

# Synthesis and Characterization of Antibacterial Polychelates of Urea–Formaldehyde Resin with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) Metal Ions

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**ABSTRACT:** We studied the reaction between urea and formaldehyde with the purpose of preparing new polychelates of Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) metal ions. These compounds were characterized by elemental analysis, IR spectroscopy, <sup>1</sup>H-NMR, electronic spectroscopy, thermogravimetric analysis (TGA), and molar conductance measurements. The percentage of metal in all of the polychelates was found to be consistent with 1:1.5 (metal/ligand) stoichiometry. The thermal behaviors of these coordination polymers were studied by TGA in a nitrogen atmosphere up to 750°C. The TGA results reveal that the complexes had higher thermal-resistance properties

compared to the common urea–formaldehyde resin. The molar conductivity and magnetic susceptibility measurements of the synthesized polychelates confirmed the geometry of the complexes. The antibacterial activity of the polychelates was also investigated with agar diffusion methods. The antibacterial activity of these polychelates was found to be reasonably good compared with standard drugs, namely, ciprofloxacin, ampicillin, and kanamycin. © 2006 Wiley Periodicals, Inc. *J Appl Polym Sci* 100: 928–936, 2006

**Key words:** resins; thermogravimetric analysis; diffusion methods

## INTRODUCTION

A significant amount of research has been dedicated to the study of organic polymers, but one of the main drawbacks of these polymer is their low thermal stability (they are generally stable up to 200°C); this has created an impetus for the development of new, thermally resistant inorganic polymeric chelates with unique combinations of properties that have not been encountered in organic polymers. Recently, a wide variety of coordination polymers have been developed that have found potential applications as catalysts,<sup>1</sup> biomedical control releasing agents,<sup>2</sup> water-treatment agents,<sup>3</sup> solid-state materials such as semiconducting substances,<sup>4</sup> and heat-resistant materials.<sup>5</sup> The use of inorganic polymeric polychelates in aerospace requirements and nanotechnology<sup>6</sup> provide an opportunity for further studies. Over the past few years, several reviews have been published on metal-containing polymers.<sup>7–9</sup>

In polymer–metal complexes, the central metal ions are surrounded by polymeric ligands, which show interesting characteristics in their catalytic activities and which are different from ordinary metal com-

plexes. The synthesis of coordination polymers are usually achieved by one of the following procedures:

1. Metal complexes may yield polymeric material during their formation because of the presence of favorable donor groups in the ligands.<sup>10</sup>
2. The ligand itself may act as an organic polymer to which metals can be suitably coordinated.<sup>11,12</sup>
3. A metal ion may be coordinated with a ligand, and the monomeric metal complex may react with another organic compound to form polymeric complexes.<sup>13</sup>

Nowadays, coordination polymers are also expected to find potential applications as antibacterial materials.<sup>2</sup>

Phenol formaldehyde resin is generally used in polymer composites as thermal insulation materials and coating materials, in the wood industry as adhesives, and so on.<sup>14–16</sup> Polychelates of phenol formaldehyde with transition-metal chlorides that showed superior heat- and mechanical-resistance properties to common phenol formaldehyde resins have been reported previously.<sup>17</sup> Indeed, urea–formaldehyde (UF) is an irreplaceable material, has wide technological applications in different emerging fields, and offers high reliability under severe circumstances. Because of the presence of multiple donor sites (amino groups and carbonyl groups per unit) in urea–formaldehyde resin (UFR),<sup>18,19</sup> one can expect that such a system may provide excellent electron donation for coordination.

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In this article, we report the syntheses and characterization of UFR and its complexes with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) metal ions. The spectral, magnetic, antibacterial, and conductivity properties and the type of geometry around the metal centers are also discussed. The antibacterial activity of polychelates of UFR were better than those of common UF and compared with standard drugs such as ciprofloxacin, ampicillin, and kanamycin in similar conditions.

## EXPERIMENTAL

### Materials

Urea, dimethyl sulfoxide (DMSO), 37% formaldehyde (S. D. Fine Chemicals, Mumbai, India), butanol, and sodium hydroxide (Qualigens) were all analytical-reagent grade and were used without further purification. The metal (II) and metal (III) chlorides (Merck India, Mumbai, India) were used as received. Organisms such as *Escherichia coli*, *Staphylococcus aureus*, *Bacillus megaterium*, *Protus vulgaris*, and *Bacillus subtilis* were isolated in suitable environments.

### Synthesis of UFR

In a 250-mL, three-necked flask equipped with a stirrer and a condenser, 12 g (0.2 mol) of urea and 15 mL (0.2 mmol) of formaldehyde (37% aqueous solution) were placed, and the pH was adjusted to 4 with an acid. The reaction mixture was heated to 95°C for 5 h under constant stirring. The process of the reaction was monitored by viscosity measurements. A viscous product of 150–200 cp viscosity was obtained and washed with a dilute NaOH solution, distilled water, and diethyl ether. The solvent was removed in vacuo with a rotary vacuum evaporator. The resin was soluble in common organic solvents, such as ethanol, xylene, toluene, and benzene, and was insoluble in water.

### Synthesis of the metal polychelates

The polymeric ligand (1.85 g, 0.75 mmol) was dissolved in 50 mL of butanol; to this solution, a sufficient amount of ethanol was added to make the volume of the solution 100 mL. An ethanolic solution of NiCl<sub>2</sub> · 6H<sub>2</sub>O (2.37 g, 1 mmol) was then added, and it was stirred again simultaneously; the color of the solution changed, and the pH was adjusted to 5–5.5. The turbid mixture was stirred at 60°C for 2 h to obtain the fused product of the polychelates. The precipitate was filtered; washed with distilled water, ethanol, and diethyl ether; and dried in a vacuum oven. The yield of the product was 75%.

