

**Some heterocyclic azo dyes as analytical reagents. II.**  
**Study of 2-(5,5-dimethyl-4,5,6,7-tetrahydrobenzthiazolyl-2-azo)-**  
**-5-hydroxyphenol and its complexes with Cu(II), Ni(II), Cd(II), Zn(II),**  
**and Pb(II)**

<sup>a</sup>J. KANDRÁČ and <sup>b</sup>E. KUCHAR

<sup>a</sup>*Department of Chemistry, Faculty of Pedagogics,  
Komenský University, 917 24 Trnava*

<sup>b</sup>*Department of Analytical Chemistry, Faculty of Natural Sciences,  
Komenský University, 801 00 Bratislava*

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*Dedicated to Professor S. Stankoviansky on his 65th birthday*

The optical and acid-base properties of 2-(5,5-dimethyl-4,5,6,7-tetrahydrobenzthiazolyl-2-azo)-5-hydroxyphenol were studied. This substance occurs in 40% aqueous solution of ethyl alcohol over the pH range from 0.15 to 12.80 in four differently coloured acid-base forms with maximum absorbances of 500 nm ( $\text{RH}_3^+$ ), 460 nm ( $\text{RH}_2$ ), 490 nm ( $\text{RH}^-$ ), and 510 nm ( $\text{R}^{2-}$ ). Furthermore, the complexes of this reagent with Cu(II), Ni(II), Cd(II), Zn(II), and Pb(II) were investigated. This reagent forms complexes with Cu(II) and Pb(II) in molar ratio 1 : 1, with Ni(II) and Zn(II) in molar ratio 1 : 2 while both these complexes are formed with Cd(II). The complexes formed with Cu(II), Ni(II), Pb(II), and Zn(II) in fairly acid region are protonized. The molar absorptivities of complexes and equilibrium constants were established by graphical analysis. The constants of stability of individual complexes were calculated.

The azo compounds, which contain the thiazol or pyridine ring in their molecules may be counted among the most studied heterocyclic *o*-hydroxyazo dyes. From this group pyridylazoresorcinol (PAR), thiazolylazoresorcinol (TAR) and their various derivatives are especially studied as reagents for spectrophotometric determination of metal ions and metallochromic indicators [1–16]. The spectrophotometric determination of zinc with some derivatives of 2-(thiazolyl-2-azo)phenol is described by Kawase [17] where the complex-forming properties of 1-(4,5,6,7-tetrahydrobenzthiazolyl-2-azo)-2-naphthol and 2-(4,5,6,7-tetrahydrobenzthiazolyl-2-azo)-4-methoxyphenol are also investigated. The spectrophotometric method has been applied to the study of acid-base properties of 2-(7-keto-5,5-dimethyl-4,5,6,7-tetrahydrobenzthiazolyl)-azo-4-hydroxybenzene and 2-(7-keto-5,5-dimethyl-4,5,6,7-tetrahydrobenzthiazolyl)-azo-2,4-dihydroxybenzene as well as complex-forming properties of these reagents [18]. The overall survey of the properties of heterocyclic azo dyes and their analytical application is presented in some reviews [19–21] and papers [22, 23].

In this study the acid-base and complex-forming properties of 2-(5,5-dimethyl-4,5,6,7-tetrahydrobenzthiazolyl-2-azo)-5-hydroxyphenol (DIBTAR) are investigated.

### Experimental

The preparation as well as the homogeneity and purity testing of DIBTAR is described in paper [24]. The solutions of reagent were prepared by diluting a  $10^{-2}$  M alcoholic stock solution. The adjustment of pH was carried out with dilute perchloric acid, dilute sodium hydroxide, Britton—Robinson buffer solution, 1 M acetate buffer solution, 1 M ammoniacal buffer solution, and 1 M formate buffer solution. The ionic strength of solutions with  $\text{pH} > 2.5$  was brought to the value of 0.1 by means of a 1 M- $\text{NaClO}_4$  solution.

The cations were used in the form of anal. grade nitrates. The concentration of solutions was checked chelatometrically [25].

The pH measurement of solutions was done with a pH-meter Radelkis-Precision Type OP-205, equipped with a glass electrode OP 711-1/A and calomel electrode OP-700. The functioning of glass electrode was checked in acid region by means of a hydrogen electrode.

The absorbance of solutions was measured with a universal spectrophotometer VSU-1 (Zeiss, Jena).

