CHAPTER - I

INTRODUCTION

Partial review of N and/or O and S chelators, physical methods used in the characterisation and the background of the present work.

1. Introduction :

A. *The Principles and Progress in Coordination Compounds :*

In inorganic chemistry renaissance finally arrived during 1940's and since then there has been great activity in all branches of science particularly in the chemistry[1]. In 1892 Prof. Alfred Werner discovered the first coordination compound, since then the sky kissing achievements particularly in the chemical sciences is worldwide accepted and rewarded till now by five Nobel Prizes : 1913, A. Werner; 1967, M. Eigen; 1973, G. Wilkinson and K. Fischer; 1983, H. Taube; 1987, D.J. Cram, L.M. Lehn, and C.J. Pederson. In broad context this field may be viewed as comprised of (1) principles and theoretical, often hypothetical relationships, (2) an experimental base and techniques for manipulations, and (3) the chemical content, classification based on ligand and enormous data base of specific informations included stoichiometry, colour and physical properties[2]. The field is divided into many branches and separately they are expanding. The main branches are bioinorganic chemistry, organometallics, homogeneous catalysis, solid state chemistry, extended mesoscopic materials, photonic materials, models for solid surfaces, separation sciences, molecular electronics, dying and photography, reactions and mechanisms and radiopharmacy.

Synthesis of compounds is the first and foremost phase of each branch. New procedures for the synthesis of inorganic complexes have made it possible to prepare several new types of compounds. The available methods are (i) direct synthesis by condensation, dehydration, substitution, elimination etc.; (ii) the template method of forming multidentate, cyclic, macrocyclic molecules; (iii) reactions of coordinated ligands[1,3].

The great growth of interest in the role of metal ions in biological processes has stimulated work in bioinorganic chemistry[4]. Coordination compounds of many of the metals involved in life processes: gold and its compounds for arth-ritis, platinum compounds for cancer, Fe(II) plays the key role in haemoglobin to transport oxygen in blood[5]. In nitrogenase[6] Mo-S-Fe bonds have been found and in DNA polymerase[7] the formation of Zn-O bonds is important. In anti-tumour therapy[8], the cure depends on the formation of Pt-N and Pt-O bonds; in the treatment of Willson's disease[9] removal of excess copper depends on the formation of both Cu-N and Cu-O bonds, In photosynthesis the main role is played by manganese and various redox cycles are constituted by organic and inorganic redox active agents[10]. Still many others are ingested inadvertently and cause disease e.g. mercury, cadmium etc.

Organometallics is one of the important branch in catalysis, solid state studies and material research. The processes are important in solving the activation of C-H bonds by metal ions particularly by transition metal compounds[11]. In the intramolecular activation of C-H bonds the complexes can be regarded as 'frozen' intermediate in metal catalysed chemical reactions and is valuable source of information about the mechanism of catalytic processes[12]. Their applications in organic synthesis[13], resolution of chiral substrate[14], to prepare compounds of liquid crystal properties[15], catalyst for hydrogenation[16] etc. are widely known.

For the industrial importance high temperature plastic polymers have come into light from late 1950's and early 1960's by using metal ions. Some coordination compounds have been used as dyes and pigments, metallted azo dyes are common in textile industry[17].

Complex formation plays an important role in analytical chemistry[18] whether the aim is to detect or determine or separate one particular species applying classical methods like gravimetry, titrimetry, liquid-liquid extraction, ion exchange through resin bed etc. or instrumental methods e.g. spectrophotometry, electroanalytical methods, chromatography etc.

2. Two constituents :

The coordination chemistry has been focused on the concept of a monoatomic, cationic central atom bound to Lewis bases called ligands. It has been a cation core focused model.

Metal ions and the ligands are inseparable constituents of the coordination compounds. Properties of metal ions change on coordination and in the same way the metal ion also changes the properties of coordinated ligands. Over the years, the coordination polyhedron has come to be recognised as the unifying concept of coordination chemistry and the species of significance is best phrased as coordination entity. The traditional coordination entity has a central (metal) atom, a number of ligands, a coordination number and a polyhedral structure. Most of the recent development in the coordination chemistry are based on the complexation reaction of the metal ion with various ligands.

A. ***About the ligands :***

Design oriented coordination chemistry generally view a chelating ligand[19] as a collection of adjustable components; the donor atoms and their intrinsic basicities, the donor functional groups and their spatial orientation and electronic, steric properties, chelate rings and their sizes, stuctures-strains relationship to each other, the substituents and their electronic steric effects, acyclic or macrocyclic etc. Ligand design[20] can be viewed as the process by which the components are varied either for curiosities sake or to control the properties of targeted system.

There is also a question of stability of the complexes both in solution and solid phase. There are many factors[21] which influence complex formation in solution viz. basicity of donor atom(s) which has been included in ligand design, covalent tendency of metal ion, charge neutralisation, increase in translational entropy which is known as chelate effect, steric effects and preorganisation of ligand which decreases solvation energies, dipole-dipole interactions etc.

Since the discovery of metal chelates in the late 19th century[1,21] a major developments in the coordination chemistry of transition or non-transition elements towards chelate complexes have been made. Unusual stability of the chelate complexes has led to synthesize of uncommon types, coordination and structures, stabilities those provide reactivities towards challenging areas[21,3(b)].

The donor centre selections is more or less driven by the nature of metal ions used in the complexation process. Usually HSAB principle provides the preliminary guideline[22]; class a metal ions prefer hard donor/class(a) bases and class(b) metal ions use class b bases. Design of ligands with properly adjustable donor centres having chelating ability with definite spatial or stereochemical arrangement insist the donor centres to intercast combination[23]. The activity of the metal centre as well as the ligating side is thus beautifully controlled.

Information relating to coordination compounds of transition metals with some bidentate or polydentate N and/or O or S chelators are presented in the tabular form. These ligand systems have received great attention at present time. There is an enormous amount of information with these donor systems and primary data are available from Comprehensive Coordination Chemistry[1]. Herein we have collected informations for the last five years from the Journals of Inorganic Chemistry of International repute(Table-I.1).

B. ***About the metal ions :***

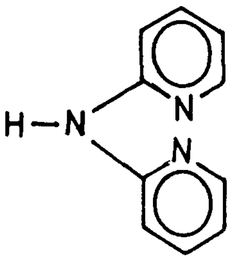
It is worthwhile mentioning that properties of d-block transition metal ions are quite sensitive to the number and arrangement of the d-electrons present. This number and arrangement are fully monitored by the ligand field symmetry and its strength[24]. In contrast, the f-orbital in lanthanides are deeply buried and the electrons are screened by the overlying shells(5s,5p) of electrons; therefore reciprocal interactions of the f-electrons and the surroundings of the ion are of relatively little chemical significance[3(b)]. The phenomena are remarkably different in actinides as they exist in great variety of oxidation states, while for the lanthanides 3+ oxidation state is the most common. The difference from the lanthanide chemistry is usually attributed to the contribution of covalent bonds involving 5f-electrons. The variety in the oxidation states pertains especially to the first half of the actinide group where the 5s, 6d, 7s and 7p orbitals (especially for Uranium to americium) can be involved in bonding. This situation is indicated by the fact that the actinides are much more prone to complex formation than the lanthanides.

The f-block metal ions generally present at very high coordination numbers particularly in actinides. The coordination number of less than six is discouraged by the size of metals. The hexa-coordination is usually found for actinides in their highest oxidation states, which correspond to a minimum ionic radius; hepta, octa and nona-coordination are common. Obviously the type of polyhedron obtainable is influenced by the nature of the ligand and the spatial arrangement of the donor centres[25(a)].

