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NOTE

Synthesis, Crystal Structure and Property of $(CdCl_3)_n \cdot nH_3O$ With a One-Dimensional Infinite Chain-like Structure

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A cadmium chloride with protonated water molecules, $(CdCl_3)_n \cdot nH_3O$ (**1**), has been synthesized *via* hydrothermal reaction and structurally characterized by single crystal X-ray diffraction. Compound **1** features a one-dimensional (1-D) infinite chain-like structure, which is constructed from edge-shared $CdCl_6$ octahedra. Compound **1** displays an optical gap of 1.56 eV.

Keywords: Band gap, Cadmium, Crystal, Hydrothermal, Semiconductor.

Transition metal compounds play an important roles in the fields of chemistry and biology and thus, they have attracted great attention[1-4]. Group 12 (IIB) transition metal compounds are particularly attractive for several reasons, such as, the variety of coordination geometries provided by the d^{10} configuration of the IIB metal ions, the vital role in biological systems of zinc and so forth. Many IIB metal compounds are potential materials due to their novel photoelectric and fluorescent properties. We report herein the hydrothermal synthesis, crystal structure and property of a cadmium chloride $(CdCl_3)_n \cdot nH_3O$ (**1**) with an infinite 1-D chain-like structure. It is noteworthy that compound **1** exhibits an energy band gap of 1.56 eV, indicating that compound **1** is a semiconductor.

Synthesis: $(CdCl_3)_n \cdot nH_3O$ was prepared from the reaction of CdI_2 (0.5 mmol, 180 mg), L-histidine (0.5 mmol, 78 mg), 1 mL HCl, 1 mL EtOH and 9 mL distilled water. The starting materials were loaded into a 23 mL Teflon-lined stainless steel autoclave and heated at 433 K for 10 days. After being slowly cooled down to room temperature at 6 K/h, colourless crystals suitable for X-ray analysis were obtained. Yield: 26 % (based on cadmium). The UV-visible spectrum is measured on PE Lambda 35 UV-visible spectrometer in the wavelength range of 190-1100 nm. $BaSO_4$ plate is used as a reference, on which finely ground powder of the compound is coated. The absorption spectrum is calculated from reflection spectra by the Kubelka-Munk function[5]: $\alpha/S = (1-R)^2/2R$, α is the absorption coefficient, S is the scattering coefficient and R is the reflectance.

Single-crystal X-ray diffraction experiment: X-ray diffraction data are measured on a Rigaku Mercury CCD X-ray diffractometer with graphite monochromated MoK_α radiation ($\lambda = 0.71073$ Å) using a ω scan technique. Crystal Clear software is used for data reduction and empirical absorption correction. The structure is solved by the direct method using the Siemens SHELXTL™ Version 5 package of crystallographic software. The difference Fourier maps based on the atomic positions yield all atoms. The structure is refined using a full-matrix least-squares refinement on F^2. All atoms are refined anisotropically. The summary of crystallographic data and structural analysis is listed in Table-1. The selected bond lengths and bond angles are given in Table-2. ICSD 426115.

X-ray diffraction analysis reveals that compound **1** is characterized by an infinite 1-D chain-like structure. An ORTEP drawing of **1** together with the atomic numbering scheme is given in Fig. 1. The Cd^{2+} ions are coordinated by six chloride ions, yielding an octahedron. The bond lengths of Cd-Cl are in the range of 2.5076(8) Å - 2.7104(6) Å, which is normal and comparable with those reported previously, as shown in Table-2[6,7]. Each $CdCl_6$ octahedron connects to four neighbouring one with the Cd···Cd distance between 3.9642(4) Å and 3.9872(4) Å, forming an infinite 1-D chain-like structure running along the *b*-axis (Fig. 1). Because the oxidation states of cadmium and chlorine are +2 and -1, respectively, in order to keep charge balance, the lattice water molecules must be protonated. It is noteworthy that there are O…Cl hydrogen bondings existing in compound **1** (Fig. 2). The infinite 1-D chains stack together to yield a crystal packing motif, as shown in Fig. 2.

