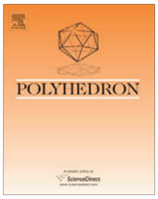
Polyhedron 28 (2009) 947–953

Contents lists available at ScienceDirect

Polyhedron

journal homepage: www.elsevier.com/locate/poly



The architectures of 1D coordination polymers with the versatile 7-chloroquinoline-4-alanine ligand mediated by anions: Syntheses, structures and luminescent properties

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ARTICLE INFO

Article history:
Received 30 October 2008
Accepted 16 December 2008
Available online 21 February 2009

Keywords:
Cadmium(II) complexes
Coordination polymers
Crystal structures
Quinoline ligands
Luminescence

ABSTRACT

Three new coordination polymers, $[Cd(cqaH)(cqa)Cl]_n$ (**1**), $[Cd(cqaH)(cqa)Br]_n$ (**2**) and $\{[Cd_2(cqa)_4] \cdot 3H_2O\}_n$ (**3**) (Hcqa = 7-chloroquinolin-4-alanine, cqaH = the Hcqa ligand, where the proton is transferred from the acid group to the imine group) have been prepared under hydrothermal conditions and characterized by X-ray structural analyses. Both complexes **1** and **2** possess 1D ribbon-like chains, and complex **3** features a 1D double-stranded chain. Various coordination fashions and supramolecular networks are observed in complexes **1–3** due to the versatile coordination modes of the ligand and the cooperative effect from anions in the assemblies. In addition, the luminescent properties for all compounds have been investigated in the solid state.

1. Introduction

There is an upsurge of interest in crystal engineering of metal–organic coordination polymers with intriguing structural features as well as useful properties [1–4], including catalysis, porosity, chirality, luminescence, non-linear optics, ferroelectrics and magnetism [5–12]. However, the influence of the factors on the self-assembly processes is still not well explored and cannot be generalized. Many investigations have indicated that the cooperative effect should be ubiquity in chemical processes, such as catalyzed reactions, biochemistry, supramolecular recognition and assembly [13–16]. The cooperative effect is commonly referred to mutual benefit for the resultant structure or properties arising from the interactions between two or more individual components. However, reports on the discussions of the structure influenced by the cooperative effect of anion and ligand are less studied so far [17,18]. Hence, it would be interesting if more work was carried out to explore the cooperative effect of anion and ligand on the supramolecular structures of coordination polymers.

The ligand 7-chloroquinoline-4-alanine (Hcqa) has versatile coordination sites from both pyridyl and carboxylate groups (Scheme 1). It can easily coordinate to Zn^{2+} and Cd^{2+} ions to form interesting neutral frameworks. In this paper, we report the syntheses and crystal structures of three 1D coordination polymers: $[Cd(cqaH)(cqa)Cl]_n$ (**1**), $[Cd(cqaH)(cqa)Br]_n$ (**2**) and $\{[Cd_2(cqa)_4] \cdot 3H_2O\}_n$ (**3**). The luminescent properties and the effects of the cooperative effect of the anions on their diverse architectures have been investigated.

2. Experimental

2.1. General remarks

All reagents and solvents were commercially available and were used without further purification. The bridging ligand 7-chloroquinoline-4-alanine (Hcqa) was synthesized according to the literature method [19]. Elemental analyses for C, H and N were taken on a CHN–O-Rapid Analyzer and an Elementar Vario Microanalyzer. The IR spectra were performed on a Bruker Vector 22 FT-IR spectrometer by using KBr disks in the 4000–400 cm^{-1} range. Thermogravimetric analyses were performed on a Perkin–Elmer Pyris 1 TGA analyzer from room temperature to 750 °C with a heating rate of 20 °C/min under nitrogen. Photoluminescence analyses for the solid samples were recorded on an AMINCO Bowman Series2 luminescence spectrometer.

2.2. Syntheses

2.2.1. $[Cd(cqaH)(cqa)Cl]_n$ (1)

A mixture of $CdCl_2 \cdot 2.5H_2O$ (0.10 mmol, 22.4 mg), Hcqa (0.10 mmol, 25.2 mg) and 10 mL of $CH_3OH/CH_3CN/H_2O$ (2:1:1 by

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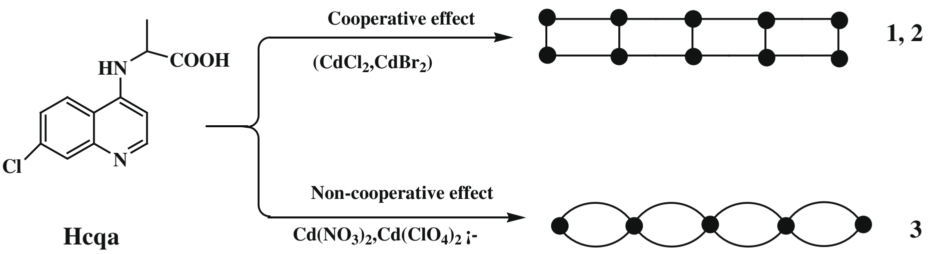
doi:10.1016/j.poly.2008.12.059