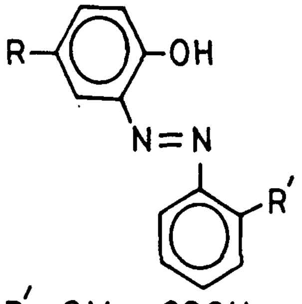
3. Present Work :

The work embodied in this thesis are divided into two parts.
The coordination chemistry of transition metals of some selected ligands will be described on the known background of the field delineated above. The ligands are N,N; O,O; O,N,O; N,S and O,N,S donor types. Majority of the work is due to f-block elements. UO_2-S coordination chemistry is explored. The complexes of lanthanides and uranium(VI) are described for N,N-chelating

Present work consists of the following ligands and resin :

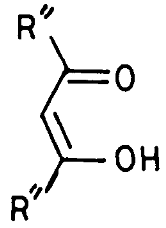


(NN)



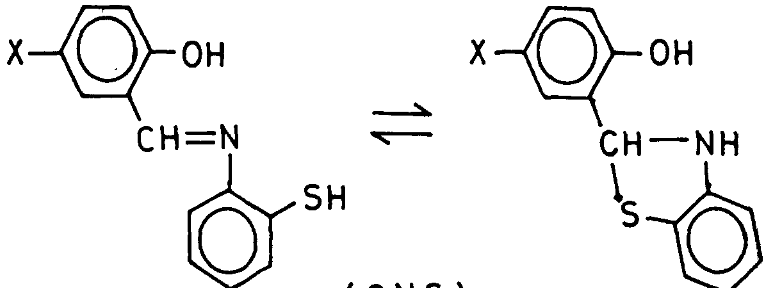
R′ = OMe, COOH

(ONO)



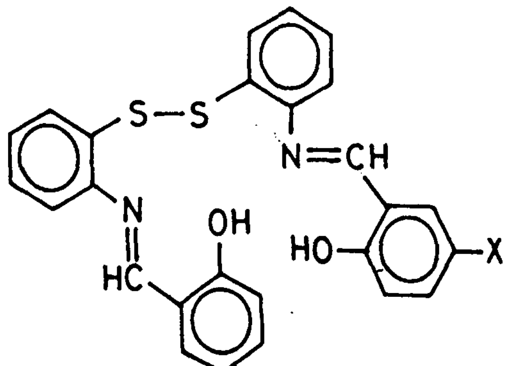
R = Me, Ph

(OO)

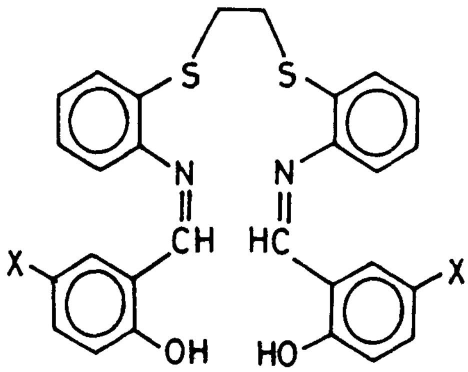


(ONS)

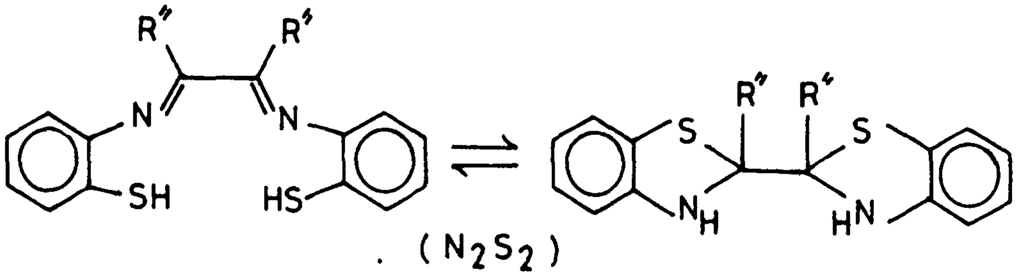
X = Cl, H



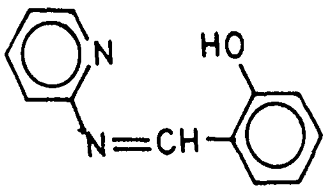
(ONSNO)



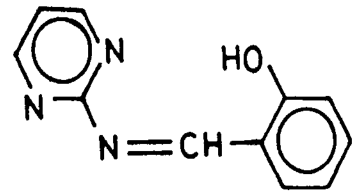
(ONSSNO)



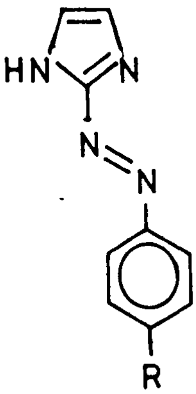
(N_2S_2)



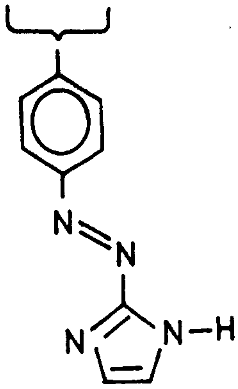
or



(NO)



(NN)



(Resin)

ligand dipyridylamine. Acetylacetonato complexes of UO_2(VI) are known, but its hetrocyclic adducts remain unknown and herein we describe synthesis and spectroscopic characterisation of adducts of hetrocyclic bases of $UO_2(acac)_2$. Uranyl complexes of ONS, NS, **O N** donor types ligands and their peroxo derivatives are critically examined. Some of the cobalt(II) complexes exhibit electrochemical responses.

In the second part, the chemistry of N,N-chelating ligand, 2-arylazoimidazoles of some transition and non-transition elements are described followed by the synthesis of new resin in which imidazolylazo group is anchord into a polymeric matrix; the presence of pyrrolic N(I)-H provide a soft donor centre and can immediately bind soft metal like Hg(II), Ag(I). The physical property of the resin is fully established and its Hg(II) and Ag(I) exchange capacity are tested radiometrically.

4. Physical Methods :

A. ***Elemental analyses*** : The elemental analyses were carried out on Perkin Elmer model 240C elemental analyser and metal analyses by standard procedure[25(b)].

B. *Conductance studies* : The conductances are meas from Phillips conductivity bridge (model PR 9500) and by u: also Systronics 304 conductivity metre.

C. *Infrared spectra* : The Infrared (IR) spectra were recorded in KBr disc on a Perkin Elmer 783, 883 and Shimadzu IR-408 Spectrophotometer.

