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SYNTHESIS, CHARACTERIZATION, AND CONDUCTANCE OF BENZIMIDAZOLYLPOLYACRYLATE Cu(II), Co(II), AND Fe(II) COMPLEXES

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INTRODUCTION

The imidazole and benzimidazole nucleus and its derivatives are known to play crucial roles in the structure and functioning of a number of biologically important molecules, generally by virtue of their being coordinated to metal ions. Thus, dimethyl benzimidazole supplies one of the five nitrogen atoms coordinated to Co(III) in vitamin B_{12} and several of its derivatives. Current evidence indicates that the manganese-oxygen evolving system in green plant photosynthesis contains at least some of the metal, not as the porphyrin complex but as manganese bound directly to a protein. In general, metal ions bind to proteins through functional groups that are substituents on the macro polypeptide backbone [1]. Metal-protein binding also involves multidentate coordination to two, three, or more of the coordination positions of the metal ions. Good models for protein-bound metals would then be complexes with multidentate ligands with phenolic oxygen and imine-like nitrogen donors, e.g., tetradentate Schiff base complexes have appeared [2] and very few systems showing the linear relationship between thermal stability of metal chelates and structure of chelating agents have been reported [3]. The present study examines the coordinating behavior of the benzimidazole nucleus, which is on the polytrichlorophenylacrylate backbone, toward metal ions.

EXPERIMENTAL

Preparation of Monomer (Addition of Acryloyl Chloride to 2,4,6-Trichlorophenol)

To 0.2 mol 2,4,6-trichlorophenol in ethyl methyl ketone, 0.2 mol triethylamine was added and stirred at 0–5 °C. To this mixture, 0.2 mol acryloyl chloride in ether was added in a dropwise manner over 45 min. Stirring was continued for 2 h. The precipitate that resulted was filtered, and the filtrate was successively washed with ether three times. The ethereal layer was evaporated to obtain 2,4,6-trichlorophenylacrylate monomer. The product was identified through NMR spectral [4] data.

^{1}H NMR (δ ppm): 5.5-6.1 ($\underline{H}$), 7.47-7.93 (2$\underline{H}$), 7.32 ($\underline{H}$). ^{13}C NMR (δ ppm): 126.177 ($^{7}\underline{C}$), 129.614 ($^{6}\underline{C}$), 161.78 ($^{5}\underline{C}$), 142.8 ($^{4}\underline{C}$) 133.9 ($^{3}\underline{C}$ and $^{5}\underline{C}$), 131 ($^{1}\underline{C}$), 128 ($^{2}\underline{C}$ and $^{6}\underline{C}$).

Polymerization of Monomer

Bead polymerization was carried out at 80 ± 2°C by using polyvinyl alcohol as the stabilizer and benzoyl peroxide as the catalyst. The controlled stirring rate of 400 rpm was maintained for 12 h. 4% Divinylbenzene was applied as the crosslinking agent. The beads that resulted were filtered and washed with petroleum ether, ethyl methyl ketone, acetone, and dichloromethane to remove unreacted monomer. The product was dried in a vacuum oven at 60°C. Yield: 80%.

The product was identified through solid-state ^{13}C-CP/MAS NMR and IR spectra.

Functionalization of Polymers

Functionalization of poly(trichlorophenylacrylate) was achieved by incorporating a benzimidazole nuclei through a postpolymerization reaction.

Crosslinked polymer (5 g) and benzimidazole (10 g) in dimethylformamide were placed in a 500-mL round-bottomed flask and refluxed for 12 h. The functionalization was maximized and attained constancy after 12 h. The contents were filtered, and the functionalized beads were collected, washed with solvents, and dried in a vacuum oven at 60°C.

Preparation of Metal Complexes

Five grams of metal salts [Cu(II), Co(II), and Fe(II) in the form of copper(II) sulfate pentahydrate, cobalt(II) chloride hexahydrate, and ammonium iron(II) sulfate hexahydrate, respectively] in a dimethylformamide-water mixture were treated with 5 g of a functionalized polymer and refluxed for 10 h in triply distilled water as the medium at a pH of 6.9 ± 0.1. The reaction mixture was filtered, and the resulting green (copper), pink (cobalt), and yellow (iron) metallated polymers were washed with hot water and solvent and dried in a vacuum oven at 60°C.

