

SPECTROPHOTOMETRIC STUDY OF THE COMPLEXATION OF Pr(III)
WITH 4-(2-THIAZOLYLAZO)RESORCINOL AND
1-(2-THIAZOLYLAZO)-2-NAPHTHOL-3,6-DISULPHONIC ACID

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Dedicated to Professor S. Stankoviansky on the occasion of his 70th birthday.

Received September 10th, 1976

The formation of PrLH^{2-} and PrL^+ complexes in 30% (v/v) ethanol solutions was found by spectrophotometric study of the complex equilibria of Pr(III) with 4-(2-thiazolylazo) resorcinol (TAR) (LH_2). A complex with the composition $\text{PrL}(\text{LH}) \cdot 6 \text{H}_2\text{O}$ was isolated in solid form. The complexes PrL and $\text{PrL}(\text{LH})^{2-}$ were found in aqueous solutions with 1-(2-thiazolylazo)-2-naphthol-3,6-disulphonic acid (TAN-3,6-S) (LH_3). The equilibrium constants of the complex equilibria and the optical properties of the individual complexes were found. The dissociation constants of both reagents were also determined.

Heterocyclic azodyes with a hydroxyl group in the *o*-position relative to the azo-group react strongly with a number of metal ions, especially with ions of rare earth elements. So far, little information has been published on the complexation of thiazole dyes with rare earth ions. Minzewski and coworkers¹ found that TAR and La(III) form 1 : 2 and 1 : 3 complexes. Navrátil² studied the extraction of Eu, Ho and Yb with 1-(2-pyridylazo)-2-naphthol and 1-(2-thiazolylazo)-2-naphthol and found complexes $(\text{MB} \cdot \text{HB})^{2+}$, $(\text{MB}_2 \cdot \text{HB})^+$ and $\text{MB}_3 \cdot \text{HB}$ in neutral medium and MB_4 in alkaline medium (M indicates the metal and B is the reagent). The chelates of pyridyl azodyes with ions of the rare earth elements were studied in greater detail³⁻⁹. Shibata³⁻⁵ studied the reaction of lanthanides with PAN reagent, Sommer and Novotná⁶ studied the reaction with 4-(2-pyridylazo)resorcinol and found 1 : 1 and 1 : 2 complexes and Munshi and Dey⁷ assume the presence of a 1 : 2 complex. Gromova and coworkers⁸ describe a method of determining Eu after reduction to Eu(II), which then reduces PAR and the decrease in the absorbance at 390 nm is measured. Spacu and coworkers⁹ studied the reaction of La and Ce with PAR. A survey of the use of the reagents for the spectrophotometric determination of the rare earths can be found in the literature¹⁰.

In this work, the complex equilibria of Pr(III) with thiazole azodyes TAR and TAN-3,6-S were studied to evaluate the possibility of analytical use of these reagents for the determination of Pr(III).

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EXPERIMENTAL

Chemicals and Instruments

The absorption spectra were measured in the recording spectrophotometer SP700 (Unicam, England); the other absorbance measurements were carried out on the SP 500 instrument (Unicam). A G 202B glass electrode was used for measuring the pH, along with a saturated calomel electrode K 401 (Radiometer) and pH meters PHM 3 (Radiometer) and OP-205 (Radelkis). In measuring the acidity of strongly acid solutions ($\text{pH} < 1$) at $1 \cdot 0\text{-NaClO}_4$, the saturated calomel electrode was separated from the measured solution by a salt bridge filled with 1M-NaNO_3 to prevent precipitation of KClO_4 on the frit of the K 401 electrode; this arrangement does not strongly affect the measured pH values as a result of the diffusion potential¹¹.

TAR (Lachema, Brno) was recrystallized from hot methanol. A chromatographic purity check¹² demonstrated that the substance was pure. The content determined by photometric titration of Cu(II) was 100% (ref.¹³).

TAN-3,6-S (Lachema, Brno) was recrystallized from hot water. The substance was then chromatographically pure and uniform¹⁴. The content found by photometric titration of Cu(II) was 98.1% (ref.¹⁵).

A standard praseodymium(III) perchlorate solution was prepared from Pr oxide, 99.9% pure (Typpi Oy Oulu, Finland) by dissolving in a small excess of 70% perchloric acid, diluted 1 : 1 with water. The solution obtained was filtered through an S4 frit while hot and the praseodymium perchlorate was recrystallized twice. The titre of the standard was determined complexometrically using xylenol orange¹⁶ and indirectly manganometrically *via* the oxalate¹⁷. The two methods agreed to within $\pm 0.35\%$ rel. Gravimetric determination of the standard (0.9296M solution) was not carried out as there is no reliable gravimetric method of determining Pr¹⁸.

Perchloric acid *p.a.* (Jenapharm, Laborchemie, Apolda) was used without further purification; sodium perchlorate *p.a.* (Xenon, Lodz, Poland) was purified by the method of Biedermann¹⁹ and recrystallized twice from water. Ethanol was redistilled and contained 3.9–4.3% methanol. The water used was distilled twice from a quartz apparatus.

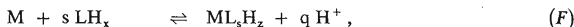
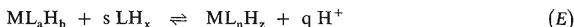
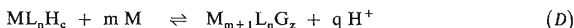
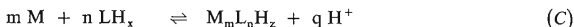
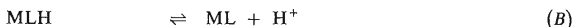
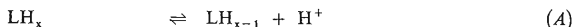
Stock solutions of 0.001M-TAR in 50% (v/v) ethanol and aqueous 0.001M-TAN-3,6-S, which were stable for at least one month were also used for solution preparation. Although it was found that the order in which the solutions are mixed has no effect on the absorbance values, the solutions were always mixed in the following order: 1. solvent (ethanol), 2. adjustment of the ionic strength, 3. preliminary adjustment of the acidity of the solution with HClO_4 or NaOH , 4. Pr(III) solution, 5. reagent, 6. final acidity adjustment. Buffers were not used. In measuring the dependence of the absorbance on the concentration of the reagent or metal, the solutions were prepared in volumetric flasks. In the measurement of the pH-curves, the titration technique and apparatus described by Havel²⁰ were used. The reproducibility and reversibility of the curves was checked by preparing several solutions in the classical way in small flasks. In alkaline and neutral media a nitrogen atmosphere was maintained over the solution surface.

