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Studies on isomerism of 1:2 iron complexed dye based on 1-(5′-nitro-2′-hydroxyphenyl)-3-cyano-5-(4″-sulphonamidophenyl)formazan

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Dedicated to Dr. A.T. Peters on behalf of his retirement as editor of *Dyes and Pigments*

Abstract

During the synthesis of previously described new 1:2 iron complexes of 1,5-diaryl-3-cyanoformazanes it was found that the metalisation process is dependent on the pH of the reaction media and in some cases two isomeric products appear. These isomers exhibited the same quantitative composition but different colours and physico-chemical properties. With the use of ^{1}H-NMR and IR analysis and the measurements of magnetic moments an attempt to attribute the chemical structure to both isomers of 1:2 type iron complex of 1-(5′-nitro-2′-hydroxyphenyl)-3-cyano-5-(4″-sulphonamidophenyl)formazan has been made. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Isomerism; Formazans; 1:2 Metal-complex dyes; Iron-dye complexes

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1. Introduction

During our previous work on iron-complexed dyes based on 1,5-diaryl-3-cyanoformazans [1] it was observed during the final conversion of the formazan dyes to their iron complexes that the main product of this reaction is often accompanied by a by-product usually of a different colour. After a number of experiments, it was found that the proportions of the two products are influenced by the reaction conditions, especially by the pH of the reaction media. It was therefore decided to examine the metal-complex formation process more closely and to determine the structure of isomeric 1:2 Fe(III) complexes of 1-(5′-nitro-2′-hydroxyphenyl)-3-cyano-5-(4″-sulphonamidophenyl)formazan (Fig. 1).

2. Results and discussion

2.1. Preparation of dyes and intermediates

Detailed methods of preparation of 1-(5′-nitro-2′-hydroxyphenyl)-3-cyano-5-(4″-sulphonamidophenyl) formazan and its 1:2 iron complex have been

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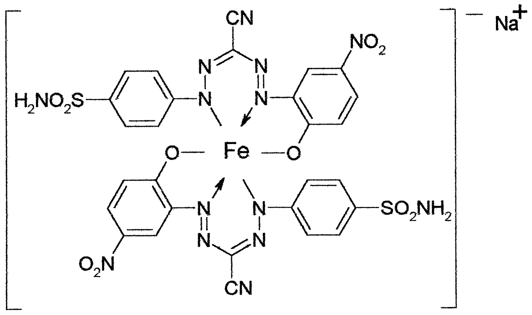


Fig. 1. 1:2 Iron complex of 1-(5′-nitro-2′-hydroxyphenyl)-3-cyano-5-(4″-sulphonamidophenyl)formazan (“classical” structure).

described previously [1]. Formation of iron complex at pH $\sim$ 2.0 gave mainly a violet-coloured dye, whilst at pH = 7–8 a brown-coloured dye predominated. Both isomers were separated and purified by column chromatography.

2.2. Characterisation of products

Visible spectra were recorded on a Perkin-Elmer Lambda 40 UV-VIS spectrophotometer. ^{1}H NMR spectra were recorded on a Brucker DPX 250 spectrometer in acetone-d_6 and acetone-d_6/trifluoroacetic acid solutions. IR spectra were recorded on Bio-Rad IR spectrometer in KBr. FAB mass spectra were recorded on a Finningam Mat MAT 94 (Switzerland) spectrometer in a glycol alcohol matrix. Magnetic susceptibility was measured at room temperature by the Faraday method on a balance constructed in Faculty of Chemistry Nicholas Copernicus University laboratory, with Hg[Co(NCS)$_4$] as a calibrant [2].

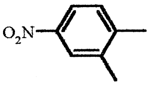
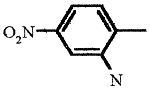
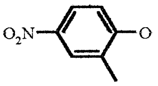
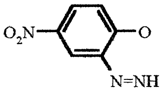
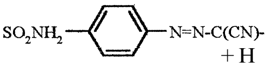
2.3. Determination of physico-chemical properties of isomeric 1:2 Fe complexes

Our first working hypothesis was that the by-product dye had a different quantitative composition from the main product i.e. it is iron–formazan complex of 1:1 or 2:3 type. However investigation of complex formation by the spectrophotometric method described by Joe [3] suggested the presence of a 1:2 complex only. This observation was confirmed by the results of negative ion FAB mass spectrometry and determination of iron contents in analysed samples of both products by AAS (atomic absorption spectroscopy) as can be seen from the data in Tables 1 and 2.

