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## Synthesis of metal containing polymers

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**ABSTRACT:** The remarkable growth in the applications of organic polymers in the latter half of the twentieth century can mainly be attributed to their ease of preparation, and the useful mechanical properties and unique propensity for fabrication. Polymers containing metallic elements offer a wider range of novel characteristics and provide potential access to new processible functional polymeric materials and thus, study on the synthesis and prospective applications of metallopolymers have become an area of interest to polymer chemists. In this review, the procedures for the synthesis of organometallic polymers have been categorized in to three. These are: Polymerization through pre-formed metal complexes, Coordination of a metal ion by a preformed polymer containing chelating groups and Coordination reaction of a ligand which can attach itself simultaneously to two metal atoms or ions. Various literature reported under the above three headings were extensively reviewed.

**Keywords:** Organic polymers; Polymerization; Metal coordination.

### Introduction

The presence of metals in polymeric materials leads to new physical properties and potential applications (Ismet, 2008). Several different possible types of metal-containing polymer structures exist depending on where the metal atoms are incorporated and the nature of the linkages between them. A major subdivision of linear polymers involves a consideration of the location of the metallocenters. For example, the metal can be in the side-group or directly in the main chain of the polymer. Dendrimers and hyperbranched polymers represent another structural class of growing interest. In this case, the metallocenters can be located throughout the structure or, alternatively, in the core or at the periphery (Manners, 2007).

Coordination polymers are light in weight and possess high thermal stability (Kaya, 2002). Polymeric metal complexes have a variety of geometries that are not observed in organic polymers (Ismet, 2008); some combine the properties of anisotropy with photo responsive behavior that give rise to applications in areas such as optical storage, optical switching, diffractive optical elements, non-linear optical devices, liquid crystal displays (LCD's) etc. (Freiberg, 2003; Matczyszyn, 2002; Davidenko, 2005).

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Metal Containing polymers have important applications in medical sciences; they play an important role in controlled drug delivery systems (Roy, 2003), artificial organs (Yang, 2004) and protein synthesis (Cao, 2003). Some of the oligophenol derivatives of Schiff base compounds have been used as antimicrobial agents (Kaya, 2002). In the field of crystal engineering, they are considered very vital due to their fascinating architectures and potential applications such as magnetism, electric conductivity, molecular adsorption and catalysis. Some can be made to be electrically conductive and offer potential uses for the semiconductor industry and as lightweight electrodes and electrolytes for batteries for automotive and aerospace applications.

### Synthesis of Coordination Polymers

The literature reveals three possible methods of preparing metal coordination polymers (Marcos, 1992): The first method involves polymerization through pre-formed metal complexes through functional groups where the polymer forming step is typically a condensation or an addition reaction. The second method includes the coordination of a metal ion by a preformed polymer containing chelating groups. In the third method, a metal coordination polymer is formed by a coordination reaction of a ligand, which can attach itself simultaneously to two metal atoms or ions (Ismet, 2008).

In theory and in practice, a myriad of ligands can be employed for such procedures. This can be seen as a means through which various architectures can be produced covering a wide circle of many metal atoms and ions. Some typical ligands are displayed in table 1.

Table 1: Some ligand groups with examples, typically used in the synthesis of metal containing polymers (Batten *et al.*, 2008).

Ligand class	Example(s)
Amides	4-(methylamino)benzoic acid
Carboxylate based	Acetate, Carboxylate
Nitrile based	1,3,5-tris(4-ethynylbenzonitrile) benzene, 1,3,5-tris(3-ethynylbenzonitrile)benzene
Pseudohalide	Cyanide, Azide
Sulfonate containing	4-sulfo-benzoate, naphthalene-1,5-disulfonate
5 membered heterocyclic	Pyrazole, Triazole
6 membered heterocyclic	Pyrazine, Piperazine, Pyrimidine

Ligands bind metal atoms mainly through nitrogen or oxygen where the binding modes affect the conformation of the metal containing polymers. Figure 1 shows a number of binding functional groups through which the ligands bond the central metal atoms or ions.

