

Water-insoluble polyacrylamide XII : Polychelates based on poly (N-methacryloyl-*m*-amino benzoic acid)

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Abstract. Six new polychelates of Fe(II), Co(II), Ni(II), Cr(III), UO₂(II) and Zn(II) were prepared from the chelex poly(N-methacryloyl-*m*-amino benzoic acid). All these polychelates are coloured, amorphous powders, insoluble in all common organic solvents. They are characterized by electronic reflectance spectra, IR spectra elemental analyses and magnetic susceptibility measurements. All the polychelates show a six co-ordinated structure and suggest octahedral geometry. Conductometric studies indicated that these polychelates are non-electrolytes. Their thermal stabilities were established by thermogravimetric studies.

Keywords. Poly(N-methacryloyl-*m*-aminobenzoic acid); chelex; polychelate; diffuse reflectance Spectra; thermal stability; conductance.

1. Introduction

Literature concerning water-insoluble polyacrylamides (Joshi 1962; Patel *et al* 1985a) revealed that such polymers may find interesting applications. Only sparse reports have appeared (mostly in patents) about acryloyl-amino-benzoic acids and their polymers (Frantisek *et al* 1975; Yoshikazu *et al* 1975). Such polymeric ligands have provided a basis for the syntheses of polychelates from transition metals (Mykytiuk *et al* 1980; Kraus and Moore 1953; Desai and Suthar 1985). Chelex is a polymer containing pendant functional groups which act as chelating groups in binding polyvalent metal ions. Such properties of chelex have been exploited in diverse applications such as ion exchangers (Patel and Patel 1979), in metal separations (Dunn *et al* 1980) and preconcentration of metals (Mykytiuk *et al* 1980) and as therapeutic complexes in many biological models (Haner *et al* 1984). To understand such functions we have reported a series of metal chelates from chelex based on N-substituted carboxyphenyl acrylamide polymers (Patel and Suthar 1985a, 1985b; Patel *et al* 1985b). The present communication deals with the syntheses of the polychelates of Fe(II), Co(II), Ni(II), Cr(III), UO₂(II) and Zn(II) with chelex poly(N-methacryloyl-*m*-aminobenzoic acid). We have studied their diffuse reflectance spectra, infrared spectra, magnetic susceptibilities, elemental analyses and thermogravimetric properties.

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2. Experimental

2.1 Materials

All chemicals used were of analytical grade purity. N-methacryloyl-*m*-aminobenzoic acid (MMAB) was synthesized from *m*-aminobenzoic acid according to Patel *et al* (1985b). MMAB was recrystallized from alcohol, m.p. 190°C, yield 86%. It is soluble in alcohol, dioxane THF, DMF and DMAC.

Analysis: N 6.78%; C₁₁H₁₁NO₃ requires 6.83% N.

The chelex poly(N-methacryloyl-*m*-aminobenzoic acid) (PMMAB) was prepared and characterized according to Patel *et al* (1985a).

2.2 Preparation of polychelates

All the metal polychelates were prepared as follows: Poly(N-methacryloyl-*m*-aminobenzoic acid, PMMAB) (5 g) was dissolved in dimethyl formamide (50 ml). To this solution, metal nitrate (3 g in 50 ml DMF) was added. Sodium acetate (1 g) was then added to the reaction mixture. It was refluxed for 6 hr. The precipitated material was filtered, washed with boiling DMF followed by hot water and finally with ethanol.

The Fe(II) polychelate was prepared according to the method mentioned above using ferrous ammonium sulfate instead of ferrous nitrate. All the polychelates were dried in an oven at around 60°C.

2.3 Analytical methods

All the physico-chemical measurements were made at 30°. The diffuse reflectance spectra were obtained on a Beckman DU Spectrophotometer. IR spectra were recorded on a Perkin Elmer 983 Spectrophotometer as KBr pellets. Magnetic measurements were made on a Sartorius semi-micro Gouy Balance. The thermogravimetric analyses were carried out using a Du Pont 951 thermal analyser at a heating rate of 10°C/min in air. Conductances were measured on a Konduktoskop Metrohm Herisau, Switzerland, conductometer. For estimating elemental composition, the metal content in each polychelate was determined by independent gravimetric and volumetric methods. Carbon, hydrogen and nitrogen analyses were made on a Coleman C-H-N analyser.

3. Results and discussion

All the polychelates were dark coloured solids. They were insoluble in all common organic solvents including water. Hence, it was not possible to characterize them by conventional methods such as viscometry and osmometry. It was also not possible to determine their conductances. However, the low values of specific conductance indicated that all the polychelates were non-electrolytes. The elemental analyses of all these polychelates (table 1) indicated 1:2 (metal:ligand) stoichiometry. Thus the structures of the polychelates may be as proposed in figure 1.

