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A new 2,6-di(anthracen-9-yl)pyridine ligand and its complexes with Ag(I) ions: Synthesis, structure and photocatalytic activity ☆

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A new 2,6-di(anthracen-9-yl)pyridine ligand **L** reacts with various silver(I) salts to give three new complexes: mononuclear [Ag**L**(NO_3)] and [Ag**L**(*i*-PrOH)$_2$](BF_4), and dinuclear [Ag**L**(μ-H_2O)Ag**L**](BF_4)$_2$·3CH_2Cl_2. The complexes have been characterized by spectroscopic techniques and elemental analysis. The solid state structures of the complexes have been determined by X-ray diffractometry. Methylene blue (MB) degradation was studied by UV–Vis spectrophotometry. The new complexes of silver(I) are active photocatalysts of MB degradation under sunlight irradiation.

1. Introduction

In recent years, the synthesis of supramolecular complexes has become one of the most active fields in coordination chemistry due to their special chemical and physical properties, fascinating structures and their potential applications as functional materials [1–6]. Silver(I) ions are able to have different coordination numbers and geometries, this variety is in the part due to the lack of stereochemical preference that arises from their d^{10} configuration [7]. Depending on the nature of the ligands, anions, solvents and metal-to-ligand ratio [8], silver(I) ions are known to form various types of supramolecular complexes, such as coordination polymers [9,10], grids [11], helicates [12,13], cyclic helicates [14], metallamacrocycles [15] and clusters [16,17]. In view of the strong ability of nitrogen atoms to coordinate to silver ions [18], we wondered if some derivatives of anthracene pyridines could be used to obtain new coordination networks.

The textile industry generates a large amount dyes, which are generally toxic and quite resistant to destruction. Various chemical and physical processes, such as chemical precipitation, coagulation, electrocoagulation, adsorption, etc., are applied for dye removal from effluents. These methods only transfer the contamination from one phase to another. Methods that are able to decompose dyes are needed [19]. Methylene blue (MB) is a cationic dye used for dyeing cotton, wool, silk, etc. MB reveals very harmful effects to animals and people [20]. The IUPAC name of MB is 3,7-bis(dimethylamino)-phenothiazin-5-ium chloride ($C_{16}H_{18}N_3SCl$). In recent years, photocatalytic decomposition of MB was proposed as an alternatives method for its disposal. As photocatalysts, TiO_2 and doped TiO_2 were commonly used [21]. TiO_2/Ag [22] and a few Ag contained compounds were used as photocatalysts in MB decomposition, namely Ag[$Li_{1/3}Ti_{2/3}$]O_2 and Ag[$Li_{1/3}Sn_{2/3}$]O_2 synthesized from layered $Li_2Ti(Sn)O_3$ using molten $AgNO_3$ [23], helical [24] and polymeric Ag(I) complexes with 2,3-bis(6′-methyl-2,2′-bipyridin-6-yl)pyrazine [25]. Much attention needs to be focused on achieving the utilization of visible light because of UV light accounts for only about 2–3% of the total sunlight, whereas visible light accounts for 45%.

MB was used a model for the organic dye, because it is considered by the International Organization of Standardization as a standard method for testing and comparing the efficiency of photocatalytic coatings and it is commonly adopted to evaluate the catalytic activity of a catalyst [26].

Herein, we reported a synthetic route to a new N-heterocyclic ligand containing an anthracene moiety (Fig. 1) and its Ag(I) complexes [Ag**L**(NO_3)] (**1**), [Ag**L**(μ-H_2O)Ag**L**](BF_4)$_2$·3CH_2Cl_2 (**2**) and [Ag**L**(*i*-PrOH)$_2$](BF_4) (**3**), which we designed on being inspired by our previous experiences with helical [26] and polymeric silver(I)

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[25] complexes, performing complexation reactions with a metal:ligand ratio of 1:1. The photocatalytic activity of the Ag complexes **1**–**3** were also examined under UV–Vis light and sunlight.

