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Synthesis, characterization and catalytic activity of Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) complexes of 4-((3-formyl-4-hydroxyphenyl)diazenyl)-*N*-(4-methyloxazol-2-yl) benzenesulfonamide

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ABSTRACT

The sulfonamide derivative, 4-((3-formyl-4-hydroxyphenyl)diazenyl)-*N*-(4-methyloxazol-2-yl) benzenesulfonamide (FDMB), was synthesized and characterized. Additionally, its Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) complexes were prepared and their structures were investigated by elemental analysis, thermal analysis and (IR, electronic and EPR) spectroscopy. The mode of binding indicates that the ligand binds to the metal ion through carbonyl oxygen and OH phenolic with displacement of its proton. The Co(II) complex was applied for the hydrolysis of nerve agent-like compound, *bis*-(*p*-nitrophenyl) phosphate (BNPP). The results showed a significant rate enhancement of 2.5 million fold with respect to the auto-hydrolysis of BNPP under the same conditions.

1. Introduction

Sulfonamide moiety has a vital functionality because of its wide varieties of reported biological [1,2] and pharmacological activities such as anticancer [3,4], carbonic anhydrase inhibitory [5,6], antibacterial [7,8], antimalarial [9], antitumor [10], antihypertensive [11], and anti-inflammatory [12]. Sulfonamide has been also reported to possess good herbicidal [13] and corrosion inhibitory properties [14,15]. At the same time, *N*-salicylideneamino acidato metal complexes with different organic ligands have been prepared, characterized [16-18] then the chemical nuclease property of these metal complexes that intercalates into the DNA grooves [19] have been introduced. Some ternary salicylaldehyde-amino acid Schiff base complexes of Cu(II) with 1,10-phenanthroline and 2,2'-bipyridine exhibit antitumor activity as tumor chemo-therapeutic agents and tumor radio-imaging [20]. It is well known that the phosphoester bond is considered as backbone of the pesticides and nerve agents. Hydrolytic chemistry can play very important role in degradation of phosphoester pesticides and nerve agents, including the G-agents (Sarin and Salman) and the VX-agent [21]. Recent efforts to design synthetic metalloenzymes and elucidate the mechanisms by which metal ions promote hydrolysis have focused primarily on metal complexes [22]. A large number of metal complexes have been synthesized in recent years as models of metallohydrolases, for the purpose of effective hydrolysis of phosphoesters such as DNA and nerve agent-like compounds [23,24].

In this study, we prepared and characterized 4-((3-formyl-4-hydroxyphenyl)diazenyl)-*N*-(4-methyloxazol-2-yl) benzene sulfonamide and its metal complexes. The Co(II) complex has been used as heterogeneous catalyst on the hydrolysis of phosphodiesters *bis*-(*p*-nitrophenyl)phosphate as a nerve agent like compound.

2. Experimental

2.1. Physical measurements

Cu(II), Co(II), Ni(II), Mn(II) and Fe(III) ions were determined by complexometric titration using xylenol orange as indicator [25,26]. Carbon, hydrogen and nitrogen contents were determined at the Microanalytical Unit, Cairo University, Egypt. IR spectra of the ligand and its solid complexes were recorded in KBr disc on a Mattson 5000 FT-IR spectrometer. The electronic spectra of the ligand and its solid complexes were recorded in DMSO in UV/Vis range (195-1100) nm using Perkin Elmer Lambda 35 UV/Vis Spectrometer. Magnetic moments were determined using a Johnson Matthey balance at room temperature (25 °C) with $Hg[Co(NCS)_4]$ as a calibrant. The diamagnetic corrections for the ligand and the metal atoms were computed using Pascal's constants [27]. Thermal analysis measurements TGA were recorded on a Shimadzu thermo-gravimetric analyser model TGA-50H, using 20 mg samples. The flow rate of nitrogen gas and heating rate was 20 mL/min and 10 °C/min, respectively.

