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Selective high capacity adsorption of Congo red, luminescence and antibacterial assessment of two new cadmium(II) coordination polymers

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ABSTRACT

Coordination polymers [CdCl(NCS)L]n (**1**) and $\{[Cd_2I_4(L)_2]\cdot H_2O\cdot DMF\}_n$ (**2**) (where L = 1, 1-(1,4-butanediyl) bis(1,3-dihydro-3-methyl-1H-imidazole- 2-thione)) were synthesized and structurally characterized. Compounds **1** and **2** both possess a tetrahedral arrangement with CdS_2NCl and CdS_2I_2 cores, respectively. In these structures, the flexible thione ligands adopt a μ- bridging coordination mode to form 1D chains along the b-axis. The 1D chains are join together by C–H—Cl hydrogen bonds (in **1**) and water molecules (in **2**) to create a 2D supramolecular framework with an ABAB...packing mode. Remarkably, compounds **1** and **2** in particular polymer **1** exhibit excellent capacity to adsorb Congo red (CR) with high selectivity. The experimental data demonstrate that the mechanism of sorption process can be described by the Elovich and pseudo second order kinetic models for **1** and **2**, respectively. Furthermore, the possible mechanism of CR absorption was investigated by UV–Vis and solid state fluorescence spectra for the title polymers. In addition, the antibacterial assessment of these compounds have also been studied.

1. Introduction

A considerable amount of work has been performed on the synthesis and characterization of metal complexes containing heterocyclic thiones as ligands in the past two decades [1]. The chemical interest of the monodentate thiones lies in the fact that they are potentially ambidentate or multi-functional donors with the exocyclic S and heterocyclic N donor atoms available for coordination. The biological interest of these compounds arises from their structural analogy to thiolated nucleosides [2]. In view of our interest on d^{10} metal complexes of coordination chemistry with monodentate terminal thione ligands, we have focused for some time on coordination compounds of Cu^I, Ag^I, Cd^{II} and Zn^{II} ions with a range of heterocyclic thiones such as 1-methylimidazoline-2(3H)thione (Hmimt) [3], imidazolidine-2-thione (Imt) [4] and seven-membered heterocyclic bulky ligand 1,3-diazepane-2-thione (Diap) [5]. On one hand, the construction of coordination polymers containing metal ions and flexible organic ligands have attracted much attention not only because of their intriguing variety of structures, but also for their potential applications in many fields. Coordination polymers containing two bio-active and drug used of 3-3methylimidazole-2- thione rings have not been studied in depth in spite of the potential that these species might have in biomedical applications [6]. On the other hand, cadmium(II) complexes of thiones are important as simple structural model for metal binding site in metallothioneins [7]. The design and synthesis of coordination polymers containing Cd^{II} metal centers have received remarkable attention for two main reasons: their non-linear optical properties and the convenient preparation of semi-conducting materials based on CdS through the thermal decomposition of these complexes [8]. This type of compounds possess a variety of structures, ranging from four to six coordinated species with tetrahedral and octahedral geometries, respectively [9]. By considering the aforementioned points, we have synthesized and structurally characterized two new 2D non-covalent supramolecular cadmium(II) compounds with the flexible thione ligand. These polymers are antibacterial active, have a potential to degrade cyanide into thiocyanate and are also able to absorb CR from the wastewater with high selectivity and effectively. The removal of organic dyes from industrial wastewater is an interesting research topic, because these compounds not only reduce the water quality, but also are toxic for human health [10–12]. The UV–Vis and solid state fluorescence spectra of the flexible thione ligand, Cd^{II} polymers and CR-Cd^{II} polymers were also investigated in detail.

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2. Experimental

2.1. Materials and physical measurements

All experiments were carried out in air. Starting materials were reagent grade and used as commercially obtained without further purification. Infrared spectra (4000–400 cm^{-1}) were recorded from KBr discs with a BOMEN MB102 FT-IR spectrometer. Elemental analyses for C, H, N and S were performed on Thermo Finigan Flash EA 1120 CHN analyzer. UV–Vis spectra were measured with a JASCO model 7850 spectrophotometer. Fluorescence spectra of the solid samples were recorded on a Hitachi F-7000 fluorescence spectrophotometer. The TG for **1**, **2** and their CR-Cd^{II} corresponding ones were performed on a Perkin–Elmer TGA7 instrument under flowing of O_2 with a heating rate of 10 °C min^{-1}. X-ray powder diffraction patterns were recorded on a Philips X'Pert Pro diffractometer (Cu Kα radiation, λ = 1.54184 Å) in the 2θ range 5–80°. The flexible thione ligand was prepared by the reaction of butilene-bridged methylimidazolium dicholoride with sulphur powder in methanol as a solvent [13].

2.2. Preparation of $[CdCl(NCS)L]_n$ (1)

$CdCl_2$ (0.025 g, 1 mmol) and KSCN (0.005 g, 1 mmol) were added to a methanol solution (15 mL). The mixture was stirred at room temperature for 20 min. The flexible thione ligand (0.032 g 1 mmol) was added to the solution and then heated under reflux for 8 h. The resulting white color precipitate was filtered off. Colorless cubic single crystals suitable for X-ray crystallography were obtained at room temperature by recrystallization from DMF after four days (0.09 g, yield: 56% based on Cd). The crystals were collected and vacuum dried. Mp = 215 °C. Anal. calcd. (%) for $C_{13}H_{18}CdClN_5S_3$: C 29.80, H 3.46, N 13.36, S 18.36; found: C 30.09, H 3.45, N 13.35, S 17. 95. Selected IR (KBr, cm^{-1}): ν (-CH_2- of spacer) 3155 −2941 (m), ν (CN) 2059 (s), 1564 (s), 1471 (s), 1417 (s), 1230 (s), 1181 (m), 767 (m), 724 (s), 687 (s), ν (C=S) 521(m), 473 (m). UV–Vis spectrum (DMF ,λmaxin nm): 276(π→π*in L). Fluorescence: The complex was excited at 282 nm and emission was observed at 550.2 nm.

