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STUDIES ON ALIZARIN MAROON, ALIZARIN SAPHIROL B AND ALIZARIN HELIOTROPE COMPLEXES OF Mn(II), Fe(II), Co(II), Ni(II) AND Cu(II)

CONSIDERABLE interest has been shown recently in the complex formation by amino-anthraquinone dyes and their related compounds¹⁻⁵. In the present paper we have studied the possibility of alizarin maroon (AZM), alizarin saphirol B (AZSB) and alizarin heliotrope (AZH) to form stable complexes with some divalent transition metal ions. The composition and structure of the complexes formed are studied using spectral and conductivity data.

Experimental

The solid complexes were prepared by mixing the appropriate amount of the ligand solution (10⁻³ M) with the accurately weighed quantity of the metal salt (dissolved in ethanol). The mixture was refluxed for 10 min. on a water bath and cooled. The solids were filtered off, washed with acetone, dried and analysed. The solid complexes having the metal:ligand ratios 1:1 and 1:2 were isolated.

The absorption spectra of solutions were recorded on a UNICAM S.P. 8000 spectrophotometer and the i.r. spectra were recorded on a Beckman Infrared Spectrophotometer as KBr discs.

Results and Discussion

The visible spectrum of AZH in ethanol shows a main absorption band at 480 nm⁶ which shows a red shift on addition of metal ions.

The formation of AZM and AZSB metal complexes are pH-dependent. The results indicate that the optimum pH is ~ 7.5 for the formation of Fe(II) and Cu(II) complexes and 8-8.5 for the Mn(II), Co(II) and Ni(II) complexes. The obvious red shift of the bands shown by AZM and AZSB complexes in comparison with those of the free ligands^{6,7} at the same pH, indicates the complex formation. In Table I, are given the values of λ_{max} for the different complexes.

The stoichiometry of the mixed ligands in solution was determined by Job's continuous variation⁸ and also by molar ratio⁹, straight line¹⁰, slope 4ratio¹¹ and limiting logarithmic¹² methods. The results indicated two types of complexes for the metal ions with stoichiometric ratios 1:1 and 1:2 (M:L).

The apparent stability constant β_n is determined from the results of the mol ratio⁹, straight line¹⁰, continuous variation⁸ and limiting logarithmic¹² methods. The mean values of log β as well as the values of ΔG° are also given in Table I.

The metal chloride solutions (10⁻⁴ M) were titrated with 10⁻³ M AZM, AZSB or AZH in aqueous or ethanolic medium, and the conductance-molar ratio curves indicated the formation of 1:1 and 1:2 complexes. The complex formation appears to be accompanied by the liberation of the proton from the α -OH substituent as gathered from the increase of the electrical conductance when the reagent is added to the metal ion solution.

TABLE I
 Values of λ_{max} , log β and $-\Delta G^\circ$ for AZM, AZSB and AZH complexes

Complex	λ_{max} (nm)	log β_1	$-\Delta G^\circ$ K cal/mole	log β_2	$-\Delta G^\circ$ K cal/mole
Mn(II)-AZM	620	4.70	6.4	10.01	13.6
Fe(II)-AZM	630	4.60	6.3	10.40	14.2
Co(II)-AZM	630	5.20	7.1	10.40	14.2
Ni(II)-AZM	620	5.08	6.9	10.60	14.4
Cu(II)-AZM	620	4.70	6.4	10.04	13.7
Fe(II)-AZSB	700	5.02	6.8	9.10	12.4
Co(II)-AZSB	680	4.50	6.1	9.10	12.4
Ni(II)-AZSB	650	5.20	7.1	9.80	13.4
Cu(II)-AZSB	690	4.90	6.6	9.30	12.6
Co(II)-AZH	425, 590	4.80	6.5	9.40	12.8
Ni(II)-AZH	425, 590	4.70	6.4	9.30	12.7
Cu(II)-AZH	400, 600	5.01	6.0	9.5	12.9

TABLE II
Some IR bands of AZM, AZSB, AZH and their metal chelates

Ligand	Mn ²⁺	Fe ²⁺	Co ²⁺	Ni ²⁺	Cu ²⁺	Assignment
~ 3600	3600	3600	3600	3600	3600	ν_{NH_2}
~ 3400	3200	3220	3250	3250	3300	ν_{OH} (bonded)
1610-1635	1570	1580	1585	1585	1600	$\nu_{\text{C=O}}$ (bonded)
1500	1500	1500	1500	1500	1500	δ_{NH}
1435-1460	1410	1420	1425	1425	1430	δ_{OH} (bonded)
~ 1270	1250	1255	1260	1260	1265	δ_{CH}

The important I.R. band frequencies for the free ligands and their metal chelates are given in Table II. The bands corresponding to the ν_{OH} become broadened, less intense and suffer a frequency shift when the ligand is bonded to the metal ions to give the chelates. All the spectra of the metal chelates show an overlap of the bonded $\nu_{\text{C=O}}$ with $\nu_{\text{C=C}}$ near 1600 cm^{-1} and a red shift is observed. This indicates that the quinone structure is influenced by the substituents; that is to say it lowers the C=O character and increases the C-C bond order. The intensity of the bands due to δ_{OH} decreases apparently due to the displacement of a proton from the α -OH group on complex formation.

From the foregoing results as well as those obtained from the elemental analysis of the solid chelates, we conclude that the reaction between the metal ions and the complexing agents under investigation occurs via the formation of a covalent linkage with the oxygen of the α -OH group and the carbonyl group.

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INVESTIGATION ON THE TOXICITY OF SOME CARBAZOLE DERIVATIVES AND PLANT EXTRACTS

PREVIOUS studies on the insecticidal properties of carbazole derivatives¹ revealed that tetrahydrocarbazole, 2-methyl tetrahydrocarbazole and 3-methyl tetrahydrocarbazole are more toxic to houseflies (*Musca domestica* L.) than the corresponding carbazoles. Such high toxicity of tetrahydrocarbazole derivatives is due to the presence of partially reduced carbazole moiety¹. This¹ interested us to study the toxicity of tetrahydrocarbazole(I), carbazole(III), glycozoline(IV) and glycozolidine(V) (carbazole alkaloids), along with extract of root-bark of *Glycosmis pentaphylla* (Retz) DC (which contains two carbazole alkaloids—glycozoline and glycozolidine) on mosquito larvae (*Culex* Sp.). The percentage of mortality of house-flies (*Musca domestica* L.) at different concentrations of tetrahydrocarbazole(I) and 2-methyl tetrahydrocarbazole(II) are also presented in this communication.

Tetrahydrocarbazole(I) and 2-methyl tetrahydrocarbazole(II) were prepared by Borsche method described previously¹. The dried and powdered root-bark of *Glycosmis pentaphylla* (Retz.) DC was extracted with benzene in a Soxhlet for 48 hours. The benzene extract was freed from solvent and used for toxicity tests on mosquito larvae. The neutral mass of this extract (after the separation of acidic and basic constituents by washing with alkali and acid respectively) was also used for toxicity tests. Glycozoline²(IV) and glycozolidine³(V) were isolated from the neutral mass of the benzene extract of the root-bark of *Glycosmis pentaphylla* (Retz.) DC. by chromatography and characterised in the usual way.