Proc. Indian Acad. Sci., Vol. 88 A, Part 1, Number 1, February 1979, pp. 63-67,
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Magnetic and electrical properties of coordination polymers of 4,4′-dihydroxy-3,3′-diacetyl-biphenylbenzidine

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MS received 24 July 1978; revised 17 November 1978

Abstract. A poly (Schiff base) has been prepared by the condensation of 4,4′-dihydroxy-3,3′-diacetyl-biphenyl and benzidine. Cu(II), Ni(II) and Co(II) coordination polymers of PSB have been synthesised. The magnetic moment and the electrical resistivity have been reported.

Keywords. Poly (Schiff base); coordination polymers; Ni-PSB; Co-PSB; Cu-PSB.

1. Introduction

The good thermal stability, catalytic activity and electrical conductivity of coordination polymers (D'Alelio *et al* 1967; Gooding 1976; Horowit *et al* 1965) encouraged the development of new polymeric materials either from polymeric or monomeric ligands. Much progress has been made in this field and a number of reviews have appeared (Hartel *et al* 1973; Keirr *et al* 1962).

The present study deals with the magnetic and electrical properties of poly-Schiff base (PSB) and its Cu(II), Ni(II) and Co(II) coordination polymers.

2. Experimental

2.1. *Synthesis*

The poly (Schiff base) was prepared by the condensation of 1 : 2 mole quantities of hydroxy ketone (4,4′-dihydroxy-3,3′-diacetyl biphenyl) and aromatic diamine (benzidine) in ethyl alcohol and refluxed for 8 hr at 80° C (chart 1). The polymer was purified by soxhlet extraction with benzene for 24 hr.

PSB was pale yellow in colour and found to be insoluble in the usual organic solvents except in dimethyl formamide (DMF), dimethylsulfoxide (DMSO) and H_2SO_4. The molecular weight estimation was made from the elemental analysis and the order of n was found to be 15.

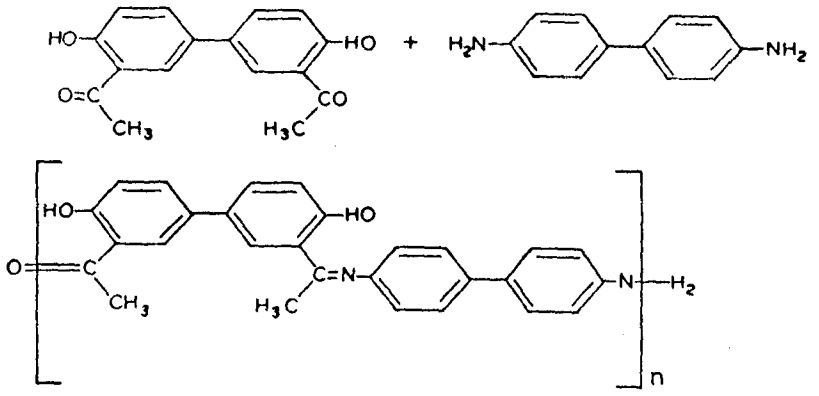
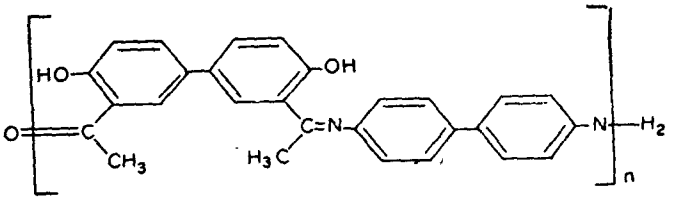


Chart 1

The intrinsic viscosity [η] in 1% DMF solution was found to be 0·092 dl/g at 25° C. The infrared spectrum of PSB showed the characteristic -C=N- band at 1605 cm^{-1} and weak carbonyl and amine bands at 1700 cm^{-1} and 3365 cm^{-1} respectively. The bands around 1500 cm^{-1} showed the presence of aromatic groups.

The coordination polymers of copper, nickel and cobalt were prepared by dissolving equimolar quantities of the ligand and the metal acetate salts in DMF (chart 2) and refluxing the contents for 8 hr. The hot solution was cooled, diluted with water and filtered, washed with water and dried. The Cu(II), Ni(II) and Co(II) polymers were in the form of powder having black, greenish-yellow and



$$+ M(CH_3COO)_2 \cdot xH_2O \xrightarrow[\text{reflux}]{DMF} \text{coordinated polymers}$$

Chart 2

grey colour respectively. All of them were found to be insoluble in common organic solvents and could not therefore be purified by crystallisation. The coordination polymers were then extracted with methanol to remove DMF and any alcohol-soluble constituents. The products were dried under vacuum at 100° C for 24 hr. The data on elemental analyses are given in table 1.

2.2. *Magnetic susceptibility*

Static magnetic susceptibility of the PSB and its coordination polymers was measured by Gouy's method at room temperature. The results are given in table 2.

