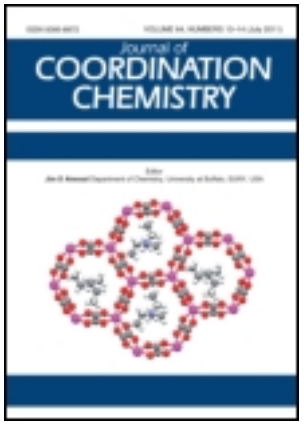

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Aggregation of two different coordination polymers by reacting zinc nitrate and cadmium chloride with N,N′-ethylenebisacetamide

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Aggregation of two different coordination polymers by reacting zinc nitrate and cadmium chloride with N,N′-ethylenebisacetamide

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Two different coordination polymers are obtained from d^{10} metal ions [Zn(II) and Cd(II)] and N,N′-ethylenebisacetamide (EBA). $\{[Zn(EBA)_{1.5}(NO_3)]\cdot(NO_3)\}_n$ (**1**) is a 1-D coordination polymer assembled from zinc ions and EBA molecules acting as a bridging ligand. $Cd(H_2O)_2Cl_2(EBA)$ (**2**) is constructed from 1-D inorganic polymeric chains $\{Cd(OH_2)_2Cl_2\}_n$ and uncoordinated N,N′-ethylenebisacetamide molecules. These chains are interconnected through hydrogen bonds resulting in a 3-D supramolecular network. The luminescent properties of the organic molecule EBA, as well as of the coordination polymers **1**, and **2** have been investigated.

Keywords: N,N′-Ethylenebisacetamide; Coordination polymers; Hydrogen bonds; Luminescence

1. Introduction

Coordination polymers are intensively investigated nowadays due to their interesting properties like luminescence, porosity, magnetism, etc. [1–9]. A plethora of coordination polymers of different topologies and dimensionalities were assembled exploiting the coordination abilities of ligands and stereochemical preferences of the metal ions [10–13]. Ditopic, *exo*-bidentate ligands, of which the most popular are 4,4′-bipyridyl and bis-(4-pyridyl) derivatives, are suitable to build 1-D coordination polymers [14–21]. Less common are 1-D coordination polymers constructed from amide divergent ligands with oxygen donor atoms [22, 23]. Usually, the amide derivatives play a stabilizing role of the crystal lattice, creating 3-D supramolecular frameworks through hydrogen bond interactions [24–28].

Only a few coordination systems containing N,N′-ethylenebisacetamide or its derivatives and first row transition metals have been obtained. Mononuclear complexes

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of Mn(II), Co(II), and Ni(II) were described by means of FTIR and UV-Vis spectroscopy [29]. Three X-ray structures of network arrays of Co(II) [30] and 3-D inorganic-organic hybrid systems of Mn(II) and Cu(II) were reported to date [31].

In this article, we report the synthesis and X-ray structures of two new compounds obtained by reacting N,N′-ethylenebisacetamide (scheme 1) with $Zn(NO_3)_2$ and $CdCl_2$: $\{Zn(EBA)_{1.5}(NO_3)\}_n \cdot n(NO_3)$ (**1**) and $Cd(H_2O)_2Cl_2(EBA)$ (**2**). Their luminescent properties have been investigated.

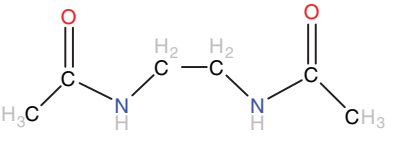
2. Experimental

All chemicals were obtained from commercial sources and used as received. N,N′-ethylenebisacetamide was synthesized from ethylenediamine and acetic acid distilled at 15 mm Hg, 3 h. The resulting solid was recrystallized from isopropyl alcohol. Anal. Calcd for $C_6H_{12}N_2O_2$ (%): C, 50.00; H, 8.33; N, 19.44. Found: C, 50.78; H, 8.78; N, 19.65. ^{1}H-NMR (DMSO-d_6, δ_{ppm}, J (Hz)): 1.78 (s, 6H); 3.04 (m, 2.75, 4H); 7.88 (s, 2H). ^{13}C-NMR (DMSO-d_6, δ_{ppm}): 169.35 (C=O), 38.38 (–CH_2–), 22.59 (–CH_3). UV-Vis (nm): 230, 320.