D. *UV - VIS spectra* : The UV-VIS spectral data were recorded on Hitachi 330 and Schimadzu UV-160A spectrophotometer.

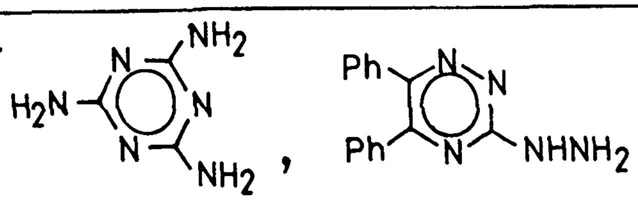
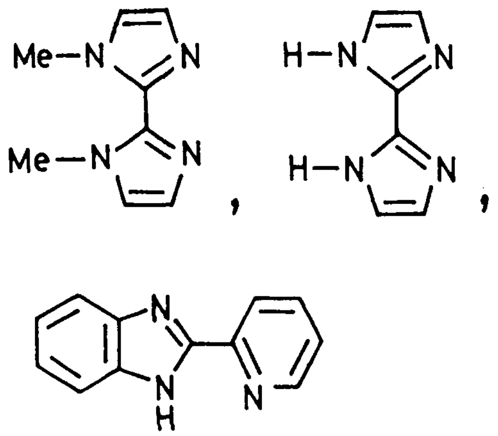
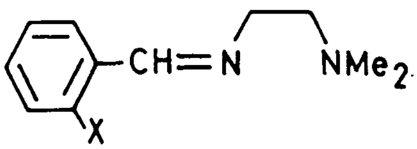
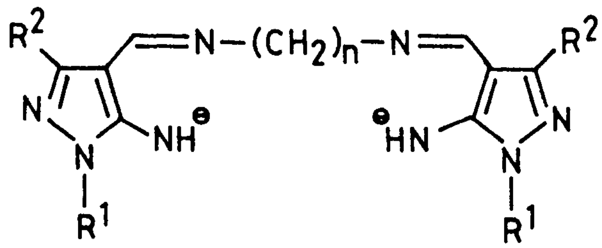
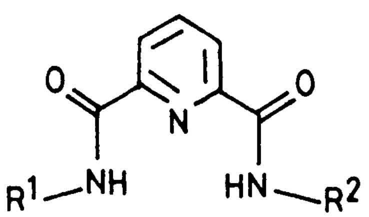
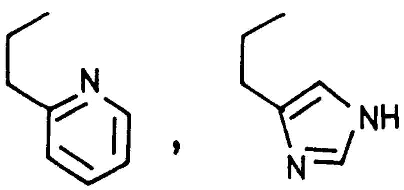
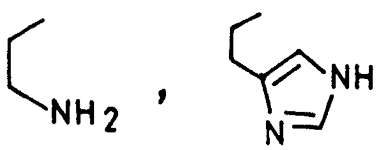
E. *^{1}H NMR spectra* : ^{1}H NMR spectral data were collected in different solvents $CDCl_3$, DMSO-d6 (wherever it is necessary) using Varian XL200 MHz, Bruker 300-MHz; JEOL, JNM, GX270 and JEOL 100-MHz FT NMR spectrometers.

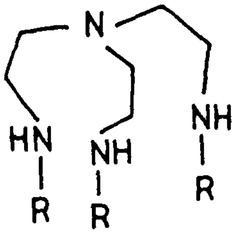
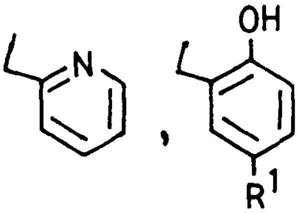
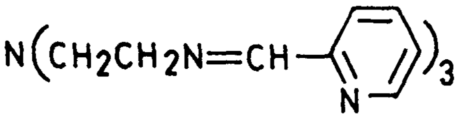
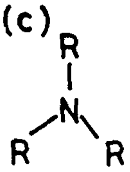
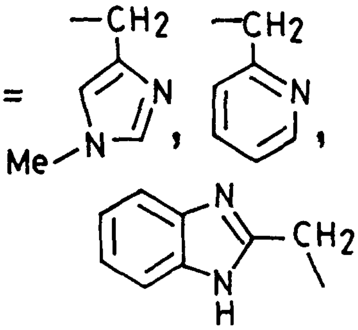
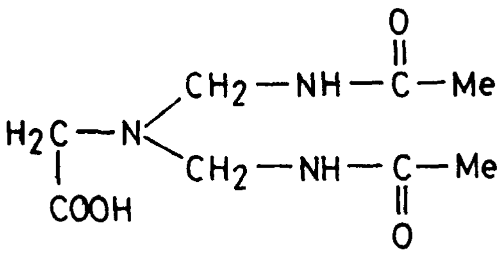
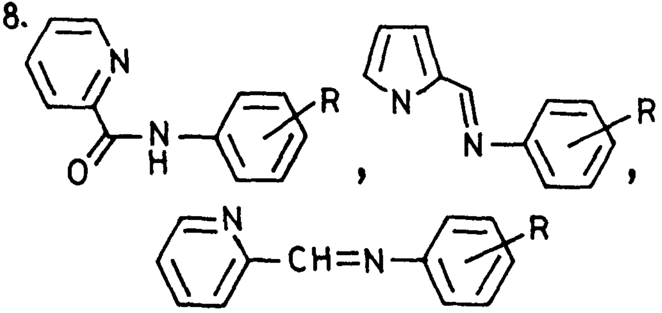
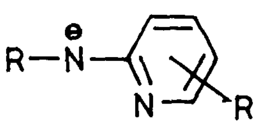
F. *Thermal analyses* : Thermoanalytical data were obtained using Shimadzu TG50/DT50, DT30 and DT40 thermal analyser.

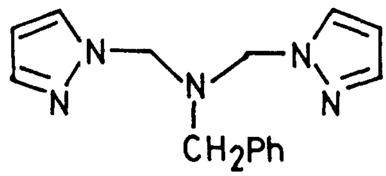
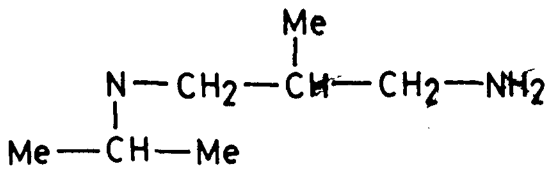
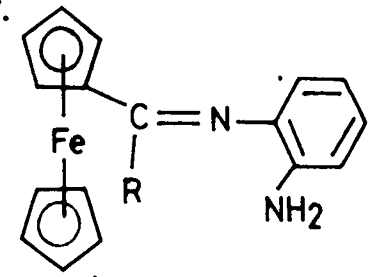
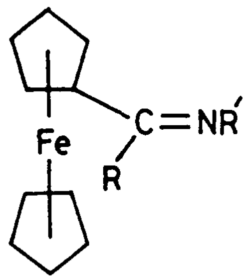
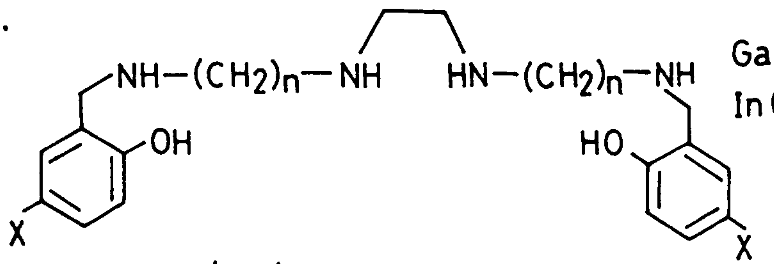
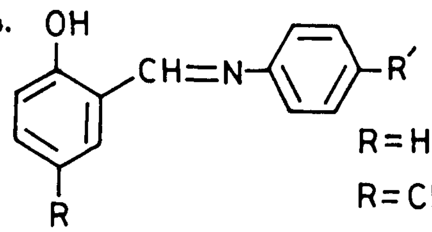
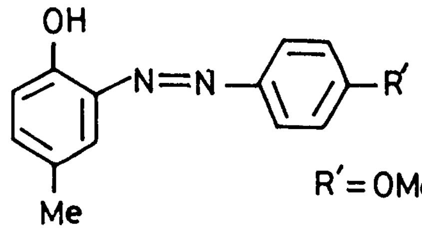
G. *Magnetic susceptibility* : The magnetic susceptibilities were measured on a PAR 155 vibrating sample magnetometer.

