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PHYSICAL METHODS OF INVESTIGATION

Crystal Structure and Fluorescence of Supramolecular Compound $[Cd_3Cl_6C_6N_2O_8H_{22}]_n$[1]

Ge Guo, Ruzhong Sun, and Yuanlin Dang

College of Chemistry and Pharmacy Engineering, Nanyang Normal University, Nanyang, Henan, 473061, China

e-mail: yuanlindang@yahoo.com.cn

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Abstract—A novel trinuclear supramolecular compound of $[Cd_3Cl_6C_6N_2O_8H_{22}]_n$ has been synthesized under alanine with cadmium chloride to the reaction in aqueous solution conditions, and characterized by elemental analyses, FT-IR spectroscopy, X-ray diffraction, DTA-TG. Its crystal structure was determined from single crystal X-ray diffraction. The title compound crystallizes in monoclinic system with space group $P2_1/n$. The crystal structure of the compound is characterized by forming a trinuclear 3D supramolecular structure with three cadmium(II) ions, six chloride ions, two molecules D, L-alanine in salt, two coordinated water molecules and two crystal water molecules. Cd(1) is distorted octahedrally coordinated with two oxygen atoms (from the adjacent amino acid and water molecule) and four chloride ions; Cd(2) is smaller extent distorted octahedrally coordinated with two oxygen atoms (from the adjacent amino acids) and four chloride ions. Cd(1) and Cd(2) connected by the bridge bonds of μ_2-Cl, μ_3-Cl and the carboxyl oxygen into ID chain structure, which further connected by hydrogen bonds to form 3D supramolecular network. Fluorescence test showed that the compound has a good photoluminescence property, respectively.

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Cadmium is an important environmental and industrial toxins, it also is a very long half-life multi-organ, multi-system poison [1, 2]. Amino acids are an important component of biological organisms, it's the basic unit of peptide and protein composition, it also is the metabolic processes of biological organisms in the basic materials, it has important physiological functions. As we all know, we study the composition and structure of complexes with the cadmium and the amino acid is benefit of the physiological role of organism. Moreover, cadmium is one of the semiconductor materials, which compounds are mostly good photoluminescence properties [3, 4]. The inorganic-organic supramolecular compound is a new material, which has wide application areas of optical, catalytic, magnetic materials, conductors, semiconductors, nonlinear optical materials and molecular recognition [5–8]. To investigate the compounds of cadmium(II) and amino acid form a supramolecular structure and photoluminescence properties, the compound [2-(3-pyridy1)benzimidazole$H_2]^{4+} \cdot [Cd_2Cl_8]^{4-}$ has been synthesized under been synthesized under hydrothermal conditions in literature [9], and its structure and fluorescence properties have been studied. In this paper, we report a supramolecular compound of $[Cd_3Cl_6C_6N_2O_8H_{22}]_n$ (**I**) has been synthesized under alanine with cadmium chloride to the reaction in aqueous solution conditions at 323 K, and characterized by elemental analyses, FT-IR spectroscopy, X-ray diffraction, DTG-TG and fluorescence spectra. Its crystal structure was determined from single crystal X-ray diffraction, to our knowledge, the structure of the type not been reported.

EXPERIMENTAL SECTION

Reagents. $CdCl_2$ (mass fraction ≥ 0.996), DL–alanine (Ala) (mass fraction ≥ 0.998).

Equipment and conditions. C, H and N analyses were carried out with a Vario EL III CHNOS element analysis instrument. The IR analysis was conducted on a Nicolet 5700 spectrometer (KBr discs). Thermal characterization of the new compound was undertaken with a SDT Q600 V8.0 thermal analysis apparatus (TG-DTG) that worked with a heating rate of 10 K/min under a N_2 atmosphere with a flow rate of 100 cm^3/min; X-ray diffraction (XRD) measurements were performed by a D/Max-3C diffractometer using CuK_α radiation, 50 kV and 80 mA, at room temperature, in air. The diffraction data of the structure analysis was collected by a Bruker Smart Apex-ll CCD diffractometer using a graphite monochromatized MoK_α radition (λ = 0.071 073 nm), at room temperature. Broker); CARY Eclipse fluorescence spectrophotometer (VARIAN), light flashing-type is xenon lamp, its scanning speed of 12000 nm min^{-1}. Excitation and emission slits were 5.0 nm.

