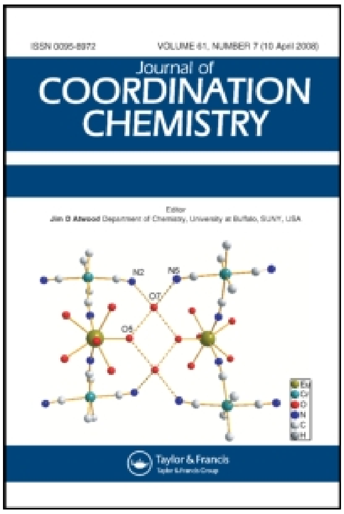

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COMPLEXATION BETWEEN COBALT(II), NICKEL(II) AND 4-(4′,5′-DIMETHYL-2′-THIAZOLYLAZO)-2-METHYLRESORCINOL. A SPECTROPHOTOMETRIC STUDY

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Complexation equilibria between Co(II) and Ni(II) and 4-(4′,5′-dimethyl-2′-thiazolylazo)-2-methylresorcinol have been studied spectrophotometrically. Graphical as well as numerical calculation methods have been used to establish the species in solution and stability constants have been determined at 25°C and $I = 0.25$M (Co: $\log\beta_{111} = 9.90 \pm 0.04$, $\log\beta_{101} = 12.30 \pm 0.08$, $\log\beta_{102} = 14.83 \pm 0.09$; Ni: $\log\beta_{111} = 19.89 \pm 0.05$, $\log\beta_{101} = 12.21 \pm 0.04$).

Keywords: Cobalt, nickel, complexes, heteroazoligands, stability

INTRODUCTION

Heteroazo compounds have been widely used as chromogenic reagents as well as metallochromic indicators for several metal ions but only in a few cases have the equilibria involved been studied.[1,2] The ligand 4-(4′,5′-dimethyl-2′-thiazolylazo)-2-methylresorcinol, DMTAMR, has been previously synthesized and its acid-base equilibria and complexation equilibria with several metal ions studied,[3–7] in 40% (v/v) methanol/water.

In this paper the acid-base equilibria of DMTAMR and its complexation equilibria with Co(II) and Ni(II) in 20% (v/v) acetone/water at $I = 0.25$M ($NaClO_4$) are reported. Graphical as well as numerical calculation methods are used to establish the nature of the complex species in solution and to calculate stability constants which have not been hitherto reported in the literature.

EXPERIMENTAL

Absorbance measurements were made using a Beckman 25 or a Perkin-Elmer 550S recording spectrophotometer with 1 cm matched quartz cells. A Radiometer PHM64 digital pH meter with glass-calomel combination electrode was used for pH measurements at 25°C. Calculations were carried out on a Digital VAS/VMX 11/780 (V.4.O) computer. Standard 10^{-1}M solutions of $Co(ClO_4)_2$ and $Ni(ClO_4)_2$ were prepared from the nitrates by perchloric acid treatment and standardized complexometrically. A 10^{-3}M DMTAMR solution in acetone was used as the ligand source. Analytical reagent grade chemicals and distilled water were used throughout with no further purification.

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TABLE I

Values of pK_{ax} and molar absorptivities of DMTAMR species obtained by graphical and numerical calculation methods (20% v/v acetone/water medium, $I = 0.25M\ NaClO_4$, 25°C).

		Graphical Method		Numerical Method**	
Species	λ_{max}(nm)	$\varepsilon x10^{-4}$*	pK_{ax}	ε*	$pK_{ax} \pm 3SD$
H_3R^+	500	2.14		22,000 ± 80	
H_2R	460	1.33	$pk_{a1} = 1.61 \pm 0.02$	27,000 ± 100	1.60 ± 0.13
HR^-	525	2.67	$pk_{a2} = 7.06 \pm 0.04$	12,300 ± 200	6.98 ± 0.05
R^{2-}	550	2.01	$pk_{a3} = 11.19 \pm 0.08$	22,000 ± 70	11.81 ± 0.20

* $1\ mol^{-1}cm^{-1}$; ** for $\sigma(A) = 0.009$, and $U = 7.51 \times 10^{-3}$.

RESULTS AND DISCUSSION

Acid-base equilibria of DMTAMR

To study the acid-base behaviour of DMTAMR in 20% (v/v) acetone/water medium at $I = 0.25M\ NaClO_4$ and at 25°C a method of graphical analysis of the absorbance-pH experimental curves was first used.[8] Values calculated for pK_{ax} together with the optical characteristics of each species are listed in Table I. The experimental data were further refined using the LETAGROP-SPEFO numerical calculation method.[9] The results obtained are included in Table I. Good agreement between both methods is apparent.

