

Cobalt (II), Nickel (II), and Copper (II) Complexes of Polystyrene-Supported Schiff Bases

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Received 27 December 2002; revised 25 May 2003; accepted 10 August 2003

ABSTRACT: Two novel polystyrene-supported Schiff bases, PSOPD and PSHQAD, were synthesized. A polymer-bound aldehyde was condensed with *o*-phenylenediamine to prepare the Schiff base PSOPD, and a polymer-bound amine was condensed with 3-hydroxyquinoxaline-2-carboxaldehyde to prepare the Schiff base PSHQAD. This article addresses the study of cobalt (II), nickel (II), and copper (II) complexes of these polymer-bound Schiff bases. All the complexes were characterized, and the probable geometry was

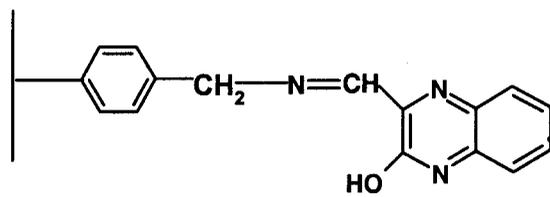
suggested using elemental analysis, diffuse reflectance ultraviolet, Fourier transform infrared spectroscopy, thermal studies, surface area studies, and magnetic measurements. © 2004 Wiley Periodicals, Inc. *J Appl Polym Sci* 91: 3710–3719, 2004

Key words: polystyrene-bound Schiff base; *o*-phenylenediamine; 3-hydroxyquinoxaline-2-carboxaldehyde; polymer-metal complexes; supported complexes

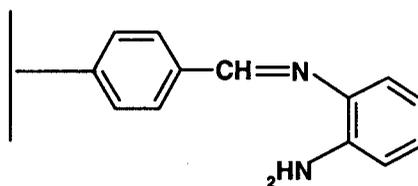
INTRODUCTION

Metal complexes are supported on polymers to give an organic polymer inorganic function.¹ Such complexes may show a specific type of catalytic activity reflecting the properties of polymers. In metalloenzymes, such as hemoglobin and oxidase, where the metal complex is the active site, the organic part plays an important role in the reactivity.^{2–4} Such catalysts are used extensively now in emerging areas such as

triphasic catalysis.⁵ Schiff bases, an important class of ligands obtained by condensation of aldehyde with amine, play a significant role in such applications.^{6–8} We report herein the synthesis of cobalt (II) [Co(II)], nickel (II) [Ni(II)], and copper (II) [Cu(II)] complexes with the polymer-anchored Schiff bases I and II and their characterization using various physicochemical techniques.



I



II

EXPERIMENTAL

Chloromethylated polystyrene [3.1 mmol Cl/g (Merck)] crosslinked with 2% divinyl benzene was used as the starting material. The amine-bound⁹ and the aldehyde-bound¹⁰ polystyrene was synthesized from the chloromethylated polystyrene according to the literature procedure. *o*-Phenylenediamine was

purchased from CDH Laboratories and was purified by recrystallization from its hot solution, which was treated with activated charcoal. 3-Hydroxyquinoxaline-2-carboxaldehyde was prepared according to a reported procedure.¹¹ All metal chlorides were Merck samples and were used as such.

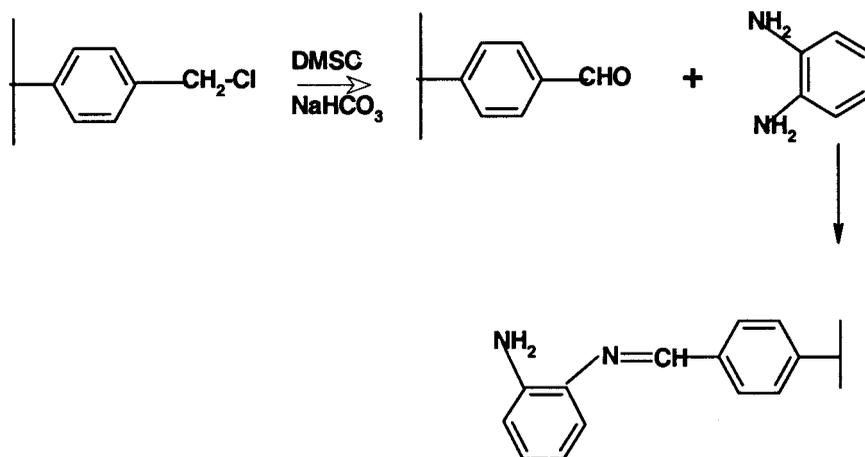
Synthesis of polymer-anchored schiff base of *o*-phenylenediamine

The polymer-bound benzaldehyde (4 g) was swelled in ethanol for 1 hour. *o*-Phenylenediamine (1.08 g) was dissolved in ethanol (50 mL). This was then refluxed

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on a water bath for 6 hours. The resulting Schiff base, PSOPD, was filtered, washed with ethanol several

times, and dried in vacuum over anhydrous calcium chloride.



Synthesis of cobalt, nickel, and copper complexes

The polymer-bound Schiff base PSOPD (3 g) was swelled in chloroform (25 mL) for 1 hour. It then was filtered and refluxed with a solution of the metal chloride (1.70 g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 2.37g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, or 2.37g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 100 mL ethanol) on a water bath for approximately 6 hours. All these complexes then were washed several times with ethanol and dried in vacuum over anhydrous calcium chloride.

