



Synthesis, Characterization and Catalytic Activity of Chromone Derivative Schiff Base Complexes; Rapid Hydrolysis of Phosphodiester in an Aqueous Medium.

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ABSTRACT

The Schiff base 5-Iodo-2-[(5-methoxy-2-methyl-4-oxo-4*H*-chromen-6-ylmethylene)-amino]-benzoic acid, IMMCAB has been prepared from condensation of chromone derivative 6-formyl-5-methoxy-2-methylchromon with 3-Iodo-6-aminobenzoic acid. Co(II), Ni(II), Zn(II), Cu(II) and Fe(III) of IMMCAB have been prepared and characterized by means of IR, UV/Vis, ¹H-NMR, thermal analysis and magnetic moment measurements. IR spectroscopy reveals that the IMMCAB behaves as a bidentate ligand towards these metal ions. The metal to ligand ratio is found to be 1 : 2 in case of Cu(II) and Zn(II) complexes. The Ni(II) and Co(II) complexes have been used as heterogeneous catalysts in the hydrolysis of phosphodiester compound bis(*p*-nitrophenyl) phosphate (BNPP) in an aqueous medium at pH = 8. The hydrolysis of BNPP here shows a significant enhancement rate of 3.6×10^5 and 1.1×10^6 fold for Ni(II) and Co(II) complexes respectively with respect to the autohydrolysis of BNPP under the same conditions.

KEYWORDS: Chromone, Schiff base, hydrolysis, phosphodiester.

INTRODUCTION

The development of Schiff base compounds has attracted a lot of interest in the fields of coordination chemistry and material sciences [1,2]. Schiff base compounds can accommodate different metal centers involving various coordination modes, thereby allowing successful synthesis of homo and hetero metallic complexes with varied stereochemistry [3]. This feature is employed for modeling active site centers in metalloenzymes in the biological systems [4,5]. Additionally, they have wide applications such as antibacterial and antifungal agents [6]. These compounds also find many important catalytic applications, e.g. their ability to reversibly bind oxygen [7], solid phase extraction of metal ions [8] as well as complexing ability toward toxic metals [9] and preparation of ion selective electrodes [10,11].

Visnagin (precursor of chromone derivatives) obtained from ammi visnaga have a great medicinal uses. It has been used in the treatment of asthma, angina, coronary arteriosclerosis and kidney stones[12].

Hydrolytic chemistry has been one of the most attractive areas of chemistry studies due to industrial and biological importance and applications. Some of those important biological processes are protein degradation, protein maturation, hormone regulation and their relation to the health problems. The half-life for hydrolysis of the phosphodiester bond has been estimated to be 100 years for RNA and 130,000 years for DNA at room temperature and neutral pH at 25 °C [13]. This stability which makes these linking bonds so useful in biopolymers can also be a problem. For example, foreign DNA and proteins, once recognized, need to be destroyed. Mutation in native DNA needs to be excised and repaired. Messenger RNA must be hydrolyzed so that the protein it encodes is not synthesized unnecessarily. Of course, all of this must be accomplished on utilizes a class of enzymes called hydrolases[14]. Hydrolytic chemistry also can play very important role in degradation of phosphoester pesticides and nerve agents, including the G-agents (Sarin and Salman) and the VX-agent[15,16]. Recent efforts to design synthetic metalloenzymes and elucidate the mechanisms by which metal ions promote hydrolysis have focused primarily on metal complexes[17-19]. A large number of metal complexes, including those of Co(III), Cu(II), Zn(II), and lanthanides (III), have

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been synthesized in recent years as models of metallohydrolases, and as catalysts for the purpose of effective hydrolysis of phosphoesters, such as DNA and nerve agent-like compounds[20-23]

In this study we prepared and characterized a chromone derivative Schiff base and its metal complexes. Co(II) and Ni(II) complexes have been used as heterogeneous catalysts on the hydrolysis of phosphodiester bis (*p*-nitrophenyl)phosphate.

EXPERIMENTAL

Physical measurements

Cu(II), Zn(II), Ni(II), Fe (III) and Co(II) ions were determined by complexometric titration using xylenol orange as indicator [24,25]. 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 FTIR 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 at Al-Azhar University. 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 [26]. Thermal analysis measurements TGA were recorded on a Shimadzu thermogravimetric 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. The ¹H-NMR spectra were recorded in *d*₆-DMSO using ovarian F.T-300 MHz spectrometer using TMS as internal standard. The mass spectrum of the legend was recorded on a Shimadzu GC-S-QP 1000 EX spectrometer using a direct inlet system. TGA, ¹H-n.m.r., mass spectra and magnetic moments were carried out at Cairo University, Egypt. The kinetic measurements for hydrolysis of phosphodiester were performed using Perkin Elmer Lambda 35 UV/Vis Spectrometer. The conductance of metal complexes (1.0 mM) dissolved in methanol, DMF or DMSO was measured using WTWD -812-Weilheim –conductivity meter model LBR, fitted with a cell mode LTA 100 at faculty of science, Al Azhar University, Cairo, Egypt.

