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A novel azo-azomethine based fluorescent dye and its Co(II) and Cu(II) metal chelates

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ABSTRACT

Cobalt(II) and copper(II) complexes of a novel Schiff base ligand containing two –N=N– chromophore groups, derived from the condensation of 2-hydroxy-5-[(*E*)-phenyldiazenyl]benzaldehyde with *p*-aminoazobenzene were synthesized and characterized by analytical and spectroscopic methods. The X-ray powder diffraction analysis was used to determine the unit cell parameters of the synthesized ligand and its metal complexes. Self-isomerization via intramolecular proton transfer was investigated by UV–Vis and theoretical calculations. The effect of solvent polarity on UV–Vis was examined. The electronic structures of compounds were also predicted with computational chemistry methods. Theoretical vibrational and electronic spectra of the metal complexes were obtained from these structures. Binding energies of the metal complexes were obtained by quantum chemical calculations. Upon irradiation the ligands and their metal complexes gave blue light. The (***1a***) azo-aldehyde and (***2a***) azo-azomethine ligands revealed quantum yields of 35 and 41% and their excited-state lifetimes were 3.26 and 3.86 ns, respectively. Decreases in photoluminescence intensity and quantum yield upon complexation with metal ions were noted. The thermal behavior to include activation energy (E), entropy (ΔS^*), enthalpy (ΔH^*) and Gibbs free energy change (ΔG^*), using Coats–Redfern (CR) and Horowitz–Metzger (HM) methods, were examined.

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1. Introduction

Schiff bases derived from aromatic amines and aromatic aldehydes and their metal complexes have a wide variety of applications in the fields of biology [1], catalysis [2], materials [3] and inorganic [2] and analytical chemistry [4]. These compounds have been found to possess a wide range of biological activities such as antibacterial [5], antifungal [6], antimalarial [7], anticancer [8], antitubercular [9], anti-inflammatory [10], and antiviral [11].

Azo dyes are key chromophores in the chemical industry as dyes and pigments [12], food additives [13], indicators [14], radical reaction initiators [15] and therapeutic agents [16]. The azo azomethine compounds are commonly prepared by the condensation between primary amine or hydrazine and aromatic aldehyde or ketone-linked –N=N– chromophore group. Recent years have a great deal of interest in the preparation and characterization of azo azomethines and their metal complexes [17–22].

Research and development for new organic materials as light emitting devices continue [23–25]. Organic polymers having strong luminescence and using insignificant voltages, for flat panel displays prove to be important [26,27]. Aromatic amines and polymeric arylamines have been used as hole transport layers for electroluminescent technology [28,29]. A fluorescent dioxime-type ligand and its complexes have been reported in the literature [30]; fluorescence emission intensity of the ligand decreased with metal ion complex formation, where decreases in emission intensities were reported to be a result of the coordination complex of *N*-atom of the ligand with the metal ions. Further, fluorescent studies using metal complexes have been explored, for example, metal complexes in excited states have been studied as components of luminescent sensors and switches [31,32]. Developments in photochemistry and photophysics using Ru(II)–polypyridine complexes have been reported by Balzani and Juris, where these complexes helped to explain important electronic phenomena and interactions [33]. Balzani et al. have also given a detailed discussion of photoactive dendrimers containing metal complexes [34]. A multitude of research have been carried out on fluorescent sensors and metal ions, for example, the transduction mechanisms for metal ion detection by fluorescence were outlined by Formic et al. [35]. Small molecule fluorescent sensors for the detection of several molecular components of oxidative stress have also been reviewed by Hyman [36], where design, function and application of probes to detect metal cations, reactive oxygen species, and intracellular thiol-containing compounds were addressed. Also the development of luminescent transition metal

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complexes as chemosensors for cations and anions is presented in the literature [37].

As part of our continuing interest in azo-azomethine chemistry, we synthesized numbers of such compounds [38–40]. We now report on the successful synthesis of a novel azomethine ligand containing –N═N– moiety and its Co(II) and Cu(II) metal chelates and their photoluminescence properties were investigated. The structures of the prepared compounds were confirmed by spectroscopic techniques to include UV–Vis, FT-IR, ^{1}H and ^{13}C NMR data and elemental analysis. The theoretical study of the synthesized compound and its metal complexes was carried out by using different programs and methods. The crystallinity of the prepared compound and its metal complexes was studied by X-ray powder diffraction. The thermal stability of the prepared ligands and its metal complexes was also investigated using a thermogravimetric analysis (TGA), along with the kinetics and thermodynamic data evaluation.

