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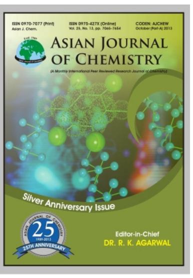

Gadolinium Complex of Schiff Base as Efficient Suppression Ratio for Hydroxyl Radical

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This paper described the synthesis and characterization of a novel gadolinium complex of Schiff base derived from *o*-vanillin and *o*-phenylenediamine, which were characterized by elemental analysis, the infrared spectroscopy (IR) and UV-VIS spectroscopy, fluorescence spectrometer, antioxidative activity. The UV-visible spectroscopy showed that the ligand has two intense absorption bands appeared at 219 and 272 nm which were attributed to n-π^* or π-π^* transition of conjugation system. Fluorescence spectrometer analysis showed that the Schiff base ligand exhibits strong fluorescence emission with the peak maximum at 598 nm in comparison to the complex. The complex has the maximum excitation at 466 and 526 nm, respectively. The antioxidative activity data show that the ligand and complex can not only scavenge $OH^{\bullet}$, but also increases with increasing complex concentration which their inhibition rates were up to 50.55 and 39.22 %.

Key Words: Gadolinium complex, Fluorescence, UV-VIS spectroscopy.

INTRODUCTION

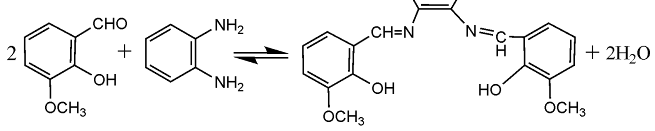
Luminescent rare earth Schiff base complexes have been subject of several studies due to not only their important properties and applications but also their relatively straightforward synthesis[1-3]. Since these compounds can be applied as phosphors and as starting materials with laser properties, their luminescence behaviour has become an important area of research. The possibilities of design novel photoluminescent materials have impelled numerous investigations dealing with new lanthanide complexes. The optical and photoluminescent properties of gadolinium(III) complex with the different kind of aromatic ambidentate ligands were already reported by several authors[4,5]. Moreover, a series of gadolinium compounds having different coordination numbers was also studied through its photoluminescent and optical properties, which were correlated to their structures[3]. Aime *et al.*[6] have published a promising new ligand 6-amino-6-methylperhydro-1,4-diazepinetetraacetic acid (AAZTA) and its gadolinium(III) complexes $[Gd(H_2O)_2AAZTA]^-$. The complex $[Gd(H_2O)_2AAZTA]^-$ shows good thermodynamic and kinetic stability and high relaxivity in aqueous solutions. Recently, they have reported the first X-ray structures of the AAZTA ligand and its gadolinium(III) complex[7]. Despite the mono-anionic nature shown in the aqueous solutions, the complex crystallizes as a dimeric $[Gd(H_2O)(AAZTA)]_2^{2-}$ complex with decacoordinated Gd(III) centers and one water molecule associated with each gadolinium(III) center.

In spite of the greatest effort and success in the study of Schiff base of gadolinium complexes, such complexes still attract much attention due to their interesting properties and the relative simplicity of their synthesis. From this point of view, the results presented here are of interest. In this paper, our research group reported the synthesis and characterization of a novel gadolinium coordination complex based on the new Schiff base ligand (N,N'-*bis*(2-oxy-3-methoxybenzylidene)-1,2-phenylenediamine), which were characterized by elemental analyses, IR and ultraviolet-visible spectrometer. Furthermore, the luminescence of the complex and the antioxidative activity are also presented.

EXPERIMENTAL

All materials and solvents were of reagent grade quality and were used without further purification. Elemental analyses (C, H, N) were performed on a Vario EL III analyzer. Infrared spectra on KBr pellets were recorded on a Nicolet 5700 spectrophotometer in the range 4000-400 cm^{-1}. Electronic spectra and the antioxidative activity were recorded on Lambda 35 UV-visible spectrophotometer (Perkin Elmer). LS55 spectrofluorimeter (Perkin Elmer), equipped with a dual monochromator was used for the steady state fluorescence measurements of the complex and Schiff base ligand at room temperature.

General procedure: The synthesis of the ligand is shown in **Scheme-I**. *o*-Vanillin (10 mmol), dissolved in methanol (20 mL), was added dropwise with stirring at 60 ºC to a solution of *o*-phenylenediamine (20.2 mmol) in methanol. The reaction mixture was then cooled to room temperature. The jaffa orange crystals formed were filtered and washed with 10 mL of acetone. Yield: 65 %, elemental analysis (%): Anal. calcd. for $C_{22}H_{20}N_2O_4$: C, 70.20; H, 5.36; N, 7.44; O, 17.0. Found (%): C, 69.27; H, 5.45; N, 7.48. ^{1}H NMR (400 MHz, MeOH-d_4): δ (PPm) 8.75 (s, 2H), 7.36(m, 2H), 7.18(m, 2H), 7.02(m, 4H),6.82(m, 2H), 3.89(s, 6H).