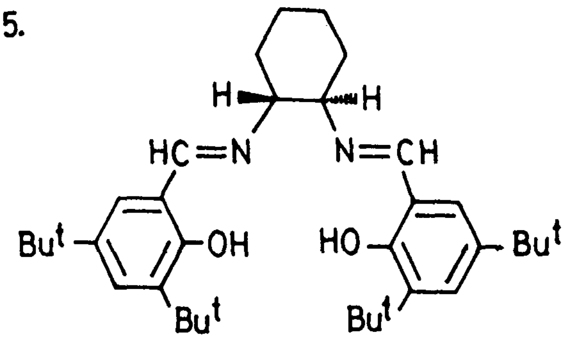
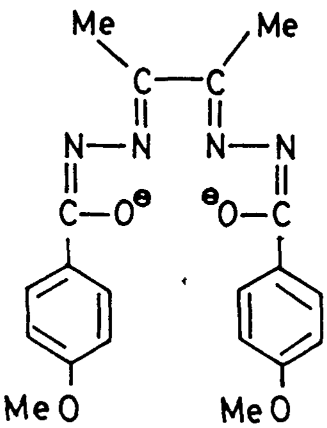
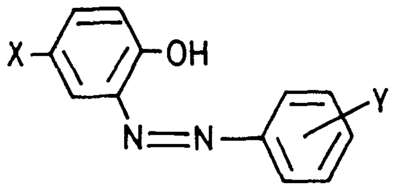
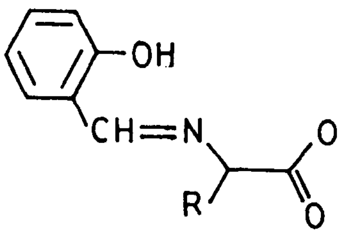
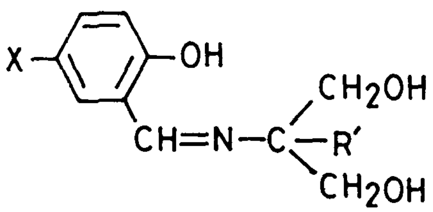
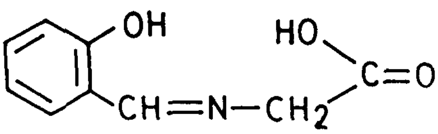
H. *Electrochemical studies* : The electrochemical studies were carried out with the help of PAR Model 370-A electrochemistry system, Model 174A polarographic analyser, Model 175 Universal programmer, Model REOO 74XY recorder, Model 377 A cell system under nitrogen atmosphere in a three electrode system using planar Beckman Model 39273 platinum as working electrode referenced to the saturated calomel electrode at 298K. For coulometry, a platinum wire-gauge working electrode was used.

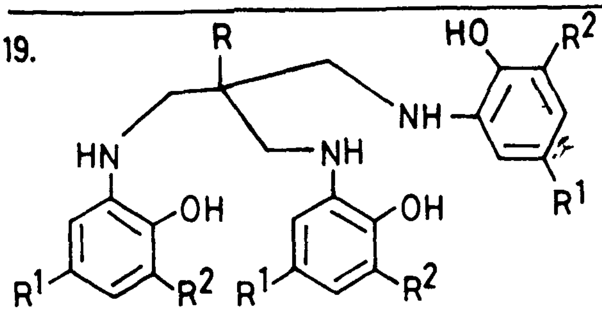
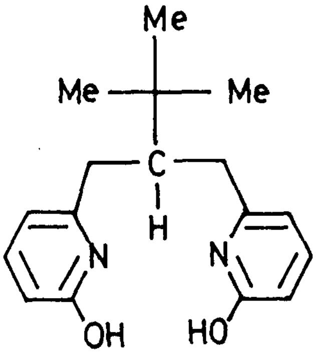
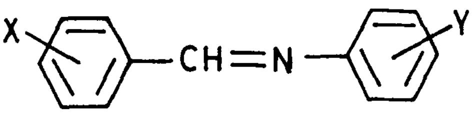
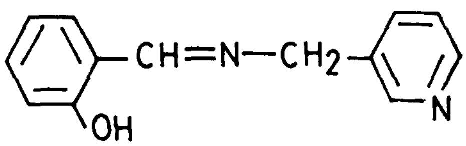
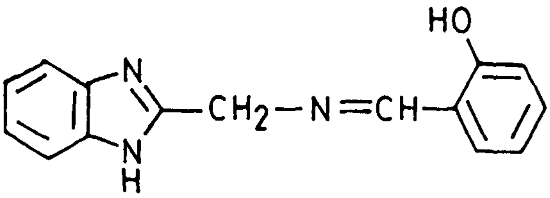
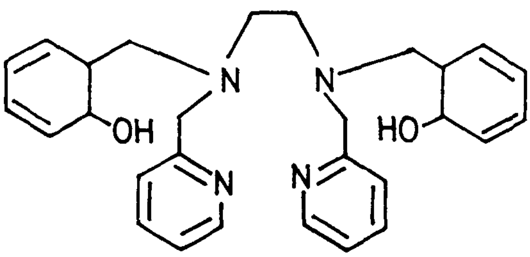
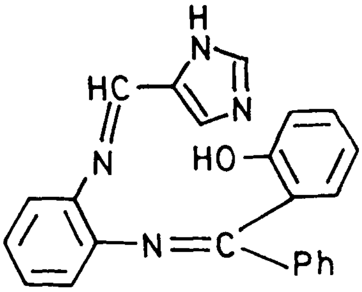
Table - I.1

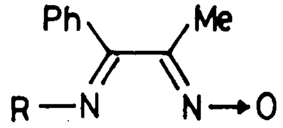
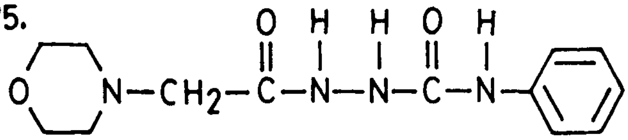
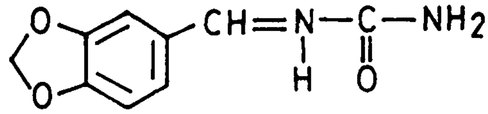
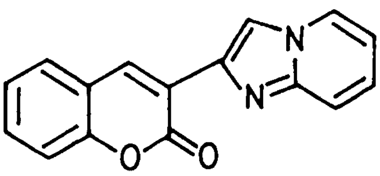
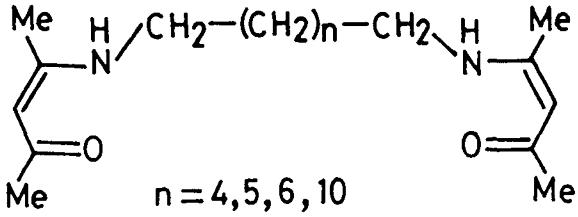
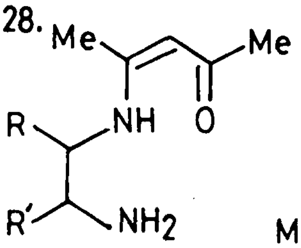
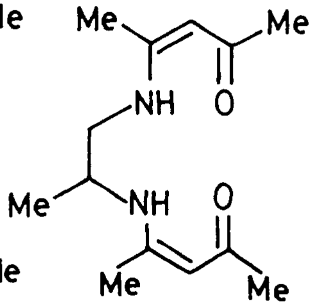
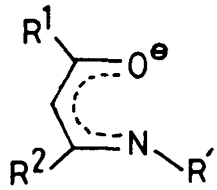
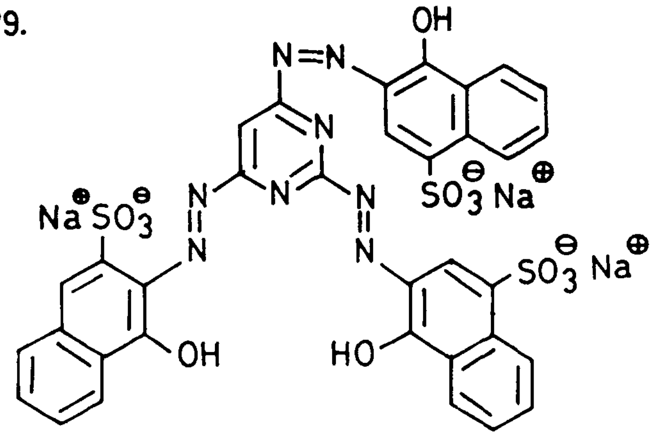
Ligands	Metal ions	References
1.  and similar types.	Cu(II)	26
2. 	Pt(II), UO_2(VI)	27
3. 	Pt(II)	28
4.  $n = 2-4$, $R^1 = Me/Ph$, $R^2 = Ph$	Cu(II) Ni(II)	29
5.  $R^1 =$  $R^2 =$ 	Cu(II)	30

