A Spectrophotometric Study on Equilibria of *p*-(4-Hydroxy-1-naphthylazo)nitrobenzene with Proton and of *p*-(2,4-Dihydroxyphenylazo)nitrobenzene with Proton and Copper(II) in Aqueous Solution

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The protonation constants of *p*-(2,4-dihydroxyphenylazo)nitrobenzene (' Magneson I ') and *p*-(4-hydroxy-1-naphthylazo)nitrobenzene (' Magneson II ') have been determined by spectrophotometric methods at 25 °C and *I* = 1.0 mol dm^{-3} (KCl). The equilibria between Cu^{II} and *p*-(2,4-dihydroxyphenylazo)nitrobenzene have also been investigated in acidic medium under the same conditions. The mixed cumulative stability constants of the protonated species have been refined with two different computer programs: a modified version of the program SQUAD and the program SPEFO (an application of LETAGROP to spectrophotometric data). The spectrophotometric characteristics and equilibrium constants for the various species are reported. The least-squares values of the protonated species and the formation constants of the complexes are log β_{011} = 11.816(4), log β_{021} = 21.590(17), log β_{111} = 23.327(33), and log β_{102} = 35.706(64) for Magneson I and log β_{011} = 12.474(37) for Magneson II. The experimental spectra are in good agreement with the calculated ones and the constants are discussed in connection with those of similar compounds reported in the literature.

PROTOLYTIC equilibria play an important part in azo-dyes. On one hand, some azo-compounds are much used as acid–base indicators in analytical chemistry, but, on the other, these very indicator properties provide some obstacles to their universal application as dyestuffs. The indicators described in this paper were selected and studied in order to investigate their protonation and complex formation equilibria. In this study, therefore, two procedures of refinement have been applied for this same purpose. When spectrophotometry is utilized, a wavelength is usually selected where only one species is absorbing in order to obtain a direct measure of its concentration. These methods are limited to systems with mononuclear complex species, because when many complexes are involved the data elaboration certainly implies an error accumulation. Although there is a number of somewhat general graphical methods,[1-9] nowadays the wide use of digital computers for the analysis of chemical equilibria from spectrophotometric measurements has been developed by several authors.[10-19] It is useful to process spectral data at several wavelengths in these computations, obtaining, in such a way, a graphical display of the results with an automatic PLOTTER CALCOMP 936. Spectrophotometric methods and refinement procedures have been used to determine the protonation constants of *p*-(2,4-dihydroxyphenylazo)nitrobenzene, ' Magneson I ' (H_2L^1), and *p*-(4-hydroxy-1-naphthylazo)nitrobenzene, ' Magneson II ' (HL^2), in an ionic medium of 1.0 mol dm^{-3} at 25 °C. The complexing capacity of Magneson I with Cu^{II} is also investigated.

EXPERIMENTAL

TABLE 1

Initial concentration (mol dm^{-3}) and the measured pH of the different solutions

Magneson I		Magneson II	
[H_2L^1]	pH	[HL^2]	pH
0.000 042 5	7.457	0.000 518 4	11.342
0.000 063 7	9.356	0.000 277 2	12.118
0.000 042 5	9.385	0.000 314 9	12.247
0.000 070 8	10.524	0.000 323 4	12.263
0.000 070 8	11.147	0.000 382 3	12.380
0.000 070 8	11.347	0.000 381 7	12.468
0.000 070 8	11.674	0.000 420 3	12.470
0.000 070 8	11.857	0.000 429 9	12.538
0.000 070 8	11.982	0.000 604 2	12.573
0.000 070 8	12.134	0.000 612 6	12.596
0.000 070 8	12.278	0.000 666 5	12.665
0.000 070 8	12.397	0.000 715 9	12.671
0.000 070 8	12.530	0.000 558 7	12.741
0.000 042 5	12.959	0.000 573 0	12.782
0.000 056 6	13.284	0.000 618 5	12.934
0.000 042 5	13.464	0.000 762 7	13.102