Synthesis. The title compound was synthesized from a mixture of 1.8331 g of $CdCl_2$ in 30 mL of H_2O, 0.5934 g of Ala in 30 mL of H_2O, the $CdCl_2$ and Ala in

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Table 1. Bond lengths [Å] and angles [deg] for **I**

Cd(1)–O(1)	2.273(4)	Cd(2)–Cl(1)#3	2.5880(15)
Cd(1)–O(2W)	2.321(4)	Cd(2)–Cl(2)	2.6419(14)
Cd(1)–Cl(2)#1	2.8401(15)	O(2)–C(2)#2	1.272(7)
Cd(2)–O(2)	2.301(4)	O(2W)–H(2)	0.81(8)
O(1)Cd(1)O(2W)	83.25(16)	O(2)Cd(2)Cl(1)#3	93.88(11)
O(1)Cd(1)Cl(2)	103.44(11)	O(2)Cd(2)Cl(2)	86.68(11)
O(2W)Cd(1)Cl(2)	170.71(12)	Cl(1)#1Cd(2)Cl(2)	84.84(5)
O(2W)Cd(1)Cl(1)	82.79(13)	O(2)Cd(2)Cl(2)#2	93.32(11)
O(1)Cd(1)Cl(2)#1	78.43(11)	Cl(2)Cd(2)Cl(2)#2	180.00(6)
O(2W)Cd(1)Cl(2)#1	87.01(12)	Cd(1)Cl(2)Cd(2)	102.94(5)
Cl(3)Cd(1)Cl(2)#1	172.83(5)	Cd(1)Cl(2)Cd(1)#1	91.95(5)
Cl(2)Cd(1)Cl(2)#1	88.05(5)	Cd(2)Cl(2)Cd(1)#1	92.29(4)
Cl(1)Cd(1)Cl(2)#1	80.36(4)	Cd(2)#4Cl(1)Cd(1)	98.79(5)
O(2)#2Cd(2)O(2)	180.0(2)	C(2)#2O(2)Cd(2)	129.6(4)
O(2)#2Cd(2)Cl(1)#1	93.88(11)	Cd(1)O(2W)H(1)	109(5)
O(2)Cd(2)Cl(1)#1	86.12(11)	Cd(1)O(2W)H(2)	112(5)
O(2)#2Cd(2)Cl(1)#3	86.12(11)	–	–

Note: Symmetry code: #1 $-x-2, -y, -z$; #2 $-x-1, -y, -z$; #3 $x+1, y, z$; #4 $x-1, y, z$. (CCDC number–CCDC 729398).

the molar ratio of 3 : 2. Ala solution will slowly add drops of $CdCl_2$ solution, constantly mixed at 323 K about 8 h, and then vacuum evaporation. The resulting columnar colorless crystals were collected and dried in air at ambient temperature. Analysis calculated for the title compound: C 9.00, H 2.75, N 3.50%; found: C 9.09, H 2.56, N 3.42%.

