

Complexation of Lanthanoids with 4-(2-Thiazolylazo)-6-bromoresorcinol

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4-(2-Thiazolylazo)-6-bromoresorcinol (TAR-Br) was synthesized and its usefulness for spectrophotometric determination of 14 lanthanoid(III) ions was examined. The acid dissociation constants of the reagent and the stability constants of the complexes (1:1) were determined, and the complexing behavior was studied. The optimum pH for complexation lies between 6.8–8.7. Beer's law holds up to about 2.5 ppm of each lanthanoid, with a molar absorptivity of $6 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$ level near 553 nm. The addition of ethanol produced some sensitization effect, due to solvation with the complexes. Both the molar absorptivities and the stability constants were larger in light lanthanoids with the atomic number, but the latter were slightly lower in heavy lanthanoids. TAR-Br was classified as a second ligand group member according to the Moeller's type classification.

Keywords 4-(2-Thiazolylazo)-6-bromoresorcinol, lanthanoids, spectrophotometry, lanthanoid contraction

The analytical utility of heterocyclic azo compounds is well-known. Thiazolylazo derivatives are especially attractive, because the complexing behavior is often peculiar.^{1,2} In previous studies, we synthesized a series of 4-(2-thiazolylazo)resorcinol (TAR) derivatives and found that both the bathochromic shifts and the molar absorptivities of the complexes were enhanced by the inductive effect of the *meta*-substituents to the azo group.^{3,4} From these findings, highly selective spectrophotometric methods for determination of iron(II) were proposed and the extraction mechanism of the complex was kinetically clarified.⁵

In the present study, a new reagent, 4-(2-thiazolylazo)-6-bromoresorcinol (TAR-Br), with a bromine introduced into *meta*-position of TAR, was synthesized. The complexing behavior with lanthanoid(III) ions was investigated to develop the sensitive spectrophotometric methods. The stability constants of lanthanoid complexes were examined to understand the connection with the lanthanoid contraction.

Experimental

Reagents and apparatus

TAR-Br was synthesized by the diazotization of 2-aminothiazole with nitrous acid and subsequent coupling with 4-bromoresorcinol at 0°C. The dark red product was purified by repeated crystallization with ethanol and was identified by elementary analyses. A 0.05% TAR-Br solution was prepared by dissolving in 0.01 M NaOH. The standard lanthanoid(III) solutions

were prepared by dissolving high purity oxides (> 99.9%) or salts in 0.1 M HCl and were standardized by EDTA titration. One molar ammonia or acetate buffer solutions were used for pH adjustment. All other reagents used were of analytical reagent or better grade. A Shimadzu Model UV-200S spectrophotometer and a Hitachi-Horiba M-5 pH meter equipped with a combined glass electrode were used.

Analytical procedure

Transfer the sample solution containing up to 100 µg of lanthanoid ion into a 50-ml volumetric flask. Add 5 ml of 0.05% TAR-Br solution and adjust the pH within the optimum range for each metal by using 5 ml of buffer solution. Dilute the solution to the volume and measure the absorbance near 553 nm against the reagent blank.

Results and Discussion

Acid dissociation constant

TAR-Br is soluble in a 5% dioxane solution and is orange in strongly acidic solution, yellow to orange in acidic or neutral solutions, and red in alkaline solution. The acid dissociation constants were determined spectrophotometrically; they were found to be $pK_{a1}=0.85 \pm 0.12$, $pK_{a2}=5.20 \pm 0.08$, $pK_{a3}=9.25 \pm 0.05$ (25°C, $\mu=0.1$, KCl). The constants are to some extent smaller than those of TAR, especially in pK_{a2} that corresponds to the deprotonation of the *para*-hydroxyl group. The inductive effect of *meta*-bromo group in the resorcinol

ring may contribute to the smaller basicity of TAR-Br.