### Results and discussion

In the pH range from 0.15 to 12.80 DIBTAR occurs in four differently coloured acid-base forms. At  $\text{pH} < 2.6$ , the atom of heteronitrogen is protonized and the neutral form  $\text{RH}_2$  is transformed into the orange-red form  $\text{RH}_3^+$ . The yellow undissociated form  $\text{RH}_2$  occurs in the solution at  $\text{pH} 3-5$ , as obvious from Fig. 1. At  $\text{pH} > 5$ , the hydrogen

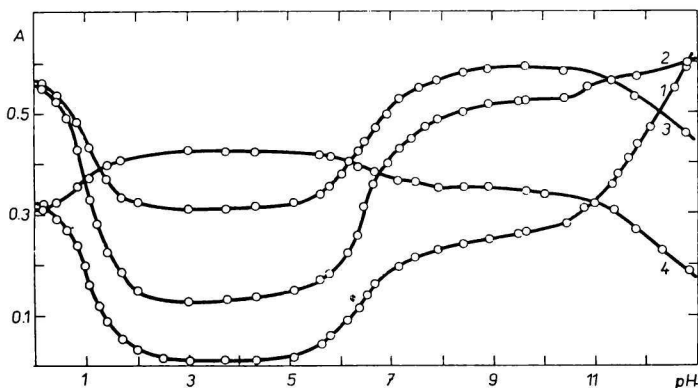
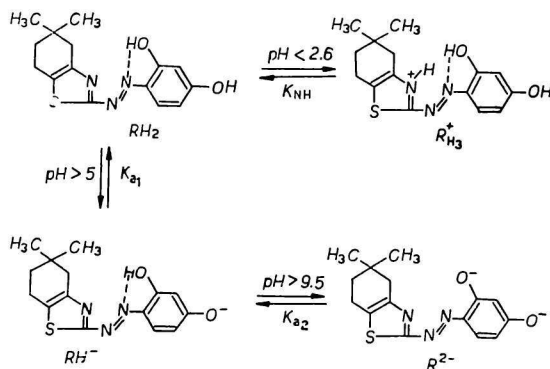


Fig. 1. Absorbance as a function of pH for DIBTAR.

$$c_R = 1.6 \times 10^{-5} \text{ M}; l = 1.00 \text{ cm.}$$

1. 540 nm; 2. 510 nm; 3. 490 nm; 4. 440 nm.

atom of the hydroxyl group in *p*-position with respect to azo group dissociates what leads to the gradual colour change of the yellow form  $\text{RH}_2$  into the red form  $\text{RH}^-$ . Above  $\text{pH} 9.5$ , the hydroxyl group which is in *o*-position with respect to azo group also dissociates. Thus the reagent is transformed into the violet-red form  $\text{R}^{2-}$ . The equilibria concerning particular acid-base forms of DIBTAR may be expressed as shown in Scheme 1.



Scheme 1

Thus it follows that the absorption spectrum of DIBTAR exhibits in visible region four absorption maxima, which correspond to individual forms of the reagent

$$\lambda(\text{RH}_3^+) = 500 \text{ nm}, \lambda(\text{RH}_2) = 460 \text{ nm}, \lambda(\text{RH}^-) = 490 \text{ nm}, \lambda(\text{R}^{2-}) = 510 \text{ nm}.$$

The absorption spectrum shows isosbestic points, which give proof of the existence of simple equilibria between the above-mentioned forms of reagent

$$\lambda_1 = 467 \text{ nm} \text{ corresponds to the equilibrium } \text{RH}_3^+ \rightleftharpoons \text{RH}_2 + \text{H}^+,$$

$$\lambda_2 = 454 \text{ nm} \text{ corresponds to the equilibrium } \text{RH}_2 \rightleftharpoons \text{RH}^- + \text{H}^+,$$

$$\lambda_3 = 505 \text{ nm} \text{ corresponds to the equilibrium } \text{RH}^- \rightleftharpoons \text{R}^{2-} + \text{H}^+.$$

The acidity of the hydroxyl group in *o*-position with respect to azo group is lower owing to the existence of hydrogen bond. In comparison with 2-(5,5-dimethyl-4,5,6,7-tetrahydrobenzthiazolyl-2-azo)-4-methylphenol (DIBTAK) [26] which also possesses a hydroxyl group in *o*-position with respect to azo group, the hydroxyl group of DIBTAR is less acid. That is evidently due to the fact that the molecule of DIBTAK is without any effect of the negative charge of phenolate ion before the dissociation of this group.

The protonization and deprotonization of DIBTAR produce a colour change and a bathochromic shift of absorption maxima. The relation between protonization or deprotonization and the change in the constitution of the whole molecule is still more evident owing to the fact that the molecules of the reagent investigated are conducting systems. That is why *e.g.* the negative charge on hydroxyl oxygen atom is delocalized over all the molecule after dissociation of hydrogen ion. The delocalization of electric charge in these molecules results in an intensification of *p*- $\pi$  conjugation what may be considered to be the cause of the bathochromic effect in the case of DIBTAR.