Both isolated 1:2 Fe complexes were characterised by their electronic absorption spectra in the visible region (Fig. 2). The results of these measurements are presented in Table 3.

As mentioned above, the proportions of both products in the reaction mixture were influenced

Table 1
FAB analysis data of isomeric 1:2 iron complexes of 1-(5′-nitro-2′-hydroxyphenyl)-3-cyano-5-(4″-sulphonamidophenyl)formazan

Assignment		m/z	Relative abundance[a]	
			Brown dye	Violet dye
M		853	16.29	5.98
[M–Na]	–	830	45.46	10.65
		121	2.38	3.18
	+H	122	8.78	10.74
	+2H	123	2.46	2.38
		135	3.33	2.98
	+H	136	4.40	4.11
		137	5.34	4.97
	+H	138	7.77	6.83
		166	17.19	10.35
	+2H	168	25.78	19.61
		222	2.80	7.91
	+H	223	–	4.39

[a] Ion abundances are expressed relative to the base peak $m/z = 152$ (3-nitrobenzyl alcohol, 100%).

Table 2
Analytical results of iron content of isomeric 1:2 iron complexes of 1-(5′-nitro-2′-hydroxyphenyl)-3-cyano-5-(4″-sulphonamidophenyl)formazan

Isomer	Sample weight (mg)	Fe_{calcd} (mg)	Fe_{est} (mg)	Correlation Fe_{calcd}/Fe_{est}
Brown	47.2	2.984	3.099	0.963
Violet	51.2	3.312	3.361	0.985

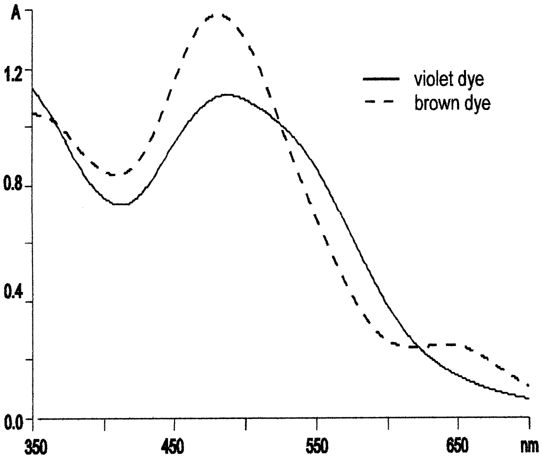


Fig. 2. Absorption spectra of isomeric 1:2 iron complexes of 1-(5′-nitro-2′-hydroxyphenyl)-3-cyano-5-(4″-sulphonamidophenyl)formazan (1 cm path length, conc. 4.73 x 10^{-5} mol x dm^{-3}, 50% aqueous ethanol).

Table 3
Spectral properties of isomeric 1:2 iron complexes of 1-(5′-nitro-2′-hydroxyphenyl)-3-cyano-5-(4″-sulphonamidophenyl) formazan

Isomer	λ_{max} (nm)	$\varepsilon_{max} \times 10^{-4}$
Brown	480	2.92
	642	0.53
Violet	490	2.34

by the reaction conditions and especially by the pH of the reaction media. Moreover, it was found that the isolated violet dye was partially converted to the brown isomer when stored in aqueous ethanol solutions for prolonged time, finally reaching some equilibrium state. The rate of this process was increased at elevated temperatures. The same process was observed in the case of the isolated brown dye but at a much slower rate. Different spectral properties of the isomers allowed the equilibrium constant of this conversion at pH $\geqslant 2$ to be determined. Below this pH value some decomposition of the complexes to the initial formazan was also observed. Spectophotometric measurements carried out in the temperature range of 20–70°C and pH 2.0–10.0 in buffered ethanol solutions of constant ionic activity enabled the summary reaction rate constant k and its components, the decomposition constant of the violet dye k' and formation constant of the brown dye k'' to be determined according to the equations:

$$-\frac{d[A]}{dt} = (k' + k'')[A] - -k''[A]_o$$

$$\ln\frac{[A]_o - [A]_\infty}{[A] - [A]_\infty} = kt$$

where

$[A]_o$ — initial concentration of violet dye;
$[A]$ — concentration of violet dye after time t;
$[A]_\infty$ — equilibrium concentration;
k — summary reaction constant;
k' — decomposition constant of violet dye;
k'' — formation constant of brown dye.

