Synthesis and identification of N-[(2-pyridyl)methyliden]-6-coumarin complex of Pt(IV)

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Abstract

Coumarin derivatives have blood-thinning, anti-fungicidal, anti-tumor and anticoagulant activities. Photophysics and photochemistry of coumarin derivatives are also important. With reaction between 6-aminocoumarin and pyridine-2-carboxaldehyde, we synthesized N-[(2-pyridyl)methyliden]-6-coumarin(L). The ligand, L, reacts with hexachloroplatinic acid to synthesize a Pt(IV) complex of formulae, $[Pt(L)_2]Cl_6$ and $[Pd(L)_2]Cl_2$, respectively. On the other hand, all reactions in the attendance of pyrocatechol has isolated $[Pt(L)(1,2\text{-dihydroxybenzene})_2]Cl_6$. This compound is characterized by FTIR, UV–Vis and ^{1}H NMR spectroscopic data.

Keywords: Synthesis of N-[(2-pyridyl)methyliden]-6-coumarin, hexachloroplatinic acid

Introduction:

Coumarin is found in a variety of plants such as Tonka bean, lavender, sweet clover grass, licorice and also occurs in food plants such as strawberries, apricots, cherries, cinnamon. Coumarin derivatives have blood-thinning, anti-fungicidal, anti-tumor and anticoagulant activities [1–3].

Photophysics and photochemistry of coumarin derivatives are also important and have been used as dye lasers [4-7]. Considerable effort has been given at present to functionalize coumarin so that metal–coumarin complexes may be synthesized and could display interesting excited state properties and be used in designing artificial photosynthetic systems, chemical sensors and molecular level devices [8]. We are interested to anchor diimine (–N=C–C=N–) function to coumarin backbone so that the molecule may act as bidentate N,N-chelator. We have prepared coumarin based ligand, N-[(2-pyridyl) methyliden]-6-coumarin (L), which reacts with hexachloroplatinic acid to synthesize $[M(L)_2]^+$. All these compounds are characterized by spectroscopic methods.

Experimental:

Hexachloroplatinic acid and pyridine-2-carboxaldehyde were purchased from Aldrich Chemical Co. Coumarin was available from S.D. Fine Chem. Ltd. Solvents were purified by standard procedure [9]. All other chemicals and solvents were of reagent grade and were used without further purification.

Physical measurements

Spectroscopic data were 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.

Synthesis of N-[(2-pyridyl)methyliden]-6-coumarin (L)

There are three steps in the preparation of ligand (Scheme 1): 6-nitrocoumarin (step 1), 6-aminocoumarin (step-2) and condensation with pyridine-2-carboxaldehyde (step-3). All the steps are shown in Scheme 1.

Step-1: synthesis of 6-nitrocoumarin

Coumarin was nitrated with mixed acid in an ice bath. Coumarin was dissolved in H_2SO_4 and then mixed acid (HNO_3 and H_2SO_4) was added. The mixture was stirred keeping at room temperature. A white precipitate of 6-nitrocoumarin was obtained. It was then filtered and washed thoroughly with water and dried over $CaCl_2$. Yield, 9.2 g (88%). m.p.

185° ± 2 °C; ^{1}H NMR (300 MHz, CD3CN) d 8.54 (1H, s), 8.38 (1H, d, 7.5 Hz), 7.98 (1H, d, 7.5 Hz), 7.49 (1H, d, 7.0 Hz), 6.55 (1H, d, 8.0 Hz); IR (KBr, cm_1) 3096, 3071, 1751, 1620, 1564, 1536, 1480, 1436; UV (kmax, nm (e, 103 M_1 cm_1) in CH_3CN) 327 (1.80), 314 (2.13), 268 (6.93), 259 (9.51); Anal. Calc. for $C_9H_5NO_4$: C, 56.54; H, 2.62; N, 7.33. Found: C, 56.45; H, 2.67; N, 7.28%.

