FLUORESCENCE PROPERTIES OF METAL COMPLEXES OF 2-*N*-ANILINOPYRIMIDINE

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Abstract

2-N-anilinopyrimidine was used as specific binder towards selected transition metals ion such as Mn(II), Ni(II) and Cr(II) in a 1 : 2 ratio (metal : ligand) to give their respective complexes. The structures of the ligand and complexes were confirmed by spectroscopic analysis. Fluorescence studies of metal complexes of 2-N-anilinopyrimidine and the ligand itself were carried out under various conditions using methanol as the solvent. In general, metal ions, especially paramagnetic ions, are able to quench the fluorescence of organic ligands. The fluorescence intensity was studied based on several factors such as pH, capped and uncapped conditions. The compounds showed higher intensity in capped samples compared to uncapped samples.

Abstrak

2-N-anilinopyrimidina digunakan sebagai ligan di dalam pembentukan kompleks logam – logam peralihan seperti Mn(II), Ni(II) dan Cr(II) mengikut nisbah 1 : 2 (logam : ligan). Struktur sebatian – sebatian ini kemudiannya dikenalpasti secara analisis spektroskopi. Kajian pendafluoran dilakukan dengan menggunakan metanol sebagai pelarut dalam keadaan sampel bertutup dan sampel dalam keadaan terbuka. Puncak pendafluoran menunjukkan penurunan bagi sampel terbuka berbanding sampel bertutup.

Keywords: 2-N-anilinopyrimidine, fluorescence, metal complexes, pH effect, capped samples, uncapped samples

Introduction

Pyrimidine is a heterocyclic aromatic organic compound containing two nitrogen atoms at positions 1 and 3 of the six-membered ring (Figure 1). Compounds containing pyrimidine rings play a significant role in many biological systems [1]. The pyrimidine ring system, present in nucleic acids, several vitamins, coenzymes and antibiotics, provides potential binding sites for metal ions, and any information on their coordinating properties is important as a means of understanding the role of the metal ions in biological systems. Since pyrimidine bases are minor constituents of nucleic acids, the chemistry of pyrimidine has been the subject of much research owing to their applications in molecular biology and medicine [2]. Moreover, some divalent transition metal complexes of pyrimidine play an important role in the maintaining of functionality of DNA, as well as being used in the preparation of pesticides.

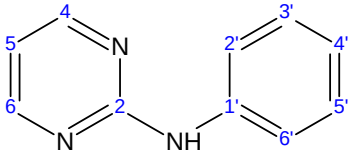


Figure 1: Two nitrogen atoms at positions 1 and 3 of six-membered ring

In general, molecular fluorescence spectrometry can be used for quantification of aromatic, or highly unsaturated, organic molecules present at trace concentrations, especially in biological and environmental samples. It also can be extended to a wide variety of organic and inorganic compounds via chemical labeling and derivatization procedure [3].

It is known that some heterocyclic compounds are fluorescent but the fluorescence-structure relationship is less investigated. Investigations on the fluorescence of these compounds are made difficult because their fluorescence characteristics are often dependant on the nature of the solvents used [4]. In general, compounds tend to be fluorescent in polar solvents. Under these condition, the lone pair of electrons are bonded and the longest absorption wavelength is due to $\pi \rightarrow \pi^*$ transition, instead of $n \rightarrow \pi^*$.

There are several factors that affect fluorescence intensity of a compound, such as influence of solvents and the structure of the compound itself. In general, metal ions, especially paramagnetic ions, are able to quench the fluorescence of organic ligands by enhancing the rate of same non-radiative processes that compete with fluorescence, such as intersystem crossing [5].

Quenching of fluorescence of a ligand by transition metal ions during complexation is a rather common phenomenon which is explained by processes such as magnetic perturbation, redox-activity, electronic energy transfer and etc. [6 – 7].

This paper will report on the preparation of 2-*N*-anilinopyrimidine and its metal complexes and a study of their fluorescence characteristics for capped and uncapped samples.

Experimental

Synthesis

2-N-anilinopyrimidine

2-Chloropyrimidine (0.5160 g , 0.0045 mol) was added to aniline (5 cm^3 , 0.0045 mol) and heated in an oil bath at 140^oC for about 3 hours. The mixture was then cooled and dissolved in a minimum volume of water. The aqueous layer was then extracted with ether (3x10 cm^3). The ether layer was washed with water and dried over anhydrous sodium sulphate. Evaporation of ether gave the product, yellow powder. Yield 0.4740 g, 70 % .

