

## The Structures and Properties of Lakes of some Azo Dyes\*

JENNIE CHING-I LIU† and JOHN C. BAILAR, JR.\*\*

Department of Chemistry, University of Illinois, Urbana, Ill. 61801, U.S.A.

(Received August 26, 1987)

### Abstract

The azo group by itself is a weak ligand, but when it is part of a chelate ring it often forms quite stable complexes in which the azo group occupies a single coordination position. The other coordinating member (or members) of the chelate ring (or rings) may be parts of neutral groups (e.g.  $\text{NH}_2$  or  $\text{OCH}_3$ ) or potentially negative groups (e.g.  $-\text{OH}$ ,  $-\text{SH}$  or  $-\text{COOH}$ ). Thus, a variety of structures can be constructed, depending upon the nature of the metal and the functionality of the azo dyes. This article describes some lakes of azo dyes in which the dye contains three coordinating atoms, one of which is acidic.

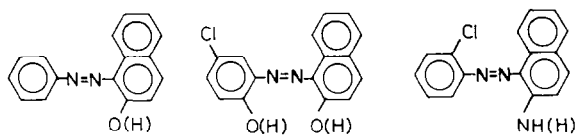
### Introduction

Commercial azo dyes are usually 'metallized' to increase their stability toward sunlight and laundering. The metal lakes so formed are typical coordination compounds, as has been shown by several investigators [1]. In order to give sufficient stability, the azo group is made part of one or two chelate rings by putting functional groups in the *ortho* positions on the adjacent aromatic groups. If these functional groups lose protons when they coordinate, they also serve to reduce the charge on the complex ion. Thus, benzene-azo- $\beta$ -naphthol fills two coordination positions and contributes a charge of  $-1$ , whereas 5-chloro-2-hydroxybenzene-azo- $\beta$ -naphthol is expected to fill three coordination positions and contribute a charge of  $-2$ . The latter gives the more stable lakes because of the double negative charge and the formation of fused rings. Carboxyl groups behave in the same way as phenolic groups and in some cases, amino, alkoxy and aryloxy groups do, also, the latter two because they hydrolyze to  $-\text{OH}$  [2]

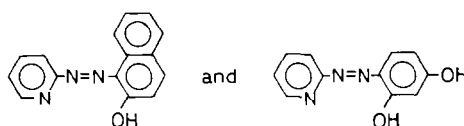
\*The work described in this paper was done some years ago, and should have been published then.

†Present address, Research Center for Eco-Environmental Sciences, Academia Sinica, P.O. Box 934, Beijing, China.

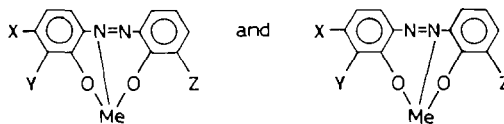
\*\*Author to whom correspondence should be addressed.



This paper describes dyes of an unusual sort — those which can fill three coordination positions, but contribute only  $-1$  to the charge. These are  $\alpha$ -pyridyl-azo- $\beta$ -naphthol and  $\alpha$ -pyridyl-azo-resorcinol



The azo group occupies only one coordination position, but it is hard to say which of the two nitrogen atoms takes part in the chelate ring formation. Alcock *et al.* [3] have suggested that the double bond of the azo group is involved, in analogy to the well known coordination compounds of the isoelectronic  $-\text{CH}=\text{CH}-$  group (as in Zeise's salt). X-ray studies by Jarvis [4] and by Prince and Spencer [5] have shown that in dyes containing one hydroxy group *ortho* to the azo group, the nitrogen atom furthest from that group takes part in the lake formation; this forms a six membered ring. However, Pfitzer [6] has reported that unsymmetrical azo dyes lakes containing two  $-\text{OH}$  groups in the *ortho* positions can exist in two isomeric forms, depending upon which of the nitrogen atoms takes part in the ring formation



In the cases we have examined, the nitrogen atom adjacent to the hydroxy group is almost certainly the one which is involved; otherwise, a four membered chelate ring would be formed. The copper and nickel lakes obtained from  $\alpha$ -pyridyl-azo- $\beta$ -naphthol each contain one molecule of dye per metal atom, whereas

the cobalt(III) and chromium(III) lakes each contain two. The magnetic moments of the nickel lakes show that they are tetrahedral, whereas the cobalt(III) and chromium lakes are octahedral. The iron(III) lake was not obtained in pure form, but it, too, apparently contains two molecules of dye for each iron atom, and is octahedral.