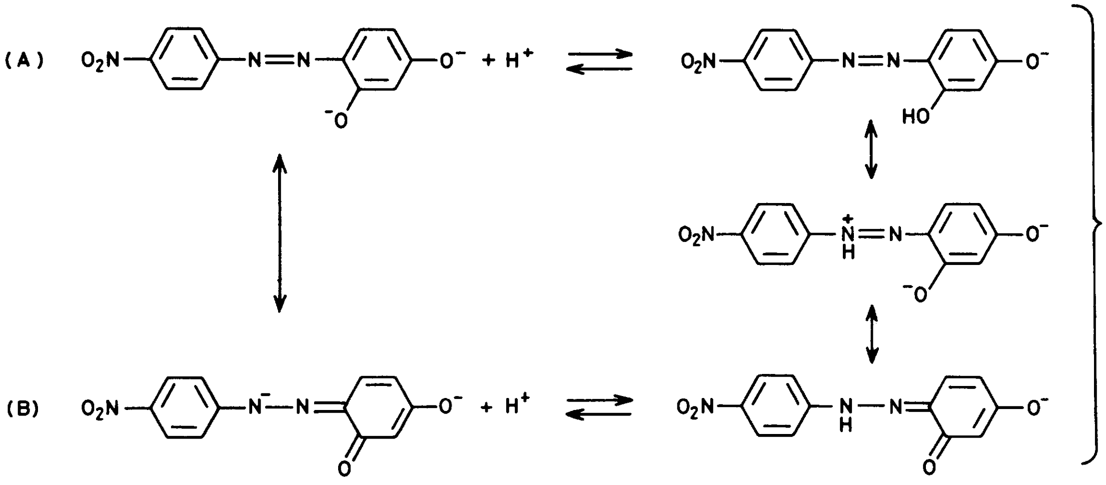
Cu^{II}–Magneson I

	[Cu^{II}]	[H_2L^1]	pH
1	0.004 719 6	0.000 113 3	2.236
2	0.001 287 2	0.000 084 9	3.564
3	0.002 574 3	0.000 212 4	2.265
4	0.002 145 3	0.000 269 0	2.474
5	0.000 858 1	0.000 070 8	5.625
6	0.000 858 1	0.000 070 8	5.624
7	0.000 429 1	0.000 070 8	6.090
8	0.000 086 1	0.000 099 1	5.850
9	0.002 145 3	0.000 141 6	5.072
10	0.001 287 2	0.000 146 1	5.543