$\{[Zn(EBA)_{1.5}(NO_3)]\cdot(NO_3)\}_n$: A methanolic solution (15 mL) of 0.57 g (4 mmol) N,N′-ethylenebisacetamide was added to an aqueous solution (10 mL) of 0.378 g (2 mmol) $Zn(NO_3)_2 \cdot 4H_2O$. The resulting mixture was stirred for 3 h at 60°C and left undisturbed at room temperature. Crystals were formed after 3 weeks. Anal. Calcd for $C_{18}H_{36}Zn_2N_{10}O_{18}$ (%): C, 26.63; N, 17.26; H, 4.43. Found: C, 26.53; N, 17.18; H, 4.51. ^{1}H-NMR (DMSO-d_6, δ_{ppm}, J (Hz)): 1.78 (s, 6H); 3.04 (m, 2.75, 4H); 7.85 (s, 2H). ^{13}C-NMR (DMSO-d_6, δ_{ppm}): 169.44 (C=O), 38.49 (–CH_2–), 22.73 (–CH_3). UV-Vis (nm): 250, 320.

$(Cd(OH_2)_2Cl_2)(EBA)$: A methanolic solution (15 mL) of 0.72 g (5 mmol) N,N′-ethylenebisacetamide was added to an aqueous solution (15 mL) of 0.57 g (2.5 mmol) $CdCl_2 \cdot 2.5H_2O$ and the resulting mixture was stirred for 2 h at 60°C. The solution was left undisturbed for 2 weeks at room temperature and the transparent crystals formed were filtered and washed with methanol. Anal. Calcd for $CdC_6H_{16}O_4N_2Cl_2$ (%): C, 19.83; N, 7.70; H, 4.40; Cl, 19.56. Found: C, 20.70; N, 7.36; H, 4.05; Cl, 20.57. ^{1}H-NMR (DMSO-d_6, δ_{ppm}, J (Hz)): 1.77 (s, 6H); 3.03 (m, 2.5, 4H); 7.85 (s, 2H). ^{13}C-NMR (DMSO-d_6, δ_{ppm}): 169.59 (C=O), 38.49 (–CH_2–), 22.73 (–CH_3). UV-Vis (nm): 225, 320.

Elemental analyses were carried out on a *Carlo Erba* M1106 Elemental Analyzer. The NMR spectra were performed on a Varian Gemini 300 apparatus at 300 MHz (^{1}H) and 75 MHz (^{13}C) using TMS as internal standard, in DMSO-d_6. Absorption spectra were



Scheme 1. Structure of N,N′-ethylenebisacetamide.

recorded on a JASCO V-670 spectrophotometer and the fluorescence measurements were carried out on a Jasco FP6500 spectrofluorimeter at room temperature.

X-ray diffraction measurements were performed on a Bruker Apex 2 diffractometer for **1** and on a STOE-IPDS II diffractometer for **2**, both operating with Mo-Kα ($\lambda = 0.71073$ Å) X-ray tube with graphite monochromator. The structures were solved (SHELXS-97) by direct methods and refined (SHELXL-97) by full matrix least-square procedures on F^2 [32]. The crystallographic data and other pertinent information are collected in table 1.

3. Results and discussion

3.1. *Description of the structures*

The crystallographic investigation of **1** reveals a 1-D coordination polymer, $[Zn(EBA)_{1.5}(NO_3)]_n$, assembled from zinc ions and N,N′-ethylenebisacetamide, acting as a divergent ligand through both oxygen atoms. The principal bond lengths and angles are listed in table 2. Positively charged $[Zn(EBA)_{1.5}(NO_3)]^+$ coordination units are accompanied by NO_3^- counter ions. Each zinc ion is pentacoordinated by three oxygen atoms arising from the organic ligands and two oxygen atoms from a chelating nitrato ligand. The Zn–O distances vary between 1.937(4) and 2.168(9) Å, the Zn–$O_{nitrato}$ [O(4) and O(5)] bonds being longer than Zn–O_{EBA} [O(1), O(2) and O(3)] bonds.

Table 1. Summary of crystallographic data for **1** and **2**.