In the study of the acid-base equilibria of the reagent, EDTA was added to the solution in a 10 fold excess with respect to the reagent to prevent formation of chelates with traces of metal impurities which might be present. The pH values measured in 30% (v/v) ethanol were not corrected.

Method of Interpreting the Experimental Absorbance Dependences

Graphical methods of analyzing the experimental dependences, *i.e.* absorbance – pH curves or the dependence of the absorbance on the concentration of reagent

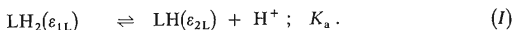
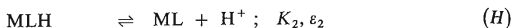
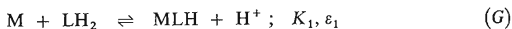
or metal have already been described²¹. Classical graphical procedures have recently been made more effective by using a computer with the PRCEK program (ref.^{22,23}), whose use has already been described^{24,25}. In this work the PRCEK-T200 version (ref.²⁶) was used in the Fortran language on the Tesla 200 computer which included all the transformations²¹ enabling calculation of the most common complex equilibria, represented by equations (A)–(F):



where M indicates the metal cation and LH_x is the ligand in the weak acid form (the charges of the complexes, metal and ligand have been omitted).

As opposed to the graphical method, the PRCEK program expresses the given dependence as a straight line constructed by the linear regression method and thus, in addition to constants and molar absorption coefficients (from slopes and intercepts), it is also possible to determine the standard deviations of the determined parameters. The computations can be carried out both for absorbance-pH curves in equimolar solutions or with small or large excesses of one of the components as well as for the dependence of the absorbance on the concentration of some component, provided only one complex equilibrium is involved in addition to possible reagent dissociation.

In this work, transformations were newly derived for graphical and logarithmic analysis of absorbance curves in excess reagent, if two complex equilibria (G) and (H) occur simultaneously and the reagent simultaneously dissociates according to equilibrium (I). So far, such transformations have been derived only for the similar case of two complexes being produced simultaneously, but for a reagent which does not absorb²⁷.



If $Z = 1 + K_a/[H^+]$, $\bar{\epsilon}_L = \epsilon_{1L} + K_a\epsilon_{2L}/[H^+]$, $\alpha = 1 + Z[H^+]/(c_L K_1)$ and the reagent bound in the complex is ignored, $c_L = Z[LH_2]$, then for the differential absorbance curves $\Delta A = A - A_{0L} = \epsilon_1[MLH] + \epsilon_2[ML]$, then transformations (1)–(3) are valid:

$$\Delta A = \epsilon_2 c_M - [H^+] (\alpha \Delta A - \epsilon_1 c_M) / K_2 \quad (1)$$

$$\alpha \Delta A = \epsilon_1 c_M + (\epsilon_2 c_M - \Delta A) K_2 / [H^+] \quad (2)$$

$$\log \frac{\alpha \Delta A - \epsilon_1 c_M}{\epsilon_2 c_M - \Delta A} = \text{pH} + \log K_2, \quad (3)$$

where c_M and c_L are the overall (analytical) concentrations of the metal and the reagent and A_{0L} is the overall absorbance of the reagent alone.

Curves in the regions where several complex equilibria occur simultaneously were solved using the SPEKTFOT program (ref.²⁸) which employs the LETAG minimization procedure (ref.²⁷) and is analogous to the general minimization program LETAGROP-SPEFO (ref.³⁰). The SPEKTFOT program enables solutions of systems containing at most four complexes and three dissociation equilibria of the reagent.

The JOB program (ref.³¹) was used for evaluating the continuous variation curves which, on the basis of the linear regression method of the transformation of continuous variation curves, permits calculation of the conditional stability constant and molar absorption coefficient for 1 : 1 complexes and the more general minimization program JOBCON (ref.³²) was used for the same purpose. Calculation of the distribution diagram for complex equilibria from known values of equilibrium constants was carried out on a MINSK 22 computer using the HALTAFALL-SPEFO program (ref.³³).

All calculations were carried out in the Computers laboratory of the Technical University, 600 00 Brno.

Acid-Base Equilibria of the Reagents

The dissociation constants of TAR were measured in 30% (v/v) ethanol at $I = 0.1$ ($\text{Na}^+ + \text{H}^+$) ClO_4 in nitrogen atmosphere. The dissociation constant of the protonated form of the reagent (LH_3^+) was measured at $I = 1.0$ ($\text{Na}^+ + \text{H}^+$) ClO_4 and at wavelengths of 500, 520, 534 and 550 nm. In both cases the concentration of TAR was $4.998 \cdot 10^{-5} \text{M}$. The absorbance pH curves were evaluated using the PRCEK-T200 program (ref.²⁶). In Table I the results obtained are given which are the average of determinations at 4 wavelengths and the values are compared with those from the literature. Values of the dissociation constants in various media are given in reference³⁴.

The molar absorption coefficients of the individual acid-base forms of the reagent at wavelengths at which the constants were determined are given in Table II.

From the acid-base equilibria of TAN-3,6-S, only the dissociation constant of the hydroxyl group was determined, in aqueous media at $I = 0.1$ ($\text{Na}^+ + \text{H}^+$) ClO_4 for the reagent concentration $4.986 \cdot 10^{-5}\text{M}$. The average value obtained by the PRCEK-T200 program for four wavelengths was $\text{p}K = 7.83 \pm 0.02$, which is in good agreement with the literature data¹⁵ ($\text{p}K = 7.86 \pm 0.02$). The molar absorption coefficients at 540, 560, 570 and 580 nm had the following values: $\epsilon_{\text{LH}_2} = 6550 \pm 60$, 650 ± 110 , 0 ± 110 , and 0 ± 30 ; $\epsilon_{\text{L}_3^+} = 17980 \pm 20$, 15970 ± 40 , 13680 ± 45 and 10850 ± 70 , resp.

