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METAL COMPLEXES OF 4-(2′-THIAZOLYLAZO)-RESORCINOL

A COMPARATIVE STUDY WITH 4-(2′-PYRIDYLAZO)-RESORCINOL*

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Summary—The acid dissociation constants of 4-(2′-thiazolylazo)-resorcinol (TAR) and the formation constants of the metal complexes formed by this reagent with Cu(II), Ni(II), Co(II), Zn(II) and Mn(II) have been determined potentiometrically at 25° in 50% v/v mixtures of dioxane and water. The values obtained for TAR and the metal complexes are contrasted with similar values for the reagent 4-(2′-pyridylazo)-resorcinol (PAR). Differences and similarities between the co-ordinating tendencies of these two reagents are revealed in terms of the proton displacement constant and the acid dissociation constants of the metal complexes. Evidence is presented which suggests that both TAR and PAR may act as terdentate ligands toward some bivalent metal ions.

THE wide interest exhibited in the application of organic compounds in analytical chemistry has been summarized by May and Schubert.[1] One of the main characteristics and advantages of organic reagents is the predictable alteration in reactivity which may be achieved by appropriate substitution in the reagent. These substitutions result in a wide range of electronic and steric effects which may be manifested in those factors controlling the formation of metal complexes. Two such factors are the formation constant of the metal complex and the acid dissociation constant of the ligand. Since these constants are inter-related it seems preferable to consider them simultaneously through the proton displacement constant, K_{pd}, defined by Sun *et al.*[2] Other properties which may be affected by alterations in the organic residue surrounding a selected donor group are the solubility and colour of the resulting metal complexes.

The orthohydroxyazo dyes, in particular 1-(2′-pyridylazo)-2-naphthol (PAN)[3–5] and 4-(2′-pyridylazo)-resorcinol (PAR)[5,6] have received attention as metallochromic indicators. Recently, 4-(2′-thiazolylazo)-resorcinol (TAR) has been synthesised and its utility as a metallochromic indicator investigated empirically by Jensen.[7] In order to fully exploit TAR as an analytical reagent, information on the stoichiometries, proton displacement constants and acidities of the metal complexes of TAR must be available, and it was therefore considered worthwhile obtaining this information.

Since TAR and PAR have the same reactive group, $-N{=}CN{=}N-C-\overset{\|}{C}-O^-$, available for possible co-ordination to the metal ion, it is of interest to compare the reactivities of these two compounds and thus assess the effect of the thiazole sulphur atom on metal complex formation.

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EXPERIMENTAL

Reagents and apparatus

TAR was prepared as described by Jensen,[7] and purified by dissolution in sodium hydroxide, extraction with ether, and reprecipitation with dilute hydrochloric acid or carbon dioxide. The equivalent weight of the monohydrate was found by potentiometric titration to be 240·0 (theoretical 239·3).

PAR (G. F. Smith Chemical Co.) was purified in the same manner as TAR. The equivalent weight found potentiometrically was 215·6 (theoretical 215·2).

The preparation of the standard solutions of the metal perchlorates, perchloric acid and sodium hydroxide has been previously described, and so has the apparatus.[8]

The 1,4-dioxane (Fisher Scientific) was purified by the method described by Pease,[9] and then distilled from sodium wire through a 6-ft column packed with glass helices.

Potentiometric titrations

The general titration procedure was to add 50·0 ml of 0·01*M* perchloric acid and 55·0 ml of dioxane to a weighed amount of TAR or PAR in the titration vessel and then to add 5·0 ml of water or 5·0 ml of 0·01*M* metal ion depending on whether acid dissociation constants of the reagents or complex formation constants were being determined. The contents of the titration vessel were maintained at 25·0° ± 0·1°. Prepurified nitrogen gas was passed through the solution, and an atmosphere of nitrogen was maintained above the solution throughout the titration. The standard sodium hydroxide solution was added to the stirred solution in small increments together with equal volumes of dioxane. All pH measurements were made with a Radiometer pHM_4C pH meter equipped with a Beckman E-2 glass electrode and a saturated calomel electrode. The system was calibrated with Beckman buffers at pH 4·01 and 7·00.