Kinetic studies

The hydrolytic reaction solutions were prepared by adding Co(II) or Ni(II) complexes of IMMCAB in 50 mM HEPES buffer solution (pH 8.0, 25 °C). The substrate (bis *p*-nitrophenyl phosphate), BNPP dissolved in the same buffer, was added. The heterogeneous mixture has been stirred using magnetic bar and 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 due to releasing a *p*-nitrophenolate as a hydrolytic product ($\epsilon = 17500 \text{ M}^{-1}\text{Cm}^{-1}$) was followed with the time. The reference cell contained substrate without metal complex has been used to correct for background hydrolysis. Experiment was repeated three times to ensure accuracy.

Synthesis of 5-Iodo-2-[(5-methoxy-2-methyl-4-oxo-4*H*-chromen-6-ylmethylene)-amino]-benzoic acid (IMMCAB); The Schiff base was prepared by refluxing equimolar amounts of 6-formyl-5-methoxy-2-methylchromon (str.1) with 3-Iodo-6-aminobenzoic acid (str. 2) in ethanol for two hrs as described earlier[27].

Preparation of solid metal complexes:

A hydrated metal nitrate Fe(NO₃)₃·9H₂O, Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, Cu(NO₃)₂·2.5H₂O and Zn(NO₃)₂·6H₂O (232- 502 mg, 1.0 mmole) were dissolved in ~ 30 ml methanol. This solution was added dropwise to 463 mg (1.0 mmol) of the ligand dissolved in ~ 30 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 vacuum at 60 °C, the physical properties of the metal complexes are listed in the table 1.

RESULTS AND DISCUSSION

The IR spectrum of 5-Iodo-2-[(5-methoxy-2-methyl-4-oxo-4*H*-chromen-6-ylmethylene)-amino]-benzoic acid (IMMCAB) shows the most intense band at 1590 cm^{-1} corresponds to stretching frequency absorption of $\nu\text{C}=\text{N}$ of azomethine group [28]. The band appears at 1650 cm^{-1} is in a good agreement with $\nu\text{C}=\text{O}$. The infrared spectrum of IMMCAB shows the disappearance of the vibrational absorption characteristic of amino group together with appearance of vibrational absorption bands at 1230 and 760 cm^{-1} assignable to the deformation vibration of OCH_3 [29]. $^1\text{H-NMR}$ of IMMCAB in $d_6\text{-DMSO}$ shows signals at $7.43\text{-}7.84$ ppm attributed to aromatic protons. The spectrum shows the OH proton signal at 10.21 ppm. The signal appears at 8.13 ppm is accompanied to azomethine proton. The protons of methoxy group as well as methyl group appear at 3.89 and 1.88 ppm respectively. The molecular weight of IMMCAB was determined by mass spectroscopy. The mass spectrum (Fig. 1) shows a peak at $m/e = 463$ representing the molecular ion peak M^+ ($\text{C}_{19}\text{H}_{14}\text{O}_5\text{NI}$) with (16.9%) abundance. All these data together with the elemental analysis (%C found/calc. = $49.13/49.23$, %H found/calc. = $3.21/3.02$ and %N found/calc. = $3.31/3.03$) are supporting the proposed structure for IMMCAB. Mass fragmentation pattern of IMMCAB scheme 1 can be used as an additional evidence to confirm the structure of the ligand.

By comparing the IR spectra of the ligand with its metal complexes, it is found that the IMMCAB binds Co(II) and Ni(II) through azomethine nitrogen atom with carboxylic oxygen atom after deprotonation forming tetrahedral structure geometry. At the same time IMMCAB behaves as a bidentate ligand through the deprotonated carboxylic group and azomethine nitrogen atom to form an octahedral structure around the Cu(II), Fe(III) and Zn(II) ions. The mole ratio between ligand and metal is 1:1 in case of Co(II), Ni(II) and Fe(III) while it is 2 : 1 (ligand to metal) in case of Zn(II) and Cu(II) (structures 3,4,5). This assumption is supported by the following data. The absorption band $\nu\text{C}=\text{N}$ which appear at 1590 cm^{-1} in IMMCAB is shifted to lower frequency ($1519 - 1575\text{ cm}^{-1}$) in the metal complexes. The coordination of azomethine nitrogen atom is also consistent with presence of new bands at ($417 - 474\text{ cm}^{-1}$) due to $\nu\text{M}-\text{N}$. The IR spectra (table 2) show broad band observed at ($3350 - 3428\text{ cm}^{-1}$) assigned to νOH stretching vibration of water molecules. Also new two bands observed at 1518 and 1380 cm^{-1} are in a good agreement with $\nu(\text{NO}_3)$ vibrations [30]. The existence of those two bands suggests the monodentate nature of the NO_3 group. The proposed structures are confirmed by presence of new bands at ($530 - 540\text{ cm}^{-1}$) attributed to $\text{M}-\text{O}$. All these foundations together with the results of elemental analyses (table 1) suggest the chemical formula of the metal complexes.

