

Synthesis and Characterization of Schiff Base Metal Complexes and Reactivity Studies with Maleimide Epoxy Resin

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A novel maleimide epoxy containing Co(II), Ni(II) and Cu(II) ions have been synthesized by curing maleimide epoxy resin (MIEB-13) and Co(II), Ni(II) and Cu(II) complexes of macrocyclic bis-hydrazone Schiff base. The Schiff base was synthesized by reacting 1,4-dicarbonyl phenyl dihydrazide with 2,6-diformyl-4-methyl phenol. The Schiff base and its Co(II), Ni(II) and Cu(II) complexes have been characterized by elemental analyses, spectral (IR, ¹H NMR, UV-vis., FAB mass, ESR), thermal and magnetic data. The curing reaction of maleimide epoxy compound with metal complexes was studied as curing agents. The stability of cured samples was studied by thermo-gravimetric analyses and which have excellent chemical (acid/alkali/solvent) and water absorption resistance. Further, the scanning electron microscopy (SEM) and definitional scanning calorimetric (DSC) techniques were confirmed the phase homogeneity of the cured systems.

Key Words : Schiff base, Metal complex, Maleimide, Curing

Introduction

Hydrazone is a special group of compounds in the Schiff base family. They are characterized by the presence of >C=N-N=C<. The presence of two inter linked nitrogen atoms separates this from imines, oximes, etc. Compound to simple hydrazone Schiff bases, acyl, aroyl and heteroacroyl Schiff bases have an additional donor sites >C=O. The additional donor sites make them more flexible and versatile. It is this versatility that has made hydrazones good polydentate chelating agents that can form a variety of complexes with various transition and inner transition metals and has attracted the attention of many researchers.^{1,2}

Hydrazones are used as plasticizers and stabilizers for polymers, polymerization initiators, antioxidants, etc., they act as intermediates in preparative chemistry. In analytical chemistry, hydrazones find application in detection, determination and isolation of compounds containing the carbonyl group. More recently, they have been extensively used in detection and determination of several metals. They also find applications as indicators and spot test reagents.^{3,4}

One of the major synthetic efforts in the field of epoxy resin to improve to words the heat, chemical and moisture resistant of epoxy polymers. The need for such polymers is their potential use as materials for air-craft, spacecraft, automotive and electronic components.^{5,6} Incorporation of transition metals into polymer chains offers a possibility to access new useful heat-resistant polymers. The methods to prepare metal-containing epoxy polymers are the use of metal chelates as the curing agents⁷⁻⁹ use of organotransi-

tion-metal complexes as additives¹⁰⁻¹² and synthesis of epoxy resins containing transition metal ions.¹³⁻¹⁷ It has been found that the metal-containing epoxy polymers possess higher strength and thermal stability, and which can be used for industrial production of one-plate glass-reinforced plastic springs for large-loaded motor vehicles.¹⁸

On the other hand, epoxy resins modified with maleimide compounds also received attractive attentions, due to the similar curing conditions and processing properties of the epoxy resins and maleimides. Maleimide-epoxy resins usually showed appropriate properties between epoxy and maleimide resins. Thus, both the intercrossed and the interpenetrating systems (IPN) based on bis-maleimides and epoxy resins were prepared and which exhibited good thermal and mechanical properties additionally, since imide groups could provide char formation in the condensed phase to improve polymers flame retardant properties, epoxy resins modified with imide compounds through chemical reactions or physical blending have been reported to show good flame retardant properties.¹⁹⁻²²

A survey of the literature revealed that no work has been carried out on the synthesis of metal complexes with macrocyclic hydrazone are used as curing agents in maleimide epoxy resins. However the Co(II), Ni(II) and Cu(II) complexes with macrocyclic hydrazone Schiff base were used as curing agents in maleimide epoxy resin. So it is considered worthwhile to study the synthesis of Schiff base metal complexes and reactivity studies with maleimide epoxy resin. Each of the reactive groups might form cross-linking networks under thermal curing reaction with these Schiff base

metal complexes to bring about high cross-linking density. The cured samples are found to have good thermal stability, chemical resistance and water absorption resistance. However, these cured samples exhibited homogeneity with no phase separation which was confirmed by scanning electron microscopy (SEM) and definitional scanning calorimetric (DSC) studies.

Experimental Section

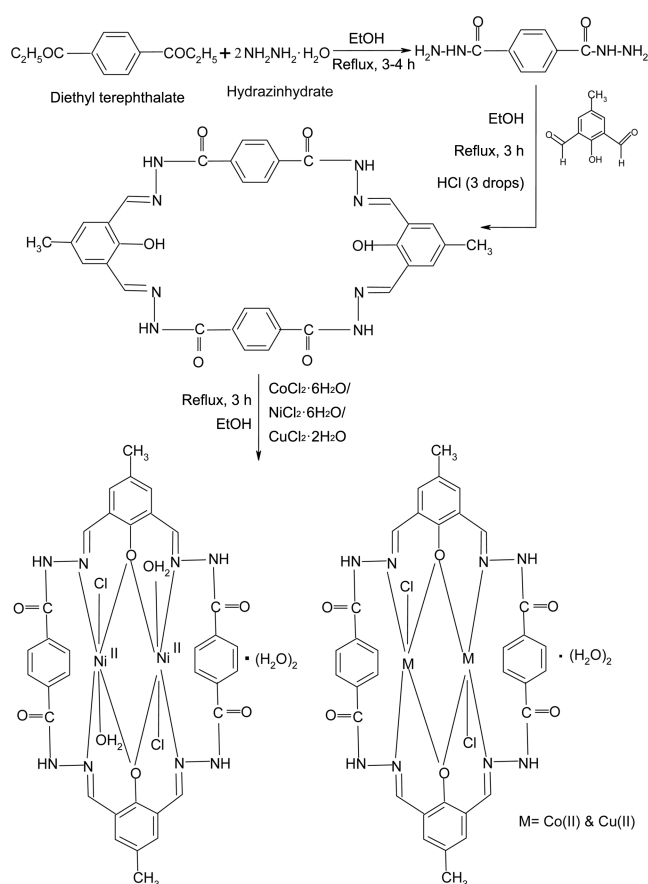
Materials and Methods. All chemicals and solvents used were of analytical grade (AR). All metal(II) salts were used as their chlorides. Further remaining pure reagents were purchased from Ranbaxy chemicals. The chlorides and metal contents were determined gravimetrically by the known method.

