

Optical detection of sodium salts of fluoride, acetate and phosphate by a diacylhydrazine ligand by the formation of a colour alkali metal complex

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Abstract. A solution of N, N'-diacylhydrazine ligand in organic solvent is potential for colourimetric detection of F⁻/AcO⁻/PO₄³⁻ via -NH deprotonation, tautomerization and its stabilization as a colour alkali metal complex.

Keywords. Anion sensing; colourimetric detection; alkali metal complex; single crystal X-ray; deprotonation.

1. Introduction

Anions like fluoride, acetate and phosphate play an important roles in a wide range of chemical and biological systems and they are also of health concern.^{1,2} Many synthetic chromogenic and/or fluorogenic sensors for fluoride, acetate and phosphate have been reported in recent years.³ Colourimetric sensing of anions by these systems are mostly explained *via* deprotonated receptors and their stabilization upon delocalization. Thus, most of the above sensors are not suitable for colourimetric sensing of these anions even in the presence of a trace quantity of water in the system and are not applicable in many bio-analytical applications. Of course, colourimetric detection of fluoride in aqueous medium through chemodosimetric approach has been reported scarcely.⁴ Gunnlaugsson and other group have also developed few systems which are capable of binding acetate in competitive solvent like water along with 'naked eye' colour change.⁵ To the best of our knowledge colourimetric detection of fluoride or phosphate *via* deprotonation mechanism in the presence of water is not known. Here, we describe a new approach for the colourimetric detection of fluoride, acetate and phosphate *via* deprotonation, tautomerization followed by complex formation which is established by single crystal X-ray structural analysis.⁶

2. Experimental

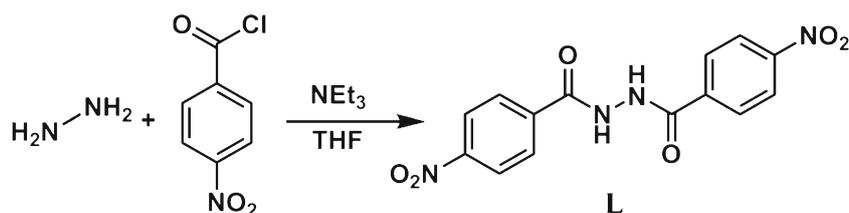
2.1 Materials and methods

¹H NMR and ¹³C NMR spectra for **L** and complex **1** were recorded on Bruker 300 MHz FT-NMR spectrometer (model: DPX-300) in DMSO-*d*₆ at 25°C. HRMS measurements were carried out on QToF-Micro YA 263 instruments. Elemental analyses were performed on a CHN 2400 Ser II Elemental Analyzer. UV/Vis spectra were recorded on a Perkin-Elmer Lambda 950 UV/Vis Spectrometer and with a quartz cuvette (path length: 1 cm). Acetonitrile (MeCN), dimethyl formamide (DMF) and all the sodium salts were purchased from Spectrochem Ltd., India. Chemical shifts for ¹H and ¹³C NMR were reported in parts per million (ppm), calibrated to the residual solvent peak set, with coupling constants reported in Hertz (Hz).

2.2 Synthesis of ligand, **L**

L was synthesized by a modified literature procedure (scheme 1).⁷ To a solution of hydrazine hydrate (0.4 ml) in dry THF was added triethylamine (3.2 ml) in ice cold condition and the solution stirred for 15 min. To the stirred solution 4-nitrobenzoyl chloride (3 g) in dry THF was added, a yellow precipitate appeared after sometime and the solution was stirred overnight and finally refluxed for 3 h. The whole solution was then evaporated *in vacuo* and thoroughly washed with H₂O to remove triethylammonium chloride and excess acid

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Scheme 1. Synthesis of **L**.

chloride and finally washed with diethyl ether. Molecular receptor **L** was obtained as a pale yellow colour solid (90% yield). ^1H NMR (300 MHz, DMSO-d_6): 11.00 (s, $-\text{NH}$), 8.38 (d, $J = 8.58$ Hz, 4H), 8.15 (d, $J = 8.61$ Hz, 4H). ^{13}C (75 MHz, DMSO-d_6) 164.69, 149.91, 138.31, 129.44, 124.24. HRMS: 331 ($\text{M}+\text{H}^+$), 353.3573 ($\text{M}+\text{Na}^+$), 369.3293 ($\text{M}+\text{K}^+$). Anal. Calcd. for $\text{C}_{14}\text{H}_{10}\text{N}_4\text{O}_6$: C, 50.66; H, 3.13; N, 16.77. Found: C, 50.92; H, 3.13; N, 16.96.

