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Dicopper Complexes of Polyethyleneimine and Polyvinylamine Vinylsulfonate

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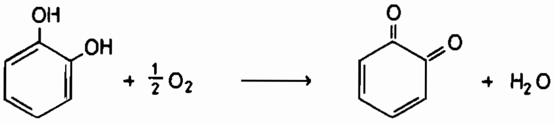
Binuclear copper(II) complexes prepared with the binucleating ligand 2,6-diformyl-4-methyl-phenol were attached as pendant groups to the polymers polyethyleneimine and polyvinylaminevinyl sulfonate sodium salt. The polymer–copper(II) complexes were characterized from optical and magnetic studies and their catecholase activities were measured in water. Polyvinylamine–vinylsulfonate–copper(II) is insoluble in water and showed little if any catecholase activity. The polyethyleneimine–copper complexes were reasonably soluble in water and demonstrated good catecholase activity. The catecholase activity of the polyethyleneimine–copper complexes increased in activity with an increase in the ratio of polymer-to-copper content (based on a constant copper concentration).

Introduction

Simple dicopper complexes have recently received renewed attention. They have been shown to catalyze several important industrial reactions [1, 2]. They have also been studied as type 3 copper ions in model enzyme studies [3, 4]. Interest in our laboratory has been concerned with the latter [4, 5]. We previously prepared simple dicopper complexes which catalyzed the dioxygen oxidation of catechols (eqn. 1) and thus mimic the behavior of polyphenoloxidase:



Others have shown that dicopper complexes attached to polymers may offer advantages in catalysts over the simple dicopper analogs [6]. By attaching our previously prepared simple dicopper complexes to polyethylene (PEI, Fig. 1) and the copolymer poly(vinylamine-vinylsulfonate sodium salt) (PVA, Fig. 2) we hoped to enhance the catecholase activity of the system and at the same time immobilize the simple complex.

We report the synthesis and characterization of polyethyleneimine-dicopper complexes, (PEI Cu) and poly(vinylamine-vinylsulfonate) dicopper complexes (PVA Cu) (Fig. 3) which are analogs of the previously prepared simple dicopper complexes in Fig. 4. Because the PEI Cu complexes are moderately

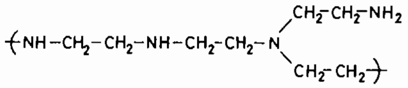


Fig. 1. Polyethyleneimine.

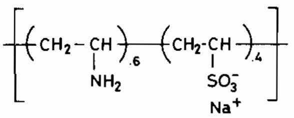
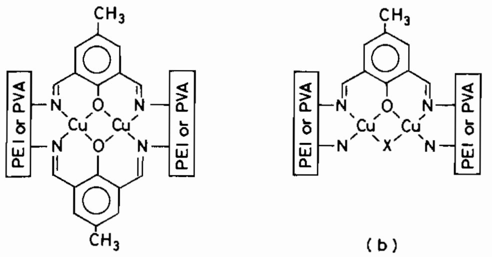
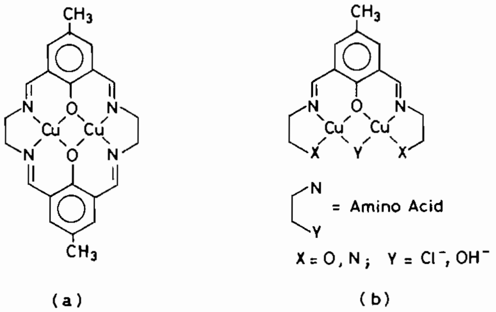


Fig. 2. Copolymer of poly(vinylamine-vinyl-sulfonate sodium salt), 60% amine/40% sulfonate.



(a) (b)

Fig. 3. PEI Cu complexes.



(a) (b)

Fig. 4. Simple dicopper complexes.

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soluble in water, attempts to insolubilize the complexes by crosslinking the polymer amines with dibromobutane were attempted. The results only served to increase the solubility of the PEI Cu complexes. Thus, the catecholase activity and the oxygen uptake studies reported in this work utilize the PEI Cu complexes as homogeneous. catalysts. The PVA Cu complexes were insoluble in water and are studied as heterogeneous catalysts.

Experimental

Synthesis

The ligand 2,6-Diformyl-4-methylphenol was prepared by the method in reference [7].

