Structure and Fluorescence Properties of a Novel Supramolecular Zinc Complex

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Hydrothermal reaction of $Zn(NO_3)_2 \cdot 6H_2O$ and 2-hydroxypyridine-3-carboxylic acid afforded a novel supramolecular complex, $[Zn(C_6H_4NO_3)_2(H_2O)_2]$ (**1**). The complex has been characterized by macroanalysis, IR spectra, and thermogravimetric and differential thermal analysis (TG/DTA). Single crystal X-ray analysis shows that complex **1** crystallizes in the monoclinic space group $P2_1/c$ with the cell dimensions $a = 7.534(6)$, $b = 12.289(1)$, $c = 7.534(6)$ Å, $\beta = 100.51°$, $V = 685.85(1)$ Å^3, and $Z = 2$. The six-coordinated Zn atom is in a severely distorted octahedral geometry. The complex molecules are assembled *via* strong O–H···O and N–H···O hydrogen bonding interactions into a three-dimensional supramolecular framework. Compared with the free ligand, complex **1** exhibits strong fluorescence in the solid state at room temperature.

Key words: Zinc(II), Crystal Structure, Supramolecular, Fluorescence Properties

Introduction

In recent years, rational design and construction of novel supramolecular systems with specific properties has been one of the most popular research subjects in modern coordination chemistry and materials science [1 – 3]. Non-covalent interactions, such as hydrogen bonding and aromatic π-π stacking interactions, play very important roles in supramolecular systems [4]. Particularly, hydrogen bonding interaction has been investigated because it is responsible for many phenomena in chemistry and biology [5 – 6]. 2-Hydroxypyridine-3-carboxylic acid, a preferred rigid multifunctional nitrogen- and oxygen-donor connector with diverse chelating and bridging modes for constructing coordination complexes, can be utilized to generate lower- and higher-dimensional supramolecular metal-organic frameworks. However, there are only few reported crystal structures of metal 2-hydroxypyridine-3-carboxylate complexes [7 – 12]. In this contribution I present a novel supramolecular complex, $[Zn(C_6H_4NO_3)_2(H_2O)_2]$ (**1**).

Experimental Section

Measurements of physical properties

All chemicals of p. a. grade were commercially available and used without further purification. C, H and N microanalyses were performed with a Perkin-Elmer 2400-CHNS/O elemental analyzer. FT-IR spectra were recorded from KBr pellets in the range 4000 – 400 cm^{-1} on a Shimadzu FTIR-8900 spectrometer. The combined measurement on thermogravimetric and differential thermal analysis (TG/DTA) was carried out in the range 25 – 800 °C on powdered samples using a Perkin Elmer TGS-2 analyzer with a heating rate of 10 °C min^{-1}. All the excitation and emission spectra were measured with an F-4500 fluorescence spectrophotometer with a xenon arc lamp as the excitation light source for the solid samples at r. t.

Preparation of $[Zn(C_6H_4NO_3)_2(H_2O)_2]$ (1)

A mixture of $Zn(NO_3)_2 \cdot 6H_2O$ (0.291 g, 1.0 mmol), 2-hydroxypyridine-3-carboxylic acid (0.069 g, 0.5 mmol), and 15 mL of H_2O was sealed in a 25 mL stainless-steel reactor with Teflon liner and heated to 160 °C and then kept at this temperature for 120 h, prior to slow cooling to r. t. Orange block-shaped crystals suitable for single crystal X-ray diffraction were obtained in 45 % yield (based on the initial $Zn(NO_3)_2 \cdot 6H_2O$ input). – $C_{12}H_{12}ZnN_2O_8$: calcd. C 38.14, H 3.18, N 7.42; found C 38.09, H 3.21, N 7.45. – IR: ν = 3430m, 3118m, 3078m, 1638s, 1598s, 1550s, 1468s, 1417s, 1395m, 1320m, 1130w, 1054w, 905w, 890w, 835w, 784m, 660w, 564w cm^{-1}.