Electronic spectra

The electronic spectrum of $[\text{Co}(\text{L-H})\text{NO}_3 \cdot \text{H}_2\text{O}]5\text{H}_2\text{O}$ complex shows two bands at 390 and 430 nm assignable to $^4\text{T}_{1g(f)} \rightarrow ^4\text{A}_{2g(f)}$ transitions. The magnetic moment value 4.52 B.M. is in conformity with tetrahedral structure. The electronic spectrum of $[\text{Cu}(\text{L-H})_2]5\text{H}_2\text{O}$ shows a maximum at 676 nm which can be assigned to $d_{xz,yz} \rightarrow d_{xy}$ and $d_{x^2-y^2} \rightarrow d_{xy}$ transitions in D_{2h} symmetry [31,32]. The relatively high $U_{\text{eff}} = 2.3\text{ B.M.}$ suggests the relatively high tetrahedral distortion. The magnetic moment of $[\text{Ni}(\text{L-H})\text{NO}_3 \cdot \text{H}_2\text{O}]3\text{H}_2\text{O}$ $U_{\text{eff}} = 3.2\text{ B.M.}$, together with The two bands at 390 and 430 nm in the electronic spectrum of the complex are consistency with tetrahedral structure around Ni(II) [33]. Finally, the U_{eff} for $[\text{Fe}(\text{L-H})(\text{NO}_3)_2 \cdot (\text{H}_2\text{O})_2]3\text{H}_2\text{O}$ (2.3 B.M.) suggests a low-spin octahedral structure around the Fe(III) ion. The broad band observed in the U.V. spectrum of the Fe(III) complex at 580 nm is assigned to $^2\text{T}_2 \rightarrow ^2\text{A}_2$ transition and a low -spin octahedral configuration [34] around the Fe(III) ion. The two bands at 400 and 355 nm are assigned to charge-transfer.