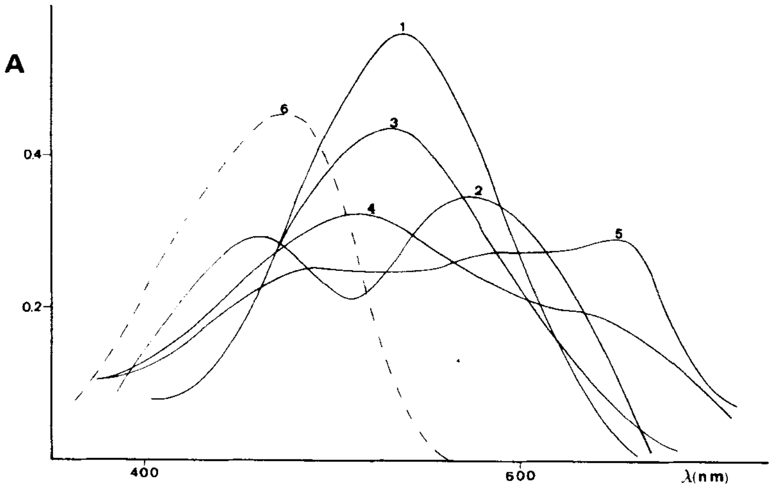

FIGURE 1 Absorption spectra of the Ni(II)-DMTAMR system as a function of pH, 20% (v/v) acetone/water, $I = 0.25M\ (NaClO_4)$, 25°C. $C_R = 2 \times 10^{-5}M$, $C_{Ni} = 1 \times 10^{-3}M$, pH: 1) 7.55, 2) 5.80; $C_M = 0.95 \times 10^{-5}M$, pH: 3) 7.25, 4) 6.77, 5) 4.47; R) reagent alone, $C_R = 2 \times 10^{-5}M$, at pH 5.40.

Complexation equilibria between Co(II), Ni(II) and DMTAMR

Solutions containing Co(II) and DMTAMR appear brown-violet and at pH $\leqslant 4$ show an absorption band at 590–675 nm in solutions which have either metal ion or reagent in excess, Fig. 1. A well-defined maximum at 540 nm is found for pH $\geqslant 5$. In equimolar solution at pH $\leqslant 5$ two absorption maxima at 500 and 550 nm and a shoulder at 590 nm can be seen.

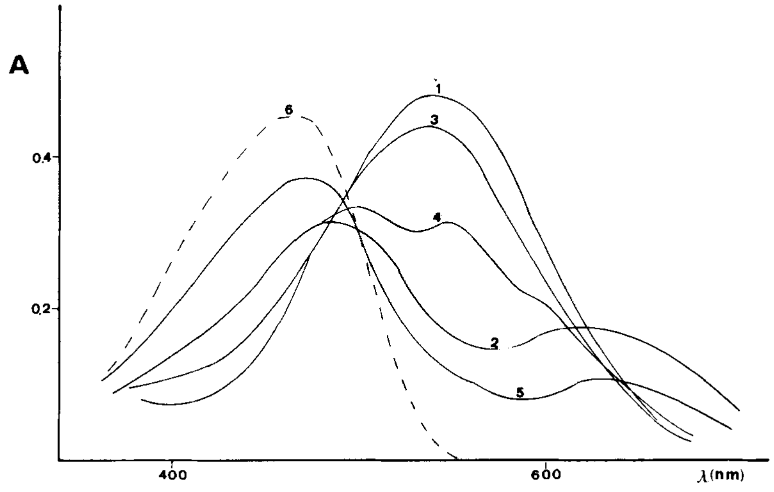

FIGURE 2 Absorption spectra of the Co(II)-DMTAMR system as a function of pH, 20% (v/v) acetone/water, $I = 0.25$M (NaClO$_4$), 25°C. $C_R = 2 \times 10^{-5}$M, $C_{Co} = 7.7 \times 10^{-3}$M, pH: 1) 7.60, 2) 2.50; $C_{Co} = 0.96 \times 10^{-5}$M, pH: 3) 7.06, 4) 5.24, 5) 3.32; R) reagent alone, $C_R = 2 \times 10^{-5}$M, at pH 5.40.

Ni(II) and DMTAMR give violet coloured solutions at pH $\geqslant 5$. In solutions with metal ion in excess, Fig. 2, an absorption maximum at 560 nm appears which shifts to 540 nm as the pH increases. With reagent in excess a broad absorption band at 560–675 nm is seen at pH $\leqslant 5$ which changes to a well-defined absorption maximum at 540 nm as the pH increases. Thus for both systems the presence of at least two complex species in solution is apparent.

The absorbance-pH curves for several C_{Ni}/C_R ratios at the absorption maxima, Fig. 3, clearly show the presence of at least two species in solution. For the Co(II)-DMTAMR system no such clear conclusion can be drawn although the corresponding A-pH curves do indicate the presence of more than one complex species.

The stoichiometries of the complexes for each system were established by the continuous variation and mole ratio methods and show the presence of 1 : 1 (Ni : R) and 1 : 2 (Co : R) complex species.