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Table 1. Physical properties and elemental analysis of the synthesized metal complexes.

Complex	M.wt, g	Color	Yield, %	Melting point, °C	%C Calcd./Found	%H Calcd./Found	%N Calcd./Found	%M Calcd./Found
$Cu(L\text{-}H)_2(H_2O)_3$	887	Bluff	72	>300	45.9/45.9	3.6/4.3	12.6/12.2	7.1/7.5
$Mn(L\text{-}H)_2\ (H_2O)_6$	931	Brown	65	>300	43.8/43.6	4.1/3.3	12.0/11.4	5.9/6.3
$CoL\text{-}H\ (Ac)MeOH.3H_2O$	589	Brown	75	>300	40.7/41.5	4.4/4.0	9.5/10.3	10.0/10.5
$NiL\text{-}H\ (Ac)MeOH.1.5H_2O$	562	Brown	73	>300	42.7/42.7	4.1/4.2	9.9/10.2	10.5/10.0
$FeL\text{-}H\ (OH)_2(H_2O)_2$	511	Black	70	176	39.9/40.1	3.7/3.8	10.9/10.9	10.9/11.0

The ^1H NMR spectra were recorded in DMSO-d_6 using ovarian FT-300 MHz spectrometer using TMS as internal standard. The mass spectrum of the ligand was recorded on a Shimadzu GC-S-QP 1000 EX spectrometer using a direct inlet system. The kinetic measurements for hydrolysis of phosphodiester were performed using Perkin Elmer Lambda 35 UV/Vis Spectrometer.

2.2. Synthesis of 4-((3-formyl-4-hydroxyphenyl)diazenyl)-N-(4-methyloxazol-2-yl)benzenesulfonamide (FDMB)

Sulfamethoxazole (0.01 mol) was mixed with HCl (10 mL) and water (16 mL) and then digested on a water bath for 30 min. The sulfamethoxazole hydrochloride was cooled to 5 °C and diazotized with ice-cold aqueous $NaNO_2$ solution (5 g, 20 mL). A cold solution of salicylaldehyde (0.01 mol) dissolved in 10% NaOH solution (50 mL) was added to the cold diazonium salt solution with vigorous stirring. A red colour developed immediately and the stirring was continued for 1 h. The reaction mixture was kept overnight in a refrigerator, followed by 3 h at room temperature, and then acidified with dilute acetic acid. The yellow orange precipitate separated out. The precipitate was filtered, washed several times with water to remove excess acetic acid and water-soluble materials, and finally dried in air. The crude product was washed with hexane to remove any tarry materials, dried in vacuum and recrystallized from methanol to yield yellow prismatic crystals of Ligand FDMB.

4-((3-Formyl-4-hydroxyphenyl)diazenyl)-N-(4-methyloxazol-2-yl)benzenesulfonamide (**FDMB**): Color: Light brown. Yield: 70%. M.p.: 204 °C. FT-IR (KBr, ν, cm^{-1}): 3072 (OH), 1658 (C=O), 1614 (C=N), 1401 (SO_2), 3420 (NH), 1476 (N=N). ^1H NMR (300 MHz, DMSO-d_6, δ, ppm): 2.31 (s, 3H, CH_3), 6.19 (s, 1H, C*H*-oxazole), 7.20-8.03 (m, 7H, Ar-*H*), 8.22 (s, 1H, C*H*O), 10.37 (s,1H, N*H*), 11.64 (s, 1H, O*H*). MS (EI, *m/z* (%)): 386 (M$^+$, 12).

