SPECTRAL STUDY OF THERMOCHROMISM OF 1-PHENYL-3-0-METHOXYPHENYL-5-(2-BENZOTHIAZOLYL)-FORMAZANATES OF ZINC AND CADMIUM

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In a previous publication, we described certain zinc and cadmium formazanates that have thermochromic properties. Here we are presenting data from a spectral study of the behavior of 1-pheny1-3-o-methoxypheny1-5-(2-benzothiazoly1)formazanates of zinc  $[Zn(F-H)_2, II]$  and cadmium  $[Cd(F-H)_2, III]$ , and also the original formazane (F, I), in propanol with added amines, at various temperatures.



Formazane I is a weak acid,  $pK_{\alpha NH-H}$  = 10.17 [2]. In the spectrum of a buffered propanol solution of I (50% solution, boric acid-base buffer) at pH  $\sim$ 9.5, absorption bands are observed from the un-ionized form ( $\lambda_{max}$  = 395 nm) and the anion ( $\lambda_{max}$  = 510 nm). Upon heating, the intensity of absorption at 510 nm increases, and that at 395 nm decreases. When the solution is cooled, its color returns to the original (Fig. 1); i.e., under these conditions, the formazane I has positive thermochromism, similar to other aryl- and hetarylformazanes [3].

The formazane I behaves differently in the presence of amines. The addition of excess ammonia or methylamine ( $\circ$ 1000-fold excess) to a propanol solution of I leads to complete ionization of the formazane; only the band of the anion at 510 nm is observed in the spectrum (Fig. 2 and Table 1). Heating of the solution is accompanied by a decrease in the intensity of absorption by the anion and an increase in absorption by the un-ionized form (color changes from red to yellow). Upon cooling, the original red color of the solution is restored (Fig. 2, Table 1). Here, we have negative thermochromism. This means that, depending on the character of the base (caustic or amine\*), we can observe either positive or negative thermochromism of the formazane I, the reason for which is found in the displacement of the acid-base equilibrium when the temperature is changed, in the direction of the ionized or un-ionized form of the formazane,

> $F + OH^{-} \xrightarrow{\text{heating}} (F - H)^{-} + H_2O,$  $F + H_3CNH_2 \xrightarrow{\text{cooling}} (F - H)^{-} + H_3CNH_3.$

The zinc and cadmium formazanates (II, III) were obtained by the interaction of hot solutions of the formazane I and the respective metal acetates in dimethylformamide. They are deeply colored crystalline substances (Table 1). Elemental analyses of II and III indicate

<sup>\*</sup>In this article, the term "amine" is apparently used in a loose sense to denote either methylamine or ammonia - Translator.

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Fig. 1. Electronic spectra of I in buffered propanol solution at 20°C (1) and 50°C (2) and after cooling from 50°C to 15°C (3).  $C_{\rm I} = 5 \cdot 10^{-5}$  mole/liter, pH = 9.5.

Fig. 2. Electronic spectra of I in propanol (1) and with added methylamine at 20°C (2), 44°C (3), 54°C (4), 70°C (5), and 76°C (6), and after cooling from 76°C to 18°C (7).  $C_{\rm I}$  = 4.2·10<sup>-5</sup>,  $C_{\rm CH_3NH_2}$  = 0.08 mole/ liter.

that they have the composition 2Lig:1M,\* and the IR spectra of these compounds do not have the  $v_{\rm NH}$  absorption band of the original formazane. We can assume that the complexes II and III have a chelate structure. When an amine is added in an excess of  $(4-12)\cdot10^3$  to a solution of II or III in propanol, the color changes from blue to red (Table 1). The spectral picture of the titration is characterized by two iso-points; the interaction of II and III with the amine proceeds in steps. The equilibrium shift method [4] was used to calculate the ratio of initial reactants; it was found that within the interval of amine concentrations from 0 to  $1.5\cdot10^{-3}$  mole/liter, this ratio is  $1M(F-H)_2:1$  amine. We can assume that a ligand exchange of the following type takes place:

$$M(F-H)_{2} \xrightarrow{CH_{3}NH_{2}} [M(F-H)(CH_{3}NH_{2})]^{+} + (F-H)^{-} \xrightarrow{CH_{3}NH_{2}} [M(CH_{3}NH_{2})_{2}]^{2+} + 2(F-H)^{-},$$

and the appearance of absorption at 510 nm is due to the presence of the anion in the reaction medium. The addition of caustic to the solution of II or III is also accompanied by a change in color from blue to red (Table 1); however, the solutions become cloudy, evidently because of the formation of cadmium or zinc hydroxide.