Absorption spectra

TAR-Br reacts with 14 lanthanoid(III) ions to form water soluble and reddish-brown complexes. Figure 1 shows the absorption spectra of lanthanoid complexes and a reagent blank at pH 8.0. The complexes have only one absorption maximum, which is focused near

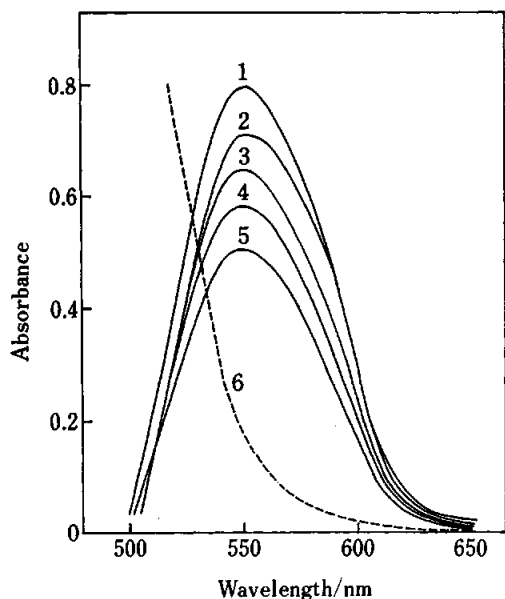


Fig. 1 Absorption spectra of TAR-Br complexes. 0.05% TAR-Br, 2 ml; pH, 8.0. 1, Sm(104 μg); 2, Ho(90 μg); 3, Eu(82 μg); 4, Pr(77 μg); 5, La(99 μg); 6, TAR-Br.

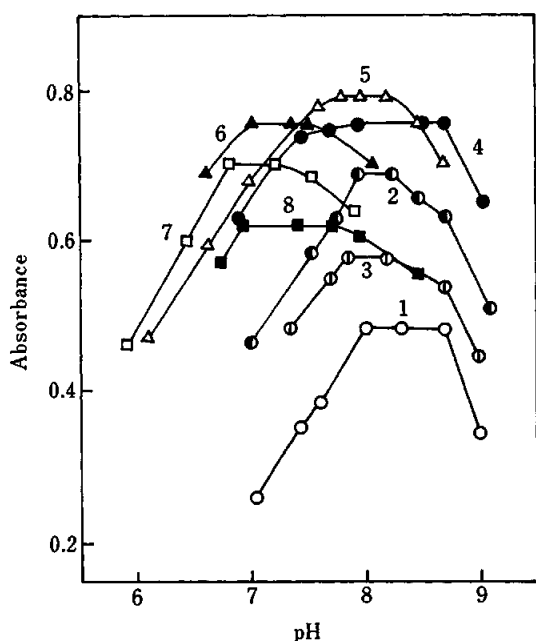


Fig. 2 Effect of pH. 0.05% TAR-Br, 2 ml; wavelength, 550 nm. 1, La(99 μg); 2, Ce(96 μg); 3, Pr(77 μg); 4, Nd(110 μg); 5, Sm(104 μg); 6, Dy(88 μg); 7, Tm(86 μg); 8, Lu(88 μg).

553 nm. The TAR-Br blank shows absorption at a little beyond 550 nm.

Effect of pH

The effect of pH on the absorbances of the complexes was examined, as shown in Fig. 2. Constant absorbances were obtained over the pH range from 6.8 to 8.7. The light lanthanoids form stable complexes in a more alkaline region than the heavy lanthanoids. The constant range is the narrowest in cerium, while is the widest in neodymium and lutetium. Ammonia buffer was finally chosen for pH adjustment.

Effect of other experimental variable

The effect of TAR-Br concentration was examined. The constant absorbances were obtained by adding about 2 to 10 ml of 0.05% solution for 100 μg of respective lanthanoids. The complexation reactions were completed immediately after addition of the reagent. The absorbances of the complexes remained constant even after 12 h at room temperature. We found that the molar absorptivities were raised by the addition of ethanol, as shown in Fig. 5. The sensitization effect was pronouncedly recognized for the elements from neodymium (increasing rate, 9.0%) to thulium (4.3%). Though the effect would be mainly produced by solvation of ethanol to lanthanoid complexes, cerium and ytterbium, whose valences are easily changeable, showed lower absorbances.

Calibration graphs

The calibration graphs of each lanthanoid were made under the optimum conditions. The curves pass through the origin and Beer's law holds approximately up to 2.5 ppm of each lanthanoid. The molar absorptivities exceed $5 \times 10^4 \text{ l mol}^{-1} \text{ cm}^{-1}$, except that of lanthanum, and the sensitivities for determination of lanthanoids are quite high. TAR-Br is more sensitive than the common reagents, such as Arsenazo-III, Xylenol Orange and Bromopyrogallol Red.⁶

Composition of lanthanoid complexes

The results obtained by the continuous variation method are shown in Fig. 3; it is confirmed that cerium, gadolinium and ytterbium form a 1:2 complex with TAR-Br. The complexes will be an inner-sphere complex of the six-coordinate octahedral type⁷, because thiazolylazo compounds usually act as a tridentate ligand.

