

FIGS. 2-3. Fig. 2. Absorption curves of  $\alpha$ -naphthol ( $\sim 0.1\%$  by weight) in the boric acid glass (A) before irradiation, (B) and (C) after irradiating with UV light for 3 and 60 minutes respectively. (Wavelength in  $m\mu$ .) Fig. 3. Absorption curves of  $\beta$ -naphthol ( $\sim 0.1\%$  by weight) in the boric acid glass (A) before irradiation, (B) and (C) after irradiating with UV light for 3 and 60 minutes respectively. (Wavelength in  $m\mu$ .)

spectrum of naphthalene cation is very similar to the spectrum of naphthalene anion, as expected theoretically.<sup>2-6</sup>

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### SPECTROPHOTOMETRIC INVESTIGATIONS OF SOME METAL COMPLEXES OF OXIMIDOBENZOTETRONIC ACID

OXIMIDOBENZOTETRONIC ACID (OBTA) has already been reported as an analytical reagent<sup>1-6</sup> for the spectrophotometric and gravimetric determination of a number of metal ions. The present communication deals with spectrophotometric investigations on OBTA complexes with Mn(II), Fe(II) and (III), Co(II), Ni(II) and Cu(II).

Fresh alcoholic or acetone solutions of OBTA<sup>7</sup> were used. Stock solutions of Mn(II), Fe(II) (in presence of hydroxylamine hydrochloride), Fe(III), Co(II), Ni(II) and Cu(II) were prepared from B.D.H. (A.R.) or Merck (pro Analysis) Grade chemicals and standardized gravimetrically.

The pH of the solution was adjusted with dilute HClO<sub>4</sub> acid and NaOH solution and measured with Beckman pH meter model H-2.

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TABLE I  
Spectrophotometric characteristics of OBTA complexes with some metal ions

Metal ion taken	Colour of the complex	$\lambda_{\max}$ , m $\mu$	Molar extinction coefficient ( $^{\circ}$ M) per mole metal	pH range where the complex is stable	Molar composition	Some properties of the complex
Mn (II)	Bluish-green	625	50 (a)	3.2- 5.7	1 : 1	Stable for only 10 min. Not extractable by CHCl <sub>3</sub> or C <sub>6</sub> H <sub>6</sub>
Fe (II)	Deep blue	625	$1.92 \times 10^4$ (a)	3.0-10.0	1 : 3	Extractable in CHCl <sub>3</sub> , but not in C <sub>6</sub> H <sub>6</sub> and ether
Fe (III)	Greenish-blue	640-660	$6.8 \times 10^3$ (b)	3.0- 7.2	1 : 2	Extracted by CHCl <sub>3</sub> but not by C <sub>6</sub> H <sub>6</sub>
Co (II)	Green	405, 580	$1.4 \times 10^4$ , $2.9 \times 10^3$ (c)	..	1 : 1	Stable for only 10 min. in 95% acetone, unstable if >5% water is present
	Dark red	480	$1.32 \times 10^4$ (b)	10.2	1 : 2*	Not extracted by C <sub>6</sub> H <sub>6</sub> or CHCl <sub>3</sub>
	Yellow	410	$6.2 \times 10^3$ (d)	3.0- 6.1	1 : 3†	Neutral, extracted by CHCl <sub>3</sub> , CH <sub>2</sub> , Ether, CH <sub>3</sub> CO <sub>2</sub> C <sub>2</sub> H <sub>5</sub> , etc.
Ni (II)	Yellow-brown	425	$3.2 \times 10^3$ (b)	4.2- 9.2	1 : 2	Stable for 15 min., extracted by CHCl <sub>3</sub> and C <sub>6</sub> H <sub>6</sub>
Cu (II)	Orange-brown	390-395	$6.3 \times 10^3$ (a)	2.3- 5.3	1 : 2	Stable for 30 min. Opalescence in solutions having 30% ethanol. Complex extracted by CHCl <sub>3</sub> and C <sub>6</sub> H <sub>6</sub>

(a)=40% ethanol; (b)=30% ethanol; (c)=95% acetone; (d)=60% acetone.

\* To prevent precipitation of Co (II) by hydrolysis at high pH, citrate ions (0.016 M) were added. Cobalt (II) does not form any mixed complex with OBTA and citrate ions.

† At lower ethanol or acetone concentration, a red-brown precipitate, which after drying at 120° corresponds to a 1 : 3 composition, is obtained. The complex is diamagnetic showing Co is in + 3 oxidation state.

