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Polychelates of poly(acrylic acid-*co*-acrylamide)with Cu(II), Co(II), and Ni(II)

Synthesis and properties

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SUMMARY

Polychelates were obtained by addition of an aqueous solution of the poly(acrylic acid-*co*-acrylamide) to an aqueous solution of Cu(II), Co(II), and Ni(II). All the polychelates were insoluble in water and in common organic solvents. The polychelates were characterized by elemental analysis, FT-IR spectroscopy thermogravimetry, and showed tetrahedral arrangement for Co(II) and Ni(II). Magnetic and conductivity studies for all the polychelates were also carried out. The poly(acrylic acid-*co*-acrylamide) behaved as semiconductor.

INTRODUCTION

Polymer-metal complexes have been the subject of increasing interest in the fields of catalytic reactions, mining separations and in connection with biochemistry and environmental chemistry (1-7).

Extensive literature is available on the formation and coordination number of polymer-metal complexes in aqueous solution. Poly(vinyl alcohol) is a simple synthetic water-soluble polymer which shows a green color at pH>6 with Cu(II) with a remarkable decrease of viscosity. This was interpreted as a result of the formation of stable mononuclear copper(II) complexes with the hydroxyl groups of poly(vinyl alcohol).

Four-coordinate square-planar structures are known for Cu(II) ion with poly(vinyl amine) (8-9). Formation of the four-coordinate complex is easily accomplished since their ligands are small and no steric hindrance is encountered. Poly(allyl amine) forms in aqueous solution complexes with Ni(II), Co(II), Cu(II), Zn(II) (10). One of the most versatile polyamine is branched poly(ethylene imine) (BPEI) which forms polychelates with different geometric arrangements: Cu-BPEI square planar, Ni-BPEI tetrahedral, and Co-BPEI octahedral (11). On the other hand, Cu(II) ion forms two coordinate complexes with poly(acrylic acid), which has a negative charge and bulky structure (12). Its complex formation is affected by electrostatic repulsion and steric hindrance among ligands.

The present paper reports, the preparation and characterization of polychelates from poly(acrylic acid-*co*-acrylamide) with the divalent metal ions Cu(II), Co(II), and Ni(II).

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EXPERIMENTAL PART

Materials

All the reagents used were of analytical grade. Poly(acrylic acid-*co*-acrylamide), PAA-Am, was synthesized by radical initiator according to the literature (13). Aqueous solutions of the divalent metal ions Cu(II), Co(II), and Ni(II) were prepared from their chloride salts.

Preparation of the polychelates

The metal polymers have been synthesized by mixing equimolar aqueous solutions of the metal salts and the ligand chelates. The mixture was heated at 60°C under stirring for 6h and the solids separated were filtered and washed with water and ethanol to remove unreacted rectants. The three solids were dried under vacuum at 40°C until constant weight.

Measurements

Elemental analysis of the polychelates were carried out using a Series II CHNS/O analyzer 2400 Perkin Elmer. The infrared spectra (4000-500 cm^{-1}) were obtained employing a Nicolet Magna 550 FT-IR spectrophotometer using KBr pellets. Magnetic susceptibility was determined at room temperature by the Gouy method (14) using $Hg[Co(SCN)]_4$ as a calibration standard according to the relation $\mu_{eff} = 2.84 = \sqrt{X_m}T$. The thermal stability of the polychelates was studied by TGA. The samples were heated in aluminum crucibles under N_2 by heating from 25 up to 550°C at 10°C/min.

RESULTS AND DISCUSSION

Poly(acrylic acid-*co*-acrylamide) was synthesized by radical polymerization (13) and employed as macromolecular reagent support to obtain polychelates with Cu(II), Co(II), and Ni(II) through the two potential ligand groups.

All these polychelates are intensely colored solids, insoluble in water and in common organic solvents. Hence it was not possible to characterize them by conventional methods. The analytical data presented in Table 1 clearly indicate that all polychelates conform to the formula and include the chlorine atom. The molecular mass of the repeating unit was used as the basis for the calculations.

Table 1. Analytical data of the polychelates.

Main unit	Color	Elemental Analysis found (calcd.) C	H	N	Molar mass of repeating unit (calcd.) (g/mol)
$CuCl_2L_2$	Green	43.17 (44,25)	6.38 (6.28)	6.79 (6.66)	420.45
CoClL	Violet	31.62 (30.33)	5.43 (5.79)	5.23 (5.89)	237.35
NiClL	Light green	26.63 (30.36)	5.43 (3.80)	5.40 (5.90)	237.15

L= PAA-Am

FT-IR spectroscopic analysis

Despite the fact that the FT-IR spectra of the ligand and its polychelates are similar (see Figure 1), the following tentative differences have been extracted after careful analysis of the spectra. The signals in the 3500-3100 cm^{-1} region are assignable to the stretching of the hydroxyl of carboxylic acid and N-H of amide group. The signals around 2900, 1470, 1300, 1100, and 950 cm^{-1} correspond to C-H vibrations.

