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Stoichiometry of Polymer Complexes

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1. Introduction

Polymer complexes have been attracting interest in many scientific and technological fields in recent years. Polymer complexes have found wide applications in bioinorganic industry (Fenger & Le Drian, 1998), wastewater treatment (Mizuta et al., 2000), pollution control (Orazzhanova et al., 2003), hydrometallurgy (Varvara et al., 2004), preconcentration (Ro et al., 2003), anionic polyelectrolyte hydrogels (Varghesa et al., 2001), cation-exchange resins (Ahmed et al., 2004) etc. Moreover, they recently showed potential applications in material science as catalytic, conductive, luminescent, magnetic, porous, chiral or non-linear optical materials (Janiak, 2003; James, 2003; Maspoch et al., 2004; Batten & Murray, 2003).

Although various extensive investigations on polymer complexes have been reported, most of these complexes are too complicated to be discussed quantitatively due to the non-uniformity of their structure. These compounds include not only "complexes of macromolecules" but also the structurally labile "metal complex". Before detailed information can be obtained about the properties of polymer complexes, in particular about the reactivity and the catalytic activity, their structure must be elucidated. A polymer complex possessing a uniform structure may be defined as follows:

- The structure within the coordination sphere is uniform, i.e. the species and the composition of the ligand and its configuration are identical in any complex unit existing in the polymer complex;
- The primary structure of the polymer ligand is known.
- If the structure within the coordination sphere is identical in a polymer and in a monomeric complex, their reactivity ought to be the same even though the complex is bound to a polymer chain. However, it is clear that the reactivity is sometimes strongly affected by the polymer ligand that exists outside the coordination sphere surrounding the metal complex. The effect of polymer ligands can be explained in terms of two factors:
- the steric effect, which is determined by the conformation and density of the polymer ligand chain;
- the special environment constituted by a polymer ligand domain.

Hence, it is possible to prepare polymer complexes having different use and applications by varying the polymer chain, the nature of the ligand and the metal ion.

A polymer complex is composed of synthetic polymer and metal ions, with the metal ions bound to the polymer ligand by a coordinate bond. A polymer ligand contains anchoring sites like nitrogen, oxygen or sulphur obtained either by polymerization of monomer possessing the coordinating site or by a chemical reaction between a polymer and a low molecular weight compound with coordinating ability. The synthesis results in an organic polymer with inorganic functions. The metal atoms attached to the polymer backbone are bound to exhibit a characteristic catalytic behavior, distinctly different from their low molecular weight analogues. Indeed, many synthetic polymer complexes have been found to possess high catalytic activity, in addition to semiconductivity, heat resistance and biomedical potentials.

This review will focus mainly on the stoichiometry and the characterization of polymer complexes structure by using elemental analyses, electronic spectra, magnetic susceptibilities, FT-IR, IR, ^{1}H-NMR, ESR and thermogravimetric analyses.

2. Classification of polymer metal complexes

The polymer complexes may be classified into three different groups according to the position occupied by the metal, which is decided by the methods of preparation:

1. Complexation of polymeric ligand with metal ions which could be divided into two categories:
   a. Pendant metal polymer complexes.
   b. Inter/intra-molecular bridged polymer complexes.
2. Complexation of multifunctional ligands with a metal.
3. Polymerization of metal containing monomers.

2.1 Complexation of polymeric ligand with metal ion

Only decades ago polychelats derived from polymeric ligands and transition metal ions attracted the attention of many investigators. Bamford, Jenkins and Johnson (Bamford et al., 1958) were the first who noticed and described that radical polymerization of vinyl monomers is accelerated by addition of an inorganic salt not participating in redox reactions. They showed that the rate of polymerization of acrylonitrile (AN) initiated by azobisisobutyronitrile (AIBN) in dimethyl formamide (DMF), increases when lithium chloride is dissolved in the reaction mixture. According to the kinetic measurements, the effect was ascribed to an increased propagation of the rate constant and explained by the complexation of the nitrile groups at the radicals with lithium chloride.

A number of authors (Tazuke & Okamura, 1966; Tazuke et al. 1966; Tazuke & Okamura, 1967) have studied radical polymerization of this type. From a kinetic point of view methyl methacrylate (MMA) and AN-metal salt ($AlCl_3$, $AlBr_3$, $ZnCl_2$, $GaCl_2$, etc) systems were most intensively investigated (Imoto et al., 1963; Bamford et al., 1966a & Zubov et al., 1968). The increased reactivity of the complexed monomer has been attributed to the delocalization of the electrons in the double and triple bonds of the acceptor monomer as a result of the complexation with the electron accepting metal halide (Fig. 1) (Lazuke et al., 1967).

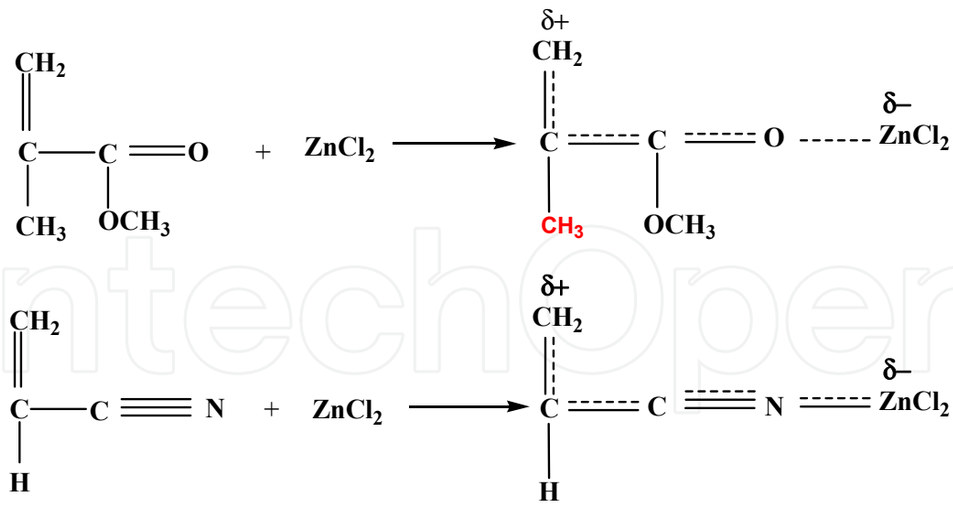


Fig. 1.

The new electrophilic acceptor monomer has an increased rate constant and an unchanged termination rate constant resulting in a more rapid rate of propagation and in the formation of a higher molecular weight polymer (Banford et al., 1966b). The kinetics of polymerization were extended to methyl acrylate (MA) with transition metal bromides (El-Sonbati et al., 1992). The presence of Cu(II), Ni(II) and Zn(II) bromides retards the rate of polymerization. This retardation effect of the polymerization of MA is attributable to the formation of addition products, which must be inactive in initiating the polymerization of MA and decrease the rate of polymerization in the order MA-$ZnBr_2$ < MA-$CuBr_2$ < MA-$NiBr_2$.

The enhanced reactivity of the complex monomer extends to copolymerization with olefinic or allylic monomer, which is poorly responsive to free radical initiated polymerization (Imoto et al., 1965; Serniuk & Thomas, 1965; Serniuk & Thomas, 1966). The free radical initiated copolymerization of such monomers which a metal halide complexed polar monomer results in an increased concentration of olefinic monomer in the polymer as compared with that obtained in the absence of the complexing agent, as well as an increase in the polymer molecular weight.

The reaction of polymer ligands with metal ions usually results in various coordination structures, which are divided into pendant and inter- and/or intra-molecular bridged complexes.

2.1.1 Pendant polymer complexes

The metal ion in a pendant metal complex is attached to the polymer ligand function, which is appended on the polymer chain. Based on the chelating abilities of the ligands, pendant complexes are classified as monodentate or polydentate polymer metal complexes.

a. Monodentate pendant polymer complexes

A metal ion or a metal complex has only one labile ligand, which is easily substituted by a polymeric ligand, and when other coordination sites are substitution inactive, the complex formed has a simple structure of monodentate type as shown in Fig. 2.

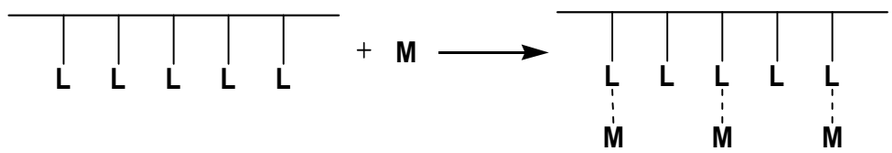
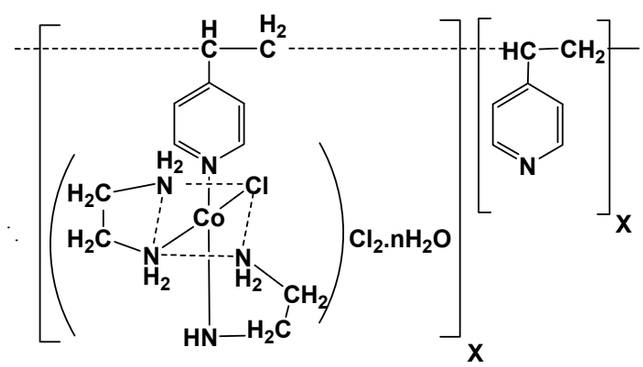


Fig. 2.

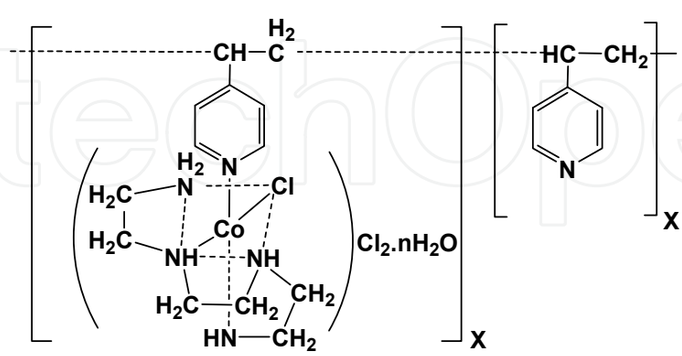
If the metal ion or metal complex has more than two labile ligands, it is often possible to realize a monodentate complex structure by selecting an appropriate reaction condition (Kaneko & Tsuchide, 1981). Important characteristics of this type of polymer complexes are:

i. The coordination is very clear.
ii. The effect of the polymer chain is clearly exhibited.
iii. The polymer complex is very often soluble in water or in organic solvents.

The reaction of poly(4-vinylpyridine)(PVP) with various metal chelates such as cis[$Co(en)_2Cl_2$]Cl.H_2O (en = ethylendiamine), cis-α-[$Co(trien)Cl_2$]Cl.H_2O, (trien = triethylenetetramine) and cis-[$Co(en)_2PyCl$]Cl_2 (Py = pyridine) gives simple structures of monodentate type (Fig. 3) (Kurimura et al., 1971; Tsuchide et al., 1974).



cis-[$Co(en)_2$ PVPCl] $Cl_2.nH_2O$



cis-[$Co(trien)_2$PVPCl]$Cl_2.nH_2O$

Fig. 3.

Soluble copper chloride complexes of poly(2-vinylpyridine) (P2VPy) were prepared (Lyons et al., 1988) in a methanol-water solution. Solubility was achieved with the proper solvent

system due to the sterically hindered environment of the ligand, allowing only one pyridine moiety to complex each copper cation. Partial reduction of the cupric cation occurred during sample preparation, as observed by X-ray photoelectron spectroscopy (XPS) and magnetic susceptibility measurements.

b. Polydentate pendant polymer complexes

When the polymer pendant coordination group has a polydentate structure, the coordination structure of the polymer metal complex is very clear, and high stability can be expected as shown in Fig. 4.

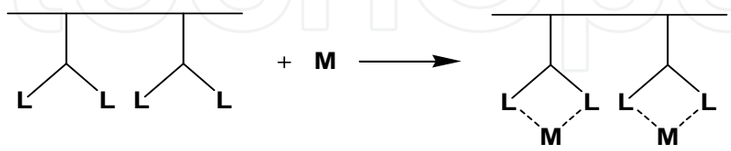
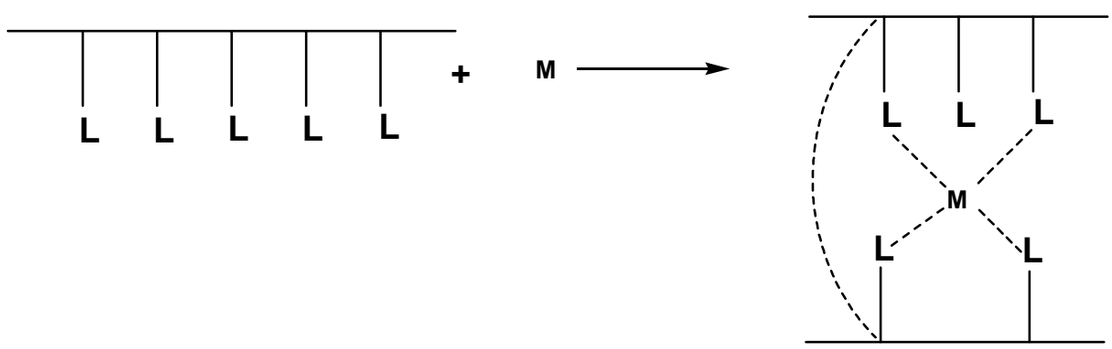


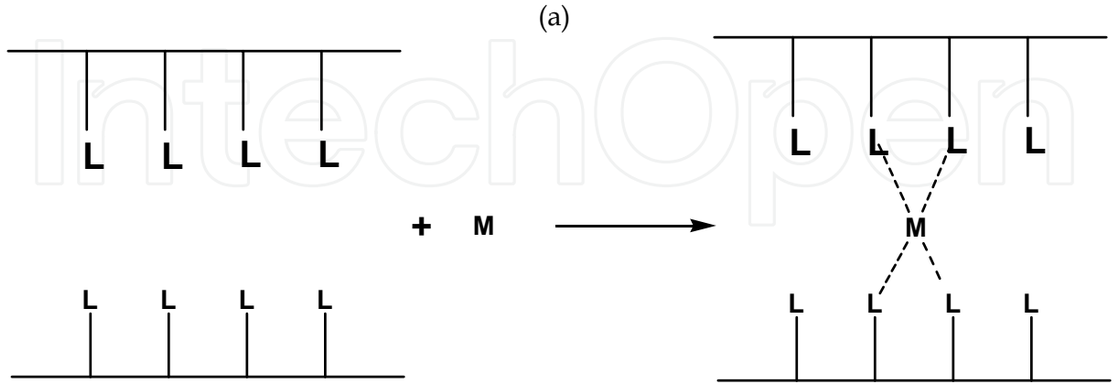
Fig. 4.

2.1.2 Inter-and/or intra-molecular bridging polymer complexes

The reaction of polymer ligands with metal ions very often results in inter-and/or interamolecular bridging (Fig. 5).



(a)



(b)

L : Coordinate atom (or) group, M = Metal ion, a : intra-polydentate, b : inter-polydentate

Fig. 5.

The coordination structure of the resulting polymer metal complex is not clear in this case, and the polymer complex is sometimes insoluble in water or in organic solvent. It is usually difficult to distinguish between the inter and intra-molecular bridging. The fact that it is not often easy to elucidate the polymer effect in studying the characteristics of the polymer complex. The simplest example of this type of polymer complex is the poly(vinyl alcohol)(PVA)-Cu(II) complex (Fig. 6) (Hojo & Shiria, 1972).

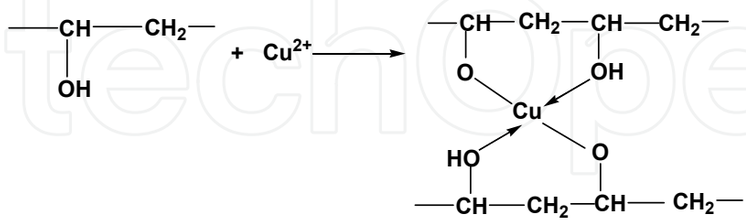


Fig. 6.

The coordination reaction is generally affected by the polymer ligand tacticity. The different coordination behavior of atactic poly (4-vinylpyridine)(PVP) and isotactic (2-vinylpyridine)(P2VP) with $M(II)Cl_2$, where M=Co, Ni, Cu or Zn, is reported (Agnew, 1976). Atactic PVP and $NiCl_2$ precipitated a mixture of a tetrahedral structure having stoichiometry $Ni(PVP)_2Cl_2$. Isotactic P2VP gave no precipitation with $NiCl_2$ in ethanol, showing no coordination in UV and visible spectra as shown in Fig. 7.

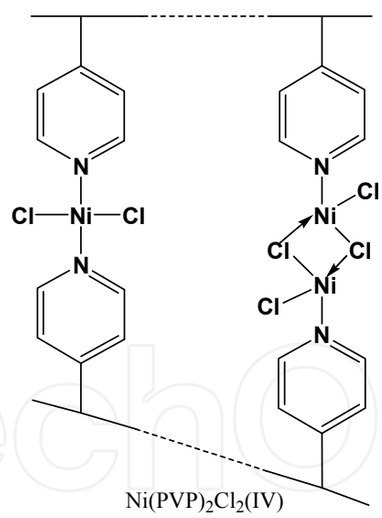


Fig. 7.

2.1.3 The chain linked through complexation of bifunctional ligands with metal ions

When bifunctional ligands form a complex with metal ions having more than two labile ligands, i.e. easily replaceable a polymer complex (Fig. 8) is formed through metal ion bridging.

This type of polymer metal complex has been synthesized as semiconducting organic materials (Katon, 1970), heat resistant organic polymer or polymer catalysts. Bridged ligands

able to form polymer metal complexes of this type are classified as follows : (i) compounds having more than two coordinating groups, and (ii) simple compounds having more than two coordinating atoms, or simple ions which are able to function as bridged ligands. When the complex formation of ligands having four coordinating groups induces chemical reaction between the ligands, the resulting polymer complex sometimes has a network structure.

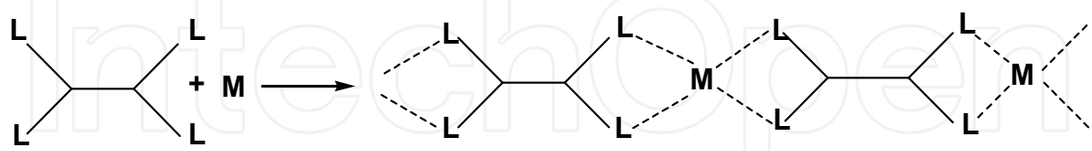


Fig. 8.

a. Linear coordinated polymer

i. Linked by a bifunctional ligand

Dithiooxamide (rubeanic acid) is a typical bifunctional ligand which forms a linear-type polymer metal complex with metal ions (Fig. 9) (Amon & Kane, 1950).

