition and are diamagnetic. The electronic spectra of complexes reveal a charge transfer bands $\pi-\pi$ and $n-\pi$ transitions in the vicinity of the Schiff base ligand at 288, 285 and 293, 278 nm for both complexes; and 387, 389 and 360, 374 cm^{-1} , respectively suggesting an octahedral structure which is common for d^{10} systems.

HNMR spectra:-

The NMR spectra of Schiff bases were recorded in dimethyl sulfoxide (DMSO) solution, using tetramethylsilane (TMS) as an internal standard. Chemical shifts were reported as δ -values in parts per million (ppm) relative to Si $(CH_3)_4$ as relative reference ($\delta = 0$ ppm) and to the solvent as internal reference.

The formation of the complex **iiic M₃** from its ligand (**iiib**) is shown in **Figure 1 and 2**.

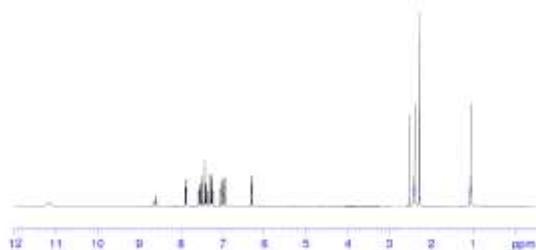


Figure 1: (**iiib**)

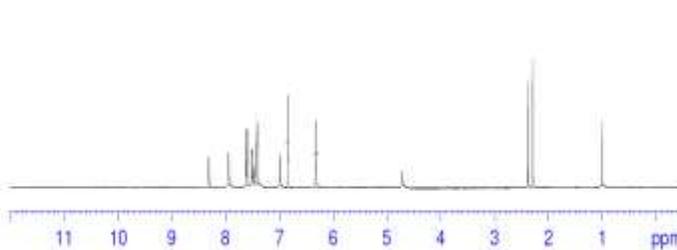


Figure 2: **iiic M₃**

The proton NMR spectrum shows a singlet peaks at 1.03 and 1.01, 1.02 (3H) ppm, which corresponds to the $[N=C-CH_3]$ group of the ligand **iiib** and its Zn(II) **iiic M₃** and Cd(II) **iiic M₄** complexes. The singlet peaks of methyl protons (coumarin) appeared at 2.34 and 2.22, 2.20 ppm in the 1H NMR spectra of the ligand **iiib** and its Zn(II) **iiic M₃** and Cd(II) **iiic M₄** complexes respectively. The singlet peaks of aromatic methyl protons appeared at 2.56 and 2.37, 2.33 ppm in the 1H NMR spectra of the ligand **iiib** and its Zn(II) **iiic M₃** and Cd(II) **iiic M₄** complexes respectively. The two singlet peaks of protons (coumarin) appeared at 6.38, 7.95 (**iiib**) and 6.32, 7.85 (**iiic M₃**), 6.18, 7.78 (**iiic M₄**) ppm in the 1H NMR spectra of the ligand and its Zn(II) and Cd(II) complexes respectively. The doublet peaks of aromatic protons appeared at 6.96 and 6.80, 6.81 ppm in the 1H NMR spectra of the ligand **iiib** and its Zn(II) **iiic M₃** and Cd(II) **iiic M₄** complexes respectively. The singlet peaks of aromatic proton appeared at 7.07 and 7.00, 7.01 ppm in the 1H NMR spectra of the ligand **iiib** and its Zn(II) **iiic M₃** and Cd(II) **iiic M₄** complexes respectively.

Both the ligand and complexes show a group of multiplet at 7.3-7.4(4H) **iiib**, 7.4-7.5(4H) **iiic M₃** and 7.2-7.3(4H) **iiic M₄** for aromatic protons respectively. The singlet peaks at 8.67 and 8.27, 8.58 (H) ppm which corresponds to the $[N=C-H]$ group of ligand **iiib** and its Zn(II) **iiic M₃** and Cd(II) **iiic M₄** complexes. The proton NMR spectrum shows two phenolic-OH groups at 11.27 ppm which are absent in the spectra of M(II) complexes. This indicates that the deprotonated phenolic-O atom is involved in chelation.