The molar absorptivities of individual forms of reagent as well as the dissociation constants were found by the graphical analysis of the rising part of the curves expressing absorbance as a function of pH [27, 18] and subsequently by calculation. Some molar absorptivities were calculated from the horizontal parts of these plots by using unit width of layer according to the formula

$$a_{\text{R}} = \frac{A}{c_{\text{R}}} \cdot \quad (1)$$

To calculate the dissociation constants, the expressions deduced from the fundamental relationships valid for the dissociation constants of weak acids were used

$$K_{\text{NH}} = \frac{(a_{\text{R1}} c_{\text{R}} - A) [\text{H}^+]}{A - a_{\text{R2}} c_{\text{R}}}, \quad (2)$$

$$K_{\text{a1}} = \frac{(A - a_{\text{R2}} c_{\text{R}}) [\text{H}^+]}{a_{\text{R3}} c_{\text{R}} - A} \quad (3)$$

$$K_{\text{a2}} = \frac{(A - a_{\text{R3}} c_{\text{R}}) [\text{H}^+]}{a_{\text{R4}} c_{\text{R}} - A} \quad (4)$$

The individual molar absorptivities  $a_{\text{R2}}$ ,  $a_{\text{R3}}$ , and  $a_{\text{R4}}$  were calculated from the absorbances of solutions of the individual forms of reagent according to the relationship (1).

The subsequent equations of straight line obtained by a convenient rearrangement of expressions (2), (3), and (4) were used for graphical analysis (Fig. 2).

$$\frac{c_{\text{R}}}{A} = \frac{1}{a_{\text{R1}}} + \frac{(A - a_{\text{R2}} c_{\text{R}}) K_{\text{NH}}}{a_{\text{R1}} [\text{H}^+] A} \quad (5)$$

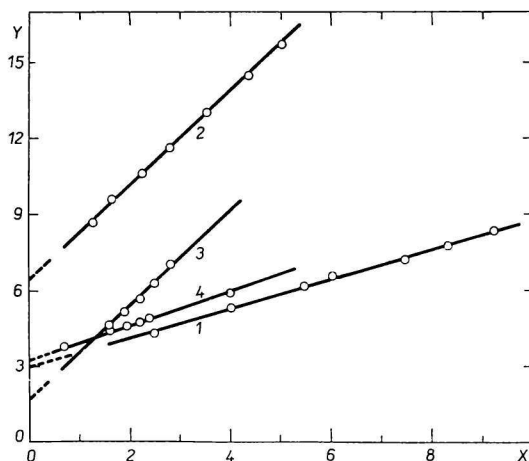


Fig. 2. Graphical analysis of the curve  $A = f(\text{pH})$  for DIBTAR.

$$y = \frac{c_{\text{R}}}{A} \cdot 10^5.$$

$$1. \ 540 \text{ nm}; \ x = \frac{A - a_{\text{R2}} c_{\text{R}}}{[\text{H}^+] A}.$$

$$2. \ 540 \text{ nm}; \ x = \frac{(A - a_{\text{R2}} c_{\text{R}}) [\text{H}^+]}{A} \cdot 10^7.$$

$$3. \ 510 \text{ nm};$$

$$4. \ 540 \text{ nm}; \ x = \frac{(A - a_{\text{R3}} c_{\text{R}}) [\text{H}^+]}{A} \cdot 10^{12}.$$

$$\frac{c_R}{A} = \frac{1}{a_{R3}} + \frac{(A - a_{R2} c_R) [H^+]}{K_{a1} a_{R3} A}, \quad (6)$$

$$\frac{c_R}{A} = \frac{1}{a_{R4}} + \frac{(A - a_{R3} c_R) [H^+]}{K_{a2} a_{R4} A}. \quad (7)$$

The dissociation constants were also estimated by logarithmic analysis of the curves expressing absorbance as a function of pH [28] by using the following relations

$$pK_{NH} = pH - \log \frac{a_{R1} c_R - A}{A - a_{R2} c_R}, \quad (8)$$

$$pK_{a1} = pH - \log \frac{A - a_{R2} c_R}{a_{R3} c_R - A}, \quad (9)$$

$$pK_{a2} = pH - \log \frac{A - a_{R3} c_R}{a_{R4} c_R - A} \quad (10)$$

The molar absorptivities and dissociation constants of DIBTAR are given in Table 1.

Table 1

Molar absorptivities and dissociation constants of DIBTAR

Form of reagent	$\lambda_{max}$ [nm]	$a_R \cdot 10^{-4}$	$\lambda$ [nm]	$pK_{NH}$	$pK_{a1}$	$pK_{a2}$
$RH_3^+$	500	3.56	540	0.34 (5)	6.50 (6)	10.97 (7)
$RH_2$	460	2.5	540	0.47* (8)	6.47* (9)	11.20* (10)
$RH^-$	490	3.68	490		6.70 (3)	
$R^{2-}$	510	3.60				

\* Used for the calculation of the constants of complexes.

### Analytical reactions of DIBTAR

DIBTAR reacts with metal ions even in acidic or slightly acidic medium under formation of red or red-violet solutions. At  $pH < 1$  this reaction involves Bi(III) and Cu(II) as representatives of common cations. In the case of Ni(II), Co(II), Zn(II), Pb(II), Cd(II), U(VI), Ag(I), and Fe(III) this reagent reacts in the pH range from 2 to 5. Among common cations it is Mn(II) which reacts at  $pH > 5$ .

