CHELATING POLYMERS

A : LINEAR CONDENSATION POLYMERS

II INTRODUCTION

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Natural chelating polymers :

Alginic acid is a polyuronide found in brown sea-weeds and its chemical formula is suggested as (II- S-1). The alginate in sea-weed behaves as a base exchange material and is present as mixed salt of cations, mostly calcium, able to render it insoluble. The amount of divalent ions necessary to obtain precipitation of alginates increases in the order, Pb, Cu < Ca < Co, Ni, Zn Mn[1]. Through divalent ions, alginic acid may also be combined to other substances[2,3]. As alginate was found to be a very effective agent for inhibiting intestinal strontium uptake, it was proposed for prevention and therapy of strontium radio contamination[4].

Chromatography of metal ions and organic substances on alginic acid has been studied by Cozzi and co-workers[5,6,7].

Chiten is a polysaccharide constituted of β(1-4) 2-acetamido-2-deoxy-D-glucose units, some of them being deacetylated. It can be called poly-N-acetyl-D-glucosamine and be represented as (II- S-2).

It occurs widely in lower animals, fungi, etc. The exoskeletons of crabs, lobsters, (arthropods) etc. are good sources of chiten[8]. Metal concentration factors in zooplankton support Bowen's statement that among cations the order of affinity for living matter is tetravalent elements, trivalent elements divalent transition element divalent group IIA elements group IA elements[9].

Chitosan is deacetylated chitin, and is conceived as a clarification aid and viscosity builder in solutions for rapid settling of suspended solids[10]. It can also be obtained as a chelating membrane. Chitosan membranes generally show lower capacity than chitosan powder[11]. It is possible to use chitosan, as a polymer for collection of trace metals by chelation accompanied by coprecipitation[12].

Many polysaccharide derivatives have been studied as natural chelating polymers[13]. The polyanions are

Polyguluronate, polymannuronate, pectate, hyauronate, etc. Polysaccharides are present in soil humus[14] also. Ligand groups in soil organic matter may be found in arrays sterically favourable for the chelation of particular metal ions[15,16].

Metal - cordination - complex formation in cartilage, elastin, etc. is important in primary calcification process[17]. Wool is a complex protein containing hydroxyl, amino, amido, carboxyl, sulphydryl and disulphide groups. Wool protein has been investigated[18] for thin layer chromatography. Nucleic acids are also known to interact with various metal ions[19-22].

Synthetic chelating polymers :

a, Linear addition polymers :

Linear polymers containing chelating sites can be obtained by addition polymerisation or condensation polymerisation.

Linear addition polymers containing chelating groups would have vinyl backbone. Styrene may be copolymerised with malic anhydride to produce (II- S-3). Polystyrene may be chloromethylated and then treated with (i) a suitable chelating diamine to yield (II- S-4) or (ii) iminodiacetate to yield (II- S-5). Dowex A-1 chelating

resin has the polymer backbone structure of (II- S-5) and has metal chelating properties similar to IDA itself[23]. Amino acid chelating resin structures have been prepared containing amino dipropionate[24], glycine[25], anthranilic acid[26], pyridine dicarboxylic acid[27], hydroxamic acid[28], etc.

b. Linear coordination/chelate polymers are obtained from bis-bidentate ligands and bivalent metal ions as shown in (II- S-6)[29-31], (II- S-7)[32-41], (II- S-8)[42-47], (II- S-9)[48-51], (II- S-10)[52-58], (II- S-11)[59-61], (II- S-12)[62-69], (II- S-13)[70] and (II- S-14)[71-72].

Linear condensation polymers containing complexing sites are obtained by condensing bifunctional complexing ligand with an appropriate bifunctional reagent. Some of these products are shown as (I- S-6)[73], (I- S-7)[74-75], (II- S-15)[76,77], (II- S-16)[78], (II- S-17)[79], (II- S-18)[80], (II- S-19)[81] and (II- S-20)[82].

Present work :

While studying coordination polymers[83] and semiconducting chelate polymers[48], we observed that very few condensation polymers with chelating properties have been prepared and studied. Hence we believed that there is a wide scope for investigations on chelating (condensation) polymers. We also believed that three-dimensional network produced by polycondensation reactions would involve the

intermediate formation of linear polymers, which by cross-linking would yield three-dimensional polymeric network. Hence we decided to concentrate first on the formation and study of linear condensation chelating polymers.

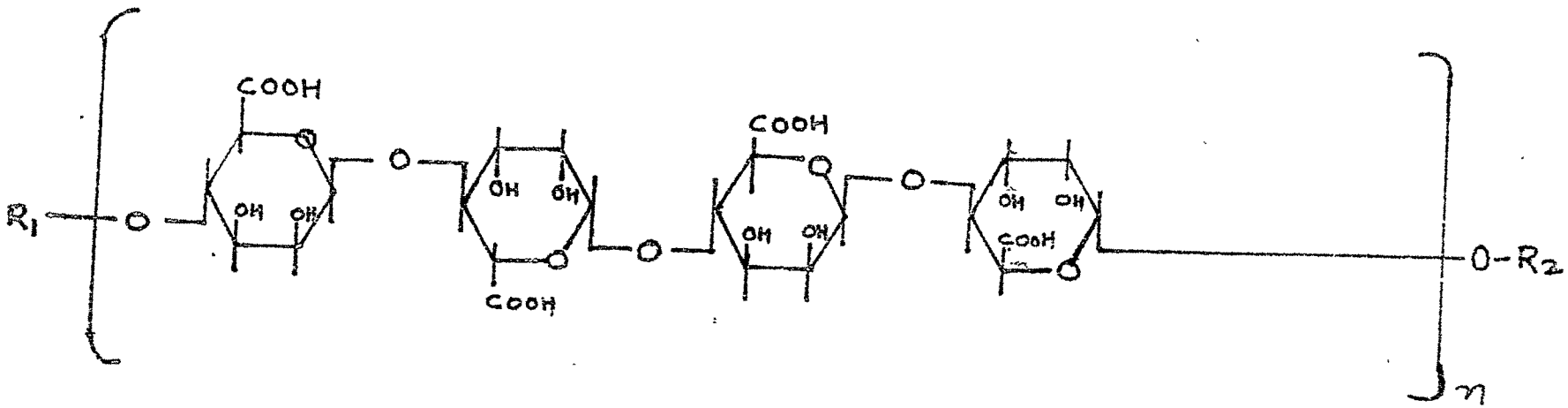
We planned the work as follows :

(i) preparation of bifunctional condensing agent;

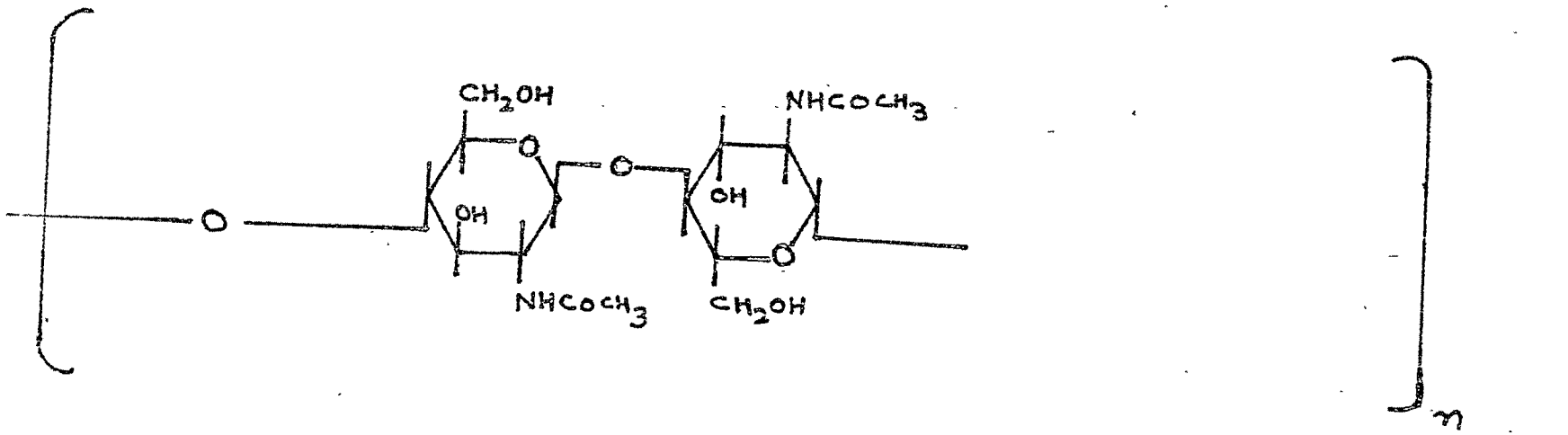
(ii) condensation of the reagent with a chelating ligand to give linear condensation chelating polymer;

(iii) study of the relative chelation of these polymers to bivalent transition metal ions in presence of different anions.

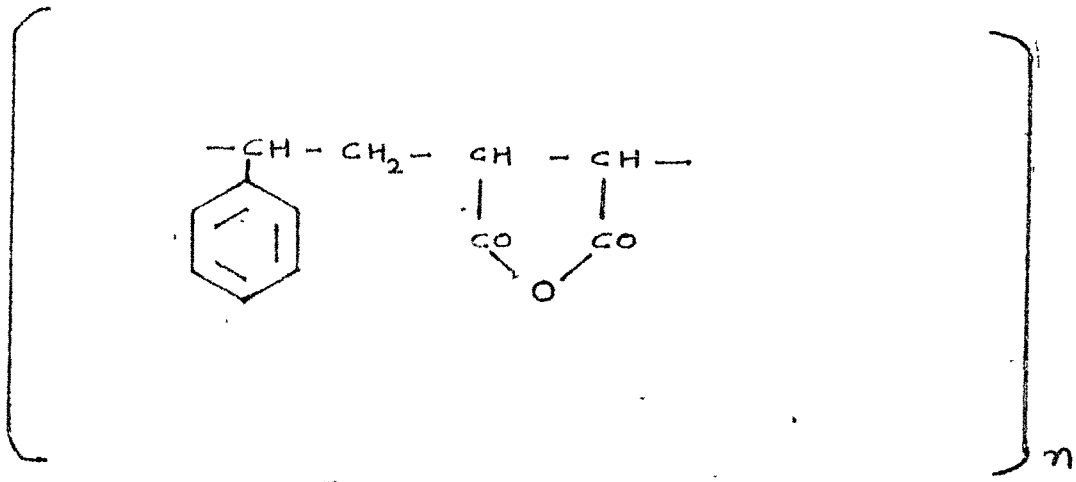
Experiments carried out and results obtained are presented and discussed in the following pages.



