# Synthesis, Characterization, and Antimicrobial Studies of Newly Developed Metal-Chelated Epoxy Resins

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**ABSTRACT:** A series of novel metal-chelated epoxy resins have been synthesized by the condensation of epichlorohydrin (1-chloro-2, 3 epoxy propane) with bisphenolic metal chelates in alkaline medium. The bisphenolic chelates were initially prepared by the reaction of 3-formyl-4, 4'-dihydroxy diphenyl methane and diamine (ethylenediamine/$o$-phenylenediamine) in 1:2 molar ratio and then with Cu(II), Ni(II), and Co(II) acetate. The metal-chelated epoxy resins were characterized by various instrumental techniques, such as elemental analysis, DSC and TGA, electronic, FTIR, ^{1}H-NMR, and ^{13}C-NMR spectra. The physicochemical properties, viz., epoxide equivalent weight (eq/100 g), hydroxyl value (eq/100 g), refractive index, specific gravity, and specific viscosity were measured by standard procedures. The antimicrobial activities of these chelated resins were screened against *Escherichia coli, Staphylococcus aureus, Bacillius subtilis* (bacteria), and *Candida albicans, Mucor species* (yeast) by using agar well diffusion method. All the polymeric chelates show promising antimicrobial activities. Among these polymeric chelates (ERPD)-Cu(II) shows better antimicrobial activities, which can be attributed to higher stability constant of Cu(II) chelate than others. © 2006 Wiley Periodicals, Inc. J Appl Polym Sci 101: 1347–1355, 2006

**Key words:** chelates; epoxy resin; physicochemical; antimicrobial activity; agar diffusion method

## INTRODUCTION

Despite the fact that the discovery of epoxy resin is half century old,[1] the chemistry and technology associated with it continues to fascinate the researchers. The search for the development of high thermal resistant and biologically active polymers is on the rise to meet the growing demand of rapidly evolving high technology field. Epoxy resin is gifted with attractive physicomechanical as well as physicochemical properties, which make it highly processible.[2] However, one of the major drawbacks associated with organic polymers resins is that they have poor thermal stability.[3] Metal-containing polymers on the other hand are thermally stable and impart high flexibility owing to the presence of organic moiety, as well as high thermal stability due to presence of inorganic functional groups in the same polymeric backbone.[4] The association of these properties makes them highly useful for industrial and scientific applications. The incorporation of metal ions in the polymeric backbone is not only affecting their physical properties but also alter chemical properties of the polymers.[5] Previously a number of metal-chelated polymers with Schiff base complexes,[6] crown ether complexes,[7] and ferrocene complexes[8] have been prepared and reported. These polymers are widely being used in the surface coating,[9] semiconductor devices,[10] and in the field of nanotechnology.[11] The metal-chelated polymers also have biological significance since they can also act as antimicrobial agents; these polymers are reported to show superior antimicrobial activity than do organic polymers.[12]

Literature survey reveals that no work has been reported on metal-chelated epoxy resin synthesized from bisphenolic metal chelates of ethylenediamine and $o$-phenylenediamine. The present article reports on the synthesis, characterization, and antimicrobial activities of newly developed metal-chelated epoxy resins. These compounds were synthesized by the reaction of epichlorohydrin with bisphenolic metal chelates of Cu(II), Ni(II), and Co(II) acetate and characterized by using various spectral techniques such as, electronic, FTIR, ^{1}H-NMR, and ^{13}C-NMR. Thermal stability of these compounds has also been determined by using TGA and DSC techniques. The antimicrobial activity of these resin were tested against *Escherichia coli, Staphylococcus aureus, Bacillius subtilis* (bacteria), and *Candida albicans, Mucor species* (yeast) by using agar disk diffusion method.[13]

## EXPERIMENTAL

### Material

Salicylaldehyde, phenol, ethylenediamine. *o*-phenylenediamine (Merck India), and Copper(II), Nickel(II),

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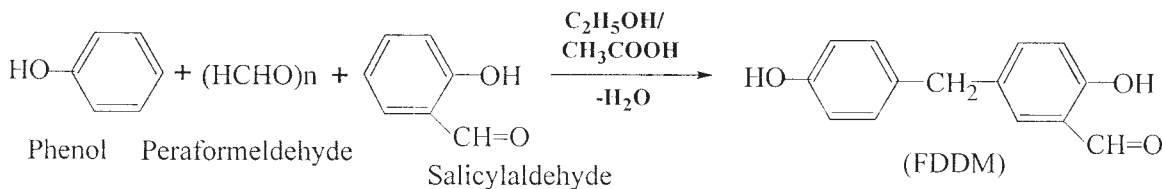
**Scheme 1**

and Cobalt(II) acetate, trioxane (trimer of formaldehyde), and epichlorohydrin (s. d. fine) were used without further purification. Solvents like dimethylformamide (DMF), dimethylsulphoxide (DMSO), ethyl alcohol, methanol, and acetone (Qualinges India) were distilled before use. The organisms such as *Escherichia coli, Staphylococcus aureus, Bacillius subtilis* (bacteria), and *Candida albicans, Mucor species* (yeast) were provide by the culture collection of Microbiology Laboratory, Department of Biosciences (J.N.U. New Delhi).

### Preparation of fddm

3-formyl 4,4'-dihydroxy diphenyl methane (FDDM) was prepared by reported method.[14] The overall route of synthesis is given in Scheme 1.