The proton NMR spectrum shows a singlet peaks at 1.05 and 1.00, 1.01 (6H) ppm, which corresponds to the $[N=C-CH_3]$ group of ligand **iv** and its Zn(II) **v M₈** and Cd(II) **v M₉** complexes. The singlet peaks of four methyl protons (coumarin) appeared at 2.45, 2.54 (**iv**) and 2.27, 2.47 (**v M₈**), 2.29, 2.47 (**v M₉**) ppm in the 1H NMR spectra of the ligand and its Zn(II) and Cd(II) complexes respectively. The singlet peaks of four protons (coumarin) appeared at 6.23, 7.92 (**iv**) and 6.17, 7.87 (**v M₈**), 6.20, 7.89 (**v M₉**) ppm in the 1H -NMR spectra of the ligand and its Zn(II) and Cd(II) complexes respectively. Both the ligand and complexes show a group of multiplet at 7.32-7.39(4H) **iv**, 7.25-7.35(4H) **v M₈** and 7.23-7.38(4H) **v M₉** for aromatic protons respectively.

The proton NMR spectrum shows two phenolic-OH groups at 10.40 ppm which are absent in the spectra of M(II) complexes. This indicates that the deprotonated phenolic-O atom is involved in chelation.

The chemical shift data of the ligands and their metal complexes are presented in **Table 6 and 7**.

Table 6 :-¹H NMR spectral data of Schiff base ligands and their metal complexes:

Compound	δ (N=C-CH ₃)	δ (Cou-CH ₃)	δ (Ar-CH ₃)	δ (H ₂ O)	δ (Cou-H)	δ (Ar-H)	δ (Ar-H)	δ (Ar-H)	δ (Cou-H)	δ (N=C-H)	δ (O-H)
C ₂₇ H ₂₄ N ₂ O ₄ (iiib)	1.03	2.34	2.56	-	6.38	6.96	7.07	7.3-7.4	7.95	8.67	11.27
C ₂₇ H ₂₂ N ₂ O ₄ Zn(H ₂ O) ₂ (iiic M₃)	1.01	2.22	2.37	4.72	6.32	6.80	7.00	7.4-7.5	7.85	8.27	-
C ₂₇ H ₂₂ N ₂ O ₄ Cd(H ₂ O) ₂ (iiic M₄)	1.02	2.20	2.33	4.54	6.18	6.81	7.01	7.2-7.3	7.78	8.58	-

Table 7:-¹H NMR spectral data of Schiff base ligands and their metal complexes:

Compound	δ (N=C-CH ₃)	δ (Cou-CH ₃)	δ (Ar-CH ₃)	δ (H ₂ O)	δ (Cou-H)	δ (Ar-H)	δ (Cou-H)	δ (O-H)
C ₃₂ H ₂₈ N ₂ O ₆ (iv)	1.05	2.45	2.54	-	6.23	7.32-7.39	7.92	10.40
C ₃₂ H ₃₀ N ₂ O ₈ Zn(H ₂ O) ₂ (v M₈)	1.00	2.27	2.47	4.51	6.17	7.25-7.35	7.87	-
C ₃₂ H ₃₀ N ₂ O ₈ Cd(H ₂ O) ₂ (v M₉)	1.01	2.29	2.47	4.60	6.20	7.23-7.38	7.89	-

Mass spectral studies:-

The mass spectra of Schiff base ligands (**iiib**, **iv**) exhibited parent peaks due to molecular ions (M⁺). The proposed molecular formula of these complexes was confirmed by comparing their molecular formula weights with m/z values. The mass spectrum for the Schiff base ligands **iiib** and **iv** (**Figure 3**) showed a molecular ion peak at m/z = 440, 536 respectively.