The absorption bands at 1045 and 500 cm^{-1} are attributed to C-N stretching and metal-N stretching vibrations, respectively (15-16).

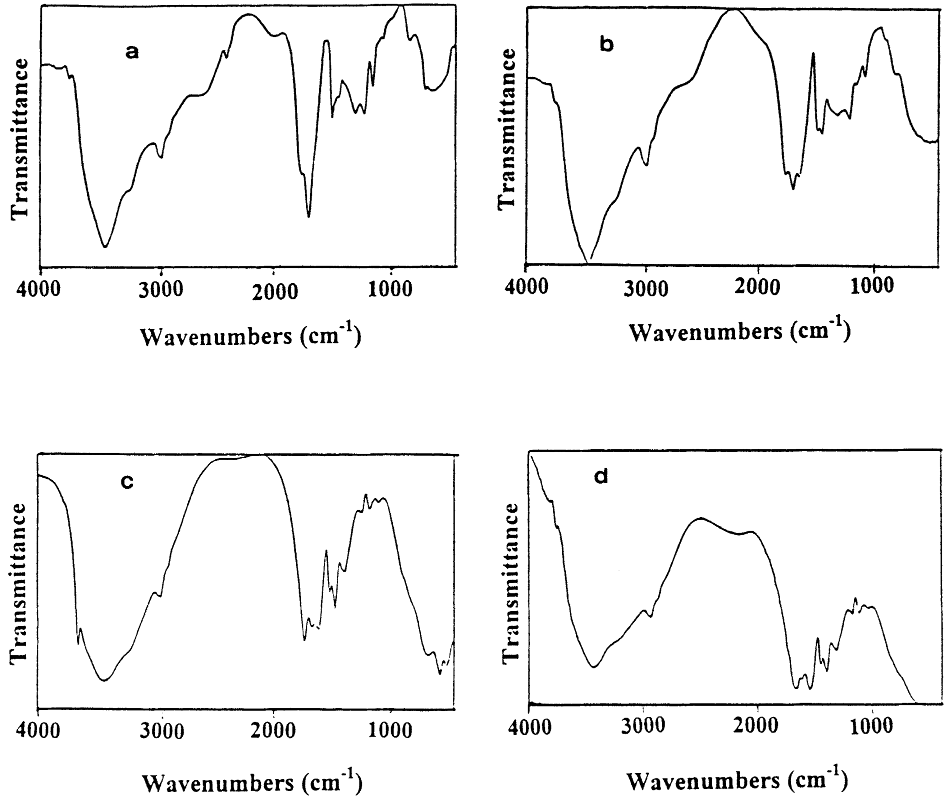


Figure 1. FT-IR spectra (KBr) of (a) poly(acrylic acid-*co*-acrylamide) and its polychelates with (b) Cu(II), (c) Ni(II), and (d) Co(II).

The spectrum of PAA-Am shows absorption bands at 1719 cm^{-1} and 1659 cm^{-1} attributed to stretching bands of C=O coming from carboxylic acid and amide group.

The polychelate with Cu(II) shows in the 1600-1700 cm^{-1} region a splitting of the bands appearing three absorption bands placed at 1726 cm^{-1} (C=O of carboxylic group); 1660 cm^{-1} (C=O of amide) and 1600cm^{-1} assignable to N-H deformation.

The last absorption band is shifted to lower frequency due to coordination. The last band was not observed in PAA-Am because it is probably coupled with the stretching band of C=O from the amide group. On the other hand, the C-N vibration of amide group was split in two bands at 1461 and 1408 cm^{-1}. With these data it is possible to postulate the coordination of the Cu(II) ion with the copolymer ligand through the nitrogen of the amide group. In the spectra of the polychelates of Co(II) and NI(II) did not show signals at 1730 and 1250 cm^{-1} corresponding to the vibrations of the carboxylic group, however, two bands appear due to carboxylate group at 1550 cm^{-1} assigned to the asymmetric vibration and at 1407 cm^{-1} to the symmetric vibration. The last band increases in intensity in the spectrum of the polychelate with Ni(II). In the 1400 cm^{-1} region the vibrations from amide and carboxylic groups are observed. Thus it is possible that the C-N vibrations of amide group and those of C-O of carboxylic group are coupled. With these data it is also possible to postulate that the PAA-Am ligand coordinates the metal ion Ni(II) and Co(II) through the carboxylic group.

Other important bands and their assignments are given in Table 2.

Table 2. FT-IR spectral data (cm^{-1}) of poly(acrylic acid-*co*-acrylamide), PAA-Am, and its polychelates.

