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Synthesis, characterization of poly(allylamine)chelates with Cu(II), Co(II) and Ni(II)

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SUMMARY

The parent polymer, poly(allylamine) as ligand polymer was employed to synthesize polychelates of heavy metal ions. The functional poly(allylamine) and its Ni(II), Co(II) and Cu(II) metal chelates were characterized by elemental analysis, FT-IR spectroscopy, TGA, and SEM. For the polychelates magnetic and conductivimetry studies were also carried out.

INTRODUCTION

The polymeric metal complexes which are composed for polymeric ligands and metal ions differ from the corresponding monomeric complexes in their specific properties and chemical reactivities. Many polymeric metal complexes have been reported (1-6), however, few of these complexes have a uniform structure, and no more than the outward properties of the complexes have been studied.

One of the very interesting metal complexing polymer is poly(allylamine), (PAAm) which possesses an amino group in the side chain that is highly reactive and oxidizes in air (7-9). The chelating properties in solution of PAAm for heavy metal ions like Ni(II), Cu(II), Cd(II), Zn(II) and UO_2^{2+} have been reported. Lee et al. (10) prepared a poly(allylamine)/poly(vinyalcohol) blend chelate membrane for future use in gas separation. The metal incorporated was Co(II).

In the present paper, we report the preparation and characterization of polychelates from poly(allylamine) with the divalent metal ions, Cu(II), Co(II) and Ni(II).

EXPERIMENTAL PART

Materials

All reagents used were of analytical grade. Poly(allylamine), PAAm (Aldrich Co.) was used as a 30% aqueous solution. Solutions of Cu(II), Co(II), and Ni(II) were prepared from their chloride salts.

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Preparation of polychelates

The solid complexes were prepared by adding an aqueous solution of the PAAm to the aqueous solution of the metal salts. The molar ratio employed was metal to PAAm, 1:4. The pH was adjusted to 8. Methanol was added and the mixture was stirred at room temperature to obtain a solid. These solid metal complexes were separated by filtration, washed with a 1:1 ethanol/water mixture and dried in an oven at 40°C and under vacuum.

Measurements

Elemental analyses (Table 1) of polychelate samples were carried out on a C, H, O, N rapid elemental analyzer. The analyses of metal ions polychelates were carried out by decomposition of a known amount of polychelate by mineral acids (11).

The FT-IR spectra of all polymer samples were taken in KBr on a Nicolet Magna FT-IR spectrophotometer. The magnetic susceptibility was determined at room temperature by the Gouy method (12) using $Hg[Co(SCN)_4]$ as a calibration standard and the following relation:

$$\mu_{eff} = 2.84 \sqrt{X_M T}$$

The thermal stability of the PAAm and metal-PAAm complexes was studied by TGA. The measurements were performed with a Polymer Laboratories STA-625 Thermal Analyzer. The samples were heated in aluminium crucibles under N_2 by heating from 25 up to 550°C at $5°C{\bullet}min^{-1}$. The electron micrographs were obtained by using a scanning electron microscope, ETEC Autoscan U-1 Model. The surface of the polychelate was coated with gold for 3 min to obtain a 150 Å thickness using an Edwards S 250 sputter coater.

RESULTS AND DISCUSSION

All the PAAm-metal(II) polychelates were colored solids and insoluble in water.

The analytical data, conductivity and magnetic moment of the three polychelates are summarized in Table 1. The molecular mass of the repeat unit was used as the basis for the calculations.

Table 1. Analytical data, conductivity and magnetic moment of the polychelates.

Main unit L = PAAm	Color	Elemental Analyses Found (Calc.)			Molecular mass repeat unit ($g{\bullet}mol^{-1}$)	μ_{eff} (BM)	Λ_M (mhos cm^2/ml)
		C	H	N			
$[CuL_2Cl_2]{\bullet}H_2O$	Blue	28.63(27.02)	614(6.00)	10.95(10.51)	266.4	1.72	-
$[NiL_3Cl]Cl{\bullet}H_2O$	Light green	31.09(32.08)	7.74(7.42)	11.94(12.47)	336.54	1.84	1.86
$[CoLCl_2H_2O]$	Dark green	17.33(17.57)	5.48(4.39)	5.75(6.83)	204.83	4.02	-

The magnetic moment of the Cu(II)-PAAm is 1.72 BM which is typical for one unpaired electron in compounds with a strongly covalent metal-ligand (13).

The Co(II)-PAAm polychelate shows μ_{eff} = 4.02 BM. The limits expected for three unpaired electrons varied between 3.87 BM, considering only the spin, and 5.2 BM considering spin-orbital coupling. The magnetic moments observed for octahedral complexes of high spin varied between 4.7 and 5.2 BM but for the tetrahedral varied between 4.4 and 4.8 BM. According to the stoichiometry of the polychelate, Co(II) may present a coordination number of 4, which would indicate a tetrahedral geometry with a coordinated water molecule.

