

## 1-(2'-Thiazolylazo)-2-Oxyaryl Compounds as Complexometric Metal Indicators

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By the coupling of diazotized 2-aminothiazole with  $\beta$ -naphthol  $\beta$ -naphthol-6-sulphonic acid, *p*-cresol, resorcinol, orcinol and *m*-dimethylaminophenol a series of 1-(2'-thiazolylazo)-2-oxyaryl compounds have been prepared. Their properties as metal-indicators for  $\text{Th}^{4+}$ ,  $\text{La}^{3+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$ ,  $\text{Cd}^{2+}$ ,  $\text{Mg}^{2+}$  and  $\text{Ca}^{2+}$  ions have been investigated. The compounds seem to be especially suited for the direct titration of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions with ethylenediaminetetraacetic acid (EDTA) in acid solutions.

The complexometric metal-indicator PAN (1-(2'-pyridylazo)- $\beta$ -naphthol) was introduced by Cheng and Bray<sup>1</sup> who applied the dye to a few complexometric metal determinations. Later its great versatility as a metal-indicator was confirmed by works of Flaschka *et al.*<sup>2,3</sup> and Cheng *et al.*<sup>4,5</sup> Recently a number of new pyridylazo-dyes have been prepared which also show promise as metal-indicators and colorimetric reagents<sup>6-10</sup>.

PAN acts as a tridentate ligand which accounts for the rather high stabilities of its metal-complexes.

By the replacement of the pyridine nucleus in PAN by a thiazole nucleus it should be possible to obtain a chelating agent with similar chelating properties. Hence the dye 1-(2'-thiazolylazo)- $\beta$ -naphthol (TAN) has been prepared and investigated as a metal-indicator in complexometric titrations (Fig. 1).

By the coupling of diazotized 2-aminothiazole with  $\beta$ -naphthol-6-sulphonic acid, *p*-cresol, resorcinol, orcinol and *m*-dimethylaminophenol the following compounds were also prepared for further investigations.

1-(2'-thiazolylazo)- $\beta$ -naphthol-6-sulphonic acid	TAN-6-S
2-(2'-thiazolylazo)- <i>p</i> -cresol	TAC
6-(2'-thiazolylazo)-resorcinol	TAR
6-(2'-thiazolylazo)-orcinol	TAO
6-(2'-thiazolylazo)-1-oxy-3-dimethylaminobenzene	TAM

The diazotization of 2-aminothiazole took place at 0°C in *ca.* 6 N hydrochloric acid. The diazotate is so reactive that the couplings with the phenols

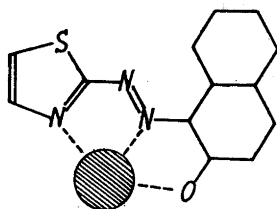


Fig. 1. Shows how 1-(2'-thiazolylazo)- $\beta$ -naphthol may act as a tridentate ligand.

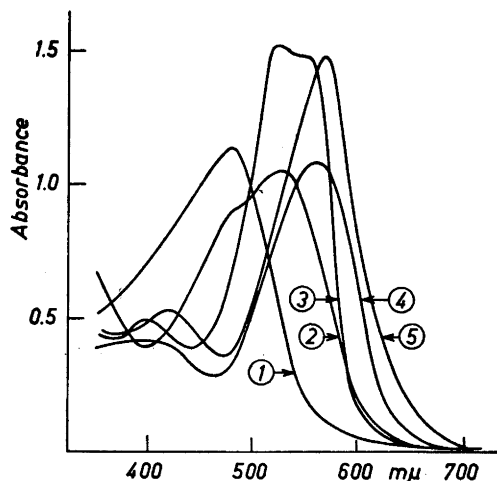


Fig. 2. Spectra of ca.  $10^{-4}$  M solutions of TAN-6-S in acid (1) and in basic (2) solutions together with the spectra of its chelates of Zn (3), Pb (4) and Cu (5) in slightly acid solution.

had to be performed in cold acetic acid solutions or in 4 N hydrochloric acid solutions producing the dyes in crystalline form immediately.

Coupling of the diazotate with the phenols under alkaline conditions as is the normal case, produced large amounts of dark coloured by-products and only very low yields of the pure compounds could be obtained.

The pure compounds were obtained by recrystallizations from methanol or ethanol. The dye TAN-6-S was isolated as its sodium salt which was easily salted out from water by sodium chloride.

Previously only TAN and TAR seem to have been prepared.<sup>11</sup>

All the compounds form intensively coloured metal chelates in neutral or slightly acid solutions with  $\text{Th}^{4+}$ ,  $\text{La}^{3+}$ ,  $\text{UO}_2^{2+}$ ,  $\text{Hg}^{2+}$ ,  $\text{Pb}^{2+}$ ,  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$ ,  $\text{Ni}^{2+}$ ,  $\text{Zn}^{2+}$  and  $\text{Cd}^{2+}$  ions.