An example of these measurements at pH = 9.04 and temperature range 293–343 K are presented in Fig. 3 and Table 4. It can be seen that the reaction equilibrium constant K_C, which can be expressed as k'/k'', is temperature independent and approximately equal to 3. In other experiments it was found to be pH independent. In Fig. 4, the results of spectrophotometric measurements of this process taken at pH = 9.04, temperature 343 K and over of 2.5 h are presented.

It seemed obvious that the various colouristic properties of both isomers are the result of different metal-ligand interactions inside the complex. The observed dependence of the proportions of the products on the pH during complex formation gave assumption to hypothesis that this phenomenon may be the result of structural changes of the substrate formazan of a keto–enol equilibrium type as shown in Fig. 5. The above assumption was confirmed by the results of ^{1}H-NMR analysis of formazan in neutral (acetone-d_6) and acidic environment (acetone-d_6/trifluoroacetic acid) (Table 5).

Chemical shift values of protons H_d and H_e which are present in the aromatic ring with a sulphonamide group are the same both in neutral and in acidic environment. On the other hand, signals of the protons H_a and H_c which are located in the other aromatic ring in *ortho* positions to

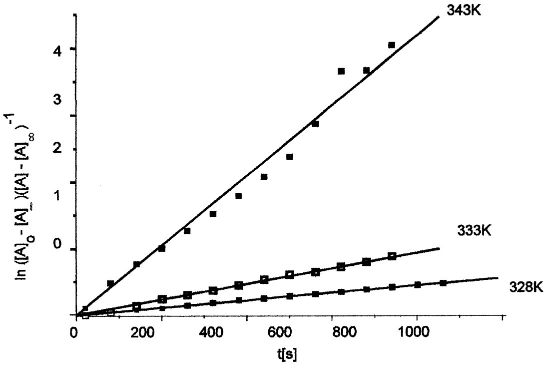


Fig. 3. The dependence $\ln([A]_o - [A])_\infty([A] - [A_\infty])^{-1} = f(t)$ for different temperatures at pH = 9.04.

Table 4
Summary reaction constant k and its components k' and k'' at pH = 9.04 and equilibrium constant K_c

Temperature (K)	k (s^{-1})	k' (s^{-1})	k'' (s^{-1})	K_c
293	1.03 10^{-6}	7.50 10^{-7}	2.53 10^{-7}	2.96
328	5.57 10^{-5}	4.18 10^{-5}	1.40 10^{-5}	2.98
333	1.27 10^{-4}	8.82 10^{-5}	2.89 10^{-5}	3.05
343	5.25 10^{-4}	3.95 10^{-4}	1.30 10^{-4}	3.03

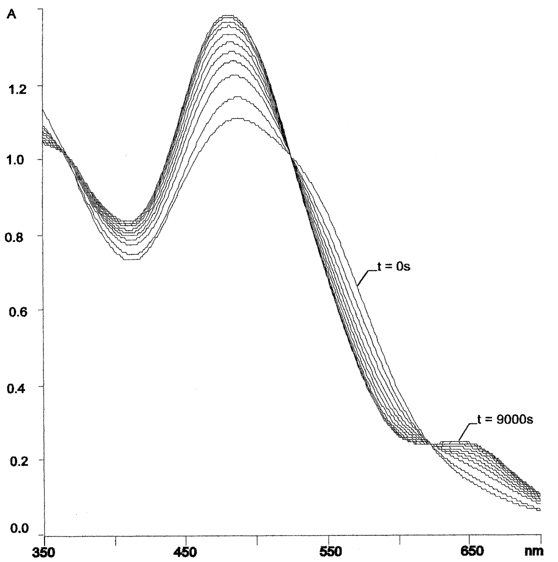


Fig. 4. Spectrophotometric data for conversion of the violet dye to its brown isomer [1 cm path length, conc. 4.73 × 10^{-5} mol dm^{-3}, $T = 343$ K, $\Delta t = 900$ s, pH 9.04)].

hydroxyl group and nitrogen atom of the formazan chain are doubled in acidic environment with signals from both the enol and ketone tautomers. According to the presented data the ratio of the signals indicates that the amount of ketone present is about 30%.

