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Structure, fluorescence, redox properties and theoretical interpretation of heteroleptic copper(I) and silver(I) complexes of N-[(2-pyridyl) methyliden]-6-coumarin and triphenylphosphine

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ABSTRACT

[MX(L)(PPh_3)] (L = N-[(2-pyridyl)methyliden]-6-coumarin; M = Cu(I), Ag(I); X = Cl, Br, I, N_3, SCN) are characterized by spectroscopic data. The X-ray structure of [CuCl(L)(PPh_3)] shows CuN_2PCl distorted tetrahedral coordination (L acts N,N chelator). The complexes show emission and the emission efficiency is dependent on nature of M and X; Cu(I) complexes (d^{10}) are more emissive than Ag(I) complexes which may be due to heavy atom effect of silver. [Cu(SCN)(L)(PPh_3)] shows highest emission intensity in the series. The cyclic voltammogram of [CuX(L)(PPh_3)] shows Cu(II)/Cu(I) quasireversible redox couple while [AgX(L)(PPh_3)] exhibits deposition of Ag(0) on the electrode surface together with irreversible ligand reduction. Coulometric oxidation of [CuX(L)(PPh_3)] has synthesised copper(II) derivatives. Theoretical calculations are applied in modelling of complexes studied and UV–Vis spectra simulation.

1. Introduction

Copper(I)-polypyridine complexes have been extensively studied because of their potential redox and luminescence properties [1–3]. Towards the target of designing efficient emissive complexes and of longer lifetime, the mixed ligand complexes of triphenylphosphine (PPh_3) and polypyridine based diimine (–N=C–C=N–) ligand of copper(I) have been used [4–8]. Use of potentially photoactive organic moiety attached to diimine function is an attractive synthetic protocol in this regard. Coumarin, a phytochemical, is an interesting photoactive molecule and has been used as laser dye [9]. They are antifungal and antibacterial, and there are a number of commercially available coumarinyl-antibiotics [10–13]. Coumarin derivatives have been used to synthesize polydentate ligands so that metal complexes of these ligands may be useful for displaying excited state properties [14–16] and photostability. With this objective we have synthesised N-[(2-pyridyl)methyliden]-6-coumarin (L) and its copper(I) and silver(I) complexes [17].

The ligand, L, a bidentate N, N′-chelating agent (N refers to N(pyridyl) and N′ refers to N(imine)) is used for the synthesis of complexes [MX(L)(PPh_3)] (M = Cu(I), Ag(I) and X = Cl, Br, I, N_3, SCN). All these compounds are characterized by spectroscopic data. The structural analysis of one of the complexes, [CuCl(L)(PPh_3)], is carried out by single crystal X-ray diffraction measurement. The effect of halide (Cl, Br, I) and pseudohalide (N_3, SCN) on luminescence properties are examined. The DFT and TD-DFT computation processes are employed for the evaluation of electronic structure and the simulation of UV-vis spectra in solution is used to interpret the spectra and redox activity of the complexes.

2. Experimental

2.1. Materials

$AgNO_3$, CuX (X = Cl, Br, I), ammonium thiocyanate and pyridine-2-carboxaldehyde were purchased from Aldrich Chemical Co. Coumarin was obtained from S.D. Fine Chem. Ltd., Boisar. PPh_3 and NaN_3 were purchased from Merck, India. $[Cu(MeCN)_4]ClO_4$ was prepared by standard procedure [18]. Dinitrogen was purified by bubbling through an alkaline pyrogallol solution. Solvents were purified by standard procedure [19]. All other chemicals were of reagent grade and were used without further purification.

2.2. Physical measurements

Microanalytical data (C, H, N) were collected on Perkin–Elmer 2400 CHNS/O elemental analyzer. Spectroscopic data were

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obtained using the following instruments: UV–Vis spectra by Perkin Elmer UV–Vis spectrophotometer model Lambda 25; FTIR spectra (KBr disk, 4000–400 cm^{-1}) by Perkin Elmer FT-IR spectrophotometer model RX-1; the ^{1}H NMR spectra by Bruker (AC) 300 MHz FTNMR spectrometer. Electrochemical measurements were performed using computer-controlled CH-Instruments, Electrochemical workstation, Model No CHI 600D (SPL) with Pt-disk electrodes. All measurements were carried out under nitrogen environment at 298 K with reference to Ag/AgCl electrode in acetonitrile using [nBu$_4$N]ClO$_4$ as supporting electrolyte. Controlled potential coulometry was performed to know the number of electrons involved in the oxidation of Cu(I) in CH$_3$CN medium. It was carried out in an electrochemical cell using suitable platinum wire gauge electrode, Pt-counter, and Ag/AgCl reference electrodes. In case of coulometry, an CH$_3$CN solution of Cu(I) complex (**1a**, **1b** and **1c**) was electrolyzed against a constant potential of 0.9 V for 1 h. The total charge (C) provided during electrolysis of Cu(I) complex was monitored against time in seconds and the results were analyzed. 0.1 M tetrabutylammonium perchlorate (TBAP) was used for CH$_3$CN media. Nitrogen gas was used to maintain inert atmosphere and proper stirring was ensured. The reported potentials are uncorrected for junction potential. Emission was examined by LS 55 Perkin Elmer spectrofluorimeter at room temperature (298 K) in CH$_3$CN solution under degassed condition.