STUDY OF THE COMPLEX EQUILIBRIA OF Pr(III) WITH TAN-3,6-S

Solutions with Excess of Metal Ions

In solutions with excess Pr(III) in the pH interval 2–6 a red chelate is formed with an absorption maximum at 545 nm, which is shifted by 60 nm relative to the

TABLE I

Values of the Dissociation Constant of TAR Calculated from Curves of the $A = A(\text{pH})$ Dependence ($c_{\text{L}} = 4.998 \cdot 10^{-5}\text{M}$; $c_{\text{EDTA}} = 5 \cdot 10^{-4}\text{M}$) by the PRCEK-T200 Program, Compared with the Literature

σ ($\text{p}K_{\text{an}}$) is the average value of the standard deviation of the $\text{p}K_{\text{an}}$ value; $\text{p}K_{\text{an}}$ is the average value of the values found for various wavelengths.

Equilibrium	$\text{p}K_{\text{an}} \pm \sigma(\text{p}K_{\text{an}})^*$	Conditions	Reference
$\text{LH}_3^+ \rightleftharpoons \text{LH}_2 + \text{H}^+$	0.879 ± 0.018	1.0 (Na, H) ClO_4 ; 25°C ; 30% ethanol (v/v) λ 500, 520, 534 a 550 nm	this work
	0.75 ± 0.01	0.1M-KNO_3 ; 30% ethanol (v/v)	35
	0.75	30% ethanol	36
$\text{LH}_2 \rightleftharpoons \text{LH} + \text{H}^+$	6.36 ± 0.08	0.1M-NaClO_4 ; 30% ethanol (v/v); 25°C λ 400, 496, 526 a 550 nm	this work
	6.51 ± 0.04	0.1M-KNO_3 ; 30% ethanol (v/v)	35
	6.56	30% ethanol	36
	5.9		37
	6.40	20% dioxane	38
$\text{LH} \rightleftharpoons \text{L}^{2-} + \text{H}^+$	10.68 ± 0.03	0.1M-NaClO_4 ; 30% ethanol (v/v) 25°C ; λ 433, 526, 550 a 570 nm	this work
	10.67 ± 0.02	0.1M-KNO_3 ; 30% ethanol (v/v)	35
	10.52	20% dioxane	38–40

maximum of the undissociated form of the reagent. As the dependence of the absorption curves on the pH exhibited a single isosbestic point at 508 nm, a single complex equilibrium could be assumed. In order to determine the nature of this equi-

TABLE II

Values of the Molar Absorption Coefficient of Individual Acid-Base Forms of TAR Calculated by the PRCEK-T200 Program

λ , nm	Values $\epsilon \pm \sigma(\epsilon)^a$			
	LH_3^+	LH_2	LH^-	L^{2-}
400	—	$18\,290 \pm 150$	$13\,950 \pm 35$	—
433	—	—	$20\,690 \pm 70$	$7\,770 \pm 210$
496	—	$3\,160 \pm 260$	$25\,690 \pm 140$	—
500	$23\,930 \pm 90$	$3\,490 \pm 35$	—	—
520	$14\,800 \pm 160$	590 ± 40	—	—
526	—	270 ± 40	$10\,960 \pm 75$	$35\,690 \pm 470$
534	$8\,880 \pm 30$	207 ± 9	—	—
550	$3\,405 \pm 20$	154 ± 6	$1\,845 \pm 6$	$23\,560 \pm 310$
570	—	—	0 ± 62	$10\,605 \pm 130$

^a $\sigma(\epsilon)$ is the standard deviation of the determined value of the molar absorption coefficient.

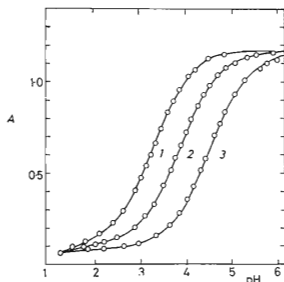


FIG. 1

Absorbance-pH Curve for the TAN-3,6-S-Pr(III) System I 0.1 NaClO₄; λ 560 nm, $c_L = 4.986 \cdot 10^{-5} \text{M}$; $c_M = 1.9622 \cdot 10^{-3} \text{M}$
 2 $2.406 \cdot 10^{-4} \text{M}$ 3 $4.811 \cdot 10^{-4} \text{M}$.

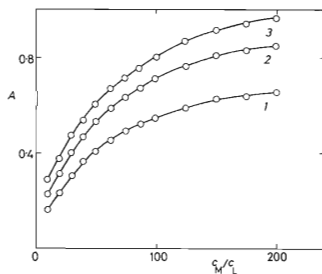


FIG. 2.

Dependence of the Absorbance on the Concentration of Pr(III) in the TAN-3,6-S-Pr(III) System $A = A(c_M)$

I 0.1 NaClO₄; $c_L = 4.986 \cdot 10^{-5} \text{M}$; pH 3.80, λ : 1 580 nm, 2 570 nm, 3 560 nm.

librium, the dependence of the absorbance on the pH was measured for three different Pr(III) concentrations; the dependence of the absorbance on the concentration of Pr(III), $A = A(c_M)$, was measured at constant pH value (Fig. 1 and 2). The colouration of the solution is independent of time and is stable for at least 24 h.

By preliminary graphical analysis of the dependence for one wavelength using the usual transformations²¹, it was found that equilibrium (C) occurs, where $m = n = q = 1$, i.e. complex with composition ML is formed. On this basis, all the curves were evaluated using the PRCEK-T200 program (Table III).

