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SYNTHESIS OF A NOVEL DIAZO FUNCTIONALISED OXIME LIGAND AND ITS Cu(II) AND Fe(III) COMPLEXES

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ABSTRACT

N-Phenyl-3-oxo-butanamide, (**1**), which is used in dyes and pigment synthesis, on reaction with hydroxylamine gives *N*-phenyl-3-hydroxyimino-butanamide (**2**). This compound reacts with diazonium salts to give diazo products which coordinate to copper(II) and iron(III). The intermediate obtained from the preparation of the ligand, the ligand itself and the metal complexes were characterised by magnetic susceptibility, spectroscopic techniques such as IR, ^{1}H NMR, UV-Vis. and microanalytical data.

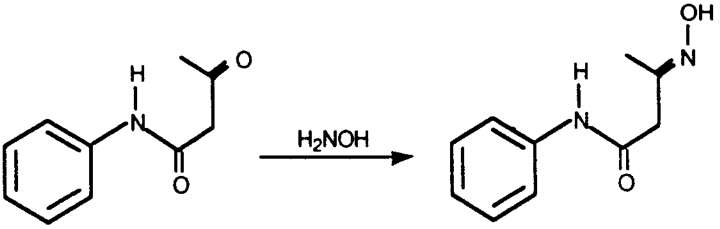
INTRODUCTION

The starting compound (**1**) for many years [1] has been used as coupling component in azo dyes and pigment synthesis by coupling via the active methylene group. The compound also reacts with nitrous acid and hydroxylamine to give a *vic*-dioxime, *N*-phenyl-2,3-dihydroximino-butanamide. The nickel(II) complex of this compound shows pigment properties.[2, 3, 4] It has been reported that oximes react with diazonium compounds.[5] Since both the active methylene and oxime groups of compound (**2**) could react with diazonium salts, the reactions of (**2**) with diazonium salts could be interesting. In the present work, compound (**2**) has been treated with the diazonium salt of *N'*,*N''*-diethyl-3-amino-4-methoxyphenylsulphonamide (**3**) under various reaction conditions to give *N*-phenyl-2-[2-methoxy-5-(*N'*,*N''*-diethylsulphonamide)phenylhydrazo]-3-hydroxyiminobutanamide (**4**). The copper(II) and iron(III) complexes of (**4**) also have been prepared and characterised.

RESULTS AND DISCUSSION

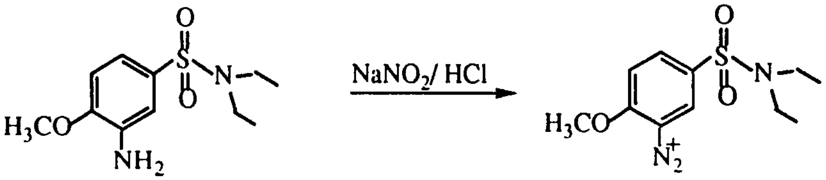
The reported studies state that carbonyl groups adjacent to nitrogen do not react with hydroxylamine.[6] Thus, compound (**1**) has been treated with hydroxylamine to give compound (**2**) (Scheme 1) whose IR spectrum shows only one carbonyl group at 1685 cm^{-1} which is in agreement with amide carbonyl.[7] The ^1H NMR spectrum of (**2**) also confirms that only one carbonyl group of (**1**) reacted with hydroxylamine to give an oxime by showing a singlet at 10.4 ppm which is characteristic of the oxime proton.[8]

Treatment of (**2**) with the diazonium salt (**3a**) derived from (**3**), as shown in Scheme 2, at various pH values afforded different diazo compounds. The spectral data of the reaction products obtained at pH 7 and 9 showed a mixture of the compounds which were formed by coupling via either the oxime nitrogen or the active methylene. Whereas the reaction at pH 5 showed only one product, (**4**), as shown in Scheme 3, coupled via the active methylene group. This has been explained by blocking of the oxime nitrogen in acidic media. The product (**4**) could exist in different tautomeric forms due to the fact that the hydrogen atoms may be involved in tautomerism. There have been many reported studies on the characterisation of butanamide derived diazo compounds.[9] Recently, single crystal X-ray diffraction studies on butanamide derivative pigments have shown that these compounds could exist in seven different tautomeric forms.[10] The disappearance of the active methylene proton in the ^1H NMR spectrum of (**4**) showed that the compound forms one



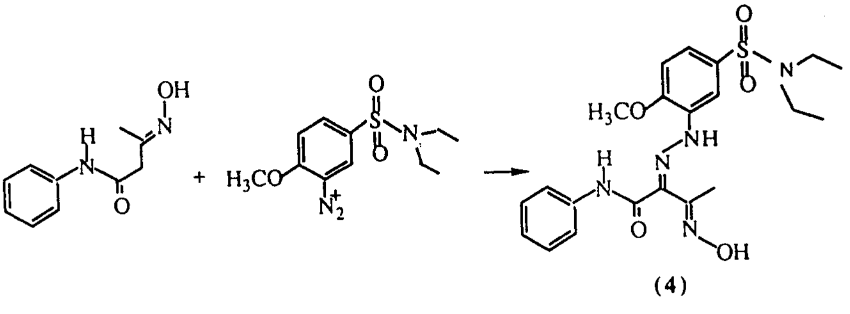
(1) (2)

Scheme 1



(3) (3a)

Scheme 2



(4)

Scheme 3

of the hydrazo forms as shown in Fig. 1 a and b.[11,12] In addition to that, the presence of a C=O band in the IR spectrum and the absence of other enolic protons in the ^1H NMR spectrum, except the oxime proton, indicated that the compound was in the keto form of the hydrazo forms as in structure (**4b**) in Fig. 1.