The initial concentrations used in the determination of the acid dissociation constants of TAR and PAR were: TAR—$2{\cdot}8 \times 10^{-3}M$, perchloric acid—$4{\cdot}5 \times 10^{-3}M$; PAR—$3{\cdot}1 \times 10^{-3}M$; sodium hydroxide—0·1011*M*. For the determination of the formation constants the initial concentrations of TAR and metal ion ranged from $9{\cdot}0 \times 10^{-4}$ to $2{\cdot}5 \times 10^{-3}M$ and 4·9 to $9{\cdot}0 \times 10^{-4}M$ respectively. The initial concentration of PAR was $9{\cdot}0 \times 10^{-4}M$, the perchloric acid was $4{\cdot}2 \times 10^{-3}$–$4{\cdot}0 \times 10^{-3}M$, and the sodium hydroxide was 0·1008–0·1011*M*. The ionic strength, μ, used in this investigation was initially <0·01.

Determination of pH meter correction in 50% v/v aqueous dioxane

A $4{\cdot}5 \times 10^{-3}M$ solution of perchloric acid in 50% v/v aqueous dioxane was titrated with 0·1008*M* sodium hydroxide at 25·0 ± 0·1°. The difference between the calculated p_cH and the corresponding pH meter reading at every point in the titration was tabulated, and plotted as correction factor *vs.* pH meter reading. The differences varied with the individual electrode calibrated, but were in the range 0·03–0·13 ($p_cH >$ pH meter reading) for low pH meter readings, and covered the range 0·45–0·51 for pH meter readings >11. The autoprotolysis constant used, $p_cK_w = 16{\cdot}16$, was extrapolated from the data of Harned and Owen.[10] The large correction factor in the alkaline region may be attributed to two causes; one, the glass electrode is responding to the sodium ion present in the solution,[11] and two, the value $p_cK_w = 16{\cdot}16$ is too large for the solvent system employed. It has recently been shown that for $\mu = 0{\cdot}1$, $p_cK_w = 15{\cdot}38$ for this solvent system.[12]

Spectrophotometric titration

Copper(II) was titrated spectrophotometrically in 50% v/v aqueous dioxane with TAR by the method of Pease[9] at a wavelength of 520 mμ and a slit width of 0·010 mm. The initial concentration of copper(II) was $8{\cdot}528 \times 10^{-6}M$ and of TAR $2{\cdot}030 \times 10^{-3}M$. The instrument used was a Beckman Model DU equipped with power supply, photomultiplier and matched 1·0-cm silica cells.

METHODS OF CALCULATION

Chelate formation constants

If K_{NH}, K'_{OH} and K_{OH} are the acid dissociation constants of the hetero-ring nitrogen, *p*-hydroxy and *o*-hydroxy groups, respectively, in TAR and PAR, it can be shown that $\bar{n}$, the average number of ligand molecules bound to a bivalent metal ion, is:

$$\bar{n} = \frac{1}{T_M}\left[T_{H_2L} - S\left\{\frac{K_{NH}[H^+] + [H^+]^2 + K'_{OH}K_{NH}}{K_{NH}[H^+] + 2[H^+]^2}\right\}\right] \qquad (1)$$

where T_M = total metal ion concentration, T_{H_2L} = total reagent concentration, and S is defined by

$$S = T_{H_2L} - 2T_M - [H^+] - [Na^+] + [OH^-] + [ClO_4^-].$$

The stepwise formation constants, $\log K_1$ and $\log K_2$, for the neutral TAR and PAR chelates were obtained by plotting $\bar{n}$ against $-\log [HL^-]$ where

$$[HL^-] = \frac{S \,.\, K_{NH} \,.\, K_{OH}}{2[H^+]^2 + K_{NH}[H^+]}\,. \tag{2}$$

Log K_1 and log K_2 were obtained from the values of $-\log [HL^-]$ at the points where $\bar{n} = 0{\cdot}5$ and $1{\cdot}5$ respectively.

For the copper(II)-PAR complex, which is 1:1 (*vide infra*), the formation constant k_1 is given by:

$$k_1 = \frac{\bar{n}}{[HL^-][1 - \bar{n}]}\,. \tag{3}$$

For the copper(II)-TAR complex, which is also 1:1, since the *p*-hydroxy group of the complex tends to dissociate in the pH range of complex formation, the formation constant, k_1, is given by:

$$k_1 = \frac{[H^+]^3 \left\{[H^+] + K_{NH}\right\}\left[T_{H_2L} - Q\left\{\dfrac{[H^+] + K_{NH}}{[H^+]}\right\}\right]}{K_{NH}K_{OH}T_M(1 - \bar{n})(T_{H_2L} - \bar{n}T_M)[(2K_{a_1} + [H^+])([H^+] + K_{NH}) + [H^+]([H^+] + K_a)]} \tag{4}$$

where K_{a_1} is the acid dissociation constant of the *p*-hydroxy group in the chelate, and Q is defined by $Q = [ClO_4^-] + [OH^-] - [H^+] - [Na^+] - 2T_M$.

