SUMMARY

Synthesis and Characterization of Multidentate Schiff base Podands and their use as Chemosensors and Catalysts

The present thesis consists of two parts. For convenience in presentation, the results of this research work have been discussed in the following four chapters.

Part A

Chapter 1: Chemosensors for ions: A review of literature

Chapter 2: Synthesis, spectroscopic/structural characterization and cation/anion recognition studies of some mono, di and tripodal receptors

Part B

Chapter 3: Transition metal complexes and their role in catecholase activity and phosphodiester cleavage: An introduction

Chapter 4: Synthesis, X-ray crystal structure analysis, spectral & magnetic studies and catalytic activity of Cu(II), Ni(II) and Zn(II) complexes with di- and tri-podal ligands

Part A

Chapter 1: Chemosensors for ions: A review of Literature

An appropriate definition of a chemosensor is the so-called “Cambridge definition” Chemical sensors are miniaturized devices that can deliver real time and on-line information on the presence of specific compounds or ions in even complex samples. Chemical sensors employ specific transduction techniques to yield analyte information. The most widely used techniques employed in chemical sensors are optical absorption, luminescence, redox potential etc.
Various neutral and ionic species find widespread use in physiology, medical diagnostics, catalysis and environmental chemistry. As cations and anions are prevalent in both heavy industry and in farming, and as such in the environment, the chemosensors are beginning to find many applications. Different cations and anions are relevant in different fields. Therefore finding new selective ion receptor systems is an important goal which involves sensor development, environmental remediation, selective separation and extraction of chemical species.

Design of the chemosensors consist of three components; a chemical receptor capable of recognizing the guest of interest usually with high selectivity; a transducer or signaling unit which converts that binding event into a measureable physical change and finally a method of measuring this change and converting it to useful information. There are three different approaches which have been used by various groups in pursuing the synthetic receptors, which differ in the way the first two units are arranged with respect to each other. The two units can be covalently attached or intermolecularly linked to each other (binding site- signaling subunit approach) or non-covalently linked (displacement approach). In the third chemodosimeter approach a specific anion-induced chemical reaction occurs which results in an optical signal. Out of these three approaches the first one has been widely exploited and this is the one which would be pursued presently.

Depending on the type of signals produced on the binding event, sensors may be put into two categories; Electronic sensors or Optical sensors. The former produce signals in the form of changes in the electrochemical properties whereas the latter bring changes in the optical properties. The present thesis reports the investigations carried on potential optical sensors.

Optical sensors - The optical sensors further can be classified into two categories.

(A) Chromogenic chemosensors. In such type of chemosensors the coordination site binds the guest in such a way that signaling unit shows the changes in color.

(B) Fluorogenic chemosensors. In fluorogenic chemosensors the interaction between the coordination site and the guest moiety shows the changes in fluorescence behavior of the signaling unit.
A wide variety of optical chemosensors have been reported for the cation, anion and neutral molecules. Based on the nature of analyte being detected, irrespective of the photophysical phenomenon the receptors follows, the chemosensors may be broadly classified into 3 categories; **Cations sensors, Anions sensors, Neutral sensors.** The work presented is restricted to the optical chemosensors for cations and anions. **The first chapter contains a review of literature in their context only.**

**Chapter 2: Synthesis, spectroscopic/structural characterization and cation/anion recognition studies of some mono, di and tripodal receptors**