The lakes prepared from  $\alpha$ -pyridyl-azo-resorcinol are not as stable as those from the naphthol, and some of them were not obtained in highly pure form. The copper compound was obtained both as the monohydrate and in anhydrous form. The nickel lake, unlike the one from  $\beta$ -naphthol, contains two molecules of dye for each nickel atom. Analysis suggests that the cobalt(III) and chromium(III) lakes each consist of a cation containing one molecule of dye and an anion containing two. Thus these resemble the cobalt(III) lake of 2-hydroxybenzal-2-hydroxy-*o*-chloroaniline [1b]. However, in the case of the cobalt complex prepared in this research, part of the coordinated water has been lost in drying and in the case of the chromium lake, some extraneous water remains.

## Procedure

Spectrophotometric determinations were made on a Cary Recording Quartz Spectrophotometer, Model II, No. 46 made by the Applied Physics Corporation. Magnetic susceptibilities were measured on a modified Curie-Cheveneau balance, using ferrous ammonium sulfate as the standard. Elemental analyses for carbon, hydrogen, nitrogen and metal were performed by standard methods.

## Experimental

### Preparation of the Dyes\*

The diazotization of  $\alpha$ -aminopyridine does not proceed readily under the usual diazotization procedures, but it is readily effected by the reaction of the aminopyridine and butyl nitrite under reflux in the presence of sodium alcoholate [7]. The diazotate couples readily with aromatic phenols such as  $\beta$ -naphthol and resorcinol. The orange-red naphthol compound,  $\alpha$ -pyridyl-azo- $\beta$ -naphthol, is insoluble in water, but soluble in alcohol, acetone and in dilute mineral acids. It melts at 137 °C. The resorcinol compound,  $\alpha$ -pyridyl-azo-resorcinol, is slightly soluble in water and easily soluble in alcohol. It decomposes at 186–188 °C.

In each case, the coupling reaction was carried out in absolute ethanol while a stream of carbon dioxide was passed through the solution. After standing overnight, the precipitate was removed by filtration and the dye was dissolved in absolute ethanol. It was

filtered from the sodium carbonate, evaporated to a smaller volume and cooled, whereupon, crystals separated.

### Preparation of lakes of $\alpha$ -Pyridyl-azo- $\beta$ -naphthol

In general, for the preparation of the metallic derivatives, the nitrates of the metals were used as they are readily soluble in ethanol. An excess of metal salt was used. To a solution of the dye in boiling ethanol, a solution of the metal salt was added dropwise, and the mixture was refluxed for several hours. Upon cooling, the metal lake separated. This was filtered and dried. In each case, the lake was analyzed and, where useful, its magnetic moment was measured. From these data, the structure was inferred (Table I).

Several attempts were made to form a copper azo-naphthol lake containing ammonia in place of the coordinated water. Treatment of the anhydrous lake with gaseous ammonia did not effect any change; immersion in liquid ammonia gave a mixture of lake and the tetraamine. However, when the lake was prepared in the presence of pyridine (50 ml in 150 ml of  $C_2H_5OH$ ) the tris-pyridine hydroxide was formed.

The preparation of the cobalt(III) lake differed from that of the others in that the source of the metal was  $[Co(NH_3)_6]Cl_3$  and for solubility reasons, the solvent was 70% alcohol instead of 95%.

