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Synthesis, characterization and biocidal activities of Schiff base polychelates containing polyurethane links in the main chain

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ABSTRACT

The concept of combining metallo-polymers with urethanes offers a versatile approach for the synthesis of new polymeric materials. Polyurethane containing transition metals was synthesized by the reaction of Schiff base metal complex with toluene 2,4 diisocyanate. The proposed structures were confirmed by elemental analysis, ¹H NMR, ¹³C NMR and FT-IR. The geometry is determined by UV–Visible spectra and magnetic moment measurements, which reveals that the Mn(II), Co(II) and Ni(II) complexes have octahedral geometry while square planer geometry is reported for Cu(II) and tetrahedral for Zn(II) complex. The antimicrobial activities are determined using the agar well diffusion method with *Staphylococcus aureus, Escherichia coli, Bacillus subtilis* (bacteria), *Aspergillus niger, Candida albicans* and *Aspergillus flavus* (yeast). All the polymeric metal complexes show comparatively good biocidal activity, which is further enhanced after polymerization.

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Introduction

In polymer science, there is continuous requirement for the development of materials that are stronger, durable and inhibit microbes. From the last few years, extensive efforts have been made, both in academics and in industry to develop the Schiff base polymers, as they possess high thermal stability, complex forming ability and semiconducting properties. The incorporation of transition metals into polymeric Schiff bases not only affects their physical characteristics, but also their chemical activity [1]. Complexation of a metal ion to functional polymeric ligand changes its activity due to polymeric effect, which has led to a variety of applications such as aqueous thickeners, impregnates, textile seizers, adhesives, additives, resins and catalysts [2-4]. Their catalytic actions in a variety of organic reactions have been known for a long time [5,6]. Polyurethanes are the most versatile family of polymeric materials due to the fact that they are used in many forms and find their way into many applications [7,8]. Polyurethane coatings mainly moisture-cured are applied on products to improve their appearance, lifespan, scratch and corrosion resistance [9,10]. Modification of polyurethanes by incorporating metal and functional groups are used extensively to improve various typically desired properties of materials, such as enhanced thermal stability, fire redundancy, flexibility and solubility [11]. These are also extensively used in biological applications such as artificial

heart, blood pumps and valves. Several metallo-polymers containing metals in the backbone of the polymer chain have already been prepared [12,13]. So the synthesis and structural studies of new compounds of this type have much interest as a first step in the search for new Schiff base polymers as potential antimicrobial agents. Keeping the foregoing facts in mind and in continuation to our research work in this domain [14–17], novel Schiff base polyurethane containing transition metal ions in the main chain has been synthesized, and their spectral, magnetic and antimicrobial properties have been discussed.

Experimental

Materials

Semicarbazide and toluene-2,4-diisocyanate, salicylaldehyde, formaldehyde (37–41%) and dimethylsulfoxide were obtained from S.D. fine chemicals and Merck India, while Manganese(II) acetate tetrahydrate, cobalt(II) acetate tetrahydrate, nickel(II) acetate tetrahydrate, copper(II) acetate monohydrate and zinc(II) acetate dihydrate were purchased from Qualigens fine chemicals, India. These chemicals were all used as received.

Synthesis

Synthesis of monomeric ligand

Semicarbazide (0.01 mol, 1.11 g) was dissolved in minimum amount of distilled water in 250-mL three-necked round-bottom flask and was attached to the ice-cooled reflux condenser fitted

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Fig. 1. Monomeric ligand [SSF].

over the magnetic stirrer and maintained at 50 °C. Salicylaldehyde (0.02 mol, 2.44 mL) was dissolved in 20 mL ethanol and added drop wise by a burette to the semicarbazide solution, and the reaction mixture was stirred continuously for about 2 h. Solvent was removed by filtration, washed with distilled H₂O and diethyl ether several times and finally dried at 30–40 °C in vacuum oven for 8 h to give Schiff base semicarbazone (2.15 g, 76.2% yield). Its melting point is 110 °C.

The dried Schiff base (2.15 g, 0.01 mol) was further dissolved in DMSO and heated at 60 °C. Formaldehyde (37–40%) (0.15 mL, 0.02 mol) was added to this hot solution of Schiff base in the three-necked round-bottom flask attached to a water condenser, the reaction mixture was further heated at this temperature for 2 h. Monomeric ligand [SSF] was obtained after washing it with distilled water, diethyl ether and drying at 40 °C. Its melting point was approx. 115 °C. Proposed structure of monomeric ligand is represented in Fig. 1.