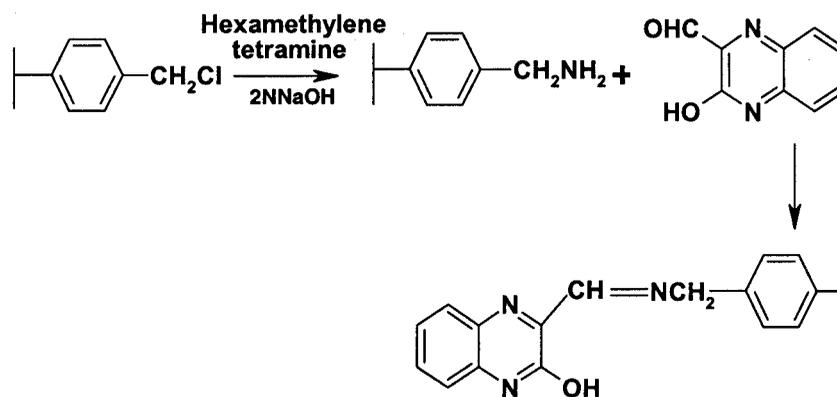
bound amine (5 g) for approximately 8 hours. The resulting Schiff base was filtered and washed with water and alcohol and dried in vacuum over anhydrous calcium chloride.

Synthesis of CO(II), NI(II), and CU(II) complexes

The polymer-bound Schiff base PSHQAD (3 g) was swelled in chloroform for 1 hour. After swelling, it was filtered and refluxed with a solution metal chloride 1.70g of $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 2.37g of $\text{CoCl}_2 \cdot 6\text{H}_2\text{O}$, or 2.37g of $\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$ in 100 mL ethanol) for approximately 6 hours. The complexes thus formed were washed with ethanol several times, filtered, and dried in vacuum over anhydrous calcium chloride.

Synthesis of polymer-anchored schiff base of 3-hydroxyquinoxaline-2-carboxaldehyde

3-Hydroxyquinoxaline-2-carboxaldehyde [500 mL of 0.005% (w/v)] solution was refluxed with polymer-



Analytical methods

Microanalysis for C, H, and N were carried out on a Perkin Elmer 2400 elemental analyzer. Metal analyses were carried out by ICP measurements after digesting the samples in Conc. HNO_3 . The percentage of chlo-

rine in the sample was determined using the Volhards method after digesting the samples in pyridine.¹² Magnetic susceptibility of the complexes was determined at RT using the Gouy method, using $\text{Co}[\text{Hg}(\text{NCS})_4]$ as standard. Electronic spectra were obtained using a Cary Win UV-Vis spectrophotometer in

TABLE I
Elemental Analysis Data of the Ligand
and Polymer-Bound Complexes

Compound	%C	%H	%N	%M	%Cl
PSOPD	77.76	7.36	3.32	—	—
CoPSOPD	74.66	6.58	2.88	2.2	2.5
NiPSOPD	77.59	7.11	2.48	1.5	—
CuPSOPD	74.45	7.04	2.61	1.5	—
PSHQAD	77.57	6.80	4.43	—	—
CoPSHQAD	72.36	6.70	3.00	2.3	3
NiPSHQAD	76.35	6.79	3.77	1.3	3
CuPSHQAD	73.91	6.73	3.31	1.1	—

the diffuse reflectance mode at RSIC, IIT, Chennai. Infrared spectra of the complexes were taken in region 400–4000 cm^{-1} as KBr discs using a Shimadzu 8100 FTIR spectrophotometer. The ESR spectra of the complexes were recorded at liquid N_2 temperature using E-109X/Q band ESR spectrometer. The calibration was carried out using DPPH (1,1, diphenyl-2-picrylhydrazyl) as the field marker. Surface area measurements were carried out using the BET method using a Micromeritics Gemini 2360 surface area analyzer. Thermogravimetric analysis was carried out on a Shi-

TABLE II
EPR and Magnetic Moment Data for the Complexes

Complexes	g_{\perp}	g_{\parallel}	Magnetic moment (BM)
CoPSHQAD	2.20	2.70	2.2
NiPSHQAD	2.023	—	3.0
CuPSHQAD	2.07	2.27	2.1
CoPSOPD	2.004	2.20	2.5
NiPSOPD	2.004	2.076	3.3
CuPSOPD	2.06	2.20	1.8

madzu TGA-50 at a heating rate of 20°C under N_2 atmosphere.