A series of new trimethy/ethylbenzene core moiety based tripodal, dipodal and monopodal ligands (scheme 1) containing aza-thioethers, phenol, catechol, urea and thiourea as binding groups have been synthesized. These receptors have high selectivity for different cations and anions. The recognition/sensing behavior of the receptors with various cations and anions has been evaluated by using UV-Vis, fluorescence and NMR spectral techniques in solution at 25°C.
\[
\text{(a)} = o-\text{NO}_2, \quad \text{(b)} = m-\text{NO}_2, \quad \text{(c)} = p-\text{NO}_2, \quad \text{(d)} = o-\text{Cl}, \quad \text{(e)} = p-\text{Cl}
\]
Receptor 4, 5 and 6 were synthesized by the reaction of tripodal and dipodal bromide with 2-aminothiophenol under phase transfer catalytic and dry conditions. The compounds 8 and 9 were prepared by the reaction of 1 mmol of 4 and 5 in dry acetonitrile with 3 mmol azosalicylaldehyde intermediates in chloroform respectively. Compounds 10 a-b were synthesized by reacting respective azosalicylaldehyde intermediates with N,N-dimethylethylenediamine. A condensation reaction of tripodal amines 4 and 5 with salicylaldehyde, in the presence of a catalytic amount of zinc perchlorate gave receptor 12 and 13, respectively. The receptors 15 and 16 were synthesized by Schiff base condensation reaction of 4 with 3 mmol and 1 mmol of 2, 3-dihydroxy benzaldehyde, respectively in chloroform-methanol mixture in the presence of catalytic amount of zinc perchlorate. Thiourea and urea based dipodal and tripodal receptors 18 and 19 were synthesized by reacting tripodal 4, 5 and dipodal 6 amines with 4-nitrophenyl isothiocyanate or 4-nitrophenyl isocyanate in dichloromethane. All the receptors were characterized by various spectroscopic techniques such as IR, $^1$H NMR, $^{13}$C NMR and elemental analyses. The X-ray crystal structures of the receptors 5, 13 and 15 have been solved and shown in Fig. 1.
Cation recognition studies for receptor 8a, 8b, 8d and 10 have been performed. To obtain a quantitative insight into metal affinity of the chromogenic tripodal ligands, the wavelength changes upon complexation of various metal ions were determined. The solvent system used was dioxane : water in 1:9 (V:V) ratio, so that all the studies were performed virtually in an aqueous system at 25°C at neutral pH. The receptor 8a and 8b show a band at $\lambda_{\text{max}}$ 394 nm (10.9 x 10$^3$ M$^{-1}$ cm$^{-1}$) and 425 nm (6.2 x 10$^3$ M$^{-1}$ cm$^{-1}$) in water: dioxane 9:1 mixture of solvent. It was found that there were no significant changes in the spectra upon addition of Li$^+$, Na$^+$, K$^+$, Sr$^{2+}$, Ca$^{2+}$, Cd$^{2+}$, Zn$^{2+}$, Hg$^{2+}$, Pb$^{2+}$, Ni$^{2+}$ and Cu$^{2+}$ metal ion solutions. However there is significant a change in $\lambda_{\text{max}}$ on addition of Ag$^+$ ion solution to the chromogenic receptor 8a and 8b with the appearance of a new band at 460 nm.

In continuation to above work the effect of anchoring group on recognition behavior upon complexation of various metal ions have been studied by synthesizing 1,3,5-triethylbenzene based azo-coupled chromogenic receptors 9a-e in dioxane:water 1:9 (V:V) at neutral pH (HEPES buffer) and in the presence of 0.1 M potassium nitrate (to maintain the constant ionic strength). There was a marked change in $\lambda_{\text{max}}$ in 9c upon addition of 10 equivalent of Cu$^{2+}$ with the appearance of a new band at 452 nm with a visual color change of the solution from yellow ($\lambda_{\text{max}}$ = 384 nm) to red ($\lambda_{\text{max}}$ = 452 nm) and no significant change was observed upon the addition of Li$^+$, Na$^+$, K$^+$, Sr$^{2+}$, Ca$^{2+}$, Cd$^{2+}$, Zn$^{2+}$, Hg$^{2+}$, Pb$^{2+}$, Ni$^{2+}$ and Ag$^+$ metal ion. The receptors 8 and 9 were able to detect
the Ag(I) and Cu(II) ion visually and in a concentration of $1 \times 10^{-5}$ M respectively, with the help of UV-Vis spectrophotometer, in the presence of other interfering metal ions.

To evaluate the metal binding affinity of receptor $13$, the changes in fluorescence intensity of $13$ upon addition of a different metal salts were recorded. A marked enhancement in fluorescence intensity has been observed upon addition of silver salt. On the other hand, no such significant changes in fluorescence spectra were observed when receptor $13$ was exposed to $\text{Cu}^{2+}$, $\text{Ni}^{2+}$, $\text{Co}^{2+}$, $\text{Zn}^{2+}$ or $\text{Hg}^{2+}$ salts under the same experimental conditions. Upon complexation of the $\text{Ag}^+$ ion, the N of the $\text{–C}=\text{N}$ group and O of the OH group are involved in coordination with the metal ion hindering the PET phenomenon and fluorescence is restored resulting in an off-to-on signal.

Thus the fluorogenic chemosensor $13$ was selective and sensitive for Ag(I), capable of detecting the metal ion in a concentration of $1\times10^{-5}$ M with the help of fluorescence spectrophotometer, in the presence of other interfering metal ions. The tripodal amine $5$ has also been successfully used to extract and transport Ag(I) and the receptor has been shown to be useful for repeated extraction and transportation experiments.