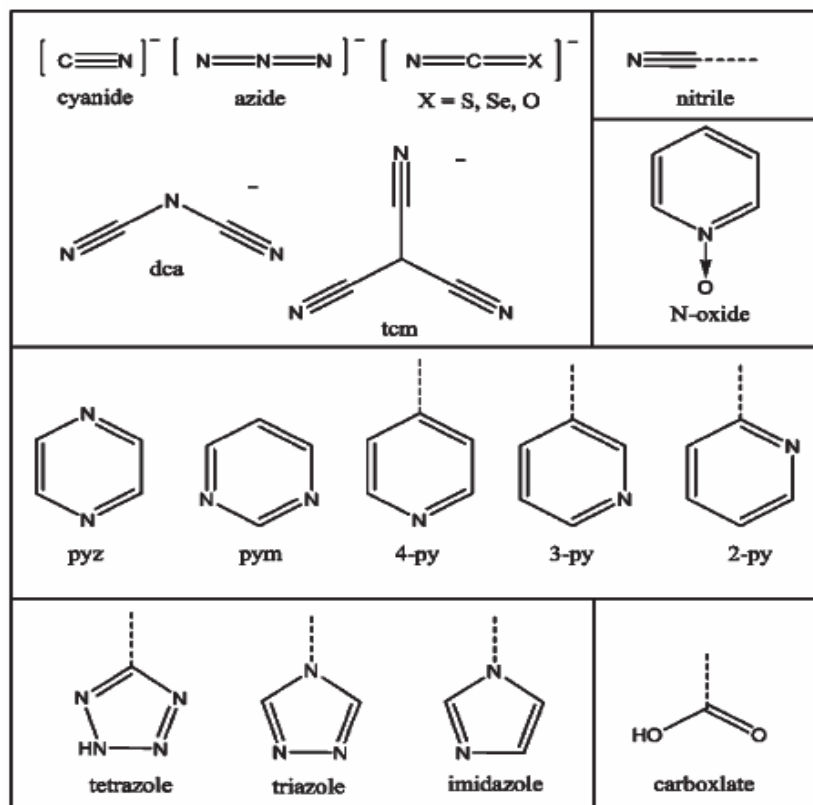
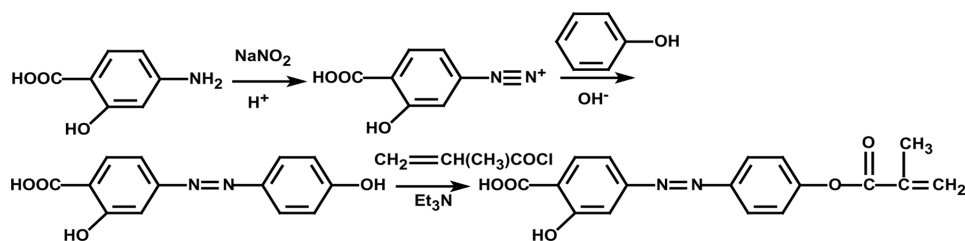


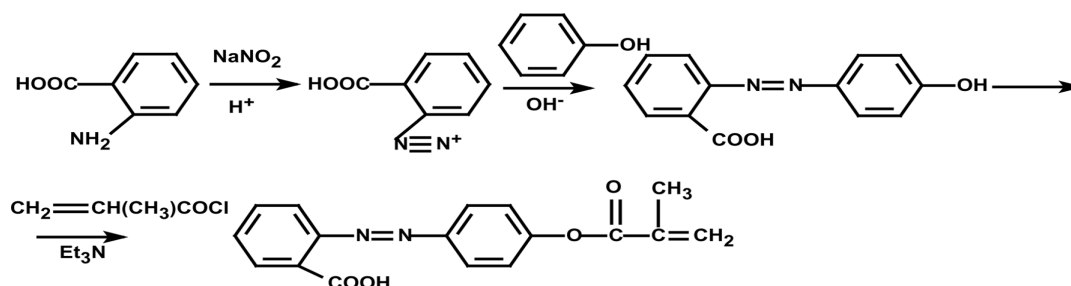
Figure 1: Some typical ligand functional groups used in the synthesis of metallopolymer (Batten et al, 2008)