Chelate dissociation constants

With the exception of the copper(II)-TAR and copper(II)-PAR chelates, it may be shown that if $\bar{n}_H$ is the average number of protons bound per molecule of chelate, defined by:

$$\bar{n}_H = \frac{1}{T_M}\left[Z + \frac{(T_{H_2L} - 2T)_M([H^+]K'_{OH} + 2K'_{OH}K_{OH})}{[H^+]^2 + [H^+]K'_{OH} + K'_{OH}K_{OH}}\right] \tag{5}$$

where $Z = 2T_M - [Na^+] - [H^+] + [ClO_4^-] + [OH^-]$, then a plot of $\bar{n}_H$ against p$_c$H will give the dissociation constants of the chelates, pK_{a_1} and pK_{a_2}.[13]

For the case of the copper(II)-PAR and copper(II)-TAR complexes, it can be shown that the dissociation of the *p*-hydroxy group in the chelates is given by:

$$K_{a_1} = \frac{[H^+][V([H^+]^2 + [H^+]K_{NH} + K_{NH}K'_{OH}) + (T_{H_2L} - T_M)([H^+]^2 - K_{NH}K'_{OH})]}{(T_M - V)([H^+]^2 + [H^+]K_{NH} + K_{NH}K'_{OH}) - (T_{H_2L} - T_M)([H^+]^2 - K_{NH}K'_{OH}} \tag{6}$$

where $V = T_M - [ClO_4^-] - [OH^-] - [Na^+] - [H^+]$.

Hydroxo-complexes

The formation constant associated with the hydroxo form of the 1:1 copper-ligand chelates can be treated as a simple acid dissociation constant:

$$K_H = \frac{[H^+](T_M - T_{H_2L} - [ClO_4^-] - [OH^-] + [Na^+] + [H^+])}{T_{H_2L} + [ClO_4^-] + [OH^-] - [Na^+] - [H^+]}. \qquad (7)$$

All the terms referred to throughout the equations are expressed as molar concentrations, and hence the constants are molarity quotients. Goldberg's method[14,15] was used to assess the effect of the ionic strength of the medium on the magnitude of these constants.

RESULTS

The acid dissociation constants determined are reported in Table I, where pK_{NH} refers to the dissociation of the protonated species, pK'_{OH} to the dissociation of the hydroxy group *para* to the azo group, and pK_{OH} to the dissociation of the hydroxy group *ortho* to the azo group.

TABLE I.—ACID DISSOCIATION CONSTANTS OF TAR AND PAR IN 50% v/v AQUEOUS DIOXANE AT 25·0°C

	pK_{NH}	pK'_{OH}	pK_{OH}
TAR	1·65 ± 0·11 (1·65)	7·37 ± 0·03 (7·61)	12·80 ± 0·04 (13·07)
PAR	2·31 ± 0·02 2·3* (2·31)	6·87 ± 0·01 6·9* (7·08)	13·42 ± 0·01 12·4* (13·70)

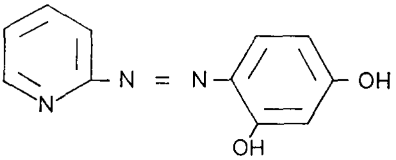
The precision is expressed as the standard deviation. For TAR, the least amount of data involved three separate determinations, and a total of 43 distinct points (pK_{NH}). For PAR, only one determination is reported, which involves a minimum of 13 distinct points (pK_{NH}). The values in parenthesis have been corrected for the ionic strength of the medium according to Goldberg.[14,15]

* Corsini *et al.*[5]

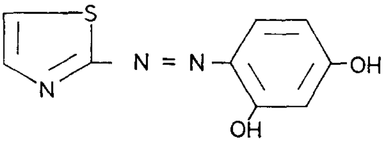
The rationale for the respective assignments of pK_{NH}, pK'_{OH} and pK_{OH} of PAR has been presented by Geary *et al.*[16] in an elegant spectrophotometric study, and substantiated by Corsini[5] through a potentiometric comparison of the acidities of PAR and 1-(2-pyridylazo)2-naphthol (PAN). In view of the structural similarity between PAR and TAR shown in Fig. 1 the assignment of the constants in this work has been the same for both compounds.