The magnetic moment of Ni(II)-PAAm, 1.84 BM, is very low corresponding to almost the theoretical value of one unpaired electron. The complexes of Ni(II) show two unpaired electrons either in a tetrahedral and octahedral field. This observed value, 1.84 BM, is also lower than that observed for the Ni(II)-branched poly(ethyleneimine), 1.94 BM (14). However, for Ni(II)-complexes with plane square geometry have reported magnetic moments between zero and 3.2 BM, the usual value for octahedral complexes. In these compounds, the octahedral is achieved by bridge ligands. One example of this type of compound corresponds to the yellow form of Ni(2,3-butylendiamine)$_2$Cl$_2$ with a μ_{eff} = 1.7 BM (15).

Due to the insolubility in water of Cu(II)-PAAm and Co(II)-PAAm, only the electrical conductivity of Ni(II) was measured. The 180 [mhos cm^2/mol] value may be attributed to an electrolyte 1:1.

The FT-IR spectral data of the polychelates in comparison with those of the uncomplexed PAAm give some information about the bonding site of the ligand moieties to the central metal ion (see Table 2 and Fig. 1).

The broad band around 3400 cm^{-1} refers to the stretching vibration of the NH group. The symmetric and asymmetric vibrations of this group are around 1600 and 1350 cm^{-1}, respectively. The signals around 2900, 1450, 1300, 1180, 860 cm^{-1} correspond to C-H vibrations. The N-H and C-N absorption bands of PAAm are shifted in the metal-PAAm polychelates indicating that the amino group is coordinating to the metal atom.

In all spectra, free ligand PAAm and metal-PAAm polychelates show an absorption band at 2000 cm^{-1} which may be attributed to crystallization water.

The FT-IR spectrum of Co(II)-PAAm shows among other bands, two bands at 3710 cm^{-1} and 680 cm^{-1} which correspond to OH stretching vibration and a wagging of the coordinated water molecule, respectively (16-18).

At lower temperatures (< 300°C) the polychelates showed a similar weight of loss which was higher than that of PAAm. From 400°C, all the polychelates were more stable than PAAm, particularly Co-PAAm which lost only a 38.2% of weight at 500°C as compared with 94.55% loss for the PAAm (see Table 3). The exothermic peaks should be caused by oxidation, decomposition of the complexes and formation of metal oxides.

Table 2. FT-IR spectral data (cm^{-1}) of poly(allylamine) and its metal complexes[a].

Assignment	PAAm=L	Cu-L	Ni-L	Co-L
Stretching NH	3445 s	3447 s	3465 s	3471 s
		3230 m		
		3131 m		
Stretching CH_2	3040 s			
	2930 s	2921 s	2930 m	2936 m
Deformation NH	1602 s	1585 s	1613 s	1640 m
	1512 s	1506 ms	1522 s	1529 m
	1398 w	1394 m	1383 mw	1360 w
Bending CH_2	1450 sh	1453 ms	1445 sh	1465 sh
Wagging CH_2	1300 w	1320 w	1300 sh	
Twisting CH_2	1180 mw	1137 m	1170 w	1160 w
Wagging NH_2	1125 w	-	1110 w	1090 w
	1070 w			
Stretching C-N	994 m	1012 ms	1014 m	1005 m
Rocking CH_2	868 mw	845 sh	860 sh	855 sh
Rocking NH_2	730 w	-	760 sh	

a) s = strong, m = medium; w = weak; sh = shoulder.

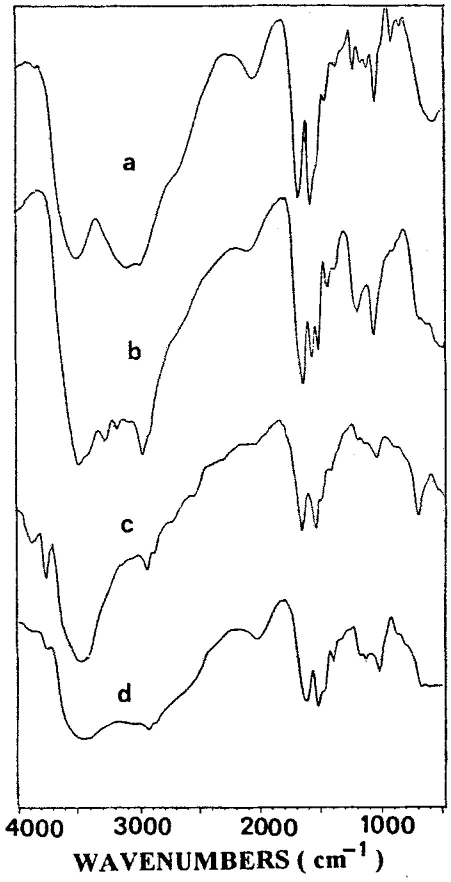

Figure 1. FT-IR spectra of: a) PAAm; b) Cu-PAAm; c) Co-PAAm; and d) Ni-PAAm.

Table 3. Thermal stability of poly(allylamine), PAAm, and its metal complexes.

