



Spectroscopic and fluorescence studies on Mn(II), Co(II), Ni(II) and Cu(II) complexes with NO donor fluorescence dyes

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ARTICLE INFO

Article history:

Received 9 December 2010

Received in revised form 24 April 2011

Accepted 16 May 2011

Keywords:

Metal complex dyes

Fluorescence study

Thermal properties of dyes

Naphthalimid

Spectrophotometry

ABSTRACT

The reactions of the two common dyes [2TMPACT and 4PENI] with Mn(II), Co(II), Ni(II) and Cu(II) ions were done. All the isolated complexes have been characterized by physicochemical and spectroscopic techniques. The IR data reflect the bidentate mode of 2TMPACT towards the mononuclear complex [Mn(II)] even its tetradentate in binuclear complexes [Co(II) and Cu(II)]. However, the bidentate mode is the only behavior of 4PENI ligand towards each metal ion in its mononuclear complexes. The UV–vis spectral analysis beside the magnetic moment measurements are proposed different geometries concerning each metal ions with the two ligands under investigation, as the Mn(II)–2TMPACT complex is an octahedral but Mn(II)–4PENI is a tetrahedral geometry. All the synthesized compounds are thermogravimetrically investigated. The proposed thermal decomposition was discussed for each compound with each step as well as, the kinetic parameters were calculated for all preferable decomposition steps. The mass spectroscopy tool was used to emphasis on the suitable molecular formula proposed and the fragmentation patterns were displayed. The fluorescence properties of the synthesized ligands and their complexes were studied in DMSO at room temperature.

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1. Introduction

The compounds containing heterocyclic rings play an important role in many biological systems [1], where they exist in nucleic acids, several vitamins, coenzymes and antibiotics. These provide 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. Furthermore, it has been suggested that the presence of metal ions in biological fluids, could have a significant effect on the therapeutic action of drugs [2,3]. Many diverse applications of metal species are aimed at understanding the natural roles of metal ions or exploiting the unique properties of metal centers in the study of the biology or biochemistry of nucleic acid and nucleic acid constituent [4]. The macrocyclic ligands and their metal complexes have attracted interest among the coordination chemists [5]. The metal ions direct the reaction preferentially towards cyclic rather than oligomeric or polymeric products [6]. The study of synthetic macrocyclic compounds is a very important area of chemistry in view of their presence in many biological significance naturally occurring metal

complexes [7]. This present work concerning the preparation of new complexes using fluorescence macrocyclic dyes. Verifying the structure of the isolated compounds by different spectral and analytical tools was done. Fluorescence spectral studies were carried out for the free ligands and their complexes. As well as, throw light on the effective biological activity expected for such complexes, but in this paper we are satisfying with the fluorescence application only.

2. Experimental

2.1. Reagents

All chemicals used for the study were of analytically reagent grade, commercially available from Fulka and used without previous purification as CoCl₂·6H₂O, MnCl₂·4H₂O, CuCl₂·H₂O and NiCl₂·6H₂O, compounds, which represents the metal ions in concern for the complexation. All the used solvents were pure or spectroscopic grade.

2.2. Synthesis of ligands

2.2.1. Synthesis of 2TMPACT

The compound 2TMPACT was synthesized as before [8]. Cyanuric chloride (1.85 g, 0.01 mol) dissolved in dichloromethane

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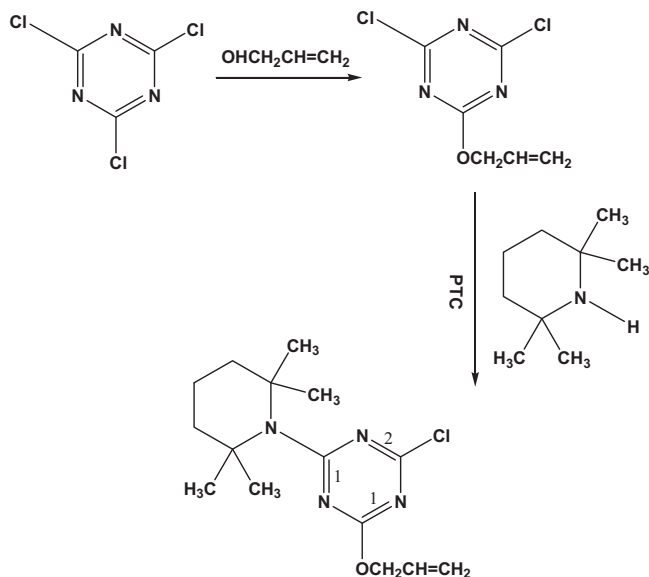


Fig. 1. The synthesis steps of commonly fluorescence dye, (2,2,6,6-tetramethylpiperidin-1-yl)-4-allyloxy-6-chloro-1,3,5-triazine (2TMPACT).

(15 ml) was added dropwise to a mixture of allyl alcohol (0.58 g, 0.01 mol) dichloromethane solution (15 ml), 50% hydrous sodium hydroxide solution (10 ml) and tetra butylammonium bromide (TBAB) (0.32 g, 0.001 mol) under vigorous stirring. The resulting mixture was stirred for 15 min at 10 °C and then diluted in 20 ml of water. Organic layer was separated, washed with water, dried over anhydrous sodium sulphate and evaporated in vacuum to give pure allyloxy-s-triazine in quantitative yield. To a solution of 2,2,6,6-tetramethyl piperidine (0.01 mol) in 40 ml of glacial acetic acid 1.5 g (0.01 mol) of sodium acetate and allyloxy-s-triazine above obtained were added at room temperature under PTC (Phosphorus tri chloride) conditions. The resulting mixture was stirred for an hour at 80 °C and then after cooling, poured into 40 ml of water. The crude precipitated product was filtered off and dried. The m.p. was exhibited as 115 °C. The procedure of the synthesized 2TMPACT was described (Fig. 1).