Scheme-I: Synthesis of Schiff base

The ligand (1 mmol) was dissolved in acetonitrile (5 mL). After 5 min, 1 mmol $Gd(NO_3)_3·6H_2O$ (1 mmol), dissolved in methanol (20 mL), was added into the ligand solution and the resulting mixture was stirred for *ca.* 2 h at 60 ºC. An orange precipitate was separated from the solution by suction filtration, purified by washing several times with methanol and dried for 3 h in the vacuum. Yield: 75 %. Elemental analysis (%): Anal. calcd. for $C_{22}H_{18}N_2O_4Gd$: C, 45.58; H, 3.13; N, 4.83. Found (%): C, 45. 55; H, 3.12; N, 4.81. ^{1}H NMR (400 MHz, MeOH-d_4): δ (ppm) 9.17(s, 2H), 7.86 (m, 2H), 7.56(m, 2H), 7.09 (d, 2H),6.49(t, 2H), 3.85(s, 6H).

The hydroxyl radical in aqueous media was generated through the Fenton reaction. The solution of the tested compounds were prepared with DMF. The reaction mixture contained 1.0 mL 0.05 M Tris-HCl buffer (pH 4.1), 1.0 mL, 0.1 mmol/L methyl violet, 1.0 mL, 0.5 mmol/L $FeSO_4$, 0.50 mL 3 % H_2O_2 and the 0.5 mL tested compound solution. The sample without the tested compound was used as the control. Absorbances (A_i, A_0, A) at 576 nm were measured. The suppression ratio for $HO^•$ was calculated from the following expression: Suppression ratio $\eta = [(A_i - A_0)/(A-A_0)] \times 100$ %. Where A_i is the absorbance in the presence of the tested compound; A_0 is the absorbance in the absence of the tested compound; A is the absorbance in the absence of the tested compound, $FeSO_4$ and H_2O_2.

RESULTS AND DISCUSSION

IR spectra: FTIR spectra obtained for the samples are shown in Figs. 1 and 2. In the free ligand, The broad band observed around 3346 cm^{-1} is assigned to ν(O-H) absorption, the strong band at 1617 due to ν(C=N) of imine, which indicates that the Schiff base ligand has been obtained. In gadolinium(III) complex, azomethine band ν(C=N) was shifted to lower frequencies (1602 cm^{-1}) after complexation. This blueshift could be attributed to a weakening of the C=N bonds on adduct formation and this can be explained by the donation of electrons from nitrogen to the empty *d*-orbitals of the metal ions[8]. The strong bands at 1298 and 1236 cm^{-1} in the free Schiff base ligands are due to the phenolic C-O stretchings. On complex formation, these bands are blueshifted to 1439 and 1247 cm^{-1} indicating coordinations through the phenolic oxygens. This shift can be explained by the fact that the two nitrogen atoms of ligands donate a pair of electrons each to the central metal forming a coordinate covalent bond.