2. Experimental

2.1. General procedure

Silver nitrate, silver tetrafluoroborate and 2,6-dibromopyridine were used as supplied from Aldrich without further purification. The synthesis of 2-(anthracen-9-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane) (**A**) has been reported in our previous paper [27]. NMR spectra were measured using a Varian Gemini (300 MHz) spectrometer. The instrument was calibrated against the residual protonated solvent signals ($CDCl_3$ δ 7.24) and the shifts are given in ppm. Mass spectra for acetonitrile solutions, $\sim 10^{-4}$ M, were determined using a Waters Micromass ZQ spectrometer. IR spectra in the 4000–400 cm^{-1} region were measured with a Perkin–Elmer 580 spectrophotometer. KBr pellets were used for each measurement. Diffuse reflectance spectra of the solids were recorded on a Jasco V650 UV–Vis recording spectrophotometer. The spectra were recorded at room temperature in the wavelength range of 250–800 nm.

The photocatalytic activity was evaluated by photocatalytic degradation of MB under natural sunlight irradiation. The experiments were performed on the window ledge under direct solar radiation (5 h every sunny day). The average intensity of sunlight was about 0.0014 $W\,cm^{-2}$ (determined using a radiometer). The amount of synthesized material was insufficient to perform photocatalytic experiments in dye solution. Tests were performed on 4 cm^2 glass plates covered by 4 mg of the Ag complexes. A water solution of MB (1 $g\,dm^{-3}$) was dropped onto every plate. The plates were first dried in the dark and then exposed to natural sunlight. The photocatalytic degradation of methylene blue was determined by means of UV–Vis spectrophotometry through monitoring the color disappearance of the solid phases. A calibration curve (not presented here) was obtained at 665 nm wavelength with different concentrations of the MB solution. At specific time intervals, the dye blanching was measured by UV–Vis spectroscopy. Blank experiments were carried out in the dark and without catalysts, where no degradation of MB was observed.

2.2. Preparation of 2,6-di(anthracen-9-yl)pyridine (**L**)

A solution of 2,6-dibromopyridine (0.47 g, 2.0 mmol) in degassed toluene (25 mL) and water (3 mL) was added consecutively, by syringe, to a mixture of 2-(anthracen-9-yl)-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (**A**) [27] (1.37 g, 4.5 mmol), $[Pd(PPh_3)_4]$ (0.23 g, 0.2 mmol) and $Ba(OH)_2{\cdot}8H_2O$ (2.52 g, 8.0 mmol) under an argon atmosphere. The reaction was refluxed and stirred at 100 °C for 24 h with protection from light, then the toluene was evaporated and the residue was taken up in dichloromethane (100 ml) and washed with water (3 × 60 ml). The organic layer was dried over anhydrous $MgSO_4$ and the solvent was evaporated. 2,6-Di(anthracen-9-yl)pyridine **L** was purified by column chromatography (SiO_2; CH_2Cl_2/hexane 2:8). Yield: 83% (0.71 g). ESI-MS: *m*/*z* (%): 470 (15) $[L+K]^+$, 454 (40) $[L+Na]^+$, 432 (100) $[L+H]^+$. ^1H NMR ($CDCl_3$, 400 MHz) δ (ppm): 8.4 (s, 2H), 8.1 (t, 1H, *J* = 8.10 Hz), 7.9–8.0 (m, 4H, *J* = 7.96 Hz), 7.7–7.8 (m, 4H, *J* = 7.75), 7.6 (d, 2H, *J* = 7.64 Hz), 7.3–7.4 (m, 8H, *J* = 7.37 Hz). ^{13}C NMR ($CDCl_3$, 400 MHz) δ (ppm): 158.6, 136.6, 134.9, 131.4, 130.2, 128.5, 127.6, 126.0, 125.9, 125.5, 125.0. IR (KBr) ν (cm^{-1}): $\nu(C–H)_{ar}$ 3079, 3056, 3027, 2998; $\nu(C{=}C)$ 1580, 1564, 1517, 1456; $\nu(C{=}N)$ 1442, 1400, 1346, 1311; $\rho(C–H)$ 1198, 1170, 1143, 1085, 990, 952, 885; $\gamma(C–H)$ 837, 806, 789, 762, 735, 641, 608, 548, 438, 414. *Anal.* Calc. for $C_{33}H_{21}N$ (431.53): C, 91.85; H, 4.91; N, 3.25. Found: C, 91.87; H, 4.95; N, 3.24%.