RESULTS AND DISCUSSION

The chloromethylated polystyrene containing approximately 13% Cl, the starting material for the preparation of Schiff base, on treatment with dimethyl sulphoxide and sodium bicarbonate yielded polymer-bound benzaldehyde, which was evidenced by the positive test with Borsche's reagent. The chlorine content of the polymer-bound aldehyde was negligible,

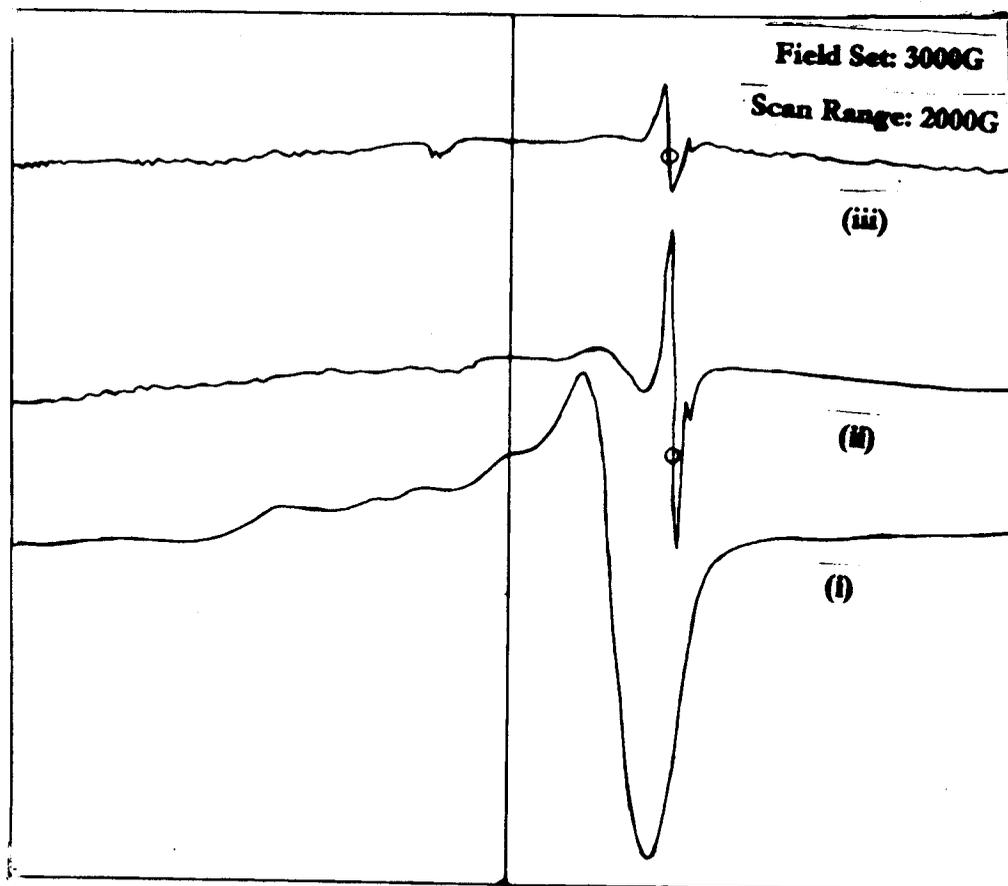


Figure 1 EPR spectra of Polymer bound OPD complexes i) CuPSOPD ii) NiPSOPD iii) CoPSOPD.