Evidence for an keto–enol equilibrium is also apparent from the IR spectra of samples of the same formazan crystallised from acetone/aqueous ammonia (enol form predominant) and glacial acetic acid (dominated by ketone form) [4].

Especially interesting are the results of the IR analysis of the isomeric dyes. The spectra presented in Fig. 6 show that the majority of absorption peaks are shifted towards lower wave numbers for the brown dye which is probably the result of more deformed structure of the complex.

Moreover according to literature data, similar hypsochromic shifts of absorption peaks were observed in Raman spectra during a change from low-spin to high-spin iron complexes [5–7]. The assumption that the observed isomers may be the complexes of low-spin and high-spin iron were considered earlier when comparing the measurements of their relative magnetic susceptibility by the nuclear magnetic resonance method described by Evans [8,9]. The relative magnetic susceptibility of the brown dye was found to be $\chi = -0.508\ 10^{-6}$ $cm^3\ g^{-1}$. The violet isomer exhibited different magnetic properties with $\chi = 0.773\ 10^{-6}$ $cm^3\ g^{-1}$.

The only information in the literature relative to magnetic properties of iron-complexed formazan dyes were found in recent work by Lye and coworkers [10] in which iron complexes of 1-(5′-chloro-2′-hydroxyphenyl)-3-phenyl-5-(4″sulfonamidophenyl)formazan and 1-(2′-hydroxy-5′-sulphonamidophenyl)-3,5-diphenylformazan, were investigated along with work on azo dyes. Measurements of magnetic moments of these dyes showed also some differences. The first dye with experimental magnetic moment $\mu_{expt} = 2.141$ BM was found to be a low-spin complex, but the second dye with experimental magnetic moment $\mu_{expt} = 4.061$ BM was suggested to be a low-spin complex possibly contaminated with a high-spin impurity.

In our work, effective magnetic moments of the violet and brown isomers were measured with the use of magnetic balance and calculated according to equation:

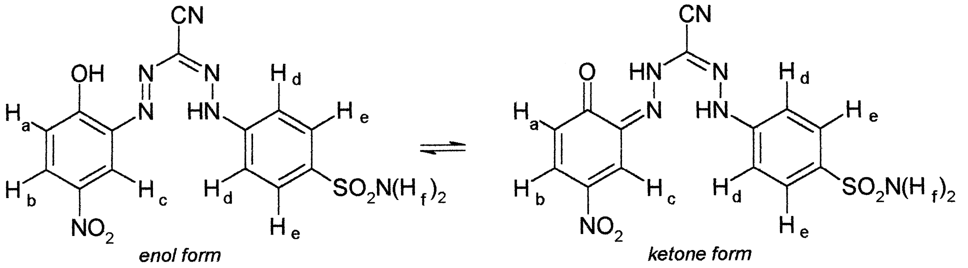


Fig. 5. Keto–enol isomers (one of the two possible enol forms shown) of 1-(5′-nitro-2′-hydroxyphenyl)-3-cyano-5-(4″-sulphonamidophenyl)formazan.