Assignment	PAA-Am (Ligand, L)	L-Cu	L-Co	L-N
stret. N-H	3438 s	3443 s	3435 s	3423 s
	3200 sh			
stret. C-H	2933 m	2926 m	2928 m	2930 m
stret. COOH	1719 m	1726 m	1555 s	1553 ms
			1405ms	1406m
stret. C=O	1659s	1659ms	1659s	1664ms
def. NH_2		1600m	1603w	1603ms
stret. C-N amide	1449mw	1460mw	1450m	1451mw
stret. COOH	1399sh	1407mw		
stret.C=O acid	1250mw	1250mw	1322m	1326mw
acid	1175mw	1169mw	1179w	
	1106mw	1403w	1117w	
	798w			
	600mw			620ms
	606mw			
				519s
				462ms

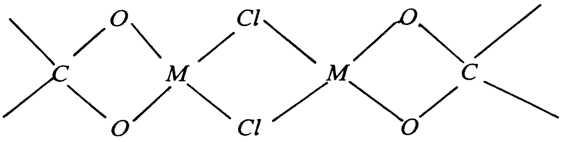
m= medium; s= strong; sh= shoulder; w= weak.

Magnetic moments

The Cu(II)-polychelate shows a magnetic moment 1.77 BM at room temperature which is in close agreement to the spin only value (1.73 BM) for one unpaired electron. This polymer metal-complex correspond to a magnetically dilute polychelate. It occurs usually when the Cu(II) ions are well separated (>0.73Å).

On the other hand, the values between 1.72 and 1.82 BM are common for strong covalent bonds in coordination compounds (17).

The polychelates with Ni(II) and Co(II) show magnetic moment of 3.47 and 4.80 BM respectively. Both values fall in the range of an octahedral and tetahedral environment (18-19). However, from elemental analysis it is possible to postulate for both metal ions a tetrahedral geometry involving chlorine atoms as bridge ligands.



Conductivity measurements

These measurements in the solid state at 20ºC show that PAA-Am behaves as a semiconductor with high resistance (see Table 3).

Table 3. **Electrical conductivity of poly(acrylic acid-*co*-acrylamide), and its polychelates.**

Polymer sample	s at 20ºC (ohm cm)$^{-1}$
PAA-Am (L)	2.85 x10^{-11}
L-Cu(II)	1.23 x10^{-10}
L-Ni(II)	2.60 x10^{-11}
L-Co(II)	3.80 x10^{-11}

One can expect that the introduction of a metal ion at the polymer by coordination would increase the conductivity due to the tendency to ionize the metal, or to the delocalization of d electrons of the metal ion. It is usually observed in square planar complexes (20).

The electrical conductivity of polychelates with Co(II) and Ni(II) does not change significantly in respect to PAA-Am. Only the polychelate with Cu(II) shows a somewhat higher conductivity (see Figure 2 and Table 3). This could be attributed to the absence of a pure planar geometry or to the behavior as a magnetically dilute system.

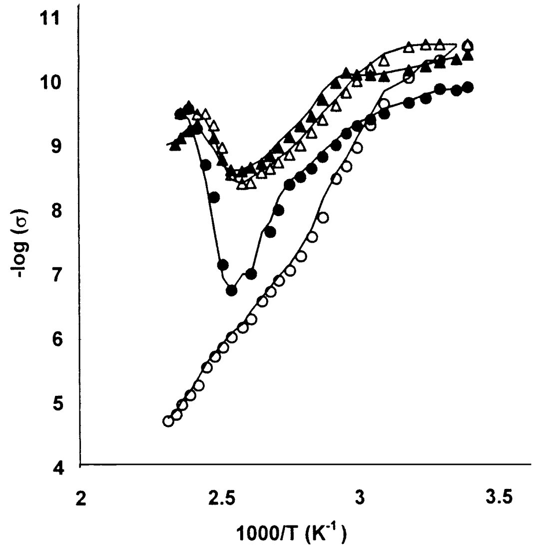


Figure 2. Electrical conductivity of poly(acrylic acid-*co*-acrylamide (-o-) and its polychelates with Cu(II) (-△-), Ni(II) (-●-), and Co(II) (-▲-) at different temperatures.

Thermal stability

PAA-Am and their polychelates with Cu(II), Co(II), and Ni(II) show a weight-loss between 0-100ºC attributed to occluded water. In general, the polychelates show higher thermal stability than PAA-Am, specially in the 300-500ºC range. (see Table 4).

Table 4. Thermal stability of PAA-Am, and its polychelates.

Polymer sample	%Weight loss at different temperatures (ºC)				
	100	200	300	400	500
PAA-Am, L	6.1	16.4	27.3	54.1	86.5
L-Cu	0.0	4.2	19.0	39.1	61.8
L-Ni	5.5	14.0	21.8	31.2	52.2
L-Co	13.3	19.3	25.1	32.8	52.7

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