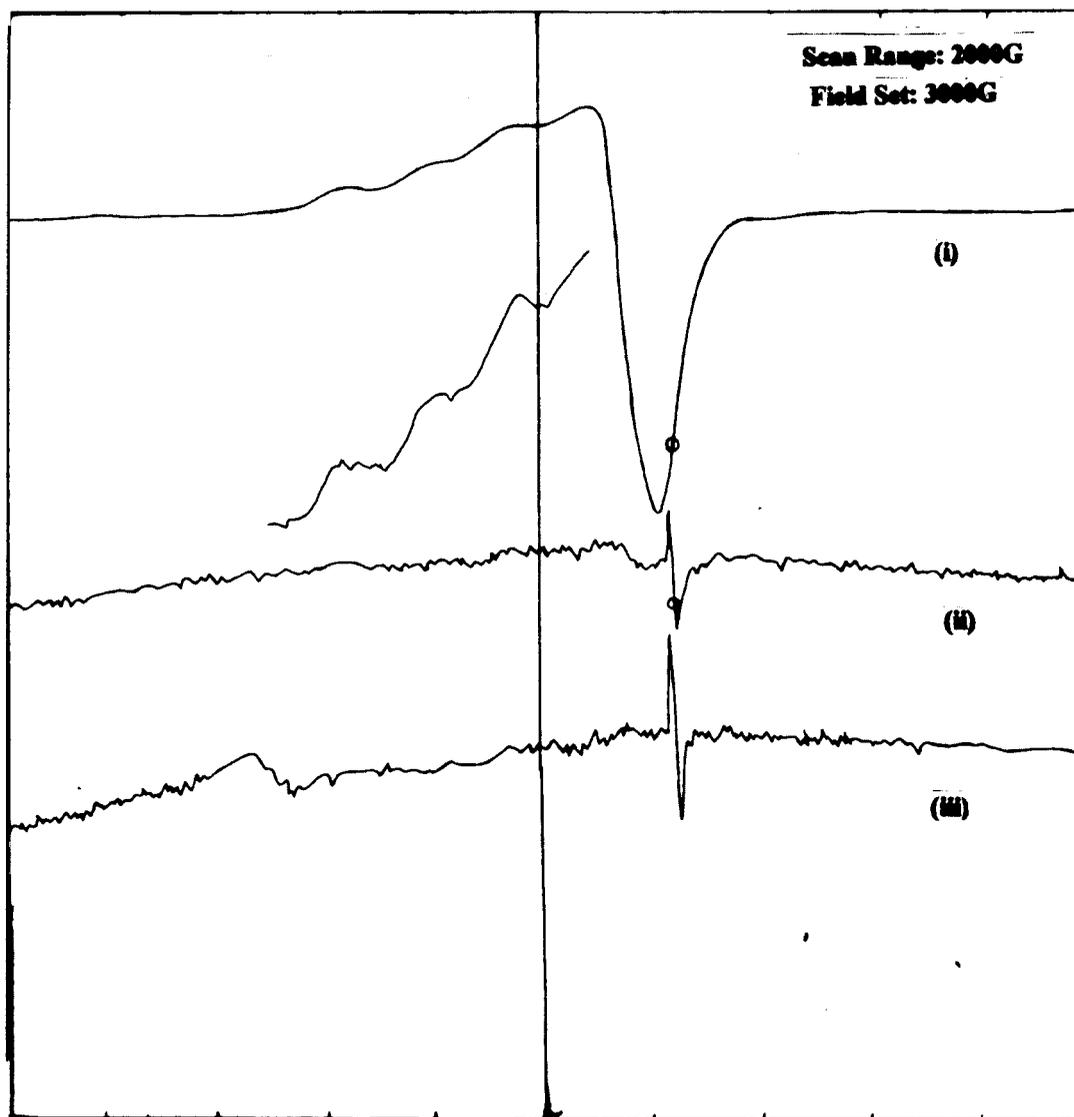


Figure 2 EPR spectra of complexes i) CuPSHQAD ii) NiPSHQAD iii) CoPSHQAD.

which indicates that almost all chloromethylene groups are converted into aldehyde. Aminomethyl polystyrene prepared by the polymer analog of delipine reaction as indicated in the scheme above gave

TABLE III
Thermogravimetric Analysis Data of PSHQAD and Metal Complexes

Compound	Temperature Range	% Weight Loss
PSHQAD	110–405	39.5
	405–600	53.7
CoPSHQAD	110–406	38.4
	406–500	47.5
NiPSHQAD	110–405	41.6
	405–538	47.2
CuPSHQAD	110–385	41.1
	385–447	48.2

a positive test for the presence of amino group (a deep blue color with Ninhydrin reagent). The percentage of nitrogen indicates that there is only 14% conversion. The nitrogen percentage in the Schiff base indicates that the azomethine group units are approximately 7 to 8 units apart. The metal binding capacity was found to be highest for cobalt. The porous structure of the polymer seems to be blocked, which is indicated by the drastic decrease in surface area from 154 to 200 m^2/g to approximately 45 to 50 m^2/g in the case metal complexes.

Magnetic susceptibility measurements

For calculation of magnetic susceptibility, the Guoy method was used. Magnetic susceptibility of all the complexes showed a negative value, probably the

TABLE IV
Thermogravimetric Analysis Data of PSOPD and Metal Complexes

Compound	Temperature range	% Weight loss
PSOPD	265–600	25
	600–800	48
CoPSOPD	376–424	25
	424–500	15
	500–800	42
NiPSOPD	376–425	20
	425–500	20
	500–800	30
CuPSOPD	378–413	22
	413–457	20
	457–800	20

result of the low concentration of the metal and the very large diamagnetic susceptibility of the atoms present in the polymer complex. However, the approximate molecular weight and empirical formula of the repeating complex unit containing one metal atom was calculated using a reported procedure.¹³ The magnetic moments μ_{eff} of the different complexes calculated on the basis of these values are given in the Table II. The cobalt complex Co(II)-PSOPD has a magnetic moment of 2.5 BM. Magnetic moment values of 2.0 to 2.5 usually are reported for square planar Co(II) complexes. This higher magnetic moment value (when compared with that expected for one unpaired electron) for low-spin square planar complexes corresponds to the spin-only value for one unpaired electron multiplied by a factor of $[1 + (2\lambda / \delta)]$. Here, λ is the single electron spin-orbit coupling constant, and δ is the separation between the d_{xy} orbit and its neighboring levels. Such high values are reported for square planar complexes like $\text{Co}(\text{PET}_3)_2(\text{NCS})_2$, which has a magnetic moment value of 2.3 BM.¹⁴ Cobalt complexes of the ligand Salen also are planar, with a magnetic moment value of 2.2 BM. Thus, the present Co(II)-PSOPD complex can be considered to have a square planar structure. Ni(II)PSOPD has a μ_{eff} of 3.3 BM, which suggests an octahedral structure, and Cu(II)-PSOPD has a magnetic moment of 1.8 BM, indicating a distorted octahedral structure.

Among the complexes of PSHQAD, the Co(II)-PSHQAD has a magnetic moment of 2.2 BM, indicat-

ing a square pyramidal geometry for the complex. The Ni(II)PSHQAD exhibits a magnetic moment value of 3.0 BM, which is suggestive of an octahedral structure. Cu(II)PSHQAD exhibits a slightly higher magnetic moment value of 2.1 BM, indicating a tetrahedral geometry for this complex.

EPR spectra

EPR spectra of the complexes were recorded at liquid nitrogen temperature. EPR parameters of the complexes are given in the Table II.

