



Synthesis, Metal Complexation and Spectroscopic Characterization of Three New Azo Compounds

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Abstract

The synthesis of azo compounds [4-(*N'*-2-thiazol-2-ylsulfanyl)-4'-hydroxyazo benzene (**1**), 4-(*N'*-2-thiazol-2-ylsulfanyl)-2'-hydroxy-5-tert-butylazobenzene (**2**), 7-[4-(*N'*-2-thiazol-2-ylsulfanyl)phenylazo-8-hydroxy quinoline (**3**)] have been carried out by reacting phenol, 4-tert-butyl phenol and 8-hydroxy quinoline with *N'*-2-thiazol-2-ylsulfanylamine as coupling component. The resulting ligands (**2** and **3**) were treated with two transition metal salts (e.g., CuCl₂·2H₂O and NiCl₂·6H₂O). Cu(II) and Ni(II) complexes of the azo derivative of phenol were obtained and characterised by IR, UV-Vis, ¹H NMR, spectroscopic and elemental analysis techniques. All the complexes have a metal : ligand ratio of 1 : 2 and are square-planar.

Introduction

Azo compounds are an important class of organic colorants and consist of at least a conjugated chromophore azo (—N=N—) group and two or more aromatic rings. The colour properties of organic dyes depend on both the presence of the chromophore groups and the crystallographic arrangement of molecules in the solid state [1].

It has been known for many years that azo compounds are the most widely used class of dyes due to their versatile application in various fields such as the dyeing of textile fiber, the colouring of different materials, coloured plastics, biological-medical studies and advanced applications in organic synthesis [2–9].

Diazo coupling reactions of calyx[4]arene were studied by Morita *et al.* and Shinkai *et al.* and they described their NMR spectra [10, 11]. In our recent work, we synthesised five diazo coupling derivatives of calix[4]arene [12–15].

In the present study, we have described the synthesis of three new azo compounds (**1**, **2** and **3**) which are obtained by diazotization of *N'*-2-thiazol-2-ylsulfanyl amide and then coupling this with phenol, 4-tert-butyl phenol and 8-hydroxy quinoline (Schemes 1 and 2).

Experimental

Chemicals used in all ligand synthesis were purchased from Merck or Carlo-Erba Company and are chemically pure.

All melting points were determined with an Electro-thermal IA9100 digital melting point apparatus and are uncorrected. The ¹H-NMR spectra were recorded on a Varian

EM 360L NMR Spectrometer in CDCl₃ with TMS as an internal standard. IR spectra were recorded using a Mattson 1000 FT-IR Spectrometer as KBr pellets. UV-Vis spectra were obtained with an Epson LK 300 UV-1600 UV-visible recording spectrophotometer. The elemental analysis were performed in the TUBITAK Laboratory (Center of Science and Technology Research of Turkey).

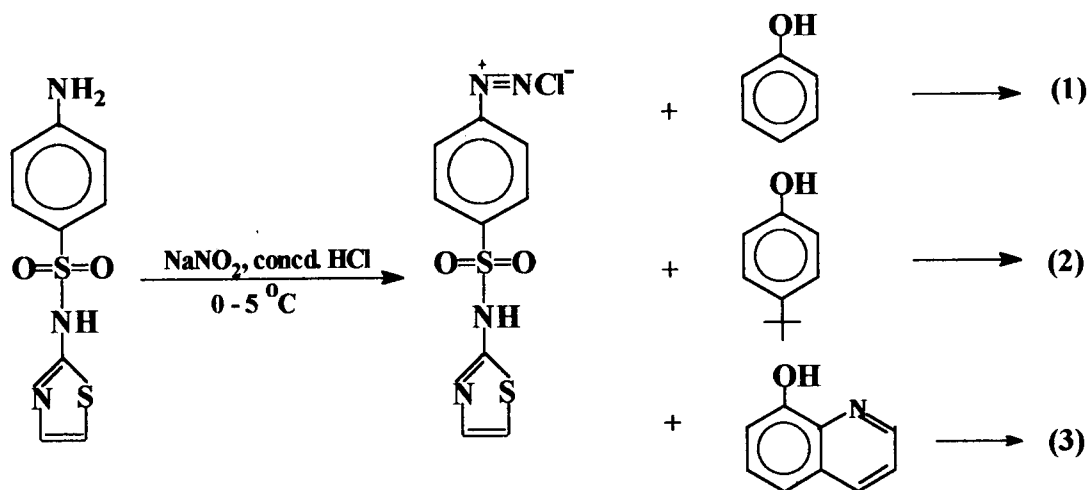
Preparation of *N'*-2-thiazol-2-ylsulfanyl diazonium chloride