The polyethyleneimine–dicopper complexes (PEI Cu) were prepared in a manner similar to the simple dicopper complexes [4]. The PEI polymer was purchased from Aldrich Company as a 30% solution in water (see Fig. 1). The appropriate amount of PEI solution was added to 30 ml volume of ethanol containing the diformyl ligand and $Cu(ClO_4)_2 \cdot 6H_2O$. The amounts of reactants in solution used to prepare the PEI Cu complexes were as follows:

Weight Ratios, grams

	PEI /	Cu /	L	% Cu found
PEI #10	0.480	0.37	0.164	8.80
PEI #12	0.960	0.37	0.164	8.11
PEI #14	1.920	0.37	0.164	5.60
PEI #16	2.880	0.37	0.164	3.75

L = 2,6-diformyl-4-methylphenol, $Cu=Cu(ClO_4)_2 \cdot 6H_2O$

The mixture was warmed for 10 minutes to 60 °C and precipitates were formed which varied in texture from a powder (PEI #10) to a tacky solid (PEI #16). The precipitates were washed with ethanol and dried at 40 °C in a vacuum oven. The analysis for the % copper found in the complexes is given above.

The PEI Cu complexes were found to be moderately soluble in water and other polar solvents. When the complexes were heated for one hour and then allowed to return to room temperature, the saturated solutions were found to be at least 3.0×10^{-4} *M* in dicopper. The concentrations of these solutions were approximated spectrophotometrically by using a molar extinct coefficient of $\epsilon = 120$ for λ_{max} at about 600 nm.

An attempt was made to render the complexes completely insoluble by the addition of 1–4-dibromobutane commonly used to crosslink polymeric amines. Various amounts of dibromobutane were added to a mixture of PEI Cu complex in tetrahydrofuran ranging from 3% (per mol of amine) to 100% dibromobutane. The reactants were stirred for 24 hours. No significant change in the PEI Cu complex was observed at low concentrations of dibromobutane. At higher concentrations a noticeable change in the texture took place with a corresponding increase in the water solubility of the complexes. No further attempts were made to render the complexes soluble in water.

The preparation of the poly(vinylamine-vinylsulfonate)–dicopper complexes (PVA-Cu) were performed in a manner similar to the simple dicopper complexes previously prepared in this laboratory [4]. The PVA polymer was added to 30 ml of ethanol. The PVA solution was then added to 30 ml of ethanol solution containing the diformyl ligand and $Cu(ClO_4)_2 \cdot 6H_2O$. The amounts of reactants in solution used to prepare the PVA-Cu complexes were as follows:

Weight Ratio, grams

	PVA	Cu	L	% Cu found
PVA #10	0.480	0.37	0.164	10.15
PVA #12	0.960	0.37	0.164	9.35
PVA #14	1.920	0.37	0.164	8.25
PVA #16	2.880	0.37	0.164	7.10

L = 2,6-diformyl-4-methylphenol, $Cu=Cu(ClO_4)_2 \cdot 6H_2O$

The mixture was warmed for 10 minutes to 60 °C. The resulting powdery green precipitates were filtered and washed well with ethanol and then dried at 40 °C in a vacuum oven. The complexes were analyzed for copper and the results are given in the table above.

Infrared Analysis

The infrared spectra of the ligands and complexes were run on a Perkin-Elmer PE 283 IR spectrometer. Samples were prepared in both KBr pellet and in nujol.

Ultra-Violet–Visible–Near Infrared

Optical spectra in the uv–vis–ir regions were run on a Cary 17 spectrophotometer. The spectra were run in solutions of water and DMSO.

Magnetic Moments

The magnetic moments of Cu^{+2} were calculated from measurements made on the solid using a Gouy type method developed by Eaton [8] and in solutions of DMSO using the NMR method of Evans [9].

TABLE I. Electronic Spectra and Magnetic Moments.

Complexes	Magnetic Moments		Electronic Spectra			
	μ_{eff} DMSO	(per Cu), B.M. Solid	$\pi \rightarrow \pi^*$ Benzene Ring	$\pi \rightarrow \pi^*$ Azomethine	Charge Transfer	Copper(II) d–d Band
PEI #10	1.67	1.75	250/270	405	450	610
PEI #12	1.57	1.65	250/270	400	450	620
PEI #14	1.60	1.60	218/250/270	395	430	620
PEI #16	1.69	1.48	215/250/270	395	420	620
PVA #10		2.23	230/260	380	410	650
PVA #12		1.53	230/260	385	415	625
PVA #14		1.48	230/260/275	390	420	625
PVA #16		1.64	220/250/260	395	430	620
FSAL(Gly)		1.71	225/250	385	410	655
FSAL(PN)		0.59	215/250	385	405	590

[a] PVA Cu electronic spectra were run in DMSO, PEI Cu electronic spectra were run in water. [b] Spectral data of FSAL (Gly) and FSAL (PN) were taken from reference [4].