Table 1. Characterization of polychelates from poly(N-methacryloyl-*m*-aminobenzoic acid).

Sample code	Analysis (%) [*]				μ_{eff} (B.M.)	Specific conductance (10 ⁶) (mho cm ⁻¹)	Decomposition temperature (°C)
	C	H	N	Metal			
Chelex-PMMAB	64.46 (64.39)	5.36 (5.37)	6.86 (6.83)	—		1.40	310
Fe(II)-PMMAB	57.10 (56.92)	4.40 (4.31)	6.12 (6.04)	12.20 (12.04)	40.70	1.50	440
Co(II)-PMMAB	56.64 (56.54)	4.28 (4.28)	6.02 (5.99)	12.62 (12.58)	4.70	1.20	415
Ni(II)-PMMAB	56.72 (56.57)	4.32 (4.29)	6.02 (5.99)	12.66 (12.58)	3.60	0.98	368
Cr(III)-PMMAB	57.87 (57.39)	4.40 (4.35)	6.12 (6.09)	11.50 (11.30)	3.96	1.30	362
UO ₂ (II)-PMMAB	39.24 (38.94)	2.99 (2.95)	4.10 (4.13)	39.99 (39.83)	Dia	1.38	410
Zn(II)-PMMAB	55.82 (55.79)	4.30 (4.23)	5.99 (5.92)	13.90 (13.81)	Dia	1.40	450

* Theoretical values in bracket.

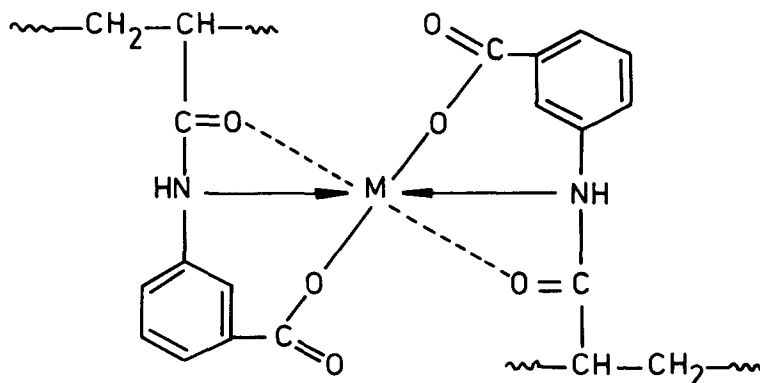


Fig. 1.

3.1 Reflectance spectra

The diffuse reflectance spectrum of chelex PMMAB shows two high intensity bands at 21400 and 19506 cm^{-1} which may be attributed to $\pi \rightarrow \pi^*$ and $n \rightarrow \pi^*$ transitions respectively (Rao 1975).

Iron (II) : The diffuse reflectance spectrum of the Fe(II) polychelate shows bands at 9620, 11270 and 15600 cm^{-1} . The latter two bands may be attributed to the spin allowed ${}^5T_{2g} \rightarrow {}^5E_g$ transition in an octahedral stereochemistry (Prabhakaran and Patel 1972). The former low energy band is presumed to be due to the low

symmetry ligand field (Mani 1979). The Fe(II) polychelate shows very high magnetic moment (40 B.M.) indicating its ferromagnetic behaviour.

Cobalt (II): The diffuse reflectance spectrum of the Co(II) polychelate indicates bands at 8600, 15630, 21220 and 22700 cm^{-1} . The first two bands may be safely assigned to ${}^4T_{1g} \rightarrow {}^4T_{2g}$ and ${}^4T_{1g} \rightarrow {}^4A_{2g}$, respectively, in an octahedral stereochemistry. The highly intense and moderately broad band in the region 21400–20100 cm^{-1} may be the $n \rightarrow \pi^*$ band of the ligand itself. However the observed bathochromic shift compared with that of the ligand may be attributed to the extensive conjugation of the co-ordinated ligand through the metal ions. The magnetic moment (4.7 B.M.) of the Co(II) polychelate is in the range required for octahedral stereochemistry (Rastogi and Sharma 1974).

Nickel (II): The diffuse reflectance spectrum of the Ni(II) polychelate exhibits broad absorption at 9360 and 15950 cm^{-1} which may be assigned to ${}^3A_{2g} \rightarrow {}^3T_{2g}$ and ${}^3A_{2g} \rightarrow {}^3T_{1g}$ transitions respectively. The Ni(II) polychelate shows high magnetic moment (3.6 B.M.) for octahedral stereochemistry (Calvin and Barkenlew 1964).

Chromium (III): The diffuse electronic spectrum of the Cr(III) polychelate exhibits bands at 11300 cm^{-1} and 16090 cm^{-1} . The former band may be due to ${}^4A_{2g} \rightarrow E_g$ transition (Foster 1969) while the latter may be due to ${}^4A_{2g} \rightarrow {}^4T_{2g}$ transition in an octahedral stereochemistry (Koenig 1971). The magnetic moment is in agreement with the octahedral stereochemistry.