2.2.2. Synthesis of 4PENI

The synthesis of 4-piperidino-N-ethanolamine-1,8-naphthalimide (4PENI) has been described previously [9]. To a solution of 4-bromo-1,8-naphthalic anhydride (0.005 mol) in 50 ml of glacial acetic acid were added (0.005 mol) of sodium acetate and (0.005 mol) of ethanolamine. The resulting mixture was stirred for 8 h at 120 °C and then after cooling the precipitated product was filtered off, washed with water and dried. A solution of 4-bromo-N-ethanoamine-1,8-naphthalimide (0.01 mol) and piperidine (0.01 mol) in 80 ml of glacial acetic acid was stirred under reflux in the presence of PTC conditions for 12 h. The crude product which precipitated on cooling was treated with 100 ml of 5% aqueous sodium hydroxide to give after filtration, washing with water and dry. The m.p. was exhibited as 135 °C. The procedures of the synthesized of 4PENI were described (Fig. 2).

In the ¹H NMR spectrum of 4PENI ligand, the OH proton exhibited signal at $\delta = 8.44$ ppm (s, 1H). A characteristic proton signal at $\delta = 7.81$ –7.29 ppm range (m, 5H) for aromatic protons. In addition, the triplet signals at $\delta = 4.83$, 4.12 ppm assigned to CH₂ groups in aliphatic terminal chain, as well as signals at $\delta = 3.59$ –3.19 ppm range (m, 6H) assigned to piperidine 3(CH₂)² protons. The other 2(CH₂)¹ protons at 1.81–1.66 ppm range (m, 4H). The ¹H NMR spectrum of its Co(II) complex was done and gave broad resonances commensurate with paramagnetic species.

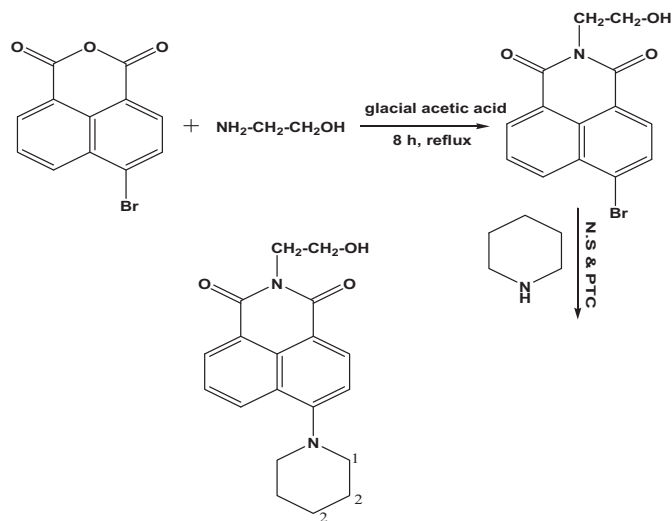


Fig. 2. The synthesis steps of commonly fluorescence dye, 4-piperidino-N-ethanolamine-1,8-naphthalimide (4PENI).

2.3. Synthesis of metal ion complexes of 2TMPACT and 4PENI ligands

The mentioned complexes were prepared by adding of the appropriate metal salts (0.3 mmole; in 10 ml 99% methanol) to a hot solution of each ligand (0.3 mmole; in 20 ml 99% CH₃OH) with molar ratio 1:1. The resulting solutions were stirred and heated on a hot plate at 60–70 °C for 30 min, the volume of the obtained solutions was decreased to one-half by evaporation carefully till obtaining the colored solid of the mentioned complexes that were prepared and isolated as powdered materials. Concerning, the Co(II)–2TMPACT complex, the color solution before precipitation was pink and a greenish-blue ppt complex was formed by yield = 0.1642 g (99%). While, Cu(II)–2TMPACT complex, the solution color before precipitation was faint-green and dark-green ppt was formed after precipitation process by yield = 0.1304 g (94%). On the other hand, the Mn(II)–2TMPACT complex has a faint-yellow color in the solution state but after precipitation the color turned to brownish-yellow ppt by yield = 0.1498 g (98%). At the time of addition process in case of, Mn(II)–4PENI complex, the color of solution before precipitation was yellow and reddish-orange ppt was obtained by yield = 0.050 g (96%), for Co(II)–4PENI complex, the solution was colored before precipitation by faint yellow and brown ppt complex was formed by yield = 0.053 g (94%). On the other hand, concerning, Ni(II)–4PENI complex, the solution color before precipitation was yellow and become orange after ppt was formed by yield = 0.045 g (80%), while the Cu(II)–4PENI complex, has a faint-yellow color before precipitation and reddish-brown after precipitation. The complex was obtained by yield = 0.0451 g (95%).

2.4. Physical measurements

Carbon, hydrogen and nitrogen contents were determined using a Perkin-Elmer CHN 2400. The copper(II), cobalt(II), nickel(II), and manganese(II) contents were determined gravimetrically by direct ignition of the complexes at 1000 °C for 3 h till constant weight. The residue was then weighted in the forms of metal oxides and verified complexometrically according to standard methods [10]. IR spectra were recorded on Bruker FTIR Spectrophotometer (4000–400 cm⁻¹) in KBr pellets. The UV–vis spectra were studied in the DMSO solvent for the ligands and their complexes and available fluorescence by help of Jenway 6405 Spectrophotometer with

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