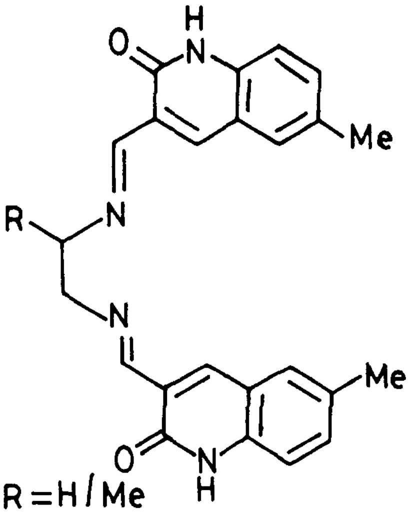
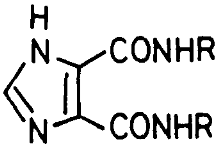
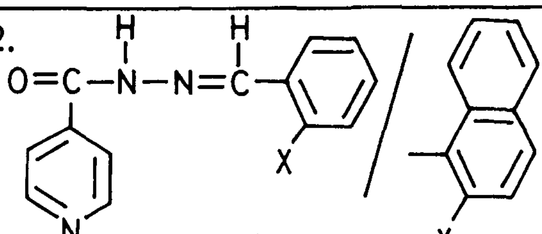
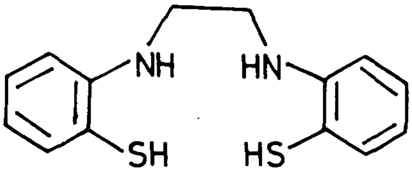
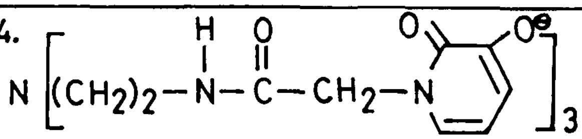
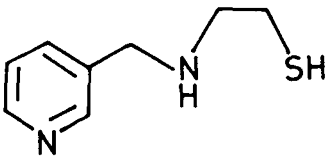
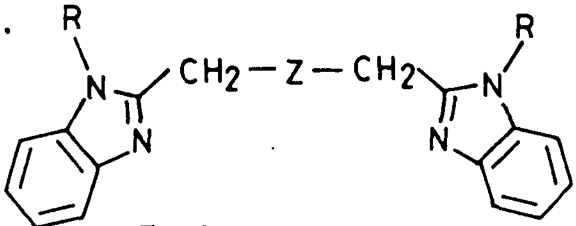
Ligands	Metal ions	References
6.(a)  R = 	Mn(II) Ga(III) In(III)	31
(b) 	Cu(I) Cu(II)	
(c)  R = 	Cu(II) Mn(II)	
7. 	Zn(II), Ni(II) Cu(II), Co(II)	32
8. 	Ru(III) Re(III)/(IV) Co(II)/(III)	33
9.  R = Me/Ph	Ti(III)	34

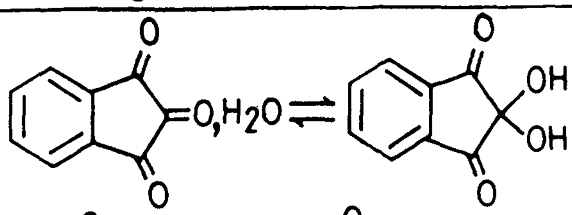
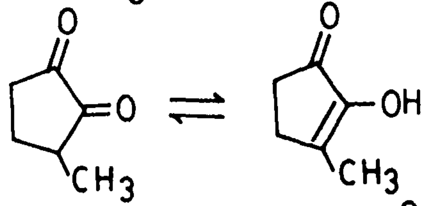
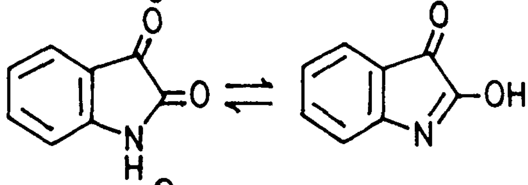
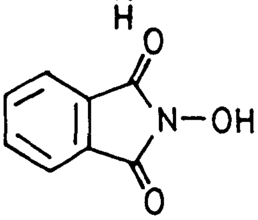
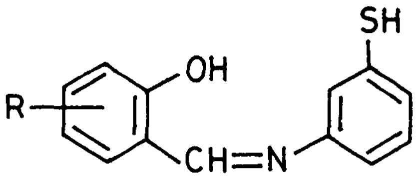
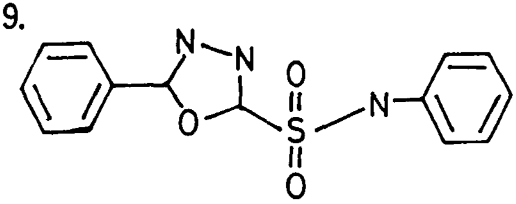
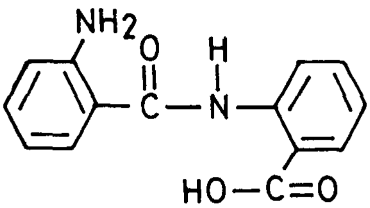
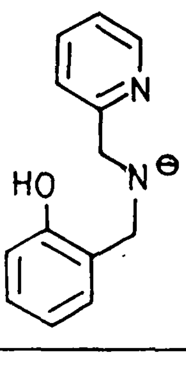
Ligands	Metal ions	References
10. 	Cu(I), Fe(II), Zn(II), Co(II), Ni(II)	35
11. 	Ni(II)	36
12.  ,  R = H/Me , R′ = o-C_6H_4OH / o-C_6H_4COOH	Cu(II) Co(II)/(III) Ni(II)	37
13.  X = H / Cl / Br; n = 2 and 3	Ga(III) In(III)	38
14.  R = H, R′ = OMe / Me / Cl / H; R = CH_3, R′ = H  R′ = OMe / Me / Cl / H	Ru(II)	39