$^1$H-NMR-(300 MHz, DMSO, $\delta$) 13.25 (1H, OH), 9.95 (1H, CH=O), 6.53 (1H, OH), 7.26–6.80 (7H, ArH), 3.9 (2H, Ar—CH$_2$—Ar), FTIR (KBr pallets) $\nu_{max}$ (cm$^{-1}$) 3370–3250, 1632, 1257, 1132. Anal. calcd for C$_{14}$H$_{12}$O$_3$: C, 73.65; H, 5.29. Found: C, 73.64; H, 5.30.

### Preparation of bisphenolic complexes

#### Preparation of bisphenolic Schiff base of ethylenediamine and Schiff base of *o*-phenylene diamine

The monomeric bisphenolic Schiff base {bis- [2-hydroxy (3-formyl 4,4'-dihydroxy diphenyl methane)-ethylenediamine]} (BHFED) was synthesized by the reaction of FDDM (4.56 g, 0.02 mol) dissolved in 25 mL methanol with 0.67 mL (0.01 mol) of ethylene diamine in the presence of 0.05 g of anhydrous sodium acetate. The mixture was refluxed for 1 h at 70°C, the progress of the reaction was monitored by TLC, using ethanol as an eluent. When the reaction was completed, the resulting mixture was poured into ice cooled water and allowed to stand for 30 min, resulting yellow-colored precipitate was filtered off, washed rapidly by demineralized water, ethanol and dried in vacuum at 70°C for 2 h.

$^1$H-NMR (300 MHz, DMSO, $\delta$) 13.10 (2H, OH), 6.60 (2H, OH) 7.52–6.87 (14h, ArH); 8.26 (2H,CH=N); 4.01–3.60 (8H, Ar—CH$_2$—Ar, =N—CH$_2$); FTIR (KBr pallets) $\nu_{max}$ (cm$^{-1}$) 3324–3235, 3055, 2962–2850, 1630, 1502, 1265, 748, 620, 540. Anal. calcd for

C$_{30}$H$_{28}$O$_4$N$_2$: C, 74.97; H, 5.87; N, 5.83. Found: C, 74.94; H, 6.85; N, 5.80.

Bifunctional monomer bis-[2-hydroxy-(3-formyl 4,4'-dihydroxy diphenyl methane) *o*-phenylenediamine] (BHFPD) was synthesized from FDDM and *o*-phenylenediamine in 2:1 molar ratio. The reaction was carried out under the similar experimental conditions applied for preparing BHFED.

$^1$H-NMR (300 MHz, DMSO, $\delta$) 12.81 (2H, OH), 6.80 (2H, OH), 7.55–6.80(18h, ArH); 8.26 (2H,CH=N); 4.08–3.75 (8H,Ar—CH$_2$—Ar); FTIR (KBr pallets) $\nu_{max}$ (cm$^{-1}$) 3325–3240, 3058, 2975–2850, 1640, 1500, 1270, 748, 615, 543. Anal. Calcd for. C$_{34}$H$_{28}$O$_4$N$_2$: C, 77.23; H, 4.97; N, 5.50. Found: C, 77.28; H, 4.95; N, 5.54.

### Preparation of bisphenolic chelates with metal salts

The bisphenolic chelates of ethylendiamine (BHFED)-M(II) [M=CO(II), Ni(II),and Cu(II)], and bisphenolic chelates of *o*-phenylenediamine (BHFPD)-M(II) were prepared according to the reported procedure.[15] To a solution of 4.80 g (0.01 mol) BHFED, 5.26 g (0.1 mmol) BHFPD and 1.99 g copper acetate in the molar ratio 1:1 were dissolved together in ethanol (for a 10% w/v solution) and heated at 40°C, with stirring for 2 h. The brown-colored precipitate of copper-chelated bisphenol was filtered, washed off, and dried in vacuum oven at 70°C for 2 h. The similar procedure was employed for the synthesis of Ni(II)- and Co(II)-chelated bisphenolic monomer. The overall route for the synthesis of BHFED-M(II), BHFPD-M(II) and their metal chelates is represented in Scheme 2.

$^1$H-NMR (300 MHz, DMSO, $\delta$) 13.13 (2H, OH), 7.43–6.56(14h, ArH); 8.24 (2H,CH=N); 4.04–3.50 (8H,Ar—CH$_2$—Ar, =N—CH$_2$); FTIR (KBr pallets) $\nu_{max}$ (cm$^{-1}$) 3330–3235, 3050, 2961–2852, 1633, 1502, 1266, 748, 620, 540. Anal. calcd For. C$_{34}$H$_{26}$O$_4$N$_2$-Cu(II): C, 69.87; H, 4.48; N, 4.95; M, 10.07. Found: C, 69.87; H, 4.49; N, 4.94; M, 10.12.

