

Self-Assembly of a Cd^{2+} Compound with 4-Pyridylthioacetic Acid: Structural and Luminescence Properties

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Dedicated to Professor Hubert Schmidbaur on the occasion of his 70th birthday

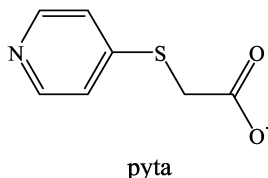
An interesting 3-D supramolecular architecture has been constructed through $\text{O-H}\cdots\text{O}$ and $\text{S}\cdots\text{S}$ weak interactions based on a neutral 1-D coordination polymer, $[\text{Cd}(\text{pyta})_2(\text{H}_2\text{O})]_n$ (pyta = pyridylthiocarboxylate), by self-assembly of the Cd^{2+} ion and Hpyta ligand. This supramolecular approach is achieved in combination of coordinative bonds, $\text{O-H}\cdots\text{O}$ and $\text{S}\cdots\text{S}$ interactions. The tetragonal unit of 1-D coordination polymers forms a 1-D channel structure with a dimension of $5.35 \times 6.86 \text{ \AA}^2$ in the solid state, leading to the formation of zeolite-like materials. In combination with the zeolite-like nature of the title compound as well as its luminescence behavior, it is expected to find useful applications in luminescence sensing for VOCs (volatile organic compounds).

Key words: Self-Assembly, Luminescence, Supramolecular, Coordination Polymers, Volatile Organic Compounds

Introduction

The widespread use of the coordinative-bond approach in the construction of supramolecular coordination compounds by self-assembly is well established [1, 2]; moreover, it is able to parallel the use of the highly directional hydrogen bonds as a means of controlling self-assembly in supramolecular systems. In this context, the combination of the coordinative-bond approach, hydrogen bonding and / or other weak interactions has recently been recognized as a very powerful and versatile strategy in the material synthesis [3]. So far, a variety of discrete and a wide range of one- and multi-dimensional infinite solid-state coordination architectures with hydrogen-bonded frameworks have been achieved in the last decade [4, 5].

4-Pyridylthioacetic acid (Hpyta) is chosen as a building block for the construction of supramolecular architectures in this work, because it has a flexible backbone containing bifunctional binding sites (both pyridyl and carboxylate groups upon deprotonation) as well as a strong capability of forming hydrogen bonding and / or $\text{S}\cdots\text{S}$ weak interactions, playing an important role in the assembly of supramolecular compounds. Although the crystal engineering work of



Scheme 1.

many metal complexes of pyta has been published so far [6], the luminescence properties and the Cd^{2+} analogue are not studied yet. In continuing our research interest in crystal engineering and luminescence studies [7], we report here the solid-state luminescence of the Cd^{2+} complex of pyta as well as its interesting structural motif in the solid state.

Experimental Section

Synthesis

$[\text{Cd}(\text{pyta})_2(\text{H}_2\text{O})]_n$ **1**: $\text{Cd}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ [25 mg, 0.08 mmol] dissolved in 2 ml of CH_3CN was carefully layered onto an aqueous solution of pytaH [27 mg (0.16 mmol), dissolved in 2 ml of H_2O]. The colorless crystals were obtained within one week in a 51% yield. Analysis for $\text{C}_{14}\text{H}_{14}\text{CdN}_2\text{O}_5\text{S}_2$: calcd. C 36.02, H 3.02, N 6.00; found C 35.86, H 3.35, N 6.31.

Table 1. Crystallographic data for [Cd(pyta)₂(H₂O)]_n.

