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Three different configurations of d^{10} complexes based on benzoxazole pyridyl ligand: Synthesis, structures and properties

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ABSTRACT

Three different coordination complexes containing 2-(3′-pyridyl)-benzoxazole (3-PBO) and 2-(4′-pyridyl)-benzoxazole (4-PBO) ligands, namely $[Cd(3\text{-}PBO)_2(NO_3)_2(H_2O)_2]CH_3CN$ (**1**), $[Zn(4\text{-}PBO)_2(NO_3)_2]$ (**2**) $[Ag(4\text{-}PBO)_2Pic]_n$ (Pic = Picric acid) (**3**) have been synthesized and characterized. Single crystal X-ray structure analysis reveals that complex **1** is distorted seven-coordinated pentagonal-bipyramidal geometry, and complex **2** is a twisted six-coordinate octahedral structure, while complex **3** is a four-coordinated one-dimensional linear coordination polymer. A wide range of hydrogen bonding (of the O–H···O and O–H···N types) and π–π stacking interactions are also present in the crystal structure. These arrangements lead to the formation of three supramolecular structures. By careful inspection of the structures of **1** and **2**, the ion radius of metal centers adopting various coordination modes is a crucial factor for the formation of the different structures. Cyclic voltammograms of **3** indicate a quasi-reversible Ag^+/Ag couple. Moreover, the fluorescence properties of the ligands and complexes **1**–**3** were studied in solid state. Strong photoluminescence is observed in complexes **1** and **2** at room temperature and the complexes may be good candidates for potential luminescence materials.

1. Introduction

Over the past decade, the rational design and assembly of metal–organic frameworks have extensive interest in coordination and supramolecular chemistry because of its intriguing structure and potential applications in functional materials [1–3]. However, the ability to predict and control supramolecular assembly is still a long-term challenge the due to the fact that the self-assembly process is frequently influenced by various factors, including inbeing of the metal ions and the predesigned organic ligands as well as other factors such as medium, template, temperature and counterion [4,5]. With regard to the efforts to pursue the supramolecular framework synthesis strategy, some noncovalent forces, such as π–π stacking interactions and hydrogen bonding interactions, also intensively impact the supramolecular topology and dimensionality [6,7]. The ligands containing 2-substituded benzimidazoles/benzoxazoles have a wide range of interest for their antiviral activity [8], luminescent properties [9,10], multifunctional coordination patterns, and the potential to form supramolecular aggregates through π–π stacking interactions [10,11].

Complexes of d^{10} metal ions such as zinc(II), cadmium(II), and silver(I) have recently drawn global attention due to these metals playing important roles in many newer functional materials [12–14]. Zinc-containing compounds are particularly noticeable as luminescent materials for organic light-emitting diodes [15], and promote the various structures that can be used for sensory materials to detect alkaloids [16] and nitro aromatics [17]. Cd (II) is usually used in the field of optics such as fluorescent probes and nonlinear optical materials [18–21]. Ag(I) ions are more compatible with the electrical, photographic, imaging and pharmaceutical industries [22,23], the complexes of which exhibit different coordination geometries and luminescent properties [24].

In our previous work, we have investigated a series of V-shaped bis-benzimidazole ligands and their complexes [25]. However, little is known on the use of the title ligands. Hence, in this work, we wish to report the synthesis, structure, fluorescence studies, and electrochemical properties of three d^{10} metal complexes containing benzoxazole pyridyl ligands.

2. Experimental details

2.1. Materials and methods

All chemicals and solvents were reagent grade and were used without further purification. The C, H and N elemental analyses were performed using a Carlo Erba 1106 elemental analyzer. The

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thermal analysis of the complexes **1**–**3** were carried out under nitrogen atmosphere with a heating rate of 10 °C/min on METTLER TOLEDO TGA1. The IR spectra were recorded in the 4000–400 cm^{-1} region with a Nicolet FT-VERTEX 70 spectrometer using KBr pellets. Electronic spectra were taken on a Lab-Tech UV Bluestar spectrophotometer. Absorbance was measured with the Spectrumlab 722sp spectrophotometer at room temperature. 1H NMR spectra were recorded on a Varian VR300-MHz spectrometer with TMS as an internal standard. Fluorescence measurements were performed on a 970-CRT spectrofluorophotometer. Electrochemical measurements were performed on a LK2005A electrochemical analyser under nitrogen at 283 K. A glassy carbon working electrode, a platinum-wire auxiliary electrode and a Ag/AgCl reference electrode ($[Cl^-] = 1.0$ mol/L) were used in the three-electrode measurements. The electroactive component was at 1.0×10^{-3} mol·dm^{-3} concentration with tetrabutylammonium perchlorate (TBAP) (0.1 mol·dm^{-3}) used as the supporting electrolyte in DMF. Ag(Pic) is obtained by reacting silver carbonate with picric acid.

2.2. Synthesis of the ligands and complexes *1–3*

The ligands 3-PBO and 4-PBO (Scheme 1) were synthesized according to the reported method [26].

Three complexes were prepared using a similar procedure. Complex **1** was prepared by the following reaction. A solution of 3-PBO (0.0392 g, 0.2 mmol) in 3 mL of dichloromethane was very carefully placed on the bottom of the tube. 1 mL of dichloromethane as the buffer was slowly layered onto the ligand solution. A clear solution of $Cd(NO_3)_2 \cdot 4H_2O$ (0.0308 g, 0.1 mmol) in 3 mL of acetonitrile was then very carefully layered on the top of the buffer solution. After 1 week, colorless block crystals of **1** were collected by filtration and dried in vacuo. The synthesis of complex **2** is similar to **1** except for using 4-PBO (0.0392 g, 0.2 mmol) and $Zn(NO_3)_2 \cdot 6H_2O$ (0.0291 g, 0.1 mmol) instead of 3-PBO and $Cd(NO_3)_2 \cdot 4H_2O$. Complex **3** was synthesized similar to **2**, but using Ag(Pic) (0.0336 g, 0.1 mmol) instead of $Zn(NO_3)_2 \cdot 6H_2O$.