The Infrared spectroscopy (IR) spectra of the Schiff base and its Co(II), Ni(II) and Cu(II) complexes were recorded on a HITACHI-270 IR spectrophotometer in the 4000-350 cm^{-1} region in KBr discs. The electronic spectra of the complexes were recorded in Dimethylformamide (DMF) on a VARIAN CARY 50-BIO UV-spectrophotometer in the region of 200-1100 nm. The ^1H NMR spectra of Schiff base and complexes were recorded in $\text{DMSO}-d_6$ on a BRUKER-300 MHz spectrometer at room temperature using Tetramethylsilane (TMS) as an internal reference. Fast atom bombardment (FAB) mass spectra were recorded on a JEOL SX 102/DA-6000 mass spectrometer/data system using Argon/Xenon (6 KV, 10Am) as the FAB gas. The accelerating voltage was 10 KV and the spectra were recorded at room temperature; *m*-nitrobenzyl alcohol was used as the matrix. The mass spectrometer was operated in the positive ion mode. Thermogravimetric data were measured from room temperature to 1000 $^\circ\text{C}$ at a heating rate of 10 $^\circ\text{C min}^{-1}$. The data were obtained by using a PERKIN-ELMER DIAMOND TG/DTG instrument. Molar conductivity measurements were recorded on an ELICO-CM-82 T conductivity bridge with a cell having cell constant 0.51; magnetic moments were determined on a Faraday balance.

Synthesis of Diethyl Terephthalate. Terephthalic acid (1.6 g) in super dry ethanol (60 mL) containing 2-3 drops of conc. H_2SO_4 (AR) was refluxed till it dissolves. Then, the reaction mixture was poured on to ice cold water, immediately a solid started separating from the clear solution. To this a solution of sodium bicarbonate was added till the effervescence ceases. The ester thus obtained was filtered and washed with water for several times (mp 44 $^\circ\text{C}$).

Synthesis of Dihydrazone of terephthalic Acid. A mixture of diethyl ester of terephthalic acid (2.22 g) and hydrazine hydrate (98% 2 cc) in ethanol was refluxed for 4-5 h. The reaction mixture was allowed to cool to room temperature then, the cooled solution was poured on to ice cold water. The dihydrazone of terephthalic acid thus obtained was filtered and recrystallized from ethanol.

Preparation of 2,6-Diformyl-4-methylphenol. The 2,6-diformyl-4-methylphenol was prepared by reported method.^{23,24}

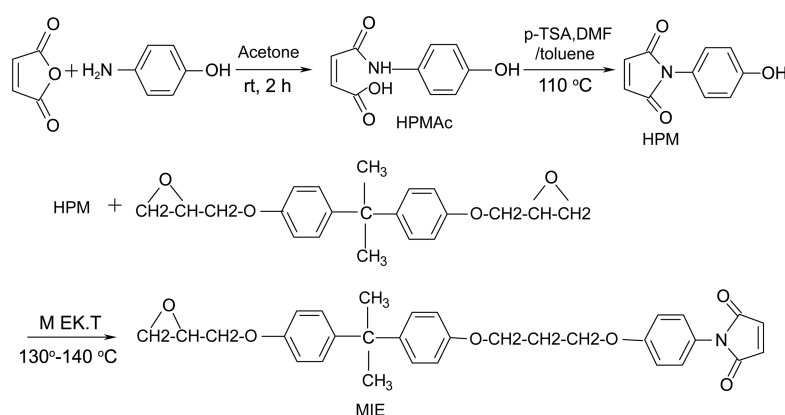


Scheme 1. Preparation of Schiff base and its Co(II), Ni(II) and Cu(II) complexes.

Synthesis of Macrocyclic Terephthalic Acid Hydrazone Schiff Base. 2,6-Diformyl-4-methylphenol (2 mmol) in ethanol (20 mL) was added to an ethanolic solution of 1,4-dicarbonyl phenyl dihydrazide (2 mmol, 30 mL) containing a few drops of concentrated HCl. The reaction mixture was refluxed for 3 h. The mixture was cooled to room temperature and the solvent removed under reduced pressure until a solid product (Scheme 1) was formed that was washed with cold ethanol and dried under vacuum. Yield (70-75%).

Synthesis of Co(II), Ni(II) and Cu(II) Complexes. A mixture of ligand (0.01 mole) and metal chloride (0.02 mole) was refluxed for an hour in alcohol. To the reaction mixture sodium acetate (0.02 mole) in water was added and the reaction was continued for another 2 h. The complex was precipitated by adding distilled water. The complex separated (Scheme 1) was filtered, washed with water, then with hot alcohol and finally dried in vacuum desiccator over P_2O_5 (yield 60-70%).

Synthesis of Maleimide Epoxy Compounds (MIEB-13). Experimental procedure for the synthesis and characterization of MIEB-13 is the same as given in previous reports^{21,22} (Scheme 2). Elemental analysis: found % (calcd %) C: 69.21(69.87), H: 5.80 (5.72), N: 2.88 (2.96). IR (KBr, cm^{-1}): 3471 (O-H), 1636 (C=O), 1638 (C=C), 1367 (C-N), and 917 (oxirane ring). ^1H NMR (ppm, in $\text{DMSO}-d_6$): 1.54 (s, 6H), 2.64-2.66 (t, 1.2H), 2.77-2.81 (t, 1.2H), 3.25-3.28



Scheme 2. Preparation of MIEB-13 compound.

Table 1. Curing conditions and thermal stability of cured systems evaluation with TGA and DSC under air atmosphere

Sl. No	System	Curing conditions	Thermal stability		DSC data	
			IDT °C	IPDT °C	T _{endo} °C	T _{exo} °C
1	MIE+Cu(II) complex	110 °C (1 h), 150 °C (2 h)	420	580	60	340
2	MIE+Ni(II) complex	110 °C (1 h), 150 °C (2 h)	420	570	70	350
3	MIE+Co(II) complex	110 °C (1 h), 150 °C (2 h)	400	560	80	360

(m, 1.2H), 3.43 (m, 0.8H), 3.71-3.77 (m, 1.2H), 3.95 (b, 3.2H), 4.20-4.25 (m, 1.2H), 5.39 (b, 0.8H), 6.71-7.29 (m, 12.8H). Softening point: 110-112 °C. Epoxy equivalent weight (MIEB-13) = 451 (calculated value 445).