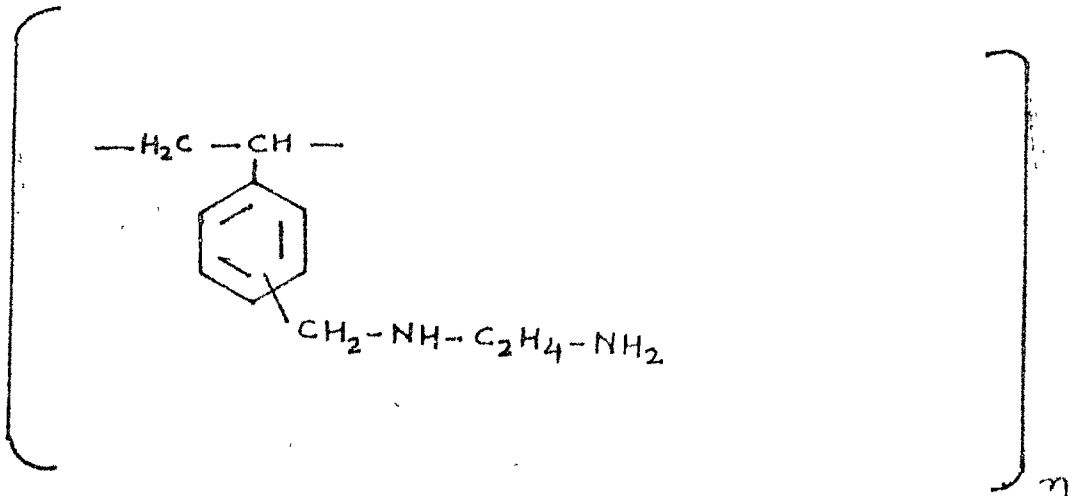
II-S-1
Alginic acid



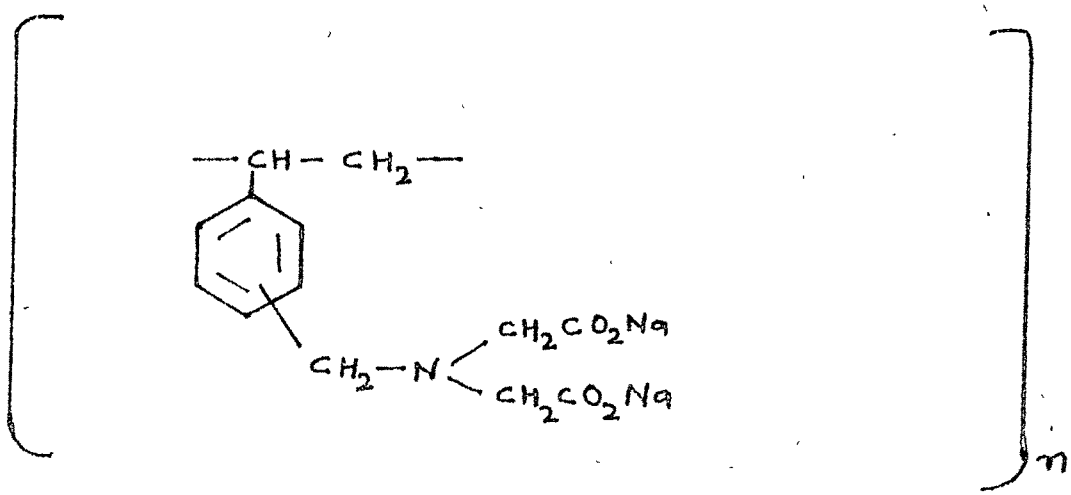
II-S-2
Chitin



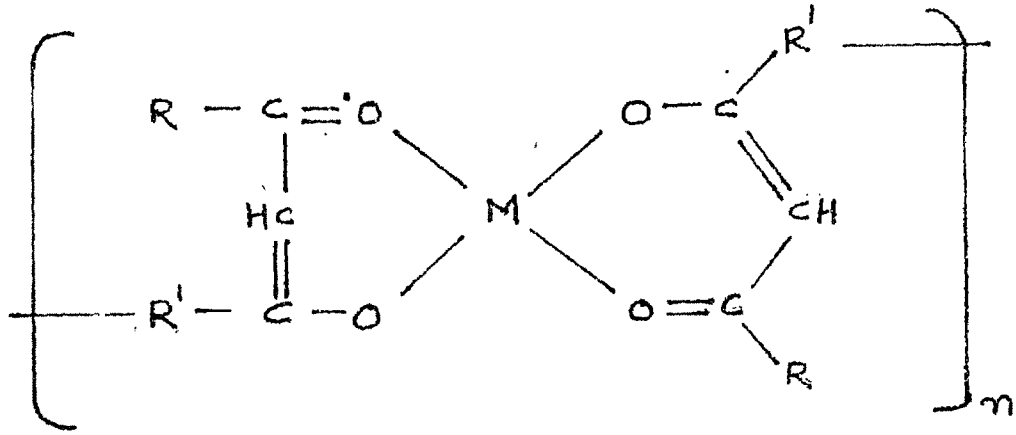
II - S - 3



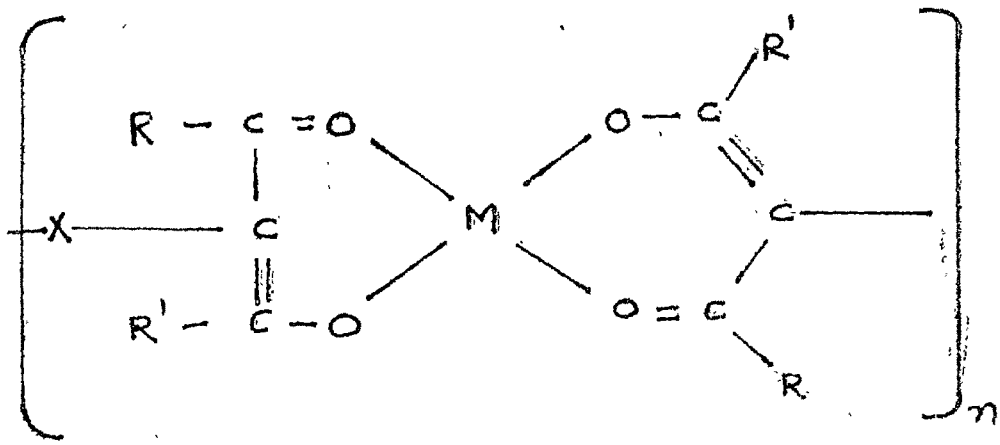
II - S - 4



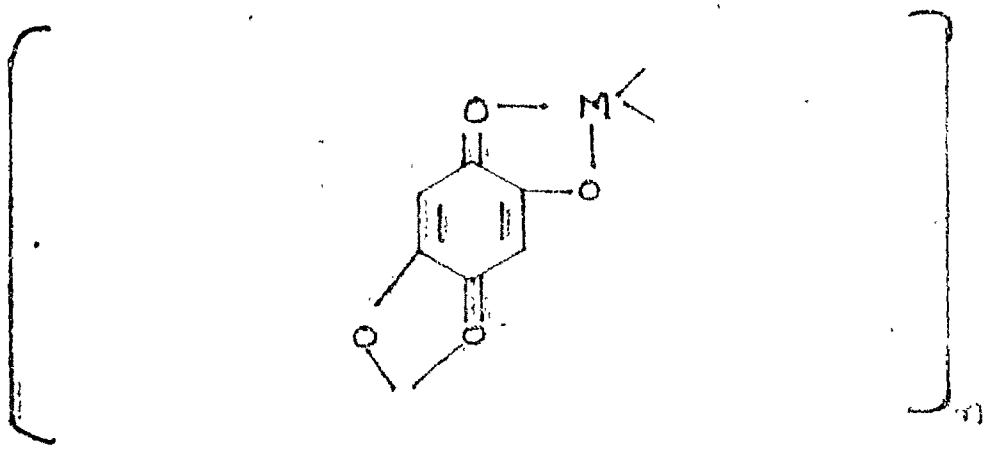
II - S - 5.



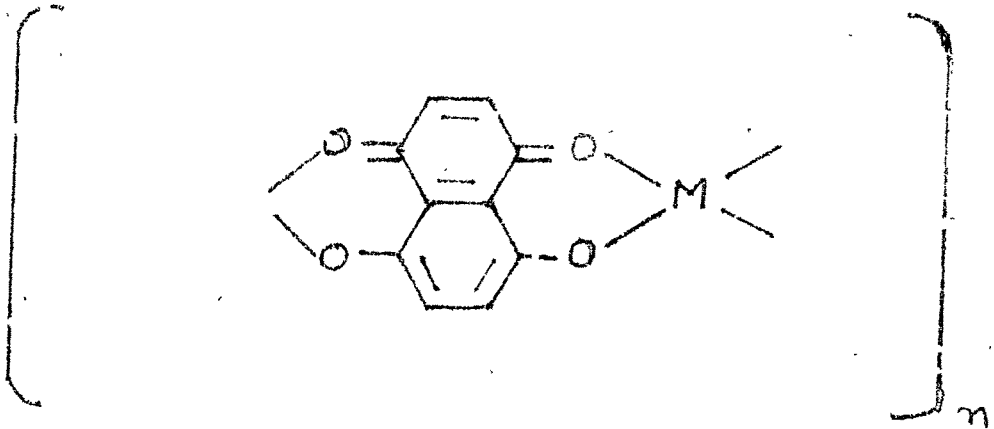
II-s-6



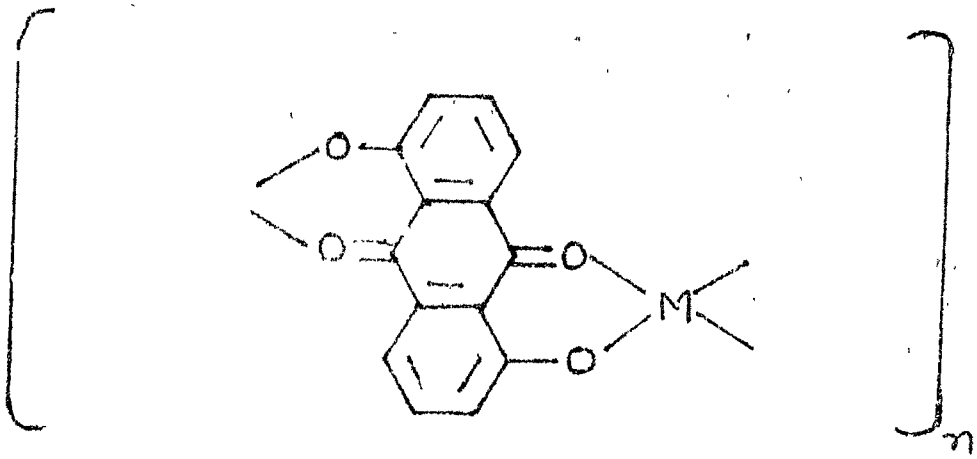
III-s-7



II-s-8



II - S - 9



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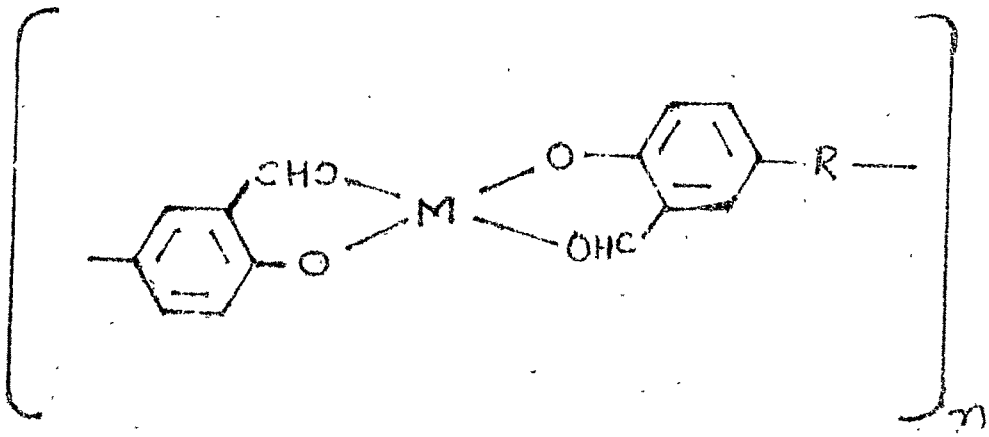
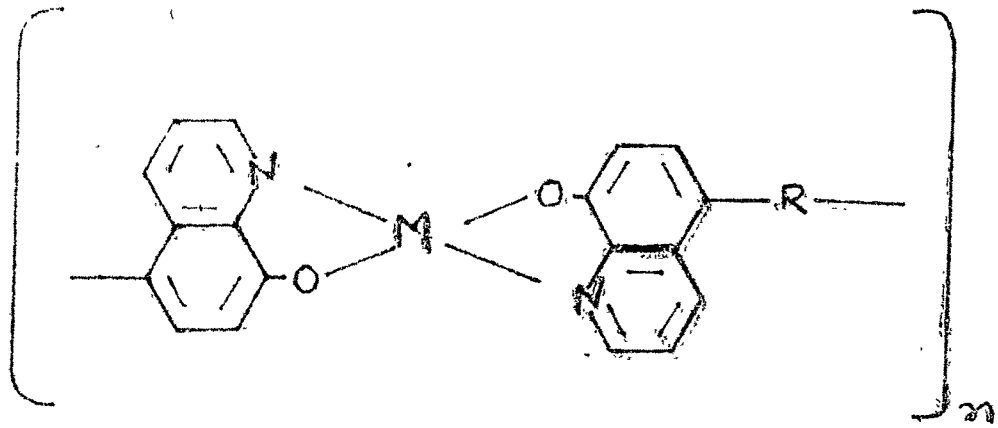
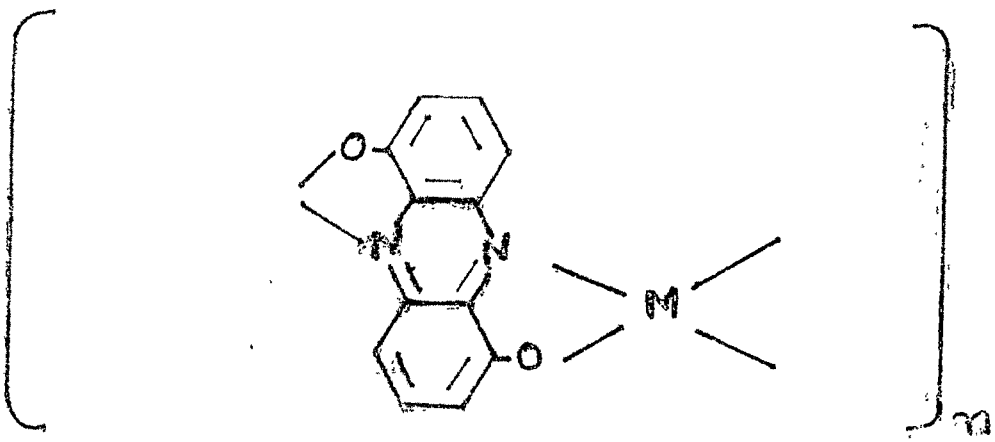