2.3 Synthesis of complex, **1**

To a DMF (10 ml) solution of molecular receptor **L** (50 mg), aqueous solution of Na_2CO_3 (100 mg in 10 ml water) was added. The solution immediately turned to reddish colour. It was then filtered and kept for crystallization; pink colour crystal was obtained within 24 h (65% yield). ^1H NMR (300 MHz, DMSO-d_6): 10.66 (br, $-\text{NH}$), 8.32 (d, $J = 10.53$ Hz, 4H), 8.11 (d, $J = 8.07$ Hz, 4H). Anal. Calcd. for $\text{C}_{28}\text{H}_{34}\text{N}_8\text{O}_{20}\text{Na}_2$: C, 39.63; H, 4.04; N, 13.20. Found: C, 39.39; H, 3.94; N, 12.76.

2.4 X-ray crystallographic analyses

The crystallographic data and data collection details for complex **1** was given below. A crystal of suitable size was selected from the mother liquor and immersed in partone oil, then mounted on the tip of a glass fibre and cemented using epoxy resin. Intensity data for the crystal were collected using Mo K_α ($\lambda = 0.7107$ Å) radiation on a Bruker SMART APEX diffractometer equipped with CCD area detector at 120 K. The data integration and reduction were processed with SAINT^{8a} software. An empirical absorption correction was applied to the collected reflections with SADABS.^{8b} The structure was solved by direct methods using SHELXTL⁹ and was refined on F^2 by the full-matrix least-squares technique using the SHELXL-97¹⁰ program package. Graphics are generated using PLATON,¹¹ MERCURY 2.2¹² and ORTEP3v2. The non-hydrogen atoms are

treated anisotropically. Wherever possible, the hydrogen atoms are located on a difference Fourier map and refined. In other cases, the hydrogen atoms are geometrically fixed. Crystallographic data for complex **1**: Triclinic, P-1, $a = 7.761(9)$ Å, $b = 9.182(11)$ Å, $c = 13.791(17)$ Å, $\alpha = 73.221(11)^\circ$, $\beta = 86.963(12)^\circ$, $\gamma = 74.063(12)^\circ$, $V = 904.4(19)$ Å³, $Z = 1$, $D_c = 1.558$ g/cm³, $T = 120$ (2) K, $\mu = 0.153$ mm⁻¹, GOF on F2 = 1.080, $R = 0.0699$, $wR = 0.2052$ [$I > 2\sigma(I)$]. CCDC 781918 contains the supplementary crystallographic data for complex **1**.

3. Results and discussion

The molecular receptor **L** was synthesized and characterized by NMR, ESI-MS and elemental analyses. Complex **1** was synthesized by the reaction of **L** with Na_2CO_3 in a DMF solution. Pink coloured single crystals of complex **1** suitable for X-ray crystallographic analysis is obtained after slow evaporation of the solvent. All compounds were obtained in good yield. The detailed solution and structural analysis of the complex was described below.

Here, we explored **L** for colourimetric sensing of different inorganic anions in a semi-aqueous solvent system. Colourimetric and UV-Vis experiments were carried out with different anions as their sodium salts. When 0.3 ml of 10^{-2} (M) anions in water was added to 2.7 ml solution of **L** (1×10^{-4} M) in MeCN/DMF (4.9 : 0.1)(v/v), colour changes from colourless to yellow in cases of fluoride, acetate and phosphate (figure 1), whereas the other anions induced negligible responses. In cases of fluoride, acetate and phosphate a new absorption peak at 401 nm appear with molar extinction coefficient ($\epsilon_{401\text{nm}}$) values of 5,050, 9,000 and 17,365 $\text{M}^{-1} \text{cm}^{-1}$, respectively (figure 1). It was important to note that yellow colour persists even in the presence of significant amount of water in the system. To determine the detection limit and selectivity of these anions further UV-Vis as well as colourimetric experiments for fluoride, acetate and phosphate