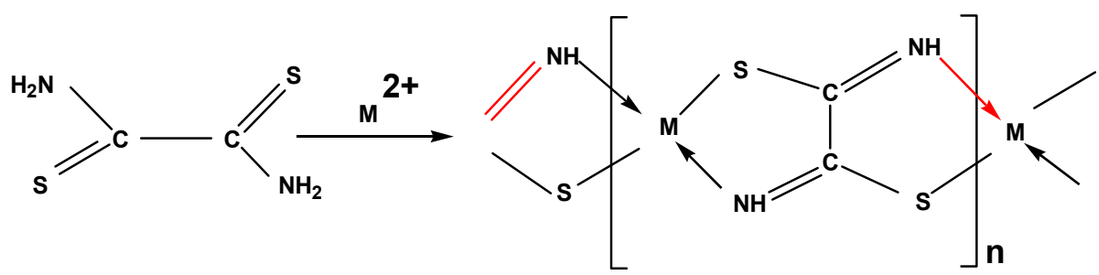


Fig. 9.

ii- Linked by simple compound or ion

A simple ion or compound can work as a bridging ligand giving a polymeric structure. A metal salt such as cupric chloride forms an associated structure (Fig. 10) in a very concentrated aqueous solution of hydrogen chloride (Wertz & Tyvoll, 1974) with the chloride ions occupying as bridging ligands both the axial and equatorial coordination sites of Cu^{2+}.

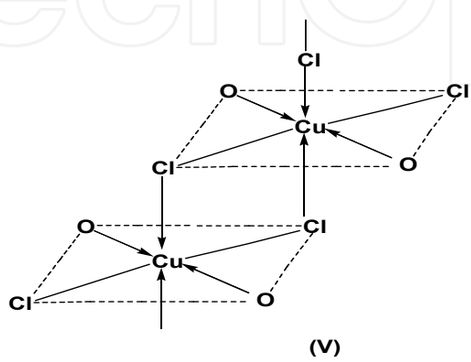


Fig. 10.

b. Network-coordinated polymers

The most usual method to prepare this type of complexes is use a "template reaction". This is a reaction between two functional groups of the ligand induced by their coordination to the metal ion, resulting in a chelated-type metal complex (Fig. 11).

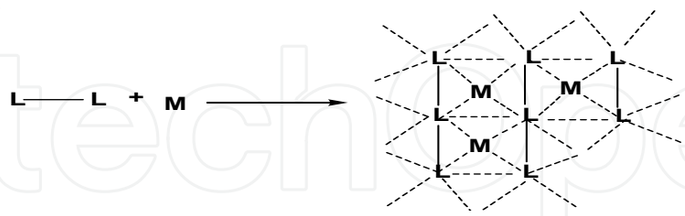


Fig. 11.

A typical example is poly(metal phthalocyanine) formed during the reaction of tetracyanobenzene with metal halides catalyzed by urea as shown in Fig. 12 (Epstein & Wildi, 1960).

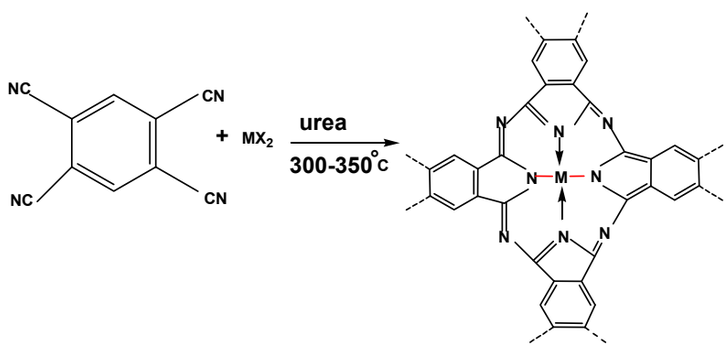


Fig. 12.

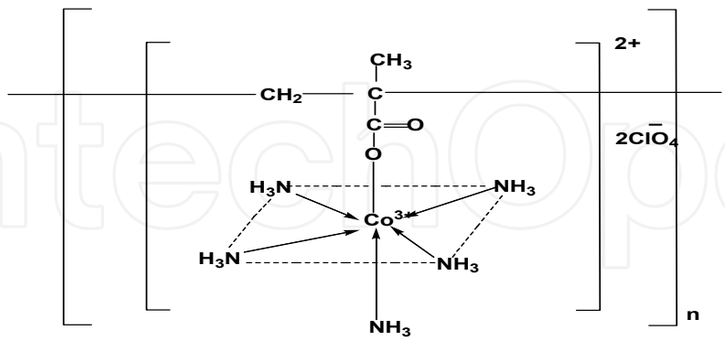
2.1.4 Formation through polymerization of metal complexes

Polymer containing the metal as part of a pendent or substituent group may be formed when complex possessing functionalized ligands undergo polymerization. The most widely studied are vinyl complexes and their derivatives, formed through radical polymerization of vinyl monomer containing transition metal ions. Vinyl compounds of metal complex are polymerized giving polymer metal complexes as shown in Fig. 13.

Fig. 13.

This type of polymer complex is characterized by its clear coordination structure. Nevertheless, the limitations of the vinyl compounds, and the metal complex tendency to hinder the vinyl polymerization, may constitute an obstacle in this type of polymerization.

Methacrylate monomer coordinated to Co(III) complex, e.g. methacrylato-pentaamine cobalt (III) perchlorate, was radically polymerized giving the polymer (VI) (Fig. 14) (Osada, 1975; Osada, 1976a; Osada, 1976b; Osada & Ishida, 1976).

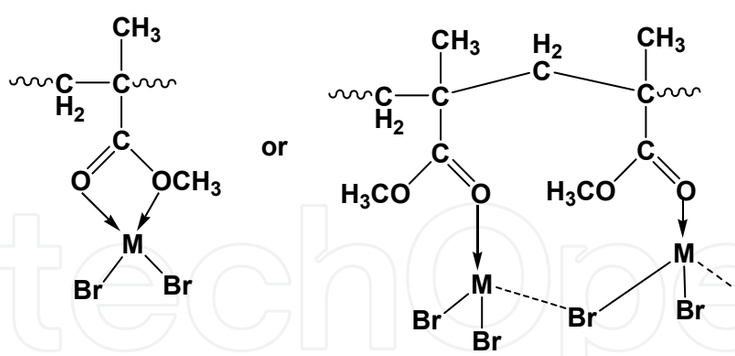


(VI)

Fig. 14.

The free radical initiated polymerization of polar monomers containing pendant nitrile and carbonyl groups, e.g. acrylonitrile and methyl methacrylate, in the presence of metal halides such as $ZnCl_2$ and $AlCl_3$ is characterized by an increased rate of polymerization. On the contrary, the formation of polymers with considerably higher molecular weight is likely in the absence of the metal halide (Bamford et al, 1957; Bovey, 1960; Arthur & Blouin, 1964).

The reaction of methyl methacrylate (MMA) with transition metal bromides gives examples of bidentated polymer complexes (El-Sonbati & Diab, 1988a) as shown in Fig. 15.



M = Cu(II), Co(II) and Ni(II)

Fig. 15.

This behavior is similar to the one suggested (Kabanov, 1969) for the polymerization of MMA in presence of inorganic salts such as $ZnCl_2$ and $AlBr_3$.

The polymerization of acrylonitrile (AN) in presence of Cu(I), Cu(II), Co(II), Ni(II) and Cd(II) bromides was studied (El-Sonbati & Diab, 1988b & 1988c). The IR spectrum of the formed AN-Cu(II) bromide polymer complex shows the absence of the C≡N band and the presence of two new bands corresponding to NH_2 and OH groups. These bands are not

found with the other metal bromide polymer complexes (Fig. 16). It seem that Cu(II) is reduced to the stable Cu(I) during the polymerization of AN-Cu(II) bromide.

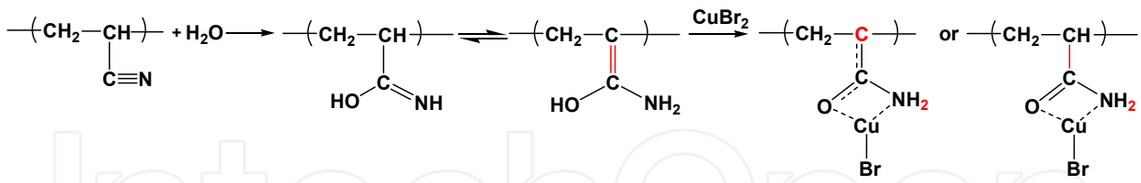
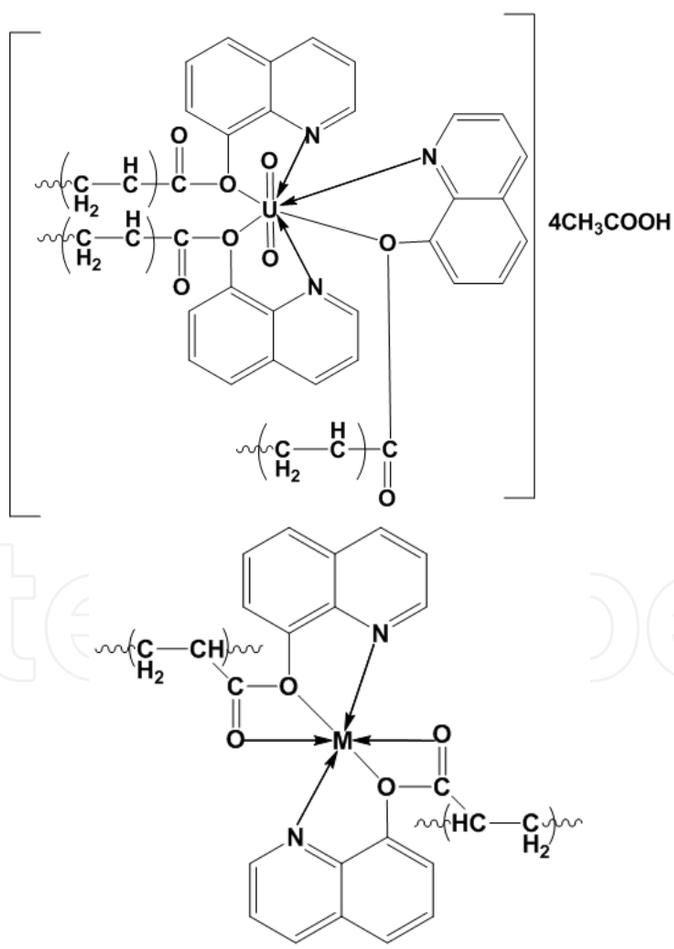


Fig. 16.

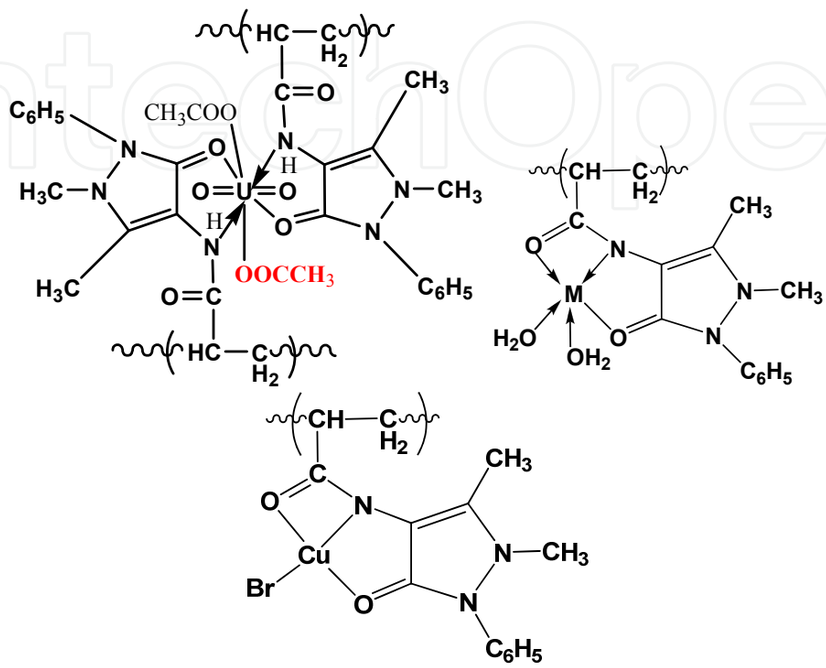
Poly(8-quinolyl acrylate)(P8-QA) and the polymers of the complexes of 8-quinolyl acrylate (8-QA) with some transition metal bromides and uranyl acetate have been prepared and characterized (El-Sonbati & Diab, 1988d). Dioxouranium(VI) acetate dehydrate reacts with 8-QA monomer in a 1:3 metal:ligand molar ratio. On the other hand, 8-QA reacts with Cu(II), Ni(II) and Co(II) bromides in such a way that the polychelates have 1:2, metal:ligand stoichiometry as shown in Fig. 17.



M = Cu(II), Co(II) and Ni(II)

Fig. 17.

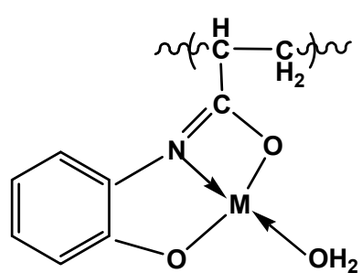
Poly(acrylamido-4-aminoantipyrinyl)(PAA) homopolymer and polymer complexes of acrylamido-4-aminoantipyrinyl (AA) with some transition metal bromides and uranyl acetate have been prepared (El-Sonbat et al., 1989)). Dioxouranium(VI) acetate dehydrate reacts with AA in a 1:2 and with $CuBr_2$, $NiBr_2$ and $CoBr_2$ in 1:1 metal:ligand molar ratios and the polychelates of the types shown in Fig. 18.



M = Co(II) and Ni(II)

Fig. 18.

Poly(2-acrylamidophenol)(PAP) homopolymer and polymer complexes of 2-acrylamidophenol (AP) with Cu(II), Ni(II), Co(II), Cd(II) chlorides and uranyl acetate were prepared and characterized (Diab et al., 1988). The phenolic C-O IR band has been shifted of ± 15 cm^{-1}, indicating that it is involved in the coordination of AP-$CuCl_2$ and AP-$CdCl_2$ polymer complexes (Fig. 19). There is a change in the position of NH band to lower frequency, indicating the recruitment of these groups in the coordination of AP-$CoCl_2$ and AP-$NiCl_2$ polymer complexes. The possible structures of AP-Cu(II), AP-Ni(II), AP-Co(II), AP-Cd(II) chlorides and uranyl acetate are the following:



M = Cu(II) and Cd(II)

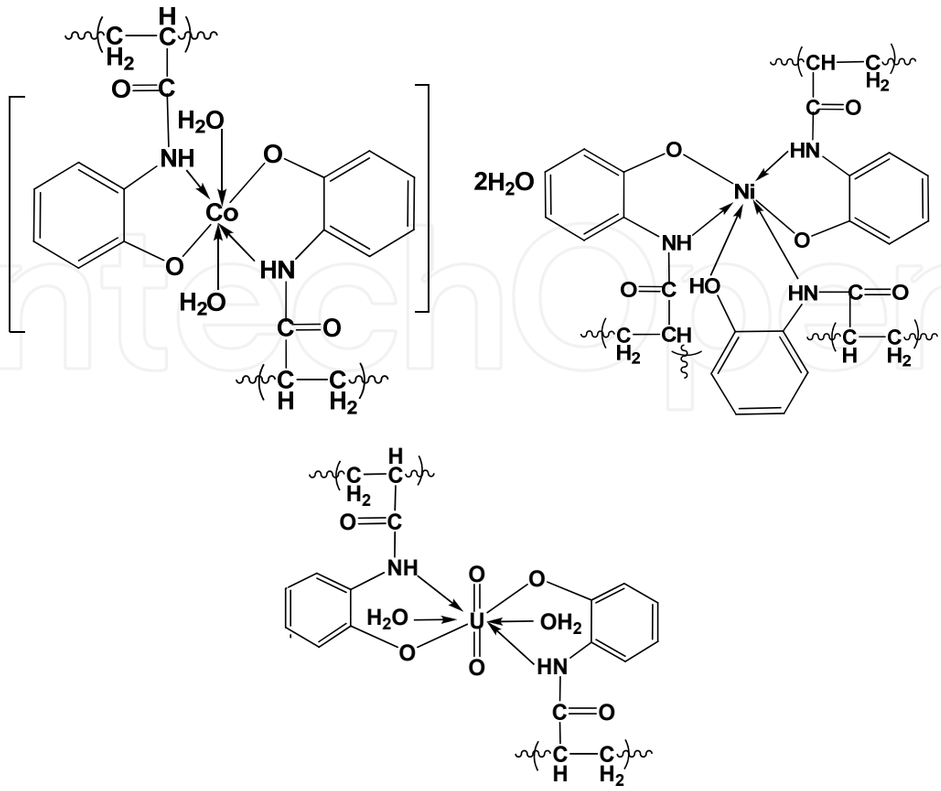


Fig. 19.

Poly(2-acrylamidopyridine)(PAP) homopolymer and polymer complexes of 2-acrylamidopyridine (AP) with some transition metal chlorides have been prepared and characterized (Diab et al., 1989a). IR spectrum of PAP homopolymer indicates two tautomeric forms are shown in Fig. 20.

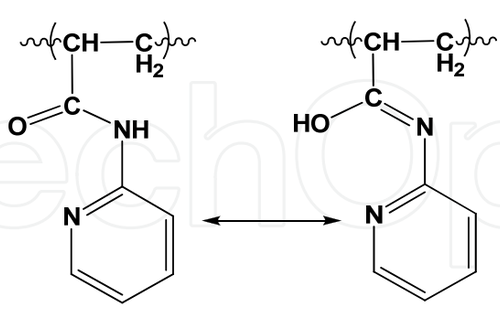


Fig. 20.

The IR spectrum of AP-$CuCl_2$ polymer complex shows a lowering of the OH stretching frequency by about 10-15 cm^{-1} indicating that the OH group is involved in the coordination (Fig. 21). An increase in the frequency of the pyridine nitrogen indicates that it takes part in the bond formation. Moreover, new bands appeared in the spectrum assigned to υ(M-O), υ(M-N) and υ(M-Cl). It may be deduced that the probable structure of AP-$CuCl_2$ polymer complex is:

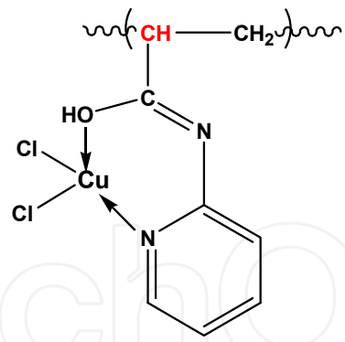
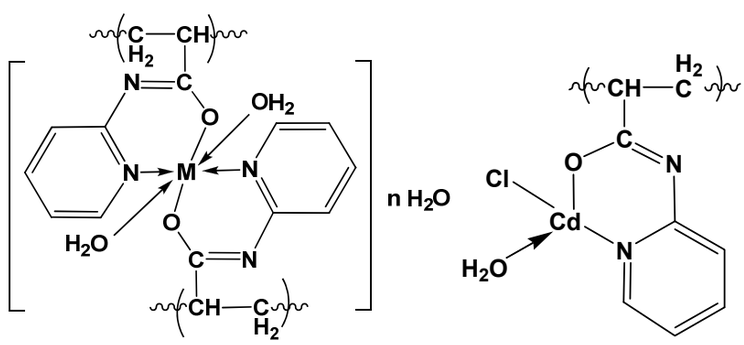


Fig. 21.