II - S - 11



II - S - 12



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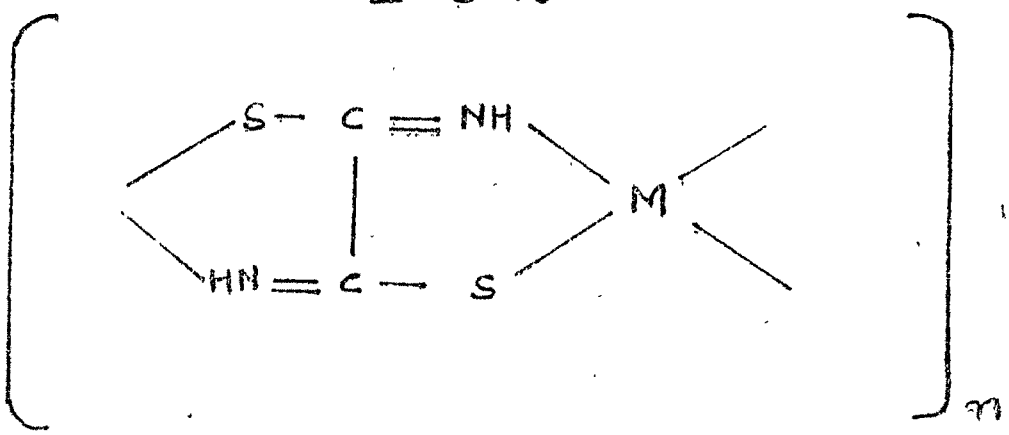
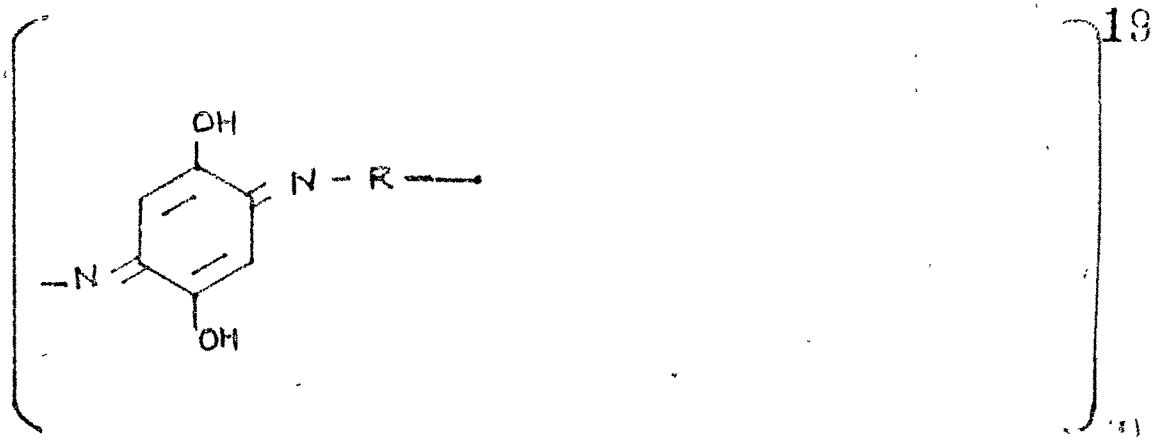
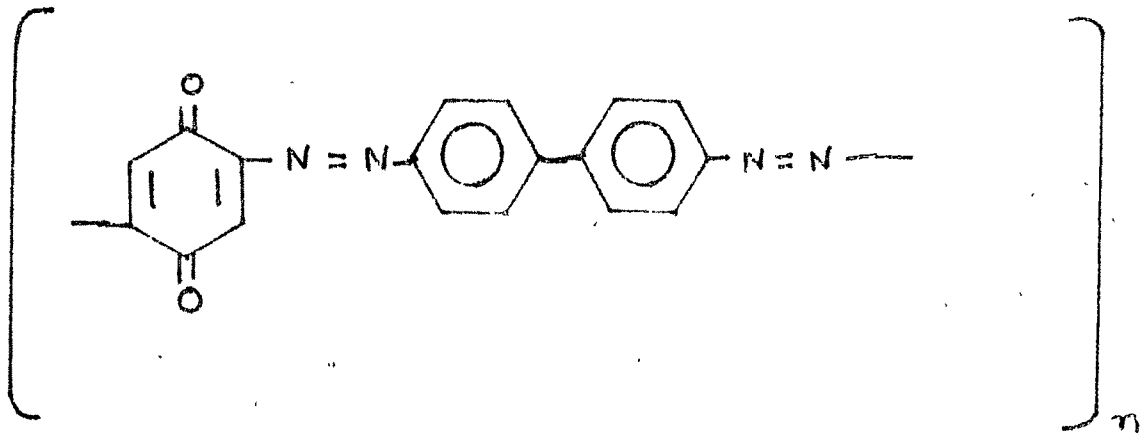


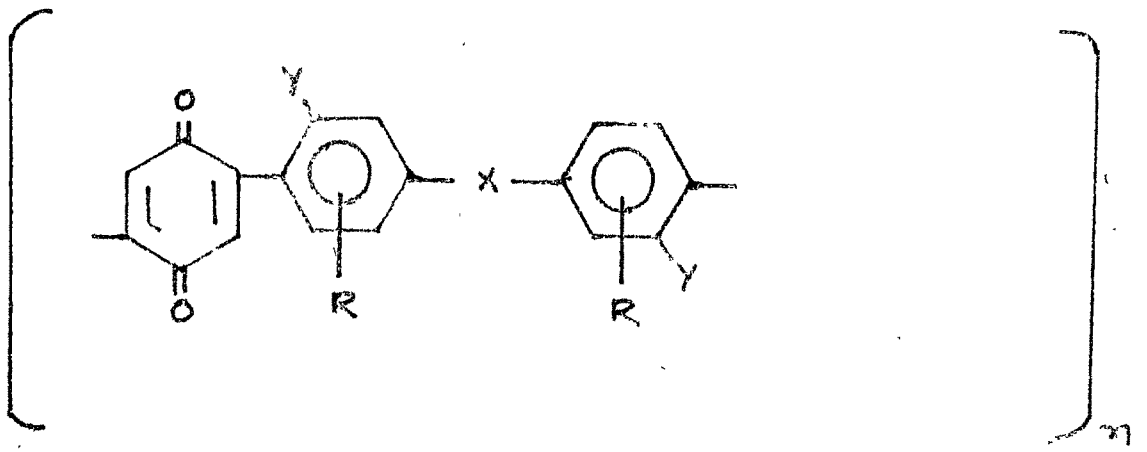
II - S - 14



II – S – 15

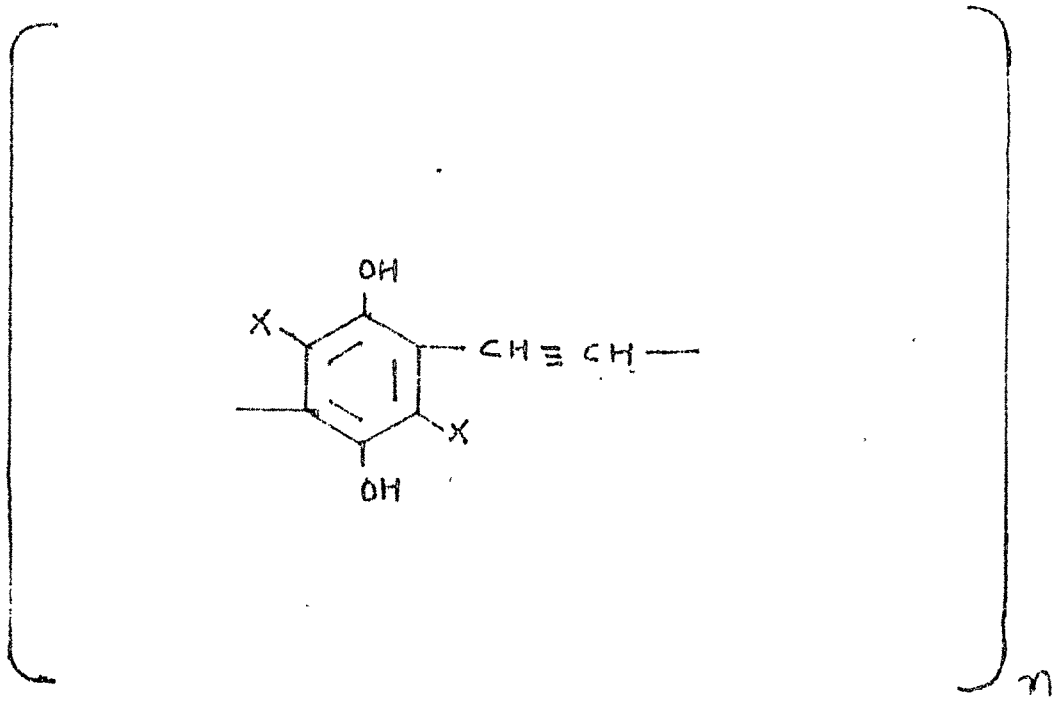


II – S – 16



X = – CH = CH – or absent

II – S – 17



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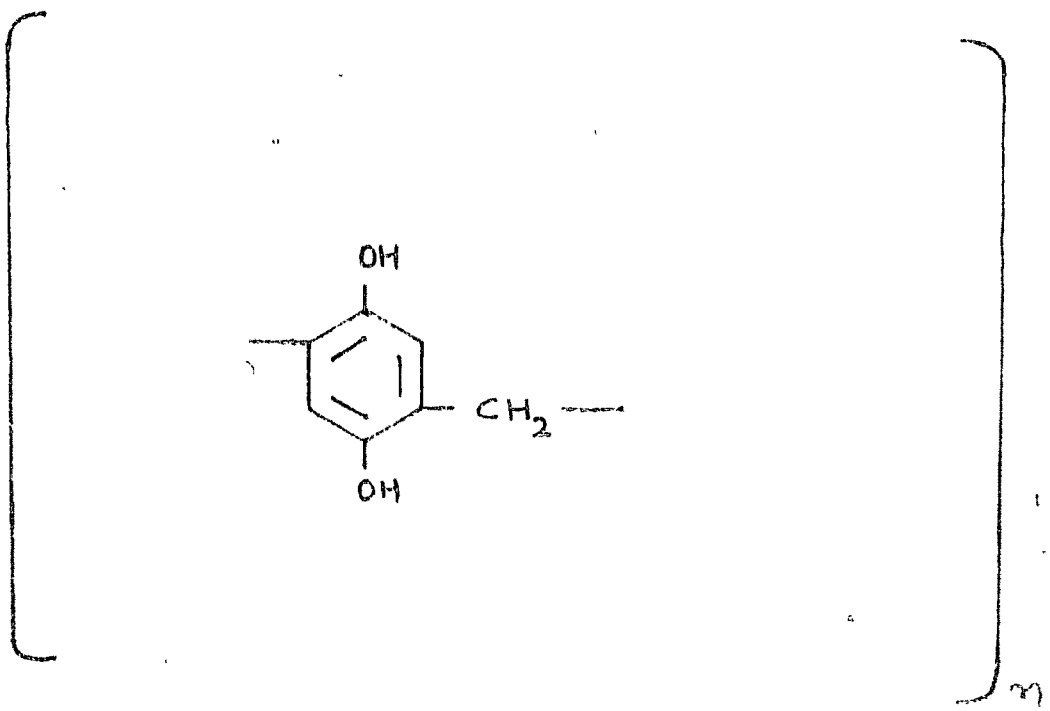