Scheme 1. Molecular structure of the ligand Hcqa and the topologies of its 1D coordination polymers.

volume) was sealed in a Teflon-lined stainless steel reactor, heated at 100 °C for 3 days and cooled to room temperature. Colorless plate-like single crystals of **1** were obtained and washed with distilled water. Yield: 35%. *Anal.* Calc. for $C_{24}H_{22}CdCl_3N_4O_4$: C, 44.40; H, 3.42; N, 8.63. Found: C, 44.21; H, 2.99; N, 8.86%. IR (KBr, cm^{-1}): 3341(m), 3279(m), 2987(m), 1618(s), 1584(vs), 1557(s), 1453(s), 1403(vs), 1368(s), 1028(w), 949(w), 902(w), 870(m), 812(m), 762(w), 688(m).

2.2.2. [Cd(cqaH)(cqa)Br]$_n$ (**2**)

Compound **2** was prepared by a similar method to **1**, except for using $CdBr_2 \cdot 4H_2O$ instead of $CdCl_2 \cdot 2.5H_2O$. Yield: 22%. *Anal.* Calc. for $C_{24}H_{22}CdCl_2BrN_4O_4$: C, 41.55; H, 3.20; N, 8.08. Found: C, 41.94; H, 3.21; N, 7.86%. IR (KBr, cm^{-1}): 3336(m), 3283(m), 2982(w), 1615(s), 1583(vs), 1559(s), 1453(s), 1402(s), 1367(vs), 1033(w), 949(w), 902(w), 865(m), 812(m), 763(w), 686(m).

2.2.3. {[$Cd_2(cqa)_4$] · $3H_2O$}$_n$ (**3**)

Compound **3** was prepared by a similar method to **1**, except for using $Cd(NO_3)_2 \cdot 4H_2O$ instead of $CdCl_2 \cdot 2.5H_2O$. Yield: 26%. *Anal.* Calc. for $C_{48}H_{42}Cd_2Cl_4N_8O_{11}$: C, 45.12; H, 3.31; N, 8.77. Found: C, 44.93; H, 3.07; N, 8.96%. IR (KBr, cm^{-1}): 3448(br), 3276(s), 2986(w), 1579(vs), 1456(m), 1406(s), 1368(s), 1041(w), 950(w), 914(m), 867(m), 812(m), 763(m), 660(w). This compound could also be obtained in various yields under the same hydrothermal conditions, by using $Cd(ClO_4)_2 \cdot 6H_2O$, $Cd(OAc)_2$, $Cd(SCN)_2$, CdI_2 and $CdSO_4 \cdot 8/3H_2O$ instead of $Cd(NO_3)_2 \cdot 4H_2O$.

2.3. Caution

Although we have experienced no problems in handling perchlorate compounds, these should be handled with great caution due to the potential for explosion.

2.4. X-ray structure determinations

X-ray intensity data of **1–3** were collected on a Bruker SMART APEX CCD diffractometer [20] using graphite monochromatized Mo Kα radiation (λ = 0.71073 Å) at 291(2) K. The raw data were reduced and corrected for Lorentz and polarization effects using the SAINT program and for absorption using the SADABS program. The structures were solved by direct methods and refined with the full-matrix least-squares technique using SHELXTL version 5.1 [21]. Anisotropic thermal parameters were assigned to all non-hydrogen atoms. Hydrogen atoms were placed in calculated positions and refined using a riding model. The crystallographic data are shown in Table 1. Selected bond lengths and bond angles are given in Table 2.

Table 1
Crystallographic data and details of refinements for complexes **1**–**3**.