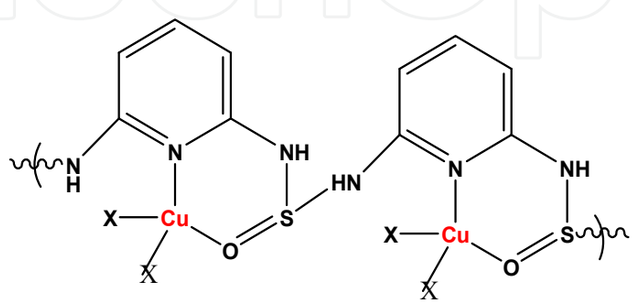
The IR spectra of AP-$CoCl_2$, AP-$NiCl_2$ and AP-$CdCl_2$ polymer complexes have the characteristic features of coordination between the nitrogen atom of the pyridine ring and the oxygen atom of the hydroxyl group. AP reacts with $NiCl_2$, $CoCl_2$ in a 2:1 ratio and with $CdCl_2$ in a 1:1 ratio. The possible structures of AP-$NiCl_2$, AP-$CoCl_2$ and AP-$CdCl_2$ polymer complexes (Fig. 22) are the following:



For M = Ni(II); n = 0
For M = Co(II); n = 4

Fig. 22.

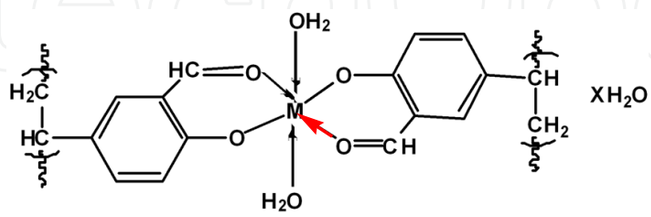
It was found that poly[bis(2,6-diaminopyridine sulphoxide)](PDPS) homopolymer and polymer complexes of bis(2,6-diaminopyridine sulphoxide)(DPS) with $CuCl_2$, $CuBr_2$ and CuI_2 were prepared and characterized (Diab et al., 1989b). The mode of complexation of the polymer complexes of PDPS with copper halides is derived as shown in Fig. 23.



X = Cl, Br and I

Fig. 23.

Poly(5-vinyl salicylaldehyde)(PVS) homopolymer and polymer complexes of 5-vinylsalicylaldehyde (VS) with $CuCl_2$, $CoCl_2$, $NiCl_2$ and uranyl acetate were synthesized and characterized (El-Hendawy, 1989). The IR spectrum of VS-$CuCl_2$ polymer complex shows a shift of υ(C=O) to a lower frequency by about 15 cm^{-1} and the υ(C-O) of the phenolic group is shifted to a higher frequency by about 25 cm^{-1} indicating that both groups are involved in the complexation. From the spectroscopic data, the magnetic moments and the elemental analysis, it is concluded that VS reacts with $CuCl_2$, $CoCl_2$ and $NiCl_2$ in the ratio 2:1. The possible structure of the polymer complexes VS-$CuCl_2$, VS-$CoCl_2$ and VS-$NiCl_2$ may be as shown in Fig. 24.



M = Cu (II), X = 0
= Co (II), X = 2
= Ni (II), X = 4

Fig. 24.

VS reacts with uranyl acetate in 1:2 metal:ligand stoichiometry (Fig. 25).

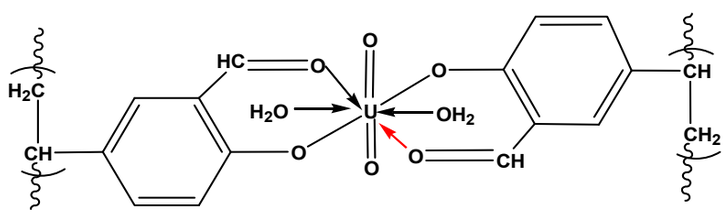


Fig. 25.

Polymer complexes of 2-acrylamidobenzoic acid (ABA) with transition metal chlorides and uranyl acetate were prepared and characterized (Diab et al., 1990a). ABA reacts with uranyl ions in a 2:1 molar ratio. The chelation occurs through one of the two oxygens of the carboxylate ion, which is represented as a tautomeric form as shown in Fig. 26.

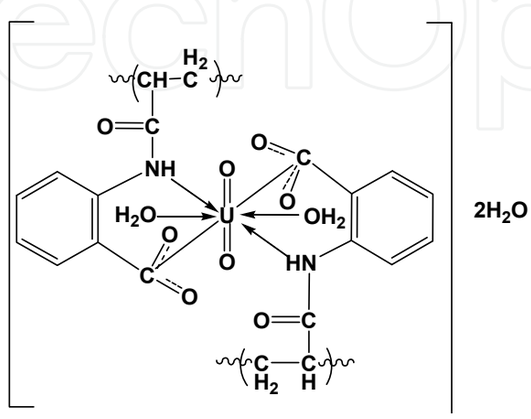
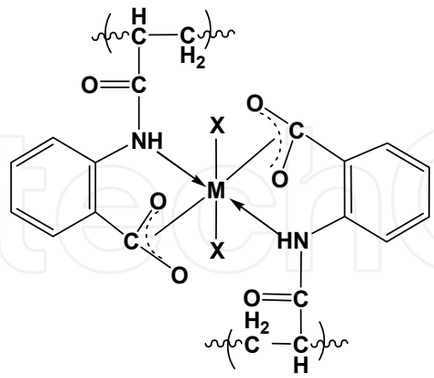


Fig. 26.

ABA reacts with Cu(II), Co(II), and Ni(II) in a 2:1 molar ratio of monomer unit: metal. The structure of the polychelates (Fig. 27) is of the type:



M = Co(II); X = H_2O
M = Cu(II) and Ni(II); X = 0

Fig. 27.

Poly(5-vinylsalicylidene anthranilic acid)(PVSA) homopolymer and polymer complexes of 5-vinylsalicylidene anthranilic acid (VSA) with some transition metal chlorides and uranyl acetate were prepared (Diab et al., 1990b). The IR spectrum of VSA-uranyl acetate polymer complex shows a change in the position of azomethine nitrogen and carboxylate ion groups indicating their involvement in coordination. Elemental analysis and IR spectrum reveal that VSA reacts with uranyl acetate, $NiCl_2$, $CuCl_2$ and $CoCl_2$ to form the structures shown in Fig. 28.

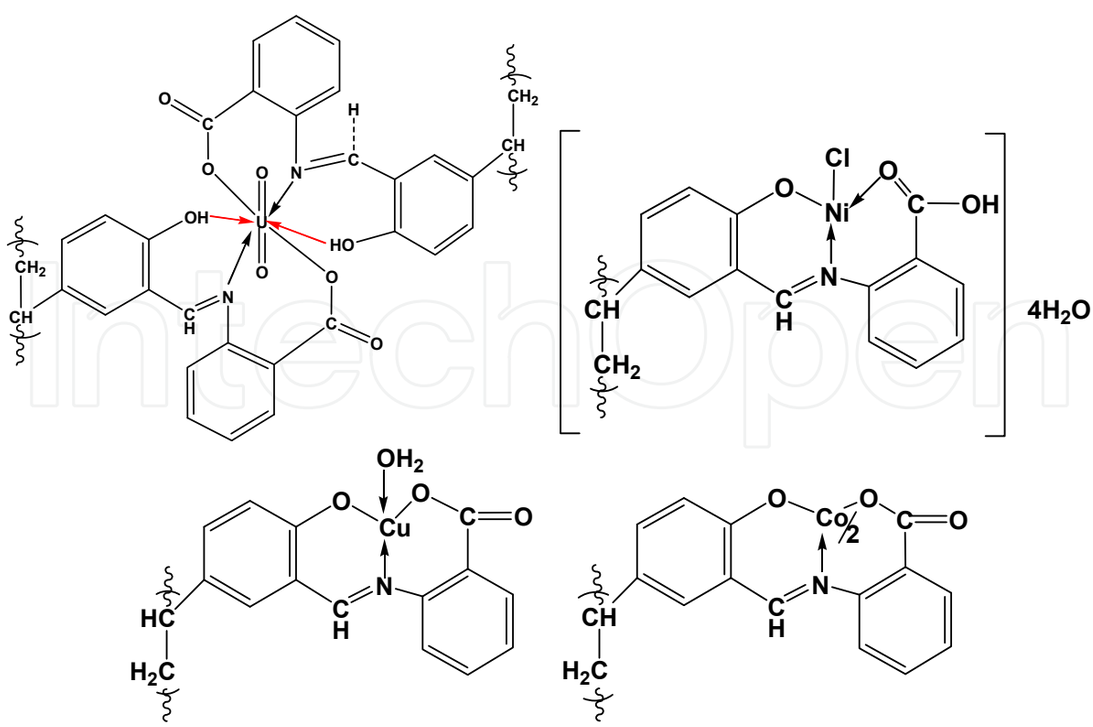
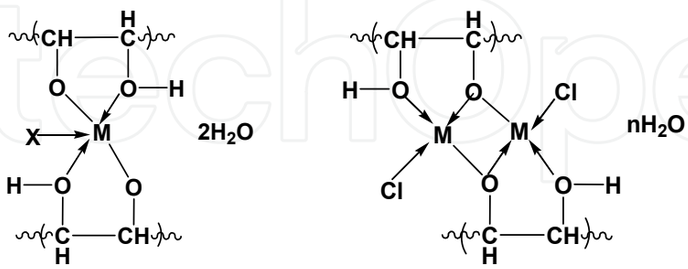


Fig. 28.

Poly(ethylene glycol)(PEG) reacts with Cu(II), Co(II), Ni(II) and Cd(II) chlorides to form polymer complexes in 2:1, ligand:metal molar ratios (Diab & El-Sonbati, 1990). The IR bands due to C-O are shifted to higher frequencies in the formed polymer complexes. This shift may be due to the increased covalence resulting from metal ion coordination. On the basis of the analytical data, electronic and IR spectral data, PEG reacts with $CuCl_2$, $CoCl_2$, $NiCl_2$ and $CdCl_2$ as shown in Fig. 29.



M = Cu(II); X = H_2O M =Co(II); n = 3
M = Ni(II); X = zero M =Co(II); n = 6

Fig. 29.

Polymer complexes of 5-vinylsalicylidene aniline (VSA) with Cu(II), Co(II), Ni(II), Cd(II) and UO_2(II). VSA reacts with uranyl nitrate in a 2:1 ratio and with uranyl acetate in a 1:1 ratio were found (El-Sonbati, 1992). A possible structure for the polymer complexes is shown in Fig. 30.

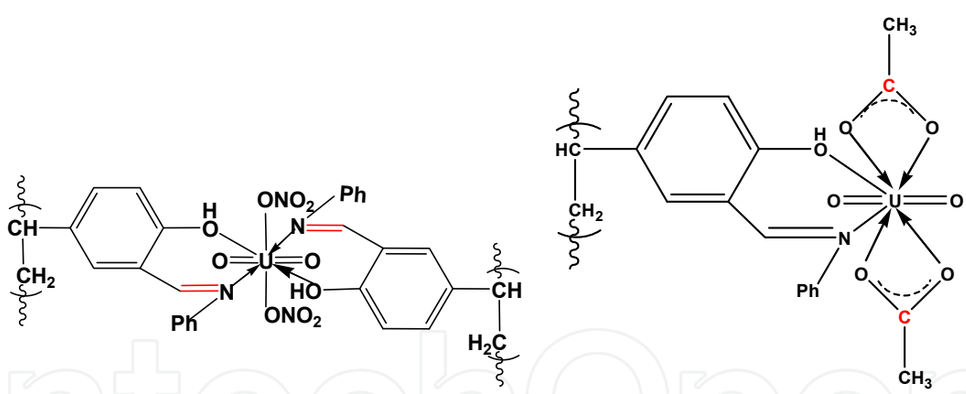


Fig. 30.

The IR, electronic spectra and elemental analyses data indicate that copper(II) salts react with VSA monomer in a 1:1 molar ratio (Fig. 31).

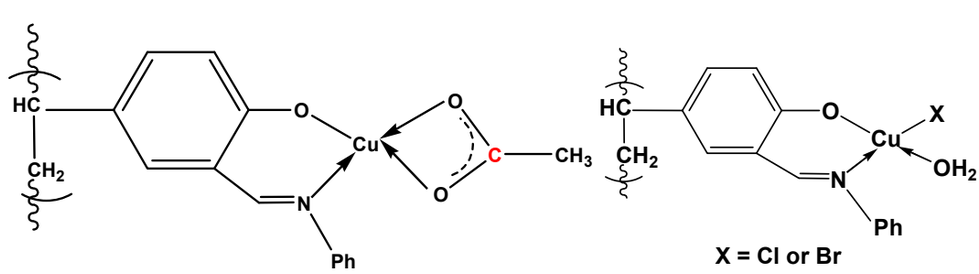


Fig. 31.

VSA reacts with Ni(II) and Co(II) in a 2:1 molar ratio and with Cd(II) in a 1:1 ratio (Fig. 32).

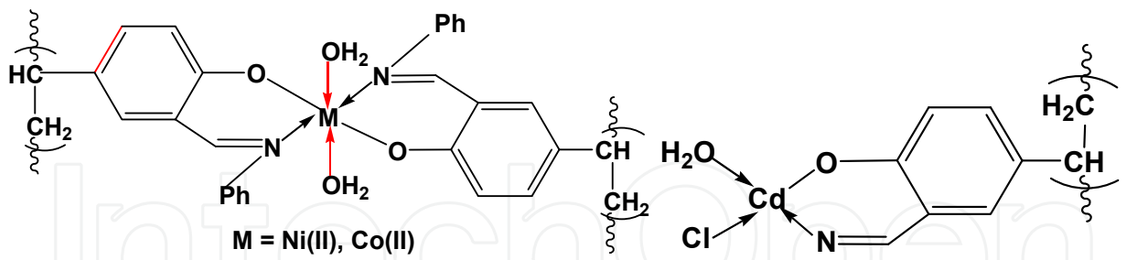
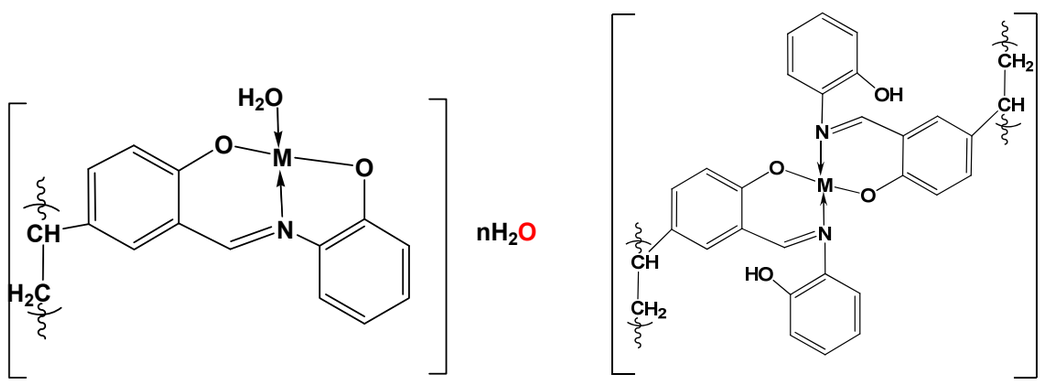


Fig. 32.

Homopolymer of 5-vinylsalicylidene-2-aminophenol (PVSA) and polymer complexes of 5-vinylsalicylidene-2-aminophenol (VSA) with transition metal acetate have been prepared and characterized (El-Sonbati, 1991a). The absence of the phenolic υ(O-H) in the copper(II), nickel(II), cadmium(II) and zinc(II) polymer complexes indicates the phenolic proton is lost upon metal ion complexation VSA appears to react with Cu(II), Ni(II), Cd(II) and Zn(II) acetate in a 1:1 ratio and with Co(II) and uranyl acetate in a 2:1 molar ratio. A possible structure for the polymer complexes is shown in Fig. 33.



M =Cu(II); n = 2, M = Ni(II), Cd(II), Zn(II); n = 0 M = UO_2(II) or Co(II)

Fig. 33.

Polymer complexes derived from 5-vinylsalicylidene hydrazine-S-benzyl dithiocarbocarbazate (VSH) with $CuCl_2$, $NiCl_2$, $CdCl_2$ and uranyl acetate were prepared and characterized by elemental analyses, spectroscopic and magnetic measurements (El-Sonbati, 1991b). The IR spectra of VSH-$NiCl_2$ and VSH-$CdCl_2$ polymer complexes show the disappearance of the NH group and the appearance of new bands at 1625-1630 cm^{-1} which could be attributed to the stretching vibrational mode of the conjugated C=N-N=C group. There is a strong broad band at 3460-3350 cm^{-1} which is attributable to the associated water molecules. The absence of the phenolic υOH is an indication that the phenolic proton is lost upon complexation. Furthermore, it was found that there is a band around 1495 cm^{-1}, suggesting that the *o*-hydroxy group has entered into the band formation with metal ions. According to these results beside the electronic spectra and elemental analysis, the possible structure of the products of reaction of VSH with $NiCl_2$ and $CdCl_2$ as shown in Fig. 34.

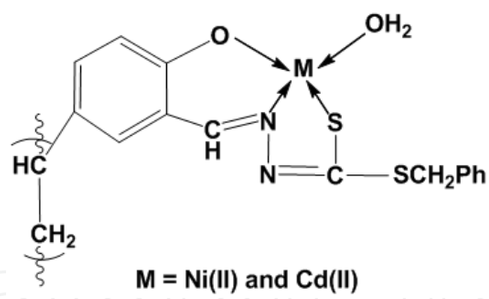


Fig. 34.

The IR spectrum of the VSH-$CuCl_2$ polymer complex shows the disappearance of the bands attributed to C=S and OH groups, suggesting that enolization occurred through the thioketonic group. The shift of the phenolic υ(C-O) to higher frequencies by about 15-20 cm^{-1} suggests the formation of an oxygen-bridge structure (Fig. 35). The structure appear to be of the following type:

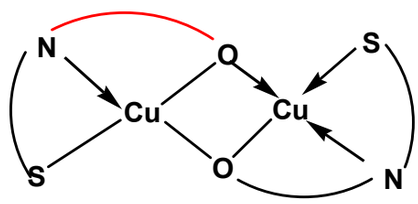
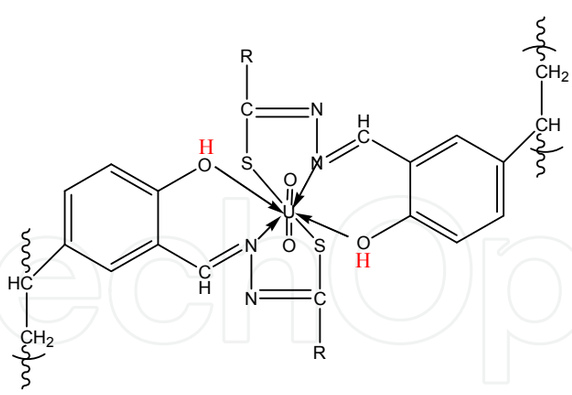


Fig. 35.