We synthesized the polychelates of Cr(III), Mn(II), Fe(III), Co(II), Cu(II), and Zn(II) by mixing 2.66, 1.97,

2.70 g, 2.37, 1.70, and 1.36 g, respectively, of these metals ions with 1.85 g of UFR in a 1 : 1.5 ratio by a method similar to that mentioned previously. The different colored precipitates were obtained for different metals, as shown in Table I. The colors and the solubility of the metal ions changed on complexation. They were soluble in polar solvents, namely, DMSO and dimethylformamide.

### Measurements

The percentages of C, H, and N of the ligand and its metal polychelates were determined with a PerkinElmer model 2400 elemental analyzer (CDRI, Lucknow, Boston, MA). The percentages of metals in the UF metal polychelates were determined by complexometric titration with ethylenediaminetetraacetic acid after decomposition with fuming HNO<sub>3</sub>, and the percentage of Cl was estimated gravimetrically.<sup>20,21</sup> IR spectra were taken on a PerkinElmer IR spectrophotometer (model 621) with KBr pellets in the range 5000–500 cm<sup>-1</sup>. A PerkinElmer Lambda E2201 was used to measure the electronic spectra of the complexes; magnetic susceptibility measurements were done with a vibrating sample magnetometer, and NMR spectra were recorded on a Bruker spectropin DPX-30 MHz (Ontario, Canada). The thermogravimetric analysis (TGA) was done on a TA Analyzer 2000 (TA Instruments, New Castle, DE).

### Preparation of the microbial culture

Antibacterial activity assays of the newly synthesized polychelates was carried out with the cup plate agar diffusion method.<sup>22</sup> All of the compounds were screened in vitro for their antimicrobial activity against a variety of bacterial strains, including *E. coli*, *S. aureus*, *B. megaterium*, *P. vulgaris*, and *B. subtilis*. One loopfull of bacteria was inoculated in 10 mL of a nutrient broth (peptone 5 g/G, pH 6.8) and incubated at 37°C for 28 h in a test-tube shaker at 100 rpm. Nutrient agar (20 mL) was poured into a sterile Petri plate and allowed to solidify at room temperature. After solidification, 0.1 mL of the bacterial culture was spread on the nutrient agar. A circular well (9 mm in diameter) was made at the center of each Petri plate with a sterilized steel borer. UFR and its metal complex test sample were prepared with DMSO as a solvent at a concentration of 25 µg/mL. Then, 0.1 mL of each test solution was added, and they were incubated at about 37°C for 24 h. The antibiotics, including ampicillin, kanamycin, and ciprofloxacin, were used as positive controls and DMSO was used as a negative controls. Inhibition of growth was measured in millimeters and compared with standard drugs for positive control.

TABLE I  
Analytical Data of UFR Ligand and Its Polychelates with the Metal Ions Cr (III), Mn (II), Fe (III),  
Co (II), Ni (II), Cu (II), and Zn (II)

Compound	C (%)	H (%)	Cl (%)	M (%)	N (%)	Color
1. C <sub>8</sub> H <sub>11</sub> N <sub>4</sub> O <sub>2</sub>						
Calcd	49.00	5.60			28.7	White
Found	48.06	5.65			28.4	
2. (C <sub>8</sub> H <sub>9</sub> N <sub>4</sub> O <sub>2</sub> Cr · 2H <sub>2</sub> O) <sub>n</sub> · nCl						
Calcd	30.15	4.08	11.14	16.33	17.58	Green
Found	30.28	4.01	11.20	16.39	17.73	
3. (C <sub>8</sub> H <sub>9</sub> N <sub>4</sub> O <sub>2</sub> Mn · 2H <sub>2</sub> O) <sub>n</sub>						
Calc.	33.57	4.54		19.20	19.58	Brown
Found	33.85	4.47		20.34	19.60	
4. (C <sub>8</sub> H <sub>9</sub> N <sub>4</sub> O <sub>2</sub> Fe · 2H <sub>2</sub> O) <sub>n</sub> · nCl						
Calcd	29.78	4.03	11.01	17.31	17.37	Wooden
Found	30.12	4.08	11.00	17.10	17.56	
5. (C <sub>8</sub> H <sub>9</sub> N <sub>4</sub> O <sub>2</sub> Co · 2H <sub>2</sub> O) <sub>n</sub>						
Calcd	33.11	4.58		20.31	19.31	Pink
Found	33.58	4.49		20.54	19.48	
6. (C <sub>8</sub> H <sub>9</sub> N <sub>4</sub> O <sub>2</sub> Ni · 2H <sub>2</sub> O) <sub>n</sub>						
Calcd	33.13	4.48		20.26	19.33	Light Green
Found	33.45	4.46		20.50	19.40	
7. (C <sub>8</sub> H <sub>9</sub> N <sub>4</sub> O <sub>2</sub> Cu · 2H <sub>2</sub> O) <sub>n</sub>						
Calcd	32.59	4.41		21.70	19.01	Green
Found	32.62	4.40		21.00	19.13	
8. (C <sub>8</sub> H <sub>9</sub> N <sub>4</sub> O <sub>2</sub> Zn · 2H <sub>2</sub> O) <sub>n</sub>						
Calcd	32.50	4.40		22.13	18.95	White
Found	32.65	4.43		21.55	19.80	