Metal complexes of 2-N-anilinopyrimidine

Each acetate salts of Mn(II) and Cr(II) and the carbonate of Ni(II) in acetic acid was refluxed and stirred for about an hour. 2-*N*-anilinopyrimidine was then added to the metal ion solution in ratio 1 : 2 (metal : ligand), the mixture was then stirred and refluxed for another 8 hours. The resultant solution was evaporated to dryness. Colored complexes of pale brown for Mn(II) complex (0.3217g, 67%), pale green for Ni(II) complex (0.2394g, 58%) and dark green for Cr(II) complex (0.3914g, 73%) were obtained.

Spectroscopic analysis

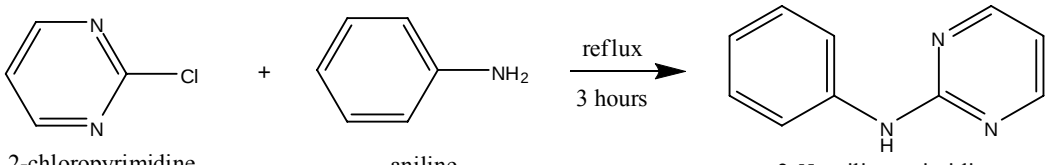
Infrared spectra were recorded as KBr discs(solids) on a Perkin Elmer 298 Infrared Spectrometer and FTIR Perkin Elmer 1600 Series. ^{1}H-NMR and ^{13}C-NMR spectra were measured on JEOL JNM-LA400FT NMR System in $CDCl_3$ with TMS as internal standard at 25 ^oC.

Fluorescence Studies

2-*N*-anilinopyrimidine and its metal complexes with the same concentration of $2.5x10^{-4}$ M were prepared in methanol. The fluorescence measurement was carried out in a quartz cell, using Fluorescence Spectrometer Model F-2000 Hitachi at room temperature with the same instrument setting.

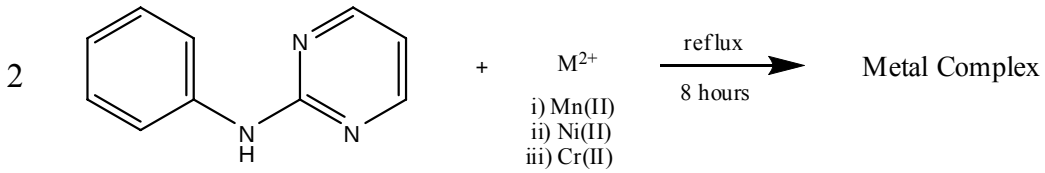
Results and discussion

2-*N*-anilinopyrimidine was obtained when commercially available 2-Chloropyrimidine was reacted with aniline, as shown in Scheme 1. 2-*N*-anilinopyrimidine was then used as specific binder towards the transition metal ions, Mn(II), Ni(II) and Cr(II) in a 1 : 2 ratio (metal : ligand) to give their respective complexes, as shown in Scheme 2.



2-chloropyrimidine aniline 2-*N*-anilinopyrimidine

Scheme 1



2-*N*-anilinopyrimidine

Scheme 2

The ^{1}H-NMR spectrum of 2-*N*-anilinopyrimidine showed a doublet at 8.40, which was due to H_4 and H_6 of pyrimidine ring. A doublet at 7.59 was due to $H_{2'}$ and $H_{6'}$ of the benzene ring. A triplet was recorded at 7.34, was due to proton resonance at $H_{3'}$, $H_{5'}$ and N-H group. A triplet peak was observed at 7.03 was due to $H_{4'}$ of the benzene ring and another triplet was recorded at 6.69 was due to proton resonance at H_5 of the pyrimidine ring. The ^{13}C-NMR spectrum showed a relatively low intensity absorption peak at 160.193, which was due to C_2 of the pyrimidine ring. A peak at 157.980 was assigned to C_4 and C_6 of pyrimidine ring. One absorption peak at 139.329 was due to $C_{1'}$ of benzene ring. A strong absorption peak at 128.921 was assigned to $C_{2'}$ and $C_{6'}$ of benzene ring. One peak at 122.743 was due to $C_{4'}$ of benzene ring. A medium absorption peaks at 119.575 and 112.475 were assigned to $C_{3'}$ and $C_{5'}$ of the benzene ring and C_5 of pyrimidine ring.

Table 1 show the fluorescence characteristic of 2-*N*-anilinopyrimidine and its metal complexes studied under the condition of capped and uncapped samples.