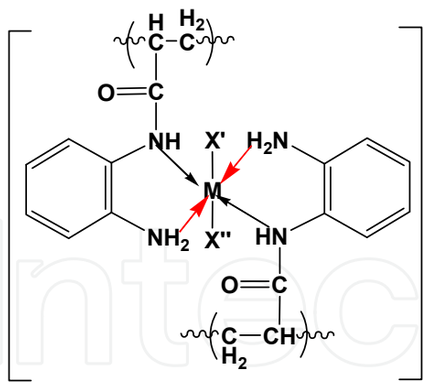
The stoichiometry between uranyl acetate and VSH are in agreement with a 1:2 molar ratio and the following type of structure is proposed (Fig. 36).

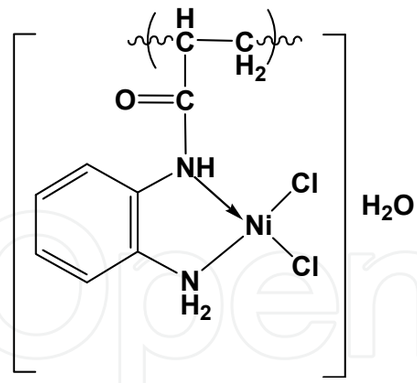


R = SCH_2Ph

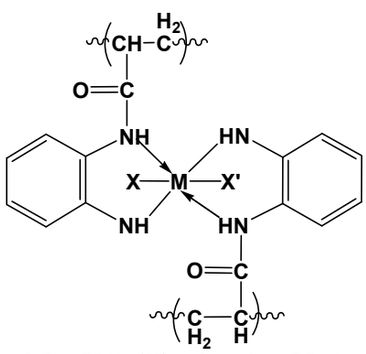
Fig. 36.

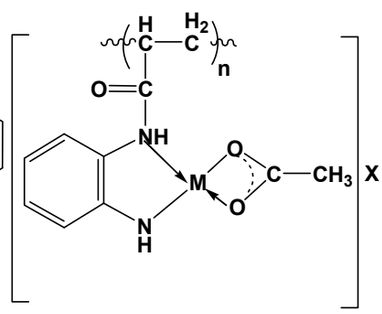
It was found that, 2-acrylamido-1,2-diaminobenzene (AAB) reacts with Cu(II), Ni(II), Zn(II) and UO_2(II) chlorides or acetate to give polymer complexes with different stoichiometry (El-Sonbati et.al., 1991), depending on the metal salt and the reaction conditions. The cobalt(II) polymer complexes may be classified into two groups. Those with the 1:1 composition are derived from ADB-Co(II) acetate and those with 1:2 stoichiometry are derived from ADB-Co(II) chloride. All these observations suggest the structures as shown in Fig. 37.

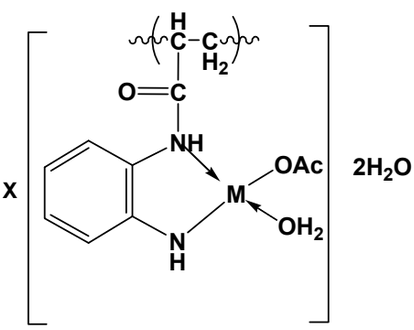




M = Cu(II) X = Cl X′ = X″ = nill
M = Co(II) X = nill X′ = X″ = Cl



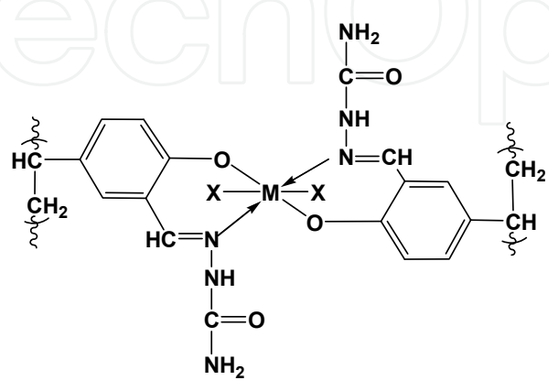




M = UO_2(II); X = X` = H_2O M = Co(II); X = nill M = Cd(II) or Zn(II)
M = Cu(II); X = X` = nill M = Ni(II) ; X = H_2O

Fig. 37.

Polymer complexes of 5-vinylsalicylidene semicarbazone (VSSc) with Cu(II), Co(II), Ni(II), Cd(II), Zn(II) and UO_2(II) acetates were synthesized by mixing stoichiometric quantities (0.02 mol) of the VSSc in 30 ml DMF, the metal salt (0.01 mol) in 20 ml DMF and adding 0.1 w/v % 2,2`-azobisisobutyronitrile (AIBN) as initiator (El-Sonbati, 1991c). VSSc reacts with metal ions and uranyl acetate in a 2:1 molar ratio and a possible structure for the polymer complexes is shown in Fig. 38.



M = Cu(II), Co(II), Ni(II), Cd(II) or Zn(II); X = H_2O, M = UO_2(II); X = nill

Fig. 38.

Polymer complexes of 5-vinylsalicylidene-2-benzothiazoline ($VSBH_2$) with Cu(II), Ni(II), Co(II), Fe(II), Mn(II), Zn(II), Pd(II) and UO_2(II) were prepared and characterized (El-Sonbati & Hefni, 1993). Two IR bands of medium intensity at 1580 and 1530 cm^{-1} can be assigned to the thiazolines ring vibration. Therefore, $PVSBH_2$ homopolymer exists in benzothiazoline form as shown in Fig. 39.

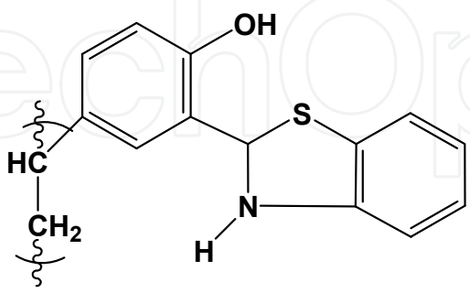
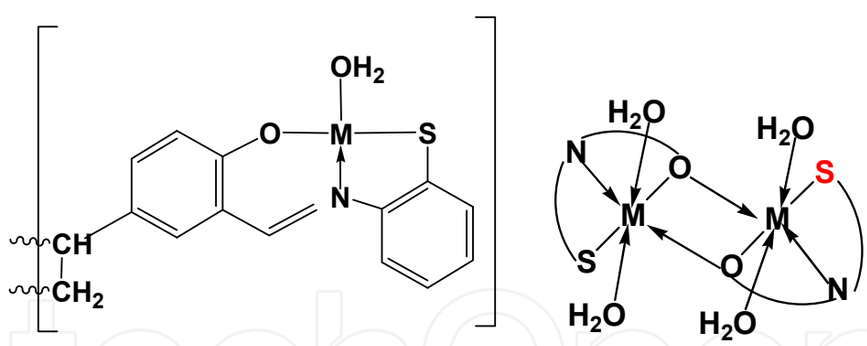


Fig. 39.

The electronic spectral data concluded that the five coordinate polymeric metal complexes of the general formula $[M(VSBH_2\text{-}2H).2H_2O]_n$ (M = Ni(II), Co(II), Mn(II) or Fe(II)) are dimetallic with octahedral geometry, while the remained ones are monomeric and present a square or tetrahedral structure (Fig. 40).

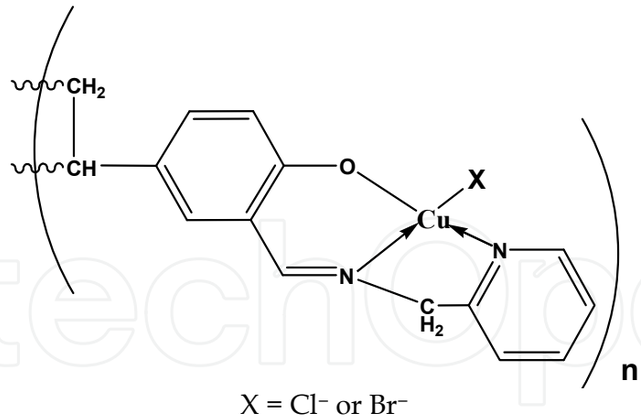


M = Fe(II), Mn(II), Co(II) or Ni(II) M = Cu(II) or Zn(II)

Fig. 40.

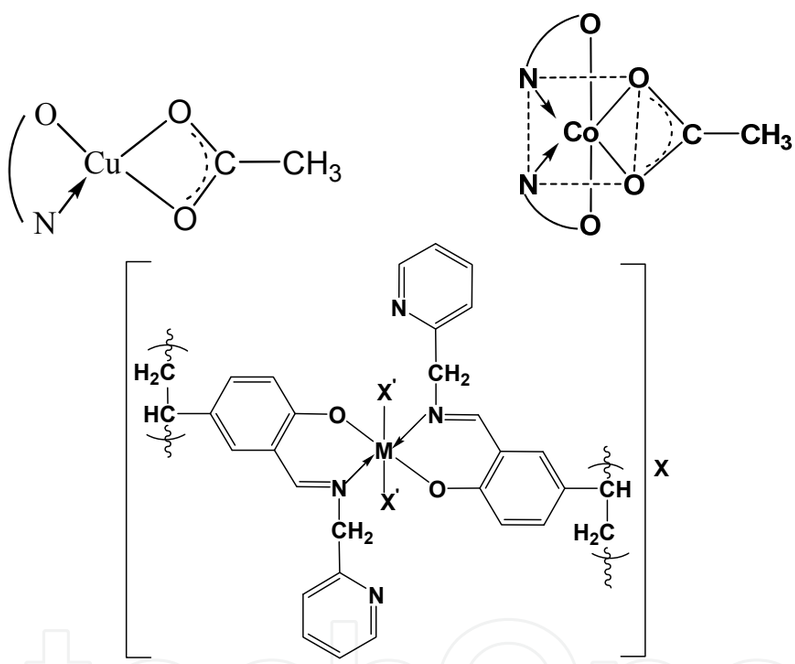
Polymer complexes derived from 5-vinylsalicylidene-2-aminomethylpyridine (VSAPH) with some transition metal salts were prepared and characterized (El-Bindary et al., 1993). All the IR and analytical data are commensurate with the structure shown in Fig. 41.

VSAPH may also act as a bidentate ligand, coordinating to the metal ion *via* the azomethine nitrogen and phenolic oxygen atoms. Loss in a proton from the latter group would allow formation of a six-membered chelate ring. The uranyl polymer complexes can be formulated as $[UO_2(VSAP)_2]$ and $[UO_2(VSAPH)(OAc)_2]$, indicating a probable coordination number of 6 for the uranium(VI) ion. The following structures are suggested (Fig. 42) for the polymer complexes:

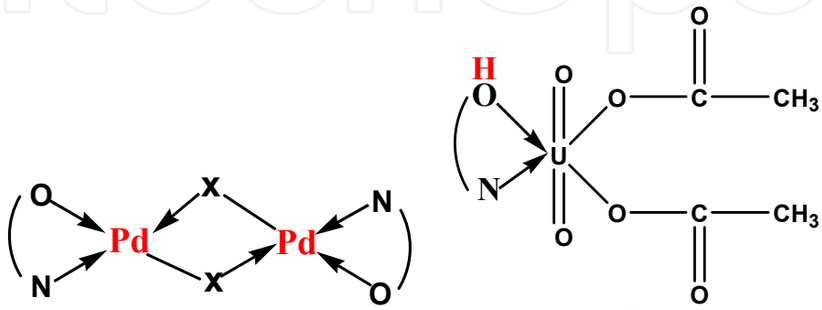


X = Cl^- or Br^-

Fig. 41.



M = Co(II); X = Cl^- or Br^-; X′ = H_2O; M = Ni(II); X = nil; X′ = H_2O; M =Cd(II), Hg(II), UO_2(II); X = X′ = nill



X = Cl^- or Br-

Fig. 42.

Poly (cinnamaldehyde)-2-anthranilic acid (PCA) homopolymer and polymer complexes of cinnamaldehyde-2-anthranilic acid with Cu(II), Ni(II), Co(II), Zn(II), Cd(II) and Hg(II) has been synthesized and characterized (Fig. 43) (El- Sonbati et al., 1993a).

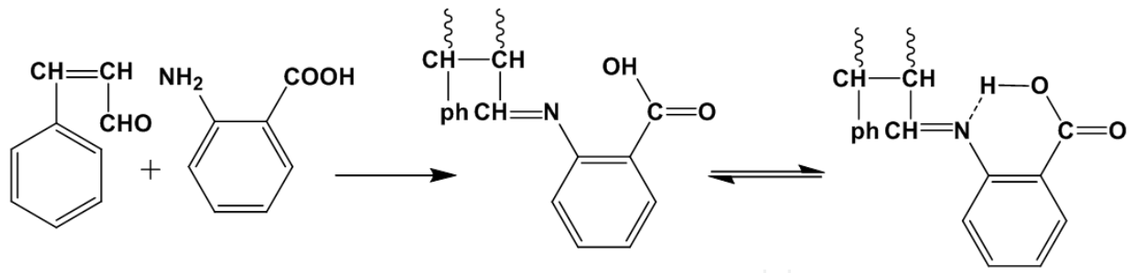


Fig. 43.

The analysis of the chelates show their formulae to be [M (PCA)- $H)_2$.2X], where M = Cu (II), Co(II); and M = Zn(II), Hg(II) and Cd(II) at X = nill, [M(PCA)-H]OAc.2X and [Ni(PCA)-H]XY] where M = Cu(II), Co(II), Ni(II) and X = H_2O, Y = Cl or Br. Their solubility varies in different common organic solvents. The 1:1 and 1:2 stoichiometries of the polymer complexes have been deduced from their elemental analyses. The presence of coordinated water was confirmed by TG data when a loss in weight corresponding to one water molecule was found for Ni(II) and two water molecules for Cu(II), Co(II) and Ni(II). No coordination water molecules were found in the case of Zn(II), Hg(II) and Cd(II) polymer complexes.

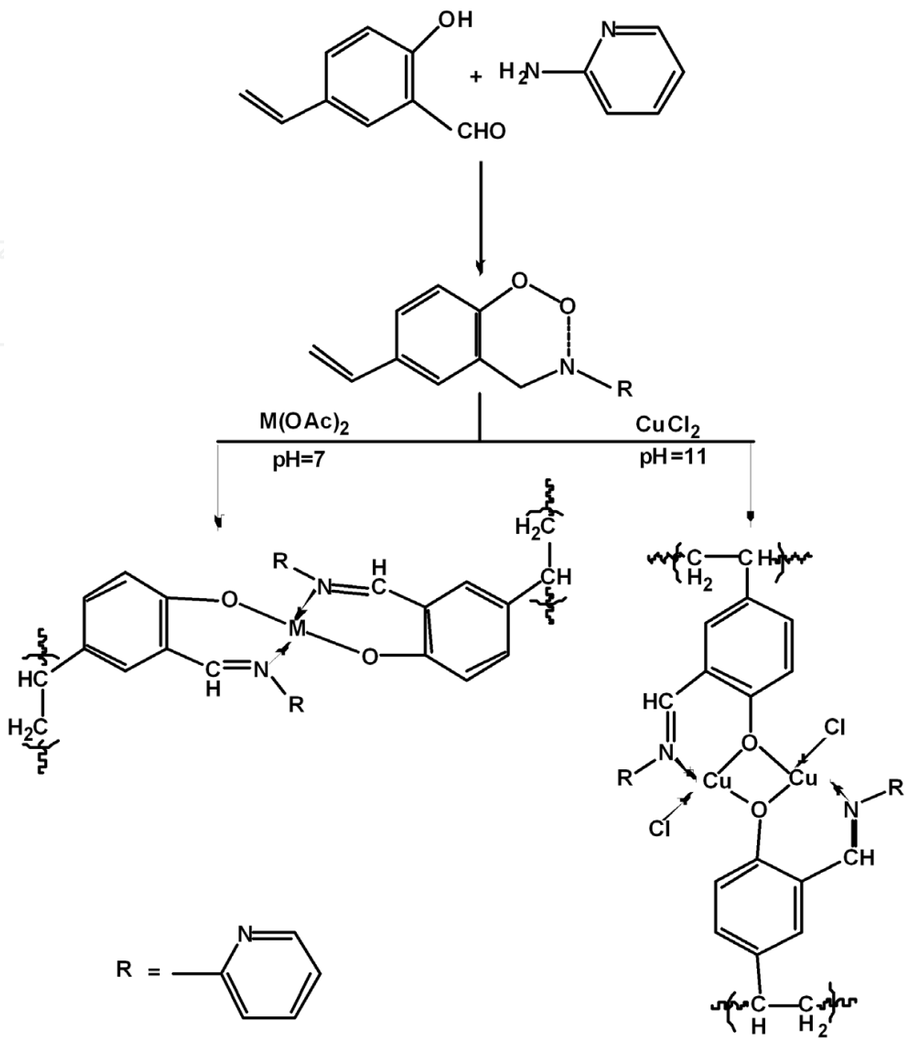
Polymer complexes of N,N`-*o*-phenylenediamine bis(cinnamaldehyde) (L) with Cu(II), Co(II), Ni^{II}, Zn^{II},UO_2^{II} and Pd^{II} were prepared and characterized (El-Sonbati et al., 1993b). A bidentate methine nitrogen atoms coordination of the ligand is assigned in the isolated complexes. The μ_{eff} values of cobalt(II) and nickel(II) polymer complexes are normal and indicate an octahedral stereochemistry around the metal ion, the moments for the cobalt and nickel complexes are in a range expected for six-coordination metal ions, with much orbital contribution. The electronic spectra are summarized in Table 1, together with the proposed assignments, ligand field parameters, magnetic susceptibilities and suggested geometries.

Mononuclear and binuclear complexes of poly(5-vinylsalicylidene-2-aminopyridine) (PVSA) were prepared by the reaction of the homopolymer with copper(II), cobalt(II), nickel(II), dioxouranium(VI) and palladium(II) salts (El-Sonbati et al., 1994a). Metal(II) acetates and palladium chloride were found to give mononuclear complexes, while cupric chloride gave a binuclear complex. The stereochemistry and the nature of the polymer complexes are markedly dependent upon the molar ratios of the reactants, the pH of the system and the nature of the anions involved. In all of the complexes the homopolymer was chelated to the metal ion through the nitrogen atom of the azomethine group and the oxygen atom of the phenolic group. The stoichiometric of the complexes indicate that the copper(II) complexes fall into two distinct categories. The reaction of metal acetate with the VSP monomer gives compounds with formulae which correspond to $[M(VSP\text{-}H)_2]_n$ while the reaction of $CuCl_2$ with VSP in the presence of an excess of ammonium hydroxide gives a compound with the formula $[Cu_2(VSP\text{-}H)_2Cl_2]_n$. The mononuclear and binuclear polymer complexes may be represented as shown in Fig. 44.