The sensitivity of analytical reactions of DIBTAR was tested as follows: ethyl alcohol (1.5 ml) and the solution of a cation (1 ml), the original concentration of which was  $2 \times 10^{-3}$  M, were added into a  $2 \times 10^{-3}$  M solution of reagent (1 ml). The volume was made up to 5 ml with a buffer solution. The colour arisen was compared with the colour of the reagent alone at equal pH. The results are compiled in Table 2.

The data found correspond to optimum demands on the sensitivity of analytical reactions.

Table 2

Colour and sensitivity of the reaction of some complexes with DIBTAR

Cation	Cu(II)	Pb(II)	Ni(II)	Co(II)	Zn(II)	Cd(II)	Bi(III)
pD	6.6	5.5	6.6	6.4	6.4	6.2	5.8
Colour	v	v	rv	rv	rv	rv	r
Cation	U(VI)	Ag(I)	Mn(II)	Fe(III)			
pD	5.7	5.4	5.3	4.7			
Colour	rv	r	rv	rv			

rv — red-violet, r — red, v — violet.

The character of the absorption curves of DIBTAR with an excess of  $\text{Cu}^{2+}$  as well as of the curves expressing  $A$  as a function of pH [ $A = f(\text{pH})$ ] indicates a successive formation of two complexes, which absorb at different wavelengths. In the pH range between 0.7 and 1.8 the complex of blue-violet colour with absorption maximum at 575 nm is formed (Fig. 3, curve 5; Fig. 4, curve 1). The second red-violet complex with absorption maximum at 540 nm is formed at pH ranging from 3 to 6 (Fig. 4, curve 2; Fig. 3, curve 2). The absorption curves exhibit two isosbestic points, at  $\lambda_1$  460 and 575 nm. The composition of complexes corresponds to molar ratio 1 : 1 (Fig. 5d).

The absorption spectrum of DIBTAR solutions with an excess of  $\text{Ni}^{2+}$  (Fig. 6) shows that two complexes are successively formed in the pH region between 2 and 8. The absorption maximum of the first complex is at 550–560 nm. The series of the absorbance curves corresponding to this complex exhibits an isosbestic point ( $\lambda_1$ ) at 500 nm. Owing to the formation of complex, the yellow colour of solution turns into blue-violet. The second red-violet complex with absorption maximum between 520 and 530 nm starts to be formed above pH 4.7. Two isosbestic points ( $\lambda_1$ ) at 580 and 440 nm pertain to the series of the absorbance curves.

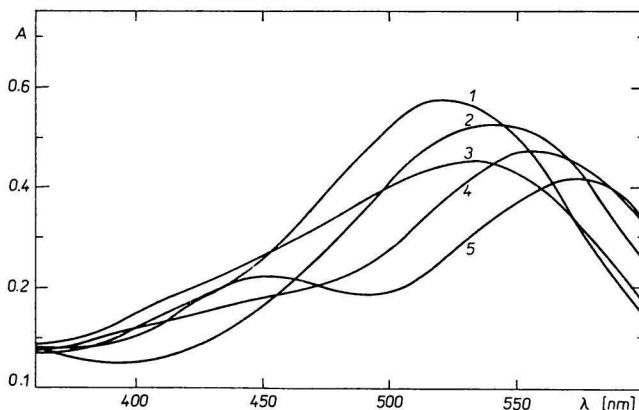


Fig. 3. Absorption curves of the solutions containing DIBTAR complexes.

 $c_R = 1.6 \times 10^{-5} \text{ M}; l = 1.00 \text{ cm}.$ 

 1.  $c_{\text{Cd}} = 8 \times 10^{-4} \text{ M}$ , pH = 7.02; 2.  $c_{\text{Cu}} = 1.2 \times 10^{-3} \text{ M}$ , pH = 5.67;

 3.  $c_{\text{Zn}} = 8 \times 10^{-4} \text{ M}$ , pH = 6.01; 4.  $c_{\text{Pb}} = 8 \times 10^{-4} \text{ M}$ , pH = 5.40;

 5.  $c_{\text{Cu}} = 1.2 \times 10^{-3} \text{ M}$ , pH = 1.85.

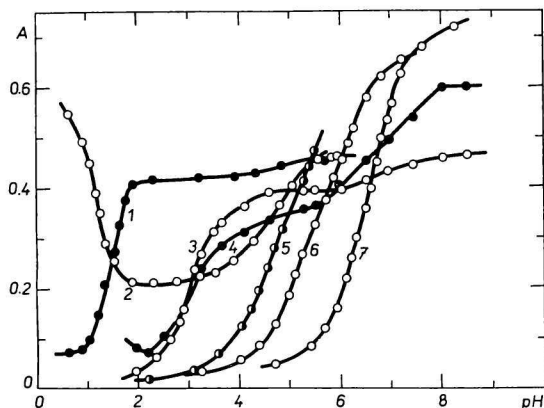


Fig. 4. Absorbance as a function of pH for DIBTAR complexes.  
 1. (Cu) 570 nm; 2. (Cu) 510 nm; 3. (Ni) 560 nm; 4. (Ni) 530 nm; 5. (Pb) 560 nm;  
 6. (Zn) 530 nm; 7. (Cd) 530 nm.