## RESULTS AND DISCUSSION

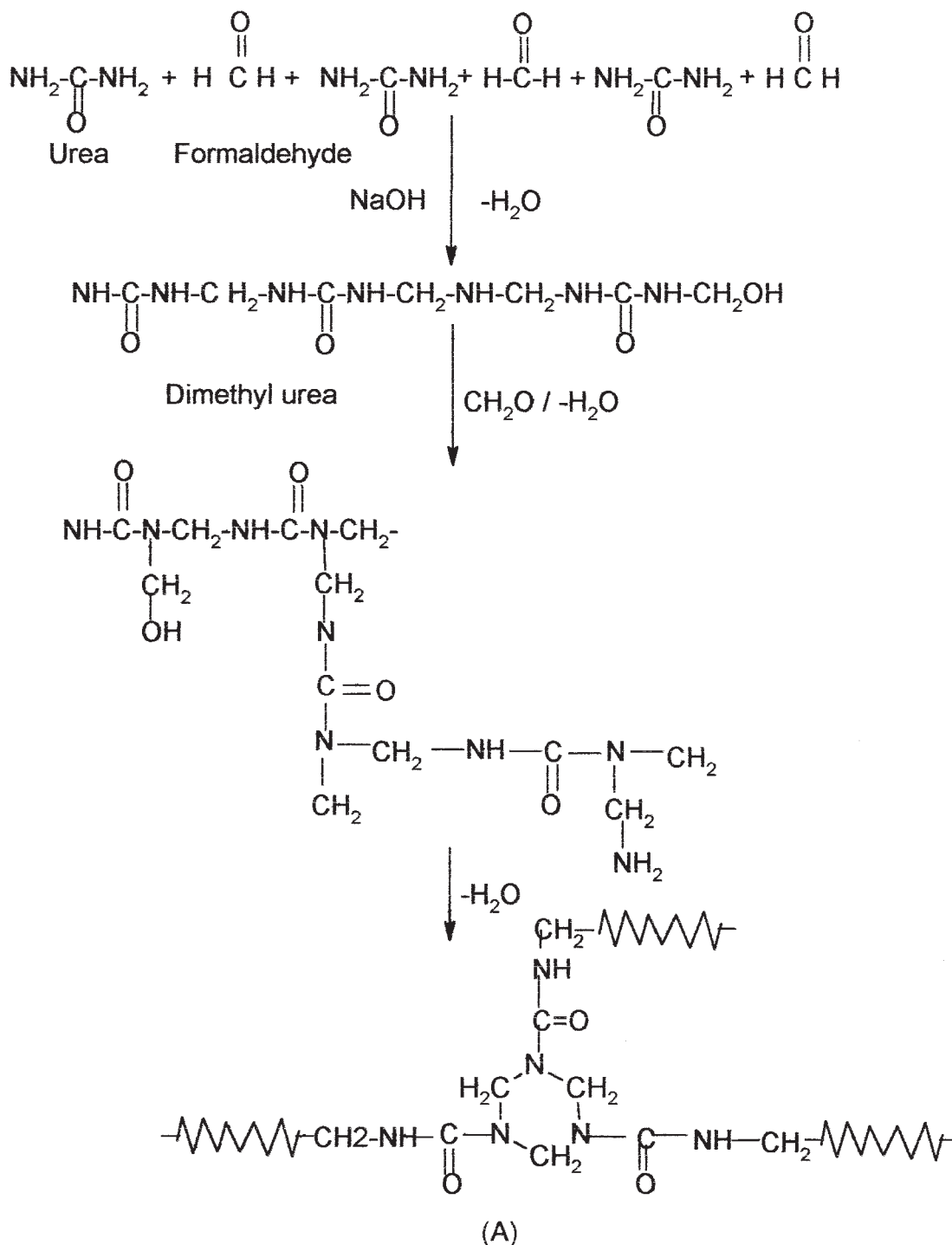
We obtained UFR in a good yield (75%) by reacting urea with formaldehyde in a basic medium (Scheme 1). Polymeric complexes were prepared by the reaction of UFR with divalent and trivalent transition metals (Scheme 2). The percentage of chlorine in polymeric complexes indicates that only the trivalent metal complexes have chlorine. All the polychelate resins were colored; insoluble in water and common organic solvents, such as ethanol, xylene, and toluene; and soluble in DMSO and ethyl methyl ketone. The analytical data agreed with the 1 : 1.5 metal-to-ligand ratio as expected for a branch polymer. Two molecules of water were coordinated per metal ion, which indicated the association of water in all of polymeric complexes, which has been reported by other workers. The analytical data and colors of UFR and its first-row transition-metal complexes are given in Table I.

### FTIR spectra

The IR Spectra are given in Fig. 1 and important bands and their assignments based on IR studies on UFR and its metal polychelates are listed in Table II. In the IR spectra of UFR, two broad bands appeared in the region 3450–3250 cm<sup>-1</sup> due to νNH vibrations of amide groups,<sup>23</sup> and the ν(OH) of the terminal hydroxyl group of UFR as formaldehyde was in excess

during the synthesis. Furthermore, the decreasing frequencies and the broadening of this band in this region suggested intermolecular hydrogen bonding,<sup>24</sup> which was possible between the carbonyl oxygen and amide hydrogen.

Two strong bands appeared at 2945–2850 cm<sup>-1</sup> due to the asymmetric and symmetric stretching modes of the —CH<sub>2</sub> groups.<sup>25</sup> Two strong bands of νC=O and amide II groups appeared at 1676 cm<sup>-1</sup> and the 1540–1565 cm<sup>-1</sup> region, respectively.<sup>26</sup> The band at 1470 cm<sup>-1</sup> was assigned to the δC—H bending of >N—CH<sub>2</sub>—N<.<sup>27</sup> The spectra of the UF metal complexes showed a hump or a very broad band around 3250 cm<sup>-1</sup>; the broadening of this band greater than that of the UFR was attributed to the merge of —NH metal coordination.<sup>28</sup> The presence of coordinated water molecules in the complexes was further confirmed by the appearance of bands in the region 1600–1540 cm<sup>-1</sup> of δHOH deformation and in the 670–650-cm<sup>-1</sup> region for the rocking modes of coordinated water.<sup>29</sup> In the νC=O and δN—H complexes, the bands shifted to a lower frequency region (ca. 25–30 cm<sup>-1</sup>), and the δN—H became more broad. This suggested the participation of these groups in coordination. The participation of oxygen and nitrogen in all of complexes was further supported by the appearance νM—O and νM—N modes in the 658–640 cm<sup>-1</sup> and 564–540-cm<sup>-1</sup> regions, respectively.<sup>30</sup>



