A Photoluminescent *zig-zag* 1D Coordination Polymer with Mixed Ligands [Zn(absa)(pcih)](CH_3OH)

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A novel 1D zinc(II) coordination polymer [Zn(absa)-(pcih)](CH_3OH) (**1**) (Habsa = 4-aminobenzenesulfonic acid, Hpcih = 2-pyridinecarbaldehyde isonicotinoylhydrazone) has been synthesized by solvothermal reaction at 72 °C and structurally characterized. Each Zn^{2+} ion is five-coordinated by three N atoms and one O atom from two pcih ligands, and one O atom of an absa ligand, forming a distorted square-pyramidal geometry. Zn^{2+} ions are bridged by pcih ligands in a *zig-zag* arrangement generating infinite chains with appended absa ligands. Photoluminescent studies have shown that **1** exhibits an emission at 535 nm (λ_{ex} = 492 nm).

Key words: Coordination Polymer, Photoluminescent Properties, Solvothermal Synthesis, Crystal Structure

Introduction

Recently, coordination polymers have received a great deal of attention because of their intriguing structural motifs coupled with potential applications in the areas of absorption, catalysis, nonlinear optics, molecular magnetization and others [1 – 5]. Many interesting coordination polymeric frameworks (such as 1D chains [6], 2D grids [7] and 3D diamond networks [8]) have been constructed by rational selection of multi-dentate bridging organic ligands as 'spacers' and the metal ions as 'nodes'. Habsa and its derivatives are good candidates for the construction of coordination polymers, as exemplified by [Tl_2(absa)$_2$](H_2O) [9], [Ba(abse)$_2$(H_2O)$_6$] (abse = 4′-aminoazobenzene-4-sulfonate) [10], [Na(abse)(μ_2-H_2O)(H_2O)] [11], [Na_2(dabs)$_2$(methanol)] (dabs = 4′-dimethylaminoazobenzene-4-sulfonate) [10], and [Ca_2(hbs)$_4$(H_2O)$_4$](H_2O)$_4$ (hbs = 4-(4′-hydroxyphenylazo)benzenesulfonate) [11]. The *d*-block metals as coordination centers in coordination polymers of these ligands have been neglected in favor of studying *s*-(or *p*-) block metals. Furthermore, Hpcih and its derivatives are also interesting ligands and may coordinate to metal cations in versatile binding modes, such as chelating bidentate, chelating tridentate and bridging tetradentate, generating diverse molecular architectures [12 – 17]. However, the solvothermal synthesis of coordination polymers involving Hpcih and Habsa simultaneously as bridging and terminal ligands has not been reported until now to the best of our knowledge. Herein, we report the preparation, the crystal structure and the properties of the 1D coordination polymer [Zn(absa)(pcih)](CH_3OH) (**1**) with mixed ligands.

Results and Discussion

The crystal structure of this title compound consists of 1-D [Zn(absa)(pcih)] *zig-zag* chains and free methanol molecules. The coordination geometry of the Zn^{2+} center is best described as distorted square-pyramidal comprising three N atoms and one O atom from two deprotonated Hpcih ligands, and one O atom of one fully deprotonated Habsa ligand (Fig. 1). The Zn–O and Zn–N bond lengths varying from 1.965(1) to 2.192(1) Å lie within the range reported in the literature (Table 1) [1, 18].

Two adjacent Zn^{2+} ions are linked by the pcih ligands as tetradentate bridging 'spacers' to form an infinite *zig-zag* chain along the [010] direction. The absa ligands, just like grapes, are regularly appended to both sides of the chain (grapevine), connected by the O atoms of the sulfonate groups. The methanol molecules are involved in intermolecular O–H···O and N–H···O hydrogen bonds with adjacent -NH_2 and -SO_3 groups (Table 2), resulting in a layered arrangement parallel to the (100) plane (Fig. 2). In addition, a number of C–H···O hydrogen bonds and π-π aromatic stacking interactions play an important role in stabilizing **1** in the solid state (Fig. 3).