X-Ray structure analysis

The intensities of a suitable single crystal of **1** were collected at 298(3) K using a Bruker SMART Apex II CCD area detector single crystal diffractometer, with graphite-mono-

Table 1. Crystal and refinement data for $[Zn(C_6H_4NO_3)_2(H_2O)_2]$ **1**.

Formula	$C_{12}H_{12}ZnN_2O_8$
M_r	377.63
Crystal size, mm^3	$0.45 \times 0.35 \times 0.15$
Crystal system	monoclinic
Space group	$P2_1/c$
a, Å	7.534(6)
b, Å	12.289(1)
c, Å	7.534(6)
β, deg	100.51(2)
V, Å^3	685.8(10)
Z	2
D_{calcd}, g cm^{-3}	1.828
$\mu(MoK_\alpha)$, cm^{-1}	1.838
$F(000)$, e	384
hkl range	$-8 \le h \le 9$, $-15 \le k \le 15$, $-9 \le l \le 9$
θ_{max}, deg	27.4
Refl. meas./unique	5712/1359
R_{int}	0.101
Param. refined	107
$R1(F)/wR2(F^2)$[a] (all refls.)	0.037/0.099
GoF (F^2)	1.139
$\Delta\rho_{fin}$ (max/min), e Å^{-3}	0.49/−0.58

[a] $R1 = \|F_o| - |F_c\|/\Sigma|F_o|$, $wR2 = [\Sigma w(F_o{}^2 - F_c{}^2)^2/\Sigma w(F_o^2)^2]^{1/2}$, $w = [\sigma^2(F_o{}^2) + (0.056P)^2 + 0.000P]^{-1}$, where $P = (F_o{}^2 + 2F_c{}^2)/3$.

Table 2. Selected interatomic distances (Å) and angles (deg) for **1**.

Distances				
Zn1–O1	2.134(2)	Zn1–O2		1.991(2)
Zn1–O4	2.109(3)			
Angles				
O1–Zn1–O1$^{\#1}$	180.0	O2–Zn1–O2$^{\#1}$		180.0
O4–Zn1–O4$^{\#1}$	180.0			
O2–Zn1–O1	87.98(6)	O2–Zn1–O4		87.55(5)
O4–Zn1–O1	93.23(8)	O2–Zn1–O4$^{\#1}$		92.45(5)
O1–Zn1–O2$^{\#1}$	92.02(6)	O1–Zn1–O4$^{\#1}$		86.77(8)
Hydrogen bonding contacts				
D–H···A	D–H	H···A	D···A	D–H···A
O4–H4A···O3$^{\#2}$	0.90	1.82	2.704(3)	172.5
O4–H4B···O3$^{\#3}$	0.90	1.91	2.772(3)	163.3
N1–H1A···O1$^{\#4}$	0.86	2.06	2.892(3)	162.4

Symmetry code: $^{\#1}$ $-x, -y, -z$; $^{\#2}$ $-x, -1/2+y, -1/2-z$; $^{\#3}$ $-x, 1/2-y, 1/2+z$; $^{\#4}$ $1-x, -y, -z$.

chromatized MoK_α radiation (λ = 0.71073 Å) in the $\varphi/2\vartheta$ scan mode. An absorption correction was applied using the program SADABS [13]. The structure was solved with Direct Methods using SHELXS-97 [14] and refined by full-matrix least-squares methods on F^2. All H atoms attached to C and N atoms were positioned geometrically and treated as riding with C–H = 0.93, N–H = 0.86 Å and U_{iso}(H) = $1.2 \times U_{eq}$(C, N). The H atoms of the water molecules were located in difference Fourier maps and included in the subsequent refinement cycles using restraints [O–H = 0.90 Å and U_{iso}(H) = $1.5 \times U_{eq}$(O)]. All non-hydrogen atoms were finally refined with anisotropic displacement parameters by full-matrix least-squares techniques using SHELXL-97 [15]. Detailed information about the crystal data and structure determination is summarized in Table 1. Selected interatomic distances and bond angles are given in Table 2.

CCDC 699889 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.