If the solution obtained by mixing II or III with the amine is heated, the color of the solution changes from red to yellow-green. In the spectrum, the intensity of the absorption at 510 nm decreases, and that at 395 and 600 nm increases (Fig. 3, Table 1). Upon cooling, the original color is restored. We can assume that temperature changes produce the following conversions:

$$F \xrightarrow[\text{cooling}]{} \underbrace{M(CH_3NH_2)_2^{2+} + 2(F-H)}_{\text{cooling}} \xrightarrow[\text{heating}]{} M(F-H)_2 + 2CH_3NH_2$$

$$\lambda = 395 \text{ nm} \qquad \lambda = 510 \text{ nm} \qquad \lambda = 600 \text{ nm}.$$

Either water or propanol is evidently the proton donor that is necessary for conversion of the anion to the formazane.

Still more striking thermochromic transitions are observed in systems consisting of the complex II or III, methylamine hydrochloride, and propanol as the solvent. Thus, the addition of a saturated solution of methylamine hydrochloride in propanol to a propanol solution of II or III gives little change in color (Fig. 4). However, when this mixture is heated we observe a color change from blue to yellow, the original color being restored upon cooling

\*M = metal.

No.	without added	HUH+	- ⊢ -	l₄OH*	+0+	I <sub>3</sub> NH <sub>2</sub>	+CH <sub>3</sub> N	H2.HCI*	+11C1
	substance		20	7.0	20	70	20	20	-
T	395(1,8)	510(5,2)	395(0,24) 510(1,28)	395(0,44) 510(0,70)	395(0,36) 510(1,20)	395(0,66) 510(0,51)	395(0, 6v)	395(0,65)	395(1,8)
II	600(3,5)	510	395(0,70) 510(0,99) 600(0,16)	395(0,80) 510(0,35) 600(0,12)	395(0,44) 510(1,25) 600(0,43)	395(0,64) 510(0,65) 600(0,48)	395(0,27) 600(0,49)	395(0,51) 600(0,20)	395(1,8)
III	615(3,9)	510	395(0,34) 510(0,85) 615(0,25)	395(0,47) 510(0,38) 615(0,34)	395(0,18) 510(1,32) 615(0,27)	395(0, 35) 510(0, 77) 615(0, 34)	395(0,36) 615(0,53)	395(0,57) 615(0,15)	395(1,8)
IV	468(2,9)	605(4,9)	468(0,77) 605(0,79)	$\begin{array}{c} 468(0,82) \\ 605(0,34) \end{array}$	$ \begin{array}{c} 468(0,40) \\ 605(1,14) \end{array} $	$\begin{array}{c} 468(0,44) \\ 605(0,92) \\ \end{array}$	468(2,90)	468(2,90)†	468(2,9)
>	645(3,9)	605	645(1,22) 605(1,70)	645(0,80) 605(1,20)	605(1,64) 645(1,14)	605(1,20) 645(0,80)	645(0,50) 468(0,58)	645(0,21) 470(0,72)†	468(2,9)

TABLE 1. Spectral Characteristics of Compounds I-V in Propanol with Different Added Substances and at Different Temperatures (°C)



Fig. 3. Changes in absorption spectrum of III in propanol with added NH<sub>4</sub>OH at 20°C (1), 30°C (2), 40°C (3), 50°C (4), 60°C (5), and 70°C (6), and after cooling from 70° to 10°C (7).  $C_{\rm III} = 2.7 \cdot 10^{-4}$  mole/liter,  $C_{\rm NH_4OH} = 2.1$  mole/liter.

Fig. 4. Changes in absorption spectrum of II in propanol with added methylamine hydrochloride at 20°C (1), 30°C (2), 45°C (3), 55°C (4), 62°C (5), and 70°C (6), and after cooling from 70°C to 8°C (7).  $C_{II} = 5 \cdot 10^{-5}$  mole/liter,  $C_{CH_3NH_2}$ ·HCl =  $2 \cdot 10^{-3}$  mole/liter.

(Fig. 4). The absorption band at 395 nm is due to the presence of the formazane I in the mixture (the absorption is identical in frequency and intensity). Evidently the following processes take place upon heating and cooling:

$$CH_{3}NH_{2} \cdot HCl \xrightarrow{\text{heating}} CH_{3}NH_{2} + HCl,$$
  

$$\xrightarrow{\text{cooling}} M(F-H)_{2} + 2HCl \xrightarrow{\longrightarrow} MCl_{2} + 2F.$$

In order to confirm this hypothesis, we titrated propanol solutions of II and III with a hydrochloric acid solution. The spectra showed the same changes as when II or III was heated with methylamine hydrochloride, i.e., a gradual change of the color from blue to yellow.

