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Synthesis, structure, fluorescence spectra study of two kinds of coordination supramolecular zinc compounds

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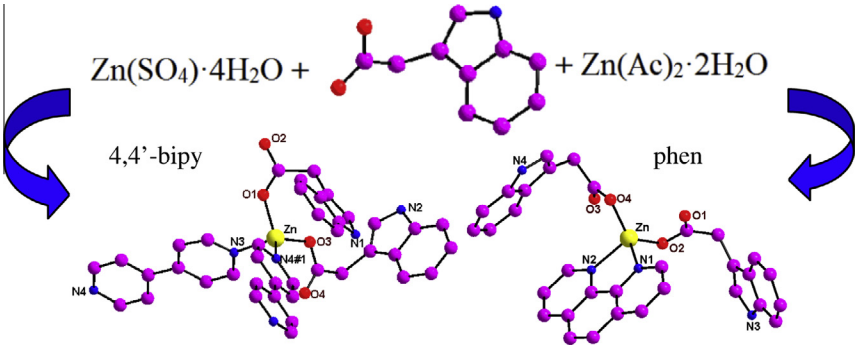
HIGHLIGHTS

- Synthesizing two zinc complexes constructed from indoleacetic acid.
- Discussing the UV–vis absorption spectra.
- Discussing the photoluminescent properties of two complexes.

GRAPHICAL ABSTRACT

Two kinds of novel compounds $[Zn(IAA)_2(phen)$ (HIAA = indole-3-acetic acid, phen = 1,10-phenanthroline) (**1**) and $[Zn(IAA)_2(4,4'\text{-bipy})](4,4'\text{-bipy} = 4,4'\text{-bipyridine})$ (**2**) have been synthesized by the reaction of $Zn(Ac)_2{\cdot}2H_2O$ or $Zn(SO_4){\cdot}4H_2O$ as metal source, IAA as the first ligand and phen or 4,4′-bipy as the second ligand at room temperature. Compounds **1** and **2** are both crystallizing in monoclinic, space group $P2_1/c$. The fluorescence spectra of the two compounds had been studied in detail.



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ABSTRACT

Two novel compounds $[Zn(IAA)_2(phen)$ (HIAA = indole-3-acetic acid, phen = 1,10-phenanthroline) (**1**) and $[Zn(IAA)_2(4,4'\text{-bipy})](4,4'\text{-bipy} = 4,4'\text{-bipyridine})$ (**2**) were synthesized by the reaction of $Zn(Ac)_2{\cdot}2H_2O$ or $Zn(SO_4){\cdot}4H_2O$ as a metal source, HIAA as the first ligand and phen or 4,4′-bipy as the second ligand in the system of methanol or the mixed solution of methanol and water at room temperature. They were characterized by elemental analysis, IR spectroscopy, UV–vis spectra and single-crystal X-ray diffraction. Structural analysis shows that the center metal Zn(II) for the compound **1** is four-coordinated, displaying a distorted tetrahedron; the metal center coordinated model for compound **2** is similar to that of **1**, in which the structural unit of $Zn(IAA)_2$ was connected by bridging the 4, 4′- bipy ligand to form an infinite 1D chain. In the packing of the compounds, there are some hydrogen bonding interactions and by the hydrogen bonding, 1D and 2D supramolecular structures were formed. Additional, we have studied the fluorescent properties of the two compounds.

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Introduction

Transition metal zinc is not only an important element of life, but also an essential trace element to human body. The compounds containing N, S donor atoms are an important organic component of organism. It is worth to mention that zinc compounds and bioactive organic ligands have received continuing attention since their unique characteristics in the process of gene expression, immunization, cell proliferation and differentiation, as well as in the process of metabolism [1–3]. In addition, zinc also plays a key role in catalysis and regulate, as well as take part in many biological functions, such as keeping the synthesis and degradation about sugar, fat, protein and nucleic acid [4,5]. Consequently, designing and synthesizing zinc complexes with bioactive molecule and mimicking the hydrolytic enzyme as well as inferring the reaction mechanism are a hot topic in recent years [5,6].