The transition of the first complex into the second one is very distinct in the case of the curves giving absorbance as a function of pH in solutions containing an excess of  $\text{Ni}^{2+}$  (Fig. 4, curves 3, 4). The composition of complexes corresponds to the molar ratio  $M : R = 1 : 2$  (Fig. 5b).

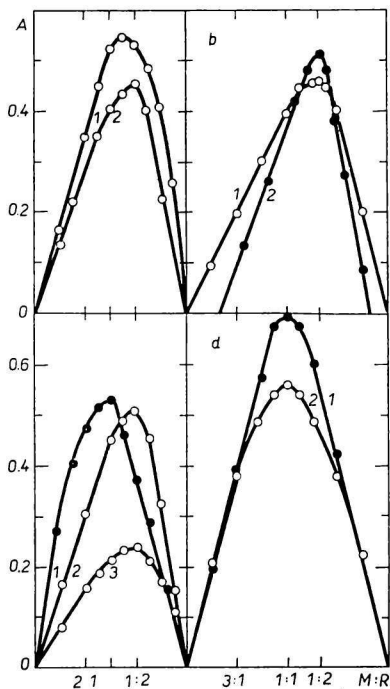


Fig. 5. The Job's curves for DIBTAR complexes.

$$c_R^0 = c_M^0 = 2 \times 10^{-3} \text{ M.}$$

- a) (Cd) 1. pH = 6.80,  $l = 2.00$  cm, 530 nm;  
 2. pH = 8.62,  $l = 1.00$  cm, 530 nm.  
 b) (Ni) 1. pH = 5.15,  $l = 1.00$  cm, 520 nm;  
 2. pH = 8.20,  $l = 1.00$  cm, 540 nm.  
 c) (Pb) 1. pH = 5.25,  $l = 1.00$  cm, 560 nm;  
 (Zn) 2. pH = 8.35,  $l = 1.00$  cm, 540 nm;  
 (Zn) 3. pH = 5.40,  $l = 1.00$  cm, 540 nm.  
 d) (Cu) 1. pH = 5.13,  $l = 1.00$  cm, 580 nm;  
 2. pH = 2.95,  $l = 1.00$  cm, 540 nm.

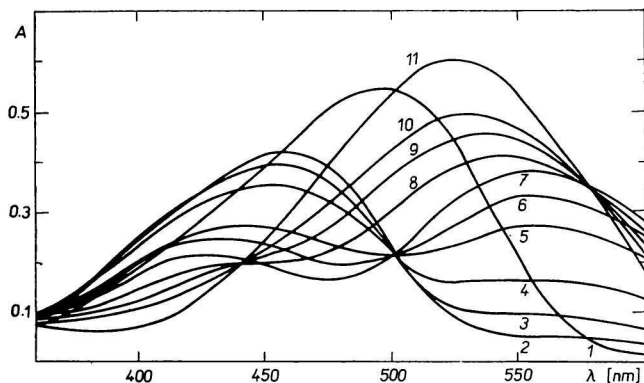


Fig. 6. Absorption curves of the complexes of Ni with DIBTAR.

$$c_R = 1.6 \times 10^{-5} \text{ M}; c_M = 8 \times 10^{-4} \text{ M}; l = 1.00 \text{ cm.}$$

pH: 1. 0.4; 2. 2.19; 3. 2.50; 4. 2.92; 5. 3.25; 6. 3.62; 7. 4.63; 8. 5.99; 9. 6.48;  
10. 6.92; 11. 8.03.

According to the course of the curve expressing the dependence of absorbance on pH in the solutions of DIBTAR with an excess of  $\text{Cd}^{2+}$  ions (Fig. 4, curve 7), the complex is formed on condition that  $\text{pH} > 5$ . The most rapid increase in the absorbance and thus in the concentration of complex appears in the pH region between pH 6 and pH 7. The curves expressing absorbance as a function of pH [ $A = f(\text{pH})$ ] do not indicate, in contrast to the curves obtained with Cu(II) and Ni(II) any formation of complexes with different absorption. The fact that the formation of a complex effects an increase in the acidity of hydroxyl group in *p*-position confirms the statement that a normal complex with absorption maximum at 520 nm (Fig. 3, curve 1) is formed in the reaction of DIBTAR with  $\text{Cd}^{2+}$  in the pH range from pH 5.5 to pH 7. The isosbestic point ( $\lambda_i$ ) is at 478 nm and the composition of the complex of DIBTAR with  $\text{Cd}^{2+}$  corresponds at higher pH to the molar ratio  $M : R = 1 : 2$ . A decrease in pH shifts the composition even in equimolar solutions towards the ratio 1 : 1 (Fig. 5a). In solutions containing an excess of  $\text{Cd}^{2+}$ , a complex of the composition of 1 : 1 is supposed to be formed.