Preparation of Cured Epoxy Resins. The cured epoxy resin is obtained from thermally curing of maleimide epoxy resin (MIE) with Schiff base metal complexes was mixed together in methylethylketone as a solvent and cured in oven. The conditions of curing reactions are listed in Table 1.

Moisture Absorption and Chemical Resistance Measurements. The above cured system was cut into small specimens of 25 × 25 mm and the thickness around 5 to 10 mm. The edges of specimens were coated with the same matrix system in order to avoid the moisture absorption through cut edges by capillary action. All the specimens were weighed bone dry in Sartorius balance. To start with, the initial weights were noted at room temperature. The samples were then immersed in water/alkali/solvent/acid for different intervals of time and then taken out, wiped with tissue paper and weighed.

Results and Discussion

All the Co(II), Ni(II) and Cu(II) complexes are colored non-hygroscopic solids, stable in air. They are sparingly soluble in common organic solvents, but soluble in DMF and DMSO. The elemental analyses show that the Co(II), Ni(II) and Cu(II) complexes have stoichiometry of the type $[M_2LX_2] \cdot 2H_2O$ (M=Co(II), Cu(II) and X=Cl) and $[Ni_2LX_2(H_2O)_2] \cdot 2H_2O$. The molar conductance values are too low to account for any dissociation of non-electrolytes in DMF.

I.R. Spectra. The important infrared frequencies of Schiff

base and its Co(II), Ni(II) and Cu(II) complexes. It is well established that the Schiff base having O-hydroxy group either on aldehyde or on aniline residue can form intramolecular hydrogen bonding.^{25,26} This has direct impact on the $\nu(OH)$ vibration, and shifts to the lower frequency with broadening. The extent of shift depends on the strength of hydrogen bonding.

The broad band at 3439 cm^{-1} , a strong band at 1626 and 1687 cm^{-1} in the IR spectrum of the Schiff base are assigned to H-bonded $\nu(OH)$ stretching, $\nu(C=N)$ of azomethine and carbonyl $\nu(C=O)$ vibrations, respectively. An intense band at 3100 cm^{-1} is due to the $\nu(NH)$ vibrations of the hydrazine group, a broad medium intense band was observed at 2921 cm^{-1} due to methyl groups and the band at 1,068 cm^{-1} is assigned to hydrazinic $\nu(N-N)$ of the free ligand.

For the Co(II), Ni(II) and Cu(II) complexes, we observed the following changes: the high intense band due to phenolic $\nu(OH)$ appeared in the region at 3439 cm^{-1} in the Schiff base was disappeared in the complexes. These observations support the formation of M-O bonds *via* deprotonation. So the H-bonded $\nu(OH)$ groups have been replaced by the metal ion. The presence of broad stretching vibrations in the 3598-3570 cm^{-1} region can be attributed to coordinated or lattice water molecules in all these complexes. The medium intense band at 1601 cm^{-1} due to $\nu(C=N)$ indicates that the C=N of the ligand coordinates to the metal through nitrogen. A broad band at 3565 cm^{-1} in addition to a medium to high intense band at 850 cm^{-1} are attributed to the symmetric and antisymmetric-OH stretching modes of coordinated water.²⁷ The unaltered position of the $\nu(C=O)$ (carbonyl) confirms non involvement in coordination. The $\nu(M-O)$ and $\nu(M-N)$ bands have been assigned in the region 540-550 cm^{-1} and 425-450 cm^{-1} , respectively.^{28,29}

¹H-NMR Spectral Studies. The Schiff base exhibits signals at 13.42 ppm due to NH protons.³⁰ These protons are D₂O exchangeable and confirming the assignment. It also exhibits resonance due to phenolic-OH protons around 11.30 ppm.³¹ The other characteristic resonance due to azomethine proton in the Schiff base appears at 8.20 ppm. In addition to above all observed signals in the region 6.80-7.75 ppm due to aromatic protons. A signal in the region 2.50-2.82 ppm is assigned to methyl protons. All these observations support the infrared conclusions.

Electronic Spectral Studies. The electronic spectra of Co(II) complex exhibits absorption bands in the region 11015, 17212 and 20032 cm⁻¹ which can be assigned to the transitions ⁴A₂ + ⁴E → ⁴B₁, ⁴A₂ + ⁴E → ⁴E (P) and ⁴A₂ + ⁴E → ⁴A₂ (P) respectively which are characteristic of square pyramidal geometry.²⁹ The Ni(II) complex shown three bands around 10882, 16752 and 26342 cm⁻¹ which are assigned to ³A_{2g} (F) → ³T_{2g} (F) (ν₁), ³A_{2g} (F) → ³T_{1g} (F) (ν₂) and ³A_{2g} (F) → ³T_{1g} (P) (ν₃) transition respectively, indicating octahedral geometry.³¹ The ligand field parameters of Ni(II) complex are listed in Table 2. The Cu(II) complex exhibited a high intensity band at 27523 cm⁻¹ in the UV-region. Appearance of this band is due to π → π* transition associated with the azomethine linkage and L → M charge transfer transition. The electronic spectrum of Cu(II) complex shown three bands at 10952, 14798 and 23228 cm⁻¹, these bands have been assigned to the transition ²B₁ → ²A₁ (ν₁), ²B₁ → ²B₂ (ν₂) and ²B₁ → ²E (ν₃) respectively. These transitions are characteristic of square pyramidal geometry.³²

Magnetic Studies. The magnetic moments of the Co(II), Ni(II) and Cu(II) complexes obtained at room temperature are listed in Table 3. The Co(II) and Ni(II) complexes shown magnetic moment values around 3.87 and 2.83 BM respectively which are lower than the respective spin values only and indicates weak antiferromagnetic coupling interaction between the metal ions which further confirm the dinuclear nature of the complexes. The Cu(II) complex showed a magnetic moment around 1.45 BM which is considerably lower than the spin only value for Cu(II) complexes. The low value of the magnetic moment is attributed for the

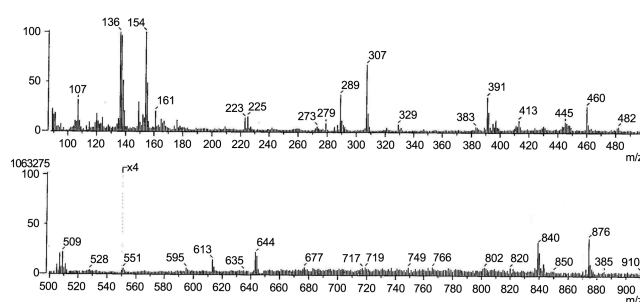


Figure 1. FAB-mass spectrum of Schiff base.