Table 1: Fluorescence characteristic of` 2-*N*-anilinopyrimidine and its metal complexes in methanol.

Condition	Compound	Excitation wavelength (nm)	Fluorescence Wavelength (nm)	Intensity (I)
Capped	2-*N*-anilinopyrimidine	378	757	0.729
	Mn(II) Complex	351	701	8.987
	Ni(II) Complex	348	707	1.610
	Cr(II) Complex	352	709	0.602
Uncapped	2-*N*-anilinopyrimidine	378	757	0.531
	Mn(II) Complex	351	738	0.006
	Ni(II) Complex	348	741	0.009
	Cr(II) Complex	357	712	0.559

For both capped and uncapped samples, 2-*N*-anilinopyrimidine emit at the same wavelength 757 nm when excited at 378 nm. It can be seen from Table 1 that the intensities in capped sample is higher than the uncapped sample. The spectra for each of the compounds in capped and uncapped samples are given in Figure 2, 3, 4 and 5.

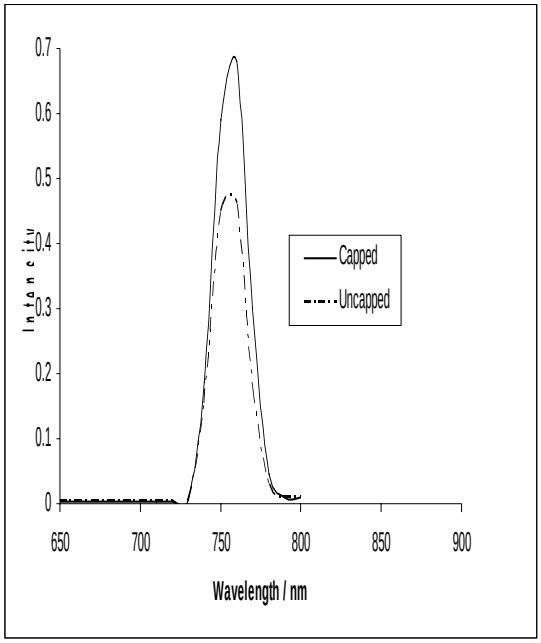
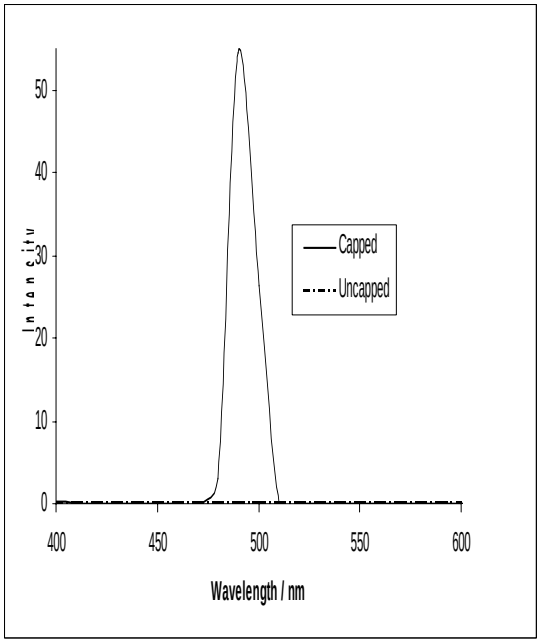
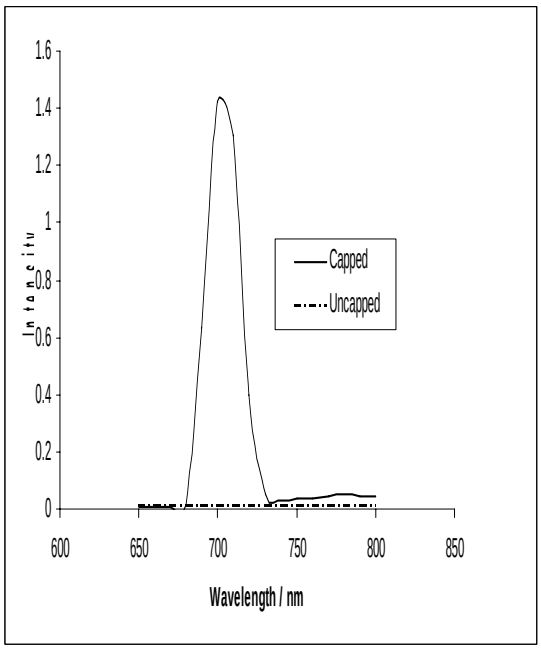