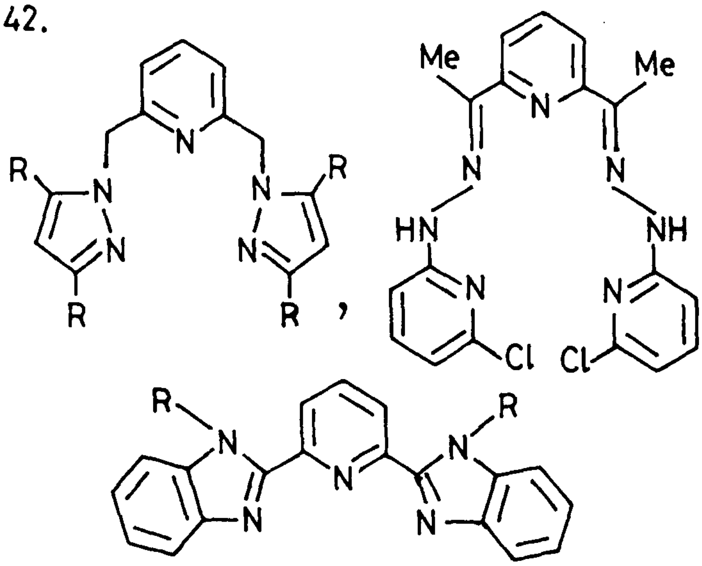
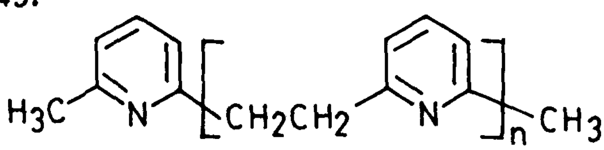
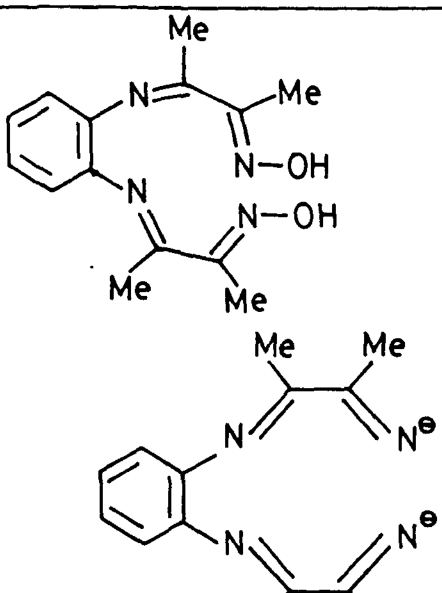
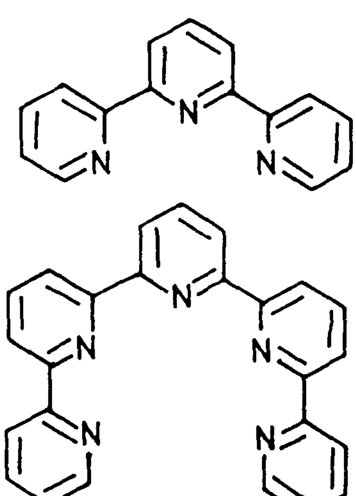
Ligands	Metal ions	References
15. 	Co(II) Ru(III)	40
16. 	Co(II)/(III)	41
17.  X = Me/Cl, Y = 4-Me	Rh(III)	42
18.  R=H/Me/$CHMe_2$/CH_2Ph  	VO^{2+} Cu(II) Mo(VI)	43

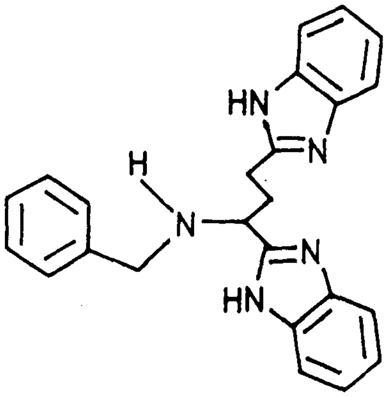
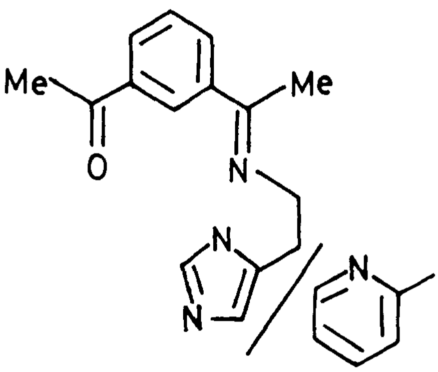
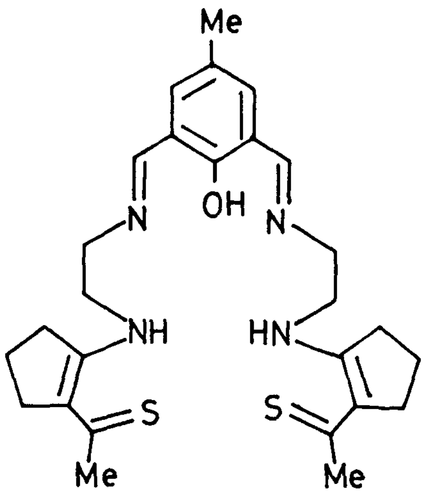
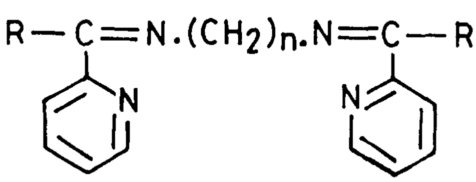
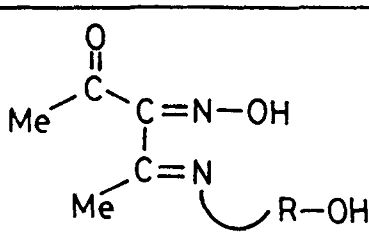
Ligands	Metal ions	References
19.  	Ga(III) In(III) Ln(III)	31b, 44
20.  	Pt(II)	45
21. 	Cu(II)	46
22. 	Ru(II)	47
23. 	Ni(II) Fe(II)	48

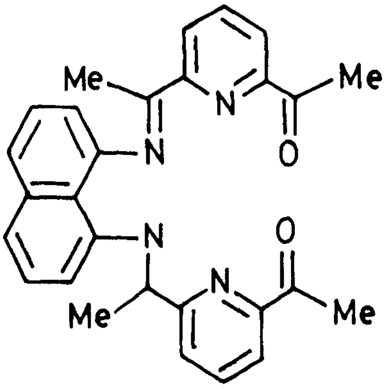
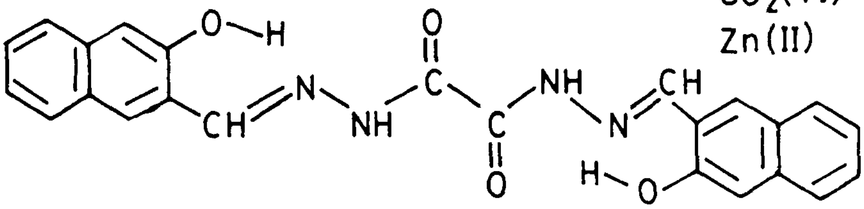
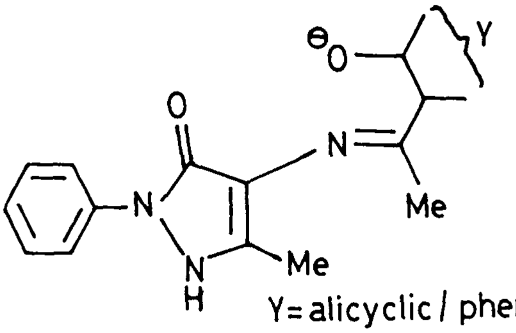
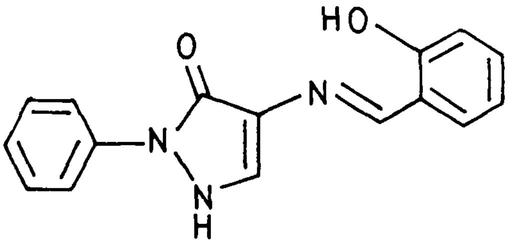
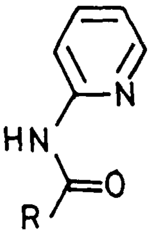
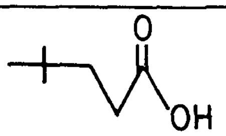
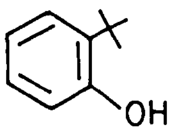
Ligands	Metal Ions	References
24. 	Ni(II) Cu(II)	49
25.  	Fe(III), Co(II) Th(IV), Ni(II) Cu(II), Si(IV) Cd(II), UO_2(VI)	50
26. 	Cu(II), Ni(II) Co(II), Zn(II) Cd(II), VO(IV)	51
27.  n = 4, 5, 6, 10	Cu(II), Zn(II)	52
28.   R = H/Me, R′ = H/Me  R′ = alkyl/aryl group R^1 = Me R^2 = Ph/Me	Ni(II) Cu(II)	53
29. 	In(III)	54