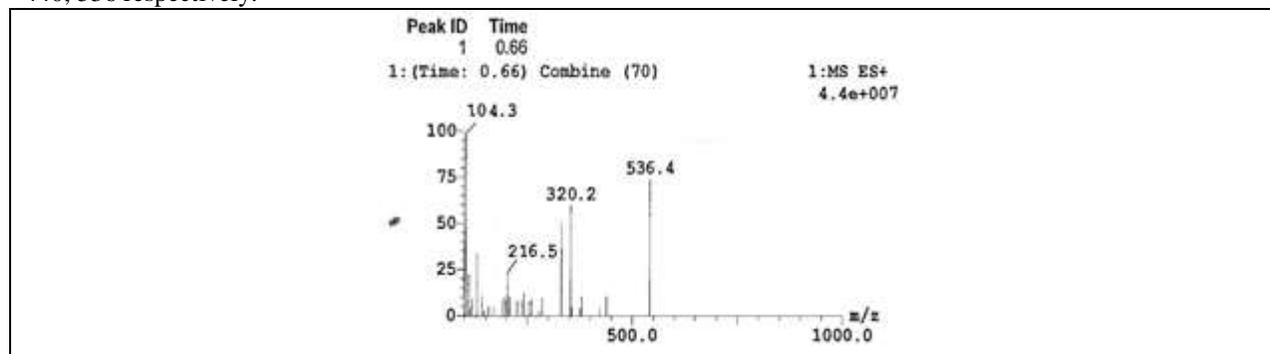


Figure 3:-Mass spectrum of ligand di[1,2-7-hydroxy-6-(1-imino-ethyl)]-4,8-dimethyl-chromen-2-one]benzene(**iv**):

Thermal analysis:-

In the present investigation, heating rates were suitably controlled at 10°C min⁻¹ under nitrogen atmosphere, and the weight loss was measured from the ambient temperature up to 800°C. The data are provided in **Table 8**. The TGA and DTG curve of complex **iiic M₁** is given in **Figure 4**. The weight loss for each chelate was calculated within the corresponding temperature ranges.

The stages of decomposition, temperature range, decomposition products as well as observed and calculated mass loss percentages of all the complexes are illustrated in **table 8**.

Table 8:-Stepwise thermal degradation data obtained from TGA curves and their composition.

Complex	Process	Temp. range (°C)	Degrada-tion Products	% Weight loss		No. of Moles	% Residue		Nature
				Calcd	Expt		Calcd	Expt	
C ₂₇ H ₂₂ N ₂ O ₄ Co(H ₂ O) ₂ (iiic M ₁)	I	120-180	H ₂ O	5.5	5.8	2	12.10	10.7	CoO
	II	185-340	Ligand	82.4	83.5	1			
C ₂₇ H ₂₂ N ₂ O ₄ Ni(H ₂ O) ₂ (iiic M ₂)	I	80-170	H ₂ O	5.5	6.4	2	12.4	10.47	NiO
	II	175-330	Ligand	82.08	83.45	1			
C ₂₇ H ₂₂ N ₂ O ₄ Zn(H ₂ O) ₂ (iiic M ₃)	I	115-156	H ₂ O	5.4	5.8	2	8.00	8.70	ZnO
	II	290-398	Ligand	86.6	85.5	1			
C ₂₇ H ₂₂ N ₂ O ₄ Cd(H ₂ O) ₂ (iiic M ₄)	I	110-185	H ₂ O	4.6	5.10	2	20.10	20.34	CdO
	II	250-480	Ligand	74.82	74.56	1			
C ₂₇ H ₂₂ N ₂ O ₄ Cu(H ₂ O) ₂ (iiic M ₅)	I	157-230	H ₂ O	5.4	6.3	2	7.7	8.2	CuO
	II	270-420	Ligand	86.9	85.5	1			
C ₃₂ H ₃₀ N ₂ O ₈ Co(H ₂ O) ₂ (v M ₆)	I	100-170	H ₂ O	5.71	6.02	2	9.22	9.98	CoO
	II	180-320	Ligand	85.07	84.0	1			
C ₃₂ H ₃₀ N ₂ O ₈ Ni(H ₂ O) ₂ (v M ₇)	I	125-160	H ₂ O	5.61	6.50	2	9.37	9.00	NiO
	II	265-450	Ligand	85.02	84.50	1			
C ₃₂ H ₃₀ N ₂ O ₈ Zn(H ₂ O) ₂ (v M ₈)	I	150-210	H ₂ O	5.66	5.51	2	10.07	10.49	ZnO
	II	295-520	Ligand	84.27	84.0	1			
C ₃₂ H ₃₀ N ₂ O ₈ Cd(H ₂ O) ₂ (v M ₉)	I	110-180	H ₂ O	6.71	6.50	2	14.7	15.15	CdO
	II	280-445	Ligand	78.59	78.35	1			
C ₃₂ H ₃₀ N ₂ O ₈ Cu(H ₂ O) ₂ (v M ₁₀)	I	155-205	H ₂ O	5.67	5.00	2	9.79	11.50	CuO
	II	270-430	Ligand	84.54	83.50	1			