Chemical formula	$C_9H_{18}ZnN_5O_9$ (**1**)	$C_6H_{16}CdN_2O_4Cl_2$ (**2**)
Formula weight	405.65	363.51
Temperature (K)	297(2)	293(2)
Wavelength (Å)	0.71073	0.71073
Crystal system	Triclinic	Monoclinic
Space group	*P*–1	*C*2/*c*
Unit cell dimensions (Å, °)		
a	7.4420(8)	17.479(2)
b	10.6283(11)	11.5536(16)
c	12.4321(13)	7.6665(9)
α	107.056(2)	90.00
β	104.004(2)	112.830(8)
γ	102.655(2)	90.00
Volume (Å^3), *Z*	866.40(16), 2	1427.0(3), 4
Calculated density (g cm^{-3})	1.555	1.692
Absorption coefficient (mm^{-1})	1.469	1.902
F(000)	418	720
Crystal dimensions (mm^3)	0.28 × 0.26 × 0.23	0.5 × 0.4 × 0.3
θ range for data collection (°)	2.11–25.00	3.19–33.39
Limiting indices	$-8 \le h \le 8$; $-12 \le k \le 12$; $-14 \le l \le 14$	$-24 \le h \le 26$; $-17 \le k \le 17$; $-11 \le l \le 11$
Reflections collected/unique	8434/3044 [*R*(int) = 0.0337]	8490/2689 [*R*(int) = 0.0302]
Refinement method	Full-matrix least-squares on F^2	
Data/constraints/parameters	3044/0/233	2689/0/81
Goodness-of-fit on F^2	1.104	1.085
Final *R* indices [$I > 2\sigma(I)$]	$R_1 = 0.0668$, $wR_2 = 0.1541$	$R_1 = 0.0432$, $wR_2 = 0.0752$
R indices	$R_1 = 0.0786$, $wR_2 = 0.1602$	$R_1 = 0.0335$, $wR_2 = 0.0787$

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

Zn(1)–O(1)	1.937(4)
Zn(1)–O(2)	1.948(4)
Zn(1)–O(3)	1.938(4)
Zn(1)–O(4)	2.168(9)
Zn(1)–O(5)	2.099(8)
C(1)–O(1)	1.249(6)
C(1)–N(1)	1.305(8)
N(4)–O(5)	1.087(11)
N(4)–O(4)	1.168(11)
N(4)–O(6)	1.180(8)
N(1)–C(3)–C(6)#1	111.9(5)
N(2)–C(6)–C(3)#1	112.5(5)
O(2)–C(4)–N(2)	119.8(5)
O(2)–C(4)–C(5)	121.6(5)
O(1)–Zn(1)–O(3)	105.61(17)
O(3)–Zn(1)–O(2)	103.27(18)
O(3)–Zn(1)–O(5)	132.1(4)
O(2)–Zn(1)–O(4)	134.4(3)
O(5)–Zn(1)–O(4)	48.4(4)

$\#1 = -x+1, -y+1, -z+2$.

Goodgame *et al.* obtained a Co(II) coordination compound, $[Co(EBA)_2(H_2O)_2]Br_2$, in which the organic ligand EBA connects six-coordinated Co(II) centers and generates a polymeric rhombohedral network [30a]. The axial positions of the octahedral $[Co(EBA)_2(H_2O)_2]^+$ cationic units are occupied by oxygen atoms from EBA ligands. Although the ionic radii of Co(II) and Zn(II) are equal, $Co–O_{EBA}$ bond lengths (2.095(4) and 2.103(4) Å) are significantly shorter than Zn–O distances most likely as a consequence of the coordination geometry.

The polymeric chain shows a very interesting topology that can be described as being built from $[Zn_2(EBA)_2]$ 18-member metallacycles, which are further connected by EBA ligands (figure 1). The ligands which connect the metallacycles adopt the *anti* conformation, while those forming the metallacycles display *gauche* conformation. EBA molecules bridging the metallacycles are disposed diagonally. The distance between the zinc ions within a metallacycle is 6.1363(11) Å. The shortest distance between metal ions belonging to two different metallacycles is 9.7649(13) Å.

Analysis of the packing diagram shows the superposition of the metallacycles, generating channels along the *c*-axis (figure 2). The diagonal disposition of EBA connectors prevents the inclusion of guest molecules into the channels.