All the complexes of PSOPD are seen to be EPR active (Figure 1). For the Co(II)PSOPD complex, g_{\parallel} and g_{\perp} values are found to be 2.004 and 2.20, respectively. These values suggest a square planar structure. The assignment of this geometry is supported by the magnetic moment value of 2.5 BM. The Ni(II)PSOPD is EPR active, and g_{\perp} and g_{\parallel} values for this complex are 2.004 and 2.076, respectively.¹⁵ This suggests an octahedral structure for this complex. The EPR spectrum of the polymer-anchored Cu(II)PSOPD complex shows two g values ($g_{\parallel} = 2.28$ and $g_{\perp} = 2.08$), indicating a tetragonal symmetry or a distorted octahedral structure. The A_{\parallel} and A_{\perp} values for Cu(II)PSOPD are found to be $150 \times 10^{-4} \text{ cm}^{-1}$ and $66 \times 10^{-4} \text{ cm}^{-1}$.

The EPR spectra of all the complexes of PSHQAD are depicted in Figure 2. The EPR spectrum of Co(II)-PSHQAD gives two g values, $g_{\parallel} = 2.70$ and $g_{\perp} = 2.02$, indicating a square pyramidal structure. The EPR spectrum exhibiting a g value of 2.023 was observed in the case of Ni(II)PSHQAD. This may be the result of the octahedral structure for the complex. The Cu(II)-PSHQAD complex also exhibits two g values, $g_{\parallel} = 2.26$ and $g_{\perp} = 2.06$, and the A_{\parallel} and A_{\perp} values are $133 \times 10^{-4} \text{ cm}^{-1}$ and $60 \times 10^{-4} \text{ cm}^{-1}$.

The polymer-anchored CU(II) complexes exhibit a covalent environment as indicated by a g_{\parallel} value less than 2.3.¹⁶ The strength of the ligand can be assessed from the G value, which can be calculated using the following equation¹⁷:

$$G = \frac{g_{\parallel} - 2.002}{g_{\perp} - 2.002}$$

If it is less than 4, the ligand forming the CU(II) complex is regarded as a strong field ligand. In the

TABLE V
FTIR Spectral Data (in cm^{-1}) of PSOPD and Metal Complexes

Compound	N-H stretching	Azomethine C=N stretching	C-N stretching		M-N stretching
PSOPD	3436	1650	1268	1162	
CoPSOPD	3436	1635	1275	1175	552
NiPSOPD	3436	1640	1275	1175	539
CuPSOPD	3436	1626	1275	1175	565