The composition of the chelate formed was confirmed by the method of continuous variations at wavelengths of 540, 560 and 590 nm and at pH 6. The continuous variation plots were also evaluated numerically using the JOB³¹ and JOBCON³² programs. The values of the molar absorption coefficient calculated from the continuous variation curves are lower than those curves with excess of metal ions, while

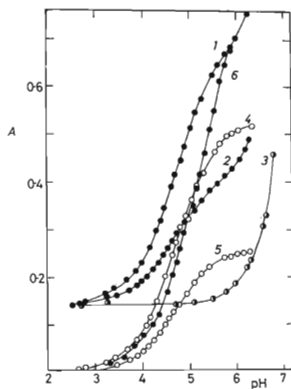


FIG. 3

Absorbance-pH Curves for the TAN-3,6-S-Pr(III) System in Solutions with Excess Reagent for λ 480 nm

I 0.1 NaClO₄; c_M : 1 $2.00 \cdot 10^{-5}M$ 2 $1.00 \cdot 10^{-5}M$ 3 $0.042 \cdot 10^{-5}M$ 4 $2.00 \cdot 10^{-5}M$ 5 $1.00 \cdot 10^{-5}M$ 6 $5.00 \cdot 10^{-5}M$; c_L : 1-5 3.99 $\cdot 10^{-4}M$ 6 $1.00 \cdot 10^{-4}M$. For curve 3 $c_{EDTA} = 0.005M$. Curves 4 and 5 are difference curves. (The curve of the reagent alone was subtracted from curves 1 and 2, i.e. curve 3).

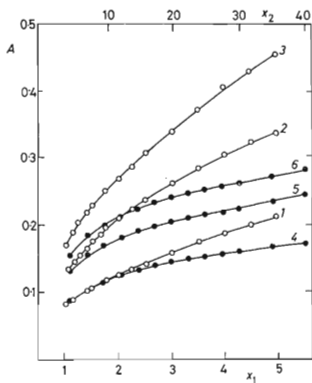


FIG. 4

Dependence of the Absorbance on the Reagent Concentration in the TAN-3,6-S-Pr(III) System at pH 6.00

I 0.1; c_M : 1-3 $2.00 \cdot 10^{-5}M$ 4-6 $1.00 \cdot 10^{-5}M$; λ , nm: 1, 4 570 2, 5 580 3, 6 590. Scale x_1 is valid for curves 1-3 and scale x_2 for curves 4-6.

TABLE III
Equilibrium Constant Values for the $\text{Pr}^{3+} + \text{LH}^{2+} \rightleftharpoons \text{PrL} + \text{H}^+$ Reaction and Values of the Molar Absorption Coefficients of the PrL Complex Calculated by the PRCEK Program for Various Experimental Dependences in the TAN-3,6-S-Pr(III) System

Curve No	Experimental conditions, mol/l	Type of dependence	ϵ (540 nm)	ϵ (560 nm)	ϵ (570 nm)	ϵ (580 nm)	ϵ (590 nm)	$\log k_1$
1	c_L $4.986 \cdot 10^{-5}$	$A = f(\text{pH})$	$24\,370 \pm 100$	$23\,100 \pm 85$	$21\,060 \pm 75$	$17\,315 \pm 70$	—	-1.19 ± 0.03
	c_M $4.811 \cdot 10^{-4}$							
2	c_L $4.986 \cdot 10^{-5}$	$A = f(\text{pH})$	$24\,190 \pm 25$	$23\,580 \pm 23$	$21\,870 \pm 90$	$18\,010 \pm 90$	—	-1.25 ± 0.02
	c_M $2.408 \cdot 10^{-3}$							
3	c_L 4.986 ± 10^{-5}	$A = f(\text{pH})$	$24\,360 \pm 94$	$23\,660 \pm 20$	$21\,890 \pm 16$	$17\,610 \pm 20$	—	-1.28 ± 0.03
	c_M $9.632 \cdot 10^{-3}$							
4	c_L $4.986 \cdot 10^{-5}$	$A = f(c_M)$	—	$24\,840 \pm 75$	$21\,580 \pm 50$	$16\,870 \pm 22$	—	-1.22 ± 0.03
	pH = 3.80 ± 0.01							
5	c_L $9.974 \cdot 10^{-5}$	$A = f(\text{pH})$	—	—	$23\,400 \pm 300$	$18\,340 \pm 110$	$11\,410 \pm 30$	-1.25 ± 0.01
	c_M $4.985 \cdot 10^{-5}$							
6	c_M $1.999 \cdot 10^{-5}$	$A = f(c_L)$	—	—	—	$18\,400^c$	—	-1.23 ± 0.03
	pH = 6.00 ± 0.01							
7	$c_0 c_M + c_L = 2 \cdot 10^{-4}$	variation	$15\,600 \pm 200^a$	$19\,800 \pm 330^a$	$19\,420 \pm 140^a$	$16\,100 \pm 200^a$	$11\,600 \pm 240^a$	-1.17 ± 0.85^a
	pH = 6.00 ± 0.01							
8	c_L $1.995 \cdot 10^{-4}$	$A = f(\text{pH})$	—	—	$19\,440^b$	$16\,260^b$	$10\,940^b$	-1.29 ± 0.08^b
	c_M $1.00 \cdot 10^{-5}$							
Average			$24\,310 \pm 70^c$	$23\,800 \pm 520^c$	$21\,960 \pm 580^c$	$17\,680 \pm 490$	$11\,320 \pm 250$	-1.24 ± 0.03

^a Calculated by the JOB program (the constants obtained for this program were not included in the average because of their large deviation; ^b calculated by the JOBCON program; ^c graphical calculation; ^d calculated by the SPEKTFOT program; ^e because of their deviation, the values obtained from the variation were not included in the average.

the equilibrium constant values agree very well (Table III). Consequently, the same complex is formed in equimolar solutions as in solutions with excess Pr(III).

Equilibria in Solutions with Excess of the Reagent

In solutions with a small excess of reagent ($c_L/c_M = 2$) the principal complex is the ML chelate (Table III, series 5) as the results of analysis assuming formation of this complex are in good agreement with the results obtained by analysis of the dependences in the presence of excess Pr(III).

In solutions with large excesses of the reagent ($c_L/c_M = 20$ and 40), a new isosbestic point at 540 nm appears on the series of absorption curves for various pH values; the absorption maximum of the red-purple solution is 565 nm, compared with λ_{\max} 545 nm in solutions with excess metal ions. This fact indicates that, in solutions with excess reagent, another compound is formed in addition to the ML complex.