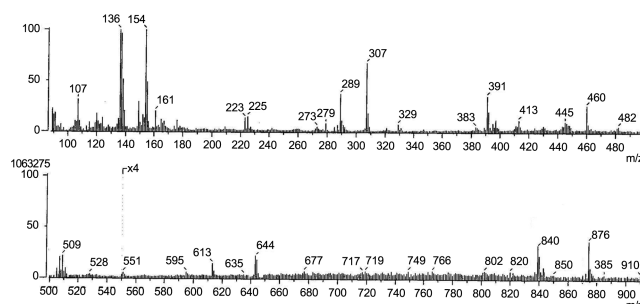


Figure 2. FAB-mass spectrum of Cu(II) complex.

antiferromagnetic coupling interaction between two metal ions. This fact suggests the dinuclear nature of the Cu(II) complexes.³³

FAB-Mass Spectrum. The FAB-mass spectrum of the Schiff base has been depicted in Figure 1. The spectrum showed a molecular ion peak at *m/z* 645 which is equivalent to its molecular weight [L+H]⁺. The FAB mass spectrum of Cu(II) complex has been depicted in Figure 2. The spectrum showed a molecular ion peak M⁺ at *m/z* 876, which is equivalent to its molecular weight of the Cu(II) complex. The molecular ion peak fragmentation with the loss of two water molecules, gave a peak A₁ at *m/z* 840 due to the fragment ion [Cu₂(C₃₄H₂₆N₈O₆)Cl₂]⁺. Further, the fragments leading to the formation of the species [Cu₂L]⁺ which under goes demetallation to form the species [L+H]⁺ gave fragment ion at *m/z* 644. All these fragmentation patterns are well observed in the FAB-mass spectrum. These entire frag-

Table 2. Ligand field parameters of Ni(II) complex

Complex No.	Transitions (cm ⁻¹)			ν ₂ calcd. cm ⁻¹	Dq cm ⁻¹	B ¹ cm ⁻¹	% Distortion	ν ₂ /ν ₁	LFSE	μ _{eff} calcd. BM	β	β ^o %
	ν ₁	ν ₂	ν ₃									
[Ni(C ₃₄ H ₂₆ N ₈ O ₆)Cl ₂ ·2H ₂ O]·2H ₂ O	10882	16752	26342	16782.48	1088.2	698.56	0.182	1.539	37.32	3.15	0.662	33.84

Table 3. Analytical, magnetic and molar conductance data of 3-Substituted-4-amino-5-hydrazino-1,2,4-triazole and its Co(II), Ni(II) and Cu(II) complexes

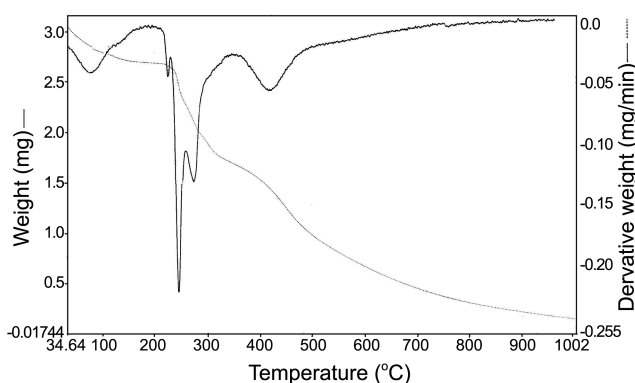
Empirical formula	M%		C%		H%		N%		λ _m cm ² Ω ⁻¹ mol ⁻¹	μ _{eff} (BM)	% Yield
	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.	Obsd.	Calcd.			
(C ₃₄ H ₂₈ N ₈ O ₆)	-	-	63.29	63.35	4.30	4.34	17.32	17.39	-	-	78
[Co(C ₃₄ H ₂₆ N ₈ O ₆)Cl ₂ ·2H ₂ O]	13.30	13.41	47.12	47.16	3.05	3.00	12.50	12.59	25	4.28	66
[Ni(C ₃₄ H ₂₆ N ₈ O ₆)Cl ₂ ·2H ₂ O]	12.79	12.87	45.22	45.28	2.83	2.88	12.36	12.43	32	3.34	68
[Cu(C ₃₄ H ₂₆ N ₈ O ₆)Cl ₂ ·2H ₂ O]	14.35	14.40	46.57	46.62	2.91	2.97	12.75	12.80	21	1.45	62

Table 4. Thermogravimetric data of Co(II), Ni(II) and Cu(II) complex

Empirical formula	Decomposition temperature	% Weight loss		Inference
	°C	Obsd.	Calcd.	
[Co(C ₃₄ H ₂₆ N ₈ O ₆)Cl ₂ ·2H ₂ O]	110-120	04.11	04.14	Loss of adhered water molecules
	200-210	43.95	43.93	Loss of hydrazine moieties
	240-250	30.32	30.28	Loss of aldehyde moieties
[Ni(C ₃₄ H ₂₆ N ₈ O ₆)Cl ₂ ·2H ₂ O]·2H ₂ O	200-210	03.86	03.99	Loss of coordinated water molecules
	230-235	42.22	42.17	Loss of hydrazine moieties
	280-290	14.58	14.53	Loss of one aldehyde moiety
	410-450	14.55	14.53	Loss of one aldehyde moiety
[Cu(C ₃₄ H ₂₆ N ₈ O ₆)Cl ₂ ·2H ₂ O]	115-125	04.16	04.11	Loss of adhered water molecules
	210-220	43.49	43.42	Loss of hydrazine moieties
	250-260	29.89	29.94	Loss of aldehyde moieties

mentation patterns are well observed in the FAB mass spectrum (Fig. 2). It clearly indicates dinuclear nature of the complex and two Cu(II) ions are held in the macrocyclic compartment of the Schiff base. The metal ions are bonded to two phenoxo bridges, which endogenously coordinated to the metal ions and the other coordinating sites in the ligand are the azomethine nitrogen atoms. Both phenoxide and azomethine groups surround the two metal ions, which are in close proximity within the ligand molecule to form a square base. A chloride ion coordinates to each metal ion from opposite sides to give square pyramidal configuration to the metal ions. The FAB mass spectrum confirms the dinuclear nature of the metal complex.