In order to calculate the stability constants for each complex the method of graphical analysis of the absorbance-pH dependences of Sommer *et al.*,[10,11] was first used. For the two systems the presence of the species NiHR ($\log \beta_{111} = 19.90 \pm 0.05$, $\varepsilon_{111} = 1.01 \times 10^4$ l mol^{-1}cm^{-1}), NiR ($\log \beta_{101} = 13.27 \pm 0.09$, $\varepsilon_{101} = 3.04 \times 10^4$), CoHR ($\log \beta_{111} = 19.00 \pm 0.05$, $\varepsilon_{111} = 1.75 \times 10^4$) and CoR$_2$ ($\log \beta_{102} = 27.80 \pm 0.09$, $\varepsilon_{102} = 4.5 \times 10^4$) was established.

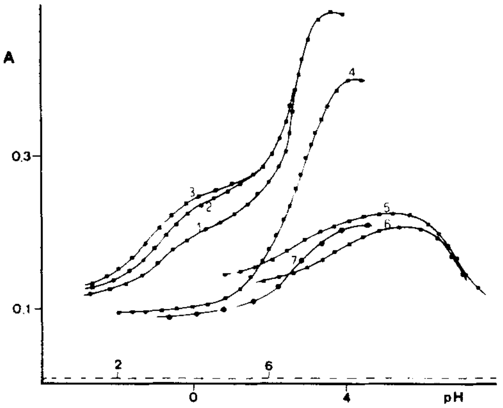

FIGURE 3 Absorbance–pH curves for the system Ni(II)–DMTAMR at 540 nm: 1) $C_R = 1 \times 10^{-3}$M, $C_{Ni} = 2 \times 10^{-5}$M; 2) $C_R = 2 \times 10^{-5}$M, $C_{Ni} = 1.6 \times 10^{-6}$M; 3) $C_R = 2 \times 10^{-5}$M, $C_{Ni} = 2 \times 10^{-3}$M; 4) $C_R = 4 \times 10^{-5}$M, $C_{Ni} = 1 \times 10^{-5}$M; 620 nm: 5) $C_R = 2 \times 10^{-5}$M; $C_{Ni} = 1 \times 10^{-3}$M; 6) $C_R = 2 \times 10^{-5}$M, $C_{Ni} = 1.6 \times 10^{-3}$M; 7) $C_R = 2 \times 10^{-5}$M, $C_{Ni} = 0$, at 540 nm.

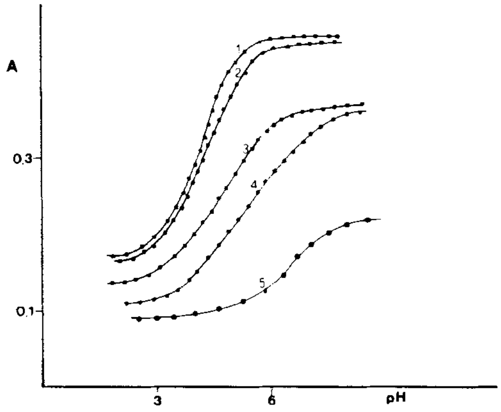

FIGURE 4 Absorbance–pH curves for the system Co(II)–DMTAMR at 540 nm; $C_R = 2 \times 10^{-5}$M, C_{Co}: 1) 1×10^{-5}M, 2) 2×10^{-5}M, 3) 2×10^{-4}M, 4) 8×10^{-4}M, 5) 0.

The experimental data for both systems were subsequently analysed by applying the LETAGROP-SPEFO[8] numerical calculation method. Initially the values obtained for β_{pqr} in each system by the graphical method were used as starting values and then the species model was modified by introducing new species in order to establish which of the proposed models would fit the experimental data with minimum error. From the values obtained for the minimization function

$$U = \sum_{Np} (A_{calc} - A_{exp})^2$$

and the standard deviation σ(A) it is seen in Table II that for the Ni(II)–DMTAMR system the model containing the species NiHR and NiR simultaneously fits the experimental data much better than models containing only one species. For the Co(II)–DMTAMR system only the model containing (simultaneously) the species

CoHR, CoR and CoR_2 did fit the experimental data. Calculations for other models assuming, in addition to the species previously established, the formation of hydroxo complexes, mixed ligand species, polynuclear species and/or more protonated species, did not converge. Calculated values for log β_{pqr} and ε_{pqr} for each complex in every system are included in Table II.

TABLE II
Results from the numerical calculation method for the complexes of Ni(II) and Co(II) with DMTAMR.

Species model	U	σ(A)	ε (l $mol^{-1}cm^{-1}$)	log β ± 3SD
HNiR			10.353 ± 70	19.98 ± 0.11
NiR	0.61×10^{-2}	0.009	30.598 ± 240	12.66 ± 0.20
HNiR				
NiR	0.114	0.12		
NiR_2				
CoR	0.73×10^{-1}	0.04		12.93 ± 0.18
CoR_2				21.9 Max 26.5
HCoR				18.12 Max 18.36
CoR	0.51×10^{-1}	0.03		11.83 Max 12.39
HCoR			12.904 ± 224	18.68 ± 0.05
CoR	0.74×10^{-2}	0.009	18.000 ± 70	13.71 ± 0.14
CoR_2			49.836 ± 417	28.45 ± 0.20

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