IR (KBr): 3424 cm⁻¹(sb, OH), 1173 cm⁻¹(m, C–O), 1720 cm⁻¹(s, C=O), 1566 cm⁻¹(m, CH=N), 3389 cm⁻¹(mb, NH), 1626 cm⁻¹(w, NH).

(sb = strong and broad, m = medium, mb = medium and broad, w = weak).

¹H-NMR: 7.89 ppm(2H, CH=N), 2.7 ppm(4H, CH₂), 10.06 ppm(4H, OH), 7.02 ppm(1H, NH), 6.12–6.70 ppm(6H, C_6H_3) for the azomethine linkage, methylene, hydroxyl, NH and phenyl groups, respectively.

Synthesis of monomeric metal complexes

A series of transition metal complexes of Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) were prepared from the monomeric ligand [SSF]. A typical procedure for the preparation of manganese monomeric complex is as follows:

The monomeric Schiff base [SSF] was dissolved in 20 mL DMSO and heated at 70 °C in a round-bottom flask fitted to an ice-cooled condenser. Manganese(II) acetate tetrahydrate (1.27 g, 0.01 mol) dissolved in DMSO was added to this hot solution and refluxed for 6–7 h, slight change in color appears. It was precipitated in distilled H₂O, filtered and washed several times with distilled H₂O and diethyl ether. It was oven-dried at 45 °C for 8–10 h to obtain the monomeric metal complex of manganese [SSF-Mn(II)] of light yellow color.

Similar procedure was used to isolate the Co(II), Ni(II), Cu(II) and Zn(II) complexes. Analytical data of these complexes are given below:

 $\label{eq:constraint} \begin{array}{ll} \mbox{[} C_{17} \mbox{H}_{19} \mbox{N}_{3} \mbox{O}_{7} \mbox{Mn(II)}\mbox{]:} & \mbox{C}^{\ast} = 47.23 & (46.21), & \mbox{H}^{\ast} = 4.43 & (3.98), \\ \mbox{N}^{\ast} = 9.72 & (9.01), & \mbox{Mn(II)}^{\ast} = 12.70 & (13.11); & \mbox{Call}. \end{array}$

IR (KBr): 1161 cm⁻¹ (w, C–O), 1720 cm⁻¹ (m, C=O), 1551 cm⁻¹ (m, CH=N), 3376 cm⁻¹ (m, ν NH), 1628 cm⁻¹ (w, δ NH), 515 cm⁻¹ (m, M–O), 447 cm⁻¹ (m, M–N), M–H₂O(rocking)=980 cm⁻¹, M–H₂O(wagging)=742 cm⁻¹.

 $[C_{17}H_{19}N_3O_7Co(II)]$: C% = 46.80 (45.10), H% = 4.39 (3.11), N% = 9.63 (8.52), Co(II)% = 13.50 (12.72); Cal.(Found).

IR (KBr): 1160 cm⁻¹ (w, C–O), 1721 cm⁻¹ (m, C=O), 1550 cm⁻¹ (m, CH=N), 3380 cm⁻¹ (m, ν NH), 1625 cm⁻¹ (w, δ NH), 520 cm⁻¹ (m, M–O), 449 cm⁻¹ (m, M–N), M–H₂O(rocking)=981 cm⁻¹, M–H₂O(wagging)=746 cm⁻¹.

 $[C_{17}H_{19}N_3O_7Ni(II)]$: C% = 46.72 (44.98), H% = 4.39 (3.61), N% = 9.63 (8.24), Ni(II)% = 13.46 (12.90); Cal.(Found).

IR (KBr): 1162 cm⁻¹ (w, C–O), 1722 cm⁻¹ (m, C=O), 1548 cm⁻¹ (m, CH=N), 3375 cm⁻¹ (m, vNH), 1626 cm⁻¹ (w, δ NH), 521 cm⁻¹ (m, M–O), 448 cm⁻¹ (m, M–N), M–H₂O(rocking)=981 cm⁻¹, M–H₂O(wagging)=749 cm⁻¹.