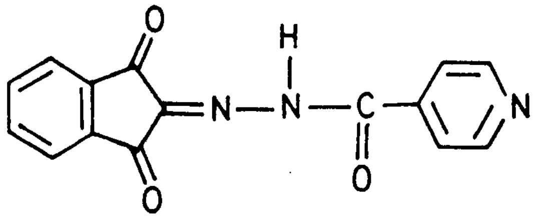
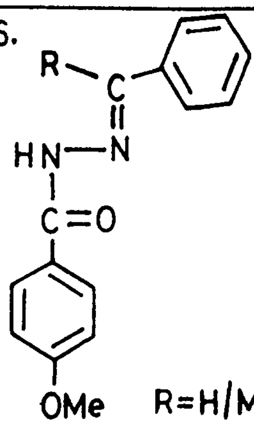
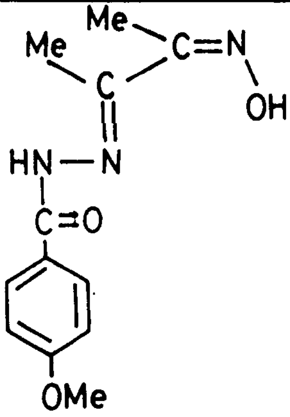
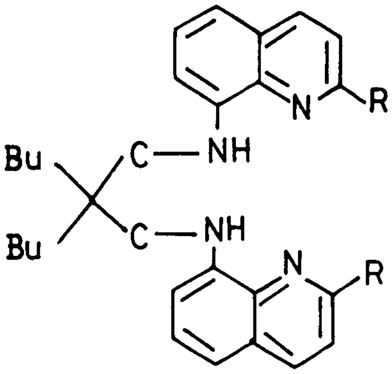
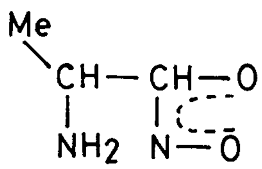
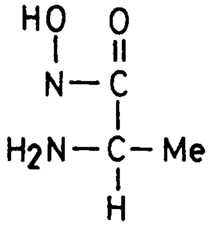
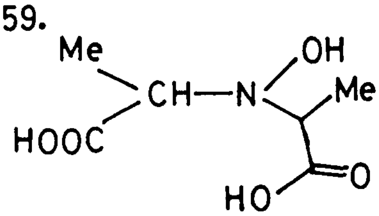
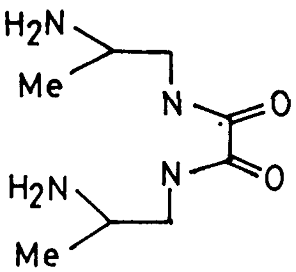
	Ligands	Metal ions	References
30.	 R = H / Me	Ni(II) UO_2(VI)	55
31.		Cu(II) Ni(II)	56
32.	 X = H / OH	Th(IV) UO_2(VI)	57
33.		ReO(V) TcO(V)	58
34.		Fe(III)	59
35.		Zn(II)	60
36.	 Z = O, R = H Z = S, R = H	Fe(III)	61

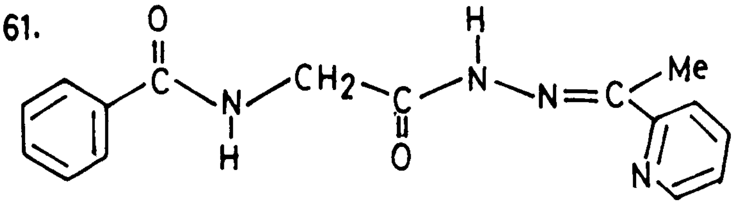
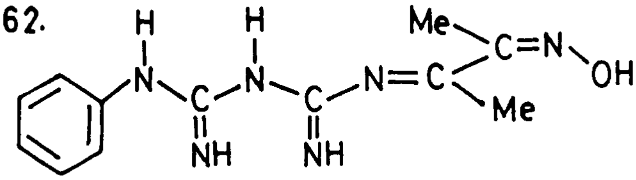
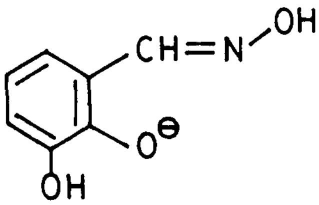
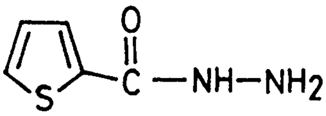
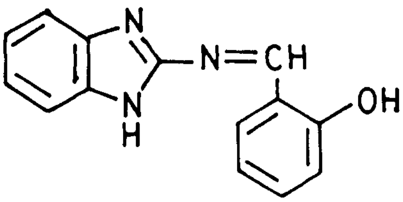
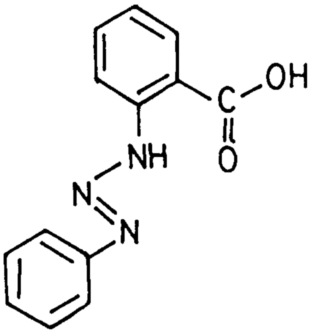
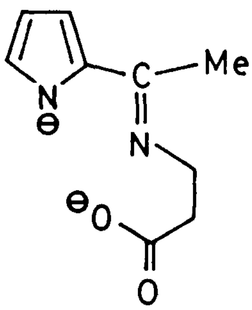
Ligands	Metal ions	References
37. (a)  (b)  (c)  (d) 	Fe(II)	62
38.  R = H / 5-Cl / 5-Br / 5-NO_2 / 5,6-Benzo	Zr(IV)	63
39.  and hydrazine derivative	Mn(II), Fe(II) Co(II), Ni(II) Cu(II), Zn(II)	64
40. 	Fe(II), Co(II) Ni(II), Cu(II) Ru(II/III), Rh(III) Pd(II)	65
41. 	Zn(II)	66