	Cd(pyta) ₂ (H ₂ O)
Empirical formula	C ₁₄ H ₁₄ CdN ₂ O ₅ S ₂
Formula weight	466.79
Crystal system	monoclinic
Space group (No.)	C2/c
<i>a</i> [Å]	21.6169(3)
<i>b</i> [Å]	6.5940(1)
<i>c</i> [Å]	15.6015(3)
β [°]	133.057(1)
<i>V</i> [Å ³], <i>Z</i>	1624.91(5), 4
ρ_{calc} [g cm ⁻³]	1.908
<i>F</i> (000) (e)	928
μ (Mo-K α) [mm ⁻¹]	1.629
<i>T</i> [K]	150(1)
Reflections collected	8586
Observed reflections (<i>F</i> _o ≥ 2σ(<i>F</i> _o))	1872
Refined parameters	111
<i>R</i> ^a , <i>R</i> _w ^b	0.031, 0.071
ρ_{fin} (max/min) [e Å ⁻³]	0.738 / -1.503
Goodness-of-fit on <i>F</i> ²	1.021
No. frames	1,800

^a $R = \sum ||F_o| - |F_c|| / \sum |F_o|$; ^b $wR_2 = \{[\sum w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$; $w = 1/[\sigma^2(F_o^2) + (0.0451P)^2 + 0.0000P]$; where $P = (F_o^2 + 2F_c^2)/3$.

X-ray crystallography

A suitable single crystal of complex **1** was mounted on a glass capillary. Data collection was carried out on a Bruker SMART CCD diffractometer with Mo radiation (0.71073 Å) at 150 K. A preliminary orientation matrix and unit cell parameters were determined from 3 runs of 15 frames each, each frame corresponding to 0.3° scan in 15 s, followed by spot integration and least-square refinement. Data were measured using an ω scan of 0.3° per frame for 20 s until a complete hemisphere had been collected. Cell parameters were retrieved using SMART [8] software and refined with SAINT [9] on all observed reflections. Data reduction was performed with the SAINT software and corrected for Lorentz and polarization effects. Absorption corrections were applied with the program SADABS [10]. The structure was solved by direct methods with the SHELX93 [11] program and refined by full-matrix least-squares methods on *F*² with SHELXL-PC V 5.03 [11]. All non-hydrogen atomic positions were located in difference Fourier maps and refined anisotropically. The hydrogen atoms were placed in their geometrically generated positions. Detailed data collection and refinement of complex **1** are summarized in Table 1.

Results and Discussion

Although the structural work of many metal complexes (Co²⁺ [6f], Cu²⁺ [6f], Ag⁺ [6f], Zn²⁺ [6a, 6b], Mn²⁺ [6e, 6f], Pb²⁺ [6f], Sn⁴⁺ [6c] and Pd²⁺ [6g]) of pyta has been published, the luminescence study re-

garding this family of compounds is still absent. The Cd²⁺ complexes are particularly of interest and attraction for their rich luminescence due to intraligand (IL) or charge-transfer (CT) transitions [12] and versatile coordination modes, where the Cd²⁺ ion can have a coordination number up to 7, expected to have structural versatility contributing to crystal engineering. Consequently, the above mentioned reasons prompted us to initiate this study.