Spectrophotometric measurements were made with Unicam spectrophotometer model SP 600.

The molar composition of the metal-OBTA complexes was determined by Job's method<sup>8</sup> of continuous variations as modified by Vosburgh and Cooper<sup>9</sup> as well as by the slope-ratio method.<sup>10</sup> The relevant data along with other characteristics of the complexes are given in Table I.

The stability constant ( $\beta_n$ ) of the metal-OBTA complexes was determined by (i) Harvey and Manning's method,<sup>10</sup> (ii) Foley and Anderson's method<sup>11</sup> and (iii) from Bjerrum's formation curves obtained spectrophotometrically<sup>12</sup> using Bjerrum's method<sup>13</sup> and correction term method.<sup>13</sup> The results are given in Table II.

The  $pK_a$  of the reagent was determined spectrophotometrically from the absorption spectrum of the reagent at different pH values as well as by a pH metric titration against NaOH, and was found to be  $3.50 \pm 0.05$  in 40% aqueous ethanol at 25° C. (ionic strength,  $\mu = 0.1$  mole, maintained by using NaClO<sub>4</sub>).

In Table II, it is observed that cobalt (II) gives 1 : 1 and 1 : 2 complexes with the reagent besides a 1 : 3 complex containing the metal in + 3 oxidation state, while in

TABLE II

Stability constants ( $\log \beta_n$ ) of OBTA-metal complexes at 25° C  $\pm$  2° C, ionic strength  $\mu = 0.1$  M (NaClO<sub>4</sub>) in 40% aqueous ethanol

Metal ions	Composition of the complex (Metal : OBTA)	$\log \beta_n$		
		Method (1)	Method (2)	Method (3)
Mn (II)	1 : 1	3.1	3.0	..
Fe (II)	1 : 3	14.0	13.8	13.7
Fe (III)	1 : 2	8.3	8.5	..
Co (II)	1 : 1	4.3 (a)	4.6 (a)	..
	1 : 2	6.5 (c)	6.9 (c)	..
Co (III)	1 : 3	15.8 (b)	15.4 (b)	16.2
Ni (II)	1 : 2	7.3	7.1	7.2
Cu (II)	1 : 2	9.4	9.2	9.1

(a)=95% acetone in absence of any NaClO<sub>4</sub>; (b)=60% acetone; (c)=in presence of 0.016 M Na citrate.

other cases only one complex has been detected. The order of stability constants for 1 : 2 complexes with bivalent metal ions (determined in 40% aqueous ethanol,  $\mu = 0.10$  mole) has been found to be  $Co^{+2} < Ni^{+2} < Cu^{+2}$ .

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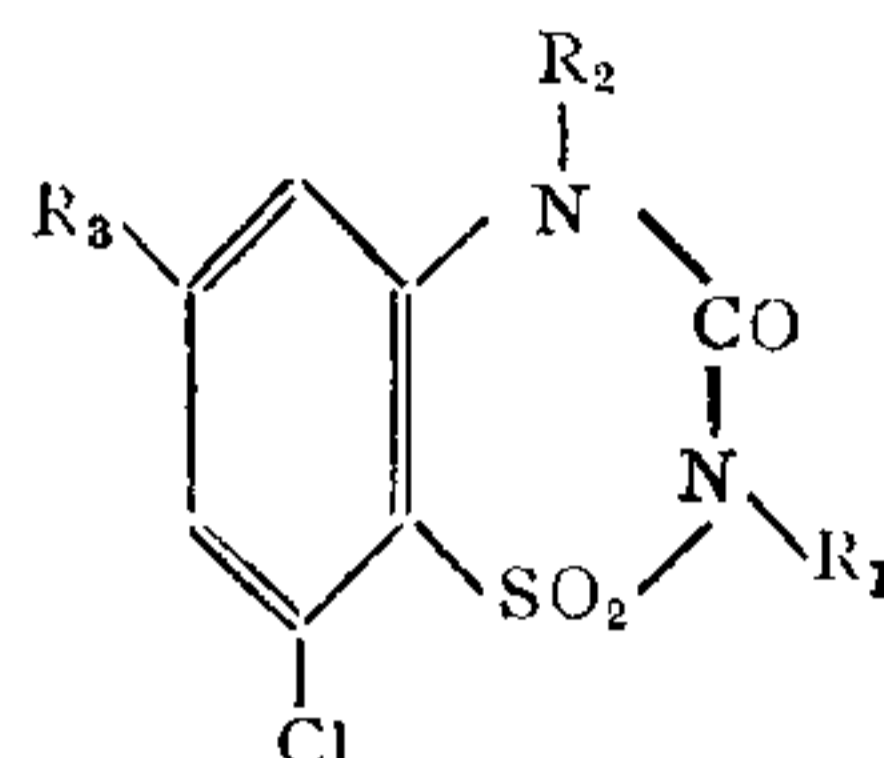
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### SUBSTITUTED 1, 2, 4-BENZO- THIADIAZIN-3-ONES