### Polymerization through pre-formed metal complexes

In this concept, a metal complex is prepared from the reaction of a ligand with a metal ion. The prepared metal complex is then polymerized through the various polymerization reaction mechanisms. This is as reported by Irina (2008), on the synthesis and electro optical properties of metal-containing azopolymers and the influence of steric factors on the electro-optical effect in polycomplexes of azobenzene derivatives with Cobalt. The synthesis was achieved by first, synthesizing the azo compounds 4-hydroxy-(4'-carboxy-30-hydroxy)-azobenzene and 4-hydroxy-(2'-carboxy)-azobenzene. The synthetic route for the target monomers is shown by schemes 1 and 2. Complexes of 4-methacroyloxy-(40-carboxy-30-hydroxy)-azobenzene and 4-methacroyloxy-(20-carboxy)-azobenzene with Cobalt were synthesized by the exchange reaction between acetates of the corresponding metal and monomers. The polymers were finally obtained by free-radical polymerization with AIBN as free radical initiator. The polymers show photoinduced optical anisotropy which is as a result of irradiation by linearly polarized light, which causes trans-cis isomerization of azobenzene groups. There was an orientation of the light-induced dipole moments of these groups by an external electric field, causing the electro-optic effect at wavelengths near the long-wave absorption edge of the polymers.



Scheme 1: Synthesis of 4-methacroyloxy-(40-carboxy-30-hydroxy)-azobenzene



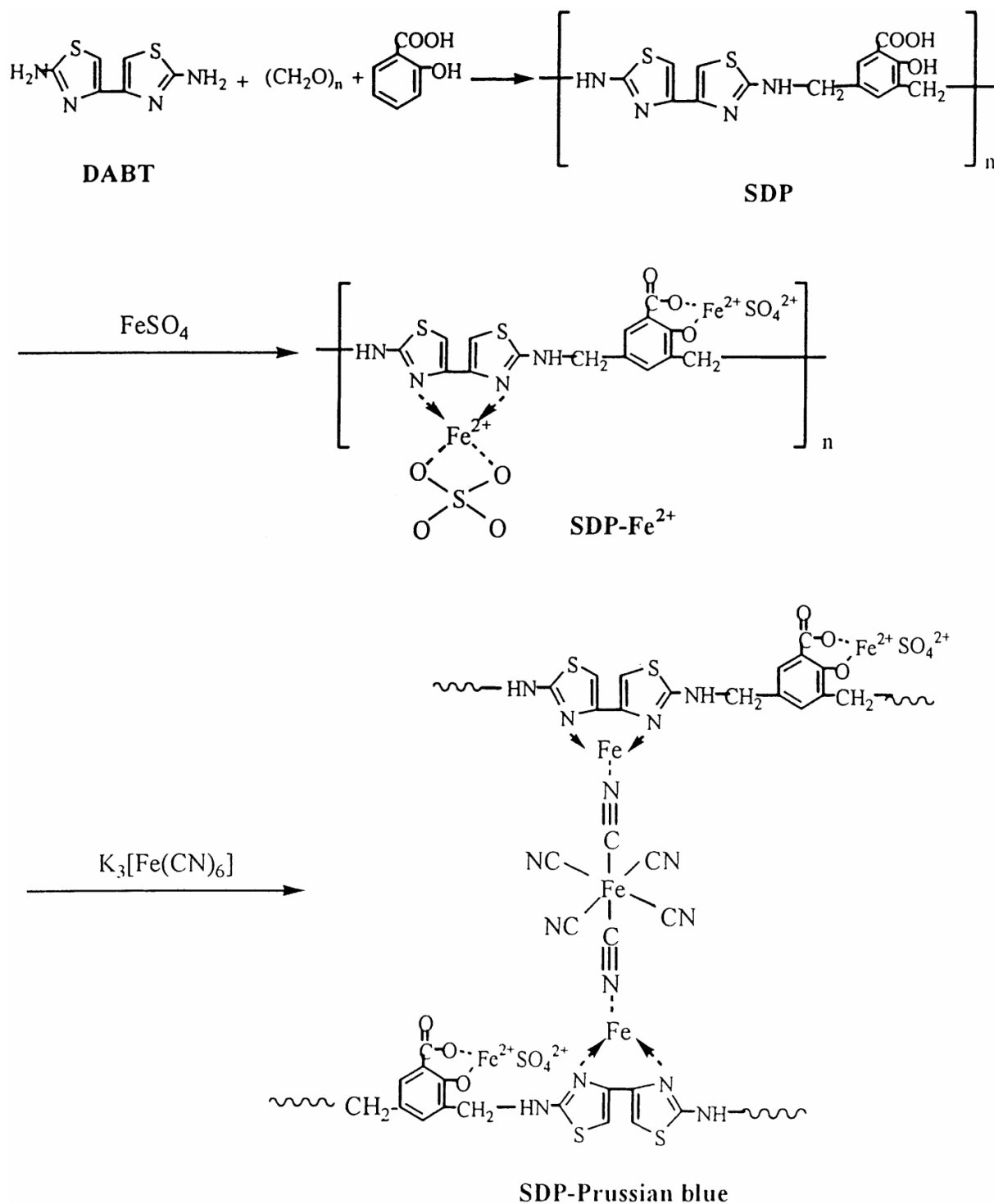
Scheme 2: Synthesis of 4-methacroyloxy-(20-carboxy)-azobenzene