Step-2: synthesis of 6-aminocoumarin

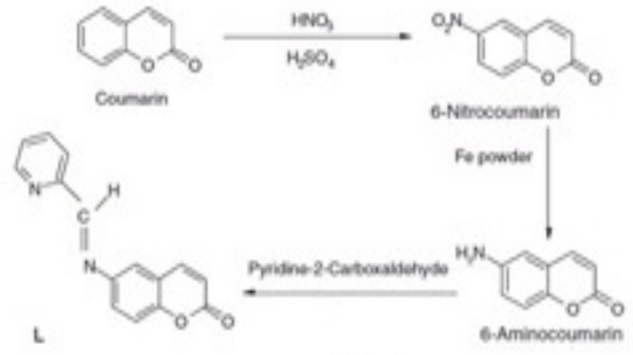
Reduction of 6-nitrocoumarin was done with Fe-powder in water. 6-Nitrocoumarin in water (150 cm^3) was treated with Fe-powder. The mixture was kept in water bath. A dark brown precipitate was obtained. After evaporation yielded a silky yellow precipitate of 6-aminocoumarin (m.p. 158°C). It was then recrystallized from dil. HCl solution as 6-aminocoumarin hydrochloride. Yield, 5.1 g (76%). m.p. >260 _C; ^{1}H NMR (300 MHz, CD_3CN) d 7.71 (1H, d, 7.5 Hz), 7.09 (1H, d, 7.5 Hz), 6.88 (1H, d, 7.5 Hz), 6.77 (1H, s), 6.30 (1H, d, 8.0 Hz), 4.26 (2H, s); IR (KBr, cm^{-1}) 1705, 1635, 1570, 1490, 1451; UV (kmax, nm (Ɛ , 10^3 M^{-1} cm^{-1}) in CH_3CN) 370 (3.54), 280 (11.43), 253 (21.44); Anal. Calc. for $C_9H_7NO_2$: C, 67.08; H, 4.35; N, 8.70. Found: C, 67.12; H, 4.25; N, 8.65%. 3.1.3.

Step-3: N-[(2-pyridyl)methyliden]-6-coumarin (L)

6-Aminocoumarine and pyridine-2-carboxaldehyde was taken in methanol. Slow evaporation of the solution separated a straw color crystalline compound of yield 0.7 g (90%); m.p. 152° ± 2 C; MS m/z = 249 (M$^+$); FT-IR (KBr, m, cm^{-1}) ʋ (COO), 1714; ʋ (C=N), 1629; ʋ(C=C), 1581, 1566, 1472, 1437. Anal. Calc. for $C_{15}H_{10}N_2O_2$: C, 72; H, 4; N, 11.2. Found: C, 71.8; H, 4.1; N, 11.15%

Preparation of $[Pt(L)_2]Cl_6$ (3)

To H_2PtCl_6 solution in MeOH, L was added in MeOH. The solution was magnetically stirred, yellow precipitate filtered, residue was collected and dried. The complex was obtained in 0.090 g (90%) yield; decomposition temperature >250° C. FT-IR (KBr, cm^{-1}) 1721, 1561, 1384. The structural characterization has been carried out by ^{1}H NMR spectral data (Table 1).



Scheme 1.

Table 1: ^{1}H NMR spectral data of the complex.

δ ppm (J, Hz)									
3-H^{a}	4-H^{a}	5-H^{b}	7-H^{a}	8-H^{a}	10-H^{b}	13-H^{a}	14-H^{c}	15-H^{a}	16-H^{a}
6.43 (9.60)	7.76 (9.64)	7.54	7.32 (8.68)	7.59 (8.68)	8.84	8.86 (6.7)	8.13	8.13	8.00 (7.73)

In DMSO-d$_6$ ^{a} Doublet ^{b} Singlet ^{c} Multiple

Results and discussion

N-[(2-pyridyl)methyliden]-6-coumarin (L) Nitration of coumarin and its subsequent reduction to 6-aminocoumarin has been carried out by Fe powder. The condensation of pyridine-2-carboxaldehyde with 6-aminocoumarin has isolated straw yellow crystalline compound (Scheme 1). Infrared spectra of 6-aminocoumarin shows two υ (NH$_2$) bands at 3329 and 3409 cm^{-1} which is eliminated in the condensation product and a new band appears at 1582 cm^{-1} that is corresponding to υ (C=N) at 328 and 289 nm in acetonitrile. These are assigned to n→π* and π→π* transitions.

The reaction of L with H$_2$PtCl$_6$ in dry methanol for 2 h has isolated yellow colored [Pt(L)$_2$]Cl$_6$. The complex was characterized by FTIR and ^{1}H NMR spectra which confirm the presence and coordination of L to Pt(IV)

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