2.3. Preparation of metal complexes

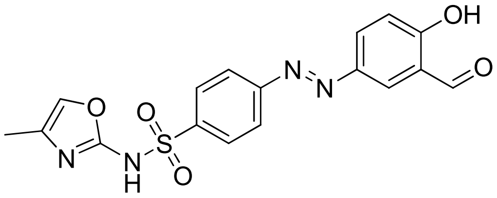
Metal chlorides (Fe(III) and Mn(II)) or metal acetates (Cu(II), Co(II), Ni(II)) (1.0 mmol) were dissolved in ~60 mL methanol. This solution was added dropwise to (0.2 mmol) of the ligand dissolved in ~40 mL methanol with continues stirring. The mixture was heated under reflux for 2.0 hrs. The precipitate was formed and filtered off, washed with diethyl ether and finally dried in an open air. The physical properties of the metal complexes are listed in Table 1.

2.4. Kinetic reactions for phosphoester hydrolysis

The hydrolytic reaction was performed using solid complexes as heterogeneous catalysts in 50 mL of *N*-2-hydroxyethylpiperazine-*N*'-2-ethanesulfonic acid (HEPES) buffer solution (50 mmol, pH = 8.0). The substrate *bis*-(*p*-nitrophenyl) phosphate (BNPP), dissolved in 50 mmol of HEPES buffer solution (pH = 8.0) was added to the previous solution. The heterogeneous mixture has been stirred using a magnetic stirrer. The mixture was centrifuged and the absorbance of the supernatant has been measured using spectrophotometer at 405 nm. The increase in absorbance at 405 nm was followed with time. The reference cell contains substrate without the complex has been used to correct the background hydrolysis. Experiments were repeated three times to ensure accuracy.

3. Results and discussion

The structure of the organic ligand FDMB was elucidated on the basis of its analytical and spectral data. The infrared spectrum of FDMB reveals absorption bands at 1658, 1476, 1401 and 1614 cm^{-1} corresponding to $\nu_{C=O}$, $\nu_{N=N}$, ν_{SO2}, and $\nu_{C=N}$, respectively. The ^1H NMR of this compound showed signal at δ 2.31 (s, 3H, CH_3), 6.19 (s, 1H, CH-oxazole), 7.20-8.03 (m, 7H, Ar-H), 8.22 (s, 1H, CHO), 10.37 (s, 1H, NH) and 11.64 (s, 1H, OH). All these data together with the mass spectrum which showed a molecular ion peak at *m/z* = 386, and base peak at *m/z* = 121 suggest the proposed structure of the ligand FDMB (Scheme 1).



4-((3-Formyl-4-hydroxyphenyl)diazenyl)-*N*-(4-methyloxazol-2-yl)benzene sulfonamide (**FDMB**).

Scheme 1

3.1. IR spectra

By comparing the IR spectral data of the ligand and their metal ion complexes, one finds that the whole metal ions bind to the organic ligand through phenolic OH group with the liberation of its hydrogen atom and the oxygen atom of the aldehydic group. This assumption is supported by disappearance of the ν_{OH} band which was appeared at 3072 cm^{-1}. At the same time the carbonyl band ν_{CO} was shifted to higher wavenumber. Both Co and Ni complexes have two bands at (1320-1340) and (1515-1520) cm^{-1} corresponding to acetate group ν_{sym}COO and ν_{asym}COO. On the other hand the negative test for the chloride ion in the iron complex indicates the liberation of two chloride ions with the formation of two hydroxo Fe^{3+} compound due to a partial hydrolysis of $FeCl_3$. The band observed at 950 cm^{-1} which is obscured in the spectra of the ligand and the above mentioned complexes may attribute to δ_{OH} hydroxo [28]. The proposed structures also were supported by existence of C=N, SO_2, NH and N=N bands at their positions in the ligand spectrum without changes (Table 2) which indicate that these functional groups are not participating in the binding. The band appears at (3480-3490) cm^{-1} was attributed to water molecules in all metal complexes. The mode of binding in these metal complexes reveals that the copper and manganese coordinate to the ligand FDMB in the ratio of 1:2 (M:L) where M = Cu or Mn and L = FDMB. Whereas the coordination of the cobalt, nickel and iron complexes are founded to be in the mole ration of 1:1 (M:L).

Table 2. IR bands of the ligand and its metal complexes.