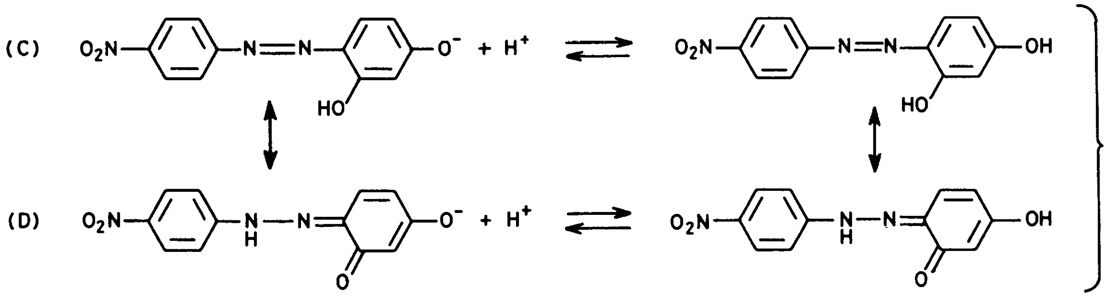
The copper(II) chloride (AnalaR) solution (0.107 049 mol dm^{-3}) was standardized by electrolytic procedure. Potassium chloride (AnalaR) was recrystallized twice from distilled water. AnalaR hydrochloric acid and potassium hydroxide (carbonate-free) were used to reach the desired pH. Magneson I and Magneson II were obtained from Carlo Erba. The pH measurements were made using a digital Radiometer PHM84 Research pH meter, having an accuracy of about ±0.002 pH unit. A combined electrode Radiometer GK2351B was standardized against the buffer solutions, prepared from ' National Bureau of Standards ' buffer chemicals, using the procedure of the two-buffers adjustment. The electrode utilized was chosen owing to its ability to operate reliably over the range pH 0—14. Careful calibration of the electrode was necessary, the main advantage of its glass membrane being its use in the range pH 0—14 without correction. All the measurements were carried out at 25 °C and at an ionic strength of 1.0 mol dm^{-3} (KCl), regulated by addition of potassium chloride. Spectrophotometric determinations were made with a Jasco Spectrophotometer, model UVIDEC-505, equipped with a digital printer DP-101. Matched quartz cells of pathlength 1.0 cm, calibrated before use, were employed. During the measurements, the cuvette assembly was thermostatted to 25.0 ± 0.1 °C by a Paratherm II electronic (Julabo) circulating water bath. Absorption spectra were obtained for 16 or 10 different solutions of Magneson I systems and 16 for Magneson II in doubly distilled water. The initial concentration and the measured pH value of various solutions for the two compounds are reported in Table 1. The absorbance data were collected for each solution (to three decimal places) on a digital printer with a stepping of 10.0 nm in the ranges 240—740 nm, or 340—600 nm, obtaining 51 or 27 absorbance values respectively for each solution. For the two ligands investigated a ' mixed ' protonation constant, β_{0x1}, was determined where $\beta_{0x1} = [H_xL]/[L^{x-}][H^+]^x(\gamma_{H^+})^x$, with x = 1 or 2. β_{0x1} is related to the protonation constant at a definite ionic strength (β'_{0x1}) by $\beta_{0x1} = \beta'_{0x1}/(\gamma_{H^+})^x$.

RESULTS AND REFINEMENT

The mixed protonation constants of Magneson I at 25 °C and at I = 1.0 mol dm^{-3} (KCl) are log β_{011} = 11.816(4) for the equilibrium (1) and log K_2^H = 9.774(17) for the equilibrium (2). For Magneson II only one equilibrium (3) is present, whose mixed protonation constant is log β_{011} = 12.474(37). The assignment of the protons to the sites in the tautomeric forms of the two ligands can be done on the



(1)



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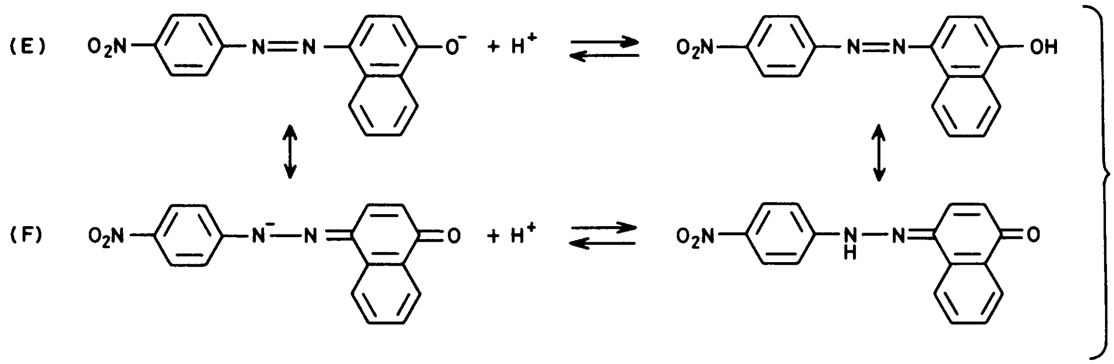