RESULTS AND DISCUSSION

Elemental Analysis

Elemental analysis data are presented in Table 1. The data show that the conversion of functionalization is 22% and that of metallation is 100, 94, and 34%, respectively, for the Cu(II), Co(II), and Fe(II) complexes. It is evident that each benzimidazole nuclei is metallated in a 1:1 ratio.

Solid-State ^{13}C-CP/MAS NMR Spectroscopy

The ^{13}C-NMR spectra of the crosslinked polymer as recorded on a Bruker 300 MSL CP-MAS at IISC, Bangalore, are shown in Fig. 1. The backbone methylene carbon appeared as a very broad peak at 38.66 ppm in the solid-state NMR and at 45.89 ppm as a very sharp peak in the solution (monomer) state NMR. The $-C=C$ of the phenyl ring appeared at 141.59 ppm in the crosslinked polymer and at 142.88 ppm in the monomer as a sharp line and as a broad peak, respectively. The $^2\underline{C}$ and $^6\underline{C}$ of the phenyl ring give lines at 126.17 ppm in the monomer and 127.14 ppm in the crosslinked system. The carbonyl carbon of the ester [5] appears as a broad peak in the crosslinked system at 169.55 ppm and as a small but sharp line at 161.78 ppm for

TABLE 1.

	C, %	H, %	N, %
TCPA-Bz	31.765	4.101	3.463 (16.271)[a]
TCPA-Bz-Cu(II) complex	16.621	2.151	1.047 (1.07)[a]
TCPA-Bz-Co(II) complex	35.482	2.563	4.252 (9.276)[a]
TCPA-Bz-Fe(II) complex	50.214	3.012	1.023 (6.142)[a]

[a] For 100% calculated value.