Treatment of the ligand (**4**) with copper(II) and iron(III) salts dissolved in ethanol afforded the metal complexes (**5**) and (**6**), respectively, Fig. 2. On the basis of the microanalytical data of the complexes, the metal:ligand ratio was found to be 1:1. The IR spectra of (**5**) and (**6**) indicated that the complexes were formed through the coordination of the carbonyl group and the nitrogen atom of the oxime group of the ligand. On comparison of the infrared spectra of the ligand itself and the metal complexes, significant shifts were observed for the carbonyl (C=O) and C=N of oxime groups. The carbonyl band of the ligand appeared at 1715 cm^{-1} and was observed at 1660 cm^{-1} for the Cu(II) complex and at 1680 cm^{-1} for Fe(III) complex. Similarly, the C=N band of ligand also shifted from 1550 cm^{-1} to 1540 cm^{-1} for the Cu(II) and to 1535 cm^{-1} for Fe(III) complexes, respectively. These shift could be interpreted as coordination of the ligand to the metal centre through the carbonyl and C=N of oxime, in accordance with reported studies.[7,13] Elementel analyses of the complexes proved that the metal ligand ratio was 1:1 in the formation of complexes. The magnetic susceptibility of the Cu(II) complex was found to be 1.83 BM which corresponds to one unpaired electron, whereas for the Fe(III) complex it was found to be 5.91 BM which corresponds to three unpaired electrons. Qualitative chlorine analysis of the complexes showed no detectable chloride and the moleculer weight determination of the metal complexes also gave results which are very close to the calculated value for mononuclear complexes. The complexes, therefore, are assumed to be monomeric rather than dimeric or polymeric based on these experimental results. The ^1H NMR spectra could not be obtained due to the paramagnetism of the complexes.

EXPERIMENTAL

N-Phenyl-3-oxo-butanamide, hydroxylamine hydrochloride, copper(II) chloride and iron(III) chloride were used as purchased from Merck. The

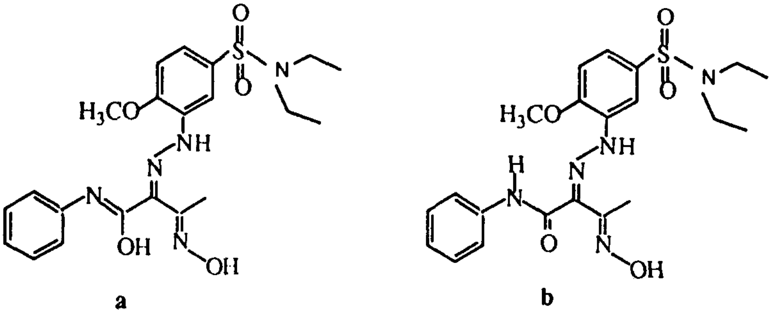
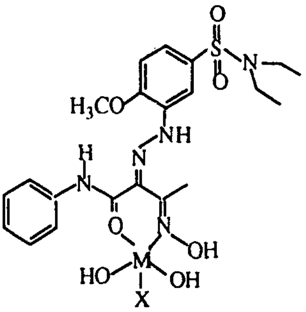


Fig. 1. Enol (a) and Keto (b) Forms of Compound (4)



M = Cu, X = H_2O (5)
M = Fe, X = OH (6)

Fig. 2. Metal Complexes of Compound (4)

solvents were supplied commercially. The ^1H NMR spectra were measured in DMSO-d_6 on a Brucker AC 2001 spectrometer operating at 200 MHz with TMS as internal standard. Magnetic susceptibilities were measured by the Gouy method at room temperatute using Hg[Co(SCN)$_4$] as calibrant. The solution IR spectra were recorded on a Perkin Elmer 983 spectrophotometer in $CHCl_3$. The microanalytical data of C, H, N were obtained on a Carlo Erba Elemental Analyser Model 1106 and the metals copper and iron were determined on a Perkin Elmer atomic absorption spectrophotometer. The moleculer weights of the compounds were determined by the boiling point elevation method in toluen.