The formation constants for the reactions between TAR and bivalent metal ions are reported in Table II. For comparative purposes similar values for PAR are included.

The stoichiometry of the complexes formed between the bivalent metal ions and TAR was deduced from the potentiometric titration curves (Fig. 2) for all the metal ions tested except copper(II). In any of the titrations approximately 5 ml of 0·1*N* sodium hydroxide were required to neutralize the excess of perchloric acid and any protonated species present; consequently, the displacement of the TAR, perchloric acid, and metal ion curve from the TAR and perchloric acid curve after the addition of 5 ml of base must be due to proton release, which in the absence of metal ion hydrolysis must depend on the reaction between TAR and the metal ion. All metal



4-(2′-PYRIDYLAZO)-RESORCINOL
(PAR)



4-(2′-THIAZOLYLAZO)-RESORCINOL
(TAR)

FIG. 1.—Structures of PAR and TAR.

TABLE II.—COMPLEX FORMATION CONSTANTS OF TAR AND PAR IN 50% v/v AQUEOUS DIOXANE AT 25·0°C

	TAR			PAR	
Metal ion	log K_1	log K_2	log β_2	log K_1	log K_2
Copper(II)	14·19 ± 0·26 (14·42)*	—	—	15·44 ± 0·17 16·4† (15·68)*	— 8·9†
Nickel(II)	12·94 ± 0·08 (13·15)*	11·82 ± 0·04 (12·05)*	24·76 (25·22)*	13·2‡	12·8‡
Cobalt(II)	12·05 ± 0·10 (12·28)*	11·23 ± 0·06 (11·46)*	23·28 (23·74)*	>12‡	—
Zinc(II)	11·08 ± 0·04 (11·31)*	10·11 ± 0·02 (10·34)*	21·19 (21·62)*	12·4‡	11·1‡
Manganese(II)	9·43 ± 0·02 (9·66)*	8·6 ± 0·2 (8·8)*	18·0 (18·46)*	9·79 9·7‡ (10·02)*	9·13 9·2‡ (9·36)*

Precision is expressed as the standard deviation. All values are an average of a minimum of three separate determinations at various mole ratios of TAR to metal ion. Each determination involves from 5 to 28 individual points.

* Values in parenthesis have been obtained by correcting for the ionic strength of the medium according to Goldberg.[14,15]

† Geary *et al.*[6]

‡ Corsini *et al.*[5]

ions titrated in this study show an equivalent weight corresponding to half the atomic weight. Hence, it could be concluded that all the complexes have a 2:1 ratio of TAR to metal ion.

In the case of the TAR and copper(II) reaction, the spectrophotometric titration (Fig. 3) indicated that a 1:1 complex was formed. Since light of wavelengths below 300 mμ caused photodecomposition of TAR and hence could not be used, confirmatory evidence for the 1:1 stoichiometry of the TAR-copper(II) complex was taken from the application of equation (4) to the system. This equation was derived