No	Species	Band position (cm^{-1})	Assignment	μ_{eff} (B.M)	Geometry
1	$[Co\ L_2Cl_2]\ 2X$	8300 17350 19000 23450	$^4T_{1g} \rightarrow {}^4T_{2g}(F)\ \upsilon_1$ $^4T_{1g} \rightarrow {}^4A_{2g}(F)\ \upsilon_2$ $^4T_{1g} \rightarrow {}^4T_{1g}(P)\ \upsilon_3$	4.31	Octahedral
2	$[Co\ L_2Br_2]\ X$	8050 16600 18700 23500	$^4T_{1g} \rightarrow {}^4T_{2g}(F)\ \upsilon_1$ $^4T_{1g} \rightarrow {}^4A_{2g}(F)\ \upsilon_2$ $^4T_{1g} \rightarrow {}^4T_{1g}(P)\ \upsilon_3$	4.05	Octahedral
3	$[Ni\ L_2Cl_2]$	10206 15272 22222	$^3A_{1g} \rightarrow {}^3T_{2g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(P)$	3.37	Octahedral
4	$[Ni\ L_2\ Br_2]\ X$	10000 15625 24800	$^3A_{1g} \rightarrow {}^3T_{2g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(F)$ $^3A_{2g} \rightarrow {}^3T_{1g}(P)$	3.21	Octahedral
5 6	$[Cu\ L_2Cl_2]$ $[CuL_2\ Br_2]\ X$	13900 – 16900 22200 - 24200	$^2E_g \rightarrow {}^2T_{2g}$ $^1A_g \rightarrow {}^1B_{1g}$	1.93 1.89	Octahedral
7 8 9	$[Pd\ LCl_2]$ $[Pd\ L_2]\ Cl_2$ $[Pd\ L]\ [PdCl_4]$	22200 – 24200 29000 - 31000	$^2E_g \rightarrow {}^2T_{2g}$ $^2A_g \rightarrow {}^1B_{1g}$	dia.	Square planner
11	$[UO_2\ L_2(NO_3)_2]$	21730	$E \rightarrow {}^2\Pi_4$	dia.	Octahedral

Polymer complexes (1-9) X = Cl or Br.

Table 1. Electronic spectral bands, assignments, ligand field parameters and proposed geometries for the polymer complexes.



M = Cu(II), Fe(II), Co(II), Ni(II), Pd(II), Cd(II) and Zn (II)

Fig. 44.

Poly(5-vinylsalicylidene)-1,2-diaminobenzene (PVSB) homopolymer behaves as a monobasic tridentate chelating ligand and mixed ligand of PVSB and pyridine as a bidentate species. Polymer complexes of these ligands with Cu(II), Fe(II), Co(II), Ni(II), Pd(II), Cd(II) and Zn(II) were prepared and characterized (El-Sonbati & Hefni, 1994). In PVSB homopolymer, the principal IR bands of interest are two strong bands at 3365 and 3175 cm^{-1} attributed to the symmetric and asymmetric NH_2 stretching vibrations (Fig. 45). The frequencies of these bands are observed at a considerably lower wavenumber in the polymer complexes of the nitrogen atom of the amino group with metal ions. The absence of large systematic shifts of $\upsilon_{as}(NH_2)$, $\upsilon_s(NH_2)$ and $\delta(NH_2)$ bands in the spectra of mixed ligand polymer complexes, i.e. 2:1 species, implies that there is no interaction between the amino group nitrogen atom and the metal ions.

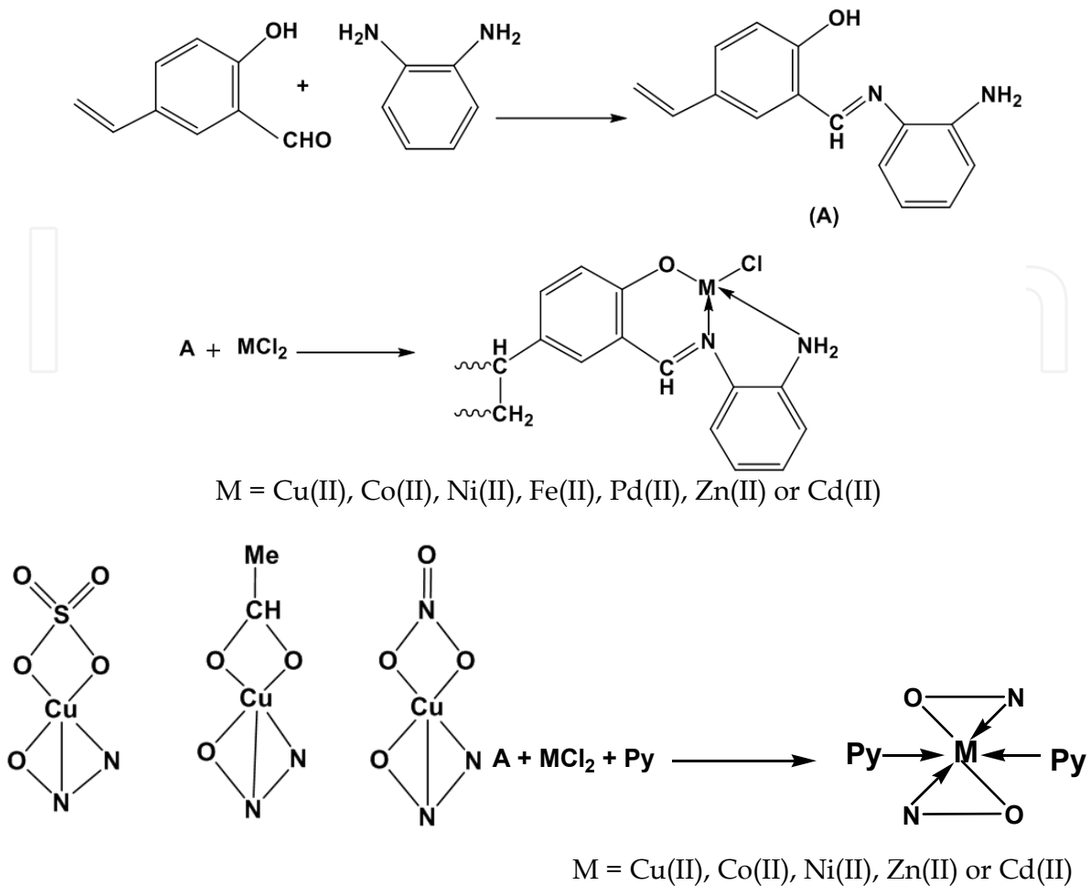


Fig. 45.

Polymer complexes of 2-acrylamido-1-phenyl-2-aminothiourea (APATH) with Rh(II) and Ru(II) ions in the presence and absence of N-heterocyclic bases as mixed ligand have been prepared and characterized through chemical analyses, thermal, electronic and infrared spectral studies (El-Sonbati et al., 1994b). The homopolymer shows three types of coordination behavior. In the mixed valence paramagnetic trinuclear polymer complexes $Rh_3(APATH)_2Cl_8$ (**1**) and $Ru_3(APATH)_2Cl_8$ (**2**), and in the mononuclear polymer compound $Ru(APATH)_2Cl_3$ (**3**) it acts as a neutral bidentate ligand coordinating through the thiocarbonyl sulphur and carbonyl oxygen atoms. In the mixed ligand paramagnetic polychelates, which are obtained from the reaction of APATH with $RuCl_3$. XH_2O in the presence of N-heterocyclic bases [B = H_2O, pyridine (Py)/or *o*-phenylendiamine (*o*-phen), DMF] consisting of polymer complexes $[Ru(APAT)_2(H_2O)Py]XCl$ (**7**) and $Ru(APAT)Cl_2$(*o*-phen.) H_2O (**8**) and in mononuclear compounds $Ru(APAT)_2Cl.DMF$ (**6**) and $Ru(APAT)_2Cl(H_2O)_2$ (**8**), it behaves as a monobasic bidentate ligand coordinating through the same donor atoms. In mononuclear compounds $[Ru(APAT)(APATH)Cl]2H_2O$ (**4**) and $[Ru(APAT)\ (APATH)Cl_2]2H_2O$ (**5**) it acts as a monobasic and neutral bidentate ligand coordinating only through the same donor atoms. Monometric distorted octahedral or trimeric chlorine-bridged, approximately octahedral structures are proposed for these polymer complexes. The polychelates are of 1:1, 1:2 and 3:2 (metal: poly-Schiff base) stoichiometry and exhibit five and six coordination (Fig. 46).

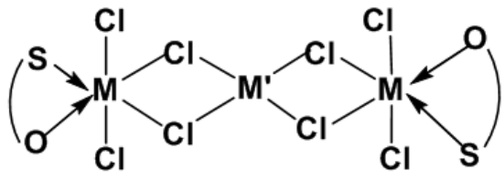


Fig. 46.

In the other hand, mononuclear and hetero bi-trinuclear polymer complexes of nickel(II), copper (II) and oxovanadium(VI) chloride with APATH monomer derived from amidation of acryloyl chloride with 2-amino-1-phenylthiourea have been prepared (El-Sonbati el al., 1995a). The elemental analyses show that these homonuclear polymer complexes have 2:1 and in bimetallic polymer complexes 2:1:1 (homopolymer: metal: metal), stoichiometry. These indicate that they fall into two distinct categories. The first is mononuclear, while the second is heterobinuclear. The following structures shown in Fig. 47 are suggested:

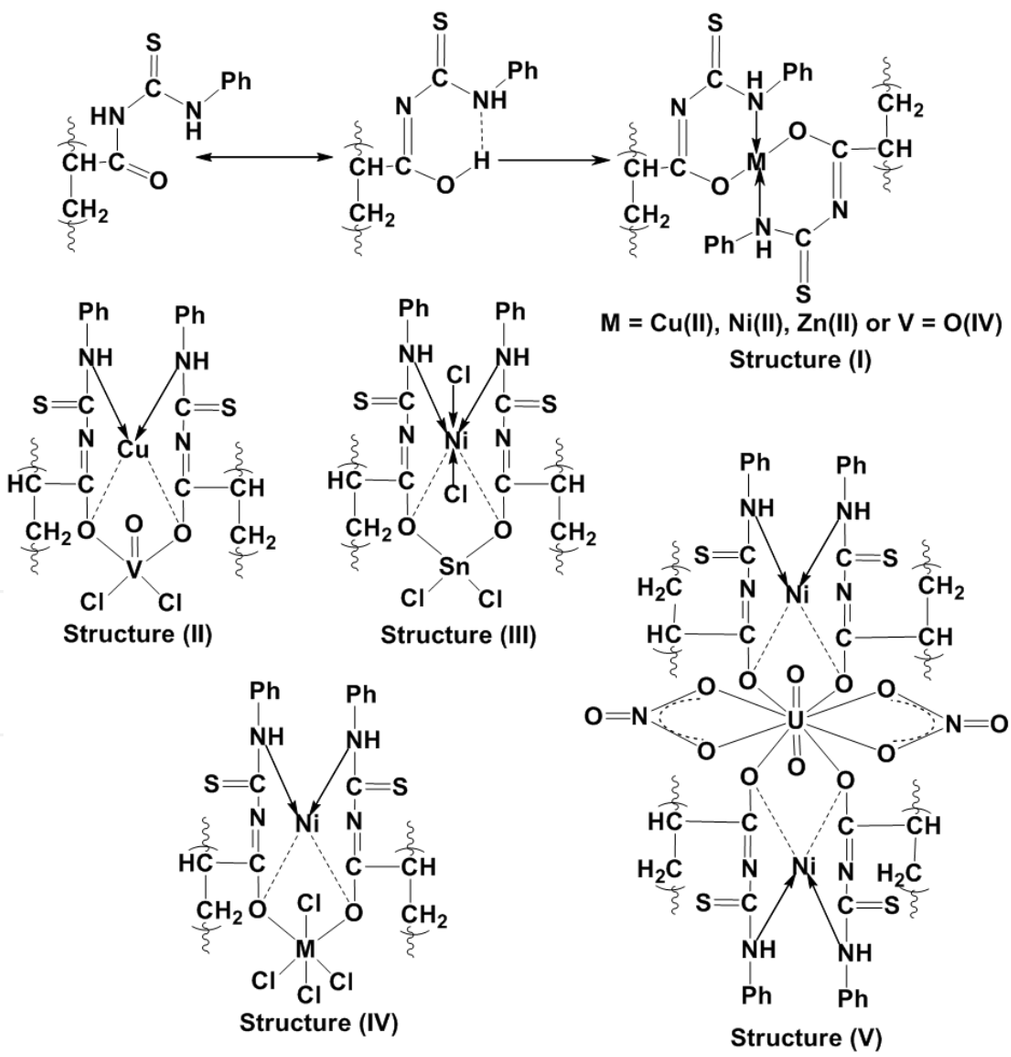


Fig. 47.

Poly[1-acrylamido-2(2-pyridyl)ethane)] (PAEPH) homopolymer and polymer complexes of 1-acrylamido-2(2-pyridyl) ethane AEPH with a number of bi and tetravalent transition metals have been prepared and characterized using spectral (^{1}H and ^{13}C-NMR, IR, UV-Vis) and thermal analysis, and magnetic measurements (El-Sonbati et al., 1995b). The stoiciometries of the polymer complexes have been deduced from their elemental analyses. These indicate that the metal-polymer complexes fall into two distinct categories, namely 1:1 and 1:2 (ligand: metal). PAEPH is mononucleating and hence requires one metal ion for coordination. The formation of the polymer complexes may be represented by the following reactions:

$$MX_2 + 2\ AEPH \longrightarrow [M\ (AEP)_2] + 2HX\ (M = Pd, Pt \text{ or } UO_2,\ X = Cl \text{ or } CH_3COO)$$

$$ZrCl_2 + AEPH \xrightarrow{1:1\ (6h \text{ or } 9h)} [Zr\ (AEP)\ Cl_3]_n\ \mathbf{A} \text{ or } \mathbf{C}$$

$$ZrCl_2 + AEPH \xrightarrow{1:2\ (12h \text{ or } 15h)} [Zr\ (AEP)_2\ Cl_2]_n\ \mathbf{B} \text{ or } \mathbf{D}$$

(Where AEP represents the anion of the corresponding monofunctional bidentate AEPH).

The reactions appear to proceed only up to a 1:2 molar ratio. Even on prolonged refluxing (~ 32 h) of 1:3 or 1:4 reaction mixture, replacement of a third chloride group by the homopolymer was not observed. This is probably due to steric factors. Plausible structures (Fig. 48) are given for the products (**A**, **C**) and (**B**, **D**) obtained from the reaction of 1:1 and 1:2 molar ratios, respectively.

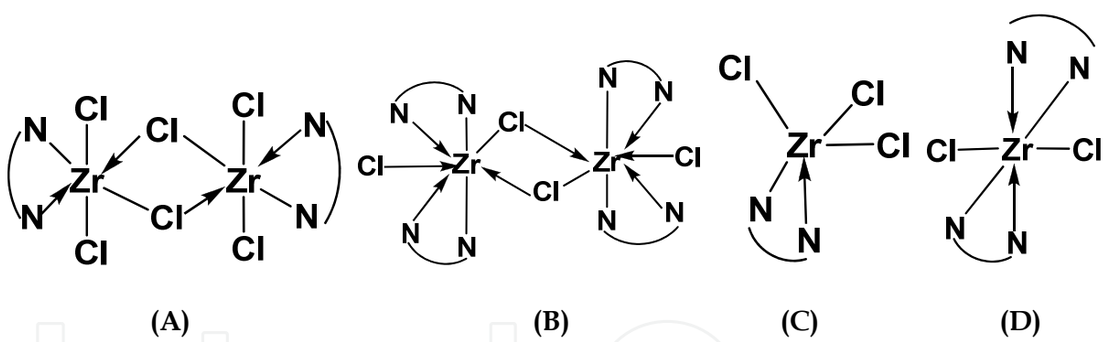
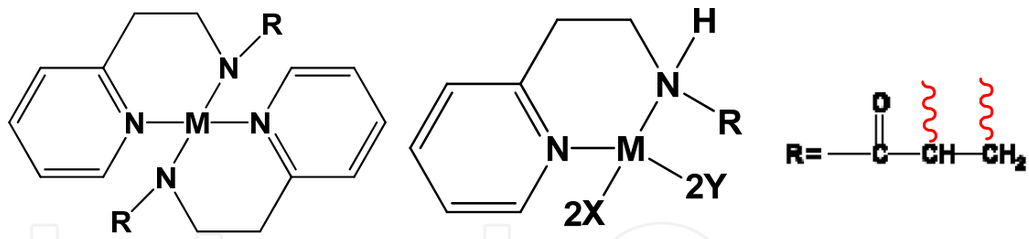


Fig. 48.

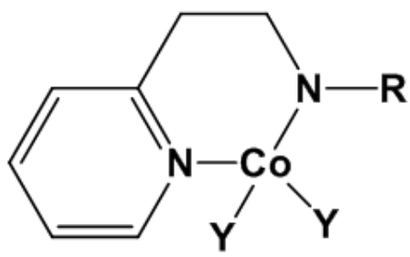
The zirconium atoms appear to be hexa-(**A**, **B**) and hepta-(**B**, **C**) coordinated. In the polymer complexes of zirconyl isopropoxide, zirconium exhibits a coordination number of 5. The $[UO_2(AEP)(AcO)(OH_2)]$ polymer complex spectrum exhibits characteristic bands for the monodentate acetate group at 1620 and 1395 cm^{-1} with $\Delta\upsilon$ = 235 cm^{-1}. The spectrum also exhibits three bands at 907, 790 and 275 cm^{-1} assigned to υ_3, υ_1 and υ_2 of the dioxouranium ion.

Trying to deepen the knowledge of this ligand, a studied polymer complexes of AEPH with copper(II), nickel(II), cobalt(II) and Zn(II) (El-Sonbati & El-Bindary, 1996). From IR and elemental analyses, the possible structures of the products of reaction of AEPH with transition metal ions shown in Fig. 49 are as follows:



M = Cu(II) for $Cu(AEP)_2$
= Ni(II) for $Ni(AEP)_2$
= Zn(II) for $Zn(AEP)_2$

M = Cu(II), Ni(II) or Zn(II);
X = NO_3, Y = OH_2 for
$Cu(AEPH)(NO_3)_2(OH_2)_2$,
$Ni(AEPH)(NO_3)_2(OH_2)_2$ and
$Zn(AEPH)(NO_3)_2(OH_2)_2$;
M = Co(II); X = OAc; Y=OH_2 for $Co(AEPH))OAc)_2(OH_2)_2$
M = Zn(II); X = OAc;Y= nil for $Zn(AEPH)(OAc)_2$
M = Co(II); X = NO_3; Y= OH_2 for $Co(AEPH)(NO_3)_2(OH_2)_2$



Y = OH_2 for $Co(AEP)(OH_2)_2$

Fig. 49.