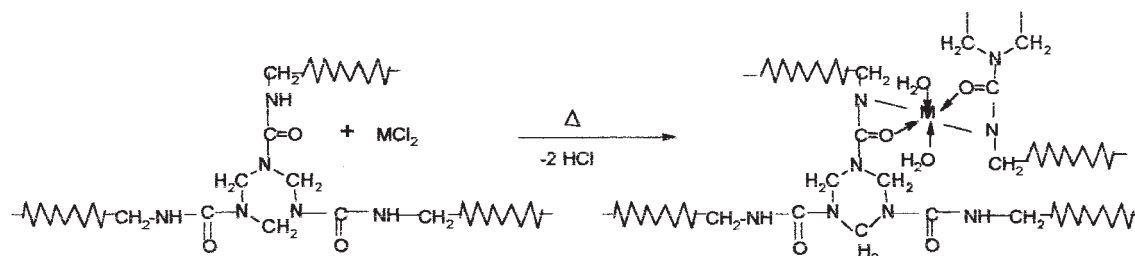
Scheme 1 Synthesis of UFR.

#### Electronic spectra and magnetic measurement studies

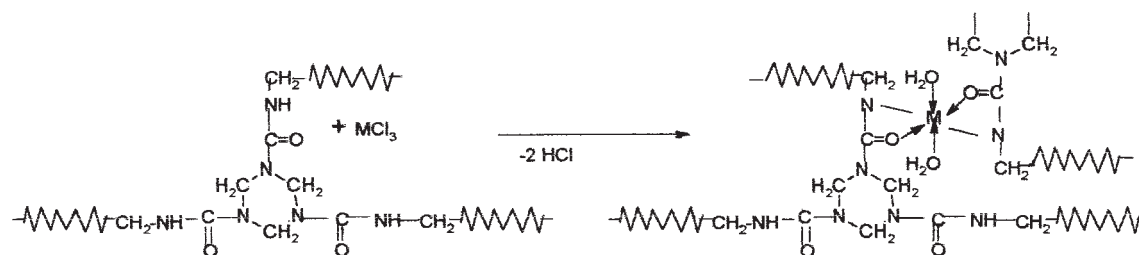
The electronic spectra of the synthesized complexes of  $10^{-3}$  M solutions were recorded in DMSO (Table III). The magnetic moment of the green polychelate of Cr(III) was  $3.80 \mu_B$ , which suggested the presence of three unpaired electrons. The electronic spectra showed three bands at 17,760, 26,200, and 36,400  $\text{cm}^{-1}$ , which were assigned to the  ${}^4T_{2g}(\text{F}) \leftarrow$

${}^4A_{2g}(\text{F})(\nu_1)$ ,  ${}^4T_{1g}(\text{F}) \leftarrow {}^4A_{2g}(\nu_2)$ , and  ${}^4T_{1g}(\text{P}) \leftarrow {}^4A_{2g}(\nu_3)$  transitions, respectively, for octahedral geometry.<sup>31</sup>

The previous data was used to calculate  $D_q$ , Racah parameter ( $B$ ), and  $\beta$  values. The value  $D_q$  was obtained directly from lower energy transition and was found to be 17,750  $\text{cm}^{-1}$ .  $B$  was 692  $\text{cm}^{-1}$ , which indicated that the magnitude of interelectronic repulsion between various levels in the gaseous ions and  $\beta$  was evaluated to 0.75. The complex of Mn(II) exhibited



Where-  
M = Mn(II), Co(II), Ni(II), Cu(II) and Zn(II).



Where-  
M = Cr(III), and Fe(III).

Scheme 2 Preparation of the complexes of metal salts.

three bands at 18,870, 22,980, and 25,300  $\text{cm}^{-1}$  due to the  ${}^4T_{1g}(G) \leftarrow {}^6A_{1g}(F)(\nu_1)$ ,  ${}^4T_{2g}(G) \leftarrow {}^6A_{1g}(F)(\nu_2)$ , and  ${}^4A_{1g}(G) \leftarrow {}^6A_{1g}(F)(\nu_3)$  transitions, respectively, in an octahedral environment.<sup>32</sup> The magnetic moment of the Fe(III) polychelate was 5.97  $\mu_B$ , corresponding to

five unpaired electrons and a high spin state of the Fe(III) ion. Three bands at 14,235, 20,740, and 24,780  $\text{cm}^{-1}$  corresponded to  ${}^4T_{1g}(G) \leftarrow {}^6A_{1g}(F)(\nu_1)$ ,  ${}^4T_{2g}(G) \leftarrow {}^6A_{1g}(F)(\nu_2)$ , and  ${}^4E_g(G) \leftarrow {}^6A_{1g}(F)(\nu_3)$ . This suggested an octahedral geometry. The Co(II) polychelate

TABLE II  
Important IR Spectra Bands and Their Assignments for the UFR Ligand and Its Metal Complexes with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) ( $\text{cm}^{-1}$ )