### Preparation of metal-chelated epoxy resin

Metal-chelated epoxy resins of ethylene diamine (ERED)-M(II) were synthesized by the reaction of 5.38 g (0.01 mol) (BHFED)-M(II) dissolved in 20 mL DMF and 10 mL of epichlorohydrin in basic medium.
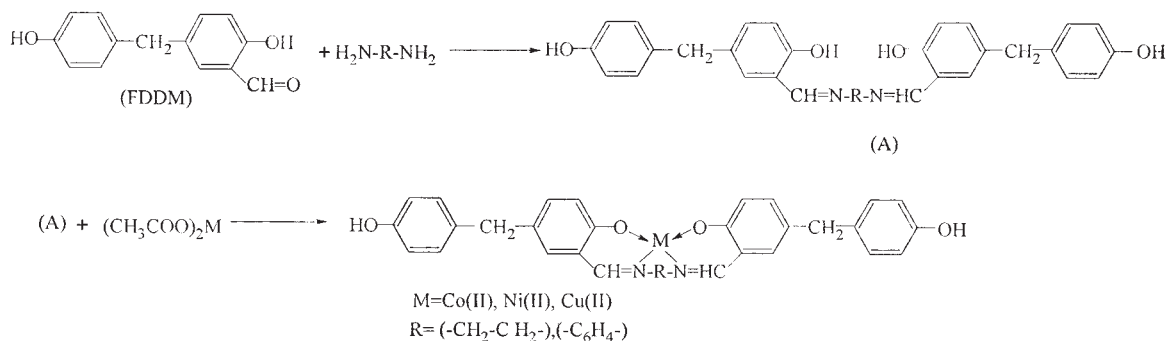
**Scheme 2**

10 mL of 2*N* NaOH was added dropwise in the reaction mixture. The system was heated between 80 and 90°C with continuous stirring for 2 h. The progress of the reaction was monitored by TLC technique and epoxide equivalent weight. As the heat evolution was slowed, the solution was poured in to ice cooled ether. The resulting precipitate of metal-chelated epoxy resin was filtered, washed with water and methanol respectively. After that the final product was dried in vacuum oven at 100°C for 2 h.

The metal-chelated epoxy resin of *o*-phenylenediamine (ERPD)-M(II) was synthesized by the same procedure as mentioned above in the preparation of (ERED)-M(II). Schematically, the overall route for the synthesis of metal-chelated epoxy resin is represented in Scheme 3.

### Preparation of microbial cultures

The antimicrobial activity of metal-chelated epoxy resin was carried out against *Escherichia coli, Staphylococcus aureus, Bacillius subtilis* (bacteria) and *Candida albicans, Mucor species* (yeast). Bacteria strains were nourished in nutrient broth (Difco, Sparks, MD, USA) and yeasts in malt extract broth (Difco) and incubated for 24 and 48 h respectively. According to agar disk diffusion method bacteria were inoculated on Mucller

Hinton Agar and yeast on Sobered dextrose agar. A circular well was made at the center of each petri plate with a sterilized steel borer. Metal-chelated epoxy samples were prepared using DMSO as a solvent at a concentration of 25 $\mu$g/mL. Then 0.1 mL of each test solution was added to the well and incubated at about 36°C for 24 h and the yeast sample were incubated at 25°C for 72 h. DMSO-absorbed disks were used for control only. The resulting inhibition zones on the palates were measured in mm by using Imipenum as a standard drug for the antibacterial activity and Miconazol for antifungal activity.

### Characterization

The elemental analysis of metal-chelated epoxy resins was carried out on a Perkin–Elmer Model-2400 elemental analyzer (CDRI, Lucknow). The metal percentage of the chelated polymers was determined by complexometric titration against EDTA after decomposing with concentrated nitric acid ($HNO_3$). The FTIR Spectra were recorded over the ($4000–500$ cm$^{-1}$) range on a Perkin–Elmer infrared spectrophotometer Model 621 by using KBr pellets. $^1$H-NMR and $^{13}$C-NMR spectra were recorded on a JEOL–GSX-300 MHz, FX–1000 FT-NMR spectrometer using DMSO as a solvent and tetramethylsilane (TMS) as an internal standard. The
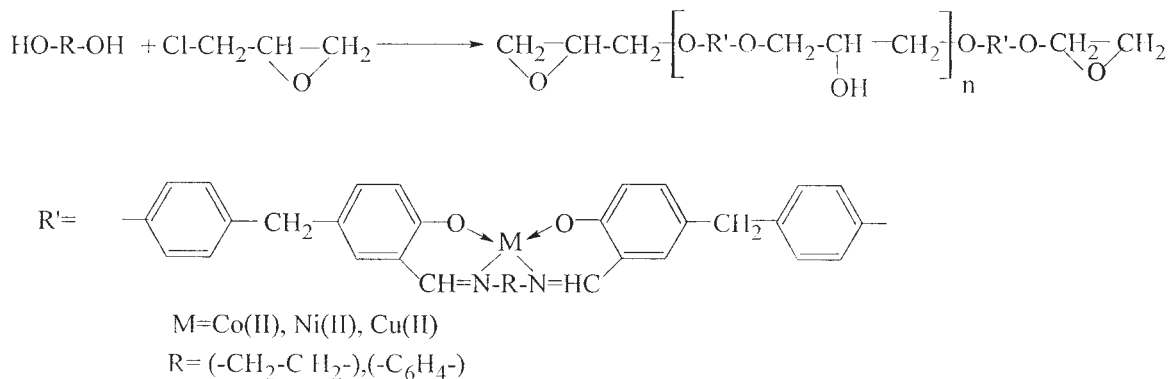