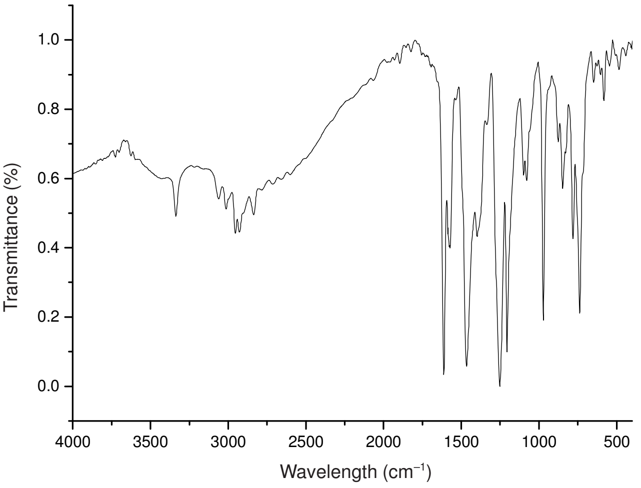


Fig. 1. IR spectrum of free ligand

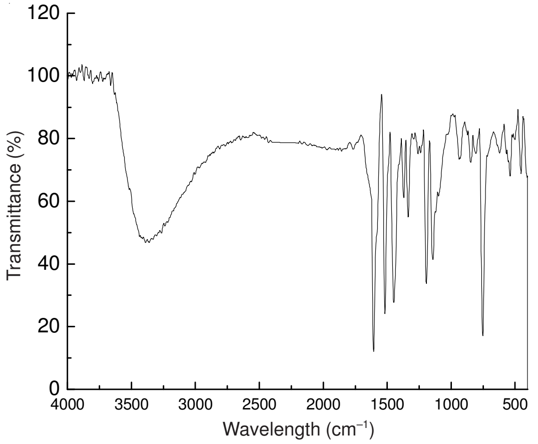


Fig. 2. IR spectrum of Gd(III) complex

Electronic absorption spectra: UV/visible data of the ligand and its Gd(III) complex are shown in Fig. 3 at the room temperature. In the ligand, there are two intense absorption bands appeared at 219 and 272 nm, respectively. The band of 272 nm may be assigned to n-π* transition of conjugation between lone-pair electron of *p*-orbital of N atom in C=N group and a conjugated π bond of benzene ring. Another peak at 219 nm is attributed to a π-π* transition of the conjugation system of Schiff base. The absorption spectra of complex measured in $CHCl_3$ solvent have three absorption peaks, which appeared at 206, 249 and 346 nm, respectively. The first two characteristic absorption peaks are assigned to the n-π* transition of conjugation between alone pair electron of the N atom in the C=N group and π bond of the benzene ring. The peak at 346 nm is attributed to ligand to metal charge transfer (LMCT), which indicates that the complex has formed. In the absorption spectra of complex, a low intensity band presented at 320-360 nm caused red shifts of the long wavelength absorption band by 60-80 nm. It is understandable that the protonation of the ligand would cause enhancement of the π-acceptor properties.

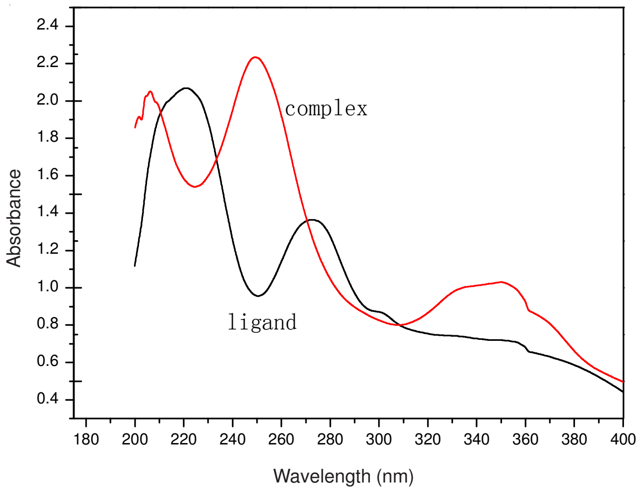


Fig. 3. Electronic optical absorption spectrum of ligand and complex

Energy gap determination: Fig. 4 shows the $(\alpha hn)^2$ *versus* hν curves of the complex, which was calculated from their UV-visible absorbance. Usually, the optical absorption method is used for investigating the optically induced transition and for providing information about the band structure of the compounds. The nature of the optically induced transitions can be determined from the UV spectra. The direct band gap energy (E_g) of complex was calculated by the Wood and Tauc method[9]. Theoptical bandgap is associated with the absorbance and photonenergy by the following equation: $(\alpha h\nu)^n = B(h\nu - E_g)$, where α, h, n and E_g are the absorbance, Planckconstant, frequency and opticalbandgap. E_g of complex was evaluated by extrapolating the linear portions of the curves to the zero absorbance. The energy band gap is 4.39 eV.

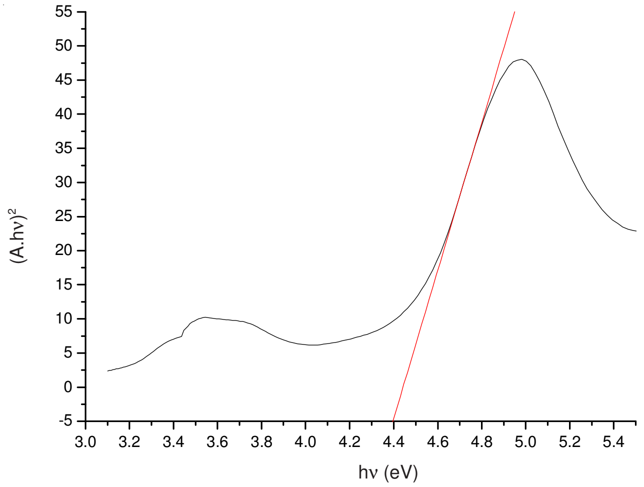


Fig. 4. Plot of $(\alpha h\nu)^2$ *versus* photon energy hν. (The band-gap energy is deduced from the extrapolation of the straight line up to $(\alpha h\nu)^2$ = 0)