The fluorescence quantum yield of the complexes was determined using carbazole (ϕ_R = 0.42 in benzene) [20] and anthracene (ϕ_R = 0.27 in ethanol) [21]. The complex and the reference dye were excited at same wavelength, maintaining nearly equal absorbance (~0.1), and the emission spectra were recorded. The area of the emission spectrum was integrated using the software available in the instrument and the quantum yield was calculated according to the following equation:

$$\phi_S/\phi_R = [A_S/A_R] \times [(\mathrm{Abs})_R/(\mathrm{Abs})_S] \times [\eta_S^2/\eta_R^2] \qquad (1)$$

Here, ϕ_S and ϕ_R are the fluorescence quantum yield of the sample and reference, respectively. A$_S$ and A$_R$ are the area under the fluorescence spectra of the sample and the reference respectively, (Abs)$_S$ and (Abs)$_R$ are the respective optical densities of the sample and the reference solution at the wavelength of excitation, and η_S and η_R are the values of refractive index for the respective solvent used for the sample and reference.

Fluorescence lifetimes were measured using a time-resolved spectrofluorimeter from IBH, UK. The instrument uses a picosecond diode laser (NanoLed-07, 370 nm) as the excitation source and works on the principle of time-correlated single photon counting [22]. The instrument responses function is ~230 ps at FWHM. To eliminate depolarization effects on the fluorescence decays, measurements were done with magic angle geometry (54.7°) for the excitation and emission polarizers. The observed decays of [CuCl(L)(PPh$_3$)] (**1a**), [CuBr(L)(PPh$_3$)] (**1b**), [CuI(L)(PPh$_3$)] (**1c**), [Cu(N$_3$)(L)(PPh$_3$)] (**1d**) and [Cu(SCN)(L)(PPh$_3$)] (**1e**) fit with single exponential decay whereas [AgCl(L)(PPh$_3$)] (**2a**), [AgBr(L)(PPh$_3$)] (**2b**), [AgI(L)(PPh$_3$)] (**2c**), [Ag(N$_3$)(L)(PPh$_3$)] (**2d**) and [Ag(SCN)(L)(PPh$_3$)] (**2e**) fit with a bi-exponential decay as in the following equation, where τ's are the fluorescence lifetime and α is the pre-exponential factor. For the fits, the reduced χ^2 values were within 1.02–1.32 and the distribution of the weighted residuals were random among the data channels. τ_f is mean fluorescence life time (meaning of the symbols are usual) [23].

$$I(t) = [a_1 \exp(-t/\tau_1) - a_2 \exp(-t/\tau_2)] \qquad (2)$$

$$\tau_f = a_1\tau_1 + a_2\tau_2 \qquad (3)$$

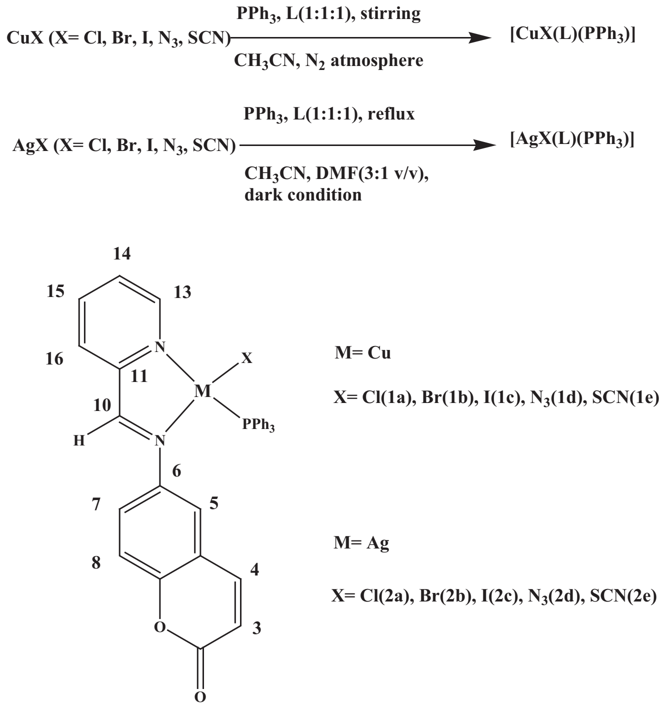
2.2.1. Synthesis of [CuX(L)(PPh$_3$)] [X = Cl (**1a**), Br (**1b**), I (**1c**), N$_3$ (**1d**), SCN (**1e**)]