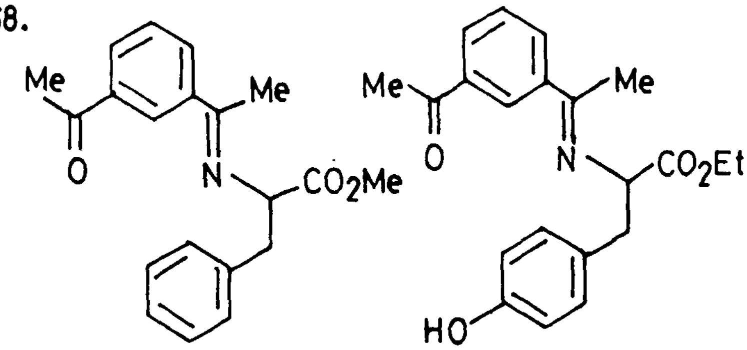
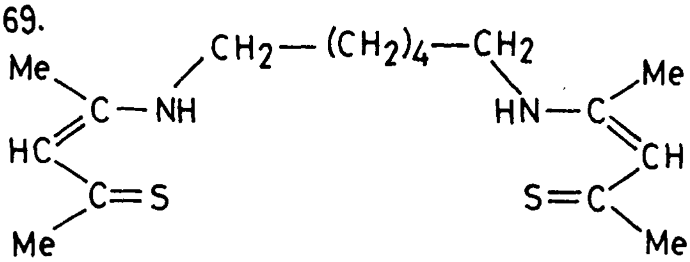
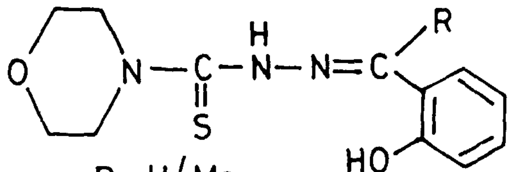
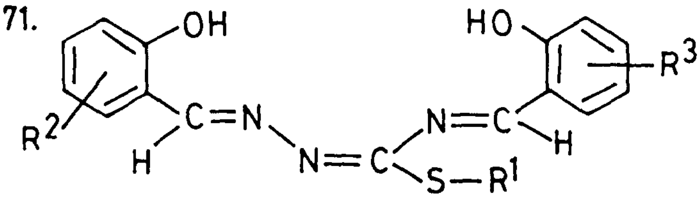
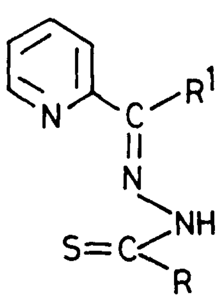
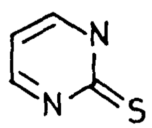
Ligands	Metal ions	References
42. 	Ni(II) Co(II) Ag(I)	67
43.  n = 1, 2, 3	Cu(I), Co(II) Zn(II)	68
44. 	Co(III) Cu(II)	69
45. 	Mg(II) Ag(I)	70

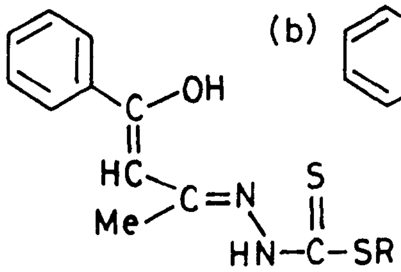
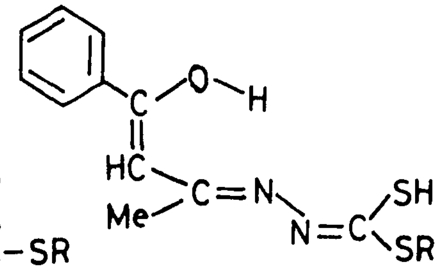
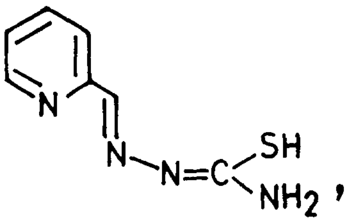
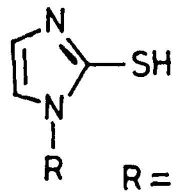
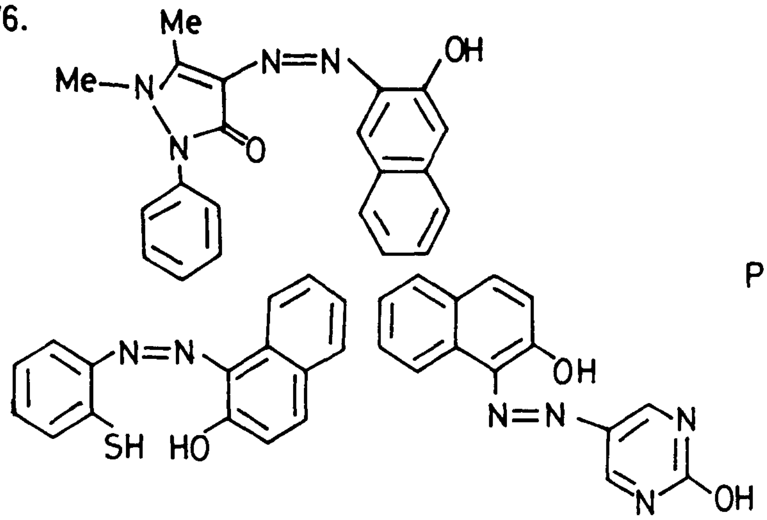
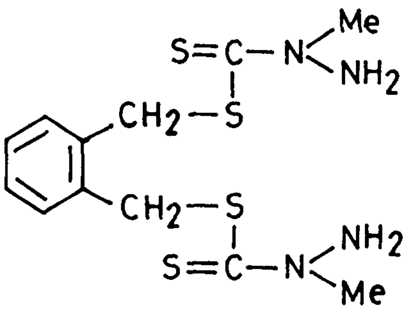
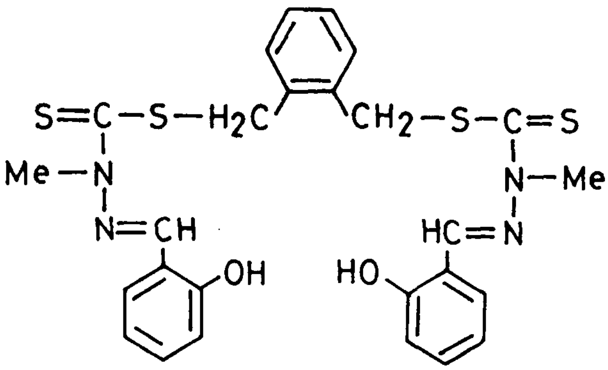
Ligands	Metal ions	References
46. 	Fe(II) Cu(II)	71
47. 	Cu(II)	72
48. 	Co(II) Ni(II) Zn(II) Cu(II)	73
49. 	UO_2(VI)	74
50.  R= $-C_6H_4-$/$-(CH_2)_2-$	Ni(II),Cu(II)	75

Ligands	Metal ions	References
51. 	Ca(II) Ba(II) Sr(II)	76
52. 	UO_2(VI) Zn(II)	77
53.  Y= alicyclic / phenyl 	Cu(II) Ni(II)	78
54.  R=  / 	Co(II)	79

Ligands	Metal ions	References
55. 	Cr(III), Co(II) Ni(II), Cu(II) Mo(VI)	80
56.  R=H/Me 	Co(II) Co(III)	81
57. R= H/Me 	Cu(II), Ni(II) Pd(II), Cd(II)	82
58.  	Cu(II)	83
59. 	VO(IV)	84
60. 	Cu(II) Co(II)	85

	Ligands	Metal ions	References
61.		Ln(III)	86
62.		Cu(II) Ni(II)	87
63.		Fe(II/III) Co(II),Co(III) Ni(II),Cu(II)	88
64.		Ln(III)	89
65.		Mn(II),Co(II) Ni(II),Cu(II)	90
66.		Zn(II)	91
67.		Co(II),Ni(II),Cu(II) VO(IV), UO_2(VI) Zn(II), Cd(II)	92

Ligands	Metal ions	References
68. 	Cu(II)	47
69. 	Ni(II), Cu(II) Zn(II)	93
70.  R = H / Me	Ni(II), Cu(II) Co(II), Co(III)	94
71.  R^1 = Me / Et / n-Bu, R^2 = H / 5-Cl, R^3 = H / 5-Cl / 3,5-Cl_2 / 3-OMe	Zn(II)	95
72.  R^1 = H / Me; R = NHMe / NMe_2 / SMe / NC_8H_{14}	Cu(II)	96
73. 	Pd(II)	97

Ligands	Metal ions	References
74. (a)  (b) 		98
75.  ,  R = H / Me	Cu(II)	99
76. 	Pd(II)	100
77.  	Ni(II), Cu(II) Zn(II), Cd(II)	101

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