The sulfonate groups of Habsa and its derivatives usually adopt bridging coordination modes, including η^2, μ_2-SO_3 and η^3, μ_3-SO_3 bridges, which lead to 1D-3D alkali or alkaline earth coordination polymers [10 – 11]. In contrast, the sulfonate group is seldomly observed as a terminal ligand. Examples exist in mononuclear [Ca(abse)$_2$(H_2O)$_4$] [11], which has one termi-

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

Zn1–O2	1.965(1)	Zn1–N4$^{\#1}$	2.042(1)
Zn1–N1	2.192(1)	Zn1–O4	2.116(1)
Zn1–N2	2.040(2)		
O2–Zn1–N2	132.3(1)	O2–Zn1–N4$^{\#1}$	115.9(1)
N2–Zn1–N4$^{\#1}$	111.6(1)	O2–Zn1–O4	94.6(1)
N2–Zn1–O4	75.3(1)	N4$^{\#1}$–Zn1–O4	96.5(1)
O2–Zn1–N1	102.8(1)	N2–Zn1–N1	76.1(1)
N4$^{\#1}$–Zn1–N1	96.1(5)	O4–Zn1–N1	151.4(5)

Symmetry transformation used to generate equivalent atoms: $^{\#1}$ $-x+2, y-1/2, -z+1/2$.

Table 2. Hydrogen bonding parameters (Å, deg) for **1**.

D–H···A	d(D–H)	d(H···A)	d(D···A)	∠(DHA)
N5–H5···O5^{i}	0.86	2.08	2.907(3)	162.0
N5–H5···O3^{ii}	0.86	2.34	3.117(2)	151.1
O5–H5···O1^{ii}	0.82	2.48	2.730(2)	99.3
C2–H2···O4^{ii}	0.93	2.56	3.365(2)	145.3
C6–H6···O3^{iii}	0.93	2.50	3.126(2)	124.7
C17–H17···O1	0.93	2.50	3.896(2)	105.5

Symmetry code: ^{i} $1-x, 1-y, 1-z$; ^{ii} $x, 3/2-y, 1/2+z$; ^{iii} $-1+x, y, z$.

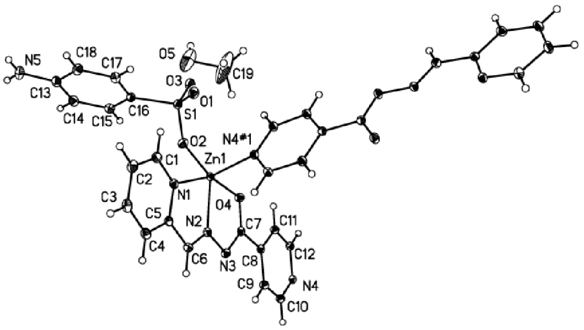

Fig. 1. ORTEP representation of the structure of **1** with labeling scheme and 30 % probability ellipsoids (symmetry codes: #1 $-x+2, y-1/2, -z+1/2$).

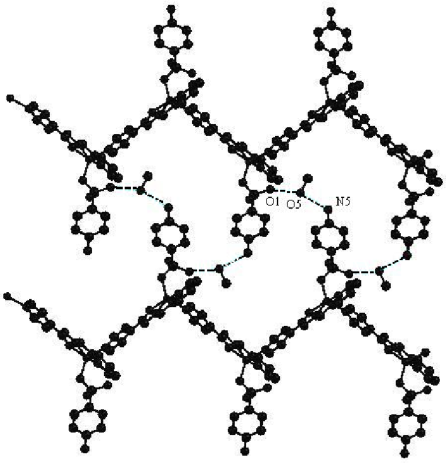

Fig. 2. Part of the crystal structure of **1**, showing the formation of a (100) sheet constructed from N–H···O and O–H···O hydrogen bonds. All H atoms have been omitted for clarity.