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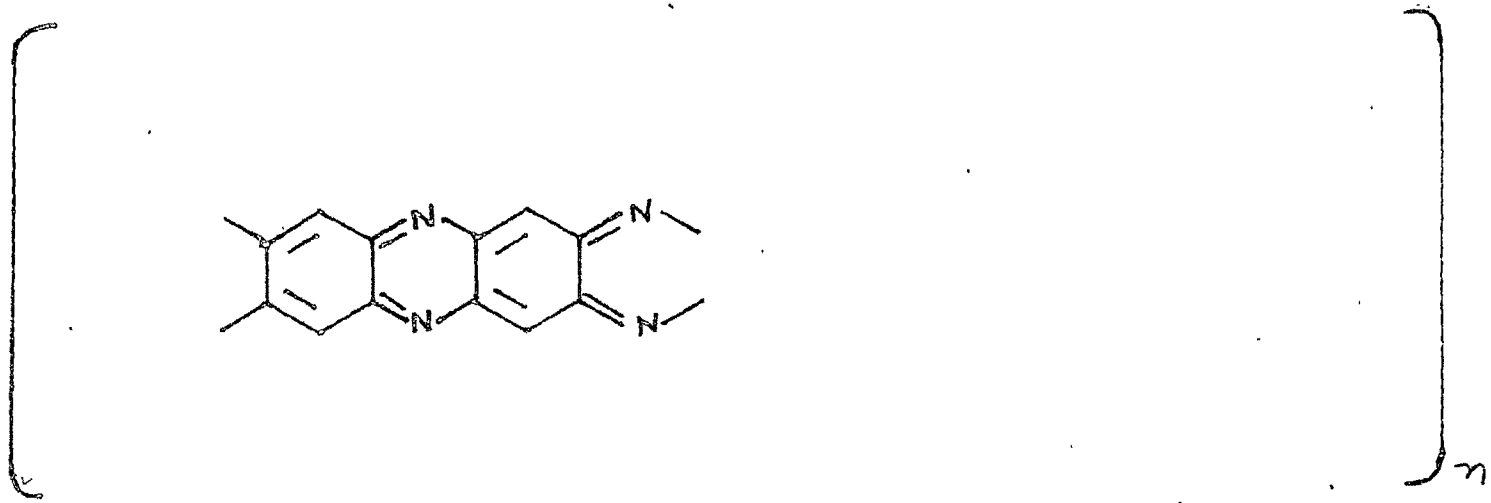
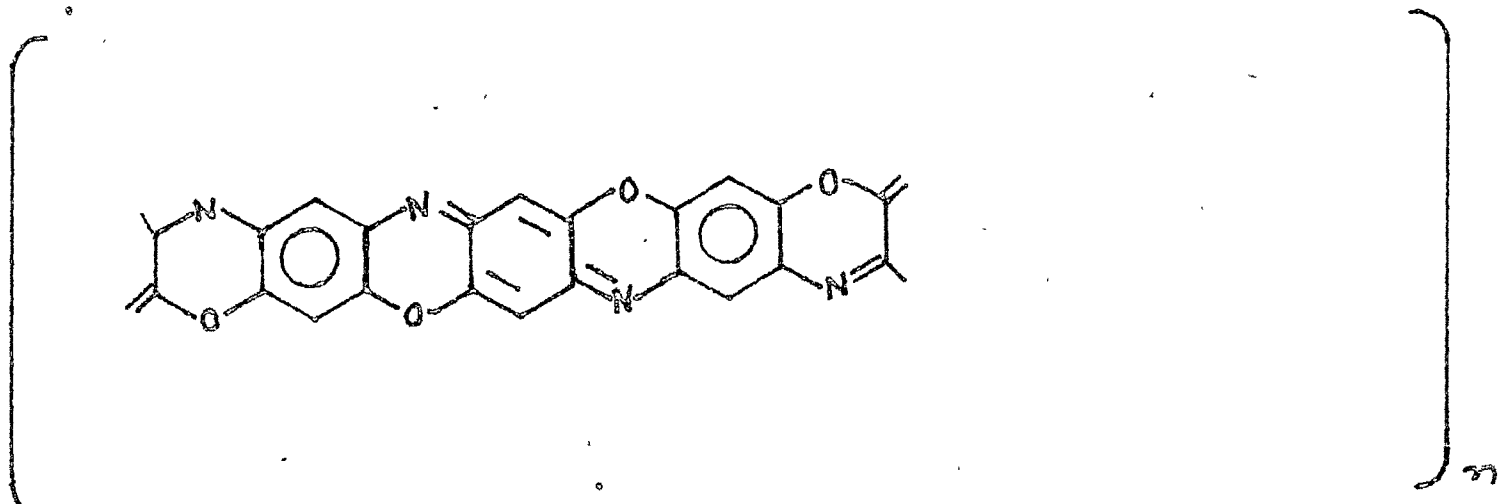


II-S-20(a)



II-S-20(b)

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III EXPERIMENTAL

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III EXPERIMENTAL

III (a). Condensation product of salicylic acid with dimethylol urea and its transition metal complexes :

1. Preparation of dimethylol urea (DU):

Urea (1 mole) was dissolved in 37% aqueous formaldehyde (2.2 moles) which was previously adjusted to pH 7.5 by the addition of aqueous sodium hydroxide (excess of formaldehyde was used to reduce the formation of monomethylol urea). Reaction took place spontaneously

without the application of heat and was complete within 24 hours. The product separated as a dense white solid. It was filtered, washed with ethanol and dried under vaccume. M.P. 138 - 140°C.

Analysis: Found: %C = 30.61; %H = 6.99; %N = 23.85.

$C_3H_8N_2O_3$ requires %C = 30.00; %H = 6.67 %N = 23.33.

2. Condensation of salicylic acid and dimethylol urea (SADU) :

Salicylic acid (1 mole) and dimethylol urea (1 mole) were dissolved separately in hot water and then mixed in 250 ml. round bottom flask fitted with a condenser. The contents of the flask were heated on a [illegible] sand -bath till the solid separated. Concentrated hydrochloric acid (2 to 3 ml.) was added as catalyst. The resultant hard mass was crushed and washed with hot water till unreacted salicylic acid and dimethylol urea were removed. It was obtained as pink powder by recrystallisation from hot dimethyl formamide. It is insoluble in water and all common organic solvents except dimethyl formamide and dimethyl sulphoxide. M.P. 225°C (decomposed).

Analysis; Found: %C = 48.15; %H = 4.55; %N = 10.52

$C_{10}H_{13}N_2O_{5.5}$ requires %C = 48.19; %H = 5.22; %N = 11.24.

3. Thermolysis of the condensation product (SADU) :

Condensation product of salicylic acid and dimethylol urea (SADU) was heated in an oven at 180 - 200°C. The product is white, insoluble in various solvents and does not melt up-to 300°C.

Analysis: Found: %C = 60.32; %H = 4.77; %N = 8.23.

$C_{17}H_{14}N_2O_6$ requires %C = 59.64; %H = 4.09; %N = 8.18.

4. Spectroscopic studies :

Ultra violet absorption spectrum of the condensation product (SADU) was determined in dimethyl formamide, and is presented in Fig. III- F-1.

IR spectra of the condensation product were studied in the form of KBr pellet and in nujol mull, and the important absorption peaks are presented in Table III- T-1.

5. Cu (II), Ni (II), Co (II), Mn (II), and Zn (II) complexes of the condensation product of salicylic acid and dimethylol urea in presence of acetate ion in dimethyl formamide :

Condensation product of salicylic acid and dimethylol urea (SADU) dissolved in dimethyl formamide was mixed with calculated amount of metal acetate in dimethyl formamide (salt: ligand:: 1:1). The mixture became turbid,

gradually forming slimy precipitates and was left overnight. The precipitates were carefully filtered, washed with methanol and little dimethyl formamide and dried. They are insoluble in water and all organic solvents. The colour, M.P., analysis, etc. of these complexes are presented in Table III- T-2.

6. Cu (II), Ni (II), Co (II), and Zn (II) complexes of the condensation product of salicylic acid and dimethylol urea in presence of chloride ion in dimethyl formamide :

SADU dissolved in dimethyl formamide was mixed with calculated amount of metal chloride in dimethyl formamide (salt: ligand::1:1). The mixture became turbid and was left overnight. The precipitates were filtered, washed with methanol and little dimethyl formamide and dried. The colour, M.P., analysis, etc. of these complexes are presented in Table III- T-3.

7. Cu (II), Ni (II), Co (II), Zn (II), and Mn (II) complexes of the condensation product of salicylic acid and dimethylol urea in presence of sulphate ion in dimethyl formamide :

SADU dissolved in dimethyl formamide was mixed with calculated amount of metal sulphate in dimethyl formamide (salt: ligand:: 1:1). The mixture became turbid and was

left overnight. The precipitates were filtered, washed with methano methanol, and little dimethyl formamide and dried. The colour, M.P., analysis, etc. of these complexes are presented in Table III- T-4.

III (b). Condensation product of salicylaldehyde and dimethylol urea and its transition metal complexes :

1. Condensation of salicylaldehyde and dimethylol urea (SDU) :

Salicylaldehyde (1 mole) and dimethylol urea (1 mole) were dissolved separately in hot water and then mixed in 250 ml. round bottom flask fitted with a condenser. The contents of the flask were heated on a sand-bath till the solid separated. Concentrated hydrochloric acid (2 to 3 ml.) was added as catalyst. The resultant hard mass was crushed and washed with hot water and ethanol till unreacted salicylaldehyde and dimethylol urea were removed. It was obtained as pale yellow powder by recrystallisation from hot dimethyl formamide. It is insoluble in water and all common organic solvents except dimethyl formamide and dimethyl sulphoxide. It does not melt upto 300°C. (decomposed).

Analysis: Found: %C = 50.6; %H = 5.31; %N = 16.34.

$C_{13}H_{18}N_4O_6$ requires %C = 48.00; %H = 5.52; %N = 17.23.

2. Thermolysis of the condensation product :

Condensation product (SDU) was heated in an oven at 150-80°C. There was evolution of water. The product is insoluble in various solvents and does not melt upto 300°C.

Analysis: Found: %C = 52.80; %H = 5.25; %N = 18.7.

$C_{13}H_{16}N_4O_5$ requires %C = 50.81; %H = 5.18; %N = 18.2.

3. Spectroscopic studies :

IR spectrum of SDU in KBr pellet was obtained and the characteristics absorption peaks are presented in Table III- T-5.

4. Cu (II), Ni (II), and Co (II) complexes of the condensation product of salicylaldehyde and dimethylol urea in presence of acetate ion in dimethyl formamide :

Condensation product of salicylaldehyde and dimethylol urea (SDU) dissolved in dimethyl formamide was mixed with calculated amount of metal acetate in dimethyl formamide (salt: ligand:: 1:1). The mixture became turbid , gradually forming slimy precipitates and was left overnight. The precipitates were carefully filtered, washed with ethanol and little dimethyl formamide and dried. They are insoluble in water and all organic solvents. Colour, M.P., analysis, etc. of these complexes are presented in Table

III- T-6.

5. Cu (II), Ni (II), Co (II), Zn (II) and Mn (II) complexes of the condensation product of salicylaldehyde and dimethylol urea in presence of chloride ion in dimethyl formamide:

Condensation product of salicylaldehyde and dimethylol urea (SDU) dissolved in dimethyl formamide was mixed with calculated amount of metal chloride in dimethyl formamide (salt: ligand:: 1:1). The mixture became turbid, gradually forming slimy precipitates and was left overnight. The precipitates were carefully filtered, washed with ethanol and little dimethyl formamide and dried. They are insoluble in water and all organic solvents. Colour, M.P., analysis, etc. of these complexes are presented in Table III- T-7.

6. Cu (II),Ni (II), and Co (II) complexes of the condensation product of salicylaldehyde and dimethylol urea in presence of sulphate ion in dimethyl formamide :

Condensation product of salicylaldehyde and dimethylol urea (SDU) dissolved in dimethyl formamide was mixed with calculated amount of metal sulphate in dimethyl formamide (salt: ligand:: 1:1). The mixture became turbid,

gradually forming slimy precipitates and was left overnight. The precipitates were carefully filtered, washed with ethanol and little dimethyl formamide and dried. They are insoluble in water and all organic solvents. Colour, M.P., analysis, etc. of these complexes are presented in Table III- T-8.

III (c). Oxime of the condensation product of salicylaldehyde and dimethylol urea and its transition metal complexes :

1. Oxime of the condensation product of salicylaldehyde and dimethylol urea (SODU) :

Concentrated aqueous solution of hydroxylamine-hydrochloride and sodium acetate (0.5 gm.) was added to the solution of condensation product of salicylaldehyde and dimethylol urea (1.5 gm.) in dimethyl formamide and the mixture was heated on sand-bath for 3 to 4 hours. The precipitates were filtered, washed with water and ethanol and dried. The product was recrystallised from dimethyl-formamide. It is insoluble in water and all common organic solvents except dimethyl formamide and dimethyl sulphoxide. M.P. 252°C (decomposed).

Analysis: Found: %C = 49.0; %H = 5.85; %N = 23.95.

$C_{13}H_{17}N_5O_5$ requires %C = 48.2; %H = 5.26; %N = 21.67.

2. Cu (II), Ni (II)and Co (II) complexes of oxime of condensation product of salicylaldehyde and dimethylol urea in presence of acetate ion in dimethyl formamide :

Oxime of condensation product of salicylaldehyde and dimethylol urea (SODU) dissolved in dimethyl formamide was mixed with calculated amount of metal acetate in dimethyl formamide (salt: ligand::1:1). The mixture became turbid, gradually forming slimy precipitates and was left overnight. The precipitates were carefully filtered, washed with ethanol and little dimethyl formamide and dried. They are insoluble in water and all organic solvents. The colour, M.P., analysis, etc. of these complexes are presented in Table III- T-9.