The spectra of TAN-6-S alone and in combination with some metal ions are shown in Fig. 2. The effect of complex-formation seems to be a shift towards longer wave-lengths.

The dyes are also pH indicators. Only TAR and TAO do not change colour in an ammonia-buffer (pH = 10) indicating that their  $\text{p}K_a$  values are larger than 10. For TAN-6-S the  $\text{p}K_a$  value has been determined to 7.9<sup>12</sup>.

With the exception of TAN-6-S the compounds are only slightly soluble in water but show appreciable solubility in water-ethanol or water-dioxane mixtures.

The dyes were tested as metal-indicators in complexometric titrations of several metal ions with 0.1 M EDTA solutions. Acetate-acetic acid, pyridine pyridinium chloride and ammonia-ammonium chloride buffers were used. The

changes of their colour at satisfactory endpoints were noted and are listed in Table 1. The amount of indicator used in the titrations was 4–5 drops of a 0.1 % solutions of the dye in methanol.

With all the compounds sharp end-points were obtained in direct titrations of  $\text{Cu}^{2+}$ ,  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions in acetate and in pyridine buffers. The  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions, however, reacted satisfactorily only in hot solutions. The addition of methanol or ethanol often improved the colour changes with TAN, TAC, TAR, TAO and TAM because of the increased solubility of the indicators in the mixed solvents.

No direct complexometric titrations of  $\text{Co}^{2+}$  and  $\text{Ni}^{2+}$  ions in acid solutions seem to have been reported in the literature until now.

The direct titrations of  $\text{Zn}^{2+}$  and  $\text{Pb}^{2+}$  ions were easily performed in the pyridine buffer but not in the acetate buffer. The direct titration of the  $\text{Cd}^{2+}$  ion in those two buffers was unsatisfactory.

In pyridine buffer the  $\text{Th}^{4+}$ ,  $\text{Zr}^{4+}$  and  $\text{UO}_2^{2+}$  ions formed intensively coloured chelates with all the compounds. However they could not be titrated with EDTA as larger amounts of the titrant were needed to change the colour of the indicator than that corresponding to equivalence.

With TAN, TAN-6-S and TAR the colour changes at the endpoints of the titrations were easily observed with all the metal ions mentioned. With TAO and TAC especially the endpoints in the  $\text{Cu}^{2+}$  ion titrations were good. When TAM was used as an indicator the colour changes were difficult to observe as the changes usually were from red-violet to pink.

It was found possible to increase the number of metal ions which could be titrated directly by the use of a  $\text{Cu}^{2+}$  ion-EDTA-dye combination as an indicator. A similar  $\text{Cu}^{2+}$  ion-EDTA-PAN indicator combination has been described by Flaschka.<sup>3</sup>

One drop of a Cu-salt solution was added to the buffer-indicator mixture and then so much EDTA solution that the indicator just changed colour. The metal ion solution to be determined was pipetted into the mixture where the  $\text{Cu}^{2+}$  ion was displaced from its EDTA complex in amounts large enough to reverse the colour change of the indicator. Depending on the buffer system used and the metal ion added the accurate determination of the latter was often possible by titration with EDTA to a new colour change.

In Table 2 some successful titrations are shown which have been made in this way with TAN-6-S, TAR and TAO.

Owing to the small  $pK_a$  value of TAN-6-S (7.9<sup>12</sup>) this indicator could not be used in the ammonia buffer (pH = 10) and therefore it could not be used in the determination of  $\text{Mg}^{2+}$ ,  $\text{Ca}^{2+}$  and  $\text{Cd}^{2+}$  ions. With TAR and TAO these ions were successfully titrated in an ammonia buffer.

The 1-(2'-thiazolylazo)-2-oxyaryl compounds are also useful as colorimetric reagents. A detailed procedure for the determination of uranium with TAN and TAM will be published in the near future<sup>13</sup>.

Recently the synthesis of 2-(2'-methylthiazolylazo)-*p*-methoxyphenol and its colour reactions with several metal ions have been described<sup>14</sup>.

Table 1.

Compound	Metal ion	Buffer	Colour-change
TAN	Cu Co Ni	Acetate or pyridine	blue to orange to yellow violet to orange to yellow violet to orange to yellow
TAR	Cu Co Ni		violet to yellow-green violet to dirty yellow red-violet to yellow
TAO	Cu Co Ni		red to yellow red to yellow red to yellow
TAC	Cu Co Ni		Blue-green to yellow smoke to yellow blue-green to yellow
TAM	Cu Co Ni		red-violet to pink red-violet to pink red-violet to pink
TAN-6-S	Cu Co Ni		blue to yellow-green violet to dirty yellow violet to yellow
TAN	Zn Pb	Pyridine	pink to yellow violet to yellow
TAR	Zn Pb		pink to yellow violet to yellow
TAO	Zn Pb		smoke to yellow blue-green to yellow
TAM	Zn Pb		
TAN-6-S	Zn Pb		red-violet to yellow blue-violet to yellow

Table 2.