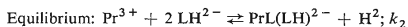
To clarify the complex equilibria in solutions with excess reagent, the absorbance-pH curves and curves of the dependence of the absorbance on the reagent concentration were measured (Fig. 3 and 4).

By preliminary graphical analysis using transformation²¹, assuming equilibrium (C) for the series of A-pH curves, it was found that one proton is dissociated during complex formation and that the reagent is coordinated directly to the metal ion. The dissociation of one proton as during the formation of the ML complex and the fact that, in the pH region 3-6, the reagent is present as LH^{2-} led to the assumption that complex ML(LH) is formed, where the addition of a further reagent molecule is not associated with proton dissociation. The results of numerical analysis by the PRCEK-T200 program, assuming the formation of a 1:2 complex with this composition, are given in Table IV. The assumptions were confirmed by analysis of the dependence on the reagent concentration (pH 6.0, λ 580 nm) using the transformation introduced above²¹. It was demonstrated that two complexes are actually formed. At low reagent concentrations, the ML complex is formed directly from the reaction components, as it is reflected in the zero value of the transformation limit for the determination of the values of ϵ_{1,c_M} (Fig. 5, curve 2). The transformation for the determined values of the absorption coefficient of the complex formed has two branches, of which the first (Fig. 5, curve 1) at low reagent concentrations has a limiting value corresponding to the molar absorption coefficient of the ML complex ($\epsilon = 1.89 \cdot 10^4$) and the second (Fig. 5, curve 1') has a limit corresponding to the value of the molar absorption coefficient of the second chelate, ML(LH) ($\epsilon = 2.71 \cdot 10^4$). The results of the analysis are given in Table IV.

The correctness of these conclusions was also confirmed by calculation of the A(pH) curves for solutions with excess reagent ($c_L/c_M = 20$) using the SPEKTFOT²⁸ minimization program assuming simultaneous formation of the two complexes,

TABLE IV

Values of Equilibrium Constants and Molar Absorption Coefficients of the $\text{PrL}(\text{LH})^{2-}$ Complex Calculated for Various Experimental Dependences in the TAN-3,6-S-Pr(III) System



Type of dependence	Experimental conditions, mol/l	ϵ (570 nm)	ϵ (580 nm)	$\log k_2$
$A = f(\text{pH})$	$c_L 3.99 \cdot 10^{-4}$	$34\,600 \pm 150^a$	$28\,040 \pm 140^a$	2.10 ± 0.01^a
	$c_M 2.00 \cdot 10^{-5}$	—	$27\,400^b$	2.06 ± 0.03^b
		—	$27\,600 \pm 1\,170^c$	2.12 ± 0.02^c
$A = f(\text{pH})$	$c_L 3.99 \cdot 10^{-4}$	$30\,150 \pm 300^a$	$27\,220 \pm 50^a$	2.17 ± 0.04^a
	$c_M 1.00 \cdot 10^{-5}$			

Equilibrium: $\text{PrL} + \text{LH}^{2-} \rightleftharpoons \text{PrL}(\text{LH}^{2-}); k_3$				$\log k_3$
$A = f(c_L)$	$c_M 1.00 \cdot 10^{-5}$ pH 6.00 ± 0.02	—	$30\,500^b$	3.37^b $\log k_2 = 2.13$
Average		$32\,380 \pm 2\,000$	$28\,150 \pm 940$	2.12 ± 0.04 ($\log k_2$)

Equilibrium: ^a Calculated by the PRCEK-T200 program; ^b graphical procedure; ^c calculated by the SPEKTFOT program.

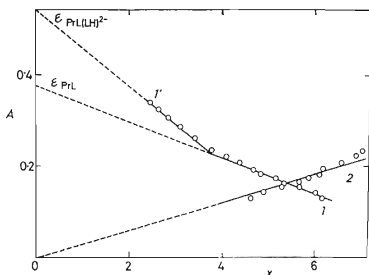


FIG. 5

Graphical Analysis of the $A = A(c_L)$ Dependence in the TAN-3,6-S-Pr(III) System at pH 6.00 and 580 nm

$c_M = 2.00 \cdot 10^{-5} \text{M}$; x : 1 and $1' A/(\epsilon_2 c_L - A) \cdot 10^2 (A_{02} - A) (\epsilon_2 c_L - A) \cdot 10^2$, where value A_{02} was obtained by extrapolation of curve 1 to the A axis.

ML and ML(LH) (Table V). A schematic picture of the formation of the individual complexes in the Pr(III)-Tan 3,6 S system follows from the distribution diagrams calculated from the equilibrium constant values of the individual acid-base and complex equilibria using the HALTAFALL SPEFO program³³. It follows from the diagrams given in Fig. 6a,b that, in solutions with excess of Pr(III), the PrL complex actually predominates (Fig. 6a) whereas, in solutions with excess reagent (Fig. 6b) both complexes are formed simultaneously and at pH 6 almost the same amounts of complexes PrL and PrL(LH)²⁻ are formed. According to the calculated distribution diagram (Fig. 6b) the 1 : 2 complex should gradually disappear in solutions with pH > 6 and should be converted into the 1 : 1 complex. It should be added that, in the region pH > 6, no experimental data could be measured because of the high absorbance of the reagent itself; consequently, the possibility of the formation of a 1 : 2 complex with composition PrL₂³⁻ cannot be excluded.