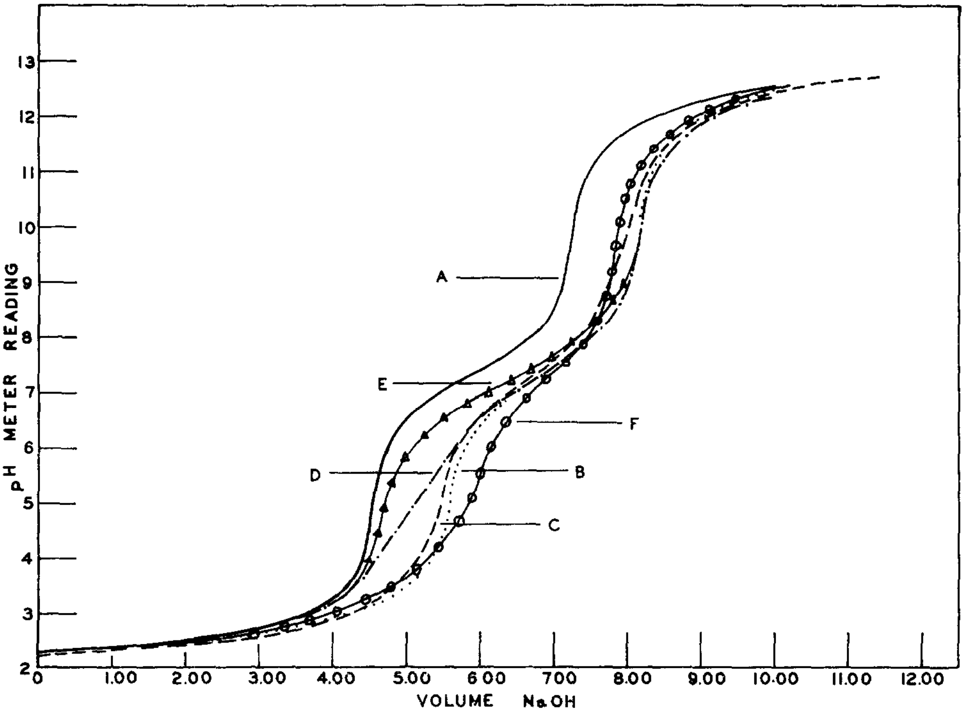


FIG. 2.—Titration curves of TAR and 0·457 mmole of perchloric acid with 0·1007*N* sodium hydroxide in 50% v/v aqueous dioxane at 25·0°C.
A—0·27 mmole TAR
B—0·27 mmole TAR, 0·053 mmole nickel(II)
C—0·27 mmole TAR, 0·53 mmole copper(II)
D—0·27 mmole TAR, 0·053 mmole zinc(II)
E—0·27 mmole TAR, 0·053 mmole manganese(II)
F—0·27 mmole TAR, 0·055 mmole cobalt(II)

on the basis that formation of the complex and dissociation of the *p*-hydroxy group of the complex overlap. This overlapping of the formation and dissociation constants did not occur with the other metal ions and TAR nor with PAR and copper(II), *vide infra.*

The further displacement of the TAR-perchloric acid-metal ion curves, other than that for copper(II), from the TAR-perchloric acid curve after the addition of about 7 ml of alkali may be attributed to the dissociation of the *p*-hydroxy group in the metal chelate. This phenomenon then gives rise to the chelate acid dissociation constants which are summarised in Table III.

In the reaction of copper(II) with TAR or PAR, this further displacement of the curves is attributed to the dissociation of a bound water molecule in the 1 : 1 complex. This situation is more clearly revealed in Fig. 4. The p*K* values obtained are 10·13 ± 0·06 for the copper-TAR system, 10·09 ± 0·06 for copper-PAR, and 8·98 ± 0·03 for zinc-TAR, in 50% aqueous dioxane at 25°. No evidence of dissociation of the bound water molecules in chelates of TAR with nickel(II) or cobalt(II) could be obtained, in the former case owing to the high pH value at which metal hydrolysis

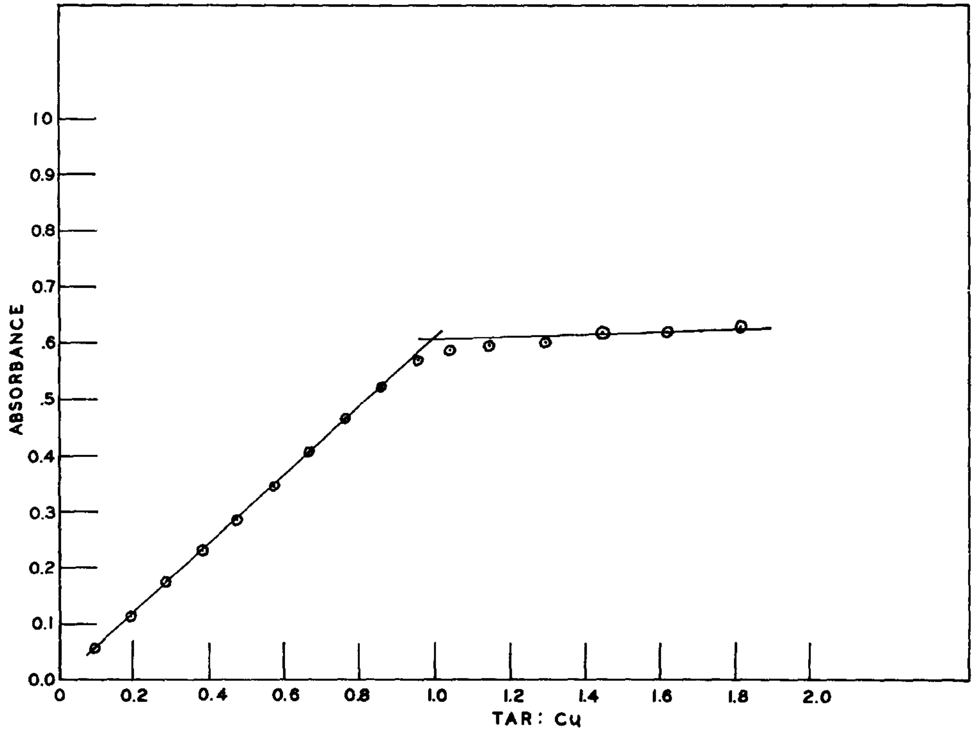


FIG. 3.—Spectrophotometric titration curve

$$\text{TAR: Cu} = \frac{\text{mmole TAR}}{\text{mmole Cu(II)}}$$

Wavelength = 520 mμ.