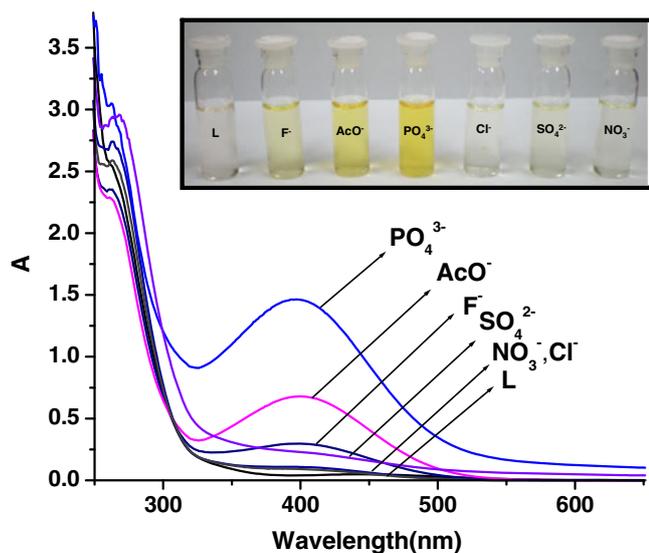


Figure 1. UV-Vis spectra and colour changes (inset) observed upon addition of 0.3 ml of 10^{-2} M aqueous solution of anions to the solution of **L** (10^{-4} M) in MeCN/DMF (4.9:0.1 v/v, 2.7 ml).

were carried out in two different experimental conditions where final anion concentration and the amount of water play important roles. Figure 2 showed UV-Vis and colourimetric experimental results when 0.03 ml of 5×10^{-3} (M) anion solution was added to 2.97 ml of 10^{-4} (M) solution of **L**. In this case a yellow colouration was observed only for acetate and phosphate where

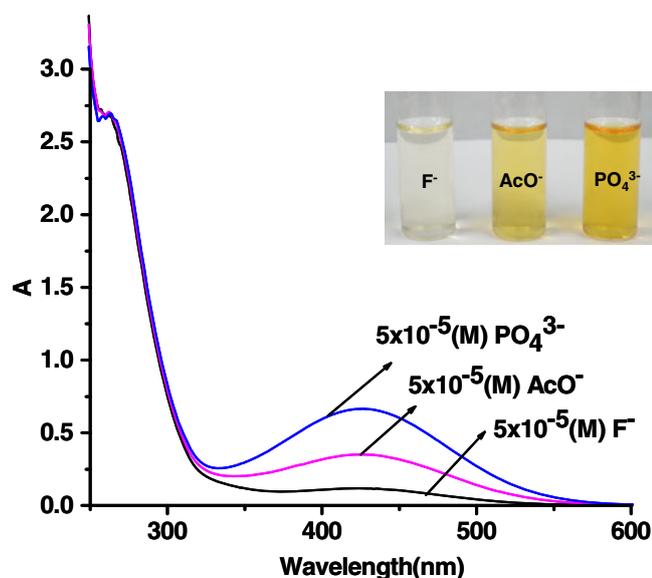


Figure 2. UV-Vis spectra and colour changes (inset) observed upon addition of 0.03 ml 5×10^{-3} M aqueous solution of anions to the solution of **L** (10^{-4} M) in MeCN/DMF (4.9:0.1 v/v, 2.97 ml).