A solution of *N'*-2-thiazol-2-ylsulfanylamine (2.77 g, 10.80 mmol) in 100 mL water and 9 mL concentrated HCl (37%) was stirred until a clear solution was obtained. This solution was cooled to 0–5 °C and while maintaining the temperature below 5 °C a solution of sodium nitrite (0.75 g, 10.80 mmol) in 10 mL water was then added dropwise. The resulting mixture was stirred for 45 min in an ice bath and excess nitrite was destroyed by addition of urea [12]. This solution was buffered with solid sodium acetate.

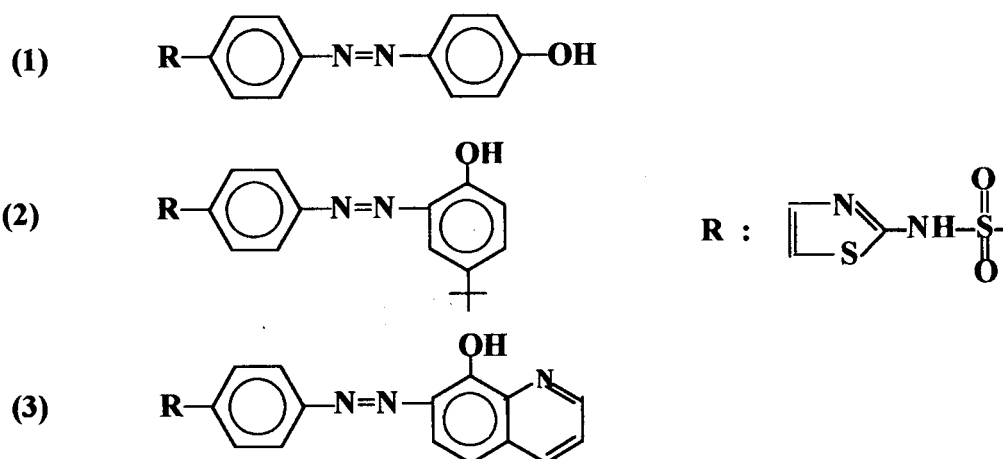
Synthesis of 4-(*N'*-2-thiazol-2-ylsulfanyl)-4'-hydroxyazobenzene (**1**)

Phenol (1.02 g, 10.80 mmol) was dissolved in 10 mL water with sodium acetate and cooled to 0–5 °C in an ice bath. This solution was added gradually to the solution of the cooled *N'*-2-thiazol-2-ylsulfanyl diazonium chloride and the resulting mixture was continually stirred at 0–5 °C for an hour. The yellow-orange crude precipitate was filtered and washed several times with water and then dried in vacuum. Yield was 3.75 g, 96%. The resulting product was recrystallized from glacial acetic acid to achieve a product of m.p. 240 °C.

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Scheme 1. Synthesis of diazo coupling reactions.



Scheme 2. The structures of the azo compounds.

$^1\text{H-NMR}$ (CDCl_3 , $25\text{ }^\circ\text{C}$): δ : 1.25–1.54 (2H, d, =CH—), 5.73 (1H, s, —NH), 5.80 (1H, s, —OH), 6.51–8.16 (8H, m, Ar—H).

Compound (1) is soluble in 10% NaOH, EtOH, acetone, acetic acid, CHCl_3 , DMSO, and insoluble in water, 10% HCl, diethyl ether. The elemental analysis, IR and UV-vis data of the compound are given in Tables 1–3.

Synthesis of 4-(N'-2-thiazol-2-ylsulfanyl)-2-hydroxy-5-tert-butylazobenzene (2)

When 4-tert-butyl phenol (1.62 g, 10.80 mmol) was added to 20 mL water with 10% sodium hydroxide, a suspension was obtained. This suspension was cooled to $0\text{--}5\text{ }^\circ\text{C}$ in an ice bath. This suspension was gradually added to the solution of the cooled N'-2-thiazol-2-ylsulfanyl diazonium chloride. Using the same procedure as described above for **1**, compound **2** was obtained. Yield was 3.31 g, 74%. The brown-red crude product was recrystallized from glacial acetic acid to give a product of m.p. $224\text{ }^\circ\text{C}$.