### Preparation of Lakes of $\alpha$ -Pyridyl-azo-resorcinol

This red dye is easily soluble in alcohol, but only slightly soluble in water. In general, the lakes were prepared in the same manner as those of the  $\beta$ -naphthol compound. The hydroxy group *para* to the azo group takes no part in the coordination, but it tends to lose its proton, and thus reduce the charge on the complex. The cobalt(III) lake was prepared from sodium hexanitro cobaltate(III),  $Na_3[Co(NO_2)_6]$ . All of these lakes are a deep purple color. The results of the experiments are summarized in Table II.

## Conclusions

Metallized azo dye lakes are readily formed from dyes which contain one or two coordinating atoms in the *ortho* positions of the two aromatic rings adjacent to the azo linkage. The charge on the

\*These dyes were first prepared in the course of this work. At that time, a sample of the naphthol compound was given to a friend who was looking for an indicator for use in heavy metal titrations. He found it useful and described it in the literature [8]. It has been used frequently by other chemists and is now available from chemical supply houses under the name 'PAN'. The analogous resorcinol compound (PAR) which was also first prepared in the research described here, has likewise found wide use as an indicator [9].

TABLE I. Lakes of  $\alpha$ -Pyridyl-azo- $\beta$ -naphthol

Metal	How dried	Analysis: Found(calc.) (%)				Suggested formula	Magnetic moment (Bohr magnetons)	Solubility
		C	H	N	Me			
Cu(II)	air	46.38 (45.95)	3.10 (3.06)	14.04 (14.30)	16.29 (16.24)	[Cu dye H <sub>2</sub> O]NO <sub>3</sub>	2.02	Slightly in H <sub>2</sub> O and ether. Very sol. in pyridine.
Cu(II)	100 °C	48.24 (48.19)	2.84 (2.68)	14.38 (14.99)	17.00 (17.02)	Cu dye NO <sub>3</sub>	2.10	Same as above
Cu(II) in pyridine	air	64.33 (63.65)	4.33 (4.59)	14.87 (14.85)	11.03 (11.24)	[Cu dye py <sub>3</sub> ]OH	2.13	
Ni(II)	100 °C	48.70 (48.43)	2.65 (2.71)	15.10 (15.19)	15.78 (15.91)	Ni dye NO <sub>3</sub>	3.23	Sol. in alcohol, acetone.
Ni(II)	air	47.62 (46.51)	3.51 (3.10)	13.95 (14.48)	15.87 (15.15)	[Ni dye H <sub>2</sub> O]NO <sub>3</sub> tetrahedral	3.33	
Co(II)		contains some Co(III) lake					2.15	
Co(III)	desiccator	61.25 (60.98)			9.72 (9.98)	[Co dye <sub>2</sub> ]Cl octahedral	Diamagnetic	Easily in hot C <sub>2</sub> H <sub>5</sub> OH.
Cr(III)		58.79 (59.01)	3.39 (3.28)	16.10 (16.07)	8.68 (8.53)	[Cr dye <sub>2</sub> ]NO <sub>3</sub> octahedral		Slightly in C <sub>2</sub> H <sub>5</sub> OH, H <sub>2</sub> O.
Fe(III)	air	47.94 (58.6)	3.56 (3.2)	15.12 (15.9)	7.67 (9.1)	[Fe dye <sub>2</sub> ]NO <sub>3</sub> (?)		Sol. H <sub>2</sub> O, C <sub>2</sub> H <sub>5</sub> OH. Slightly sol. ether, acetone, dil. H <sup>+</sup>