Assignments	UFR complexes							Ligand
	Cr(III)	Mn(II)	Fe(III)	Co(II)	Ni(II)	Cu(II)	Zn(II)	
NH (asymmetric and symmetric) and terminal OH	3250– 3450 (br)	3250– 3450 (br)	3250– 3450 (br)	3250– 3450 (br)	3250– 3450 (br)	3250– 3450 (br)	3250– 3450 (br)	3360– 3340 (br)
CH <sub>2</sub>								
Asymmetric	2962 (s)	2970 (s)	2964 (s)	2970 (s)	2963 (s)	2962 (s)	2950 (s)	2945 (s)
Symmetric	2850 (s)	2850 (s)	2850 (s)	2850 (s)	2850 (s)	2850 (s)	2850 (s)	2850 (s)
Amide I, mainly due to $\nu C=O$	1645 (s)	1640 (s)	1648 (s)	1642 (s)	1643 (s)	1640 (s)	1640 (s)	1676
$\delta$ HOH (water)	1610 (br)	1610 (br)	1600 (br)	1610 (br)	1620 (br)	1610 (br)	1600 (br)	1600
Amide II mixture of C–N and N–H def.; the contribution of NH def. is higher	1540 (s)	1545 (s)	1540 (s)	1545 (s)	1540 (s)	1540 (s)	1548 (s)	1565 (s)
$\delta$ CH bending due to –N–CH <sub>2</sub> –N	1471 (m)	1472 (m)	1470 (m)	1470 (m)	1471 (m)	1469 (m)	1469 (m)	1470 (m)
$\delta$ CH of CH <sub>2</sub> OH	1390 (s)	1385 (s)	1387 (s)	1385 (s)	1390 (s)	1390 (s)	1390 (s)	1380
$\delta$ C–N mode/amide III	1370/ 1260	1370/ 1261	1365/ 1262	1375/ 1260	1375/ 1262	1268/ 1261	1365/ 1260	1365/ 1260
$\delta$ OH in CH <sub>2</sub> OH	1015 (m)	1010 (m)	1000 (m)	1005 (m)	1005 (m)	1010 (m)	1010 (m)	1020 (m)
$\nu$ M–O	650 (s)	640 (s)	650 (s)	620 (s)	658 (s)	654 (s)		
$\nu$ M–N	550 (m)	545 (m)	540 (m)	564 (m)	564 (m)	543 (m)	650 (s) 540 (m)	

s = strong; br = broad; m = medium. def = deformation.

TABLE III  
Electronic Spectra, Magnetic Moments, Electrical Conductivities, and Ligands Field Parameters of the Complexes

Complex	Electrical conductivity ( $\Omega^{-1} \text{ cm}^2 \text{ mol}^{-1}$ )	$\mu_{\text{eff}}$ ( $\mu_{\text{B}}$ )	Frequency ( $\text{cm}^{-1}$ )	Assignment	$D_q$ ( $\text{cm}^{-1}$ )	$B$ ( $\text{cm}^{-1}$ )	$\beta$	$\beta \%$
$(\text{C}_8\text{H}_9\text{N}_4\text{O}_2\text{Cr} \cdot 2\text{H}_2\text{O})_n \cdot n\text{Cl}$	95	3.80	36,400 26,200 17,760	${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{A}_{2g}(\text{F})$ ${}^4\text{T}_{1g}(\text{F}) \leftarrow {}^4\text{A}_{2g}(\text{F})$ ${}^4\text{T}_{2g}(\text{F}) \leftarrow {}^4\text{A}_{2g}(\text{F})$	932	692	0.75	25
$(\text{C}_8\text{H}_9\text{N}_4\text{O}_2\text{Mn} \cdot 2\text{H}_2\text{O})_n$	10	6.17	25,300 22,980 18,870	${}^4\text{A}_{1g}(\text{G}) \leftarrow {}^6\text{A}_{1g}(\text{F})$ ${}^4\text{T}_{2g}(\text{G}) \leftarrow {}^6\text{A}_{1g}(\text{F})$ ${}^4\text{T}_{1g}(\text{G}) \leftarrow {}^6\text{A}_{1g}(\text{F})$	782	637	0.81	19
$(\text{C}_8\text{H}_9\text{N}_4\text{O}_2\text{Fe} \cdot 2\text{H}_2\text{O})_n \cdot n\text{Cl}$	120	5.97	24,780 20,740 14,235	${}^4\text{E}_g(\text{G}) \leftarrow {}^6\text{A}_{1g}(\text{F})$ ${}^4\text{T}_{2g}(\text{G}) \leftarrow {}^6\text{A}_{1g}(\text{F})$ ${}^4\text{T}_{1g}(\text{G}) \leftarrow {}^6\text{A}_{1g}(\text{F})$	1143	984	0.85	14
$(\text{C}_8\text{H}_9\text{N}_4\text{O}_2\text{Co} \cdot 2\text{H}_2\text{O})_n$	30	4.97	20,400 14,080 9,800	${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ ${}^4\text{A}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$ ${}^4\text{T}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})$	1100	787	0.71	29
$(\text{C}_8\text{H}_9\text{N}_4\text{O}_2\text{Ni} \cdot 2\text{H}_2\text{O})$	10	2.97	23,809 12,155 8,335	${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}(\text{F})$ ${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$ ${}^3\text{T}_{2g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})$	982	767	0.78	22
$(\text{C}_8\text{H}_9\text{N}_4\text{O}_2\text{Cu} \cdot 2\text{H}_2\text{O})_n$	30	2.2	25,000 15,380 13,560	Charge-transfer spectra ${}^2\text{E}_g \leftarrow {}^2\text{B}_{1g}$ ${}^2\text{E}_g \leftarrow {}^2\text{B}_{1g}$				
$(\text{C}_8\text{H}_9\text{N}_4\text{O}_2\text{Zn} \cdot 2\text{H}_2\text{O})_n$		Dimagnetic						

$\mu_{\text{eff}}$  = effective magnetic moment in BM.