(3)

basis of the following arguments. The effects of *ortho* and *para* substituents on protonation equilibria of the azo-group have been investigated by Haselbach[20] whose results support the classical view that the protonation takes place at a particular nitrogen atom with formation of a N–H σ bond (equilibria B, F, AB). The structure of conjugate acids of Magneson I is of interest as the proton can be accommodated either on the azo-nitrogen or the phenolic oxygen. The protonation of the β-azo-nitrogen is favoured in this case by the greater basicity of the azo-nitrogen interpreted in terms of mesomerism between equilibria A and B. Generally, the product of the monoprotonated form is regarded as a tautomeric mix of A, B, and AB. Moreover, the tautomeric equilibrium favours increasingly the hydrazone form as the number of rings becomes greater in going from derivatives of phenol, to those of 1-naphthol, *etc.* Substituents in the diazo-component influence the tautomeric equilibrium greatly, the participation of the hydrazone form increasing in the series p-OCH_3 < p-CH_3 < H < Cl < p-NO_2 and being therefore favoured by acidifying groups. This conclusion is supported by the study of i.r. spectra of azophenols and azonaphthols.[21]

The mixed protonation constants for Magneson I and Magneson II have been obtained through the refinement of several measurement sets with two different computer programs, SQUAD and LETAGROP version SPEFO. Preliminary protonation constants have been obtained by graphical methods according to the Yatsimirskii procedure[22] and then refined with the generalized least-squares programs.

According to the Bouguer–Lambert–Beer law, the optical density $A_c(i,k)$ of the ith solution at the kth wavelength for hypothetical equilibria involving the species metal (M), ligand (L), and hydrogen which absorb radiation in the u.v.–visible region is defined by the relation (4), where $\varepsilon(k)_{pqr}$ is

$$A_c(i,k) = l \cdot \sum_0^p \sum_0^q \sum_0^r [M_pH_qL_r]_i \cdot \varepsilon(k)_{pqr} \qquad (4)$$

the molar absorption coefficient at the kth wavelength for the $[M_pH_qL_r]_i$ species and l is the pathlength (cm). This

$$A_c(i,k) = l \cdot \sum_0^p \sum_0^q \sum_0^r \beta_{pqr}[M]_i^p[H]_i^q[L]_i^r \cdot \varepsilon(k)_{pqr} \qquad (5)$$

leads to equation (5). Thus, given sufficient values of $A_o(i,k)$, it is possible, in principle, to evaluate β_{pqr} and $\varepsilon(k)_{pqr}$ for any system. The computer programs SQUAD and LETAGROP–SPEFO differ from one another either in the mathematical method of finding the minimum of the

$$U = \sum_{ik} |\Delta_{ik}|^2 = \sum_{ik} (X_{c,ik} - X_{0,ik})^2 \cdot w_k \qquad (6)$$