TABLE II. Lakes of  $\alpha$ -Pyridyl-azo-resorcinol

Metal	How dried	Analysis: Found(calc.) (%)				Suggested formula	Magnetic moment (Bohr magnetons)	Solubility
		C	H	N	Me			
Cu(II)	air	45.14 (44.81)	2.97 (3.05)	14.31 (14.22)	22.03 (21.58)	[Cu dye H <sub>2</sub> O] <sup>o</sup>		Slightly in H <sub>2</sub> O, C <sub>2</sub> H <sub>5</sub> OH. Very sol. in ammonium hydroxide and in mineral acid.
Cu(II)	100 °C	46.17 (47.73)	2.80 (2.53)	15.23 (15.18)	22.06 (22.98)	Cu dye	2.08	Slightly in H <sub>2</sub> O, C <sub>2</sub> H <sub>5</sub> OH. Very sol. in ammonium hydroxide and in mineral acid.
Ni(II)	air	51.86 (51.39)	3.54 (3.69)	16.45 (16.33)	11.01 (11.41)	2H <sup>+</sup> [Ni dye <sub>2</sub> ] <sup>2-</sup> 1.5H <sub>2</sub> O octahedral	3.17	Sol. in H <sub>2</sub> O, C <sub>2</sub> H <sub>5</sub> OH. Very sol. in ammonium hydroxide and mineral acids. Insol. in acetone
Co(III)	air	50.28 (50.51)	3.49 (3.06)	15.92 (16.07)	14.81 (15.04)	[Co(dye)(H <sub>2</sub> O) <sub>3</sub> ] [Co dye <sub>2</sub> ]·3H <sub>2</sub> O both octahedral	diamagnetic	Sol. in H <sub>2</sub> O, C <sub>2</sub> H <sub>5</sub> OH.
Cr(III)	air	46.35 (46.53)	4.08 (3.98)	15.34 (14.81)	11.49 (12.22)	[Cr dye(H <sub>2</sub> O) <sub>3</sub> ] [Cr dye <sub>2</sub> ]·3H <sub>2</sub> O both octahedral		Sol. in H <sub>2</sub> O, C <sub>2</sub> H <sub>5</sub> OH. Insol. in acetone, benzene, dioxane, nitrobenzene. Very sol. in mineral acids.

resultant lake is determined by the charge on the metal and the number of protons lost from the dye molecule, irrespective of whether these are coordinated to the metal or not. Dyes containing a pyridyl

nitrogen atom *ortho* to the azo group coordinate firmly to copper(II), nickel(II), cobalt(III) or chromium(III), but apparently, less firmly to iron(III) or cobalt(II).

## References

- 1 (a) C. F. Callis, N. C. Nielsen and J. C. Bailar, Jr., *J. Am. Chem. Soc.*, **74**, 3161 (1952); (b) J. C. Bailar, Jr. and C. F. Callis, *J. Am. Chem. Soc.*, **74**, 6018 (1952); (c) H. D. K. Drew and J. K. Lundquist, *J. Chem. Soc.*, 242 (1938); H. D. K. Drew and R. E. Fairbairn, *J. Chem. Soc.*, 823 (1938); W. F. Beech and H. D. K. Drew, *J. Chem. Soc.*, 603, 608 (1940); H. D. K. Drew and F. G. Dunton, *J. Chem. Soc.*, 1064 (1940).
- 2 V. I. Mur, *J. Gen. Chem. U.S.S.R.*, **25**, 355 (1955); *Chem. Abstr.*, **50** 2460c (1956).
- 3 N. W. Alcock, R. C. Spencer, R. H. Prince and O. Kennard, *J. Chem. Soc.*, 2383 (1968).
- 4 J. A. J. Jarvis, *Acta Crystallogr.*, **14**, 961 (1961).
- 5 R. H. Prince and R. C. Spencer, *J. Chem. Soc. A*, 2383 (1968).
- 6 H. Pfitzer, *Angew. Chem., Int. Ed. Engl.*, **11**, 312 (1972).
- 7 A. E. Tschitschibabin, *J. Russ. Phys. Chem. Ges.*, **50**, 513 (1918); *Chem. Zent.*, **II**, 1022 (1923).
- 8 Kuang Lu Cheng and R. H. Bray, *Anal. Chem.*, **27**, 782 (1955).
- 9 T. Yotsuyanagi, R. Yamashita and K. Aomura, *Anal. Chem.*, **44**, 1091 (1972), and refs. therein.