**Scheme 3**

**TABLE I**
**Physico chemical Properties of Metal-Chelated Epoxy Resins**

| Characterization | (ERED)-Co(II) | (ERED)-Ni(II) | (ERED)-Cu(II) | (EDEP)-Co(II) | (ERPD)-Ni(II) | (ERPD)-Cu(II) |
|---|---|---|---|---|---|---|
| Epoxy equivalent (eq/100 g) | 840 | 840 | 847 | 856 | 865 | 878 |
| Hydroxyl value (eq/100 g) | 4.125 | 4.035 | 4.083 | 4.083 | 4.056 | 4.064 |
| Specific viscosity (at 30°C) | 1.325 | 1.462 | 1.534 | 1.532 | 1.585 | 1.612 |
| Refractive index (at 30°C) | 1.4230 | 1.432 | 1.463 | 1.497 | 1.493 | 1.483 |
| Specific gravity | 1.786 | 1.785 | 1.821 | 1.832 | 1.832 | 1.848 |
| Physical state | crystalline | crystalline | crystalline | crystalline | crystalline | crystalline |
| Color | light pink | rust brown | greenish blue | wooden | brown | wooden |

solubility of the chelated polymers in various solvents was checked at room temperature. The specific viscosity of polyepoxide in DMSO dimethylsulphoxide (20%) 30°C was determined with the help of Ubbelhde viscometer. Various physical and chemical properties such as refractive index, hydroxyl value, and epoxy equivalent weight were determined by standard procedures. Thermal properties (viz., thermo- gravimetric analysis and differential scanning calorimetric analysis) of the metal-chelated epoxy resins were carried out on a TA analyzer 2000 in nitrogen atmosphere. TGA and DSC were performed at a heating rate of 20°C/min and 10°C/min, respectively. The antibacterial and antifungal activities of the chelated epoxy resins were observed on different bacteria and fungus by using agar well diffusion methods, the results are reported according to their growth profile.

## RESULTS AND DISCUSSION

### Chemistry

The monomeric FDDM was obtained by treating 1:1 molar ratio of phenol and salicylaldehyde with trioxane in acid ($CH_3COOH$ + conc. $H_2SO_4$) solution. A similar procedure was already used by Smith for the preparation of 3-carboxy 4,4'-dihydroxy diphenyl methane from salicylic acid.[16] Phenol and salicylaldehyde to trioxane ratio must be very high in order that the FDDM be formed rather than a polymeric product in acidic medium, according to Scheme 1.

Metal-chelated bisphenol was prepared by the reaction of FDDM with ethylenediamine/o-phenylenediamine in 2:1 molar ratio and then Co(II), Ni(II), and Cu(II) acetate in 1:1 molar ratio.

Metal-chelated epoxy resins of (ERED) and (ERPD) were obtained in good yield by the reaction of epichlorohydrin (1-chloro-2,3 epoxy propane) with Co(II)-, Ni(II)-, and Cu(II)-chelated bisphenol in the presence of NaOH solution as a catalyst. The reaction was monitored by TLC and occurred at the boiling point of epichlorohydrin. All chelated epoxy resins are insoluble in common organic solvents, but soluble in DMSO and DMF.

### Physicochemical properties and composition

An examination of physicochemical properties of all the chelated epoxy resins are given in Table I and the results of elemental analysis of these polyepoxides are given in Table II with the theoretical composition based on assumed structure. A Slight deviation in elemental analysis may be due to the polymeric nature of the complexes, as the value of end groups are not taken in to account for theoretical calculation. The hydroxyl value (eq/100 g) of metal-chelated resin was found to be about 4.000 by using following equation.

Hydroxyl value

$$= \frac{\text{Weight of sample}}{\text{Normality of KOH} \times (V_2 - V_1) \times 170}$$

**TABLE II**
**Elemental Analysis of Metal-Chelated Epoxy Resin**

| Compounds | Yield in (%) | Elemental analysis[a] | | | |
|---|---|---|---|---|---|
| | | Carbon | Hydrogen | Nitrogen | Metal |
| (ERED)-Co(II) | 80 | 66.16 (66.21) | 5.17 (5.20) | 4.70 (4.72) | 9.90 (9.90) |
| (ERED)-Ni(II) | 83 | 66.16 (66.07) | 5.17 (5.13) | 4.70 (4.74) | 9.87 (9.91) |
| (ERED)-Cu(II) | 82 | 65.65 (65.67) | 3.13 (3.16) | 4.67 (4.70) | 10.57 (10.91) |
| (ERPD)-Co(II) | 85 | 68.33 (68.67) | 4.87 (4.86) | 4.42 (4.42) | 9.31 (9.34) |
| (ERPD)-Ni(II) | 84 | 68.33 (68.39) | 4.87 (4.83) | 4.42 (4.43) | 9.28 (9.26) |
| (ERPD)-Cu(II) | 86 | 67.79 (67.80) | 4.83 (4.86) | 3.39 (3.32) | 9.96 (9.95) |

[a] The calculated, (Found) values.