Thermal Studies Metal Complexes. TG and DTG studies were carried out for Co(II), Ni(II) and Cu(II) complexes. These complexes decompose gradually with the formation of respective metal oxide above 500 °C. The nature of proposed chemical change with the temperature range and the percentage of metal oxide obtained are given in the Table 4. The thermal decomposition of respective Co(II) and Cu(II) complexes takes place in three steps as indicated by DTG peaks around 110-120, 200-210 and 240-250 °C corresponding to the mass loss of two coordinated water molecules, two aldehyde moieties and two bis hydrazine moieties respectively Figure 3. Whereas, one representative Ni(II) complex decomposes in four steps as indicated by DTG peaks around 200-210, 230-235, 280-290 and 410-450°C

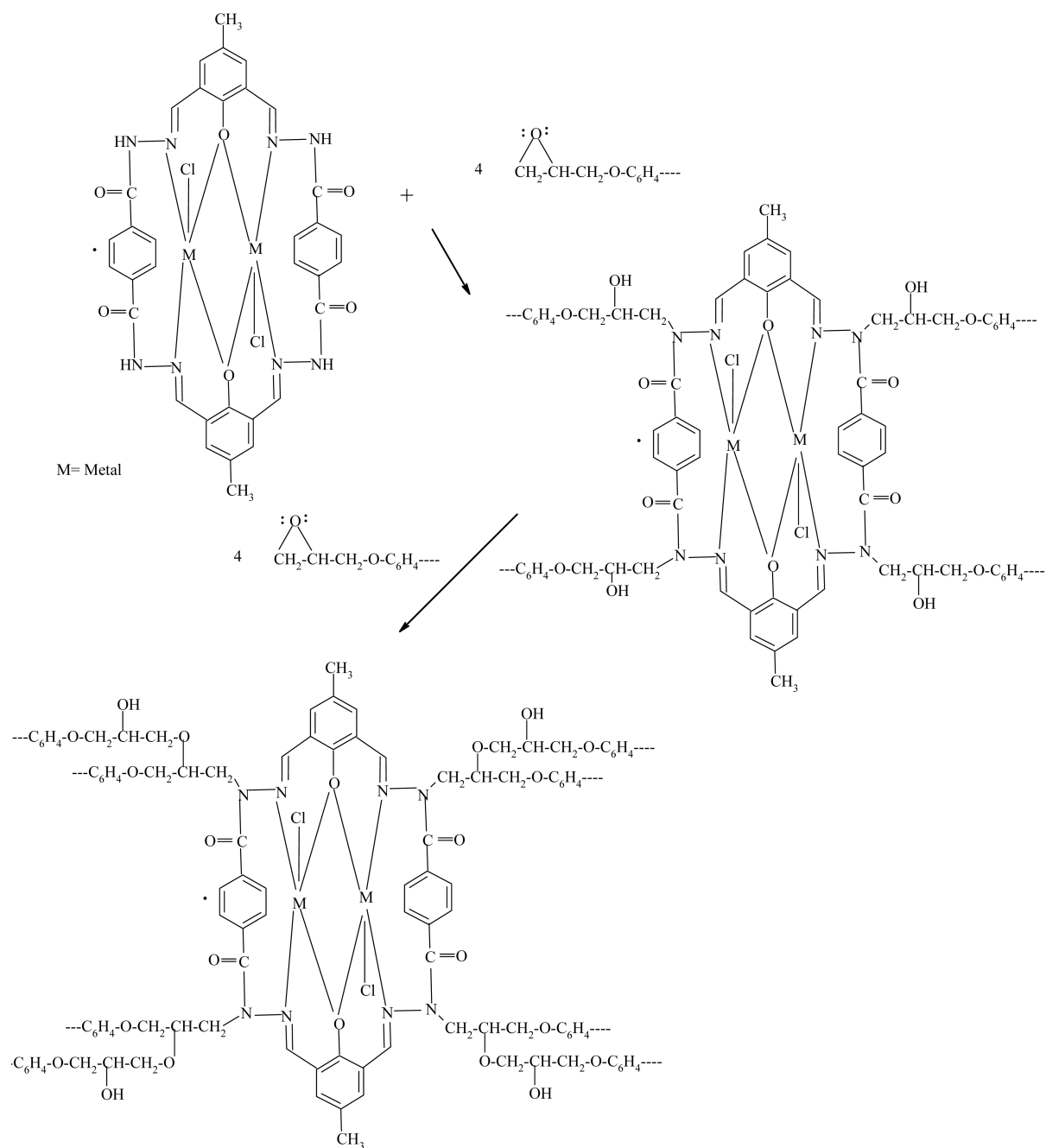
**Figure 3.** TG/DTG spectrum of Ni(II) complex.

corresponding to the mass loss of two coordinated/adhered water molecules, two aldehyde moieties and two bis hydrazine moieties respectively.