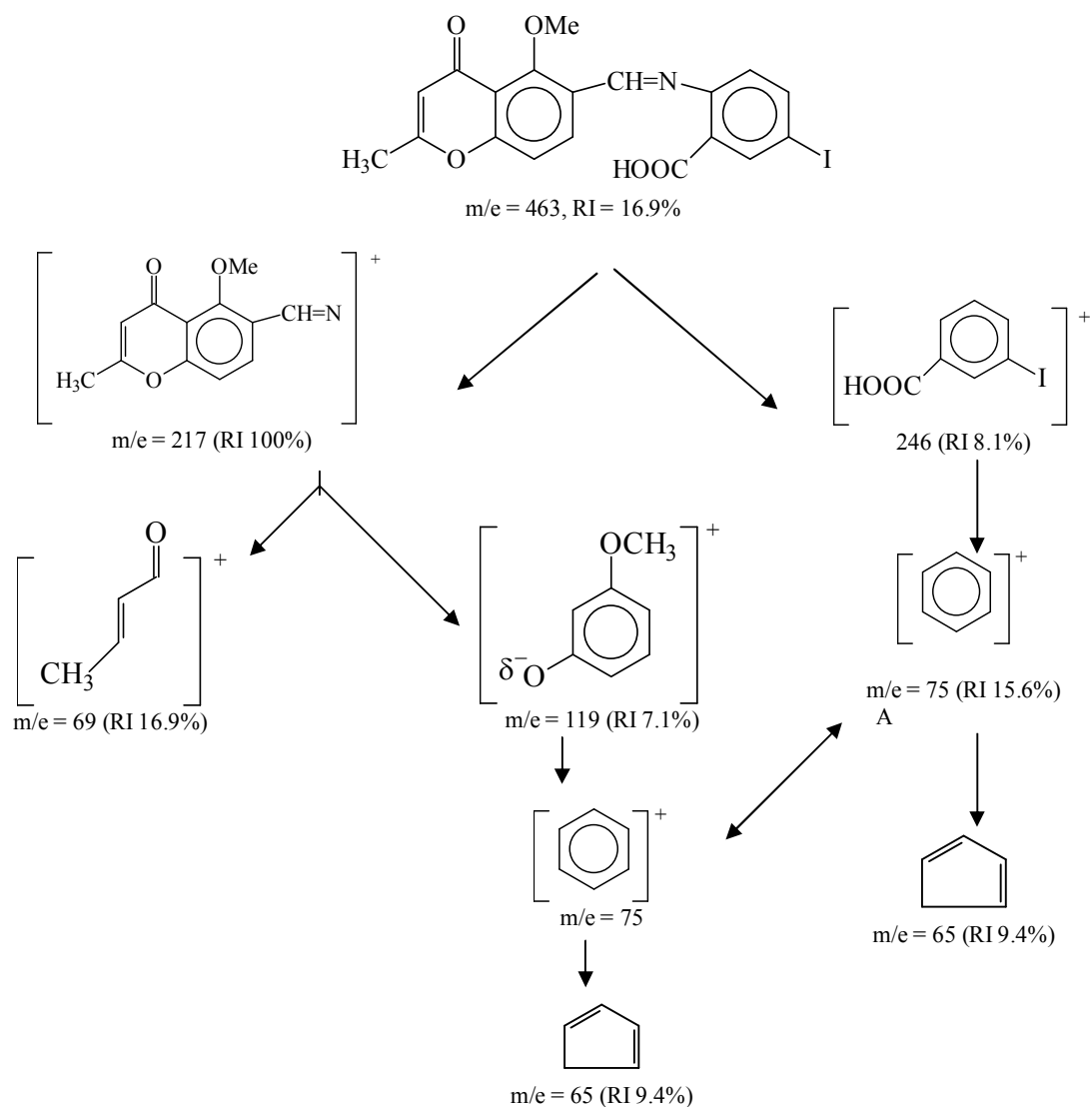
Thermal analysis

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 thermogram of IMMCAB shows three stages of mass loss at temperature range $25\text{-}800^\circ\text{C}$. These stages involved mass loss of 95.04% for first, second and third step of decomposition respectively. TGA of $[\text{Ni}(\text{L-H})\text{NO}_3 \cdot \text{H}_2\text{O}]3\text{H}_2\text{O}$ complex shows six decomposition steps within temperature range $25\text{-}800^\circ\text{C}$. The inflection in the temperature range $25\text{-}100^\circ\text{C}$ corresponds to removal of three water molecules outside the coordination sphere (weight loss calc. = 8.2% , found = 7.4%). The second peak in the temperature range $100\text{-}200^\circ\text{C}$

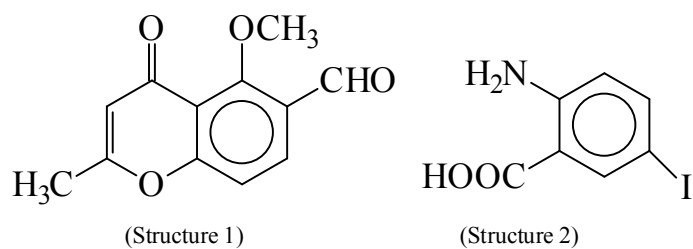
corresponds to removal of one water molecule as well as nitrate group and CO₂ molecule with weight loss = 18.9% (calc = 19.1). The subsequent steps involve loss of organic part of the ligand with mass losses 59.5% (calcd 59.6%) leaving NiO₂ as metallic residue. The thermogram of [Fe(L-H)(NO₃)₂(H₂O)₂]3H₂O complex shows four decomposition steps within temperature range 25-800°C. The first step in the temperature range 25-125 °C corresponds to removal of the hydration and coordination water molecules with weight loss = 13.8% (calc. = 13.3%). The second and third steps from 140- 360 °C are assigned to removal of two molecules of nitrate, two molecules of methane and one molecule of carbon dioxide with weight loss of 28.9% (calc. = 29.5%). The temperature range 400-800 °C for subsequent step involve losses of organic part of ligand leaving 3/5 Fe₂O₃ as residue.

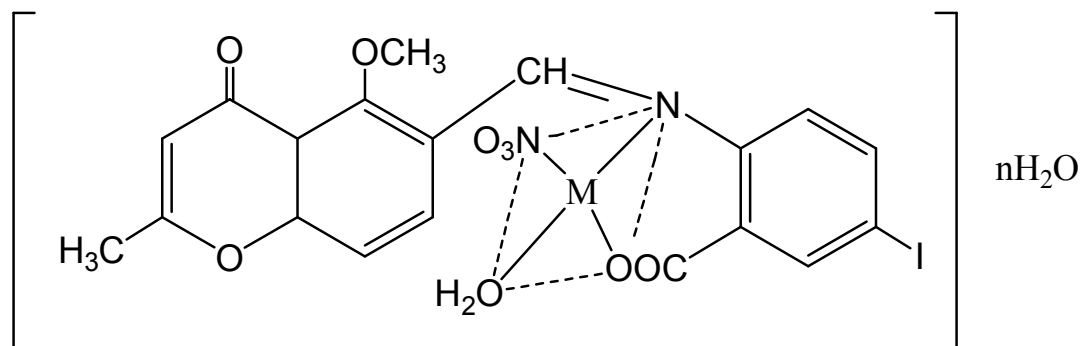
Hydrolysis of phosphodiester by Ni(II) and Co(II) complexes