Complexes	**1**	**2**	**3**
Empirical formula	$C_{24}H_{22}CdCl_3N_4O_4$	$C_{24}H_{22}CdBrCl_2N_4O_4$	$C_{48}H_{42}Cd_2Cl_4N_8O_{11}$
Mr	649.21	693.67	1273.50
Crystal system	triclinic	triclinic	trigonal
Space group	$P\overline{1}$	$P\overline{1}$	$R\overline{3}$
a (Å)	9.997(2)	10.039(4)	20.301(4)
b (Å)	11.236 (1)	11.488(5)	20.301(4)
c (Å)	11.871(3)	11.866(5)	32.781(8)
α (°)	106.045(3)	105.983(7)	90
β (°)	106.171(2)	106.705(7)	90
γ (°)	97.565 (1)	98.265(8)	120
V (Å^3)	1198.9(4)	1222.6(9)	11 700(4)
Z	2	2	9
D_{calc} (g/cm^{-3})	1.798	1.884	1.627
μ (mm^{-1})	1.287	2.787	1.090
θ range (°)	1.89–26.00	1.90–26.00	1.70–26.00
Reflections collected/unique (R_{int})	6629/4638 (0.0314)	6563/4660 (0.0344)	21 061/5121 (0.0446)
Data/restraints/parameters	4638/0/327	4660/0/327	5121/0/354
F(000)	650	686	5742
T (K)	291(2)	291(2)	291(2)
R_1[a], wR_2[b] [I > 2σ(I)]	0.0587, 0.1159	0.0613, 0.1303	0.0451, 0.0946
R_1[a], wR_2[b] [all data]	0.0814, 0.1196	0.0842, 0.1356	0.0628, 0.0988
Goodness-of-fit	1.003	1.014	1.097
Largest difference in peak and hole (e Å^{-3})	1.409, −0.750	0.687, −1.263	0.273, −0.989

[a] $R_1 = \sum||F_o| - |F_c||/\sum|F_o|$.
[b] $wR_2 = [\sum w(|F_o^2|-|F_c^2|)^2/\sum w(|F_o^2|)^2]^{1/2}$.

Table 2
Selected bond lengths (Å) and angles (°) for **1**–**3**.

Complex **1**			
Cd(1)–O(3)	2.228(4)	Cd(1)–N(1a)	2.282(5)
Cd(1)–O(4b)	2.341(4)	Cd(1)–O(2)	2.345(4)
Cd(1)–O(1)	2.514(4)	Cd(1)–Cl(1)	2. 537(1)
O(3)–Cd(1)–N(1a)	100.6(2)	O(3)–Cd(1)–O(4b)	90.7(1)
N(1a)–Cd(1)–O(4b)	87.0(2)	O(3)–Cd(1)–O(2)	154.1(2)
N(1a)–Cd(1)–O(2)	102.4(2)	O(4b)–Cd(1)–O(2)	78.8(1)
O(3)–Cd(1)–O(1)	100.5(1)	N(1a)–Cd(1)–O(1)	151.9(2)
O(4b)–Cd(1)–O(1)	74.4(1)	O(2)–Cd(1)–O(1)	54.0(1)
O(3)–Cd(1)–Cl(1)	92.6 (1)	N(1a)–Cd(1)–Cl(1)	104.7(1)
O(4b)–Cd(1)–Cl(1)	167.0(1)	O(2)–Cd(1)–Cl(1)	92.9(1)
O(1)–Cd(1)–Cl(1)	92.93(9)		
Complex **2**			
Cd(1)–O(3)	2.232(5)	Cd(1)–N(1a)	2.296(6)
Cd(1)–O(4b)	2.342(5)	Cd(1)–O(2)	2.345(5)
Cd(1)–O(1)	2.509(5)	Cd(1)–Br(1)	2.676(1)
O(3)–Cd(1)–N(1a)	99.3(2)	O(3)–Cd(1)–O(4b)	154.2(2)
O(1)–Cd(1)–Br(1)	92.7(1)	N(1a)–Cd(1)–Br(1)	104.6(2)
Complex **3**			
Cd(1)–O(2b)	2.212(3)	Cd(1)–O(4a)	2.257(3)
Cd(1)–O(3a)	2.486(3)	N(1)–Cd(1)	2.285(3)
N(3)–Cd(1)	2.285(3)		
O(2b)–Cd(1)–O(4a)	105.1(1)	O(2b)–Cd(1)–N(3)	108.0(1)
O(4a)–Cd(1)–N(3)	95.5(1)	O(2b)–Cd(1)–N(1)	102.5(1)
O(4a)–Cd(1)–N(1)	134.7(1)	N(3)–Cd(1)–N(1)	109.4(1)
O(2b)–Cd(1)–O(3a)	149.5(1)	O(4b)–Cd(1)–O(3a)	54.1(1)
N(3)–Cd(1)–O(3a)	97.0(1)	N(1)–Cd(1)–O(3a)	84.9(1)

Symmetry codes: (a) $x - 1, y, z$; (b) $-x, -y + 2, -z$ for **1** and for **2**; (b) $x - 1, y, z$ for **2**; (a) #1 $- x + 1, -y, -z$; (b) $-x + 2/3, -y + 1/3, -z + 1/3$ for **3**.