Compound	**νC=O**	**νC=N**	**νN=N**	**νC-O**	**νSO_2**	**νNH**
Ligand	1658	1614	1476	1092	1401	3420
$Cu(L\text{-}H)_2(H_2O)_3$	1795	1611	1471	1103	1398	3423
$Mn(L\text{-}H)_2\ (H_2O)_6$	1795	1618	1467	1109	1396	3424
CoL-H (Ac)MeOH. $3H_2O$	1791	1620	1468	1101	1398	3423
NiL-H (Ac)MeOH. $1.5H_2O$	1865	1616	1474	1101	1397	3421
FeL-H $(OH)_2(H_2O)_2$	1796	1618	1468	1109	1397	3419

3.2. Electronic and EPR spectra

The electronic spectrum of [CoL-H (Ac)MeOH].$3H_2O$ complex shows two bands at 380 and 453 nm assignable to $^4T_{1g}(f) \rightarrow {}^4A_{2g}(f)$ transitions The magnetic moment value 4.5 B.M. is in conformity with tetrahedral structure. The magnetic moment measurement of the Ni(II) complex [NiL-H (Ac)MeOH].$1.5H_2O$ at room temperature shows that the nickel complex is a diamagnetic. The band appears at 450 nm with the diamagnetic nature corresponding to a square planar geometry around the Ni(II) ion. The manganese complex $[Mn(L\text{-}H)_2](H_2O)_6$ shows intense absorption band at 340 nm assigned to ligand centered transition while two weak transitions are observed at 375 nm and 460 nm may be referred to a combination of MLCT and *d-d* transition ($^4A_1 \rightarrow {}^4T_1$), suggesting tetrahedral geometry of the complex. The magnetic moment value of the manganese(II) complex 5.6 BM may also support a high spin tetrahedral complex [29]. The magnetic moment (1.9 BM) of the Cu(II) complex $[Cu(L\text{-}H)_2](H_2O)_3$ at room temperature corresponds to one unpaired electron [30]. The electronic spectrum of the copper (II) complex recorded in ethanol reveals an absorption band at 495 nm. This band can be attributed to *d-d* transition ($^2B_{1g} \rightarrow {}^2A_{1g}$), which supports square-planar geometry around the metal ion [31]. The bands at 280 and 370 nm can be assigned to a CT band from filled orbitals Cu(II) to the anti-bonding π* orbitals of the ligand [32]. The EPR spectrum of the complex $[Cu(L\text{-}H)_2](H_2O)_3$ was recorded as a polycrystalline sample at room temperature. The spectrum of the complex exhibits a single anisotropic broad signal. The analysis of the spectrum (Figure 1) gives the $g_{||}$ = 2.1212 and $g_{\perp}$ = 2.0811. These values indicate that the ground state of Cu(II) is predominately $dx^2\text{-}y^2$, which supports a square planar structure [33,34]. The observed $g_{||}$ value for the copper(II) complex is less than 2.3, thus, indicating that the bonds between the organic ligand and copper ion have a covalent character more than the ionic one. According to Hathaway and Billing [35,36] the $G = (g_{||} - 2)/(g_{\perp} - 2)$, which measures the exchange interaction between the copper centers in a polycrystalline solid has been calculated and found to be less than 4.0. This value indicates to a considerable exchange interaction in solid complex.

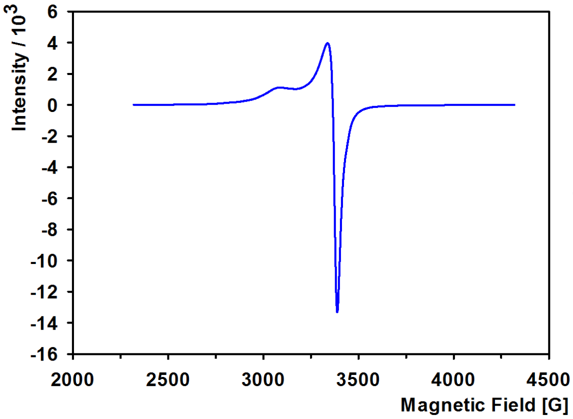


Figure 1. EPR spectrum of Cu(II) complex.