**Anion recognition**

Some neutral tripodal and dipodal receptors based on catechol and urea/thiourea which have the potential to act as colorimetric anion sensors are reported.

**Catechol based receptors**

The anion binding affinity of receptor $15$ was determined by the changes in absorption spectra of receptor $15$ upon addition of various anions such as $\text{F}^-$, $\text{Cl}^-$, $\text{Br}^-$, $\Gamma$, $\text{NO}_3^-$, $\text{CN}^-$, $\text{ClO}_4^-$, $\text{AcO}^-$, $\text{HSO}_4^-$ and $\text{H}_2\text{PO}_4^-$ (Fig. 2). In the absence of anions, the receptor $15$ in DMSO showed a band at $\lambda_{\text{max}}$ 274 nm ($\varepsilon_{\text{max}}$ 44600 M$^{-1}$ cm$^{-1}$) and two shoulders at $\lambda_{\text{max}}$ 306 nm ($\varepsilon_{\text{max}}$ 30400 M$^{-1}$ cm$^{-1}$) and $\lambda_{\text{max}}$ 353 nm ($\varepsilon_{\text{max}}$ 19200 M$^{-1}$ cm$^{-1}$). Addition of $\text{F}^-$ ion brings significant changes in the spectrum, on the other hand, no change was observed with $\text{Cl}^-$, $\text{Br}^-$, $\Gamma$, $\text{NO}_3^-$, $\text{CN}^-$, $\text{ClO}_4^-$, $\text{AcO}^-$, $\text{HSO}_4^-$ and $\text{H}_2\text{PO}_4^-$ ions. On addition of $\text{F}^-$ ion in the solution of $15$ the highest energy band shows a slight
hypsochromic shift whereas the shoulder at 353 nm disappears and a new band appears at λ_max 433 nm.

Fig. 2. Showing changes in the UV-vis spectrum of 15 in DMSO (10 μM) on addition of (100 μM) various anions, inset shows the visual color change on addition of F⁻ ion.

The receptor 15 was supposed to provide anion recognition through H-bonding interactions employing –OH groups of catechol only. However the results show that the deprotonation rather than the H-bonding is the key factor triggering the chromogenic effect. This deprotonation is being facilitated by the high intrinsic acidity of catechol groups, highly basic F⁻ ion and a polar solvent like DMSO. Fluoride ion though is a weak base, the extreme stability of [HF₂]⁻ is well documented and it is known to behave as a very strong base and can cause the deprotonation of catechol groups. The deprotonation forms the stable [HF₂]⁻ anion. The existence of [FHF]⁻ is unequivocally proved by the presence of a well formed triplet at ~ δ16.07 ppm in the proton nmr of 15 in the presence of 12 equivalents F⁻ ion. Thus the receptor 15 forms an example of a highly selective and efficient naked eye sensor for F⁻ ion at a concentration of 10 μM. The results obtained with the tripodal receptor 15 were also compared with the analogous monopodal receptor 16 containing just one catechol moiety. Comparison of the sensing ability of tripodal receptor 15 with monopodal receptor 16 has showed that the former gives a much enhanced response towards the fluoride ion.

Thiourea derivatives-

On addition of F⁻ ion into thiourea ligands 18a, 18b, 19a the absorption band at ~ 360 nm disappears and a new band at ~ 417 nm appears with a red shift of Δλ_{max} ~ 57
nm. The complex formation on addition of F⁻ ion solution can be visually perceived through a color change from pale to bright yellow.

In the spectrophotometric titrations of 18a, 18b and 19a (Fig. 3) a gradual decrease in the intensity of the band at ~355 nm with a simultaneous increase in the intensity at ~410 nm was seen on increasing the concentration of F⁻ ion solution for all three receptors. Fitting the changes in UV-vis spectra of these receptors gave a good fit and showed that for all receptors, species with 1:1 stoichiometry is the most stable in solution form. The binding constants calculated for receptors 18 and 19. The stoichiometry of these complexes formed was also determined by Job’s plot and was found to be 1:1. The selective recognition of tripodal 18a, 18b and dipodal 19a with F⁻ was also evident in ¹H NMR titration experiment.

Fig. 3. Changes in absorbance spectra of 19a (10 μM) upon addition of TBAF (0-100 μM) in DMSO. Inset- Shows a plot of absorption vs. concentration of F⁻.