Results and Discussion

IR spectra

The IR spectra show the ν(N–H) stretching vibration at 3430 cm^{-1}, and the ν(O–H) stretching vibrations of coordinated water molecules at 3118 and 3078 cm^{-1}. The absorptions at 1638 and 1395 cm^{-1} can be assigned to the $\nu_{as}(CO_2{}^-)$ and $\nu_s(CO_2{}^-)$ stretching vibrations, respectively. A comparison with the characteristic carboxylate stretching vibrations of 2-hydroxypyridine-3-carboxylic acid shows a significant blue-shift attributed to the coordination interaction. The strong absorptions located at 1598 and 1550 cm^{-1} may be assigned to pyridyl vibrations.

Structure description

Complex **1** consists of $Zn(C_6H_4NO_3)_2(H_2O)_2$ molecules. In the crystal, **1** has crystallographic centrosymmetry. The octahedrally coordinated Zn atom is surrounded by six oxygen atoms, of which two come from two carboxylate groups and two from the keto groups of the 2-oxopyridinium-3-carboxylate ligands, and the remaining two from two water molecules. This means that the ligand is attached in its pyridone form, *i. e.*, as the isomer with the protonated N atom and a keto group. The apical positions are occupied by the coordinated water molecules, as shown in Fig. 1. The

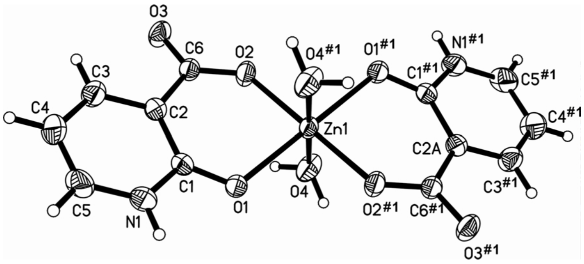

Fig. 1. ORTEP view of **1** and crystallographic numbering scheme used (displacement ellipsoids at the 30 % probability level; symmetry transformation used to generate equivalent atoms: #1 = $-x, -y, -z$).

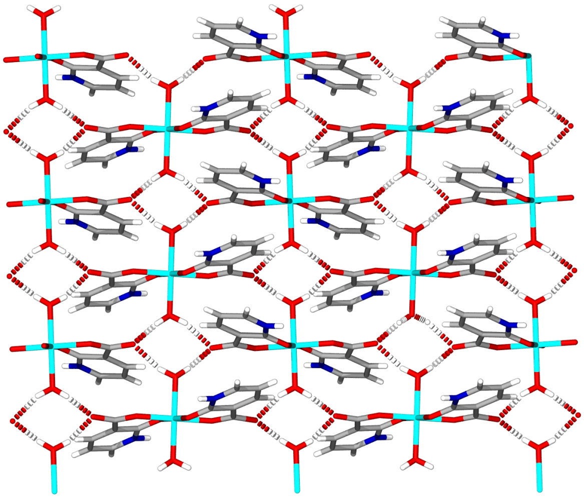

Fig. 2. The 2D structure of **1** along (001) built from O–H$\cdots$O hydrogen bonding interactions.

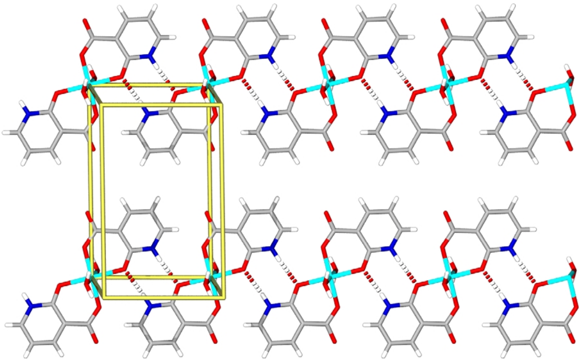

Fig. 3. Partial packing view of compound **1**, showing the formation of chains along [100] *via* N–H$\cdots$O hydrogen bonding interactions.