Figure 2 : 2-*N*-anilinopyrimidine



*** Figure 3 : Mn(II) complex**



*** Figure 4: Ni(II) complex**

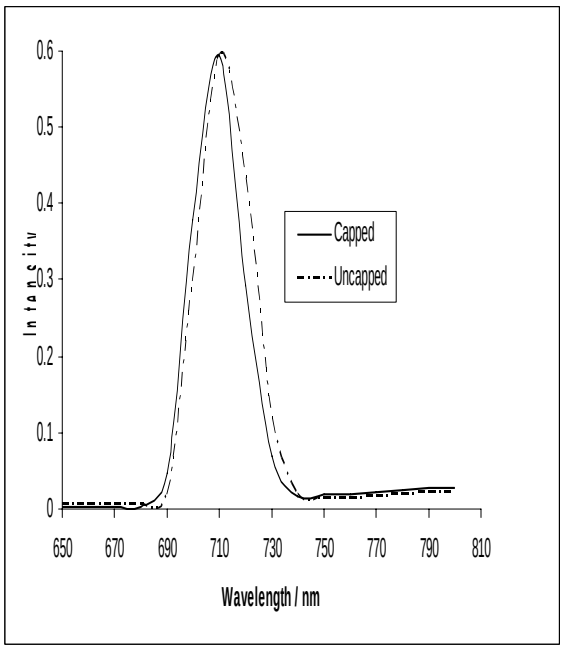


Figure 5 : Cr(II) complex

* Plotted area in uncapped condition for Mn(II) and Ni(II) complexes cannot be seen in the Figure 3 and 4 as the intensity values are very low (refer to Table 1).

Generally, under capped condition, the metal complexes emit at about 10 – 40 nm lower wavelengths than the uncapped samples, as shown in Figure 6.

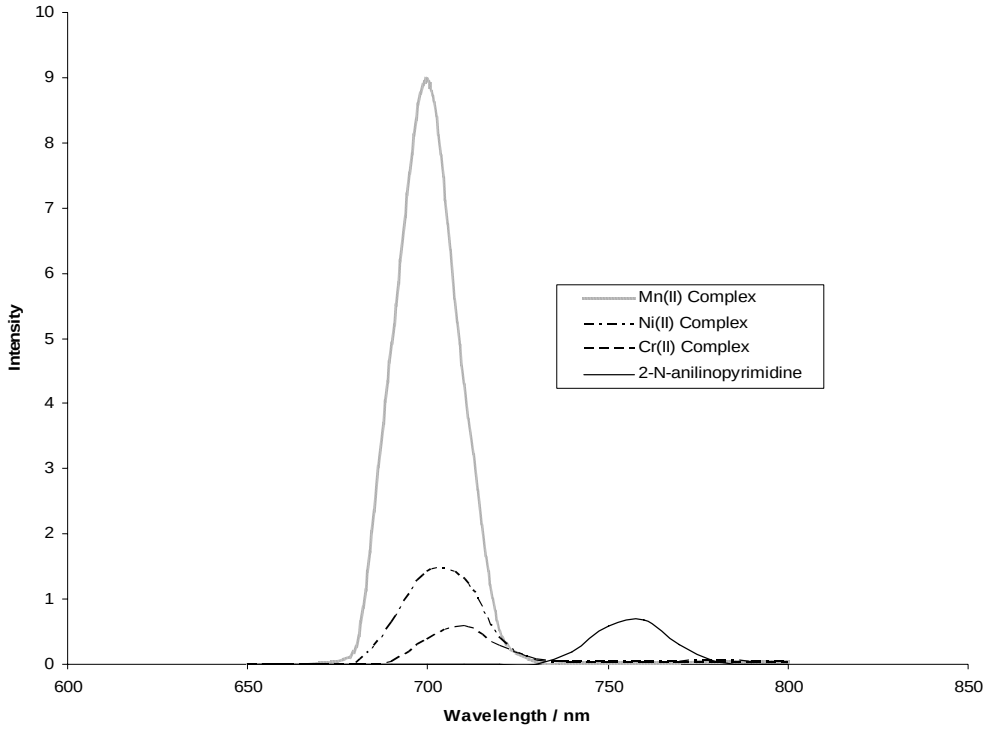


Figure 6: Fluorescence spectrum of 2-*N*-anilinopyrimidine and its metal complexes under capped condition.