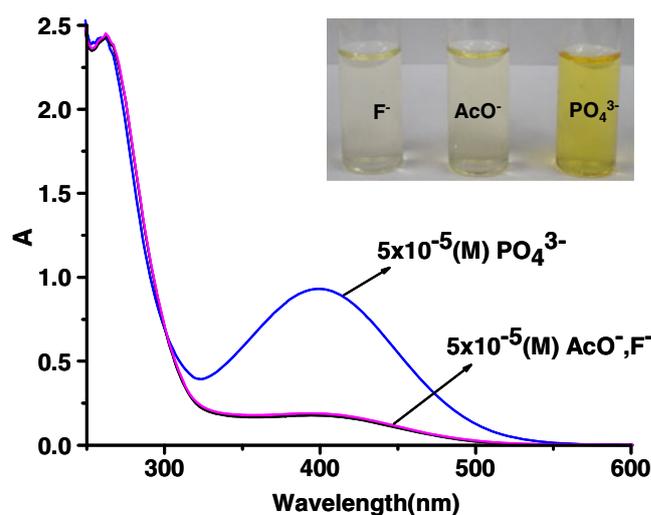
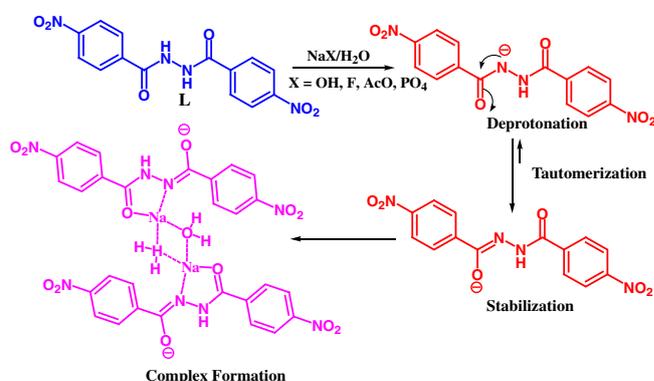


Figure 3. UV-Vis spectra and colour changes (inset) observed upon addition of 0.3 ml 5×10^{-4} M aqueous solution of anions to the solution of **L** (10^{-4} M) in MeCN/DMF (4.9:0.1 v/v, 2.7 ml).

final anion concentration is 20 times dilute and water content is 10 times less than the previous case.

Keeping the final anion concentration fixed and upon increasing the water content by 10 times with respect to figure 2, only phosphate ion showed selective colour and spectral change (figure 3). Further we have carried out experiment where the colour sustainability and selectivity even in the presence of 20% water was obtained *via* distinct and selective colour change for phosphate (figure S1). It was clear from above three experiments that in a particular condition, absorption maxima for all the anions were same with different molar extinction coefficient values. This clearly indicates that the origin of colour appearance could be the



Scheme 2. The proposed mechanism for complex formation in aqueous solution.

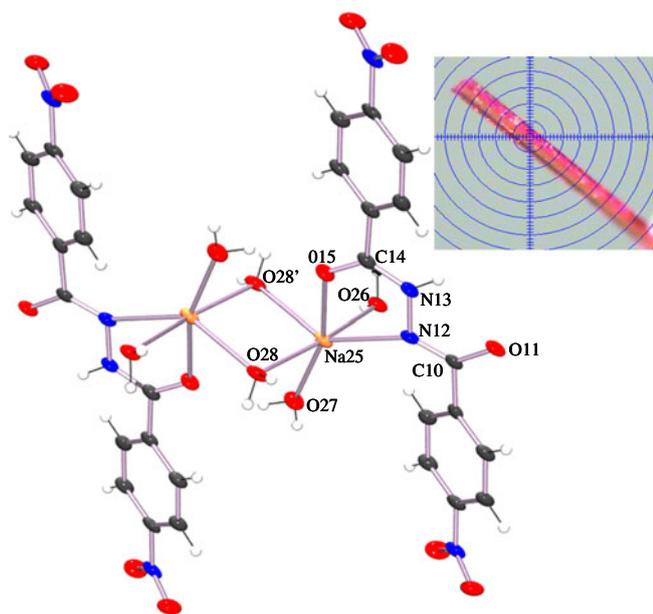


Figure 4. Single crystal X-ray structure of complex **1**; inset shows the crystal of complex **1** (orange:Na; black:C; red: O; deep blue: N; white: H.).

same for these three anions and that could be due to the proton dissociation equilibrium. To test this phenomenon, NaOH/Na₂CO₃ solution was added to the solution of **L** (figure S2) in similar experimental conditions and a similar colour change was also observed. This indeed indicates deprotonated species of the receptor must be involved for the colour generation. Sustainability of the colour in the presence of significant amount of water suggests stabilization of the deprotonated species in aqueous medium *via* tautomerization (scheme 2). Efforts have been made to isolate the crystals of the colour complexes of the chemosensor with sodium salts of fluoride, acetate, phosphate, carbonate and hydroxide in DMF-water mixture. A pink colour