Urea derivatives-
The results with the urea derivatives 18c, 18d, 18e and 19b are similar yet different in many ways and more interesting and intriguing as well. The UV-vis spectrophotometric titrations of the receptors 18c-18e with tetrabutylammonium salts of various anions show chromogenic response towards F⁻ ion. On addition of increasing amount of TBAF the absorption band at ~ 351 nm of receptors 18c, 18d (Fig. 4) and 18e decreases and a new
band at $\lambda_{\text{max}}$. 474 nm ($\Delta\lambda \sim 125$ nm) emerges with a visual color change from pale to dark yellow.

Fig. 4. Showing changes in absorbance spectra of 18d (10 $\mu$M) upon addition of TBAF (0-1100 $\mu$M) in DMSO.

There are three important differences in the behavior of urea and thiourea derivatives here. First is that the thiourea derivatives start responding at lower molar equivalents of the added anion solution. Secondly the original band decreases in absorbance but it does not disappear completely at any time and sustains even at saturation of 474 nm band which is achieved at ten times higher concentration of the anion. Finally the spectral changes are transient and go back to the original situation shortly and the visual color of the solution also reverts back. Similarly to investigate the binding behavior of urea based receptors 18c, 18d, 18e and 19b the NMR titrations have been also performed.

Surmising the above result it has been found that thiourea derivatives are proved to be very selective and sensitive towards small and spherical F$^-$ ion with some interference from tetrahedral H$_2$PO$_4^-$ ions. Their recognition act involves stable H-bonded complexes. Urea derivatives on the other hand, are also selective for F$^-$ ions but have very low sensitivity and work only at relatively higher concentrations of the anion. Their sensing process is simply based upon Lewis acid-base reaction which is completely reversible with time. The chapter contains the synthesis & characterization of some mono, di and tripodal receptors and their ion recognition studies.
Part B

Chapter 3: Transition metal complexes and their role in catecholase activity and phosphodiester cleavage: An introduction

An important goal in supramolecular chemistry is the synthesis of molecules that exhibit catalytic activity analogous to the activity of enzymes. Such artificial enzymes have same catalytic function but these are more stable and structurally less complex than enzymes. The synthetic enzyme models are helpful in understanding the mechanistic aspects of enzyme action. Thus the studies on the model compounds mimicking are very useful and promising for the development of new, more efficient bioinspired, environment friendly catalysts. Biochemically important processes like catalytic oxidation of 3,5-di-tert-butylcatechol to quinone (catecholase activity) and hydrolytic reactions, i.e. hydrolysis of phosphodiester bond (phosphodiester cleavage) are of considerable importance and are a topic of discussion presently.

1. Catecholase activity

Catecholase activity is the oxidation of a broad range of catechols to quinones through the four-electron reduction of molecular oxygen to water undertaken by catechol oxidase. Dinuclear copper proteins like hemocyanin, tyrosinase and catechol oxidase are known as type-3 copper(II) proteins. The active site contains dicopper core in which both copper ions are surrounded by three nitrogen donor atoms of histidine residues. The characteristic feature of these enzymes is the ability to reversibly bind dioxygen at ambient conditions.

In literature four approaches have been used in the mechanistic studies on the model compounds for studying catecholase activity.

- Substrate-binding studies
- Structure-activity relationship
- Kinetic studies on catalytic reactions
- Stoichiometric oxidation of catechol substrates by the peroxo- and oxo-dicopper complexes
Out of these, the approach of structure activity has been more frequently employed by various groups. Under this approach the relationships between metal-metal distance; electrochemical properties; exogenous bridging ligand; ligand structure and solvent nature, with the catecholase activity have been exploited.

2. **Phosphodiester cleavage**

Hydrolytic reactions have received considerable attention as an important biochemical process, for example hydrolysis of amino acid esters, peptides, and phosphate esters by esterases, peptidases and phosphoesterases, respectively. Out of them the phosphate diester cleavage is of particular interest. Hydrolytic enzymes such as phospholipase C, nuclease P1, RNAase A, alkaline phosphatase, DNA polymerases, phosphotriesterase, recombinases, topoisomerases, reverse transcriptases, that cleave phosphate ester bonds efficiently often have in their active site two or three divalent transition metal ions such as Zn(II), Mg(II), Mn(II), Ni(II), or Fe (III) that act as Lewis acid sites in the catalysis and generally facilitated by cooperative action of two metal ions. There are two modes prevalent for the catalysis of phosphate diester cleavage namely *hydrolysis* or *transesterification*. Various metal ions in the active sites are responsible for performing some crucial functions such as

- Act cooperatively as Lewis acid sites
- Activate the nucleophile and substrate cooperatively
- Stabilize the pentacoordinate transition state
- Stabilize the leaving group.