Table 5
^{1}H NMR data of 1-(5′-nitro-2′-hydroxyphenyl)-3-cyano-5-(4″-sulphonamidophenyl)formazan taken in neutral and acidic environment

	δ (ppm), J (Hz)[a]	δ (ppm), J (Hz)[b]
H_a	d; 1H; δ 7.34; J=9.25	d; 0.3H; δ 7.29; J=9.25 d; 0.7H; δ 7.35; J=9.25
H_b	dd; 1H; δ 8.30; J=9.25, J=2.75	dd; 1H; δ 8.31; J=9.25, J=2.75
H_c	d; 1H; δ 8.55; J=2.75	d; 0.7H; δ 8.55; J=2.75 d; 0.3H; δ 8.59; J=2.75
H_d	d; 2H; δ 7.74; J=8.75	d; 2H; δ 7.73; J=8.75
H_e	d; 2H; δ 7.94; J=8.75	d; 2H; δ 7.97; J=8.75
H_f	s; 2H; δ 6.63	s; 2H; δ 6.61

[a] In acetone-d_6,.
[b] In acetone-d_6/trifluoroacetic acid.

$$\mu_{\text{eff}} = 2.828\left(\chi_M^{\text{corr}} \cdot T\right)^{1/2}$$

where χ_M^{corr} is the corrected molar magnetic susceptibility [cm^3 mol^{-1}] calculated as:

$$\chi_M^{\text{corr}} = \chi_M - \sum \chi_P$$

where χ_M is the measured molar magnetic susceptibility [cm^3 mol^{-1}] and χ_P the empirical Pascal's diamagnetic constants [11]

The magnetic susceptibilities of the investigated dyes were estimated by the extrapolation of the results to infinite magnetic field intensity. In the case of the violet dye μ_{eff}=2.02 BM is close to literature data 2.0–2.6 BM [12] and to the theoretical value for formazan low-spin Fe complex of 1.73

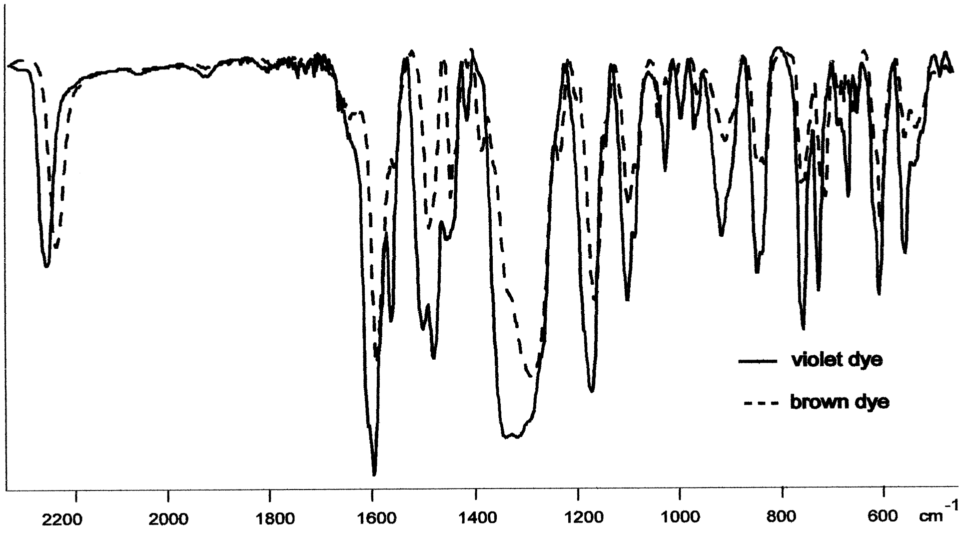


Fig. 6. IR spectra of isomeric 1:2 iron complexes of 1-(5′-nitro-2′-hydroxyphenyl)-3-cyano-5-(4″-sulphonamidophenyl)formazan.

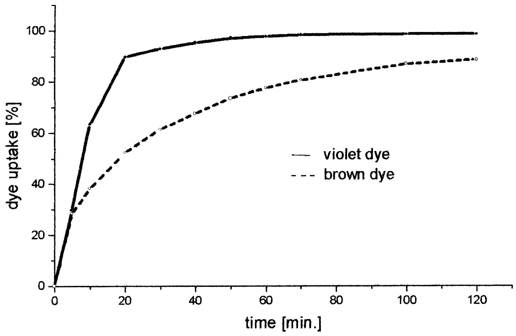


Fig. 7. Dyeing properties of isomeric dyes 1:2 iron complex of 1-(5′-nitro-2′-hydroxyphenyl)-3-cyano-5-(4″sulphonamidophenyl) formazan (polyamide fabric, temperature 55°C, 1% dye concentrations, pH of the dyebath 5.0).