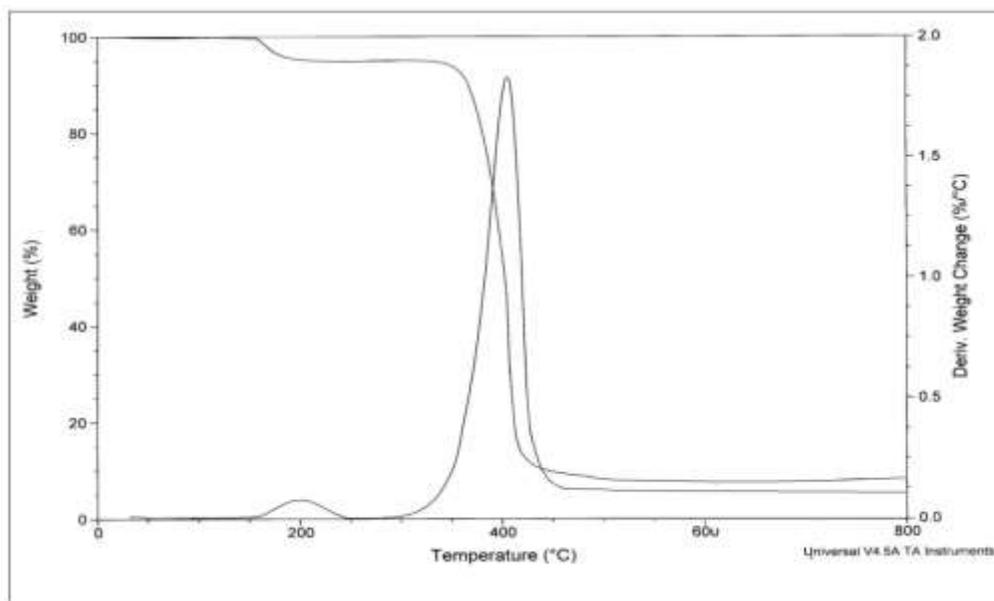


Figure 4:-TG curves of cobalt complex of 7-hydroxy-6-(1-{2-[(2-hydroxy-5-methyl-benzylidene)-amino]-phenylimino]-ethyl)-4,8-dimethyl-chromen-2-one (iiic M₁)

Racah parameters:-

For the octahedral complexes the ligand field parameters Dq , B and C were found (Table 9) by solving the secular equation and possible to simplify the problem to that of solving a quadratic equation in Dq , v_1 , v_2 , v_3 and v_4 only. These parameters indicate the significant covalent character of the metal ligand bonds.

Table9:- Ligand field parameters of Schiff base complexes.

Complex	λ_{\max} (nm)	Dq (nm)	B (nm)	C (nm)
$C_{27}H_{22}N_2O_4Co(H_2O)_2$ (iiic M ₁)	270, 325, 430	27.0	44.9	----
$C_{27}H_{22}N_2O_4Ni(H_2O)_2$ (iiic M ₂)	330, 380, 420, 470	33.0	46.53	78.0
$C_{27}H_{22}N_2O_4Cu(H_2O)_2$ (iiic M ₅)	310, 350, 460	31.0	47.8	----
$C_{32}H_{30}N_2O_8Co(H_2O)_2$ (v M ₆)	280, 340, 460	28.0	47.73	----
$C_{32}H_{30}N_2O_8Ni(H_2O)_2$ (v M ₇)	380, 390, 460, 480	38.0	49.00	81.0
$C_{32}H_{30}N_2O_8Cu(H_2O)_2$ (v M ₁₀)	350, 430, 490	35.0	54.3	----

Biology:-

The antimicrobial screenings of the synthesized compounds were undertaken using disc diffusion method. The screening results of the tested compounds against the gram positive bacteria, gram negative bacteria in addition to the pathogenic fungi microorganisms are summarized in Table 10-13.

The obtained data revealed that most of the compounds showed moderate to excellent activities against the tested microorganisms. Complexes **ivM₁**, **ivM₃**, **ivM₉**, **ivM₂**, **ivM₄** and **ivM₁₀** were shown maximum zone of inhibition in both the bacterial and fungal strains compared to remaining compounds in the series with respect to standard Streptomycin and Ciprofloxacin in the case of bacterial, Fluconazole and Ketoconazole with respect to fungal strains. A comparative study of ligand and their metal complexes indicates that some of the metal chelates exhibits higher antimicrobial activity than the free ligands. The increase in antimicrobial activity of metal chelates is due to the presence of metal ion in the complexes.