The $\text{UO}_2(\text{II})$ and $\text{Zn}(\text{II})$ polychelates are found to be diamagnetic in nature as is expected.

3.2 Infrared spectra

The IR spectra of chelex and all the metal polychelates (figure 2) resemble each other in general appearance. However, there is a noticeable difference in certain vibrational frequencies.

Examination of the IR spectrum of chelex PMMAB shows a medium broad band around 3400–3100 cm^{-1} which may be assigned to the carboxylic –OH and amide –NH stretching vibrations (Silverstein *et al* 1981). This obscured region may be due to the mixing of intermolecular and intramolecular H bonding due to –NH and –OH groups. The chelex shows strong bands at 1685 and 1665 cm^{-1} which may be attributed to the carbonyl stretching frequencies of the aromatic carboxylic and amide groups. All the polychelates show the absence of the band at 1695 cm^{-1} and a shift in the band of the amide group around 1665–1635 cm^{-1} . It is quite possible that the band due to the carboxylic carbonyl group is involved in co-ordination with metal ions while the amide carbonyl group is not participating in direct metal-chelex bonding. The IR spectra of all the polychelates reveal the presence of two bands around 1600 and 1460 cm^{-1} . This may be due to the carboxylate ion (Nakamoto *et al* 1961). It is well established that the band around 1600 cm^{-1} is due to the antisymmetric stretching and the band around 1460 cm^{-1} is due to the symmetric stretching vibrations of the carboxylate (Sandhu *et al* 1969).

A strong band around 1280 cm^{-1} in the spectrum of chelex may be due to H-bonded OH in-plane bending vibration. All the polychelates show this band shifted to 1250 cm^{-1} which may be due to –O–M suggesting co-ordination through the carboxylic oxygen (Bellamy 1958).

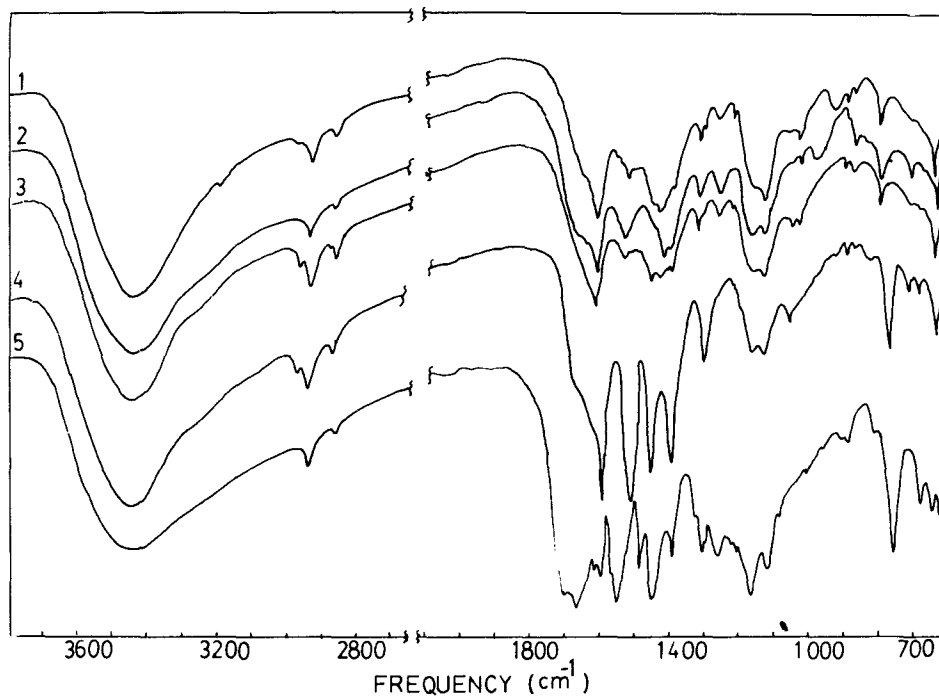
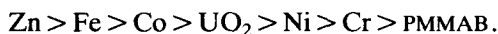


Fig. 2.

3.3 Thermogravimetric

The thermograms of all these polychelates were compared with that of chelex PMMAB. The polychelates are more stable than chelex PMMAB. The examination of the thermograms of the polychelates indicates the absence of water molecules in the co-ordination sphere. The loss in weight of Fe(II), Co(II), Ni(II), Cr(III), UO₂(II) and Zn(II) polychelates at 400°C are 7, 10, 15, 50, 10 and 6% respectively. The decomposition temperatures are listed in table 1 and reveal the following trend in thermal stabilities:



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