III (d). Condensation product of 8-hydroxyquinoline with dimethylol urea and its transition metal complexes:

1. Condensation of 8-hydroxyquinoline and dimethylol urea (OQDU) :

8-Hydroxyquinoline (1 mole) and dimethylol urea (1 mole) were dissolved separately in hot water and then mixed in 250 ml. round bottom flask fitted with a condenser. The contents of the flask were heated on a sand-bath till

solid separated. Concentrated hydrochloric acid (2 to 3 ml.) was added as catalyst.The resulting mass was washed with hot water and then alcohol. It was obtained as yellow powder by recrystallisation from hot dimethyl sulphoxide. It is insoluble in water and all common organic solvents except dimethyl sulphoxide. It does not melt upto 300°C.

Analysis: Found: %C = 49.53; %H = 4.89; %N = 14.04.

$C_{12}H_{18}N_3O_{5.5}$ requires %C = 49.41; %H = 6.14; %N = 14.38.

2. Spectroscopic studies :

IR spectra of the condensation product (OQDU) in KBr pellet form and in nujol mull were obtained and characteristic absorption peaks are presented in Table III- T-10.

3. Cu (II), Ni (II) and Co (II) complexes of condensation product of 8-hydroxyquinoline and dimethylol urea in presence of acetate ion in dimethyl sulphoxide :

Condensation product of 8-hydroxyquinoline and dimethylol urea (OQDU) dissolved in dimethyl sulphoxide was mixed with calculated amount of metal acetate in dimethyl - sulphoxide (salt: ligand:: 1:1). The mixture became turbid, gradually forming slimy precipitates and was left overnight.

The precipitates were filtered, washed with ethanol and little dimethyl sulphoxide and dried. They are insoluble in water and all organic solvents. M.P. and analysis of these complexes are presented in Table III- T-11.

4. Cu(II), Ni(II) and Co(II) complexes of condensation product of 8-hydroxyquinoline and dimethylol urea in presence of chloride or sulphate ions in dimethyl-sulphoxide :

Condensation product of 8-hydroxyquinoline and dimethylol urea (OQDU) dissolved in dimethyl sulphoxide was mixed with calculated amount of metal chloride or sulphate in dimethyl sulphoxide (salt: ligand:: 1:1). The mixture became turbid, gradually forming slimy precipitates and was left overnight. The precipitates were filtered, washed with ethanol and little dimethyl sulphoxide and dried. They are insoluble in water and all organic solvents. M.P. and analysis of these complexes are presented in Table III- T-12.

Table- III T-1

IR absorption bands (cm^{-1})

of SADU

KBr pellet	Nujol mull
660 w	660 w
710 w	715 w
750 w	760 sh
800 m	795 m
1050 m	
1090 m	
1125 m	
1200 b s	
1260 b s	1240 s
1345 m	
1380 m	1370 s
1450 m	1440 s
1550 b m	
1660 s	
2900 s	
3360 s	

Table III- T-2

Analysis, formula, etc. of metal acetate complexes of SADU

M. P. >300°C

NO.	Complex	Formula	Analysis							
			Required				Found			
			%C	%H	%N	%M	%C	%H	%N	%M
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
1.	SADU-Cu-A	$C_{12}H_{20}N_2O_{10}Cu$	34.3	4.8	6.7	15.1	34.2	3.9	6.5	15.3
2.	SADU-Ni-A	$C_{13}H_{20.5}N_2O_{10}Ni_{0.75}$	38.1	5.0	6.8	10.9	38.1	5.2	6.7	11.1
3.	SADU-Co-A	$C_{12}H_{18}N_2O_9Co$	36.9	4.6	7.2	15.1	36.1	4.7	6.6	15.4
4.	SADU-Zn-A	$C_{12}H_{15}N_2O_7Zn_{0.5}$	43.7	4.5	8.5	9.9	44.7	4.5	7.7	10.1
5.	SADU-Mn-A	$C_{12}H_{15}N_2O_7Mn_{0.5}$	43.7	4.5	8.5	8.3	43.0	4.0	8.2	8.7

Table III- T-3

Analysis, formula, etc. of metal chloride complexes SADU

M. P. >300°C

No.	Complex	Formula	Analysis							
			Required				Found			
			%C	%H	%N	%M	%C	%H	%N	%M
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
1.	SADU-Cu-C	$C_{10}H_{13.5}N_2O_6Cu_{0.5}Cl_{0.5}$	38.7	4.4	9.0	10.2	39.0	3.8	7.6	10.2
2.	SADU-Ni-C	$C_{10}H_{13.6}N_2O_6Ni_{0.4}Cl_{0.4}$	40.7	4.4	9.4	8.0	42.1	4.5	9.6	8.6
3.	SADU-Co-C	$C_{10}H_{11.5}N_2O_5Co_{0.5}Cl_{0.5}$	41.4	4.0	9.6	10.2	41.9	4.6	10.2	10.3
4.	SADU-Zn-C	$C_{10}H_{13.5}N_2O_6Zn_{0.5}Cl_{0.5}$	38.7	4.4	9.9	10.5	37.3	3.7	8.5	10.5

Table III- T-4

Analysis, formula, etc. of metal sulphate complexes of SADU

M. P. >300°C

NO.	Complex	Formula	Analysis							
			Required				Found			
			%C	%H	%N	%M	%C	%H	%N	%M
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
1.	SADU-Cu-S	$C_{10}H_{11.6}N_2O_{5.8}S_{0.2}Cu_{0.4}$	42.1	4.1	9.8	8.9	40.9	4.7	10.4	8.8
2.	SADU-Ni-S	$C_{10}H_{11.5}N_2O_6S_{0.25}Ni_{0.5}$	41.0	4.0	9.6	10.0	43.1	4.7	8.7	9.2
3.	SADU-Co-S	$C_{10}H_{11.6}N_2O_{5.8}S_{0.2}Co_{0.4}$	42.6	4.1	9.9	8.4	44.1	4.8	10.4	9.5
4.	SADU-Zn-S	$C_{10}H_{11.5}N_2O_6S_{0.25}Zn_{0.5}$	41.0	4.0	9.6	11.2	44.3	4.7	8.5	10.5
5.	SADU-Mn-S	$C_{10}H_{11.6}N_2O_{5.8}S_{0.2}Mn_{0.4}$	42.9	4.2	10.0	7.9	44.5	5.0	9.9	8.5

Table III- T-5

IR absorption bands (cm^{-1})

of SDU

KBr pellet	Nujol mull
750 m	720 w
795 w	795 w
990 w	1025 w
1145 m	1150 m
1175 m	
1275 s	1300 m
1380 m	1375 s
1440 m	1460 s
1490 s	
1540 m	
1650 s	1640 b m
2920 m	
3380 b m	3300 b w

Table III- T-6

Analysis, formula, etc. of metal acetate complexes of SDU

M.P. >300°C

NO.	Complex	Formula	Analysis					
			Required			Found		
			%C	%H	%M	%C	%H	%M
1.	2.	3.	4.	5.	6.	7.	8.	9.
1.	SDU-Cu-A	$C_{15}H_{22}N_4O_9Cu$	39.1	4.8	13.8	40.1	4.8	13.2
2.	SDU-Ni-A	$C_{15}H_{20}N_4O_8Ni$	40.0	4.4	13.1	42.4	4.9	13.5
3.	SDU-Co-A	$C_{15}H_{30}N_4O_{13}Co$	34.0	5.7	11.1	34.6	5.7	10.7

Table III- T-7

Analysis, formula, etc. of metal chloride complexes of SDU

M. P. >300°C

NO.	Complex	Formula	Analysis							
			Required				Found			
			%C	%H	%N	%M	%C	%H	%N	%M
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
1.	SDU-Cu-C	$C_{13}H_{15}N_4O_5Cl\ Cu$	38.9	3.8	13.9	15.5	40.5	4.0	13.2	15.0
2.	SDU-Ni-C	$C_{13}H_{15}N_4O_{5.5}Ni$	41.8	4.2	15.0	15.7	45.0	4.9	15.7	15.7
3.	SDU-Co-C	$C_{13}H_{15.5}N_4O_5Co_{0.5}$	46.7	4.5	16.6	8.8	49.0	4.8	17.6	9.6
4.	SDU-Zn-C	$C_{13}H_{15}N_4O_5Zn_{0.5}$	46.0	4.4		9.6	47.5	4.4		10.1
5.	SDU-Mn-C	$C_{13}H_{15}N_4O_5Mn_{0.5}$	46.7	4.5		8.2	49.5	4.6		8.3

Table III- T-8

Analysis, formula, etc. of metal sulphate complexes of SDU

M. P. > 300°C

NO.	Complex	Formula	Analysis							
			Required				Found			
			%C	%H	%N	%M	%C	%H	%N	%M
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
1.	SDU-Cu-S	$C_{13}H_{19}N_4O_7Cu_{0.5}$	41.6	5.0	14.9	8.5	39.7	4.7	15.9	8.2
2.	SDU-Ni-S	$C_{13}H_{17}N_4O_6Ni_{0.5}$	43.1	4.7	16.0	8.2	43.4	4.6	16.4	7.8
3.	SDU-Co-S	$C_{13}H_{15}N_4O_5Co_{0.5}$	45.9	4.4		8.7	46.0	4.8		8.2

Table III- T-9

Analysis, formula, etc. of metal acetate complexes of SODU

M. P. > 300°C

NO.	Complex	Formula	Analysis							
			Required				Found			
			%C	%H	%N	%M	%C	%H	%N	%M
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.	11.
1.	SODU-Cu-A	$C_{15}H_{19}N_5O_7Cu$	40.4	4.3	15.5	14.1	41.5	4.9	14.9	13.5
2.	SODU-Ni-A	$C_{15}H_{19}N_5O_7Ni$	40.9	4.3	15.9	13.4	41.1	4.8	15.5	13.8
3.	SODU-Co-A	$C_{15}H_{19}N_5O_7Co$	40.9	4.3	15.9	13.4	42.1	4.7	15.6	14.0

Table III- T-10

IR absorption bands (cm^{-1})

of OQDU

KBr pellet	Nujol mull
650 w	
710 w	715 w
785 m	785 w
945 w	955 m
1015 m	1015 m
1155 m	1155 m
1260 m	1270 b m
1360 m	1380 s
1410 m	
1480 s	1460 s
1500 s	1500 w
1545 w	
1630 b m	1630 b w
2920 m	
3370 b s	3300 b m

Table III- T-11

Analysis, formula, etc. of metal acetate complexes of OQDU

M. P. $> 300^{\circ}C$

NO.	Complex	Formula	Analysis					
			Required			Found		
			%C	%H	%M	%C	%H	%M
1.	2.	3.	4.	5.	6.	7.	8.	9.
1.	OQDU-Cu-A	$C_{12}H_{14}N_3O_4Cu_{0.5}$	48.0	4.7	10.6	50.4	5.1	10.6
2.	OQDU-Ni-A	$C_{12}H_{12}N_3O_3Ni_{0.5}$	51.4	4.3	10.5	51.4	5.0	11.3
3.	OQDU-Co-A	$C_{12}H_{14}N_3O_4Co_{0.5}$	49.6	4.8	10.2	48.6	4.6	10.0

Table III- T-12

Analysis, formula, etc. of metal complexes of OQDU

M. P. > 300°C

NO.	Anion	Complex	Formula	Analysis					
				Required			found		
				%C	%H	%M	%C	%H	%M
1.	2.	3.	4.	5.	6.	7.	8.	9.	10.
1.	Sulphate	OQDU-Cu-S	$C_{12}H_{10}N_3O_2Cu_{0.5}$	55.4	3.8	12.2	55.1	3.9	13.8
2.	Sulphate	OQDU-Co-S	$C_{12}H_{10}N_3O_2Co_{0.5}$	55.4	3.8	11.4	57.1	4.3	12.3
3.	Chloride	OQDU-Ni-C	$C_{12}H_{10}N_3O_2Ni_{0.5}$	55.4	3.8	11.4	57.1	4.0	13.0