Table10:-In-vitro antibacterial activity of compounds ivM₁-ivM₁₀

Compound	Zone of inhibition in mm							
	Gram positive bacteria				Gram negative bacteria			
	M. <i>luteus</i>	S. <i>aureus</i> (MRS A)	S. <i>aureus</i>	E. <i>erogenes</i>	S. <i>typhimurium</i>	S. <i>Paratyphi-B</i>	P. <i>vulgaris</i>	K. <i>pneumonia</i>
C ₃₁ H ₃₀ N ₂ O ₂ (iiiia)	9	8	9	10	8	8	10	9
C ₃₁ H ₂₈ N ₂ O ₂ Co(H ₂ O) ₂ (ivM ₁)	23	23	21	21	15	15	15	24
C ₃₁ H ₂₈ N ₂ O ₂ Ni(H ₂ O) ₂ (ivM ₃)	15	12	23	21	15	13	73	17
C ₃₁ H ₂₈ N ₂ O ₂ Zn(H ₂ O) ₂ (ivM ₅)	14	15	13	17	11	14	11	8
C ₃₁ H ₂₈ N ₂ O ₂ Cd(H ₂ O) ₂ (ivM ₇)	10	8	8	9	15	9	12	8
C ₃₁ H ₂₈ N ₂ O ₂ Cu(H ₂ O) ₂ (ivM ₉)	21	23	23	21	17	16	21	13
C ₂₉ H ₂₄ N ₂ O ₂ Cl ₂ (iiib)	10	9	8	9	10	10	9	8
C ₂₉ H ₂₂ N ₂ O ₂ Cl ₂ Co(H ₂ O) ₂ (ivM ₂)	19	23	26	25	24	19	21	21
C ₂₉ H ₂₂ N ₂ O ₂ Cl ₂ Ni(H ₂ O) ₂ (ivM ₄)	19	24	25	21	18	19	19	21
C ₂₉ H ₂₂ N ₂ O ₂ Cl ₂ Zn(H ₂ O) ₂ (ivM ₆)	9	16	16	10	10	9	11	12
C ₂₉ H ₂₂ N ₂ O ₂ Cl ₂ Cd(H ₂ O) ₂ (ivM ₈)	11	13	18	17	13	14	9	11
C ₂₉ H ₂₂ N ₂ O ₂ Cl ₂ Cu(H ₂ O) ₂ (ivM ₁₀)	21	23	21	23	21	21	21	23
Streptomycin	24	23	25	27	26	25	21	24

Table 11:-Minimum inhibitory concentration (µg/ ml).

Compounds	Gram positive bacteria				Gram negative bacteria			
	M. <i>luteus</i>	S. <i>aureus</i> (MRS A)	S. <i>aureus</i>	E. <i>aerogenes</i>	S. <i>typhimurium</i>	S. <i>Paratyphi-B</i>	P. <i>vulgarius</i>	K. <i>pneumonia</i>
C ₃₁ H ₂₈ N ₂ O ₂ Co(H ₂ O) ₂ (ivM ₁)	16.52	30.15	62.5	16.52	16.52	125	16.52	62.5
C ₃₁ H ₂₈ N ₂ O ₂ Ni(H ₂ O) ₂ (ivM ₃)	30.15	62.5	16.52	125	30.15	125	62.5	16.52
C ₃₁ H ₂₈ N ₂ O ₂ Cu(H ₂ O) ₂	62.5	125	16.52	62.5	30.15	500	125	500

(ivM ₉)								
C ₂₉ H ₂₂ N ₂ O ₂ Cl ₂ Co(H ₂ O) ₂ (ivM ₂)	16.52	125	62.5	62.5	30.15	125	125	500
C ₂₉ H ₂₂ N ₂ O ₂ Cl ₂ Ni(H ₂ O) ₂ (ivM ₄)	125	62.5	16.52	125	30.15	125	62.5	16.52
C ₂₉ H ₂₂ N ₂ O ₂ Cl ₂ Cu(H ₂ O) ₂ (ivM ₁₀)	30.15	16.52	16.52	62.5	16.52	125	16.52	62.5
Streptomycin	6.25	>100	6.25	25	30	6.25	ni	6.25
Ciprofloxacin	<0.78	>100	<0.78	>100	>100	<0.78	6.25	<0.78

Table12:- In-vitro antifungal activity of compounds ivM₁-ivM₁₀.