2. Experimental

2.1. Reagents

Salicylaldehyde was purchased from Merck and used as received. Dimethylformamide (DMF), chloroform ($CHCl_3$), dichloromethane (CH_2Cl_2), carbon tetrachloride (CCl_4), hexane, toluene, methanol, ethanol, 9,10-diphenylanthracene, acetone and diethyl ether were purchased from Aldrich Chem. Co. and Merck and used as received. Reagents used were purchased from Aldrich, Fluka and Merck and used without further purification. The azo-aldehyde compound, 2-hydroxy-5-[(*E*)-phenyldiazenyl]benzaldehyde (***1a***) was prepared according to the published paper [38].

2.2. Techniques

The melting points of the azo-azomethine compounds were determined with an Electrothermal LDT 9200 apparatus. Infrared spectra were recorded on a PerkinElmer FT-IR spectrophotometer using KBr discs. ^{1}H and ^{13}C NMR spectra were collected using Bruker AC spectrometer 600 MHz, with samples dissolved in $CDCl_3$, and chemical shifts expressed in δ with TMS as an internal standard. Elemental analysis for C, H and N was performed on a PerkinElmer 240 elemental analyzer in Inonu University, Malatya, Turkey. The synthesized azo-azomethine ligand and its Co(II) and Cu(II) complexes were examined in spectrophotometric grade different solvents. The UV–Vis spectra were recorded from 190 to 1100 nm using a PG Instruments Ltd T80+ UV/VIS scanning spectrophotometer on 2.0×10^{-5} mol/L sample concentrations, prepared in spectrophotometric grade different solvents, and contained in 1 cm optical path quartz cuvette. The X-ray powder diffraction patterns were recorded on a vertical type Rigaku D-max/B diffractometer with CuKα radiation generated at 30 kV and 30 mA. Samples were measured from 20° to 50° (2θ) with a step size of 0.02 ´I and a count time of 1 s per step. Ligand and complex fluorescence spectra were obtained using a PerkinElmer LS55 spectrometer. Samples were prepared in spectrophotometric grade DMF, where solution concentrations were 1.0×10^{-5} mol/L and excitation was achieved at 338 nm. The standard 9,10-diphenylanthracene was used for quantum efficiency calculations [41,42]. Thermogravimetric analysis (TG and DTG) and differential thermal analysis (DTA) experiments were performed using a SII Exstar TG/DTA 6200 in the temperature range of 25–1000 °C with a heating rate of 20 °C min^{-1} under flowing dry air atmosphere (30 mL/min).

2.3. Preparation of 4-[(E)-phenyldiazenyl]-2-[(E)-({4-[(E)-phenyldiazenyl]phenyl}imino) methyl]phenol (**2a**)

A hot solution (60 °C) of *p*-aminoazobenzene (0.197 g, 1 mmol) in 10 mL of MeOH + 10 mL of $CHCl_3$ mixture was mixed with a hot solution (60 °C) of 2-hydroxy-5-[(*E*)-phenyldiazenyl]benzaldehyde (***1a***) (0.226 g, 1 mmol) in the same solvent. The reaction mixture was then refluxed for 2 h. A solid product was obtained and separated by filtration, then purified by crystallization from EtOH, washed with Et_2O, and then dried. Yield, 0.259 g (64%). m.p.: 188–189 °C. Λ_m: 2.70 Ω^{-1} cm^2 mol^{-1}. Elemental analyses for $C_{25}H_{19}N_5O$ (405.45 g/mol): Found: C, 74.15; H, 5.096; N, 17.06%. Calcd.: C, 74.06; H, 4.72; N, 17.27%. IR (KBr, cm^{-1}): 3450 υ(O–H), 3049 υ(aromatic C–H), 1616 υ(C═N), 1480 υ(N═N). ^{1}H NMR (ppm, in $CDCl_3$): 13.672 (s, 1H, OH), 8.846 (s, 1H, CH═N), 8.121 (s, 1H, Ar–H), 7.204–7.189 (m, 1H, Ar–H). ^{13}C NMR (ppm, in $CDCl_3$): 164.045, 162.78, 152.67, 152.59, 151.51, 149.92, 145.70, 131.19, 130.68, 129.16, 129.13, 128.15, 127.92, 124.32, 122.94, 122.66, 122.04, 118.86, 118.28.