Determination of crystal structure. A suitable single crystal with dimensions 0.12 × 0.10 × 0.08 mm was selected for the crystal structure measurements. The X-ray diffraction intensities were recorded by a Bruker Apex-II CCD diffractometer with graphite monochromatized MoK_α radiation ($\lambda = 0.071073$ nm), at a temperature of 296(2) K. A total of 5203 reflection

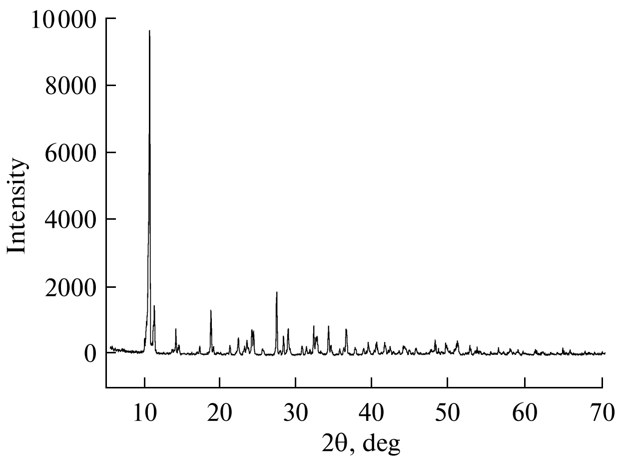

Fig. 1. X-ray powder diffraction spectrum of $[Cd_3Cl_6C_6N_2O_8H_{22}]_n$.

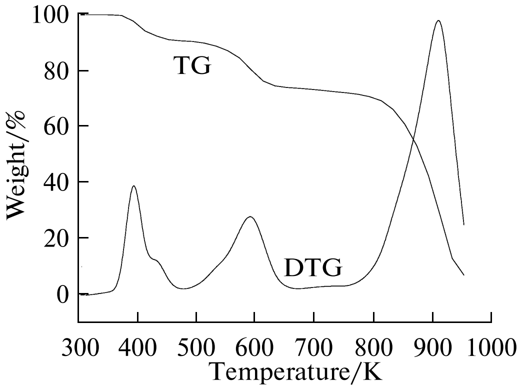

Fig. 2. Thermo-gravimetric curve of $[Cd_3Cl_6C_6N_2O_8H_{22}]_n$.

Table 2. Hydrogen bonds for A [Å and deg]

D–H···A (Å)	*d*(D–H)	*d*(H···A)	*d*(D···A)	<(DHA)
N(1)–H(1A)···Cl(3)#5	0.86	2.65	3.250(5)	128
N(1)–H(1B)···O(1W)#6	0.86	2.32	3.005(7)	137
N(1)–H(1B)···Cl(1)#7	0.86	2.82	3.337(5)	120

Note: Symmetry code: #5 $-x-2, -y-1, -z$; #6 $-x-3/2, y-1/2, -z-1/2$; #7 $x+1/2, -y-1/2, z-1/2$.

intensities, of which 1889 were independent ($R_{\text{int}} = 0.0292$), were collected within the range $2.40 < \theta < 24.99$ deg for the compound. All data were corrected and experience *Lp* absorption correction factor. Positions of the hydrogen atoms attached to carbon and nitrogen atoms were fixed at their ideal positions, and those attached to water hydrogen atoms were not located. All non-hydrogen atoms were refined anistropically. The final cycle of refinement performed on afforded residuals $R_1 = 0.0381$ and $wR_2 = 0.1691$. The structures were solved using direct method and refined by full-matrix least-squares methods on F^2 by using SHELXL-97 program package [10, 11].