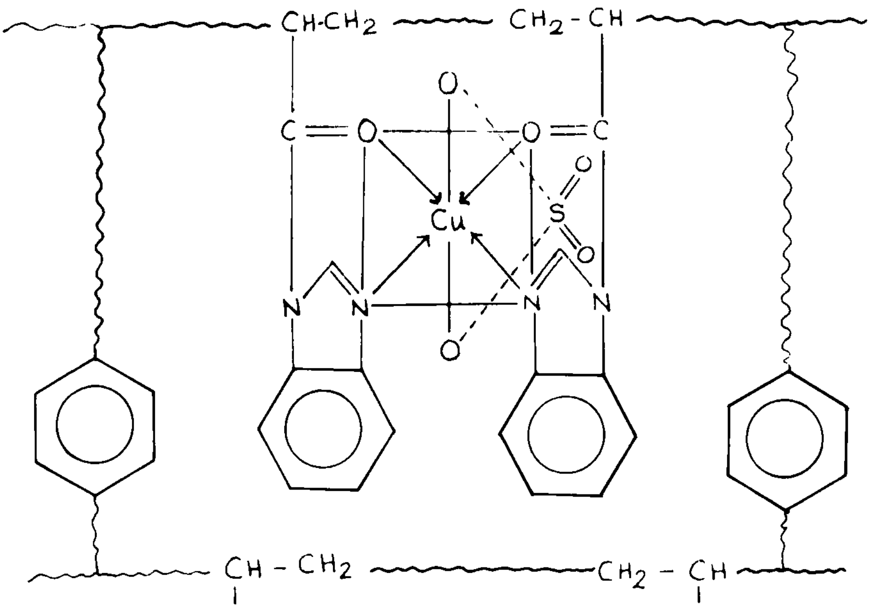

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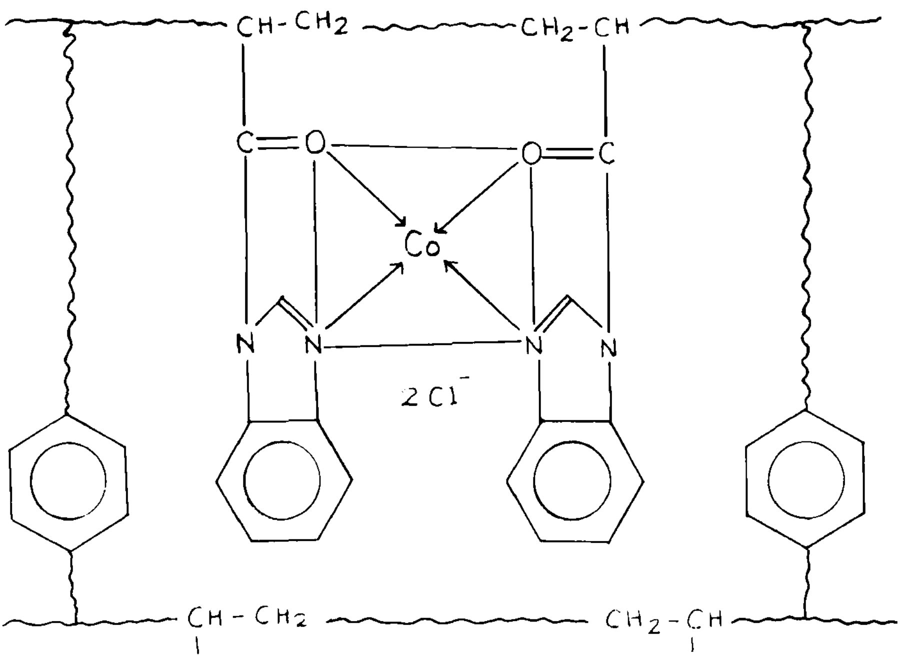
TABLE 1. Continued.



the monomer. Despite the broadness of the aromatic peaks in the crosslinked polymers, the individual peaks for the aromatic carbon atoms can be very precisely and unambiguously identified. The O=C—N group appears at 172 ppm in the case of the TCPA-Bz system. It is not present in the TCPA-DVB system.

IR SPECTRAL STUDIES

The IR frequencies of the polymer, the functionalized polymer, and its copper(II), cobalt(II), and iron(II) complexes are shown in Table 2.

From Table 2 it can be inferred that the frequency of $>C=N$ in the functionalized polymer shows a downfield shift which indicates its participation in coordination. The carbonyl oxygen also participates in coordination due to the highfield shifts of $\Delta 12$, $\Delta 15$, and $\Delta 17$ cm^{-1} in the cases of Cu(II), Co(II), and Fe(II) complexes, respectively. The C—N frequency in the spectra did not undergo any change. The =CH—COOR group shows highfield shifts of $\Delta 9$, $\Delta 8$, and $\Delta 11$ cm^{-1} in the cases of the Cu(II), Co(II), and Fe(II) complexes, respectively, which indicates functionalized polymer coordination to the metal ion. The very broad peak at 1040 cm^{-1} in the case of the Cu(II) complex and at 1088 cm^{-1} in the case of the Fe(II) complex is direct proof of the presence of sulfate ions.

EPR Studies

The EPR parameters calculated by the Kneubuhl [14] method for the complexes are shown at the top of page 178.