Shagisultanova (1996) reported the synthesis and properties of photoactive and electroactive polymers based on transition metal complexes. Electrochemical reduction of iron, ruthenium and osmium complexes containing 5-Cl-Phen as ligand leads to the growth of metallopolymers on the metal surface. The polymers were found to be very stable to repeated electrochemical cycling and were highly reproducible.

#### Coordination of a metal ion by a pre-formed polymer containing chelating groups

In this aspect, a polymer is formed by any of the conventional polymerization mechanisms. The pre-formed polymer, containing chelating groups is then coordinated to the metal ion. This was demonstrated by Weilin *et al* (2003) who worked on the synthesis and ferromagnetic property of Bithiazole based polymer and its ferro complex containing hexacyanoferrate (III) group.

The polymer (referred to as SDP) was prepared according to the reaction scheme 3. The precipitate thus produced was collected by suction filtration, followed by washing successively with water, methanol, and ether and dried in vacuo at 60°C for 24hrs to give a yellowish-green powder (yield 90%). Ferro-Complex (SDP-Fe<sup>2+</sup>) was prepared from the reaction of SDP and FeSO<sub>4</sub> in DMSO for 5 days at room temperature under a purified nitrogen atmosphere. SDP-Prussian blue complex was prepared from reaction of K<sub>3</sub>[Fe(CN)<sub>6</sub>] in DMSO with SDP-Fe<sup>2+</sup> complex and the resulting suspension was allowed to react for 3 days at room temperature. Elemental analysis yields the formula [C<sub>15</sub>H<sub>12</sub>N<sub>4</sub>O<sub>3</sub>S<sub>2</sub>(FeSO<sub>4</sub>)0.23]*n* and {C<sub>15</sub>H<sub>12</sub>N<sub>4</sub>O<sub>3</sub>S<sub>2</sub>[KFeFe(CN)<sub>6</sub>]0.20}*n* for both complexes. The presence of ferromagnetic coupling between iron ions through cyano bridging linkage in SDP-Prussian blue is proposed based on the electron spin resonance spectroscopy (ESR).



Scheme 3: Synthetic route of SDP, SDP- $Fe^{2+}$  and SDP-Prussian blue and suggested structures.

Vaishali (2006) reported the Preparation, characterization, magnetic and thermal studies of some chelate polymers of first series transition metal ions. A modified method (Priyadarshini and Tandon, 1967) based on Schotten Baumann reaction was used for the preparation of hydroxamic acid (Ukey, 2003). The chelate polymers

were prepared according to the procedure described by (Ukey, 2005). Figure 2 shows the proposed structure of the chelate polymers. On the basis of elemental analyses, infrared (IR) spectra, reflectance spectra, magnetic moment data and thermal studies, the  $[\text{Zn(II)(ABHA)}]_n$  chelate polymers have tetrahedral geometry, whereas  $[\text{Mn(II)(ABHA)(H}_2\text{O)}_2]_n$ ,  $\{[\text{Ni(II)(ABHA)-(H}_2\text{O)}_2] \cdot (\text{H}_2\text{O})\}_n$  and  $\{[\text{Co(II)(ABHA)(H}_2\text{O)}_2] \cdot (\text{H}_2\text{O})\}_n$  chelate polymers have octahedral geometry and order of reactions has been found to be approximately one and have thermal stability in the order  $\text{Ni(II)} > \text{Mn(II)} > \text{Zn(II)} > \text{Co(II)}$ .