TABLE-2
SELECTED BOND LENGTHS (Å) AND BOND ANGLES (°)

Cd(1)-Cl(1)	2.5076(8)	Cl(2)-Cd(1)-Cl(3)#2	88.09(2)
Cd(1)-Cl(2)	2.6405(6)	Cl(2)#1-Cd(1)-Cl(3)#2	88.09(2)
Cd(1)-Cl(3)	2.7104(6)	Cl(1)-Cd(1)-Cl(3)	92.83(2)
Cd(1)-Cl(2)#1	2.6405(6)	Cl(2)-Cd(1)-Cl(3)	172.67(3)
Cd(1)-Cl(3)#2	2.6544(8)	Cl(2)#1-Cd(1)-Cl(3)	83.18(2)
Cd(1)-Cl(3)#3	2.7104(6)	Cl(3)#2-Cd(1)-Cl(3)	84.73(2)
Cl(1)-Cd(1)-Cl(2)	94.28(2)	Cl(1)-Cd(1)-Cl(3)#3	92.83(2)
Cl(1)-Cd(1)-Cl(2)#1	94.28(2)	Cl(2)-Cd(1)-Cl(3)#3	83.18(2)
Cl(2)-Cd(1)-Cl(2)#1	98.05(3)	Cl(2)#1-Cd(1)-Cl(3)#3	172.67(3)
Cl(1)-Cd(1)-Cl(3)#2	176.38(3)	Cl(3)-Cd(1)-Cl(3)#3	94.70(3)
Symmetry codes: # 1 x, y + 1, z; # 2–x + 4, -y + 1, -z-1; #3 x, y-1, z			

TABLE-1
CRYSTAL DATA

Empirical formula	H_3CdCl_3O
Formula weight	237.78
Crystal system	orthorhombic
Space group	Pnma
Unit cell dimensions	a = 9.0128(8) Å b = 3.9872(4)Å c = 14.8973(12) Å
Z	4
V	535.35(8) $Å^3$
D_c	2.950 Mg/m^3
Absorption coefficient	5.416 mm^{-1}
Crystal size	0.21 × 0.13 × 0.11 mm
No. of reflections ollected/unique	2630/693 [$R_{(int)}$ = 0.0338]
Goodness-of-fit on F^2	0.985
Final R indices	R_1 = 0.0235, wR_2 = 0.0591
R indices (all data)	R_1 = 0.0240, wR_2 = 0.0595
$(\Delta/\sigma)_{max}$	0.001

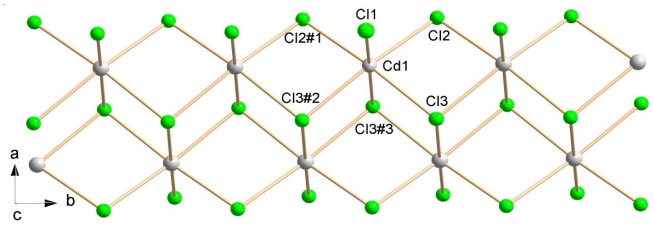

Fig. 1. An ORTEP drawing of **1** with 50 % thermal ellipsoids. Lattice water molecules were omitted for clarity

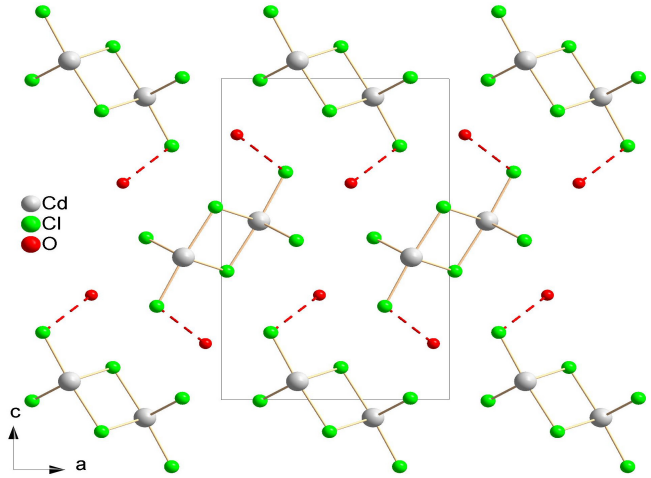

Fig. 2. Packing diagram of **1** with the dashed lines representing hydrogen bondings (Å): O1W…Cl1(-1/2 + x, -1/2-y, -3/2-z) 3.268 and O1W…Cl1(-1/2 + x, 1/2-y, -3/2-z) 3.268

The solid-state diffuse reflectance spectrum of **1** reveals the existence of an optical band gap of 1.56 eV, indicating that compound **1** is a semiconductor. The gradual slope of the absorption edge suggests an indirect transition[8]. It should be pointed out that the energy band gap of 1.56 eV is close to those of $CuInS_2$ (1.55 eV), CdTe (1.5 eV) and GaAs (1.4 eV), all of them are highly efficient photovoltaic materials[9-12].

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