To acetonitrile solution (20 ml) of CuCl (0.025 g, 0.25 mmol) was added PPh$_3$ (0.066 g, 0.25 mmol) under nitrogen environment and stirred for one hour. Then acetonitrile solution (5 ml) of N-[(2-pyridyl)methyliden]-6-coumarin (L) (0.063 g, 0.25 mmol) was added. The solution was stirred for another two hours; the reaction mixture was filtered and kept undisturbed for slow evaporation. Reddish brown single crystal of [CuCl(L)(PPh$_3$)] (**1a**) obtained after two weeks. Brown [CuBr(L)(PPh$_3$)] (**1b**) and reddish brown [CuI(L)(PPh$_3$)] (**1c**) were synthesized following the same procedure. Upon addition of NaN$_3$/NH$_4$SCN to [Cu(MeCN)$_4$]ClO$_4$ solution in dry methanol Cu(N$_3$)/Cu(SCN) might be prepared in situ and was used to synthesize [Cu(N$_3$)(L)(PPh$_3$)] (**1d**) and [Cu(SCN)(L)(PPh$_3$)] (**1e**) (Scheme 1).

Caution!! Azide compounds are explosive. A small amount of compound has been used in the synthesis.

*[CuCl(L)(PPh$_3$)] (**1a**):* 0.107 g (70%) yield; decomposition temperature >234 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.45 (1H, d, 9.4 Hz, 3-H), 7.76 (1H, d, 9.2 Hz, 4-H), 7.5 (1H, s, 5-H), 7.35 (1H, d, 8.3 Hz, 7-H), 7.43 (1H, d, 8.22 Hz, 8-H), 9.71 (1H, s, 10-H), 8.36 (1H, d, 7.95 Hz, 13-H), 7.91 (1H, m, 14-H), 7.91 (1H, m, 15-H), 8.86 (1H, d, 6.5 Hz, 16-H), PPh$_{3,}$ 7.25-7.35; FT-IR (KBr, ν cm^{-1}) ν(CO)$_{\mathrm{lactone}}$, 1728; ν(C=N), 1566, 1599; ν(PPh$_3$) 1095, 697, 526; UV ($\lambda_{\max}$, nm (ε, 10^3 M^{-1} cm^{-1}) in CH$_3$CN), 454 (5.9), 334 (7.5), 285 (14.8), 271 (17.3); *Anal.* Calc for C$_{33}$H$_{25}$ClCuN$_2$O$_2$P: C, 64.78; H, 4.09; N, 4.58. Found: C, 64.72; H, 4.02; N, 4.61%. .

*[CuBr(L)(PPh$_3$)] (**1b**):* 0.047 g (65%) yield; decomposition temperature >230 °C. ^{1}H NMR (300 MHz, CDCl$_3$) δ 6.43 (1H, d, 9.2 Hz, 3-H), 7.43 (1H, d, 9.1 Hz, 4-H), 7.55 (1H, s, 5-H), 7.43 (1H, d, 8.11 Hz, 7-H), 7.51 (1H, d, 8.15 Hz, 8-H), 9.70 (1H, s, 10-H), 8.35 (1H, d, 7.92 Hz, 13-H), 7.95 (1H, m, 14-H), 7.95 (1H, m, 15-H), 8.84 (1H, d, 6.3 Hz, 16-H), PPh$_{3,}$ 7.22-7.36; FT-IR(KBr, ν cm^{-1}) ν(CO)$_{\mathrm{lactone}}$, 1723; ν(C=N), 1566, 1593; ν(PPh$_3$) 1096, 696, 524; UV ($\lambda_{\max}$, nm (ε, 10^3 M^{-1} cm^{-1}) in CH$_3$CN), 453 (4.9), 334 (7.9), 290 (12.9), 276 (14.9); *Anal.* Calc for C$_{33}$H$_{25}$BrCuN$_2$O$_2$P: C, 60.38; H, 3.81; N, 4.27. Found: C, 60.35; H, 3.86; N, 4.20%.



Scheme 1. Syntheses of the complexes.