Catecholase Activity

By heating the PEI Cu complexes in aqueous solution to 60 °C and allowing the solutions to cool, solutions with PEI Cu concentrations of at least 3×10^{-4} *M* could be prepared. The dicopper concentration was estimated spectrophotometrically at λ_{max} = 620 nm and molar absorptivity of 120 M^{-1} cm^{-1}. These saturated solutions were adjusted to 10^{-4} *M* in dicopper. The initial rate of catechol oxidized to *o*-quinone was measured optically by following the *o*-quinone peak at λ = 390 nm (ϵ = 1417 M^{-1} cm^{-1}) using a reaction mixture of 10^{-4} *M* dicopper and 10^{-3} *M* catechol in a 10 mm cuvette of a Cary 17 spectrometer.

Because of their insolubility in water, the activity of the PVA Cu complexes was measured in a specially built reaction vessel located outside the sample compartment of the spectrophotometer. The PVA Cu complex was powdered by crushing with the tip of a spatula and 0.0212 g was placed in the reaction vessel containing 47.2 ml of buffer solution at pH = 7.0. Enough catechol was injected into the stirred vessel containing the heterogeneous PVA-Cu to make a 10^{-3} *M* solution in catechol. A small amount of the reacting mixture was continuously pumped from the vessel through a filter into a flow-through cell in the spectrometer where the production of *o*-phenol was measured at λ = 390 nm.

A cell was constructed to measure the oxygen uptake of the reactions catalyzed by the PEI Cu and the PVA Cu complexes. It was constructed with an Orion Model 97-08 Oxygen probe in contact with the reaction solution (47.2 ml). The solution was completely devoid of air above the solution level, and this allowed for a small amount of concentrated catechol solution to be introduced into a buffer solution (pH = 7.0) containing PEI Cu or PVA Cu. The PEI Cu was placed in the cell as a 10^{-4} *M* buffered solution but the PVA Cu was powdered with a spatular tip and 0.0212 g were dispersed in the buffer solution. The cell was equipped with a magnetic stirring bar. Upon injection of the concentrated catechol solution, the kinetics of the oxygen depletion caused by the catechol oxidation were measured.

Results and Discussion

Synthesis

The PEI Cu complexes were prepared with varying amounts of PEI polymer. The first complex, PEI #10, was prepared with stoichiometric mixtures of PEI (calculations were based on primary amines), Cu^{+2} and 2,6-diformyl-4-methyl phenol. The PEI #10 complex formed with a somewhat crystalline green texture after drying in a vacuum oven. PEI Cu complexes prepared with larger ratios of the PEI polymer showed less crystalline character of the complex. PEI #16 which contained the largest amount of PEI polymer resembled solid green glass, which appeared to be tacky when wet. Analysis showed a decrease in copper from PEI #10 to PEI #16.

The PVA Cu complexes were prepared in a manner similar to the PEI Cu complexes. They were medium green in color and could be powdered with the tip of a spatula. The complexes were found to be slightly soluble in dimethylsulfoxide but insoluble in water.

Infrared Spectra

The ir spectra of each of the PEI Cu complexes were very similar, probably because of the large amount of polymer material in the complexes. The ClO_4^- bands were found at around 600 cm^{-1} and

1100 cm^{-1} in both nujol and KBr matrices. These bands were found to be weaker and broader in the PEI Cu complexes than the ClO_4^- bands found in $Cu(ClO_4)_2 \cdot H_2O$. The bands suggest that the counter ions for Cu^{+2} are ClO_4^- ions rather than OH^-, as may sometimes be found for such polymeric complexes. A band at 1530 cm^{-1} was assigned to ν (skeleton) of the benzene ring and a band at 1630 cm^{-1} was assigned to the ν(C=N). These peaks demonstrate the presence of the 2,6-diformyl-4-methylphenol moiety and its participation in the Schiff Base reaction with primary amines of the PEI polymer.

The infrared spectra of the PVA Cu complexes showed little or no sign of the ClO_4 ion. The presence of the $-SO_3^-$ ion was seen at 1200 cm^{-1} and replaced the ClO_4 ion as the counter ion to Cu^{+2}. A band at 1625 cm^{-1} was observed and is assigned to the Schiff Base ν(C=N). The ν(skel) and ν(C–O) of the diformyl ligand are identified from bands at 1550 cm^{-1} and 1350 cm^{-1}

Ultra-Violet–Visible–Near Infrared Spectra

The optical electronic spectra for PEI Cu and PVA Cu complexes are given in Table I. Both sets of complexes show a series of bands between 215 and 270 nm. The bands are assigned to the $\pi \rightarrow \pi^*$ transitions of the benzene ring of the diformyl ligand. Two other groups of transitions are found at around 390 nm and 420 nm. The transitions found around 390 nm are assigned to the $\pi \rightarrow \pi^*$ of the (C=N) formed by the Schiff Base reaction between the polymer amine and the diformyl ligand [10]. The lower energy transitions at around 420 nm are probably M → L charge transfer bands, but may also result from $\pi \rightarrow \pi^*$ of the C=N group. These results clearly show the presence of the diformyl ligand in the polymer complex.