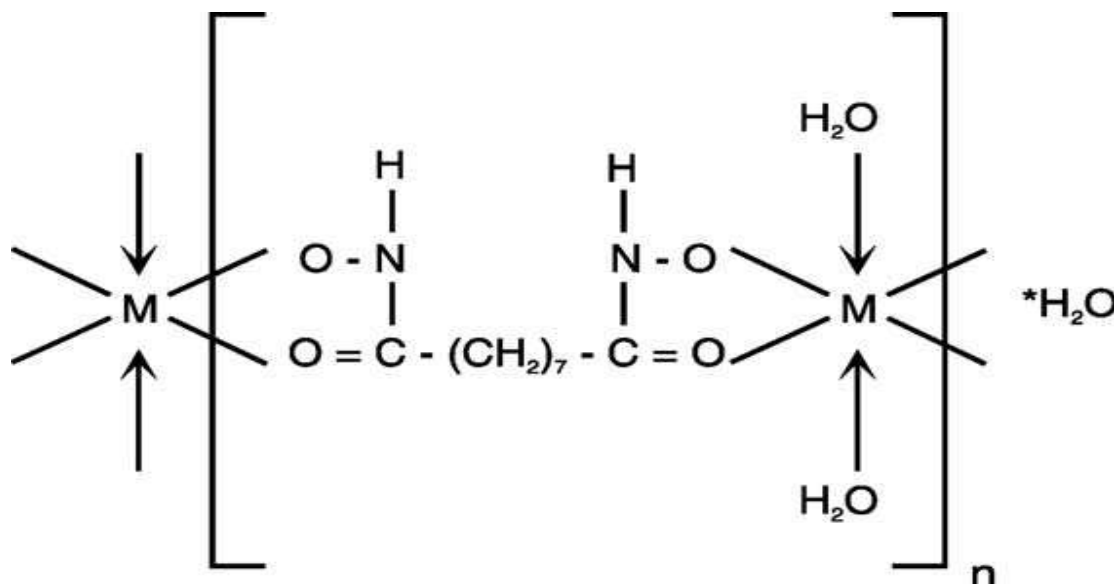


Figure 2: Proposed structure of the chelate polymers of azelaoyl-bis-hydroxamic acid, where  $\text{*H}_2\text{O}$ —water of hydration and  $\text{H}_2\text{O}$ —water of coordination.  $\text{M}$ = metal ion,  $\text{Mn(II)}$ ,  $\text{Co(II)}$ ,  $\text{Ni(II)}$  and  $\text{Zn(II)}$ .  $\text{*H}_2\text{O}$  is absent in case of  $\text{Mn(II)}$  ABHA chelate. Both  $\text{H}_2\text{O}$  and  $\text{*H}_2\text{O}$  molecules are absent in the case of  $\text{Zn(II)}$  ABHA chelate polymer.