Table 1. Elemental analysis data for poly (Schiff base) and its coordination polymers

No.	Ligand	Metal salt	C%	H%	N%	M%
1.	Poly (Schiff base)	..	80·12	6·10	6·80	..
2.	Poly (Schiff base)	Cu Ac_2 H_2O	69·13	4·32	5·45	12·16
3.	Poly (Schiff base)	Ni Ac_2 $4H_2O$	73·70	4·20	5·89	8·95
4.	Poly (Schiff base)	Co Ac_2 $4H_2O$	73·15	4·15	5·78	8·88

Ac = CH_3COO^-

Table 2. Magnetic and electrical data for poly (Schiff base) and its coordination polymers

No.	Polymer	Mass magnetic susceptibility (30° C) $\chi_g \times 10^6$ c.g.s. units	$\log_{10} \rho$ (40° C)	E_a (eV)
1.	PSB	0·66	14·65	0·90
2.	Cu-Polymer	1·88	12·45	0·84
3.	Ni-Polymer	2·43	13·65	0·61
4.	Co-Polymer	3·61	14·40	0·61

2.3. *Electrical resistivity*

The electrical resistivity of the ligand and its coordination polymers over a range of temperature was determined using Hewlett-Packard 4329 A, high resistance meter. The results are also given in table 2 and shown graphically in figure 1.

2.4. *Electron spin resonance spectra*

The ESR spectrum of PSB was obtained in DMF solution at 9·55 GHz and 100 kHz magnetic field modulation using a Varian E-4 ESR spectrometer. The typical ESR spectrum is shown in figure 2.

3. Results and discussion

The PSB shows paramagnetism and the magnetic moment per unit was calculated as 1·07 B.M. The magnetic behaviour was also retained in solution and is $7·38 \times 10^{-6}$ e.m.u./g in 0·33M solution of DMF. This indicates that the paramagnetism is related to the individual repeating unit rather than the polymer as a whole.

The ESR spectrum shows hyperfine structure (band width = 6·5 G) which may be because of the interaction between phenolic proton and nitrogen nuclei.

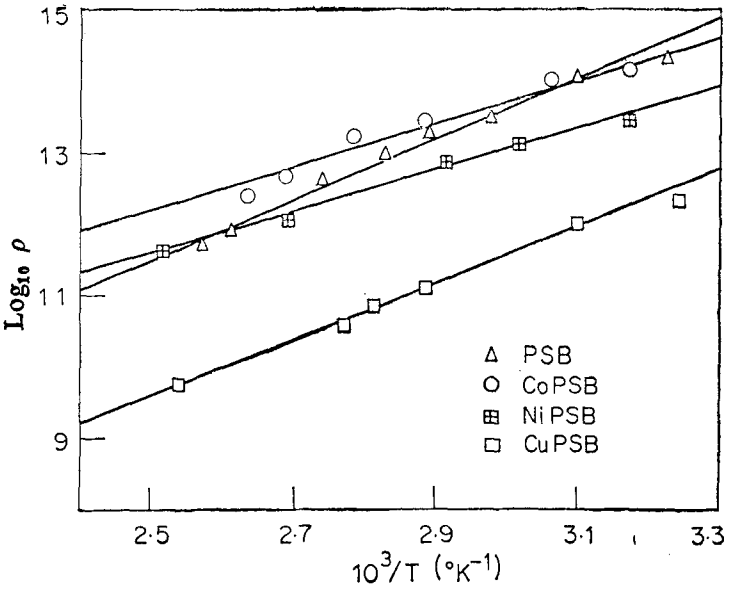


Figure 1. Plots of $\log_{10} \rho$ vs $10^3/T$.

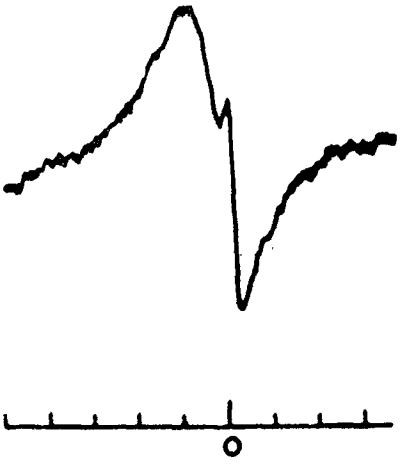


Figure 2. Typical ESR spectrum of poly-Schiff base.

In PSB the signal would be attributed to the unpaired electrons in the -C=N- moiety (Kajiwara *et al* 1975).

The magnetic moments per copper, nickel and cobalt atom are found to be 1·73, 2·23 and 3·27 B.M. respectively. This indicates that copper possesses a square planar, while nickel and cobalt possess a tetrahedral configuration.

The electrical resistivity (ρ) of an organic semiconductor is given by the relation

$$\rho = \rho_0 \exp(E_a/kT) \tag{1}$$

where E_a and ρ_0 are respectively the activation energy and resistivity at infinite temperature. The plots of $\log_{10}\rho$ vs reciprocal temperature (figure 1) are linear as required by (1).

All the coordination polymers of PSB have lower resistivity than their parent ligand (table 2). The values of E_a calculated from the plots are given in table 2. The values of E_a follow the order

$$\text{PSB} > \text{Cu-PSB} > \text{Ni-PSB} \simeq \text{Co-PSB}$$

and the values have the following order

$$\text{PSB} > \text{Co-PSB} > \text{Ni-PSB} > \text{Cu-PSB}.$$

The resistivity was found to decrease by two orders of magnitude for copper by one order for nickel. The resistivity was the same for cobalt coordination polymer in comparison to that of the ligand. The high resistivity of PSB may be ascribed to low molecular weight and unusual morphology while pressing into hard brittle pellet for the measurement.

Acknowledgement

One of us (JTD) is grateful to UGC, New Delhi, for a fellowship.

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