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# studies chelation and micro determination of some rare elements with some organic compounds

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In the first chapter, a literature survey of the previous studies on Schiffbases and their complexes with different metal ions is given. This survey includes spectrophotometric, potentiometric, conductometric and polarographic studies on Schiff bases and their chelates. It includes also the use of some Schiff bases as analytical reagents for detection and determination of lanthanide and transition metal ions spectrophotometrically and polarographically. 2- The experimental part (chapter II) includes the preparation of the Schiffbases under investigation. It comprises also information about the instruments used for spectrophotometric, potentiometric, conductometric, polarographic, IR,  $^1\text{H-NMR}$ , EPR, magnetism as well as thermal analysis measurements. 3- Chapter III includes the results and discussion and consists of two parts, the first part (A), includes the studies in solutions of complexes formed between Schiff bases under investigation with lanthanide ions  $\text{La}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Gd}^{3+}$  and transition metal ions ( $\text{Cu}^{2+}$ ,  $\text{Ag}^{+}$  and  $\text{Au}^{3+}$ ). The studies include conductometric, potentiometric, spectrophotometric and polarographic techniques. From conductometric measurements the stoichiometry of the different complexes is obtained. Potentiometric titration of  $\text{La}^{3+}$ ,  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Gd}^{3+}$  with Schiff bases and  $\text{Ag}^{+}$  and  $\text{Au}^{3+}$  ions are performed in a medium of perchloric acid and sodium perchlorate. The proton-ligand stability constants  $\log K_{\text{HL}}$  are determined as well as the formation constants of the complexes  $\log K_{\text{f}}$ . From the data obtained from the polarographic study of the complexes of  $\text{Sm}^{3+}$ ,  $\text{Eu}^{3+}$  and  $\text{Gd}^{3+}$  with all ligands in NaClO<sub>4</sub> solutions containing 30% (v/v) ethanol, the values of the stability constants of metal complexes are given. The stoichiometry and stability constants of metal complexes are also evaluated from spectrophotometric methods namely the molar ratio, straight line and continuous variation methods. The optimum conditions for the complex formation are investigated, universal buffer of 30% (v/v) ethanol was found to be the best medium for spectrophotometric studies. Optimum pH values, suitable wavelength, effect of time and temperature as well as the sequence of addition were also studied. The results obtained indicate that a satisfactory agreement is observed between stability constant values evaluated using the three different methods. 4- Part (B) of chapter (III) includes studies of the solid chelates which include elemental analysis, molar conductivity measurements, TGA, DTA, IR,  $^1\text{H-NMR}$ , electronic absorption spectra, EPR and

magnetic measurements. The molar conductance of the complexes in DMF show that these chelates are electrolytes in nature and display different oxidation states. The chemical formula of the solid chelates were determined using the data obtained from thermal methods of analysis (TGA and DTA) as well as dehydration and elemental analysis. The spectra of the metal chelates are studied and compared with those of the free ligands which indicate that the coordinate and covalent bonds occur through the nitrogen atom of the azomethine group and the oxygen atom of the hydroxyl group of the salicylidene part of the molecule respectively. Their spectra of the metal chelates exhibit a very broad band at high frequency (3300-3450 cm<sup>-1</sup>) which is due to the water molecules coordinated to the central metal ions. 1. The <sup>1</sup>H-NMR spectra of La<sup>3+</sup> chelates with the ligands under investigation were studied in DMSO and compared with those of the free ligands. The main signals due to the proton of the phenyl ring, CH, CH<sub>2</sub> and OCH<sub>3</sub> groups are detected. It is found that the signals of protons of the OH group of the salicylidene part were completely disappeared indicating the contribution of this OH group in chelation through proton displacement. 2. The magnetic susceptibilities of some representative solid Cu<sup>2+</sup> chelates are measured using the Gouy method, from which the magnetic moments (μ<sub>B</sub>) and the number of unpaired d-electron in the Cu<sup>2+</sup> ion are determined. The stereochemistry of these chelates were then detected using Pauling's theory. The absorption spectra of the solid chelates are studied in both nujol mull and DMF. The variation of the position of the CT band in the two media indicates the variation of the environment of the central metal ion in DMF solution than in solid state. Some new bands are observed which are assigned and related to the spin allowed d-d transition for transition metal ion or f-f transition for lanthanide metal ions. The CT band due to L-M or M-L transition appears at longer or shorter wavelength to CT band of the ligand confirming the interaction between the metal ions and the ligands. The EPR spectra of some chelates of Cu<sup>2+</sup> metal ions and ligands are recorded. The calculated G-values indicate that the ligands environment is the same for Cu<sup>2+</sup> metal ions. 5- Chapter (N), includes the analytical microdetermination of lanthanide 3+, 3+, 3+, 3+, 2+, + ions (La, Sm, Eu and Gd) and transition metal ions (Cu, Ag and Au<sup>3+</sup>) with Schiff bases under investigation using the spectrophotometric techniques (calibration curve, EDTA titration and Ringbom method). It includes also the use of such compounds in the polarographic microdetermination of metal ions under consideration.