As we known, indoleacetic acid is a significant plant somatotropin which plays a vital role in the growth of plants [7,8]. The mechanization about indoleacetic acid has received continuing attention, particularly the mechanism about compounds of plant hormones and metal [9]. In addition, indole ring is an aromatic ring characterization with a high electron cloud density, it could take part in many reactions with enzyme with better physiological activity [10–13]. Although a number of transition metal compounds containing carboxylic acid as ligands have been reported, transition metal compounds with indoleacetic acid ligands are relatively rare [11–14]. In addition, the compounds may be potential application in the field of biological fluorescence probe. In order to further study various the structures and functional properties of the compounds with indoleacetic acid ligands, in this work, two novel compounds [Zn(IAA)$_2$(phen)] (HIAA = indole-3-acetic acid, phen = 1,10-phenanthroline) (**1**) and [Zn(IAA)$_2$(4,4′-bipy)] (HIAA = indole-3-acetic acid, 4,4′-bipy = 4,4′-bipyridine) (**2**) were synthesized by the reaction of Zn(Ac)$_2$·2H$_2$O or Zn(SO$_4$)·4H$_2$O, IAA as the first ligand and phen or 4,4′-bipy as the second ligand at room temperature. The compounds were characterized by single-crystal X-ray diffraction and IR spectra, UV–vis spectra, and the fluorescence spectroscopy of them were also studied.

Experimental section

Materials and methods

All the chemicals used were analytical grade and without further purification. Elemental analyses for C, H, and N were carried out on a Perkin Elmer 240C automatic analyzer. The infrared spectra were recorded on a JASCO FT/IR-480 spectrometer with pressed KBr pellets in the range 200–4000 cm^{-1}. UV–vis spectra were recorded on JASCO V-570 spectrometer (200–1100 nm, in form of solid sample). The luminescence spectra were recorded on a JASCO F-6500 spectrofluorimeter (solid).

Synthesis of the complexes

*[Zn(IAA)$_2$(phen)] (**1**)*

A methanol solution of 1, 10-phen (0.05 g, 0.25 mmol) and HIAA (0.09 g, 0.5 mmol) was added to an methanol solution (7.5 ml) of Zn(Ac)$_2$·2H$_2$O (0.066 g, 0.3 mmol) with continuous stirring at room temperature for 2 h, and a few drops of HAc were added to the mixed solution so that the solution became clear light yellow. Then, the mixture was placed at room temperature for several days, light yellow crystals suitable for X-ray diffraction were obtained. Yield (based on Zn): 0.120 g, 67.8%. Anal. Calc. for C$_{32}$H$_{24}$N$_4$O$_4$Zn: C, 64.65 (64.71); H, 4.01 (4.07); N, 9.39 (9.43). IR (KBr pellet, ν [cm^{-1}]): 3396(ν_{N-H}); 3058(ν_{Ar-H}); 2925, 2875 ($\nu_{-(CH2)-}$); 1595(ν_{asCOO-}); 1381(ν_{sCOO-}); 1519($\nu_{C=N}$); 1496($\nu_{C=C}$); 1162(ν_{C-C}); 1105(ν_{C-N}); 1050(ν_{C-O}); 870, 799, 723(δ_{Ar-H}); 521(ν_{Zn-N}); 425(ν_{Zn-O}).