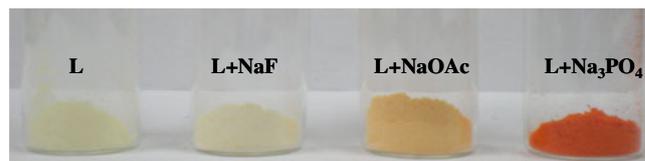


Figure 5. Colour changes observed upon grinding 4 equivalents of NaF, NaOAc and Na₃PO₄ with **L**.

needle-like crystal of complex **1** in case of Na₂CO₃ was isolated and characterized by single crystal X-ray, ¹H-NMR and elemental analyses. X-ray crystal structural analysis of complex **1** clearly showed the evidence of -NH deprotonation which further stabilizes upon tautomerization and followed by alkali metal complex formation. Single crystal X-ray structural analysis (figure 4) reveals complex **1** as a di-sodium aquo-bridged complex of **L** where each sodium ion was in six-coordination state and showed a distorted octahedral geometry around the metal centre (table 1). Two water molecules bridge two Na⁺ with a Na⁺Na separation of 5.341 Å. Deprotonated -NH in the complex **1** was identified from the N-C and C-O bond distances. The C(10)-N(12) and C(14)-O(15) bond distances are 1.306 Å and 1.253 Å which are significantly shorter than the C(14)-N(13) and C(10)-O(11) bond distances 1.315 Å and 1.301 Å, respectively.

Shorter distances in C(10)-N(12) and C(14)-O(15) can be explained due to the partial double bond character after deprotonation and its delocalization. From the solution and single crystal X-ray analysis, we propose the possible mechanism (scheme 2) for the persistence of colour even in the presence of water in the system as diacylhydrazine ligand. Interestingly, this system can also be used for colourimetric detection of phosphate ion in the solid phase. When a 1:4 mixture of molecular receptor, **L** and sodium salts of respective anions were

Table 1. Hydrogen bonding interactions in complex **1**.

D-H...A	D-H (Å)	H...A (Å)	D...A (Å)	∠D-H...A (°)
N13-H1...O26	0.788	2.275	3.043(5)	165.17
O26-H26A...O11	0.915	1.873	2.762(6)	163.21
O26-H26B...O29	0.764	2.037	2.799(6)	174.82
O27-H27A...O15	0.902	1.978	2.797	150.13
O27-H27B...O1	0.692	2.387	3.068	168.37
O28-H28A...O29	0.818	2.149	2.951	166.73
O28-H28B...O11	0.909	2.041	2.891	155.07
O29-H29A...O11	0.805	1.968	2.725	156.53
O29-H29B...O23	0.837	2.239	3.067	170.16

grinded, a distinct red colour appeared only for phosphate ion whereas, yellowish colour was detected for acetate ion (figure 5).

4. Conclusion

In summary, we have described a simple N, N'-diacylhydrazine molecular receptor which can detect fluoride, acetate and phosphate colourimetrically in a semi-aqueous solvent system and it shows selectivity towards phosphate at lower concentration. Further, single crystal X-ray structural analysis confirms –NH deprotonation in the presence of basic anions and its stabilization through tautomerization in aqueous medium and subsequent formation of a colour alkali metal complex. It has been found that in the case of phosphate the colour intensity is maximum among the anions. This could be due to the most basic nature of tri-negative phosphate anion which could deprotonate **L** easily and effectively. Consequently, the formation of the disodium complex **1** (i.e., concentration of **1**) in solution becomes maxima in the case of phosphate.

Supplementary data

Experimental section and spectral data (¹H, ¹³C NMR and ESI-MS) for **L** and (¹H NMR) complex **1** are provided. Crystallographic table, selected geometric parameter and hydrogen bonding table for complex **1** are also provided for reference. The electronic supplementary information can be seen in www.ias.ac.in/chemsci.

Acknowledgements

PG gratefully acknowledges the Department of Science and Technology (DST), New Delhi, India for financial support; PB and RD would like to acknowledge Council of Scientific and Industrial Research (CSIR), New Delhi, India for fellowships. X-Ray crystallography was performed at the Facility in the Department of Inorganic Chemistry, IACS. DST-funded National Single Crystal X-ray Diffraction.

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