physicochemica studies of some multidenate azo dyes and their chelates with transition metal ions

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1- In the first chapter (the introduction) a literature surveyfor the previous studies of the physical properties of mono azoand azo-azomething dyes and their chelates with transition metals ”is given.2- The second chapter includesthe experimental part of the worksuch as preparation of the azo-compounds under investigation, thestock solutions together with their standardization. It comprisesalso information about the equipments used for the ir-, uv.- vis,lH_nmr or epr spectroscopy, potentiometric and conductometric titrationsas well as TGA - DTA measurements.3- Chapter III includes the studies of electronic structure ofligands using the electronic spectra in organic solvents, ir- and1H-nmr spectra.a- The electronic absorption spectra of the ligands in ethanolexhibit four different bands. These bands result from local excitationof 7l-electrons of the phenyl ring, local excitation dueto JZ -electrons of the wN=N- linkage or charge transfer transitionsthrough the whole molecule. The change in the colour of theligands or the position of the CT band in different organic solventsof protic and aprotic nature is discussed in terms of differentimperical solvent polarity parameters which are termedmicroscopic characteristicS e.g polarity (If), acidity (0( ) ,basecity (p) as well as the Er or Z-values of the solvent molecules.Also, the so-called macroscopic solvent polarity parameterswhich characterise the bulk properties of the solvent medium suchas dielectric constant or refractive index were employed. It wasfound that no main factor predominates and can affect directly thechange in band position. The contribution of these factors as wellas the solute-solvent interaction through H-bond formation playsan important role in changing the postion of the CT band.b- The ir-spectra show that the ligands exhibit an intramolecularH-bond and the shift in band position of each of POH’)/C=0 or thatof N=N gives a qualitative indication for the strength of the H-bondAlso a ke~enol tautomerism is liable to exist with these compoundseven in the solid state.1 6C- The H-nmr spectra of the free ligands are studied in d - DMSObefore and after d~tion •. The main signals due to the protons ofthe phenyl ring, OH, COOH, AsO(OH)2 or CH groups are detected.4- In chapter IV, the chelation of monoazo and azo-azomethine dyesunder investigation with Mn2+, Fe3+, C02+, Ni2+, Cu2+ and Zn2+ionsare studied in solution,and solid state.a- Conductometric titration of the azo dyes with the metal ions inethanol solution are measured to determine the stoichiometry ofthe chelates. The stoichiometry of the type 2:1, 1:1, 1:2 and even1:3 (M:L) are detected.b- Potentiometric titration of the monoazo-and the azo-azomethinedyes with metal ions are performed in a medium of perchloric acidand sodium perchlorate. The half interpolation method is applied.The stepwise formation constant pK as well as the overall formationconstants of these che1ates are determined. Also, the proton-ligandstability constants pKR are determined.c- The measurements of the molar conductance of solutions of the 2:1and 1:1 solid chelates dissolved in DMF show that these che1ates aree1ectro1ytesin.nature and display different oxidation numbers. Thechemical formula of the solid che1ates can be determined using thedata obtained from thermal methods of analysis TGA and DTA as well asdehydration and elemental analysis.d- The ir- spectra of the metal che1ates are studied and comparedwith those of the free ligands. The spectra exhibit a pronounced shiftin the stretching vibration bands of the C:O, N:N to lower wavenumberswhile those of the OR bands display broadening or disappear. Thespectra showed also the appearance of new bands at lower frequencies(600 - 300 cm-1) which are due to the stretching vibration of theM-O or M-N bands. The ir-spectra of the samples exhibit also a verymuadband at high frequency which is due to the water molecules coordinatedto the central metal ions.e- The 1R-nmr spectra of the Zn - chelates are studied and comparedwith those of the free ligands. The signals due to the proton of theOR, COOR or AsO(OR)2 group become broadened or disappeared on chelation,denoting the contribution of the OR groups in chelation throughproton displacement.f- The magnetic susceptibilities of some representative solid chelatesare measured using the Gouy method, from which the magnetic moments(~ eff) and the number of unpaired d-electron in the metal ion aredetermined. The stereochemistry of these complexes were then detectedusing pauling’s theory.g- The absorption spectra of the solid chelates are studied in bothnUjol mull and DMF. The variation of the position of the CT band inthe two media indicates the variation of the environment of the centralmetal ion in DMF solution than in solid state. Some new bands areobserved which are assigned and related to the spin allowed d _ dtransition of the metal ion according to crystal field splitting. TheCT band due to L - M or M --- L transition appears at longer or shorterwavelength compared to CT band of the ligand confirming the interactionbetween the metal ions and the ligands.h- The epr spectra of some chelates of different metal ions and ligandsarerecorded. The calculated g- values indicate that the metal environmentis different for such complexes.