TABLE III.—ACID DISSOCIATION CONSTANTS OF METAL CHELATES OF TAR AND PAR IN 50% v/v AQUEOUS DIOXANE AT 25·0°C

	TAR		PAR	
Metal Ion	pK_1	pK_2	pK_1	pK_2
Copper(II)	4·34 ± 0·06	—	5·56 ± 0·01 5·5*	—
Nickel(II)	6·84 ± 0·07	8·55 ± 0·10	7·7*	9·2*
Zinc(II)	7·12 ± 0·10	8·74 ± 0·11	7·7*	9·3*
Manganese(II)	7·88 ± 0·05	9·38 ± 0·11	8·8*	10·3*

Precision is expressed as the standard deviation. Three separate determinations are averaged and reported. The minium number of points involved in any one deteimination is 7, and the maximum is 22.

* A. Corsini, Q. Fernando and H. Freiser, *Inorg. Chem.*, 1963, **2**, 224.

ordinarily starts and in the latter, owing to uncertainty regarding the composition of the system.

DISCUSSION

The formation constants presented in Table II were calculated on the assumption that for the equilibria shown in Fig. 5, pK^* = pK_{OH}. It was necessary to make this

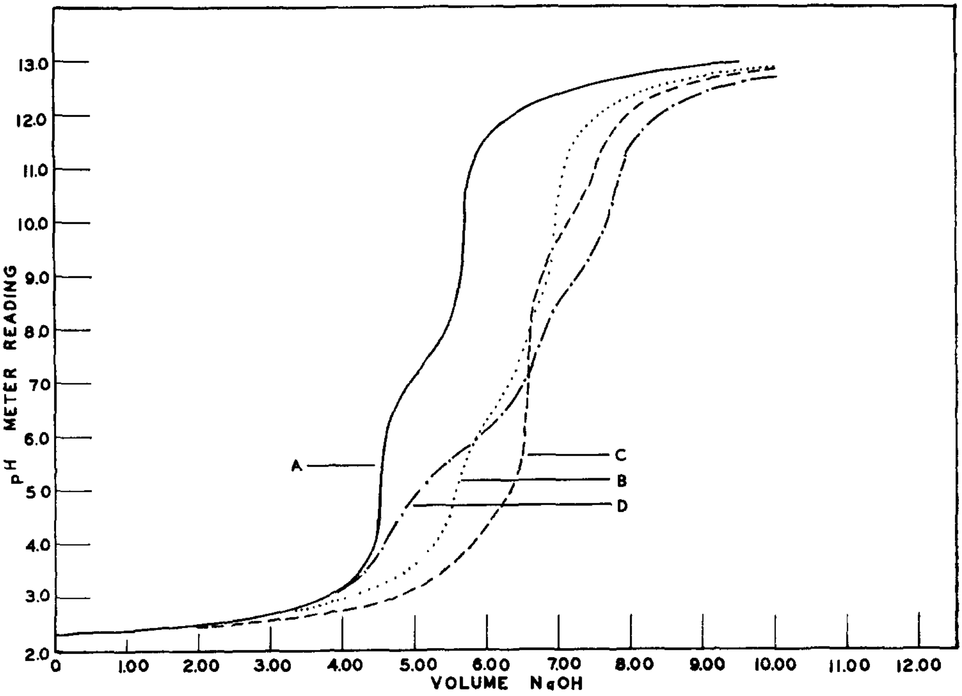


FIG. 4.—Titration curves of TAR and 0·457 mmole of perchloric acid with 0·1007*N* sodium hydroxide in 50% v/v aqueous dioxane at 25·0°C.
A—0·11 mmole TAR
B—0·11 mmole TAR, 0·11 mmole nickel(II)
C—0·11 mmole TAR, 0·11 mmole copper(II)
D—0·11 mmole TAR, 0·11 mmole zinc(II).