RESULTS AND DISCUSSION

The FT-IR spectrum of the pure D, L-alanine and the complexes are recorded from KBr tablet in the region of 100–4000 cm^{-1}. Compared with that of the pure Ala, the spectrum of the as-formed complexes displays several significant differences: (1) The adsorption peaks at 3086 and 2958 cm^{-1} are resulted from the asymmetrical stretching vibration and the symmetrical stretching vibration of NH_3^+; however, as to the complexes, these adsorption bands become broadened and are shifted to 3130 cm^{-1}, which reveals the existence of strong hydrogen bonds between amino groups and H_2O. (2) As shown in the spectrum of the complexes, the adsorption bonds at 1624 and 1410 cm^{-1}, assigned to the asymmetrical and symmetrical stretching vibrations of COO^- in D, L-alanine, are shifted to 1619 and 1464 cm^{-1}, respectively. The results indicate that these carboxyl groups of the complexes are double coordination. (3) The band around 3444 cm^{-1} is attributed to the stretching vibration of –OH in the H_2O molecular. The band observed near 531 cm^{-1} is the wagging vibration of H_2O, which indicates that H_2O molecular take part in coordination. (4) The complexes also exhibit some medium intensity bands at the low wavelength range. For example, the bands around 369 and 357 cm^{-1} are assigned to the symmetrical stretching vibration of Cd–O, and the peaks around 283, 266, 260 cm^{-1} are ascribed to the symmetrical stretching vibration of Cd–Cl, which suggested that the oxygen atoms and chlorine atoms also take part in coordination.

The X-ray powder diffraction pattern of the **I** compound obtained is shown in Fig. 1. It is neither the same as $CdCl_2$ or Ala, nor the simple superposition of $CdCl_2$ and Ala. This demonstrates that I is formed from a reaction between $CdCl_2$ and Ala.

TG-DTG curves for the title compound ispresented in Fig. 2. It can be seen clearly from the mass-loss curve that three steps existed in the process of the thermal decomposition for **I**. The solid complex was

Fig. 3. One-dimensional chain of the complex for a.

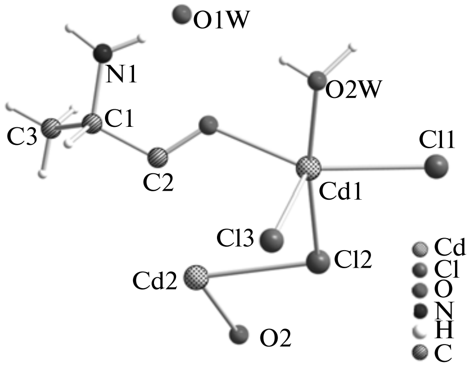

Fig. 4. Asymmetric unit structure.

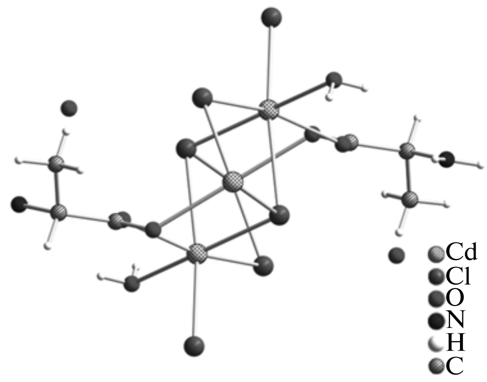

Fig. 5. Molecular structure of complex $[Cd_3Cl_6C_6N_2O_8H_{22}]_n$.

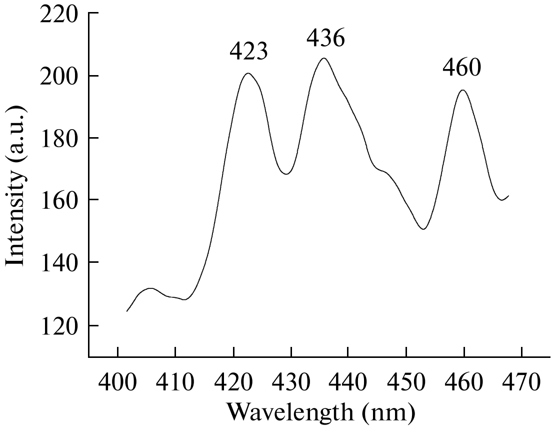

Fig. 6. Fluorescence spectra of compound $[Cd_3Cl_6C_6N_2O_8H_{22}]_n$.

stable below 360 K and started decomposition at this point. The first mass-loss took place in the range of 360 to 475 K, the second mass-loss occurred in the temperature range 508 to 643 K, and the third mass-loss arose at 782 K. These results were well in accord with those obtained by DTG curve. The first mass-loss was 9.19%, and the second mass-loss was 17.12%. According to the mass-loss in each step, it was assumed that the first mass-loss peak was associated with the loss of water, the second mass-loss peak corresponded to the decomposition of Ala, and the third mass-loss peak represented the sublimation of cadmium chloride. The first mass-loss value was in agreement with the theoretical dehydration value of 9.00%.