**TABLE III**
**The IR Spectral Bands and Their Assignments of Chelated Epoxy Resin**

| | | | | | Assignments[a] | | | | |
|---|---|---|---|---|---|---|---|---|---|
| Samples | vO—H | vAr—CH | —CH (sym) | —CH (asym) | vC=N | vO=C | vC—O—C | vM—N | vM—O |
| (ERED)-Co(II) | 3350–3400(b) | 3050(m) | 2943(m) | 2860(m) | 1650–1600(s) | 1560(m) | 1060(m) | 640(s) | 520(s) |
| (ERED)-Ni(II) | 3352–3400(b) | 3055(m) | 2940(m) | 2860(m) | 1650–1640(s) | 1550(m) | 1060(s) | 650(m) | 530(s) |
| (ERED)-Cu(II) | 3350–3400(b) | 3050(m) | 2940(m) | 2860(m) | 1660–1600(s) | 1540(m) | 1060(s) | 650(s) | 520(s) |
| (ERPD)-Co(II) | 3355–3405(b) | 3052(b) | 2940(m) | 2865(m) | 1650–1630(s) | 1565(s) | 1060(m) | 655(s) | 520(m) |
| (ERPD)-Ni(II) | 3350–3402(b) | 3050(m) | 2942(m) | 2860(m) | 1650–1600(s) | 1563(m) | 1060(m) | 650(m) | 540(s) |
| (ERPD)-Cu(II) | 3355–3408(b) | 3054(m) | 2940(m) | 2864(m) | 1650–1600(s) | 1560(m) | 1060(s) | 650(s) | 520(s) |

[a] s, strong; m, medium; w, week; sym, symmetric; asym, asymmetric;

Where $V_1$ = volume of KOH used for blank; $V_2$ = volume used for sample

Thus the number of repeat unit is four, because one unit contains one OH atom as shown Figure 1. The observed molecular mass of metal-chelated resin could not be determined by using TLC because these were not completely soluble in THF but the molecular weight is calculated by end group techniques using following formula.

$$Mw = Functionality \times W \times 1000/N \times V$$

where Mw = molecular weight; $V$ = volume of KOH used; $N$ = normality of KOH solution; Functionality = number of reactive groups in each molecule.

Calculated molecular mass was found to be 2974–2997 and 3161–3284 for (ERED)-M(II) and (ERPD)-(II) respectively, by using end groups analysis.[17]

**FTIR spectra**

The important IR bands of metal-chelated epoxy resin and their assignments are summarized in Table III. A broad band appears in the region 3400–3350 cm$^{-1}$ due to vOH vibration of the hydroxyl groups and a strong band at 1105 cm$^{-1}$ appears, which indicate C—O vibration on the secondary alcohol. The presence of methylene group was confirmed by the appearance of two strong bands at 2945 and 2860 cm$^{-1}$ due to vCH *symmetric* and *asymmetric* stretching and a band at 1410 cm$^{-1}$ due to δCH$_2$ bending mode. All chelated epoxy resins show characteristic bands at 3050 cm$^{-1}$ due to aromatic vC-H stretching. These polychelates display strong bands in the region 1630–1650 cm$^{-1}$ and 1540–1560 cm$^{-1}$ that were ascribed to vC=N of the azomethine and vC=C aromatic ring stretching respectively. Two other bands of ether —C—O—C—
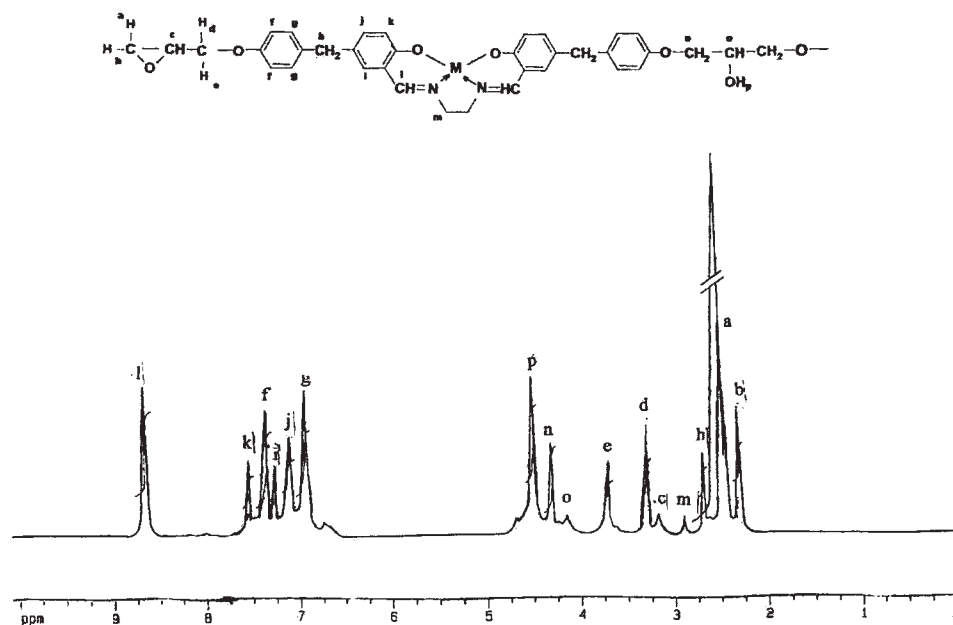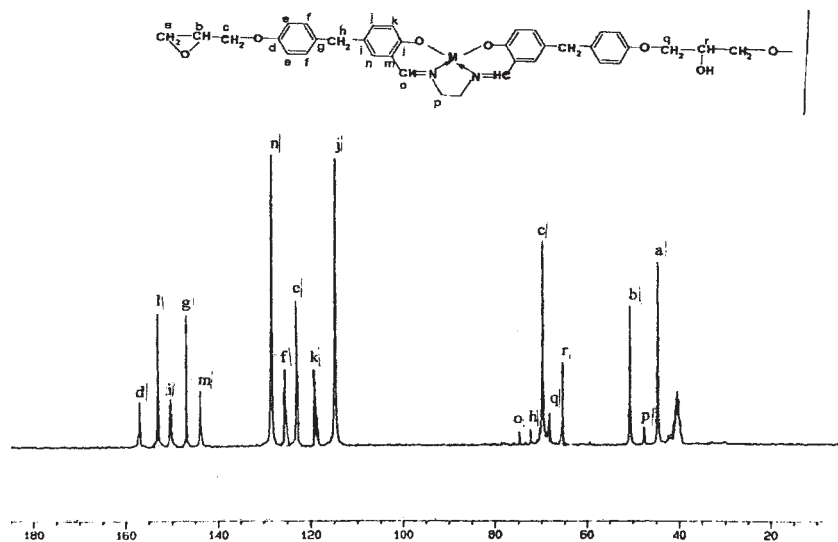