3.3. Thermal analysis

The thermograms TGA confirms the amount of solvent inside and outside the coordination sphere and gives some information about the stability of this compound. The thermograms of all metal complexes (Figure 2) have two or three decomposition stages from 25 to 1000 °C. These stages involved mass loss of ~75 %. TGA of the all prepared complexes show first stages from 25-95 °C corresponds to removal of water molecules outside the coordination sphere with weight loss calc. = 4.8-11.6%, found = 5.2-11.0 % indicating to 1.5-6.0 molecules of water. The second inflection point stars at around 400 °C with starting the decomposition of the metal complexes with weight loss of about 68-70% of the whole complex leaving the metallic residue for metal oxide or metal carbide. The elemental analysis, IR and electronic spectra with thermal analysis suggest the complexes structures given in Scheme 2-4.

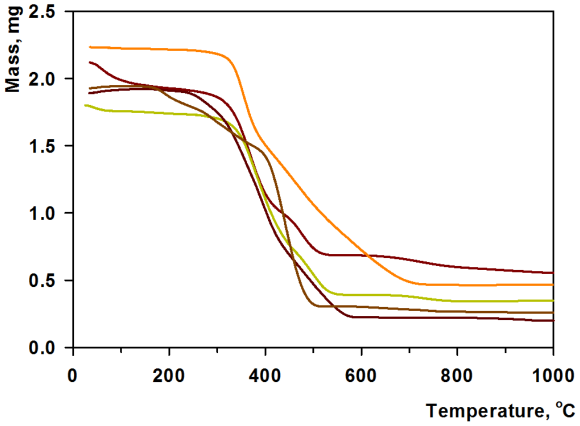
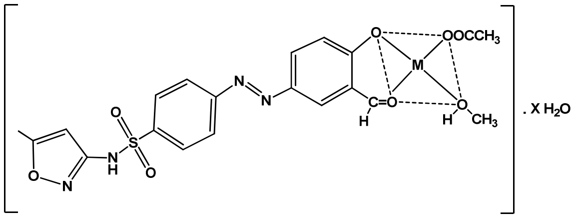


Figure 2. TGA for Cu(II) (dark brown), Co(II) (reddish brown), Ni(II) (orange), Mn(II) (green) and Fe(III) (buff) complexes.

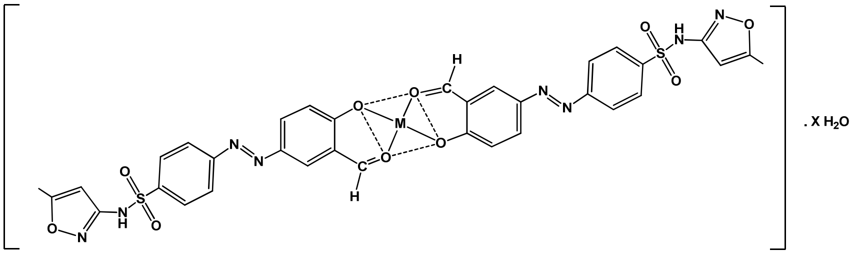


M = Co, X = 3 and M= Ni, X = 1.5

Scheme 2

3.4. Hydrolysis of phosphodiester by Co(II) complex

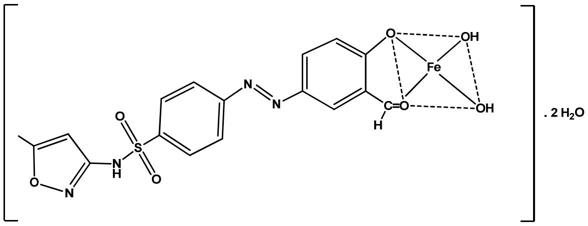
Since phosphate diesters are generally highly resistant toward the hydrolysis cleavage, therefore, catalysts reactive enough to hydrolyze the target bonds rapidly under physiological conditions represent a major challenge.