2.4. Preparation of copper(II) complex (**2b**)

$Cu(CH_3COO)_2 \cdot H_2O$ (0.10 g, 0.5 mmol) in 10 mL of hot MeOH–$CHCl_3$ (1:1) was added to 20 mL of the azo-azomethine ligand (***2a***) (0.405 g, 1.0 mmol) in $CHCl_3$. The mixture was refluxed for 3 h on water bath. The volume of the solution was reduced to one-third of its original volume and left overnight. The dark green precipitate was filtered off, washed with cold MeOH and Et_2O and dried. Yield, 0.62 g (79%). m.p.: 275 °C. Λ_m: 3.10 Ω^{-1} cm^2 mol^{-1}. $\mu_{eff} = 1.78$ B.M. Elemental analyses for $C_{50}H_{36}CuN_{10}O_2$ (872.43 g/mol): Found: C, 68.21; H, 4.42; N, 15.58%. Calcd.: C, 68.83; H, 4.16; N, 16.05%. IR (KBr, cm^{-1}): 3049 υ(aromatic C–H), 1611 υ(C═N), 1472 υ(–N═N–), ~556 υ(M–O), 513 υ(M–N).

2.5. Preparation of cobalt(II) complex (**2c**)

To a solution of (0.202 g, 0.5 mmol) 4-[(*E*)-phenyldiazenyl]-2-[(*E*)-({4-[(*E*)-phenyldiazenyl]phenyl}imino)methyl]phenol (***2a***) in 20 mL $CHCl_3$, 10 mL of $CoCl_2 \cdot 6H_2O$ (0.0059 g, 0.25 mol) was added. The solution was refluxed at 40–50 °C with stirring for 2 h, and the resulting mixture was kept in the refrigerator for one day. The reddish brown complex was filtered and washed with cold MeOH and dried under vacuum. Yield, 0.309 g (70%). m.p.: 254 °C. Λ_m: 51 Ω^{-1} cm^2 mol^{-1}. $\mu_{eff} =$ 3.33 B.M. Elemental analyses for $C_{51}H_{46}ClCoN_{10}O_6$ (989.36 g/mol): Found: C, 61.86; H, 4.960; N, 14.08%. Calcd.: C, 61.91; H, 4.696; N, 14.16%. IR (Kr, cm^{-1}): 3320 υ(O–H-hydrated and methanol), 3058 υ(aromatic C–H), 2930 (Me–H), 1612 υ(C═N), 1480 υ(–N═N–), 826 (coordinated water), 549 υ(M–O), 510 υ(M–N).

2.6. Computational method

All calculations were made by Gaussian 09 package programs [43–45]. Hartree–Fock (HF) and density functional theory (DFT/B3LYP) methods with 3-21G and LANL2DZ basis sets were used for obtaining the optimized structure of tautomers and copper(II) and cobalt(II) complexes. The calculated vibrational frequencies were scaled by 0.9, 0.9393, 0.964 [46] and 0.9978 [47] for HF/3-21G, HF/LANL2DZ, B3LYP/3-21G and B3LYP/LANL2DZ, respectively. The best level was found as HF/3-21G level from the correlation of experimental and calculated vibrational frequencies. Tautomer interacting with metal cation was determined by calculating the orbital character of HOMO and HOMO-1. Time dependent-HF (TD-HF) method was used for UV–Vis spectra calculations. The UV–Vis spectra were calculated in vacuum, water and chloroform. Solute–solvent interactions were taken into account by the conductor-like polarizable continuum model (CPCM) [48].

3. Results and discussion

3.1. Synthesis and solubility

The synthesized ligand and its metal complexes were characterized by IR, UV–Vis, NMR spectra, magnetic susceptibility measurements and

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