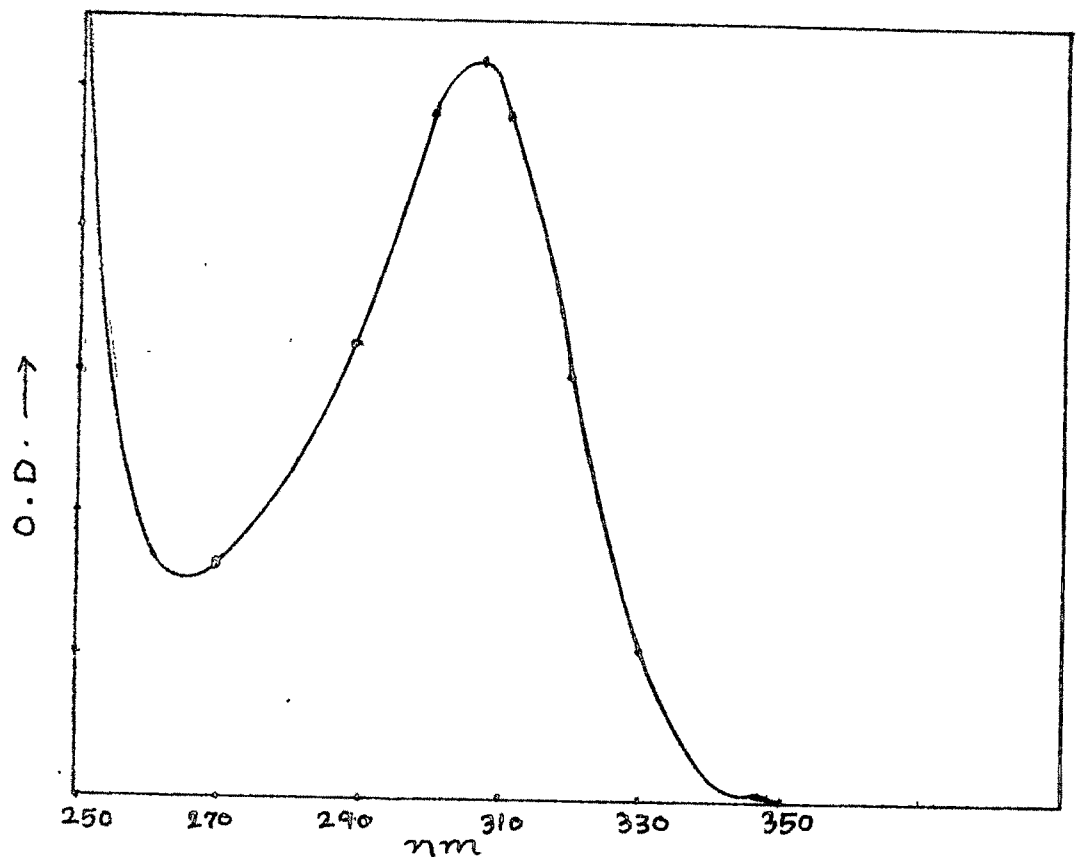


Fig - III - F - 1 : UV absorption spectrum of SADU

CHELATING POLYMERS

A : LINEAR CONDENSATION POLYMERS

IV DISCUSSION

CHELATING POLYMERS

A: LINEAR CONDENSATION POLYMERS

IV DISCUSSION

IV (a) Dimethylol urea (DU):

Dimethylol urea (DU) was prepared by the known method[84] from urea and formaldehyde (IV- E-1).

$NH_2\ CO\ NH_2 + 2\ HCHO \rightarrow HO\ CH_2\ NH\ CO\ NH\ CH_2\ OH$ (IV- E-1).

Earlier studies[85] have shown that the reaction of formaldehyde with urea proceeds in steps with the final product of tetramethylol urea. Conditions of the reactions were so adjusted that the maximum yield of (DU) was obtained. On thermolysis at 150-80°C, it decomposes with the possible loss of H_2O and CO_2 .

IV (b) Linear condensation product of salicylic acid with dimethylol urea (SADU) :

Salicylic acid condenses with dimethylol urea with the formation of a linear condensation polymer (IV- S-1a). The analysis indicates that the product contains 1.5 water molecules per molecule of salicylic acid and has a degree of polymerisation of about 10 with terminal ligand molecule. On thermolysis at 150-80°C it decomposes to (IV- S-1b).

From the ultraviolet absorption spectrum of SADU, the absorption band of SADU is found at 305 nm. IR absorption bands of SADU are also recorded.

IV (c) Complexes of Cu(II), Ni(II), Co(II), Mn(II), and Zn(II) with SADU :

IV (c-i) Complexes formed in presence of acetate anion :

Complexes of Cu(II), Ni(II), Co(II), Mn(II) and Zn(II) with SADU were formed from dimethyl formamide solutions of reagents in presence of acetate anion and are represented as (IV- S-2).

IV (c-ii) Complexes formed in presence of chloride anion :

Complexes of Cu(II), Ni(II), Co(II) and Zn(II) with SADU were formed from dimethyl formamide solutions of reagents in presence of chloride anion and are represented as (IV- S-3).

IV (c-iii) Complexes formed in presence of sulphate anion:

Complexes of Cu(II), Ni(II), Co(II), Zn(II) and Mn(II) with SADU were formed from dimethyl formamide solutions of reagents in presence of sulphate anion and are represented as (IV- S-4).

IV (c-iv) Complexes of SADU :

We find that the presence of the anion such as sulphate, chloride or acetate has a definite influence on the reactivity of the resin. Thus, in presence of chloride or sulphate anion, substitution reaction takes place and a fraction of metal-valancy is satisfied by the resin. On the other hand in presence of acetate ion, substitution reaction is observed in case of Cu(II) and Co(II) wherein one of the metal-valancies is satisfied by the resin and addition reaction is observed in case of Ni(II), Zn(II) and Mn(II). In case of substitution reaction in presence of different anions, the extent of substitution increases in order

chloride : Ni $<$ Co, Cu, Zn.

sulphate : Mn, Co, Cu $<$ Ni, Zn

and in case of addition reaction, the extent of addition increases in order

Zn, Mn $<$ Ni

IV (d) Linear condensation product of salicylaldehyde with dimethylol urea (SDU) :

Salicylaldehyde was condensed with dimethylol urea. The product is represented as (IV- S-5). Condensation of salicylaldehyde with DU is relatively less, the molecular proportion being 1:2. Its degree of polymerisation is about 10. When thermolysed at 150-80°C, it loses water and its degree of polymerisation increases to about 40. Increased length of polymer chain is reflected in its increased temperature of decomposition and reduced solubility. IR absorption bands of SDU are recorded.

IV (e) Complexes of Cu(II), Ni(II), Co(II), Zn(II) and Mn(II) with SDU :

IV (e-i) Complexes formed in presence of acetate anion :

Complexes of Cu(II), Ni(II) and Co(II) with SDU were formed from dimethyl formamide solutions of reagents in presence of acetate anion and are represented (IV- S-6).

IV (e-ii) Complexes formed in presence of chloride anion:

Complexes of Cu(II), Ni(II), Co(II), Zn(II) and Mn(II) with SDU were formed from dimethyl formamide solutions of the reagents in presence of chloride ion and are represented as (IV- S-7).

IV (e-iii) Complexes formed in presence of sulphate anion:

Complexes of Cu(II), Ni(II) and Co(II) with SDU were formed from dimethyl formamide solutions of reagents in presence of sulphate ion and are represented as (VI-S-8).

IV (e-iv) Complexes of SDU :

We find that in case of SDU, substitution reaction is observed in presence of acetate, chloride or sulphate ions. Thus in presence of sulphate ion, both valencies of Cu, Ni and Co are satisfied by the polymer anion. In presence of acetate ion, substitution reaction takes place partly, wherein one of the metal-valancies is satisfied by the resin. On the other hand, in presence of chloride ion the behaviour is complex partial substitution is observed with Cu, partial substitution is followed by hydrolysis and oxobridge formation with Ni and complete substitution is observed with Mn, Co and Zn.

IV (f) Oxime of the linear condensation product of (SDU) : salicylaldehyde with dimethylol urea (SODU) :

Oxime of SDU is prepared from SDU and is represented as (IV-S-9). Its degree of polymerisation may be considered to be the same as of SDU.

IV (g) Complexes of Cu(II), Ni(II) and Co(II) with SODU formed in presence of acetate anion :

Cu(II), Ni(II) and Co(II) complexes of SODU were formed from dimethyl formamide solutions of the reagents in presence of acetate anion and are represented as (IV- S-10). We find that SODU behaves similar to SDU, i.e. substitution reaction takes place partly, wherein one of the metal-valancies of Cu, Ni or Co is satisfied by the polymer.

IV (h) Linear condensation product of 8-hydroxy quinoline and dimethylol urea (OQDU) :

8-Hydroxy quinoline was condensed with dimethylol urea. The product is represented as (IV- S-11).

IV (j) Complexes of Cu(II), Ni(II) and Co(II) with OQDU :

IV (j-i) Complexes in presence of acetate ion :

Complexes of Cu(II), Co(II) and Ni(II) with OQDU were formed from dimethyl formamide solutions of the reagents in presence of acetate anion and are represented as (IV- S-12).

IV (j-ii) Complexes in presence of sulphate of chloride ion:

Complexes of Cu(II), Ni(II) and Co(II) with OQDU were formed from dimethyl formamide solutions of the reagents in presence of chloride or sulphate ion and can be represented as (IV- S-12) without water molecules.

IV (j-iii) Complexes of OQDU :

We find that complete substitution reaction is observed, irrespective of the nature of the anion present.

IV (k) General :

The results have been generalised and presented in table IV. T-1. We find that the linear chelating polymer prepared from 8-hydroxyquinoline is quite similar to the chelating ligand in behaviour in monomeric and polymeric forms[36] and forms complexes with Cu(II), Ni(II) and Co(II) of the same structure irrespective of the nature of the anion used. The chelation with these metal ions introduces characteristic cross-linking of linear chains and hence the product will possess outstanding properties. Thus, they can have capacity to absorb ammonia and can be useful in waste-liquor treatment.

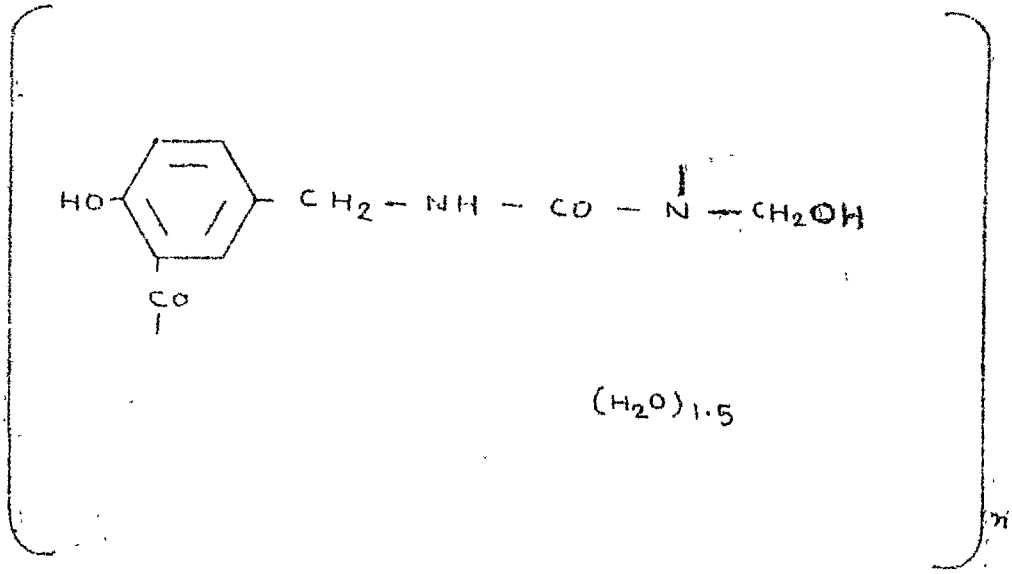
The chelating polymer prepared from salicylicaldehyde forms complexes with Cu(II), Ni(II) and Co(II), whose nature depends on the nature of anion used. Thus highly cross-linked metal-chelated polymer would be formed when prepared in presence of sulphate anion, whereas cross-linking through metal ion is considered to be absent when prepared in presence of acetate ion. In presence of chloride ion, the metal ions exhibit variation in behaviour and cross-linking through metal ion is considered to increase in order

Cu Ni Co

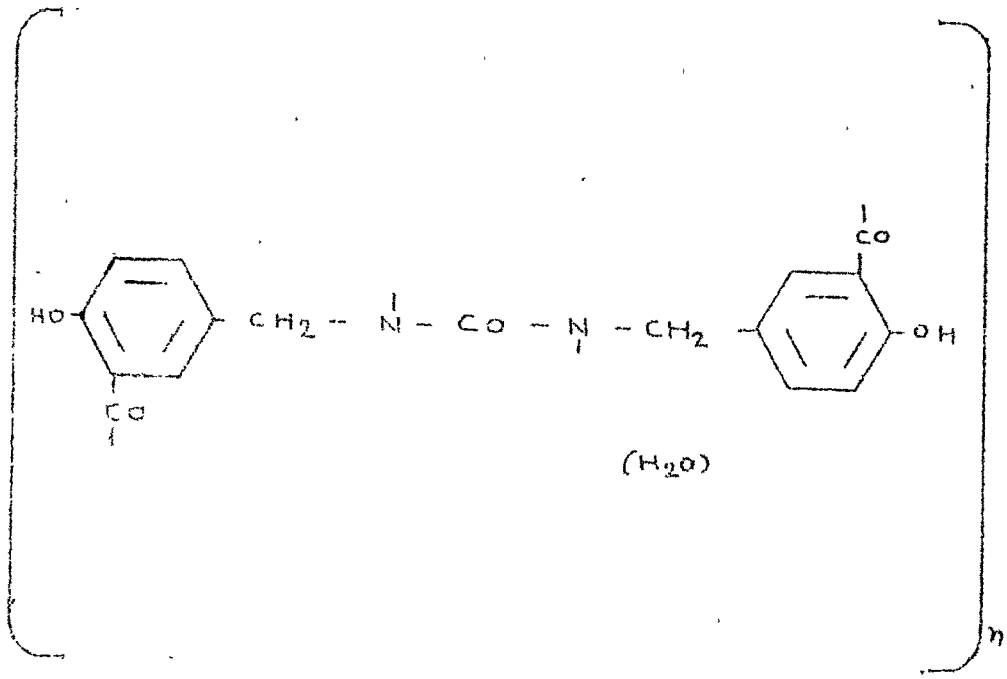
The chelating polymer prepared from salicylic acid forms complexes with transition metal ions, which do not exhibit cross-linking through metal ion, and whose nature depends on the nature of the anion used. Thus fractional

substitution of the acidic proton of the ligand is observed in presence of sulphate or chloride anion, while fractional addition of salt is observed in case of acetates of zinc, nickel and manganese and substitution in case of acetates of copper and cobalt. The formation of metal-chloro-complexes with the chelating resin CHELEX-100 has been observed recently.[87]