Description of crystal structure

As shown in Figure 1(a), each Cd²⁺ ion is coordinated by two pyridyl nitrogen atoms [Cd-N of 2.321(2) Å], two slightly asymmetric carboxylic oxygen atoms [Cd-O of 2.396(2) and 2.461(2) Å], and a water molecule [Cd-O of 2.325(3) Å], which reach a 7-coordination configuration, a common coordination geometry for the Cd²⁺ ion. Hpyta is deprotonated to give rise to pyta even in the absence of any base during the reaction process. The structure of complex **1** displays a 1-D coordination-polymer framework in which two adjacent Cd²⁺ ions are linked through two bent pyta ligands to form a tetragonal unit with a size of 5.35 × 6.86 Å² and the Cd...Cd distance of 8.73 Å. It can also be described as two zig-zag chains (one-stranded) interconnected at the Cd²⁺ ions leading to the formation of 1-D coordination polymers (two-stranded). The packing of the molecules reveals the existence of only one type of O-H...O hydrogen bonds as shown in Fig. 1(b) and weak inter-chain S...S interactions, where a pair of inter-chain head-to-tail O-H...O hydrogen bonds [O(3)-H(3A)...O(1) : O(3)-H(3A) 0.850 Å, H(3A)...O(1) 1.979 Å, C(11')...O(4) 2.744(3) Å; O(3)-H(3A)...O(1) 149.3°] between the coordinated water molecule in each chain and the carboxylic oxygen atoms from the adjacent chain are observed, resulting in a 2-D sheet structure. In addition, the nonbonding S...S distance between two adjacent 2-D hydrogen-bonded frameworks is 3.550 Å (less than the sum of the van der Waals' radii of two S atoms, 3.6 Å) [13], indicating the presence of weak S...S interactions. In this context, in combination of the hydrogen-bonding and S...S interactions, these 1-D coordination chains are further extended into an interesting 3-D supramolecular architecture. Although a similar 3-D supramolecular network through O-H...O and S...S weak interactions has been constructed from a neutral 1-D coordina-

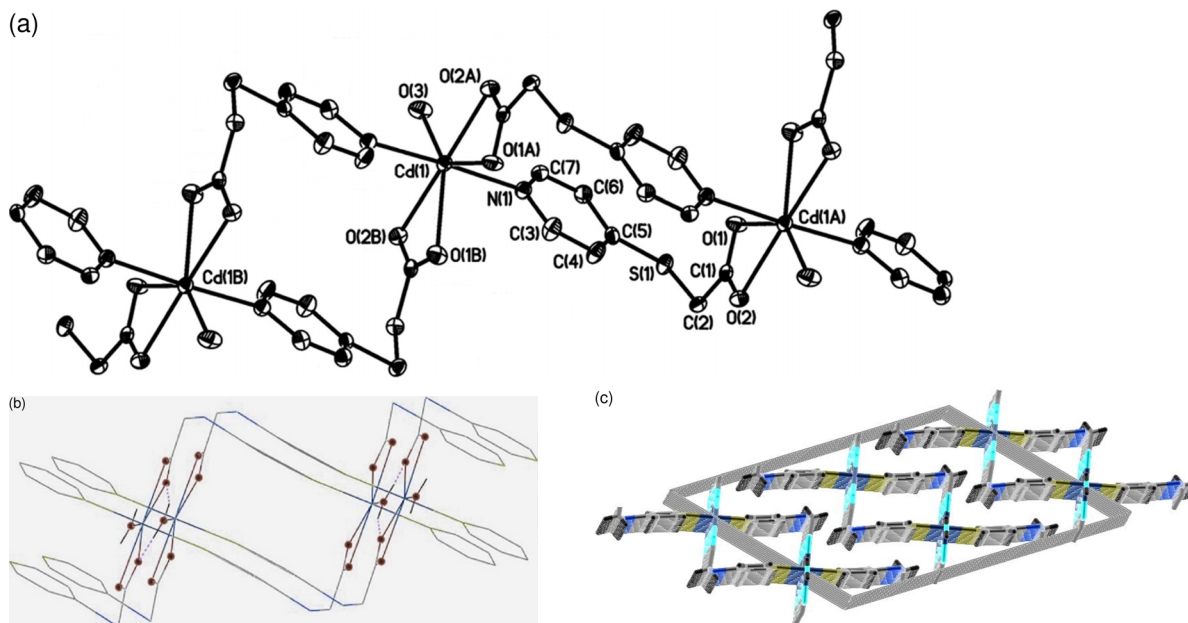


Fig. 1. (a) Molecular structure of complex **1**. ORTEP diagram shows 50% probability ellipsoids. Selected bond lengths (\AA) and angles ($^\circ$): Cd(1)-N(1) 2.321(2), Cd(1)-O(1) 2.461(2), Cd(1)-O(2) 2.396(2), Cd(1)-O(3) 2.325(3), C(1)-O(1) 1.255(3), C(1)-O(2) 1.256(3), N(1)-Cd(1)-O(3) 92.55(6); (b) a pair of inter-chain head-to-tail O-H \cdots O hydrogen bonds between the coordinated water molecule and the carboxylic oxygen atoms, and (c) combining the hydrogen-bonding and S \cdots S weak interactions, these 1-D coordination chains are further extended into an interesting 3-D supramolecular architecture showing a 1-D channel structure with a dimension of $5.35 \times 6.86 \text{ \AA}^2$ in the solid state.