The crystal structure of **2** consists of purely inorganic neutral 1-D chains, $[Cd(OH_2)_2Cl_2]_n$, and uncoordinated EBA molecules (figure 3). The cadmium ions are double bridged by chloride ions and the aqua ligands are disposed in *trans* positions. The infinite chains run along the crystallographic *c*-axis. The metal–metal distance along the resulting chain of edge sharing octahedra is 3.8353(5) Å. We recall here that similar inorganic–organic hybrid systems were obtained by reacting $MnCl_2$ and $CuCl_2$ with EBA [31]. In these cases, interatomic distances between two metal ions from neighboring units of the polymeric chains are 3.7850(8) and 3.7930(8) Å, respectively. It seems that the formation of such systems is favored when starting from metal(II) chlorides. This is due to the rather poor coordinating abilities of the amides and the stability of metal chloride inorganic chains.

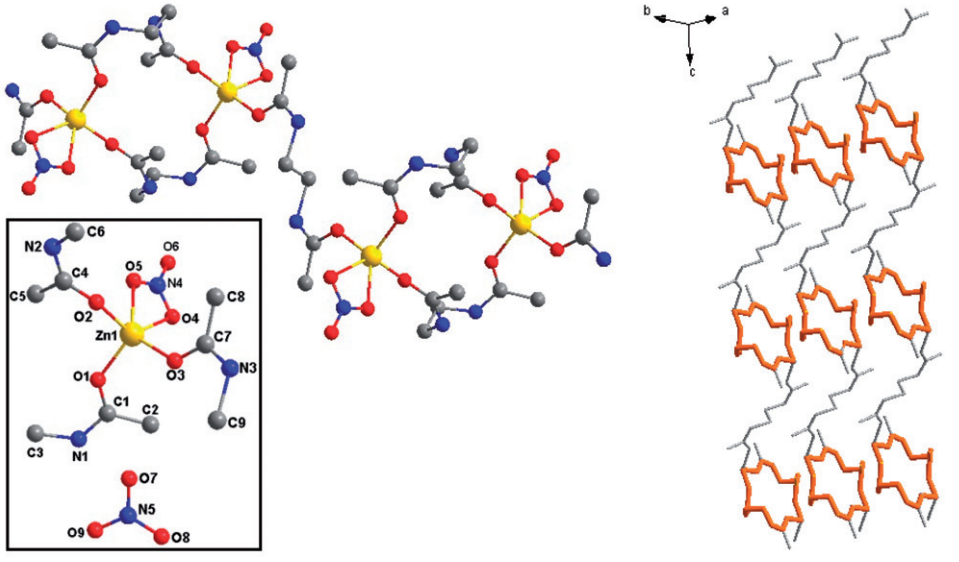


Figure 1. Crystal structure of **1**. Left: perspective view of a chain. Inset: asymmetric unit along with the atom-numbering scheme. Right: packing diagram.

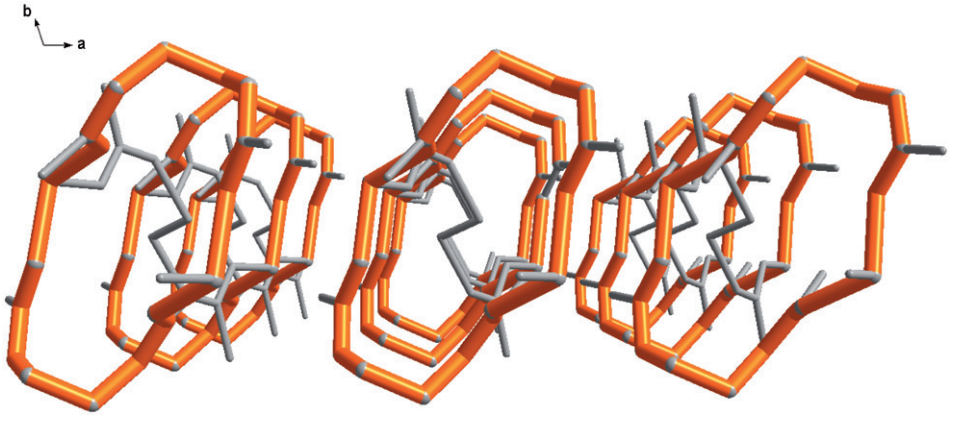


Figure 2. Packing diagram for **1** – view along the crystallographic *c*-axis.