 $[C_{17}H_{15}N_3O_5Cu(II)]$: C% = 50.41 (51.21), H% = 3.73 (3.06), N% = 10.37 (11.71), Cu(II)% = 15.69 (14.98); Calc. (Found).

IR (KBr): 1159 cm⁻¹ (w, C–O), 1720 cm⁻¹ (m, C=O), 1548 cm⁻¹ (m, CH=N), 3382 cm⁻¹ (m, ν NH), 1620 cm⁻¹ (w, δ NH), 525 cm⁻¹ (m, M–O), 452 cm⁻¹ (m, M–N).

(m = medium, w = weak).

 $\label{eq:constraint} \begin{array}{ll} \textbf{[C_{17}H_{15}N_3O_5Zn(II)]:} & C\% = 50.20 & (48.96), & H\% = 3.71 & (3.01), \\ N\% = 10.33 & (9.27), & Zn(II)\% = 16.07 & (15.11); & Cal.(Found). \end{array}$

IR (KBr): 1161 cm⁻¹ (w, C–O), 1720 cm⁻¹ (m, C=O), 1552 cm⁻¹ (m, CH=N), 3377 cm⁻¹ (m, vNH), 1626 cm⁻¹ (w, δ NH), 516 cm⁻¹ (m, M–O), 450 cm⁻¹ (m, M–N).

(m = medium, w = weak).

Elemental analysis and FT-IR spectral data suggest that the disappearance of phenolic OH peak and shifting of azomethine and hydroxyl carbon peak to lower frequency is due to the coordination of metal to the hydroxyl oxygen and azomethine nitrogen. Proposed structure for monomeric metal complexes has been provided in Fig. 2.

Synthesis of metal containing polyurethane [SPU-M(II)]

Above prepared monomeric metal complex, as for Mn(II), 2.87 g, 0.01 mol, was dissolved in DMSO and taken in a three-necked round-bottom flask. The temperature of the flask was set up to 80 °C and stirred magnetically. Then, toluene 2,4-diisocyanate (TDI) (0.01 mol, 1.74 mL) was added to this solution in the presence of 2–3 drops of di-*n*-butyltindilaurate (DBTDL) as catalyst. The reaction mixture was stirred at this temperature for 6 h. It was precipitated and washed with distilled water, then with diethyl ether and dried at room temperature for 24 h to give metal-chelated polyurethane [SPU-Mn(II)] in 68.9% yield. Synthetic route to metal containing polyurethane is represented in Scheme 1.

Preparation of microbial culture

The antimicrobial activities of the metal containing polyurethanes were tested against various microorganisms in DMSO as the solvent. The sample concentration was 50 μ g/mL for antibacterial studies and 100 μ g/mL for antifungal studies. The antibacterial activity was screened against *Staphylococcus aureus*, *Bacillus subtilis* (Gram-positive) and *Escherichia coli* (Gram-negative), while antifungal screening was done against *Aspergillus niger*, *Candida albicans* and *Aspergillus flavus*.

Bacterial strains were nourished in a nutrient broth (Difco) and yeasts in malt extract broth (Difco) and incubated for 24 and 48 h, respectively. According to the agar-diffusion method [18,19], bacteria were incubated on Mueller–Hinton agar and yeast on Sabouraud dextrose agar. The wells were dug in the media with the help of a sterile steel borer, and then 0.1 mL of each sample was introduced in the corresponding well. Standard drugs, kanamycin and



M"=Mn(II),Co(II) and Ni(II) M'=Cu(II) and Zn(II) X =H₀O

Fig. 2. Proposed structure of monomeric metal complexes [SSF-M(II)].



Scheme 1. Synthetic route to metal containing polyurethane [SPU-M(II)].

miconazole, were taken as control for bacteria and fungi, respectively. After incubation, the zone of inhibition was measured, and according to the zone of inhibition and clarity of the zone, results are represented as inactive, mildly active, moderately active and highly active.