**Figure 1** $^1$H-NMR spectra of ERED-Ni(II)

**Figure 2** $^{13}$C-NMR spectra of ERED-M (II)

and epoxy appear at 1050 cm$^{-1}$ and 909 cm$^{-1}$ respectively. The appearances of well-defined absorption in the range 620–635 cm$^{-1}$ and 540–545 cm$^{-1}$ were assigned to an $\nu$M—O and $\nu$M—N.[18]

## $^1$H-NMR spectra

The $^1$H-NMR spectra of Ni-chelated epoxy resins, ERED-Ni(II), are shown in Figure 1. The $^1$H-NMR signals for N=C$H$ proton of the imines groups appear around 8.69–8.80 ppm for (ERED)-Ni(II) and at 8.50–8.60 ppm for (ERPD)-Ni(II),complexes.[19] The aromatic protons of $o$-phenylenediamine show resonance signal at 6.96–7.04 ppm, while the methylene protons of ethylenediamine appear at 3.25–3.38 pmm. The methylene groups of Ar—O—C$H_2$—, methyne, and methylene protons of epoxy show signal at 4.63–3.82, 3.3–3.4, and 3.51–2.57 ppm, respectively.[20] The protons of

CH$_2$ groups attached between two-phenyl groups show a signal at 2.8 ppm. The OH protons appear at 4.5 ppm and aromatic protons in asymmetric patterns at 7.02–6.68 ppm. The polymerization of epoxide through phenol is confirmed by the absence of its hydroxyl group peaks. A visual evaluation of signals of equal number of aromatic protons is due to the intermolecular interaction toward metal ions and variation in the $\pi$-electron density around the proton.

## $^{13}$C-NMR spectra

The $^{13}$C-NMR spectra of metal-chelated epoxy resin (ERED)-M(II) is shown in Figure 2 where M represent metal ion. The peaks at 136.6–105 ppm and 130–115 ppm are due to the aromatic carbons of $o$-phenylenediamine-based resins (ERPD) and for ethylenediamine based resins, (EDER)-M(II), respectively. The N=CH

## TABLE IV
### Magnetic Moment and Electronic Spectral Data of Polymeric Metal Complexes

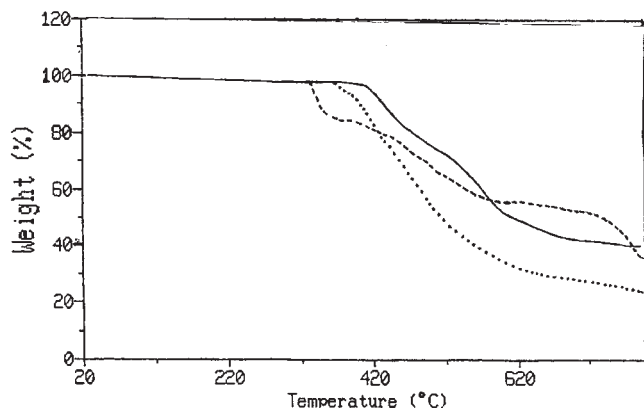| Compounds | Magnetic moment in B.M. | Electronic spectral data | | Geometry |
|---|---|---|---|---|
| | | Electronic transition (cm$^-$) | Assignment | |
| (ERED)-Co(II) | 4.68 | 8810 | $^4T_1(F)\leftarrow{^4}A_2$ | Tetrahedral |
| | | 15900 | $^4T_1(P)\leftarrow{^4}A_2$ | |
| (ERED)-Ni(II) | diamagnetic | 17010 | $^1A_{2g}\leftarrow{^1}A_{1g}$ | Squareplanar |
| | | 23000 | $^1B_{1g}\leftarrow{^1}A_{1g}$ | |
| (ERED)-Cu(II) | 1.79 | 15625 | $^2A_{1g}\leftarrow{^2}B_{1g}$ | Squareplanar |
| | | 25380 | Charge-transfer | |
| (ERPD)-Co(II) | 4.65 | 9210 | $^4T_1(F)\leftarrow{^4}A_2$ | Tetrahedral |
| | | 17200 | $^4T_1(P)\leftarrow{^4}A_2$ | |
| (ERPD)-Ni(II) | diamagnetic | 17050 | $^1A_{2g}\leftarrow{^1}A_{1g}$ | Squareplanar |
| | | 23080 | $^1B_{1g}\leftarrow{^1}A_{1g}$ | |
| (ERPD)-Cu(II) | 1.78 | 15820 | $^2A_{1g}\leftarrow{^2}B_{1g}$ | Squareplanar |
| | | 25485 | Charge-transfer | |