DURING the course of our work on benzothiadiazines,<sup>1</sup> we had occasion to synthesize a few N-substituted o-aminobenzenesulphonamides. In view of the hypnotic and tranquilliser properties reported<sup>2</sup> for 2H-3, 4-dihydrobenzo-1, 2, 4-thiadiazin-3-one-1, 1-dioxides, the synthesis of the following 8-chloro- and 6, 8-dichlorobenzothiadiazinones was undertaken.

The compounds listed in Table I were easily synthesized by heating the appropriate

(2 g.) and n-propylamine (4 ml.) were heated in a sealed pyrex tube for four hours at 140°. The reaction product was triturated with 2N hydrochloric acid. The residue (1.3 g.) was crystallised from benzene-hexane to obtain the title product; m.p. 125-26°. Found: N, 9.92; Calc. for C<sub>9</sub>H<sub>12</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>2</sub>S; N, 9.90%.



4-Propyl-6, 8-dichloro-2H-3, 4-dihydro-3-keto-1, 2, 4-benzothiadiazin-1, 1-dioxide.—2-propylamino-4, 6-dichlorobenzenesulphonamide (2 g.) was mixed thoroughly with urea (4 g.) and heated at 200° for four hours. The reaction product was cooled and triturated with dilute hydrochloric acid. The solid residue was taken up in 2N sodium hydroxide solution, clarified with carbon and acidified to obtain the crude title product (1 g.). It was crystallised from ethanol; m.p. 191-93. Found: N, 9.21; Calc. for C<sub>10</sub>H<sub>10</sub>Cl<sub>2</sub>N<sub>2</sub>O<sub>3</sub>S; N, 9.06%.

2-Methyl-4-phenylethyl-8-chloro-2H-3, 4-dihydro-3-keto-1, 2, 4-benzothiadiazin-1, 1-dioxide.—4-Phenylethyl-8-chloro-2H-3, 4-dihydro-3-keto-1, 2, 4-benzothiadiazin-1, 1-dioxide

TABLE I

No.	R <sub>1</sub>	R <sub>2</sub>	R <sub>3</sub>	m.p. °C.	Nitrogen %	
					Found	Calc.
I	H	C <sub>3</sub> H <sub>7</sub>	H	188-89	10.31	10.20
II	H	C <sub>4</sub> H <sub>9</sub>	H	167-68	9.61	9.71
III	H	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	H	214-15	8.51	8.68
IV	H	CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	H	180-82	8.39	8.32
V	CH <sub>3</sub>	CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	H	88-90	8.32	8.00
VI	H	C <sub>3</sub> H <sub>7</sub>	Cl	191-93	9.21	9.06
VII	H	CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	Cl	239-40	7.65	7.85
VIII	H	CH <sub>2</sub> CH <sub>2</sub> C <sub>6</sub> H <sub>5</sub>	Cl	191-93	7.67	7.55

o-aminobenzenesulphonamide with excess of urea at 200° for 4-5 hours. Attempts to synthesize them by reacting the sulphonamides with potassium cyanate under neutral, alkaline or acidic conditions met with no success.

A few typical experiments are described below.

2-Propylamino-4, 6-dichlorobenzenesulphonamide.—2, 4, 6-Trichlorobenzenesulphonamide

(1.7 g.) was taken in 5% sodium hydroxide solution (60 ml.). Dimethyl sulphate (2.5 g.) was added to the former solution at 60° under stirring over 15 minutes. The reaction mixture was stirred and heated at 70° for 45 minutes and then cooled. The alkali-insoluble material (1.1 g.) was crystallised from aqueous ethanol to obtain the title product; m.p. 88-90°. Found: N, 8.32; Calc. for C<sub>10</sub>H<sub>10</sub>Cl<sub>3</sub>N<sub>2</sub>O<sub>3</sub>S; N, 8.00%.