Compounds	Zone of inhibition in mm			
	<i>B. cinerea</i>	<i>C. albicans</i>	<i>M. pachydermatis</i>	<i>C.krusei</i>
C ₃₁ H ₃₀ N ₂ O ₂ (iiiia)	8	9	11	10
C ₃₁ H ₂₈ N ₂ O ₂ Co(H ₂ O) ₂ (ivM ₁)	16	23	21	16
C ₃₁ H ₂₈ N ₂ O ₂ Ni(H ₂ O) ₂ (ivM ₃)	15	21	24	15
C ₃₁ H ₂₈ N ₂ O ₂ Zn(H ₂ O) ₂ (ivM ₅)	8	10	12	14
C ₃₁ H ₂₈ N ₂ O ₂ Cd(H ₂ O) ₂ (ivM ₇)	11	21	9	14
C ₃₁ H ₂₈ N ₂ O ₂ Cu(H ₂ O) ₂ (ivM ₉)	13	20	19	13
C ₂₉ H ₂₄ N ₂ O ₂ Cl ₂ (iiib)	8	8	9	10
C ₂₉ H ₂₂ N ₂ O ₂ Cl ₂ Co(H ₂ O) ₂ (ivM ₂)	16	23	23	17
C ₂₉ H ₂₂ N ₂ O ₂ Cl ₂ Ni(H ₂ O) ₂ (ivM ₄)	13	22	24	18
C ₂₉ H ₂₂ N ₂ O ₂ Cl ₂ Zn(H ₂ O) ₂ (ivM ₆)	13	15	10	11
C ₂₉ H ₂₂ N ₂ O ₂ Cl ₂ Cd(H ₂ O) ₂ (ivM ₈)	8	10	11	12
C ₂₉ H ₂₂ N ₂ O ₂ Cl ₂ Cu(H ₂ O) ₂ (ivM ₁₀)	15	22	20	18
Ketoconazole	17	24	25	19

Table13:-MIC (mg/ml) of compounds against tested fungi.

Compounds	Minimum inhibitory concentration (µg/ ml)			
	<i>B. cinerea</i>	<i>C. albicans</i>	<i>M. pachydermatis</i>	<i>C. krusei</i>
C ₃₁ H ₂₈ N ₂ O ₂ Co(H ₂ O) ₂ (ivM ₁)	16.52	135	30.15	135
C ₃₁ H ₂₈ N ₂ O ₂ Ni(H ₂ O) ₂ (ivM ₃)	60.5	135	30.15	16.52
C ₃₁ H ₂₈ N ₂ O ₂ Cu(H ₂ O) ₂ (ivM ₉)	16.52	30.15	135	60.5

$C_{29}H_{22}N_2O_2Cl_2Co(H_2O)_2$ (ivM ₂)	16.52	135	30.15	60.5
$C_{29}H_{22}N_2O_2Cl_2Ni(H_2O)_2$ (ivM ₄)	135	60.5	30.15	16.52
$C_{29}H_{22}N_2O_2Cl_2Cu(H_2O)_2$ (ivM ₁₀)	16.52	30.15	60.5	60.5
Fluconazole	ni	>100	13.5	13.5
Ketoconazole	25	25	15	15

ni = no inhibition.

Significant MIC values were observed against gram positive; gram negative bacteria and antifungal activity are summarized in **Table 10-12**. Compounds ivM₁, ivM₂, ivM₅, ivM₆, ivM₇ and ivM₁₀ exhibited good MIC result among the series. In comparison, compound ivM₆, ivM₇ and ivM₁₀ with halogen substituted is more potent and showed better activity for most of the tested bacteria and fungi.

Conclusion:-

A series of metal (II) complexes have been synthesized from the Schiff base. The ligand (iiib, iv) and their complexes (iiic M₁-M₅, v M₆-M₁₀) were characterized by analytical and spectral techniques like IR, ¹H NMR, UV-VIS, elemental analysis, molar electric conductance, magnetic susceptibility and thermal studies. Molar conductance values in DMF indicate the non-electrolytic nature of the complexes. Mass spectral data are in agreement with the structures confirmed by other spectroscopic techniques.

The antimicrobial activity of synthesized complex compounds was screened against eight bacteria and four fungi using in vitro disc diffusion method respectively. The results revealed that most of the synthesized complex compounds exhibited good biological activities due to the presence of metal ion in the complexes.

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