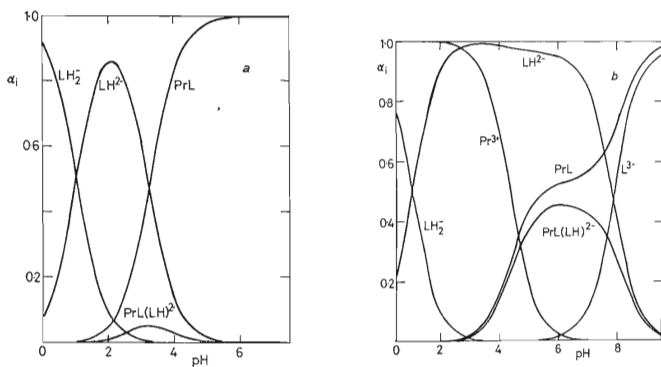


FIG. 6

Distribution Diagram for the Complex Equilibria of the Complex of Pr(III) with the TAN-3,6-S Reagent and the Acid-Base Forms of the Reagent in Solutions with Excess Metal Ions (a) and Excess Reagent (b)

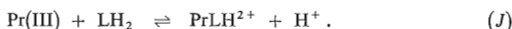
$a: c_M = 9.632 \cdot 10^{-3} M; c_L = 4.99 \cdot 10^{-5} M; b: c_M = 1 \cdot 10^{-5} M; c_L = 3.99 \cdot 10^{-4} M$. The curves were calculated using the dissociation constant values for the reagent given in this work and the values of the complex equilibrium constants given in Tables III and IV. $\alpha_i = [M_q L_r] / c_L$ for a and $q[M_q L_r] / c_M$ for b where $[M_q L_r]$ are the concentrations of the species formed with stoichiometric coefficients of the metal and the reagent q and r , resp. For b the α_i values of the individual reagent forms LH_i are given by the $[LH_i] / c_M$ ratio.

STUDY OF THE COMPLEX EQUILIBRIA OF Pr(III) WITH TAR

Complex Equilibria in Solutions with Excess Pr(III)

Because of the low solubility of the reagent, the complex equilibria were studied in 30% (v/v) ethanol. In this medium and in solutions with excess Pr(III) a soluble, red-orange chelate with λ_{\max} 525 nm is formed in the pH range 2–6 and an isobestic point at 475 nm is observed.

The experimental dependences of the absorbance on the pH and on c_M (Fig. 7, Fig. 8) were analyzed by the PRCEK-T200 program, assuming equilibrium (C), where the best results were obtained for $m = n = q = 1$. Analysis of the dependence of the absorbance on the concentration of Pr(III) at pH 5.0 showed that one Pr(III) ion reacts with the reagent during complex formation. The results of the analysis of both dependences are given in Table VI and indicate that complex equilibrium (J) is established in solutions with excess Pr(III):



The stoichiometric ratio 1 : 1 in equimolar solutions was also confirmed by the method of continuous variations at pH 6.50 ($c_0 = 1.0 \cdot 10^{-4} \text{M}$). The curves exhibited maximum at a component ratio of 1 : 1 for $\lambda = 560, 570, \text{ and } 580 \text{ nm}$.

TABLE V

Comparison of the Experimental $A = f(\text{pH})$ Curves with the Curve Calculated by the SPEKTFOT Program from the Values of the Equilibrium Constant and Molar Absorption Coefficients

$c_L 4.00 \cdot 10^{-4} \text{M}$, $c_M 2.00 \cdot 10^{-5} \text{M}$; 580 nm; $\epsilon_{\text{PrL}} 17\,230$, $\epsilon_{\text{PrL(LH)}-2} 27\,600$; $\log k_1 -1.23$; $\log k_2 2.12$. Optical path length, d 1.00 cm.

pH	A_{exp}	A_{calc}	$\Delta = A_{\text{exp}} - A_{\text{calc}}$	pH	A_{exp}	A_{calc}	$\Delta = A_{\text{exp}} - A_{\text{calc}}$
4.15	0.088	0.0946	-0.0066	5.58	0.248	0.2463	+0.0017
4.40	0.105	0.1124	-0.0074	5.65	0.258	0.2534	+0.0047
4.57	0.125	0.1282	-0.0032	5.74	0.262	0.2622	-0.0002
4.62	0.129	0.1334	-0.0044	5.86	0.273	0.2738	-0.0008
4.82	0.155	0.1563	-0.0013	5.99	0.288	0.2868	+0.0012
4.94	0.170	0.1711	-0.0011	6.04	0.295	0.2920	+0.0030
4.99	0.176	0.1773	-0.0013	6.09	0.299	0.2975	+0.0015
5.12	0.196	0.1937	+0.0023	6.23	0.311	0.3145	-0.0035
5.19	0.204	0.2023	+0.0017	6.38	0.337	0.3368	+0.0002
5.29	0.218	0.2144	+0.0036	6.51	0.358	0.3612	-0.0032
5.38	0.228	0.2248	+0.0032	6.57	0.370	0.3745	-0.0045
5.48	0.238	0.2358	+0.0022	6.73	0.408	0.4182	-0.0102

TABLE VI

Values of the Equilibrium Constant of the $\text{Pr}^{3+} + \text{LH}_2 \rightleftharpoons \text{PrLH}^{2+} + \text{H}^+$ Reaction and Molar Absorption Coefficients of the PrLH^{2+} Complex Calculated from Various Experimental Dependences by the PRCEK-T200 Program. Pr(III)-TAR System, Solutions with excess of Pr(III)

$\sigma \log k_1$ is the standard deviation of the logarithm of the constant; the values of $\log k$ given are the average values found at the given wavelength.

Type of dependence	Experimental conditions, mol/l	ϵ , 400 nm	ϵ , 433 nm	ϵ , 550 nm	ϵ , 570 nm	ϵ , 580 nm	$\log k_1 \pm \sigma_{\log k_1}$
$A = f(\text{pH})$	c_M $4.811 \cdot 10^{-4}$	8 560 ± 95	8 130 ± 70	25 220 ± 220	—	11 330 ± 45	-2.50 ± 0.06
	c_L $4.998 \cdot 10^{-5}$						
$A = f(\text{pH})$	c_M $2.390 \cdot 10^{-3}$	7 550 ± 30	8 910 ± 40	22 480 ± 110	—	8 670 ± 20	-2.54 ± 0.06
	c_L $4.998 \cdot 10^{-5}$						
$A = f(\text{pH})$	c_M $9.622 \cdot 10^{-3}$	8 090 ± 15	8 700 ± 30	22 350 ± 100	—	8 860 ± 10	-2.34 ± 0.08
	c_L $4.998 \cdot 10^{-5}$						
$A = f(\text{pH})$	c_L $4.998 \cdot 10^{-5}$	—	—	20 300 ± 15	13 240 ± 30	9 520 ± 30	-2.43 ± 0.02
	pH = 5.00 ± 0.02						
Average		8 070 ± 330	8 580 ± 300	22 600 ± 1 400	13 240 ± 30	9 600 ± 905	-2.45 ± 0.06