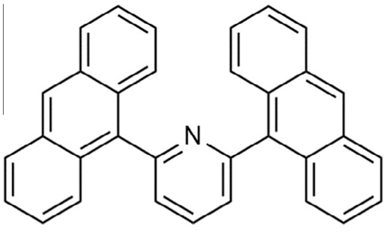

Fig. 1. The ligand **L** ($C_{33}H_{21}N$).

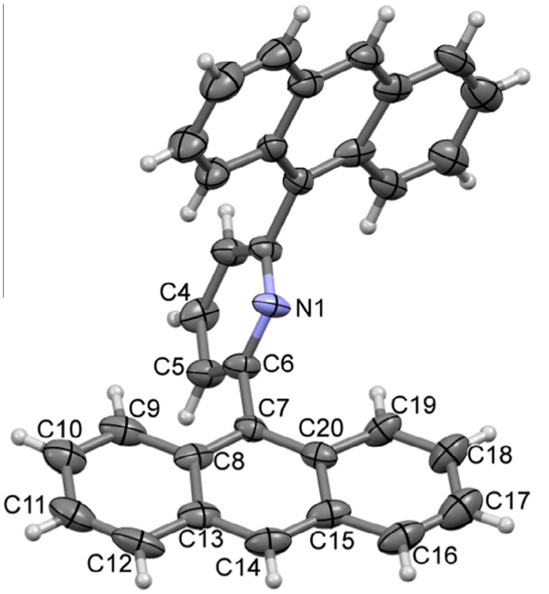

Fig. 2. Perspective view of the ligand **L**; ellipsoids are drawn at the 50% probability level, hydrogen atoms are depicted as spheres of arbitrary radii. The unlabelled part of the molecule is related to the labelled one by the symmetry operation 1 − *x*, *y*, 1/2 − *z*.

2.3. Preparation of the complexes

$[AgL(NO_3)]$ **1**: A mixture of $AgNO_3$ (7.9 mg, 46 μmol) and the ligand **L** (20.0 mg, 46 μmol) in a mixture of $CH_3CN{:}CH_2Cl_2$ in a 1:1 volume ratio (20 mL) was stirred at room temperature for 48 h under normal atmosphere. The product was isolated by evaporation of the solvent and recrystallisation of the residue from a minimum volume of CH_3CN by the gradual addition of diethyl ether to obtain complex **1** as a yellow solid. ESI-MS *m*/*z* (%): 538 (10) $[AgL]^+$, 432 (90) $[L+H]^+$. IR (KBr) ν (cm^{-1}): $\nu(C–H)_{ar}$ 3068, 3049, 2962; $\nu(NO_3^-)$ 1623, 1260, 1016, 780, 736; $\nu(C{=}C)$ 1593, 1559, 1458; $\nu(C{=}N)$ 1395, 1374, 1278; $\rho(C–H)$ 1159, 1083, 911, 857; $\gamma(C–H)$ 814, 603, 545, 440, 414. *Anal.* Calc. for $[Ag(C_{33}H_{21}N)]NO_3$ (601.39): C, 65.91; H, 3.52; N, 4.66. Found: C, 65.92, H, 3.51; N, 4.67%.

$[AgL(\mu\text{-}H_2O)AgL](BF_4)_2\ 3CH_2Cl_2$ **2**: A mixture of $AgBF_4$ (9.0 mg, 46 μmol) and the ligand **L** (20.0 mg, 46 μmol) in a mixture of $CH_2Cl_2{:}CH_3CN$ in a 10:2 volume ratio (12 mL) was stirred at room temperature for 48 h under normal atmosphere. The product was isolated by evaporation of the solvent and recrystallisation of the residue from a minimum volume of CH_3CN by the gradual addition of diethyl ether to obtain the complex **2** as a yellow solid. ESI-MS *m*/*z* (%): 971 (20) $[AgL_2]^+$, 547 (10) $[Ag_2L_2(H_2O)]^{2+}$, 538 (5) $[AgL]^+$, 432 (90) $[L+H]^+$. IR (KBr) ν (cm^{-1}): $\nu(O–H)_{H2O}$ 3463; $\nu(C–H)_{ar}$