had a magnetic moment of 4.97  $\mu_{\text{B}}$  due to four unpaired electrons and showed three bands at 9800, 14,080, and 20,400  $\text{cm}^{-1}$  due to  ${}^4\text{T}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})(\nu_1)$ ,  ${}^4\text{A}_{2g}(\text{F}) \leftarrow {}^4\text{T}_{1g}(\text{F})(\nu_2)$ , and  ${}^4\text{T}_{1g}(\text{P}) \leftarrow {}^4\text{T}_{1g}(\text{F})(\nu_3)$  transitions, respectively, which suggested an octahedral environment around the Co(II) ion. The  $\nu_3 : \nu_2$  value for the compound was 2.08, which occurred in the useful range 2.0–2.80 reported for the majority of Co(II) octahedral compounds.<sup>33</sup> The spectral parameters of the compounds were  $D_q = 1100 \text{ cm}^{-1}$ ,  $B' = 787 \text{ cm}^{-1}$ , and  $\beta = 0.81$ . The reduction in  $B$  from the free ion value of 971 to 787  $\text{cm}^{-1}$  and the value of  $\beta$  (0.81) indicated the presence of covalence in the compound. Ni(II) showed three bands at 8335, 12,155, and 23,808  $\text{cm}^{-1}$  assigned to the spin allowed transitions  ${}^3\text{T}_{2g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})(\nu_1)$ ,  ${}^3\text{T}_{1g}(\text{F}) \leftarrow {}^3\text{A}_{2g}(\text{F})(\nu_2)$ , and  ${}^3\text{T}_{1g}(\text{P}) \leftarrow {}^3\text{A}_{2g}(\text{F})(\nu_3)$ , respectively, in an octahedral geometry. The  $\nu_1 : \nu_2$  value for this compound was 1.64 and corresponded to the usual range (1.6–1.82) reported for the octahedral geometry of Ni(II) compounds.<sup>32</sup>

The spectral parameters were  $D_q = 982 \text{ cm}^{-1}$ ,  $B' = 767 \text{ cm}^{-1}$ , and  $\beta = 0.73$ ; the covalency parameter  $\beta^0$  value was a 27% reduction of  $B$  from the free-ion value of 1056–767  $\text{cm}^{-1}$  and a  $\beta$  value of 0.73 indicated the covalent nature of the compound. The previous discussion indicates an octahedral geometry around the central metal ion in all of complexes that accounted for the occupation of two coordinating sites by  $\text{H}_2\text{O}$  out of six in making the octahedral environment. The electronic spectra of the Cu(II) complexes exhibited bands at 13,650, 15,380, and 25,000  $\text{cm}^{-1}$ , which indicated a distorted octahedral geometry. Thus, the electronic spectral study further supported the structure proposed for the polymeric complexes in Scheme 2.

### ${}^1\text{H-NMR}$ spectra

The  ${}^1\text{H-NMR}$  spectral data and their assignments are given in Figure 2. The  ${}^1\text{H-NMR}$  spectral data of the ligand exhibited signals at 2.5, 4.3, 5.5, and 6.8 ppm, which

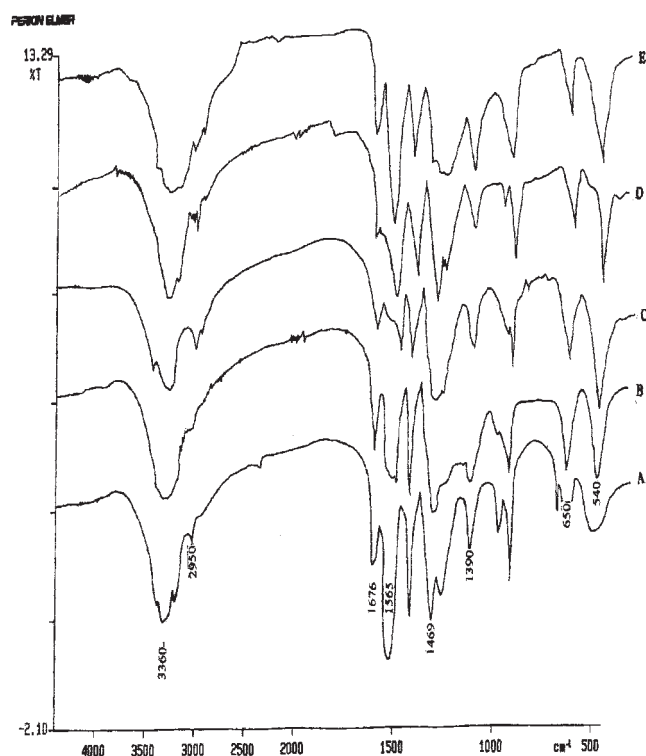


Figure 1 FTIR spectra of UFR and its metal complexes: (A) UFR, (B) UFR–Fe(III), (C) UFR–Co(II), (D) UFR–Ni(II), and (E) UFR–Cu(II).