In all of the cases examined, the thermochromic transitions can be repeated many times without any change in intensity.

Cases of extracoordination of DMSO or amines by zinc complexes of porphyrins have been described in the literature [5, 6]. We can assume that in the present case as well, for compounds II and III, when amines are added, extracoordination takes place with the formation of complexes of the type  $M(F-H)_2(amine)_2$  that absorb in the 510-nm region. In order to test this hypothesis, we synthesized and investigated 1-p-nitrophenyl-3-o-methoxyphenyl-5-(2-benzo-thiazolyl)formazane (IV) and its zinc complex, (V) (Table 1). If extracoordination takes place when amines are added to the zinc complex, then we should find that for V the addition of the amine will be accompanied by the appearance of an absorption band in the spectrum at approximately 500-520 nm, since it is known [5] that the introduction of substituents into the ligand has almost no effect on the spectrum of the extra complex. However, the titration of V with methylamine is accompanied by the disappearance of the absorption at 645 nm and an increase in the intensity of absorption at 605 nm pertaining to the anion of IV (Table 1). This means that the addition of amines to Zn and Cd complexes leads not to extracoordination, as in the case of porphyrins, but to ligand exchange.

Thus, we have found new compounds with positive and negative thermochromism with transitions that are characterized by a high degree of contrast.

The electronic spectra of compounds I-V in propanol were taken for solutions with C =  $(2-5) \cdot 10^{-5}$  mole/liter in Specord UV VIS and Beckman UV 5270 double-beam recording spectro-

photometers. The lightpath was 1 cm. The spectra were taken at T = 20-70 °C in thermostated cuvettes.

The IR spectra were taken for solutions in  $CHCl_3$  (C  $\sim 10^{-3}$  mole/liter) in a UR-20 spectrophotometer.

 $\underline{\text{Zinc 1-Phenyl-3-o-methoxyphenyl-5-(2-benzothiazolyl)formazanate (II).}$  To a hot solution of 0.002 mole of the formazane I in 10 ml of dimethylformamide (DMF), a hot solution of 0.001 mole of zinc acetate in 5 ml of DMF was added, the color of the solution changing from red to blue. After 10 min, the complex was precipitated with hot water. The precipitate (which had a metallic luster) was filtered off and dried at 100°C. T<sub>m</sub> = 157°C. Yield 80%. Found (%): C 59.9, H 4.3, N 16.2. C<sub>4.2</sub>H<sub>3.2</sub>N<sub>1.0</sub>O<sub>2</sub>S<sub>2</sub>Zn. Calculated (%): C 60.2, H 3.8, N 16.7.

Cadmium 1-Phenyl-3-o-methoxyphenyl-5-(2-benzothiazolyl)formazanate (III). Obtained by procedures analogous to those for II.  $T_m = 204^{\circ}C$ . Yield 75%. Found (%): C 56.7, H 3.6, N 15.8, S 7.1.  $C_{42}H_{32}N_{10}O_2S_2Cd$ . Calculated (%): C 57.0, H 3.6, N 15.9, S 7.3.

<u>1-p-Nitrophenyl-3-o-methoxyphenyl-5-(2-benzothiazolyl)formazane (IV)</u>. To a solution of 2.8 g (0.01 mole/liter) of the 2-benzothiazolylhydrazone of o-methoxybenzaldehyde in 20 ml of DMF, there was added with stirring, at a temperature no higher than 5°C, a solution of a diazonium salt obtained from 2 g of p-nitroaniline, 20 ml of HCl (1:1), and 1 g of NaNO<sub>2</sub> in 10 ml of H<sub>2</sub>O. Then the reaction mixture was made alkaline with 2 N NaOH to pH  $\sim$  8, held for 40 min, and neutralized with 2 N HCl. The precipitate was filtered off, dried, and recrystallized from ethanol. T<sub>m</sub> = 203-205°C. Found (%): C 58.4, H 3.9. C<sub>21</sub>H<sub>16</sub>N<sub>6</sub>SO<sub>3</sub>. Calculated (%): C 58.3, H 3.7.

The spectrophotometric titration was performed as follows: To 25 ml of solutions of compounds I-V in propanol, the appropriate reagent (amines, HCl, methylamine hydrochloride) was added in portions while stirring, by means of an automatic micropipette. After each addition and a holding period of 3-10 min, the light absorption curve was recorded. The titration was continued until a constant light absorption was obtained.

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