Two types of hydrogen bonds are established in the crystal lattice between: (i) aqua ligands and oxygen atoms of the organic molecule [O(1)···O(2), 2.710(3) Å; O(1)···O(2), 2.721(4) Å] and (ii) chlorido ligand and NH group of EBA [N(1)···Cl(1), 3.335(3) Å] (figure 4).

Supramolecular layers are formed from inorganic chains that interact one to each other through hydrogen bonds involving half of the organic molecules, EBA (figure 3). The supramolecular layers are further interconnected through hydrogen bonds established by the remaining EBA molecules, resulting in a 3-D supramolecular architecture (figure 5).

The geometrical parameters associated with hydrogen bonds are gathered in table 3. Selected bond distances and angles for compound **2** are presented in table 4.

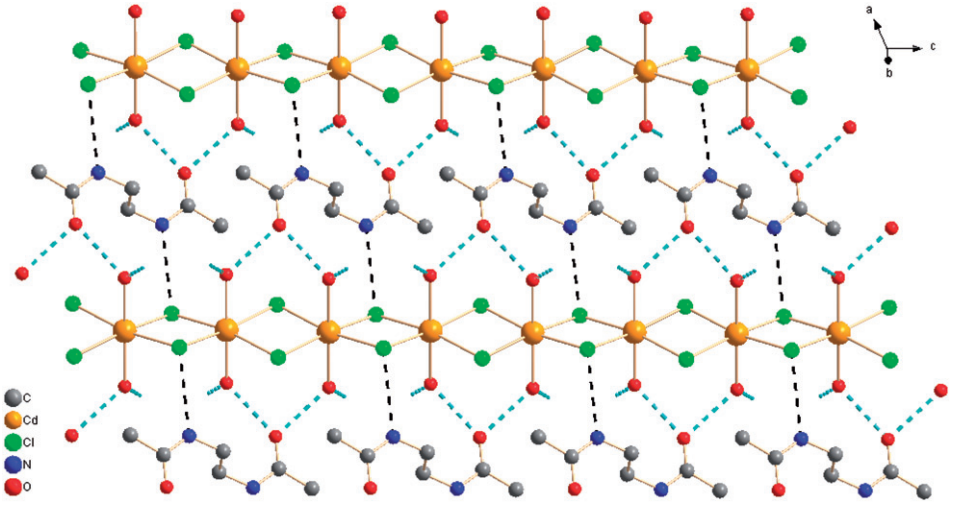


Figure 3. Perspective view of **2** showing the formation of supramolecular layers through hydrogen bonds established between the inorganic chains and the organic molecules.

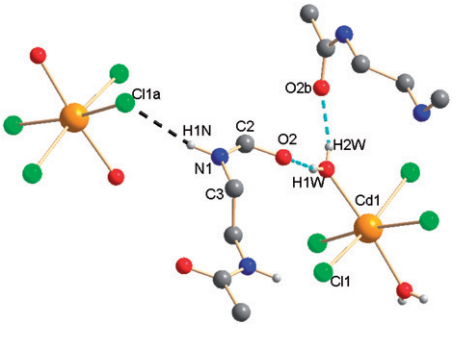


Figure 4. Detail of the crystal structure of **2** showing the hydrogen-bond interactions and the atom-numbering scheme.

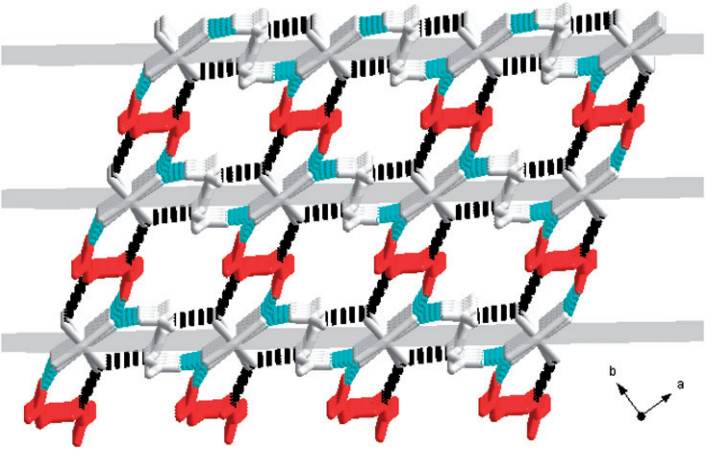


Figure 5. The 3-D supramolecular architecture in crystal **2**: the supramolecular layers (highlighted in grey) are connected by hydrogen-bonded EBA molecules (between the layers).