2.3. Preparation of $[\{[Cd_2I_4(L)_2]\cdot H_2O\cdot DMF\}_n$(2)

The flexible thione ligand (0.018 g, 1 mmol) was added to a solution of CdI_2 (0.024 g, 1 mmol) in acetone (15 mL). The reaction mixture was heated under reflux for 6 h. The resulting white color precipitate was filtered off. Colorless cubic single crystals suitable for X-ray crystallography were obtained at room temperature by recrystallization the sample from DMF after four days (0.18 g, yield: 61% based on Cd). The crystals were collected and vacuum dried. Mp = 135 °C. Anal. calcd. (%) for $C_{27}H_{45}Cd_2I_4N_9O_2S_4$: C 22.21, H 2.79, N 8.63, S 9.88; found: C 22.45, H 2.88, N 8.87, S 9.47. Selected IR (KBr, cm^{-1}): ν (-CH_2- of spacer) 3148 −2951 (m), ν (C=O of unbounded DMF) 1713 (s), 1358 (w), 1245 (w), 1851(m), 1131 (w), 1091 (w), 733 (m), 687 (m), ν (C=S) 512 (m). UV–Vis spectrum (DMF ,λmaxin nm): 274 (π→π*in L). Fluorescence: The complex was excited at 282 nm and emission was observed at 547.2 nm.

2.4. An attempt for preparation of [CdCl(CN)L]n

In the reaction similar to **1,** KCN was used instead of KSCN. X-ray crystallography and elemental analysis illustrated that CN is converted to SCN and the product of this reaction is the same as compound **1**.

2.4.1. Dye adsorption and separation

Adsorption experiments with the synthesized Cd^{II} coordination polymers were carried out using batch method. The experiments were conducted individually for each dye by using an aliquot of 10 mL of the dye solutions with selected initial concentration (30–80 ppm) was transferred into each of the beakers. A dosage of 10 mg of compounds **1** and **2** were added to the beakers. The resulting mixture was stirrer for 1 min and then centrifuge. A concentration of the dye residue in the supernatant was recorded by UV–Vis spectrometer. The absorbance before and after adsorption of the dye were measured. The percent adsorption of each dye and the dye removal efficiency of Cd^{II} coordination polymers, were calculated by Eq. (1).

$$\%Absorbtion = \frac{(C0 - Cf)}{C0}\times 100 \tag{1}$$

Where C0 and Cf represent the initial and final (after adsorption) dye concentration in the aqueous phase, respectively. All tests were performed in duplicate at 25 °C.

2.4.2. Procedure for determination of chloride and iodide

Each of the Cd^{II} polymers (10 mg) separately was added to the freshly prepared CR dye solution (60 ppm). After stirring for 1 min the mixture was centrifuged and the supernatant was used to measure the concentration of the appropriate halogen ion in the solution.

2.4.3. X-ray crystallography

Single crystal data collections and corrections were done at 100(2)K with Bruker D8Venture diffractometer using graphite mono chromated MoKa (λ = 0.71073 Å). The structures were solved by direct methods with SIR97 [14] and refined with full-matrix least-squares techniques on F^2 with SHELXL-97 [15]. The molecular structure plots were prepared using ORTEPIII, DIAMOND and Mercury [16].

2.4.4. Antibacterial activity assessments

The antibacterial properties of free ligand and the title complexes were evaluated according to Kirby-Bauer disc diffusion method as described by CLSI guidelines. So, sterile blank discs (6.4 mm) were saturated by 5, 10, 20 and 40 mg mL^{-1} concentrations of the prepared mentioned compounds in DMSO. As a result 0.2, 0.4, 0.8 and 1.6 mg effective doses per disc were achieved. Escherichia coli (ATCC25299), Pseudomonas aeruginasa (ATCC9027), Bacillus subtilis (ATCC6633) and Staphylococcus aureus (ATCC6538) were used as target bacteria. The saturated discs were placed on the lawn culture of 0.5 McFarland suspension of each species on Mueller-Hinton agar (MHA, Merck, Germany) and plates were incubated at 37°C for 24 h. In order to find the possible effect of solvent, a DMSO saturated disc was also used as negative control.

2.4.5. MIC and MBC indices

Minimum Inhibitory Concentration (MIC) and Minimum Bactericidal Concentration (MBC) are indices which quantify the least concentration of a compound that is able to inhibit bacterial growth or kill it. So, these indices were investigated for polymers **1** and **2** against two gram positive and two gram negative bacteria using macro broth dilution assay. For this purpose, serial two -fold dilutions from 0.5 to 32 mg/mL of each compounds were prepared in Mueller-Hinton broth and inoculated with 100 μl of 0.5 McFarland suspensions of mentioned bacteria and incubated for 24 h at 37 °C, the least concentration at which no visible growth was detected, regarded as MIC. From growth negative tubes a culture was prepared on Mueller- Hinton agar and the least concentration at which colony formation was unsuccessful, regarded as MBC.

2.4.6. DNA cleavage assessment

The chromosomal and plasmid DNA were treated with 20 mg mL^{-1} concentration of **1** and **2** in DMSO. For this purpose, 5 μl of template DNA was mixed with 2.5 μl of each of the prepared solutions and incubated at 37 °C for 2 h. 2 μl of this solution was then mixed with loading dye and electrophoresed at 80 V and 45 min in 1% agarose gel containing DNA safe stain. Finally, the results were documented using UVI Tech gel documentation.