**Figure 3** TGA thermograms of . . . . . . (ERED)-Co(II), ——— (ERED)-Ni(II), and ▬ (ERED)-Cu(II), in nitrogen atmosphere; the heating rate is 20°C/min.

imines carbons show peak at 154–155 ppm. The peak at 54 ppm is due to Ar—CH$_2$—Ar group. The peaks at 64.3–65.2 ppm, 68.3–63.5 ppm and 50.4–45.8 ppm are due to methylene and methyne carbon of epoxy groups, respectively.[20] The peak of Ar—O—CH$_2$— appears at 68.3–68.5 ppm, suggesting that methylene group of epichlorohydrin groups are linked with phenolic groups of Schiff base by removal of hydrochloric acid as a by product. A sharp peak at 64.2 ppm is assigned to —CH(OH)— function, which was generated by the reaction of epoxy moiety with phenolic group.

## Electronic spectra and magnetic property

The electronic spectra and magnetic properties of metal-chelated epoxy resin are depicted in Table IV. The electronic spectra of these chelated polymers are recorded in DMSO. The magnetic moment of Co-chelated resin (ERED) is 4.68 BM and two bands due to $^4T_1(P) \leftarrow ^4A_2$ and $^4T_2$ (F)$\leftarrow ^4A_2$ transition appeared at 15,900 and 8810 cm$^{-1}$ respectively, which indicates the tetrahedral environment around Co(II) ion. The diamagnetic complex (ERED)-Ni (II) exhibits two bands at 17,010 and 23,000 cm$^{-1}$, which is characteristic of square planar environment due to $^1A_{2g} \leftarrow ^1A_{1g}$ and $^1B_{1g} \leftarrow ^1A_{1g}$ transitions. The copper complexes exhibit bands at 15,625 and 25,380 cm$^{-1}$ due to $^2A_{1g} \leftarrow ^2B_{1g}$ and charge transfer spectra and 1.79 B.M. magnetic moment of complexes shows square planar geometry.

Among the complexes of (ERPD)-M(II) the cobalt complex showed two bands at 9210 and 17,200 cm$^{-1}$, which indicates tetrahedral geometry reported.[21] The Ni(II) complexes exhibit bands at 17,050 and 23,080 cm$^{-1}$ with $^1A_{2g} \leftarrow ^1A_{1g}$ and $^1B_{1g} \leftarrow ^1A_{1g}$ assignment, characteristic of a square planar environment around the Ni(II) ions. Cu(II) complexes exhibit bands at 15,820 and 25,485 cm$^{-1}$ transition and were assigned

to $^2A_{1g} \leftarrow ^2B_{1g}$ and charge transfer spectra respectively, and 1.78 BM magnetic moment of complexes show square planar geometry. The results of electronic spectra indicate that there was a little deviation in the electronic transition of monomeric metal complexes because of their polymerization by epoxy resin. These deviations are too little to affect the geometry of the central metal ions.

## Thermal analysis

The TGA traces of (ERED)-M(II) and (ERPD)-M(II) metal chelates are shown in Figures 3 and 4. The thermal behaviors of all polymers in nitrogen environment provide information about their thermal stability and nature of degradation of products at various temperatures. The glass transition temperature ($T_g$), Char. % weight at 800°C, and the temperature at which all the chelated resins show a weight loss of 10–50% in nitrogen are tabulated in Table V. The thermal stability of aromatic-based chelated resin (ERPD)-M(II) [M = Co(II), Ni(II), and Cu(II)] is higher than that of epoxy resins based on aliphatic amine because of higher resonance energy. The chelated epoxy resins were stable up to 325°C, then a continuous mass loss was observed up to 620°C, indicate the decomposition of the organic part of the polyepoxied complexes. The Cu(II) complexes of (ERPD) were more stable than the other polyepoxide[22] because of higher successive stability constant of Cu(II) complexes. The thermal stability of the epoxy resins are in the order (ERPD)Cu(II) >(ERPD)Ni(II) >(ERED) Cu(II)>(ERPD)Co(II) >(ERED)Ni(II) >(ERED)Co(II).

The $T_g$ of the epoxy resin are listed in Table V. DSC evaluation are used to measure percentage crystallinity of the metal-containing epoxy resins with the help of following equation (r).
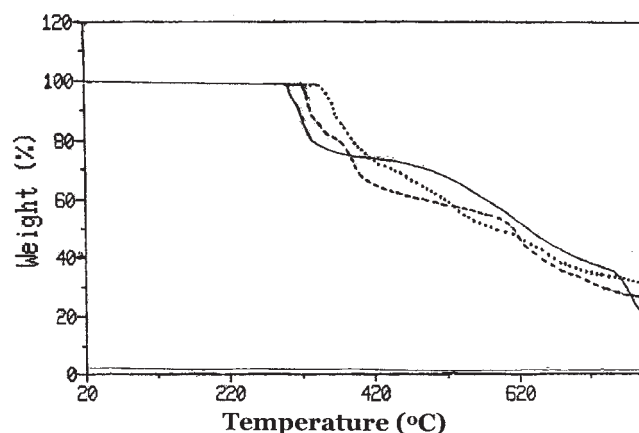


**Figure 4** TGA thermograms of . . . . . . (ERPD)-Cu(II), - - - (ERPD)-Ni(II), and ▬ (ERPD)-Co(II), in nitrogen atmosphere; the heating rate is 20°C/min.