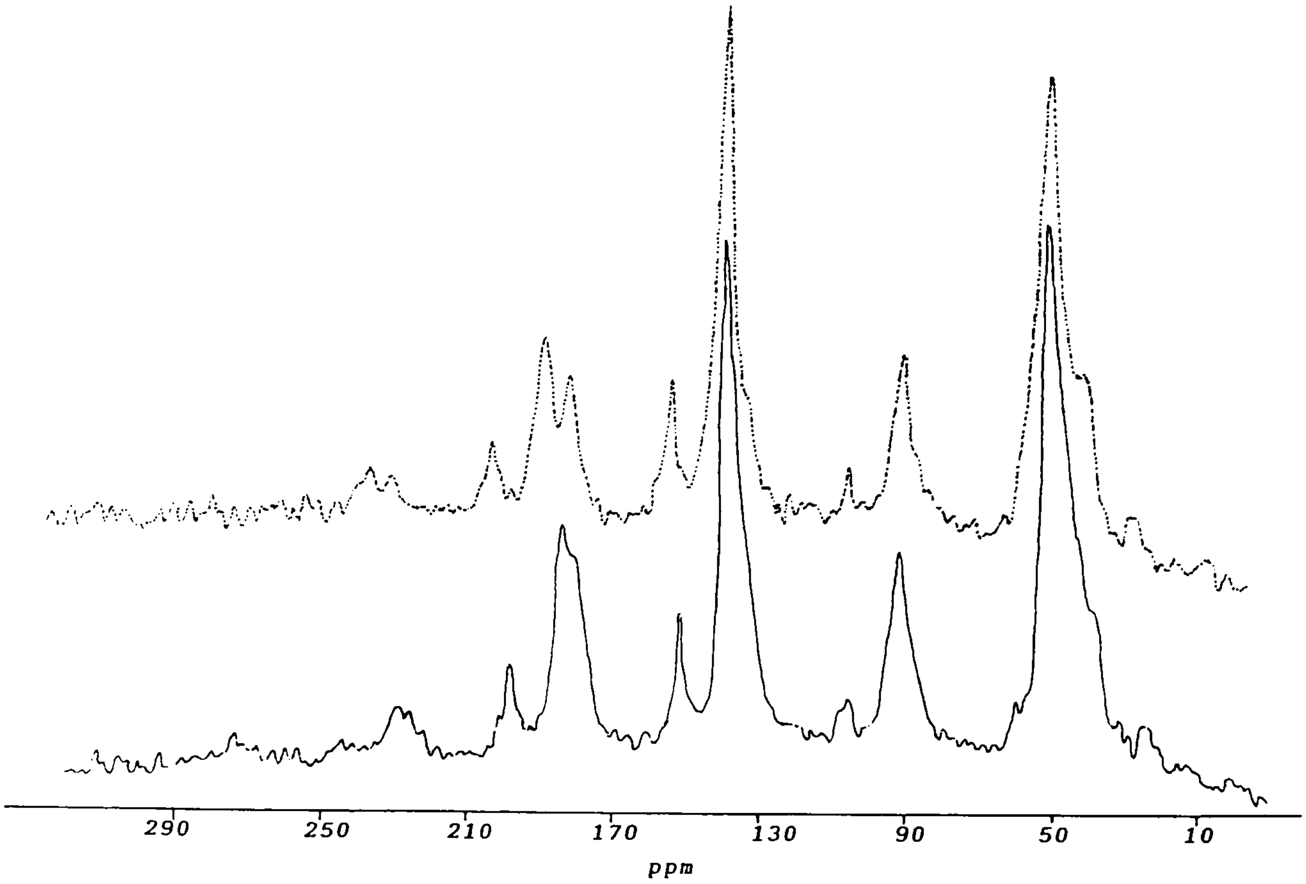


FIG. 1. Solid-state ^{13}C-CP/MAS NMR of TCPA-DBV (· · ·) and TCPA-DVB-Bz (—).

Complexes	A	$g_{\parallel}$	$g_{\perp}$
Cu(II)	72 G	2.22	2.12
Co(II)	24 G	2.21	2.11

The EPR spectra of Cu(II) and Co(II) are presented in Fig. 2. The EPR spectra of the cupric complex show a strong signal characteristic of bivalent copper [15]. The signal of the copper complexes of univalent copper is zero. It is shown in the literature that the lower part of the strong signal is a doublet for bivalent cooper in a square planar belonging to dsp^2 coordination. Our complex did not show any doublet in the lower part of the strong signal. Therefore, we assume an almost planar cupric [16] ion in the center with the nitrogen, carbonyl oxygen, and sulfate groups on the X and Y axes. Molecules of water are weakly coordinated along the Z axis according to the reaction conditions. Thus, the results of EPR measurements have corroborated the conclusions from our analysis of the IR spectra.

Low spin Co(II) in an octahedral field with tetragonal distortion is expected to have spin orbit coupling parameter $\lambda < 0$, and as a consequence, $g_{\perp} > g_{\parallel}$ [17]. In such cases, the unpaired electron solely occupies the d_z^2 orbital. For example, for cobalt phthalocyanine, $g_{\perp} = 2.68$ and $g_{\parallel} = 2.016$, and for $[Fe(CN)_5NOH]^{2-}$, $g_{\perp} = 2.074$ and $g_{\parallel} = 2.0669$. It is reasonable to conclude that the g value in such compounds lies very close to that of a free electron. In our present investigation, $g_{\perp} = 2.11$ and $g_{\parallel} = 2.21$. $g_{\perp}$ is far from the free electron and very close to the electrons in a tetrahedral environment, thus confirming a total spin of 3/2.

The EPR signal corresponding to an Fe(II) complex is not observed at room temperature, and this may be due to a low percentage of metallation (34%).