Mn(II) complex and Ni(II) complex in capped samples showed an increased in fluorescence intensity whilst Cr(II) complex showed a decrease in intensity compared to its ligand as shown in Table 1. The increase in fluorescence intensity for Mn(II) and Ni(II) complexes can be explained by metal to ligand charge transfer when 2-*N*-anilinopyrimidine complexes with the metal [8]. The decrease in intensity for Cr(II) complexes may be explained by ligand to metal charge transfer. The relative intensities for complexes in capped samples decreases in order, Mn(II) > Ni(II) > Cr(II).

The intensities of complexes of 2-*N*-anilinopyrimidine in uncapped samples however, is decreased. This is probably due to quenching effect of the transition metal, which bound to the ligand during complexation whereby the charge transfer transition occurred between ligand and metal ion [9]. This can also be accounted for by the effect of unlimited amount of oxygen available, and therefore quenched the fluorescence intensity of the complexes [10]. Oxygen, which has an unusually large diffusion coefficient, and on prolong exposure of the solution to the atmosphere, could result in large quantity of oxygen diffusing into solution [11]. The intensities of the complexes decreases in order, Cr(II) > Ni(II) > Mn(II). The spectra for uncapped condition is given in Figure 7.

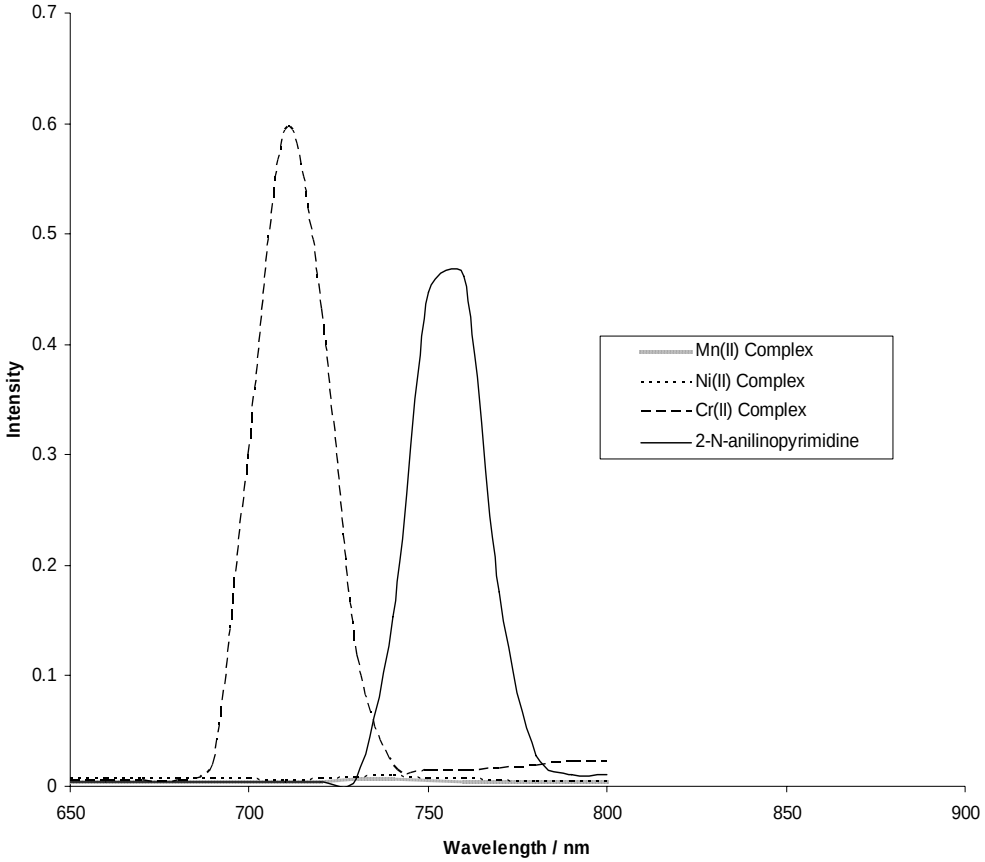


Figure 7: Fluorescence spectrum of 2-*N*-anilinopyrimidine and its metal complexes under capped condition.

Conclusion

In general, the compounds showed higher intensity in capped samples compared to uncapped samples. The relative intensities for complexes in capped samples decreases in order, Mn(II) > Ni(II) > Cr(II) whilst for uncapped samples, the intensities of the complexes decreases in order, Cr(II) > Ni(II) > Mn(II). Further study on the 2-*N*-anilinopyrimidine is in progress before any concrete conclusion can be made on complex – fluorescence relationship.

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