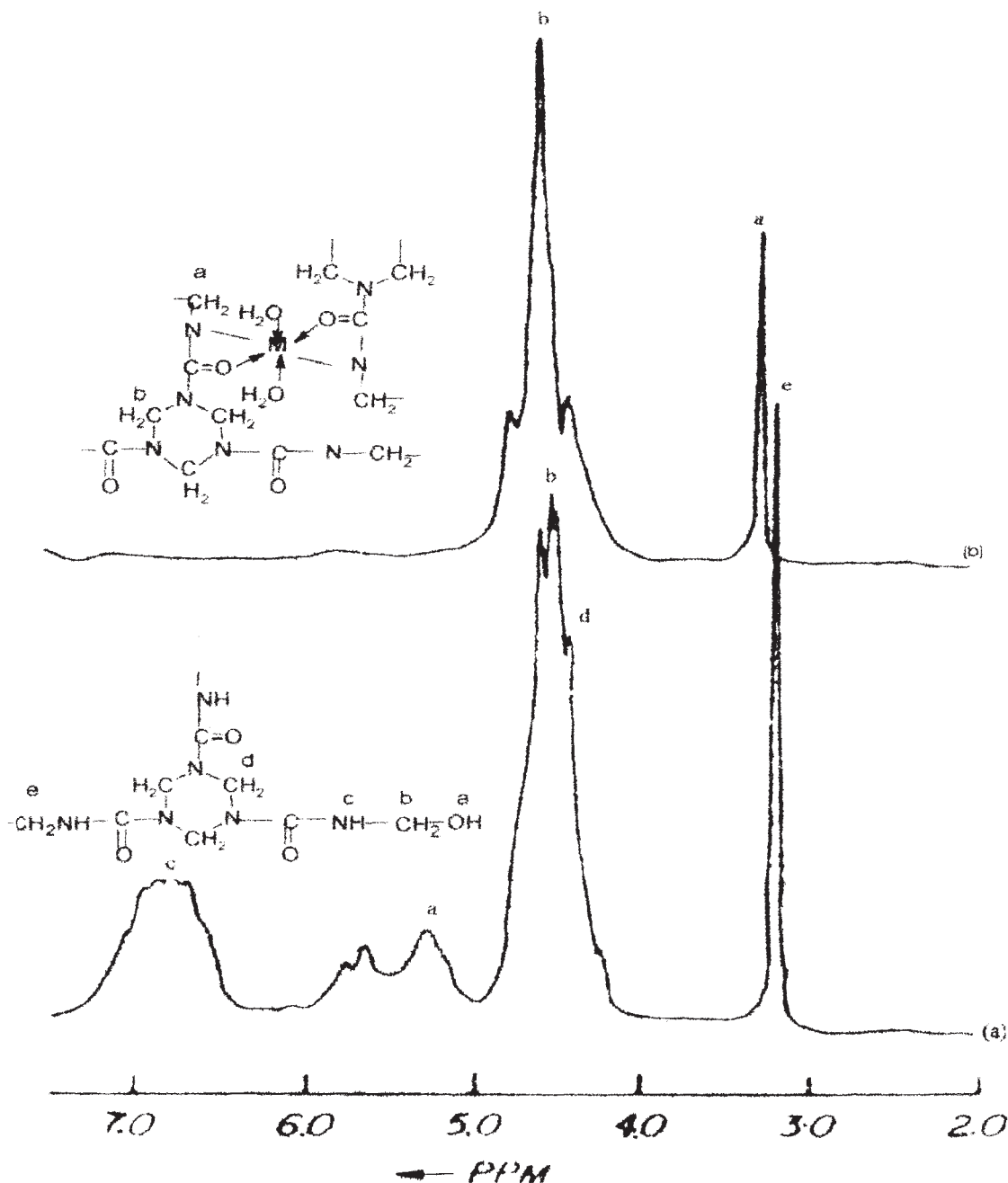


Figure 2  $^1\text{H-NMR}$  spectra of (a) UFR and (b) its complexes.

showed the presence of  $-\text{N}(\text{CH}_2)_2$ ,  $>\text{N}-\text{CH}_2-\text{N}<$ ,  $\text{O}=\text{C}-\text{NH}_2$ , and  $\text{O}=\text{C}-\text{NH}-$ , respectively.<sup>34</sup> On complexation, the signals shifted downfield, and  $\text{O}=\text{C}$ ,  $-\text{NH}-$  groups signals were more shifted, which suggested the involvement of these groups in coordination.

#### Thermal analysis

The thermal decomposition of these coordination polymers was studied by the thermogravimetric method. The thermogravimetry curve of UF and its complexes are depicted in Figure 3, and the thermal

analytical data are listed in Table IV. All of the compounds were highly heat resistant and did not decompose easily, even at high temperatures.

The thermogravimetry curves confirmed the presence of water molecules in all of the chelates, except that of  $\text{Cu}(\text{II})$ , according to the literature.<sup>35</sup> That water was eliminated below  $150^\circ\text{C}$  may have been due to its coordination to the metal atoms in the chelates. In this study, the removal of water from the  $\text{Ni}(\text{II})$  and  $\text{Mn}(\text{II})$  chelates was complete up to  $130^\circ\text{C}$ ; this water was probably crystalline water. The removal of water took place from the  $\text{Cr}(\text{III})$  and  $\text{Fe}(\text{III})$  chelates above  $150^\circ\text{C}$ .

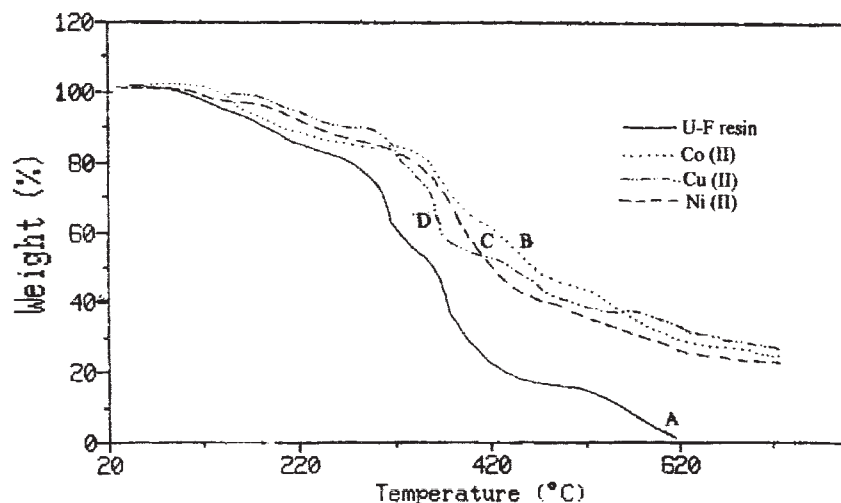


Figure 3 TGA of UFR and its metal complexes: (A) UFR, (B) UFR-Co(II), (C) UFR-Ni(II), and (D) UFR-Cu(II).