Magnetic Studies

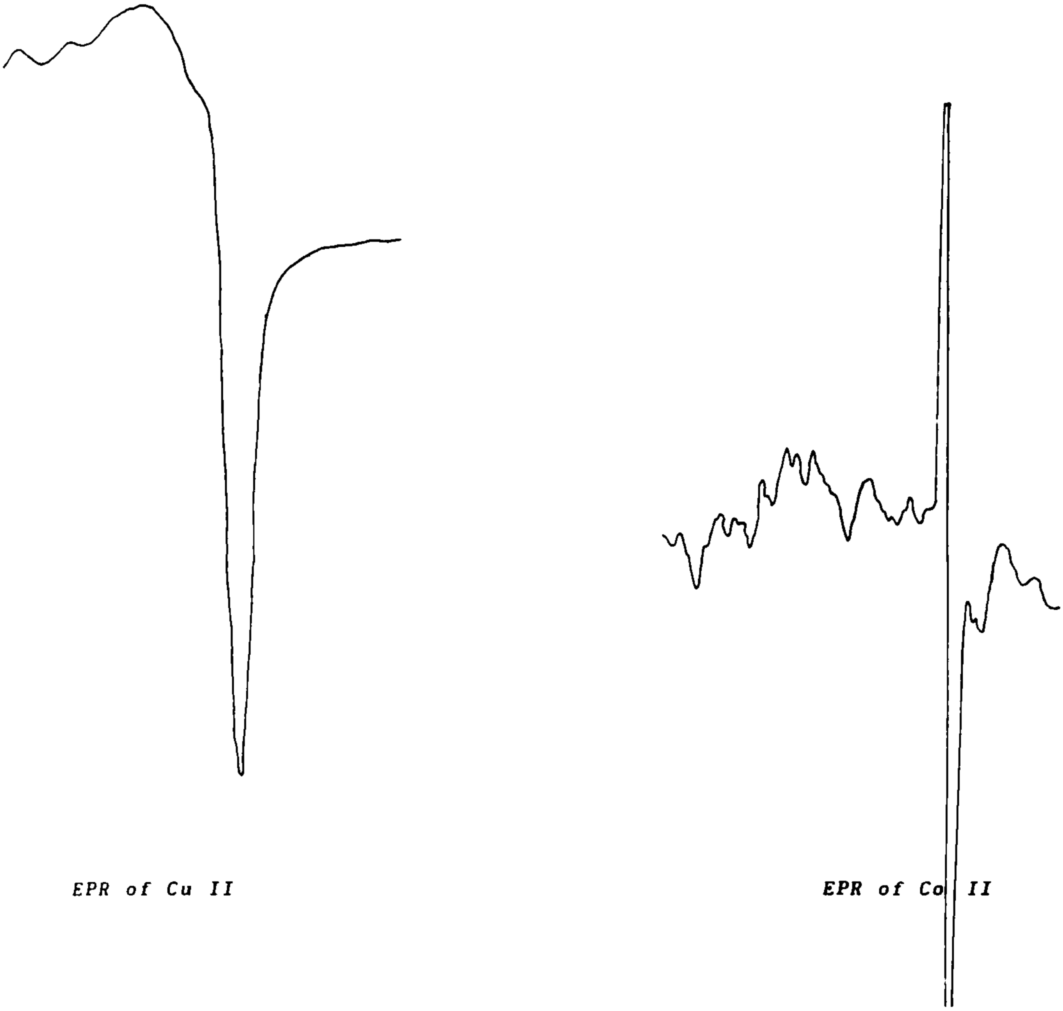
The magnetic data reveal that the three complexes are paramagnetic. The values are given in Table 3.

Optical Microscopy

The spherical nature of the beads was observed by optical microscopy. These microphotographs are presented in Fig. 3.

TABLE 2. IR Frequencies (cm^{-1})

Polymer	Functionalized polymer	Copper(II) complex	Cobalt(II) complex	Iron(II) complex	Assignment	Refs.
1771	1771	1780	1779	1782	=CH−COOR	6
1440	1440	1440	1438	1447	C=C	
—	1560	1540	1565	1565	C=N	
—	1360	1360	1360	1360	C−N	7-9
1708	1708	1720	1723	1725	C=O	10-12
—	—	1040	—	1088	SO_4^{2-}	13