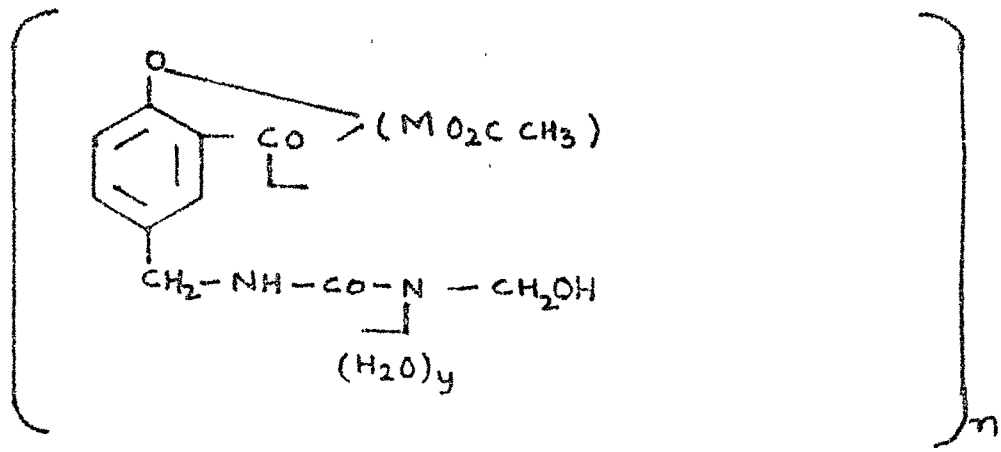
To our knowledge, the linear chelating polymers based on urea-formaldehyde resin reactions are reported for the first time. We consider that these chelating polymers can find some applications in the extraction of metal ions from various sources, and the chelated polymers for the extraction of amines.



IV- 5-1 (a)
SADU

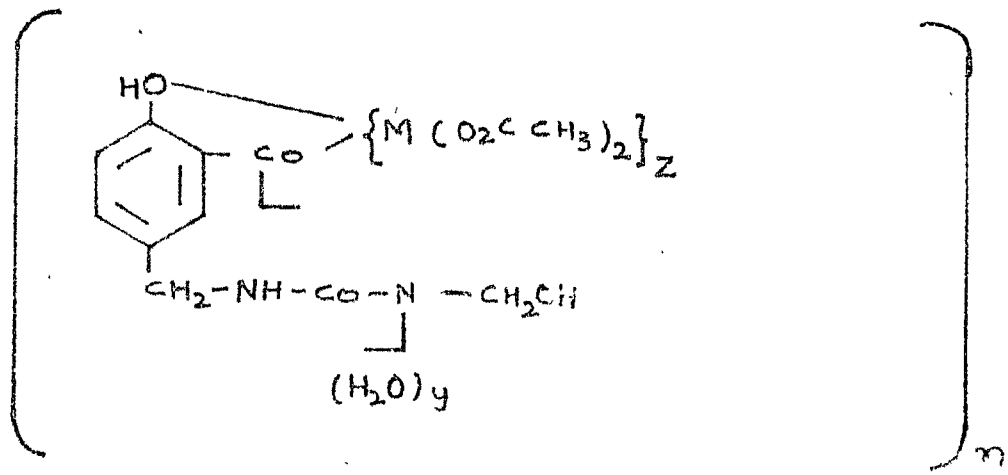


IV- 5- 1.(b)
SADU-Py



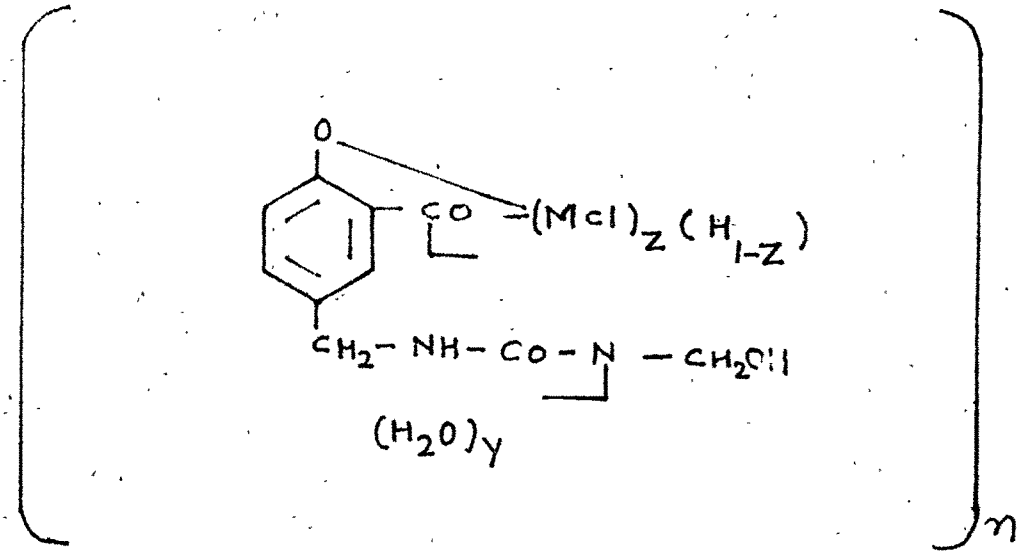
M =	Cu	Co
y =	4	3

IV - S - 2 (a)



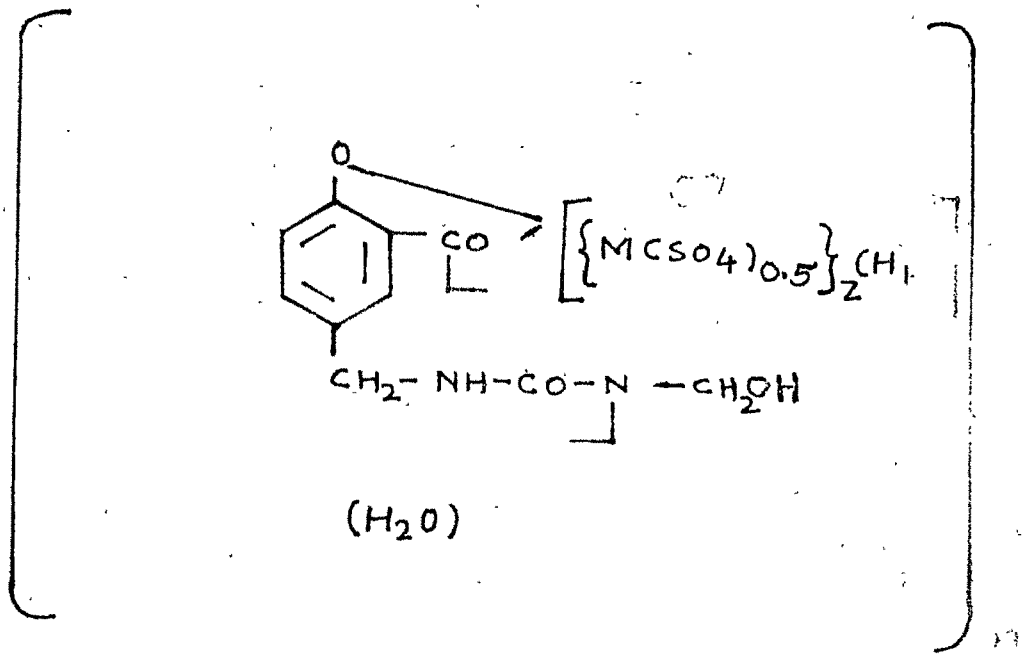
M =	Ni	Zn	Mn
y =	3	1	1
z =	0.75	0.5	0.5

IV - S - 2(b)



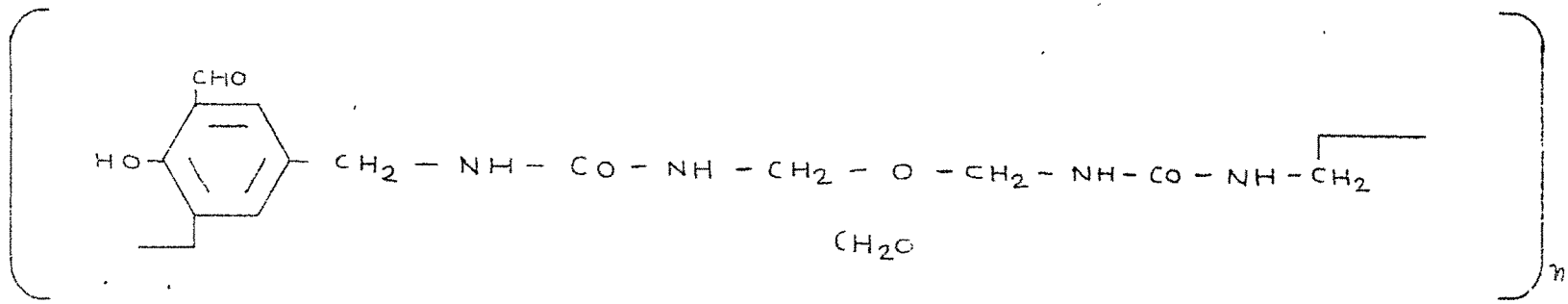
M	=	Cu	Ni	Co	Zn
Z	=	0.5	0.4	0.5	0.5
Y	=	2	2	1	2

IV - S - 3

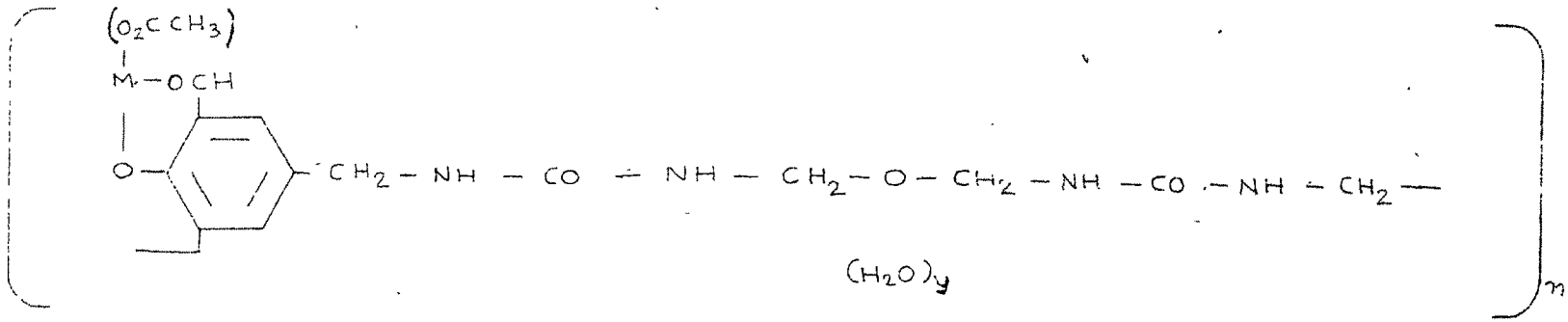


M =	Cu	Ni	Co	Zn	Mn
Z =	0.4	0.5	0.4	0.5	0.4

IV - 5 - 4.