Some binary and ternary novel polymer complexes dioxouranium(VI) with 5-vinylsalicylaldehyde (VSH) have been prepared and characterized by various physico-chemical techniques (El-Sonbati et al., 2002). Addition of ammonia to an ethanolic solution of uranyl nitrate give uranyl ammine complex which on treatment with VSA result in the formation of the imine complex (**C**). The reaction of the compound **C** with 1,2-diaminoethane and/or 1,2-diaminobenzene yield symmetrical tetradentate Schiff base complex of type (**1C**) as shown in Fig. 50.

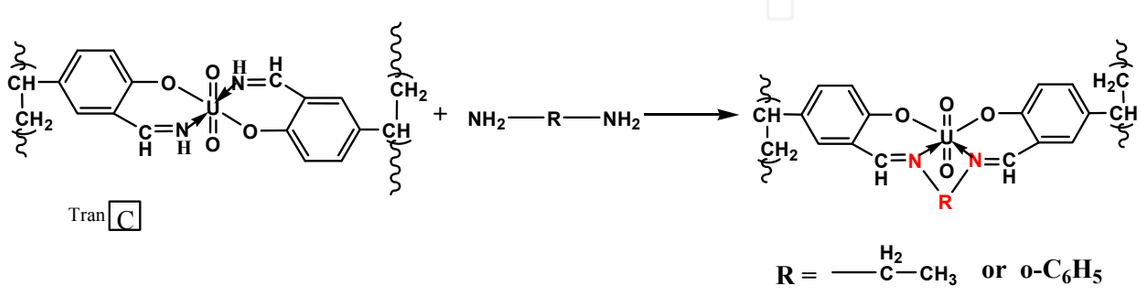


Fig. 50.

Reaction of $ZrCl_4$ with [Cu(VSR)] give heterobinuclear complexes Cu(VSED)$ZrCl_4$. [Cu(VSR)] has an additional lone pair of electron at each of the coordinated phenolic O^- and hence, it acts as a ligand and gets coordinated with $UO_2(CH_3COO)_2.2H_2O$. The Cu(II) band in the binuclear complex shows a shift from its value in mononuclear complex [Cu(VSR)] (Fig. 51). This lowering in the ligand field band of [Cu(VSR)] may be due to exchanges in the planarity of (VSR) and also to reduction in strength of Cu-O bond on the formation of second bond with metal(II) halides.

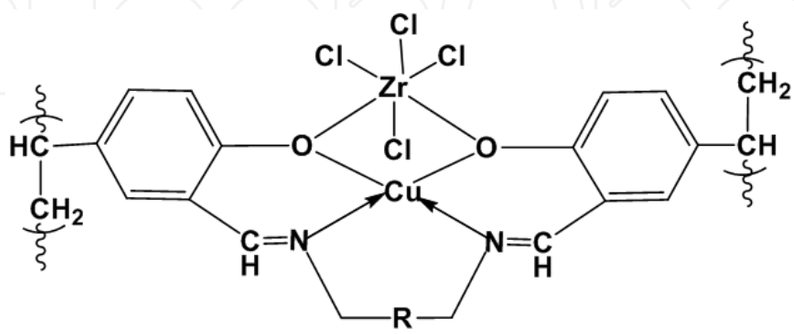


Fig. 51.

Novel seven, nine and ten-coordinated rare earth polymer complexes of N-acryloyl-1-phenyl-2-thiourea (APT) of the composition $[Ln(NO_3)_3(APT)_2]_n$ (Ln = La, Sm, Tb, Pr and Nd) and $[Ln(NCS)_3(APT)_x]_n$ (where Ln = La or Pr at X = 2 and Ln = Nd, Sm and Tb at X = 3) have been prepared and characterized on the basis of their chemical analyses, magnetic measurements, conductance, visible and IR spectral data (Mubarak & El-Sonbati, 2006). The data of elemental analysis indicate that the stoichiometric ratio for the reaction of monomer with various LnX_3 is 1:2 and 1:3 (Ln: monomer). The polymer complexes do not contain any water of coordination are all occupied by donor centers from the ligand groups. Therefore, the reaction between LnX_3 and ligand can be represented as follows:

$$LnX_3 + nAPT \rightarrow [Ln(NO_3)_3(APT)_2]_n$$

$$\rightarrow [Ln(NCS)_3(APT)_2]_n$$

$$\rightarrow [Ln(NCS)_3(APT)_3]_n$$

These data suggest that three nitrato and isothiocyanato ions are within the coordination sphere.

The build-up of polymer metallic supramolecules based on homopolymer 1-acrylamido-2-(2-pyridyl)ethane (AEPH) and ruthenium, rhodium, palladium as well as platinum complexes has been pursued with great interest (El-Sonbati et al., 2003a). AEPH is found to be a polyfunctional planar molecule with a delocalized π electronic system, with two nitrogen atoms which may act as basic centers and two labile N-H bands. The molecule may present in several tautomers and conformers. The equivalent conformers are the principle contributors to the molecular structure of this molecular in solution; they are in equilibrium and established by intramolecular hydrogen bonds. In the solid state reveals widely used intramolecular hydrogen bonding, which gives rise to six-membered ring (Fig. 52).

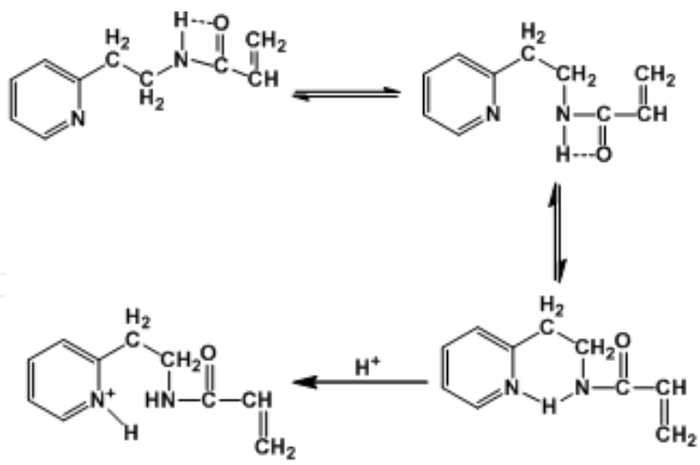
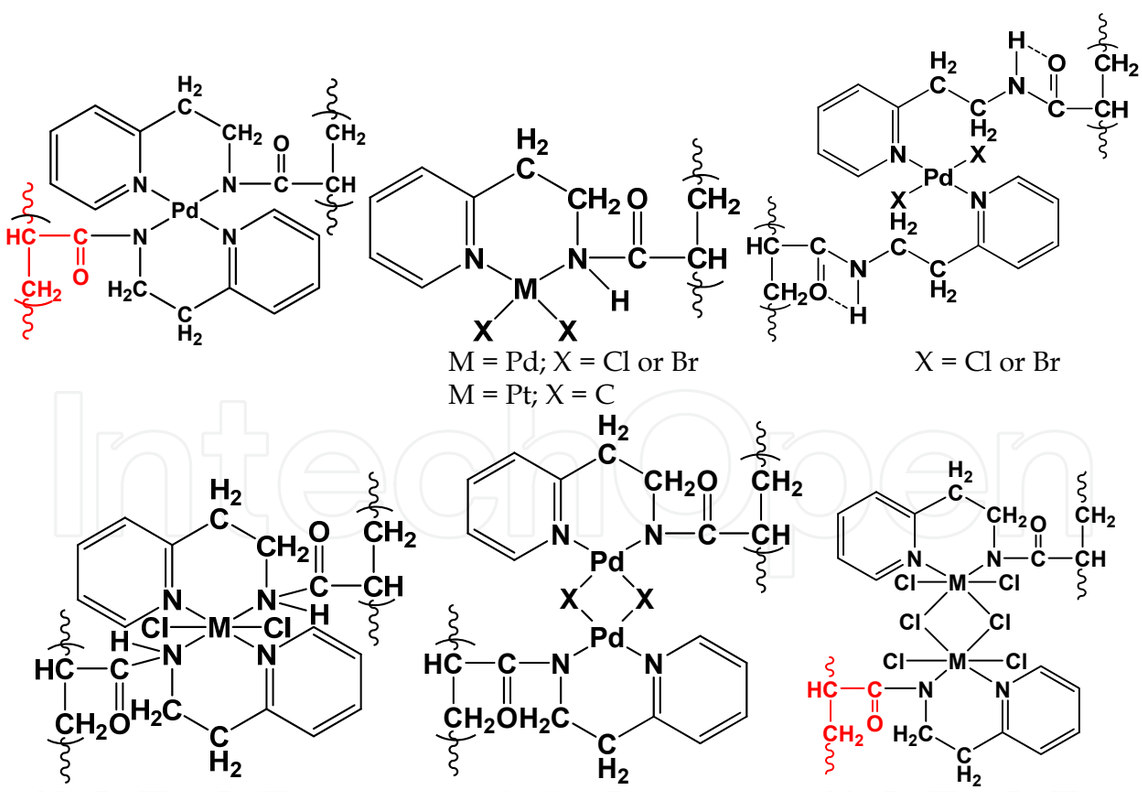


Fig. 52.

From the stoichiometries of all complexes, it is clear that the AEPH ligand function as bidentate N-N donors. Construction of molecular models suggest that the formation of a stable six-membered ring system with the central metal ions having N-N donor function taking one of the N-pyridyl ring and the N-imino (NH) of the monomer residue as bonding sites is the most probable proposition as shown in Fig. 53.

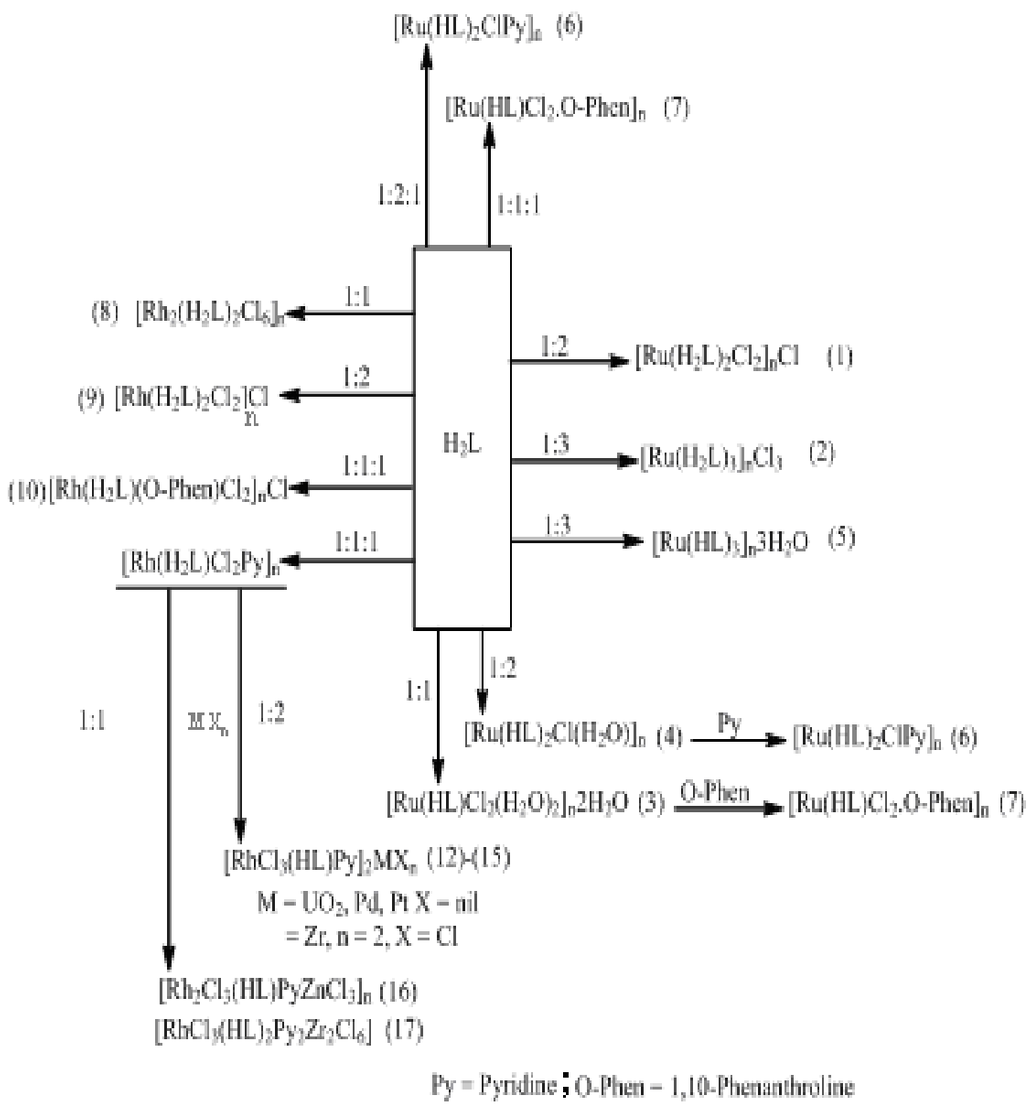


Coordination compounds of PAEPH with transition metal ions

Fig. 53.

Monomeric distorted octahedral or trimeric chlorine-bridged, approximately octahedral structures are proposed for these polymer complexes.

Mono, bis and tris-polymer complexes of ruthenium(III) and rhodium(III) chloride with 3-hydroxy-2-N-acrylamidopyridine (H_2L) monomer, derived from amidation of acryloyl chloride with 2-amino-3-hydroxypyridine have been proposed (El-Bindary et al., 2003). A few bimetallic mixed ligand polymer complexes have also been obtained by the reaction of rhodium(II) bidentate poly-chelate mixed ligand with palladium(II), platinum(II) or zirconium(IV) chlorides and uranyl acetate. The homopolymer shows three types of coordination behavior. The poly-chelates are of 1:1, 1:2 and 1:3 (metal:homopolymer) stoichiometry and exhibit six coordination.



From the spectroscopic investigation of the rhodium complexes, it was concluded that the rhodium atom in each complex exists in an octahedral environments (Fig. 54).

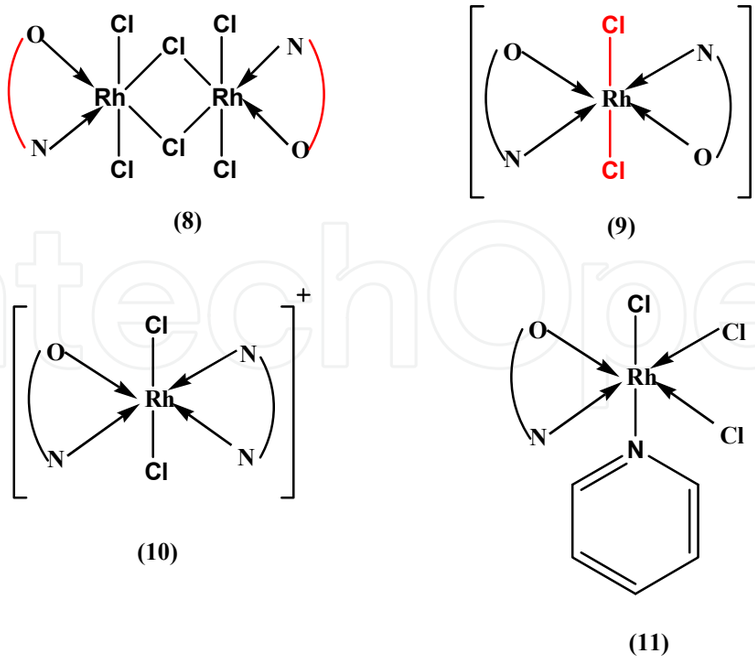


Fig. 54.

Plausible structures are given for the structures obtained from the reaction of 1:1 and 1:2 molar ratios (Fig. 55).

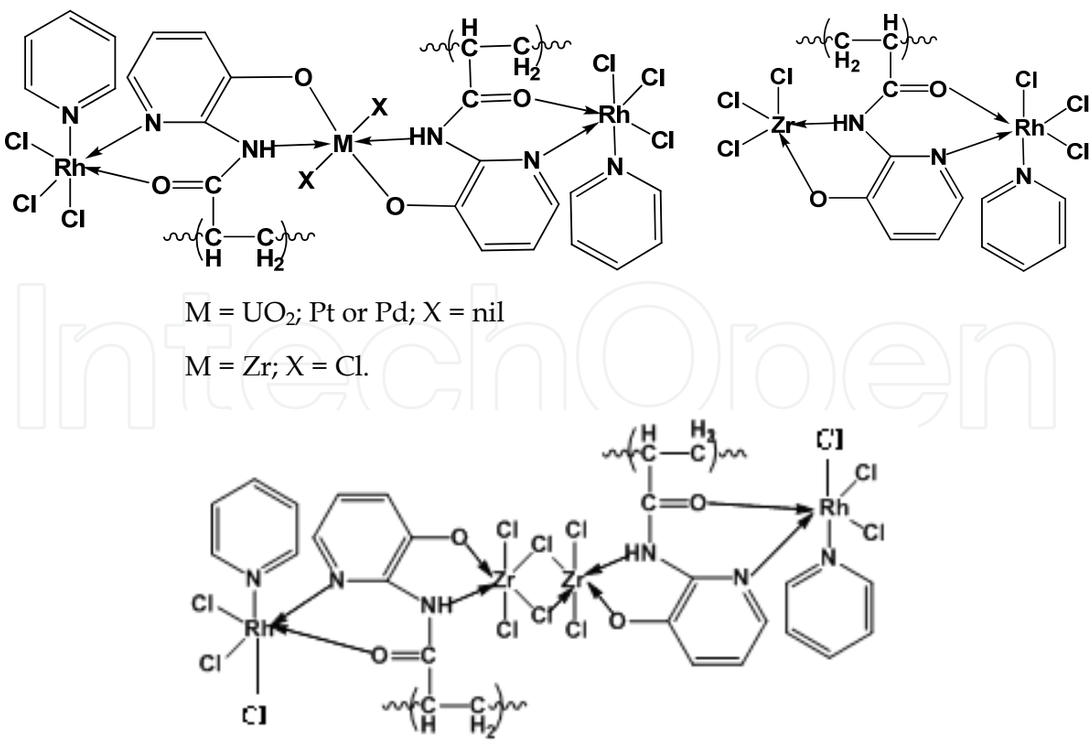
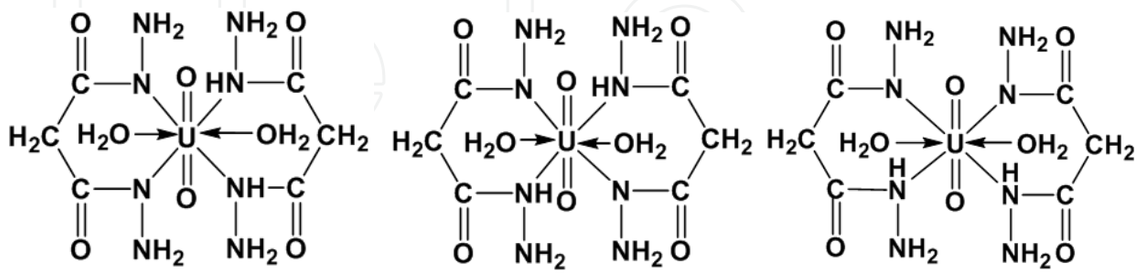


Fig. 55.