According to the character of the curves giving the dependence of absorbance on pH in the solutions of DIBTAR containing an excess of  $\text{Zn}^{2+}$  ions (Fig. 4, curve 6) a complex is formed in the pH range from pH 4 to pH 7. The absorption maximum shifts with increasing pH of solution from the value of 550 nm to shorter wavelengths. At pH 5.27, the absorption maximum is established at the value of 530 nm (Fig. 3, curve 3). It is obvious that a protonized complex comes into existence at lower pH and successively with increasing pH is transformed into a "normal" complex. In the series of curves giving the absorbance of equimolar solutions the shift in the maximum of complex is not observable. The composition of the complex corresponds to the molar ratio  $M : R = 1 : 2$  (Fig. 5c, curves 2, 3).

The complex of DIBTAR with an excess of  $\text{Pb}^{2+}$  starts to be formed at as few as pH 3 (Fig. 4, curve 5). In this pH region a protonized complex is formed. That is confirmed by the character of the plots giving the absorbance in the solutions with an excess of  $\text{Pb}^{2+}$  ions as well as in equimolar solutions. The curves of absorbances in the presence of excess  $\text{Pb}^{2+}$  ions show the absorption maximum at 560 nm (Fig. 3, curve 4) and as early



as at pH 5.40 this maximum shifts to shorter wavelengths what might be due to a deprotonization of the complex. The series of the curves of absorbances in equimolar solutions with absorption maxima at 540–550 nm confirms this idea. The composition of the complex of DIBTAR with  $Pb^{2+}$  corresponds to the molar ratio 1 : 1 (Fig. 5c, curve 1).

Provided all components absorbing under the conditions of the reaction are taken into consideration, it is possible to deduce some relationships for the equilibrium constants of the reactions of reagent with the cations studied ( $K_{11H}$ ,  $K_{12H}$ ,  $K_{22H}$ ,  $K_{22}$ , and  $K_{11}$ ) which are valid in the presence of excess cations. These relationships may be given the following forms of the equations of straight line [27] valid for the unit width of layer

$$\frac{c_R}{A} = \frac{1}{a_{1H}} + \frac{\left\{ A \left( 1 + \frac{K_{NH}}{[H^+]} \right) - a_{R1} c_R \right\} [H^+]^2}{K_{12H} c_M a_{1H} A}, \quad (11)$$

$$\frac{c_R}{A} = \frac{1}{a_{1H}} + \frac{\left\{ A \left( \frac{[H^+]}{K_{NH}} + 1 \right) - a_{R1} \frac{[H^+]}{K_{NH}} c_R \right\} [H^+]^2}{K_{11H} c_M a_{1H} A} \quad (12)$$

$$\frac{c_R}{A} = \frac{1}{a_1} + \frac{\left\{ A \left( \frac{[H^+]}{K_{a1}} + 1 \right) - \left( a_{R2} \frac{[H^+]}{K_{a1}} + a_{R3} \right) c_R \right\} [H^+]^2}{K_{11} c_M a_1 A} \quad (13)$$

$$\frac{c_R}{A} = \frac{2}{a_{2H}} + \frac{\sqrt{A a_{2H} \cdot [H^+]}}{\sqrt{K_{22H} c_M a_{2H} A}} \quad (14)$$

$$\frac{c_R}{A} = \frac{1}{a_{1H}} + \frac{(A - a_{R2} c_R) [H^+]}{K_{11H} c_M a_{1H} A}. \quad (15)$$

The molar absorptivities of individual complexes  $a_{1H}$ ,  $a_{2H}$ , and  $a_1$  as well as the equilibrium constants were obtained on the basis of above relationships (Fig. 7) by using the graphical analysis of rising parts of the curves expressing absorbance as a function of pH. The molar absorptivity of the Zn-DIBTAR complex ( $a_2$ ) was calculated according to expression (1) and the equilibrium constant according to following equation

$$K_{22} = \frac{[H^+]^2 \left\{ a_2 \left[ A \left( \frac{[H^+]}{K_{a1}} + 1 \right)^2 - \left( \frac{[H^+]}{K_{a1}} + 1 \right) \left( a_{R2} \frac{[H^+]}{K_{a1}} + a_{R3} \right) c_R \right] - 2A \left( a_{R2} \frac{[H^+]}{K_{a1}} + a_{R3} \right) \left[ \left( \frac{[H^+]}{K_{a1}} + 1 \right) + 2c_R \left( a_{R2} \frac{[H^+]}{K_{a1}} + a_{R3} \right) \right] \right\}}{c_M (a_2 c_R - 2A)^2}$$

The number of the hydrogen ions split off during the formation of complexes was verified on the basis of the following equations by using logarithmic analysis