Compound	Metal ion	Buffer
TAN-6-S	Hg, Zn, Pb La	Acetate or pyridine
TAR TAO	Mg, Ca, Mn Cd Mg, Ca, Mn Cd	Ammonia

## EXPERIMENTAL

All the compounds were prepared by essentially the same method. The synthesis of TAM will serve as an example. Owing to the possibility of coupling in positions 2 and 4 with *m*-dimethylaminophenol only a rather low yield of TAM was obtained.

6-(2'-Thiazolylazo)-3-dimethylaminophenol (TAM). 5 g of 2-aminothiazole were dissolved in 40 ml of 6 N hydrochloric acid and cooled in ice. 3.5 g of sodium nitrite were dissolved in a small amount of water. After the addition of crushed ice to both solutions the nitrite solution was slowly poured into the other solution while stirring with a glass spatula. The mixture was left in an icebath for 10 min. The solution of the diazotate was then poured slowly while stirring into a well cooled solution of 7 g of *m*-dimethylaminophenol in 100 ml of 4 N hydrochloric acid (or in acetic acid). An intense colour immediately developed in the mixture and soon yellow-brown crystals of the hydrochloride of TAM were formed.

After 1/2 h in the refrigerator 100 g of sodium acetate in 300 ml of water were added. The colour changed into intense red-violet and after 2–3 h the precipitate formed was filtered with suction on a Büchner-funnel. The filtrate which was almost pure red in colour was discarded. The filter cake was recrystallized from an acetic acid-water mixture yielding the pure product as dark violet needles. Yield 6.3 g (53 %), m. p. 216°C. (Found: C 53.22; H 4.87. Calc. for  $C_{11}H_{11}N_4OS$ : C 53.45; H 5.09.)

1-(2'-Thiazolylazo)- $\beta$ -naphthol (TAN). Yield 75 %, m. p. 140°C. (Found: C 61.17; H 3.55. Calc. for  $C_{13}H_9N_2OS$ : C 61.30; H 3.57.)

1-(2'-Thiazolylazo)- $\beta$ -naphthol-6-sulphonic acid, sodium (TAN-6-S). Yield 50 %, m. p. (decomp.). (Found: C 41.55; H 2.83. Calc. for  $C_{13}H_8N_2O_4S_2Na$ ,  $H_2O$ : C 41.65; H 2.68.)

6-(2'-Thiazolylazo)-resorcinol (TAR). Yield 35 %, m. p. 235°C (decomp.). (Found: C 48.87; H 3.19. Calc. for  $C_9H_7N_2O_2S$ : C 49.00; H 3.38.)

6-(2'-Thiazolylazo)-orcinol (TAO). Yield 47 %, m. p. 250°C (decomp.). (Found: C 51.06; H 3.85. Calc. for  $C_{10}H_7N_2O_2S$ : C 51.00; H 3.93.)

2-(2'-Thiazolylazo)-*p*-cresol (TAC). Yield 57 %, m. p. 129°C. (Found: C 54.79; H 4.13. Calc. for  $C_{10}H_9N_2OS$ : C 54.70; H 4.18.)

*Titrations.* The 0.1 M solutions of the metal salts were prepared by dissolving calculated amounts of analytical grade metal nitrates or chlorides in water. The 0.1 M EDTA solution was prepared according to standard procedures<sup>7</sup>. The buffers were made by mixing 1 M solutions of the acids and bases in the proper ratios.

In the titration experiments 5–10 ml of the metal salt solution were pipetted into 30–40 ml of a buffer solution and diluted to ca. 100 ml distilled water. 4–5 drops of a 0.1 % solution of the indicator in methanol were added.

The titrant was added from a 10 ml burette, rapidly at first but dropwise near the expected end-point.

The end-point was taken as the point where further addition of titrant did not change the colour.

A titration was regarded as satisfactory when the experimental endpoint did not deviate more than 1 % from the calculated.

All melting-points were measured on a Kofler hot-bench. The spectra were taken with a Perkin-Elmer Spectracord 4 000 recording spectrophotometer.

*Acknowledgements.* The author wishes to thank Mr. P. Hansen at the Chemical Laboratory at the University of Copenhagen for performing the microanalyses and Mr. O. Jørgensen for valuable technical assistance.

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Received December 14, 1960.