ESR Studies. The X-band ESR spectrum of Cu(II) complex was recorded at room temperature using DPPH as a reference standard. The g_{\parallel} and g_{\perp} values have been found to be 2.25 and 2.09 respectively. In general, dinuclear Cu(II) complexes give broad ESR peaks and the broadening is assigned to a dipolar interaction.³⁴ The observed ESR spectrum is characteristic of square pyramidal geometry. The g_{av} value was calculated to be 2.14. The existence of $g_{\parallel} > g_{\perp}$ suggests that $d_{x^2-y^2}$ orbital is in the ground state and d^9 configuration is $(eg)^4(a_{1g})^2(b_{2g})^2(b_{1g})^1$. The 'g' values are related to the axial symmetry and $g_{\parallel} > g_{\perp}$ suggests square pyramidal geometry of Cu(II) complex. The axial symmetry parameter $G=2.542$ which has less than 4.0 indicates considerable exchange interaction between metal ions in the solid complex³⁵ which further supports the dinuclear nature of the Cu(II) complex.

Curing Reactions of MIEB-13 with Metal Complexes. Epoxy resin can be cured using amines, anhydrides, fatty acids, acrylics, and amide as curing agents to study the effect on their curing rate and related properties to obtain epoxy polymers.³⁶⁻³⁸ Therefore, the Schiff base metal complexes, which also contain amine groups in their molecules, were then applied as curing agents for MIEB-13. The curing systems were obtained by reacting between MIEB-13 with Schiff based metal complexes, was carried out based on their hydrogen equivalent weights. MIEB-13 resin and metal complexes was taken on an aluminum foil of about 10 cm diameter were dissolved in methylethylketone to form a homogeneous solution. After evaporating the solvent at ambient temperature the mixture was cured with specific curing condition to result in cured resins. The curing process converts the maleimide epoxy resins into a hard, infusible and rigid material; the curing conditions are listed in Table 1.

The curing mechanism of MIEB-13 E with the metal complexes is proposed to involve a ring opening of the epoxy group of MIEB-13 by the amine groups of the complex to give a alcohol, which can then open another epoxy group of maleimide epoxy resin resulting to form a highly



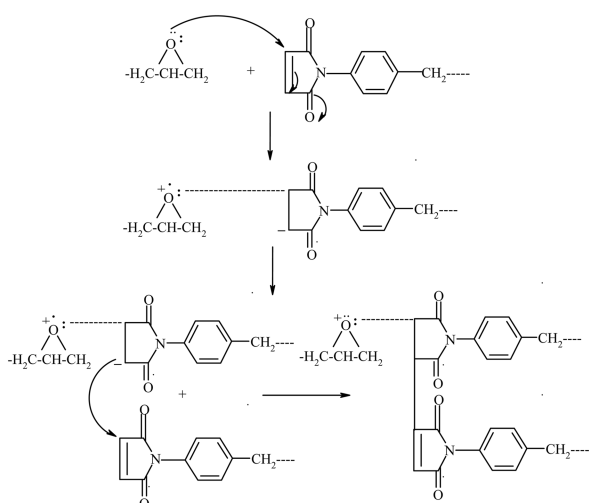
Scheme 3. The reaction mechanism of amine with oxirane ring.

cross linked, three dimensional network. These reactions occur repeatedly to produce the cross-linked metal-containing maleimide epoxy compounds as shown in Scheme 3.

Maleimide group of MIEB-13 is well known that, the maleimide groups might crosslink through self-addition reaction (Scheme 4) under heating. Therefore, while curing MIEB-13 with metal complexes, all the three above-mentioned reactions might occur. In this work, the curing compositions were taken with the same stoichiometric amounts of the amine curing agent and oxirane groups. Therefore, most of the amine groups are expected to react with oxirane groups at low temperature region. Since almost no amino group was left to react with maleimide group, only self-

addition reaction occurred for maleimido groups in the curing reaction. The resulting products obtained were therefore supposed to have high cross linking densities.

Detection of Curing Time and Exothermic. The curing reaction between MIEB-13 with Schiff based metal complexes based on their hydrogen equivalent weights. MIEB-13 resin was taken on an aluminum foil of about 5 cm diameter then add methylethylketone metal complexes (depending on their hydrogen equivalent weight) was added and mixed thoroughly for a minute using a thin wooden stick. In all the cases, the temperature of the reaction mixture at different intervals of time was measured using an infrared gun and the completion of the curing process is indicated



Scheme 4. Self-addition reaction of maleimide groups of MIEB-13 compound.

Table 5. Reactivity studies data MIEB-13 compound with amines

Sl. No	System	Wight of MIEB-13 (g)	Weight of amine (g)	Curing Time in min	Exotherm (°C)
1	MIE+Cu(II) complex	10	0.35	50 ± 1	49 ± 0.2
2	MIE+Ni(II) complex	10	0.64	45 ± 1	53 ± 0.3
3	MIE+Co(II) complex	10	0.76	38 ± 1	58 ± 0.4

when the reaction mixture became non-sticky to the wooden stick. The results are listed in Table 5.

Differential Scanning Calorimetric (DSC) Studies of Cured Systems. Dynamic DSC thermograms of cured maleimide epoxy containing copper, nickel and cobalt ions are represented in Figure 4. The dynamic scans were performed at a heating rate of 10 °C/min and the data are summarized in Table 1. From the figure it is clear that all the cured systems exhibit similar behaviour. The endothermic peak at 80 °C corresponds to the melting point of the cured epoxy systems. The exothermic peak at around 280 to 300

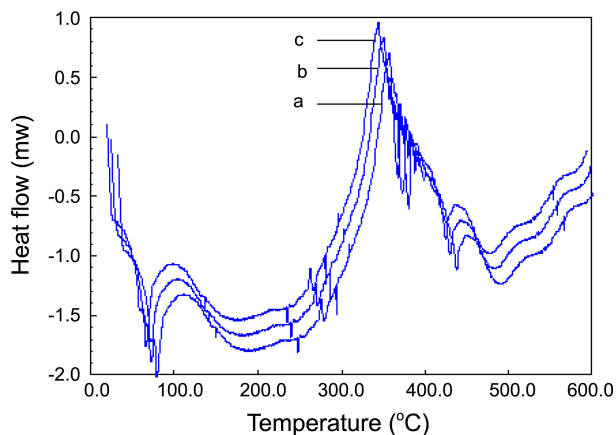


Figure 4. Dynamic DSC thermograms of the three systems a. MIEB-13 +Cu(II) complex, b. MIEB-13+Ni(II) complex, c. MIEB-13+Co(II) complex.