Fluorescence spectral studies: It is known that Ln^{3+} complexes with Schiff bases or aromatic heterocyclic ligands exhibit interesting luminescence properties. Under identical experimental conditions, the fluorescence properties of the Schiff base ligand and its Gd(III) complex were studied at room temperature which are listed in Fig. 5. It can be seen that Schiff base ligand exhibits strong fluorescence emission with the peak maximum at 598 nm in comparison to complex. The complex has the maximum excitation at 466 and 526 nm, respectively. It is interesting that the Gd(III) complex shows lower intensity than that of the free ligand. Metal ions can quench the fluorescence emission of some Schiff base ligands containing aromatic ring. Quenching of fluorescence of a ligand by metal ions during complexation is a rather common phenomenon which is explained by processes such as magnetic perturbation, redox activity and electronic energy transfer. For Gd(III) complex, no emission originating from metal-centered MLCT/LMCT excited states are expected, since Gd(III) ion is difficult to oxidize or reduce due to its *f* configuration. Thus, the emission observed in the complex is tentatively assigned to the π-π* intraligand fluorescence.

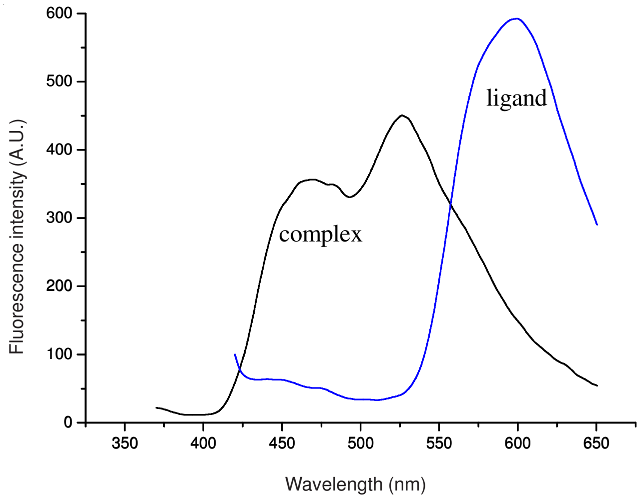


Fig. 5. Emission spectra of ligend and complex at room temperature

Suppression ratio (%) for HO•: Reactive oxygen species (ROS), such as hydroxyl radical (HO•), is generated by all aerobic cells during normal oxygen metabolism and cumulative information obtained has proved that the oxidation induced by ROS is involved in the pathogenesis of various diseases through direct effects on DNA directly and by acting as a tumor promoter[10]. In this paper, the antioxidant activity of the ligand and its Gd(III) complexe were studied by comparing their scavenging effect on hydroxyl radical. Fig. 6 shows that the ligand and complex can not only scavenge OH•, but also increase with complex concentration. The research indicated the complex and the ligand inhibition rate were up to 50.55 and 39.22 %, respectively when the concentrations were 10 mg/mL. It is clearly shown that metal complex exhibits more considerable scavenging activity than the ligand. Therefore, the scavenging effect of the complex studied in *o*-vanillin Schiff base should be further investigation.

Conclusion

In this work, we have succeeded in synthesizing Gd(III) complex with the Schiff base. The energy band gap of the complex is 4.39 eV, the Gd(III) complex and the ligand each displays intense fluorescence at room temperature. It is suggested that the complex exhibits the potential for use in applications as photochromatism materials. Furthermore, present results suggest that the scavenging effect of the complex increases with increasing complex concentration. Metal

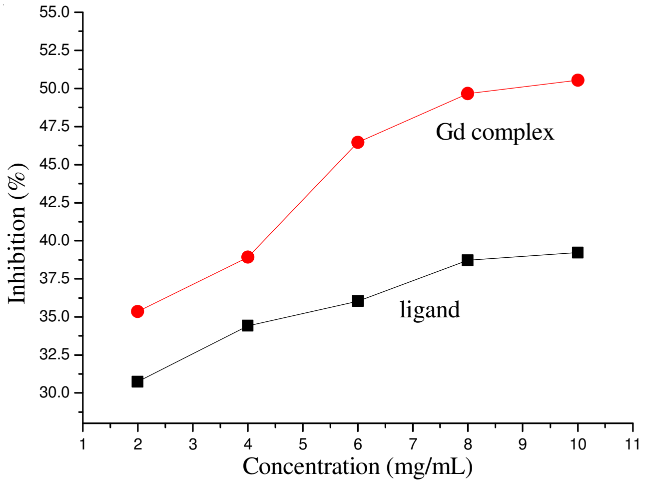


Fig. 6. Ligand and it's complex Suppression ratio for OH•

complex exhibits more considerable scavenging activity than the ligand.

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