Most of the polychelates started to decompose with weight losses from 7 to 10 wt % at 200°C, which was due to the elimination of water molecules. The thermogram in Figure 3 indicates that the decomposition of the polychelates was very slow in the initial state, but above 300°C, the weight loss became fast. The thermal data indicated that the thermal stability of the polychelates were in the order Ni(II), Cu(II), Mn(II), Cr(III), and Fe(III); moreover, the decomposition was completed at about 750°C in all of coordination polymers. The polychelates were thermally stable up to 300°C.

#### Antibacterial activity studies

The results of the antibacterial activity studies were expressed as inactive, mildly active, moderately active, and highly active and are shown in Table V as reported in literature.<sup>36</sup> The complexes of Co(II) and Cu(II) exhibited high activity (18 and 16 mm, respectively), the ligand showed mild activity (5 mm), and the others complexes were moderately active (12, 10, and 13 mm). All of the polychelates showed lower activity than ciprofloxacin and kanamycin, but the activity of the Co(II) complexes against *E. coli* was equal to that of ampicillin. The compounds of Fe(III)

and Ni(II) were highly active (15 and 17 mm, respectively) against *S. aureus*. The complexes of Mn(II) and Zn(II) displayed promising activity (14 and 13 mm, respectively) against *E. coli*. The Co(II), Cu(II), and Ni(II) complexes also showed moderate activity (14, 13, and 14 mm, respectively) against *P. vulgaris*. All of the metal polychelates {excluding Co(II) polychelates} were moderately active against *B. mega*. The antibacterial activity of these polychelates was due to the presence of nitrogen and oxygen donor groups. It has been suggested that compounds with N and O donor systems 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. Coordination reduces the polarity of the central ion, and because partial shearing of its positive charge with the donor groups and possible  $\pi$  electron delocalization within the chelate ring also increases the lipophilic nature of the central atom, this favors its permeation through the lipid layer of the membrane.

The results of antibacterial activity reveal that the Cu(II) polychelate showed the highest antibacterial activity against *B. subtilis*. This result may have been due to the higher stability constant of Cu(II) than the other polychelates.<sup>37</sup> According to the stability con-

TABLE IV  
Thermal Behavior of the Coordination Polymers

Compound	Weight loss percentage at certain temperatures (°C)						
	150	200	300	400	500	600	700
$(C_8H_9N_4O_2Cr \cdot 2H_2O)_n \cdot nCl$	6	10	22	35	68	68	85
$(C_8H_9N_4O_2Mn \cdot 2H_2O)_n$	8	12	18	35	65	77	80
$(C_8H_9N_4O_2Fe \cdot 2H_2O)_n \cdot nCl$	6	10	15	30	62	77	82
$(C_8H_9N_4O_2Co \cdot 2H_2O)_n$	4	11	20	35	60	72	83
$(C_8H_9N_4O_2Ni \cdot 2H_2O)_n$	3	9	17	30	59	65	84
$(C_8H_9N_4O_2Cu \cdot 2H_2O)_n$	—	8.5	15	38	55	65	83



**TABLE V**  
**Antibacterial Activity of UFR Ligand and Its Polychelates with the Metal Ions Mn(II), Fe(III), Co(II), Ni(II), and Cu(II)**

Compound	Antibacterial activity <sup>a</sup>				
	<i>E. coli</i>	<i>S. aureus</i>	<i>B. megaterium</i>	<i>P. vulgaris</i>	<i>B. subtilis</i>
C <sub>8</sub> H <sub>11</sub> N <sub>4</sub> O <sub>2</sub>	5	8	7	6	10
(C <sub>8</sub> H <sub>9</sub> N <sub>4</sub> O <sub>2</sub> Mn · 2H <sub>2</sub> O) <sub>n</sub>	12	11	14	13	11
(C <sub>8</sub> H <sub>9</sub> N <sub>4</sub> O <sub>2</sub> Fe · 2H <sub>2</sub> O) <sub>n</sub> · nCl	10	15	12	12	14
(C <sub>8</sub> H <sub>9</sub> N <sub>4</sub> O <sub>2</sub> Co · 2H <sub>2</sub> O) <sub>n</sub>	18	10	9	14	13
(C <sub>8</sub> H <sub>9</sub> N <sub>4</sub> O <sub>2</sub> Ni · 2H <sub>2</sub> O) <sub>n</sub>	13	17	11	12	15
(C <sub>8</sub> H <sub>9</sub> N <sub>4</sub> O <sub>2</sub> Cu · 2H <sub>2</sub> O) <sub>n</sub>	16	14	13	14	19
DMSO	—	—	—	—	—
Ciprofloxacin	25	24	20	22	22
Ampicillin	18	22	15	20	20
Kanamycin	26	25	22	26	25

0–5 = inactive; 5–10 = mildly active; 10–15 = moderately active; >15 = highly active. Ciprofloxacin, ampicillin, and kanamycin were used as standard drugs. DMSO was used as a control.

<sup>a</sup> Zone of inhibition in 0–25 mm at a concentration of 25 µg/mL.

stant, the Cu(II) ion was made up of stronger interactions with N and O donor atoms, by which its lipophilic nature was increased. All of the polychelates showed lower antibacterial activities than the known antibiotics, namely, ciprofloxacin, ampicillin, and kanamycin, in similar conditions.

### CONCLUSIONS

Polychelates of UFR and complexes with Cr(III), Mn(II), Fe(III), Co(II), Ni(II), Cu(II), and Zn(II) metal ion in acidic medium were prepared successfully. These polychelates showed octahedral geometries, as depicted by the electronic spectra, and were thermally stable up to 300°C. The fairly good antibacterial activities exhibited by these metal polychelates may help them find potential application as effective antibacterial coating materials.

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