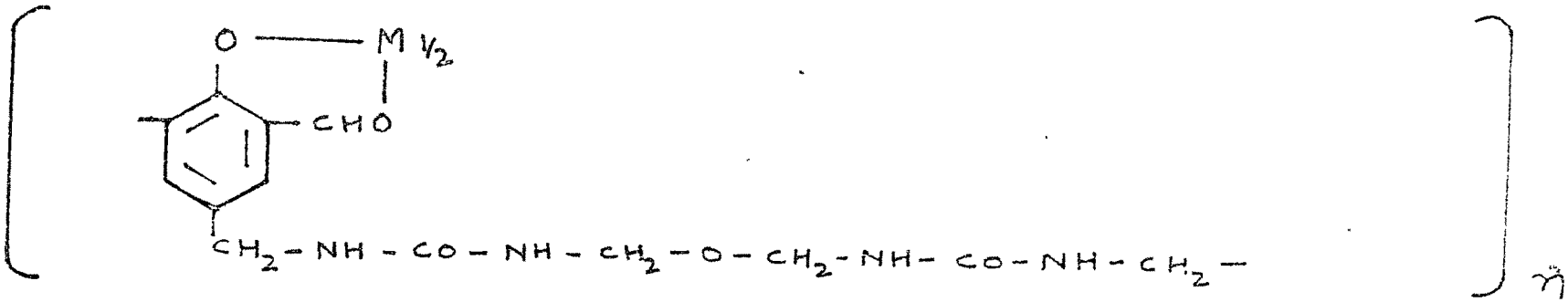


IV-5-5
SDU

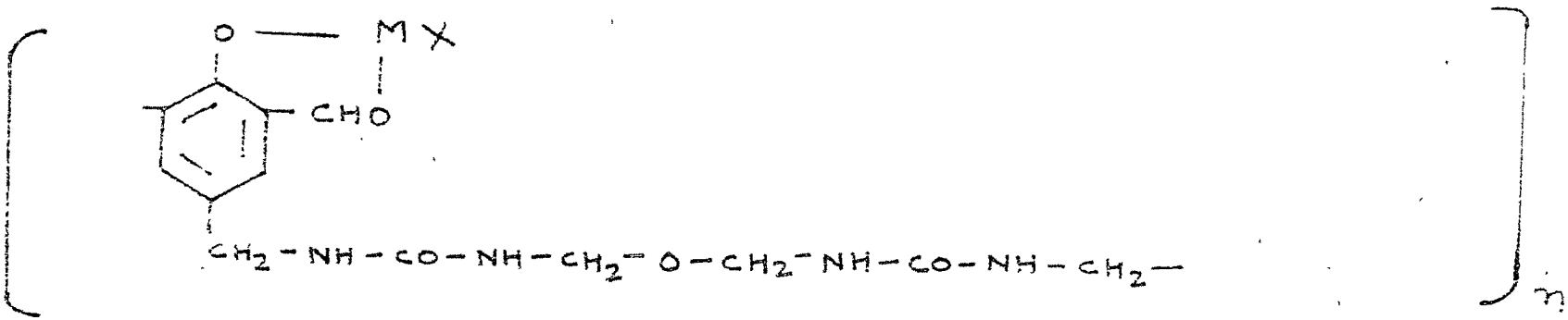


IV-5-6

M = Cu Ni Co
Y = 2 1 6

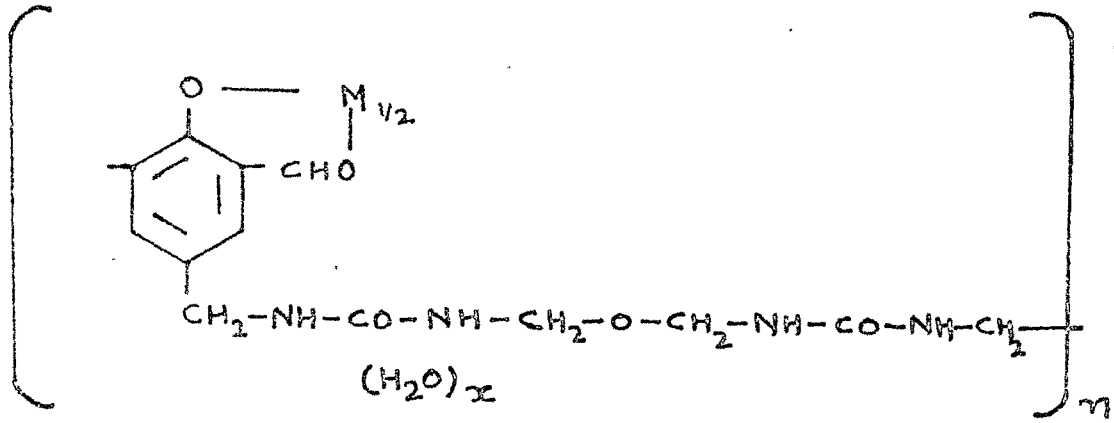


M = Co Zn Mn



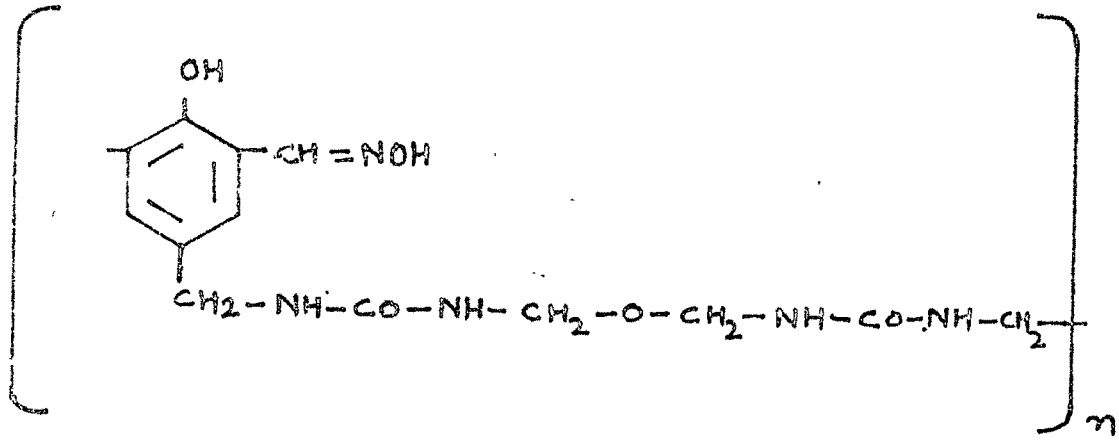
M = Cu Ni
X = Cl O ½

IV - S - 7

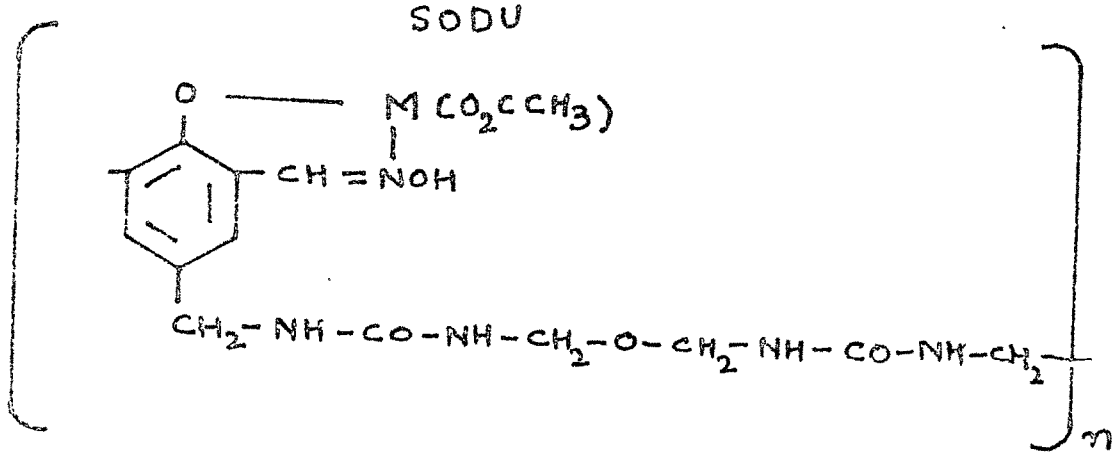


M = Cu Ni Co
x = 2 1 0

IV-S-8

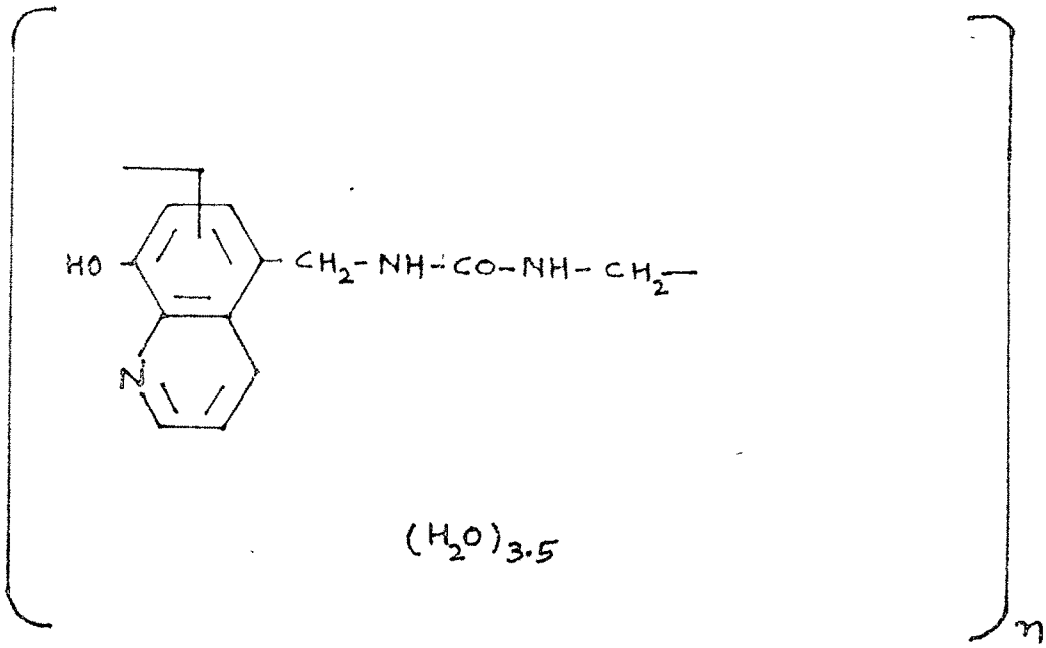


IV-S-9
SODU

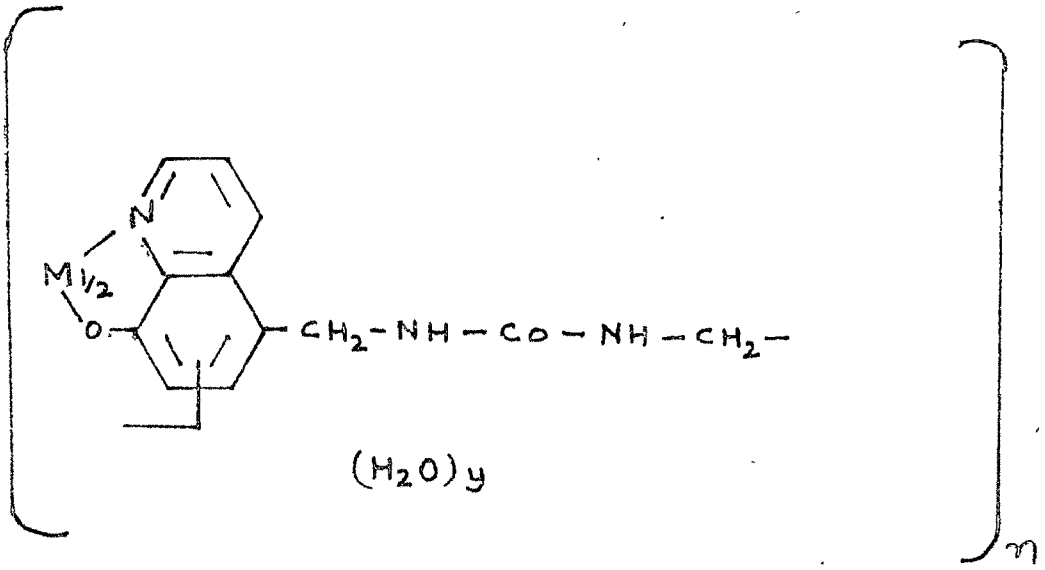


M = Cu Ni Co

IV-S-10



IV - S - 11



M =	Cu	Ni	Co
Z =	0.5	0.5	0.75
y =	2	1	2

IV - S - 12

Table V.- T-1

Reagent	metal ion				
	Mn	Co	Ni	Cu	Zn
1.	2.	3.	4.	5.	6.
		anion - Ac			
SADU	a*	p	a*	p	a*
SDU		p	p	p	
SODU		p	p	p	
OQDU		s	s	s	
		anion - Cl			
SADU		p*	p*	p*	p*
SDU	s	s	s≠	p	s
OQDU			s		
		anion - SO_4			
SADU	p*	p*	p*	p*	p*
SDU		s	s	s	
OQDU		s		s	

a = addition of salt to reagent
p = p. subst. of anion of salt by reagent anion
s = substitution of anion of salt by reagent anion
* = fractional
≠ = hydrolysis and dehydration

CHELATING POLYMERS

A : LINEAR CONDENSATION POLYMERS

V REFERENCES

CHELATING POLYMERS

A: LINEAR CONDENSATION POLYMERS

V REFERENCES

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