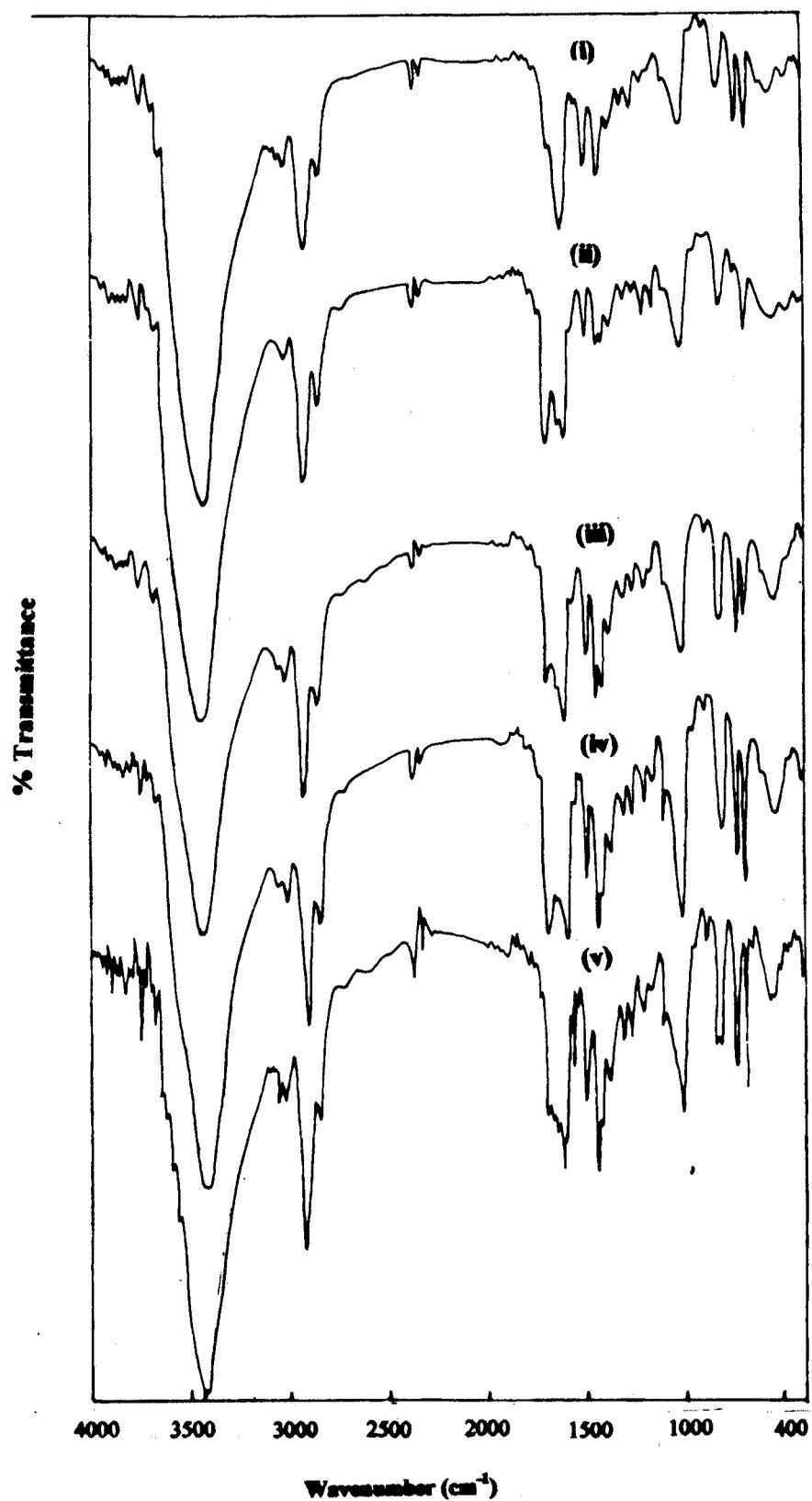


Figure 3 IR spectra of PSOPD complexes i) PSCHO ii) PSOPD iii) CoPSOPD iv) NiPSOPD v) CuPSOPD.

TABLE VI
FTIR Spectral Data (in cm^{-1}) of PSHQAD and the Metal Complexes

Complex	O-H stretching	Aliphatic C-N stretching	C-O stretching	Azomethine C=N stretching	Aldehydic C-H stretching	Aromatic ring C-N
PSHQAD	—	1029	1573	1660	2740	1460
CoPSHQAD	3549	1023	1560	1645	2727	1454
NiPSHQAD	—	1023	1566	1650	2733	1454
CoPSHQAD	—	1016	1566	1650	2727	1447

present case, it was observed to be less than 4 [G value is 3.79 for Cu(II)PSHQAD and $G = 3.56$ for Cu(II)-PSOPD], indicating the strong field nature of the ligands. The in-plane covalence parameter $\alpha^2\text{Cu}$ was found to be 0.7676 and 0.6992 for Cu(II)PSOPD and Cu(II)PSHQAD, respectively, which also supports covalent nature.

Thermal analysis

Thermal analysis of the PSHQAD complexes was carried out to find the stability of the complexes. All the complexes were stable up to 110°C . At less than 100°C , there appears to be a small decrease in weight corresponding to a weight loss of 4%. This may be the result of the loss of physisorbed water. Therefore, the complexes can be considered to decompose in two stages (Table III). There was an approximately 40% weight loss during the second stage of decomposition. The decomposition of the Schiff base PSHQAD is almost complete at 600°C , whereas the decomposition of the complexes was found to be complete at a lower temperature. The lower decomposition temperature in the case of the complexes may be the result of the catalytic activity of the metal ion in the decomposition of the polymer part.

The PSOPD complexes are stable up to 350°C . Up to 350°C , there is only an 8% weight loss resulting from adsorbed water or solvent molecules. Further decomposition of the complexes occurs in three stages (Table IV). Among the complexes, the cobalt complex, Co(II)-PSOPD, was found to be of lower stability. It may be seen that the PSOPD complexes were more stable than the PSHQAD complexes.

Infrared spectra

Infrared spectra of the ligands and the polymer-supported complexes were taken as KBr pellets in the region of 400 to 4000 cm^{-1} . The infrared frequencies of PSOPD and its complexes are given in Table V, and the spectra are depicted in Figure 3. It is seen that PSOPD exhibits a band at 1650 cm^{-1} , which can be assigned to the azomethine¹⁸ C = N

linkage of the Schiff base. This band is observed to show a negative shift by 10 to 25 cm^{-1} in the complexes, indicating the coordination of this nitrogen to the metal in the complexes. The bands at 1268, 1162 cm^{-1} resulting from stretching of the C-N bond (the bond between the aromatic ring and the free amino group) seem to be shifted to a higher frequency. This is probably the result of the shift in electron density from the benzene ring through resonance as the nitrogen is coordinated to the metal. The bands, observed at 552 cm^{-1} for the cobalt complex, at 539 cm^{-1} for the nickel complex, and at 569 cm^{-1} for the copper complex, may be the result of M-N stretching modes.

The spectral data for PSHQAD and its complexes are given in Table VI, and the spectra are represented in Figure 4. In the case of PSHQAD complexes also, the azomethine band at 1660 cm^{-1} for PSHQAD undergoes a red shift on complexation, indicating the coordination of this group. There is an additional peak at 3549 cm^{-1} for Co(II)PSHQAD resulting from O-H stretching. The hydroxyl proton may be retained in this case, whereas in all the other cases, O-H group is deprotonated during the complex formation. The C-O stretching frequencies at 1573 cm^{-1} shifted toward a lower frequency, indicating the coordination of oxygen to the metal. The C-N stretching of the aromatic ring nitrogen at 1460 cm^{-1} also shows a shift toward lower frequencies. This may be the result of the shift in the electron density from the quinoxaline ring as a result of the coordination of oxygen and nitrogen to the metal. The metal oxygen stretching frequencies are at 691, 590, and 698 cm^{-1} for cobalt, nickel, and copper complexes, respectively.