The Co(II), Ni(II), Zn(II), Fe(III), and Cu(II) complexes of IMMCAB have been investigated to hydrolyze the phosphodiester bis(*p*-nitrophenyl)phosphate (BNPP) at pH 8.0 and 25°C. All metal complexes show negligible activity toward the heterogeneous hydrolysis of BNPP except those of Ni(II) and Co(II) complexes which show an observed rate constant of 6.49×10^{-5} and 2.59×10^{-5} mM/sec respectively. Heterogeneous catalysis has been well recognized to be a convenient process in industry and laboratory owing to easy separation of the products, recovery of the catalysts, and incorporation into a continuous flow process. In order to establish the rate law for the heterogeneous hydrolysis of bis(*p*-nitrophenyl)phosphate by [Ni(L-H)NO₃.H₂O]3H₂O and [Co(L-H)NO₃.H₂O]5H₂O, the rate is further determined at various BNPP concentration values (Figs. 2,3) at pH 8.0 and 25 °C. The rate of BNPP hydrolysis is found to be non linear and show saturation with respect to BNPP concentration, suggesting the possibility of a pre-equilibrium kinetics. This kinetics can be described as the binding of the substrate BNPP (S) to the metal center of the complex to form the intermediate M²⁺ complex-S, followed by the conversion of the bound substrate into products. The metal coordinated water molecule may used as intramolecular general acid catalyst[35](str 6). The first order rate constant k_{cat} was found to be 3.98×10^{-5} ($t_{1/2} = 4.8$ h) and 1.18×10^{-4} s⁻¹ ($t_{1/2} = 1.6$ h) for Ni(II) and Co(II) complexes respectively. The catalytic efficiency k_{cat}/K' have been calculated as second order rate constants and found to be = 0.28 M⁻¹s⁻¹ and 0.29 M⁻¹s⁻¹ for Ni(II) and Co(II) complexes respectively. The autohydrolysis of BNPP is extremely slow with rate constant K_0 of 1.1×10^{-10} s⁻¹ ($t_{1/2} = 200$ years) at pH 8.0 and 25 °C [36]. The hydrolysis of BNPP here thus shows a significant rate enhancement of 3.6×10^5 and 1.1×10^6 fold with respect to the autohydrolysis of BNPP under the same conditions for Ni(II) and Co(II) complexes respectively. To investigate the effect of catalyst concentration on the hydrolysis of BNPP, different concentrations of Ni (II) and Co(II) complexes have been used. The observed rate constant of the hydrolysis of BNPP increases with the increasing of the concentration of the complex.



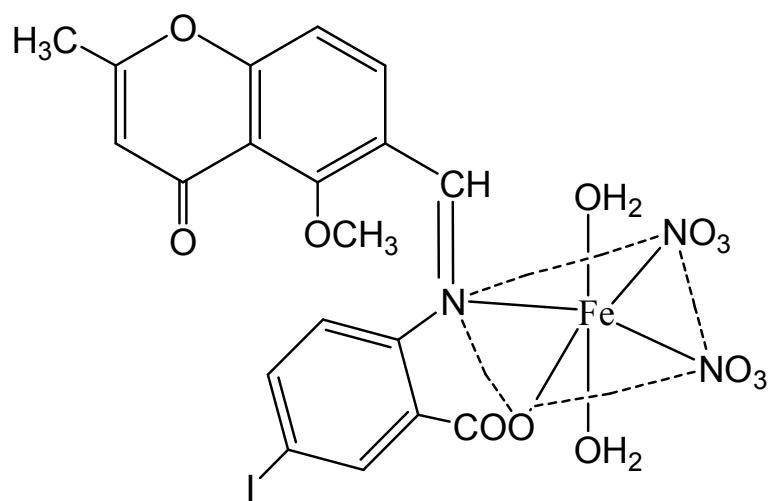
Scheme (1): Mass fragmentation pattern of IMMCAB