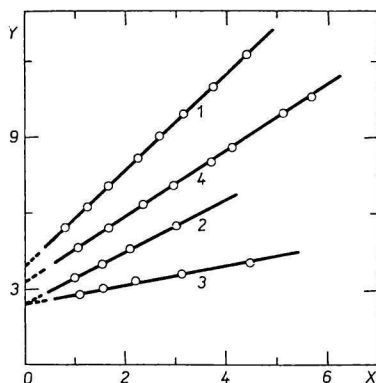
$$\log \frac{A \left( 1 + \frac{K_{NH}}{[H^+]} \right) - a_{R1} c_R}{a_{1H} c_R - A} = \log K_{12H} + \log c_M + 2 \text{ pH}, \quad (16)$$

$$\log \frac{A \left( \frac{[\text{H}^+]}{K_{\text{NH}}} + 1 \right) - a_{\text{R1}} \frac{[\text{H}^+]}{K_{\text{NH}}} c_{\text{R}}}{a_{1\text{H}} c_{\text{R}} - A} = \log K_{11\text{H}} + \log c_{\text{M}} + \text{pH}, \quad (17)$$

$$\log \frac{A - a_{\text{R2}} c_{\text{R}}}{a_{1\text{H}} c_{\text{R}} - A} = \log K_{11\text{H}} + \log c_{\text{M}} + \text{pH}, \quad (18)$$

$$\log \frac{A \left( \frac{[\text{H}^+]}{K_{\text{a1}}} + 1 \right) - \left( a_{\text{R2}} \frac{[\text{H}^+]}{K_{\text{a1}}} + a_{\text{R3}} \right) c_{\text{R}}}{a_1 c_{\text{R}} - A} = \log K_{11} + \log c_{\text{M}} + \text{pH}, \quad (19)$$

$$\log \frac{A a_{2\text{H}}}{(a_{2\text{H}} c_{\text{R}} - 2A)^2} = \log K_{22\text{H}} + \log c_{\text{M}} + 2 \text{pH}. \quad (20)$$



*Fig.* Graphical analysis of the curves  $A = f(\text{pH})$  for DIBTAR with an excess of cation.

$$y = \frac{c_{\text{R}}}{A} \cdot 10^5$$

$$1. \text{ (Ni) } 560 \text{ nm}; x = \frac{[\text{H}^+] \sqrt{A}}{A} \cdot 10^3$$

$$2. \text{ (Cu) } 570 \text{ nm}; x = \frac{\left\{ A \left( 1 + \frac{[\text{H}^+]}{K_{\text{NH}}} \right) - a_{\text{R1}} c_{\text{R}} \frac{[\text{H}^+]}{K_{\text{NH}}} \right\} [\text{H}^+]}{A} \cdot 10^2$$

$$3. \text{ (Cd) } 530 \text{ nm}; x = \frac{\left\{ A \left( \frac{[\text{H}^+]}{K_{\text{a1}}} + 1 \right) - \left( a_{\text{R2}} \frac{[\text{H}^+]}{K_{\text{a1}}} + a_{\text{R3}} \right) c_{\text{R}} \right\} [\text{H}^+]}{A} \cdot 10^7$$

$$4. \text{ (Pb) } 560 \text{ nm}; x = \frac{(A - a_{\text{R2}} c_{\text{R}}) [\text{H}^+]}{A} \cdot 10^5$$

The graphical representation of these relationships gave straight lines the slopes of which ( $k$ ) indicated the number of the protons abstracted during the reaction (Fig. 8).

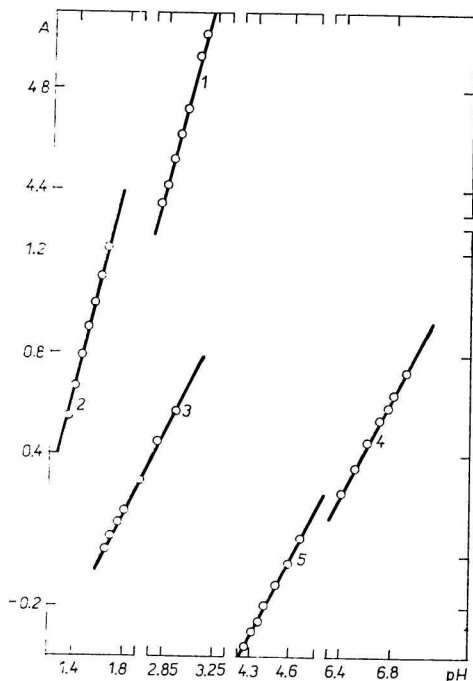


Fig. 8. Logarithmic analysis of the curves  $A = f(\text{pH})$  for the solutions containing DIBTAR with an excess of cation.

1. Ni (according to (20)); 2. Cu (according to (16)); 3. Cu (according to (17)); 4. Cd (according to (19)); 5. Pb (according to (18)).

For the stability constants of the complex a relationship may be deduced from the relations between the overall equilibrium and the partial equilibria [27]

$$K_{1H} = \frac{K_{12H}}{K_{NH} K_{a2}} \quad (21)$$

$$K_{1H} = \frac{K_{11H}}{K_{a2}}, \quad (22)$$

$$K_{2H} = \frac{K_{22H}}{(K_{a2})^2} \quad (23)$$

$$K_1 = \frac{K_{11}}{K_{a2}} \quad (24)$$

$$K_2 = \frac{K_{22}}{(K_{a2})^2}. \quad (25)$$

The results of graphical and logarithmic analysis are compiled in Table 3.