Diffuse reflectance ultraviolet spectra

Because the polymer samples are insoluble in solvents, the spectra were recorded in the diffuse reflectance mode.¹⁹ The diffuse reflectance spectrum is a plot of %R versus wavelength. A Kubelka Munk analysis was performed on the reflectance data.

The diffuse reflectance spectra of PSOPD complexes are presented in Figure 5. Copper complexes of

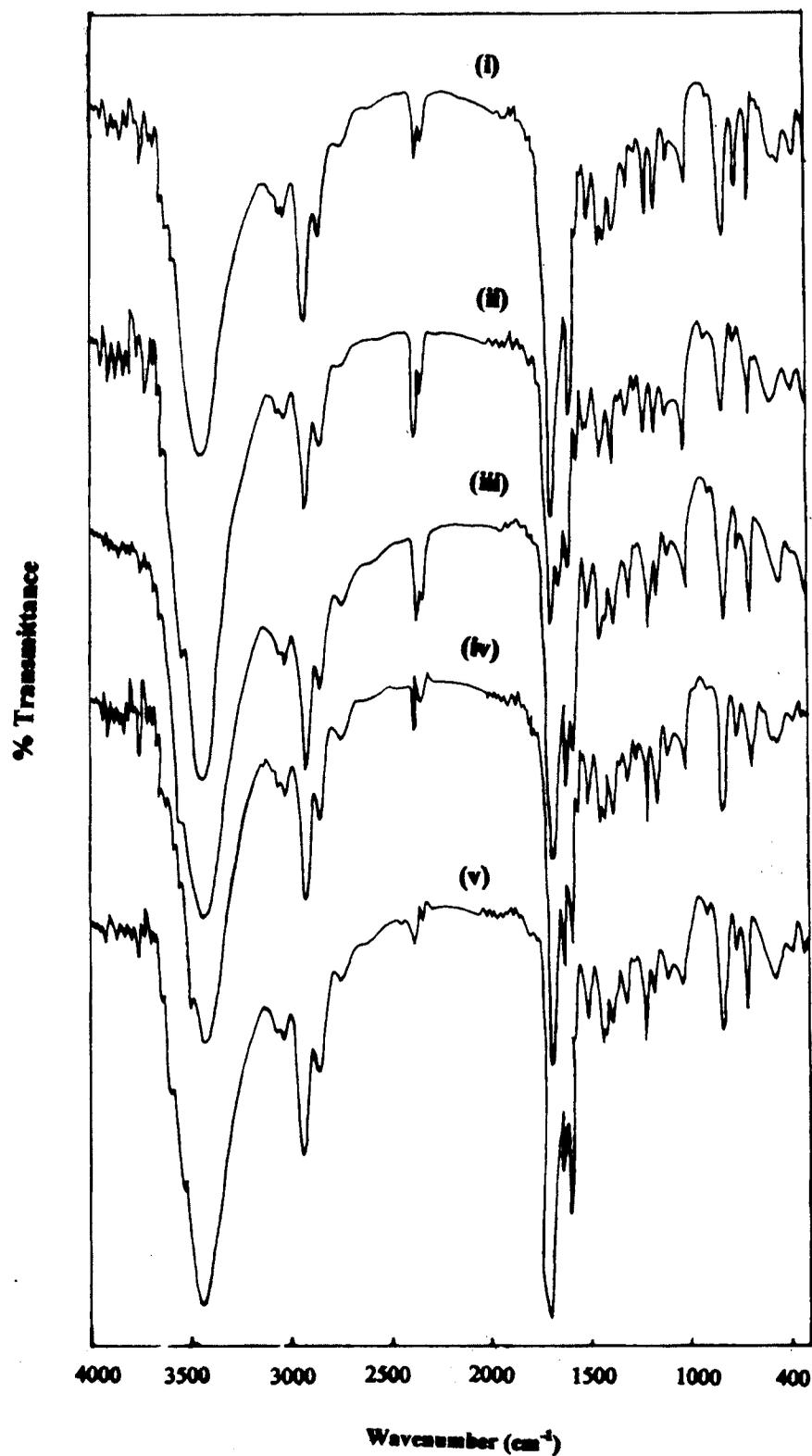


Figure 4 IR spectra of PSHQAD complexes i) PSNH_2 ii) PSHQAD iii) CoPSHQAD iv) NiPSHQAD v) CuPSHQAD.