Zn–O bond lengths range from 1.991(2) to 2.134(2) Å, indicating that the coordination sphere is significantly distorted. The Zn–O bond lengths are similar to those in the related complex $[\mathrm{Zn(C_9H_6O_5)(H_2O)}]_n$ [16].

Parallel to (001), the $\mathrm{Zn(C_6H_4NO_3)_2(H_2O)_2}$ complex molecules are assembled into two-dimensional layers by O–H$\cdots$O hydrogen bonding interactions, in which the coordinated water molecules donate hydrogen atoms to the uncoordinated carboxylate O3 atoms, generating centrosymmtric $R_4^2(8)$ rings (Fig. 2, Table 2) [17] [$d(\mathrm{O4}\cdots\mathrm{O3}^{\#2})$ = 2.704(3) Å, $\angle(\mathrm{O4{-}H4A}\cdots\mathrm{O3}^{\#2})$ = 172.5°; $d(\mathrm{O4}\cdots\mathrm{O3}^{\#3})$ = 2.772(3) Å, $\angle(\mathrm{O4{-}H4B}\cdots\mathrm{O3}^{\#3})$ = 163.3°; for the symmetry code see Table 2]. The layers are interlinked by N–H$\cdots$O hydrogen bonding interactions into a three-dimensional supramolecular metal-organic framework. Fig. 3 shows the isolated supramolecular chains along the [100] direction, where the protonated pyridyl N atoms donate H atoms to the carboxyl O1 atoms of neighboring layers to form $R_2^2(8)$ rings [$d(\mathrm{N1}\cdots\mathrm{O1}^{\#4})$ = 2.892(3) Å, $\angle(\mathrm{N1{-}H1A}\cdots\mathrm{O1}^{\#4})$ = 162.4°].

Thermal behavior

Compound **1** is air-stable at r. t. The DTA curve exhibits one endothermic peak centered at 164 ℃, and two exothermic peaks at 242 and 319 ℃. The TGA curve indicates that a weight loss of 10.4 % occurs in the temperature range from r. t. to 164 ℃, which agrees well with the calculated value of 9.5 % for release of two moles of H_2O per complex molecule, suggesting complete dehydration. In the range of 300 – 600 ℃, the observed weight loss of 70.1 % is comparable to the calculated value of 68.9 % for release of the two moles of organic ligands. The powder X-ray diffraction pattern confirms the white residue of 19.5 % left at 600 ℃ to be ZnO (calcd. 21.6 %).

Fluorescence properties

The solid-state fluorescence spectrum of complex **1** at r. t. is depicted in Fig. 4. The complex has a maximum fluorescence emission at *ca.* 390 nm upon excitation at 248 nm, which can be assigned to the ligand-ligand charge transfer $\pi_\mathrm{L} \rightarrow \pi_\mathrm{L}^*$ transition from the 2-oxopyridinium-3-carboxylate groups. The fluorescence intensity of **1** is stronger than that of the free ligand. The fluorescence enhancement of compound **1** may be due to the coordination interactions and the

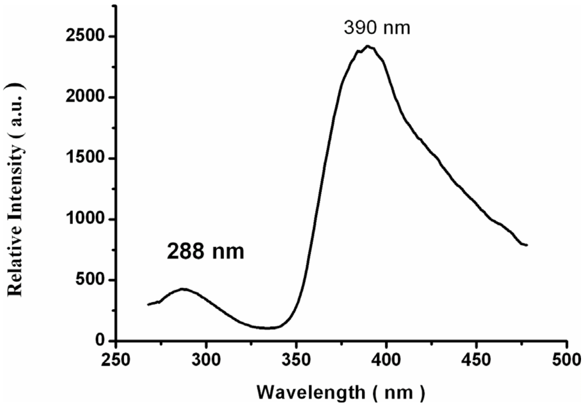

Fig. 4. Fluorescence spectrum of **1** in the solid state at room temperature.

packing interactions in the solid state, which effectively increase the rigidity of the ligand and reduce the energy loss by radiationless decay of the intraligand excited state [18].

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