In the medium of 40% aqueous solution of ethyl alcohol DIBTAR forms with metal ions complexes, which are of different composition (1:1 and 1:2). At lower values of pH the protonized complexes are formed.

Table 3

Absorption maxima, molar absorptivities, equilibrium constants, the slopes of logarithmic transformation and the constants of stability of the complexes containing DIBTAR

Complex	$\lambda_{\max}$ [nm]	$\lambda_i$ [nm]	Equilibrium constant	$k$	$10^{-4}$	$\log K$
CuRH <sup>+</sup>	575	500	9.03	2.14	4.10	12.3
			(11)	(16)	(11)	(21)
			19.20	1.04	4.10	12.2
			(12)	(17)	(12)	(22)
CuR	540	460				
		575				
Ni(RH) <sub>2</sub>	560	500	65.40	1.96	5.12	23.8
			(14)	(20)	(4)	(23)
NiR <sub>2</sub> <sup>2-</sup>	530	580				
		440				
CdR	525	478	$8.25 \times 10^{-4}$	0.98	4.08	7.9
			(13)	(19)	(13)	(24)
ZnR <sub>2</sub> <sup>2-</sup>	530	469	0.229	—	4.06	21.3
					(1)	(25)
PbRH <sup>+</sup>	560	495	$3.10 \times 10^{-2}$	1.01	3.08	9.5
			(15)	(18)	(15)	(22)
PbR	540					

The protonized complexes possess a hydrogen atom bonded with the oxygen atom in *p*-position with respect to azo group. This hydrogen atom is more acidic in complex than it is in the reagent itself. For this reason the protonized complex dissociates at lower pH than pure reagent. Only the complex-forming reaction may be responsible for the increase in the acidity of *p*-hydroxyl group. Between the heteronitrogen as well as the nitrogen of azo group and the central ion some coordination relations are operative which reduce locally the electron density. Because of conjugation an equalization of electron density occurs in the whole molecule what results in an intensification of *p*- $\pi$  conjugation and thus in an increase in the acidity of hydroxyl group. The increase in acidity of the *p*-hydroxyl group is proportional to the stability of the complex formed with Cu(II), Pb(II), Cd(II), Ni(II), and Zn(II) what is in agreement with the results obtained in other studies [3, 29].

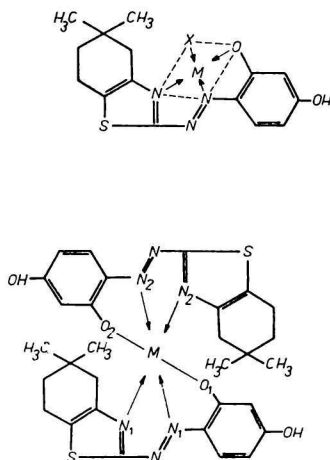
In all cases under investigation the formation of complex is accompanied by a bathochromic effect. The dissociation of protonized complexes is usually accompanied by a hypsochromic effect.

DIBTAR gives more stable complexes than DIBTAK. The cause of higher stability consists in the effect of another hydroxyl group occurring in the molecule of DIBTAR. In contrast to TAR, DIBTAR is insoluble in water. Therefore an aqueous-alcoholic medium must be used for the study of DIBTAR and its complexes.

In general, the heterocyclic *o*-hydroxyazo dyes are assumed to be triple-donor ligands. The results obtained conform with this general conclusion. If, *e.g.*, the coordination number 4 is characteristic of Cu<sup>2+</sup> [30], then the composition 1 : 1 of the complex containing DIBTAR gives evidence for its triple-donor character. If DIBTAR were of double-donor character, the composition 1 : 2 would be more likely for the complexes with Cu<sup>2+</sup> showing the coordination number equal to 4.

The structure of the complexes formed by central ions and heterocyclic *o*-hydroxyazo dyes is not unequivocally stated in literature. It is evidently due to the fact that the problem of mechanism of the formation of complexes with azo compounds is still in the stage of discussion [31]. Assuming that the mutual reaction between central ions and azo compounds consists virtually in the interaction between the external electron spheres of ions as well as donor atoms of azo compounds, then the electron structures of central ions as well as reagents themselves represent the essential factors in the solution of this problem.

The space disposition of the complexes of DIBTAR with normal structure may be figured for the composition  $M : R = 1 : 1, 1 : 2$  (Scheme 2).



Scheme 2

It is supposed that the complex of DIBTAR with Cu(II) is planar. The individual donor atoms of the reagent as a conjugated system (heteronitrogen, nitrogen of azo group, and hydroxyl oxygen) are situated in three apices of a square; the fourth coordination position is taken by a molecule of solvent. The equal space disposition of donor atoms is also supposed for the complexes of other metals the composition of which corresponds to molar ratio 1 : 1. For the composition of chelates corresponding to molar ratio 1 : 2 an octahedral disposition of six donor atoms in two planes perpendicular to each other is supposed.

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