squares of the residuals [equation (6), where $X_{c,ik}$ and $X_{0,ik}$ are the calculated and the observed values of the ith solution at the kth wavelength] or in the employed X quantity. A weighting factor, w_k, is used in the SQUAD program. The derivation of a suitable value of w_k is left to the individual user. Unit weights have been used in all the calculations. The computer program SQUAD is based on the non-linear Gauss–Newton least-squares method,[23] introduced by Tobias and Yasuda[24] and developed by Perrin and other workers. This procedure uses the conventional least-squares approach to calculate the shifts in the equilibrium constants, the partial derivatives being obtained numerically by incrementing the constants. The Newton–Raphson method is also employed in the subroutine COGSNR of the SQUAD program. The LETAGROP–SPEFO program, due to Sillén and Warnquist,[25] uses the 'pit-mapping' approach. According to this technique the problem is still to minimize an error square sum, but now this is defined as a function of the n variable, which may be expressed as a paraboloid in $(n + 1)$ dimensional space, and the calculation is designed to seek the minimum or 'pit' in such a surface. The Newton–Raphson method, employed in the subroutine COGSNR of the program SQUAD, is also used to determine the concentrations of every species in solution. These programs are therefore able to yield, from appropriate absorbance data, protonation constants, metal-ion hydrolysis constants, and cumulative stability constants of simple and polynuclear complexes. At the same time, a set of molar absorptivities are calculated according to the obtained β_{pqr} values. The two mathematical methods, which differ in their speed of convergence, give comparable results (Table 2). Small differences in the results are found when different $X_{i,k}$ quantities are employed. The calculated absorbance is the $X_{i,k}$ value, taken to measure the agreement in both programs SQUAD and LETAGROP–SPEFO. The Cu^{II}–Magneson I system has been also investigated in detail by means of spectrophotometric methods using the same procedure of calculation. It is also noted that the Cu^{2+} ion absorbs in the range 340—600 nm. Hence ε_{Cu} has been previously determined and then introduced in the programs. All the calculations have been carried out on the CDC CYBER 70/76 computer of the 'Consorzio per la gestione del Centro di Calcolo Elettronico Interuniversitario dell'Italia Nord-Orientale,' Casalecchio, Bologna, with the financial support of the University of Parma. Complete lists of the experimental data, calculated molar absorption coefficients of the various species and Cu^{II} complexes at all wavelengths selected, and plots of ε_{pqr} ($p = 0$) are available as Supplementary Publication No. SUP 23272 (17 pp.).*

TABLE 2

Stepwise and total mixed protonation and formation constants for Magneson I and Magneson II at 25 °C and $I = 1.0$ mol dm^{-3} (KCl) using different refinement programs; estimated standard deviations are given in parentheses

	Magneson I	Magneson II
SQUAD		
log β_{011}	11.816(4)	12.474(37)
log β_{021}	21.590(17)	
log K_2^H	9.774(17)	
LETAGROP–SPEFO		
log β_{011}	11.816(4)	12.472(38)
log β_{021}	12.591(17)	
log K_2^H	9.775(17)	
SQUAD		
log β_{111}	23.327(33)	
log β_{102}	35.706(64)	
LETAGROP–SPEFO		
log β_{111}	23.327(33)	
log β_{102}	35.707(64)	

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* For details see Notices to Authors No. 7, *J. Chem. Soc., Dalton Trans.*, 1981, Index issue.

DISCUSSION

Protonation Equilibria.—The refinement of the protonation constants in aqueous solution gives the values reported in Table 2. The recorded spectra (Figures 1 and 2) show the absorption bands in the ranges 450—462 and 551—554 nm for Magneson I and at 570 nm for Magneson II. These bands are usually associated with $\pi \rightarrow \pi^*$, $n \rightarrow \pi^*$, or charge-transfer transitions. In acid, neutral, and weak-basic media the absorption spectra for Magneson I show that the yellow colour originates from the single band at *ca.* 450 nm, while for pH values greater than 9.4 the colour changes from yellow, to orange, to reddish purple to a pure purple. The colouration is reversible with an isosbestic point at 490 nm. A small bathochromic shift is observed from 450 to 462 nm when the pH increases. Although the two species H_2L^1 and $(HL^1)^-$ absorb at very close wavelengths this spectrophotometric method permits the two determinations of β_{0x1}. The only colour variation observed for Magneson II is from pale yellow, in acid solution, to violet in strongly alkaline media. The refined mixed protonation constants (Table 2), together with the calculated molar absorptivities of the corresponding species for Magneson I and Magneson II, have been used to plot the spectra of the different solutions. Figures 2 and 3 show the comparison between some computed and experimental spectra. Use of the calculated spectra is a particularly valuable method of testing the correctness of the selected model and the values of the refined protonation constants. The standard deviation (*s*) in the absorbance data based on the final constants [$s = (U/N_{d.f.})^{\frac{1}{2}}$, where $N_{d.f.}$ are the degrees of freedom of all data] is 0.0128 and 0.0156 absorbance units for Magneson I and Magneson II, respectively. The protonation constant log β_{011} (Magneson I), which corresponds to the protonation of the phenolic oxygen in the *ortho* position, including the hydrogen-bonded system with the β-azo-nitrogen atom, is in good agreement with a corresponding value from a series of substituted phenylazoresorcinol compounds studied in earlier work:[26,27] *e.g.* for 4-(*p*-nitrophenylazo)resorcinol at 15 °C, $I = 0.1$, log $\beta_{011} = 11.74(1)$; 4-phenylazoresorcinol at 15 °C, $I = 0.1$, log $\beta_{011} = 12.13(1)$; 4-(*m*-nitrophenylazo)resorcinol at 15 °C, $I = 0.1$, log $\beta_{011} = 11.63(3)$; 2′,4′-dihydroxyazobenzene-4′-sulphonic acid at 15 °C, $I = 0.1$ mol dm^{-3}, log $\beta_{011} = 12.00(5)$.