Complex Equilibria in Solutions with Excess of the Reagent

In solutions with excess reagent the absorption spectra exhibit a shift of the maximum from 525 to 535 nm, with simultaneous increase in the colour intensity increasing pH values; these changes suggest the simultaneous presence of several complex equilibria. At $\text{pH} > 6.5$ an almost black, crystalline precipitate, which is almost insoluble in water and in the common solvents, is formed. It was found by graphical analysis of the dependence of the absorbance on the reagent concentration^{21,31} at $\text{pH} 5.53$ (Fig. 9) that the transformations are linear only on the assumption that one molecule of the reagent is bound to each Pr(III) atom, *i.e.* that a 1 : 1 complex is formed. However, it was found during analysis of the dependence of the absorbance on the pH (Fig. 10) that the transformations are linear for equilibrium (*F*) ($s = 1$) but that the logarithmic dependences then yield a non-integral number of the dissociated hydrogen ions. Good agreement was obtained if it was assumed that two 1 : 1 complexes are formed, *i.e.* assuming equilibria (*G*), (*H*) and (*I*) and applying the transformation relationships according to equations (1) and (2). The results of the graphical analysis are given in Table VII.

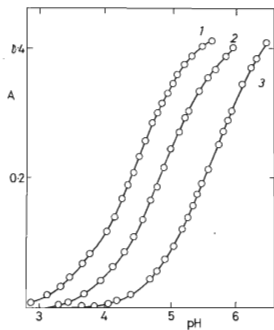


FIG. 7

Absorbance-pH Curves in the TAR-Pr(III) System for Solutions with Excess Pr(III) at λ 580 nm

I 0.1 NaClO₄; 30% (v/v) ethanol; $c_L = 4.998 \cdot 10^{-5} \text{ M}$; c_M : 1 9.622 · 10⁻³ M 2 2.39 · 10⁻³ M 3 4.811 · 10⁻⁴ M.

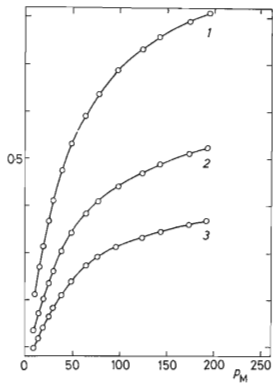


FIG. 8

Dependence of the Absorbance on the Concentration of Pr(III) in the TAR-Pr(III) System at $\text{pH} = 5.00 \pm 0.02$

I 0.1 NaClO₄; 30% ethanol (v/v); $c_L = 4.998 \cdot 10^{-5} \text{ M}$; λ , nm: 1 550 2 570 3 580.
 $p_M = c_M/c_L$.

In solutions with a small excess of the reagent, equilibrium (G) is suppressed and satisfactory agreement was obtained by assuming only equilibrium (F) (for $s = 1$ and $q = 2$). The results obtained are in good agreement with the results of analysis of the other dependences (Table VII)

The conclusions on the study of the complex equilibria of Pr(III) with TAR are supplemented by the distribution diagram calculated from the values of the constants for the complex equilibria found and from the dissociation constants of the reagent, by means of the HALTAFALL-SPEFO program³³ for the solutions with excess of Pr(III) (Fig. 11a) and for the solutions with excess of the reagent (Fig. 11b).

Isolation of the Complex of Pr(III) with TAR in Solid State

The complex was isolated from solutions of $\text{pH} = 6.5-7$ ($c_M 4 \cdot 10^{-4}\text{M}$, $c_L 1.2 \cdot 10^{-3}\text{M}$). In more acid solutions or at higher reagent concentrations the reagent

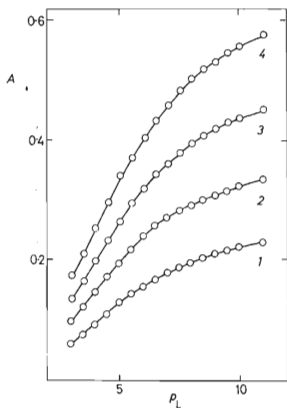


FIG. 9

Dependence of the Absorbance on the Reagent Concentration in TAR-Pr(III) System in 30% Ethanol at $\text{pH} = 5.53 \pm 0.02$

$I 0.1 \text{ NaClO}_4$; $c_M = 4.0 \cdot 10^{-5}\text{M}$; λ , nm
1 580 2 570 3 560 4 550. $p_L = c_L/c_M$.

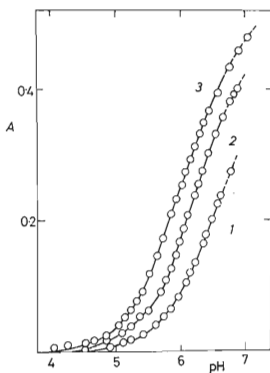


FIG. 10

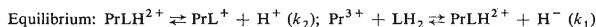
Absorbance-pH Curves in the TAR-Pr(III) System for Solutions with Excess Reagent for $\lambda 580 \text{ nm}$

$I 0.1 \text{ NaClO}_4$; 30% ethanol (v/v); $c_M = 2.0 \cdot 10^{-5}\text{M}$; $c_L: 1.9995 \cdot 10^{-5}\text{M}$ 2 2.00 $\cdot 10^{-4}\text{M}$ 3 4.00 $\cdot 10^{-4}\text{M}$.

is also precipitated in addition to the complex. The complex is not formed instantaneously but begins to crystallize out after about 1–2 h. The precipitate was filtered off the following day, it was washed with small amounts of cold water, ethanol, and ether and it was dried in the air. The content of crystallization water found by drying to a constant weight (several days) at 110–120°C; the Pr content was determined complexometrically¹⁶ after evaporation with concentrated sulphuric and perchloric acids; the C, H and N contents were found by elemental microanalysis. The results of the analysis correspond best to the composition PrL(LH).6 H₂O (calculated 31.40% C, 3.36% H, 12.21% N; 20.45% Pr; found 30.91% C, 2.92% H, 11.14% N, 22.26% Pr, 15.61% H₂O, the results of the analyses are the average of 2–4 determinations) which also follows from the calculated empirical coefficient values. For PrL(LH) · 6 H₂O it was calculated: C₁₈H₁₁N₆O₄Pr₁S₂(H₂O)₆ and found: C_{17.7}H_{7.96}Pr_{1.09}N_{5.48}(H₂O)_{5.97}.