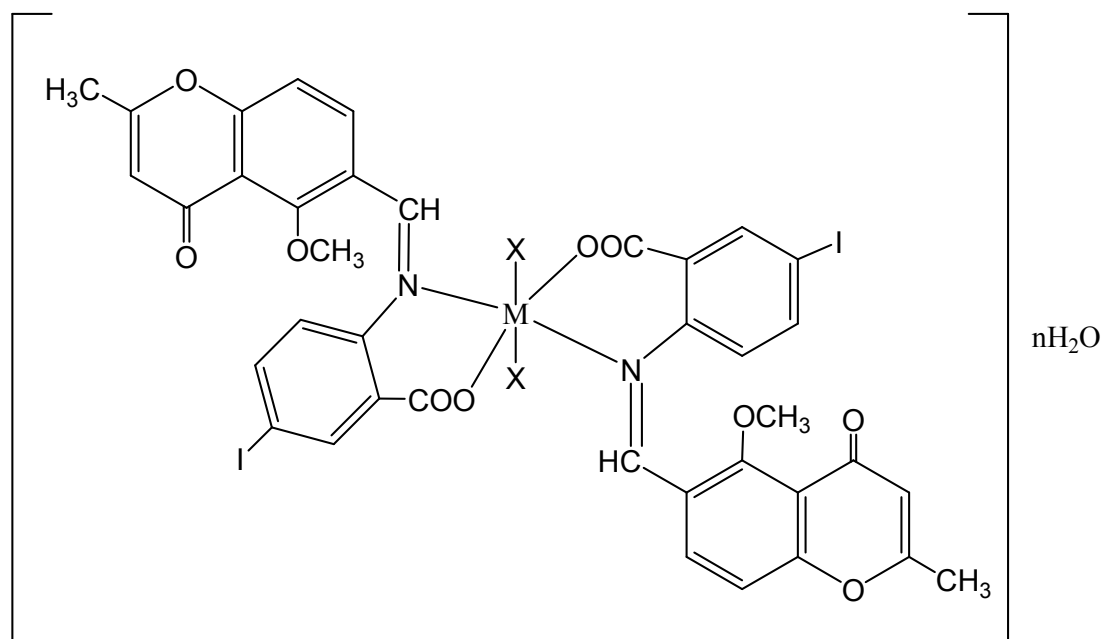


(Structure 3)

M	n
Co	5
Ni	3

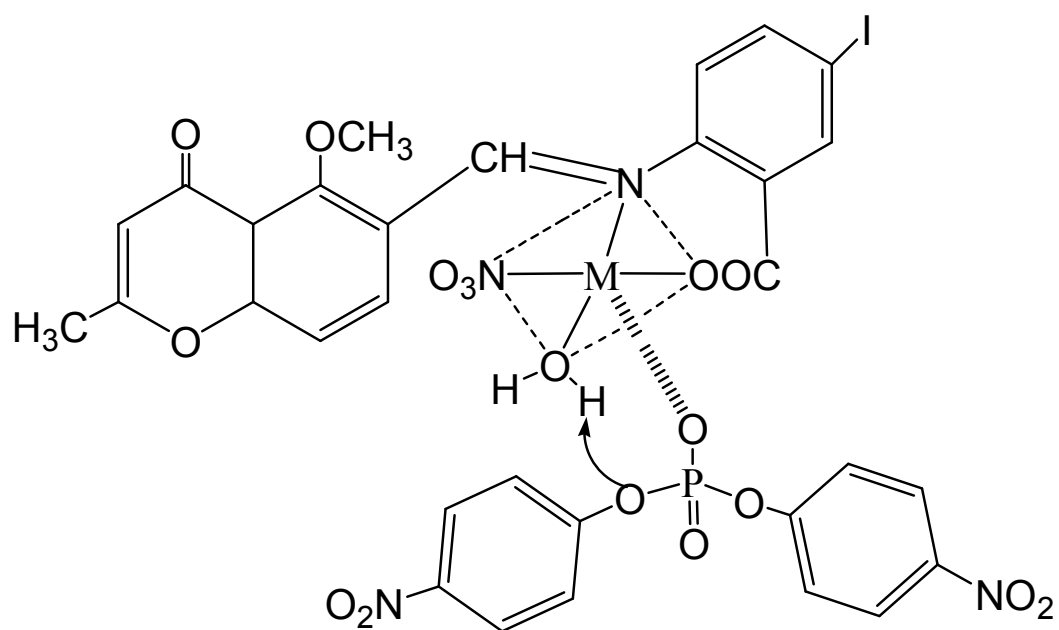


(Structure 4)



(Structure 5)

M	X	n
Cu	-	5
Zn	H ₂ O	2



(Structure 6)