The synthetic models for dinuclear metallo-phosphoesterases are dinuclear transition metal complexes in which the two metal centers are kept at a particular distance by selecting an appropriate spacer. Thus the molecular scaffolds with a proper preorganization of multiple catalytic groups and appropriate flexibility are highly required for these synthetic models. The distance between the two metal ions is very crucial parameter for the catalytic activity. The synthesis and design of models with a high degree of cooperative action between two metal centers is highly required. Thus a number of synthetic models for dinuclear hydrolytic metallo-enzymes have been developed and their biomimetic activity has been investigated. **The chapter includes an**
overview on transition metal complexes which have been used for these two types of catalytic studies.

Chapter 4: Synthesis, X-ray crystal structure analysis, spectral & magnetic studies and catalytic activity of Cu(II), Ni(II) and Zn(II) complexes with di- and tri-podal ligands

Nine complexes \([\{\text{Cu}(L1)\}_2(\mu-\text{CH}_3\text{COO})_2]\) (1), \([\{\text{CuL2}\}(\text{CH}_3\text{COO})]\) (2), \([\{\text{Cu(CH}_3\text{COO})\}_2(\mu-L3)_2]\) (3), \([\{\text{Cu}(L4)\}_2(\mu-(\text{CH}_3\text{COO})_2]\) (4), \([\text{Cu}_3(L5)(\text{CH}_3\text{COO})_3]\) (5), \([\{\text{Ni}(\mu-\text{L1})(\text{CH}_3\text{COO})(\text{H}_2\text{O})_2\}]\) 0.25 H_2O (6), \([\{(\text{Ni}(\mu-L2)(\text{CH}_3\text{COO})\}_2(\mu-\text{H}_2\text{O})]\) (7), \([\{\text{ZnL2})(\text{CH}_3\text{COO})]\) (8), \([\text{Zn}_2(L4)(\mu-\text{CH}_3\text{COO})_2, (\text{CH}_3\text{COO})\}] (9) of Cu (II), Ni (II) and Zn (II) acetate with Schiff base ligands and their reduced products (scheme 2) have been synthesized and characterized by various spectroscopic methods.

Scheme 2. Showing the ligands used for the complexation

Synthesis of receptors

All the compounds have been characterized by elemental analysis, IR and UV-vis spectroscopy. Whenever possible the NMR (for 8 and 9), ESI Mass, thermal analyses and molar conductivity have also been determined. The X-ray crystal structures of 1, 2, 3, 6, 7, 8 and 9 have been solved. The room temperature magnetic moments of all the complexes have been measured and variable temperature magnetic susceptibilities have
been calculated for 1 and 3 which have been confirmed to exist as weak dimers by X-ray diffraction methods. The molar conductivity measurements show that compounds 1-5 are non-electrolytes.

**Spectral Characterization**

The IR spectra of 1, 2, 5, 6, 7 and 8 show –C=N characteristic bands around 1649- 1608 cm⁻¹, which are absent in the reduced products 3, 4 and 9. The latter three complexes show medium to weak broad bands due to N-H stretching frequency. The νC=N stretching band shifts to a lower frequency by 10, 26, 58, 28, 31 cm⁻¹ and to a higher frequency by 14 cm⁻¹ in 1, 2, 5, 7, 8 and 6 clearly showing its participation in coordination.

The electronic absorption spectra of complexes 1-5 show strong red shifted (cf. spectra of ligands) charge transfer bands in the range 369-423 nm which have been tentatively assigned to ligand to metal transitions. Compounds 1 to 5 show weak d-d bands in the range λmax. 647– 690 nm in the visible region. The electronic absorption spectra of complexes 6-7 suggest that each complex has octahedral environment for the Ni(II) ions. A red shifted charge transfer bands in the range 211-368 nm have been assigned to ligand to metal transitions. Complexes 6 and 7 show weak d-d bands at λmax 886 & 600 and 1032& 634 nm respectively. The broadness of the absorption maxima and low intensity are suggestive of d – d transitions and can be assigned to the 3A2g → 3T1g (F) and 3T2g (F) transitions, respectively. Another spin-allowed d-d transition assigned to the 3A2g → 3T1g (P) is not visible as it merge into ligand charge transfer transition. The 1H NMR spectra of complexes 8 and 9 show shifts w.r.t the spectra of free ligands which serves as evidence for complexation.