TABLE VII

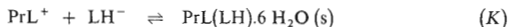
Values of the Equilibrium Constants and Molar Absorption Coefficients of Complexes at 580 nm, Calculated from Various Experimental Dependences in Solutions with Excess Reagent, Pr(III)–TAR System



Type of dependence	Experimental conditions, mol/l	$\epsilon_{\text{PrLH}^{2+}}$	ϵ_{PrL^+}	$\log k_2^a$	
$A = f(\text{pH})$	c_L $4.00 \cdot 10^{-4}$ c_M $2.00 \cdot 10^{-5}$	10 800	21 300	–5.82	
$A = f(\text{pH})$	c_L $2.00 \cdot 10^{-4}$	11 000	22 900	–5.95	
Equilibrium: $\text{Pr}^{3+} + \text{LH}_2 \rightleftharpoons \text{PrL}^+ + 2 \text{H}^+; k_3$				$\log k_3$	
$A = f(\text{pH})$	c_L $9.995 \cdot 10^{-5}$ c_M $2.00 \cdot 10^{-5}$	—	19 600	–8.49	–6.04 ^b
$A = f(c_L)$	c_M $4.00 \cdot 10^{-5}$ pH 5.53 ± 0.02	—	20 700	–8.39	–5.94 ^b
<i>Average</i>		$10\,900 \pm 50$	$21\,130 \pm 1\,000$	-8.44 ± 0.05 – 5.94 ± 0.06	

^a The value of k_1 given in Table VI ($-2.45 = \log k_1$) was used in the calculation of k_2 ; ^b the value of $\log k_2$ was calculated from the k_3 value found according to the relationship $\log k_2 = \log k_3 - \log k_1$.

TAR also yields insoluble 1 : 2 chelates with Cd, Zn and Pb (ref.³⁵). The formation of a 1 : 2 complex with Pr(III) is also understandable as, at pH > 6.5 in solutions with excess reagent, most of the Pr is present as the PrL^+ complex and the reagent is present as LH^- (Fig. 11b). The complex is formed through the equilibrium (K):



CONCLUSIONS

Both the reagents studied, TAR and TAN-3,6-S, yield intensively coloured complexes with Pr(III). In solutions with excess Pr(III) complexes with component ratios of 1 : 1 are formed; in solutions with excess reagent the reaction is somewhat different. In the whole concentration range at pH 2–6.5, TAR forms a 1 : 1 complex, which is gradually deprotonized as the pH increases. The formation of the 1 : 2 complex was found only in solid form by isolation of the $\text{Pr}(\text{LH}) \cdot 6 \text{H}_2\text{O}$ complex, which is almost insoluble in water and common solvents. In solutions with excess reagent, TAN-3,6-S forms both a 1 : 1 complex and a complex with the

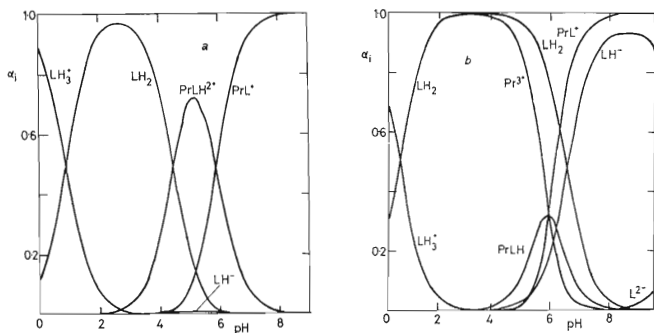


FIG. 11

Distribution Diagram for the Complex Equilibria of the Pr(III) Complex with TAR and the Acid-Base Equilibria of the Reagent in Solutions with Excess Metal Ions (a) and Excess Reagent (b)

a: $c_L = 5.00 \cdot 10^{-5} \text{M}$; $c_M = 9.62 \cdot 10^{-3} \text{M}$; b: $c_L = 4.00 \cdot 10^{-4} \text{M}$; $c_M = 2.00 \cdot 10^{-5} \text{M}$. The curves were calculated using the dissociation constant values given in Table I and the complex equilibrium constant values given in Tables VI and VII. $\alpha_i = r[M_q^r L_r] / c_L$ for a and $q[M_q L_r] / c_M$ for b where $[M_q L_r]$ are the concentrations of the species formed with stoichiometric coefficients q and r . For b the α_i values of the individual reagent forms LH_i are given by the $[\text{LH}_i] / c_L$ ratio.

composition $\text{PrL}(\text{LH})^{2+}$; however, relatively high reagent concentrations are necessary for the formation of the latter. The formation of the PrL_3^{3+} complex in solution was not demonstrated. While the chelates of Pr(III) have relatively high absorption coefficients, they are not particularly suitable for the spectrophotometric determination of Pr(III). With TAR, horizontal section of the $A(\text{pH})$ curve cannot be attained even in 30% ethanol because of the low solubility of the 1 : 2 complex formed; with TAN-3,6-S the λ_{max} of the dissociated form of the reagent practically obscures the λ_{max} of the 1 : 2 complex. In the pH region 8–9, where according to the distribution diagram the PrL complex should be formed quantitatively, the reagent absorbs very strongly. Consequently, the use of pyridylazodyes is far more suitable for the determination of the lanthanides¹⁰.

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Translated by M. Štulíková.