tion polymer $\{[\text{Cu}(\text{pyta})_2(\text{H}_2\text{O})] \cdot 0.5\text{H}_2\text{O}\}_n$ [6f] consisting of rectangle units by reaction of $\text{CuCl}_2 \cdot \text{H}_2\text{O}$ with Hpyta, it shows a distinct structural motif compared with that of complex **1**. The difference in coordination numbers (7 for Cd^{2+} and 5 for Cu^{2+}) results in a different hydrogen-bonding mode due to the coordinated and semi-coordinated water molecules for the Cd^{2+} and Cu^{2+} complexes respectively, where the former has a symmetric hydrogen-bonding mode and the latter an asymmetric one between the coordinated or semi-coordinated water molecules and the carboxylic oxygen atoms. It is noted that the tetragonal unit also forms a 1-D channel structure in the solid state as shown in Figure 1(c), leading to the formation of a zeolite-like structure.

Solid-state emission spectra

Figure 2 shows the solid-state emission spectra of complex **1** and Hpyta measured at room temperature. Upon photoexcitation at 350 nm complex **1** shows a low-energy emission with a maximum at 547 nm, whereas Hpyta displays only a high-energy one at

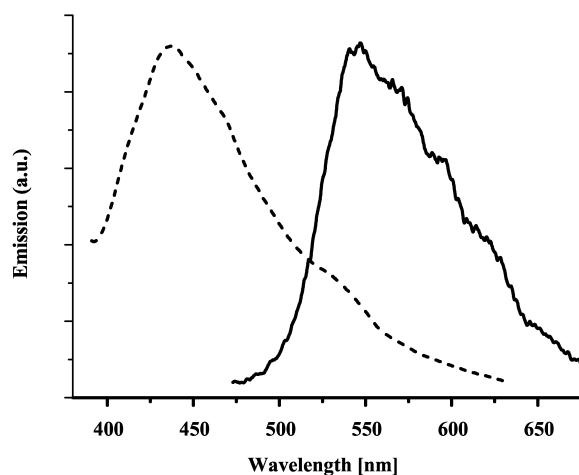


Fig. 2. The solid-state emission spectra of complex **1** (solid line) and Hpyta (dash line) measured at room temperature with an excitation wavelength at 350 nm.

436 nm. Given a significant red shift from pyta to complex **1**, the low-energy emission is unlikely to originate from pyta itself (IL). With reference to previous studies [12], this low-energy emission would be tentatively

assigned as a ligand-to-metal charge-transfer (LMCT) transition. The charge-transfer excited states of Cd^{2+} complexes with a low-energy emission are still rare compared with those of IL, and thus in combination with the zeolite-like nature of complex **1**, it is expected to find useful applications in luminescence sensing for VOCs.

Conclusion

We report here an interesting 3-D supramolecular architecture through $\text{O-H}\cdots\text{O}$ and $\text{S}\cdots\text{S}$ weak interactions constructed from a neutral 1-D coordination

polymer by self-assembly of the Cd^{2+} ion and Hpyta ligand. It is noted that the tetragonal unit of 1-D coordination polymers forms a 1-D channel structure with a dimension of $5.35 \times 6.86 \text{ \AA}^2$ in the solid state leading to the formation of zeolite-like materials. In combination with the zeolite-like nature of the title compound and its luminescence behavior, it is expected to find useful applications in luminescence sensing.

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