$^1\text{H-NMR}$ (CDCl_2 , $25\text{ }^\circ\text{C}$): δ : 0.94 (9H, s, — $\text{C}(\text{CH}_3)_3$), 1.15–1.46 (2H, d, =CH—), 5.90 (1H, s, —NH), 6.75–8.28 (7H, m, Ar—H), 12.92 (1H, s, —OH).

Compound (2) is soluble in 10% NaOH, EtOH, acetone, acetic acid, CHCl_3 , DMSO, and slightly soluble in diethyl ether, and insoluble in water and 10% HCl. The elemental analysis, IR and UV-vis data of the compound are given in Tables 1–3.

Synthesis of 7-[4-(N'-2-thiazol-2-ylsulfanyl)phenylazo]-8-hydroxy quinoline (3)

When 8-hydroxy quinoline (1.57 g, 10.80 mmol) was added to 20 mL water with 10% sodium hydroxide, a suspension was obtained. This suspension was cooled to $0\text{--}5\text{ }^\circ\text{C}$ in an ice bath. This suspension was gradually added to the solution of the cooled N'-2-thiazol-2-ylsulfanyl diazonium chloride. Using the same procedure as described above for **1**, compound **3** was obtained. Yield was 2.94 g, 66%. The dark-red crude product was recrystallized from glacial acetic acid to achieve a product of m.p. $>300\text{ }^\circ\text{C}$ (dec.).

$^1\text{H-NMR}$ (CDCl_3 , $25\text{ }^\circ\text{C}$): δ : 1.20–1.48 (2H, d, =CH—), 5.95 (1H, s, —NH), 6.90–8.12 (9H, m, Ar—H), 12.85 (1H, s, —OH).

Compound (3) is soluble in 10% NaOH, acetone, acetic acid, CHCl_3 , DMSO, and slightly soluble in EtOH, diethyl ether, and insoluble in water and 10% HCl. The elemental

Table 1. The colours, formulas, melting points, yields and elemental analytical results of the compounds and their complexes

Compound	Formula	MW	Colour	m.p.	Yield	Calcd. (found) %				
						C	H	N	S	M
1	C ₁₅ H ₁₂ N ₄ S ₂ O ₃	360.41	Yellow-orange	240	96	50.00 (49.61)	3.33 (3.22)	15.55 (15.18)	17.77 (17.02)	–
2	C ₁₉ H ₂₀ N ₄ S ₂ O ₃	416.51	Brown-red	224	74	54.81 (54.46)	4.81 (4.41)	13.46 (13.68)	15.38 (15.66)	–
2 ·Cu·2H ₂ O	C ₃₈ H ₄₂ N ₈ S ₄ O ₈ Cu	929.50	Dark brown	>300	84	49.06 (48.69)	4.52 (4.79)	12.05 (12.14)	13.77 (13.43)	6.83 (6.48)
2 ·Ni·H ₂ O	C ₃₈ H ₄₀ N ₈ S ₄ O ₇ Ni	906.71	Dark red	>300	76	50.29 (50.23)	4.41 (4.56)	12.35 (12.67)	14.12 (14.33)	6.47 (6.32)
3	C ₁₈ H ₁₃ N ₅ S ₂ O ₃	411.45	Dark red	>300 (dec.)	66	52.49 (51.31)	3.15 (3.30)	17.01 (16.65)	15.55 (15.32)	–
3 ·Cu·2H ₂ O	C ₃₆ H ₃₂ N ₁₀ S ₄ O ₉ Cu	939.50	Pale brown	>300	89	45.98 (45.74)	3.41 (3.63)	14.90 (14.67)	13.62 (13.72)	6.76 (6.43)
3 ·Ni·H ₂ O	C ₃₆ H ₂₈ N ₁₀ S ₄ O ₇ Ni	898.70	Dark red	>300	83	48.07 (48.29)	3.12 (3.27)	15.58 (15.27)	14.24 (13.96)	6.53 (6.21)

Table 2. Characteristic IR bands of the compounds as KBr pellets (cm⁻¹)

Compound	$\nu(\text{H}_2\text{O})$	$\nu(-\text{OH})$	$\nu(-\text{CH}_3)$	$\nu(-\text{N}=\text{N}-)$	$\nu(-\text{SO}_2)$
1	–	3200–3500	–	1448	1165
2	–	3200–3500	2927–2978	1448	1165
2 ·Cu·2H ₂ O	3420	–	2918–2934	1415	1160
2 ·Ni·H ₂ O	3430	–	2908–2946	1415	1160
3	–	3300–3600	–	1448	1148
3 ·Cu·2H ₂ O	3420	–	–	1412	1140
3 ·Ni·H ₂ O	3430	–	–	1412	1140

