Summary

Summary

1- Chapter I includes the introduction containing a literature suvery for the previous studies of the physical properties of azo compounds and their chelates with transition metals. It also includes different spectrophotometric methods for determination of transition metal ions.

Inorganic ion exchangers, absorption and precipitation have received attention for the treatment of radioactive waste. It has been done in an attempt to prepare inorganic ion exchangers that can help in various areas of nuclear feuel cycle. Also knowing information helping to understand and improve the ion exchange process. To satisfy these purposes different silicon (IV) antimonates are propared. Silicon (IV) antimonates which is amonge several ion exchange materials, double salts of polybasic acids with tetravalent metal types is very promising.

2- Chapter II includes the experimental part of the work such as preparation of the azo compounds under investigation, The stock solutions together with their standardization. It also describes different spectroscopic and conductometric methods along with the instrumentation, the analytical techniques, TGA-DTA and magnetic measurement procedures used in this thesis are also described. Also a detalied discription of the prepared different silicon (IV) antimonates which are used in this thesis is also presented.

3- Chapter III includes the studies of electronic structure of ligands using the electronic spectra in organic solvents, IR and ^{1}HNMR spectra.

a– The electronic absorption spectra of the ligands in ethanol exhibit four different bands. These bands result from either local excitation due to π electrons of naphthyeal ring or charge transfer transition through the whole molecule. The change in the colour of ligands or the position of the CT band in different organic solvents of protic and aprotic nature can be disscussed in terms of different emperical solvent polarity parameters which are termed microscopic character e.g polarity (π), acidity (α), basicity (ß) of solvent molecules as well as E_T or Z – values of them. Also, the so-called macroscopic solvent polarity parameters which characterise the bulk properties of the solvent medium such as dielectric constant and refractive index were employed. These parameter are plotted against λ_{max} (nm)or Δύ (cm^{-1}) and it was found that no main factor predominates and can affect directly the change of band position. But the contribution of these factors as well as the solute solvent interaction through H- bond formation play important role in changing the position of the bands.

b– In aqueous buffer solutions of various pH values containing 20% ethanol, the CT bands of the ligands exhibit a shift in λ_{max} and variation in molar absorptivity indicating that the aqueous medium may ionise these ligands and consequently changes their formula and subsquently the colour. The pK_a values for SO_3H, OH and COOH groups were determined by appling three different methods.

c- The ir spectra show that the ligands exhibit an intramolecular H-bond of these compounds and the ir band position of each ν_{OH} or $\nu_{C=O}$ or that of N=N gives a qualitative indication for the strength of H- bond. Also the quinone hydrazone tautomerism is liable to exist with these compounds in the solid state.

d- The ^1H NMR spectra of the free ligands are studied in $CDCl_3$ or DmSO-d_6 before and after deuteration. The main signals due to the protones of naphthyl ring, CH, OH COOH and SO_3H groups which gives satisfactory structural informations.

4- In chapter IV, the chelation of azo compounds with Mn^{2+}, Fe^{3+}, Co^{2+}, Ni^{2+} and Cu^{2+} ions are studied in solution and in solid state.

a- The IR spectra of the metal chelates are studied and compared with those of the free ligands. The spectra exhibit a pronounced shift in the stretching vibration bands of the C=O, N=N to lower wave number. The results reveal that new bands appear at lower frequencies (510-375 cm^{-1}) and (510-360 cm^{-1}) which were interpreted as being due to the stretching vibrations of M-O and M-N bonds, respectively. The ir spectra of the samples exhibit also a very broad band at high frequency which is due to the water molecules coordinated to the central metal ions. The latter is confirmed by the new band observed at (830-875) cm^{-1} for chelates due to the coordinated water.

b- The measurements of the molar conductance of DMF of solution of solid chelates show that these chelates are electrolytes in nature and display different oxidation numbers. The chemical formula of the solid chelates can be determined using data obtained from thermal methods of analysis TGA and DTA as well as dehydration and elemental analysis.

c- Conductometric titrations of azo compounds with metal ions in ethanol solution are measured to determine the stoichiometry of the chelates. The stoichiometry of the type 1:1 and 1:2 (M:L) are detected.

d- The optimum conditions favouring the complexation process are studied spectrophotometrically. These are resulted by studying each of the following: effect of pH, determination of λ_{max} at which complex species absorb, stoichiometries of complexes, effect of time and temperature. The values of stability constants are also determined using spectrophotometric technique. Validity of Becr's law is also studied.

The magnetic susceptibilities of some selected metal chelates were determined by Gouy method, from which the moments were calculated using the equation

$$\mu_{eff.} = 2.84\sqrt{x_m . T}\ \text{BM}$$

the data obtained are summarized in Table (23). The stereochemistry of these complexes were then detected, which show that the μ_{eff} for complexes of Mn^{2+}, Fe^{3+} with ligands (I-VI) give μ_{eff} rang in the 5.69-6.02 BM of high spin (except for Mn-I complexes = 1.92 BM indicate the low spin).