The presence of copper(II) ions is also obvious in the green complexes. The d–d transitions of the copper(II) ions in the PEI Cu complexes are generally at 620 nm. Much weaker and more poorly defined bands are also found at around 850 nm and 1050 nm. The bands are found in the same region as those found in the simple dicopper complexes illustrated in Fig. 4, but they are found to be broader. The broadness is characteristic of metal complexes prepared in polymeric ligands, but it also raises some doubt as to the structure of copper(II) ions in the polymer. It is possible that more than one copper(II) site exists in the polymer complex.

The d–d transitions of the copper(II) ions in the PVA Cu complexes are also comparable to the transition found for the simple dicopper complexes given in Table I. Again, the transitions are broad and may be due to the effect of the polymer ligand, but it is also possible that the copper ions are not all in the same site symmetry.

TABLE II. Catecholase Activity.

Complex	Initial Rates	
	o-Quinone produced (mol/L min × 10^7)	Oxygen uptake (mol/L min × 10^7)
PEI #10	0.31	1.0
PEI #12	1.0	2.7
PEI #14	1.0	5.6
PEI #16	6.2	15.3

$[Cu_2] = 10^{-4}$ *M*, [Catechol] = 10^{-3} *M*.

Magnetic Moment

Reduced magnetic moments of copper(II) ions (from values of μ 1.85 B.M.) were previously used to demonstrate binuclearity of two copper(II) ions in simple dicopper complexes [4]. Examples of the magnetic moments of the simple dicopper complexes FSAL(Gly) and FSAL(PN) were found to be 1.71 B.M. and 0.59 B.M. respectively. Their structures are given in Fig. 4a, 4b. The PVA Cu and PEI Cu complexes are expected to have similar structures (proposed structures are given in Fig. 3a, 3b). The magnetic moments of the PVA Cu and PEI Cu complexes are listed in Table I and range below 1.85 B.M. The low magnetic moments and the expected structures of PVA Cu and PEI Cu complexes suggest that the copper(II) ions (or most of them) are in dicopper sites similar to those in the simple dicopper complexes. Bands between 590 and 655 nm are the d–d bands of Cu(II).

Catecholase Activity

The PVA Cu complexes demonstrated little or no catalytic activity using the optical method for measuring the production of *o*-quinone. The oxygen uptake method is more sensitive and did demonstrate some activity for the PVA Cu complexes but not nearly so much as was found from the PEI Cu studies.

The results of the PEI Cu activities are shown in Table II. The results of the optical method are given as mol *o*-quinone produced per liter minute. PEI #16, which is highest in polymer content, has the highest rate while PEI #10 containing the lowest amount of polymer has the lowest rate. Thus, activity of a PEI complex increases with increase in PEI polymer in the complex. It would appear that rather than impeding the catechol's access of the dicopper site, the polymer increases the PEI Cu activity. This role however is not well understood.

The oxygen uptake rate for PEI Cu is also reported in Table II. The rates for the complexes parallel those found using the optical method. The number of mol of oxygen uptake are greater than the mol of *o*-quinone produced. Just the reverse is expected from eqn. 1 if only *o*-quinone was produced. Apparently *o*-quinone is not the only oxidation product. This phenomenon was previously observed in similar studies [3, 4].

Summary and Conclusions

Polymeric dicopper complexes were prepared using the binucleating ligand 2,6-diformyl-4-methylphenyl with polyethyleneimine and the copolymer poly(vinylamine-vinylsulfonate). The PEI Cu complexes were found to be reasonably soluble in water but the PVA Cu complexes were insoluble in water. Although the copper(II) ions are for the most part magnetically coupled and located in the binucleating ligand as shown in Fig. 3a, they may also be located in a coordination site similar to those shown in Fig. 3b. This site difference may account for the broadening of the copper(II) d–d bands. A third copper(II) site alternatively may be that of several polymeric amines.

The PEI Cu complex containing the largest quantity of PEI ligand demonstrated the highest activity. The polymer enhancement of the activity may result from a polymer concentration of the catechol in the neighbourhood of the dicopper site. This, however, may only be speculation at the moment.

The PVA Cu complexes showed little or no activity. The lack of activity is due most likely to a tightly coiled polymer which prevents catechol access to the dicopper sites. The slight activities observed for two of the PVA Cu complex resulted from surface effects.

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