Stability constants

It is well known that lanthanoids(III) simultaneously form protonated and normal type 1:1 complexes with TAR according to the pH.^{8,9} In the case of a great excess of lanthanoid ion against TAR-Br, the formation of $[\text{LnHR}]$ species would be predominated at $\text{pH} < \text{p}K_{a2}$. The successive stability constant of LnHR can be calculated by Eq. (1).

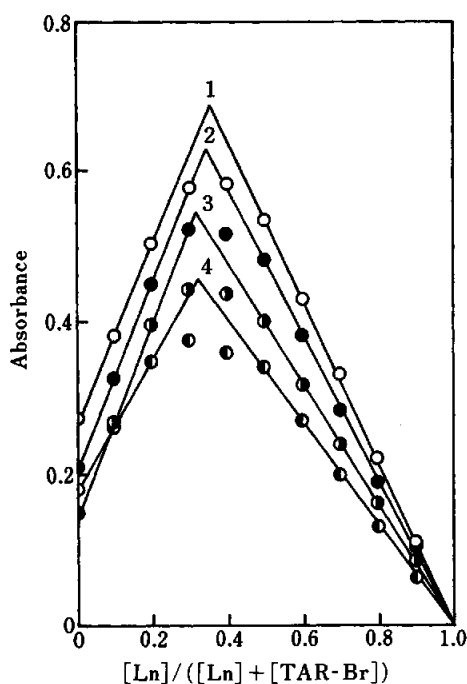


Fig. 3 Continuous variation method. 1, $[\text{Ce}] + [\text{TAR-Br}] = 3.43 \times 10^{-5} \text{ M}$, 540 nm; 2, $[\text{Gd}] + [\text{TAR-Br}] = 2.61 \times 10^{-5} \text{ M}$, 540 nm; 3, $[\text{Yb}] + [\text{TAR-Br}] = 2.63 \times 10^{-5} \text{ M}$, 550 nm; 4, $[\text{La}] + [\text{TAR-Br}] = 3.43 \times 10^{-5} \text{ M}$, 550 nm. Reference, water.

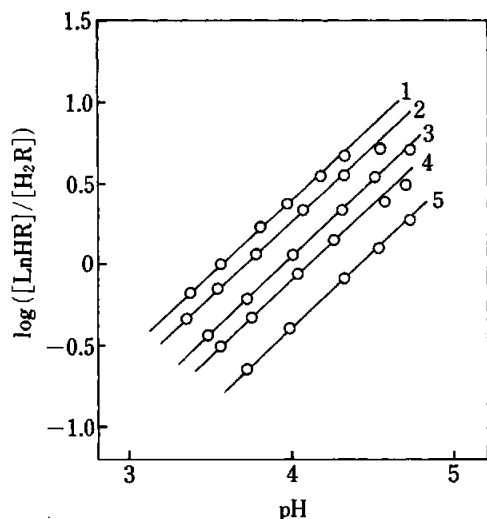


Fig. 4 Plots of $\log([\text{LnHR}]/[\text{H}_2\text{R}])$ vs. pH. Ln(III), $1 \times 10^{-3} \text{ M}$; TAR-Br, $2 \times 10^{-5} \text{ M}$; wavelength, 530 nm; $\mu = 0.1$ (Na_2ClO_4). 1, Sm; 2, Lu; 3, Dy; 4, Gd; 5, Ce.

$$\log K_{\text{LnHR}} = \log[\text{LnHR}]/[\text{H}_2\text{R}] + p\text{Ln} + pK_{\text{a3}} - \text{pH}, \quad (1)$$

where the charges are omitted for simplicity. The $\log K_{\text{LnHR}}$ values were determined spectrophotometrically by plotting $\log[\text{LnHR}]/[\text{H}_2\text{R}]$ versus pH, as shown in Fig. 4. The plots gave a straight line with a slope of unity, which suggests that Eq. (1) is reasonable. The constants obtained are listed in Table 1. The values are