The μ_{eff} Co^{2+} complexes with ligands I-VI are within the range 4.44-5.12 BM due to the presence of three unpaired electrons, whereas for Ni^{2+} complexes with all ligands the magnetic moment (μ_{eff}) in range 2.67-3.19 BM is evidence of two unpaired electrons. For Cu^{2+} chelates the μ_{eff} ranging 1.90-2.09 indicate that the complexes have one unpaired of electron for octahedral or tetrahedral geometry.

The electronic absorption spectra of the solid chelates are studied both in Nujol mull and in DMF solution. The measurements of electronic spectra of Mn^{2+} chelates in nujol mull show mainly three bands. The first band within the range 22727-25614 cm^{-1} is due to the $^6A_{1g}\rightarrow{}^4E_g$, $^4A_{1g}$ transition within octahedral configuration. The second band within the range 24096-33003 cm^{-1} is due to the transition $^6A_{1g}\rightarrow{}^4E_{2g}$ (D) while the third band within the range 38462-40160 cm^{-1} is due to the $^6A_{1g}\rightarrow{}^6E_{1g}$ (D) in the octahedral arrangement. Also Fe^{3+} chelates in nujol mull show mainly three bands. The first band within the range within the range 22223-25644 cm^{-1} is due to the $^6A_{1g}\rightarrow{}^4E_g$, $^4A_{1g}$ transition within octahedral configuration. The second band within the range 24364-29412 cm^{-1} is due to the transition $^6A_{1g}\rightarrow{}^4E_{2g}$ (D) while the third band within the range 38150-40165 cm^{-1} is due to the $^6A_{1g}\rightarrow{}^6E_{1g}$ (D) in the octahedral arrangement. The electronic spectra of the complexes Co-I, Co-III and Co-VI in nujol mull show three bands at the ranges 22727-24096, 24390-29586, 38461-40715 cm^{-1} corresponding to the transition from $^4T_{1g}$ ground state to $^4T_{2g}$ and $^4T_{1g}$ (P) states respectively in octahedral field. for Co-II, Co-IV and Co-V show two bands at 24272-25615 and 26247-330003 cm^{-1} corresponding to the transition from $^4A_2$ ground state to the $^4T_1$ (F) and $^4T_1$ (P) exited states, respectively in tetrahedral arrangement. The absorption spectra of Ni(II) complexes show three bands at 23801-24076 cm^{-1} corresponding to $^3A_2\rightarrow{}^3T_2$, 25412-25445cm^{-1} due to $^3A_2\rightarrow{}^3T_1(F)$ and 32462-35166 cm^{-1} due to to $^3A_2\rightarrow{}^3T_1(p)$ transitions within the tetrahedral field. On the other hand, Ni(II) complexes with ligands IV, V and VI show that the three bands within the ranges 25637-25660, 25126-27027 and 40055-40801 cm^{-1} correspond to the transitions in octahedral field respectively.

$$^3A_{2g}\rightarrow{}^3T_{2g}$$

$$^3A_{2g}\rightarrow{}^3T_{1g}(F)$$

$$^3A_{2g} \rightarrow {}^3T_{1g}(g)$$

The electronic spectra of all Cu(II) complexes except Cu-I and Cu-III show broad band at 16739-18256 cm^{-1} and small one at 19463-22440 cm^{-1} which can be assigned to the $^2E_g \rightarrow {}^2B_{1g}$ and $^2A_{1g} \rightarrow {}^2B_{1g}$ transitions in a tetragonally distorted octahedral configuration.

The Cu(II) complexes with ligands I and III show broad bands in the range 16083-17973 cm^{-1} due to the $^2A_{1g} \rightarrow {}^2B_{1g}$ transition in square planar geometry.

e- The prepared different silican (IV) antimonates is characterized using X-ray diffraction and ir spectroscopy.

The results showed that the prepared samples has a semicrystalline structure, silicon (IV) antimonats has thermal stability. The results of solubility showed that the prepared samples are very stable in water, HNO_3 and HCl.

These results indicate that the SiSb has a good thermal and chemical stability compared with the other inorganic ion exchangers.

The capacity measurements of different silicon (IV) antimonates for both Cesium and Cobalt cations under different conditions (molority, drying temperature), shows that, as the acidity of the medium increases the hydrolysis of H^+ become more easly. By introducing another factor (drying temperature), The capacities of different silicon (IV) antimonates samples dried at different temperatuers for Cobalt and Cesium at 0.1 M are studied. The results show that the capacity of SiSb and MSiSb (where M= Cs^+,

Co^{2+} and Eu^{3+}) slightly decreases by increasing the drying temperature from 50 to 200 °C. At 400 °C. It is seen that the capacity generally largely increases. It is appear from these results also that the capacity of the exchanger for Cobalt ion is higher than that for Cesium ion due to the specific electrostatic interactions of the multivalent ions with the fixed exchange sites in the exchangers as the reason for the higher affinity to these ions. Also the chemical in–situ precipitation of Cs^{+}, Co^{2+} and Eu^{3+} ions with Silicon (IV) antimonate produce a new ion exchange materials with relatively higher capacities for Cs^{+} and Co^{2+} than SiSb.