Table 3. The electronic spectra of the compounds (in DMF)

Compound	λ_{max} nm (ϵ)
1	362 (21782)
2	334 (12226) 403 (5561)
2 ·Cu·2H ₂ O	432 (8364) 542 (2376)
2 ·Ni·H ₂ O	409 (8142) 521 (2564)
3	397 (13489) 410 (4830)
3 ·Cu·3H ₂ O	488 (8857) 568 (2879)
3 ·Ni·H ₂ O	472 (8546) 551 (3088)

analysis, IR and UV-vis data of the compound are given in Tables 1–3.

Synthesis of the metal complexes

A solution of 2.0 mmol metal salt [0.344 g of CuCl₂·2H₂O and 0.476 g of NiCl₂·6H₂O] in 20 mL of ethanol was added to a solution of **2** (2.083 g, 5 mmol) or **3** (2.057 g, 5 mmol) in 10 mL of THF-ethanol (3 : 1). After addition of a 1% KOH solution in ethanol to raise the pH to 4.5–5.0, the mixture was stirred on a water bath at 35–45 °C for 10 min. The pre-

cipitated complex was filtered, washed with water, ethanol and THF and dried *in vacuo*.

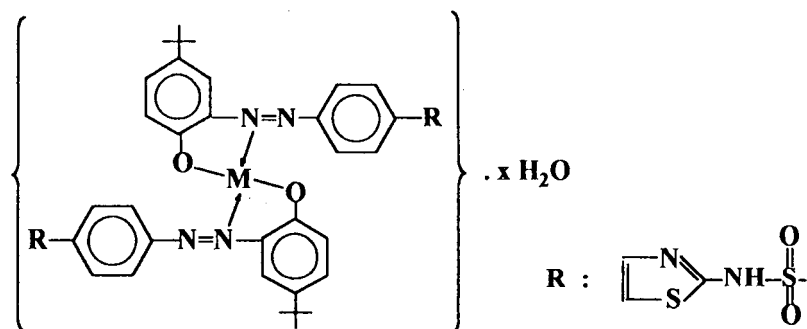
The elemental analysis, IR and UV-vis data of the compounds are given in Tables 1–3.

Results and discussion

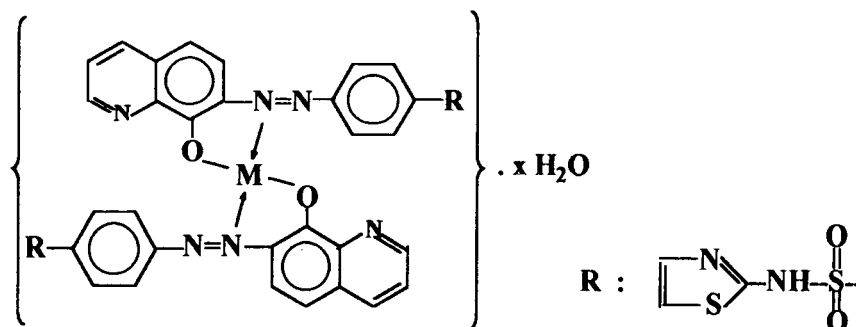
In this work, three new azo compounds and their complexes were synthesised from *N'*-2-thiazol-2-ylsulfanylamine and phenol, 4-*tert*-butyl phenol or 8-hydroxy quinoline. These compounds and their complexes are shown in Schemes 2 and 3.

4-(*N'*-2-Thiazol-2-ylsulfanyl)-4'-hydroxy azobenzene (**1**) was obtained by the diazo-coupling. The coupling reaction of phenol with *N'*-2-thiazol-2-ylsulfanyl diazonium chloride in water gave 4-(*N'*-2-thiazol-2-ylsulfanyl)-4'-hydroxy azobenzene in 96% yield.

The 4-(*N'*-2-thiazol-2-ylsulfanyl)-2'-hydroxy-5-*tert*-butyl azobenzene (**2**) and 7-[4-(*N'*-2-thiazol-2-ylsulfanyl)phenylazo]-8-hydroxy quinoline (**3**) compounds were obtained by the same method. However, the yields of these azo compounds were 74% and 66%, respectively. The yields are in agreement with the literature [9]. The azo dyes obtained were purified by recrystallization from glacial acetic acid and their purity was examined by thin-



Scheme 3a. Square-planar Cu(II) and Ni(II) complexes of **2**. For M = Cu, $x = 2$; for M = Ni, $x = 1$.