Measurements

Elemental analysis of C, H and N was carried out on an elemental analyzer system GmbH Vario ELIII, while the percentage of metal was obtained by complexometric titration with EDTA after digestion with conc. HNO₃ at room temperature. The magnetic susceptibility measurements are recorded on a vibrating sample magnetometer model 155 at room temperature. FT-IR spectra are obtained on a Perkins Elmer IR spectrophotometer model 621 using KBr pellets. Proton and carbon nuclear magnetic resonance spectra (¹H NMR and ¹³C NMR) are 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 UV–Visible spectra are carried on a Perkins Elmer Lambda EZ-201 spectrophotometer using DMSO as a solvent.

Results and discussion

The monomeric ligand and its metal polychelates are synthesized by the reaction of semicarbazide with salicylaldehyde, and then formaldehyde is attached to the formed Schiff base. Here, one thing is to be taken care of that the ratio of formaldehyde to Schiff base must be 1:1 in order to avoid polymerization [20]. The ligand formed is tetradentate, with oxygen of salicylaldehyde and nitrogen of semicarbazide being involved in coordination. All the metal complexes are hydrated with the exceptions of the Cu(II) and Zn(II) complexes. Polyaddition of toluene 2,4-diisocyanate (TDI) with metal-chelated Schiff base [SSF-M(II)] is done in the presence of DBTDL to obtain metal-chelated polyurethane [SPU-M(II)]. Reaction between diols and diisocyanates is catalyzed by DBTDL, and it takes place via the formation of a ternary complex between the reagents and the catalyst [21]. To avoid cross-linking of the polymers, the mole ratio of mixtures of diols and diisocyanates is taken as 1:1. The elemental analysis data of all the polymers show that the experimentally determined percentage values of C, H, N and M are within the calculated values, results being depicted in Table 1.

Solubility data

The synthesized Schiff base polychelates [SSF-M(II)] and polyurethanes containing metal [SPU-M(II)] are soluble in DMSO and DMF, while these are insoluble in THF and other common organic solvents such as benzene, toluene, ethanol, methanol and water.

FT-IR analysis

The IR spectrum of Schiff base [SSF] shows a characteristic absorption peak at 1566 cm⁻¹ for the formed azomethine linkage, while a very broad absorption peak is observed at 3424 cm⁻¹ for the OH group with a small shoulder which is for the overlapping of N—H peak with OH peak. Thereafter, Mn(II), Co(II), Ni(II), Cu(II) and Zn(II) complexes are prepared. The IR spectra of the metal complex show two additional peaks in the range of 447-452 and 515-525 cm⁻¹ due to M—N and M—O bond formation while azomethine band shifts slightly to lower frequency (15-20 cm⁻¹), revealing the complexation of metal ion to ligand. Coordinated water peaks appear at 980-982 cm⁻¹ and 742-747 cm⁻¹.

IR absorption bands for SPU-M(II) are illustrated in Table 2. The IR spectrum show peaks at 1720 cm⁻¹ due to carbonyl stretching (-C=0) [22] and the absorption band at 1159–1161 cm⁻¹ due to phenolic (C–O). The peak at 3374–3382 cm⁻¹ is due to –NH stretching and at 1628–1620 cm⁻¹ due to NH bending. Carboxylate ions (-COO) give two broad peaks in the range of 1552–1559 cm⁻¹ and 1462–1466 cm⁻¹. The characteristic C=O peak is observed at 1720 cm⁻¹ while and CH=N peaks observed at 1566 cm⁻¹ [23] is shifted to 15–25 cm⁻¹ to lower frequency after chelation, indicating that nitrogen is involved in bond formation with the metal. The coordination of metal ion to the polymeric ligand is supported by the appearance of M–N, M–O and M–H₂O stretching vibrations at 447–452 cm⁻¹, 515–525 cm⁻¹ and 980–982 cm⁻¹(rocking), 742–747 cm⁻¹(wagging) for coordinated water, respectively [24].

NMR analysis

¹H NMR spectrum of SPU-Zn(II) is shown in Fig. 3. The spectrum shows signals for NH proton of the urethane group (-NH-C= O-O-) at around 9.05 ppm. Resonance signals in the range of 6.40–7.96 ppm appeared due to the aromatic protons of TDI and benzene ring. The peak at 8.14 is for the proton linked to the carbon of salicylaldehyde (-CH=N-) [25]. NH- protons of semicarbazide appear at 7.05 ppm. Methyl and methylene protons appear at 2.3 and 2.9 ppm, respectively.