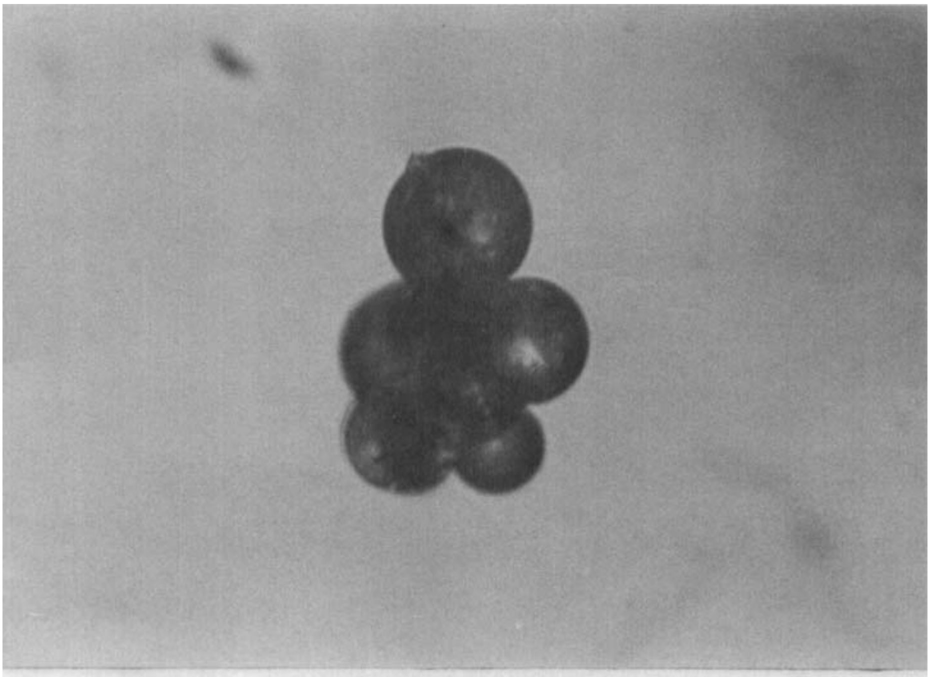
EPR of Cu II

EPR of Co II

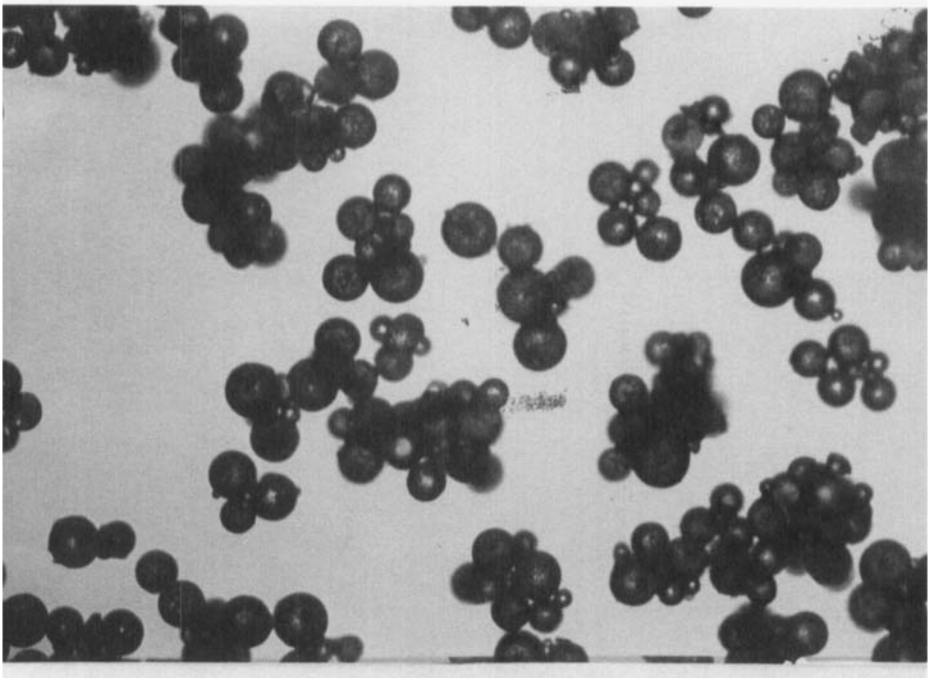
FIG. 2.

TABLE 3.