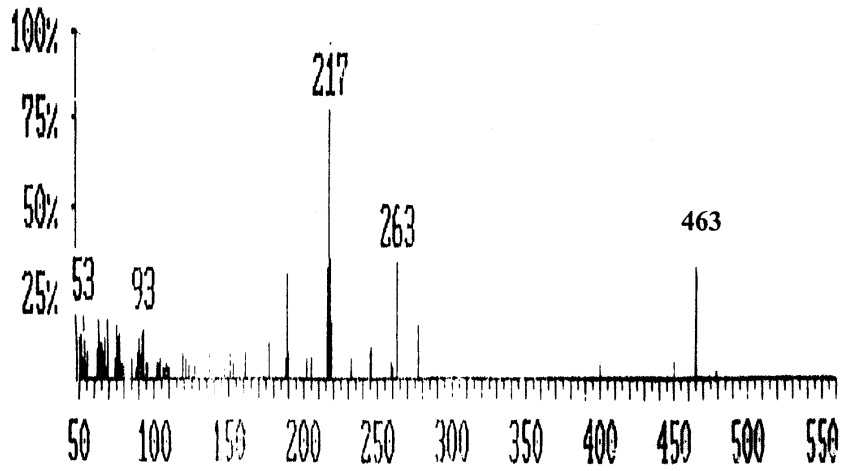


Fig. 1; Mass spectrum of IMMCAB

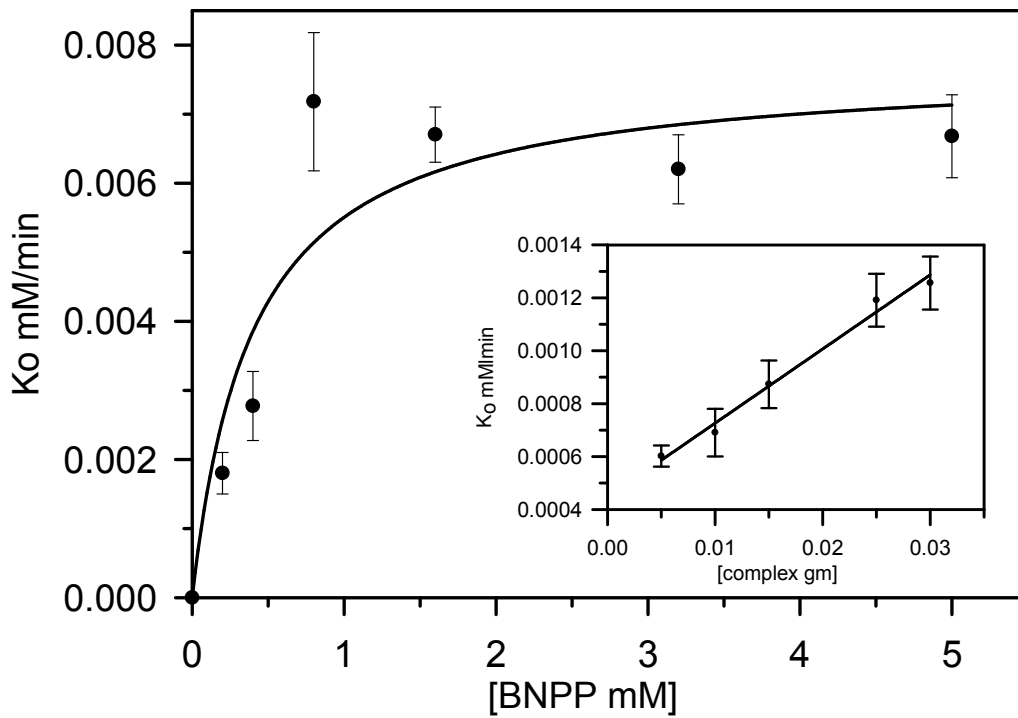


Fig 2; Hydrolysis of different concentration of BNPP using Co(II) complex in 50 mM HEPES buffer solution at pH = 8. Inset, Hydrolysis of 1.0 mM BNPP by using different concentrations of the catalyst Co(II) complex