Table 3. Geometrical parameters (Å, °) associated with hydrogen bonds in **2**.

Donor - - - H · · · Acceptor	D–H, Å	H · · · A, Å	D · · · A, Å	D H · · · A, °
N(1) - - - H(1N) · · · Cl(1)a	0.95(6)	2.40(6)	3.335(3)	168(5)
O(1) - - - H(1W) · · · O(2)	0.78(5)	1.94(5)	2.710(3)	171(6)
O(1) - - - H(2W) · · · O(2)b	0.76(5)	1.98(5)	2.721(4)	166(5)

a = $-1/2+x,1/2-y,-1/2+z$; b = $x,-y,1/2+z$.

Table 4. Selected bond lengths (Å) and angles (°) for **2**.

Cd(1)–O(1)#2	2.279(2)
Cd(1)–Cl(1)#2	2.6194(6)
Cd(1)–Cl(1)#4	2.6258(6)
Cl(1)–Cd(1)–Cl(1)#4	86.03(2)
Cl(1)–Cd(1)–Cl(1)#3	170.48(2)
Cd(1)–O(1)–H(2W)	120(4)
H(1W)–O(1)–H(2W)	115(5)
O(1)–Cd(1)–O(1)#2	175.04(16)
O(1)–Cd(1)–Cl(1)#2	91.42(8)
O(1)–Cd(1)–Cl(1)#3	86.08(6)

#2 = $-x+1, y, -z+3/2$; #3 = $x, -y, z+1/2$; #4 = $-x+1,-y, -z+1$.

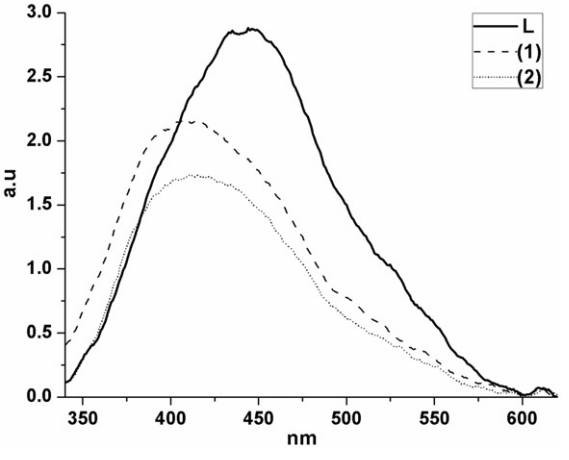


Figure 6. Emission spectra of EBA, **1**, and **2** upon excitation at 320 nm.

3.2. *Luminescent properties*

The luminescence properties of the organic molecule as well as of compounds **1** and **2** were determined in the solid state at room temperature (figure 6). The UV-Vis spectra show, in all cases, a strong, broad absorption band located at 320 nm. N,N′-ethylenebisacetamide exhibits strong violet-blue luminescence at 450 nm upon excitation at 320 nm. Compounds **1** and **2** display violet luminescence upon excitation at 320 nm. The luminescence of N,N′-ethylenebisacetamide arises from a π^*–π transition.

For **1** and **2**, the fluorescence bands appear as a result of the intra-ligand transition. These bands are shifted to lower wavelengths compared with the free ligand, at 410 and 420 nm, because of the involvement of amide chromophore in coordination and in hydrogen bonds, respectively.

4. Conclusion

Two new coordination systems were obtained by reacting zinc nitrate and cadmium chloride with N,N′-ethylenebisacetamide (EBA). Their structural features and optical properties were discussed. The structure of zinc derivative consists of 1-D coordination polymer of metallacycles formed between Zn(II) and *exo*-dentate EBA ligand, and connected by EBA ligands. The cadmium compound presents a supramolecular 3-D structure formed by $[Cd(OH_2)_2Cl_2]_n$ coordination chains, connected by organic molecules EBA through hydrogen bonds. The organic molecule EBA exhibits a strong violet-blue luminescence which undergoes hypsochromic shifts in the two complex systems.

Supplementary material

Crystallographic data for the structural analysis have been deposited with CCDC Nos 795964, 693902.

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