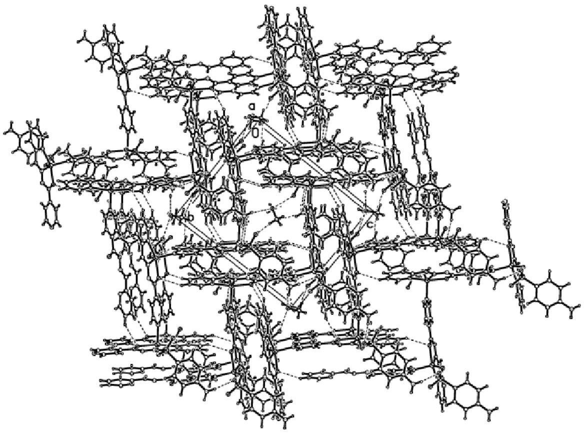

Fig. 3. Packing diagram of **1**, showing the hydrogen bond scheme and aromatic π-π stacking interactions.

nally bonded sulfonate and one η^2 bonded sulfonate where both O atoms are bound to the same metal atom, and in mononuclear $[Ca(azo)_2(OH_2)_x]$ species (x = 3, 4; azo = 4-(4-R-aminophenylazo)benzenesulfonate (R = bis-(2-hydroxyethylamino), amino, hydroxy, or dimethylamino) [10]. Coordination polymers containing terminal sulfonate groups of these ligands have not been reported till now. Complexes of Hpcih ligands are generally discrete molecules, mainly because the coordination sphere of the metal ion is completed by two tri-(or bi-)dentate Hpcih ligands with a non-coordinating pyridyl N atom [13–16]. Coordination polymers with Hpcih ligands are rare, the only two examples exist in $[Zn(Hpcih)SO_4]$ [16] and $[Pb(Hpcih)]_2(NO_3)_2(H_2O)$ [17].

In the IR spectrum of **1** there are no bands corresponding to stretching of hydrazinic N–H and carbonyl C=O bonds in the complex, which is in accordance with the deprotonation of the enolic form of Hpcih. Similar phenomena have been observed in $[Co(pcih)_2\text{-}CoCl_3]\cdot 2H_2O$ [16], $[Cu(pcih)_2]$ [16], $[Ni(pcih)_2]_2H_2O$ [16] and $[Co(Hpcih)(pcih)](NO_3)_2\cdot H_2O \cdot 0.5CH_3OH$ [16]. The excitation and emission spectra of **1** in the solid state at r. t. are shown in Fig. 4. The strong absorption bands at about 492 nm can be assigned to the metal-perturbed intraligand π*-π transition of the absa and pcih ligands. **1** exhibits an intense emission at 535 nm when excited at 492 nm. This emission can be caused by the metal-perturbed π*-π transition of both ligands [19, 20]. The thermal behavior of **1** is shown in Fig. 5. An initial weight loss of 5.82 % be-

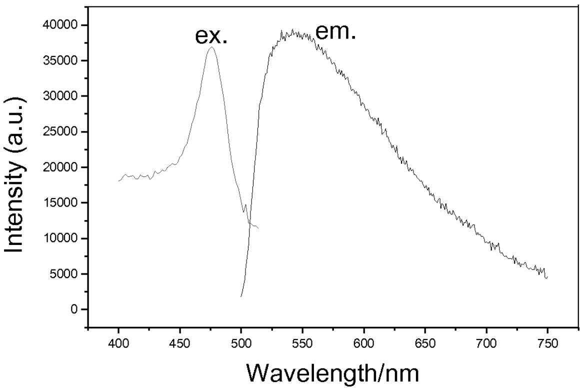

Fig. 4. The solid-state excitation and emission spectra of **1** at room temperature.

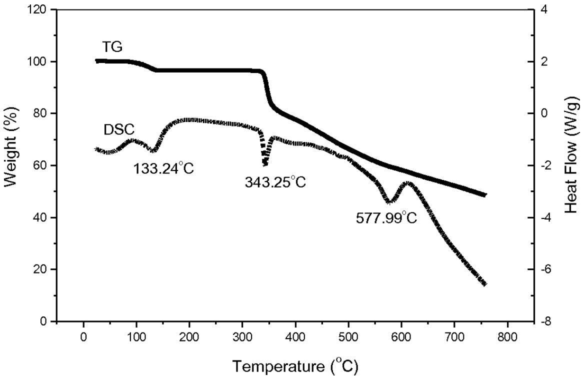

Fig. 5. TG-DSC curves of **1**.

tween 90 and 140 °C is assigned to the departure of the CH_3OH molecules (calculated 6.46 %). Then the residue remains nearly intact up to 320 °C, beyond which the compound begins to decompose.