Field (kG)	Moment (EMU)		
	Cu(II)	Co(II)	Fe(II)
3	0.025×10^{-2}	0.078×10^{-2}	0.070×10^{-2}
4	0.028×10^{-2}	0.101×10^{-2}	0.088×10^{-2}
5	0.032×10^{-2}	0.122×10^{-2}	0.105×10^{-2}
6	0.042×10^{-2}	0.124×10^{-2}	0.108×10^{-2}
7	0.056×10^{-2}	0.127×10^{-2}	0.108×10^{-2}

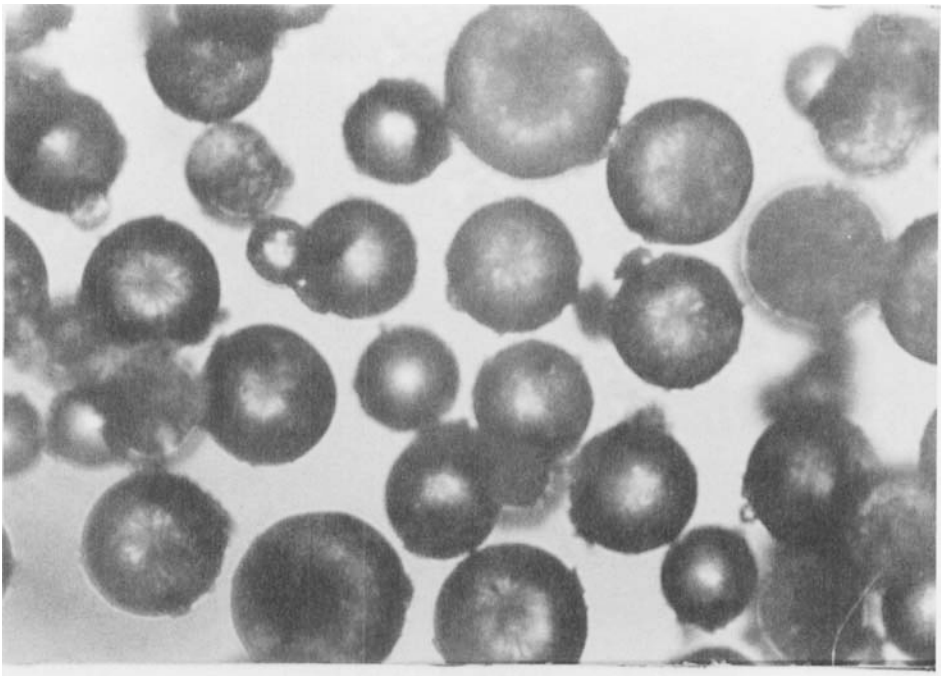


TCPA - DVB - Bz
complex

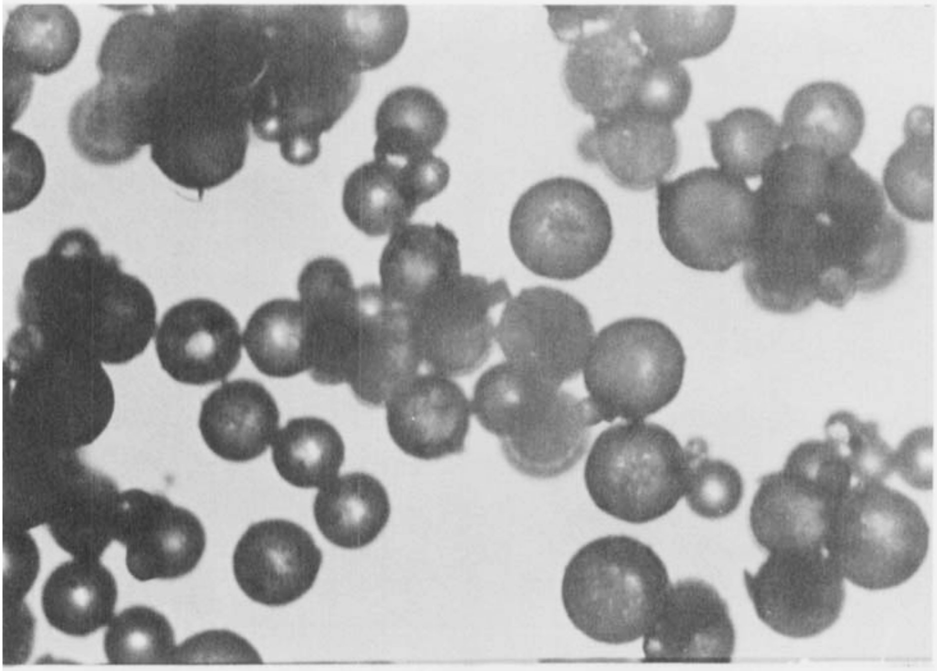


TCPA - DVB - Bz - Cu (II)
complex

FIG. 3.