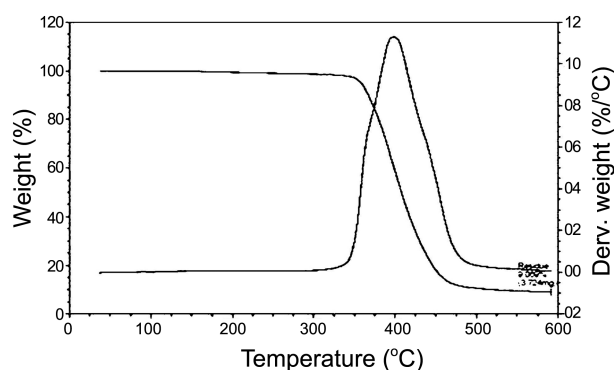


Figure 5. Thermogravimetric analysis of cured systems a. MIEB-13+Cu(II) complex.

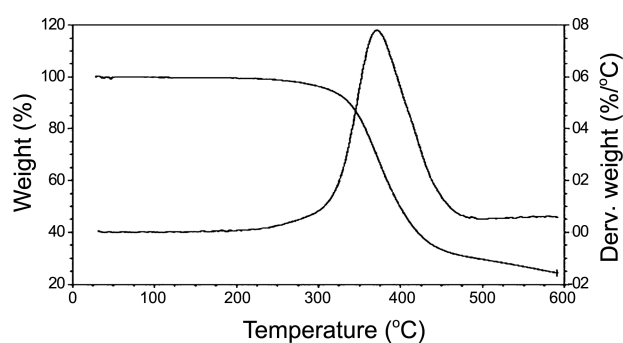


Figure 6. Thermogravimetric analysis of cured systems a. MIEB-13+Ni(II) complex.

°C is attributed to the exothermic curing reactions of the above mentioned epoxy and metal complexes systems and the maximum of the exothermic peak obtained at 330-350 °C. After 410 °C, the completion of curing process indicates the absence of exotherm peaks in the post cure in epoxy amine systems.

Thermal Properties of the Cured Systems. The thermal stability of the cured maleimide epoxy containing copper, nickel and cobalt ions was investigated with thermogravimetric analysis (Figs. 5-7). The enhancement of the thermal stability due to incorporation of metal ions into MIEB-13 was thus demonstrated. The thermo grams of the cured

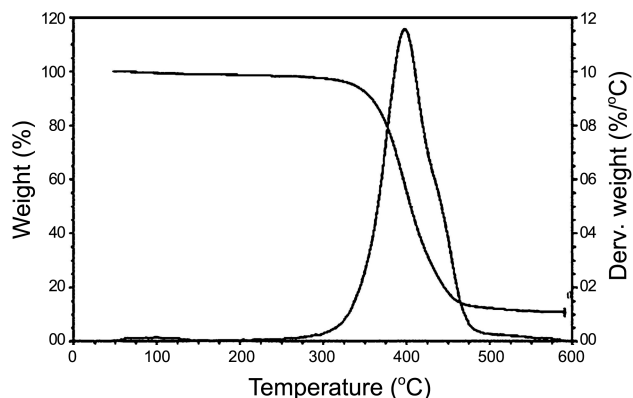


Figure 7. Thermogravimetric analysis (TGA) of MIEB-13+Co(II) complex.

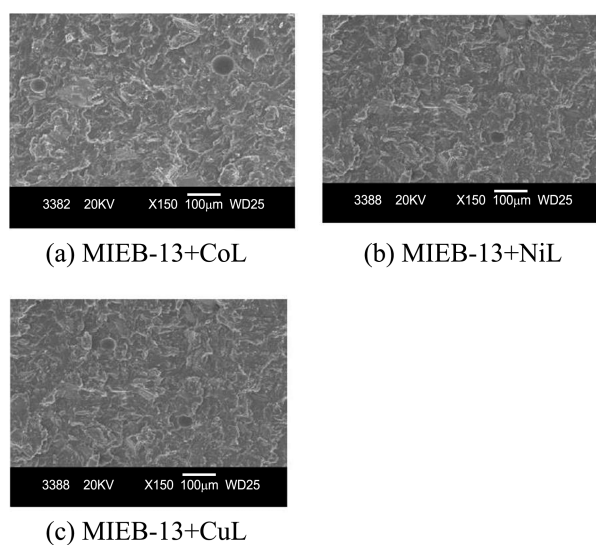


Figure 8. Fractured morphology analysis of cured systems (a) MIEB-13+Co(II) complex, (b) MIEB-13+Ni(II) complex, and (c) MIEB-13+Cu(II) complex.

maleimide epoxy containing metal ions clearly indicate that the thermal stability of cured resins was improved with the incorporation of metal ions into the maleimide epoxy resin. With the incorporation of the metal ions into MIEB-13 which increases the initial decomposition temperature (IDT) of the maleimide epoxy containing metal ions. On the other hand, the integral procedural decomposition temperature (IPDN) also systematically increased with incorporation of metal ions. Due to the presence of the metal ions in the epoxy network, this shows more resistance even in higher temperature. The high IPDT indicates that the cured maleimide epoxy containing copper, nickel and cobalt ions shows good thermal stability even in high temperature.

Morphology Studies of Cured Systems. The morphology of fracture surfaces of cured maleimide epoxy containing copper, nickel and cobalt ions were examined using scanning electron microscope. All the systems exhibit similar

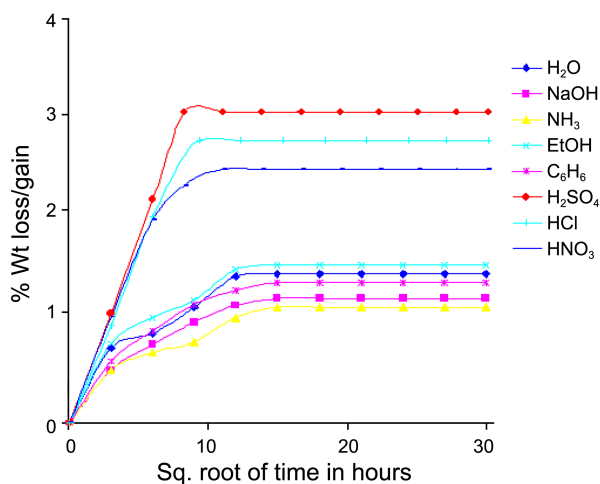


Figure 9. Water/Acid/Alkali/Solvent resistance of MIEB-13 with Cu(II) complex.