*[Zn(IAA)$_2$(4,4′-bipy)] (**2**)*

A methanol solution of 4,4′-bipy (0.04 g, 0.25 mmol) and HIAA (0.09 g, 0.5 mmol) was added to an aqueous solution (10 ml) of ZnSO$_4$·4H$_2$O (0.09 g, 0.5 mmol) with continuous stirring at room temperature for 3 h, then, the mixed solution were placed five days at room temperature, finally the yellow crystals suitable for X-ray diffraction analysis were obtained. Yield (based on Zn): 0.10 g, 56.1%. Anal. Calc. for C$_{30}$H$_{24}$N$_4$O$_4$Zn: C, 63.17 (63.23); H, 4.18 (4.24); N, 9.77 (9.83). IR (KBr pellet, ν [cm^{-1}]): 3296(ν_{N-H}); 3056(ν_{Ar-H}); 2927, 2901($\nu_{-(CH2)-}$); 1613(ν_{asCOO-}); 1397(ν_{sCOO-}); 1590, 1491($\nu_{C=N}$); 1456($\nu_{C=C}$); 1173(ν_{C-C}); 1105(ν_{C-N}); 1048 (ν_{C-O}); 878, 813, 746(δ_{Ar-H}); 529(ν_{Zn-N}); 428(ν_{Zn-O}).

X-ray single crystal structural determination

Suitable single crystals of the two compounds were mounted on glass fibers for X-ray measurement. Reflection data were collected at room temperature on a Bruker AXS SMART APEX II CCD diffractometer with graphite monochromatized Mo Kα radiation (λ = 0.71073 Å). All the measured independent reflections

Table 1
Crystal structure parameters for compounds **1** and **2**.[a]

Compounds	1	2
Formula	C$_{32}$H$_{24}$N$_4$O$_4$Zn	C$_{30}$H$_{24}$N$_4$O$_4$Zn
M_r	593.92	569.90
Crystal system	Monoclinic	Monoclinic
Space group	$P2_1/c$	$P2_1/c$
a (Å)	12.298 (3)	8.352 (2)
b (Å)	12.554 (3)	18.073 (5)
c (Å)	17.669 (3)	19.376 (5)
α (°)	90	90
β (°)	105.965 (4)	102.001 (4)
γ (°)	90	90
V (Å^3)	2623 (1)	2687 (1)
Z	4	4
Crystal size (mm)	0.25 × 0.22 × 0.10	0.20 × 0.18 × 0.12
D (g cm^{-3})	1.504	1.323
F (000)	1224	1176
μ (Mo Kα) (mm^{-1})	0.984	0.899
Reflections collected	9814	13041
Independent reflections ($I > 2\sigma(I)$)	3195 (2095)	4926 (3217)
Parameters	370	352
$(\Delta\rho)_{max}$, $(\Delta\rho)_{min}$ (e Å^{-3})	0.367 and −0.381	0.335 and −0.299
Goodness of fit	0.982	1.057
R, wR_2 [$I > 2\sigma(I)$][a]	0.0438, 0.0788	0.0466, 0.0927
R, wR_2 (all data)[a]	0.0828, 0.0976	0.0697, 0.1002

[a] $R = \Sigma||Fo| - |Fc||/\Sigma|Fo|$, $wR_2 = [\Sigma(w(Fo^2 - Fc^2)^2/[\Sigma(w(Fo^2)^2)^{1/2}$; $[Fo > 4\sigma(Fo)]$.

Table 2
Selected bond lengths (Å) and angles (°) for title compounds **1** and **2**.[a]

*Compound **1***			
Zn1—O4	1.956 (3)	Zn1—O2	1.959 (3)
Zn1—N1	2.085 (4)	Zn1—N2	2.089 (4)
O4—Zn1—O2	129.95 (13)	O4—Zn1—N1	107.26 (13)
O2—Zn1—N1	107.86 (14)	O4—Zn1—N2	105.93 (14)
O2—Zn1—N2	114.11 (15)	N1—Zn1—N2	80.45 (15)
*Compound **2***			
Zn1—O3	1.922 (5)	Zn1—O1	1.934 (5)
Zn1—N3	2.056 (6)	Zn1—N4$^{\#1}$	2.039 (6)
O3—Zn1—O1	113.3 (3)	O3—Zn1—N4$^{\#1}$	122.8 (2)
O1—Zn1—N4$^{\#1}$	104.3 (2)	O3—Zn1—N3	111.1 (2)
O1—Zn1—N3	96.9 (2)	N4$^{\#1}$—Zn1—N3	105.0 (3)

[a] Symmetry code: #1: $-x$, $y + 1/2$, $-z + 1/2$.