Two novel supramolecular complexes of types $UO_2(L)(H_2L)(OH_2)_2$ and $UO_2(HL_n)_2(OAc)_2$ (H_2L is a potential four-dentate ligand derived from hydrazine hydrate and malonylchloride and HLn is a potential bidentate ligand derived from coupling of allylazo-β-diketone have been synthesized and characterized by elemental analyses, conductance and spectral measurements (El-Sonbati et al., 2004a). Alcoholic solutions of uranyl acetate and malonic dihydrazide were refluxed for 8-9 h forms uranyldihydrazide complex as shown in Fig. 56.



(A) (B) (C)

Fig. 56.

To the uranyl complex, an allyl-β-diketone was added using AIBN as initiator; the polymer complexes (Fig. 57) were characterized by IR spectroscopy:

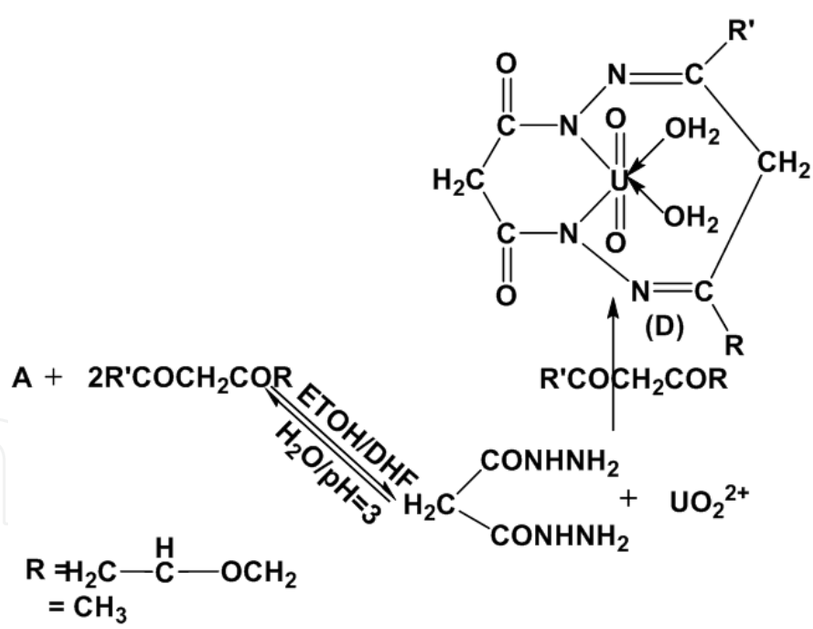
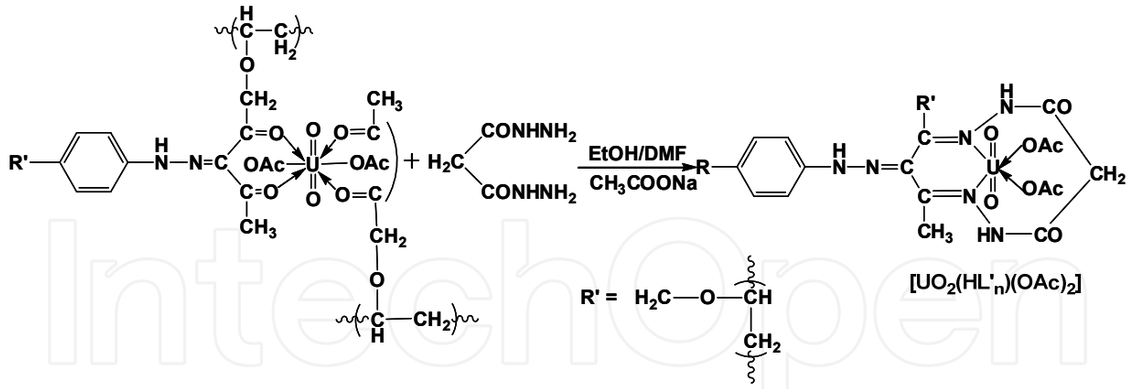


Fig. 57.

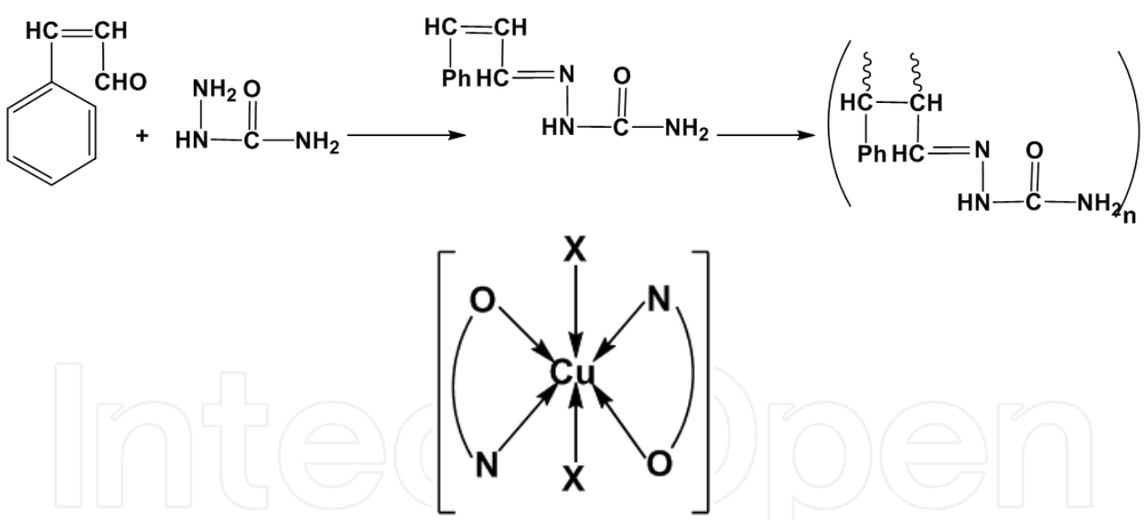
Polymer complexes of $[UO_2(HL_n)(OAc)_2]$ were prepared by refluxing a 0.5 M solution of the metal salt with the monomer using AIBN as initiator. The products of condensation reaction of allyl propenyl-2-(4-derivatives phenylazo) butan-3-one polymer complexes with malonyldihydrazide in ethanol/DMF in the presence of sodium acetate results in macrocyclic uranyl polymer complexes (Fig. 58).



n =1(R = OCH_3), n =2(R=CH_3), n=3(R=H), n=4(R=Br), n=5(R=NO_2)

Fig. 58.

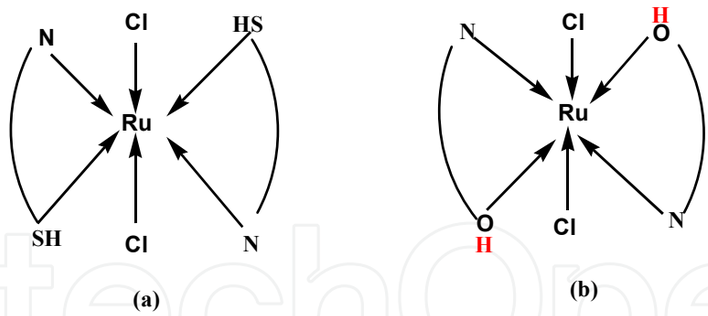
Copper(II) polymer complexes of emprical formula [Cu(ligands)$_2$X$_2$] (Fig. 59) (where X=Cl, Br, I, NO_3 and 1/2 SO_4) and [Cu(ligand)(CH_3COO)$_2$] have been prepared with poly(3-phenylacrylidine semicarbazone) (El-Sonbati et al., 2003b). It is propose that the uncomplexed polymer behaves as a bidentate coordinated ligand through the oxygen of the carbonyl and the nitrogen of azomethine.



X = Cl, Br, I, NO_3

Fig. 59. Molecular structures proposed for poly(3-phenyl-acrylidine semicarbazone) and [Cu(ligand)$_2$X$_2$] complexes.

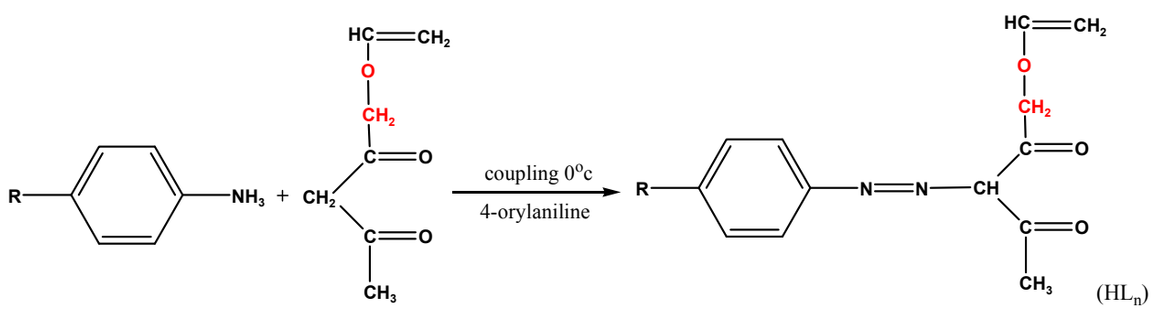
Poplymer complexes of N-(3-phenylacrylidene)-2-mercaptoaniline (HL_1) and cinnamaldehyde-2-aminophenol (HL_2) with Cu(II), Pd(II), Pt(II), UO_2(II), Rh(II), Ru(III), and Pd(IV) have been synthesized and characterized (Fig. 60) (El-Sonbati et al., 2003b). The electronic spectra of the derivatives of types [Ru(HL_n)Cl_3], have four bands in good agreement with the one-electron orbital schemes for trigonal bipyramidal d^5 complexes.



Molecular structures of (a) [Ru $(HL_1)_2Cl_2$] Cl, (b) [Ru $(HL_2)_2Cl_2$] Cl

Fig. 60.

Synthesis and characterization of ally propenyl-2-(4-derivatives phenylazo)butan-3-one (HL_n) are described as shown in Fig. 61 (Mubarak et al., 2006).



n = 1 R = OCH_3 (HL_1); n = 2 R = CH_3 (HL_2); n = 3 R = H (HL_3); n = 4 R = Br (HL_4); n = 5 R = NO_2 (HL_5)

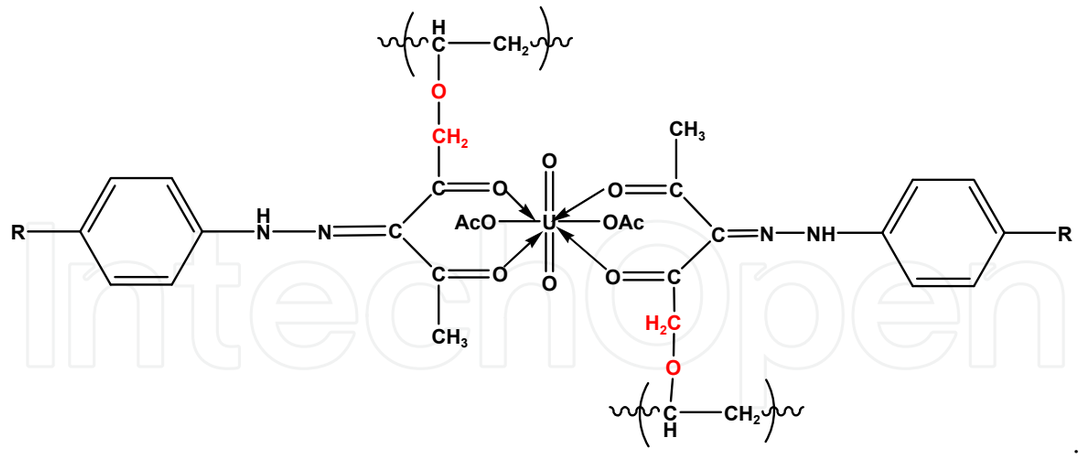
Fig. 61.

The polymer complexes were prepared by mixing the appropriate uranyl acetate with two equivalents of HL_n/H_2L in DMF according to the following reaction scheme.

$$UO_2(CH_3COO)_2.2H_2O + HL_n \xrightarrow{\textbf{DMF}} [UO_2(HL_n)_2(OAc)_2]\ (n = 1\text{-}5) \quad (1)$$

$$UO_2(CH_3COO)_2.2H_2O + H_2L \xrightarrow{\textbf{DMF}} [UO_2(HL)_2(H_2O)_2] + 2CH_3COOH \quad (2)$$

The magnetic measurements of the dioxouranium(VI) polymer complexes are independent from field strength and temperature and the ground states of dioxouranium(VI) compounds contain no unpaired electrons. Allyl propenyl-2-(4-derivatives phenylazo) butan-3-one (HL_n) is a ligand whose reactivity towards metal ions varies as a function of the 4-substituents. The products, which are usually neutral, have two coplanar O,O metal-chelate rings in an O,O(O,O) trans geometry. Consequently, in the UO_2^{2+} case, the uranyl atom should be a six-coordinate octahedral with the oxygen atom in the apical position (Fig. 62).



(n=1, R=OCH_3 (HL_1); n=2, R=CH_3 (HL_2); n=3, R=H (HL_3), n=4,R= Br (HL_4), and n=5, R=NO_2(HL_5)

Fig. 62. Molecular structure proposed for the VO $(L_n)_2$ complexes.

Novel supramolecular rare earth polymeric hydrazone complexes of 5-sulphadiazineazo-3-phenyl-2-thioxo-4-thiazolidinone (HL) of the composition $[(Ln)_2(HL)_3(NO_3)_6]_n$ where Ln = La(**1**), Y(**2**), Pr(**3**), Nd(**4**), Sm(**5**), Gd(**6**) and Ho(**7**) have been prepared and characterized on the basis of their chemical analyses, magnetic measurements, conductance, visible and IR spectral data (El-Sonbati et al., 2009). The IR spectrum of the ligand leads to assume the structure shown in Fig. 63.

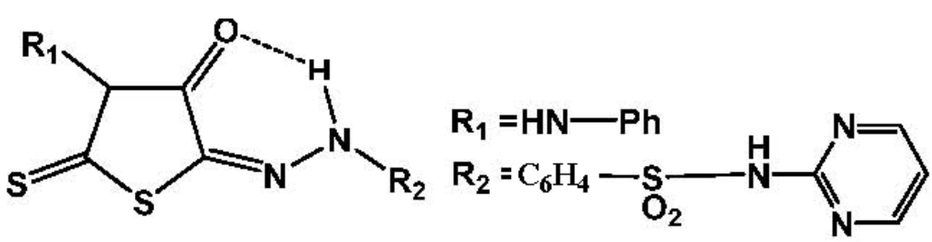
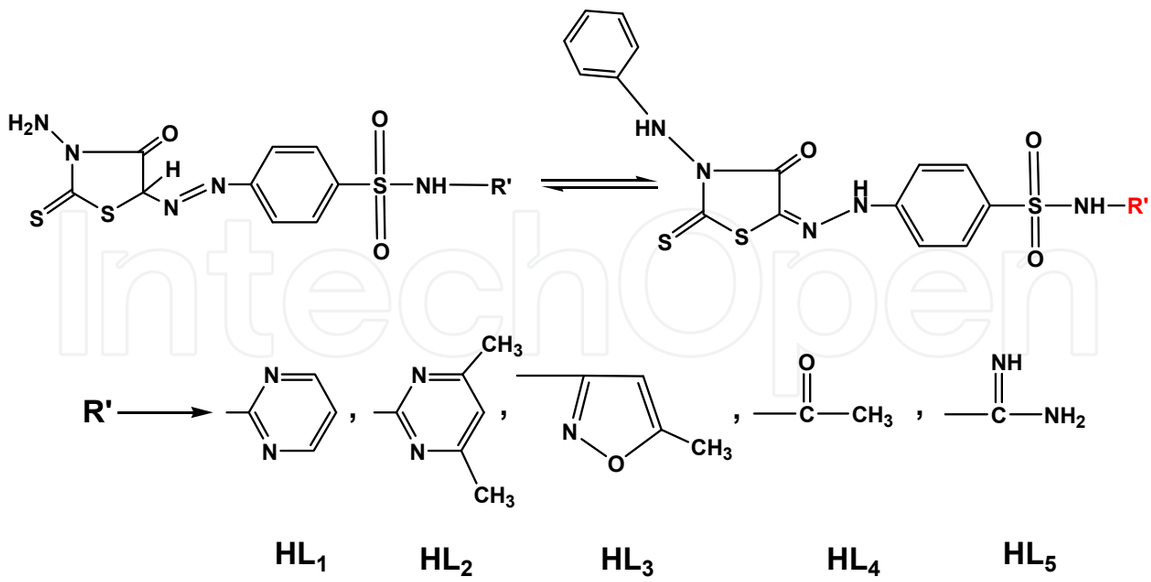


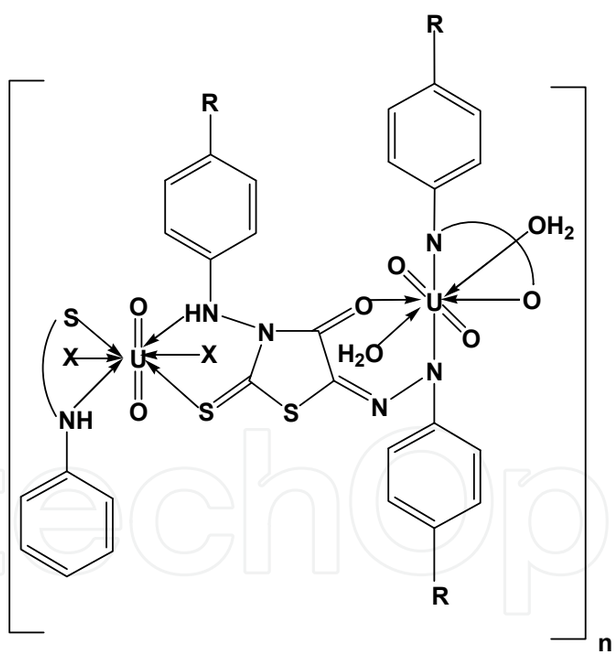
Fig. 63.

The spectral data show that all these act as tetradentate ligand. Electronic spectra indicate weak covalent character in the metal-ligand bond.