Table 1 The properties of lanthanoid(III)-TAR-Br complexes

Lanthanoid	$\lambda_{\text{max}}/\text{nm}$	$\epsilon \times 10^4 / \text{l mol}^{-1} \text{cm}^{-1}$	Optimum pH range	$\log K_{\text{LnHR}}^a$
La	555	3.56	8.0-8.7	7.94
Ce	553	5.46	8.0-8.2	8.17
Pr	554	5.69	7.8-8.2	8.49
Nd	553	5.25	8.0-8.7	8.53
Sm	554	6.51	7.8-8.2	8.65
Eu	553	6.37	7.4-8.0	8.67
Gd	553	6.81	7.4-8.0	8.61
Tb	553	6.51	7.4-8.0	8.50
Dy	553	7.04	7.0-7.5	8.45
Ho	553	6.78	7.0-7.4	8.50
Er	553	7.08	7.1-7.6	8.51
Tm	553	6.85	6.8-7.2	8.49
Yb	553	6.75	7.4-7.8	8.65
Lu	552	6.73	6.9-7.7	8.64

a. The relative errors of $\log K_{\text{LnHR}}$ are 5-10%.

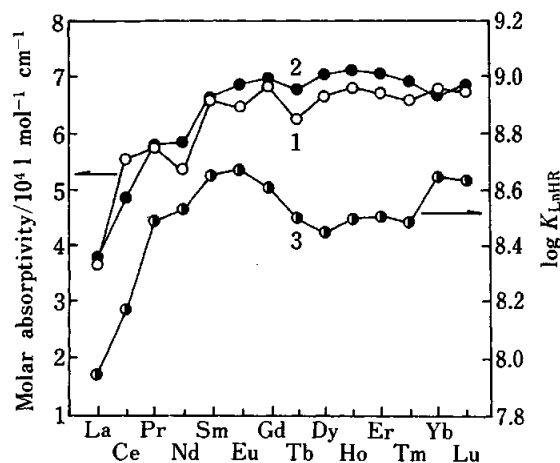


Fig. 5 Molar absorptivities and stability constants of lanthanoid(III) complexes. 1, Molar absorptivities, 0.05% TAR-Br, 5 ml; 2, molar absorptivities, 0.05% TAR-Br ethanol solution, 5 ml; 3, $\log K_{\text{LnHR}}$.

as a whole larger than those of TAR complexes⁹, but smaller than those of 2-(2-thiazolylazo)-*p*-cresol complexes.⁷ We could not determine the second successive formation constant, because accurate slopes could not be obtained.

Correlation with the lanthanoid contraction

The molar absorptivities and stability constants of lanthanoid complexes are plotted as a function of atomic number in Fig. 5. The molar absorptivities are increased with the atomic number in light lanthanoids (up to gadolinium) and are very close to each other for terbium and lutetium. The stability constants also show a similar trend, although heavy lanthanoids have slightly smaller values than those of light lanthanoids. This fact can be ascribed to the electrostatic forces

accompanying the decrease of ionic radius and thus to the stabilization of light lanthanoid complexes, but such a contraction effect is small in heavy lanthanoids.

Moeller *et al.*¹⁰ divided qualitatively the stability constants for lanthanoids whose atomic number is higher than that of gadolinium into three ligand groups: a ligand group with a regular increase in the stability constants, a ligand group with nearly the same stability constants, and a ligand group with a slight decrease in the stability constants. The stability trend of TAR-Br complexes may be classified into the second ligand group. It has also been pointed out by the same authors that the value of stability constant for the yttrium complex of the second ligand group was comparable to those for light lanthanoids. The value for yttrium was 8.24, which fell between those for cerium and praseodymium. This fact also suggests that TAR-Br belongs to the second ligand group. TAR derivatives, which are not always TAR-Br, would also form stable complexes with lanthanoids, this is now under investigation.

In conclusion, TAR-Br forms water-soluble stable complexes with lanthanoids(III); these possess high molar absorptivities. Based on these observations, simple and highly sensitive spectrophotometric methods for determination of each of 14 lanthanoids were

proposed. The complexing behavior was also examined. TAR-Br-lanthanoid complexes have both the same order of stability constants and molar absorptivities, except for lanthanum, but they are correlative to the lanthanoid contraction in light lanthanoids.

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