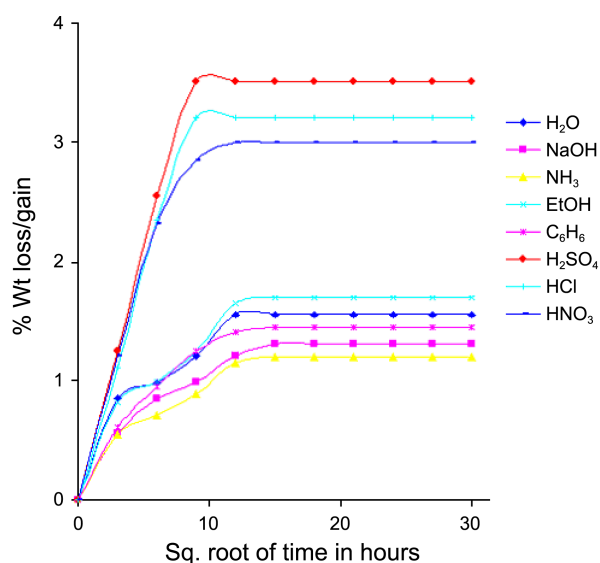


Figure 10. Water/Acid/Alkali/Solvent resistance of MIEB-13 with Ni(II) complex.

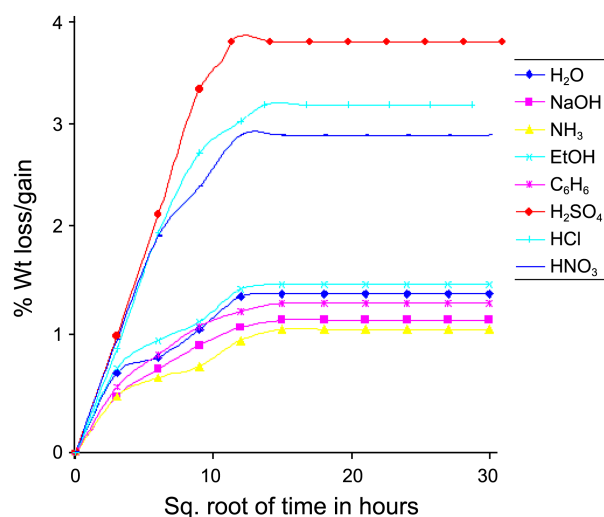


Figure 11. Water/Acid/Alkali/Solvent resistance of MIEB-13 with Co(II) complex.

morphology. From Figure 8 it is clearly seen that the fracture surfaces of the neat maleimide epoxy containing copper, nickel and cobalt ions exhibit a homogenous pattern. All the cured samples exhibit similar homogeneous network and show no formation of distinct domains, confirming the formation of a homogeneous network in all the cured maleimide epoxy containing copper, nickel and cobalt ions systems.

Moisture and Chemical Resistance Measurements of Cured Systems. The chemical and water absorption curves of the cured maleimide epoxy containing copper, nickel and cobalt ions systems are shown in Figure 9-11 and the results are tabulated in Table 6. The goal of this study was to describe the interactions between the absorbed moisture and epoxy network. The transport of moisture through the epoxy network involves cooperative motion of water molecules and 3-dimensional resin network. One of the major factors affecting water absorption is the presence or absence of

Table 6. The maximum moisture, acid, alkali and solvent resistance content under a given condition of temperature (25 °C)

Sl. No	System	% Weight gain					% Weight loss		
		H ₂ O	10%NaOH	NH ₃	C ₂ H ₅ OH	C ₆ H ₆	H ₂ SO ₄	HCl	HNO ₃
1	MIE+Cu(II) complex	1.12	1.62	1.12	1.89	1.23	3.90	3.45	3.50
2	MIE+Ni(II) complex	1.17	1.59	1.09	1.81	1.25	3.95	3.51	3.59
3	MIE+Co(II) complex	1.21	1.69	1.18	1.90	1.26	4.13	3.79	3.84

hydrophilic groups in the cross-linked network. There are same types of hydrophilic groups in the present systems. There are also other relevant factors to consider, notably free volumes, which generally increases with cross-link density because of the development of a rigid macromolecular framework.

As shown in Figure 9-11 initially there is a sharp increase in water absorption due to water penetration into structural defects and cavities on the surface of samples. After some time a slow process of water absorption reaches its equilibrium at room temperature.

In the case of chemical resistance measurements the cured systems are studied with ammonia. Same trends in weight reduction are observed for all the systems. Initially the weight reduction is faster possibly due to washing some of the unreacted epoxy from surface of the samples. The second step is a slow weight reduction which can be due to washing some of the unreacted epoxy out of the bulk of the samples. The more complex the network is, the longer it takes for ammonia to diffuse in to the system to reach to equilibrium. The plots of moisture absorption vases square root of time were constructed to note the saturation limits of the absorbed moisture. From the figures it is observed that initially the water uptake increases, and showed a flat profile exhibiting Fickian type behavior. The cured samples were found to have good chemical resistance (acid/alkali/solvent) and water absorption resistance as compared to traditional epoxy amine cured systems. This may be because of the incorporation of metal ions into MIEB-13, which provides a cyclic imide structure and high cross-linking density to the cured resins.

The maximum moisture/acid/alkali/solvent resistance contents under a given condition of temperature in case of cured maleimide epoxy containing copper, nickel and cobalt ions are shown in Table 6. These data clearly indicate that the cured maleimide epoxy containing copper, nickel and cobalt ions showed more resistance to water absorption and other chemicals.

Conclusion

The newly synthesized compound acts as hexadentate Schiff base. The metals are coordinated to azomethine nitrogen and phenolic oxygen atoms. The analytical, spectral, magnetic, and thermal studies confirm the bonding of Schiff base to metal ions. Schiff base metal complexes were found potentially curing agents for the maleimide epoxy resins MIEB-13. The cured systems exhibited excellent thermal

stability and good chemical (acid/alkali/solvent) and water absorption resistance.

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