Polymer complexes of hydrazone sulphadrugs (HL_n) extended to novel five binuclear polymeric dioxouranium(VI) of azosulphadrugs (Fig. 64) (El-Sonbati et al., 2010a). The binding modes of the azosulphadrugs ligands towards uranyl(II) ions were critically assigned and addressed properly on the basis of their IR and their uranyl(II) complexes. 5-Sulphadiazinazo-3-phenyl-2-thioxo-4-thiozolidinone(HL_1) and 5-sulphamethineazo-3-phenyl-2-thioxo-4-thiozolidinone (HL_2) act as a tetradentate dibasic ligand, binding to the metal ion through nitrogen atom of diimide (N=N) group, nitrogen of azomethine pyridine atom (sulphadrugs moiety) and enolic OH group (sulphonyl oxygen) and through deprotonated hydrogen atom of phenolic oxygen atom (rhodanine). The sulphonamidic NH does not participate in bonding due to structure complication.



$$HL_n + UO_2(NO_3)_2.2H_2O \rightarrow [(UO_2)_2(HL_n)(L_n)(NO_3)_2(OH_2)_2]_n + 2HNO_3$$



X = NO_3

Fig. 64. Geometrical formula of uranyl polymer complexes

Novel polymeric complexes with 5-sulphadiazineazo-3-phenyl-2-thioxo-4-thiazolidine (HL_1), 5-sulphamethazineazo-3-phenyl-2-thioxo-4- thiazolidine (HL_2) and 5-sulphamethoxazoleazo-3-phenyl-2-thioxo-4-thiazolidine (HL_3) and various anions were prepared (El-Sonbati et al., 2010b) according to the following scheme.

$2CuCl_2 + 3\ HL_n \rightarrow \quad [(Cu)_2(HL_n)_3(Cl)_4]_n$

$2CuSO_4 + 3\ HL_n \rightarrow \quad [(Cu)_2(HL_n)_3(SO_4)_2]_n$ where HL_n = tetradentate hydrazone, n = 1-3

The 2:3 stoichiometries of the polymeric complexes were calculated from their elemental analyses, and molar conductance reveal that three molecules of the ligand and four/two (Cl/SO_4) of the anions are coordinated to the two metal atoms in all complexes. The ligands coordinate to Cu(II) ion as an neutral and tetradentate *via* NH (hydrazone), oxygen of the carbonyl group (CO), nitrogen of the NH (3-phenylamine) and thion sulphur (CS) group.

A novel series of nickel(II) polymer complexes of 5-sulphadiazinazo-3-phenylamino-2-thio-4-thiozolidinone (HL_1), 5-sulphamethazine-3-phenylamino-2-thioxo-4-thiazolidinone (HL_2), 5-sulphamethoxazole-3-phenylamino-2-thioxo-4-thiazolidinone (HL_3), 5-sulpacetamide-3-phenyl-2-thioxo-4-thiozalidinone (HL_4) and 5-sulphaguanidine-3-phenylamino-2-thioxo-4-thiazolidinone (HL_5) were prepared and characterized (El-Sonbati et al., 2010c), IR spectra show that HL_n (n = 1-5) is coordinated to the metal ion in a neutral tetradentate manner with NSNO donor sites of NH (hydrazone`s), NH(3-phenylamine), carbonyl group and Ph-NH. The metal-to-ligand ratio of the nickel(II) polymer complexes was found to be 3:2, but all the Ni(II) polymer complexes have two additional bridged coordinated acetate molecules. So the Ni(II) ions appear to be five and hexa-coordinated acetate, and the geometry is octahedral for Ni(II) ion. The title $[Ni_3(HL_n)_2(\mu\text{-}OAc)_2(OAc)_4]_n$ consists of three Ni(II) atoms linked by interchain π-π interaction observed between aromatic rings of two (HL_n) which are further doubly bridged to two adjacent nickel atoms by acetate group. The geometrical structures of these complexes are found to be octahedral. The richness of electronic spectral in these is supporting evidence for the trinuclearity of the Ni(II) polymer complexes (Fig. 65).

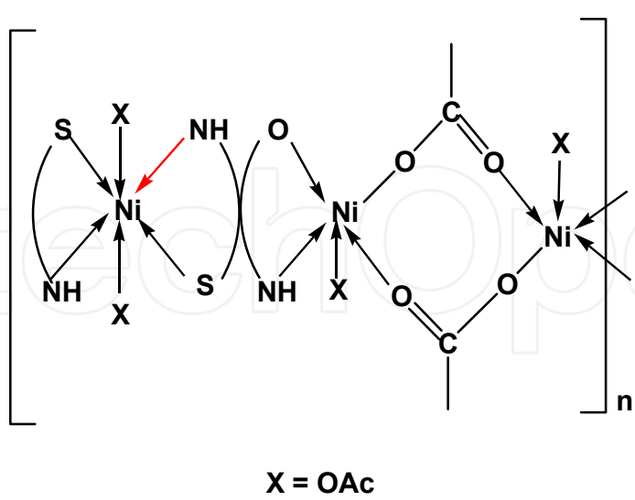


Fig. 65.

Polymer complexes of p-acrylamidyl sulphaguandine (HL) with Ni(II), Fe(II) and Pd(II) salts have been prepared (Fig. 66) (El-Sonbati et al., 2011a).

$NiX_2 + HL \rightarrow [Ni(HL)_2 X_2]_n$

where X = Cl^- (**1**), Br^- (**2**) I^- (**3**), NO_3^- (**4**) or SCN^- (**5**).

$FeSO_4 + HL \rightarrow [Fe(HL)(SO_4)(OH_2)_2]_n$ (**6**)

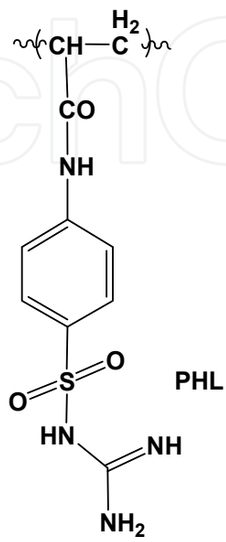


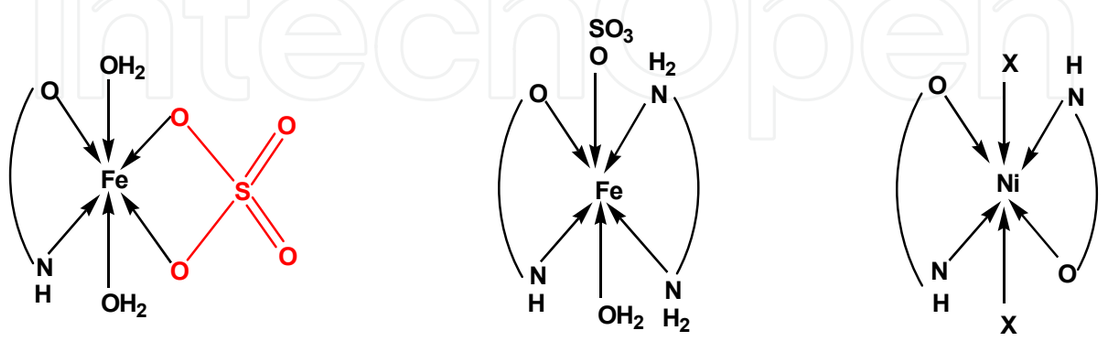
Fig. 66.

Nickel/iron mixed ligand polymer complexes were obtained by reacting pyridine (Py)/or ethylenediamine (en) with the calculated amount of trans-$[Ni(HL)_2Cl_2]$ (X = Cl^- or Br^-) as shown in Fig. 67.

$[Ni(HL)_2X_2]_n + Py \rightarrow [Ni(HL)_2(Py)_2]_nX_2$ where X = Cl^- (**7**), Br^- (**8**)

$[Fe(HL)(SO_4)(OH_2)]_n + en \rightarrow [Fe(HL)(en)(SO_4)(OH_2)]_n$ (**9**)

$PdX_2 + HL \rightarrow [Pd(LX)_2]_n$ where X = Cl^- (**10**), Br^- (**11**)



X = Cl (**1**), Br (**2**), I (**3**), ONO_2 (**4**), NCS (**5**), Py (**7**,**8**)

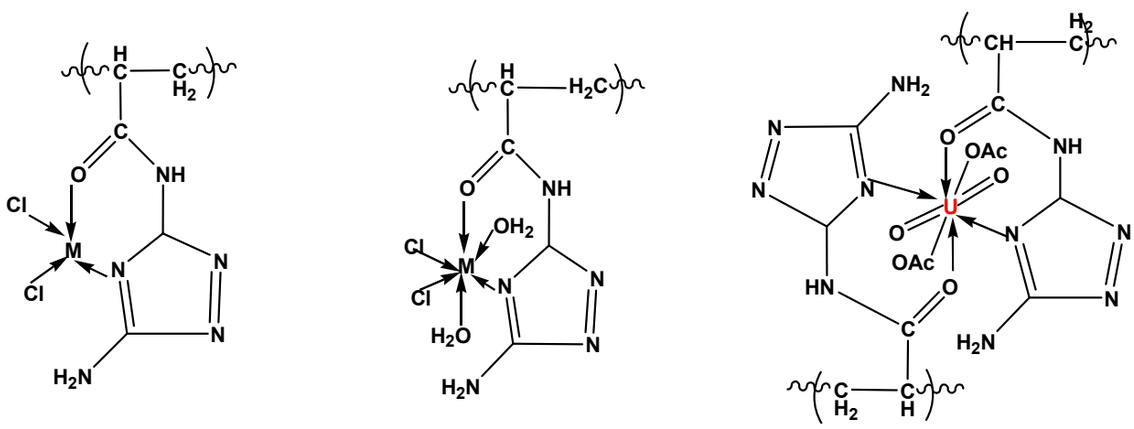
Fig. 67. Structure formulae of HL-metal polymer complexes

Novel polymer complexes of N-[3-(5-amino-1,2,4-triazolo)]acrylamide (ATA), formed by amidation of 3,5-diamino-1,2,4-triazole with acryloyl chloride were synthesized and characterized (Diab et al., 2011). Spectral studies reveal that the free ligand coordinates to the metal ion in a bidentate fashion through the oxygen of carbonyl group and a nitrogen azomethine of heterocyclic ring (Fig. 68). Elemental analyses of the polychelates indicate that the metal to ligand ratio was 1:1 and 1:2.

MCl_2 + ATA $\xrightarrow{\text{AIBN}}$ P[M(ATA)Cl_2] M = Cu(II) or Cd(II)

MCl_2 + ATA $\xrightarrow{\text{AIBN}}$ P[M(ATA)$(OH_2)_2Cl_2$] M = Co(II) or Ni(II)

$UO_2(OAc)_2$ + ATA $\xrightarrow{\text{AIBN}}$ P[UO_2(ATA)$(OAc)_2$



M = Cu(II) or Cd(II) M = Co(II) or Ni(II)

Fig. 68.

The amidation of acryloyl chloride with hydrazine hydrate in dry benzene forms acryloyl hydrazine (AH) monomer [(El-Bindary et al., 2011). Polymer complexes of AH with Cu(II), Ni(II), Co(II), Cd(II), UO_2(II) and Fe(III) salts have been prepared and characterized. AH has been shown to behave as a bidentate ligand via its nitrogen (NH_2 of the hydrazine group) and C-O/C=O (acryloyl) group in the polymer complexes, all of which exhibit supramolecular architectures assembled through weak interactions including hydrogen bonding and *π-π* staking. The elemental analyses, IR and electronic spectra data indicate that AN reacts with $CuCl_2$, $Cu(OAc)_2$, $FeCl_3$ and $CdCl_2$ in a 1:1 ratio (Structure I, III and V) and with $CoCl_2$ and $UO_2(OAc)_2$ in 2:1 molar ratios (Structure II and IV). The AH-$NiCl_2$ polymer complex is a mixture of both structure I and II. The magnetic and spectral data indicate a square planar geometry for Cu^{2+} complexes and an octahedral geometry for Co(II) and UO_2(II) complexes (Fig. 69). The ESR spectral data of the Cu(II) complexes showed that the metal-ligand bonds have considerable covalent character.

Oxovandium(IV) polymer complexes of formulation $\{[(VO)L]_2\}_n$(1) and $[(VO)LB]_n$ (2-4), where H_2L is tridentate and dianionic ligand, 3-allyl-2-thioxo-1,3-triazolidine-4,5-dione-5[*o*-hydroxylphenyl] and B is planar heterocyclic and aliphatic bases, bipyridyl (bipy); pyridine (py) and ethylenediamine (en) have been prepared and characterized (El-Sonbati et al., 2011b).

$$VOSO_4.5H_2O + H_2L \rightarrow \{[VOL]_2\}_n + H_2SO_4$$

$$VOSO_4.5H_2O + H_2L + B \rightarrow [VOLB]_n + H_2SO_4$$

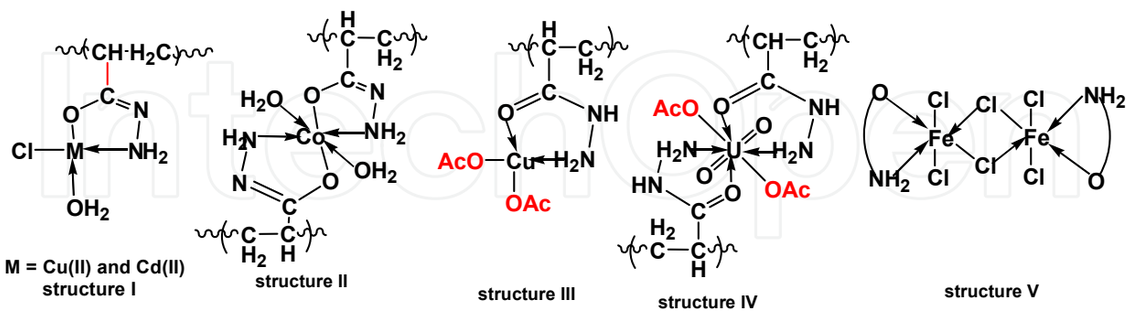


Fig. 69. Proposed structures of polymer complexes

The molecular structrure shows the presence of a vanadyl group in six-coordinate VNO_3/VN_2O_3 coordination geometry. The N,N-donor heterocyclic and aliphatic base displays an N-donor site *trans* to the vanadyl oxo-group. In all polymeric complexes (**1-4**) the ligand coordinates through oxygen of phenolic/enolic and azodye nitrogen. Formation of the polymer complexes has been done on the basis of their elemental analytical data, molar conductance values and magnetic susceptibilty data. All the complexes show 1:1$\{[VOL]_2\}_n$/1:1:1$[VOLB]_n$ metal:ligand/metal:ligand:base stoichiometry (Fig. 70).

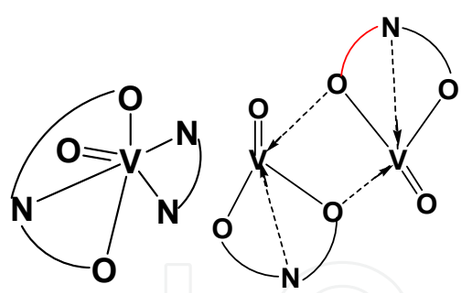


Fig. 70. Ternary structure of $[VOLB]_n$ (**2-4**) and the bases (B) used Tentative structure of polymer complex $\{[VOL]_2\}_n$ (**1**)

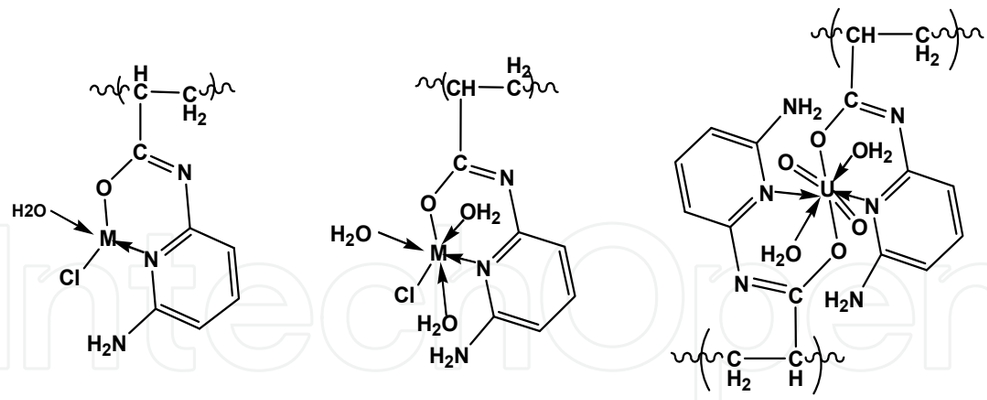
Recently, a novel ligand of N-[2-(6-aminopyridino)] acrylamide (APA) was prepared via amidation of 2,6-diaminopyridine with acryloyl chloride in dry benzene as solvent (El-Sonbati et al., 2011c). Metal-polymer complexes are reported and characterized. The formation of these polymer complexes proceeds according to the following equations:

$$MCl_2 + APA \rightarrow [M(APA)Cl.OH_2]_n \qquad M = Cu(II) \text{ or } Cd(II)$$

$$MCl_2 + APA \rightarrow [M(APA)(OH_2)_3Cl]_n \qquad M = Co(II) \text{ or } Ni(II)$$

$$UO_2(OAc)_2 + APA \rightarrow [UO_2(APA)_2(OH_2)_2]_n$$

The proposed strucrure for the polychelates is shown in Fig. 71.



M = Cu(II) or CdII) M = Co(II) or Ni(II)

Fig. 71. Proposed structure of the polymer complexes

3. Conclusions

The coordination polymer research field of study is a vast and one of the fastest growing areas of chemistry in recent times, with important work being done on a large variety of different aspects. Polymer complexes are an important class of new materials due to the coupling of the chemical, optical and electronic properties of the metal moiety to those of the polymer. This review, however, provides a uniquely broad overview of the stoichiometry of polymer complexes by using elemental analyses, FT-IR and IR spectra. The geometry of the polymer complexes was evaluated by electronic spectra (UV.-Vis.) and magnetic moment measurements.

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Stoichiometry and Research - The Importance of Quantity in Biomedicine

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The aim of this book is to provide an overview of the importance of stoichiometry in the biomedical field. It proposes a collection of selected research articles and reviews which provide up-to-date information related to stoichiometry at various levels. The first section deals with host-guest chemistry, focusing on selected calixarenes, cyclodextrins and crown ethers derivatives. In the second and third sections the book presents some issues concerning stoichiometry of metal complexes and lipids and polymers architecture. The fourth section aims to clarify the role of stoichiometry in the determination of protein interactions, while in the fifth section some selected experimental techniques applied to specific systems are introduced. The last section of the book is an attempt at showing some interesting connections between biomedicine and the environment, introducing the concept of biological stoichiometry. On this basis, the present volume would definitely be an ideal source of scientific information to researchers and scientists involved in biomedicine, biochemistry and other areas involving stoichiometry evaluation.

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