**X-ray crystal structures**

The solid state structures of 1, 2, 3, 6, 7, 8 and 9 have been determined using single crystal X-ray diffraction method (Fig.5). The compounds 1 and 3 are dinuclear complexes of the tridentate ligands, where the two Cu(II) centers have square pyramidal geometry with bridging acetate or phenoxo groups. Complex 2 is mononuclear with a square pyramidal stereochemistry. The compound 6 is mononuclear nickel complex with octahedral geometry whereas compound 7 is dinuclear nickel complex with each Ni(II)
ion being six coordinated. The compound 8 is a mononuclear five coordinated Zn(II) complex with distorted square pyramidal stereochemistry around Zn(II). The compound 9 is a dinuclear Zn(II) complex having two Zn(II) ions in two different coordination environments. The coordination geometry around one of them distorted tetrahedral but that around other may be called as a trigonal bipyramid.
**Catecholase studies**

All the copper complexes were subjected to catecholase-mimetic activities to find their capability to act as catalysts for the oxidation of alcohols to quinones, like catechol oxidase. The oxidation of 3,5-DTBC to corresponding product 3,5-di-tert-butylquinone (3,5-DTBQ) was followed by the development of a considerably stable and strong absorption band at 390 nm in methanol. All the complexes 1-5 showed activity towards the oxidation of catechols with 4 and 1 showing significant catecholase activity (Fig. 6). The kinetic experiments have been also performed to determine the dependence of the rates on the substrate concentration and various kinetic parameters. At higher concentrations, saturation kinetics was found for all the compounds. The effect is more pronounced for 4 and 1 whereas for the remaining three complexes the rates are almost independent of the substrate even at lower concentrations. The dependence on the substrate concentration indicates a catalyst-substrate binding to be an initial step in the catalytic mechanism. The rates of reactions obtained for various 3, 5-DTBC concentrations were fitted to the Michaelis–Menten equation and linearized by means of Lineweaver-Burk plot to calculate various kinetic parameters for these compounds.
Fig. 6 Increase of quinone band at 390 nm after addition of 100 equivalents of (3,5-DTBC) to a solution containing complex 4 (10⁻⁴ M) in methanol at 22 °C. The spectra were recorded after every 2 min.

**Phosphodiester cleavage studies**

The kinetic studies of bis (4-nitrophenyl) phosphate (BPNP) hydrolysis for the catalytic activity of the synthetic ligand-metal complexes were performed in the complexes 1, 2, 3, 6, 7, 8 and 9. The kinetic studies were performed in DMSO-H₂O (30 %, v/v). Studies regarding the effect of pH on the hydrolysis reaction were performed in the pH range 7.00-11.00 (HEPES pH 7.00-8.00; CHES pH 8.50-10.00; EPPS pH 10.00-11.00), under a 10-fold excess of the substrate, at 75 °C. Experiments to determine the dependence of the reaction rate on the substrate concentration were carried out at 75 °C, pH 10.00, [Complex] = 0.2 mM, [BPNP] = 2.0 to 10 mM. The effect of temperature on the reaction rate was investigated in the range 25-75 °C at pH 10.00 and a 10-fold excess of substrate (2 mM) relative to complex (0.2 mM) was maintained. The hydrolysis of BPNP to corresponding hydrolyzed product p-nitrophenolate was followed by the development of a considerably stable absorption band at 400-410 nm in 30% DMSO solution. Only 7 exhibited rate acceleration in the hydrolysis of BPNP. The rate constant values show that the rate acceleration in the hydrolysis of BPNP also depends upon the pH of the solution. The reaction rate increases with increase in pH, and finally gets saturated at higher pH 11. The complex shows very low activity at pH 7 and 8 which slightly increases at pH 9 and maximum at pH 10 (Fig. 7). The rate constants for this complex were calculated to be 2.9 x 10⁻² and 5.1 x 10⁻² at pH 9 & 10, respectively.
Fig. 7  Showing the course of absorption maxima at 406 nm with time for BPNP (2 mM) in solutions of complex 7 (0.2 mM) in 30% DMSO solution at different pH.

This pH dependent rate constant suggest that deprotonation of a coordinated water molecule is necessary to generate the catalytically active Ni(II)-coordinated hydroxo species. The chapter contains details of the characterization of these complexes and an account of their catecholase activity and phosphodiester cleavage activity.