M = Mn, X = 6 and M = Cu, X = 3.

Scheme 3

The prepared complexes in this study have been used to investigate the hydrolysis of phosphoester *bis*-(*p*-nitrophenyl) phosphate (BNPP) in an aqueous medium and under normal conditions. The Co(II) complex showed a significant activity while the other metal complexes showed negligible activities. In order to establish the rate law for the heterogeneous *bis*-(*p*-nitrophenyl)phosphate hydrolysis by the Co(II) complex [CoL-H(Ac)MeOH].3H$_2$O, the rate is further determined at various BNPP concentration values (Figure 3) at pH = 8.0 and 25 °C. The rate of BNPP hydrolysis is found to be linear in the beginning and reaching saturation at high concentration of the substrate BNPP, suggesting the possibility of a pre-equilibrium kinetics. This kinetic can be described as the binding of the substrate BNPP (S) to the metal center in the Co(II) complex to form the intermediate Co(II) complex-S, followed by the conversion of the bound BNPP into products. The first order rate constant k_{cat} and the maximal velocity V_{max} were found to be 3.1×10^{-4} s^{-1} and 0.4 mM/min, respectively. The hydrolysis of BNPP with different concentrations of the catalyst [CoL-H (Ac)MeOH].3H$_2$O (Figure 4) showed linear trend with first order rate constant 3.1×10^{-5} s^{-1}. The auto-hydrolysis of BNPP is extremely slow with rate constant K_o of 1.1×10^{-11} s^{-1} at pH = 7.0 and 25 °C [37] Thus, the hydrolysis of BNPP here shows a significant rate enhancement of 2.8 million fold with respect to the autohydrolysis of BNPP under the same conditions.



Scheme 4

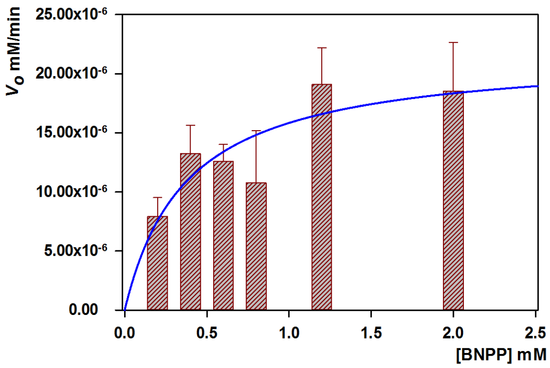


Figure 3. Hydrolysis of BNPP using Co(II) complex in aqueous medium at pH = 8 and 25 °C.

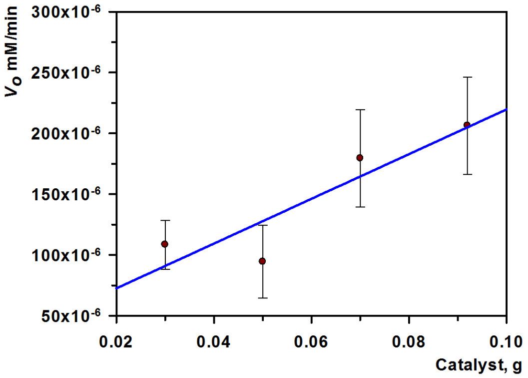


Figure 4. Hydrolysis of BNPP using different concentration of Co(II) complex in aqueous medium at pH = 8 and 25 °C.

4. Conclusions

The antibacterial sulfonamide was used in the preparation of the novel ligand FDMB. The metal complexes of this new ligand were also prepared and fully characterized by different tools to investigate their chemical structures. The electronic spectral data showed that all metal complexes are either tetrahedral or square planner. The catalytic activity of the prepared complexes was investigated towards the hydrolysis of BNPP and the Co(II) complex showed the highest activity.

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