PSOPD exhibit bands at 9500, 8300, 13,330 cm^{-1} . A copper complex, $\text{Cu}(\text{bipy})_2(\text{ONO})^+$ having absorption maxima at 9500 and 14,000 cm^{-1} , has been reported to have a cis-distorted octahedral structure.²⁰ The

present copper complex may have assigned such a structure. The complex, $\text{Co}(\text{II})\text{PSOPD}$, exhibits bands characteristic of square planar complexes at 8000 cm^{-1} and 11,500 cm^{-1} . The complex is also EPR active. The

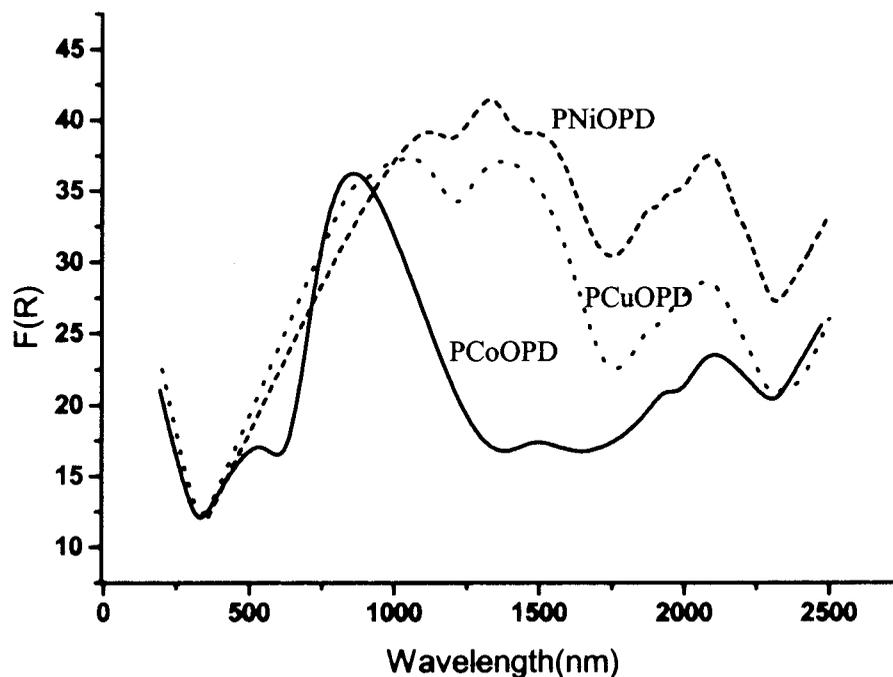


Figure 5 Diffuse reflectance spectra of PS-OPD complexes.

nickel complex showed bands at 8000 and 13,000 cm^{-1} , suggesting octahedral structure.

Among the complexes of PSHQAD, the copper complex exhibits bands (Figure 6) at 16,000, 10,500, 9500, 8000, and 5000 cm^{-1} , indicating a pseudotet-

rahedral complex reported.²¹ The nickel complex exhibits bands at 9500 cm^{-1} and 12,000 cm^{-1} , characteristic of a tetragonally distorted octahedral nickel complex. The cobalt complexes exhibit bands at 5300, 8000, 10,500, 13,300, and 17,000 cm^{-1} , indi-

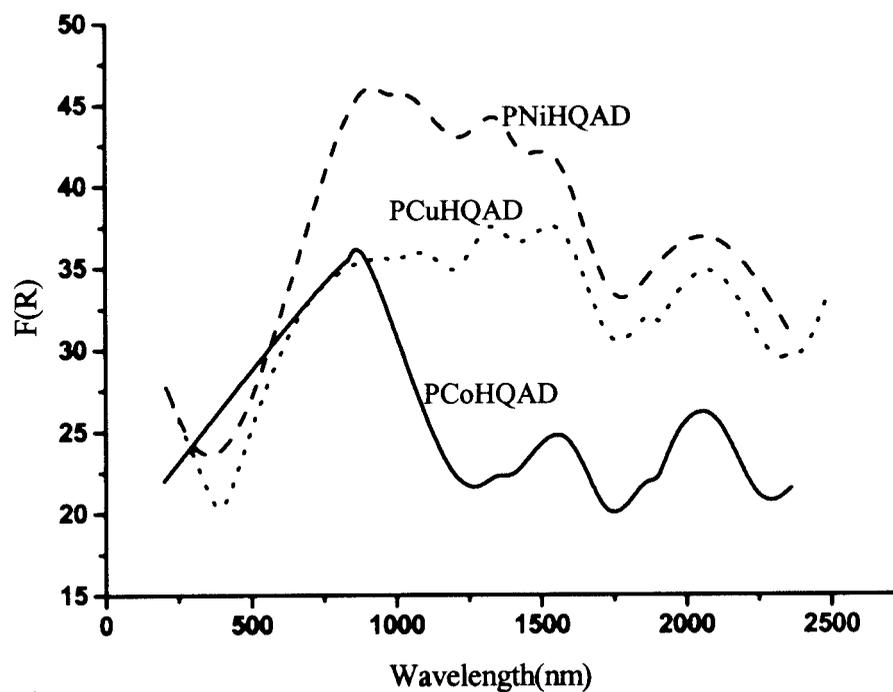


Figure 6 Diffuse reflectance spectra of PS-HQAD complex.

cating low-spin square pyramidal geometry. The complex is EPR active and has a magnetic moment value agreeing with this geometry.

The cobalt complex of Schiff-base PSHQAD is found to have square planar geometry. Such square planar complexes are found to act as catalysts in a number of reactions through reversible binding of oxygen. Thus, a series of Schiff-base complexes, which have the potential of being used as catalysts, were synthesized and were characterized using the above techniques.

One of the authors (SNR) thanks CSIR, New Delhi, India, for the award of Junior Research fellowship.

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