Scheme 3b. Square-planar Cu(II) and Ni(II) complexes of **3**. For M = Cu, $x = 2$; for M = Ni, $x = 1$.

layer chromatography. The structures of the azo compounds (**1**, **2** and **3**) were identified by IR, UV-VIS, $^1\text{H-NMR}$ and elemental analyses (Tables 1–3).

The results of the elemental analysis for nitrogen agree well with the calculated values indicating formation of the coupling product. The similarity of the reaction yields with literature values supports this.

The $^1\text{H-NMR}$ spectra of all the azo compounds exhibit a weak doublet signal in the range of 1.15–1.54 ppm, attributed to the two symmetric $=\text{CH}-$ protons in the cyclic ring. The azo compounds show peaks located in the range of 5.73–5.95 ppm which are attributed to the $-\text{NH}$ groups. It was observed that the tert-butyl protons of compound **2** resonate at 0.94 ppm. Although the compounds have two aromatic rings of different environments, they give a multiple peak due to overlapping. Also the phenyl protons were also observed as a multiplet at 6.51–8.28 ppm. The peaks of aromatic protons of the azo compounds are complicated. The lower field signals of the hydroxyl group of the two azo compounds (**2** and **3**) resonate at ca. 12.85–12.92 ppm and these are typical for intramolecular hydrogen bonding protons as reported in the literature [9, 16].

In the IR spectra of the azo compounds (**1**, **2** and **3**), characteristic stretching vibrational bands of the $-\text{N}=\text{N}-$ groups were observed at 1420–1448 cm^{-1} , which is in agreement with the literature value [3, 9]. The hydroxyl groups in the azo compounds **2** and **3** do not form an intramolecular hydrogen bond between the hydroxyl group and the azo nitrogen. This was confirmed by very low field signals at 12.85–12.92 ppm in $^1\text{H-NMR}$ spectra which are typical for hydroxyl protons involved in intramolecular hydrogen bonds. The azo compounds (**1**, **2** and **3**) showed a hydroxyl vibrational band between 3200 and 3600 cm^{-1} .

The azo compounds have characteristic strong IR absorption bands at 1148–1165 cm^{-1} ($-\text{SO}_2-$). The characteristic $-\text{CH}_3$ peak appears at 2927–2978 cm^{-1} for compound **2**.

The ultraviolet spectral behaviours of the azo compounds (**1**, **2** and **3**) were investigated in absolute ethyl alcohol. Comparing data of the UV spectra, it was found that all of the spectra show a strong absorption maximum in the 362–403 nm range with high extinction coefficients. As can be seen from Table 3, while the azo compounds **2** and **3** give two absorption bands ($\pi - \pi^*$ and $n - \pi^*$ transitions) the other azo compound **1** shows only a $\pi - \pi^*$ band because the $n - \pi^*$ transition is forbidden.

The compounds which are synthesised by diazo-coupling reaction have been defined as molecular design of chromogenic phenolic compounds in the literature [9, 15].

The metal-ligand ratio in all these complexes is 1:2. The presence of coordinated or lattice water in the Cu(II) and Ni(II) complexes is indicated by the presence of broad bands in the 3420–3430 cm^{-1} region of the IR spectra of these complexes and ascribed to O—H of water. The band in the IR spectra of the Cu(II) and Ni(II) complexes disappeared after heating at 100 °C for 6 h. This shows that water molecules are held in the crystal lattice of these complexes.

Consequently, a square-planar structure for the Cu(II) and Ni(II) complexes is proposed as shown in Schemes 3a and 3b.

The electronic spectra of the complexes exhibit intense charge-transfer bands around 409–488 nm, but weak d-d transitions are observed only for the Cu(II) and Ni(II) complexes with **2** at 542, 521 nm and with **3** at 568, 551 nm, respectively (Table 3).

On the other hand, these compounds which consist of azo groups in their structure have been interesting because

the azo groups have properties as binding sites for complexation and as chromophores of dyes. We are working on these phenolic derivatives which contain azo groups and the properties of binding the metal ions.

Conclusion

In the present study, three new azo compounds and their complexes were prepared. Moreover, the high complexation ability of chemically modified diazo compounds were studied. It is hoped that these synthesized compounds and their complexes might be used as dyes and/or coloring agents for various applications with textiles, plastics, biomedical substances, etc.

Studies concerning the production of colored cement using such compounds as synthesized in the study are underway in our laboratory.

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