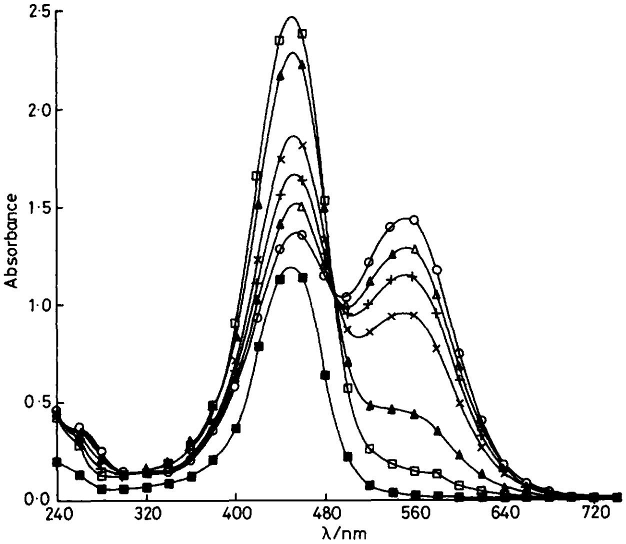


FIGURE 1 Plots of experimental absorbance data *versus* wavelength for solutions of Magneson I at 25 °C using the program VISION with the PLOTTER Calcomp 936: pH 12.134 (○), 11.982 (△), 11.857 (+), 11.674 (×), 11.147 (▲), 10.524 (□), and 9.385 (■)

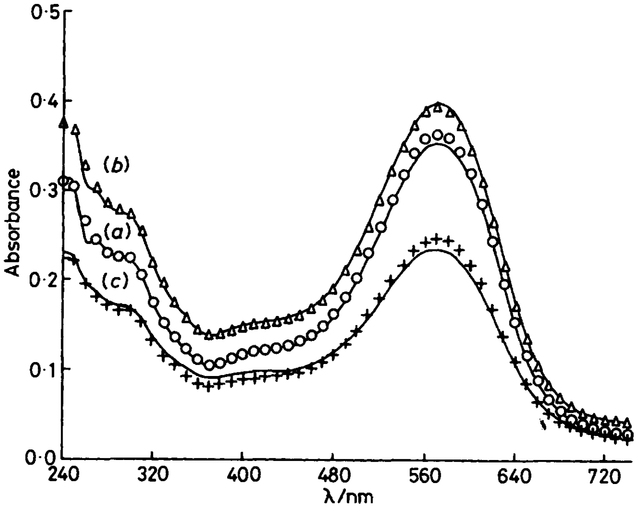


FIGURE 2 Calculated absorption spectra (——) for solutions of Magneson II (HL^2) at (*a*) pH 12.934, (*b*) 12.665, and (*c*) 12.468, plotted together with experimental points using the PLOTTER Calcomp 936, at 25 °C: $[HL^2] = 6.185 \times 10^{-4}$ (○), 6.665×10^{-4} (△), and 3.817×10^{-4} mol dm^{-3} (+). $\beta_{011} = 12.474$