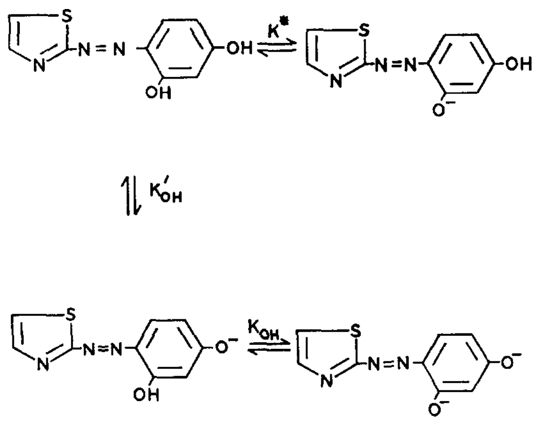


FIG. 5.—Equilibria for TAR.

assumption since potentiometry, as applied in this study, would not permit pK_{OH} to be evaluated before pK'_{OH}.

From a comparison of the visible spectra of PAR and related compounds with those of their metal complexes, Geary *et al.*[16] concluded that PAR acted as a terdentate ligand toward bivalent metal ions. In the same investigation no reference was made to the possibility that PAR could exist in a *trans*- form. In this study no evidence was obtained for the existence of a *trans*- configuration of TAR, and an extensive spectrophotometric study in the ultraviolet–visible region was precluded by the photodecomposition of the compound. Thus, it must be recognized that the results (Tables I and II) may be for the reactions of an equilibrium mixture of *cis*- and *trans*- isomers of TAR and PAR.

Evidence that TAR acts as a terdentate ligand, at least towards copper(II) in solution, is obtained from the spectrophotometric titration (Fig. 3), the magnitude of $\log k_1$ (Table II), and the acid dissociation constants of the hydroxo species. Thus $pK_H = 10{\cdot}13 \pm 0{\cdot}06$ for TAR-copper(II) and $10{\cdot}09 \pm 0{\cdot}06$ for PAR-copper(II), where pK_H refers to the equilibrium:

$$[\mathrm{Cu(L)(H_2O)}] \rightleftharpoons [\mathrm{Cu(L)(OH)}]^- + \mathrm{H}^+.$$

The similarity of these pK_H values suggests that the gross features of the bonding toward copper(II) by these reagents are the same. Thus it is concluded that it is the nitrogen in the thiazole ring of TAR rather than the sulphur that is attached to the copper(II) ion. Molecular models lend further support to the idea that if PAR acts as a terdentate ligand, then so might TAR, because they show that replacement of the pyridine ring by the thiazole ring does not significantly alter the geometry of the ligand.

TAR does not seem to behave unequivocally as a terdentate ligand toward metal ions other than copper(II). In an attempt to find any special ligand effects[17] which TAR might exhibit, a plot of $\log K_1$ for nickel *vs.* $\log K_1$ for zinc, or $\log \beta_2$ for nickel *vs.* $\log \beta_2$ for zinc, was made for a number of azo-containing reagents, including PAR,[5] PAN,[5] TAR and a large number of substituted pyrazolones.[18] It is convenient to refer to the latter by their numbers in the Table of Stability Constants,[18] *viz.*, 1035, 1036, 1038, 1039, 1041, 1049, 1054, 1056, 1058, 1067, 1070, 1075 and 1089. No irregularities were revealed by this plot, and it may be concluded that if the azo group is involved in the co-ordination of one reagent, then it is involved with them all. The reagents separate into three groups on the plot according to the ligand atoms: $\mathrm{O^-{-}C{-}N{=}N{-}C{-}C{-}O^-}$ (Group A), $\mathrm{N{-}C{-}N{=}N{-}C{-}C{-}O^-}$ (Group B) and $\mathrm{R{-}N{=}N{-}C{-}C{-}O^-}$ (Group C). It is difficult to assess the relative positions (magnitudes of $\log K$ values) of these groups on the plot, owing to differences in the solvent compositions in which the formation constants were determined. Thus Groups A and C involve a 75% aqueous dioxane system whereas Group B involves 50% aqueous dioxane. The former system gives larger values of $\log K$; nevertheless, the $\log \beta_2$ values for Group B are greater than the corresponding values for Group C, the members of which can act only as bidentate ligands, and greater than the $\log K_1$ values for Group A, the members of which for steric reasons (and from reported results) would be expected to act as terdentate ligands forming 1:1 complexes only.

The results thus suggest that PAR, TAR and PAN may act as terdentate ligands in the formation of metal complexes.