Polymer sample	% weight loss at different temperatures (°C)									
	100	150	200	250	300	350	400	450	500	550
PAAm=L	0.0	0.0	0.0	0.0	10.4	29.9	61.3	89.6	94.5	98.4
L-Cu	6.8	9.6	15.8	18.1	22.8	27.5	39.5	50.7	51.7	51.8
L-Ni	5.5	11.7	14.6	16.8	22.8	30.6	48.8	62.7	65.5	56.0
L-Co	2.5	6.5	10.8	13.5	15.2	23.1	31.7	36.5	38.2	40.8

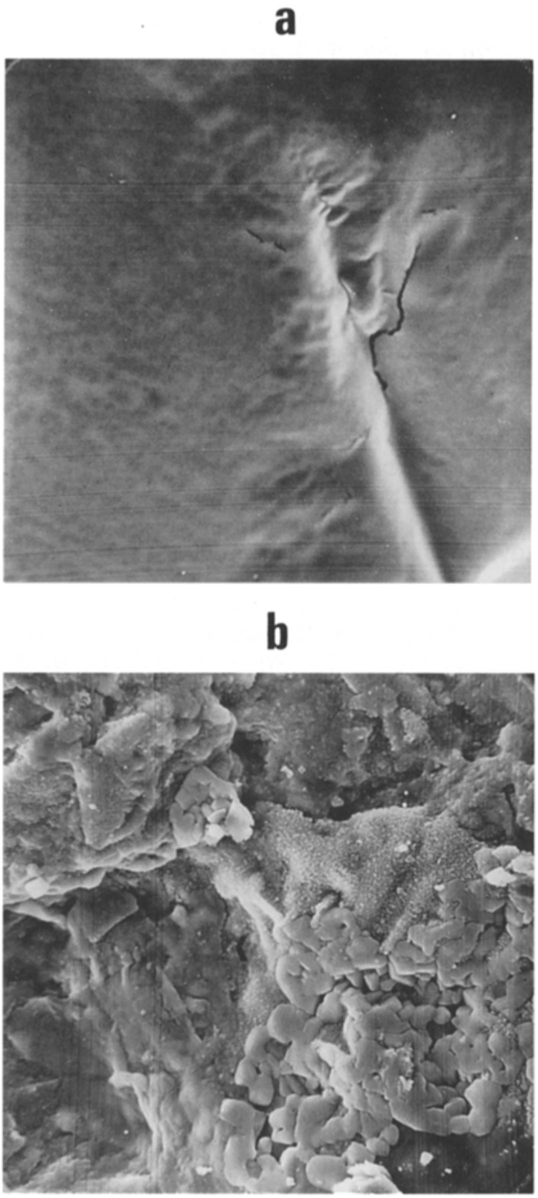

Figure 2. Scanning electron micrographs (800x) of poly(allylamine) (a) and poly(allylamine)-Co complex (b).

The electron scanning micrographs show that the ligand polymeric structure possesses a rough surface. The surface changes after complexation of metal ions. The differences among three polychelates result from the differences in the type of Cu(II), Co(II) and Ni(II)-PAAm complexes. The greatest change of the surface compared with PAAm was observed for PAAm-Co polychelate (see Figure 2).

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REFERENCES

1. A.S. Lindsey. *J. Macromol. Sci. Rev. Macromol. Rev.*, **C3**, 1 (1969).
2. J.E. Katon. Organic, Semiconducting Polymers, Marcel Dekker Inc., New York (1968).
3. E. Tsuchida, H. Nishide, M. Takeshita. *Makromol. Chem.*, **175**, 2293 (1974).
4. N. Angelova, N. Manolova, J. Rashkov. *Eur. Polym. J.*, **31**, 741 (1995).
5. K.J. Kamble, D.N. Patkar. *J. Appl. Polym. Sci.*, **56**, 1519 (1995).
6. M.M. Raj, T.B. Shab. *Pure Appl. Chem.*, **A32**, 999 (1995).
7. S. Kobayashi. *Macromolecules*, **18**, 2357 (1985).
8. R. Soto. *J. Polym. Sci., Part 1: Polym. Chem.*, **28**, 1793 (1990).
9. B.L. Rivas, G.V. Seguel (unpublished).
10. C.K. Park, M.J. Choi, Young Moo Lee. *Polymer*, **36**, 1507 (1995).
11. A.I. Vogel. A Text Book of Quantitative Inorganic Analyses, 3rd ed., Longmans, London, 1978.
12. F.A. Cotton, G. Wilkinson. Advanced Inorganic Chemistry, 3rd Ed. Wiley, New York, p. 594 (1962).
13. M. Kato, H.B. Jomassen, J.C. Fonning. *Chem. Rev.*, **64**, 39 (1964).
14. B.L. Rivas, G.V. Seguel, K.E. Geckeler. *Angew Makromol. Chem.* (in press).
15. B.N. Figgis. Introduction to Ligand Fields. Ed. Wiley, New York, p. 319 (1986).
16. K. Nakomoto. Infrared and Raman Spectra of Inorganic and Coordination Compounds. 4th Ed. J. Wiley, New York, p. 227 (1986).
17. L.J. Bellamy. The Infrared Spectra of Complex Molecules. 2nd Ed. J. Wiley, New York, p. 248 (1962).
18. K. Krishman, R.A. Plane. *Inorg. Chem.*, **5**, 852 (1966).