In the present work the stepwise protonation constant (log K_2^H) for the equilibrium (2) (C and D forms) has been also refined. The fact that the value of log K_2^H, compared with those of *o*- and *p*-hydroxyazo-dyes,[28] does not decrease much is presumably due to different factors, namely, the position of the azo-hydrazone equilibrium, the influence of the substituent ($-NO_2$) on the formation of aggregates, and the large distance of the acidifying group from the second protonation site. On the other hand, various experimental evidence suggests that Magneson II exists prevalently in the hydrazone form (F); in fact spectroscopic [29,30] and dipole moment [31] measurements indicated that the azo-hydrazone equilibrium (3) is shifted towards the hydrazone tautomer when an electron-withdrawing substituent is present in the benzene ring. The loss of the proton from (F) affords an anionic form in which the negative unit charge is highly delocalized.

Copper(II) *Complexes.*—The refinement of the formation constants of Magneson I with Cu^{2+} in aqueous solution give the values reported in Table 2. The experimental and calculated spectra for some solutions, collected in the range 340—600 nm, are shown in Figure 4. The copper(II), which probably exists as chloride complexes ($CuCl^+$, $CuCl_2$) in the chloride (KCl) solution,

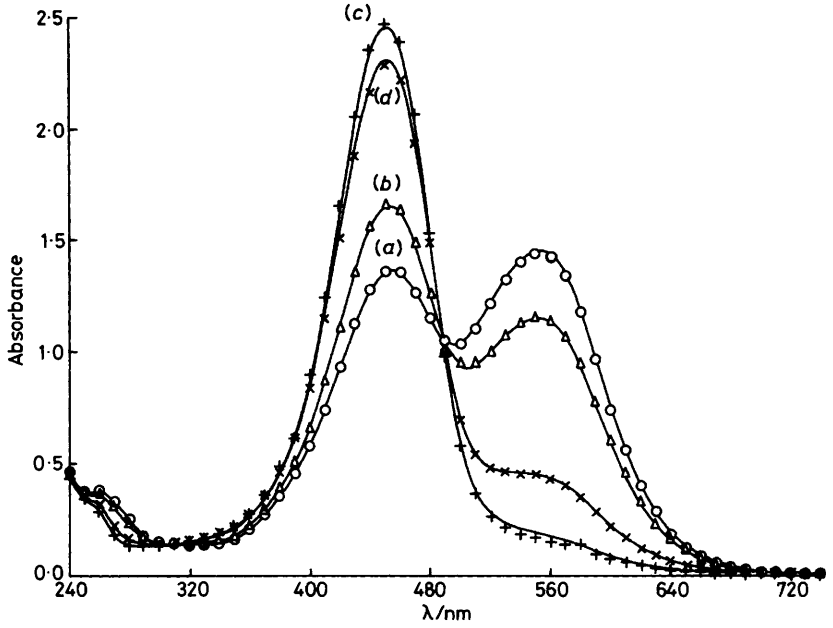


FIGURE 3 Calculated absorption spectra (——) for solutions of Magneson I [H_2L^1] at (*a*) pH 12.134, (*b*) 11.857, (*c*) 10.524, (*d*) 11.147, plotted together with experimental points using the PLOTTER Calcomp 936, at 25 °C: [H_2L^1] = 7.08 × 10^{-5} mol dm^{-3} for all curves (○), (△), (+), (×). β_{011} = 11.816, β_{021} = 21.590