In general, PAR forms slightly more stable complexes than TAR (Table II), but the proton displacement constants[2,12] for the latter ($K_{\text{pd}} = \beta_n K_{\text{OH}}{}^n$) are almost the same as the corresponding values for PAR when they may be compared. Thus for copper(II), log $K_{\text{pd}} = 1{\cdot}4$ and 2·0 for TAR and PAR respectively and for manganese(II) the corresponding values are $-7{\cdot}6$ and $-7{\cdot}9$.

The apparent similarity in reactivity of PAR and TAR toward metal ions is further revealed by a comparison of the acidity of the corresponding complexes as revealed by Table III. In general the TAR complexes are more acidic than those of PAR. The order of acidity is: Mn(II) < Zn(II) < Ni(II) < Cu(II) which parallels the stability order of the complexes. It is tempting to speculate on the origin of this acid-strengthening effect which metal complex formation exerts on the *p*-hydroxy group of TAR and PAR. There are two possible effects; the metal ion may withdraw electrons from the resorcinol ring *via* the bonding oxygen atom and hence increase the acidity of the *p*-hydroxy group, or the pyridine ring could withdraw electrons and thus stabilise the anionic metal complex. It is suggested that neither of these effects might operate to the exclusion of the other. In order to appreciate that metal complex formation does result in an increase in acidity of the *p*-hydroxy group it is convenient to consider the pK_a value for 4-(2-pyridylazo)-1-naphthol[19] (pK_a = 10·74 in 50% v/v aqueous dioxane). In this compound there is no hydroxy group *ortho* to the azo group and hence there is no electronic effect due to possible intramolecular hydrogen bonding transmitted to the *p*-hydroxy group as there is in TAR and PAR. It is therefore concluded that the values of pK'_{OH} in TAR and PAR reflect acid-strengthening effects of the *p*-hydroxy group exhibited by a "hydrogen chelate." This effect may be enhanced by replacing the proton with a dipositive metal ion if a forced planar configuration about such an ion may be attained, *e.g.*, with copper(II); the other metal ions, it seems, do not reflect such a degree of forced planar configuration and hence their effect on increase in acidity is not as marked.

The comparison of TAR with PAR as a ligand indicates that substitution of the thiazole ring for the pyridine ring does not result in a significant decrease in desirable complexing properties. Indeed, the relative magnitudes of the acidities of the metal complexes suggest that TAR might be a more useful sequestering agent than PAR It is concluded that the sulphur atom in the thiazole ring acts in such a manner as to increase the acidities in the conjugated systems but does not affect the utility of TAR as a metal complexing agent with analytical potential.

Zusammenfassung—Die Säuredissoziationskonstanten von 4-(2′-Thiazolylazo)-resorcin (TAR) und die Bildungskonstanten der Metallkomplexe diese Reagens mit Cu(II), Ni(II), Co(II), Zn(II) und Mn(II) wurden bei 25°C in 50-volumprozentigen Dioxan-Wasser-Mischungen potentiometrisch bestimmt. Die für TAR und seine Metallkomplexe erhaltenen Werte werden den entsprechenden für das Reagens 4-(2′-Pyridylazo)-resorcin (PAR) gegenübergestellt. Unterschiede und Ähnlichkeiten zwischen den Koordinationstendenzen dieser beiden Reagentien werden an Hand der Bildungs- und Säuredissoziationskonstanten der Metallkomplexe erklärt. Es werden Indizien dafür angegeben, daß TAR und PAR gegenüber einigen zweiwertigen Metallionen als dreizähnige Liganden fungieren können.

Résumé—On a déterminé potentiométriquement, à 25° en solution dans le mélange dioxane-eau 50% (v/v), les constantes de dissociation acide du 4-(2′-thiazolylazo) résorcinol (TAR) et les constantes de formation des complexes métalliques formés par ce réactif avec Cu(II), Ni(II), Co(II), Zn(II) et Mn(II). Les valeurs obtenues pour le TAR et les complexes métalliques sont opposées aux valeurs similaires correspondant au réactif 4-(2′-pyridylazo) résorcinol (PAR). Les différences et les similitudes entre les tendances à la coordination de ces deux réactifs sont révélées en fonction de la constante de déplacement du proton et des constantes de dissociation acide des complexes métalliques. On présente des arguments suggérant que le TAR et le PAR peuvent tous deux se comporter comme des ligands à trois attaches vis-à-vis de quelques ions métalliques bivalents.

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