¹³C-NMR spectrum of SPU-Zn(II) is shown in Fig. 4. The aromatic carbons of urethane group show peaks at 137.93, 119.06 and 115.99 ppm [26]. Methyl and methylene carbons show peaks at 17.32 ppm and 19.20 ppm. Carbonyl carbon of urethane group (NHCOO—) show peak at 152.68 ppm. Five carbons of benzene ring show peaks in the range of 120.11–130.02 ppm [27], while the

Table	1
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Elemental analysis data.

Compound abbreviation	Empirical formula	Elemental analysis ^a (%)			
		Carbon	Hydrogen	Nitrogen	Metal
Semicarbazone Schiff base	$C_{15}H_{13}N_3O_3$	66.44 (65.19)	4.26 (3.11)	13.67 (12.54)	-
SSF	C ₁₇ H ₁₇ N ₃ O ₅	59.46 (58.21)	4.99 (3.56)	12.23 (11.71)	-
SPU-Mn(II)	$C_{26}H_{21}N_5O_7-Mn(II)-(H_2O)_2$	51.49 (50.24)	4.15 (4.05)	11.54 (10.98)	9.05 (8.83)
SPU-Co(II)	C ₂₆ H ₂₁ N ₅ O ₇ -Co(II)-(H ₂ O) ₂	51.15 (50.26)	4.12 (3.22)	11.47 (10.11)	9.65 (9.11)
SPU-Ni(II)	C ₂₆ H ₂₁ N ₅ O ₇ -Ni(II)-(H ₂ O) ₂	51.17 (50.54)	4.12 (4.00)	11.47 (11.09)	9.61 (9.17)
SPU-Cu(II)	$C_{26}H_{21}N_5O_7$ -Cu(II)	53.93 (53.22)	3.65 (3.45)	12.09 (11.85)	10.97 (10.61)
SPU-Zn(II)	$C_{26}H_{21}N_5O_7$ -Zn(II)	53.76 (53.15)	3.64 (3.04)	12.05 (11.74)	11.25 (10.93)

(Observed) value.

^a Calculated value.

Table 2

Important FT-IR spectral bands of metal containing polyurethane with their assignments.

Assignments	SPU-Mn(II)	SPU-Co(II)	SPU-Ni(II)	SPU-Cu(II)	SPU-Zn(II)
C=O (urethane) stretching Bending	1556(s) 1462(m)	1559(s) 1465(m)	1552(s) 1466(m)	1558(s) 1462(m)	1552(s) 1466(m)
N—H (stretching) bending	3376(s) 1628(w)	3374(s) 1622(w)	3374(s) 1625(w)	3382(s) 1620(w)	3380(s) 1626(w)
C=O (carbonyl)	1720(s)	1720(s)	1720(s)	1720(s)	1720(s)
CH=N (azomethine)	1551(s)	1546 (s)	1549 (s)	1541 (s)	1546(s)
C–O (phenolic)	1161(w)	1160(w)	1160(w)	1159(w)	1159(w)
М—О	515(s)	518(s)	522(s)	525(s)	520(s)
M—N	452(s)	450(s)	447(s)	452(s)	452(s)
$M-H_2O$ (rocking)	980	982	982	-	
(wagging)	742	745	747	-	-

(s) Strong, (m) medium, (b) broad, (w) weak.



characteristic peak of phenolic carbon is observed at 155.76 ppm. The azomethine carbon (-CH=N-) show peak at 137.64 ppm.