#### **Coordination reaction of a ligand, which can attach itself simultaneously to two metal atoms or ions.**

Coordination polymers and oligomers containing dimetal clusters have not been explored as much as other coordination polymers, although numerous bridged dimetal units containing copper, rhodium, molybdenum and ruthenium are known (Craig, 2002) and recently, two reviews describing examples of dimetal tetracarboxylate unit containing one-dimensional polymers appeared (Craig, 2002). Tetrakis(carboxylato) rhodium compounds were first reported in 1960. The preparation of the polymers was achieved by the use of metal containing building block with free donor sites which can be joined together through the free binding sites to form many repeating units (polymers). Reported by Craig (2002) is the synthesis of a new mixed-metal  $\text{Mn-Rh}$  coordination polymer assembled from  $\text{Mn}$ -containing molecular building blocks and  $\text{Rh}_2(\text{OAc})_4$  dimers. The starting material  $\text{Mn(2-methylpyrazine-5-carboxylato)}_2 \cdot (\text{H}_2\text{O})_2$ , was synthesized by reacting 2-methylpyrazine-5-carboxylic acid with  $\text{MnCl}_2 \cdot 6\text{H}_2\text{O}$  in a basic solution. It was then reacted further with  $\text{Rh}_2(\text{OAc})_4$  by layering the two reactants in methanol and ethanol, respectively which yielded small red block crystals. Single crystal X-ray diffraction revealed the red crystals to be a new mixed-metal manganese/rhodium coordination polymer  $\{[\text{Mn(MePyzca)}_2(\text{MeOH})_2][\text{Rh}_2(\text{OAc})_4]\} \cdot 2\text{MeOH}$ . This new manganese–rhodium mixed metal coordination polymer complements other known systems based on the 2-pyrazinecarboxylate and 2-methylpyrazine-5-carboxylate ligands. In all cases, the ligand chelates one metal center with a carboxylate oxygen and one nitrogen donor while using the *para* nitrogens to bind a second metal.

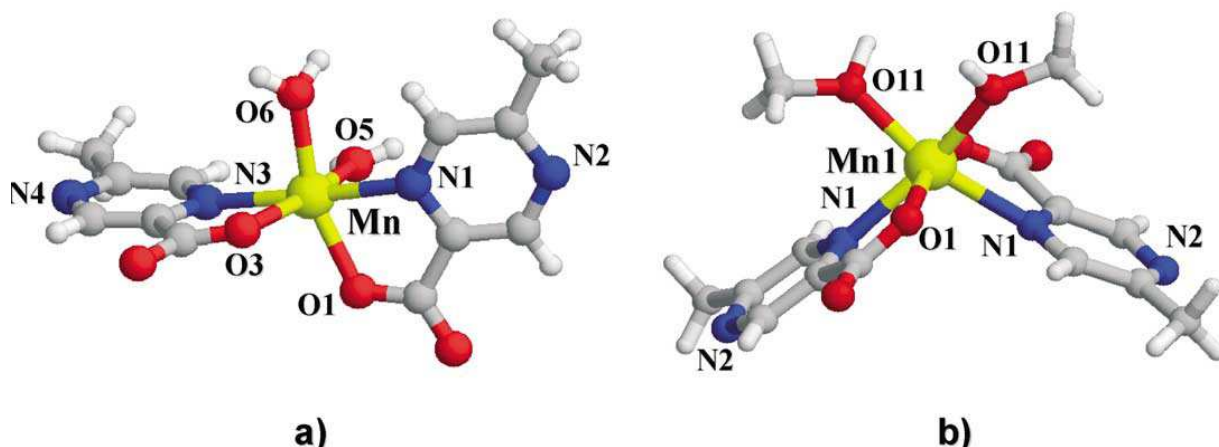


Figure 3: (a) The starting building block:  $\text{Mn}(\text{Mepyzca})_2(\text{H}_2\text{O})_2$ , **1**; (b) Coordination environment around Mn centers in the polymeric chain of **2**. Mn is shown in yellow, O in red, N in blue, C and H in grey.