BM calculated by Lye [10]. The measured magnetic moment of the brown dye $\mu_{\text{eff}} = 0.92$ BM was rather unexpected. Reduction of magnetic moment has been reported to be a result of antiferromagnetic interactions between central atoms of trivalent iron through oxygen or hydroxyl bridges but described only in the case of high-spin iron complexes [13–16]. It may thus be anticipated that the brown dye is dimerised high-spin Fe complex with antiferromagnetic interactions between two atoms of iron, probably also across the diamagnetic oxygen bridges.

The dimeric structure of the brown dye was confirmed by repeated negative ion FAB mass spectrometry analysis in extended *m*/*z* range. In the case of the brown dye we detected an additional peak of weak intensity *m*/*z* 1706 which may be the dimerized molecular ion ($2M^-$, see Table 1). No signals in this range were observed in the case of violet dye. Application tests of both products also showed some expected differences. As it can be seen on Fig. 7 the dimerized brown dye is more slowly exhausted by the polyamide fibre from the dyebath, probably due to its size. Conversely, the monomer violet dye shows practically complete uptake from the dyebath in relatively short time.

Nevertheless, at this moment all above discussed experiments did not allow also to fully attribute one of the two possible chemical structures to the violet dye. This product may be both "classic" monocentred complex of iron in low-spin state (Fig. 8a) or similar complex of low-spin Fe but with ketone form of the formazan (Fig. 8b).

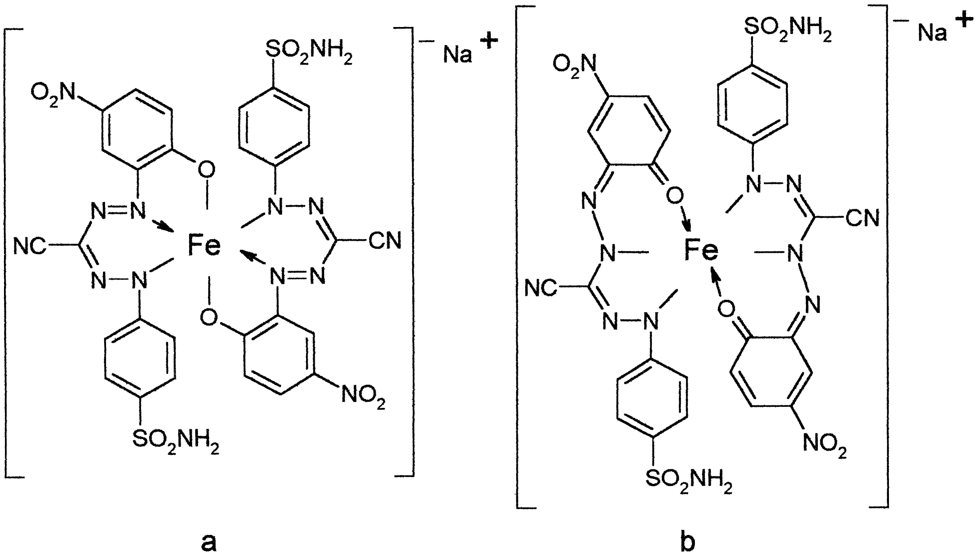


Fig. 8. Possible structures of the violet dye isomer 1:2 iron complex of 1-(5′-nitro-2′-hydroxyphenyl)-3-cyano-5-(4″-sulphonamidophenyl)formazan.

The violet dye is generated in an acidic environment where one may expect predomination of the ketone form of the formazan and formation of the Fig. 8b-type complex. The enol form of the formazan would result in a Fig. 8a-type low-spin Fe complex. On the other hand, the formation of dimeric structure takes place from the Fig. 8b-type high-spin Fe complex which may suggest the existence of such a species, probably some Drew–Pfitzner-type positional isomer of Fig. 8a. Indeed TLC monitoring of the metalisation process showed the existence of two violet spots of different intensity on the plate. The weaker spot disappeared as the reaction proceeded. The appearance of absorption curves with three isosbestic points (Fig. 4) suggests the presence of an additional product during the transformation. The definitive structure both the brown and the violet dye must await the results of an X-ray investigation.

Acknowledgements

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