does not absorb in the range 340—600 nm owing to the previous complexes not absorbing.[32] The complexes actually formed in acidic medium are [$Cu(HL^1)]^+$ and [$CuL^1_2]^{2-}$. Thus, complexation occurs with the formation of a monoprotonated [$Cu(HL^1)]^+$ and mononuclear [$CuL^1_2]^{2-}$ species with release of protons; the first species prevailing at higher acidity than the second one. [$Cu(HL^1)]^+$ can be seen as a monoprotonated complex with an internal hydrogen bond. This is confirmed by the value of the equilibrium constant log K $\{Cu^{2+} + (HL^1)^- \rightleftharpoons [Cu(HL^1)]^+\}$ = 11.511, which is comparable with that of a phenolic group (log $K_2{}^H$ = 9.774). Furthermore, the kinetic study on complex formation between Ni^{II} and similar ligands [27] has revealed that the phenolic hydrogen in the *para*-position has approximately the same log K value in the complex [$M(HL^1)]^+$ as it has in the free ligand. The structure (1) is proposed for the monoprotonated complex [$Cu(HL^1)]^+$ on the basis of the results obtained and by analogy with those known for the complexes of the azo-derivatives with Ni^{2+}.

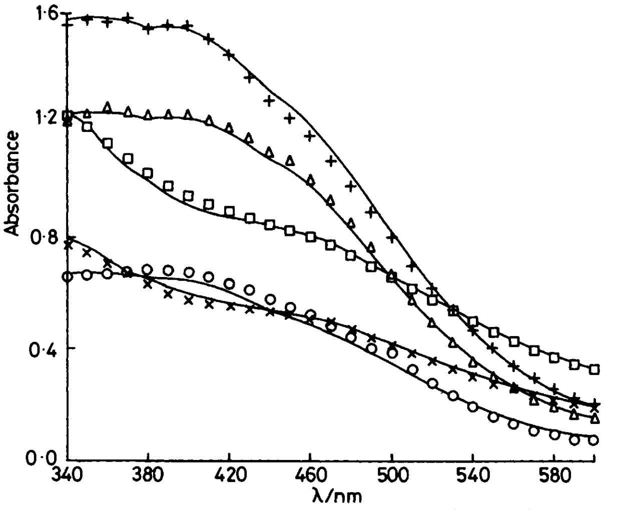
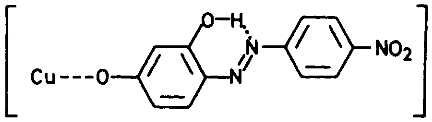
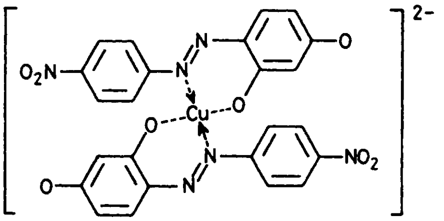


FIGURE 4 Calculated absorption spectra (——) for solutions of Cu^{II}–Magneson I at five values of pH, plotted together with experimental points using the PLOTTER Calcomp 936, at 25 °C: pH 2.236 (○), 2.265 (△), 2.474 (+), 6.090 (×), and 5.850 (□); see Table 1 for corresponding concentrations of Cu^{II} and Magneson I



(1)

At higher values of ligand concentration and of pH a second molecule of ligand is co-ordinated; the proton, involved in the internal hydrogen bond, dissociates and a much stronger chelate complex [$CuL^1_2]^{2-}$ is formed. Extensive studies on copper(II) complexes of hydroxy- and dihydroxy-azo-derivatives have been carried out by several authors (see refs. 33–36). They concluded that the azo-compounds possessing one *o*-hydroxy-group yield



(2)

preferably 1 : 2 copper complexes. The most probable structure of the $[CuL^1_2]^{2-}$ complex is represented by structure (2).

The standard deviation in the absorbance data was 0.019 59 absorbance units. Calculated and observed spectra agree satisfactorily for all the solutions. Taking into account the acidity range examined and the working conditions, the presence of hydroxo-complexes can be excluded. Equilibria between Cu^{2+} ion and Magneson II cannot be studied because precipitation occurs in the titration cuvette.

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