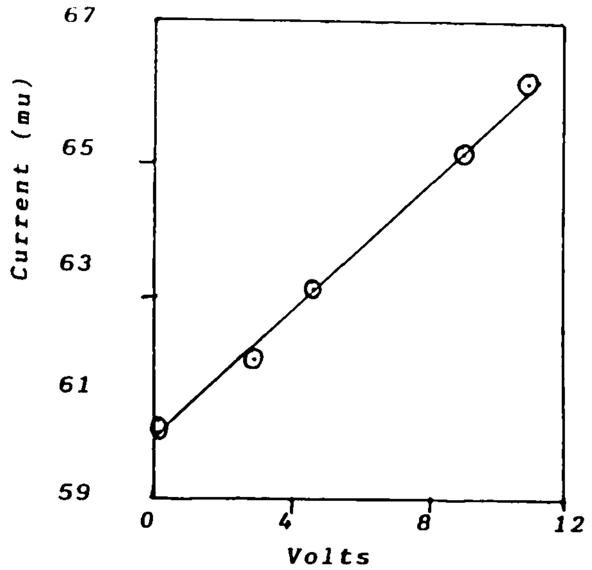


TCPA - DVB - Bz - Co (II)
complex

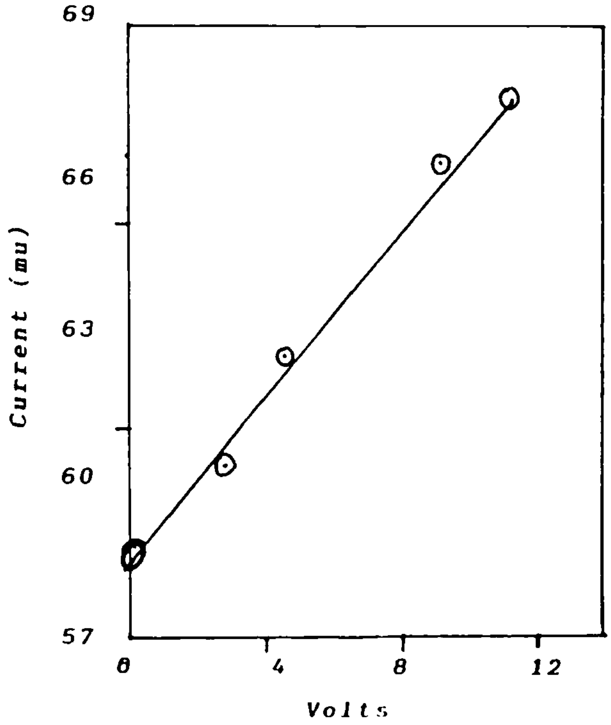


TCPA - DVB - Bz - Fe (II)
complex

FIG 3. (continued).



Conductance Measurement of Polymer



Conductance Measurement of Cu II Complex

FIG. 4.

TABLE 4.

		Polymer		Copper complex	
No.	*V*	1/*a*	*I*	1/*a*	*I*
1	2.44	3.3075	59	6.3143	57
2	5.00	3.3075	61	6.3143	60
3	6.60	3.3075	63	6.3143	63
4	11.20	3.3075	67	6.3143	69
5	13.00	3.3075	69	6.3143	71

APPLICATIONS

Electrical Conductance

The electrical conductances of the polymer and its copper complex were measured by studying the current-voltage curves of the specimens at room temperature. The potential was applied through a variable dc source and recorded on a Philips PK-5230 Voltmeter. The current was measured on a Nanoammeter model NM-122, Scientific Equipment. The graphs are shown as Fig. 4.

Table 4 show that both the polymer and its copper complex have a linear relationship for current and voltage. It has been calculated that TCPA-Bz and its copper complex have conductance values of 2.13×10^{-6} and 2.4×10^{-6} ohm^{-1}, respectively. The specific conductance values are 0.3224 and 0.3628 ohm^{-1}·cm^{-1}, respectively.

SUMMARY

Transition metal ions (Cu^{2+}, Co^{2+}, and Fe^{2+}) have been attached through coordinate bonds to a functionalized polymer backbone. The almost planar cupric ion is in the center with the nitrogen, carbonyl oxygen, and sulfate groups coordinated. Polymer synthesis was confirmed through ^{1}H-^{13}C-CP/MAS NMR spectra. From magnetic studies, all the complexes are paramagnetic. Doping of copper results in a small increase in electrical conductance. Microphotographs of metallated polymer have been compared to those of nonmetallated polymer. The copper complex is square planar while the cobalt complex is tetrahedral. Possible structures are assigned for the two complexes.

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