Conclusion

A new 1D zinc(II) coordination polymer [Zn(absa)(pcih)](CH_3OH) has been prepared under solvothermal conditions by self-assembly of the mixed ligands at the zinc(II) ion. It displays an infinite *zig-zag* chain structure with appended absa ligands and exhibits intense emission at r. t. in the solid state.

Experimental Section

Analytically pure starting materials were purchased and used without additional purification. FT-IR spectra were recorded with a Nicolet Magna-IR 550 spectrometer in dry KBr pellets. Elemental analysis was carried out on an EA-1110 elemental analyzer. The room-temperature emission and excitation spectra were recorded using a Hitachi F-4500 spectrofluorometer. Thermogravimetric (TG) analysis was conducted on a SDT 2960 TGA-DCS microanalyzer. All samples were heated under an N_2 stream of 100 mL/min with a heating rate of 5 °C min^{-1}.

Table 3. Crystal structure data for **1**.

Empirical formula	$C_{19}H_{19}N_5O_5SZn$
M_w	494.85
Crystal color	yellow
Cryst. dimens., mm^3	0.32 × 0.21 × 0.10
Cryst. system	monoclinic
Space group	$P2_1/c$
a, Å	9.7145(19)
b, Å	13.451(3)
c, Å	16.096(3)
β, deg	96.26(3)
V, $Å^3$	2090.7(7)
Z	4
T, K	293(2)
Calcd. density, Mg m^{-3}	1.572
$\mu(MoK_\alpha)$, cm^{-1}	13.17
$F(000)$, e	1016
$2\theta_{max}$, deg	54.96
Total reflns. collected	20074
Unique reflns.	4785
No. of parameters	282
$R1$ $[I \geq 2\sigma(I)]$	0.028
$wR2$ (all data)	0.073
GOF on F^2	1.016
Peak/hole, e $Å^{-3}$	0.66/−0.60

Synthesis of [Zn(absa)(pcih)](CH_3OH) (1)

2-Pyridinecarbaldehyde isonicotinoylhydrazone (Hpcih) was synthesized according to a literature method [16]. Single crystals of the complex suitable for X-ray crystallographic analysis were obtained by solvothermal reaction. $Zn(NO_3)_2\cdot 2H_2O$ (0.0439 g, 0.2 mmol), 4-aminobenzenesulfonic acid (0.0346 g, 0.2 mmol), Hpcih (0.0450 g, 0.2 mmol) and methanol (6 mL) were placed in a 15-mL Telfon-lined, stainless steel Parr bomb. The bomb was heated to 72 °C for 2 d and then cooled to r. t. at a rate of 4 K every 10 min. Yellow block-shaped crystals of [Zn(absa)(pcih)](CH_3OH) were collected by filtration, washed with ethanol, and dried in air (72 % yield based on Zn). Anal. for $C_{19}H_{19}N_5O_5SZn$: calcd. C 46.12, H 3.87, N 14.15; found: C 46.18, H 4.15, N 13.96. – IR (KBr): ν = 3442(m), 3357(m), 3242(m), 2867(w), 1622(m), 1599(s), 1571(m), 1505(s), 1466(s), 1419(w), 1316(w), 1221(m), 1156(vs), 1118(s), 1082(m), 1031(m), 1004(m), 932(w), 834(w), 765(w), 698(m), 640(vw), 572(m), 415(w) cm^{-1}.

X-Ray diffraction experiment

Data collection was performed on a Rigaku Mercury CCD diffractometer with graphite-monochromated MoK_α radiation (λ = 0.71073 Å) at 293(2) K with a maximum 2θ value of 54.96°. The intensities were corrected for Lorentz and polarization effects. The structure was solved with Direct Methods using SHELXS-97 [21], and the refinement was carried out against F^2 using SHELXL-97 [22]. All non-hydrogen atoms were refined anisotropically. The hydrogen atoms were positioned with idealized geometry and refined with fixed isotropic displacement parameters. Relevant crystal and data collection parameters and refinement results can be found in Table 3.

CCDC 682462 contains the supplementary crystallographic data for this paper. These data can be obtained free of charge from The Cambridge Crystallographic Data Centre *via* www.ccdc.cam.ac.uk/data_request/cif.

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