The main bond lengths and angles for title compound is listed in Table 1 and the details of hydrogen bonds for title compound is listed in Table 2. The asymmetric structure of the title compound consists of two Cd^{2+} cation, one amino acid molecule and water molecule as shown in Fig. 3. Figure 4 shows the one-dimensional chain of the complex along the a axis. Figure 5 shows the coordination environment of Cd atoms. Unit cell composed of three cadmium(II) ions, six chloride ions, two molecules Ala in salt, two coordinated water and two crystal water and formed 3D supramolecular compound. Cd(l) is distorted octahedrally coordinated with two oxygen atoms O(1) which from the adjacent amino acid and O(2W) which from water molecule, and four chloride ions (Cl(3) and Cl(2)#l are in the axial position). The bond length is 2.5325(15) Å for Cd(1)–Cl(3) and 2.8401(15) Å for Cd(1)–Cl(2)#l, the bond angle is 172.83(5)° for Cl(3)Cd(l)Cl(2)#l. O(2W), O(1), Cl(1) and Cl(2) are in the equatorial position, the shortest bond length is 2.273(4) Å and the longest bond length of 2.6221(15) Å. The equatorial plane diagonal atomic the largest angle is 170.71(12)° for O(2W)Cd(1)Cl(2) and 155.11(10)° for O(1)Cd(1)Cl(1). Cd(2) is smaller extent distorted octahedrally coordinated with two oxygen atoms of O(2) and O(2)#2 which from the adjacent amino acids and four chloride ions (Cl(2) and Cl(2)#2 are in the axial position). The bond length is 2.6419(14) Å for Cd(2)–Cl(2). Cl(1)#l, Cl(1)#3, O(2) and O(2)#2 are in the equatorial position, the shortest bond length is 2.301(4) Å and the longest bond length of 2.5880(15) Å. Cd(1) and Cd(2) are connected by the bridge bonds of μ_2-Cl, μ_3-Cl and formed quadrilateral shape. Cd(1) and Cd(1)#1 are connected by the bridge bonds of μ_3-Cl(2)–Cl(2), Cl(2)#2 linked to form a new four-ring. Cl(2) is connected with Cd(1), Cd(2) and Cd(1)#1 in the form of three bridges. The bonds length of 2.5938(15) Å for Cd(1)–Cl(2), 2.6419(14) Å for Cd(2)–Cl(2), 2.8401(15) Å for Cl(2)–Cd(1)#1. The bonds angles 102.94(5)° for Cd(1)Cl(2)Cd(2), 91.95(5)° for Cd(1)Cl(2)Cd(1)#1, 92.29(4)° for Cd(2)Cl(2)Cd(1)#1, while Cd(1) and Cd(2) through the carboxyl oxygen O(1), O(2) the formation of carboxylic bridge bond. The asymmetric unit connected by the bridge bonds of μ_2-Cl, μ_3-Cl and the carboxyl oxygen into 1D chain structure along the a axis, which further connected by hydrogen bonds (N(1)–H(1A)···Cl(3)#5, N(1)–H(1B)···O(1W)#6, N(1)–H(1B)···Cl(1)#7) to form 3D supramolecular network, thereby increasing the stability of the title compound.

Figure 6 is the title compound at room temperature with 255 nm excitation fluorescence spectra, and we can seen from the graph, the compound at 423, 436 and 460 nm have a relatively strong fluorescence emission peak, and the fluorescence intensity in 436 nm is greater than in the 423 and 460 nm, the causes need to be further studied.

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