**TABLE V**
**Thermal Behaviors of Polyepoxied**

| Materials | $T_g$ (°C) | Temperature °C corresponding to weight loss of | | | | | Char (%) weight at 800°C |
|---|---|---|---|---|---|---|---|
| | | 10% | 20% | 30% | 40% | 50% | |
| (ERED)-Co(II) | 186 | 300 | 325 | 480 | 505 | 620 | 20% |
| (ERED)-Ni(II) | 192 | 310 | 350 | 382 | 455 | 600 | 26% |
| (ERED)-Cu(II) | 204 | 350 | 380 | 430 | 495 | 570 | 32% |
| (ERPD)-Co(II) | 197 | 319 | 418 | 475 | 456 | 495 | 30% |
| (ERPD)-Ni(II) | 214 | 380 | 380 | 412 | 435 | 550 | 34% |
| (ERPD)-Cu(II) | 225 | 420 | 460 | 520 | 552 | 610 | 42% |

Percentage crystallinity = $H_a - H/H_a - H_c$

$H = H_t - H_c$

where $H_a$ = amorphous enthalpy; $H_c$ = Crystalline enthalpy; $H$ = Sample enthalpy; $H_t$ = Total enthalpy. The values of $H_a$, $H_c$, and $H_t$ were calculated from DSC curves.

The values of percent crystalline of metal contain epoxy resins were higher than that of common (DGEBA) epoxy resin, and the $T_g$ increases in the order (ERPD)Cu(II)>(ERPD)Ni(II)>(ERED) Cu(II)>(ERPD)Co(II) >(ERED)Ni(II) >(ERED)Co(II).

## Antimicrobial effect

The fungicidal and bactericidal effects of these metal-chelated epoxy resins were determined against three bacteria and two yeasts as described in experimental section. The agar disk diffusion method was employed for the bacteria and yeasts with respect to Imipenum and Miconazol as standard drugs. The results of activity showed that some compounds are very effective on some of the microorganisms and summarized in Table VI. The (ERPD)-Cu(II) exhibited the highest antibacterial and antifungal activities against *Escherichia coli*, 22 mm and *M. species*, 19 mm. Ni(II)-chelated epoxide display promising activity 15 mm,16 mm against, *Bacillius subtilis* (bacteria) and

*Candia albicans* (yeast). Epoxy resin containing Co(II) do not show much activity like others against these microorganisms. The result reveals that the antimicrobial activity of these metal-chelated polymers is due to the presence of nitrogen and oxygen donor groups. It has been suggested that the compound with the N and O donor system might have inhibited enzyme production because enzymes that require a free hydroxyl group for their activity appear to be especially susceptible to deactivation by the ions of the complexes.[23] The chelation reduces the polarity of the central ion and because the partial shearing of its positive charge with the donor groups and possible $\pi$ electron delocalization within the chelate ring, which also increases the lipophilic nature of the central atom, which favors its permeation through the lipid layer of the membrane. The results of antifungal and antibacterial screening indicate that (ERPD)-Cu(II) complexes show more activity than the other complexes. The result may be due to higher stability constant of Cu(II) than the other complexes. According to the stability constant, Cu(II) ion is made up of stronger interaction with N and O donor atoms by which lipophilic nature is increased. (ERPD)-Cu(II) polyepoxied show more activity then (ERED)-Cu(II) because of the presence of $\pi$ electrons, which also increase the lipophilic nature of Cu(II) ion.

**TABLE VI**
**Antimicrobial Effect of Metal-Chelated Epoxy Resin**

| Compounds abbreviations | Zone of inhibition in 0.25 mm at a of 25 $\mu$g/mL concentration | | | | |
|---|---|---|---|---|---|
| | *E. coli* | *S. aureus* | *B. subtilis* | *C. albicans* | *M. species* |
| (ERED)-Co(II) | 7 | 8 | 10 | 9 | 10 |
| (ERED)-Ni(II) | 12 | 13 | 15 | 16 | 18 |
| (ERED)-Cu(II) | 22 | 9 | 13 | 16 | 10 |
| (ERPD)-Co(II) | 13 | 14 | 11 | 11 | 13 |
| (ERPD)-Ni(II) | 17 | 19 | 10 | 9 | 18 |
| (ERPD)-Cu(II) | 22 | 18 | 14 | 10 | 19 |
| DMSO | — | — | — | — | — |
| Miconazol[a] | — | — | — | 20 | 25 |
| Imipenum[b] | 25 | 22 | 18 | — | — |

Inactive (0–8 mm), mildly active (10–13mm), moderately active (14–17mm), highly active (above 18).
DMSO (control)
[a, b] Standard drugs for antifungal and antibacterial activity.

## CONCLUSIONS

Newly developed metal-chelated epoxy compounds were prepared in good yield and characterized by various instrumental techniques. It has been observed that the attachment of metal ion in the polymeric backbone enhances thermal as well as antimicrobial activity. Because of the more toxic behavior of (ERPD)-Cu(II), they may be used as antifungal and antifouling coating in various processes.

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