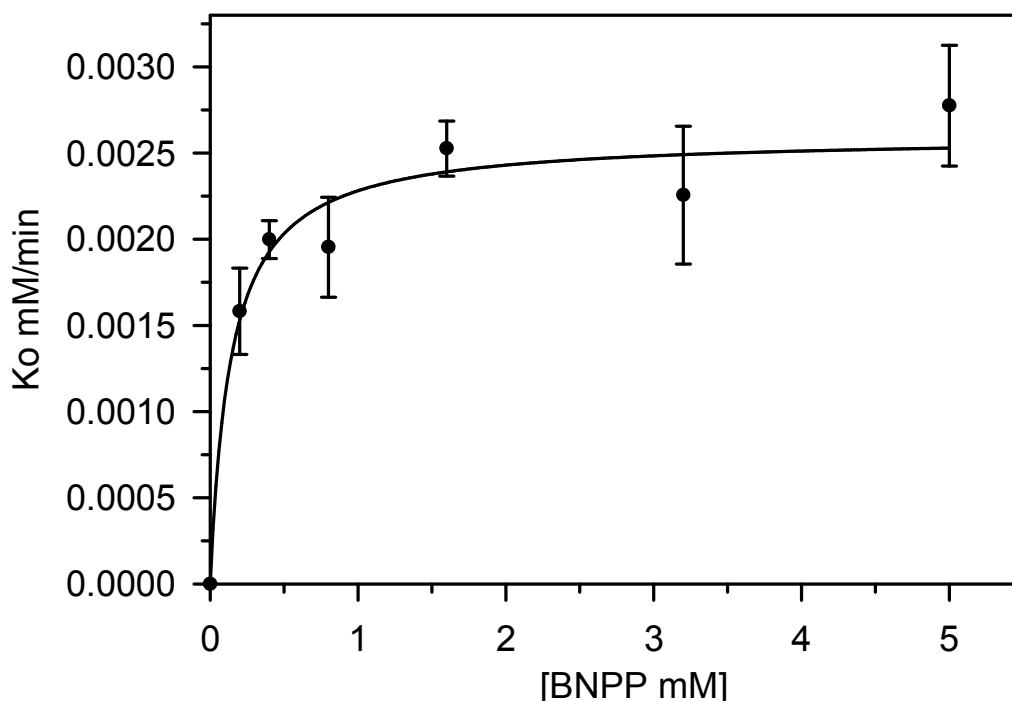


Fig.3 Hydrolysis of different concentration of BNPP using Ni(II) complex in 50 mM HEPES buffer solution at pH = 8.

Table 1; Physical properties and elemental analysis of the metal complexes

Molecular formula / molecular mass	M.P. °C	Color	A°	μ_{eff}	Elemental analysis Calc/Found			
					C	H	N	M
[Co(L-H)NO ₃ .H ₂ O]5H ₂ O 691.132	260	Brownish red	5.26	5.53	33.0	3.6	4.0	8.5
[Ni(L-H)NO ₃ .H ₂ O]3H ₂ O 654.97	>300	Brownish red	5.69	3.2	32.3	3.4	3.6	8.8
[Cu(L-H) ₂]5H ₂ O 1078.052	>300	Green	5.62	2.3	34.8	3.2	4.3	8.9
[Zn(L-H) ₂ .(H ₂ O) ₂]2H ₂ O 1034.016	260	Brownish red	5.76	-	34.5	3.3	4.0	8.8
[Fe(L-H)(NO ₃) ₂ .(H ₂ O) ₂]3H ₂ O 676.293	>300	Black	5.69	2.3	42.3	3.3	2.6	5.9
					41.2	3.1	2.8	6.3
					44.1	3.3	2.7	6.3
					44.1	4.1	3.6	5.9
					33.7	3.4	6.2	8.3
					34.0	2.7	6.0	8.8

Table 2; IR spectral data of the metal complexes

Complex	ν_{OH}	$\nu_{\text{C-H Ar}}$	$\nu_{\text{C-H Al}}$	$\nu_{\text{C=N}}$	$\nu_{\text{C=O}}$	$\nu_{\text{C=C}}$	$\nu_{\text{C-O}}$	$\nu_{\text{pH-N}}$	$\nu_{\text{M-O}}$	$\nu_{\text{M-N}}$	$\nu_{\text{C-I}}$
[Co(L-H)NO ₃ .H ₂ O]5H ₂ O	3366 b	2930 m	2800 w	1578 W	1654 S	1510 m	1197 m	1115 w	530 w	450 w	581 m
[Ni(L-H)NO ₃ .H ₂ O]3H ₂ O	3350 b	2931 m	2888 w	1569 S	1654 S	1519 m	1284 m	1081 w	524 w	474 w	525 m
[Cu(L-H) ₂]5H ₂ O	3428 b	3069 m	2827 m	1578 S	1650 S	1430 m	1197 m	1115 w	530 w	417 w	582 m
[Zn(L-H) ₂ .(H ₂ O) ₂]2H ₂ O	3393 b	2965 m	2857 m	1578 s	1650 S	1441 m	1195 m	1116 w	535 w	420 w	581 w
[Fe(L-H)(NO ₃) ₂ .(H ₂ O) ₂]3H ₂ O	3413 b	2927 m	2890 m	1575 s	1654 s	1432 m	1203 m	1116 w	540 w	425 w	572 w

Conclusion

Synthesis of Schiff base 5-Iodo-2-[(5-methoxy-2-methyl-4-oxo-4*H*-chromen-6-ylmethylene)-amino]-benzoic acid, IMMCAB and its metal complexes have been described. The ligand and its Co(II), Ni(II), Zn(II), Cu(II) and Fe(III) complexes were characterized by means of IR, UV/Vis, ¹H-NMR, thermal analysis and magnetic moment measurements. IR spectroscopy reveals that the IMMCAB behaves as a bidentate ligand toward these metal ions. The metal to ligand ratio is found to be 1 : 2 in case of Cu(II) and Zn(II) complexes. The Ni(II) and Co(II) complexes have been used as heterogeneous catalysts in the hydrolysis of phosphodiester compound bis(*p*-nitrophenyl) phosphate (BNPP) in an aqueous medium at pH = 8. Remarkable rate enhancement of 3.6×10^5 and 1.1×10^6 fold were observed for the hydrolysis of BNPP by Ni(II) and Co(II) complexes respectively with respect to the autohydrolysis of BNPP under the same conditions.

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