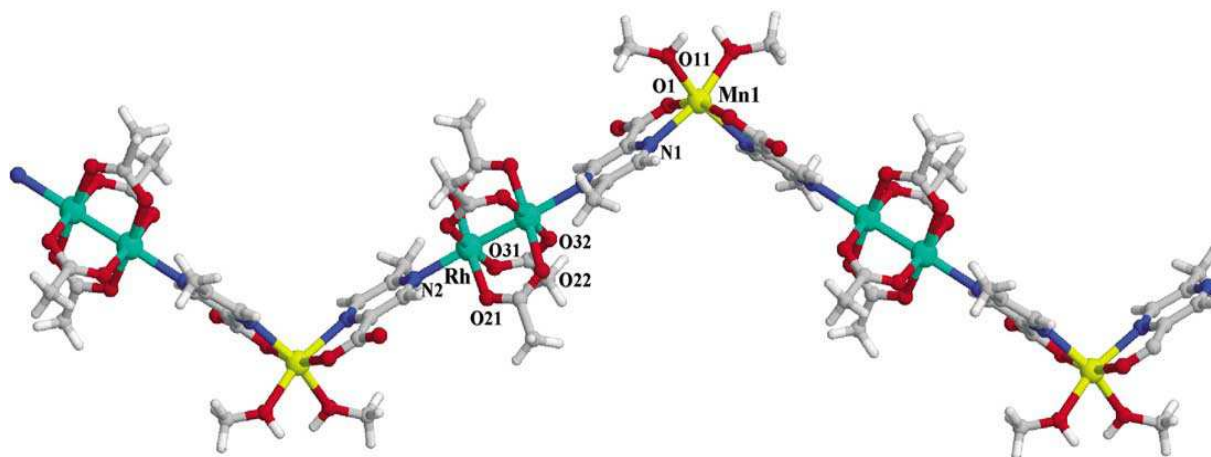


Figure 4: View of the one-dimensional zig-zag chain of **2**, oriented roughly parallel to the crystallographic *ab* plane. Rh is shown in green, Mn in yellow, O atoms in red, N in blue, C and H in grey.

Delia et al (2001) reported the synthesis of mixed-metal Ag–Co coordination polymer assembled from cobalt-containing molecular building blocks and  $\text{AgNO}_3$ . The polymer was prepared by the reaction of  $\text{Co}(\text{2-pyrazinecarboxylato})_2 \cdot (\text{H}_2\text{O})_2$  with  $\text{AgNO}_3$  in a sealed pyrex tube at  $130^\circ\text{C}$  for 24 hours. The reaction yielded two different products: yellowish block crystals and orange bar crystals. Single crystal X-ray diffraction revealed the yellow blocks to be a known three dimensional polymer,  $[\text{Ag}(\text{pyzca})]_n$  (Jaber, 1994), but determined the orange bars to be a new mixed-metal silver/cobalt coordination polymer  $\{\text{Ag}[\text{Co}(\text{pyzca})_2(\text{H}_2\text{O})(\text{NO}_3)]\}_n$ . The mixed-metal silver/cobalt coordination polymer when examined under X-ray diffractometer was found to have a polymeric structure consisting of  $\text{Co}(\text{pyzca})_2(\text{H}_2\text{O})(\text{NO}_3)-$  units linked into infinite chains by  $\text{Ag}^+$  centers (Figure 5).

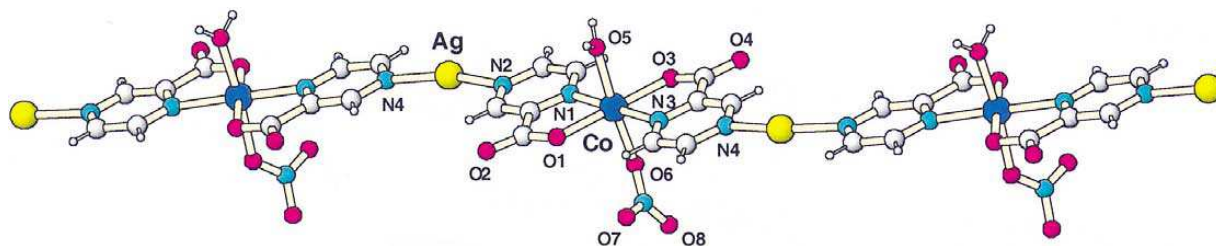


Figure: 5: View of a one-dimensional chain in  $\{Ag[Co(pyzca)_2(H_2O)(NO_3)]\}_n$ , showing the pseudo-octahedral cobalt centers and the bent two-coordinate silver centers. Co atoms are shown as large blue circles; Ag, large yellow circles; N, small blue circles; O, small red circles; C, small shaded circles.

This new silver–cobalt mixed metal coordination polymer complements other known systems based on the 2-pyrazinecarboxylate ligand. In all cases, the ligand chelates one metal center with carboxylate oxygen and one nitrogen donor while using the *para* nitrogens to bind a second metal. This cobalt–silver complex adds yet another structure type to the growing family of mixed-metal coordination polymers.

### Conclusion

The paper has pointed some three synthetic routes for the production of metallopolymer. The polymers as reported were found to have high molecular sizes and possess combined properties of coordination compounds and macromolecules. Various ligand groups can be employed to give numerous conformations while the obtained polymers have valuable properties.

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