Synthesis of *N*-Phenyl-3-hydroxyiminobutanamide (2)

An aqueous solution of hydroxylamine (1.46 g, 0.021 mol) was added to a 50 mL solution of (**1**) (3.54 g, 0.02 mol) in ethanol and the mixture was stirred for 2 hours at room temperature. Approximately 60% of ethanol was removed by passing nitrogen through the solution at 30-40 °C. Water (50 mL) was then added into the mixture to give white a precipitate which was filtered, washed with water and dried *in vacuo*. Yield 3.11 g (81%), mp. 123-125°C. The product is soluble in ethanol, chloroform, DMSO, toluene and dimethylformamide.

IR ($CHCl_3$) (cm^{-1}): 3290 (NH), 3100 (OH), 1650 (C=O), 1600 (arom.), 1550 (CN).

^{1}H NMR [(DMSO-d_6)]: δ = 10.4 ppm [s, H, OH], 9.9 ppm [s, H, NH], 7.6-7.1 ppm [m, 5H, arom], 3.2 ppm [s, 2H, CH_2], 1.8 ppm [s, 3H, CH_3].

Elemental analysis, $C_{10}H_{12}N_2O_2$ (MW = 192.19):

Calculated: C, 62.50; H, 6.25; N, 14.58.

Found : C, 62.48; H, 6.29; N, 14.57.

Synthesis of (4)

A quantity of 3.5 mL of an aqueous solution of sodium nitrite (1.4 g, 0.02 mol) was added dropwise to a solution of (**3**) (5.16 g, 0.02 mol) containing 8 mL of conc. HCl at 0°C. The excess nitrous acid in the solution was neutralised with urea and sodium acetate (5 g) was added to buffer the diazonium solution. Compound (**2**) (4.12 g, 0.02 mol) was dissolved in 50 mL of ethanol in a separate beaker and 4 mL of conc. HCl was then added. The previously prepared diazonuim solution was then added dropwise to that solution with vigorous stirring. The reaction mixture was stirred further for 30 min at 0°C. The resulting yellow precipitate was filtered and washed with dilute NaOH and HCl solutions, respectively, and dried *in vacuo*. Yield 6.74 g (80.8% based on (**2**)), mp.163-165°C. The product is soluble in acetone, chloroform, diethyl ether, toluene, DMSO and DMF.

IR ($CHCl_3$) (cm^{-1}): 3400 (NH), 3180(OH), 1715 (C=O), 1600 (arom.), 1550 (CN).

^1H NMR [($DMSO-d_6$)]: δ = 11.7 ppm [s, H, OH], 12.5 ppm [s, H, hydrazone NH], 11.39 [s, H, amide NH], 7.8-7.3 ppm [m, 8H, arom], 3.9 ppm [s, 3H, methoxy], 3.25 ppm [q, 2H, CH_2], 1.1 ppm, 2.5 ppm [s, 3H, amide CH_3][t, 3H, CH_3].

Elemental analysis, $C_{21}H_{27}N_5O_5S$ (MW = 461.52):

Calculated: C, 54.65; H, 5.89; N, 15.17.

Found : C, 54.24; H, 5.87; N, 14.92.

Synthesis of Cu(II) Complex of (4)

A solution of (4) (1.16 g, 2.5 mmol) in ethanol (50 mL) was combined with a $CuCl_2.2H_2O$ (0.43 g, 2.5 mmol) solution in ethanol (30 mL). The pH of the solution was then adjusted to 5-6 with 2N NaOH to give a yellow precipitate. The solution was stirred and boiled for 1h. The mixture was then cooled to room temperature. The precipitate was filtered, washed with water and cold ethanol, respectively, and finally dried under vacuum. Yield 1.22 g (85%), mp. >300°C. It is soluble in DMSO and DMF.

IR ($CHCl_3$) (cm^{-1}): 3420 (NH), 3500-2900 (OH), 1660 (C=O) 1600 (arom), 1540 (CN).

MW (ebullioscopic in toluene): found: 580.2 calculated: 577.09

Elemental analysis, $C_{21}H_{31}N_5O_8SCu$

Calculated: C, 43.70; H, 5.41; N, 12.13; Cu, 11.01

Found : C, 43.27; H, 5.48; N, 12.06; Cu, 10.63.

μ eff. : 1.83 B.M.

Synthesis of Fe(III) Complex of (4)

A solution of (4) (1.16 g, 2.5 mmol) in ethanol (50 mL) was combined with a $FeCl_3.2H_2O$ (0.4 g, 2.5 mmol) solution in ethanol (30 mL). The pH of the solution was then adjusted to 5-6 with 2N NaOH. The solution was stirred and boiled for 1h. The mixture was then cooled to room temperature. The brown precipitate was filtered, washed with water and cold ethanol, respectively, and finally dried under vacuum. Yield 1.11 g (77%), mp. >300°C. It is soluble in DMSO and DMF.

IR ($CHCl_3$) (cm^{-1}): 3420 (NH), 3500-2900 (OH), 1680 (C=O) 1600 (arom), 1535 (CN).

MW (ebullioscopic in toluene): found: 569.3, calculated: 568.39

Elemental analysis, $C_{21}H_{30}N_5O_8SFe$

Calculated: C, 44.37; H, 5.32; N, 12.32; Fe, 9.82.

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