UV-Visible analysis

The electronic spectra of all the synthesized polymers are recorded in DMSO solution. Various crystal field parameters 10Dq, *B*, β and β° have been calculated. The magnetic moment of SPU-Mn(II) is 5.6 B.M. corresponding to five unpaired electrons. The electronic spectrum of this complex exhibits three absorption bands at 14,380, 19,760 and 24,650 cm⁻¹, which are assigned to ${}^{4}T_{1g} \leftarrow {}^{6}A_{1g}$, ${}^{4}T_{2g} \leftarrow {}^{6}A_{1g}$ and ${}^{4}E_{g} \leftarrow {}^{6}A_{1g}$ transitions, respectively, suggesting the octahedral geometry [28]. The 10Dq and *B* are 3944.3 and 788.8 cm⁻¹, respectively, while β and β° values are 0.82 and 0.18, respectively. These values indicate the covalent nature of the compound. The polymer metal complex of Co(II) had the magnetic moment of 4.80 B.M. due to four unpaired electrons and electronic transitions at 9580, 17,586 and 19,960 cm⁻¹ corresponds to ${}^{4}T_{2g} \leftarrow {}^{4}T_{1g}$, ${}^{4}A_{2g} \leftarrow {}^{4}T_{1g}$ and ${}^{4}T_{1g}(P) \leftarrow {}^{4}T_{1g}$ transitions, respectively [29]. The spectral parameters 10Dq = 7742.7 cm⁻¹, *B* = 860.3 cm⁻¹, β = 0.88 and β° = 0.12 suggest the covalent nature of the compound. The magnetic moment of SPU-Ni(II) complex is 2.86 B.M. Three bands are observed at 8580, 12,650 and 23,380 cm⁻¹ corresponding to ${}^{3}T_{2g} \leftarrow {}^{3}A_{2g}$, ${}^{3}T_{1g} \leftarrow {}^{3}A_{2g}$ and ${}^{3}T_{1g}(P) \leftarrow {}^{3}A_{2g}$ transitions, respectively. Spectral parameters 10Dq = 8904.0 cm⁻¹, *B* = 742.2 cm⁻¹, β = 0.68 and β° = 0.32 are suggestive of the octahedral structure of the complex [30]. SPU-Cu(II) has magnetic moment of 2.18 B.M. and shows bands at 15,570 and 25,365 cm⁻¹ assigned to ${}^{2}A_{1g} \leftarrow {}^{2}B_{1g}(F)$ and charge transfer band, respectively, indicative of square planer geometry. The SPU-Zn(II) is diamagnetic and no d–d transition being observed.



Antimicrobial activity

Polymeric ligand [SSF] and its polymeric metal complexes [SPU-M(II)] are screened for their antibacterial activity against *S. aureus, E. coli* and *B. subtilis* and antifungal activity against *A. niger, C. albicans* and *A. flavus*, and the results are presented in Fig. 5. A general trend can be seen that the Cu(II) and Zn(II)-chelated polymer complexes are more active than other metal-containing polymers. SPU-Cu(II) and SPU-Zn(II) show high activity against all the tested bacteria. SPU-Cu(II) is highly active against *A. niger* and moderately active against *C. albicans*, and *A. flavus*, SPU-Zn(II) is highly active against *C. albicans* and *A. flavus*, but SPU-Co(II) is highly active against these fungi while other polychelates show mild activity. SPU-Co(II) is highly active against *E. coli*, while other polychelates are mildly to moderately active.

It is also evident that all the polymer metal complexes are more active than the polymeric ligand. This enhancement in the activity is rationalized on the basis of the structures by possessing an additional azomethine (C=N) linkage, which imparts in elucidating the mechanism of transamination and resamination reactions in biological system [31]. It has also been suggested that the ligands with nitrogen and oxygen donor systems might inhibit enzyme production, since the enzymes that require these groups for their activity appear to be especially more susceptible to deactivation by the metal ions upon chelation. Chelation reduces the polarity [32] of



Fig. 5. Antimicrobial activity analysis.

the metal ion mainly because of the partial sharing of its positive charge with the donor groups and possibly the π -electron delocalization within the whole chelate ring system thus formed during coordination. This process of chelation thus increases the lipophilic nature of the central metal atom, which in turn favors its permeation through the lipoid layer of the membrane. This in turn is responsible for increasing the hydrophobic character and liposolubility of the molecule in crossing cell membrane of the microorganism, and hence enhances the biological utilization ratio and activity of the testing drug/compound.

Conclusion

Polyurethanes containing Schiff base and metal in the main chain underwent addition polymerization giving metal containing polyurethanes in good yield. Both the ligand and metal complexes are insoluble in benzene, toluene, ethanol, methanol and H₂O but soluble in DMSO and DMF. Besides chelation, other factors such as solubility, stability influenced by metal ion may be responsible for enhanced antibacterial activity of the polychelates. Functional moieties such as the azomethine group and urethane group exhibit potential biological activities that may be responsible for the enhanced hydrophobic and lipophilic character of the molecule to cross-link the cell membrane of the microorganism and increase the biocidal activity of the polychelate.

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