$[Cd(3\text{-}PBO)_2(NO_3)_2(H_2O)_2]CH_3CN$ (**1**), Yield: 52%. Elemental analysis for $C_{26}H_{23}CdN_7O_{10}$: calculated (%): C, 44.24; H, 3.28; N, 13.89. Found (%): C, 44.33; H, 3.41; N, 13.76. Selected-IR (KBr; cm^{-1}): 1617 ν(C=C), 1401 ν(C=N), 1300 $\nu(NO_3^-)$, 1041 $\nu(NO_3^-)$, 1240 ν(C—O). UV–Vis (in DMF), λ_{max} (nm): 303.

$[Zn(4\text{-}PBO)_2(NO_3)_2]$ (**2**), Yield: 54%. Elemental analysis for $C_{24}H_{16}N_6O_8Zn$: calculated (%): C, 49.55; H, 2.77; N, 14.44. Found (%): C, 49.45; H, 2.65; N, 14.31. Selected-IR (KBr; cm^{-1}): 1628 ν(C=C), 1413 ν(C=N), 1346 $\nu(NO_3^-)$, 1032 $\nu(NO_3^-)$, 1216 ν(C—O). UV–Vis (in DMF), λ_{max} (nm): 302.

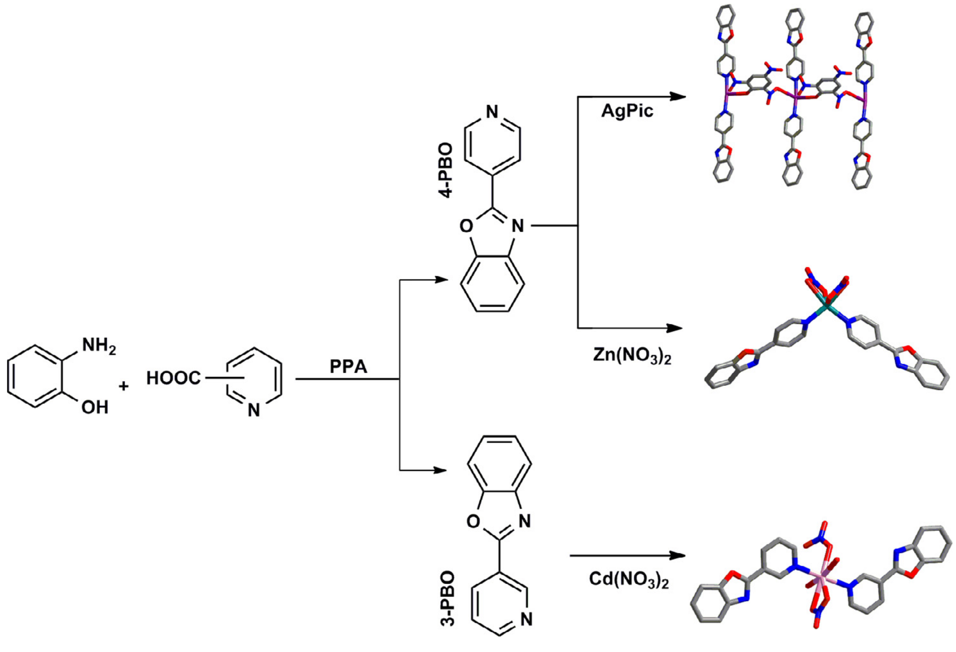
$[Ag(4\text{-}PBO)_2Pic]_n$ (**3**), Yield: 51%. Elemental analysis for $C_{30}H_{18}AgN_7O_9$: calculated (%): C, 49.47; H, 2.49; N, 13.46. Found (%): C, 49.33; H, 2.44; N, 13.55. Selected-IR (KBr; cm^{-1}): 1589 ν(C=C), 1395 ν(C=N), 1336 $\nu(Ar—NO_2)$, 1232 ν(C—O). UV–Vis (in DMF), λ_{max} (nm): 303 and 380.

2.3. X-ray crystallography

Suitable single crystals of complexes **1**–**3** were mounted on a glass fiber, and the intensity data were collected on a Bruker APEX II area detector with graphite-monochromated Mo Ka radiation ($\lambda = 0.71073$ Å) at 296(2) K. Data reduction and cell refinement were performed using the SMART and SAINT programs [27]. The absorption corrections are carried out by the empirical method. The structure was solved by direct methods and refined by full-matrix least squares against F^2 of data using SHELXTL software. [28] All H atoms were found in different electron maps and were subsequently refined in a riding-model approximation with C–H distances ranging from 0.95 to 0.99 Å. Information concerning the crystallographic data collection and structural refinements is summarized in Table 1. The relevant bond lengths and angles are listed in Table 2.

3. Results and discussion

Synthetic routes towards ligands and d^{10} metal complexes are exhibited in Scheme 1. The three complexes were obtained by the reaction of $Cd(NO_3)_2$, $Zn(NO_3)_2$ and Ag(Pic) with two ligands, namely, 3-PBO and 4-PBO, in acetonitrile and dichloromethane. They are soluble in polar aprotic solvents such as DMF, DMSO and MeCN, slightly soluble in ethanol, methanol, ethyl acetate, acetone and chloroform, and insoluble in Et_2O and petroleum ether.



Scheme 1. Synthesis of ligands and complexes **1**–**3**.